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**A TECHNIQUE TO INVESTIGATE THE MECHANISM OF UNIFORM CORROSION  
IN THE PRESENCE OF A SEMI-PERMEABLE MEMBRANE**

**TECHNIQUE D'ETUDE DU MECANISME DE CORROSION UNIFORME EN  
PRESENCE D'UNE MEMBRANE SEMI-PERMEABLE**

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**Pinawa, Manitoba R0E 1L0  
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RÉSUMÉ

On décrit une technique d'étude du mécanisme de corrosion uniforme en présence d'une membrane semi-perméable. On considère trois degrés possibles de détermination de la vitesse pour la demi-réaction anodique et la demi-réaction cathodique: la migration de l'espèce à travers la couche de diffusion entre la masse et la solution, la migration de l'espèce à travers la membrane et la réaction électrochimique elle-même. La technique repose sur la mesure du potentiel de corrosion,  $E_{CORR}$ , d'une rotrode en régime permanent. La variation de  $E_{CORR}$  en fonction de la concentration de l'oxydant, de l'épaisseur de la couche de diffusion et de l'épaisseur de la membrane sert à identifier le degré de détermination de la vitesse pour chaque demi-réaction.

On devrait employer cette technique pour étudier le comportement sous corrosion des matériaux à retenir pour les conteneurs d'évacuation des déchets nucléaires. La compréhension du mécanisme de corrosion uniforme permettra de prédire avec confiance le comportement à long terme de ces conteneurs.

L'Énergie Atomique du Canada, Limitée  
Établissement de recherches nucléaires de Whiteshell  
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A TECHNIQUE TO INVESTIGATE THE MECHANISM OF UNIFORM CORROSION IN THE  
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ABSTRACT

A technique to investigate the mechanism of uniform corrosion in the presence of a semi-permeable membrane is described. For both the anodic and cathodic half-reactions three possible rate-determining steps are considered: transport of species through the bulk solution diffusion layer, transport of species through the membrane and the electrochemical reaction itself. The technique is based on the measurement of the corrosion potential,  $E_{CORR}$ , of a rotating disc electrode under steady-state conditions. The variation of  $E_{CORR}$  with the oxidant concentration, the thickness of the diffusion layer and the membrane thickness is used to identify the rate-determining step for each half-reaction.

This technique should be of use in the study of the corrosion behaviour of candidate materials for nuclear waste disposal containers. An understanding of the mechanism of uniform corrosion will enable confident predictions to be made concerning the long-term behaviour of such containers.

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## LIST OF SYMBOLS

D	diffusion coefficient in solution ( $\text{m}^2 \cdot \text{s}^{-1}$ )
$\bar{D}$	diffusion coefficient in membrane ( $\text{m}^2 \cdot \text{s}^{-1}$ )
E	electrode potential (V)
$E^\circ$	standard electrode potential (V)
$E_{\text{CORR}}$	corrosion potential (V)
$E_{\text{eq}}$	equilibrium electrode potential (V)
F	Faraday constant ( $\text{C} \cdot \text{mol}^{-1}$ )
I	current (A)
$I_{\text{CORR}}$	corrosion current (A)
J	flux ( $\text{mol} \cdot \text{m}^{-2} \cdot \text{s}^{-1}$ )
K	partition coefficient
P	permeability ( $\text{m} \cdot \text{s}^{-1}$ )
R	gas constant ( $\text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$ )
T	temperature (K)
c	concentration in solution ( $\text{mol} \cdot \text{m}^{-3}$ )
$\bar{c}$	concentration in membrane ( $\text{mol} \cdot \text{m}^{-3}$ )
i	current density ( $\text{A} \cdot \text{m}^{-2}$ )
$i_0$	exchange current density ( $\text{A} \cdot \text{m}^{-2}$ )
$i^\circ$	standard exchange current density ( $\text{A} \cdot \text{m} \cdot \text{mol}^{-1}$ )
$i_{\text{CORR}}$	corrosion current density ( $\text{A} \cdot \text{m}^{-2}$ )
$k'$	electrochemical rate constant ( $\text{m} \cdot \text{s}^{-1}$ )
n	number of electrons
$x_B$	membrane thickness (m)
$x_D$	diffusion layer thickness (m)
$\alpha$	transfer coefficient
$\eta$	overpotential (V)
$\nu$	kinematic viscosity ( $\text{m}^2 \cdot \text{s}^{-1}$ )
$\omega$	rotation rate ( $\text{rad} \cdot \text{s}^{-1}$ )

### SUBSCRIPTS

M	membrane (permeability of)
O	oxidized form of electroactive species
R	reduced form of electroactive species
S	solution (permeability of)
a	of the anodic half-reaction
c	of the cathodic half-reaction
i	any species
m	metal dissolution product
ox	oxidant

### SUPERSCRIPTS

B	membrane/diffusion layer interface
D	diffusion layer/bulk solution interface
°	electrode surface
∞	bulk solution



## 1. INTRODUCTION

In the Canadian Nuclear Fuel Waste Management Program (CNFWMP), copper is being considered as a container material for the disposal of high-level nuclear waste. Provided the container is properly designed and fabricated, the only credible cause of container failure is corrosion. In particular, uniform corrosion and pitting attack are thought to be the two forms of corrosion most likely to limit the lifetime of a copper container [1]. Copper is thermodynamically stable in oxygen-free pure water but will corrode if oxidants and salts are present. Some oxygen will be present initially due to air trapped in the disposal vault when it is closed. Other oxidizing species may form as a result of radiolysis of the groundwater. Consequently, a copper container would undergo some corrosion in a nuclear fuel waste disposal vault.

The technique described here can be used to determine the mechanism of uniform corrosion under simulated disposal conditions. If the corrosion mechanism is known, then confident predictions can be made about the long-term corrosion behaviour of the container. For instance, in the Swedish proposal [2], the implicit assumption was made that the overall rate of corrosion would be determined by the rate of the cathodic half-reaction. The rate of the cathodic reaction, in turn, was assumed to be limited by the rate of supply of oxidizing species to the container surface. This present work will show whether the same situation will apply in the Canadian concept or whether some other mechanism will control the rate of the overall reaction. Although much of the discussion will concern the corrosion of copper, the general treatment applies to any metal provided the assumptions made in the derivation are valid.

Power and Ritchie [3] have proposed a method of determining corrosion mechanisms in bulk solution. The method is based on the measurement of the corrosion potential,  $E_{\text{CORR}}$ , of a rotating disc electrode (RDE) as a function of rotation rate and oxidant concentration. In the case of reactions with soluble corrosion products, the limiting steps for both the

anodic and cathodic reactions were considered to be either the transport of species through the solution or the electrochemical reaction itself.

In this paper, Power and Ritchie's technique is extended to include the effect of a membrane situated between the electrode and the bulk solution. The membrane simulates the compacted clay/sand buffer material, which will surround the waste disposal containers. There are then three possible rate-determining steps (rds) for the anodic and cathodic reactions: transport of species through the solution, transport of species through the membrane and the electrochemical reaction.

## 2. OUTLINE OF REACTION MECHANISMS

The RDE is a convenient tool with which to study the transport of species towards or away from an electrode surface. A schematic representation of the three layers below a membrane-covered RDE is shown in Figure 1. Due to the rotation of the electrode, two distinct regions are established within the solution. Firstly, in the bulk solution, convective and diffusive mixing produces a uniform concentration of species. Secondly, next to the surface of the membrane, transport of species is by diffusion only. This region of solution is known as the diffusion layer. The thickness of the diffusion layer,  $x_D$ , can be defined [4] and is a function of the rotation rate,  $\omega$  ( $\text{rad}\cdot\text{s}^{-1}$ ),

$$x_D = 1.612 \nu^{1/6} D_i^{1/3} \omega^{-1/2} \quad (1)$$

where  $\nu$  is the kinematic viscosity and  $D_i$  the diffusion coefficient of the electroactive species  $i$ . Transport of species across the third layer, the membrane, is assumed to be by diffusion only. The small volume of solution between the membrane and the electrode surface is assumed to be negligible.

The three possible rate-determining steps for the electrode reaction are now apparent:

- (a) transport of species through the diffusion layer,
- (b) transport of species through the membrane,
- (c) the electrochemical reaction at the metal surface.

