Multi-scale Modeling of the Corrosion of Metals
under Atmospheric Corrosion

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Abstract. A multi-scale model of atmospheric corrosion is applied to the corrosion of steel, zinc and aluminium in both the Infrastructure and Aerospace industries. The model has a modular structure and models processes from the global to the micron scale. The higher scales set the boundary conditions for the lower and the lower scales alter some of the constants in the upper scales. The model has primarily been designed for Australian conditions with a major focus on corrosion by marine aerosols. The upper level modules looks at aerosol production by the world’s oceans. This is then combined with surf-produced aerosols to give total aerosol production to estimate atmospheric aerosol concentration around Australia’s coast. The next level module looks at salt transport from the coastline across the Australian landscape to within the vicinity of infrastructure. A lower level module then looks at the deposition onto the infrastructure. Another group of modules looks at the surface response to both salt deposition and local climate including surface temperature, surface relative humidity, wetting and drying of deposited hygroscopic salts, rain deposition and rain and wind induced cleaning of the surface. The outcome of this series of modules is the ability to predict the “state” of a surface (every three hours) on different infrastructure types for locations throughout Australia. “State” could be that the surface is dry, wet from rain or wet from the wetting of hygroscopic salts.
This state model must be combined with a damage model to estimate the progression of damage since state of the surface changes with time. A number of models have been developed but they remain either probabilistic or empirical in nature. New research is being undertaken on both the experimental and modelling fronts to develop first principle models of corrosion under established oxide films. Experimental work has highlighted the importance of oxide stability within the zinc systems and indicates that the dissolution of zinc oxides can promote corrosion. Our modelling work looks at the interaction of solution chemistry, electrochemistry, mass transport, geometry and oxide growth under a marine aerosol droplet on a zinc surface. The model indicates that the drop size is a critical factor controlling the position of anodes and cathodes and the nature of oxide build up. In large droplets, the diffusion and surface availability of dissolved oxygen is higher near the edge of the droplet than at the centre. Hence preferential cathodic formation (both initiation and drifting) near the droplet edge promotes higher oxide growth near the edge. In small droplets, significant oxygen gradients are not established and the oxide growth is relatively uniform. The implication of these two modes on surface reactions and corrosion are discussed.

Introduction

From the 1970’s to 1990’s extensive studies[1-3] were undertaken to develop models of atmospheric corrosion by developing parametric models that linked climatic and pollutant parameters with mass loss as determined by field exposures. These models while accurate for the data set from which they were derived suffered from two limitations

a) Models developed from different countries were all different

b) Models could not be applied accurately in locations that were significantly different from those in which they were derived.
Partially as a result of this failure a number of workers looked at developing models based on the processes controlling corrosion. Early models of Spence and Haynie [4] and Lyon *et al.* [5] looked at processes of oxide dissolution and formation and of electrochemical processes within a droplet on a metal surface respectively. The field made a major advance with the work of Graedel [6] whose model the “Gildes” (Gas, Interface, Liquid, deposition layer, electroodic regime and solid) model looked systematically at the chemical interactions across a range of interfaces. Graedel applies the model to corrosion under moisture films on metal surfaces under relatively simple gaseous and interface regimes [6] and, therefore, a greater understanding is required of the external environment.

**Current State of Holistic Model**

The holistic approach was developed to deal with the complex environments that occur in atmospheric corrosion. It defines processes controlling atmospheric corrosion on a range of scales, from macro through meso to local, micro, micron and lastly electrochemical (Fig. 1), is one possible approach [7] to incorporating a detailed understanding of the external environment into process models. Macro refers to gross meteorological conditions (polar, subtropical etc.), “meso” refers to regions with dimensions up to 100 km², “local” is in the immediate vicinity of a building, while “micro” refers to the absolute proximity of a material surface. “Surface response” refers to largely physical responses of a surface such as deposition and retention of pollutants or condensation and evaporation. “Micron” refers to interactions within the metal/oxide/electrolyte interfaces. In the following sections the various components of the holistic model will be outlined.

