Diffusion and Uptake of Moisture through Paint Films Leading to Corrosion of Metal Substrates: A Diffusion - Adsorption Model with Reaction.

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ABSTRACT-

Corrosion occurs in response to the availability of water, oxygen and other agents at metal surfaces. The rate of corrosion depends critically upon the concentrations of these agents. At a metal surface protected by a paint layer, these concentrations are governed by diffusion through the paint film and by adsorption onto the metal surface in competition with polymer molecules of the adherent paint film. A mathematical model is developed for this problem and its behaviour and evolution in time is analysed.

The conceptual basis of this model is different from others in that it combines equations of diffusive processes with equations of paint film adherence (competitive adsorption) at the metal surface. The corrosion process is considered to arise through boundary conditions for the diffusion equations with rates governed by variables described in the competitive adsorption equations. The nonlinearity of these competitive adsorption equations is the key to describing long periods of protective action provided by paint films, with negligible corrosion of the metal substrate, followed by the sudden onset of rapidly accelerating corrosion and the consequent accumulation of corrosion product (rust). Concomitant loss of competitive adsorption (adhesion) by the paint film is a typical end result.

Electrochemical activity of the metal substrate is evaluated as a corrosion current. This is determined by concentrations of water and oxygen in the internal environment, and by chemical activity in the adsorbed layer. The mechanism of corrosion of a painted metal surface is theorised to occur through active sites not covered by adsorbed polymer, water or oxygen.

Numerical simulations were done using a detailed computer algorithm developed specifically for this purpose. These simulations give insight into the model's behaviour and aid determination of simplified constitutive relationships which lead to a simplified model which allows easy determination of the thresholds for the onset of rapid corrosion.

It turns out that the diffusion of water and oxygen through the paint film is normally very quick. The rate determining step is directly related to the competition between water, oxygen and coating polymer adherent to the metal surface, and coating polymer adherent to corrosion product. Once zinc (or any other metal) ions approach saturation in solution at the metal surface, the coating polymer approaches saturation with zinc and loses competitive adsorption onto the metal surface. Crystallinity of the adsorbed polymer declines and chemical activity coefficients in the adsorbed layer are reduced. Concentrations of water and oxygen in the adsorbed layer increase and metal active sites are exposed. The result is a surge in the rate of corrosion leading to the rapid formation of corrosion product. This in turn leads to enhanced degradation and free corrosion of the metal surface.

ACKNOWLEDGEMENTS

Note: While not referred to specifically in the text we have made general use of the following texts: Birkhoff and Rota (1962); Cesari (1963); Lefschetz (1959); Murray (1974); Roberts and Kaufman (1966); Sperb (1981); and Verhulst (1963)

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1. INTRODUCTION

1.1 BACKGROUND

A number of authors have studied corrosion of painted metal surfaces. Mayne (1957), Cherry and Mayne (1961), Maitland and Mayne (1962), Cherry and Mayne (1965), and Cherry (1974) concluded that ionic resistance rather than diffusion of water and oxygen was the rate limiting process of corrosion. Guruviah (1970) challenged Mayne's conclusions, and proposed that oxygen may be rate determining. Kresse (1973) found that water was rate determining and not oxygen or ions.

Haagen and Funke (1975) found that in general the water permeability of coatings was sufficiently great to supply all the water necessary for corrosion to proceed at the coating metal interface. However this was not always the case for oxygen where the permeation rate for oxygen may be lower than is needed for the corrosion process. Experimental data was compared for permeabilities of water, oxygen and ions which supported their case. They wrote "the permeability of anions such as Cl^- and $(SO_4)^{2-}$ is extremely low, so that underfilm corrosion caused by them must be due to contamination of the surface prior to coating and not to their diffusion through the film." They noted also that "the observation that cathodic blisters are highly alkaline provides strong evidence that paint films are impermeable also to hydroxyl ions". Nguyen et al. (1996) would reason later that mass diffusion of electrolyte may occur through tortuous transmembrane pores in a coating represented as an impermeable slab.

Parker and Gerhart (1967), Funke and Haagen (1978), and Funke (1979, 1985) found that corrosion protection depended upon adhesion. Floyd et al. (1983) found that water permeabilities and ionic conductance best predicted corrosion performance of a range of coatings (although oxygen permeability was not considered and some conflicting results were noted). Leidheiser (1983)

considered eight aspects of coatings corrosion performance, and found that cathodic delamination was generally the critical factor. Deslouis et al. (1993) and Hoffmann et al. (1993) found that specific adsorption of organic surfactants and organophosphates (respectively) inhibited corrosion. Leng et al. (1993) considered adsorbed electrolyte layers and found that corrosion depended upon both adsorbed electrolyte layer thickness and organic inhibitor concentration.

Nguyen et al. (1994) used FTIR-MIR (Fourier Transform Infra Red - Multiple Internal Reflection) spectroscopy to determine water uptake of coated substrates. They supposed that a substrate surface may consist *of* sorption sites and inferred that both water and polymer may adsorb onto these sites. They found experimentally that water entered the interfacial region where typically it displaced adsorbed polymer resulting in polymer disbondment. For Alkyd and Epoxy coatings on Germanium and Silicon they found an initial rapid uptake occurring in a period of about 10 hours, followed by a slow secondary uptake occurring over periods of hundreds of hours. It was noted that after the exposures to water the coatings had lost most of their bond strength to the substrates. They concluded that water sorption at the coating-substrate interface was the critical factor for coating performance. Exposure to water resulted in water adsorption at the interface which caused disbondment of the coating which they argued would then lead to corrosion of metallic substrates.

Wettech (1961) considered oxygen and rusting, and Fitzwater (1981) considered permeability of coatings to oxygen, water and ions in the rusting process. Katz and Munk (1969), Anderton (1970), Boxall et al. (1970), Yasheen (1970), Aithal et al. (1990), Hendricks and Balik (1990), and Xiao et al. (1990) studied permeability properties of coatings. Ulfvarson and Khullar (1971) and Fialkiewicz and Szandorowski (1974) studied ion exchange properties and Rothwell (1969) studied electrical resistance of coatings in relation to their corrosion protection, and Funke (1967) and Gowers and Scantlebury (1987) studied adhesion. Burgess et al. (1981) considered paint and polymer design as

factors affecting corrosion, Kumins (1980) considered polymer physics, Thomas (1992) considered barrier properties, and Sekine et al., (1992) considered frequency at maximum phase angle, and Bellucci and Nicodemo (1993) considered water transport in terms of Electrochemical Impedance Spectroscopy.

A number of mathematical models have been proposed to account for aspects of coatings behaviour. Diffusion of various substances has been studied and modelled by many authors (Crank, 1979). A good example of this approach is the work by Perera and Heertjes (1971 a-f) who modelled diffusion through paint films and water cluster formation. Bagda (1988) modelled water transport in coatings to obtain diffusion coefficients. The Mathematics in Industry Group (1984) considered models of diffusion through paint films and blister growth. Nguyen et al. (1991) considered blister formation to depend on diffusion in the paint - metal interface on a two dimensional basis. Rosen and Martin (1991) modelled water uptake of coatings with sorption isotherms, and Ohno et al. (1992) studied diffusion and adhesion. Barnett et al., (1984) proposed an RC (Resistance-Capacitance) equivalent circuit to describe diffusion of water, and Láng et al (1992) discussed a more complex RC equivalent circuit model. Nguyen et al. (1996) presented a cathodic blistering and delamination model based on multi-step degradation and mass diffusion of electrolyte through an impermeable slab punctured by tortuous transmembrane pores.

In contrast to diffusion processes, relatively few attempts have been made to model corrosion processes and it is only in the last few years that attention has turned to this problem on a theoretical level. Only a few studies have considered models combining corrosion processes with diffusion (eg Tang and Song 1993) and these ideas have not yet been applied to metal surfaces protected by polymeric coatings. Electrochemical theory and the general chemistry of corrosion have been known for some time and Boulton and Wright (1979), Chilton (1969), Evans (1950), and Uhlig (1948) have described the general principles of corrosion. Evans (1950) proposed a number of semi - empirical

models to account for corrosion of various metals under a variety of conditions. De Chialvo et al. (1988) studied the corrosion and passivity of copper in electrolyte solution.

Tang and Song (1993) proposed an adsorption electrochemical system for organic surfactants to model corrosion potential. They considered organic inhibitors which adsorb onto metal surfaces to form a protective layer which retards the action of corrosively active species toward the metal. The adsorption-desorption reaction was expressed as an equation. From this they used electrochemical kinetics to infer the adsorption and desorption currents based on the rate constants of the adsorption and desorption equation. Rate constants for adsorption and desorption were based on an Arrhenius type law, and they supposed that the adsorption current included a dependence upon a surface coverage fraction of the form $(1-\theta)$. They derived expressions for adsorption and desorption currents from which was derived an expression for the electrochemical potential voltage. Experimental results were compared with numerical results from the mathematical model. They found that their model can "represent well the Potentiostatic-Galvanostatic response characteristics of passive systems with adsorption".

However, most of the work in this area has been to develop empirical models of coated and uncoated metals which predict corrosion rates or concentrations on the basis of environmental factors. Ailor (1982) gives a detailed summary of these models. Spence et al. (1992) develop and evaluate a comprehensive model of this type for uncoated galvanised steel structures. They use an empirical linear zinc corrosion function combined with a competing mechanism for dissolution of corrosion product.

The studies indicated above attempting to determine what limits the rate of corrosion of painted metal surfaces (eg diffusion of water, of oxygen, of ions, etc) have typically approached the problem by comparing diffusion fluxes with

corrosion rates. A common technique is to measure the flux of water diffusing through a prepared free film of the coating under consideration, generally using high differential partial pressures. Invariably the fluxes of water or oxygen are found to be greater than required to support observed corrosion rates. In fact it is usually found that diffusion fluxes are comparable or greater than those required to support maximum corrosion rates occurring on uncoated metal surfaces. Variations of the diffusion approach have proposed the presence and diffusion of ions as empirical factors which control corrosion.

The most consistent result of these studies has been that diffusion alone does not generally appear to limit corrosion rates. Floyd et al. (1983) considered multivariate statistical analysis of various parameters and found partial correlation between diffusion and corrosion resistance. The correlation improved when coating resistance was included as a second variable in the multivariate analysis. But while some correlation was found between permeability to water and corrosion rate, the water vapour transmissions quoted exceeded in all cases the fluxes involved in freely corroding uncoated steel.

Recent studies have approached the problem by focussing on the substrate surface and the substrate-coating interface. Some researchers have looked at adsorption of organic molecules onto the substrate, for example Deslouis et al. (1993), Hu and Do (1995), Müller (1995); and others at the quantity of water or electrolyte sorbed at the substrate-coating interface, for example Nguyen et al. (1994) and Nguyen et al. (1995). Song and Cao (1990) and Tang and Song (1993) combined organic molecule adsorption dynamics with electrochemical corrosion theory to model pitting corrosion processes.

While these approaches provide vital insights into corrosion processes they address only a part of the problem. We believe that the problem to be addressed consists of two major parts: diffusion through a polymer (paint) film; and competitive adsorption of polymer and corrosive species onto a metallic

substrate. We derive corrosion activity from the state of competitive adsorption on the substrate. Additionally these two parts must be coupled together to produce a coherent system.

1.2 ADSORPTION AND CORROSION

Painted metal surfaces exhibit interaction between paint and metal substrate. One aspect of this interaction is the generation of adhesion. The adsorption (ie physisorption) and in some cases chemical reaction and chemisorption, of paint film polymer molecules onto a metal creates adhesion (Bikerman, 1967; Voyutskii and Vakula, 1963; Brewis and Briggs, 1981; Allen, 1993). In practice even very clean metal substrates contain a certain amount of metal oxide due to reaction of the metal surface with atmospheric oxygen and moisture. Coating's polymers have been shown to adsorb onto various metal oxide surfaces (Franklin et al., 1970; Hegedus and Kamel, 1993d; Idogawa and Shimizu, 1993; Sato, 1990; Sato, 1993).

Additionally interactions of polymer molecules with substrates produces modification of the polymer's natural conformation. Léger et al., 1992 found a drastic slowing down of the polymer chains in the immediate vicinity of a solid surface. Deng and Schreiber, 1991; Russell, 1991; and Vogel and Shen, 1991 found that the nature of the interface governed the orientation and conformation of polymers adjacent to the interface. Hegedus and Kamel, 1993c found that the adsorbed polymer layer thickness varied with the nature of the interaction. Long range restriction of polymer segment mobility is also revealed by nuclear magnetic resonance effects, glass transition changes, alteration in mechanical properties, and by decrease in capacity for vapour and solvent uptake (Kumins, 1980; Kumins and Kwei, 1968; Lara and Schreiber, 1991; Kumins et al., 1994). Boczar et al., 1993 showed that polymer interdiffusion occurs during film formation and during film aging and annealing, and that polymer composition

plays a large role in controlling rates of interdiffusion and hence in the resultant interfacial polymer configuration.

The extent and magnitude of segment mobility restriction influences the barrier resistance to, and diffusion and chemical potential of, diffusant molecules in this adsorbed polymer layer (Hegedus and Kamel, 1993b,d; Kumins et al., 1994). Additionally, the presence of diffusant molecules such as water leads to some desorption of polymer from the metal surface as both compete for adsorption sites. If previously adsorbed polymer cannot be easily displaced by a water molecule, the metal (iron, zinc, or whatever) corrosion rate should be less, since the sites susceptible to corrosion would be better protected by the more strongly adhering polymer molecules (Kumins, 1980; Tang and Song, 1993).

The corrosion process is treated in electrochemical theory as two chemical half reactions occurring at anodic and cathodic sites on the metal surface (Boulton and Wright, 1979). The electrical current associated with the chemical reaction is carried by electrons and ions. Typically electrons move in the metal while ions move in an adsorbed electrolyte solution. The result is a circuit connecting cathodic and anodic sites, with the energy required to maintain the process being derived from the oxidation of neutral atoms of the substrate metal (Chilton, 1969).

In a corrosion event, the first step is considered to be the production of a free electron and its transfer to an active cathodic site. Hydrogen and oxygen dissolved in the adsorbed electrolyte solution are common oxidising agents in corrosion processes. The cathodic reaction typically involves the formation of an hydroxyl ion with the consumption of an electron. An hydroxyl ion generated at an active cathodic site moves through the adsorbed electrolyte solution (under the influence of an electric field and a chemical potential gradient) to an anodic site (Evans, 1950).

The hydroxyl ion associates with a metal ion at the anodic site to form a solvated metal hydroxide molecule and the departing metal ions leave a cavity in the metal surface (Ailor, 1982). Typically this occurs in a saturated electrolyte solution so that the metal hydroxide produced will tend to supersaturate the solution and promote recrystallisation (Tyrrell, 1984). The result is the formation or growth of corrosion product adjacent to the metal surface or at the margins of the electrolyte solution (Anderson and Rubin, 1981; Haruyama, 1990; Gvirtzman and Gorelick, 1991; Hillner et al., 1992; Forcada and Mate, 1993).

The effect of adsorbed polymer molecules is twofold. First, the attachment of a polymer molecule to an active metal site acts as a physical barrier to water and oxygen and ions and thus protects the active site from chemical reaction. Second, the presence of polymer with restricted segment mobility due to adsorption, raises the chemical potential within the adsorbed layer (Tang and Song, 1993). Generally, when adsorbed on a surface, polymers achieve a crystalline state (dependent upon the nature of the polymer and the surface and on the strength of adsorption) and according to J A Barrie in 'Water in Polymers' p264 in 'Diffusion in Polymers' 1968 Crank and Park editors: "It is generally accepted that where well-defined crystallites are formed these are inaccessible to water". This leads to reduced equilibrium concentrations of water, oxygen and ions in the adsorbed layer, which reduces the rate of formation of hydroxyls and results in a reduced rate of corrosion (Kumins, 1980).

Typically, polymer molecules compete with water molecules for adsorption onto a metal surface. In addition, water molecules associate with polymer molecules, and polymer molecules associate with corrosion product. A common initial state is one where there is negligible corrosion product, so that initially a painted metal surface has mainly adsorbed polymer molecules attached, and relatively few competing water molecules. In consequence, the initial corrosion rate is very low. As the system evolves and corrosion product accumulates, polymer attachments to the metal surface are compromised by associations of polymer

molecules with corrosion product. As more active metal sites are exposed and polymer segment restriction in the adsorbed layer is compromised by desorption from the metal surface and bonding with corrosion products, more water is able to diffuse to and accumulate on the metal surface, leading to an accelerating rate of corrosion (Kumins, 1980).

1.3 DIFFUSION

Paint films consist of polymeric binders together with pigments and various low molecular weight additives. At temperatures of interest, molecules in a paint film binder are normally in motion at frequencies of about 1 THz (Kumins, 1980). Statistical fluctuations in this motion produce decompressions when polymer segments within a local group move away from each other at the same time. When polymer segments move toward each other at the same time a compression occurs. Within a paint film there is some characteristic mean spatial distribution and density of polymer molecules. Deviations below this concentration are decompressions and deviations above compressions.

On a microscopic scale the chemical potential of diffusant or wandering molecules within the paint film medium is related to the local polymer matrix density - decompressions corresponding to lower chemical potential and compressions to higher potential. As decompressions and compressions dissipate and regenerate, diffusant molecules experience fluctuating magnitudes and gradients of chemical potential. This is a non equilibrium system at microscopic scales which leads to microscopic random diffusion as diffusant molecules are continually pushed from compressions and pulled by decompressions from fluctuating regions of higher to lower chemical potential. The magnitude and extent of this microscopic motion affects molecular mobilities and bulk diffusivities.

The effect of an external concentration differential across a polymer film is to create a gradient of chemical potential through the paint film. This gradient

superimposes a drift velocity component onto the microscopic random motion and leads to macroscopic bulk diffusion or drift of diffusant molecules through the paint film as they saltate down the chemical potential gradient (Akbar, 1992). If an external concentration differential is not sustained a new state of macroscopic thermodynamic equilibrium will eventually be reached, where again microscopic motion occurs due to microscopic non equilibrium thermodynamics.

Agents or influences which increase the rate, magnitude or extent of statistical fluctuations of density and energy, or which render polymer segments more mobile, increase the mobility and therefore increase the capacity for bulk diffusion of, for example, corrosively active molecules (Hegedus and Kamel, 1993 a, b, d). Structural entities such as cross links, crystalline domains, or embedded macroscopic particles (pigments) are associated with reduced diffusant molecule mobilities and lower rates of diffusion resulting from decreased rates, magnitudes, or extents of statistical fluctuations or restrictions in polymer segment mobilities (Crank and Park, 1968; Rowland, 1980; Coughlin et al., 1990).

Additionally, there may be some interaction and temporary binding between diffusant molecules (primarily ions) and paint films. The holes and voids arising from statistical fluctuations within the polymer matrix (which constitute free volume) are not necessarily neutral. Polymer or mineral functional groups adjacent to some holes may interact with a diffusant molecule and act to capture or trap the molecule within such erstwhile holes. This interaction may affect both capture and escape and significantly modify the overall course of diffusion through a paint film (McNabb and Foster, 1963; Wu et al., 1990).

2 MODEL DESCRIPTION

2.1 INTRODUCTION

While there is some uncertainty as to whether it is oxygen or water which is the most significant factor in the corrosion process, it is generally accepted that both are important. In practice ions (such as sulphate, chloride, and sodium) are usually present, and will also diffuse through the paint film, adsorb onto the metal surface, and modify the corrosion process and rate. These factors are included in a comprehensive formulation of the model. However we will omit them initially and produce a formulation which aims to account for the essential behaviour of a painted metal surface. The model can be extended to include additional molecular and ionic species as required.

We will describe our model in terms of a coated zinc substrate where zinc ions and zinc corrosion product (primarily zinc hydroxides) are produced in the corrosion reaction. In addition to water and oxygen we include zinc as a diffusing species (the adaptation of the model to other substrates such as iron is straight forward). We thus describe the diffusion of three species: water, oxygen, and zinc with concentrations $U(x, t)$, $W(x, t)$ mol m^{-3}, and $Z_n(x, t)$ mol ratio in water. We suppose that only ionised zinc will diffuse to any significant extent.

The painted metal surface is modelled as a slab bounded by parallel planes at $x=0$ and $x=l$. We suppose that the geometry is effectively one dimensional with all diffusive transport parallel to the x direction. We assume that all diffusing substances enter and leave the slab through its plane faces. A schematic diagram is shown in *figure 1*.

Figure 1

External environment

$x = l$ ———————————————— Paint surface layer

Polymeric coating

$x = 0$ adsorbed layer
(coating-metal interface)

Metal substrate
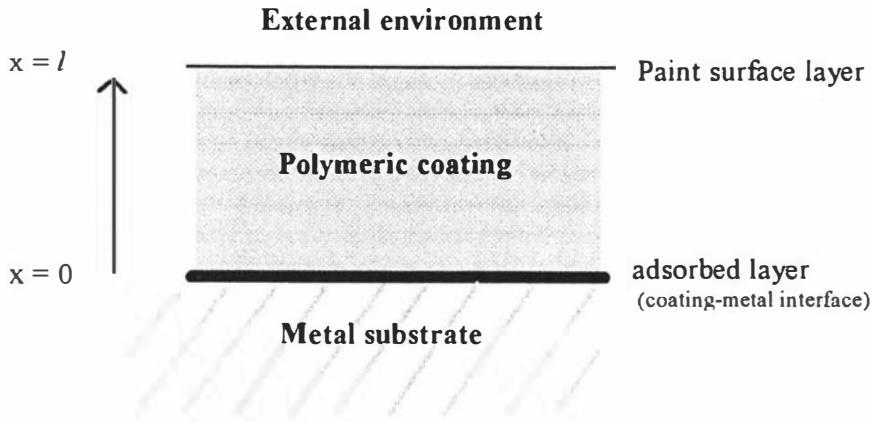
The chemical potential of a substance was first defined by Willard Gibbs in 1928 as the amount by which the capacity of a phase for doing work (other than work of expansion) is increased per mole of the substance added for an infinitesimal addition at constant entropy and volume. In general (in the absence of other potential fields) any substance tends to pass from regions of higher to regions of lower chemical potential. Chemical equilibrium between phases of a system through which each substance can freely pass, results when each substance has the same value for its chemical potential in each phase. Consequently, differences in chemical potential may be regarded as the driving force for all diffusion processes (Denbigh, 1961).

The chemical potential for ideal (ie weakly interacting) substances can be calculated from statistical thermodynamics. It is found that the chemical potential μ_i for the ith pure substance relative to some standard state of chemical potential μ_i * (eg pure substance i) is given by (Reif, 1965)

$$\mu_i - \mu_i^* = RT \ln X_i \; ; \qquad X_i \equiv \text{mole fraction} \tag{2.1.1}$$

For real systems (ie non ideal substances) activity coefficients γ_i are introduced (Denbigh, 1961; Robinson and Stokes, 1959):

$$\mu_i - \mu_i^* = RT \ln \gamma_i X_i \tag{2.1.2}$$

where the equation is taken as the definition of γ_i. In general every substance in each phase has some unique activity coefficient γ_i depending upon various factors such as the concentration of itself and other substances, temperature, and possibly the prior history and geometry of the system (Fava, 1980).

We represent activities as a product of an activity coefficient and the physical concentration (for example activity $\alpha_i = \gamma_i C_i$ for the ith substance). In the external environment we take the activity as unity so that the activity and the concentration are equal. In the paint film however the activity coefficient is effectively about 50 for a typical paint film. Consequently there are concentration discontinuities at x=0 and x=l and additionally we represent the effect of an adsorbed boundary layer with resistance at x=0 through activity coefficients at x=0 which may differ from those effective in 0<x< l. Crank and Park in 'Diffusion in Polymers' 1968 give some discussion of this effect in pages 398 and 352. Crank in 'The Mathematics of Diffusion' pp 41, and 195-200 discusses the effect of a surface skin, and Carslaw and Jaeger in 'Conduction of Heat in Solids' p23 discuss the case of transfer between two media of different conductivities. Rosen and Martin in 'Sorption of Moisture on Epoxy and Alkyd Free Films and Coated Panels' p91 state that "surface resistance contributes significantly to the movement of moisture in the films" and provide some estimates of the magnitude of the effect.

In the external environment we represent activities as equal to concentrations with symbols $U^*(t)$, $W^*(t)$, (mol m^{-3}) and $Z_w^*(t)$ (mol ratio in water) and with saturation values of U_0^*, W_0^*, Z_0^* (since the activity coefficients are approximately unity). Further we take the external environment as the reference for chemical potential and relate all activities to this frame of reference. In the paint film, 0<x<l, we represent activities as $\gamma_u U(x, t)$, $\gamma_w W(x, t)$, and $\gamma_z Z_w(x, t)$ (and physical concentrations as $U(x, t)$, $W(x, t)$, (mol m^{-3}) and $Z_w(x, t)$ (mol ratio in water)) and saturation values as $\gamma_u U_0 = U_0^*$, $\gamma_w W_0 = W_0^*$ and $\gamma_z Z_0 = Z_0^*$.

At the boundary on x=0 we represent activities as $\gamma_u^{**}U^{**}(t)$, $\gamma_w^{**}W^{**}(t)$, and $\gamma_z^{**}Z_w^{**}(t)$ and saturation values as $\gamma_u^{**}U_0^{**}=U_0^{*}$, $\gamma_w^{**}W_0^{**}=W_0^{*}$ and $\gamma_z^{**}Z_0^{**}=Z_0^{*}$. We describe this graphically in *figure 2a* and *2b* for the case of water W.

Figure 2a
concentrations

Figure 2b
activities
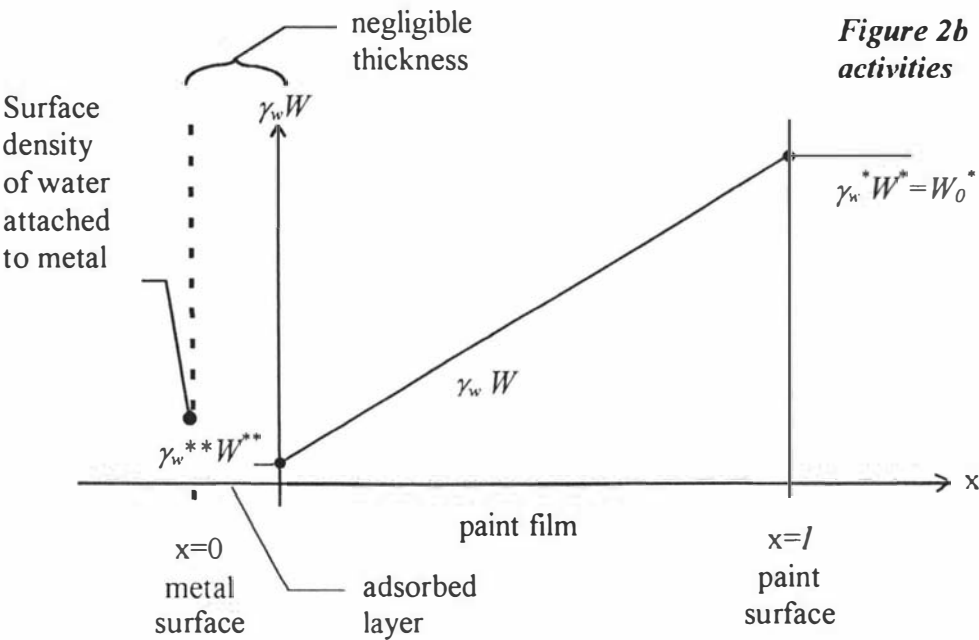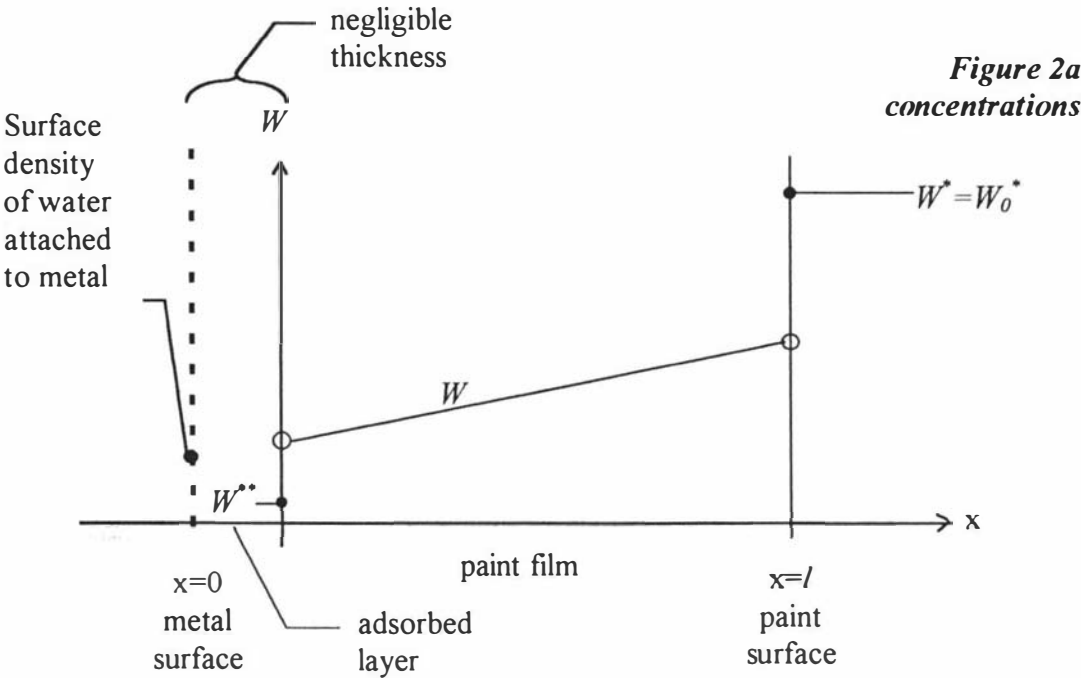
The bulk paint film ($0<x<l$) may not be internally in a state of thermodynamic equilibrium due to capacity effects, transport time lags, and fluxes into and out of the film. However we assume that the boundary layers at $x=l$ and $x=0$ are so thin that any capacitance effects in these layers are negligible. We assume also that any fluxes from one side of these boundary layers are instantaneously transmitted to the other.

Consequently we make the assumption that the boundary layers at $x=l$ and $x=0$ are in thermodynamic equilibrium with adjacent environments. So at $x=l$ we assume that the top of the paint film is always in thermodynamic equilibrium with the external environment. We shall assume that morphology of the outer boundary layer does not change with time, so that the spatial discontinuity in activity and concentration remains constant.

The surface concentrations of species adsorbed on the metal surface arise out of a system of adsorption-competition equations we shall describe shortly. We hypothesise that the adsorbed concentrations arise as a consequence of the competitive adsorption described in the model, and the concentrations of species present in the boundary layer described as the adsorbed layer. At $x=0$ we assume that species present in the adsorbed layer are always in thermodynamic equilibrium with species in the adjacent paint film.

We introduce dimensionless variables u, w, and z defined as follows:

$$u = \frac{U}{U_0} = \frac{\gamma_u U}{U_0^*} \qquad (2.1.1)$$

$$w = \frac{W}{W_0} = \frac{\gamma_w W}{W_0^*} \qquad (2.1.2)$$

$$3 = Z_w w = Z_w \frac{\gamma_w W}{\gamma_w W_0} = \frac{Z_w W}{W_0}$$

<div align="right">(2.1.3)</div>

$$z = \frac{3}{Z_0} = \frac{\gamma_z 3}{Z_0^{\cdot}} = \frac{\gamma_z Z_w \gamma_w W}{\gamma_z Z_0 \gamma_w W_0} = \frac{\gamma_z Z_w \gamma_w W}{Z_0^{\cdot} W_0^{\cdot}} = \frac{Z_w W}{Z_0 W_0}$$

Iron (and other metallic) substrates are also of great practical interest. Corrosion reactions similar to those on zinc occur on iron. However the chemistry is more complex and corrosion processes on rusty surfaces can occur in the absence of oxygen, where oxygen is supplied by reduction of γ-FeOOH to $Fe(OH)_2$ and Fe_3O_4 (Hoffmann and Stratmann, 1993). Because of this added complexity with iron chemistry, zinc was chosen as the substrate to demonstrate the essential behaviour of the model.

Some diffusing molecules may become temporarily bound: removed from the diffusing population, and added to the population of bound or trapped molecules. We will develop the model for an ideally simple paint film where polymer traps are the only significant binding sites. Often minerals (SiO_2, $CaCO_3$ etc.) are present in paint films and their surfaces may provide additional binding sites. Pigment surfaces will also adsorb polymer, water, and oxygen molecules and influence polymer packing and diffusion in the surrounding polymer matrix (Dasgupta, 1991; Kobayashi et al., 1992; Hegedus and Kamel, 1993d; Huldén and Kronberg, 1994; Müller, 1995). The model formulation can be readily extended to include these factors and we aim to demonstrate later that there is qualitative agreement between the simplified model and the more comprehensive formulation. We suppose that polymer molecules are represented by equivalent functional units each containing one binding site, and that these functional units may exist in one of four states: bound to a water molecule, bound to a zinc molecule, bound to an active site on the metal surface (only at $x=0$), or free. In the bulk paint film we consider only three states and set $P_M(x, t)=0$. The three states in the bulk film are described by concentrations $P_W(x, t)$, $P_Z(x, t)$, and $P_f(x, t)$ mol m^{-3}, and represented in dimensionless form as $p_w = P_W/P_0$, $p_z = P_Z/P_0$,

and $p_f = P_f/P_0$. In the adsorbed layer we consider four states $\mathcal{P}_W(t)$, $\mathcal{P}_Z(t)$, $\mathcal{P}_M(t)$, and $\mathcal{P}_f(t)$ mol m^{-2} represented in dimensionless form as $q_w = \mathcal{P}_W/\mathcal{P}_0$, $q_z = \mathcal{P}_Z/\mathcal{P}_0$, $q_m = \mathcal{P}_M/\mathcal{P}_0$, and $q_f = \mathcal{P}_f/\mathcal{P}_0$. P_0 mol m^{-3} represents the total volume concentration of polymer functional groups, and $\mathcal{P}_0$ mol m^{-2} represents the total concentration of polymer functional groups available to the metal surface. We shall assume that these available groups are provided by polymers present in the adsorbed layer.

A painted metal surface is typically covered with a chemically adsorbed (chemisorbed) monolayer of water, oxygen and polymer molecules. In the absence of a paint film additional multiple layers of molecules, principally water, may become physically adsorbed (physisorbed) onto the chemisorbed layer. Chemisorption is characterised by enthalpies of adsorption of order 100 kJ mol^{-1}, while physisorption arises from longer range and weaker interactions (such as Van der Waals forces) with enthalpies typically up to 20 kJ mol^{-1} (Mittal, 1975; Gregg and Sing, 1982).

The surface of a metal is believed to consist of terraces, ledges, dislocations, and other defects on an atomic scale (Atkins, 1978; Crommie et al., 1993). Defect edges and corners, and surface electric potential anomalies are hypothesised to be sites of greatest chemical and electrical corrosion activity. It is expected that there may be anodic and cathodic sites on the metal surface, but we do not distinguish these in the present version of the model, nor do we allow that some molecules may adsorb preferentially on one site rather than another.

As outlined above in section 1.3 we model the interface of a painted metal surface (*figure 3*) as discrete corrosively active sites with oxygen and water molecules, and polymer functional units competing for adsorption. Consequently active sites are modelled to exist in one of four states: attached to an adsorbed water molecule, or oxygen molecule, or polymer functional unit, or free. The active site states are described by surface concentrations $M_W(t)$, $M_U(t)$, $M_P(t)$, and $M_f(t)$

(mol m^{-2}) represented in dimensionless form by $m_w = M_W/M_0$, $m_u = M_U/M_0$, m_p $= M_P/M_0$, and $m_f = M_f/M_0$ respectively. M_0 mol m^{-2} represents the total concentration of active sites on the metal surface, which we shall consider constant.

Figure 3

Model representation

active site
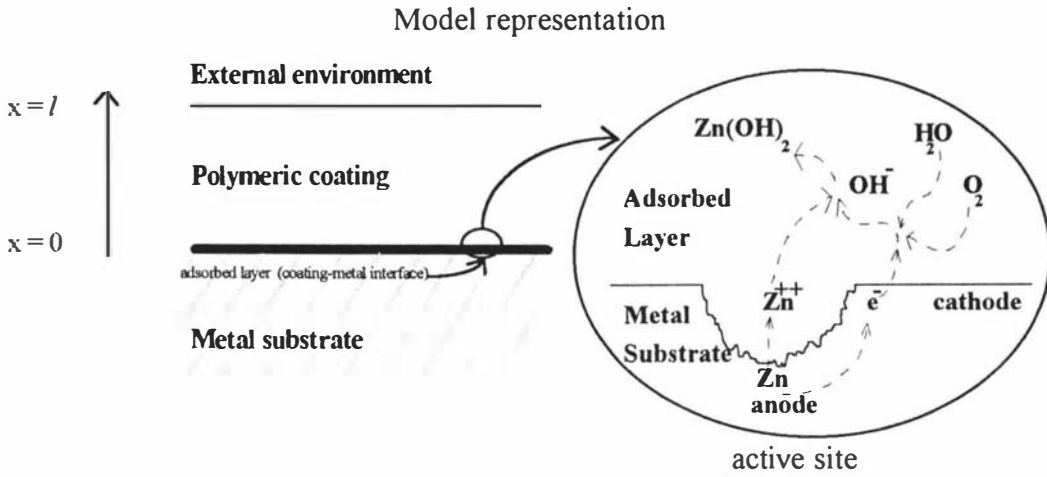
Independent variables for the model are x and t. Paint film thickness l is typically of order 100 microns (10^{-4} m), with a range usually of about 10 microns minimum (although specialist primer coatings may be 1 micron or less) to 1mm maximum (and again some specialist coatings may be 10 mm or more). We use l=5×10^{-5}m (50 microns) as a typical film thickness. Coated metal surface lifetimes vary considerably depending upon the type of coating (and metal) and upon the service environment. We refer to 'lifetime' as the time during which the metal is protected from significant corrosion. The notion of 'significant corrosion' is potentially a difficult issue to define. In practice coating lifetime is relatively easy to define because failure occurs rapidly: the transition from protection to gross failure and free corrosion typically occurs in a time very short compared to the total useful lifetime of the system. We will find later that the model produces this behaviour, and a convenient measure is the onset of accumulation of solid corrosion product. Dimensionless independent variables are defined as x=x/l where 0≤x≤1 for the model and τ=D$_w$t/l^2 where 0≤τ<∞.

2.2 MODEL CONCEPTION

The metal surface is modelled as a collection of sorption sites of which some characteristic proportion are corrosively active. Diffusing species (water and oxygen), and polymer functional groups, are considered to compete for adsorption onto these sorption sites. Our motivation for using this approach is to attempt a formulation which accounts for the chemical activities of species and to relate activities within the paint film to those in the adsorbed layer (which we suppose is of molecular dimensions). We speculate that there is some difference in activity coefficients between the bulk paint film and the adsorbed layer. Additionally we expect that the activity coefficients in the adsorbed layer will change with the state of the adsorbed layer.

Rather than attempting to estimate the activity coefficients directly we instead attempt to model the state of the adsorbed layer and use the thesis that adsorbed polymer assumes crystalline properties. We relate the activity coefficients to the proportion of polymer adsorbed onto the metal surface on the basis that this provides a simple (albeit crude) estimate of the adsorbed layer's morphology and degree of crystallinity. We attempt to depict the appearance of this crystalline layer concept in *figure 4*.

Figure 4

External environment

$x=1$

Bulk polymer

Adsorbed layer
$x=0$
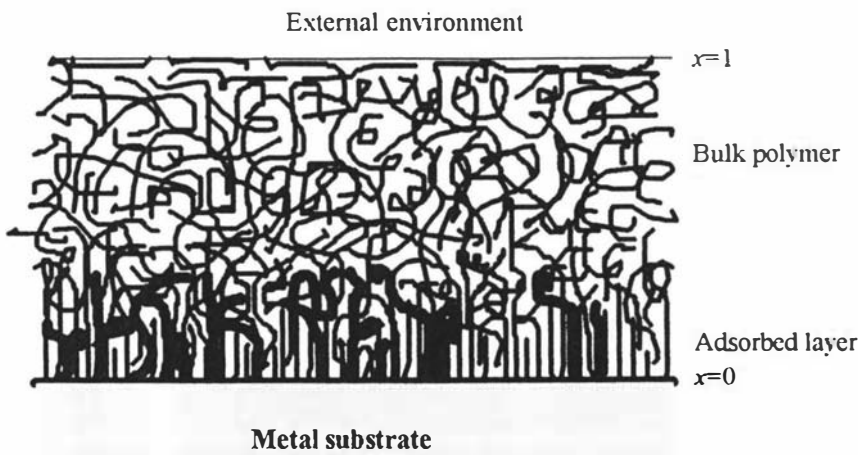
Metal substrate

We theorise that the corrosive activity of the metal substrate is governed by the quantities of water and oxygen present in the adsorbed layer. We model sorption sites in states m_u, m_w, m_p, and m_f in a competitive adsorption model in an attempt to describe the dynamic state of the adsorbed layer. The state of the adsorbed layer is taken to define the activities of species within the layer, so that we obtain estimates of the physical concentrations of water and oxygen which we suppose to be the values determining the rate of corrosion.

As we discuss later, one of the reasons for using this approach is that it allows us to relate model parameters to experimental corrosion rates. External concentrations of water and oxygen are typically readily measurable quantities. We also considered an alternative formulation where the corrosive activity of the metal substrate was related to expressions involving adsorbed quantities such as m_u and m_w. We shall discuss later the implications and consequences of these formulations.

The formulations differ in their implied corrosion mechanisms. The implied mechanism, in the formulation we have adopted, is attack of exposed active sites m_f by corrosively active species present in the adsorbed layer. We discuss in section 2.3 water uptake and corrosion and propose that corrosion is mediated principally by dissolved oxygen which may undergo cathodic reduction with the formation of hydroxyl ions (Boulton and Wright, 1979). We speculate that hydroxyl ions are present in the adsorbed layer in concentration proportional to the concentrations of water and oxygen, and make an assumption that the paint film itself regulates the effective pH. Effectively we assume that the hydroxyl ion mol ratio in water is constant. In a more comprehensive formulation of the model hydroxyl ions would be included as diffusing and reactive species. But we aim to show that water and oxygen may account for the basic phenomena we aim to represent (see *figure 5*).

We do not attempt to directly model the atomic and molecular details of the corrosion process. The main consideration is that there appears to be insufficient information available from the literature with which to develop a model on such a fundamental level. Instead we attempt a formulation where concentrations of reactants are modelled. We deduce expressions for corrosion rates from basic electrochemical dynamics and relate these expressions to observed corrosion rates. The logical consequence of this formulation are shown in *figure 5*.

We employ the least number of reacting species thought viable in formulating this model. Additional species which might be included in a more comprehensive formulation include hydroxyl, carbonate, hydrogen, sulphate, and chloride ions. Only water and oxygen, and zinc ions, are modelled on the reasoning that these could account for the essential corrosion behaviour of coated metal surfaces.

Figure 5
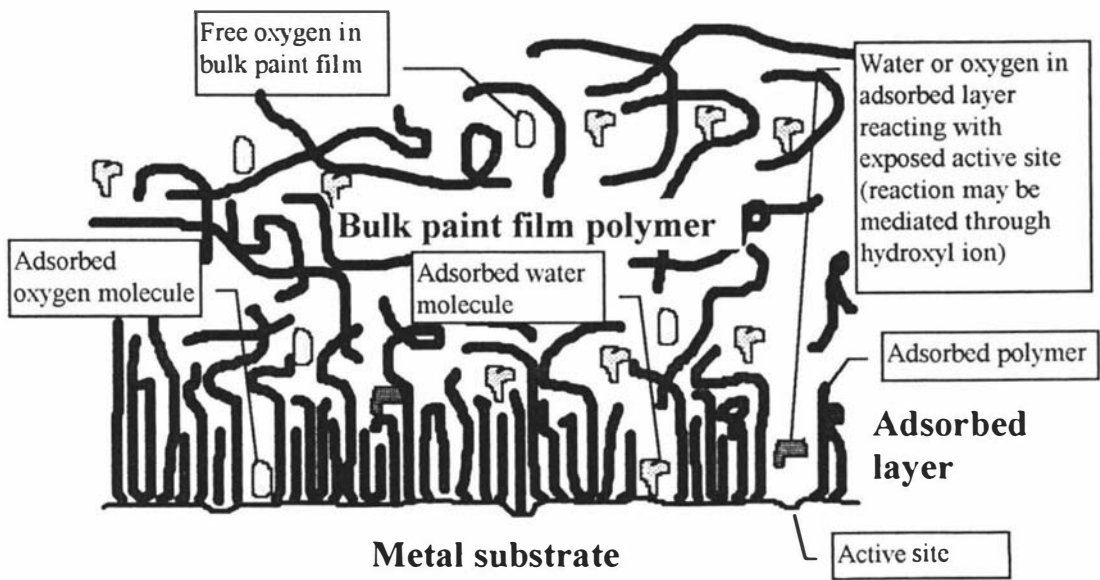
In the alternative formulation, where corrosion is mediated through adsorbed species (m_u and m_w), the implied corrosion mechanism is the direct reaction of adsorbed oxygen or water molecules with active substrate sites. We suppose that

while bound to an active site on the metal surface an adsorbed water or oxygen molecule might occasionally become reactive and produce a corrosion event. It is unclear what the trigger for such a corrosion event might be.

Physically however, this version of the formulation seems to lack features common to chemical kinetics. In particular, chemical reactions generally involve some initial potential energy barrier which is usually overcome by thermal kinetic energy. We note that corrosion does not significantly occur at temperatures below about 0°C, and in general corrosion rates do increase with increasing temperature (Slunder and Boyd, 1971). Water and oxygen (and hydroxyl) molecules in the adsorbed layer are in thermal motion and the kinetic energy of a portion of the population is thought to be sufficient to overcome a potential energy barrier to reaction.