At steady-state, the rate of the electrode reaction is determined by the rate of the slowest of the three steps. Steady-state is defined as the condition at which the concentration of species  $i$  at any point is constant, i.e.  $\partial c/\partial t = 0$ . Furthermore, at steady-state, the flux of species  $i$  reacting at the electrode surface,  $(J_i)_{ES}$ , is equal to the flux of material through the membrane,  $(J_i)_{MEM}$ , and also to the flux of material through the diffusion layer,  $(J_i)_{DL}$ . Hence,

$$J_i = (J_i)_{ES} = (J_i)_{MEM} = (J_i)_{DL} \quad (2)$$

This treatment applies equally to the transport of reactants to the electrode surface as to the transport of products away from the electrode. In this section, we will only consider the transport of reactants (oxidants) to the surface.

Assuming first order electrode kinetics, the flux at the electrode surface is given by

$$(J_i)_{ES} = k'c_i^{\circ} \quad (3)$$

where  $k'$  is an electrochemical rate constant and  $c_i^{\circ}$  is the surface concentration of species  $i$ .

From Fick's 1st law and by assuming a constant (i.e., linear) concentration gradient, the flux of species through the membrane at steady-state is

$$(J_i)_{MEM} = \bar{D}_i \frac{(c_i^B - c_i^{\circ})}{x_B} \quad (4)$$

where  $\bar{c}_1^B$  and  $\bar{c}_1^\circ$  are the concentrations of  $i$  in the membrane at the membrane/diffusion layer and membrane/electrode surface interfaces, respectively,  $\bar{D}_1$  is the diffusion coefficient in the membrane and  $x_B$  is the membrane thickness. The concentrations in the membrane,  $\bar{c}_1^B$  and  $\bar{c}_1^\circ$ , are related to the concentrations in the solution phases at the respective interfaces,  $c_1^B$  and  $c_1^\circ$ . At equilibrium, the partition coefficient,  $K_1$ , is defined as the ratio of these concentrations

$$K_1 = \frac{\bar{c}_1^B}{c_1^B} = \frac{\bar{c}_1^\circ}{c_1^\circ} \quad (5)$$

Equation (4) can then be rewritten

$$(J_1)_{MEM} = K_1 \bar{D}_1 \frac{(c_1^B - c_1^\circ)}{x_B} \quad (6)$$

Similarly, for the diffusion layer at steady-state

$$(J_1)_{DL} = D_1 \frac{(c_1^\infty - c_1^B)}{x_D} \quad (7)$$

where the concentration at the diffusion layer/bulk solution interface,  $c_1^D$ , is assumed to be equal to the bulk concentration,  $c_1^\infty$ .

Using the condition that the fluxes are equal at steady-state (Equation 2), elimination of  $c_1^\circ$  and  $c_1^B$  from Equations (3), (6) and (7) and rearranging yields

$$\frac{1}{J_1} = \frac{1}{k_1 c_1^\infty} + \frac{1}{(K_1 \bar{D}_1 c_1^\infty)/x_B} + \frac{1}{(D_1 c_1^\infty)/x_D} \quad (8)$$

From Equation (8), the conditions under which each of the possible rds limits the rate of the overall reaction can be seen. If  $k'c_1^\infty$  is much smaller than both  $(K_1\bar{D}_1c_1^\infty/x_B)$  and  $(D_1c_1^\infty/x_D)$  then  $J_1 \approx k'c_1^\infty$  and the rate of the overall reaction is controlled by the rate of the electrochemical step. Alternatively, if  $(K_1\bar{D}_1c_1^\infty/x_B)$  is much smaller than  $k'c_1^\infty$  and  $(D_1c_1^\infty/x_D)$ , the reaction is controlled by diffusion through the membrane. Finally, if  $(D_1c_1^\infty/x_D)$  is much smaller than both  $k'c_1^\infty$  and  $(K_1\bar{D}_1c_1^\infty/x_B)$  the reaction is controlled by diffusion through the diffusion layer.

In a rigorous derivation, the concentration terms above would be replaced by activities. For simplicity, concentrations will be used instead of activities.

### 3. ELECTROCHEMICAL EXPRESSIONS FOR EACH RDS

The overall rate of both the anodic and cathodic half-reactions can be limited by one of the three rds. In this Section, expressions are given which relate the rates of these reactions to various electrochemical parameters. The derivations of Equations (9) to (14) are given in Appendix A.

We shall assume that the products of the anodic (metal dissolution) and cathodic reactions are soluble. The source of oxidants is the bulk solution phase. In addition, it is assumed that the rds is much slower than the other two processes, i.e., we shall not consider reactions under mixed control.

#### 3.1 RATE CONTROLLED BY TRANSPORT THROUGH THE DIFFUSION LAYER

##### (1) Anodic reaction

In this case, the rate of the anodic reaction is limited by the rate of transport of the soluble product, m, across the diffusion layer. At steady-state, the electrode potential, E, is given by

$$E = E_a^\circ - \frac{RT}{n_a F} \ln (0.52 n_a F D_m^{2/3} \nu^{-1/6} \omega^{1/2}) + \frac{RT}{n_a F} \ln i_a \quad (9)$$

where  $E_a^\circ$  is the standard electrode potential of the anodic reaction,  $n_a$  is the number of electrons involved in the anodic reaction,  $i_a$  is the anodic current density and R, T and F have their usual meanings.

(ii) Cathodic reaction

The rate of the cathodic reaction is controlled by the rate of transport of oxidant (subscript ox) across the diffusion layer and, at steady-state, the current density is given by

$$i_c = -0.62 n_c F D_{ox}^{2/3} \nu^{-1/6} \omega^{1/2} c_{ox}^\infty \quad (10)$$

where  $i_c$  is the cathodic current density and  $n_c$  is the number of electrons involved in the cathodic reaction.

3.2 RATE CONTROLLED BY TRANSPORT THROUGH THE MEMBRANE

(i) Anodic reaction

Similarly, if the anodic rate is controlled by transport through the membrane, the steady-state electrode potential is

$$E = E_a^\circ + \frac{RT}{n_a F} \ln i_a - \frac{RT}{n_a F} \ln (n_a F K_m \bar{D}_m) + \frac{RT}{n_a F} \ln x_B \quad (11)$$

Equation (11) is analogous to Equation (9) with  $x_D$  (Equation 1) replaced by  $x_B$ .

(ii) Cathodic reaction

The steady-state cathodic current density for membrane transport control is

$$i_c = - \frac{n_c F K_{ox} \bar{D}_{ox} c_{ox}^{\infty}}{x_B} \quad (12)$$

Again, Equation (12) is equivalent to Equation (10) with  $x_D$  replaced by  $x_B$ .

3.3 RATE CONTROLLED BY THE ELECTROCHEMICAL REACTION

(i) Anodic reaction

If the electrode kinetics follow Butler-Volmer type behaviour, the anodic electrode potential/current density relationship is

$$E = E_a^{\circ} - \frac{RT}{(1-\alpha_a)n_a F} \ln i_a^{\circ} + \frac{RT}{(1-\alpha_a)n_a F} \ln i_a \quad (13)$$

where  $\alpha_a$  is the anodic transfer coefficient and  $i_a^{\circ}$  is the anodic standard exchange current density.

(ii) Cathodic reaction

For cathodic electrochemical control the expression is

$$E = E_c^{\circ} + \frac{RT}{\alpha_c n_c F} \ln c_{ox}^{\infty} + \frac{RT}{\alpha_c n_c F} \ln i_c^{\circ} - \frac{RT}{\alpha_c n_c F} \ln |i_c| \quad (14)$$

where  $E_c^{\circ}$  is the cathodic standard electrode potential,  $\alpha_c$  is the transfer coefficient for the cathodic reaction,  $i_c^{\circ}$  is the cathodic standard exchange current density and  $|i_c|$  is the magnitude (without sign) of the cathodic current density.

### 3.4 THE MEMBRANE POTENTIAL

If a semi-permeable membrane is placed in an electrolyte solution, a potential difference will develop at the solution/membrane interface [5]. This potential difference is known as the Donnan potential. If there is a concentration gradient across the membrane as well, a diffusion potential will also exist. The membrane potential is the sum of the two Donnan potentials (one at each solution/membrane interface) and the diffusion potential [5].