**Salt Production**

In Australia, the main atmospheric pollutant is marine aerosols while marine aerosols are produced both in the open ocean and by breaking surf [7]. In the open ocean, aerosols are produced by whitecaps of ocean waves. Whitecap production varies systematically with longitude-latitude and season, being at a maximum at low latitudes in July and at a maximum at high latitudes in December, and
low all year round in tropical seas. Thus, tropical seas produce a relatively low volume of marine aerosol, resulting in decreased marine corrosion in near-equatorial regions. Experimental studies support this observation [8,9]. Surf aerosol production depends only on local wind speed and fetch [10].

Salt Transport

Factors controlling aerosol transport are also outlined in Cole et al. [7]. Aerosol residence times and thus transport distances are controlled by convection, gravity and aerosol scavenging by cloud drops, raindrops and physical objects on the ground (trees, buildings etc.). Thus, marine aerosol transport is likely to be favoured by dry climates with low rainfall and low ground coverage, while it will be restricted by humid and high rainfall climates with forest cover. Aerosols produced by surf tend to be coarse (5–20 µm) and those produced from whitecaps are generally smaller (0.5–3 µm). Thus, surf-produced aerosol rapidly deposits (due to gravity), while ocean-produced aerosol may be transported considerable distances. Experimental studies [8,9] support the terrain, climate and distance effects outlined above.

Salt Deposition

Marine aerosol deposition is primarily controlled by wind turbulence, and deposition onto an object is a function of turbulence intensity, wind speed, object shape and, to a lesser extent, aerosol size
For marine aerosols with sizes of 0.1 to 10 µm, the deposition efficiency (as a function of size) is relatively constant, while the efficiency increases rapidly for aerosol sizes above 20 µm, so that the efficiency of 100 µm aerosol is roughly four times that of the 20 µm aerosol. The size and shape of object is also important. The deposition on an exposed plate (at 45°) is likely to be more than 1.5 times that on an equivalently exposed salt candle. For complex forms such as dwellings, deposition efficiency will vary across a structure, with deposition being highest at the edges of the structure where turbulence is highest. Upstream turbulence promoted by ground roughness increases deposition by around 25% (in the case of forest).

Modes of Deposition

When an aerosol first breaks free of a wave it has seawater composition and then gradually equilibrates (and thus decreases in size). Thus, marine aerosols may take four forms [12] depending on time of flight and ambient RH, viz.: non-equilibrium near-ocean aerosol (size range 6–300 µm), wet aerosol (3–150 µm), partially wet aerosol (1–60 µm) and dry aerosol (<1–20 µm). When these aerosols are deposited on a metal surface, a number of characteristic surface “forms” result from the surface aerosol reaction [12]. These forms differ in the extent of retained salts, degree of surface alteration and in the formation of corrosion nodules. For example, when a wet aerosol impacts on an aluminium surface (limited initial reactivity), a cluster of deposited salt crystals are formed. These crystals have compositions of either NaCl, MgCl or CaSO₄, indicating that the original seawater solutions have segregated. In contrast, if the same aerosol impacts on a galvanised steel surface, there will be strong oxide growth on the surface (predominantly Simonkolleite and Gordaithe), with the retention of a NaCl crystal on this oxide layer.

GIS Formulation for Airborne Salinity

A GIS (geographical information system) system has been developed [13] to define the concentration of marine aerosol at the shoreline arising from both surf- and ocean-produced aerosol,
and then to estimate the transport of this aerosol to a given point inland. An Australia-wide map of airborne salinity has been derived and is presented in Figure 2.

Figure 2. Map of airborne salinity for Australia

Wetting and Surface Temperature

Mathematical models have been derived that estimate the surface temperature of an exposed surface considering undercooling to the night sky and daytime solar heating and convection effects [14] and validated experimentally[15]. Further work [16] predicts the RH at the metal surface and thus when hygroscopic salts (NaCl, MgCL) on the surface will wet. The evaporation of such moisture films has also been modelled [15] and validated experimentally [17] so a complete picture of moisture cycles has been developed. The role of wind and rain in removing deposited salts from the surface is also modelled [18,19].