In a further variation of this formulation we suppose that reaction might occur promptly upon initial adsorption of water or oxygen. This argument would overcome the objections raised earlier involving the kinetic energy of reactant molecules and potential energy barriers. However we realised that this concept is effectively the same as the first formulation since reaction is mediated through exposed metal active sites m_f. With our original theory that the local supply of water and oxygen is rate limiting, the reaction rate should then be proportional to the concentrations of available reactants (water and oxygen).

We conclude from this reasoning that the first formulation outlined above is more plausible, where corrosion occurs in response to the local concentrations of water and oxygen.

2.3 WATER UPTAKE AND CORROSION

Water uptake by the film is controlled by free water from the environment entering the paint film through the outer face.

At the base of the paint film the model proposes an adhesion layer of structured polymer, forming an interface between the paint film and the metal surface. This interface is the arena for corrosion reactions. Some water (and oxygen), after diffusing through the paint film, will accumulate in the adsorbed layer (Nguyen et al., 1994) and compete with polymer for adsorption onto the metal surface. Corrosion of the metal substrate occurs in proportion to the concentrations of adsorbed water and oxygen adjacent to the metal substrate. Some corrosion product is generated, and a proportional amount of water and oxygen is consumed in the chemical reaction. We consider the early history of a painted surface where the paint film is still strongly adherent: corrosion rates are small, fluxes of water and oxygen involved in the corrosion reaction are small, and the generation of corrosion product is very slow.

In general terms corrosion is considered to consist of two half reactions which are supposed to occur at an active site's anode and cathode (*Figure 6*). The anodic process is represented as

$$Zn_{(metal)} \leftrightarrow Zn^{++}_{(aqueous)} + 2e^-$$
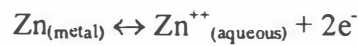
and the cathodic process as

$$H_2O + \tfrac{1}{2}O_2 + 2e^- \leftrightarrow 2OH^-$$
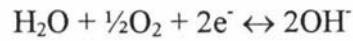
Figure 6
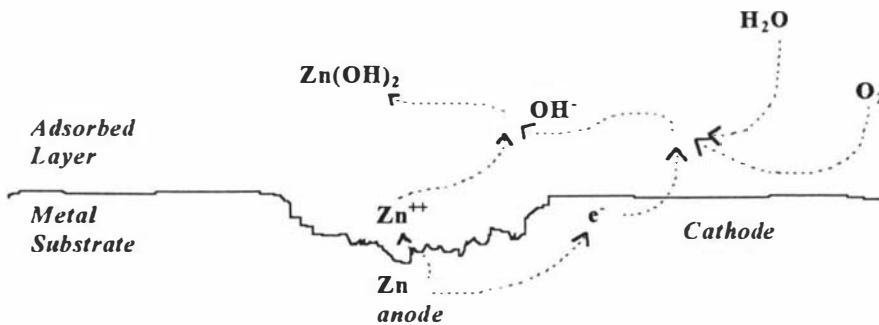
The corrosion of zinc is believed to consist of two reaction pathways:

Reaction 1

$$Zn + H_2O + O_2 \leftrightarrow Zn^{++} + 2e^- + H_2O + O_2 \leftrightarrow Zn^{++} + 2OH^- + O \leftrightarrow Zn(OH)_2 + O \qquad (2.3.1)$$

$$Zn + H_2O + O \leftrightarrow Zn^{++} + 2e^- + H_2O + O \leftrightarrow Zn^{++} + 2OH^- \leftrightarrow Zn(OH)_2 \qquad (2.3.2)$$
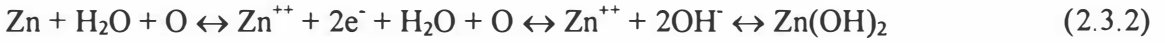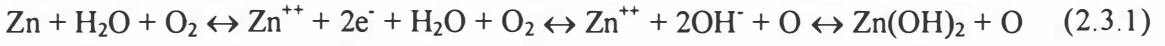
with an associated chemical rate equation R:

$$R([Zn^{++}]) = \rho_1[Zn][H_2O][O_2]^{1/2} - \rho_2'[Zn^{++}][OH^-]^2 \qquad (2.3.3)$$

where $R([Zn^{++}])$ is the net rate of formation of Zn^{++}.

and

Reaction 2

$$Zn + 2H_2O \leftrightarrow Zn^{++} + 2e^- + 2H_2O \leftrightarrow Zn^{++} + 2OH^- + H_2 \qquad (2.3.4)$$

with associated chemical rate equation R:

$$R([Zn^{++}]) = \rho_3'[Zn][H_2O]^2 - \rho_4'[Zn^{++}][OH^-]^2[H_2] \qquad (2.3.5)$$

Both Reaction 1 and Reaction 2, in the absence of external electric potentials and competing electrochemical processes, are driven by the electrochemical potential of zinc oxidation. In theory the reactions are reversible, but in practice the reverse reaction does not occur. Initially Zn^{++} generated is largely taken up by polymer (which maintains low solution Zn^{++} concentrations) and gradually modifies the polymer matrix, its morphology and its adsorption to the metal substrate. Hydrogen generated will rapidly diffuse away. Eventually excess Zn^{++} generated when the local electrolyte medium is saturated will cause precipitation of zinc corrosion product at the margins of the active site, which we expect will impair the accuracy of our modelled corrosion rates. However we theorise that for the early history of the modelled system the corrosion rates are dominated by polymer and competitive adsorption effects so that equation 2.3.5 is effectively

$$R([Zn^{++}]) = \rho_3'[Zn][H_2O]^2 \qquad (2.3.6)$$

where we have dropped the term containing hydrogen on the basis that hydrogen will rapidly disperse and the concentration will be small so that the term is negligible. Additionally [Zn] is essentially constant so

$$R([Zn^{++}]) = \rho_3[H_2O]^2 = f_{z2} \qquad (2.3.7)$$

Water (H_2O) exists in equilibrium with its dissociation products which we represent as

$$H_2O \leftrightarrow H^+ + OH^- \qquad (2.3.8)$$

with rate equation R:

$$R([OH^-]) = \rho_5[H_2O] - \rho_6[H^+][OH^-] \qquad (2.3.9)$$

We suppose that the paint film includes a metal primer with a composition which incorporates a buffering mechanism (Resene proprietary information) which maintains pH$\approx$10 so

$$[H^+] = (10^{-10} \text{ mol l}^{-1}) = 10^{-7} \text{ mol m}^{-3} \qquad (2.3.10)$$

and R([OH⁻]) is supposed zero so

$$[OH^-] = \frac{10^{-11}[H_2O]}{10^{-7}} = 10^{-4}[H_2O] \quad \text{mol m}^{-3} \qquad (2.3.11)$$

Reaction 1 becomes

$$R([Zn^{++}]) = \rho_1[H_2O][O_2]^{1/2} = f_{z1} \qquad (2.3.12)$$

where we have again dropped the second term which is considered minor on the basis that any Zn^{++} generated may readily diffuse laterally and precipitate remotely at the margins of active sites. Additionally [OH⁻] is buffered approximately constant. Finally we prefer a simpler expression and prefer to overestimate the actual reaction rate.

We suppose that the corrosion flux f_z is the sum of these two processes

$$f_z = f_{z1} + f_{z2} = \rho_1[H_2O][O_2]^{1/2} + \rho_3[H_2O]^2 \qquad (2.3.13)$$

Zinc corrodes in distilled water in the absence of oxygen at a rate of about 0.002 inches per year $= 1.1 \times 10^{-5}$ g m^{-2} s^{-1} (Uhlig, 1948).

$$f_{Z2(0)} = \rho_3 [H_2 O]^2 = \frac{1.1 \times 10^{-5} \text{g m}^{-2} \text{ s}^{-1}}{65} = 1.7 \times 10^{-7} \text{ mol m}^{-2} \text{ s}^{-1} \qquad (2.3.14)$$

$[H_2 O] = 5.6 \times 10^4$ mol m^{-3} for liquid water

$$\Rightarrow \qquad \rho_3 = \frac{1.7 \times 10^{-7}}{(5.6 \times 10^4)^2} = 5.4 \times 10^{-17} \text{ mol}^{-1} \text{ m}^4 \text{ s}^{-1} \qquad (2.3.15)$$

Zinc corrosion with oxygen and water occurs at a significantly faster rate (Uhlig, 1948) of about 0.04 inches per year $= 2 \times 10^{-4}$ g m^{-2} s$^{-1} = 3.1 \times 10^{-6}$ mol m^{-2} s^{-1}. The oxygen saturation level in distilled water is about 0.3 mol m^{-3} and

$$f_{Z(0)} = f_{Z1(0)} + f_{Z2(0)} = \rho_1 [H_2 O][O_2]^{1/2} + \rho_3 [H_2 O]^2 = 3.1 \times 10^{-6} \text{ mol m}^{-2} \text{ s}^{-1} \quad (2.3.16)$$

$$\Rightarrow \qquad \rho_1 = \frac{3.1 \times 10^{-6} - 1.7 \times 10^{-7}}{5.6 \times 10^4 \times \sqrt{0.3}} = 9.6 \times 10^{-11} \text{ mol}^{-1/2} \text{ m}^{5/2} \text{ s}^{-1} \qquad (2.3.17)$$

In general the first term in eq 2.3.16 dominates; but the second term may become significant in response to transients and in coating systems where the film is sufficiently thick and impermeable to act as a partial barrier to oxygen transport to the metal surface. Additionally oxygen may be rate limiting when some corrosion occurs, with the result that both terms may be significant.

The concentrations $[H_2 O]$ and $[O_2]$ must now be defined and the model designed so that these concentrations arise as a consequence of processes occurring in the model as a whole. We relate $[H_2 O]$ and $[O_2]$ to concentrations of water and oxygen in the adsorbed layer. With currently available information, this formulation allows us to relate corrosion rates to concentrations on the basis of experimental results. Experimental validation of the model is important. Once the viability of the model is established it is hoped that new experimental data

relating corrosion rates to surface concentrations of water and oxygen underneath paint films may become available which will allow a more sophisticated formulation of the model to be tested.

In order to determine the concentrations of water and oxygen at $x=0$ we must design an expression relating the concentrations to the chemical activities (effectively the chemical potentials since we will assume constant temperature). We have argued previously, on the basis of results reported in the literature, that the state of the adsorbed layer plays a critical role in determining the chemical potentials of substances present in each phase. Indeed the basis for this thesis is the hypothesis that adsorbed polymer of paint films on metal substrates changes state to become more crystalline. In this change of state we find that physical concentrations may vary according to the chemical activities of the substances present.

We shall assume that the polymer changes morphology immediately in response to dynamic effects arising in the competitive adsorption processes, and we shall also assume that concentrations mol m^{-3} of water and oxygen in the adsorbed layer respond immediately to changes in chemical activity so as to maintain equilibrium of chemical potential between the adsorbed layer and the adjacent bulk paint film. The basis for these assumptions is that we are primarily concerned with the initial history of the model. Corrosion rates are initially small and changes to the adsorbed layer and polymer morphology are small and gradual. Our thesis is that the time to failure is governed primarily by the initial state of the adsorbed layer and these gradual processes.

The simplest and most direct method of representing this effect of state upon chemical activity is to relate the concentration to the proportion of polymer adsorbed onto the metal surface. We model the dependence of activity between the adsorbed layer and the bulk paint film as $\dfrac{\gamma_w}{\gamma_w^{**}} = \dfrac{\left(M_0 - M_p\right)}{M_0}$ for water and

$$\frac{\gamma_u}{\gamma_u^{\ast\ast}} = \frac{\left(M_0 - M_p\right)}{M_0}$$ for oxygen. Next we equate activity in the bulk paint film to activity in the adsorbed layer.

$$\gamma_w^{\ast\ast}[H_2O] = \gamma_w^{\ast\ast}W^{\ast\ast}(t) = \gamma_w W(x=0,t)$$

From this we obtain

$$[H_2O] = \frac{\gamma_w}{\gamma_w^{\ast\ast}} W(x=0,t) = \frac{\left(M_0 - M_p\right)}{M_0} W(x=0,t) \quad \text{mol m}^{-3} \tag{2.3.18}$$

Similarly for oxygen

$$\gamma_u^{\ast\ast}[H_2O] = \gamma_u^{\ast\ast}U^{\ast\ast}(t) = \gamma_u U(x=0,t)$$

and

$$[O_2] = \frac{\gamma_u}{\gamma_u^{\ast\ast}} U(x=0,t) = \frac{\left(M_0 - M_p\right)}{M_0} U(x=0,t) \quad \text{mol m}^{-3} \tag{2.3.19}$$

where M_p and $U(x, t)$ will arise out of the adsorption - competition equations, and the diffusion equations respectively, which we will describe later.

Putting eq 2.3.18 and 2.3.19 into 2.3.13 we obtain

$$f_z = 9.6 \times 10^{-11} \left[\frac{(M_0 - M_P)}{M_0}\right]^{3/2} W(x=0,t)U^{1/2}(x=0,t) + 5.4 \times 10^{-17} \left[\frac{(M_0 - M_P)}{M_0}\right]^2 W^2(x=0,t) \tag{2.3.20}$$

It is difficult to directly relate experimentally observed corrosion rates (Guruviah, 1970; Haagen and Funke, 1975; Rosen and Martin, 1991; Ailor, 1982; Slunder and Boyd, 1971; Evans, 1950; and Uhlig, 1948) and reported parameters such as relative humidity to modelled parameters such as the water and oxygen concentrations adjacent to the metal surface. In fact this difficulty was recognised at an early stage and provided some of the stimulus to formulate the model as it now stands. We incorporate competitive adsorption of polymer, water and oxygen in a system designed to model the effective concentrations of water and oxygen at the metal surface. The measurable parameters are the concentrations of oxygen and water in the bulk medium external to, and in thermodynamic equilibrium with, the adsorbed polymer layer.

A test of the adsorption model considers a bare metal surface with oxygen and water competing for adsorption. In this case there is no discontinuity of activity since no adsorbed polymer is present. The driving force of adsorption is the concentrations of water and oxygen in the external bulk medium. From equations 2.3.18 and 2.3.19 we find

$$[H_2O] = W^{**}(t) = W(x = 0, t) \tag{2.3.21}$$

$$[O_2] = U^{**}(t) = U(x = 0, t) \tag{2.3.22}$$

and

$$f_z = \rho_1' W U^{1/2} + \rho_3' W^2 \tag{2.3.23}$$

Additionally water and oxygen will adsorb onto the metal surface with concentrations M_w and M_u. We calculate these values from the adsorption competition model we introduce in the next section. See chapter 5.7 for a discussion of a special case arising from this aspect of the model. The values of M_w and M_u arising from the adsorption competition model correspond to generalised Langmuir adsorption isotherms. We find reasonable agreement with experimentally reported sorption isotherms on metal surfaces (Rosen and Martin, 1991; Valenzuela and Myers, 1989). This relates calculated corrosion rates f_z and external bulk media concentrations W^* and U^* with experimental corrosion rates and reported concentrations of water and oxygen.

We suppose that the total zinc corrosion product concentration Z_Σ^{**} mol m^{-2} at $x=0$ is made up of a component $\mathfrak{z}^* \equiv Z_w^{**} W^{**}/W_0^{**}$ mol ratio solvated in the water present in the adsorbed polymer layer, a solid component Z_c mol m^{-2} and a polymer bound component P_z mol m^{-2}.

$$Z_\Sigma^{**} = k_3 \mathfrak{z}^* + Z_c + P_z \tag{2.3.24}$$

where k_3 is some characteristic thickness associated with the adsorbed layer.

For zinc corrosion product in solution at $x=0$ we suppose there is one source term which represents the creation of corrosion product $\mathfrak{z}^{**}$ according to equation

2.3.20. We suppose there are two sink terms: one arising from the uptake of corrosion product by polymer to form $\mathcal{P}_z$, and the other resulting from the diffusion of zinc away from the adsorbed layer at x=0. A conservation equation (eq 2.3.25) is formulated which equates the rate of change of zinc corrosion product with its rate of creation f_z, its removal to polymer bound zinc $\mathcal{P}_z$ mol m^{-2} and loss due to diffusion.

$$k_3 \frac{dz^{**}}{dt} = f_z - \frac{d\mathcal{P}_z}{dt} + D_z \frac{\partial z}{\partial x}\bigg|_{x=0} \tag{2.3.25}$$

Further we assume

1) that Z_c is only created (and exists) when $Z_w^{**} = Z_{w\ (saturation)}^{**}$ and

2) $Z_c = 0$ when $Z_w^{**} < Z_{w\ (saturation)}^{**}$.

Equation 2.3.25 can be written as two equations:

$Z_w^{**} < Z_{w\ (saturation)}^{**}, Z_c = 0 \qquad k_3 \frac{dz^{**}}{dt} = f_z - \frac{d\mathcal{P}_z}{dt} + D_z \frac{\partial z}{\partial x}\bigg|_{x=0} \tag{2.3.26}$

$Z_w^{**} = Z_{w\ (saturation)}^{**}, Z_c \geq 0 \qquad k_3 \frac{dZ_c^{**}}{dt} = f_z - \frac{d\mathcal{P}_z}{dt} + D_z \frac{\partial z}{\partial x}\bigg|_{x=0} \tag{2.3.27}$

In non-dimensional form this is:

for $z < w,\ z_c = 0$

$$-\frac{\partial z}{\partial x}\bigg|_{x=0} = -\phi_3\left(\frac{dz}{d\tau} + \kappa_5 \frac{dq_z}{d\tau}\right) + \phi_4\kappa_6\left[(1-m_p)^{3/2}wu^{1/2} + \alpha_8(1-m_p)^2 w^2\right] \tag{2.3.28}$$

and for $z = w,\ z_c \geq 0$

$$-\frac{\partial z}{\partial x}\bigg|_{x=0} = -\phi_5\left(\frac{dz_c}{d\tau} + \kappa_7\frac{dq_z}{d\tau}\right) + \phi_4\kappa_6\left[\left(1-m_p\right)^{3/2}wu^{1/2} + \alpha_8\left(1-m_p\right)^2 w^2\right] \qquad (2.3.29)$$

where : $x = x/l$ and $\tau = D_B t/l^2$,

$u = U/U_0$, $w = W/W_0$, $z = Z_W W/W_0 Z_0 = \mathcal{Z}/Z_0$, $z_c = Z_c/Zc0$, $q_z = P_Z/P_0$, $m_p = M_P/M_0$

$$\kappa_5 = \frac{P_0}{Z_0 k_3}, \kappa_6 = \frac{W_0}{Z_0}, \kappa_7 = \frac{P_0}{Z_{c0}} \qquad \phi_3 = \frac{k_3 D_W}{l D_Z}, \phi_4 = \frac{\rho_1 l U_0^{1/2}}{D_Z} \qquad \alpha_8 = \frac{\rho_2 W_0}{\rho_1 U_0^{1/2}}$$

2.4 ADSORPTION - COMPETITION

The basic hypothesis of this model is that a metal surface consists of a specific density of discrete sorption sites of size comparable to molecules considered in this model (water, oxygen, and polymer). A characteristic proportion of these sites are supposed corrosively active. When a polymer functional unit is adsorbed onto an active site, we suppose that the active site is made unreactive. In particular we consider certain chemical entities present in paint film polymers to adsorb competitively with oxygen and water onto active sites. Examples of adsorbable groups are -COOH, -OH, -NH; and a polymer functional unit is an equivalent mass of polymer containing one adsorbable group. Additionally (and in explicit detail in a more sophisticated formulation of the model) polymer functional groups may interact with other species to form more complex functional groups. For example zinc chromate may complex with polymer hydroxyl groups. In principle we could model both active sites and polymer functional groups as distribution functions. However this information is currently not readily available, and we assume that all active sites are identical and independent as are all polymer functional units. Finally we assume that each active site or polymer functional unit has the ability to adsorb only one molecule. These assumptions describe the basis for Langmuir adsorption isotherms.

On a plane surface there are approximately 10^{19} surface atoms per square metre. We suppose that a fraction σ of these are corrosively active; that adsorption occurs on all sites (10^{19}); and that all sites have equal adsorption energy. In actuality there will be a distribution of adsorption types and energies, and the surface will have some roughness and porosity. But we use as a first approximation

$$M_0 = 1.7 \times 10^{-5}\, \text{mol m}^{-2} \tag{2.4.1}$$

For water the rate of increase of adsorbed water is proportional to the collision rate of water molecules with the surface, the collision cross section, and the surface remaining uncovered (M_f). We estimate these factors in a simplistic thumb nail sketch fashion based on ideal gas dynamics

$$\left[\frac{dM_W}{dt}\right]_+ = \sqrt{\frac{kT}{2\pi m}}\frac{NW}{VW_0}\pi d^2\frac{(M_0 - M_P)}{M_0}M_f = 10^{10}\frac{W}{W_0}\frac{(M_0 - M_P)}{M_0}M_f \tag{2.4.2}$$

where k is Boltzmann's constant (1.38×10^{-23} J K^{-1}), T is degrees Kelvin ($300°$K), m is the molecular mass ($18/6 \times 10^{23}$ g), NW/VW_0 is the water molecule number density per cubic metre ($10^6 \times 6 \times 10^{23}/18 = 3 \times 10^{28}$ m^{-3}), and πd^2 is the collision cross section ($\pi \times (5 \times 10^{-10})^2 = 8 \times 10^{-19}$ m^2).

The factor $(M_0 - M_P)/M_0$ relates activity within the adsorbed layer to that outside, and we assume that the adsorbed layer is in thermodynamic equilibrium with the adjacent bulk paint film. In reality we expect the adsorbed layer to exhibit a continuous variation from its ultimate crystalline state on the metal surface to being almost amorphous at the internal boundary within the paint film at about x=100 nm. We are interested here only in the state of the adsorbed layer immediately adjacent to the metal. Our reasoning is that this is where activities of water and oxygen relevant to the corrosion process are pertinent, rather than activities at the inner face or some average applicable to the entire adsorbed layer. Additionally we are unsure how the polymer crystallinity, and hence activities of water and oxygen in the layer, may vary with position within the layer.

We suppose that the rate of decrease of adsorbed water follows an Arrhenius type law of the form $ve^{-E/RT}M_W$ where v is the molecular thermal vibration rate (typically around 10^{14} Hz), E is the energy of adsorption (around 60 kJ mol^{-1}), and R is the gas constant (8.3 J mol^{-1} K^{-1})

$$\left[\frac{dM_W}{dt}\right]_- = -10^4 M_W \qquad (2.4.3)$$

giving

$$\frac{dM_W}{dt} = r_1 \frac{W}{W_0} \frac{(M_0 - M_P)}{M_0} M_f - r_2 M_W \qquad (2.4.4)$$

where $r_1 = 10^{10}$, $r_2 = 10^4$ and which we write in nondimensional form as

$$\frac{dm_w}{d\tau} = \theta_1 \left[\alpha_1 (1 - m_p) w m_f - m_w \right] \qquad (2.4.5)$$

where: $\tau = D_W t / l^2$, $w = W/W_0$, $m_f = M_f/M_0$, $m_w = M_W/M_0$, $m_p = M_P/M_0$

$$\alpha_1 = \frac{r_1}{r_2}, \quad \theta_1 = \frac{r_2 l^2}{D_W},$$

In a more precise formulation we should account for the fact that typically multiple layers of water etc accumulate on the surface. We would accommodate this in a multilayer model with rate equations governing each layer (and there may be hundreds of layers to account for: Ailor, 1982). However we adopt a simple monolayer approach on the basis that: 1) the model is designed to account for the early history of a painted metal surface with less importance placed on the model's accuracy at late times (when multilayers are expected to dominate) and

2) adsorbed polymer is believed to inhibit the formation of multiple layers of adsorbed water.

Similarly for oxygen

$$\frac{dM_U}{dt} = r_3 \frac{U}{U_0} \frac{(M_0 - M_P)}{M_0} M_f - r_4 M_U \qquad (2.4.6)$$

where m=32/6×10²³ g, and $NU/VU_0 = PU/kTU_0 = 2\times10^4 U/kTU_0 = 4.8\times10^{24} U/U_0$, $r_3 = 10^7$, $r_4 = 10^4$, and which we write as

$$\frac{dm_u}{d\tau} = \theta_2\left[\alpha_2\left(1 - m_p\right)um_f - m_u\right] \tag{2.4.7}$$

where $m_u = M_U/M_0$, $u = U/U_0$, $\alpha_2 = \dfrac{r_3}{r_4}$, $\theta_2 = \dfrac{r_4 l^2}{D_W}$

For the rate of increase of adsorbed polymer

$$\left[\frac{dM_P}{dt}\right]_+ = \sqrt{\frac{kT}{2\pi m}}\frac{10^5}{10^2}\frac{\mathcal{P}_f N}{\mathcal{P}_0 V}\pi d^2 M_f \tag{2.4.8}$$

where $m = 10^5/6\times10^{23}$ g. We suppose that a typical polymer functional unit has equivalent weight about 100 so that there are $10^5/100=10^3$ functional units per molecule in our model polymer (with molecular weight about 10^5). $\mathcal{P}_f N/\mathcal{P}_0 V = 10^6\times6\times10^{23}/10^5 = 6\times10^{24}$ molecules m⁻³.

We allow that polymer molecules may vibrate and move within some radius of gyration related to the polymer size. Some small motion on an atomic scale is necessary to account for adsorption and desorption dynamics. However we assume that polymer molecules cannot diffuse within the paint film. Polymer molecules located initially in the adsorbed layer are assumed to be locked within the polymer matrix and to remain within the adsorbed layer indefinitely. Consequently we make no assumption of thermodynamic equilibrium for polymer species such as $\mathcal{P}_f$ in the model.

Concentrations of species such as $\mathcal{P}_f$ are instead determined by the coupled competitive adsorption equations we are describing. We suppose that the effective pressure of polymer causing adsorption is proportional to the fraction $\mathcal{P}_f$ remaining free. Then

$$\frac{dM_P}{dt} = r_5\frac{\mathcal{P}_f}{\mathcal{P}_0}M_f - r_6 M_P \tag{2.4.9}$$

where $r_5 = 10^8$, $r_6 = 60$, and we take $E \approx 70$ kJ mol⁻¹.

We write this as

$$\frac{dm_p}{d\tau} = \theta_3\left(\alpha_3 q_f m_f - m_p\right) \tag{2.4.10}$$

where $m_p = M_P/M_0$, $m_f = M_f/M_0$, $q_f = \mathcal{P}_f/\mathcal{P}_0$, $\alpha_3 = \dfrac{r_5}{r_6}$, $\theta_3 = \dfrac{r_6 l^2}{D_W}$

Finally a conservation relation exists for M_P, M_W, M_U, and M_f:

$$M_P + M_W + M_U + M_f = M_0 \tag{2.4.11}$$

In dimensionless form this is

$$m_p + m_w + m_u + m_f = 1 \tag{2.4.12}$$

We suppose that for the polymer - water interaction the adsorbed polymer layer acts like a rigid surface where $10^2/10^5 = 10^{-3}$ collisions of water molecules from the bulk paint film onto the adsorbed layer are with polymer functional units. The rate of increase of $\mathcal{P}_W$ is calculated as

$$\left[\frac{d\mathcal{P}_W}{dt}\right]_+ = \sqrt{\frac{kT}{2\pi m}}\frac{NW}{VW_0}\pi d^2 \frac{10^2}{10^5}\mathcal{P}_f = 10^7\frac{W}{W_0}\mathcal{P}_f \tag{2.4.13}$$

and

$$\frac{d\mathcal{P}_W}{dt} = r_9\frac{W}{W_0}\mathcal{P}_f - r_{10}\mathcal{P}_W \tag{2.4.14}$$

where we estimate $r_9 = 10^7$, $r_{10} = 6\times10^8$, $E \approx 30$ kJ mol^{-1} and write in nondimensional form as

$$\frac{dq_w}{d\tau} = \theta_5\left(\alpha_5 w q_f - q_w\right) \tag{2.4.15}$$

where $q_w = \mathcal{P}_W/\mathcal{P}_0$, $q_f = \mathcal{P}_f/\mathcal{P}_0$, $w = W/W_0$, $\alpha_5 = \dfrac{r_9}{r_{10}}$, $\theta_5 = \dfrac{r_{10}l^2}{D_W}$

Similarly for the polymer - zinc ion reaction we model the rate of increase of $\mathcal{P}_z$ as

$$\left[\frac{d\mathcal{P}_z}{dt}\right]_+ = \sqrt{\frac{kT}{2\pi m}}\frac{NWZ_W}{VW_0Z_0}\pi d^2 \frac{10^2}{10^5}\mathcal{P}_f \tag{2.4.16}$$

We suppose that it is the initial history of the adsorbed layer and the polymer - zinc ion interaction which is most important in determining the behaviour of the model and time to failure. Zinc ion concentrations in the bulk film and the adsorbed layer will be assumed initially zero. We argue that significant concentrations of zinc ion only arise after the adsorbed layer has degraded and reverted to a state equivalent to that of the bulk polymer.

Ideally we might formulate zinc ion and electrolyte mobility according to the approach used by Nguyen et al. (1996) where they considered mass diffusion of electrolyte through an impermeable slab (the paint film) punctured by tortuous transmembrane pores. We might include also lateral diffusion of ions and electrolyte on the metal surface (for example Nguyen et al., 1991). Instead of adapting the kinetic theory of gas dynamics to the development of our model we might properly consider quantum mechanical principles and use Fermi-Dirac and Bose-Einstein distributions rather than the classical Maxwell distribution introduced in eq 2.4.2. However with our assumptions of initially low zinc ion concentrations and thin adsorption boundary layer we suppose that any zinc ions created will first move to the bulk paint film at x=0. We suppose that there is initially a large activity gradient forcing this transport, and secondly that if any collisions should occur along the way, only 10^{-3} of them (see eq 2.4.13) are likely to be with polymer functional units. From there it follows that zinc ions either diffuse out through the bulk paint film according to a set of diffusion equations we describe later; or collide with, and become bound to, a polymer functional group of the polymer in the adsorbed layer according to the ideas described above for $\mathcal{P}_{W}$.

In dimensional form

$$\frac{d\mathcal{P}_z}{dt} = r_7 \frac{WZ_W}{W_0'Z_0} \mathcal{P}_f - r_8 \mathcal{P}_z \qquad (2.4.17)$$

assuming $E \approx 70$ kJ mol^{-1}, and with $r_7 = 10^7$, $r_8 = 10^2$.

In dimensionless form this is

$$\frac{dq_z}{d\tau} = \theta_4\left(\alpha_4 z q_f - q_z\right) \tag{2.4.18}$$

where $z = Z_W W/W_0 Z_0 = \mathcal{Z}/Z_0,$ $q_z = \mathcal{P}_Z/\mathcal{P}_0,$ $q_f = \mathcal{P}_f/\mathcal{P}_0,$ $\alpha_4 = \dfrac{r_7}{r_8},$ $\theta_4 = \dfrac{r_8 l^2}{D_W}$

We suppose that an adsorbed layer is about 100 nm $= 10^{-7}$ m thick, and the polymer density 10^6 g m^{-3} which gives

$$\mathcal{P}_0 = 10^{-3} \text{ mol m}^{-2} \tag{2.4.19}$$

$\mathcal{P}_M$ and M_P are related by:

$$\mathcal{P}_M = M_P \tag{2.4.20}$$

in dimensionless form:

$$q_m = \kappa_3 m_p \tag{2.4.21}$$

and

$$\mathcal{P}_W + \mathcal{P}_z + \mathcal{P}_M + \mathcal{P}_f = \mathcal{P}_0 \tag{2.4.22}$$

in dimensionless form:

$$q_w + q_z + q_m + q_f = 1 \tag{2.4.23}$$

2.5 DIFFUSION-GENERAL

Suppose diffusant molecules in a paint film exist in two states, free and trapped, of concentrations C and $k_C P_C$; where γ_C is the corresponding activity coefficient, and μ_C the chemical potential.

The net flux of free particles across any surface S is

$$\iint_S \frac{D_C C}{RT} \nabla \mu_C \cdot \mathbf{n} \, dS \tag{2.5.1}$$

where the current density of free particles $\mathbf{J}_Y$ is given by the product of diffusant velocity $-\dfrac{D_C}{RT} \nabla \mu_C$ and concentration C (Robinson and Stokes, 1959; Neogi, 1983 a, b; Thomas and Windle, 1982).

$$\mathbf{J}_C = -\frac{D_C C}{RT} \nabla \mu_C \tag{2.5.2}$$

Expression 2.5.2, is Fick's first equation ($\mathbf{J}_C = -D_C \nabla C$ adapted from Fourier's equation for heat conduction) incorporating non-ideal solution thermodynamics

(Neogi et al., 1986). The assumption here is that the gradient $\nabla \mu_C$ is the driving force of diffusion - the force experienced by diffusant molecules is proportional to the gradient of the chemical potential.

We have outlined in the introduction above a plausible scenario accounting for diffusion in a paint film. To properly quantify this conceptual model, a formulation of transport mechanisms in terms of thermodynamic influences and elastic stresses and strains in the film is required. A number of authors have developed various new transport models using these concepts (Carbonell and Sarti, 1990; Durning and Tabor, 1986; Herman and Edwards, 1990; Jou et al.,1991; Kim and Neogi, 1984; Larché and Cahn, 1973; Larché and Cahn, 1978; Morro et al., 1990; Neogi et al., 1986; Neogi, 1983; Oncone and Astarita, 1987). Others have adapted and extended existing formulations to include elements of mechanics or thermodynamics (Camera-Roda and Sarti,1990; Durning et al., 1985; Durning and Russel, 1985; Durning, 1985; Gostoli and Sarti, 1982; Gostoli and Sarti, 1983; Lasky et al., 1988; Petropoulos and Roussis, 1978; Petropoulos, 1984; Sarti et al., 1986; Thomas and Windle, 1982; Tsay and McHugh, 1990).

In general terms, the fundamental aspects of all diffusion models are described by the Maxwell - Cattaneo equation and this can be approximated by Fick's laws. Some authors have studied the correspondence between Fick's equations and the more general formulations of diffusion, and found that it is only in special circumstances that the Fickian formulation is incorrect (Durning and Tabor, 1986; Jou et al., 1991; Kim and Neogi, 1984; Larché and Cahn, 1982; Neogi et al., 1986; Neogi, 1983; Thomas and Windle, 1981; Vrentas and Duda, 1977). Consequently, we will follow McNabb and Foster (1973) and Wu et al. (1990), and adopt Fick's laws alluded to above, while at the same time, incorporating trapping sites to account for delayed uptake and desorption of diffusing ions and molecules, known to occur in paint films (Boxall et al., 1972; Brown and Park, 1970; Fialkiewicz and Szandorowski, 1974; Funke, 1967; Guruviah, 1970;

Katz and Munk, 1969; Kresse, 1973; Kumins, 1980; Rosen and Martin, 1991; Ulfvarson and Khullar, 1971). While our approach may not be thermodynamically rigorous or account for all the anomalous behaviour that can arise in paint films; it should provide a starting point for assessing the relative significance of some aspects of the transport and corrosion phenomena associated with paint films on metal surfaces.

Fick's second law is essentially the principle of mass conservation, and when a diffusing substance is interacting with trapped phases, the masses of all phases must be incorporated in the conservation equation. Consider an element of volume V enclosed by a surface S. The total mass Q of diffusant and trapped particles in V at any time is given by,

$$Q = \iiint_V (C + k_c P_c) dV \qquad (2.5.3)$$

If we assume the diffusing molecules are conserved (ie don't take part in chemical reactions with other diffusing ingredients within the paint film), a conservation equation is obtained by equating the rate of change of Q to the net flux of particles across the closed surface S;

$$\frac{\partial Q}{\partial t} = \iint_S \frac{D_c C}{RT} \nabla \mu_c \cdot \mathbf{n} \, dS \qquad (2.5.4)$$

Using the divergence theorem and equations 2.5.3, 2.5.4, we find

$$\iiint_V \left(\frac{\partial C}{\partial t} + k_c \frac{\partial P_c}{\partial t} \right) dV = \iiint_V \nabla \cdot \left(\frac{D_c C}{RT} \nabla \mu_c \right) dV \qquad (2.5.5)$$

and since this equation is valid for any volume V, in the paint film region,

$$\frac{\partial C}{\partial t} + k_c \frac{\partial P_c}{\partial t} = \nabla \cdot \left(\frac{D_c C}{RT} \nabla \mu_c \right) \qquad (2.5.6)$$

A second equation governing these two ingredients describes the rates of exchange of molecules between the free and bound populations. Suppose there are two rate constants (assuming one significant bound population): r_1 describing the rate of capture of free particles, and r_2 describing the rate of

escape of bound particles back into the diffusing stream. Then the rate of increase of P_C is given by,

$$\frac{\partial P_C}{\partial t} = r_1 C P_f - r_2 P_C \qquad (2.5.7)$$

where
$$P_c + P_f = P_0 \qquad (2.5.8)$$

The derivation of the rate equation 2.5.7 is based on the assumption that the rate of capture of diffusing molecules at each point of the medium is proportional to the neighbourhood concentration of diffusing molecules and to the number of unoccupied trapping sites per unit volume near the point, while the release rate at the same point is just proportional to the population density or concentration of the trapped phase.

2.6 DIFFUSION EQUATIONS

We suppose that the paint film is a slab bounded by two parallel planes at x=0 and x=l (the base and top of the film respectively). The slab is supposed thin and the medium homogeneous, so that effectively, the geometry is one dimensional with diffusive transport exclusively parallel to the x direction, with all diffusing substances entering and leaving the slab through its plane faces.

Oxygen diffusion is believed to occur essentially independently of any trapping dynamics. While some trapping probably does exist, Fickian diffusion provides an adequate representation of oxygen diffusion (Guruviah, 1970; Haagen and Funke, 1975; Kumins and Kwei, 1968; Xiao et al., 1990). We assume that the paint film is fully cured and that no further reaction occurs with oxygen. Note that some polymers cure by oxidative crosslinking, for example alkyd paints, and the reaction may proceed gradually for months and years. However we shall

assume that any residual reaction with oxygen from this source is negligible. The concentration $U(x, t)$ mol m^{-3} of oxygen is described by a linear diffusion equation

$$\frac{\partial U}{\partial t} = \frac{\partial}{\partial x}\left[\frac{D_U U}{RT}\frac{\partial \mu_U}{\partial x}\right]$$

(2.6.1)

Unlike atmospheric oxygen, water has a greater interaction with paint films (Bellucci and Nicodemo, 1993; Boxall et al., 1972; Brown and Park, 1970; Funke, 1967; Kumins and Kwei, 1968; Kunin, 1972; Perera and Heertjes, a-e 1971; Rowland, 1980; Yasheen and Ashton, 1978). Some of this interaction is associated with plasticisation and swelling. Additionally certain paint films are found to accumulate a dispersed water phase near water saturation of the film (Cherry and Mayne, 1962; Maitland and Mayne, 1962; Perera and Heertjes, a-e 1971). This dispersed water phase (when it exists) is seen microscopically to consist of discrete unconnected vesicles of water.

Initially some controversy existed as to whether or not 'pores' existed in paint films (below Critical Pigment Volume Concentration). Some early work concluded that pores did not exist. Krypton gas absorption indicated that pores in paint films were non existent or of molecular dimensions; and electron microscope studies failed to detect any evidence of pores. It was theorised that if pores did exist and if gases were passed through them the diffusion should obey Graham's Law of Diffusion. In neither dry nor wet films was Graham's Law obeyed and this was considered strong evidence for the absence of pores. Cherry and Mayne summarised these findings in 1961. However other experiments employing electrolytic and electroendosmotic techniques concluded that pores did exist.

Cherry and Mayne, 1961, and Maitland and Mayne, 1962, explained that these seemingly contradictory results arose from pores of atomic or molecular dimensions which could swell and become macroscopic under certain conditions.

Typically pores exist in the form of molecular size polymer structures (or polymer functional groups as discussed above). When the film was dry or saturated with water these molecular pores remained of molecular dimensions and were too small to significantly influence the process of diffusion through the bulk polymer film. Under the influence of electric fields and electrolyte solutions the functional groups associated with the pores become ionised and may exchange ions with the electrolyte solution. This combined with the plasticising effect of water on some polymers, can in certain paints result in inflated pores which in extreme cases appear as visible electrolyte filled vesicles.

Maitland and Mayne, 1962, discussed "fast" and "slow" changes in electrolytic resistance of paint films in electrolyte solutions. The fast change was due to sorption of water from the surrounding solution and resulted in equilibrium in times of order 10 minutes for the paint films studied. The slow change was due to ion exchange between ionogenic groups within the polymer matrix (functional groups such as -COOH) and ions in the external electrolyte. Temperature was found to have a profound effect on the rates of exchange; at elevated temperatures such as 60°C equilibrium was attained in the order of 10 hours, compared to weeks at room temperature.

Kunin, 1972, showed that at low electrolyte concentrations (10^{-3} M) ion exchange is rate limited by diffusion of ions through the bulk polymer matrix. At high concentrations (0.1 M) a particle diffusion mechanism is generally accepted. One version of this is Jenny's Contact Exchange Theory where it is postulated that ions in the polymer matrix can oscillate some finite distance and may be considered as occupying an oscillation volume. Ion transfer or exchange will occur whenever two oscillation volumes overlap. Both bulk diffusion and particle diffusion processes occur at intermediate concentrations.

Crank and Park, 1968, discuss diffusion of water in a variety of polymer systems and show that varying polymer chemistry and composition results in a spectrum

of diffusion characteristics. Although most cases are to a good first approximation represented by Fickian diffusion, anomalous response to transients can occur. Additionally changes in the polymer matrix itself (resulting from sorption of ions for example) can produce further anomalous behaviour on longer time scales.

We suppose that sorption and transport of water in paint films is represented by a combination of Fickian diffusion and Langmuir sorption dynamics. Diffusing water is denoted by $W(x, t)$ mol m^{-3}, and sorbed water by $P(x, t)$ mol m^{-3}. Polymer functional groups are considered the primary agents for sorbing water molecules, so total water in the paint film is the sum of W and P_W, which satisfy the system of equations

$$\frac{\partial}{\partial t}\left[W + k_1 P_W\right] = \frac{\partial}{\partial x}\left[\frac{D_W W}{RT}\frac{\partial \mu_W}{\partial x}\right] \tag{2.6.2}$$

$$\frac{\partial P_W}{\partial t} = r_1 \frac{W}{W_0} P_f - r_2 P_W \tag{2.6.3}$$

The units chosen for W and P_W (mol m^{-3}) make $k_1=1$. We estimate $r_1 = 10^7$ and $r_2 = 6 \times 10^8$ in a similar fashion to the rate constants for Langmuir adsorption onto the metal surface (equation 2.4.14)

We will ignore for now explicit ion exchange effects as we concentrate on the films early history, but incorporate the effect of adsorbed zinc which modifies the polymer matrix with a conservation equation

$$P_W + P_Z + P_f = P^{+}_0(x, t) \tag{2.6.4}$$

and

$$P^{+}_0(x, t) = P_0 + Z_W W/W_0 = P_0 + \mathfrak{z} \tag{2.6.5}$$

where $Z_W(x, t)$ is mol   ratio   in water. Z_W has been combined with the total polymer functional group concentration P_0 on the basis that zinc has a strong interaction with polymer functional groups (in fact much stronger than has water) and will form associations with these groups which result in modified functional units. From the work of Maitland and Mayne 1962 and Cherry and Mayne 1961

it is clear that the presence of additional ionogenic material within the polymer matrix has a strong influence on paint film properties.

Again unlike oxygen, zinc has a strong interaction with polymer films (Kunin, 1972). As with water, we suppose that the sorption and transport of water in paint films is described by a combination of Fickian diffusion and Langmuir sorption dynamics. Diffusing zinc is denoted by $Z_W(x, t)$ mol ratio in water and adsorbed zinc by $P_z(x, t)$ mol m^{-3}, so total zinc is the sum of Z_W and P_z. zinc is assumed to satisfy the system of equations

$$\frac{\partial}{\partial t}\left(\mathbf{3} + k_2 P_z\right) = \frac{\partial}{\partial x}\left[\frac{D_z \mathbf{3}}{RT}\frac{\partial \mu_z}{\partial x}\right] \tag{2.6.6}$$

$$\frac{\partial P_z}{\partial t} = r_3 \frac{W}{W_0}\frac{Z_w}{Z_0}P_f - r_4 P_z \tag{2.6.7}$$

We have supposed that unlike the paint-metal interface the bulk polymer does not allow significant corrosion product Z_c mol m^{-3} to accumulate, and that whatever zinc corrosion product exceeds the solubility level is taken up by polymer or by zinc modified polymer functional groups according to expressions 2.6.7 and 2.6.8. The units chosen for $\mathbf{3} = Z_W W/W_0$ (mol ratio in water) and P_Z (mol m^{-3}) make $k_2 = 1$. As before we estimate $r_3 = 10^7$ and $r_4 = 10^2$ in a similar fashion to the rate constants for equation 2.4.17

2.7 BOUNDARY CONDITIONS

We suppose that the painted metal surface modelled is subject to constant oxygen concentration at $x = l$

$$U(x = l, t) = U_0 \tag{2.7.1}$$

which in dimensionless form is

$$u(x=1, \tau) = 1 \tag{2.7.2}$$

and that the water concentration at $x = l$ is some function of time such as may correspond to typical atmospheric weather conditions

$$W(x = l, t) = W_0(t) \tag{2.7.3}$$

which in dimensionless form is

$$w(x=1, \tau) = w_0(\tau) \tag{2.7.4}$$

Typically zinc corrosion product diffusing to the surface will be removed by conversion to other species such as zinc carbonate or be washed away by rain water so that

$$Z(x = l, t) = 0 \tag{2.7.5}$$

which in dimensionless form is

$$z(x=1, \tau) = 0 \tag{2.7.6}$$

At the base of the paint film $(x=0)$ we suppose that gradient conditions apply such that the fluxes of zinc, water and oxygen involved in the corrosion reaction are related to the gradients at $x=0$. We now develop the equations in non dimensional form.