The value of the membrane potential at steady-state depends upon the concentration profile of the electroactive species. Let us first consider the cases in which the rates of the anodic and cathodic half-reactions are controlled by transport through the solution or by the rate of the electrochemical step. In these cases, the concentration of the electroactive species is uniform throughout the membrane. Consequently, the diffusion potential is zero. In addition, the concentrations of the electroactive species on either side of the membrane are equal, and hence, the two Donnan potentials are equal but of opposite sign. Thus, the membrane potential is zero.

However, if the anodic or cathodic reaction is controlled by transport through the membrane, the membrane potential is not zero. In these cases, the diffusion potential is a function of the concentrations and the transference numbers of the diffusing species. In addition, the sum of the two Donnan potentials is not zero. Furthermore, the overall expression for the membrane potential contains a term involving the logarithm of the ratio of the concentrations of the diffusing species in the solution on either side of the membrane [5]. In the derivation of Equations (11) and (12) the concentration is assumed to be zero on one side of the membrane. Hence, theoretically, the membrane potential is infinite.

The mathematical derivations in Appendix A are simplifications of the actual cases. In practice, the concentration gradients will not change abruptly at the membrane/diffusion layer and diffusion layer/bulk solution interfaces. Indeed, although the diffusion layer thickness,  $x_D$ , is defined



precisely, in reality, the region between the diffusion layer and the bulk solution is diffuse. Consequently, the membrane potential will be a complex and unknown function of both the membrane thickness and the rotation rate. We cannot even assume that the membrane potential will be small in comparison to the measured potentials. These problems can be overcome if the reference electrode is situated between the membrane and the working electrode (see the Discussion). Then there would be no contribution from the membrane potential to the corrosion potential being measured.

#### 4. CORRELATION BETWEEN THE CORROSION POTENTIAL AND THE CORROSION MECHANISM

At the corrosion potential the rates of the anodic and cathodic half-reactions are equal. Expressed as currents

$$I_a = -I_c = I_{CORR} \quad (15)$$

where  $I_a$ ,  $I_c$  and  $I_{CORR}$  are the anodic, cathodic and corrosion currents, respectively. The convention is used throughout that anodic currents are positive and cathodic currents are negative. The Wagner-Traud theory of corrosion states that the surface areas available for the anodic and cathodic reactions are the same and are equal to the total surface area [3]. Equation (15) can then be rewritten in terms of current densities

$$i_a = -i_c = i_{CORR} \quad (16)$$

where  $i_{CORR}$  is the corrosion current density.

We can now use Equation (16) to combine Equations (9) to (14) to yield expressions for  $E_{CORR}$  in terms of experimental parameters. There are nine possible combinations to consider. The experimental parameters are the diffusion layer thickness (which is related to the rotation rate), the membrane thickness and the bulk oxidant concentration.

Detailed derivations of Equations (17) to (25) are given in Appendix B.

Case 1 Anodic reaction solution transport controlled; cathodic reaction solution transport controlled.

Combining Equations (9) and (10), given that at

$E = E_{\text{CORR}}$ ,  $\ln i_a = \ln |i_c|$ , and rearranging yields

$$E_{\text{CORR}} = \text{const.} + \frac{RT}{n_a F} \ln c_{\text{ox}}^{\infty} \quad (17)$$

Case 2 Anodic reaction solution transport controlled; cathodic reaction membrane transport controlled.

Similarly, combining Equations (9) and (12) and rearranging gives

$$E_{\text{CORR}} = \text{const.} + \frac{RT}{n_a F} \ln c_{\text{ox}}^{\infty} - \frac{RT}{2n_a F} \ln \omega - \frac{RT}{n_a F} \ln x_B \quad (18)$$

Case 3 Anodic reaction solution transport controlled; cathodic reaction electrochemically controlled.

Combining Equations (9) and (14), and rearranging

$$E_{\text{CORR}} = \text{const.} + \frac{RT}{(n_a + \alpha n_c) F} \{ \ln c_{\text{ox}}^{\infty} - 1/2 \ln \omega \} \quad (19)$$

Case 4 Anodic reaction membrane transport controlled; cathodic reaction solution transport controlled.

Combining Equations (11) and (10), and rearranging

$$E_{\text{CORR}} = \text{const.} + \frac{RT}{n_a F} \{ \ln c_{\text{ox}}^{\infty} + 1/2 \ln \omega + \ln x_B \} \quad (20)$$

Case 5 Anodic reaction membrane transport controlled; cathodic reaction membrane transport controlled.

Combining Equations (11) and (12), and rearranging gives

$$E_{\text{CORR}} = \text{const.} + \frac{RT}{n_a F} \ln c_{\text{ox}}^{\infty} \quad (21)$$

Case 6 Anodic reaction membrane transport controlled; cathodic reaction electrochemically controlled.

Combining Equations (11) and (14), and rearranging gives

$$E_{\text{CORR}} = \text{const.} + \frac{RT}{(n_a + \alpha_c n_c) F} \{ \ln c_{\text{ox}}^{\infty} + \ln x_B \} \quad (22)$$

Case 7 Anodic reaction electrochemically controlled; cathodic reaction solution transport controlled.

Combining Equations (13) and (10), and rearranging gives

$$E_{\text{CORR}} = \text{const.} + \frac{RT}{(1-\alpha_a) n_a F} \{ \ln c_{\text{ox}}^{\infty} + 1/2 \ln \omega \} \quad (23)$$

Case 8 Anodic reaction electrochemically controlled; cathodic reaction membrane transport controlled.

Combining Equations (13) and (12) gives

$$E_{\text{CORR}} = \text{const.} + \frac{RT}{(1-\alpha_a) n_a F} \{ \ln c_{\text{ox}}^{\infty} - \ln x_B \} \quad (24)$$

Case 9 Anodic reaction electrochemically controlled; cathodic reaction electrochemically controlled.

Finally, combining Equations (13) and (14) gives

$$E_{\text{CORR}} = \text{const.} + \frac{RT}{(\alpha_c n_c + (1-\alpha_a)n_a)F} \ln c_{\text{ox}}^{\infty} \quad (25)$$

The dependencies of  $E_{\text{CORR}}$  on  $\ln c_{\text{ox}}^{\infty}$ ,  $\ln \omega$  and  $\ln x_B$  for Cases 1 to 9 are summarized in Table 1.

## 5. DISCUSSION

The technique described here permits the determination of the rds of the individual anodic and cathodic half-reactions. It does not indicate which of these half-reactions controls the rate of the overall corrosion reaction. Further experiments are necessary to determine the overall rds before the corrosion process is fully characterized.

The sign of the dependencies of  $E_{\text{CORR}}$  on  $\ln c_{\text{ox}}^{\infty}$ ,  $\ln \omega$  and  $\ln x_B$  are given in Table 2 (0 indicates no dependence). By simply determining the sign of the dependence it is possible to distinguish between six of the nine combinations of reaction mechanism. However, Cases 1, 5 and 9 are indistinguishable on this basis. These are, respectively, both reactions solution transport controlled, both reactions membrane transport controlled and both reactions electrochemically controlled. Power and Ritchie [3] have given two criteria for distinguishing between solution transport and electrochemical control. Firstly, if  $E_{\text{CORR}}$  is much closer to  $E_a^{\circ}$  than to  $E_c^{\circ}$ , the reactions are more likely to be solution transport controlled (Case 1). Secondly, if the difference ( $E_a^{\circ} - E_c^{\circ}$ ) is greater than 0.3V, the reactions are also likely to be under solution transport control. The same two criteria can be used to distinguish between the cases in which both reactions are membrane transport controlled (Case 5) and in which both reactions are electrochemically controlled (Case 9). Solution and membrane transport

control (Cases 1 and 5, respectively) can be distinguished if the permeabilities of the solution and membrane are known. The permeability of the solution,  $P_S$ , is defined as

$$P_S = \frac{D_1}{x_D} \quad (26)$$

and the permeability of the membrane,  $P_M$ , is defined as

$$P_M = \frac{K_1 \bar{D}_1}{x_B} \quad (27)$$

If the permeability of the solution is greater than that of the membrane, the two reactions are likely to be membrane transport controlled.

There are several practical difficulties associated with these measurements. Firstly, the corrosion potential must be measured under steady-state conditions. Secondly, in order to avoid errors due to the membrane potential, the reference electrode must be placed close to the working electrode. Finally, when simulating disposal vault conditions, it may be easier to use a polymer membrane rather than one made from compacted buffer material. These problems will now be discussed in turn.