Corrosion Models
To estimate the rate of corrosion the “state” of a surface is calculated on a 3 hourly basis. Four states are defined, State 1 – Dry, State 2 – Wet From Rain, State 3 – Wet From Wetting of Hygroscopic Salts, State 4 – Drying. A corrosion rate depending on pollutant levels is determined for each state from dose function tests in accelerated test chambers and then the annual corrosion is determined by summing the three hour corrosion rates. The A map of the estimated rate of corrosion of exposed zinc is presented in Figure 3. The predictions of the model are compared with measured one year data for 40 sites around Australia. The fit is quite high (R-sq= 0.82).

Figure 3. Map of corrosion rate of zinc (g/m2.year)
**Refinements to State Model**

The state model developed of Cole et al suffers a number of limitations

a) The damage module is empirical and thus cannot take into account microstructural features nor is it of use in the design of materials

b) The model assumes that marine aerosols have a sweater chemistry and that the aerosol is unaffected by transport from the source to the corroding object.

In order to address these issues research has been undertaken to

I. Look at the effect of acidified marine aerosol on atmospheric corrosion

II. Look at the physical /chemical and electrochemical mechanisms controlling droplet/metal interactions

III. Develop models of the physical /chemical and electrochemical mechanisms controlling droplet/metal interactions

The aim of this work is to replace the “state” model approach with a series of process based models that define the chemistry and electrochemistry that occur under a droplet and so predict corrosion rates from first principles. It is hoped that not only will such fully processed based multi-scale models not only be more accurate, have wider validity but will also assist in the design of new alloys and protective systems.

**Effect of marine Aerosols on atmospheric Corrosion**

Most models and experimental studies of atmospheric corrosion have assumed that metals are exposed to droplets or thin films composed of seawater or NaCl solutions. In fact as a marine aerosol is transported from its source to the corroding surface it will react with the atmosphere and may change both its pH and chemistry. A full review of this process may be found in Colet al[19].

Of particular important is the absorption in the most aerosols of acids (e.g. H$_2$SO$_4$, HCl, HNO$_3$) or
acid precursor (e.g. SO₂) which may shift the pH of the aerosol to values from 5 to 1 depending on conditions and aerosol size [19].

In order to assess the impact of acidified marine aerosol on the corrosion of zinc, a matrix of tests was undertaken in which the chemistry and size of droplets was changed (see table 1). The solution concentration were chosen as 20% represent a near saturation level of NaCl, 3.5% represent the total salt concentration in seawater, 2.4% represent the NaCl concentration in seawater, 0.05M MgCl₂ is the amount of MgCl₂ in seawater while the other MgCl₂ concentrations are to match the Cl concentrations in the NaCl solutions.

This matrix was repeated for droplets of 0.1 and 0.5 µl. The experimental method was as follows, high purity (99.9%) zinc mini plates (20 × 20 mm) were prepared by polishing with diamond particles of 9, 6, 3 and 1 micron then cleaned in ethanol and distilled water prior to application of droplets for 5 hours within a high humidity atmosphere (90%RH). At the end of experiment the droplets were allowed to evaporate in laboratory atmosphere and etched in a 20% chromium trioxide solution. The volume loss was determined by optical profilometry.

Table 1. Chemistry of Droplets and Number of Tests

<table>
<thead>
<tr>
<th>Base Solution</th>
<th>Concentration</th>
<th>HNO₃ pH = 1</th>
<th>0.1M HCl pH = 1</th>
<th>H₂SO₄ pH = 1</th>
<th>CF₃SO₂H pH = 1</th>
<th>No addition</th>
</tr>
</thead>
<tbody>
<tr>
<td>Natural seawater</td>
<td>5</td>
<td>5</td>
<td>5</td>
<td>5</td>
<td>5</td>
<td>5</td>
</tr>
<tr>
<td>NaCl</td>
<td>20%/3.42M</td>
<td>5</td>
<td>5</td>
<td>5</td>
<td>5</td>
<td>5</td>
</tr>
<tr>
<td>NaCl</td>
<td>3.5%/0.6M</td>
<td>5</td>
<td>5</td>
<td>5</td>
<td>5</td>
<td>5</td>
</tr>
<tr>
<td>NaCl</td>
<td>2.4%/0.42M</td>
<td>5</td>
<td>5</td>
<td>5</td>
<td>5</td>
<td>5</td>
</tr>
<tr>
<td>MgCl₂</td>
<td>1.7M</td>
<td>5</td>
<td>5</td>
<td>5</td>
<td>5</td>
<td>5</td>
</tr>
<tr>
<td>MgCl₂</td>
<td>0.3M</td>
<td>5</td>
<td>5</td>
<td>5</td>
<td>5</td>
<td>5</td>
</tr>
<tr>
<td>MgCl₂</td>
<td>0.05M</td>
<td>5</td>
<td>5</td>
<td>5</td>
<td>5</td>
<td>5</td>
</tr>
</tbody>
</table>