From eq. 2.3.28
for $z < w$, $z_c = 0$

$$-\frac{\partial z}{\partial x}\bigg|_{x=0} = -\phi_3\left(\frac{dz}{d\tau} + \kappa_5 \frac{dq_z}{d\tau}\right) + \phi_4\kappa_6\left[(1-m_p)^{3/2} wu^{1/2} + \alpha_8(1-m_p)^2 w^2\right] \tag{2.7.4}$$

and

for $z = w$, $z_c \geq 0$

$$-\frac{\partial z}{\partial x}\bigg|_{x=0} = -\phi_5\left(\frac{dz_c}{d\tau} + \kappa_7 \frac{dq_z}{d\tau}\right) + \phi_4\kappa_6\left[(1-m_p)^{3/2} wu^{1/2} + \alpha_8(1-m_p)^2 w^2\right] \tag{2.7.5}$$

From eq 2.3.2, 2.3.4 and 2.3.20 we find

$$\left.\frac{\partial w}{\partial x}\right|_{x=0} = \phi_1\left[\left(1-m_p\right)^{3/2} wu^{1/2} + 2\alpha_s\left(1-m_p\right)^2 w^2\right] \tag{2.7.6}$$

and
$$\left.\frac{\partial u}{\partial x}\right|_{x=0} = \phi_2\left(1-m_p\right)^{3/2} wu^{1/2} \tag{2.7.7}$$

where we assume for eq 2.7.6 that the corrosion flux (eq 2.3.13) results in the consumption of one mole water and one half mole oxygen (according to eq 2.3.2) plus 2 moles water (according to eq 2.3.4) for each mole of zinc. For eq 2.7.7 we assume only reaction 1 (equation 2.3.2) is operative and equate the gradient of oxygen at $x=0$ to the flux of oxygen due to the corrosion reaction f_{z1}.

2.8 DISCUSSION OF DIFFUSION AND ADSORPTION EQUATIONS

In general, the diffusion coefficients D are functions of the local diffusant concentrations (Fava, 1980), and in more sophisticated formulations of diffusion theory may be multicomponent, have geometric dependence and be functions of other state variables describing the paint film (Cussler, 1976; Shi and Vincent, 1993). Similarly, in formulations involving activity coefficients, the γ may be taken as functions of local diffusant concentrations and other variables.

Some tabulated values of D and γ exist (Valenzuela and Myers, 1989), as do some published experimental results (Perera and Heertjes, 1971 a-e; Bode, 1990), showing a dependence on concentration. However, if we assume as a first approximation that both D and γ are constants then expressions 2.6.1, 2.6.2 and 2.6.7 become

$$\frac{\partial U}{\partial t} = D_U \frac{\partial^2 U}{\partial x^2} \tag{2.8.1}$$

$$\frac{\partial}{\partial t}\left[W + k_1 P_W\right] = D_W \frac{\partial^2 W}{\partial x^2} \tag{2.8.2}$$

$$\frac{\partial}{\partial t}\left[\boldsymbol{z} + k_2 P_Z\right] = D_Z \frac{\partial^2 \boldsymbol{z}}{\partial x^2} \tag{2.8.3}$$

in nondimensional form these are

$$\frac{\partial u}{\partial \tau} = D_1 \frac{\partial^2 u}{\partial x^2} \tag{2.8.4}$$

$$\frac{\partial}{\partial \tau}\left(w + \kappa_1 p_w\right) = \frac{\partial^2 w}{\partial x^2} \tag{2.8.5}$$

$$\frac{\partial p_w}{\partial \tau} = \theta_6\left(\alpha_6 w p_f - p_w\right) \tag{2.8.6}$$

and
$$\frac{\partial}{\partial \tau}\left(z + \kappa_2 p_z\right) = D_2 \frac{\partial^2 z}{\partial x^2} \tag{2.8.7}$$

$$\frac{\partial p_z}{\partial \tau} = \theta_7\left(\alpha_7 z p_f - p_z\right) \tag{2.8.8}$$

where $x = x/l$, $\tau = D_W t/l^2$, $D_1 = D_U/D_W$, $u = U/U_0$, $w = W/W_0$, $z = Z_W W/W_0 Z_0 = \boldsymbol{z}/Z_0$,

$D_2 = D_Z/D_W$, $p_f = P_f/P_0$, $p_w = P_W/P_0$, $p_z = P_Z/P_0$, $\kappa_1 = \dfrac{k_1 P_0}{W_0}$, $\alpha_6 = \dfrac{r_{11}}{r_{12}}$, $\theta_6 = \dfrac{r_{12} l^2}{D_W}$,

$\kappa_2 = \dfrac{k_2 P_0}{Z_0}$, $\alpha_7 = \dfrac{r_{13}}{r_{14}}$, $\theta_7 = \dfrac{r_{14} l^2}{D_W}$.

If we consider primarily the early history of the painted metal surface so that the polymer matrix is unaffected by ion any exchange and no zinc corrosion product has accumulated, and suppose that only slowly varying functions $w(x=1, \tau)$ on the paint film surface are considered then the transport of water through the film becomes effectively a Fickian diffusion process where effects of trapping become

negligible. In a simplified version of the model we might ignore eq 2.6.3 and write for transport of w

$$\frac{\partial w}{\partial \tau} = \frac{\partial^2 w}{\partial x^2}$$

(2.8.9)

and eq 2.6.5 becomes

$$p_z + p_f = 1$$

(2.8.10)

In general we expect that diffusion will not much limit the entry of water and oxygen, so that in a further simplification expressions 2.7.6 and 2.7.7 might be approximated by zero gradient conditions on $x = 0$ when we consider the early history of the system (when corrosive fluxes are very small) so

$$\left. \frac{\partial w}{\partial x} \right|_{x=0} = 0$$

(2.8.11)

$$\left. \frac{\partial u}{\partial x} \right|_{x=0} = 0$$

(2.8.12)

Following this speculation that the paint film does not provide an effective barrier to oxygen (or water) we might make a further simplification and suppose that in general f_{zl} of expression 2.3.13 dominates and

$$f_z = \phi_4 \kappa_6 \left(1 - m_p\right)^{3/2} w u^{1/2}$$

(2.8.13)

2.8 INITIAL CONDITIONS

A typical starting point of the model is, at $\tau = 0$:

$$u = 0, \quad 0 \leq x \leq 1$$

$$w = 0, \quad 0 \leq x \leq 1$$

$$z = 0, \quad 0 \leq x \leq 1$$

$$z_c = 0, \quad x = 0$$

$$m_w = 0, \quad m_u = 0, \quad m_p = 1$$

$$q_w = 0, \quad q_z = 0$$

$$p_w = 0, \quad p_z = 0$$

3 MODEL SUMMARY

Independent variables are taken as: $x = x/l$ and $\tau = D_W t/l^2$ $\qquad$ (3.1)

The dependent variables are defined by: $\;u = U/U_0$, $\;w = W/W_0$,

$z = Z_W W/W_0 Z_0 = \mathfrak{z}/Z_0$, $\;p_f = P_f/P_0$, $\;p_w = P_W/P_0$, $\;p_z = P_Z/P_0$ $\qquad$ (3.2)

$q_f = \mathcal{P}_f/\mathcal{P}_0$, $\;q_w = \mathcal{P}_W/\mathcal{P}_0$, $\;q_u = \mathcal{P}_U/\mathcal{P}_0$, $\;q_z = \mathcal{P}_Z/\mathcal{P}_0$, $\;q_m = \mathcal{P}_M/\mathcal{P}_0$,

$m_f = M_f/M_0$, $\;m_w = M_W/M_0$, $\;m_u = M_U/M_0$, $\;m_p = M_P/M_0$, $\;z_c = Z_c/Z_{c0}$ $\qquad$ (3.3)

Dimensionless parameters are defined by: $\qquad D_1 = D_U/D_W$, $\;D_2 = D_Z/D_W$

$$\kappa_1 = \frac{k_1 P_0}{W_0},\; \kappa_2 = \frac{k_2 P_0}{Z_0},\; \kappa_3 = \frac{M_0}{\mathcal{P}_0},\; \kappa_4 = \frac{Z_0}{P_0},\; \kappa_5 = \frac{\mathcal{P}_0}{Z_0 k_3},\; \kappa_6 = \frac{W_0}{Z_0},\; \kappa_7 = \frac{P_0}{Z_{c0}}$$

$$\alpha_1 = \frac{r_1}{r_2},\; \alpha_2 = \frac{r_3}{r_4},\; \alpha_3 = \frac{r_5}{r_6},\; \alpha_4 = \frac{r_7}{r_8},\; \alpha_5 = \frac{r_9}{r_{10}},\; \alpha_6 = \frac{r_{11}}{r_{12}},\; \alpha_7 = \frac{r_{13}}{r_{14}},\; \alpha_8 = \frac{\rho_2 W_0}{\rho_1 U_0^{1/2}}$$

$$\theta_1 = \frac{r_2 l^2}{D_W},\; \theta_2 = \frac{r_4 l^2}{D_W},\; \theta_3 = \frac{r_6 l^2}{D_W},\; \theta_4 = \frac{r_8 l^2}{D_W},\; \theta_5 = \frac{r_{10} l^2}{D_W},\; \theta_6 = \frac{r_{12} l^2}{D_W},\; \theta_7 = \frac{r_{14} l^2}{D_W}$$

$$\phi_1 = \frac{\rho_1 l U_0^{1/2}}{D_W},\; \phi_2 = \frac{\rho_1 l W_0}{2 D_U U_0^{1/2}},\; \phi_3 = \frac{k_3 D_W}{l D_Z},\; \phi_4 = \frac{\rho_1 l U_0^{1/2}}{D_Z},\; \phi_5 = \frac{Z_{c0} D_W}{l Z_0 D_Z} \qquad (3.4)$$

At $x = 0$, $\tau > 0$

$$\frac{dm_w}{d\tau} = \theta_1\left[\alpha_1\left(1 - m_p\right)w m_f - m_w\right] \qquad (3.5)$$

$$\frac{dm_u}{d\tau} = \theta_2\left[\alpha_2\left(1 - m_p\right)u m_f - m_u\right] \qquad (3.6)$$

$$\frac{dm_p}{d\tau} = \theta_3\left(\alpha_3 q_f m_f - m_p\right) \qquad (3.7)$$

$$m_p + m_w + m_u + m_f = 1 \qquad (3.8)$$

$$\frac{dq_z}{d\tau} = \theta_4\left(\alpha_4 z q_f - q_z\right) \qquad (3.9)$$

$$\frac{dq_w}{d\tau} = \theta_5\left(\alpha_5 w q_f - q_w\right) \qquad (3.10)$$

$$q_m = \kappa_3 m_p \qquad (3.11)$$

$$q_w + q_z + q_m + q_f = 1 \qquad (3.12)$$

In $0 < x < 1,\ \tau > 0$

$$\frac{\partial u}{\partial \tau} = D_1 \frac{\partial^2 u}{\partial x^2} \tag{3.13}$$

$$\frac{\partial}{\partial \tau}\left(w + \kappa_1 p_w\right) = \frac{\partial^2 w}{\partial x^2} \tag{3.14}$$

$$\frac{\partial p_w}{\partial \tau} = \theta_6\left(\alpha_6 w p_f - p_w\right) \tag{3.15}$$

$$\frac{\partial}{\partial \tau}\left(z + \kappa_2 p_z\right) = D_2 \frac{\partial^2 z}{\partial x^2} \tag{3.16}$$

$$\frac{\partial p_z}{\partial \tau} = \theta_7\left(\alpha_7 z p_f - p_z\right) \tag{3.17}$$

$$p_z + p_w + p_f = 1 + \kappa_4 z \tag{3.18}$$

Boundary conditions:

$x = 0,\ \ \tau > 0$

$$\left.\frac{\partial w}{\partial x}\right|_{x=0} = \phi_1\left[\left(1 - m_p\right)^{3/2} w u^{1/2} + 2\alpha_8\left(1 - m_p\right)^2 w^2\right] \tag{3.19}$$

$$\left.\frac{\partial u}{\partial x}\right|_{x=0} = \phi_2\left(1 - m_p\right)^{3/2} w u^{1/2} \tag{3.20}$$

for $z < w,\ z_c = 0$

$$-\left.\frac{\partial z}{\partial x}\right|_{x=0} = -\phi_3\left(\frac{dz}{d\tau} + \kappa_5 \frac{dq_z}{d\tau}\right) + \phi_4 \kappa_6\left[\left(1 - m_p\right)^{3/2} w u^{1/2} + \alpha_8\left(1 - m_p\right)^2 w^2\right] \tag{3.21}$$

for $z = w,\ z_c \geq 0$

$$-\left.\frac{\partial z}{\partial x}\right|_{x=0} = -\phi_5\left(\frac{dz_c}{d\tau} + \kappa_7 \frac{dq_z}{d\tau}\right) + \phi_4 \kappa_6\left[\left(1 - m_p\right)^{3/2} w u^{1/2} + \alpha_8\left(1 - m_p\right)^2 w^2\right] \tag{3.22}$$

At $x = 1,\ \tau > 0$

$$u = 1$$
$$w = w_0(\tau) \tag{3.23}$$
$$z = 0$$

Initial conditions:

At $\tau = 0$ $\quad m_w = 0,\ \ m_u = 0,\ \ m_p = 1,\ \ q_w = 0,\ \ q_m = 0,\ \ q_z = 0,$

$$p_w = 0,\ \ p_z = 0,\ \ u = 0,\ \ w = 0,\ \ z = 0,\ \ z_c = 0 \tag{3.24}$$

NOMENCLATURE

$x = \dfrac{x}{l}$

x is distance outward from the metal surface through the coating in metres and l is the coating thickness.

$\tau = \dfrac{D_W t}{l^2}$

D_W is the diffusion coefficient $m^2 s^{-1}$ for water and t is time (seconds).

$u(x, \tau) = \dfrac{U}{U_0}$

U is the oxygen concentration in mol m^{-3} and U_0 is the internal saturation oxygen content. $U^*(t)$ is the external oxygen concentration (taken as atmospheric oxygen, U_0^*) and $U^{**}(t)$ is the oxygen concentration in the adsorbed layer.

$w(x, \tau) = \dfrac{W}{W_0}$

W is the water concentration in mol m^{-3} and W_0 is the internal saturation water content. $W^*(t)$ is the external water concentration (taken as liquid water W_0^*, or some wetting function $W_0^*(t)$) and $W^{**}(t)$ is the concentration of water in the adsorbed layer.

$w_0(\tau) = \dfrac{W_0^*(t)}{W_0^*}$

w_0 is the internal non dimensional wetting function at $x=1$ driven by some external wetting function $W_0^*(t)$

$z(x, \tau) = \dfrac{Z_W W}{W_0 Z_0}$

Z_w is the zinc ion (zinc is used in this application but the model may readily be adapted to other metals) concentration in mol ratio of water (i.e. relative to the water content of the coating), Z_0 is the saturation zinc ion concentration. $Z_w^*(t)$ is the external concentration of zinc ion, which we shall take as zero, and Z_0^* is the saturation concentration of zinc hydroxide in water. $Z_w^{**}(t)$ is the concentration of zinc ion in the adsorbed layer, and Z_0^{**} is the saturation value.

$z_c(\tau) = \dfrac{Z_C}{Z_{C0}}$

Z_C is the solid zinc corrosion product (initially zinc Hydroxide) at the coating-metal interface in mol m^{-2}. Z_{C0} is an arbitrary reference concentration in mol m^{-2} intended to represent a state of light corrosion.

D_W, D_U, D_Z Diffusion coefficients for water, oxygen, and zinc ion respectively $m^2\ s^{-1}$.

$$p_f(x,\tau) = \frac{P_f}{P_0}$$ P_f is the concentration of free (unassociated) polymer functional groups in mol m^{-3} and P_0 is the total concentration of polymer functional groups.

$$p_w(x,\tau) = \frac{P_W}{P_0}$$ P_W is the concentration of polymer functional groups associated with water in mol m^{-3}.

$$p_z(x,\tau) = \frac{P_Z}{P_0}$$ P_Z is the concentration of polymer functional groups associated with zinc ions in mol m^{-3}.

$$q_f(\tau) = \frac{\mathcal{P}_f}{\mathcal{P}_0}$$ $\mathcal{P}_f$ is the concentration of free polymer functional groups on the metal surface in mol m^{-2} and $\mathcal{P}_0$ is the total surface concentration of free polymer functional groups.

$$q_w(\tau) = \frac{\mathcal{P}_W}{\mathcal{P}_0}$$ $\mathcal{P}_W$ is the surface concentration of polymer functional groups associated with water in mol m^{-2}.

$$q_z(\tau) = \frac{\mathcal{P}_Z}{\mathcal{P}_0}$$ $\mathcal{P}_Z$ is the surface concentration of polymer functional groups associated with zinc ions in mol m^{-2}.

$$q_m(\tau) = \frac{\mathcal{P}_M}{\mathcal{P}_0}$$ $\mathcal{P}_M$ is the surface concentration of polymer functional groups associated with metal active sites on the metal surface in mol m^{-2}.

$$m_f(\tau) = \frac{M_F}{M_0}$$ M_F is the surface concentration of free (unassociated) metal active sites on the metal in mol m^{-2} and M_0 is the total concentration of metal active sites.

$$m_w(\tau) = \frac{M_W}{M_0}$$ M_W is the surface concentration of metal active sites associated with water on the metal in mol m^{-2}.

$$m_u(\tau) = \frac{M_U}{M_0}$$ M_U is the surface concentration of metal active sites associated with oxygen on the metal in mol m^{-2}.

$$m_w(\tau) = \frac{M_W}{M_0}$$

M_W is the surface concentration of metal active sites associated with water on the metal in mol m^{-2}.

$$m_p(\tau) = \frac{M_P}{M_0}$$

M_P is the surface concentration of metal active sites associated with polymer functional groups on the metal in mol m^{-2}.

Table of parameters: Table 1

$\alpha_1 = 10^6$	$\theta_1 = 10^7$	$\phi_1 = 2.7 \times 10^{-3}$	$\kappa_1 = 1.8 \times 10^{-2}$	$D_1 = 1$
$\alpha_2 = 10^3$	$\theta_2 = 10^7$	$\phi_2 = 9.5$	$\kappa_2 = 10^5$	$D_2 = 10^{-4}$
$\alpha_3 = 1.67 \times 10^6$	$\theta_3 = 6 \times 10^4$	$\phi_3 = 10$	$\kappa_3 = 8.5 \times 10^{-2}$	
$\alpha_4 = 10^5$	$\theta_4 = 10^5$	$\phi_4 = 27$	$\kappa_4 = 10^{-5}$	
$\alpha_5 = 1.7 \times 10^{-2}$	$\theta_5 = 6 \times 10^{11}$	$\phi_5 = 10^8$	$\kappa_5 = 2 \times 10^5$	
$\alpha_6 = 1.7 \times 10^{-2}$	$\theta_6 = 6 \times 10^{11}$		$\kappa_6 = 5.6 \times 10^6$	
$\alpha_7 = 10^5$	$\theta_7 = 10^5$		$\kappa_7 = 2 \times 10^{-2}$	
$\alpha_8 = 8.9 \times 10^{-2}$				

Table of constants: Table 2

$r_1 = 10^{10}$	$r_7 = 10^7$	$r_{13} = 10^7$	$Z_0^* = 10^{-2}$ mol m^{-3}
$r_2 = 10^4$	$r_8 = 10^2$	$r_{14} = 10^2$	$Z_{c0} = 10^{-2}$ mol m^{-2}
$r_3 = 10^7$	$r_9 = 10^7$	$P_0 = 2 \times 10^{-4}$ mol m^{-2}	$P_0 = 10^3$ mol m^{-3}
$r_4 = 10^4$	$r_{10} = 6 \times 10^8$	$M_0 = 1.7 \times 10^{-5}$ mol m^{-2}	$D_U = 10^{-11}$ m^2 s^{-1}
$r_5 = 10^8$	$r_{11} = 10^7$	$W_0^* = 5.6 \times 10^4$ mol m^{-3}	$D_B = 10^{-11}$ m^2 s^{-1}
$r_6 = 60$	$r_{12} = 6 \times 10^8$	$U_0^* = 8$ mol m^{-3}	$D_Z = 10^{-15}$ m^2 s^{-1}
$\rho_1 = 9.6 \times 10^{-11}$	$\rho_2 = 5.4 \times 10^{-17}$	$k_1 = 1$	$k_2 = 1$
$k_3 = 10^{-7}$	$l = 10^{-4}$ m		

4. REVIEW OF MODEL DEVELOPMENT

4.1 PREFACE

While there was some confusion in the literature as to whether it was diffusion of oxygen, or of water, or of various ions, or some combination that was most important, the common feature of all models and theories was that diffusion was the controlling factor in corrosion protection provided by coatings. It was unknown whether or not trapping and absorption within the film had much effect on diffusive processes in paint films, but it was well known, for example, that this process has a dramatic effect on diffusion of hydrogen in steel (McNabb and Foster, 1963). There has been speculation that boundary layer effects might also account for some of the observed protective action of coatings, but again the evidence was largely speculative and limited to particular coatings or experimental methods (eg Rosen and Martin, 1991).

Following this background only diffusion was considered in the initial development of the model. The paint film was modelled as a thin slab with specified concentrations of water, oxygen, and metal corrosion products (eg. zinc hydroxide etc) at the outer boundary. The boundary conditions at the metal surface posed some difficulty. We quickly eliminated simple diffusion with zero gradient conditions because if this applied the concentrations of water and oxygen within the film should reach saturation in times of order 1 hour. The metal substrate should corrode freely as concentrations of water and oxygen approached the levels of the external environment.

Possibly diffusion of water or oxygen was rate limiting. If this were the case some gradient must exist within the paint film and be related to the diffusion coefficient of water or oxygen. It seemed that diffusion of oxygen might be rate limiting in some special cases (polymers with very small diffusion coefficients) but this couldn't be a general explanation. Many coatings with relative large diffusion

coefficients are known to effectively inhibit corrosion, and diffusion in these cases cannot explain the observed low corrosion rates.

A succession of increasingly complex diffusion models was considered. Properties such as boundary layers, trapping, and discontinuous activity functions were modelled. Eventually it was concluded that none of these diffusion models was capable of describing the general corrosion protective action of paint films. However one preliminary model, based on activity step functions, appeared to have the potential to provide a general explanation. Development of this model led to the concept of competitively adsorbed polymer competing for adsorption onto corrosively active sites on the metal surface.

Preliminary analysis of the diffusion-adsorption type of model confirmed that it could potentially account for the corrosion protection of paint films observed in practice. The model was developed further and reformulated several times. A major revision and re-derivation was made following a reformulation of the estimated and calculated parameters.

4.2 OXYGEN DIFFUSION RATE LIMITING

We supposed that oxygen diffusion is rate limiting. The flux of oxygen is

$$F_U = -D_U \frac{\partial U}{\partial x} = 8 \times 10^{-7} \ mol \ s^{-1} \ m^{-2} \qquad (4.2.1)$$

where we use $U_0 = 8 \ mol \ m^{-3}$, $D_U = 10^{-11} \ m^2 \ s^{-1}$ and suppose the film thickness is $10^{-4} \ m$.

Assuming that the dominant corrosion reaction is

$$Z_n + H_2O + \tfrac{1}{2}O_2 \rightarrow Z_n(OH)_2 \qquad (4.2.2)$$

then the rate of corrosion is

$$4 \times 10^{-7} \ mol \ s^{-1} \ m^{-2} = 3 \times 10^{-5} \ g \ s^{-1} \ m^{-2} = 0.1 \ mm \ per \ year.$$

This rate of corrosion is physically possible but it corresponds to about 10% of the maximum possible rate of corrosion of bare metal immersed in oxygenated water.

While this represents some protective action it does not account for protection provided by the majority of coatings (which have diffusion constants around the value used in this calculation).

In practice many coatings achieve a useful service lifetime of several years which requires that the rate of corrosion be less than 10^{-7} g s^{-1} m^{-2}. In this case the flux of oxygen consumed in the corrosion reaction must be so small that it generates negligible gradient which in turn results in oxygen levels at the interface near their saturation values. But this would create maximum corrosion. Consequently this model can at best apply only to special cases where the diffusion constant is small and the coating offers only poor protection.

4.3 WATER DIFFUSION RATE LIMITING

We next supposed that diffusion of water was rate determining. The flux of water is

$$F_W = -D_W \frac{\partial W}{\partial x} = 5.6 \times 10^{-3} \; mol \; s^{-1} \; m^{-2} \tag{4.3.1}$$

where we use $W_0 = 5.6 \times 10^4 \; mol \; m^3$, $D_W = 10^{-11} \; m^2 \; s^{-1}$ and suppose the film thickness as before is $10^{-4} \; m$. From this we calculate the flux of corrosion product as

$$F_z = 5.6 \times 10^{-3} \; mol \; m^{-2} \; s^{-1} = 0.36 \; g \; m^{-2} \; s^{-1} \tag{4.3.2}$$

But this exceeds even the maximum rate of corrosion of uncoated metal so this model also cannot generally explain observed corrosion rates.

4.4 BOUNDARY LAYER RESISTANCE

Having eliminated the basic diffusion based models from contention as a basis for our model of painted metal surfaces we next considered boundary layer resistance effects. In this variation of the preceding models we supposed that there were very thin layers (less than 10^{-6} m) on either side of the paint film: one at the air interface

and the other at the paint-metal interface. The diffusion coefficients in these thin layers may be one or two orders of magnitude greater than in the bulk paint film.

Using analogous reasoning to that applied above, and supposing $D_U = 10^{-13}$ $m^2 s^{-1}$, interfacial layer thickness $\Delta x = 10^{-6}$m, and that the two interfacial layers account for all the diffusive resistance then

$$F_U = 10^{-13} \times \frac{8\,mol\,m^{-3}}{2 \times 10^{-6}} = 8 \times 10^{-7}\ mol\ s^{-1}\ m^{-2} \qquad (4.4.1)$$

So that the same conclusions as arrived at above apply here: this variation of the model is also incapable of accounting for general corrosion behaviour of painted metal surfaces.

4.5 ACTIVITY STEP FUNCTIONS

Next we considered thermodynamic potentials and began development of a two stage paint film. The bulk of the paint film was modelled along the lines described above and we included trapping of some species to account for diffusive delays on short time scales. We supposed that there was an interfacial layer between the paint film and the metal surface where the polymer was adsorbed onto the metal surface. From reports in the literature we recognised that this relatively thin interfacial layer could have physical properties quite different from the bulk film; Tang and Song (1993) and Nguyen et al. (1994). When strongly adherent the adsorbed layer may act as a crystalline solid where the thermodynamic activity coefficients of water and oxygen may be much larger than in the bulk paint film. As the thermodynamic potentials are generally in equilibrium between paint film and adsorbed layer, the discontinuity in activity coefficients could lead to discontinuities in physical concentrations (mol m^{-3}) of water and oxygen. It was realised that physical concentrations of water and oxygen could be sufficiently low in a crystalline polymer structure to account for the observed corrosion rates of coated metal surfaces. Even when the bulk paint film had reached saturation in oxygen and water, the adsorbed polymer layer could maintain lower physical

concentrations on the metal surface - providing that the adsorbed layer remained tightly adherent and substantially crystalline.

It was found experimentally that an initially crystalline adsorbed layer will degrade upon exposure to water and corrosion product. The experimental manifestation of this degradation is loss of adhesion, blistering, accumulation of corrosion product, and changes in polymer conformation. Accompanying degradation are changes in activity coefficients.

Initial attempts to calculate and model the activity coefficients in the adsorbed layer proved problematic and led to a profusion of variables, constants and equations. To simplify the model we supposed that the activity coefficients might be approximated by step functions which took initially some large constant value, and then at some critical state in the adsorbed layer's evolution, would swing to values near 1 to represent the degraded layer. The problem was to determine at which point in the system's evolution the activity coefficients changed from one value to the other. The initial values corresponded to extremely low rates of corrosion (metal effectively protected by a paint film), while the subsequent value corresponded to high rates of corrosion with minimal protection of the metal surface (comparable to the situation in 4.2 above).

We then explored various models of activity coefficients but found that great complexity resulted from even the simplest models and additionally the physical basis for these models was difficult to substantiate. The step function concept remained attractive and further work was done on trying to derive a plausible step time from the state of existing variables. The best measure seemed to be the concentration or quantity of corrosion product accumulated. When the concentration of corrosion product reached some critical value we set the step functions to their alternative values. The problem remaining was that we could not readily justify the model. We could choose step conditions which produced the sorts of time scales for corrosion that were expected from experiment but there was an element of having externally fixed the result by the choice of step

conditions. The worry was that the model did not itself produce a mechanism to determine the step time and step condition.

4.6 COMPETITIVE ADSORPTION

Our initial research had shown that in steady state conditions (such as immersion) diffusion was not the corrosion rate limiting mechanism. Diffusion times through paint films are usually in the range of one minute to one hour. Consequently trapping effects and diffusive time lags in non-linear diffusion will only have significant effect on these relatively short time scales. Painted metal surfaces typically display resistance to corrosion on time scales of days to years. In intermittent wetting the periods of wetness are generally longer than one hour, yet the rate of corrosion is typically kept at very low values even when the film is saturated with water and oxygen.

Experiments have been conducted on steel coupons enclosed in free standing, non adherent, paint film pockets which were stored in a humidity chamber and subsequently tested for corrosion; (Rosen and Martin (1991), and unpublished Resene Paints Ltd experimental results) More corrosion was found to occur with detached films than with adherent films where the coupons are painted directly.

One explanation for these results depends on the polymer layer adjacent to the metal surface being crystalline. When adsorbed onto the rigid metal surface, normally mobile polymer molecules become "frozen" and exhibit significantly different physical properties compared to polymer in the bulk paint film. Léger et al (1992) showed that polymers in an adsorbed layer on a solid surface were significantly slowed down compared to polymer molecules in the surrounding solution. Thermodynamic activity coefficients in crystalline solids are typically greater than in solutions or rubbery-amorphous polymers. Consequently it is arguable that concentrations of reactive molecules in a crystalline layer immediately adjacent to a metal surface may be substantially lower than the concentrations in

the adjoining bulk polymer (refer *Figure 2*). Lower concentrations of reactants at the metal surface will directly lower the rate of corrosion, reduce the ionic conductivity of the layer adsorbed onto the metal; and lower initial corrosion rates will reduce the rate of degradation of the adsorbed crystalline layer and prolong the systems time in a low corrosion regime.

A second (related) explanation arises from a novel conception of a metal surface. Traditionally it is conceived that a plane metal surface is more or less uniformly reactive to corrosively active species. In an attempt to account for the observed distribution of corrosion cells and pits in real corroding metal surfaces we proposed that the metal surface was not uniformly reactive. Instead we envisaged the surface composed of a more or less random distribution of discrete highly reactive sites of roughly atomic dimensions. In fact the size and degree of reactivity are almost certainly not constants but distributions which are characteristic of each particular piece of metal. We assumed as a first approach that we could describe a corrosively active surface as randomly scattered 'mean activity' 'mean size' active sites. When corrosion occurs it is believed to occur at an active site while the adjacent surface is passive. The passivity of the surrounding surface is speculated to arise from both inherent low reactivity, and from a shielding effect produced by intense activity at a nearby active site. This shielding is supposed to occur through diffusive depletion of corrosively active species in the vicinity of an active site, and possibly also through changes in the local electric potentials due to electrochemical processes at the active site. We speculated that the surfaces atomic topography (impurities, grain boundaries, dislocations, etc.) would govern a location's activity. Crommie et al. (1993) suggest some insight into the possible origins of active sites.

During the course of research into waterborne metal primers at Resene Paints Limited it was noticed in 1989 that freshly painted metal surfaces (mild steel, Aluminium and galvanised steel) exhibited unusual activity at discrete sites. Polymer was found to adsorb rapidly at specific sites on particular pieces of metal. When the process was interrupted before complete film formation had occurred,

and the panel gently cleaned, it was found that discrete, localised, areas of adsorbed polymer remained. When the panels were cured and recoated it was found that very little further activity remained. We hypothesised first that the original active sites corresponded to corrosively active sites. Second we hypothesised that the presence of bound (adsorbed) polymer on and around the active site inhibited ionic conduction and corrosion at the metal-polymer interface. Additionally we expect the strongly adsorbed polymer to possess significant crystallinity which results in low concentrations of reactants (water and oxygen) in contact with the metal active site. When the treated panels were subjected to more severe cleaning (scraping and scrubbing) it was found that a) more activity remained and b) additional sites appeared. We speculated from this that layers of adsorbed polymer could be physically removed, and that mechanical damage and change to the metal surface could alter reactivity.

From these observations (and the failure to otherwise explain observed corrosion rates) we formed the concept of competitive adsorption onto corrosively active sites. Basically, when polymer is adsorbed onto an active site, the site is passivated and inactivated. But when the site is unprotected by adsorbed polymer it is corrosively active. The competition equations were set up on the principles of multicomponent Langmuir adsorption isotherms. Initially we considered multilayer multicomponent adsorption. Multiple layers of water readily form on bare metal surfaces and adsorption isotherms are well documented. However little is reported concerning the adsorption isotherms of water etc. where it competes for adsorption with other species and in the presence of adsorbed polymer. We expect that up to the onset of rapid corrosion the metal surface is dominated by adsorbed polymer and hence there must be less than a mono-layer of adsorbed water. In the region of interest an assumption of single layers of adsorbed species should be satisfactory.

To account for the effects of the adsorbed layer's crystallinity on the thermodynamic activities of water and oxygen within the layer we made two assumptions. First that water and oxygen inside the layer were in thermodynamic

equilibrium with concentrations outside the layer. This is reasonable providing the bulk paint film effectively dominates the diffusion behaviour of the system, and that the adsorbed layer is thin so that it's physical capacity is small compared to that of the adjacent paint film and metal surface. Secondly we supposed that the layer's crystallinity was related to the value of M_p (the quantity of metal surface covered by adsorbed polymer). When M_p is large the crystallinity is also high, and the volume concentrations of water and oxygen are smaller than those in equilibrium outside the layer. We modelled this as

$$W^{**} = W\left(\frac{M_0 - M_p}{M_0}\right) \qquad (4.6.1)$$

$$U^{**} = U\left(\frac{M_0 - M_p}{M_0}\right) \qquad (4.6.2)$$

Where W^{**} and U^{**} are the molar volume concentrations of water and oxygen inside the adsorbed layer and W and U are the concentrations outside the layer, and M_0 is the total metal adsorption capacity. We selected this model over other variations because it displayed two desirable features. When polymer adsorption approaches M_0 we expect maximal crystallinity, and W^{**} and U^{**} should become smaller than W and U. When M_p becomes small W^{**} and U^{**} should approach the values for W and U.

4.7 CORROSION FLUX FORMULATION

The original aim was to calculate electrochemical processes directly and model the corrosion flux on electrochemical current density. From the corrosion reaction equations (eq 2.3.2, 2.3.4) and tables of standard electrode potentials we calculated an electrochemical potential for the corrosion cell depicted in *figure 6*.

Then using the Nernst equation

$$E = E^0 + \frac{RT}{F} \ln\left(\frac{a_{m_-}}{a_{m_+}}\right)$$ (4.7.1)

and Butler-Volmer equation

$$j^+(\rightarrow M, net) = je^+ \left\{ \exp\left[\frac{-z_+ \alpha \eta F}{RT}\right] - \exp\left[\frac{z_+(1-\alpha)\eta F}{RT}\right] \right\}$$ (4.7.2)

(Atkins, Physical Chemistry, 1978) we calculated current densities for the corrosion reaction related to the concentrations of the reactants. This is a common approach for electrodes in solution. But in the case of a painted metal surface the presence of the adsorbed polymer added a complication which seemed difficult to deal with. Specifically, adherent polymer added a resistance component to the electrochemical calculations. As discussed above there were difficulties and uncertainties in determining what the physical concentrations of water and oxygen were at the metal surface under an adsorbed polymer layer, particularly in the systems' early life when water concentrations were surmised to be low. With the electrochemical calculations the additional uncertainties of accounting for the effect of surface resistance in the adsorbed layer seemed insurmountable. The resistance presumably varies with water and dissolved ion content, and concentration of corrosion product; we expected also that the resistance would vary with the proportion of polymer remaining adherent as corrosion progressed. Some models were constructed but they could not be satisfactorily justified.

Next we reviewed the literature on modelling of corrosion fluxes. From a selection of sources - Spence (1992), Ailor (1982), Chilton (1969), Evans (1950) we found only empirical approaches which were based typically on either linear models (constant corrosion rate) or Poisson models (logarithmic corrosion rate). The main aim of the reported models was to predict corrosion rates for various exposure conditions of bare metal surface.

Finally a direct chemical kinetics approach was attempted. Basic chemical reactions were written (for example eqns. 2.3.2, 2.3.4) and from the molecular ratios of reactants we derived a series of chemical rate equations. Using these rate equations we could relate rates of corrosion to physical concentrations of reactants on the metal surface (ie. in the adsorbed polymer layer). Additionally we could relate these rates of corrosion to fluxes of reactants consumed in the corrosion reaction. It still remained to determine what the physical concentrations were but we could demonstrate reasonable agreement with calculated corrosion rates and available published and experimental information.

4.8 CORROSION RATE EQUATIONS

Initially we formulated the corrosion rate equations as a system of ordinary differential equations which attempted to account independently for the rates of formation and removal of every species present (Zn^{++}, $Zn(OH)^+$, OH^-, O_2, H_2O, H_2, H^+, CO_3^-, etc.). This led to some dubious assumptions and it was realised that we did not have sufficient information available to create a model on this level. The specific details of atomic reactions and molecular processes involved in the corrosion process were not sufficiently well understood - or even known.

Eventually we adopted a more pragmatic approach to the treatment of reaction rates and formulated rate equations based on the overall chemical reactions (Frost and Pearson, 1960). In general there is no guarantee that this will yield the correct form of rate equation; however some justification is found when the theoretical rates agree reasonably well with the reported rates at various concentrations of reactants. While we do not know what the detailed atomic and molecular steps in the corrosion process are, the agreement found with this rate model indicates it is a satisfactory starting point. One of the desirable features of directly modelling the corrosion reaction kinetics is that we relate corrosion flux directly to physical concentrations of reactants in the (crystalline) adsorbed layer.

One assumption made was that the pH at the interface remained constant. Some stretching of the concept of pH is required: In a solution pH has obvious meaning; but in surface systems which are substantially solid state (adsorbed polymer) the notion of pH applies only to the extent that water is present. After some trial and error we adopted a system where pH is calculated on a scale based on the physical concentration of water.

4.9 BOUNDARY CONDITIONS

Various boundary conditions have been used during the course of development. The outer boundary has generally been set at specified fixed concentrations or specified functions of time. The intention is to ultimately specify external concentrations as functions of time which represent mean weather conditions and times of wetness found in real atmospheric exposures.

The metal-paint film boundary was originally set with gradient conditions. First we used zero gradient conditions for water and oxygen; then for zinc various fixed concentrations and later flux conservation equations. When a two layer paint film model was adopted the governing equations for the layer adjacent to the metal became ordinary differential equations, and the focus on boundary conditions moved to the interface between the adsorbed layer and the bulk paint film.

Boundary conditions between the bulk paint film and adsorbed layer have mostly been gradient types based on conservation of water, oxygen and corroding species (zinc) molecules. We assumed that the adsorbed layer did not have significant capacitance and that fluxes of water and oxygen across the boundary were related to their consumption in the corrosion reaction based on equations 2.3.2 and 2.3.4. The form of the flux equations has varied as the modelling of the corrosion flux has developed. Ultimately rather awkward boundary equations have developed in an

attempt to better account for physical processes. It is likely however that simpler conditions (eg. zero gradients for water and oxygen) will be found to provide satisfactory approximations for certain stages of the modelled system's evolution. It is anticipated that the numerical solutions of the model will confirm this and allow simplifications which will aid the analytical analysis of the model. The case for the zinc boundary conditions is more complex since zinc corrosion product is generated on the metal surface and a gradient condition including a source term seems natural. There is however a possibility that the zinc corrosion product concentration rapidly rises to saturation on the metal surface. In which case further simplification could be made. Some analytical work was done on this (see later) and again it is anticipated that the numerical calculations will help clarify the type of boundary condition required, and the conditions under which they apply.

4.10 PARAMETER ESTIMATION

Estimation of parameters has been particularly difficult. In the early stages of model development the qualitative behaviour of the model was sufficient to determine that a particular model could not account for observed paint film behaviour. The parameters were of secondary importance, and their approximate values were easily accessible from the literature and from experiment.

The model has progressed through a number of generations in the pursuit of model behaviour which agrees with experimental observation. Parts of the model have remained substantially intact from the first stages along with associated parameters eg. Diffusion equations and coefficients. In developing the model to describe competitive adsorption we found that relevant experimental data was very hard to come by and at best only comparative data was available.

In the construction of the competitive adsorption portion of the model we have used parameter concepts such as rates of adsorption and desorption in a semi solid state system. While these have an immediate physical and conceptual significance they are not readily amenable to experimental determination and measurement.

The parameters involved in the corrosion flux equations have similarly been difficult to quantify. But reported experimental corrosion rates under various conditions have allowed parameters to be estimated for the corrosion equations we derived. Where reported or experimental data has not been available we have resorted to estimation from physical principles. These parameters in particular require further experimental investigation. Further, it is believed that variation of the parameters through optimisation of polymer and paint film physical properties will allow improvement in paint film performance over metal surfaces.

4.11 CORROSION PRODUCT SATURATION ON THE METAL SURFACE

It was believed from an early stage that the time for corrosion product to reach saturation on the painted metal surface must represent a significant milestone in the model's (and the painted metal surface's) evolution. We reasoned that if the levels of corrosion product remained low on the metal surface then they must also remain low throughout the entire paint film. The diffusion coefficient for corrosion product is typically small and we deduced that the rate of corrosion must also remain low while concentrations throughout the film were low. A corollary is that the time for corrosion product to reach saturation serves as a measure of the paint film's performance: the longer it takes for saturation to occur the "better" the paint film. While a painted surface may still perform satisfactorily with corrosion product at saturation on the metal surface we expect that low corrosion product levels guarantee good performance. Consequently we looked for surface

saturation times and hoped to demonstrate that the model could accommodate saturation times ranging from seconds to months.

At an intermediate stage in the model's development we determined the time for corrosion product saturation as follows:

Exploratory Model equations:

Note that the nomenclature, variables and parameters used in this section are not exactly the same as those derived earlier, and then analysed later.

$0<x<l$
$$\frac{\partial U}{\partial t} = D_U \frac{\partial^2 U}{\partial x^2} \tag{4.11.1}$$

$$\frac{\partial}{\partial t}\left(W + P_W\right) = D_W \frac{\partial^2 W}{\partial x^2} \tag{4.11.2}$$

$$\frac{\partial}{\partial t}\left(Z + P_Z\right) = D_Z \frac{\partial^2 Z}{\partial x^2} \tag{4.11.3}$$

$$\frac{\partial P_W}{\partial t} = r_1 W P_f - r_2 P_W \tag{4.11.4}$$

$$\frac{\partial P_Z}{\partial t} = r_3 Z P_f - r_4 P_Z \tag{4.11.5}$$

$$P_M + P_W + P_Z + P_f = 1 \qquad \left(x > 0, \quad P_M = 0\right) \tag{4.11.6}$$

$t=0$: $U = 0$, $W = 0$, $Z = 0$, $P_W = 0$, $P_Z = 0$, $M_U = 0$, $M_W = 0$, $M_P = M_{P_0} \approx 1$

$t>0$, $x=l$: $\qquad\qquad U = 1$, $W = f(t) = 1$, $Z = 0$

$t>0$, $x=0$:
$$D_U \frac{\partial U}{\partial x}\bigg|_{x=0} = 0.1 M_U M_W \tag{4.11.7}$$

$$D_W \frac{\partial W}{\partial x}\bigg|_{x=0} = 0.1 \, M_U M_W \tag{4.11.8}$$

for $Z < 1$
$$-D_z \frac{\partial Z}{\partial x}\bigg|_{x=0} = 0.1\, M_U M_W \tag{4.11.9}$$

At x=0, $t>0$:
$$\frac{dM_W}{dt} = r_7\, WM_f - r_8\, M_W \tag{4.11.10}$$

$$\frac{dM_U}{dt} = r_9\, UM_f - r_{10}\, M_U \tag{4.11.11}$$

$$\frac{dM_P}{dt} = r_{11}\, P_f M_f - r_{12}\, M_P \tag{4.11.12}$$

$$M_U + M_W + M_P + M_f = 1 \tag{4.11.13}$$

$$P_M = \eta\, M_P \tag{4.11.14}$$

We have omitted activity coefficients and the derivation of this preliminary version of the model. Equation 4.11.9 is shown in simplified form; in the original version of the model we considered that the equation took one of two forms depending upon the value of Z. For $Z=1$ we used an alternate form of eq 4.11.9 and introduced another variable to describe the thickness of an accumulated corrosion product layer at x=0 between the metal surface and the adsorbed layer of paint film. A number of constants and parameters have been omitted or absorbed into simplified parameters, approximated, or omitted altogether.