The equations relating  $E_{CORR}$  to  $\ln c_{OX}^{\infty}$ ,  $\ln \omega$  and  $\ln x_B$  were derived assuming steady-state conditions. At steady-state,  $\partial c / \partial t = 0$ . Before measurements can be taken, constant concentration profiles must be established within both the diffusion layer and the membrane. Steady-state is established within the diffusion layer very quickly (less than one second). The time required to reach steady-state in the membrane may be much longer and will increase with the thickness of the membrane.

The position of the reference electrode with respect to the working electrode is an important consideration. It was shown in Section 3.4

that the membrane potential is an unknown and variable quantity. This problem can be avoided by placing the reference electrode close to the working electrode, so that the membrane does not separate the two electrodes. Gough and Leyboldt [6] have described a membrane-covered rotating disc electrode in which the reference electrode was incorporated in the body of the rotating assembly. A silver-silver chloride reference electrode was used. The liquid junction between the reference electrode electrolyte and the test solution was established at a small opening close to the edge of the working electrode. An alternative approach would be to use the ring electrode of a rotating ring-disc electrode as the reference. For chloride solutions, a suitable reference would again be silver-silver chloride. The potential of the reference electrode would be stable provided the chloride ion concentration in the small volume between the membrane and the working electrode remained constant. A variation of 4% in the chloride ion activity in this volume would lead to a change of 1 mV at room temperature. To avoid interference of corrosion products with the reference electrode, the rotating ring-disc electrode should have a small collection efficiency. This can be achieved using a small disc, a thin ring and a large gap between the ring and the disc.

The nuclear waste disposal containers will be surrounded by a compacted clay/sand buffer material [7]. Membranes made from a compacted clay/sand mixture may be difficult to work with practically. The minimum thickness of such a membrane would be 2 to 3 mm. To study a range of thicknesses of even one order of magnitude would require using membranes up to 20 to 30 mm thick. The time required to reach steady-state in a 20-mm-thick membrane could be impractical. Consequently, it may prove easier to use thin polymer membranes. The diffusivity of species within the polymer should be similar to that in compacted buffer material.

This particular technique should be useful in the study of the corrosion of copper for the CNFWMP. In order to be able to make confident predictions about the very long-term corrosion behaviour of a copper container, it is essential that the mechanism of the corrosion process is understood. Only then can we attempt to predict accurately the amount of corrosion over periods of 500 to 1000 years.

Copper has been considered as the container material for the disposal of used nuclear fuel in the Swedish concept [2]. The argument was made that the total amount of metal loss could not exceed the total quantity of oxidants available in the disposal vault. The rate of metal loss was then determined from the rate of transport of oxidants to the container surface. Although the transport of oxidants through fractures in the rock was considered to be the slowest step, the transport calculations were based on oxidant transport through the compacted buffer material surrounding the container. In mechanistic terms, this is equivalent to the overall reaction being cathodically controlled with the cathodic reaction controlled by diffusion through the buffer (membrane).

The corrosion mechanism may not be the same in the Canadian concept for two reasons. Firstly, in the original Swedish concept [2] the  $\gamma$ -radiation field at the container surface was taken to be negligible (in subsequent refinements of the concept [8], using thinner walled containers, allowance was made for the  $\gamma$ -radiation field). In the CNFWMP, the nuclear waste containers are not designed to be self-shielding. The strength of the  $\gamma$ -radiation field at the container surface will depend on the container design and the waste form. It is possible that radiolysis of the groundwater may produce a net increase in the amount of oxidizing species at the container surface. If a sufficient quantity of oxidants is produced it would seem unlikely that the cathodic reaction would be transport limited. Secondly, the groundwaters found in the Canadian Shield [9] are considerably more saline than those encountered in Sweden. In chloride solutions, it is known [10-14] that the rate of copper dissolution is controlled by the rate of transport of soluble copper chloride complexes away from the metal surface. Consequently, the anodic reaction may control the rate of the overall reaction in higher salinity groundwaters.

## 6. CONCLUSIONS

A technique to determine the mechanism of uniform corrosion in the presence of a semi-permeable membrane has been described. The method is based on the variation of the corrosion potential of a rotating disc electrode. The experimentally variable parameters are the oxidant concentration, the membrane thickness and the rotation rate of the electrode. Equations are derived for the corrosion potential on the basis of the rate-determining step of the cathodic and anodic half-reactions. For each half-reaction three possible rate-determining steps are considered: transport of species through the solution diffusion layer, transport of species through the membrane and the electrochemical reaction.

Various experimental considerations have been discussed. Of these, the two most important are the establishment of steady-state conditions and the positioning of the reference electrode. The derived equations only apply to steady-state conditions. Therefore, it is essential that this condition be reached before the measurements are taken. The reference electrode should be positioned close to the working electrode. Then, the measurements are not complicated by contributions from the (unknown and variable) membrane potential. A combined working/reference electrode design has been suggested based on the rotating ring-disc electrode.

This technique should be of use in the study of the corrosion of copper for the CNFWMP. An understanding of the mechanism of uniform corrosion will enable confident predictions to be made regarding the lifetime of a copper nuclear waste disposal container.



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TABLE 1

THE DEPENDENCE OF  $E_{CORR}$  ON  $\ln c_{OX}^{\infty}$ ,  $\ln \omega$  AND  $\ln x_B$

	$\frac{\partial E_{CORR}}{\partial \ln c_{OX}^{\infty}}$	$\frac{\partial E_{CORR}}{\partial \ln \omega}$	$\frac{\partial E_{CORR}}{\partial \ln x_B}$
Case 1	$+\frac{RT}{n_a F}$	0	0
Case 2	$+\frac{RT}{n_a F}$	$-\frac{RT}{2n_a F}$	$-\frac{RT}{n_a F}$
Case 3	$+\frac{RT}{(n_a + \alpha_c n_c) F}$	$-\frac{RT}{2(n_a + \alpha_c n_c) F}$	0
Case 4	$+\frac{RT}{n_a F}$	$+\frac{RT}{2n_a F}$	$+\frac{RT}{n_a F}$
Case 5	$+\frac{RT}{n_a F}$	0	0
Case 6	$+\frac{RT}{(n_a + \alpha_c n_c) F}$	0	$+\frac{RT}{(n_a + \alpha_c n_c) F}$
Case 7	$+\frac{RT}{(1-\alpha_a)n_a F}$	$+\frac{RT}{2(1-\alpha_a)n_a F}$	0
Case 8	$+\frac{RT}{(1-\alpha_a)n_a F}$	0	$-\frac{RT}{(1-\alpha_a)n_a F}$
Case 9	$+\frac{RT}{(\alpha_c n_c + (1-\alpha_a)n_a) F}$	0	0

TABLE 2

THE SIGN OF THE DEPENDENCE OF  $E_{CORR}$  ON  $\ln c_{OX}^{\infty}$ ,  $\ln \omega$  AND  $\ln x_B$

	$\frac{\partial E_{CORR}}{\partial \ln c_{OX}^{\infty}}$	$\frac{\partial E_{CORR}}{\partial \ln \omega}$	$\frac{\partial E_{CORR}}{\partial \ln x_B}$
Case 1	+	0	0
Case 2	+	-	-
Case 3	+	-	0
Case 4	+	+	+
Case 5	+	0	0
Case 6	+	0	+
Case 7	+	+	0
Case 8	+	0	-
Case 9	+	0	0