In figure 1-2 a number of interesting comparisons are given. Full results will be presented in a later paper. In Figure 1 the variation of volume loss for a 0.5µl drop with natural seawater, either without addition or acidified to a Ph of 1 with the four different acids. Each result is the average of 5 replicates. Interestingly while acidification with HCL significantly and with H2SO4 moderately
increases the volume loss over natural seawater, acidification with HNO3 and CF3SO3H lead to a lower volume loss. In figure 2 the volume loss associated NaCl and MgCl2 solutions with variation the salinity level for 0.5µl drops. Interestingly the volume loss deceases with increases salinity for NaCl solutions while for the MgCl2 solution it reaches a maximum at chloride concentration of 0.6M (for Cl). At the higher concentration the volume losses in MgCl2 and NaCl solution are comparable.

At present the factors causing these variations are being explored, including development of oxides and passivating layers, effect of anion concentration on oxygen solubility and thus the rate of cathodic reduction.
Physical/chemical and electrochemical mechanisms controlling droplet/metal interactions.
Models of the physical /chemical and electrochemical mechanisms controlling droplet/metal interactions.

Modeling efforts have focused on addressing two problems

I. How does the geometry of a droplet affect the chemical and electrochemical reactions that occur within a droplet

II. How does the development of a porous oxide affect the chemical and electrochemical reactions occurring either at the metal surface or on the pore boundaries

The solutions to these two problems would provide the core of a corrosion damage model for atmospheric corrosion that could be integrated with the remainder of the holistic model. Such an integrated model would not only be more accurate but could also assess the impact of microstructure and oxide development on corrosion.

Droplet Model.

Since the pioneering work of Evans it has been known that a droplet can establish zones of differing oxygen concentration and thus can establish zones where cathodic or anodic activity is preferred. However despite some interesting refinement to Evans original work by Lyon et al., there has not been a rigorous treatment of the problem under droplets of varying size. This is of particular importance atmospheric corrosion where it is promoted by aerosol (size range 1-150µm) deposition or rain drop deposition (0.5 to 3 mm) as the balance of oxygen diffusion and electrochemical activity (and thus the Evans mechanisms) may be expected to vary across this range.
Model Assumptions. Fig. 1 shows half of a hemispherical aerosol droplet deposited on a bare metal surface devoid of oxide and/or other films. Oxygen diffuses through the film from the atmosphere to the metal surface and gets reduced. Zinc undergoes anodic dissolution. The species that are involved in the system are shown. The model assumes: isothermal conditions with no convection and no gas generation, dilute solution theory, the anodic and cathodic reactions can be described by the Butler-Volmer equation while no heterogeneous (incl. precipitation) or homogeneous chemical reactions occur in the film. For a full description of the governing equations see Venkatraman et al.