Non-dimensionalised formulation:

Set $\tau = 10^{-7} t$ and $x = 10^4 x$. We will use original estimates of parameters, and where appropriate adapt the current estimates of parameters to this earlier version of the model. In the process some weak links of definition and derivation will arise, but we believe this exercise demonstrates a useful conclusion derived from the model during the process of its formulation. We use the following parameter estimates

(which in some cases differ dimensionally and quantitatively from those derived later):

<div align="center">Table 3</div>

$D_U = 10^{-11}$ m^2 s^{-1}	$r_1 = 10^7$	$r_8 = 10^{-4}$
$D_W = 10^{-11}$ m^2 s^{-1}	$r_2 = 10^8$	$r_9 = 10^5$
$D_Z = 10^{-15}$ m^2 s^{-1}	$r_3 = 10^7$	$r_{10} = 10^{-4}$
$l = 10^{-4}$ m	$r_4 = 10^4$	$r_{11} = 10^8$
$\eta = 10^{-2}$	$r_7 = 10^8$	$r_{12} = 10^{-7}$

$$10^{-4}\frac{\partial U}{\partial \tau} = \frac{\partial^2 U}{\partial x^2} \tag{4.11.15}$$

$$10^{-4}\frac{\partial}{\partial \tau}\left(W + P_W\right) = \frac{\partial^2 W}{\partial x^2} \tag{4.11.16}$$

$$\frac{\partial}{\partial \tau}\left(Z + P_Z\right) = \frac{\partial^2 Z}{\partial x^2} \tag{4.11.17}$$

$$10^{-16}\frac{\partial P_W}{\partial \tau} = 10^{-2}WP_f - P_W \tag{4.11.18}$$

$$10^{-11}\frac{\partial P_Z}{\partial \tau} = 10^3 ZP_f - P_Z \tag{4.11.19}$$

$$\left.\frac{\partial U}{\partial x}\right|_{x=0} = 10^6 M_U M_W \tag{4.11.20}$$

$$\left.\frac{\partial W}{\partial x}\right|_{x=0} = 10^6 M_U M_W \tag{4.11.21}$$

$$-\left.\frac{\partial Z}{\partial x}\right|_{x=0} = 10^{11} M_U M_W \tag{4.11.22}$$

$$10^{-3}\frac{dM_W}{d\tau} = 10^{12}WM_f - M_W \tag{4.11.23}$$

$$10^{-3}\frac{dM_U}{d\tau} = 10^9 UM_f - M_U \tag{4.11.24}$$

$$\frac{dM_P}{d\tau} = 10^{15} P_f M_f - M_P \tag{4.11.25}$$

$$M_U + M_W + M_P + M_f = 1 \tag{4.11.26}$$

$$P_M + P_W + P_Z + P_f = 1 \tag{4.11.27}$$

$$P_M = \eta\, M_P \tag{4.11.28}$$

Model Approximation:

Next we produced an approximation of the model. From eqns 4.11.15 and .16 we deduced that U and W obey constant gradient conditions. Equations 4.11.18, 19, 23, and 24 are assumed to be approximated by algebraic expressions. We suppose that equation 4.11.25 is the 'governing equation' on the basis that estimates of the derivative magnitude indicate $dM_P/d\tau$ is typically greater than the other derivatives.

$$P_W = 10^{-2} P_f \tag{4.11.29}$$

$$P_Z = 10^3 Z P_f \tag{4.11.30}$$

$$M_W = 10^{12} W M_f = 10^{12} M_f \tag{4.11.31}$$

$$M_U = 10^9 U M_f = 10^9 M_f \tag{4.11.32}$$

from eq 4.11.26
$$\left(10^{12} + 10^9 + 1\right) M_f = 1 - M_P \tag{4.11.33}$$

and
$$M_f \approx 10^{-12}\left(1 - M_P\right) \tag{4.11.34}$$

from eq 4.11.25
$$\frac{dM_P}{d\tau} = 10^3 P_f\left(1 - M_P\right) - M_P \tag{4.11.35}$$

from eq 4.11.27
$$\left(1 + 10^{-2} + 10^3 Z\right) P_f = 1 - \eta\, M_P \tag{4.11.36}$$

$$P_f = \frac{1 - \eta\, M_P}{1.01 + 10^3 Z} \tag{4.11.37}$$

and
$$\frac{dM_P}{d\tau} = \frac{10^3\left(1 - M_P\right)\left(1 - \eta\, M_P\right)}{1.01 - 10^3 Z} - M_P \tag{4.11.38}$$

from eq 4.11.22

$$-\frac{\partial Z}{\partial x}\bigg|_{x=0} = 10^{11} M_U M_W = 10^{8}(1 - M_P)^2 \qquad (4.11.39)$$

Write $1 - M_P = \varepsilon$ and suppose $\varepsilon \ll 10^{-3}$ then

$$\frac{dM_P}{d\tau} = -\frac{d\varepsilon}{d\tau} = \frac{10^3(0.99 + \eta\varepsilon)\varepsilon}{10^3 Z + 1} + \varepsilon - 1 \qquad (4.11.40)$$

To a first approximation, and assuming $\eta \ll 1$,

$$\frac{d\varepsilon}{d\tau} = 1 \qquad (4.11.41)$$

$$\Rightarrow \qquad 1 - M_P = \tau \qquad (4.11.42)$$

and

$$-\frac{\partial Z}{\partial x}\bigg|_{x=0} = 10^8 \tau^2 \qquad (4.11.43)$$

from eqns 4.11.30 and 37

$$P_z = \frac{10^3 Z(1 - \eta M_P)}{1.01 + 10^3 Z} \approx \frac{Z}{Z + 10^{-3}} \qquad (4.11.44)$$

from eq 4.11.17

$$\frac{\partial}{\partial \tau}(Z + P_z) = \frac{\partial}{\partial \tau}\left(Z + \frac{Z}{Z + 10^{-3}}\right) = \frac{\partial^2 Z}{\partial x^2} \qquad (4.11.45)$$

Equations 4.11.43 and 45 together with $Z(x=1) = 0$ form an approximation of the model on scales of $t = 10^7$ s and $x = 10^{-4}$ m:

$$\frac{\partial}{\partial \tau}\left(Z + \frac{Z}{Z + 10^{-3}}\right) = \frac{\partial^2 Z}{\partial x^2} \qquad (4.11.46)$$

$$\frac{\partial Z}{\partial x}\bigg|_{x=0} = 10^8 \tau^2 \qquad (4.11.47)$$

$$Z(x = 1) = 0 \qquad (4.11.48)$$

Corrosion Saturation Times:

Our aim is to find an expression for Z at $x=0$ and determine the time required for Z to rise from zero to unity (saturation). Two cases are of immediate interest: First where $Z < 10^{-3}$ and we look for the time for Z to reach 10^{-3}, and second where $Z > 10^{-3}$ and we look for the time for Z to reach 1 (saturation).

Case 1: $Z < 10^{-3}$

$$\frac{\partial Z}{\partial \tau} = 10^{-3} \frac{\partial^2 Z}{\partial x^2} \qquad (4.11.49)$$

put $\alpha \zeta = Z$, $\beta y = x$, $\gamma t = \tau$, and $\varepsilon = 10^{-3}$

$$\frac{\partial Z}{\partial \tau} = \frac{\alpha}{\gamma} \frac{\partial \zeta}{\partial t} = \frac{\alpha \varepsilon}{\beta^2} \frac{\partial^2 \zeta}{\partial y^2} \qquad \Rightarrow \quad \beta^2 = \varepsilon \gamma$$

$$-\frac{\partial Z}{\partial x} = -\frac{\alpha}{\beta} \frac{\partial \zeta}{\partial y} = 10^8 \gamma^2 t^2 \qquad \Rightarrow \quad \alpha = 10^8 \beta \gamma^2$$

Set $\gamma = 1$, then $\beta = \varepsilon^{1/2} = 10^{-3/2}$ and $\alpha = 10^8 \beta$ giving

$$\frac{\partial \zeta}{\partial t} = \frac{\partial^2 \zeta}{\partial y^2} \qquad (4.11.50)$$

$$-\frac{\partial \zeta}{\partial y}\bigg|_{y=0} = \tau^2 \qquad (4.11.51)$$

$$\zeta(y \to \infty) = 0 \qquad (4.11.52)$$

where we use a modified condition of $\zeta = 0$ as $y \to \infty$.

Setting $\theta = y/\sqrt{t}$ and $\zeta = t^{5/2} v(\theta)$ we find a similarity solution:

$$v'' + \frac{1}{2}\theta v' - \frac{5}{2}v = 0 \qquad (4.11.53)$$

$$v'(0) = -1 \qquad (4.11.54)$$

$$v(\infty) = 0 \qquad (4.11.55)$$

We wish to find $v(0)$. Using Laplace Transforms eq 4.11.53 becomes

$$\bar{v}'(p) + \left(\frac{6}{p} - 2p\right)\bar{v}(p) = \frac{2}{p} - 2v_0 \tag{4.11.56}$$

with integrating factor

$$e^{\int\left(\frac{6}{p} - 2p\right)dp} = p^6 e^{-p^2} \tag{4.11.57}$$

and $\qquad p^6 e^{-p^2}\bar{v}(p) = 2\int p^5 e^{-p^2} dp - 2v_0\int p^6 e^{-p^2} dp + C \tag{4.11.58}$

$$\int_\infty^p q^6 e^{-q^2} dq = -\frac{1}{2}p^5 e^{-p^2} - \frac{5}{4}p^3 e^{-p^2} - \frac{15}{8}pe^{-p^2} - \frac{15}{16}\sqrt{\pi}\ erfc(p) \tag{4.11.59}$$

$$\int_\infty^p q^5 e^{-q^2} dq = -\frac{1}{2}p^4 e^{-p^2} - p^2 e^{-p^2} - e^{-p^2} \tag{4.11.60}$$

$\therefore\qquad C = 0$ in eq 4.11.58.

and $\qquad \bar{v}(p) = v_0\left\{\frac{1}{p} + \frac{5}{2p^3} + \frac{15}{4p^5} + \frac{15\sqrt{\pi}\ e^{p^2}}{8p^6}erfc(p)\right\} - \left\{\frac{1}{p^2} + \frac{2}{p^4} + \frac{2}{p^6}\right\} \tag{4.11.61}$

$\therefore\qquad v(y) = v_0\left\{1 + \frac{5y^2}{4} + \frac{5y^4}{32} + \frac{15\sqrt{\pi}}{8}\mathbf{L}^{-1}\left(\frac{e^{p^2}erfc(p)}{p^6}\right)\right\} - \left(y + \frac{y^3}{3} + \frac{y^5}{60}\right) \tag{4.11.62}$

$$v(y) = v_0\left\{1 + \frac{5y^2}{4} + \frac{5y^4}{32} + \frac{15}{8}\left(\frac{y^5}{5!} * e^{-\frac{y^2}{4}}\right)\right\} - \left(y + \frac{y^3}{3} + \frac{y^5}{60}\right) \tag{4.11.63}$$

$$\frac{y^5}{5!} * e^{-\frac{y^2}{4}} = \frac{1}{5!}\int_0^y (y-t)^5 e^{-\frac{t^2}{4}} dt = \frac{1}{5!}\sum_{r=0}^5 \binom{5}{r} y^{5-r}(-1)^r \int_0^y t^r e^{-\frac{t^2}{4}} dt \tag{4.11.64}$$

and

$$\frac{y^5}{5!} * e^{-\frac{y^2}{4}} = \frac{1}{5!}\left\{y^5\sqrt{\pi}\ erf\left(\frac{y}{2}\right) - 10y^4\left(1 - e^{-\frac{y^2}{4}}\right) - 10\left(2ye^{-\frac{y^2}{4}} - 2\sqrt{\pi}\ erf\left(\frac{y}{2}\right)\right)y^3\right.$$
$$\left. + 10\left[(2y^2 + 8)e^{-\frac{y^2}{4}} - 8\right]y^2 - 5\left[(2y^3 12y)e^{-\frac{y^2}{4}} - 12\sqrt{\pi}\ erf\left(\frac{y}{2}\right)\right]\right. \tag{4.11.35}$$
$$\left. - \left[-2y^4 + 16y^2 + 64\right]e^{-\frac{y^2}{4}} - 64\right\}$$

$\therefore$

$$v(y) = \frac{v_0}{64}\left[\sqrt{\pi}\ erf\left(\frac{y}{2}\right)(y^5 + 20y^3 + 60y) + (2y^4 + 36y^2 + 64)e^{-\frac{y^2}{4}}\right] - \left(y + \frac{y^3}{3} + \frac{y^5}{60}\right) \tag{4.11.66}$$

As $y \to \infty$, $v(y) \to 0$ provided

$$\frac{v_0}{64}\sqrt{\pi}\left(y^5 + 20y^3 + 60y\right) = y + \frac{y^3}{3} + \frac{y^5}{60} \tag{4.11.67}$$

$$\therefore \qquad v_0 = \frac{16}{15\sqrt{\pi}} \approx 0.6 \qquad\qquad (4.11.68)$$

and
$$v(y) = e^{-\frac{y^2}{4}}\left(1 + \frac{9y^2}{16} + \frac{y^4}{32}\right)\frac{16}{15\sqrt{\pi}} - erfc\left(\tfrac{y}{2}\right)\left(y + \frac{y^3}{3} + \frac{y^5}{60}\right) \qquad (4.11.69)$$

At $x = 0$
$$Z = 10^{\frac{13}{2}}\, \mathfrak{z} = 10^{\frac{13}{2}} t^{\frac{5}{2}} \frac{16}{15\sqrt{\pi}} \qquad\qquad (4.11.70)$$

Therefore time for Z to reach 10^{-3} is

$$t = \left(10^{-3} \cdot 10^{-\frac{13}{2}} \cdot \frac{15\sqrt{\pi}}{16}\right)^{\frac{2}{5}} = (5.25)^{\frac{2}{5}} = 1.9 \times 10^{-1}$$

$$\therefore \qquad T = 1.9 \times 10^3 \text{ seconds} = 30 \text{ minutes.}$$

Case 2: $Z > 10^{-3}$

$$\frac{\partial Z}{\partial \tau} = \frac{\partial^2 Z}{\partial x^2} \qquad\qquad (4.11.71)$$

put $\alpha \mathfrak{z} = Z \;\Rightarrow\; \alpha = 10^8$ and

$$\frac{\partial \mathfrak{z}}{\partial t} = \frac{\partial^2 \mathfrak{z}}{\partial y^2} \qquad\qquad (4.11.72)$$

$$-\frac{\partial \mathfrak{z}}{\partial y}\bigg|_{y=0} = \tau^2 \qquad\qquad (4.11.73)$$

$$\mathfrak{z}(y \to \infty) = 0 \qquad\qquad (4.11.74)$$

with similarity solution as before.

At $x = 0$ $\qquad Z = 10^8\, \mathfrak{z} = 10^8 t^{\frac{5}{2}} \dfrac{16}{15\sqrt{\pi}} \qquad$ and time for Z to reach 1 is

$$t = \left(1 \cdot 10^8 \cdot \frac{15\sqrt{\pi}}{16}\right)^{\frac{2}{5}} = 7.7 \times 10^{-1}$$

$$\therefore \qquad T = 7.7 \times 10^3 \text{ seconds } = 2 \text{ hours.}$$

We deduce from these results that, under these conditions, corrosion product reaches saturation at the metal-paint film interface in relatively short time.

Ricatti Equation:

Next we return to equation 4.11.38 and employ the result found above that $Z \rightarrow 1$; so that we obtain a Ricatti equation:

$$
\begin{aligned}
\frac{dM_P}{d\tau} &= 0.99(1 - M_P)(1 - \eta M_P) - M_P \\
&= a_0 + a_1 M_P + a_2 M_P{}^2 \\
&= a_2 M_P{}^2 - a_2(\rho_1 + \rho_2)M_P + a_2 \rho_1 \rho_2 \\
&= a_2(M_P - \rho_1)(M_P - \rho_2)
\end{aligned}
\tag{4.11.75}
$$

$$
\rho = \frac{-a_1 \pm \sqrt{a_1 - 4a_0 a_2}}{2a_2}
\tag{4.11.76}
$$

$$\rho_l = 0.4965 \approx 0.5 \qquad\qquad \rho_2 = 201.4$$

Suppose that $\rho_l = 0.5$ is a particular solution of eq 4.11.75 then a more general solution is

$$
M_P = \rho_1 + \omega^{-1}
\tag{4.11.77}
$$

$$
\frac{dM_P}{d\tau} = -\omega^{-2}\frac{d\omega}{d\tau} = a_2\omega^{-1}(\rho_1 - \rho_2 + \omega^{-1})
\tag{4.11.78}
$$

$$
\frac{d\omega}{d\tau} = a_2(\rho_2 - \rho_1)\omega - a_2
\tag{4.11.79}
$$

$$
\omega = ce^{a_2(\rho_2-\rho_1)\tau} + e^{a_2(\rho_2-\rho_1)\tau}\int_0^\tau -a_2 e^{-a_2(\rho_2-\rho_1)t}dt
$$

$$
= \frac{c(\rho_2 - \rho_1)e^{a_2(\rho_2-\rho_1)\tau} + 1}{\rho_2 - \rho_1}
\tag{4.11.80}
$$

$$
M_P = \rho_1 + \omega^{-1} = \frac{c\rho_1(\rho_2 - \rho_1)e^{a_2(\rho_2-\rho_1)\tau} + \rho_2}{c(\rho_2 - \rho_1)e^{a_2(\rho_2-\rho_1)\tau} + 1}
\tag{4.11.81}
$$

At $\tau = 0$ $M_P = M_{P0}$ and

$$c = \frac{\rho_2 - M_{P0}}{(\rho_2 - \rho_1)(M_{P0} - \rho_1)} \qquad (4.11.82)$$

$M_{P0} \to 1$ so

$$M_P = \frac{\rho_1(\rho_2 - 1)e^{a_2(\rho_2 - \rho_1)\tau} + \rho_2(1 - \rho_1)}{(\rho_2 - 1)e^{a_2(\rho_2 - \rho_1)\tau} + (1 - \rho_1)} \qquad (4.11.83)$$

To a reasonable approximation $c = 2$ and

$$M_P = 0.5(1 + e^{-2\tau}) \qquad (4.11.84)$$

Consequently M_P has a decay time of order $\tau = 0.5$

$\therefore \qquad T = 5 \times 10^6$ seconds $= 60$ days.

Mean Action Time

We supposed that a painted metal surface was considered to have failed when a substantial portion of the originally adsorbed polymer had become detached. The measure of adsorbed polymer is M_P, where $M_P = 1$ represents complete coverage of the metal surface with adsorbed polymer, and $M_P = 0$ represents total detachment.

Define the mean action time for a dynamical process $f(t)$ as:

$$T = \frac{\int_0^\infty t\, \dot{f}\ (t)dt}{\int_0^\infty \dot{f}\ (t)dt} \qquad (4.11.85)$$

(See McNabb and Wake, 1991)

From equation 4.11.75

$$\frac{dM_P}{d\tau} = a_2(M_P - \rho_1)(M_P - \rho_2) \qquad (4.11.86)$$

substitute $\qquad u = M_P - \rho_1 \qquad\qquad k = \rho_2 - \rho_1$

$$\frac{du}{d\tau} = a_2 u(u - k) \qquad (4.11.87)$$

with $u(t=0) = u_0$

Mean Action Time $\qquad T_{(Z \to 1)} = \dfrac{\displaystyle\int_0^\infty t\,\dot{u}\ dt}{\displaystyle\int_0^\infty \dot{u}\ dt}$ $\qquad\qquad$ (4.11.88)

$$= \frac{t u \big|_0^\infty - \displaystyle\int_0^\infty u\,dt}{u \big|_0^\infty}$$

$$= \frac{1}{u_0}\int_0^\infty u\,dt$$

$$= \frac{1}{u_0}\int_0^\infty \frac{\dot{u}}{a_2(u-k)}dt$$

$$= \frac{1}{a_2 u_0}\ln(u-k)\big|_0^\infty$$

$$= \frac{1}{a_2 u_0}\ln\frac{k}{k-u_0}$$

$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad$ (4.11.89)

so $\qquad\qquad T_{(Z \to 1)} = \dfrac{1}{a_2 u_0}\ln\dfrac{\rho_2 - \rho_1}{\rho_2 - \rho_1 - u_0}$ $\qquad\qquad$ (4.11.90)

giving $\qquad T = 0.5\tau = 5 \times 10^6$ seconds $= 60$ days, which is consistent with the result obtained from the Ricatti equation.

Conclusions:

The results obtained above from equations 4.11.1 to 4.11.14, and parameter values in Table 3, suggested that the model was capable of representing real

painted metal surfaces. With our original estimates of parameter values we found times for failure which corresponded to real life scenarios, and with variations in parameter values both shorter and longer times could be accommodated.

We then reviewed the model formulation and in particular re-derived our parameter estimates and reorganised the arguments and assumptions. Following this review the definitions of some parameters changed greatly, dimensionality changed, associated equations changed, and some values were revised by orders of magnitude. Two areas of the model were significantly altered. The equations describing the adsorbed layer were expanded to accommodate the effect of association between polymer functional groups and either water, corrosion product, or the metal surface. The belief is that initially there is typically some excess of polymer functional groups which remain unassociated (and provide the driving "pressure" for polymer attachment), while a minority associated with water molecules or adsorb onto the metal surface. As the corrosion process proceeds (slowly at first) there is gradual creation of corrosion product, which is taken up by polymer functional groups. Initially this has no significant effect on the state of the system, but eventually the polymer becomes saturated and a surplus of corrosion product arises. Our hypothesis is that this leads to a rapid desorption of polymer from the metal surface and an attendant large increase in the rate of generation of corrosion product.

The other area of revision was in the boundary conditions between the adsorbed layer and the bulk paint film. In reviewing the chemical processes involved (as far as they are known) we believed a more complex gradient condition was a better representation of the physical processes involved. While simpler conditions may also be satisfactory approximations, we aim to show that these arise as approximations of the general model.

5. SPECIAL CASES

5.1 INTRODUCTION

In certain cases the model exhibits steady state, or almost steady state, behaviour. While the special cases may not correspond to situations of much physical interest, they do allow us to isolate essential elements of the model's behaviour.

Additionally these steady and quasi-steady states allow calculation of limiting values. These values are useful for comparison with numeric calculations, and also give us some idea of how quickly certain processes might occur.

5.2 DRY FILM

In this case we suppose that water concentration is everywhere zero. The main consequence of this is that no corrosion can occur (equations 3.21 and 3.22). Additionally certain variables become fixed quantities:

$w=0$, $m_w=0$

and $q_z=0$, $q_w=0$, $p_w=0$, $p_z=0$, $z=0$, $z_c=0$

We suppose that diffusive equilibrium has been reached within the paint film so that concentrations of oxygen are constant: $u=1$ in $0<x<1$

Concentrations of adsorbed species on the metal surface must also be constant. In fact we notice that there are only two species competing for adsorption onto the metal surface: polymer, as m_p (and q_p), and oxygen as m_u.

$$m_u = \alpha_2\left(1-m_p\right)m_f \tag{5.2.1}$$

$$q_f = 1-q_m = 1-\kappa_3 m_p \tag{5.2.2}$$

$$m_p = \alpha_3 q_f m_f = \alpha_3\left(1-\kappa_3 m_p\right)m_f \tag{5.2.3}$$

$$1-m_p = m_u + m_f = \left[\alpha_2\left(1-m_p\right)+1\right]m_f \tag{5.2.4}$$

$$m_f = \frac{1 - m_p}{1 + \alpha_2 \left(1 - m_p\right)} \qquad (5.2.5)$$

$$m_p = \frac{\alpha_3 \left(1 - \kappa_3 m_p\right)\left(1 - m_p\right)}{1 + \alpha_2 \left(1 - m_p\right)} \qquad (5.2.6)$$

$$m_p^2 - \frac{1 + \alpha_2 + \alpha_3 \left(1 + \kappa_3\right)}{\alpha_2 + \alpha_3 \kappa_3} m_p + \frac{\alpha_3}{\alpha_2 + \alpha_3 \kappa_3} = 0 \qquad (5.2.7)$$

$m_p = 0.999999357 = 1 - 6.432 \times 10^{-7}$, $\qquad m_f = 6.428 \times 10^{-7}$, $\qquad m_u = 4.13 \times 10^{-10}$

From this we see that essentially all the metal surface is covered with adsorbed polymer, and that only a small proportion of the surface interacts with oxygen.

5.3 CORROSIONLESS SUBSTRATE

$f_z = 0$

and $z = 0$, $q_z = 0$, $p_z = 0$, and we suppose $\quad u = 1$, $w = 1$ in $0 < x < 1$

We suppose here that the substrate is inert so that no corrosion can occur. In equations 3.19, 3.20, 3.21, and 3.22 the parameters ϕ_1, ϕ_2, ϕ_3, ϕ_4, and ϕ_5 are all zero, so that the boundary conditions are zero gradient conditions. Consequently $z(x) = 0$; and $p_z = 0$ from eq 3.17 and $q_z = 0$ from eq 3.9.

We suppose that water and oxygen have diffused through the film and reached equilibrium within the paint film. Additionally we suppose that competitive adsorption has reached equilibrium in the adsorbed layer at $x = 0$.

$$m_w = \alpha_1 \left(1 - m_p\right) m_f \qquad (5.3.1)$$

$$m_u = \alpha_2 \left(1 - m_p\right) m_f \qquad (5.3.2)$$

$$m_p = \alpha_3 q_f m_f \qquad (5.3.3)$$

$$q_w = \alpha_5 q_f \tag{5.3.4}$$

$$q_m = \kappa_3 m_p \tag{5.3.5}$$

$$q_f = \frac{1 - \kappa_3 m_p}{1 + \alpha_5} \tag{5.3.6}$$

$$1 - m_p = m_w + m_u + m_f = \left[\alpha_1\left(1 - m_p\right) + \alpha_2\left(1 - m_p\right) + 1\right]m_f \tag{5.3.7}$$

$$m_f = \frac{1 - m_p}{1 + \left(\alpha_1 + \alpha_2\right)\left(1 - m_p\right)} \tag{5.3.8}$$

$$m_p = \frac{\alpha_3\left(1 - \kappa_3 m_p\right)\left(1 - m_p\right)}{\left(1 + \alpha_5\right)\left[1 + \left(\alpha_1 + \alpha_2\right)\left(1 - m_p\right)\right]} \tag{5.3.9}$$

$$m_p^2 - \frac{\alpha_3\left(1 + \kappa_3\right) + \left(1 + \alpha_5\right)\left(1 + \alpha_1 + \alpha_2\right)}{\alpha_3\kappa_3 + \left(1 + \alpha_5\right)\left(\alpha_1 + \alpha_2\right)}m_p + \frac{\alpha_3}{\alpha_3\kappa_3 + \left(1 + \alpha_5\right)\left(\alpha_1 + \alpha_2\right)} = 0 \tag{5.3.10}$$

$m_p=0.999998092=1-1.908\times10^{-6}$, $m_f=6.557\times10^{-7}$, $m_w=1.25\times10^{-6}$, $m_u=1.25\times10^{-9}$

$q_f=0.897$, $q_w=0.0179$, $p_{f(x=0)}=0.98$, $p_{w(x=0)}=0.0196$

As with the dry film case we see that effectively all the metal surface is covered with adsorbed polymer. We notice however that m_u is about three times larger and that m_w contributes to most of the reduction in m_p.

5.4 CORROSIONLESS SUBSTRATE WITHOUT OXYGEN

In a variation of the preceding case we suppose that oxygen is everywhere zero, and use the same assumptions of equilibrium.

$f_z=0$, $u=0$, $m_u=0$

and $z=0$, $q_z=0$, $p_z=0$, and we suppose $w=1$

$$m_w = \alpha_1\left(1 - m_p\right)m_f \tag{5.4.1}$$

$$m_p = \alpha_3 q_f m_f \tag{5.4.2}$$

$$q_w = \alpha_5 q_f \tag{5.4.3}$$

$$q_m = \kappa_3 m_p \tag{5.4.4}$$

$$q_w + q_m + q_f = 1 \quad \Rightarrow \quad q_f = \frac{1 - \kappa_3 m_p}{1 + \alpha_s} \tag{5.4.5}$$

$$1 - m_p = m_w + m_f = \left[\alpha_1(1 - m_p) + 1\right]m_f \tag{5.4.6}$$

$$m_f = \frac{1 - m_p}{1 + \alpha_1(1 - m_p)} \tag{5.4.7}$$

$$m_p = \frac{\alpha_3(1 - \kappa_3 m_p)(1 - m_p)}{(1 + \alpha_s)\left[1 + \alpha_1(1 - m_p)\right]} \tag{5.4.8}$$

$$m_p{}^2 - \frac{\alpha_3(1 + \kappa_3) + (1 + \alpha_s)(1 + \alpha_1)}{\alpha_3 \kappa_3 + \alpha_1(1 + \alpha_s)} m_p + \frac{\alpha_3}{\alpha_3 \kappa_3 + \alpha_1(1 + \alpha_s)} = 0 \tag{5.4.9}$$

$m_p=0.999998095=1-1.9048\times10^{-6}$, $m_f=6.557\times10^{-7}$, $m_w=1.249\times10^{-6}$

$q_f=0.897$, $q_w=0.0179$, $p_f=0.98$, $p_w=0.0196$

The removal of oxygen has little effect on the equilibrium values of adsorbed polymer and water. The metal surface remains substantially covered with adsorbed polymer.

5.5 POLYMERLESS SYSTEM

In this case we suppose that there is no available polymer for adsorption onto the substrate, and no available polymer for interacting with either water molecules or zinc corrosion product (either at $x=0$ or in $0<x<1$):

$m_p=0$, $q_z=0$, $q_w=0$, $q_m=0$, $q_f=0$, $p_z=0$, $p_w=0$, $p_f=0$, $p_z=0$

We are particularly interested in determining how quickly z rises from zero at $\tau=0$ to reach saturation at $z=1$. To best demonstrate this limiting case we suppose that

diffusion of water and oxygen has occurred and that the corrosion process is initially inhibited. So we first consider only water and oxygen and determine their concentrations with the boundary condition set at values which will apply when corrosion occurs.

$$\frac{\partial^2 u}{\partial x^2} = 0 \quad \Rightarrow \quad u = ax + b \tag{5.5.1}$$

$$u(x = 1) = 1 \quad \Rightarrow \quad u = 1 - a(1 - x) \tag{5.5.2}$$

$u(0) = 1-a,$ and we require $0 \le a \le 1$

$$\frac{\partial^2 w}{\partial x^2} = 0 \quad \Rightarrow \quad w = cx + d \tag{5.5.3}$$

$$w(x = 1) = 1 \quad \Rightarrow \quad w = 1 - c(1 - x) \tag{5.5.4}$$

$w(0) = 1-c,$ and we require $0 \le c \le 1$

$$\left.\frac{\partial u}{\partial x}\right|_{x=0} = a = \phi_2 w u^{1/2} = \phi_2 (1 - c)(1 - a)^{1/2} \tag{5.5.5}$$

$$\left.\frac{\partial w}{\partial x}\right|_{x=0} = c = \phi_1 \left(w u^{1/2} + 2\alpha_8 w^2\right) = \phi_1 \left[(1 - c)(1 - a)^{1/2} + 2\alpha_8 (1 - c)^2\right] \tag{5.5.6}$$

$c = 2.7 \times 10^{-3} [(1-c)(1-a)^{1/2} + 0.02 (1-c)^2] \ge 2.7 \times 10^{-3} (1-c)(1-a)^{1/2} = 2.7 \times 10^{-4} \, a$

$a = \phi_2(1-c)(1-a)^{1/2} \le \phi_2(1-2.7 \times 10^{-4} \, a)(1-a)^{1/2} \le \phi_2(1-a)^{1/2}$

$a^2 + \phi_2^2 a + \phi_2^2 \le 0 \quad \Rightarrow \quad a \le 0.990195$ and $c \approx 2.7 \times 10^{-4}$

Numeric calculation gives $a = 0.990189$ and $c = 3.2 \times 10^{-4}$

and $u(0) = 1-a = 9.811 \times 10^{-3} \quad w(0) = 1-c = 0.99968$

which suggests that diffusion of oxygen to the substrate may be the limiting process in this special case. Further, in coating systems where the adsorption of polymer is weak but the paint film may offer some barrier properties, we see that restriction of oxygen diffusion (and possibly water with appropriate parameter values) is probably the main mechanism of paint film protection.

$$m_w = \alpha_1 w m_f \tag{5.5.7}$$

$$m_u = \alpha_2 u m_f \tag{5.5.8}$$

$$m_w + m_u + m_f = 1 \tag{5.5.9}$$

$$m_f = \frac{1}{\alpha_1 w + \alpha_2 u + 1} = 1.000309 \times 10^{-6}, \quad m_w = 0.999989 = 1 - 1.08 \times 10^{-5}, \quad m_u = 9.81 \times 10^{-6}$$

We next suppose that generation of corrosion product begins and that initially $z=0$. We seek to determine how long it takes for z to reach saturation under these conditions.

$$\frac{\partial z}{\partial \tau} = D_2 \frac{\partial^2 z}{\partial x^2}, \qquad z = 0 \text{ at } x = 1$$

$$-\frac{\partial z}{\partial x}\bigg|_{x=0} = -\phi_3 \frac{dz}{d\tau} + \phi_4 \kappa_6 \left[wu^{1/2} + \alpha_8 w^2 \right] = -10 \frac{dz}{d\tau} + 1.6 \times 10^7 \tag{5.5.10}$$

set $\zeta = 6.25 \times 10^{-9} z$ and $t = \tau/D_2 = 10^{-7} t$

$$\frac{\partial \zeta}{\partial t} = \frac{\partial^2 \zeta}{\partial x^2} \tag{5.5.11}$$

$$-\frac{\partial \zeta}{\partial x}\bigg|_{x=0} = -10^{-3} \frac{d\zeta}{dt} + 1 \tag{5.5.12}$$

Use Laplace Transforms

$$-\frac{d\bar{\zeta}}{dx} = -10^{-3} q^2 \bar{\zeta} + \frac{1}{q^2} \quad \text{at } x = 0 \tag{5.5.13}$$

$$\bar{\zeta} = 0 \quad \text{at } x = 1 \tag{5.5.14}$$

$$\frac{d^2 \bar{\zeta}}{dx^2} - q^2 \bar{\zeta} = 0 \tag{5.5.15}$$

$$\bar{\zeta} = A e^{qx} - B e^{-qx} \tag{5.5.16}$$

from eq 5.5.14 $B = A e^{2q} \Rightarrow \bar{\zeta} = A e^{qx} - A e^{2q} e^{-qx}$ (5.5.17)

from eq 5.5.13

$$-\frac{d\bar{\zeta}}{dx}\bigg|_{x=0} = -Aq\left(e^{qx} + e^{q(2-x)}\right)\bigg|_{x=0} = -10^{-3} q^2 A\left(e^{qx} - e^{q(2-x)}\right)\bigg|_{x=0} + \frac{1}{q^2} \tag{5.5.18}$$

$$-Aq(1 + e^{2q}) = -10^{-3} A q^2 (1 - e^{2q}) + \frac{1}{q^2} \Rightarrow A = \frac{-10^{-3} e^{-2q}}{q^3 (10^3 + q)\left(1 + \frac{(10^3 - q)}{(10^3 + q)} e^{-2q}\right)} \tag{5.5.19}$$

$$\bar{\zeta} = \frac{10^3 e^{-qx}}{q^3(10^3+q)\left(1+\dfrac{(10^3-q)}{(10^3+q)}e^{-2q}\right)} - \frac{10^3 e^{-q(2-x)}}{q^3(10^3+q)\left(1+\dfrac{(10^3-q)}{(10^3+q)}e^{-2q}\right)}$$

$$= \frac{10^3}{q^3(10^3+q)}\left\{e^{-qx}-e^{-q(2-x)}\right\}\sum_{n=0}^{\infty}(-1)^n\frac{(10^3-q)^n}{(10^3+q)^n}e^{-2nq} \qquad (5.5.20)$$

first term ($n=0$):

$$\zeta = 2\sqrt{\frac{t}{\pi}}e^{-\frac{x^2}{4t}} - 10^{-3}(1+10^3 x)erfc\frac{x}{2\sqrt{t}} - 2\sqrt{\frac{t}{\pi}}e^{-\frac{(2-x)^2}{4t}} + \frac{(1+10^3(2-x))}{10^3}erfc\frac{(2-x)}{2\sqrt{t}}\ldots \qquad (5.5.21)$$

$$\zeta(x=0.t) \rightarrow 2\sqrt{\frac{t}{\pi}} - 10^{-3}+\ldots \qquad (5.5.22)$$

$\zeta \rightarrow 6.25 \times 10^{-9}$ in $t=(10^{-3}+6.25 \times 10^{-9})^2 \times \pi/4 = 7.85 \times 10^{-7}$ which is $z \rightarrow 1$ in $t = 8$ seconds.

We note that the metal surface is effectively covered with water. While the chosen conditions and assumptions may be artificial it seems clear that z rapidly increases and reaches saturation in very short time. In comparison with the previous special cases we see that the state of the adsorbed layer is also radically different. Where polymer is available it initially dominates the metal surface. Consequently we expect from equations 3.19 to 3.22 that the initial rate of corrosion will be exceedingly small, and that z will only very slowly increase initially.

Clearly when the polymer is either absent, or becomes bound up with corrosion product, the reactivity of the metal substrate is significantly greater. Where polymer is initially present the factor $(1-m_p)$ is of the order 10^{-6}, but without polymer this factor approaches unity. Consequently the fluxes of corrosion product and reactants are expected to change by roughly six orders of magnitude during the degradation process.

We believe that various paint film polymers differ significantly in both their effectiveness of competitive adsorption (relative to water and oxygen) and in their initial (substrate) surface density $\mathcal{P}_0$. This together with a wide range of diffusion coefficients for water, oxygen, and ions helps to explain the diversity of paint film behaviour noted in the literature (section 1.1).

5.6 ADSORBED POLYMER AND THIN PAINT FILM

We suppose the paint film so thin that its trapping capacity is negligible, that transport across the film occurs instantaneously, and that water, oxygen and zinc are in diffusive equilibrium. Effectively the system consists of adsorbed polymer on a metal substrate with a thin film of paint offering some static barrier resistance resulting in constant fluxes of water, oxygen and zinc ions. We suppose external concentrations of water and oxygen are given by $u(x=1)=1$, and $w(x=1)=1$.

Our interest here is to determine what the ultimate corrosion rate is after initial processes have occurred and the metal surface has lost all protection from adsorbed polymer. We allow that the paint film may offer some barrier properties.

We suppose that the film is in a state of equilibrium. Consequently equations 5.5.2 and 5.5.4 apply.

$$u = 1 - a(1 - x) \qquad w = 1 - c(1 - x) \tag{5.6.1}$$

Additionally we suppose that z has reached saturation at $x=0$.

$$\frac{\partial^2 z}{\partial x^2} = 0 \quad \Rightarrow \quad z = ex + f \tag{5.6.2}$$

$$z(x = 1) = 0 \quad \Rightarrow \quad z = e(1 - x) \tag{5.6.3}$$

$$z(x = 0) = 1 \quad \Rightarrow \quad z = 1 - x \tag{5.6.4}$$

From 3.22

$$\frac{dz_c}{d\tau} = \frac{\phi_4 \kappa_6}{\phi_5}(1 - c)\left[(1 - a)^{1/2} + \alpha_8(1 - c)\right] - \frac{1}{\phi_5} \tag{5.6.5}$$

which gives an actual corrosion rate of

$$\frac{dZ_c}{dt} = 2.8 \times 10^{-6} \quad mol \quad s^{-1} \quad m^{-2} \tag{5.6.6}$$

For equations 3.5 to 3.12 we have:

$$m_w = \alpha_1\left(1 - m_p\right)(1 - c)m_f \qquad (5.6.7)$$

$$m_u = \alpha_2\left(1 - m_p\right)(1 - a)m_f \qquad (5.6.8)$$

$$m_p = \alpha_3 q_f m_f \qquad (5.6.9)$$

$$m_p + m_w + m_u + m_f = 1 \qquad (5.5.10)$$

$$q_z = \alpha_4 z q_f = \alpha_4 q_f \qquad (5.6.11)$$

$$q_w = \alpha_5 q_f(1 - c) \qquad (5.6.12)$$

$$q_m = \kappa_3 m_p \qquad (5.6.13)$$

$$q_w + q_z + q_m + q_f = 1 \qquad (5.6.14)$$

$$q_f = \frac{1}{1 + \alpha_4 + \alpha_5(1 - c) + \kappa_3 m_f} \qquad (5.6.15)$$

$$A = 1 + \alpha_1(1 - c) + \alpha_2(1 - a)$$
$$B = 1 + \alpha_4 + \alpha_5(1 - c)$$
$$A\kappa_3 m_f{}^2 + \left(\alpha_3 - \kappa_3 + AB\right)m_f - B = 0 \qquad (5.6.16)$$

$$m_f = \frac{-\left(\alpha_3 - \kappa_3 + AB\right) + \sqrt{\left(\alpha_3 - \kappa_3 + AB\right)^2 + 4AB\kappa_3}}{2A\kappa_3} \approx 9.9998 \times 10^{-7}$$

$q_f \approx 9.99989 \times 10^{-6}$, $m_p \approx 1.7 \times 10^{-5}$, $m_w \approx 0.99998$, $m_u \approx 9.81 \times 10^{-6}$, $q_z \approx 0.99998$, $q_w \approx 1.7 \times 10^{-7}$

As with the case without polymer the metal surface is practically covered with adsorbed water. Some residual polymer attachment remains but it is too little to have any effect on the corrosion rate. We note that the values for m_w, and m_u are similar to the case without polymer.

In equation 5.6.6 the rate of corrosion is about 17% of the free and unrestricted rate. The paint film does provide some protection but not enough to usefully protect the metal. We note also that the predicted rate is a constant.

5.7 BARE METAL SUBSTRATE

In this case we suppose that polymer is absent altogether. We ignore diffusive processes and consider only substrate competition between water and oxygen.

$m_p{=}0,\ \ q_z{=}0,\ \ q_w{=}0,\ \ q_m{=}0,\ \ q_f{=}0,\ \ p_z{=}0,\ \ p_w{=}0,\ \ \text{and}\ p_f{=}0$

We are interested in determining equilibrium surface adsorbed concentrations m_w and m_u and in determining the resultant rate of corrosion.

From equations 3.5, 3.6, and 3.8 we find

$$m_w = \alpha_1 m_f \tag{5.7.1}$$

$$m_u = \alpha_2 m_f \tag{5.7.2}$$

$$m_u + m_w + m_f = 1 \tag{5.7.3}$$

We suppose that this special case represents a metal surface immersed in oxygenated distilled water. We further suppose that z has reached saturation at $x{=}0$ and that corrosion product z_c accumulates at $x{=}0$ and is unable to diffuse away. These assumptions are somewhat artificial but are believed to approximate the basic corrosion experiment of measuring corrosion of a metal coupon immersed in a container of oxygenated water.

$u = 1$ where $U_0 = 0.3$ mol m^{-3} is the saturation concentration of oxygen in water, and $w = 1$ where W_0 is liquid water where we use these expressions because there is no paint film and hence no internal concentrations.

We obtain

$$m_f = \frac{1}{1 + \alpha_1 + \alpha_2} \tag{5.7.4}$$

$$m_w = \frac{\alpha_1}{1 + \alpha_1 + \alpha_2} \tag{5.7.5}$$

$$m_u = \frac{\alpha_2}{1+\alpha_1+\alpha_2} \tag{5.7.6}$$

and

$m_u = 9.99 \times 10^{-4}, \quad m_w = 0.999, \quad m_f = 9.99 \times 10^{-7}$

From eq 3.22 we find

$$\frac{dz_c}{d\tau} = \frac{\phi_4 \kappa_6}{\phi_5} \left[wu^{1/2} + \alpha_8 w^2 \right] \tag{5.7.7}$$

which in dimensional form gives

$$\frac{dZ_c}{dt} = \frac{\phi_4 \kappa_6}{\phi_5} \left[wu^{1/2} + \alpha_8 w^2 \right] \times 10^{-3} \times 10^{-2} = 3.2 \times 10^{-6} \quad mol \quad m^{-2} \quad s^{-1} \tag{5.7.8}$$

If the model conditions are varied to allow oxygen at atmospheric concentrations, such as may occur in a humidity cabinet, we find that the corrosion rate becomes $1.7 \times 10^{-5} \ mol \, m^{-2} \, s^{-1}$.

6. NUMERICAL MODELLING

6.1 PREFACE

One of the aims of this project was to use the model to identify physical properties of paint films which might be varied by polymer chemical engineering or paint formulation design to produce paints which provided better corrosion protection to metal substrates. To achieve this we need to determine how the model behaves and which parameters particularly affect the protective lifetime T_c of a coating. With this information it is intended that model polymers be developed and synthesised which embody these design parameters and perform better than existing polymers.

While some special cases could be determined, and the effects of some parameters gauged, we have not found a general analytic solution for the complete model. It was expected that the model should have various simplified or reduced forms which might apply to particular regimes. It was further expected that these reduced models would allow exact solution which would allow some estimation of parameter values to best achieve large T_c values. It was clear that some model differential equations were dispensable, for example eq 3.6 and 3.10. It was also clear that diffusion was not generally the rate controlling process so eq 3.13-3.18 could be approximated by steady state expressions. But there remained several competitive adsorption equations (eq 3.5, 3.7, 3.9) and the boundary conditions 3.19 - 3.22 which have so far resisted explicit solution. It was hoped that significant simplification of the model could also be made, but again it has been difficult to determine what elements are minor and to justify omissions.

A computer programme (see appendix) was written by Dr Stephen White to numerically solve the diffusion-adsorption model. The aim was twofold: First the full model could be explored in all it's complexity, including variable external water concentrations. From this it is intended to fine tune polymer design properties to

maximise T_c. Additionally the numerical solutions could be used to test various modifications to the model, and to assist in the determination of simplified constitutive relationships.

6.2 NUMERICAL METHODS

(Adapted from "A Diffusion-Reaction Model for Corrosion of Metal Substrates Protected by Polymeric Coatings" Van Dyk, *et al.* Article to be submitted January 1997 for proposed publication in "Maths and Computer Modelling")

Equations (3.13) to (3.18) together with the boundary conditions given in equations (3.19) to (3.22) are a set of coupled ODEs (*2*), PDEs (*3*) and (possibly non-linear) algebraic equations (*4*). In order to solve this system we define a regular finite difference grid in x with N points and a corresponding dimensionless gridsize $h=1/(N-1)$.

A finite difference approximation to equations (3.13), (3.14) and (3.16) is obtained by replacing x derivatives by a central difference approximation

$$\frac{\partial^2 u}{\partial x^2}\bigg|_i \sim \frac{u_{i+1} - 2u_i + u_{i-1}}{h^2} \qquad (6.2.1)$$

This reduces the numerical problem to the solution of a mixture of ODEs and algebraic equations.