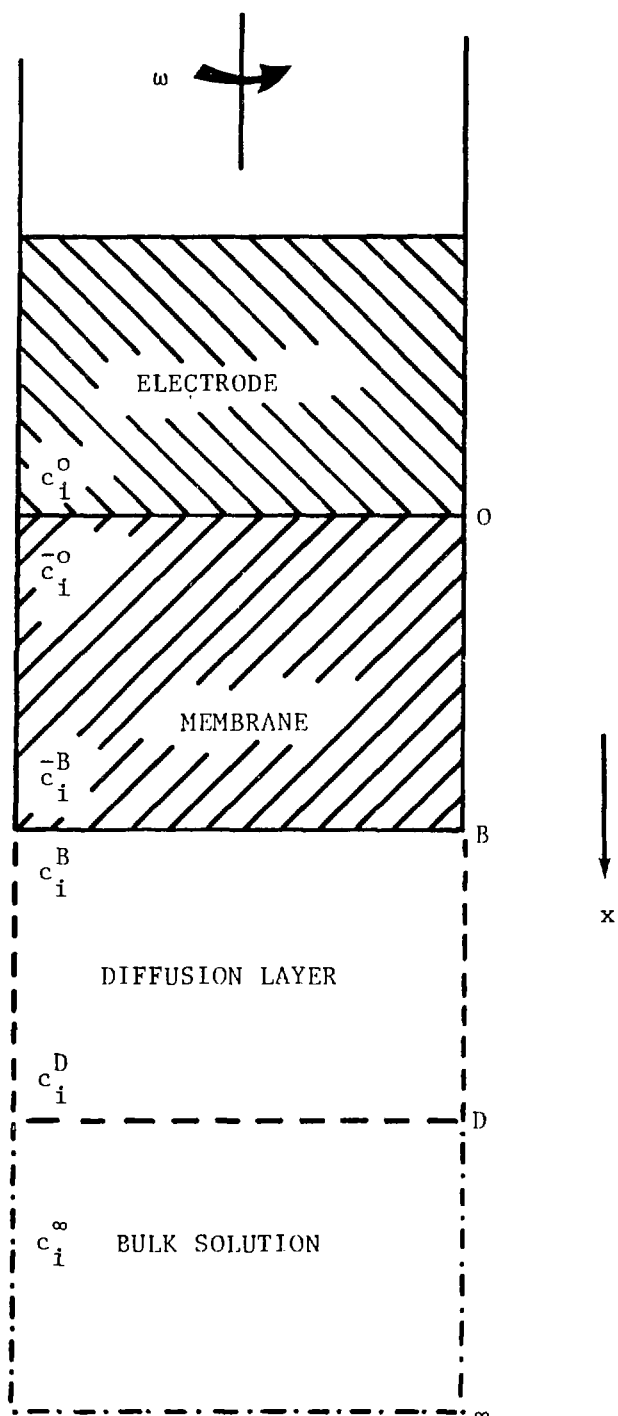


FIGURE 1: Schematic Representation of Layers Below a Membrane-Covered Rotating Disc Electrode

APPENDIX A

A.1 RATE CONTROLLED BY A TRANSPORT PROCESS

Suppose that the rates of both the anodic and cathodic electrode reactions are limited by the transport of species across either the diffusion layer or the membrane. Let  $c_i$  and  $\bar{c}_i$  be the solution and membrane phase concentrations of species  $i$ . Also, let the superscripts  $^o$  and  $B$  refer to the electrode surface/membrane and membrane/diffusion layer interfaces, respectively. Due to the stirring action, the concentration at the diffusion layer/bulk solution interface is the same as the bulk concentration,  $c_i^\infty$ . The membrane has a thickness  $x_B$  and the diffusion layer thickness is  $x_D$ .  $D_i$  and  $\bar{D}_i$  are the diffusion coefficients in the solution and in the membrane, respectively. These conditions are illustrated in Figure A.1.

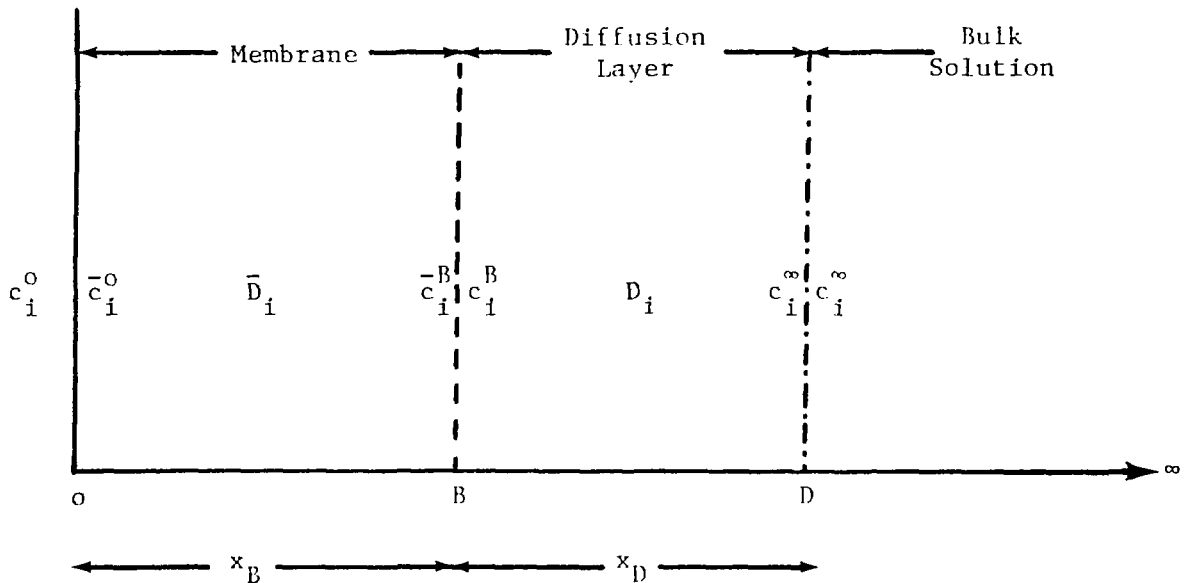


FIGURE A.1: Definition of Symbols

At steady-state, we shall assume that constant (i.e., linear) concentration gradients exist across the membrane and the diffusion layer. The flux,  $J_i$ , is given by Fick's 1st law. Hence, for the diffusion layer

$$(J_i)_{DL} = -D_i \frac{(c_i^\infty - c_i^B)}{x_D} \quad (A.1.1)$$

and for the membrane

$$(J_i)_{MEM} = -\bar{D}_i \frac{(c_i^B - c_i^o)}{x_B} = -K_i \bar{D}_i \frac{(c_i^B - c_i^o)}{x_B} \quad (A.1.2)$$

where  $K_i$  is the partition coefficient of species  $i$ .

Furthermore, at steady-state these fluxes are equal, so that

$$(J_i)_{DL} = (J_i)_{MEM} = J_i \quad (A.1.3)$$

Combining (A.1.1) and (A.1.2) by eliminating  $c_i^B$  gives

$$J_i = \frac{-K_i \bar{D}_i}{x_B} \left\{ c_i^\infty + \frac{x_D J_i}{D_i} - c_i^o \right\}$$

$$J_i \left\{ 1 + \frac{K_i \bar{D}_i x_D}{D_i x_B} \right\} = \frac{-K_i \bar{D}_i}{x_B} (c_i^\infty - c_i^o)$$

$$J_i = \frac{(D_i K_i \bar{D}_i / x_B x_D)}{\left( \frac{D_i}{x_D} + \frac{K_i \bar{D}_i}{x_B} \right)} (c_i^\infty - c_i^o) \quad (A.1.4)$$

This flux is also related to the current density,  $i$ , by

$$J = \frac{i}{nF} \quad (\text{A.1.5})$$

#### A.1.1 Rate Controlled by Transport Across the Diffusion Layer

If the permeability of the membrane is much greater than that of the diffusion layer, i.e.,

$$\frac{K \bar{D}_i}{x_B} \gg \frac{D_i}{x_D} \quad (\text{A.1.6})$$

then transport of species  $i$  across the diffusion layer will be the rate-controlling step. Equation (A.1.4) becomes

$$J_i = D_i \frac{(c_i^o - c_i^\infty)}{x_D} \quad (\text{A.1.7})$$

For a rotating disc electrode [4]

$$x_D = 1.612 \nu^{1/6} D_i^{1/3} \omega^{-1/2} \quad (\text{A.1.8})$$

##### (i) Anodic reaction

Let species  $m$  be the soluble product of the anodic electrode reaction. The flux of  $m$ ,  $J_m$ , is related to an anodic current density,  $i_a$ . If the experiment is arranged so that the bulk concentration of  $m$ ,  $c_m^\infty$ , is zero, Equation (A.1.7) gives

$$J_m = \frac{i_a}{n_a F} = D_m \left( \frac{c_m^o}{x_D} \right) \quad (\text{A.1.9})$$



As the electrochemical step is facile in comparison to transport across the diffusion layer it can be assumed to be at equilibrium. The Nernst equation can then be used to give  $c_m^\circ$

$$E = E_a^\circ + \frac{RT}{n_a F} \ln c_m^\circ \quad (\text{A.1.10})$$

Combining (A.1.8), (A.1.9) and (A.1.10) and rearranging gives

$$E = E_a^\circ - \frac{RT}{n_a F} \ln (0.62 n_a F D_m^{2/3} \nu^{-1/6} \omega^{1/2}) + \frac{RT}{n_a F} \ln i_a \quad (\text{A.1.11})$$