![Fig 1. Schematic of a droplet on a metal surface with oxygen in the atmosphere diffusing through it. The oxygen reduction towards the edge of the droplet causes anode-cathode separation.](image)

1. $\text{M}^{2+}$
2. $\text{OH}^-$
3. $\text{O}_2(aq)$
4. $\text{Na}^+$
5. $\text{Cl}^-$

The model predicts that in the initial stage, there is no separation of anodic and cathodic regions. Once the oxygen gradients are established, the region where there is less depletion of oxygen due to sufficient replacement by diffusion would become cathodic and vice-versa. A generalized boundary condition allowing for both the reactions to occur all over the metal surface is used. The local rate and extent of the reactions would depend on the local concentrations and overpotential and anode-cathode separation would evolve as a result. Thus we have
\[ i_{\text{Zn/Zn}^+} = i_{\text{Zn/Zn}^+} \exp \left( \frac{2}{R} \frac{1 - \alpha_{\text{Zn/Zn}^+}}{T} \frac{F}{E_{\text{corr}} - E_{\text{Zn/Zn}^+}^{\text{eq}}} \right) \]

(12)

\[ i_{\text{O/\text{OH}^+}} = -i_{\text{O/\text{OH}^+}} \exp \left( \frac{-2(1 + \alpha_{\text{O/\text{OH}^+}})F}{RT} \frac{E_{\text{corr}} - E_{\text{O/\text{OH}^+}}^{\text{eq}}}{C_{\text{O/\text{OH}^+}} - C_{\text{O/\text{OH}^+}}^{\text{eq}}} \right) \]

(28)

**Fig 2:** \( \left( \frac{C_{\text{Zn}^{2+}}}{C_{\text{Zn}^{2+}}^{\text{eq}}} \right) \) of zinc ions and arrow plot of current density vectors showing separation of metal surface into anodic and cathodic regions with time.
where $i_{\text{Zn/Zn}^2^+}$ and $i_{\text{O/H}^2^+}$ are the current densities, $i_{\text{eq,Zn/Zn}^2^+}$ and $i_{\text{eq,O/H}^2^+}$ are the equilibrium exchange current densities, $E_{\text{Zn/Zn}^2^+}^\text{eq}$ and $E_{\text{O/H}^2^+}^\text{eq}$ are the equilibrium potentials, and $\alpha_{\text{Zn/Zn}^2^+}$ and $\alpha_{\text{O/H}^2^+}$ are the transfer coefficients of zinc dissolution and oxygen reduction respectively. $E_{\text{corr}}$ is the local corrosion potential and $C_i^\text{eq}$ is the equilibrium concentration of species $i$ corresponding to the equilibrium potentials. The inward normal species flux at the metal surface is given by [3]:

$$N_n = \sum s_i F_i$$

where $s_i$ is the stoichiometric coefficient of species $i$ in the $j^{th}$ electrode reaction. The ionic fluxes at the droplet-air interface are zero whereas the concentration of oxygen at that interface is assumed to be equal to its saturation value at given temperature and pressure. The model is non-dimensionalized ($x$ and $y$ against radius $R = 10^{-6}\text{m}$ of the droplet, concentrations against the initial concentration and time $t$ against $\frac{R^2}{D_{\text{ref}}}$ where $D_{\text{ref}} = 10^{-7}\text{cm}^2\text{s}^{-1}$) and implemented in COMSOL™.

**Results**

Fig 2 shows the results of one of the simulations performed. The arrows represent the current density vectors and the contours represent the concentration of Zn$^{2+}$ ions (non-dimensionalized against initial concentration of $10^{-6}\text{M}$). The highest concentration of the zinc ions is predicted near the metal surface with an accumulation towards the cathodic region. This is attributed to the lack of any scavenging mechanism like precipitation of corrosion products namely oxides, hydroxides, chloro-hydroxides, sulfates and carbonates. Fig. 2 also shows how the current within the droplet enters from the anodic region and terminates in the cathodic region indicating separation. Figure 3 shows the oxide concentration in the droplet as a function of $kR/D$, where $k$ is the reaction rate constant, $R$ is the radius of the droplet and $D$ is the diffusion coefficient of dissolved oxygen.
If the diffusion rate was greater or of the same order as consumption, there would be insignificant variation in oxygen concentration and thus there would not be a strong drive to establish cathodic zones based on oxygen concentration. As the drop size decreases, the diffusion rate will increase, while the consumption rate will remain approximately the same. In contrast, as the consumption rate increases above the diffusion rate, sharp gradients in concentration will be established and cathodic zones will form at the edge of a drop. In Table 8 values of $kR/D$ are given as a function of drop radius and oxide porosity. This table is derived under the following assumptions:

- The annual corrosion rate is 7g/m$^2$/year with a time of wetness of 33% and thus an effective corrosion rate of 21g/m$^2$/year when the surface is wet.
- The diffusivity of oxygen is $1.97 \times 10^{-9}$ m$^2$/s at 20 deg C.