Let $u_i = u(x_i)$, $w_i = w(x_i)$, $z_i = z(x_i)$ and $p_{wi} = p_w(x_i)$, and $p_{zi} = p_z(x_i)$.

Define the components of vector $\mathbf{Y}$ to be

$$\mathbf{Y} = \begin{bmatrix} \mathbf{Y}(1) = u_1(t) \\ \mathbf{Y}(2) = w_1(t) - \kappa_1 p_w(t) \\ \mathbf{Y}(3) = z_1(t) - \kappa_2 p_z(t) \\ \mathbf{Y}(4) = p_{w1}(t) \\ \mathbf{Y}(5) = p_{z1}(t) \\ \mathbf{Y}(6) = u_2(t) \\ \vdots \\ \mathbf{Y}(5(N-1)+4) = p_{wn}(t) \\ \mathbf{Y}(5(N-1)+5) = p_{zn}(t) \\ \mathbf{Y}(5N+1) = m_w(t) \\ \mathbf{Y}(5N+2) = m_u(t) \\ \mathbf{Y}(5N+3) = m_p(t) \\ \mathbf{Y}(5N+4) = z_c(t) \end{bmatrix}$$

which we summarise as:

$$
\begin{aligned}
\mathbf{Y}(5(i-1)+1) &= u_i \\
\mathbf{Y}(5(i-1)+2) &= \left(w_i - \kappa_1 p_w \right) \\
\mathbf{Y}(5(i-1)+3) &= \left(z_i - \kappa_2 p_z \right) \\
\mathbf{Y}(5(i-1)+4) &= p_{wi} \\
\mathbf{Y}(5(i-1)+5) &= p_{zi} \\
\mathbf{Y}(5N+1) &= m_w \\
\mathbf{Y}(5N+2) &= m_u \\
\mathbf{Y}(5N+3) &= m_p \\
\mathbf{Y}(5N+4) &= z_c
\end{aligned}
\tag{6.2.2}
$$

The system of equations to be integrated can now be written as

$$\frac{d\mathbf{Y}}{dt} = \mathbf{f}(\mathbf{Y}) \tag{6.2.3}$$

where the elements of the vector $\mathbf{f}(\mathbf{Y})$ are defined as:

$$\mathbf{f}_{5(i-1)+1} = \frac{D_1\left(\mathbf{Y}_{5(i-1)-4} - 2\mathbf{Y}_{5(i-1)+1} + \mathbf{Y}_{5(i-1)+6}\right)}{h^2} \qquad i = 1\cdots N$$

$$\mathbf{f}_{5(i-1)+2} = \frac{\left(\left(\mathbf{Y}_{5(i-1)-3} - 2\mathbf{Y}_{5(i-1)+2} + \mathbf{Y}_{5(i-1)+7}\right) + \kappa_1\left(\mathbf{Y}_{5(i-1)-1} - 2\mathbf{Y}_{5(i-1)+4} + \mathbf{Y}_{5(i-1)+9}\right)\right)}{h^2} \qquad i = 1\cdots N$$

$$\mathbf{f}_{5(i-1)+3} = \frac{\left(\left(\mathbf{Y}_{5(i-1)-2} - 2\mathbf{Y}_{5(i-1)+3} + \mathbf{Y}_{5(i-1)+8}\right) + \kappa_2\left(\mathbf{Y}_{5(i-1)} - 2\mathbf{Y}_{5(i-1)+5} + \mathbf{Y}_{5i}\right)\right)}{h^2} \qquad i = 1\cdots N$$

$$\mathbf{f}_{5(i-1)+4} = \theta_6\left(\alpha_6\left(\mathbf{Y}_{5(i-1)+2} + \kappa_1\mathbf{Y}_{5(i-1)+4}\right)p_f - p_w\right) \qquad i = 1\cdots N-1$$

$$\mathbf{f}_{5(i-1)+5} = \theta_7\left(\alpha_7\left(\mathbf{Y}_{5(i-1)+3} + \kappa_1\mathbf{Y}_{5(i-1)+5}\right)p_f - p_z\right) \qquad i = 1\cdots N-1$$

$$\mathbf{f}_{5N+1} = \theta_1\left(\alpha_1\left(1 - \mathbf{Y}_{5N+3}\right)\left(\mathbf{Y}_{5(N-1)+2} + \kappa_1\mathbf{Y}_{5(N-1)+4}\right)\left(1 - \mathbf{Y}_{5N+1} - \mathbf{Y}_{5N+2} - \mathbf{Y}_{5N+3}\right) - \mathbf{Y}_{5N+1}\right)$$

$$\mathbf{f}_{5N+2} = \theta_2\left(\alpha_2\left(1 - \mathbf{Y}_{5N+3}\right)\mathbf{Y}_{5(N-1)+1}\left(1 - \mathbf{Y}_{5N+1} - \mathbf{Y}_{5N+2} - \mathbf{Y}_{5N+3}\right) - \mathbf{Y}_{5N+2}\right)$$

$$\mathbf{f}_{5N+3} = \theta_3\left(\alpha_3\left(1 - \mathbf{Y}_{5(N-1)+4} - \mathbf{Y}_{5(N-1)+5} - \kappa_3\mathbf{Y}_{5N+3}\right)\left(1 - \mathbf{Y}_{5N+1} - \mathbf{Y}_{5N+2} - \mathbf{Y}_{5N+3}\right) - \mathbf{Y}_{5N+3}\right)$$

$$\mathbf{f}_{5(N-1)+5} = \theta_4\left(\alpha_4\left(1 - \mathbf{Y}_{5(N-1)+4} - \mathbf{Y}_{5(N-1)+5} - \kappa_3\mathbf{Y}_{5N+3}\right)\mathbf{Y}_{5(N-1)+3} - \mathbf{Y}_{5N+5}\right)$$

$$\mathbf{f}_{5(N-1)+4} = \theta_5\left(\alpha_5\left(1 - \mathbf{Y}_{5(N-1)+4} - \mathbf{Y}_{5(N-1)+5} - \kappa_3\mathbf{Y}_{5N+3}\right)\left(\mathbf{Y}_{5(N-1)+2} + \kappa_1\mathbf{Y}_{5(N-1)+4}\right) - \mathbf{Y}_{5N+4}\right)$$

Boundary conditions given in equations (3.19) to (3.22) can be written in a similar fashion.

We can now use the Crank-Nicholson scheme to discretise equation (6.2.3) in time as

$$\frac{\mathbf{Y}^{t+\Delta t} - \mathbf{Y}^t}{\Delta t} = \frac{1}{2}\left(\mathbf{f}\left(\mathbf{Y}^{t+\Delta t}\right) + \mathbf{f}\left(\mathbf{Y}^t\right)\right) \tag{6.2.4}$$

Equation (6.2.4) is a non-linear system of equations and is solved using a Newton-Raphson iteration.

NUMERICAL RESULTS

6.3.1 COMPARISON WITH SPECIAL CASES

The first issue to explore is the correspondence of the numerical model results with special case results. We compare the results of section 5 with numerically calculated results. In table 4 the calculated results from section 5.2 for a dry film are compared with numerically calculated results.

Table 4 (dry film)

analytic	numerical
$m_p=0.999999357=1-6.43\times10^{-7}$	$m_p=1-6.54\times10^{-7}$
$m_f=6.43\times10^{-7}$	$m_f=6.54\times10^{-7}$
$m_u=4.13\times10^{-10}$	$m_u=4.27\times10^{-10}$

Next we compare the results of the case of a corrosionless substrate (section 5.3) with the numeric results in table 5.

Table 5 (corrosionless substrate)

analytic	numerical
$m_p=0.999998092=1-1.908\times10^{-6}$	$m_p=1-1.98\times10^{-6}$
$m_f=6.56\times10^{-7}$	$m_f=6.65\times10^{-7}$
$m_w=1.25\times10^{-6}$	$m_w=1.32\times10^{-6}$
$m_u=1.25\times10^{-9}$	$m_u=1.32\times10^{-9}$
$q_f=0.897$	$q_f=0.90$
$q_w=0.0179$	$q_w=0.015$
$p_{f(x=0)}=0.98$	$p_{f(x=0)}=0.984$
$p_{w(x=0)}=0.0196$	$p_{w(x=0)}=0.016$

Next the case of a corrosionless substrate without oxygen is compared. The results of section 5.4 are compared with numeric results in table 6.

Table 6 (corrosionless substrate without oxygen)

analytic	numerical
m_p=0.999998092=1-1.905×10^{-6}	m_p=1-1.98×10^{-6}
m_f=6.56×10^{-7}	m_f=6.65×10^{-7}
m_w=1.25×10^{-6}	m_w=1.32×10^{-6}
q_f=0.897	q_f=0.90
q_w=0.0179	q_w=0.015
$p_{f(x=0)}$=0.98	$p_{f(x=0)}$=0.984
$p_{w(x=0)}$=0.0196	$p_{w(x=0)}$=0.016

The special case of steady state corrosion offers another comparison with numerical results. In section 5.6 we considered the case of a thin film in diffusive equilibrium where adsorbed polymer had been completely degraded by corrosion product. An expression for dZ_c/dt was obtained (equation 5.6.6), and found to give $2.8×10^{-6}$ mol m^{-2} s^{-1}. From numeric calculations we obtain $1.8×10^{-6}$ mol m^{-2} s^{-1}.

6.3.2 TIME T_C TO ONSET OF CORROSION

The next issue to be resolved is: can the model account for paint protective lifetimes up to and beyond a few years? The answer to this question is shown in *figure 7*. One of the parameters, α_3, is varied from 10^5 to $2×10^6$. In the process we see that the time T_c to onset of corrosion ($z_c>0$) ranges from about $2×10^2$ seconds to about 10^9 seconds. For α_3 up to about $1.1×10^6$ T_c is limited by

diffusion. The competitive adsorption of polymer in this region is so weak that polymer is displaced by water (and oxygen) almost as quickly as water can diffuse into the paint film and arrive at the metal surface.

Figure 7
Time (T_c) to onset of Corrosion vs parameter α_3
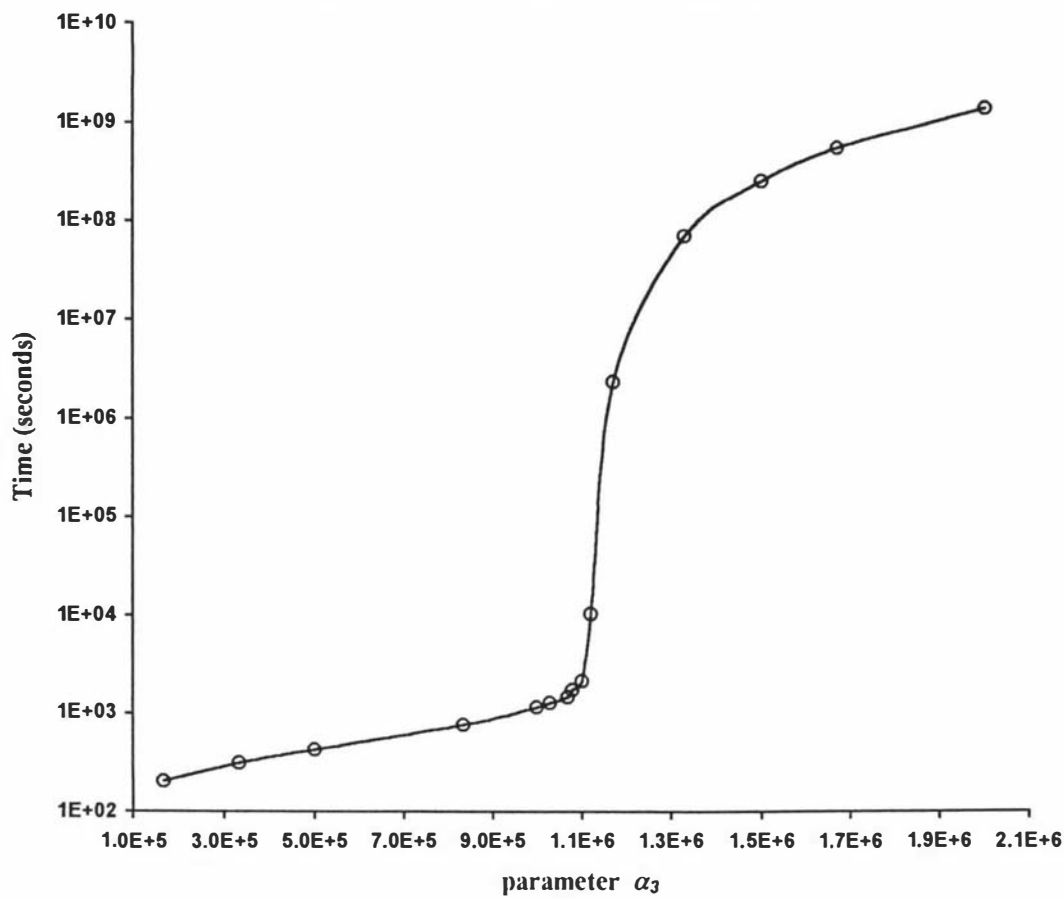
But for α_3 larger than about 1.1×10^6 we see that there is a dramatic increase in T_c. Significantly the diffusive influx of water no longer results in prompt failure. In fact the equilibrated concentrations of water and oxygen in the paint film very closely approximate constant values with zero gradients. It appears that m_p is closely related to the protective potential of the paint film. When m_p is close to unity the corrosion rate is greatly restricted and the systems protective lifetime remains long. From numerical results it is found that m_p larger than about 0.999 results in useful protective action. We interpret this to mean that with 99.9% or

more of the metal surface covered by adsorbed polymer the resulting rate of corrosion is near zero.

We see also that small variations in the relative strength of polymer adsorption in the region of $\alpha_3 = 1.1 \times 10^6$ result in large changes in the time for $z_c > 0$. This behaviour is a consequence of the nonlinearity of these competitive adsorption equations. Where competitive adsorption of one species dominates, the model's behaviour is governed largely by the dominant species. For example in *figure 7* uptake of water governs behaviour for α_3 less than about 1.1×10^6, while for α_3 greater than about 1.5×10^6 uptake of corrosion product by polymer seems to govern behaviour. In between these two regimes the model's behaviour depends sensitively upon the relative adsorptions of water and polymer.

6.3.3 MODEL BEHAVIOUR

The next issue to resolve is: does the model's behaviour correspond with reality? A characteristic of real paint film failures is that invariably the paint film provides good protection for some initial period. After this period of protection rapid degradation occurs, the metal substrate begins to rust vigorously, and the paint film itself blisters, cracks and flakes off. We have not found any diffusion limited model capable of demonstrating this type of behaviour. The model presented here (summarised in section 3) demonstrates exactly this sort of behaviour with an initial, and possibly long, period of protection followed by sudden degradation of the adsorbed layer resulting in rapid corrosion and rusting. A typical graph of corrosion product is shown in *figure 8*. We use $\alpha_3 = 1.129 \times 10^6$ along with standard values for the other parameters indicated in table 3. The numeric model used is based on equations 3.5 to 3.24.

Figure 8
Plot of z_c (solid corrosion product at $x=0$) against time
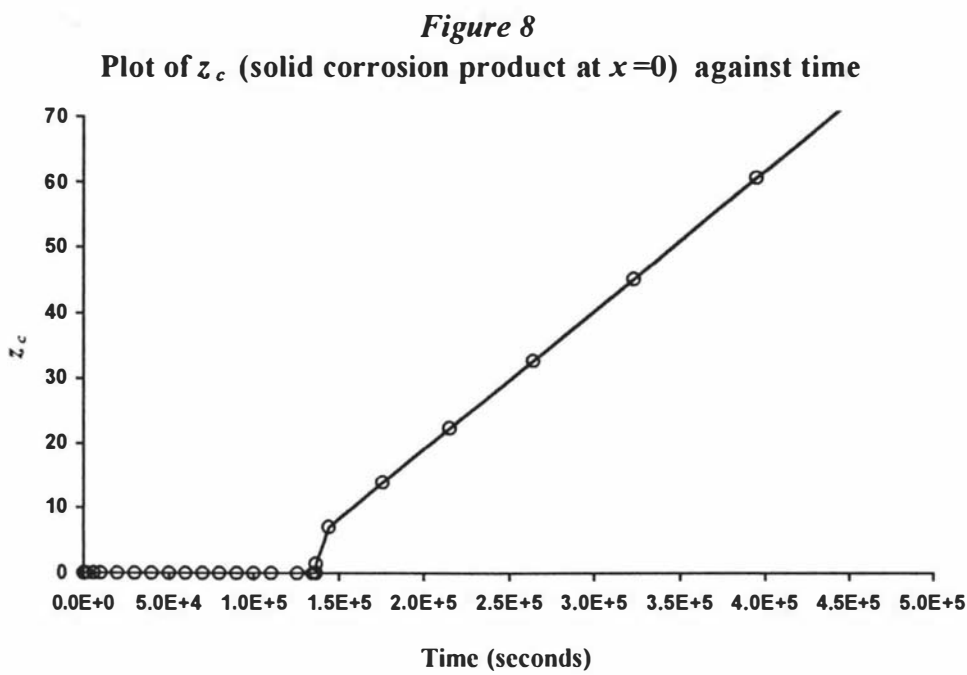
We see that up to about 1.35×10^5 seconds no corrosion product accumulates. In fact the small quantities of zinc ions that are produced are promptly absorbed by the polymer and a small proportion diffuse away from the metal surface towards the paint film surface. Once degradation of the adsorbed layer occurs we see that there is an initial rapid burst of corrosion, followed by a steady accumulation at a constant rate (which corresponds with the result of equation 5.6.6).

The initial burst of corrosion results from the sudden change of state of the adsorbed layer, in combination with a delay in the diffusive response of the paint film. At the onset of rapid corrosion the concentrations of water and oxygen near the metal surface are close to their saturation values, and there is only a small concentration gradient within the paint film. Corrosion increases so suddenly that there is insufficient time for diffusive equilibrium to be maintained. Consequently there is a brief period where the concentrations of water and oxygen at $x=0$ exceed their equilibrium values. Once diffusive equilibrium is re-established and the diffusive fluxes of water and oxygen are in equilibrium with their consumption in the corrosion reaction, we see that corrosion occurs at a constant rate.

Figure 9
Plot of m_p (metal surface covered with polymer) against time
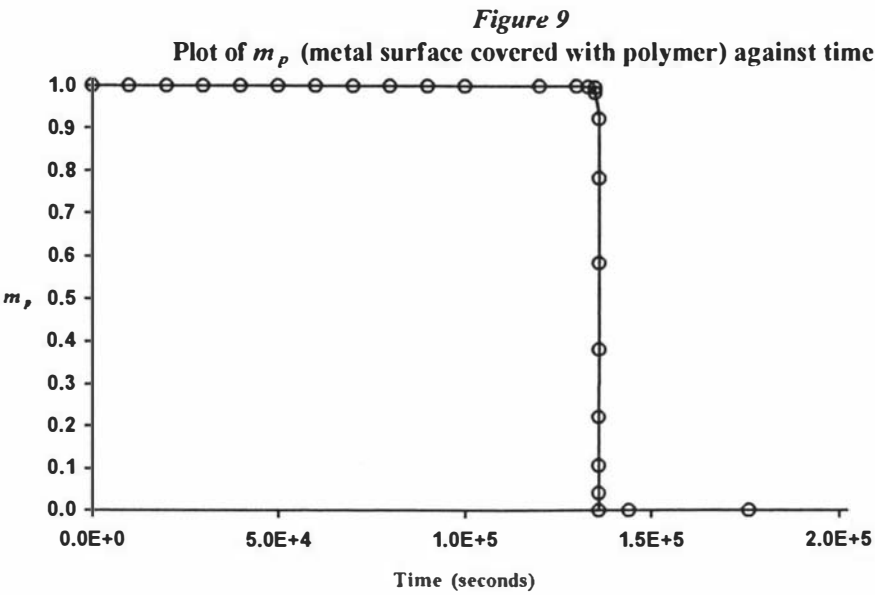
The corresponding behaviour of m_p is shown in *figure 9*. Initially there is only very slight reduction in m_p and its value remains near one throughout the protective lifetime of the paint film. At about 1.35×10^5 seconds there is sudden and catastrophic failure. In *figure 10* an enlargement of the initial behaviour of m_p is shown. The first stage up to about 1×10^3 seconds corresponds to the establishment of diffusive equilibrium as water enters the paint film from the external environment.

From about 1×10^3 to about 1×10^5 there is a very slow decrease in m_p as soluble corrosion product is taken up and immobilised by polymer. During this phase the polymer maintains protection of the metal substrate: the great majority of the metal surface remains covered with adsorbed polymer, and there remains some excess of polymer. As this excess of polymer is consumed a point is reached where there is insufficient polymer remaining to maintain significant adsorption of polymer on to the metal surface. This corresponds to the time around 1×10^5 seconds in *figure 10*. As polymer coverage decreases there is an accelerating increase in the rate of corrosion which acts to further degrade the polymer. The result is rapid desorption of polymer, accompanied by a sudden increase in the rate of corrosion.

Figure 10
Plot of m_p (metal surface covered with polymer) against time
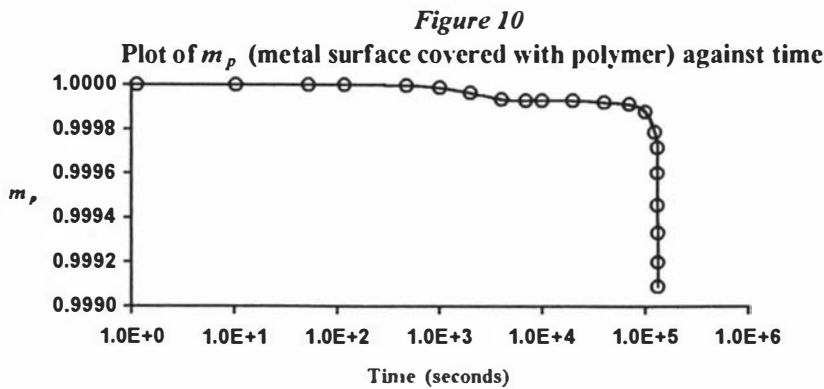
In *figure 9* we see that when degradation of the adsorbed layer is completed there is a residual small attachment of polymer to the metal surface, which in this case is about 1.1×10^{-5} for times above about 1.35×10^5. The great majority of polymer is bound to corrosion product, while small proportions are bound to water and adsorbed onto active sites on the metal surface.

In *figure 11* we plot q_f, q_w, q_z, and z against time. We see that up to about $T=2 \times 10^3$ seconds there is a steep increase in q_w, q_z, and z as diffusive equilibrium is established and oxygen u and water w reach values near unity at $x=0$. From about 10^3 to about 10^5 seconds we see a more gradual increase in q_z and z as the corrosion process develops. Note that q_w reaches a maximum at about 2×10^3 seconds and then decreases, as q_f also steadily decreases. Initially q_f is near unity at approximately $1-q_m$: almost all the polymer is in the form of free and unbound polymer functional groups. A small proportion is bound to water, and some characteristic proportion is bound to active groups on the metal surface (proportional to m_p, see equation 3.11).

The proportion of free polymer q_f steadily decreases as corrosion proceeds from 0 up to about 10^5 seconds. During this time the adsorbed layer maintains protection of the metal surface, but is steadily degrading as corrosion product is taken up. Initially this has no significant effect but beyond some critical point there remains insufficient free polymer available to produce effective competitive adsorption of polymer to the metal substrate. The result is a great surge in the rate of corrosion.

The quantity q_z of polymer bound to corrosion product rapidly reaches saturation as does z the amount of soluble corrosion product. At the same time there is a steep fall in q_f and in q_w and we note that these changes correspond to similar changes in other variables such as m_p as shown in *figures 9 and 10*.

Figure 11

Plot of q_w, z, q_z, and q_f against time

Time (seconds)
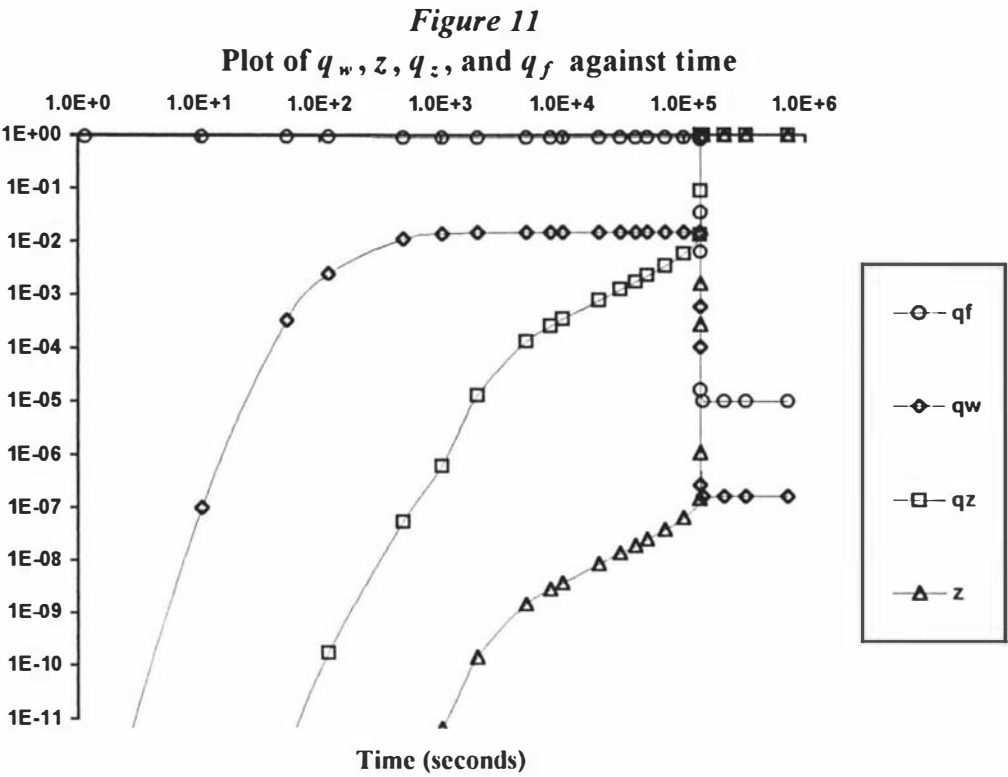
In *figure 12* m_p, m_w, m_u, and m_f are plotted against time. We see that m_f is almost constant; in fact m_f rises very slightly from about 9.7×10^{-7} to about 1.0×10^{-6}; m_f is the proportion of metal surface free and unassociated with any adsorbed species. We interpret first the near constancy to mean that there is little change in the effective total pressure of species competing for adsorption. Additionally the small value for m_f indicates that water, oxygen and polymer effectively create a high pressure: the metal surface is always densely covered with adsorbed species: initially mostly polymer m_p, and ultimately mostly water m_w.

The small decrease in m_f is produced by the removal of free polymer q_f due to uptake of corrosion product by polymer (equations 3.7 and 3.9).

We see that m_w and m_u rise initially quite steeply up to about 2×10^3 seconds as diffusive equilibrium is established. From about 2×10^3 to about 1×10^5 seconds m_w and m_u are very nearly constant which we contrast with q_z and z over the same range where there is an increase of 2 to 3 orders of magnitude (*figure 11*).

At about 1.35×10^5 seconds there is a sudden change in the model's state. The proportion of adsorbed polymer m_p drops to a small value while the proportion of adsorbed water m_w increases roughly in proportion to approach unity. The proportion of metal surface covered by oxygen m_u also increases but here (with our estimated parameters) remains at relatively low levels compared to water m_w.

Figure 12
Plot of m_p, m_w, m_u, and m_f against time
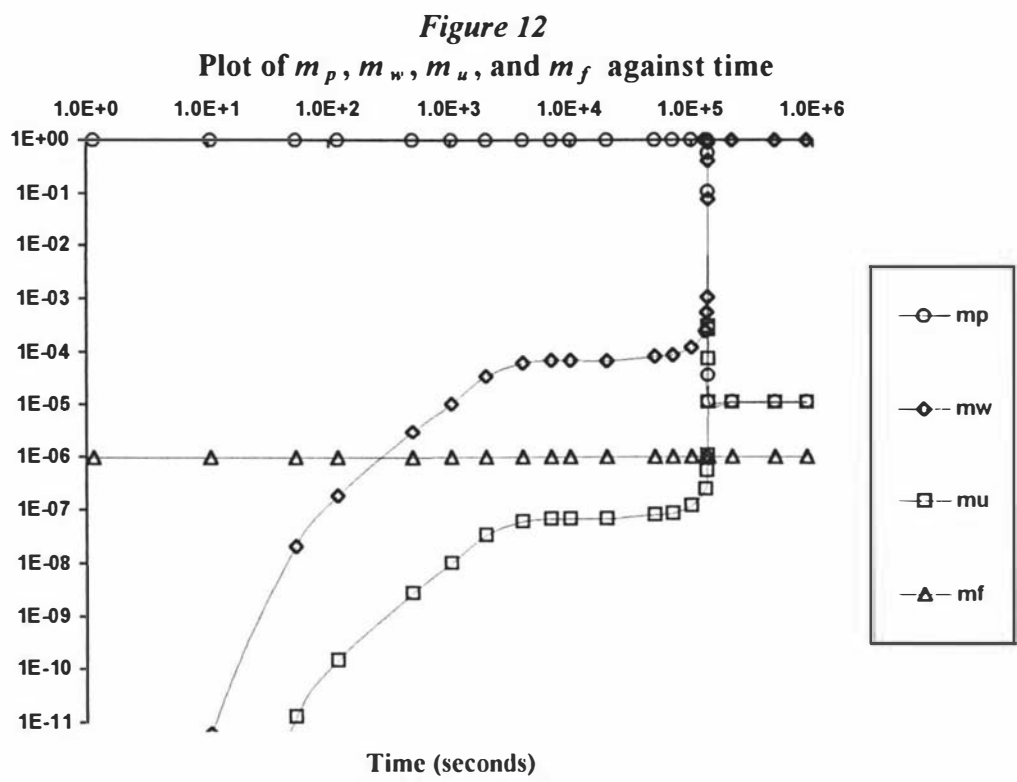
The behaviour of water w and oxygen u at $x=0$ is shown in *figure 13*. We see that saturation occurs at about 1.0×10^3 seconds for both w and u. From about 1.0×10^3

to about 1.35×10^5 seconds a state of diffusive equilibrium is maintained and w and u are maintained very close to unity (saturation). Diffusion of water and oxygen are evidently not factors governing the models behaviour in this range nor factors affecting the degradation of the adsorbed layer at $x=0$ over this same range. For times greater than about 1.35×10^5 seconds we see that water w remains near saturation, but oxygen u drops to about 1.1×10^{-2}. From this we conclude that the rate of oxygen consumption in the corrosion reaction is such that a significant gradient of oxygen occurs in the paint film which acts as the rate limiting process on this ultimate stage where steady state rusting (corrosion) ensues.

Figure 13
Plot of w and u at $x=0$ against time
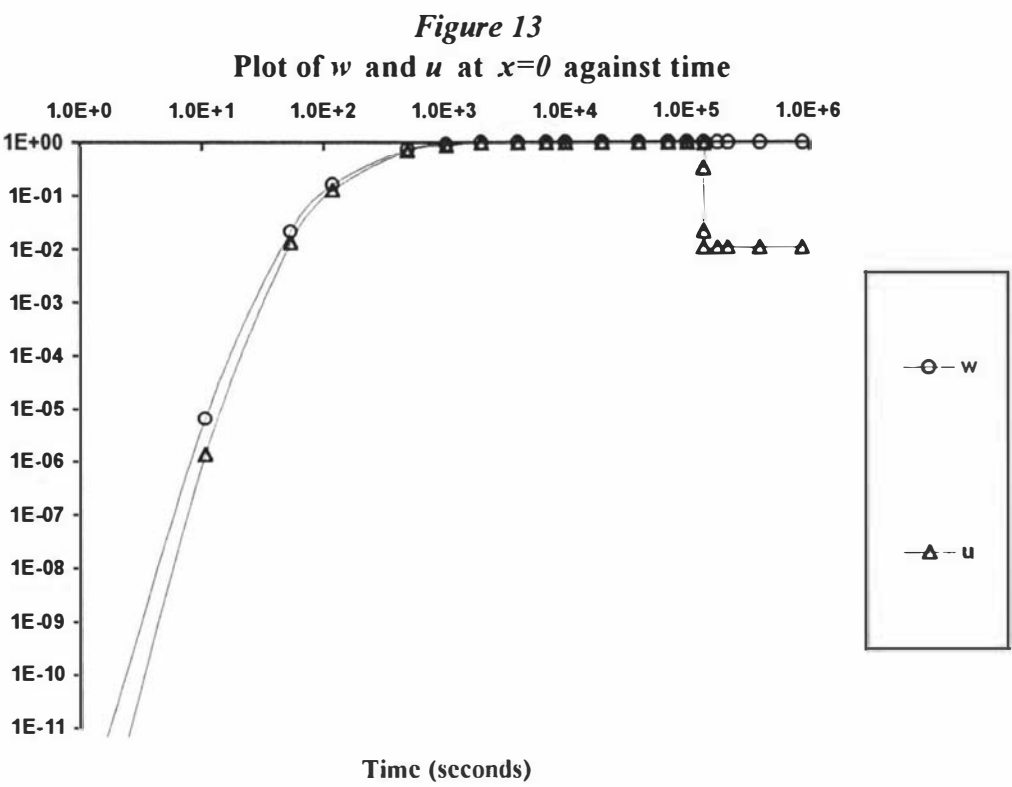
The behaviour described above is typical of painted metal surfaces. Additionally the possibility of oxygen (or water) diffusion being ultimately rate limiting agrees with many reports in the literature. Adhesion of the paint film to the metal surface and polymer interactions with ions have also been shown in the literature to be

factors in paint performance. We conclude that this model does represent the behaviour of real painted metal surfaces.

As with the real world we attempt to simulate with this model, there is a rich variety of behaviours. It has not proven possible to explore all of these variations. While we are hopeful that the model will continue to show interesting and useful parallels to real painted metal surfaces, the proof must await future study. In particular the model's response to periodic wetting functions has yet to be explored and compared with actual weather and exposure data from specific physical sites.

Also it has not been possible to study the effect of varying every parameter, nor to explore all the interactions arising from various changes to parameters and model composition. We have seen that some parameters, for example α_3, can produce dramatic change in the model behaviour even with relatively small changes in value. When the effects of periodic wetting are included we expect that diffusive processes and transient effects will considerably add to the richness of the model's behaviour.

From the rather brief review of numerical results covered in this section we next explore the behaviour of some analytic approximations arising out of reductions of the full model. These reduced models are intended to approximate the full model in certain regions of operation.

7. REDUCED MODEL

7.1 PREFACE

Our aim in formulating the model was to produce as comprehensive a formulation as possible, subject to remaining within the bounds of plausibility and capturing what was judged to be the essential elements of the problem. One major handicap was that there was not much knowledge available on models (of this type) for painted metal surfaces. A second difficulty was that we could not determine whether or not the model corresponded to reality until the model was formulated and tested. Consequently we employed a principle of "include every element which may be relevant".

We realised that the resultant model may not be analytically solvable, and may contain some redundant features. The hope was that we could study the full model and deduce what the key equations were and subsequently construct a reduced model which embodied the essential elements of the full model but without the excessive detail. One basis for this hope was that it was noted from other projects in modelling physical problems that invariably the behaviour of a system of equations, in some range of conditions, was governed by one or two differential equations. The remaining differential equations are usually found to be satisfactorily approximated by algebraic equations.

The value of a reduced model is that, ideally, it can be solved exactly. From this we can see explicitly which parameters govern, for example, the protective lifetime T_c of a particular case, and determine how they interact together. From this we can begin to apply the results of the model to real life and purposefully select and engineer polymers and paint film compositions to produce properties which the model predicts will result in longer protective lifetimes T_c. While those experienced in the field of polymer and paint formulation may have some understanding and experience of factors which typically lead to better performance there is no underlying knowledge of how paint films work. Indeed after more than

50 years of research there is still controversy about what the mechanism of protection is, and even no clear consensus as to what occurs during the failure process. We aim to show that a reduced model exists and that it predicts specific variables and factors which include many of those either recognised or suspected of playing a part in paint film protective performance.

7.2 REDUCED MODEL DERIVATION

We are interested in determining the time to failure T_c of an initially dry painted metal surface when immersed continuously in oxygenated water. We suppose the system is kept at constant temperature and ignore for now the effect of ions other than of corrosion product itself.

From *figure 13* we deduce that diffusion does not much affect T_c, at least in regions of interest where for example α_3 is larger than about 1.1×10^6 (refer *figure 7*). Consequently we assume that water and oxygen concentrations in the film are approximated by their saturation values.

$$u(x) = u_0 = 1 \tag{7.2.1}$$

$$w(x) = w_0 = 1 \tag{7.2.2}$$

consequently

$$p_w(x) = \alpha_6 w_0 p_f = \alpha_6 p_f \tag{7.2.3}$$

We specify that corrosion product is washed away from the paint film surface to maintain $z=0$ at $x=1$. Additionally we suppose that z is effectively zero throughout the film for times of interest. Eventually z will reach saturation at $x=0$ and there will develop a gradient of z as it diffuses out through the film; but we are here concerned about the initial state of the film where there is negligible corrosion product (see for example *figure 11*).

$$z(x) = z_0 = 0 \tag{7.2.4}$$

and consequently

$$p_z(x) = \alpha_7 z p_f = 0 \qquad (7.2.5)$$

Since w, u, and z are constant we suppose that the boundary conditions 3.19 to 3.22 are approximated by zero gradient conditions:

$$\left.\frac{\partial w}{\partial x}\right|_{x=0} = 0, \quad \left.\frac{\partial u}{\partial x}\right|_{x=0} = 0, \quad \left.\frac{\partial z}{\partial x}\right|_{x=0} = 0 \qquad (7.2.6)$$

Next we examine equations 3.9, 3.10, 3.7, 3.5, 3.6, and dz/dt to deduce which equation produces the greatest effect and hence is potentially a 'governing equation'. We plot in *figure 14* the derivatives dq_z/dt, dq_w/dt, dm_p/dt, dm_w/dt, dm_u/dt, and dz/dt against time for the case of best estimates for parameter values listed in table 1, in particular $\alpha_3 = 1.67 \times 10^6$. In *figure 15* we plot the derivative dq_z/dt, and $\theta_4 \alpha_4 z q_f$ (term 1), and $\theta_4 q_z$ (term 2) against time. For these parameter values we find that T_c is about 5.6×10^8 seconds (18 years) and that typically dq_z/dt is larger than the other derivatives, and much smaller than $\theta_4 \alpha_4 z q_f$, and $\theta_4 q_z$.

Figure 14

Plot of dq_z/dt, $-dq_w/dt$, $-dm_p/dt$, dm_w/dt, dm_u/dt, and dz/dt against time

Time (seconds)
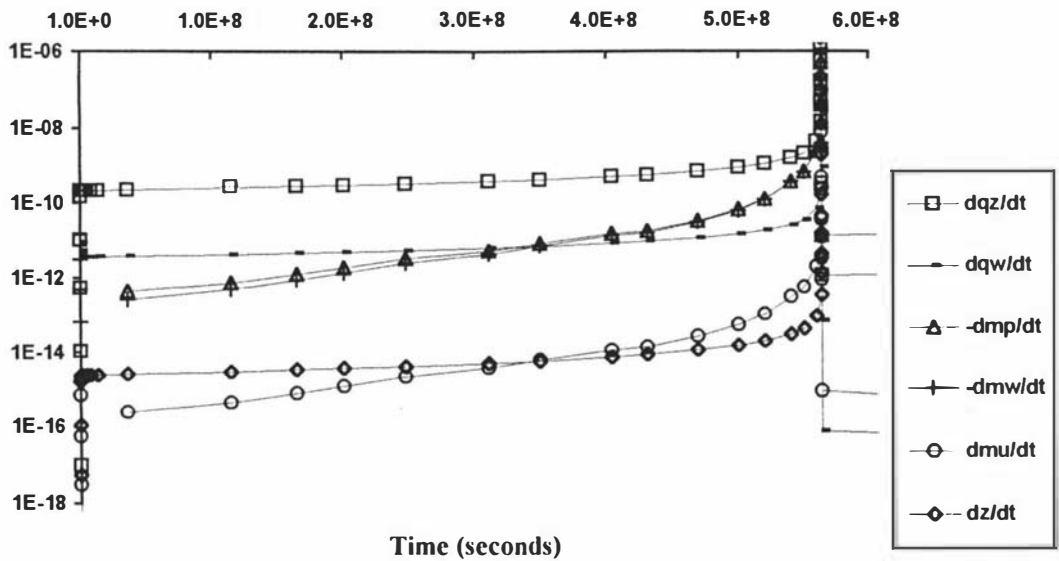
Figure 15
Plot of dq_z/dt, term 1, and term 2 of eq 7.2.7 against time

Time (seconds)
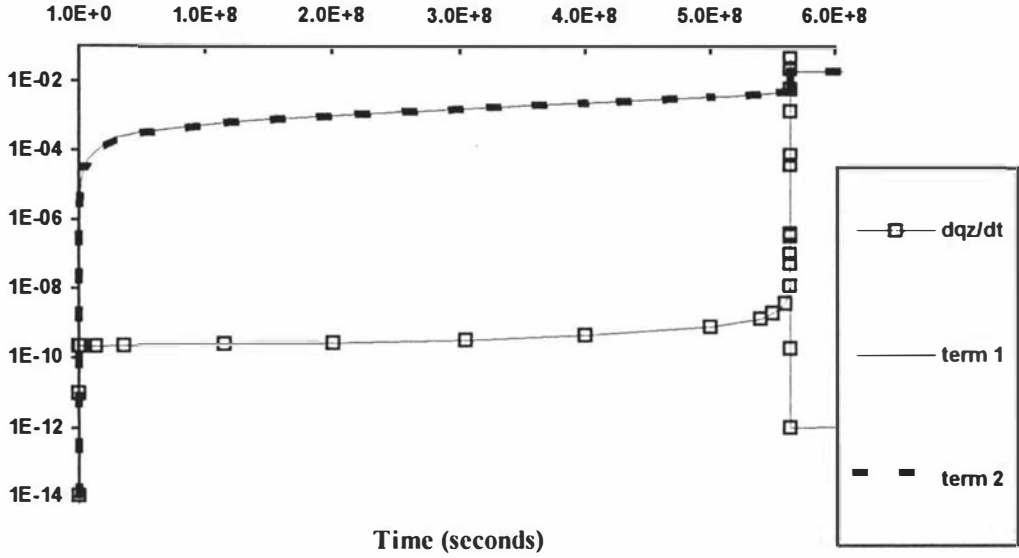
From equation 3.9 we have

$$\frac{dq_z}{d\tau} = \theta_4\left(\alpha_4 z q_f - q_z\right)$$ (7.2.7)

We find that generally $\alpha_4 z q_f$ and q_z agree to about the sixth significant digit (*figure 15*) and so we write:

$$\theta_4 \alpha_4 z q_f = \theta_4 q_z + \varepsilon\left(q_z\right)$$ (7.2.8)

We then have

$$\frac{dq_z}{d\tau} = \varepsilon\left(q_z\right)$$ (7.2.9)

and look for an expression for $\varepsilon(q_z)$ in equation 3.21 where $\varepsilon(q_z)$ is some function of q_z, considered to be small compared to the other two terms

Similarly it is found that the derivative terms are the smallest in equations 3.5, 3.6, 3.7, and 3.10 and so these are approximately in equilibrium. Hence we obtain (as quasi-steady states) the equations:

$$m_w = \alpha_1 w_0 \left(1 - m_p\right) m_f = \alpha_1 \left(1 - m_p\right) m_f \qquad (7.2.10)$$

$$m_u = \alpha_2 u_0 \left(1 - m_p\right) m_f = \alpha_2 \left(1 - m_p\right) m_f \qquad (7.2.11)$$

$$m_p = \alpha_3 q_f m_f \qquad (7.2.12)$$

$$q_w = \alpha_5 w_0 q_f = \alpha_5 q_f \qquad (7.2.13)$$

In eq 3.21 we find that generally, for this particular case of interest,

$$\frac{dz}{d\tau} \ll \kappa_5 \frac{dq_z}{d\tau} \qquad (7.2.14)$$

and

$$\alpha_8 \left(1 - m_p\right)^2 w_0^2 \ll \left(1 - m_p\right)^{3/2} w_0 u_0^{1/2} \qquad (7.2.15)$$

and we suppose that

$$-\phi_3 \left(\frac{dz}{d\tau} + \kappa_5 \frac{dq_z}{d\tau} \right) + \phi_4 \kappa_6 \left[\left(1 - m_p\right)^{3/2} w_0 u_0^{1/2} + \alpha_8 \left(1 - m_p\right)^2 w_0^2 \right] = 0 \qquad (7.2.16)$$

So that we can write

$$\frac{dq_z}{d\tau} = \frac{\phi_4 \kappa_6}{\phi_3 \kappa_5} \left(1 - m_p\right)^{3/2} w_0 u_0^{1/2} \qquad (7.2.17)$$

From eq 3.8 we find

$$1 - m_p = \frac{m_f}{1 - \left(\alpha_1 + \alpha_2\right) m_f} \qquad (7.2.18)$$