(ii) Cathodic reaction

Consider the transport of the oxidant species ox across the diffusion layer to the electrode surface where it is rapidly reduced. The fast kinetics of the electrode reaction ensure that the surface concentration,  $c_{\text{ox}}^\circ$ , is zero. The flux of oxidant to the electrode,  $J_{\text{ox}}$ , results in a cathodic current density,  $i_c$  (taken to be negative). From (A.1.7)

$$J_{\text{ox}} = \frac{i_c}{n_c F} = -D_{\text{ox}} \left( \frac{c_{\text{ox}}^\infty}{x_D} \right)$$

$$i_c = -0.62 n_c F D_{\text{ox}}^{2/3} \nu^{-1/6} \omega^{1/2} c_{\text{ox}}^\infty \quad (\text{A.1.12})$$

A.1.2 Rate Controlled by Transport Across the Membrane

If the permeability of the solution is much greater than that of the membrane, i.e.,

$$\frac{D_i}{x_D} \gg \frac{K_i \bar{D}_i}{x_B} \quad (\text{A.1.13})$$

then (A.1.4) becomes

$$J_i = \frac{K_i \bar{D}_i}{x_B} (c_i^\circ - c_i^\infty) \quad (\text{A.1.14})$$

(i) Anodic reaction

In this case, the rate of the anodic process is limited by the rate of transport of soluble corrosion product  $m$  through the membrane. Assuming the bulk concentration is zero and that the surface concentration is given by the Nernst equation, the anodic current density/potential relationship is

$$E = E_a^\circ + \frac{RT}{n_a F} \ln i_a - \frac{RT}{n_a F} \ln (n_a F K_m \bar{D}_m) + \frac{RT}{n_a F} \ln x_B \quad (\text{A.1.15})$$

(ii) Cathodic reaction

The rate of the cathodic reaction is limited by the rate of transport of oxidant to the electrode surface. Hence, the surface concentration,  $c_{\text{ox}}^\circ$ , is zero and the cathodic current density is given by

$$i_c = \frac{-n F K_{\text{ox}} \bar{D}_{\text{ox}} c_{\text{ox}}^\infty}{x_B} \quad (\text{A.1.16})$$

A.2 RATE CONTROLLED BY THE ELECTROCHEMICAL REACTION

When the rate of mass transport is fast compared to the rate of the surface reaction the concentration of the electroactive species is uniform, i.e., no concentration gradients exist. The current density/potential relationship is given by the Butler-Volmer equation [15]

$$i = i_o \left\{ e^{[(1-\alpha)nF\eta]/RT} - e^{-[\alpha nF\eta]/RT} \right\} \quad (\text{A.2.1})$$

where  $i_0$  is the exchange current density,  $\alpha$  is the transfer coefficient and  $\eta$  is the overpotential defined as

$$\eta = E - E_{eq} \quad (A.2.2)$$

where the equilibrium potential,  $E_{eq}$ , is given by the Nernst equation. The exchange current density is a function of concentration and is related to the standard exchange current density,  $i^0$  (which is not) by

$$i_0 = i^0 (c_o)^{(1-\alpha)} (c_R)^\alpha \quad (A.2.3)$$

where  $c_o$  and  $c_R$  are the concentrations of the oxidized and reduced forms of the electroactive species, respectively. Equation (A.2.1) applies to both anodic and cathodic reactions. We shall use the convention that anodic current densities and overpotentials are positive whilst cathodic current densities and overpotentials are negative.

(i) Anodic reaction

For large positive overpotentials the second term in the brackets in Equation (A.2.1) becomes small. So, for anodic electrochemical control (A.2.1) becomes

$$i_a = i_{o,a} \exp \left\{ (1-\alpha_a) n_a \frac{F}{RT} (E - E_{eq,a}) \right\} \quad (A.2.4)$$

where  $i_{o,a}$  is the anodic exchange current density and

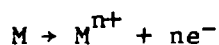
$$E_{eq,a} = E_a^0 + \frac{RT}{n_a F} \ln \frac{c_o}{c_R} \quad (A.2.5)$$

Combining (A.2.4) and (A.2.5) and substituting the standard exchange current density (Equation A.2.3) for  $i_{o,a}$  gives

$$i_a = i_a^\circ (c_o)^{(1-\alpha_a)} (c_R)^{\alpha_a} \left(\frac{c_R}{c_o}\right)^{(1-\alpha_a)} \exp\left[(1-\alpha_a) \frac{n_a F}{RT} (E-E_a^\circ)\right]$$

$$i_a = i_a^\circ (c_R) \exp\left[(1-\alpha_a) \frac{n_a F}{RT} (E-E_a^\circ)\right] \quad (\text{A.2.6})$$

For a metal dissolution reaction such as



the reduced form is the solid metal. Hence,  $c_R = 1$  and (A.2.6) rearranges to

$$E = E_a^\circ - \frac{RT}{(1-\alpha_a)n_a F} \ln i_a^\circ + \frac{RT}{(1-\alpha_a)n_a F} \ln i_a \quad (\text{A.2.7})$$

(ii) Cathodic reaction

For large negative overpotentials the first term in the brackets in Equation (A.2.1) becomes insignificant. Hence, the E/i relationship for an electrochemically controlled cathodic reaction is

$$i_c = -i_{o,c} \exp\left[-\frac{\alpha n F}{RT} (E-E_{eq,c})\right] \quad (\text{A.2.8})$$

where

$$E_{eq,c} = E_c^\circ + \frac{RT}{n F} \ln \frac{c_o}{c_R} \quad (\text{A.2.9})$$

and

$$i_{o,c} = i_c^\circ (c_o)^{(1-\alpha_c)} (c_R)^{\alpha_c} \quad (\text{A.2.10})$$

Substituting (A.2.9) and (A.2.10) into (A.2.8) gives

$$i_c = -i_c^\circ (c_o)^{(1-\alpha_c)} (c_R)^{\alpha_c} \left(\frac{c_o}{c_R}\right)^{\alpha_c} \exp \left[ -\frac{\alpha_c n_c F}{RT} (E-E_c^\circ) \right]$$
$$i_c = -i_c^\circ c_o \exp \left[ -\frac{\alpha_c n_c F}{RT} (E-E_c^\circ) \right] \quad (\text{A.2.11})$$

Using the notation in the text ( $c_{ox}^\infty$  instead of  $c_o$ ), Equation (A.2.11) rearranges to give

$$E = E_c^\circ + \frac{RT}{\alpha_c n_c F} \ln i_c^\circ + \frac{RT}{\alpha_c n_c F} \ln c_{ox}^\infty - \frac{RT}{\alpha_c n_c F} \ln |i_c| \quad (\text{A.2.12})$$

APPENDIX B

B.1 CASE 1: ANODIC REACTION SOLUTION TRANSPORT CONTROL; CATHODIC REACTION SOLUTION TRANSPORT CONTROL

The anodic half-reaction is described by

$$E = E_a^\circ - \frac{RT}{n_a F} \ln (0.62 n_a F D_m^{2/3} \nu^{-1/6} \omega^{1/2}) + \frac{RT}{n_a F} \ln i_a \quad (\text{A.1.11})$$

The cathodic half-reaction is described by

$$i_c = -0.62 n_c F D_{ox}^{2/3} \nu^{-1/6} \omega^{1/2} c_{ox}^\infty \quad (\text{A.1.12})$$

so that

$$\ln |i_c| = \ln (0.62 n_c F D_{ox}^{2/3} \nu^{-1/6}) + 1/2 \ln \omega + \ln c_{ox}^\infty \quad (\text{B.1.1})$$

$$\text{At } E = E_{CORR}, \ln i_a = \ln |i_c|$$

Substituting (B.1.1) in (A.1.11) at  $E = E_{CORR}$  gives

$$E_{CORR} = E_a^\circ - \frac{RT}{n_a F} \ln (0.62 n_a F D_m^{2/3} \nu^{-1/6} \omega^{1/2}) + \frac{RT}{n_a F} \ln (0.62 n_c F D_{ox}^{2/3} \nu^{-1/6})$$

$$+ \frac{RT}{2n_a F} \ln \omega + \frac{RT}{n_a F} \ln c_{ox}^\infty$$

$$E_{CORR} = E_a^\circ + \frac{RT}{n_a F} \ln \left( \frac{n_c D_{ox}^{2/3}}{n_a D_m^{2/3}} \right) + \frac{RT}{n_a F} \ln c_{ox}^\infty \quad (\text{B.1.2})$$