Thus significant cathodes will occur if the porosity is less 0.2 for large rain drops or 0.1 for small drops and 0.01 for 100 µm aerosol droplets. The value of $\epsilon$ varies according to the oxide structure with a typical value for zinc oxide being given by Aurian-Blajeni and Tomkiewicz$^{64}$ as 0.276. Thus this model predicts that significant oxygen differentials will only occur for oxide covered large drops.

Table 8. Values of “$kR/D$” as a function of porosity and drop diameter.

<table>
<thead>
<tr>
<th>Porosity ((\epsilon))</th>
<th>Diameter of the Droplet (D)</th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1µm</td>
<td>100 µ</td>
<td>1000 µ (1 mm)</td>
<td>3mm</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>$2.15 \times 10^{-5}$</td>
<td>$2.15 \times 10^{-5}$</td>
<td>$2.15 \times 10^{-4}$</td>
<td>$6.45 \times 10^{-2}$</td>
<td></td>
</tr>
<tr>
<td>0.8</td>
<td>$3.00 \times 10^{-5}$</td>
<td>$3.00 \times 10^{-5}$</td>
<td>$3.00 \times 10^{-4}$</td>
<td>$9 \times 10^{-2}$</td>
<td></td>
</tr>
<tr>
<td>0.6</td>
<td>$4.60 \times 10^{-5}$</td>
<td>$4.60 \times 10^{-5}$</td>
<td>$4.60 \times 10^{-4}$</td>
<td>$1.38 \times 10^{-1}$</td>
<td></td>
</tr>
<tr>
<td>0.4</td>
<td>$8.49 \times 10^{-5}$</td>
<td>$8.49 \times 10^{-5}$</td>
<td>$8.49 \times 10^{-4}$</td>
<td>$2.55 \times 10^{-1}$</td>
<td></td>
</tr>
<tr>
<td>0.2</td>
<td>$2.40 \times 10^{-4}$</td>
<td>$2.40 \times 10^{-4}$</td>
<td>$2.40 \times 10^{-3}$</td>
<td>$7.2 \times 10^{-1}$</td>
<td></td>
</tr>
<tr>
<td>0.1</td>
<td>$6.79 \times 10^{-4}$</td>
<td>$6.79 \times 10^{-4}$</td>
<td>$6.79 \times 10^{-3}$</td>
<td>$2.04$</td>
<td></td>
</tr>
<tr>
<td>0.05</td>
<td>$1.92 \times 10^{-3}$</td>
<td>$1.92 \times 10^{-3}$</td>
<td>$1.92$</td>
<td>$5.76$</td>
<td></td>
</tr>
<tr>
<td>0.01</td>
<td>$2.14 \times 10^{-2}$</td>
<td>$2.14$</td>
<td>$21.4$</td>
<td>$64.2$</td>
<td></td>
</tr>
</tbody>
</table>
Figure 8. Contours of non-dimensional oxygen concentration (top), and line plot variation of non-dimensional local concentration of oxygen along the line y=0. Note that the oxygen concentration goes to zero as the reaction rate increases in comparison with the diffusion rate (i.e. \( k/D >> 1 \)).

**Porous Model.**

A model addressing the effects of a porous oxide layer on the corrosion of metallic surface was developed (16) based on the macro-homogeneous theory of porous electrodes and dilute solution theory with a Nernst-Planck formalism. The porous electrode theory has been successfully applied to battery electrodes (17,18) and membranes to predict the concentration and current distributions but never in the context of corrosion. The theory assumes a superposition of two macroscopic continua – a solid matrix and a fluid electrolyte – and develops equations based on the interfacial reactions between the matrix and fluid and conservation of species and electric charge. In our model, we consider both the metal surface and the porous oxide to be potential sites for cathodic oxygen reduction reaction. Such a situation arises in zinc since the zinc oxide is a semiconductor and the work functions of both zinc and zinc oxide are not very different (19). Thus, the oxygen reduction reaction which needs a supply of electrons can be supported on the zinc oxide to some extent. Our model computes the extent to which such a competition between zinc oxide and zinc surface happens and also predicts the corrosion potential and corrosion current density as a function of time. Figure 6 shows a typical profile of oxygen in the porous oxide layer at various times and the associated variation of corrosion current density with time for such a system.