We shall represent m_f with a power series expansion in q_z for small values of q_z:

$$m_f(q_z) = m_{f0} + a_1 q_z + a_2 q_z^2 + \cdots \qquad (7.2.19)$$

To do this we need to solve for m_f in terms of q_z in equations 7.2.10 to 7.2.13, 3.8, and 3.12. From eq 3.12 we see that

$$q_f = \frac{1 - q_z}{1 + \alpha_5 + \alpha_3 \kappa_3 m_f} \qquad (7.2.20)$$

Figure 16
Reduced model q_f (equation 7.2.21), numeric q_f and q_z
plotted against time
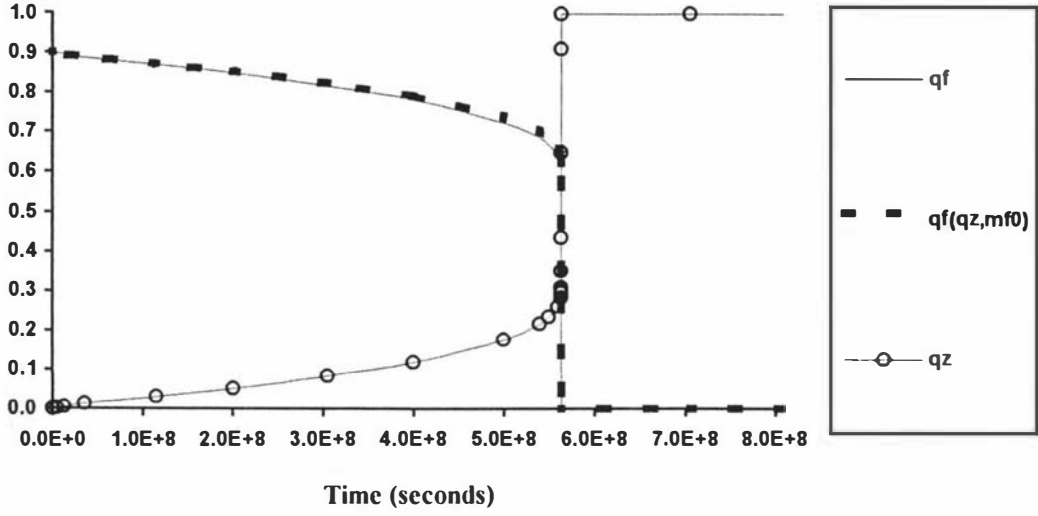
To a reasonably good approximation (see *figure 16*) we see that

$$q_f = \frac{1 - q_z}{1 + \alpha_5 + \alpha_3 \kappa_3 m_{f0}} \qquad (7.2.21)$$

where we use eq 7.2.23 for m_{f0} with $q_z = 0$. Although eq 7.2.12 might be used to express m_p, along with eq 7.2.21 and 7.2.23 we find that this does not readily lead to a useful expression for m_p; so instead substitute eq 7.2.20 into eq 3.8 to obtain

$$\alpha_3 \big[(\alpha_1 + \alpha_2)(1 - q_z) - (1 + \alpha_1 + \alpha_2)\alpha_3 \kappa_3\big] m_f^2 - \big[(1 + \alpha_1 + \alpha_2)(1 + \alpha_5) + \alpha_3(1 - \kappa_3 - q_z)\big] m_f + 1 + \alpha_5 = 0 \qquad (7.2.22)$$

and

$$m_f = \frac{\alpha_3(1 - \kappa_3 - q_z) + (1 + \alpha_1 + \alpha_2)(1 + \alpha_5) - G(q_z)}{2\alpha_3 \big[(\alpha_1 + \alpha_2)(1 + q_z) - \kappa_3(1 + \alpha_1 + \alpha_2)\big]} \qquad (7.2.23)$$

where

$$G(q_z) = \sqrt{\left[\alpha_3\left(1-\kappa_3-q_z\right)+\left(1+\alpha_1+\alpha_2\right)\left(1+\alpha_5\right)\right]^2 - 4\alpha_3\left(1+\alpha_5\right)\left[\left(\alpha_1+\alpha_2\right)\left(1+q_z\right)-\kappa_3\left(1+\alpha_1+\alpha_2\right)\right]}$$

for convenience we introduce the following constants:

$$b_1 = \left(1+\alpha_1+\alpha_2\right)\left(1+\alpha_5\right)+\alpha_3\left(1-\kappa_3\right)$$

$$b_2 = 4\alpha_3\kappa_3\left(1+\alpha_1+\alpha_2\right)\left(1+\alpha_5\right)-4\alpha_3\left(1+\alpha_5\right)\left(\alpha_1+\alpha_2\right)$$

$$b_3 = 4\alpha_3\left(\alpha_1+\alpha_2\right)\left(1+\alpha_5\right)$$

$$b_4 = 2\alpha_3\left(\alpha_1+\alpha_2\right)-2\alpha_3\kappa_3\left(1+\alpha_1+\alpha_2\right)$$

$$b_5 = 2\alpha_3\left(\alpha_1+\alpha_2\right)$$

and calculate $\dfrac{dm_f}{dq_z}$, $\dfrac{d^2m_f}{dq_z^2}$ to obtain

$$\left.\frac{dm_f}{dq_z}\right|_{q_z=0} = -\frac{\alpha_3}{b_4}-\frac{b_3-2\alpha_3 b_1}{2b_4\sqrt{b_1^2+b_2}}+\frac{b_5\left(b_1-\sqrt{b_1^2+b_2}\right)}{b_4^2} \tag{7.2.24}$$

and

$$\left.\frac{d^2m_f}{dq_z^2}\right|_{q_z=0} = -\frac{\alpha_3^2}{b_4}-\frac{\left(\alpha_3 b_1-\frac{1}{2}b_3\right)^2}{4b_4\left(b_1^2+b_2\right)^{3/2}}-\frac{2\alpha_3 b_5}{b_4^2}+\frac{b_5\left(b_3-2\alpha_3 b_1\right)}{b_4^2\sqrt{b_1^2+b_2}}+\frac{2b_5^2\left(b_1-\sqrt{b_1^2+b_2}\right)}{b_4^3} \tag{7.2.25}$$

For our best estimates of parameter values (table 1) we calculate the following quantities

$$m_{f0} = m_f\big|_{q_z=0} = 6.6555\times 10^{-7} \tag{7.2.26}$$

$$a_1 = \frac{dm_f}{dq_z}\bigg|_{q_z=0} = 7.2738 \times 10^{-7} \qquad (7.2.27)$$

$$a_2 = \frac{d^2 m_f}{dq_z^2}\bigg|_{q_z=0} = 1.5899 \times 10^{-6} \qquad (7.2.28)$$

and plot the results of linear and quadratic expressions for m_f in *figure 17*.

$$m_f(q_z) = m_{f0} + a_1 q_z \qquad (7.2.29)$$

$$m_f(q_z, q_z^2) = m_{f0} + a_1 q_z + a_2 q_z^2 \qquad (7.2.30)$$

Figure 17
Reduced model m_f (linear and quadratic expressions) and
numeric m_f plotted against time.
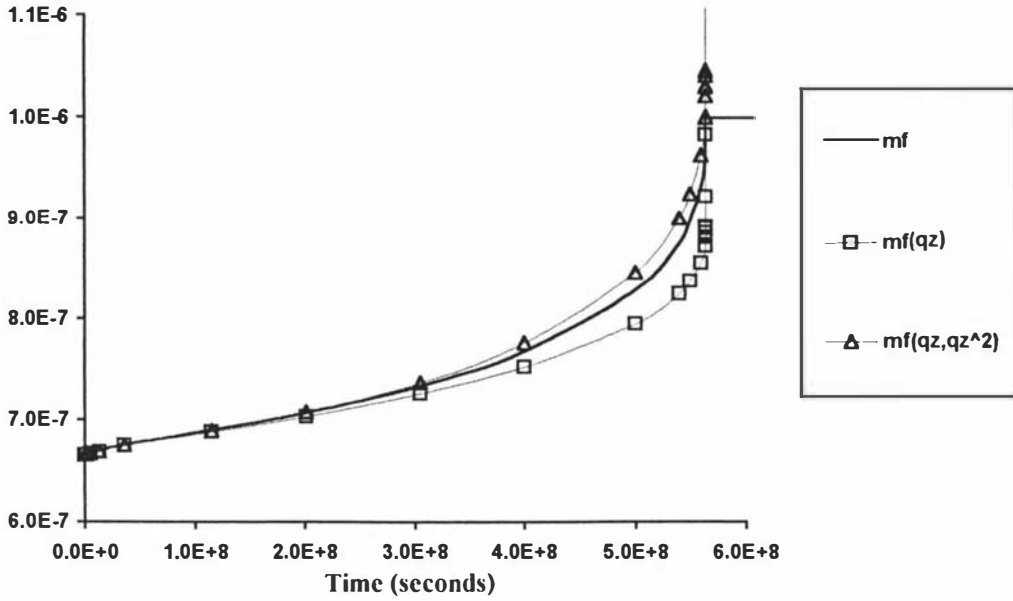
As expected eq 7.2.30 produces a better expression for m_f and we expect will under estimate T_c while eq 7.2.29 also produces a reasonable approximation for m_f which we will find is useful for producing estimates for T_c. We expect that eq 7.2.29 will lead to over estimates of T_c.

We substitute eq 7.2.29 into eq 7.2.18 and 7.2.17 to obtain a reduced model consisting of a single ODE eq 7.2.31, together with algebraic equations described above:

$$\frac{dq_z}{d\tau} = \frac{\phi_4\kappa_6}{\phi_3\kappa_5}\left(\frac{m_{f0}+a_1q_z}{1-(\alpha_1+\alpha_2)(m_{f0}+a_1q_z)}\right)^{3/2} \tag{7.2.31}$$

where we have assumed $\dfrac{\kappa_3}{\alpha_1+\alpha_2} \ll 1-q_z$ and $\dfrac{3}{2}\kappa_3+q_z \ll \left(1-\dfrac{\kappa_3}{2}\right)(\alpha_1+\alpha_2)$

Equation 7.2.31 is plotted as a function of q_z against numeric results in *figure 18*.

Figure 18
Reduced model dq_z/dt (equation 7.2.31) and numeric dq_z/dt
plotted against time.
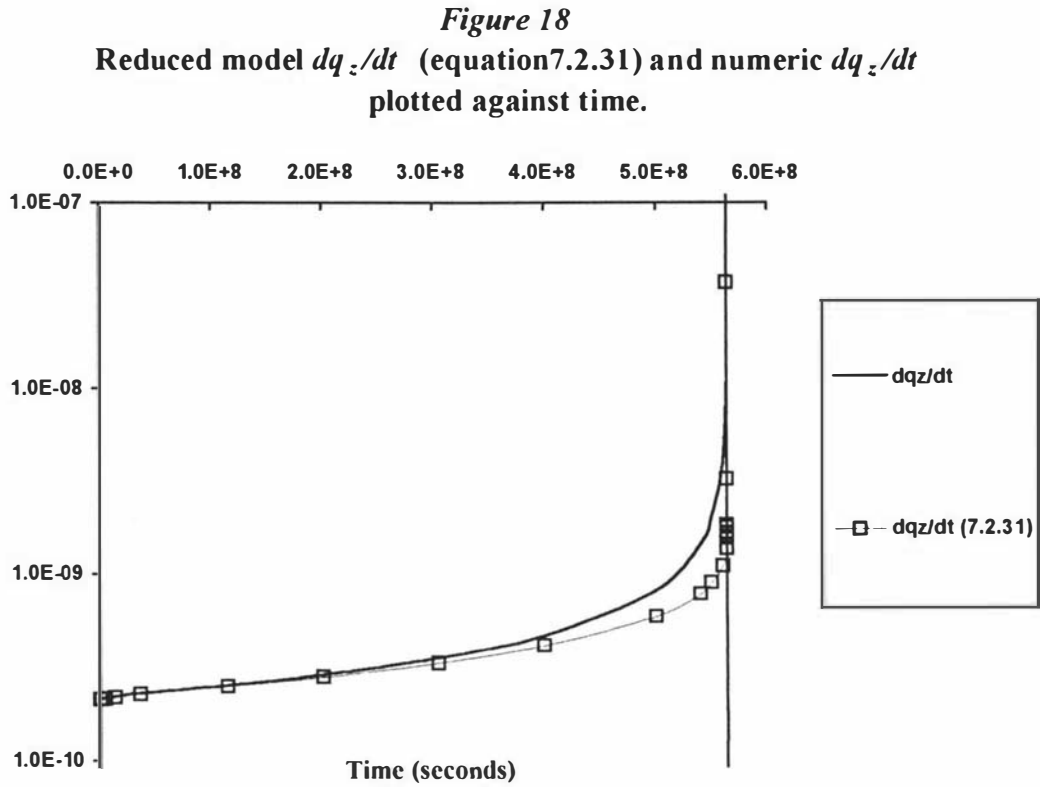
We write

$$\beta_1 = \frac{m_{f0}}{a_1}, \qquad \beta_2 = \frac{1-(\alpha_1+\alpha_2)m_{f0}}{(\alpha_1+\alpha_2)a_1}$$

and substitute

$$y = \frac{\beta_1 + \beta_2}{\beta_1 + q_z}$$

and obtain from eq 7.2.31

$$\frac{dy}{d\tau} = \frac{\phi_4 \kappa_6}{\phi_3 \kappa_5 (\beta_1 + \beta_2)(\alpha_1 + \alpha_2)^{3/2}} \frac{y^2}{(1-y)^{3/2}} \qquad (7.2.32)$$

and $\qquad y(0) = \dfrac{(\beta_1 + \beta_2)}{\beta_1}$

On integration

$$\int \frac{(y-1)^{3/2}}{y^2} dy = \int \frac{-\phi_4 \kappa_6 d\tau}{\phi_3 \kappa_5 (\beta_1 + \beta_2)(\alpha_1 + \alpha_2)^{3/2}} = \frac{-\phi_4 \kappa_6 \tau}{\phi_3 \kappa_5 (\beta_1 + \beta_2)(\alpha_1 + \alpha_2)^{3/2}} + \text{constant} \qquad (7.2.33)$$

Integrate by parts to get

$$\int \frac{(y-1)^{3/2}}{y^2} dy = \frac{-(y-1)^{3/2}}{y} + \frac{3}{2} \int \frac{\sqrt{y-1}}{y} dy \qquad (7.2.34)$$

then substitute $y = \sec^2 \theta$ to get

$$\int \frac{(y-1)^{3/2}}{y^2} dy = \frac{-(y-1)^{3/2}}{y} + \frac{3}{2} \int 2 \tan^2 \theta \, d\theta = \frac{-(y-1)^{3/2}}{y} + 3(\tan\theta + \theta) , \qquad (7.2.35)$$

and so we obtain

$$\frac{D_w \phi_4 \kappa_6 t}{\phi_3 \kappa_5 l^2 (\alpha_1 + \alpha_2)^{3/2}} + \text{constant} = \frac{(\beta_2 - q_z)^{3/2}}{\sqrt{\beta_1 + q_z}} - 3(\beta_1 + \beta_2) \left\{ \sqrt{\frac{\beta_2 - q_z}{\beta_1 + q_z}} - arc \tan \sqrt{\frac{\beta_2 - q_z}{\beta_1 + q_z}} \right\} \qquad (7.2.36)$$

where we have used $\quad \tau = \dfrac{D_w t}{l^2}$

For values of parameters in table 1 we find that $\text{constant} = -0.054$ when $t = 0$ and $q_z = 0$. The equation 7.2.31 has a singularity at $q_z = \beta_2$ which is the critical value for q_z. The time at which q_z achieves this value (with vertical tangent) is

the threshold value of the time for the onset of rapid corrosion. We suppose that t approaches T_c as q_z approaches β_2, and calculate $T_c = 7.1 \times 10^8$ which is 127% of the numerically computed value of 5.64×10^8.

$$T_c = \frac{\left[3(\beta_1 + \beta_2) \left\{ \sqrt{\frac{\beta_2}{\beta_1}} - arc \tan \sqrt{\frac{\beta_2}{\beta_1}} \right\} - \frac{\beta_2^{3/2}}{\sqrt{\beta_1}} \right] \phi_3 \kappa_5 l^2 (\alpha_1 + \alpha_2)^{3/2}}{D_w \phi_4 \kappa_6} \tag{7.2.37}$$

In the following chapters we will consider different approaches for estimating the threshold time T_c and will compare these results in a discussion of the model.

8. MODEL SIMPLIFICATION

8.1 INTRODUCTION

When formulating the model it was not known which terms were important, which equations were refinements and which were indispensable, and how the model would behave with variations in its formulation. We explore model variations in more detail in chapter 10. For the present exercise we wish to state the model in a simpler form and develop from this a second reduced model which embodies the essential behaviour of the model and which allows analytic solution.

Of particular interest is the term $(1-m_p)$ in equations 3.5 and 3.6. It is included in an attempt to represent the effect of polymer packing on activity coefficients in the adsorbed layer. There are various ways to write this effect, as we shall discuss later. One method which we considered, and ultimately abandoned, was to model the interaction of the adsorbed layer with the bulk paint film in an additional system of competition equations. The first issue which we aim to resolve here is: does the term make any difference in the model's behaviour? If it makes little difference then we should simplify our model formulation and remove it, and consequently arrive at a simplified mathematical model.

Another term which was added for completeness was $\kappa_4 z$ in equation 3.18. In theory this term might account for some additional and varying capacity for uptake of corrosion product by a polymeric paint film. The intention was to represent modification of the film by the absorbed corrosion product. Again the test of the value of this term lies in comparing results with and without it.

We consider the effect of omitting the terms $(1-m_p)$ in equations 3.5 and 3.6, and $\kappa_4 z$ in equation 3.18. The immediate effect is a drastic reduction in the model's protective properties. The simplified model produces a time to failure T_c of about 4.48×10^2 seconds, where the failure arises immediately as the uptake of water occurs through diffusion into the paint film. This parallels the behaviour of the full

model where α_3 is small (see for example *figure 7*). We find that substantial variation of parameters is required to increase T_c in the simplified model to approach significant protective lifetime values.

The parameters indicated in table 1 are the best estimates currently available; there is inevitably some uncertainty in these estimates, additionally it is believed that there is some range of values which represents the range of properties produced by different polymers and paint films. We alter the following parameters to produce a corresponding time to failure T_c which matches the case described above in *figures 8 to 13*. We set $\alpha_1=10^5$, $\alpha_3=10^8$, $\theta_3=10^3$ with remaining parameters as estimated in table 1.

The modified values for α_1, α_3, and θ_3 may still lie within the bounds of real polymers and paint films. However this simplified reduced model can at best account only for a subset of paint types of evidently lower performance. Parameter values necessary to model long times to failure T_c are unrealistic. Parameter values most likely to correspond to real paint films result in values for T_c in the range 10^3 to 10^4 seconds which is only slightly greater than the restriction imposed by diffusive processes alone.

8.2 SIMPLIFIED MODEL

The effect of varying α_3 is plotted in *figure 19* where we have also changed α_1 to 10^5 and θ_3 to 10^3. Comparing figure 19 with *figure 7* we see that this change in equations 3.5 and 3.6 has produced a significant effect in the model's behaviour. Additionally we observe that the transition from diffusion limited performance to competitive adsorption limited performance shown in *figure 7* is absent in this reduced simplified model shown in *figures 19* and *20*. A subsection of *figure 19* is graphed in *figure 20*.

Figure 19
Time (T_c) to onset of Corrosion vs parameter α_3
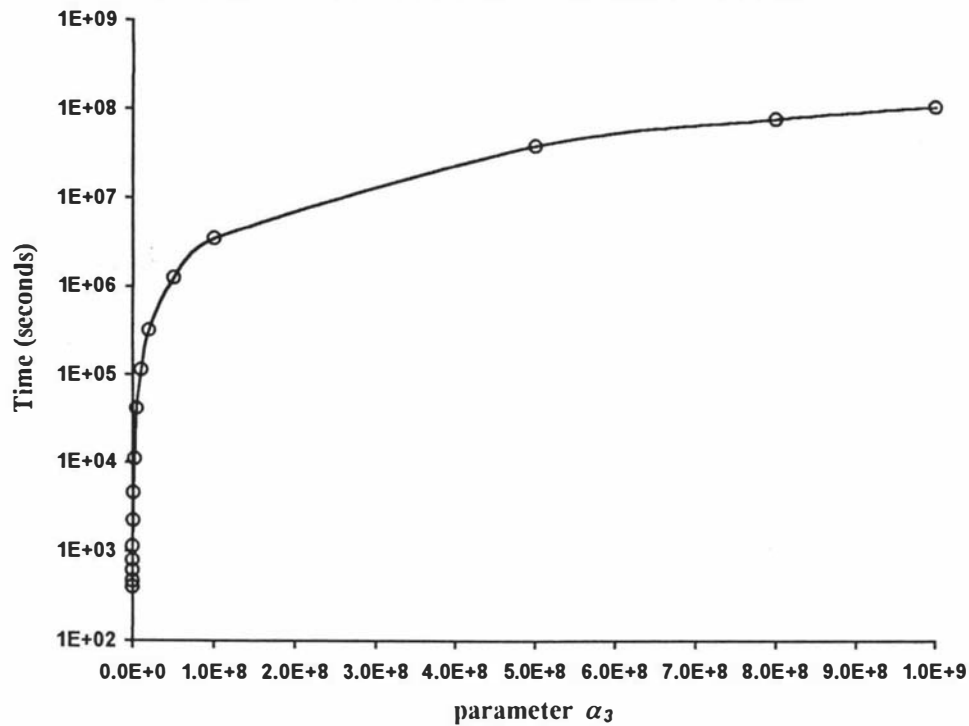
Figure 20
Time (T_c) to onset of Corrosion vs parameter α_3
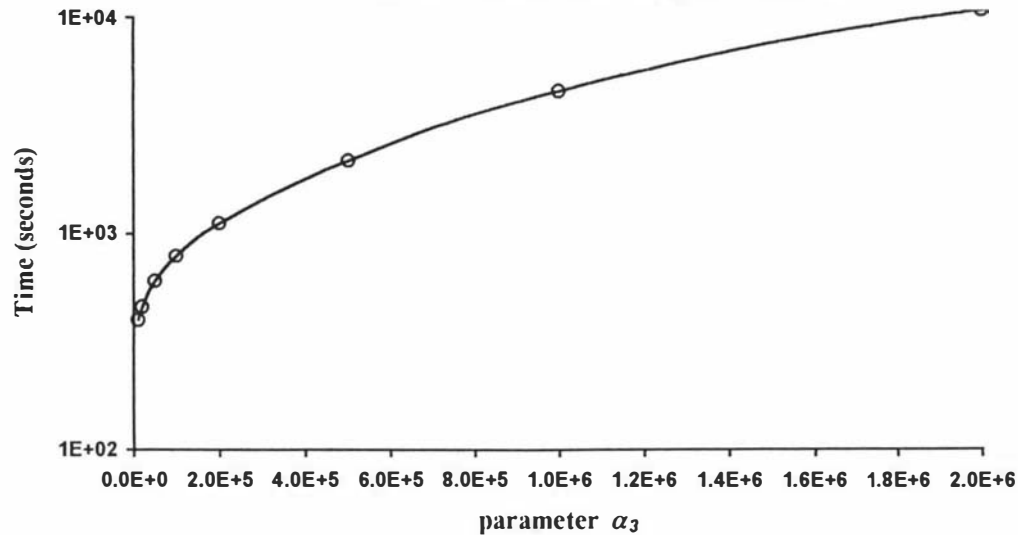
In *figure 21* we find the same behaviour as in *figure 8* for the full model. We notice that similar slope is produced ($dZ_c/dt = 1.74 \times 10^{-6}$ mol m^{-2} s^{-1} for the data in *figure 21* and $dZ_c/dt = 1.75 \times 10^{-6}$ mol m^{-2} s^{-1} for the data in *figure 8*).

Figure 21
Plot of z_c (solid corrosion product at $x = 0$) against time

Time (seconds)
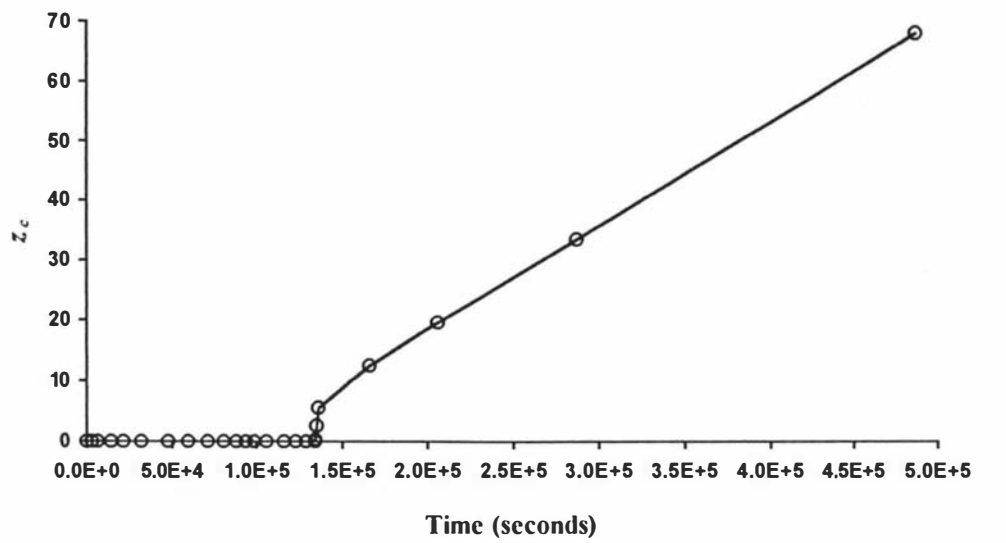
Next we plot m_p against time in *figure 22*, with an enlargement shown in *figure 23*.

Figure 22
Plot of m_p (metal surface covered with polymer) against time

Time (seconds)
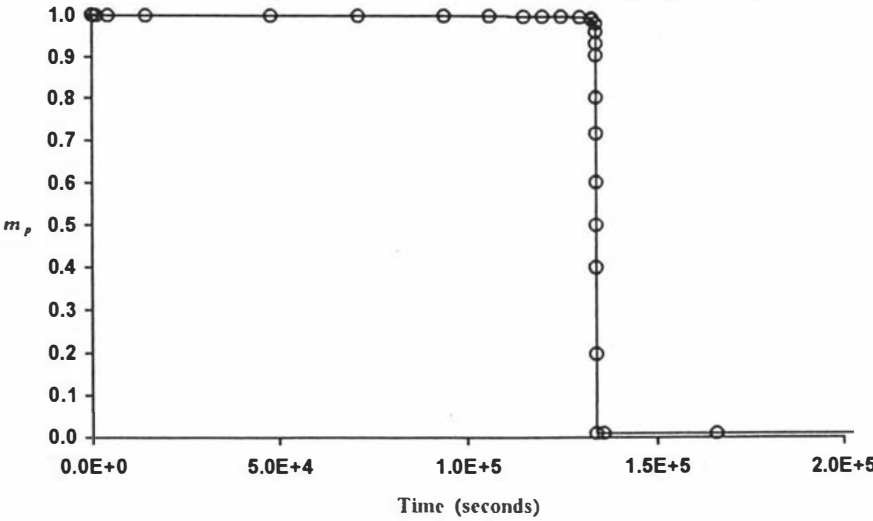
Both pairs of graphs show similar behaviour. There is the same quiescent stage up to near T_c where the polymer is gradually accumulating corrosion product as q_z increases but with m_p still near 1. Importantly there is the same sudden loss of competitive adsorption and drastic increase in the rate of corrosion as the polymer saturates with corrosion product and loses competitive adsorption onto metal active sites. We observe that m_p is held closer to unity when the term $(1-m_p)$ in equations 3.5 and 3.6 is active (*figure 10*) than when it is omitted (*figure 23*).

Figure 23
Plot of m_p (metal surface covered with polymer) against time
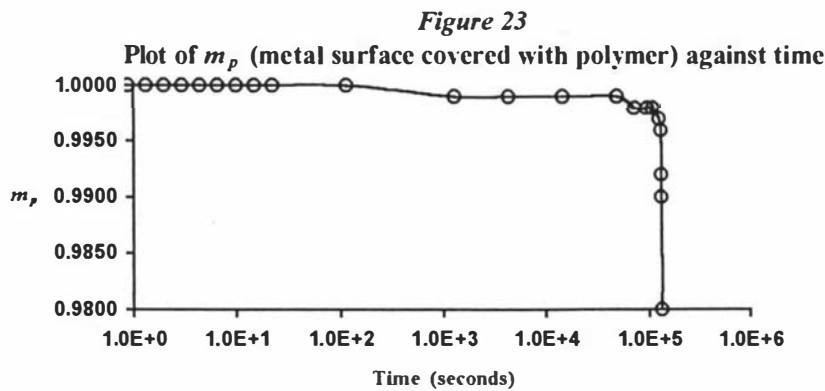
In *figure 24* we plot the corresponding information as for *figure 11*. Again it is seen that the two graphs have similar behaviour.

In comparing *figures 10* and *23* we see that the effect of the term $(1-m_p)$ in equations 3.5 and 3.6 is to constrain m_p at values closer to unity. A corollary of this is that z and q_z are constrained smaller initially than is the case for the model without the term $(1-m_p)$ in equations 3.5 and 3.6. This difference is evident when comparing *figure 24* with *figure 11*. In the full model z and q_z are smaller and rise more steeply. The main difference appears to be a more uniform increase in q_z in *figure 24* where we see q_z increases steadily from about 1×10^{-3} at about 1×10^3 seconds to about unity at 1.34×10^5 seconds. In particular the final surge in z at about 1.3×10^5 seconds ranges from 10^{-7} to saturation at unity in *figure 11*, while z ranges from about 10^{-5} to unity in *figure 24*.

Figure 24
Plot of q_w, z, q_z, and q_f against time

Time (seconds)
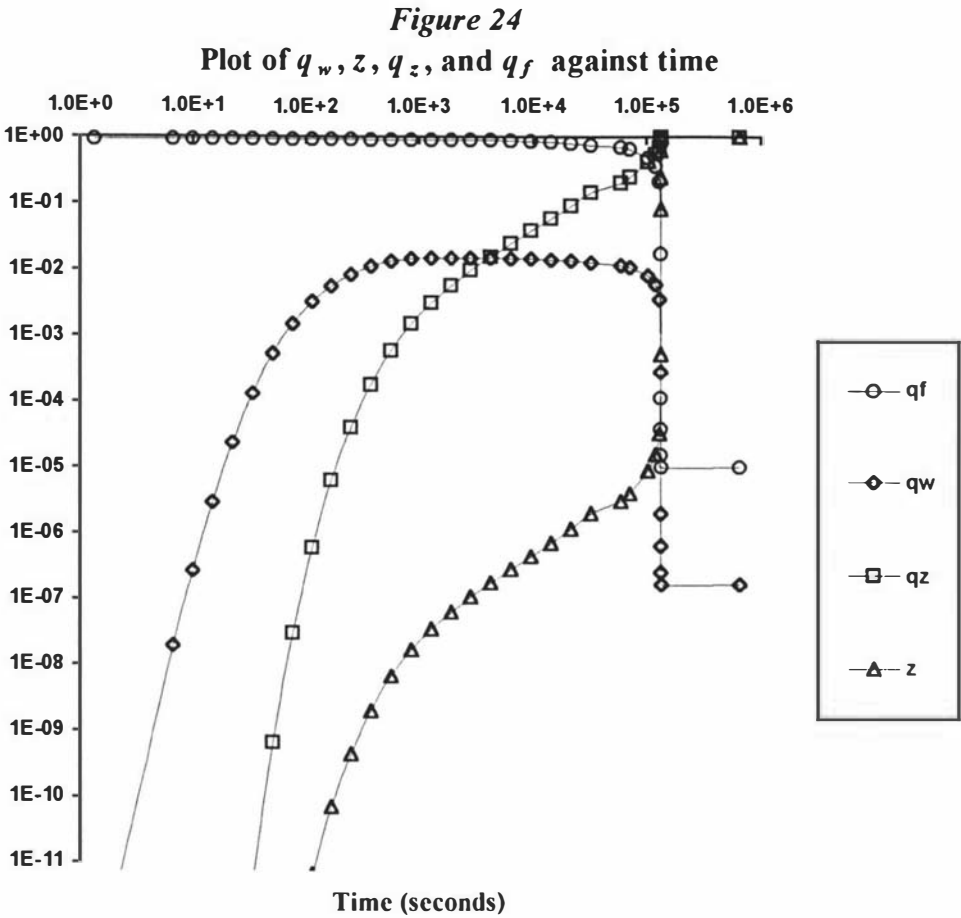
Inclusion of the term ($1-m_p$) in equations 3.5 and 3.6 is believed necessary to represent typical and high performance coatings which have moderate to very strong adsorption (i.e. adhesion) to metal substrates, and which provide effective protection against corrosion. To achieve long protective lifetimes (greater than about 10^6 seconds) with realistic values of parameters the ($1-m_p$) term is necessary. But to represent less effective coatings the simplified version appears to be realistic. Protective lifetimes up to about 10^6 are achievable with plausible variations of model parameter values.

The term $\kappa_4 z$ in equation 3.18 does not seem to result in much effect on the model's behaviour. The time to failure T_c is unaffected, and diffusion of water w, oxygen u, and zinc ions z is not significantly influenced by the term. It is possible however that for values of κ_4 somewhat larger than those estimated the term may influence diffusion of zinc ions and water.

In *figure 25* m_p, m_w, m_u, and m_f are plotted against time. The behaviour is similar to that of *figure 12*, but there are some important differences. First the increase in m_f at about 1.34×10^5 seconds is much greater at nearly three orders of magnitude than is the case in *figure 12*. We interpret this larger increase in m_f to mean that there is effectively a loss of total competitive adsorption pressure as m_p decreases to about 1×10^{-2}. For times less than $T_c = 1.34 \times 10^5$ seconds m_f is about two orders of magnitude smaller in *figure 25* compared to *figure 12*, which we interpret to mean that there is greater initial coverage of the metal surface. But after $T_c = 1.34 \times 10^5$ seconds m_f is larger by about an order of magnitude which means that the ultimate metal surface coverage must be less by a corresponding proportion.

We see that m_w and m_u rise more quickly to their plateau values at around 5×10^2 seconds compared to around 2×10^2 seconds in *figure 12*. Additionally the plateau values for m_w and m_u are larger by about an order of magnitude indicating that there is faster preliminary rate of corrosion than is the case for the full model. This is expected since if m_p is smaller and m_f is smaller there must be more of the metal surface covered with adsorbed water m_w and adsorbed oxygen m_u (by equation 3.8).

The drop in m_p at about 1.34×10^5 seconds is about two orders of magnitude to $m_p = 9.9 \times 10^{-3}$ in contrast to about five orders of magnitude to $m_p = 1.1 \times 10^{-5}$ for *figure 11*. The final surge in m_w and m_u is also smaller at about three and one order of magnitude versus four and two respectively in *figure 11*. We conclude that the omission of the term ($1 - m_p$) in equations 3.5 and 3.6 results in a version of the model with less sensitivity to the state of adsorbed polymer, and consequently less extreme effects in response to changes in m_p.

Figure 25

Plot of m_p, m_w, m_u, and m_f against time

Time (seconds)
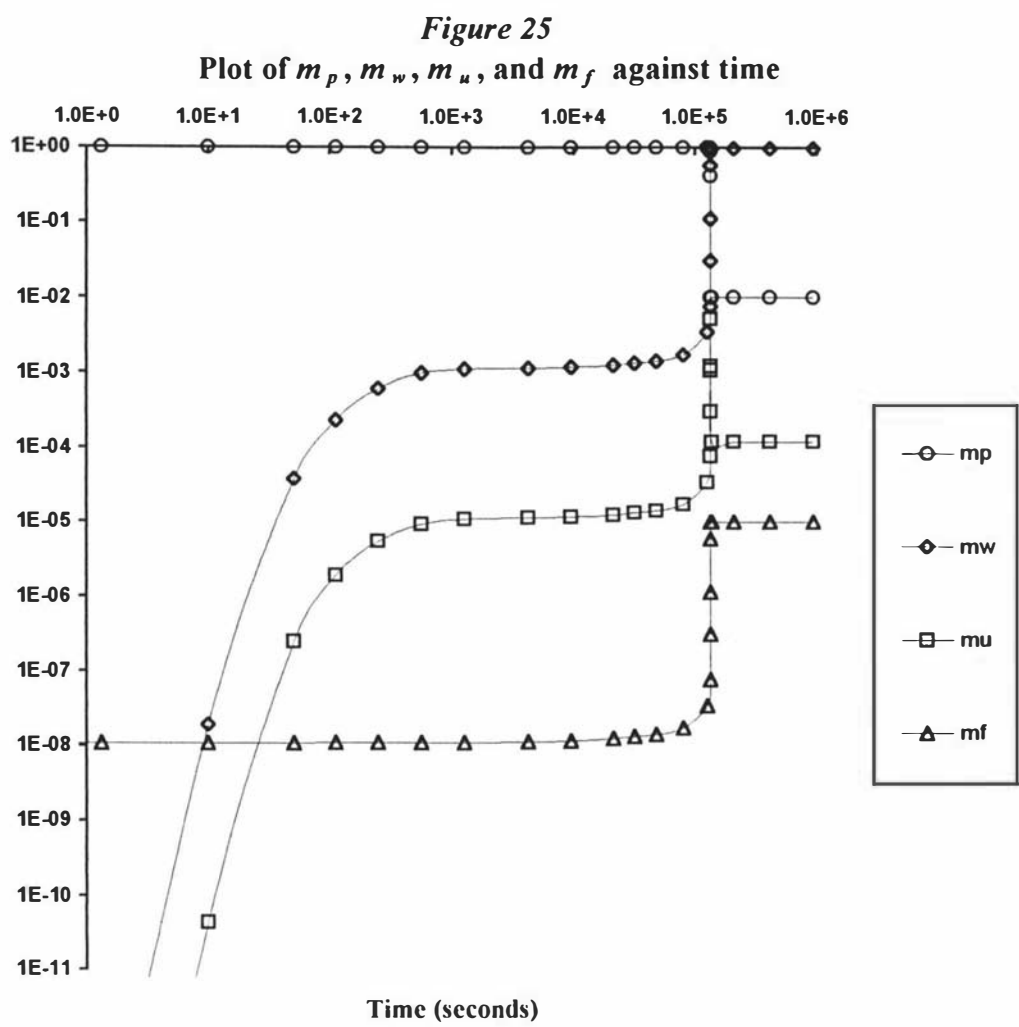
In *figure 26* we plot water w and oxygen u at $x=0$. We see that as expected this is almost identical to *figure 13*.

The boundary conditions equations 3.19 to 3.22 are also potentially simplified for certain ranges of model operation. For example equation 3.19 could be replaced by a zero gradient condition for cases where water diffusion was not rate limiting. For times up to about T_c equation 3.20 could also be replaced by a zero gradient condition with little loss of accuracy.

Figure 26
Plot of *w* and *u* at *x=0* against time

Time (seconds)
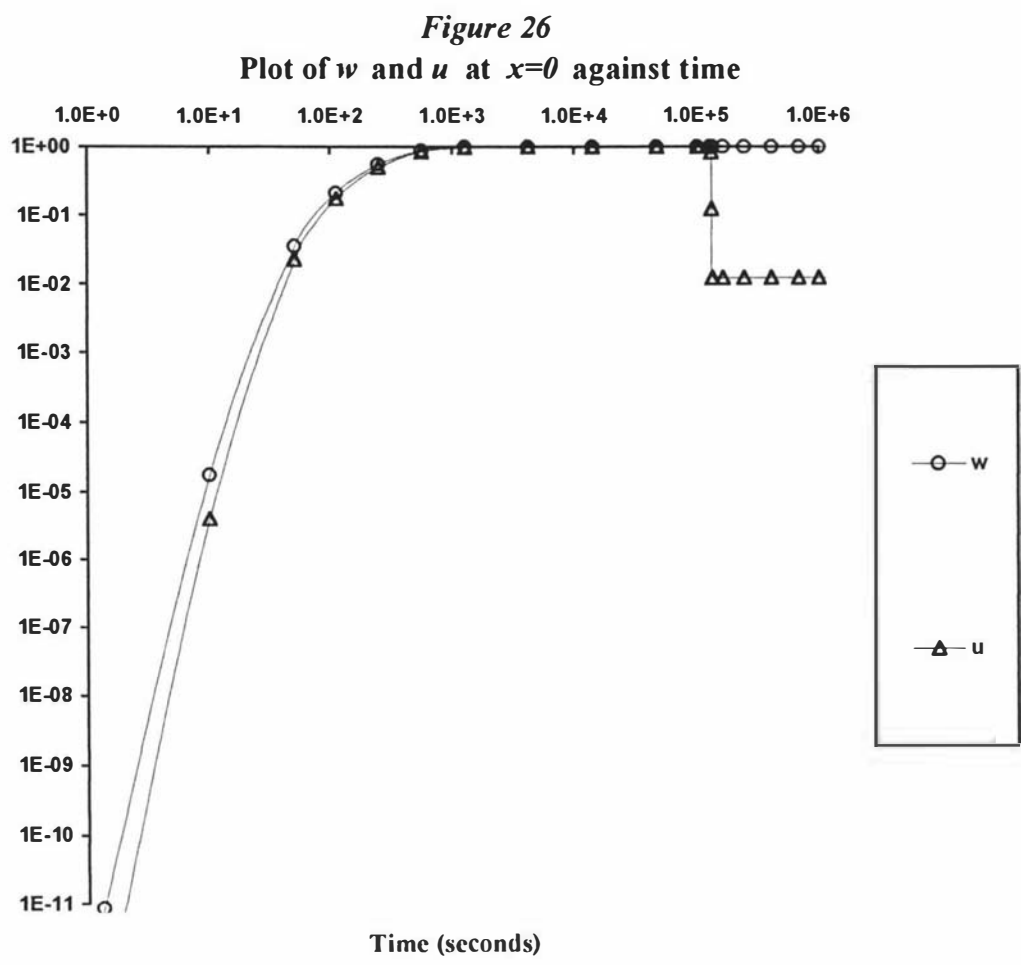
The term $\alpha_8(1-m_p)^2w^2$ in equations 3.19 to 3.22 is also found to be significant only in certain cases. When oxygen is present at $x=0$ at greater than about $0.1w$ the term $\alpha_8(1-m_p)^2w^2$ is small compared to $(1-m_p)^{3/2}u^{1/2}\,w$ and consequently is ignorable.

9 SIMPLIFIED AND REDUCED MODEL

9.1 INTRODUCTION

In chapter 8 we explored the possibility of a simplified model arising from the omission of selected terms. We found that the resulting simplified model retained some of the features present in the full model. While this version of the model may not have general applicability we suggested that it may still usefully model some paint types and situations. It is of interest to develop a reduced model for this simplified version of the model.

9.2 REDUCED SIMPLIFIED MODEL DERIVATION

First we specify environmental conditions for the reduced model. We are interested in determining the time to failure T_c of an initially dry painted metal surface when immersed continuously in oxygenated water. We ignore for now the effects of ions other than those of corrosion product from the metal itself. We also suppose the system is kept at constant temperature, and is not subject to drying nor to external electric fields. Finally we suppose that the simplified model discussed in section 8.1 is a satisfactory approximation to the full model for performances of T_c up to about 10^7 seconds (6 months immersion).

From *figure 26* we see that diffusion does not affect T_c so we assume that water and oxygen in the paint film are modelled by constant concentrations at saturation

$$u(x) = u_0 = 1 \tag{9.2.1}$$

$$w(x) = w_0 = 1 \tag{9.2.2}$$

consequently

$$p_w(x) = \alpha_6 w_0 p_f = \alpha_6 p_f \tag{9.2.3}$$

We specify that corrosion product is washed away from the paint film surface to maintain $z=0$ at $x=1$. Additionally we suppose that z is effectively zero throughout the film for times of interest. Eventually z will reach saturation at $x=0$ and there will develop a gradient of z as it diffuses out through the film; but we are here concerned about the initial state of the film where there is negligible corrosion product (see for example *figure 24*).

$$z(x) = z_0 = 0 \tag{9.2.4}$$

and consequently

$$p_z(x) = \alpha_7 z p_f = 0 \tag{9.2.5}$$

Since w, u, and z are constant we suppose that the boundary conditions 3.19 to 3.22 are approximated by zero gradient conditions:

$$\left.\frac{\partial w}{\partial x}\right|_{x=0} = 0, \quad \left.\frac{\partial u}{\partial x}\right|_{x=0} = 0, \quad \left.\frac{\partial z}{\partial x}\right|_{x=0} = 0 \tag{9.2.6}$$

Next we examine equations 3.9, 3.10, 3.7, 3.5, 3.6, and dz/dt to deduce which equation produces the greatest effect and hence is potentially a 'governing equation'. We plot in *figure 27* the derivatives dq_z/dt, dq_w/dt, dm_p/dt, dm_w/dt, dm_u/dt, and dz/dt against time for the same case discussed previously in section 8.1. For times T_c in the region of interest we find that typically dq_z/dt is larger than the other derivatives.