**B.2 CASE 2: ANODIC REACTION SOLUTION TRANSPORT CONTROL; CATHODIC REACTION  
MEMBRANE TRANSPORT CONTROL**

The anodic half-reaction is given by

$$E = E_a^\circ - \frac{RT}{n_a F} \ln (0.62 n_a F D_m^{2/3} \nu^{-1/6} \omega^{1/2}) + \frac{RT}{n_a F} \ln i_a \quad (\text{A.1.11})$$

The cathodic half-reaction is described by

$$i_c = - \frac{n_c F K_{ox} \bar{D}_{ox} c_{ox}^\infty}{x_B} \quad (\text{A.1.16})$$

so that

$$\ln |i_c| = \ln (n_c F K_{ox} \bar{D}_{ox} c_{ox}^\infty) - \ln x_B \quad (\text{B.2.1})$$

At  $E = E_{CORR}$ ,  $\ln i_a = \ln |i_c|$ . Substituting (B.2.1) in (A.1.11) gives

$$\begin{aligned} E_{CORR} &= E_a^\circ - \frac{RT}{n_a F} \ln (0.62 n_a F D_m^{2/3} \nu^{-1/6} \omega^{1/2}) \\ &\quad + \frac{RT}{n_a F} \ln (n_c F K_{ox} \bar{D}_{ox} c_{ox}^\infty) - \frac{RT}{n_a F} \ln x_B \\ E_{CORR} &= E_a^\circ - \frac{RT}{n_a F} \ln \left\{ \frac{0.62 n_a F D_m^{2/3} \nu^{-1/6}}{n_c K_{ox} \bar{D}_{ox}} \right\} + \frac{RT}{n_a F} \left\{ \ln c_{ox}^\infty - 1/2 \ln \omega - \ln x_B \right\} \end{aligned} \quad (\text{B.2.2})$$

**B.3 CASE 3: ANODIC REACTION SOLUTION TRANSPORT CONTROL; CATHODIC REACTION  
ELECTROCHEMICAL CONTROL**

The expression for the anodic half-reaction is

$$E = E_a^\circ - \frac{RT}{n_a F} \ln (0.62 n_a F D_m^{2/3} \nu^{-1/6} \omega^{1/2}) + \frac{RT}{n_a F} \ln i_a \quad (\text{A.1.11})$$

and for the cathodic reaction

$$E = E_c^\circ + \frac{RT}{\alpha_c n_c F} \ln c_{\text{ox}}^\infty + \frac{RT}{\alpha_c n_c F} \ln i_c^\circ - \frac{RT}{\alpha_c n_c F} \ln |i_c| \quad (\text{A.2.12})$$

At  $E = E_{\text{CORR}}$ ,  $\ln i_a = \ln |i_c|$ , so combining (A.1.11) and (A.2.12) gives

$$E_{\text{CORR}} = E_a^\circ - \frac{RT}{n_a F} \ln (0.62 n_a F D_m^{2/3} \nu^{-1/6} \omega^{1/2}) + \frac{RT}{n_a F} \frac{\alpha_c n_c F}{RT} \left\{ E_c^\circ - E_{\text{CORR}} + \frac{RT}{\alpha_c n_c F} \ln c_{\text{ox}}^\infty + \frac{RT}{\alpha_c n_c F} \ln i_c^\circ \right\} \quad (\text{B.3.1})$$

$$E_{\text{CORR}} \left\{ 1 + \frac{\alpha_c n_c}{n_a} \right\} = E_a^\circ + \frac{\alpha_c n_c}{n_a} E_c^\circ - \frac{RT}{n_a F} \ln (0.62 n_a F D_m^{2/3} \nu^{-1/6}) + \frac{RT}{n_a F} \ln i_c^\circ - \frac{RT}{2n_a F} \ln \omega + \frac{RT}{n_a F} \ln c_{\text{ox}}^\infty$$

$$E_{\text{CORR}} = \left\{ \frac{1}{n_a + \alpha_c n_c} \right\} \left\{ n_a E_a^\circ + \alpha_c n_c E_c^\circ - \frac{RT}{F} \ln (0.62 n_a F D_m^{2/3} \nu^{-1/6}) + \frac{RT}{F} \ln i_c^\circ - \frac{RT}{2F} \ln \omega + \frac{RT}{F} \ln c_{\text{ox}}^\infty \right\} \quad (\text{B.3.2})$$



B.4 CASE 4: ANODIC REACTION MEMBRANE TRANSPORT CONTROL; CATHODIC REACTION SOLUTION TRANSPORT CONTROL

The anodic reaction is given by

$$E = E_a^\circ + \frac{RT}{n_a F} \ln i_a - \frac{RT}{n_a F} \ln (n_a K_m \bar{D}_m) + \frac{RT}{n_a F} \ln x_B \quad (\text{A.1.15})$$

and the cathodic reaction is given by

$$i_c = -0.62 n_c F D_{ox}^{2/3} \nu^{-1/6} \omega^{1/2} c_{ox}^\infty \quad (\text{A.1.12})$$

so that

$$\ln |i_c| = \ln (0.62 n_c F D_{ox}^{2/3} \nu^{-1/6} \omega^{1/2} c_{ox}^\infty) \quad (\text{B.4.1})$$

At  $E = E_{CORR}$ ,  $\ln i_a = \ln |i_c|$ , so substituting (B.4.1) in (A.1.15) gives

$$\begin{aligned} E_{CORR} &= E_a^\circ - \frac{RT}{n_a F} \ln (n_a K_m \bar{D}_m) + \frac{RT}{n_a F} \ln x_B \\ &+ \frac{RT}{n_a F} \ln (0.62 n_c F D_{ox}^{2/3} \nu^{-1/6}) + \frac{RT}{2n_a F} \ln \omega + \frac{RT}{n_a F} \ln c_{ox}^\infty \\ E_{CORR} &= E_a^\circ + \frac{RT}{n_a F} \ln \left( \frac{0.62 n_c D_{ox}^{2/3} \nu^{-1/6}}{n_a K_m \bar{D}_m} \right) + \frac{RT}{n_a F} \left\{ \ln x_B + \ln c_{ox}^\infty + 1/2 \ln \omega \right\} \end{aligned} \quad (\text{B.4.2})$$

B.5 CASE 5: ANODIC REACTION MEMBRANE TRANSPORT CONTROL; CATHODIC REACTION MEMBRANE TRANSPORT CONTROL

The anodic reaction is given by

$$E = E_a^{\circ} + \frac{RT}{n_a F} \ln i_a - \frac{RT}{n_a F} \ln (n_a F K_m \bar{D}_m) + \frac{RT}{n_a F} \ln x_B \quad (\text{A.1.15})$$

and the cathodic reaction is given by

$$i_c = - \frac{n_c F K_{ox} \bar{D}_{ox} c_{ox}^{\infty}}{x_B} \quad (\text{A.1.16})$$

so that

$$\ln |i_c| = \ln (n_c F K_{ox} \bar{D}_{ox} c_{ox}^{\infty}) - \ln x_B \quad (\text{B.5.1})$$

At  $E = E_{CORR}$ ,  $\ln i_a = \ln |i_c|$ , so substituting (B.5.1) in (A.1.15)

$$\begin{aligned} E_{CORR} &= E_a^{\circ} - \frac{RT}{n_a F} \ln (n_a F K_m \bar{D}_m) + \frac{RT}{n_a F} \ln x_B + \frac{RT}{n_a F} \ln (n_c F K_{ox} \bar{D}_{ox}) \\ &\quad + \frac{RT}{n_a F} \ln c_{ox}^{\infty} - \frac{RT}{n_a F} \ln x_B \end{aligned}$$

$$E_{CORR} = E_a^{\circ} + \frac{RT}{n_a F} \ln \left( \frac{n_c K_{ox} \bar{D}_{ox}}{n_a K_m \bar{D}_m} \right) + \frac{RT}{n_a F} \ln c_{ox}^{\infty} \quad (\text{B.5.2})$$