Normalised time is given by:

\[ \tau = t \frac{d}{L^2} \]

where \( t \) is time (in seconds), \( d \) is the diffusion coefficient of oxygen \( (5 \times 10^{-10}) \) and \( L \) the oxide thickness. Measurement by Cole et al indicate that under a saline drop an porous oxide thickness of...
around 1µm develops after 15-30 minutes, thus \( \tau = 500 \) and thus the fall in \( i_{\text{corr}} \) indicated in figure 6 will be very rapid for the zinc system. This fall is associated with the build up of zinc ions (which is driven by the strong anodic dissolution current for zinc) in the vicinity of the anode (at the bottom of the pore) and subsequent restriction of anodic activity.

In its present form the model does not include precipitation, however the model identifies where the cathodic reactions occurs (on the metal surface or on the oxide). It would be expected that the local variations in pH would be heavily influenced by the cathodic position so that if oxygen reduction occurs on pore walls, higher pH’s would be established at that point which would promote precipitation.

Figure 6. (a) Profile of non-dimensional concentration of oxygen \( \Theta \) along the porous oxide layer at various instants of non-dimensional time \( \tau \). The metal surface is at \( \tau = 0 \) and the oxide which is
filled with electrolyte ends at \( t = 1 \). (b) Variation of nondimensional corrosion current density with non-dimensional time

Thus the model can link microstructure with oxide formation and thus electrochemical activity and oxide growth. It thus has the potential to address how corrosion rates can change with time.

**Integration of Models into Holistic Framework**

The models outlined with form the core of the electrochemical/micron scale modules of the holistic model. It is proposed that:

1. Precipitation and oxide growth be incorporated into the porous oxide model.
2. The revised porous oxide model and the droplet model be integrated into one framework

This combined electrochemical model will be able to model oxide growth and changes in oxide properties over time and how these changes and driven by and in turn effect both anodic and cathodic activity and pore and solution chemistry. It will thus be able to model corrosion rates with time under a single droplet. The holistic model requires information of corrosion rate over a whole metal surface. To provide such information the following schema is proposed. The component surface will be divided into a fine grid and for each grid a series of attributes will be defined (oxide type, thickness, and porosity, deposited salts, summed corrosion). The holistic model will be run but deposition phenomena (aerosol and rain) will be randomized onto the grid so that for each grid unit may be underplayed by part of an aerosol or raindrop or may be free of such forms. The results of the combined electrochemical model will be parameterized defining changes in oxide properties and thickness and corrosion rate as a function of droplet chemistry, pre-existing oxide and time and the parameterized rules than applied to each grid unit and a new set of characteristics determine.
This approach assumes that corrosion of the surface progresses in a uniform way into the metal surface. However the FIB work of Cole et al indicates that localized attack may occur under an oxide film while that the pencil electrode studies in this paper indicate that pits may propagate in zinc at relatively low salt concentrations. Thus it maybe necessary to develop a module that defines local attack under an oxide film (possible based on a modified Galvele approach and integrates this into the combined electrochemical model.

The revised holistic model should also be able to account for effect of acidified marine aerosols. The combined electrochemical model should be able to account for the effect of variations in droplet chemistry on oxide growth and electrochemical activity, it will however need to incorporate oxide dissolution due to the initial reactions between the oxide and the acidified drop. Consideration will also have to be made to decide how to incorporate the damage forms that result from acidic dissolution into the “attributes” that define the state of the oxide for the holistic model. For example acidic dissolution could be considered a general phenomena that changes oxide porosity.

**Conclusion**

**References**