Figure 27
Plot of dq_z/dt, $-dq_w/dt$, $-dm_p/dt$, dm_w/dt, dm_u/dt, and dz/dt
against time
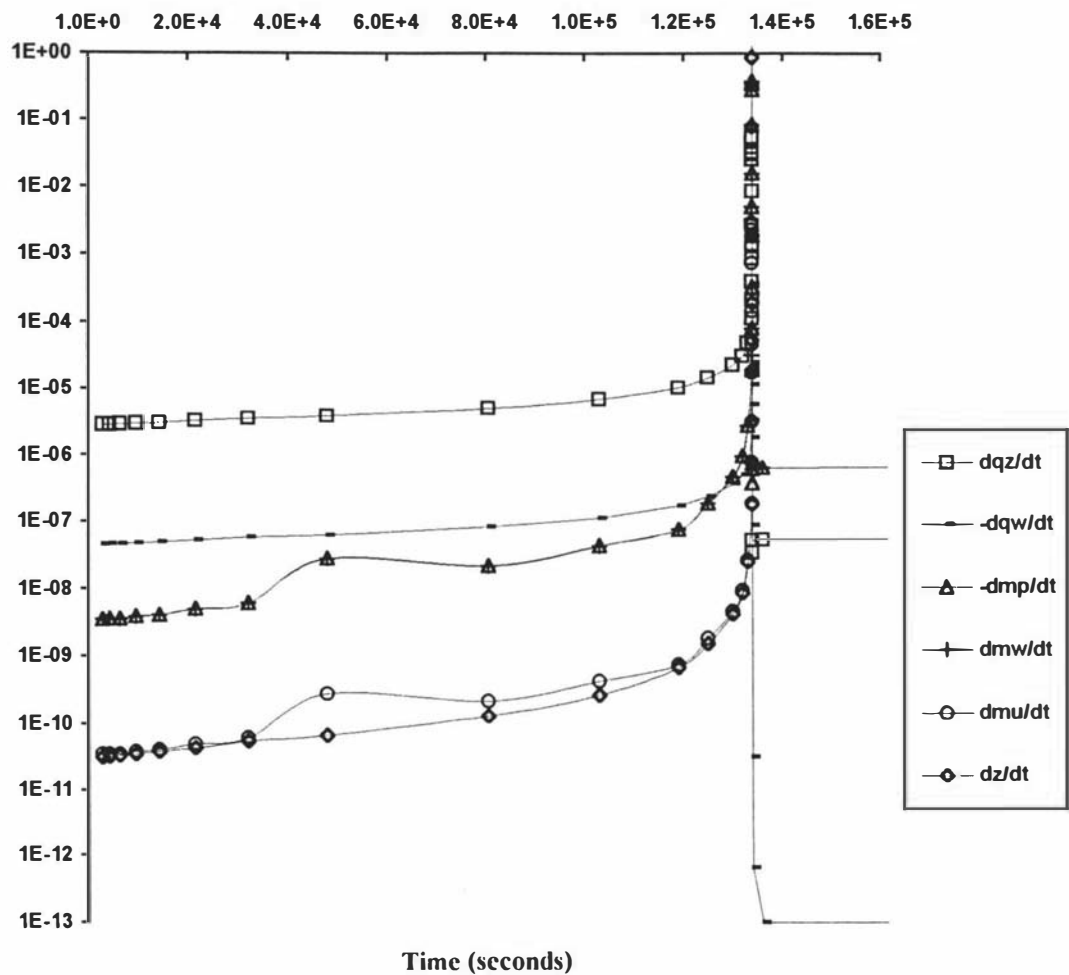
Next we plot in figure 28 the derivative dq_z/dt along with the two terms $\theta_4\alpha_4 z q_f$ (term 1) and $\theta_4 q_z$ (term 2) in eq 9.2.7 against time. We find that the terms $\theta_4\alpha_4 z q_f$ and $\theta_4 q_z$ are typically much larger than the derivative. Typically $\theta_4\alpha_4 z q_f$ and $\theta_4 q_z$ are the same value to about the third digit for the chosen parameter values, which contrasts with the case for the full model (*figure 15*) where the terms correspond to about the sixth digit.

Figure 28
Plot of dq_z/dt, term 1, and term 2 against time

Time (seconds)
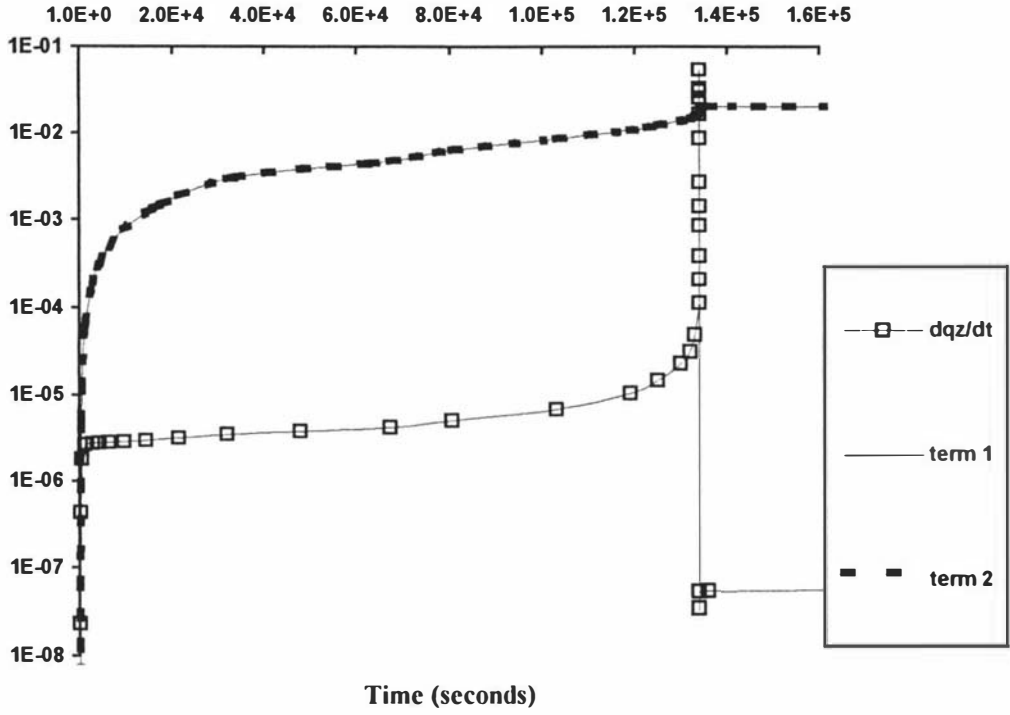
From equation 3.9 we have

$$\frac{dq_z}{d\tau} = \theta_4\left(\alpha_4 z q_f - q_z\right) \tag{9.2.7}$$

and we suppose that

$$\frac{dq_z}{d\tau} = \varepsilon\left(q_z\right) \tag{9.2.8}$$

where $\varepsilon(q_z)$ is some function of q_z. We have found that generally $\alpha_4 z q_f$ and q_z are equivalent to about the third significant figure so we write:

$$\alpha_4 z q_f = q_z + \varepsilon\left(q_z\right) \tag{9.2.9}$$

and look for an expression for $\varepsilon(q_z)$ in equation 3.21.

Equations 3.5, 3.6, 3.7, and 3.10 are written as

$$m_w = \alpha_1 w_0 m_f = \alpha_1 m_f \tag{9.2.10}$$

$$m_u = \alpha_2 u_0 m_f = \alpha_2 m_f \tag{9.2.11}$$

$$m_p = \alpha_3 q_f m_f \tag{9.2.12}$$

$$q_w = \alpha_5 w_0 q_f = \alpha_5 q_f \tag{9.2.13}$$

In eq 3.21 we find that generally, for this particular case of interest,

$$\frac{dz}{d\tau} \ll \kappa_5 \frac{dq_z}{d\tau} \tag{9.2.14}$$

and

$$\alpha_8 \left(1 - m_p\right)^2 w_0^2 \ll \left(1 - m_p\right)^{3/2} w_0 u_0^{1/2} \tag{9.2.15}$$

and we suppose that

$$-\phi_3 \left(\frac{dz}{d\tau} + \kappa_5 \frac{dq_z}{d\tau}\right) + \phi_4 \kappa_6 \left[\left(1 - m_p\right)^{3/2} w_0 u_0^{1/2} + \alpha_8 \left(1 - m_p\right)^2 w_0^2\right] = 0 \tag{9.2.16}$$

So that we can write

$$\frac{dq_z}{d\tau} = \frac{\phi_4 \kappa_6}{\phi_3 \kappa_5} \left(1 - m_p\right)^{3/2} w_0 u_0^{1/2} \tag{9.2.17}$$

Substituting from eq 9.2.12

$$\frac{dq_z}{d\tau} = \frac{\phi_4 \kappa_6}{\phi_3 \kappa_5} \left(1 - \alpha_3 q_f m_f\right)^{3/2} w_0 u_0^{1/2} \tag{9.2.18}$$

From eq 3.11 and 3.7 we find

$$q_m = \kappa_3 m_p = \alpha_3 \kappa_3 m_f q_f \tag{9.2.19}$$

Using eq 3.12 we get

$$\left(\alpha_5 + \alpha_3 \kappa_3 m_f + 1\right) q_f + q_z = 1 \tag{9.2.20}$$

and from eq 3.8

$$m_f = \frac{1}{1+\alpha_1+\alpha_2+\alpha_3 q_f}$$

(9.2.21)

From eq 9.2.20 and eq 9.2.21 we get

$$\alpha_3(1+\alpha_5)q_f^2 - \left[\alpha_3(1-\kappa_3-q_z)-(1+\alpha_5)(1+\alpha_1+\alpha_2)\right]q_f - (1+\alpha_1+\alpha_2)(1-q_z) = 0$$

(9.2.22)

and write

$$q_f = \frac{\alpha_3(1-\kappa_3-q_z)-(1+\alpha_5)(1+\alpha_1+\alpha_2)}{\alpha_3(1+\alpha_5)}\left[1+\frac{\alpha_3(1+\alpha_5)(1+\alpha_1+\alpha_2)(1-q_z)}{\left(\alpha_3(1-\kappa_3-q_z)-(1+\alpha_5)(1+\alpha_1+\alpha_2)\right)^2}+\cdots\right]$$

(9.2.23)

where to a first approximation

$$q_f = \frac{\alpha_3(1-\kappa_3-q_z)-(1+\alpha_5)(1+\alpha_1+\alpha_2)}{\alpha_3(1+\alpha_5)}$$

(9.2.24)

and

$$m_f = \frac{1+\alpha_5}{\alpha_3(1-\kappa_3-q_z)}$$

(9.2.25)

The approximation used in eq 9.2.24 should be accurate for

$$\frac{\alpha_3(1+\alpha_5)(1+\alpha_1+\alpha_2)}{\left(\alpha_3(1-\kappa_3)-(1+\alpha_5)(1+\alpha_1+\alpha_2)\right)^2} \ll 1$$

(9.2.26)

For the parameter values used here the expression evaluates to 1.2×10^{-3}.

Substituting eq 9.2.24 and 9.2.25 into eq 9.2.18 we arrive at a reduced model consisting of a single ODE eq 9.2.27, together with the algebraic equations described above:

$$\frac{dq_z}{d\tau} = \frac{\phi_4 \kappa_6}{\phi_3 \kappa_5} \left(\frac{(1+\alpha_5)(1+\alpha_1+\alpha_2)}{\alpha_3} \right)^{3/2} \frac{1}{(1-\kappa_3 - q_z)^{3/2}} \qquad (9.2.27)$$

We compare the reduced model variables q_f and m_f against numeric results in *figures 29* and *30*. The correspondence is quite good considering the various assumptions made.

Figure 29
Reduced model q_f (equation 9.2.24), numeric q_f and q_z plotted against time

Time (seconds)
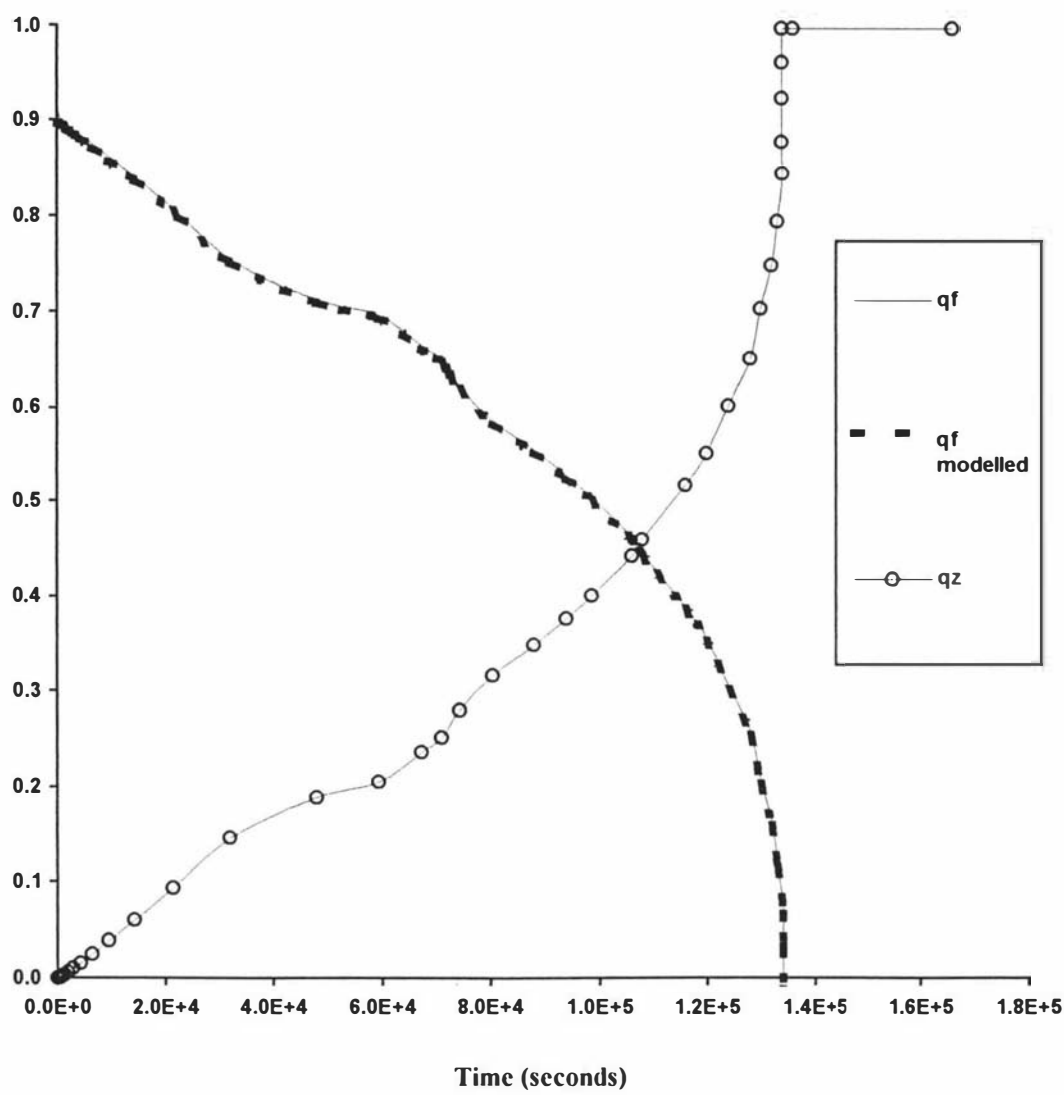
Figure 30
Reduced model m_f (equation 9.2.25) and numeric m_f plotted against time.
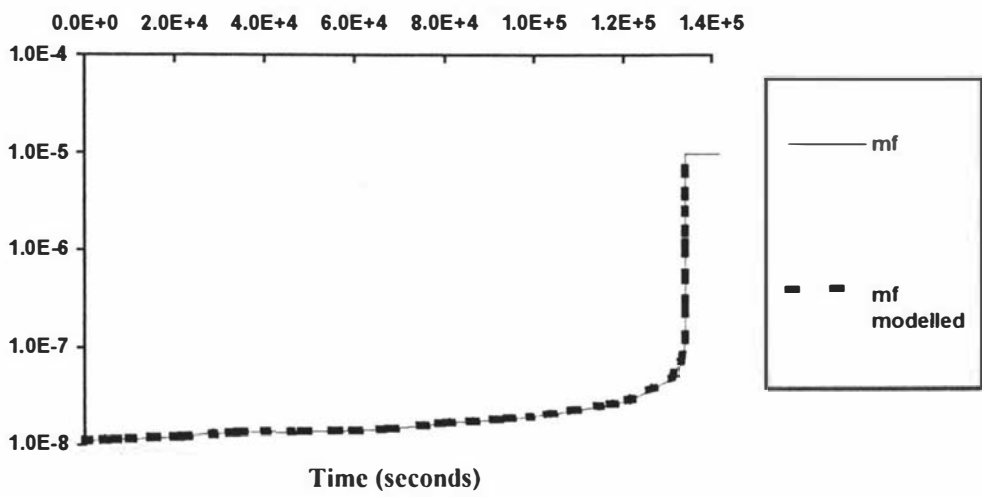
In *figure 31* we plot the reduced model dq_z/dt as a function of q_z against time and compare results to numeric calculations.

Figure 31
Reduced model dq_z/dt (equation 9.2.27) and numeric dq_z/dt plotted against time.
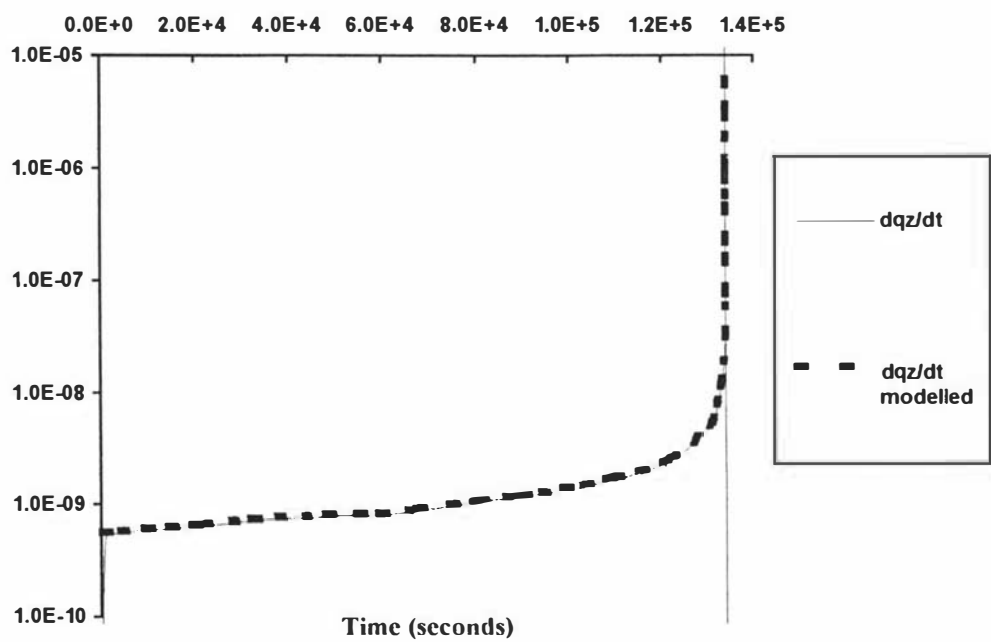
Again the correspondence is quite close. However we want to solve eq 9.2.27 in order to find q_z as a function of time. Equation 9.2.27 is readily solved and we obtain:

$$q_z = 1 - \kappa_3 - \left\{ \left(1-\kappa_3\right)^{5/2} - \frac{5\phi_4\kappa_6}{2\phi_3\kappa_5} \left[\frac{\left(1+\alpha_5\right)\left(1+\alpha_1+\alpha_2\right)}{\alpha_3} \right]^{3/2} \tau \right\}^{2/5}$$ (9.2.28)

next we get an expression (eq 9.2.29) for T_c the effective protective lifetime of the metal coating.

$$T_c = \frac{2l^2\phi_3\kappa_5}{5D_w\phi_4\kappa_6} \left[\frac{\alpha_3}{\left(1+\alpha_5\right)\left(1+\alpha_1+\alpha_2\right)} \right]^{3/2} \left(1-\kappa_3\right)^{5/2} \quad \text{seconds}$$ (9.2.29)

To compare the reduced model with numeric results we plot q_z as a function of t in *figure 32* for the reduced and numeric version of the model and compare the resultant estimates for T_c. We find from numeric calculation $T_c = 1.34 \times 10^5$ and from the reduced model $T_c = 1.28 \times 10^5$ so that the reduced model estimates T_c to 96% of the numeric value of the full model (with simplification of omission of the term $(1-m_p)$ in eq 3.5 and 3.6 plus omission of the term $\kappa_3 m_p$ in eq 3.11).

We observe that T_c depends most strongly upon α_3, α_1 and κ_3. We found in *figure 19* that increasing α_3 does increase T_c although not with the same sensitivity as in the full model (*figure 7*). Physically increasing α_3 and decreasing α_1 corresponds to increasing the competitive adsorption of polymer relative to that of water. Keeping κ_3 small also increases T_c which corresponds physically to making the proportion of available polymer functional groups large relative to the number of metal active sites on the substrate surface. We have estimated relatively smaller values for α_2 and α_5 (table 1) and consequently these parameters do not much influence T_c. However from inspection of eq 9.2.29 we see that these parameters should be made small to ensure large T_c.

Additionally we see that T_c is dependent upon the parameters

$$\frac{\phi_3 \kappa_5 l^2}{\phi_4 \kappa_6 D_w} = \frac{\mathcal{P}_0}{\rho_1 U_0^{1/2} W_0}$$. Increasing $\mathcal{P}_0$ (the total surface concentration of free

polymer functional groups) will directly increase T_c. Reducing the parameters ρ_1, U_0, and W_0 will similarly increase T_c, where T_c depends upon $U_0^{-1/2}$ and linearly upon the other parameters.

Figure 32
**Reduced model q_z (equation 9.2.28) and numeric q_z
plotted against time.**

Time (seconds)
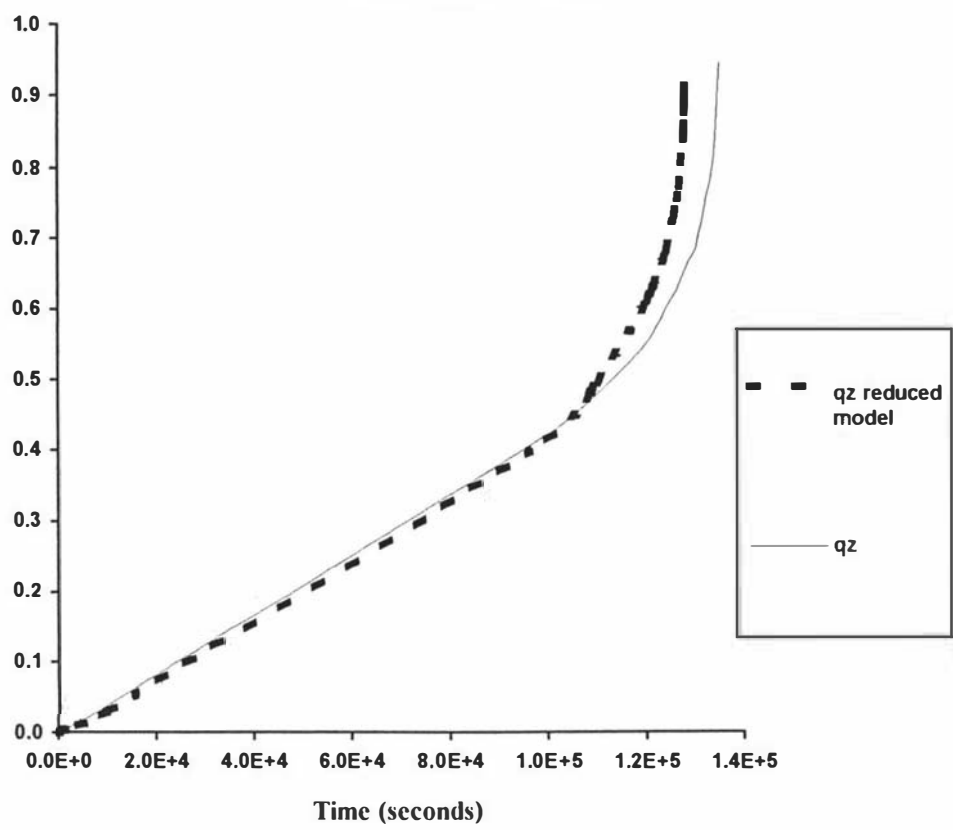
10 MODEL VARIATIONS

10.1 INTRODUCTION

Inevitably in a project such as ours decisions and choices must be made along the way. Various elements of the model may have been formulated in many ways. While we always worked to maintain consistency with the many physical and chemical issues involved it was by no means clear what the relevant issues were at the time. For every element there was always some justification; but gradually, as the project evolved, some larger issues and unifying concepts emerged. These considerations have been used to refine the model and have influenced its final form.

One issue in particular that we have dwelled on, and which has strongly coloured our development of the model, has been the physics of the adsorbed layer. We concluded at an early stage that this area must critically control the behaviour of a painted metal surface. While there is still some confusion and contradiction in the literature, a trend is developing toward exploration of the adsorbed layer. Diffusive resistance may play some role in corrosion protection, especially where transients and periodic wetting are involved. But we note that few researchers in the last decade seem to be actively pursuing diffusion as the rate controlling process.

Some concepts such as adhesion are still only poorly understood. There are many theories and concepts as to how adhesion of polymeric materials to macroscopic surfaces arises. There is also significant disagreement; and as with corrosion protection by paint films, many researchers have demonstrated that one theory is correct while another fails. A number of the elements of understanding are established. For example adsorption isotherms of many substances on to various other substances have been studied. There are various reasonably accurate models of adsorption of molecules onto solid substrates. For example adsorption of gases

on to metals is reasonably well documented and even relatively simple models can produce credible agreement with experiment. But adsorption of polymeric materials is not yet well understood. Multiple component adsorption of polymers and various molecules in a competitive situation does not seem to be very well known.

Corrosion chemistry of metal surfaces has received much attention over the years. Many researchers have made fundamental contributions toward better understanding of the processes involved. In certain situations the chemistry is fairly well defined. For example corrosion rates in solution can be accurately determined based on electrode potentials and electrochemical currents. These concepts can be applied to microscopic scales and used to model corrosion of pits and crevices on metal surfaces. Diffusion of reactants, such as oxygen, from the bulk solution to the reaction site are also found to be important factors.

Increasingly, it seems, researchers are combining elements of electrochemical potential theory with competitive adsorption of molecules. Tang and Song (1993) used this approach and found quantitative agreement with experiment. Surely this is a fruitful direction for further research. The principles of adsorption of molecules onto surfaces in gases and liquids are understood well enough to allow accurate modelling of adsorbed surface concentrations. Using these modelled surface coverages it has proven possible to calculate modifications to corrosion currents and potentials. When diffusion of reactants is included rather sophisticated models are possible.

While these approaches are effective in modelling corrosion in solution, it was not clear how they could be applied (nor even if they were valid) to the case of adherent paint films on metals. In particular we have based our thesis on the premise that initially the metal substrate is effectively dry, while the polymeric paint film remains adherent. Electrochemical currents in these circumstances seemed difficult to reconcile.

Adherent paint films may consist of microscopic adhesion defects. Our notion of active sites may correspond to these defects. When water from the external environment is available it is reasonable to expect that molecules of water will accumulate at these defect sites. Conceivable this may be the basis for the "real" process of corrosion under paint films.

Instead we have followed a more macroscopic approach. Rather than modelling the active sites themselves (as microscopic corrosion pits) we consider that they would in aggregate produce some quantifiable corrosion flux in response to available water and oxygen. Consequently we focus on quantifying the concentrations of reactants available for corrosion, and on modelling the adsorption of polymer in competition with other species. In essence we assume that an exposed active site will corrode at some maximal rate in response to available reactants (water and oxygen). We suppose that a bare metal surface will give a measure of this maximal rate for the aggregate of active sites.

We adapt chemical kinetics to produce an expression relating the rate of reaction to the available concentrations of reactants. The rate constants are obtained from experiment based on corrosion rates at various concentrations of reactants. We choose this formulation as it provides a useful means of determining the boundary conditions for the diffusion equations with which we use to model the bulk paint film.

With this quick review of some of the choices and considerations made in formulating the model we now consider some of the "what ifs". What if we model corrosion as occurring in microscopic corrosion pits? Would the inclusion of an intermediate boundary layer between the adsorbed layer and the bulk paint film help to quantify concentrations of water and oxygen in the adsorbed layer? How can the effect of the physical characteristics of the paint film be accounted for?

10.2 ACTIVE SITES AS CORROSION PITS

For this variation we imagine that a diffusion subsystem would be required. The paint film and adsorbed layer as conceived may be satisfactory. But we suppose that each exposed active site accumulates water and proceeds to corrode at a rate limited by diffusion of oxygen and water in a hemispherical region about the active site. We suppose that corrosion of the active site is in fact rate limited by diffusion of reactants from the surrounding medium (the wet paint film).

Figure 33
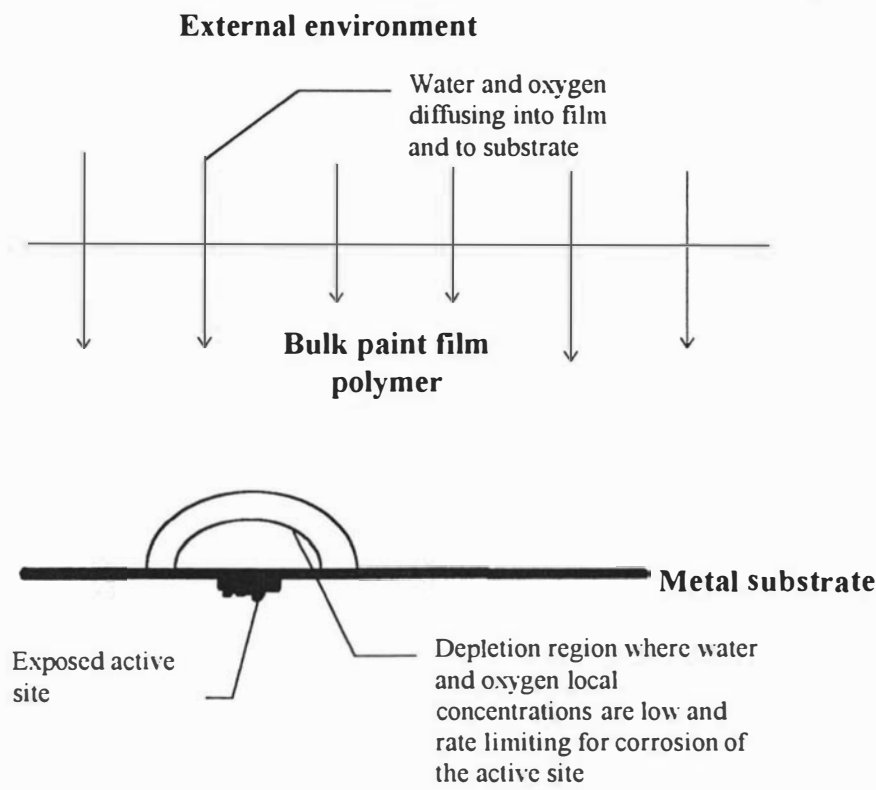
We depict this concept graphically in *figure 33*. Nguyen et al. (1991) have in fact considered something of this type of system, though without the attempt to include corrosion reaction chemistry. It is possible to include the effects of blister formation and swelling of the paint film. With this comes the possibility of

including in the modelling the paint films mechanical properties and their response to the effect of osmotic pressure.

With the formation of electrolyte blisters on active sites one could properly employ the principles of electrochemical potential theory. The rates of corrosion predicted should then have good quantitative agreement with experiment. Additionally one could include other reacting species such as hydroxyl and hydrogen ions.

In some cases this is probably closer to reality than is the model we have constructed. Blister formation on a macroscopic scale often does precede the final stages of paint film breakdown. One could reason that these macroscopic blisters grow from the microscopic defects surrounding corroding active sites. While this may be a better and more versatile model it is also significantly more complex. We theorise that the essential features of corrosion of painted metal surfaces can be embodied in the simpler formulation we choose to use.

10.3 INTERMEDIATE BOUNDARY LAYER

In this variation we consider an alternative route to determine the actual concentrations of reactants available to the corrosion reaction on the metal surface. The aim is to model the concentrations of species so that the activities arise as a dynamical equilibrium. Suppose that the adsorbed layer is subject to bidirectional adsorption processes. The first sorption process is already described by the competitive adsorption model. The second arises by considering that the adsorbed layer itself may further adsorb water and oxygen from the bulk paint film medium it is in contact with. Thus we consider concentrations W and U in the bulk paint film at $x=0$, and quantities W^{**} and U^{**} in the adsorbed layer. The concentrations W^{**} and U^{**} would then be used in the corrosion model.

We wish to include the effect of a variable adsorbed layer. We shall suppose that water and oxygen uptake occurs in molecular void spaces which result from imperfections in polymer packing. When the polymer is densely packed we assume the void volume fraction is at a minimum. While for desorbed polymer we suppose the void volume fraction is at a maximum. Models of polymer void volume fraction are described in the literature (for example Venditti et al., 1995), and Dzugutov, 1996, has described a universal scaling law applicable to atomic diffusion in condensed matter.

It is unclear how polymer packing, and hence void fraction, varies with adsorption. Experimental results demonstrating the effect are certainly convincing, but proven models are not yet well known. One approach to this obstacle is to try and adapt existing models of void fraction to include a response to the state of adsorption. Another approach is to suppose that the void fraction is proportional to the fraction of metal surface uncovered by adsorbed polymer. The former prescription is probably closer to reality, but we shall use the latter basis to develop our concept. The idea is shown graphically in *figure 34*.

Figure 34

External environment

Bulk polymer

Adsorbed layer - bulk polymer interface

Adsorbed layer - metal interface

Metal substrate
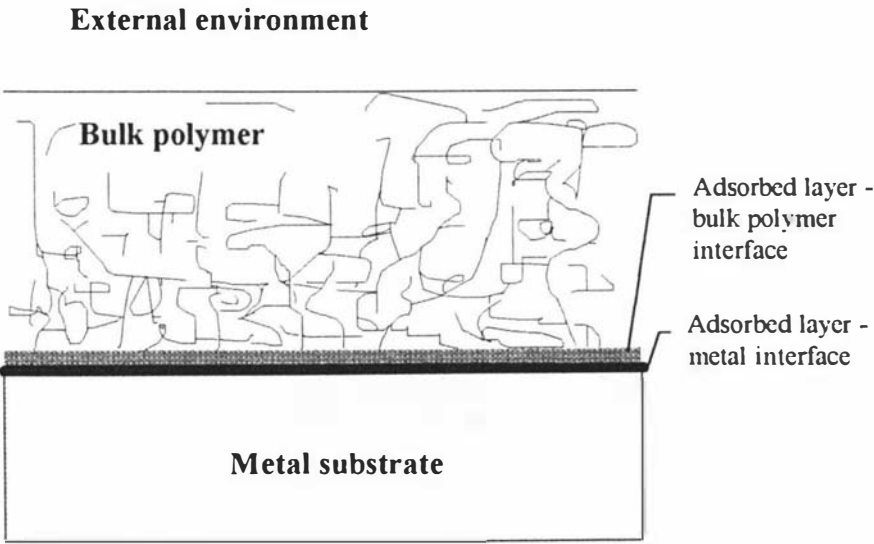
We suppose that uptake and release of water and oxygen by the adsorbed layer are governed by expressions analogous to those used to describe adsorption onto the metal surface. The assumptions conform to the prescription for Langmuir adsorption isotherms. We write

$$\frac{dW^{**}}{dt} = s_1 W F_f - s_2 W^{**} \tag{10.3.1}$$

$$\frac{dU^{**}}{dt} = s_3 U F_f - s_4 U^{**} \tag{10.3.2}$$

and

$$W^{**} + U^{**} + F_f = f(F_0) \tag{10.3.3}$$

where we suppose F_0 represents the maximum void density fraction, and $f(F_0)$ is some function that represents variation in void fraction with the state of polymer adsorption. The constants s_1 and s_3 are rates of adsorption while s_2 and s_4 are rates of desorption from the adsorbed layer. The variables W^{**}, W, U^{**}, and U have the same meaning as described previously. The variable F_f represents the fraction of void space remaining free.

We shall suppose that

$$f(F_0) = F_0 \left(\frac{M_0 - M_p}{M_0} \right) \tag{10.3.4}$$

where M_0 is the total metal surface density of available adsorption sites, and M_p is the density of sites attached to adsorbed polymer. We find that

$$W^{**} = \frac{s_1}{s_2} \frac{WF_0\left(\dfrac{M_0 - M_p}{M_0}\right)}{1 + \dfrac{s_1}{s_2}W + \dfrac{s_3}{s_4}U} \qquad (10.3.5)$$

$$U^{**} = \frac{s_3}{s_4} \frac{UF_0\left(\dfrac{M_0 - M_p}{M_0}\right)}{1 + \dfrac{s_1}{s_2}W + \dfrac{s_3}{s_4}U} \qquad (10.3.6)$$

where we assume quasi-equilibrium between the bulk paint film and the adsorbed layer. We find that these expressions are variations (possibly more realistic) of those presented in eq 2.3.18 and 2.3.19.

In principle this variation provides a better physical basis for the model. If we developed the concept in terms of molecular physics, and derived void fraction functions from basic principles, we should obtain expressions for eq 10.3.5 and 10.3.6 which would depend upon basic physical and mechanical properties of the paint film. Even if this approach should not much improve the overall accuracy, it is of immense value to relate performance to the physical and mechanical properties of the polymer and the paint film composition.

10.4 VARIATION IN CORROSION FLUX FORMULATION

We have previously adapted basic chemical dynamics to produce an expression relating the corrosion flux to the concentrations of reactants. If we followed the variation in section 10.2 we might use electrochemical potential theory to calculate corrosion flux from concentrations of available reactants.

Alternatively we might attempt a basic atomic model of the corrosion process. If we included species such as hydroxyl and hydrogen ions we could then construct a variation of the model in which hydroxyl ions for example collided with zinc atoms to produce corrosion product on an atomic level. Some dynamic system to account for quasi - equilibrium between water, oxygen, hydroxyl, and hydrogen would have to be devised. We touched on this concept in section 2.3: possibly the formulation could be expanded to include additional reacting species. In particular we could remove the assumption of a pH buffering effect and allow the pH to vary in response to the dynamical corrosion process.

As we theorised previously the probable mode of attack of the metal substrate is through exposed active sites with surface density M_f. We suppose that hydroxyl ions in the adsorbed layer have some probability of colliding with an active site (based on the density M_f) which depends upon a potential energy barrier to reaction and the estimated kinetic energy distribution of the hydroxyl ions. The hydroxyl ion concentration would also be a factor in the reaction rate. Additionally we must consider the process responsible for the creation of hydroxyl ions. Clearly the concentrations of water and oxygen are important, and conceivably these may be rate limiting when their concentrations are limited as will be the case in a strongly adherent paint film.

One difficulty with this variation, which we must overcome, is the relation of atomic collision rates with experimental corrosion rates. We have already stretched ideal gas dynamics probably beyond valid limits in the current formulation. We might further extend the notions developed previously to apply also to corrosion processes. Presumably the reaction of a hydroxyl ion with a zinc atom is effectively instantaneous. We might suppose also that the resultant intermediate species $(Zn(OH)^+)$ was ejected immediately from the atomic matrix of the metal surface.

In this fashion we would arrive at a formulation of the corrosion process based on atomic principles. Presumably the corrosion flux expression (eq 2.3.13) would

depend linearly upon the concentration of hydroxyl ions and the surface exposed to attack M_f and so

$$f_z = \rho M_f [OH^-] \qquad\qquad (10.4.1)$$

However we must still determine the concentrations of water and oxygen present in the adsorbed layer in order to determine the hydroxyl ion concentration. Additionally we must also account for the changes which occur in the adsorbed layer as it degrades and loses crystallinity through loss of adhesion.

Again this variation is probably closer to reality than is the formulation we have developed. If correct it should produce better quantitative agreement with experiment. It does however require more parameters and more complexity to account for the new species and their interactions with water, oxygen, and zinc. We chose our original formulation in the belief that supply of water and oxygen was limiting on the atomic scale. We supposed that hydroxyl ions created above some equilibrium concentration would react promptly with zinc atoms.

10.5 VARIATION IN CORROSION AND ADSORPTION FORMULATION

In this variation we consider a different formulation of the adsorbed layer and develop an alternative formulation for the corrosion flux. We begin by considering the adsorbed layer to be: very thin, not very dense or crystalline, and to not change very much during the evolution of the system. This concept differs significantly from our original formulation. In the process of developing this idea we will find some additional concepts which may usefully be incorporated into a second generation of the model.

This alternative formulation of the adsorbed layer results in several conclusions. First the concentrations of water and oxygen ($W(x=0,t)$ and $U(x=0,t)$) in the bulk polymer at x=0 must be the effective concentrations for the corrosion reaction. If the layer is thin and not very dense the mean free path for water and oxygen molecules will be sufficiently long so that there is only small probability of diffusing molecules colliding with polymer in the adsorbed layer. Instead molecules in the bulk paint film at x=0 moving perpendicular to the metal surface will often pass straight through the layer and collide directly with the metal surface. If the adsorbed layer does not change very much as corrosion proceeds and the layer loses adsorption to the metal then the activity coefficients for water and oxygen must be approximately constant, or at least have a weaker dependence upon M_p than we estimated previously.

Then eq 2.3.18 becomes

$$[H_2O] = \frac{\gamma_w}{\gamma_w^{**}} W(x=0,t) = \gamma_w{}' W(x=0,t) \tag{10.5.1}$$

where $\gamma_w{}'$ is approximately constant and approximately equal to unity. Similarly eq 2.3.19 becomes

$$[O_2] = \frac{\gamma_u}{\gamma_u^{**}} U(x=0,t) = \gamma_u{}' U(x=0,t) \tag{10.5.2}$$

where again $\gamma_u{}'$ is approximately constant and approximately equal to unity. We shall suppose that in fact $\gamma_w{}'$ and $\gamma_u{}'$ are identically equal to unity.

In this variation of the model formulation we suppose that the corrosion flux is linearly proportional to the availability of exposed active sites M_f. We write eq 10.5.3 instead of eq 2.3.20 for the corrosion flux

$$f_z = \frac{M_f}{M_{f\infty}} \left\{ 9.6 \times 10^{-11} W(x=0,t) U^{1/2}(x=0,t) + 5.4 \times 10^{-17} W^2(x=0,t) \right\} \tag{10.5.3}$$

where $M_{f\infty}=M_f(t\to\infty)$. In dimensionless form equations 3.19, 3.20, 3.21, and 3.22 become

$x = 0, \ \tau > 0$
$$\left.\frac{\partial w}{\partial x}\right|_{x=0} = \frac{\phi_1 m_f}{m_{f\infty}}\left[wu^{1/2}+2\alpha_8 w^2\right]$$
(10.5.4)

$$\left.\frac{\partial u}{\partial x}\right|_{x=0} = \frac{\phi_2 m_f}{m_{f\infty}}wu^{1/2}$$
(10.5.5)

for $z < w, \ z_c = 0$

$$-\left.\frac{\partial z}{\partial x}\right|_{x=0} = -\phi_3\left(\frac{dz}{d\tau}+\kappa_5\frac{dq_z}{d\tau}\right)+\frac{\phi_4\kappa_6 m_f}{m_{f\infty}}\left[wu^{1/2}+\alpha_8 w^2\right]$$
(10.5.6)

for $z = w, \ z_c \geq 0$

$$-\left.\frac{\partial z}{\partial x}\right|_{x=0} = -\phi_5\left(\frac{dz_c}{d\tau}+\kappa_7\frac{dq_z}{d\tau}\right)+\frac{\phi_4\kappa_6 m_f}{m_{f\infty}}\left[wu^{1/2}+\alpha_8 w^2\right]$$
(10.5.7)

In eq 2.4.2 we suppose again that $\dfrac{\gamma_w}{\gamma_{w}^{**}} = 1$ so that eq 2.4.5 becomes

$$\frac{dm_w}{d\tau} = \theta_1\left[\alpha_1 wm_f - m_w\right]$$
(10.5.8)

Similarly eq 2.4.7 becomes

$$\frac{dm_u}{d\tau} = \theta_2\left[\alpha_2 um_f - m_u\right]$$
(10.5.9)

We notice that this case is similar to that discussed in chapters 8 and 9. We suppose that an equivalent treatment is valid and adapt the derivation used in section 9.2 to find another reduced model. From eq 10.5.6 we find

$$\frac{dq_z}{d\tau} = \frac{\phi_4\kappa_6 m_f}{\phi_3\kappa_5 m_{f\infty}}w_0 u_0^{1/2}$$
(10.5.10)

and using the same manipulations employed in section 9.2 we obtain

$$m_f = \frac{1+\alpha_5}{\alpha_3\left(1-\kappa_3-q_z\right)}$$
(10.5.11)

Substituting this into eq 10.5.10 we find

$$\frac{dq_z}{d\tau} = \frac{\phi_4\kappa_6\left(1+\alpha_1+\alpha_2\right)\left(1+\alpha_5\right)}{\phi_3\kappa_5\left(1-\kappa_3-q_z\right)}$$

(10.5.12)

where we have used the result of eq 5.7.4, with an assumption that m_p goes to zero as polymer adsorption to metal fails beyond T_c, to determine $m_{f\infty}$.

$$m_{f\infty} = \frac{1}{1+\alpha_1+\alpha_2}$$

(10.5.13)

Additionally we have employed the same reasoning used previously, that w and u are approximated by their saturation values w_0 and u_0 which we take to be unity.

From eq 10.5.12 we obtain

$$T_c = \frac{\alpha_3\left(1-\kappa_3\right)^2 l^2 \phi_3\kappa_5}{2D_w\phi_4\kappa_6\left(1+\alpha_5\right)\left(1+\alpha_1+\alpha_2\right)} \quad \text{seconds}$$

(10.5.14)

where we have taken $q_z = 0$ when $\tau = 0$, and defined $t = T_c$ when $q_z = 1 - \kappa_3$.

For the parameter values used in section 9.2 we find $T_c = 5.39 \times 10^3$ seconds compared to 1.28×10^5 seconds for the simplified reduced model of section 9.2. By inspection we observe that the difference is due largely to the effect of the term raised to the power of 1.5 in eq 9.2.29 which arose from our formulation of concentrations and chemical activities of water and oxygen in the adsorbed layer.

Since the parameters used here are already about equal to the limits of plausibility for maximising T_c we must conclude that our original premise is incomplete. We assumed that the adsorbed layer did not contribute to either an increase in chemical activity or to a variable activity. We conclude that the adsorbed layer accounts for at least some increase in chemical activity coefficients, and probably for variable activity coefficients as well.

11 CONCLUDING REMARKS

We have found from our model results that most, if not all, of the conflicting results in the literature can be accounted for by corrosion resistance conferred through several different mechanisms. In some cases diffusive resistance to oxygen may indeed be the rate limiting process. Some coating compositions have inherently low oxygen and water diffusion coefficients and are typically applied as thick films (for example epoxies, vinyls, and chlorinated rubbers). These systems are traditionally used for corrosion resistant coatings.

But in general diffusive resistance alone is unlikely to provide the full story. Instead the adsorption of a coating's polymer to the metal substrate is the primary factor in the performance of a painted metal surface. We have found that the competition for adsorption between polymer, water and oxygen results in a rich complexity of behaviour which parallels that of real painted metal surfaces. Depending upon the degree and strength of adsorption by the polymer there may be more or less water and oxygen available at the metal - coating interface. From this results a greater or lesser rate of initial corrosion, and it is this initial rate which largely determines the ultimate time to failure.