B.6 CASE 6: ANODIC REACTION MEMBRANE TRANSPORT CONTROL; CATHODIC REACTION ELECTROCHEMICAL CONTROL

The anodic reaction is described by

$$E = E_a^\circ + \frac{RT}{n_a F} \ln i_a - \frac{RT}{n_a F} \ln (n_a F K_m \bar{D}) + \frac{RT}{n_a F} \ln x_B \quad (\text{A.1.15})$$

The cathodic reaction is given by

$$E = E_c^\circ + \frac{RT}{\alpha_c n_c F} \ln c_{\text{ox}}^\infty + \frac{RT}{\alpha_c n_c F} \ln i_c^\circ - \frac{RT}{\alpha_c n_c F} \ln |i_c| \quad (\text{A.2.12})$$

At  $E = E_{\text{CORR}}$ ,  $\ln i_a = \ln |i_c|$ , so substituting (A.2.12) in (A.1.15)

gives

$$E_{\text{CORR}} = E_a^\circ - \frac{RT}{n_a F} \ln (n_a F K_m \bar{D}) + \frac{RT}{n_a F} \ln x_B + \frac{RT}{n_a F} \frac{\alpha_c n_c F}{RT} \left\{ E_c^\circ - E_{\text{CORR}} + \frac{RT}{\alpha_c n_c F} \ln c_{\text{ox}}^\infty + \frac{RT}{\alpha_c n_c F} \ln i_c^\circ \right\} \quad (\text{B.6.1})$$

$$E_{\text{CORR}} \left\{ 1 + \frac{\alpha_c n_c}{n_a} \right\} = E_a^\circ + \frac{\alpha_c n_c}{n_a} E_c^\circ - \frac{RT}{n_a F} \ln (n_a F K_m \bar{D})$$

$$+ \frac{RT}{n_a F} \ln i_c^\circ + \frac{RT}{n_a F} \ln x_B + \frac{RT}{n_a F} \ln c_{\text{ox}}^\infty$$

$$E_{\text{CORR}} = \left\{ \frac{1}{n_a + \alpha_c n_c} \right\} \left\{ n_a E_a^\circ + \alpha_c n_c E_c^\circ - \frac{RT}{F} \ln (n_a F K_m \bar{D}) + \frac{RT}{F} \ln i_c^\circ + \frac{RT}{F} \ln x_B + \frac{RT}{F} \ln c_{\text{ox}}^\infty \right\} \quad (\text{B.6.2})$$

**B.7 CASE 7: ANODIC REACTION ELECTROCHEMICAL CONTROL; CATHODIC REACTION  
SOLUTION TRANSPORT CONTROL**

The anodic half-reaction is described by

$$E = E_a^\circ - \frac{RT}{(1-\alpha_a)n_a F} \ln i_a^\circ + \frac{RT}{(1-\alpha_a)n_a F} \ln i_a \quad (\text{A.2.7})$$

and the cathodic reaction by

$$i_c = -0.62n_c F D_{\text{ox}}^{2/3} \nu^{-1/6} \omega^{1/2} c_{\text{ox}}^\infty \quad (\text{A.1.12})$$

so that

$$\ln |i_c| = \ln (0.62n_c F D_{\text{ox}}^{2/3} \nu^{-1/6}) + 1/2 \ln \omega + \ln c_{\text{ox}}^\infty \quad (\text{B.7.1})$$

At  $E = E_{\text{CORR}}$ ,  $\ln i_a = \ln |i_c|$ , so substituting (B.7.1) in (A.2.7)

gives

$$\begin{aligned} E_{\text{CORR}} &= E_a^\circ - \frac{RT}{(1-\alpha_a)n_a F} \ln i_a^\circ + \frac{RT}{(1-\alpha_a)n_a F} \left\{ \ln (0.62n_c F D_{\text{ox}}^{2/3} \nu^{-1/6}) \right. \\ &\quad \left. + 1/2 \ln \omega + \ln c_{\text{ox}}^\infty \right\} \\ E_{\text{CORR}} &= E_a^\circ - \frac{RT}{(1-\alpha_a)n_a F} \ln i_a^\circ + \frac{RT}{(1-\alpha_a)n_a F} \ln (0.62n_c F D_{\text{ox}}^{2/3} \nu^{-1/6}) \\ &\quad + \frac{RT}{2(1-\alpha_a)n_a F} \ln \omega + \frac{RT}{(1-\alpha_a)n_a F} \ln c_{\text{ox}}^\infty \quad (\text{B.7.2}) \end{aligned}$$

**B.8 CASE 8: ANODIC REACTION ELECTROCHEMICAL CONTROL; CATHODIC REACTION  
MEMBRANE TRANSPORT CONTROL**

Equation (A.2.7) describes the anodic process

$$E = E_a^\circ - \frac{RT}{(1-\alpha_a)n_a F} \ln i_a^\circ + \frac{RT}{(1-\alpha_a)n_a F} \ln i_a \quad (\text{A.2.7})$$

For the cathodic reaction

$$i_c = - \frac{n_c F K_{ox} \bar{D}_{ox} c_{ox}^\infty}{x_B} \quad (A.1.16)$$

so that

$$\ln |i_c| = \ln (n_c F K_{ox} \bar{D}_{ox}) + \ln c_{ox}^\infty - \ln x_B \quad (B.8.1)$$

At  $E = E_{CORR}$ ,  $\ln i_a = \ln |i_c|$  and substituting (B.8.1) in (A.2.7)

gives

$$\begin{aligned} E_{CORR} = E_a^\circ - \frac{RT}{(1-\alpha_a)n_a F} \ln i_a^\circ + \frac{RT}{(1-\alpha_a)n_a F} \ln (n_c F K_{ox} \bar{D}_{ox}) \\ + \frac{RT}{(1-\alpha_a)n_a F} \ln c_{ox}^\infty - \frac{RT}{(1-\alpha_a)n_a F} \ln x_B \end{aligned} \quad (B.8.2)$$

B.9 CASE 9: ANODIC REACTION ELECTROCHEMICAL CONTROL; CATHODIC REACTION ELECTROCHEMICAL CONTROL

The anodic E/i relationship is

$$E = E_a^\circ - \frac{RT}{(1-\alpha_a)n_a F} \ln i_a^\circ + \frac{RT}{(1-\alpha_a)n_a F} \ln i_a \quad (A.2.7)$$

and the cathodic E/i relationship is

$$E = E_c^\circ + \frac{RT}{\alpha_c n_c F} \ln c_{ox}^\infty + \frac{RT}{\alpha_c n_c F} \ln i_c^\circ - \frac{RT}{\alpha_c n_c F} \ln |i_c| \quad (A.2.12)$$

At  $E = E_{\text{CORR}}$ ,  $\ln i_a = \ln |i_c|$  and substituting (A.2.12) in (A.2.7) gives

$$\begin{aligned}
 E_{\text{CORR}} &= E_a^\circ - \frac{RT}{(1-\alpha_a)n_a F} \ln i_a^\circ \\
 &+ \frac{RT}{(1-\alpha_a)n_a F} \frac{\alpha_c n_c F}{RT} \left\{ E_c^\circ - E_{\text{CORR}} + \frac{RT}{\alpha_c n_c F} \ln c_{\text{ox}}^\infty + \frac{RT}{\alpha_c n_c F} \ln i_c^\circ \right\} \\
 E_{\text{CORR}} \left\{ 1 + \frac{\alpha_c n_c}{(1-\alpha_a)n_a} \right\} &= E_a^\circ + \frac{\alpha_c n_c}{(1-\alpha_a)n_a} E_c^\circ \\
 &+ \frac{RT}{(1-\alpha_a)n_a F} \left\{ \ln c_{\text{ox}}^\infty + \ln i_c^\circ - \ln i_a^\circ \right\} \\
 E_{\text{CORR}} &= \left\{ \frac{1}{(1-\alpha_a)n_a + \alpha_c n_c} \right\} \left\{ (1-\alpha_a)n_a E_a^\circ + \alpha_c n_c E_c^\circ + \frac{RT}{F} \ln \left( \frac{i_c^\circ}{i_a^\circ} \right) \right. \\
 &\left. + \frac{RT}{F} \ln c_{\text{ox}}^\infty \right\} \tag{B.9.1}
 \end{aligned}$$

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