The coating's passivating effect through its adsorption and modification of the basic corrosion rate can play a significant role. Additionally the effective diffusion coefficients for the various species present, and the polymer's capacity to absorb corrosion product are also potentially important and complicating factors in the model's behaviour.

We have found in results from reduced models, and from the behaviour of the full numerical model, that the behaviour of our model depends realistically upon those parameters which experience indicates should be relevant. Further, we find that the dependencies also correspond to reality in a plausible manner. Although the experimental information available is very limited we have found reasonable

agreement: for example the model matches reported corrosion rates under various conditions, and produces times to failure consistent with experimental evidence.

Work on this project concludes with more loose ends and new avenues to explore than when we started. We attempted to formulate the simplest possible model which would account for the diverse behaviour of painted metal surfaces. Some of this behaviour has been explored, but there remain many aspects and variations of the model which have yet to be investigated. In particular the response to periodic wetting (for example simulations of actual weather conditions) remains an issue of great interest. The Fortran programme (see Appendix) is written to incorporate varying external water concentrations as a function of time. It remains the task of subsequent research to explore this aspect of the model's behaviour.

We discussed several interesting variations of the model in chapter 10. Incorporation of the alternative corrosion flux formulation (section 10.5) and an intermediate boundary layer (section 10.3) to better describe variable chemical activity in the adsorbed layer are considered to be useful improvements to the model. Elaboration of the model to describe active sites as corrosion pits is also an intriguing prospect. Another interesting variation is to represent the painted metal surface as an ensemble of models so that, for example, every $10^{-6} \times 10^{-6}$ metres is modelled by an independent model unit with its own set of parameters. Film thickness, effective diffusion coefficients, and adsorption coefficients may vary for each unit to better represent real paint films. Presumably a particular coating could be represented as a specific distribution of unit models. We expect some of the unit models to fail much sooner than others. The point of interest is how does the aggregated model behave?

Incorporation and exploration of the model variations described above are important for another reason. The variations allow additional description of the physical and mechanical properties of paint films. With this extra detail it becomes possible to realise one of the original aims of this project and design polymers and coatings which embody the physical and mechanical properties calculated to

maximise T_c, the coating's effective protective lifetime. In its current form the model addresses physical and chemical properties only through generalised parameters. For example diffusion coefficients and polymer functional groups are model parameters, but we wish to describe how these parameters arise from more basic physical and chemical properties.

With information on how the model behaves in response to the variation of properties such as polymer molecular weight, hardness, density and type of functional group, etc. it becomes possible to design and engineer better polymers for coatings. Polymers with the required properties can be identified or synthesised and compounded into paints. Also, with more detail, paint composition (such as pigment volume concentration) can be incorporated into the model so that optimum values for this physical parameter of paints can be predicted from the model. Real paints incorporating composition and properties identified by the model can then be made and evaluated.

APPENDIX

Fortran 90 (Salford FTN90, 1995) programme to numerically solve
the model equations 3.5 to 3.24
Written by Dr. Stephen White, Industrial Research Limited,
P. O. Box 3 1310, Lower Hutt, New Zealand.

```fortran
1    C
2    C    Solve the equations for corrosion under a paint film
3    C
4          BLOCK DATA
5          IMPLICIT NONE
6          DOUBLE PRECISION k1, k2, k3, Du, Dw, Dz
7          COMMON /PDE/ k1, k2, k3, Du, Dw, Dz
8          DOUBLE PRECISION r1, r2, r3, r4, r5, r6, r7, r8, r9, r10,
9         $   r11, r12, r13, r14, Alpha, Beta, Eta, Rho1, Rho2
10         COMMON /RATES/ r1, r2, r3, r4, r5, r6, r7, r8, r9, r10, r11, r12,
11        $   r13, r14, Alpha, Beta, Eta, Rho1, Rho2
12         DOUBLE PRECISION PS0, M0, W0, U0, Z0, Zc0, P0, P0S
13         COMMON /SCALE/ PS0, M0, W0, U0, Z0, ZC0, P0, P0S
14         DATA  Du /1.0D-11/, Dw /1.0D-11/, Dz /1.0D-15/, k1 /1.0D0/,
15        $    k2 / 1.0D0/, k3 /1.0D-7/, r1 / 1.0D9/, r2 / 1.0D5/,
16        $    r3 / 1.0D7/,
17        $    r4 / 1.0D4/,  r5 / 1.0D8/, r6 /6.0D0/, r7 / 1.0D7/,
18        $    r8 / 1.0D2/,
19        $    r9 / 1.0D7/, r10 / 6.0D8/, r11 / 1.0D7/, r12 / 6.0D8/,
20        $    r13 /1.0D7/, r14 / 1.0D2/, Alpha / 1.0D0/, Beta /1.0D0/,
21        $    Eta / 1.0D-1/, Rho1 /9.6D-11/, Rho2 /5.4D-17/
22         DATA PS0 /2.0D-4/, M0 / 1.7D-5/, W0 /5.4D4/, U0 /8.0D0/,
23        $    Z0 / 1.0D-2/, Zc0 / 1.0D-2/, P0 / 1.0D3/, P0S / 2.0D-4/
24         END BLOCK DATA
25         IMPLICIT NONE
26         CHARACTER*72 Title
27         CHARACTER*8  Key
28         CHARACTER*3  Type
29         DATA Title /' Jacobian Matrix'/,Key / ' Key '/,Type /'   '/
30         DOUBLE PRECISION k1, k2, k3, Du, Dw, Dz
31         DOUBLE PRECISION r1, r2, r3, r4, r5, r6, r7, r8, r9, r10,
32        $   r11, r12, r13, r14, Alpha, Beta, Eta, Rho1, Rho2
33         DOUBLE PRECISION PS0, M0, W0, U0, Z0, Zc0, P0, P0S
34         COMMON /PDE/ k1, k2, k3, Du, Dw, Dz
35         COMMON /RATES/ r1, r2, r3, r4, r5, r6, r7, r8, r9, r10, r11, r12,
36        $   r13, r14, Alpha, Beta, Eta, Rho1, Rho2
37         COMMON /SCALE/ PS0, M0, W0, U0, Z0, ZC0, P0, P0S
38         INTEGER MaxPoints
39         PARAMETER (MaxPoints = 100)
40         DOUBLE PRECISION  DX
41         INTEGER j, Kount, MKount
42         DOUBLE PRECISION Y(5 * MaxPoints + 4), F(5 * MaxPoints + 4)
43         DOUBLE PRECISION YOLD(5 * MaxPoints + 4), Matrix(50+MaxPoints*20)
44         INTEGER ROW(5*MaxPoints + 6), COL(50+MaxPoints*20), NZ
45         DOUBLE PRECISION Thickness, Time, DelTime, TOL, StartTime,
46        $    EndTime, MaxDT, MDT
47         INTEGER NoPoints, NumberOfPoints, IFAIL, MaxKount, IPrint, M
48         DATA  Thickness /1.0D-4/, NumberOfPoints /10/, EndTime /1.0D10/,
49        $    DelTime /1.0D-4/, StartTime /0.0D0/
```

```
50        $    MaxKount / 100000000000/, Iprint /200/, MaxDT /1.0D6/
51         LOGICAL ILambda, PrecipitationBegun
52         INTEGER ITest, Suspend, Imax, IGOOD, IFailTol, IFailNeg,
53        $    IFailPos
54         COMMON /FLAG/ILambda, PrecipitationBegun, ITest, Suspend, IMax
55         PrecipitationBegun = .FALSE.
56         DATA IGOOD /0/, Kount /0/, J /0/, M /0/, NZ /0/, MKount /0/,
57        $    IFailTol /2/, IFailNeg /0/, IFailPos /0/
58         NoPoints = NumberOfPoints
59         DX = Thickness / (NoPoints - 1)
60         Time = StartTime
61         open(20, file='run8.txt')
62         CALL INITIAL(NoPoints, Y)
63         CALL INITIAL(NoPoints, YOld)
64         CALL PrintSolution(Y, YOld, 5, NoPoints, DelTime)
65         M = 5 * NoPoints + 4
66     c    CALL CalculateJ(Y, YOld, DX, DelTime, NoPoints,
67     c   $    5 * NoPoints + 4, F, Time,
68     c   $    Matrix, Row, Col, NZ)
69     c    WRITE(6,*)' ***** Numerical Jacobian ******'
70     c    CALL PrintMatrix(Matrix, Row, Col, NZ, 5*NoPoints+4)
71     c    CALL SetUpMatrix(Y, DX, DelTime, NoPoints, M, Matrix, Row,
72     c   $    Col, NZ)
73     c    WRITE(6,*)' ***** Analytic Jacobian ******'
74     c    CALL PrintMatrix(Matrix, Row, Col, NZ, 5*NoPoints+4)
75         MKount = 0
76         Suspend = 0
77         DO WHILE((Time .LE. EndTime) .AND. (MKount .LT. MaxKount))
78     c   $    .AND. (Suspend .LT. 1))
79         CALL StepInTime(Matrix, Row, Col, Y, YOld, NoPoints,
80        $    DX, DelTime, Time, IFAIL)
81         IF(Ilambda) THEN
82           PrecipitationBegun = .TRUE.
83         END IF
84           Time = Time + DelTime
85         MKount = MKount + 1
86         MDT = MIN( (Time+1.0D-3)/1.0D3, MaxDT)
87         If(MKount.eq.(MKount/Iprint)*Iprint) THEN
88           CALL PrintSolution(Y, YOld, 5, NoPoints, DelTime)
89           WRITE(6,*)'Time=', Time, DelTime,MKount,IFail
90           WRITE(20,'(2(1pe16.8))', advance='no') Time, DelTime
91         END IF
92           IF(IFAIL .LT. 0) THEN
93             Time = Time - DelTime
94           DelTime = DelTime / 1.2D0
95           write(6,fmt='(a)',advance='no')'-'
96             DO j = 1, 5*NoPoints + 4
97               Y(j) = YOld(j)
98             END DO
99           ELSE IF((IFAIL .LT. 18) .AND.
100       $    (DelTime .LT. MDT)) THEN
101          DelTime = DelTime * 1.02D0
102    c      WRITE(6,*)'DT increased to ',DelTime,MDT
103          write(6,fmt='(a)',advance='no')'+'
104            END IF
105            DO j = 1, 5*NoPoints + 4
106              YOld(j) = Y(j)
107            END DO
108        END DO
109         WRITE(6,*)' Time = ', Time, DelTime
```

```fortran
110          CALL PrintSolution(Y, YOld, 5, NoPoints, DelTime)
111          STOP
112          END



113          SUBROUTINE SetUpMatrix(Y, DX, DT, N, M, Matrix, Row, Col, NZ)
114          IMPLICIT NONE
115    C
116    C     Set up jacobian matrix in CSR format
117    C
118    C   INPUT:
119    C        Y  Current solution vector
120    C        DX stepsize in X
121    C        DT stepsize in time
122    C        N  number of points in X direction
123    C        M  dimension of Matrix and COL
124    C   OUTPUT:
125    C        Matrix the Jacobian matrix
126    C        Row
127    C        Col  arrays used for sparse matrix format
128    C        NZ  number of non-zeros in Jacobian
129    C
130          INTEGER N, M, NZ, Row(M), Col(M), L, i
131          DOUBLE PRECISION Matrix(M), Y(M)
132          DOUBLE PRECISION U, W, Z, Pw, Pz, Pf, Mw, Mu, Mp, Mf, Lambda
133          DOUBLE PRECISION k1, k2, k3, Du, Dw, Dz
134          COMMON /PDE/k1, k2, k3, Du, Dw, Dz
135          DOUBLE PRECISION r1, r2, r3, r4, r5, r6, r7, r8, r9, r10,
136         $   r11, r12, r13, r14, Alpha, Beta, Eta, Rho1, Rho2
137          COMMON /RATES/r1, r2, r3, r4, r5, r6, r7, r8, r9, r10, r11, r12,
138         $   r13, r14, Alpha, Beta, Eta, Rho1, Rho2
139          DOUBLE PRECISION PS0, M0, W0, U0, Z0, Zc0, P0, P0S
140          COMMON /SCALE/ PS0, M0, W0, U0, Z0, ZC0, P0, P0S
141          DOUBLE PRECISION DX2, DX, DT, Pm, DZm1DPw, DZm1DPz, M0mMp
142          LOGICAL ILambda, PrecipitationBegun
143          INTEGER ITest, Suspend, Imax
144          COMMON /FLAG/ILambda, PrecipitationBegun, ITest, Suspend, IMax
145          DOUBLE PRECISION dfz1dMp, dfz1dW, dfz1dU, dfz2dW, dfz2dMp,
146         $           dZm1Dz
147          L = 5 * N
148          DX2 = DX * DX
149          U = MAX(Y(1), 0.0D0)
150          W = Y(2)
151          Pw = Y(3)
152          Z = Y(4)
153          Pz = Y(5)
154          Mw = Y(L+1)
155          Mu = Y(L+2)
156          Mp = MIN(Y(L+3), M0)
157          Lambda = Y(L+4)
158          Pm = Mp
159          Pf = P0S - Pw - Pz - Y(L+3)
160          Mf = M0 - Mw - Mu - Y(L+3)
161          Dfz1DMp = -3.E0/2.E0*rho1*sqrt((M0-Mp)/M0)*W*sqrt(U)/M0
162          DFz1DW = rho1*sqrt((M0-Mp)/M0)**3*sqrt(U)
163          IF(U.GT.0.0D0) THEN
164              DFz1DU = rho1*sqrt((M0-Mp)/M0)**3*W/sqrt(U)/2.0
165          ELSE
```

```
166            Dfz1DU = 0.0D0
167         END IF
168         Dfz2DW = 2*rho2*((M0-Mp)/M0)**2*W
169         Dfz2DMp = -2*rho2*(M0-Mp)/M0**2*W**2
170         NZ = 0
171    C
172    C   U
173    C
174         Matrix(NZ+1) = 1.0D0 + DT * Du / DX2 + (DT/DX) * Dfz1DU
175         Matrix(NZ+2) = + (DT/DX) * Dfz1DW
176         Matrix(NZ+3) = - DT * Du / DX2
177         Matrix(NZ+4) = + (DT/DX) * Dfz1DMp
178         COL(NZ+1) = 1
179         COL(NZ+2) = 2
180         COL(NZ+3) = 6
181         COL(NZ+4) = L + 3
182         ROW(1) = NZ + 1
183         NZ = NZ + 4
184    C
185    C   W
186    C
187    Matrix(NZ+1) =  - DFz1DU
188         Matrix(NZ+2) = - Dw / DX - DFz1DW - 2.0D0 * DFz2DW
189         Matrix(NZ+3) = Dw / DX
190         Matrix(NZ+4) = - Dfz1DMp - 2.0D0 * DFz2DMp
191         COL(NZ+1) = 1
192         COL(NZ+2) = 2
193         COL(NZ+3) = 7
194         COL(NZ+4) = L+3
195         ROW(2) = NZ + 1
196         NZ = NZ + 4
197    C
198    C   Pw
199    C
200         Matrix(NZ+1) = -DT * r9 * Pf / W0 / 2.0D0              ! d/DW
201         Matrix(NZ+2) = 1.0D0 + DT * (r9 * W / W0 + r10) / 2.0D0      ! d/dPw
202         Matrix(NZ+3) = DT * r9 * W / W0 / 2.0D0               ! d/dPz
203         Matrix(NZ+4) = -DT * r9 * W / W0 / 2.0D0              ! d/dPm
204         COL(NZ+1) = 2
205         COL(NZ+2) = 3
206         COL(NZ+3) = 5
207         COL(NZ+4) = 5*N + 3
208         ROW(3) = NZ + 1
209         NZ = NZ + 4
210         IF( .NOT.ILambda) THEN
211             Matrix(NZ+1) = 1.0D0*Dfz1DU / 2.0D0              !d/DU
212             Matrix(NZ+2) = 1.0D0*(Dfz1DW + DFz2DW) / 2.0D0      !d/DW
213             Matrix(NZ+3) = r7 * (Z / Z0) / 2.0D0         !d/DPw
214             Matrix(NZ+4) = - Dz / DX / 2.0D0 - k3 / DT    !d/DZ
215    $              -r7 * Pf / Z0 / 2.0D0
216             Matrix(NZ+5) = (r7 * (Z / Z0) + r8) / 2.0D0   !d/DPz
217             Matrix(NZ+6) = Dz * Y(9) / DX / 2.0D0         !d/DZ9
218             Matrix(NZ+7) = 1.0D0*(Dfz1DMp + Dfz2DMp) / 2.0D0   !d/dMp
219             COL(NZ+1) = 1
220             COL(NZ+2) = 2
221             COL(NZ+3) = 3
222             COL(NZ+4) = 4
223             COL(NZ+5) = 5
224             COL(NZ+6) = 9
225             COL(NZ+7) = L + 3
```

```
226              ROW(4) = NZ + 1
227              NZ = NZ + 7
228      ELSE
229         Z = Y(4)
230         W = Y(2)
231              Matrix(NZ+1) = - Z * W0 / W**2              ! d / dW
232              Matrix(NZ+2) = W0 / W                    ! d / dZ
233              Col(NZ+1) = 2
234              Col(NZ+2) = 4
235              Row(4) = NZ+1
236              NZ = NZ + 2
237      END IF
238      Matrix(NZ+1) = DT * r7 * Z / Z0 / 2.0              ! d / dPw
239      Matrix(NZ+2) = - DT * r7 * Pf / Z0 / 2.0D0          ! d / DZ
240      Matrix(NZ+3) = 1.0D0 + DT * (r7 * Z / Z0 + r8) / 2.0D0  ! d / dPz
241      Matrix(NZ+4) = DT * r7 * Z / Z0 / 2.0
242      COL(NZ+1) = 3
243      COL(NZ+2) = 4
244      COL(NZ+3) = 5
245      COL(NZ+4) = L + 3
246      ROW(5) = NZ + 1
247      NZ = NZ + 4
248      DO i = 2, N - 1
249              W  = Y((i-1)*5 + 2)
250              Pw = Y((i-1)*5 + 3)
251              Z  = Y((i-1)*5 + 4)
252              Pz = Y((i-1)*5 + 5)
253              Pf = P0 - Pw - Pz + Beta * Z
254   C
255   C    U equation
256   C
257              Matrix(NZ+1)  = - DT * Du / DX2 / 2.0D0
258              Matrix(NZ+2)  = 1.0D0 + DT * Du / DX2
259              Matrix(NZ+3)  = - DT * Du / DX2 / 2.0D0
260   C
261   C    W equation
262   C
263              Matrix(NZ+4)  = - DT * Dw / DX2 / 2.0D0
264              Matrix(NZ+5)  = 1.0D0 + DT * Dw / DX2
265              Matrix(NZ+6)  = k1
266              Matrix(NZ+7)  = - DT * Dw / DX2 / 2.0D0
267   C
268   C    Pw equation
269   C
270              Matrix(NZ+8) = - DT * r11 * Pf / W0 / 2.0D0              ! d/dW
271              Matrix(NZ+9) = 1.0D0 + DT * (r11 * W / W0 + r12) / 2.0D0 ! d/dPw
272              Matrix(NZ+10) = - Beta * DT * r11 * W / W0 / 2.0D0      ! d/dZ
273              Matrix(NZ+11) = + DT * r11 * W / W0 / 2.0D0              ! d / dPz
274   C
275   C    Z equation
276   C
277              Matrix(NZ+12)  = - DT * Dz / DX2 / 2.0D0
278              Matrix(NZ+13)  = 1.0D0 + DT * Dz / DX2
279              Matrix(NZ+14)  = k2
280              Matrix(NZ+15) = - DT * Dz / DX2 / 2.0D0
281   C
282   C    Pz equation
283   C
284              Matrix(NZ+16) = + DT * r13 * Z / Z0 / 2.0D0          ! d / dPw
285              Matrix(NZ+17) = - DT * r13 * (Pf + Beta * Z)/ Z0 / 2.0D0 ! d / dZ
```

```
286            Matrix(NZ+18) = 1.0D0 + DT * (r8 + r7 * Z/Z0) / 2.0D0 ! d / dPz
287            COL(NZ+1) = (i-1)*5 - 4
288            COL(NZ+2) = (i-1)*5 + 1
289            COL(NZ+3) = (i-1)*5 + 6
290            ROW((i-1)*5+1) = NZ + 1
291            COL(NZ+4) = (i-1)*5 - 3
292            COL(NZ+5) = (i-1)*5 + 2
293            COL(NZ+6) = (i-1)*5 + 3
294            COL(NZ+7) = (i-1)*5 + 7
295            ROW((i-1)*5+2) = NZ + 4
296            COL(NZ+8) = (i-1)*5 + 2
297            COL(NZ+9) = (i-1)*5 + 3
298            COL(NZ+10) = (i-1)*5 + 4
299            COL(NZ+11) = (i-1)*5 + 5
300            ROW((i-1)*5+3) = NZ + 8
301            COL(NZ+12) = (i-1)*5 - 1
302            COL(NZ+13) = (i-1)*5 + 4
303            COL(NZ+14) = (i-1)*5 + 5
304            COL(NZ+15) = (i-1)*5 + 9
305            ROW((i-1)*5+4) = NZ + 12
306            COL(NZ+16) = (i-1)*5 + 3
307            COL(NZ+17) = (i-1)*5 + 4
308            COL(NZ+18) = (i-1)*5 + 5
309            ROW((i-1)*5+5) = NZ + 16
310            NZ = NZ + 18
311       END DO
312       U =  Y((N-1)*5 + 1)
313       W =  Y((N-1)*5 + 2)
314       Pw = Y((N-1)*5 + 3)
315       Z =  Y((N-1)*5 + 4)
316       Pz = Y((N-1)*5 + 5)
317       Pf = P0 - Pw - Pz + Z
318  C
319  C    U Boundary condition
320  C
321       Matrix(NZ+1) = 1.0D0
322       COL(NZ+1) = (N-1)*5 + 1
323       ROW((N-1)*5 + 1) = NZ + 1
324       NZ = NZ + 1
325  C
326  C    W Boundary condition
327  C
328       Matrix(NZ+1) = 1.0D0
329       COL(NZ+1) = (N-1)*5 + 2
330       ROW((N-1)*5 + 2) = NZ + 1
331       NZ = NZ + 1
332  C
333  C    Pw equation
334  C
335       Matrix(NZ+1) = - DT * r11 * Pf / W0 / 2.0D0              ! d/dW
336       Matrix(NZ+2) = 1.0D0 + DT * (r11 * W / W0 + r12) / 2.0D0 ! d/dPw
337       Matrix(NZ+3) = - DT * r11 * W / W0 / 2.0D0              ! d/dZ
338       Matrix(NZ+4) =   DT * r11 * W / W0 / 2.0D0              ! d / dPz
339       COL(NZ+1) = (N-1)*5 + 2
340       COL(NZ+2) = (N-1)*5 + 3
341       COL(NZ+3) = (N-1)*5 + 4
342       COL(NZ+4) = (N-1)*5 + 5
343       ROW((N-1)*5 + 3) = NZ + 1
344       NZ = NZ + 4
345  C
```

```
346    C    Z Boundary conditions
347    C
348         Matrix(NZ+1) = 1.0D0
349         COL(NZ+1) = (N-1)*5 + 4
350         ROW((N-1)*5 + 4) = NZ + 1
351         NZ = NZ + 1
352    C
353    C    Pz equation
354    C
355         Matrix(NZ+1) = + DT * r13 * Z / Z0 / 2.0D0              ! d / dPw
356         Matrix(NZ+2) = - DT * r13 * (Pf + Z)/ Z0 / 2.0D0       ! d / dZ
357         Matrix(NZ+3) = 1.0D0 + DT * (r14 + r13 * Z/Z0) / 2.0D0    ! d / dPz
358         COL(NZ + 1) = (N-1)*5 + 3
359         COL(NZ + 2) = (N-1)*5 + 4
360         COL(NZ + 3) = (N-1)*5 + 5
361         ROW((N-1)*5 + 5) = NZ + 1
362         NZ = NZ + 3
363         U = Y(1)
364         W = Y(2)
365         Pw = Y(3)
366         Z = Y(4)
367         Pz = Y(5)
368         Mp = Y(L+3)            !restore Mp to current value
369         Pf = P0S - Pw - Pz - Mp
370         Mf = M0 - Mw - Mu - Mp
371    C
372    C    Mw equation
373    C
374         M0mMp = M0 - Alpha * Mp
375         Matrix(NZ+1) = - DT * r1 * (M0mMp) * Mf / M0 / W0 / 2.0D0  ! d / dW
376         Matrix(NZ+2) = 1.0D0 + DT * (r1 * (W / W0) * (M0mMp) / M0
377    $                    + r2) / 2.0D0                    ! d / dMw
378         Matrix(NZ+3) = DT * r1 * (W / W0) * (M0mMp) / M0 / 2.0D0   ! d / dMu
379         Matrix(NZ+4) = DT * r1 * W/W0 * ((M0mMp)/M0 +
380    $    Alpha * Mf/M0)/2.0D0 ! d / dMp
381         COL(NZ+1) = 2
382         COL(NZ+2) = L+1
383         COL(NZ+3) = L+2
384         COL(NZ+4) = L+3
385         ROW(N*5 + 1) = NZ+1
386         NZ = NZ + 4
387    C
388    C    Mu equation
389    C
390         Matrix(NZ+1) = - DT * r3 * (M0mMp) * Mf / U0 / M0 /2.0D0    ! d / dU
391         Matrix(NZ+2) = DT * r3 * U * (M0mMp) / U0 / M0 / 2.0D0   ! d / dMw
392         Matrix(NZ+3) = 1.0D0 + DT * (r3 * (U / U0)*((M0mMp)/M0)
393    $                    + r4) / 2.0D0              ! d / dMu
394         Matrix(NZ+4) = DT * r3 * ((U / U0) * (Alpha * Mf / M0 +
395    $    (M0mMp) / M0)) / 2.0D0                    ! d / dMp
396         COL(NZ+1) = 1
397         COL(NZ+2) = L+1
398         COL(NZ+3) = L+2
399         COL(NZ+4) = L+3
400         ROW(N*5 + 2) = NZ+1
401         NZ = NZ + 4
402    C
403    C    Mp equation
404    C
405         Matrix(NZ+1) = DT * r5 * Mf / P0S / 2.0D0              ! d / dPw
```

```
406          Matrix(NZ+2) = DT * r5 * Mf / P0S / 2.0D0          ! d / dPz
407          Matrix(NZ+3) = DT * r5 * Pf / P0S / 2.0D0        ! d / dMw
408          Matrix(NZ+4) = DT * r5 * Pf / P0S / 2.0D0        ! d / dMu
409          Matrix(NZ+5) = 1.0D0 + DT * (r5 * (Pf + Mf)
410      $        / P0S + r6) / 2.0D0                          ! d / dMp
411      COL(NZ+1) = 3
412      COL(NZ+2) = 5
413      COL(NZ+3) = L+1
414      COL(NZ+4) = L+2
415      COL(NZ+5) = L+3
416      ROW(N*5 + 3) = NZ+1
417      NZ = NZ + 5
418      IF(.NOT.ILambda) THEN
419          Matrix(NZ+1) = 1.0D0
420          COL(NZ+1) = (N*5+4)
421          ROW(N*5 + 4) = NZ+1
422          NZ = NZ + 1
423          ROW(N*5 + 5) = NZ+1
424      ELSE
425        Z = Y(4)
426          Matrix(NZ+1) = 1.0D0*Dfz1DU / 2.0D0              !d/DU
427          Matrix(NZ+2) = 1.0D0*(Dfz1DW + DFz2DW) / 2.0D0   !d/DW
428          Matrix(NZ+3) = r7 * (Z / Z0) / 2.0D0        !d/DPw
429          Matrix(NZ+4) = - Dz / DX / 2.0D0            !d/DZ
430      $              -r7 * Pf / Z0 / 2.0D0
431          Matrix(NZ+5) = (r7 * (Z / Z0) + r8) / 2.0D0  !d/DPz
432          Matrix(NZ+6) = Dz / DX / 2.0D0        !d/DZ9
433          Matrix(NZ+7) = 1.0D0*(Dfz1DMp + Dfz2DMp) / 2.0D0  !d/dMp
434        Matrix(NZ+8) = -1.D0 / DT
435          COL(NZ+1) = 1
436          COL(NZ+2) = 2
437          COL(NZ+3) = 3
438          COL(NZ+4) = 4
439          COL(NZ+5) = 5
440          COL(NZ+6) = 9
441          COL(NZ+7) = L + 3
442        COL(NZ+8) = L + 4
443          ROW(N*5+4) = NZ + 1
444          NZ = NZ + 8
445          ROW(N*5 + 5) = NZ+1
446      END IF
447      RETURN
448      END




449      SUBROUTINE CalculateF(Y, YOld, DX, DT, N, M, F, Time, IGOOD)
450      IMPLICIT NONE
451      INTEGER M, N, L, i, j, IGOOD
452      DOUBLE PRECISION Y(M), YOld(M), F(M), DX, DT, Lambda,
453      $    Lambdao, Time
454      DOUBLE PRECISION DX2, U, W, Z, Pf, Pw, Pz, Uo, Wo, Zo,
455      $    Pfo, Pwo, Pzo, Mw, Mwo, Mu, Muo, Mp, Mpo, Mf, Mfo
456      DOUBLE PRECISION k1, k2, k3, Du, Dw, Dz
457      COMMON /PDE/k1, k2, k3, Du, Dw, Dz
458      DOUBLE PRECISION r1, r2, r3, r4, r5, r6, r7, r8, r9, r10,
459      $    r11, r12, r13, r14, Alpha, Beta, Eta, Rho1, Rho2
460      COMMON /RATES/r1, r2, r3, r4, r5, r6, r7, r8, r9, r10, r11, r12,
461      $    r13, r14, Alpha, Beta, Eta, Rho1, Rho2
```

```
462        DOUBLE PRECISION PS0, M0, W0, U0, Z0, Zc0, P0, P0S
463        COMMON /SCALE/ PS0, M0, W0, U0, Z0, ZC0, P0, P0S
464        LOGICAL ILambda, PrecipitationBegun
465        INTEGER ITest, Suspend, IMax
466        COMMON /FLAG/ILambda, PrecipitationBegun, ITest, Suspend, IMax
467        DOUBLE PRECISION Zw, Zwo, temp1, temp2, fz1, fz2, Um1, Um1o, Wm1,
468     $          Wm1o, Zm1, fz1o, fz2o, zm1o, Zc, Zco, M0mMp,
469     $          M0mMpo
470        DOUBLE PRECISION WRHS
471  C
472  C    Variables are stored in the Y vector as U(i),W(i),Pw(i),Z(i),PZ(i)
473  C     i = 1...N Mw, Mu, Mp, Zc
474        DX2 = DX * Dx
475        L = 5 * N
476        Mw = Y(L+1)
477        Mu = Y(L+2)
478        Mp = MIN(Y(L+3),M0)
479        Lambda = Y(L+4)
480        Mwo = YOld(L+1)
481        Muo = YOld(L+2)
482        Mpo = MIN(YOld(L+3),M0)
483        Lambdao = YOld(L+4)
484        j = 5
485        DO i = 2, N - 1
486            U  = Y((i-1)*5 + 1)
487            W  = Y((i-1)*5 + 2)
488            Pw = Y((i-1)*5 + 3)
489            Z  = Y((i-1)*5 + 4)
490            Pz = Y((i-1)*5 + 5)
491            Uo  = YOld((i-1)*5 + 1)
492            Wo  = YOld((i-1)*5 + 2)
493            Pwo = YOld((i-1)*5 + 3)
494            Zo  = YOld((i-1)*5 + 4)
495            Pzo = YOld((i-1)*5 + 5)
496            Pf  = P0 + Beta * Z - Pw - Pz
497            Pfo = P0 + Beta * Zo - Pwo - Pzo
498  C
499  C    U equation
500  C
501            j = j + 1
502            F(j) = Y(j) - YOld(j) - DT * (Y(j+5) - 2.0D0 * Y(j) + Y(j-5)
503     $        + YOld(j+5) - 2.0D0 * YOld(j) + YOld(j-5))*Du/2.0D0/DX2
504            j = j + 1
505  C
506  C   W
507  C
508            F(j) = Y(j) - YOld(j) - DT * (Y(j+5) - 2.0D0 * Y(j) + Y(j-5)
509     $        + YOld(j+5) - 2.0D0 * YOld(j) + YOld(j-5))*Dw/2.0D0/DX2
510     $        + k1 * (Pw - Pwo)
511            j = j + 1
512  C
513  C   Pw
514  C
515          F(j) = (Y(j) - YOld(j)) - DT * ( r11 * (Pf * W + Pfo * Wo) /W0
516     $        - (r12 * (Pw + Pwo))) / 2.0D0
517            j = j + 1
518  C
519  C   Z
520  C
521            F(j) = Y(j) - YOld(j) - DT * (Y(j+5) - 2.0D0 * Y(j) + Y(j-5)
```

```fortran
522    $       + YOld(j+5) - 2.0D0 * YOld(j) + YOld(j-5))*Dz/2.0D0/DX2
523    $       + k2 * (Pz - Pzo)
524            j = j + 1
525  C
526  C    Pz
527  C
528            F(j) = (Y(j) - YOld(j)) - DT * ( rl3 * (Pf*Z/Z0 +
529    $       Pfo*Zo/Z0) - rl4 * (Pz + Pzo)) / 2.0D0
530       END DO
531       i = 1
532       U  = Y((i-1)*5 + 1)
533       W  = Y((i-1)*5 + 2)
534       Pw = Y((i-1)*5 + 3)
535       Z  = Y((i-1)*5 + 4)
536       Pz = Y((i-1)*5 + 5)
537       Uo  = YOld((i-1)*5 + 1)
538       Wo  = YOld((i-1)*5 + 2)
539       Pwo = YOld((i-1)*5 + 3)
540       Zo  = YOld((i-1)*5 + 4)
541       Pzo = YOld((i-1)*5 + 5)
542       Pf  = P0S - Pw - Pz - Y(L+3)          ! script P on boundary
543       Pfo = P0S - Pwo - Pzo - YOld(L+3)
544       IGOOD = 0
545       IF(Pf .LT. 0.0D0) THEN
546            IGOOD = 1
547            RETURN
548       END IF
549       Temp1 = (M0 - Mp) / M0
550       Temp2 = Temp1 * SQRT(Temp1)
551       FZ1 = Rho1 * Temp2 * W * SQRT(U)
552       FZ2 = Rho2 * (Temp1 * W)**2
553       Um1 = Y(6) - DX * Fz1 / Du
554       Um1o = YOld(6) - DX * Fz1 / Du
555       Wm1 = Y(7) - 2.0D0 * DX * (fz1 + 2.0D0 * fz2) / Dw
556       Wm1o = YOld(7) - 2.0D0 * DX * (fz1 + 2.0D0 * fz2) / Dw
557       Temp1 = (M0 - Mpo) / M0
558       Temp2 = Temp1 * SQRT(Temp1)
559       FZ1o = Rho1 * Temp2 * Wo * SQRT(Uo)
560       FZ2o = Rho2 * (Temp1 * Wo)**2
561       j = 1
562  C
563  C    The U equation
564  C
565       F(j) = Y(j) - YOld(j) - DT * (Y(j+5) - 2.0D0 * Y(j) + Um1
566    $    + YOld(j+5) - 2.0D0 * YOld(j) + Um1o)*Du/2.0D0/DX2
567       j = j + 1
568  C
569  C    The W equation
570  C
571  c    F(j) = Y(j) - YOld(j) - DT * (Y(j+5) - 2.0D0 * Y(j) + Wm1
572  c  $      + YOld(j+5) - 2.0D0 * YOld(j) + Wm1o)*Dw/2.0D0/DX2
573  c  $      + k1 * (Pw - Pwo)
574       F(j) = Dw * (Y(j+5) - Y(j)) / DX - FZ1 - FZ2 * 2.0D0
575       j = j + 1
576  C
577  C    The Pw equation
578  C
579       F(j) = Y(j) - YOld(j) - DT * (r9 * (Pf * W / W0 + Pfo * Wo / W0)
580    $    - r10 * (Pw + Pwo))/2.0
581       j = j + 1
```

```
582    C
583    C    The Z equation
584    C
585         IF (W .NE. 0.0D0) THEN
586             Zw = Z * W0 / W
587         ELSE
588             Zw = 0.0D0
589         END IF
590         IF((Zw .LT. Z0) .AND. .NOT. PrecipitationBegun) THEN
591             F(j) = Dz * (Y(j + 5) - Y(j)) / DX / 2.0D0
592    $        + Dz * (YOld(j + 5) - YOld(j)) / DX / 2.0D0
593    $        - k3 * (Y(j) - YOld(j)) / DT
594    $        + 1.0D0*(fz1 + fz2 + fz1o + fz2o) / 2.0D0
595    $        - (r7 * (Z / Z0) * Pf - r8 * Pz) / 2.0D0
596    $        - (r7 * (Zo / Z0) * Pfo - r8 * Pzo) / 2.0D0
597             j = j + 1
598             ILambda = .FALSE.
599         ELSE
600           IF(.NOT. ILambda) THEN
601             WRITE(6,*)' Precipitation begins '
602             Suspend = 1
603           END IF
604           F(j) = Z * W0 / W - Z0          ! Equation is Z(1) = Z0
605           j = j + 1
606             ILambda = .TRUE.
607         END IF
608    C
609    C    The Pz equation
610    C
611         F(j) = (Y(j) - YOld(j)) - DT * ( r7 * (Pf*Z/Z0 +
612    $        Pfo*Zo/Z0) - r8 * (Pz + Pzo)) / 2.0D0
613         j = 5*N+1
614         Mw = Y(j)
615         Mwo = YOld(j)
616         Mu = Y(j+1)
617         Muo = YOld(j+1)
618         Mp = Y(j+2)
619         Mpo = YOld(j+2)
620         Mf = M0 - Mw - Mu - Mp
621         Mfo = M0 - Mwo - Muo - Mpo
622         IF(Mf .LT. 0.0D0) THEN
623             IGOOD = 2
624             RETURN
625         END IF
626         IF(Mw .LT. 0.0D0) THEN
627             IGOOD = 3
628             RETURN
629         END IF
630    C
631    C    The Mw equation
632    C
633         M0mMp = M0 - Alpha * Mp
634         M0mMpo = M0 - Alpha * Mpo
635         F(j) = (Mw - Mwo) - DT * (r1 * ((W/W0) * (M0mMp)*Mf/M0
636    $        + (Wo/W0) * (M0mMpo)*Mfo/M0) - r2 * (Mw + Mwo))/2.0D0
637         j = j + 1
638    C
639    C    The Mu equation
640    C
641         F(j) = (Mu - Muo) - DT * (r3 * ((U/U0) * (M0mMp)*Mf/M0
```

```
642        $    + (Uo/U0) * (M0mMpo)*Mfo/M0) - r4 * (Mu + Muo))/2.0D0
643    C
644    C    The Mp equation
645    C
646         j = j + 1
647         F(j) = (Mp - Mpo) - DT * (r5*(Pf/P0S)*(Mf + Mfo) -
648        $    r6 * (Mp + Mpo)) / 2.0D0
649    c    WRITE(20,'(5D20.13)')Time,Mu,Mf,
650    c    $    DT * (r3 * ((U/U0) * (M0mMp)*Mf/M0
651    c    $    + (Uo/U0) * (M0mMpo)*Mfo/M0) - r4 * (Mu + Muo))/2.0D0
652    c    $    ,DT * (r5*(Pf/P0S)*(Mf + Mfo) -
653    c    $    r6 * (Mp + Mpo)) / 2.0D0
654         j = j + 1
655         Zc = Y(j)
656         Zco = YOld(j)
657         i = 1
658         U  = Y((i-1)*5 + 1)
659         W  = Y((i-1)*5 + 2)
660         Pw = Y((i-1)*5 + 3)
661         Z  = Y((i-1)*5 + 4)
662         Pz = Y((i-1)*5 + 5)
663         Uo  = YOld((i-1)*5 + 1)
664         Wo  = YOld((i-1)*5 + 2)
665         Pwo = YOld((i-1)*5 + 3)
666         Zo  = YOld((i-1)*5 + 4)
667         Pzo = YOld((i-1)*5 + 5)
668         Pf  = P0S - Pw - Pz - Y(L+3)              ! script P on boundary
669         Pfo = P0S - Pwo - Pzo - YOld(L+3)
670         IF(.NOT. Ilambda) THEN
671             F(j) = Y(j)           ! Equation is Zc=0
672         ELSE
673           Zc = Y(5*N+4)
674           Zco = YOld(5*N+4)
675             F(j) = Dz * (Y(9) - Y(4)) / DX / 2.0D0
676        $       + Dz * (YOld(9) - YOld(4)) / DX / 2.0D0
677        $       - (Zc - Zco) / DT
678        $       + 1.0D0*(fz1 + fz2 + fz1o + fz2o) / 2.0D0
679        $       - (r7 * (Z / Z0) * Pf - r8 * Pz) / 2.0D0
680        $       - (r7 * (Zo / Z0) * Pfo - r8 * Pzo) / 2.0D0
681         END IF
682         i = N
683         U  = Y((i-1)*5 + 1)
684         W  = Y((i-1)*5 + 2)
685         Pw = Y((i-1)*5 + 3)
686         Z  = Y((i-1)*5 + 4)
687         Pz = Y((i-1)*5 + 5)
688         Uo  = YOld((i-1)*5 + 1)
689         Wo  = YOld((i-1)*5 + 2)
690         Pwo = YOld((i-1)*5 + 3)
691         Zo  = YOld((i-1)*5 + 4)
692         Pzo = YOld((i-1)*5 + 5)
693         Pf  = P0 + Z - Pw - Pz
694         Pfo = P0 + Zo - Pwo - Pzo
695         F(5*(N-1)+1) = Y(5*(N-1)+1) - U0
696         F(5*(N-1)+2) = Y(5*(N-1)+2) - WRHS(Time)
697         j = 5*(N-1) + 3
698         F(j) = (Y(j) - YOld(j)) - DT * ( r11 * (Pf*W/W0 + Pfo*Wo/W0)
699        $       - (r12 * (Pw + Pwo))) / 2.0D0
700         j = j + 1
701         F(j) = Z
```

```
702        j = j + 1
703        F(j) = (Y(j) - YOld(j)) - DT * ( r13 * (Pf*Z/Z0 +
704     $        Pfo*Zo/Z0) - r14 * (Pz + Pzo)) / 2.0D0
705        RETURN
706        END



707        SUBROUTINE INITIAL(N, U)
708     C
709     C    This routine initialises spatial arrays and assigns initial conditions
710     C
711     C    INPUT
712     C    N      No of points is x direction
713     C
714     C    OUTPUT
715     C    U      Initial values for U(x), W(x), Z(x), Pw(x), Pz(x), Mw, Mu, Mp
716        IMPLICIT NONE
717        INTEGER N
718        DOUBLE PRECISION U(*)
719        INTEGER i
720        DOUBLE PRECISION  WRHS
721        DOUBLE PRECISION r1, r2, r3, r4, r5, r6, r7, r8, r9, r10,
722     $    r11, r12, r13, r14, Alpha, Beta, Eta, Rho1, Rho2
723        COMMON /RATES/r1, r2, r3, r4, r5, r6, r7, r8, r9, r10, r11, r12,
724     $    r13, r14, Alpha, Beta, Eta, Rho1, Rho2
725        DOUBLE PRECISION PS0, M0, W0, U0, Z0, Zc0, P0, P0S
726        COMMON /SCALE/ PS0, M0, W0, U0, Z0, ZC0, P0, P0S
727        DO i = 1, 5*N
728            U(i) = 0.0D0
729        END DO
730        DO i = 1, N
731            U((i-1)*5+1) =  0.0D0      !U   prev U0
732            U((i-1)*5+2) =  0.0D0      !W   prev W0
733            U((i-1)*5+3) =  0.0D0      !Pw  prev 100/6.0
734        END DO
735        U(3) =  0.0D0           !Pw0 script
736        U(5*(N-1) + 1) = U0        !U(0)
737        U(5*(N-1) + 2) = WRHS(0.0D0) !W(0)
738        U(5*(N-1) + 3) = WRHS(0.0D0) * r11 * P0 /(r11 + r12)/W0  !P0/61=16.393
739        U(5*N + 1) = 0.0D0         !Mw
740        U(5*N + 2) = 0.0D0         !Mu
741        U(5*N + 3) = M0 - 1.09344D-11    !Mp M0 - 1.115D-8
742        U(5*N + 4) = 0.0D0         !Pz?
743        RETURN
744        END



745        SUBROUTINE PrintSolution(U, UOld, NPDE, NoPoints, DTime)
746        IMPLICIT NONE
747        DOUBLE PRECISION U(*), UOld(*)
748        INTEGER NPDE, NoPoints, i, j, Suspend, ITest, IMax
749        LOGICAL ILambda, PrecipitationBegun
750        DOUBLE PRECISION Pf(NoPoints)
751        DOUBLE PRECISION Pw, Pz, Mf, Z, MfOld, DTime
752        DOUBLE PRECISION r1, r2, r3, r4, r5, r6, r7, r8, r9, r10,
```

```
753        $    r11, r12, r13, r14, Alpha, Beta, Eta, Rho1, Rho2
754         COMMON /RATES/r1, r2, r3, r4, r5, r6, r7, r8, r9, r10, r11, r12,
755        $         r13, r14, Alpha, Beta, Eta, Rho1, Rho2
756         DOUBLE PRECISION PS0, M0, W0, U0, Z0, Zc0, P0, P0S
757         DOUBLE PRECISION T1, T2, T3, T4, T5, T6, T7, T8, T9,
758        $    T10, T11, T12, T13, Mwm, Mum, Mpm,Mfm,
759        $    DEMw, DEMu, DEMp, DEPz, DEPw, DEZ, DEZc
760         COMMON /SCALE/ PS0, M0, W0, U0, Z0, ZC0, P0, P0S
761         COMMON /FLAG/ILambda, PrecipitationBegun, ITest, Suspend, IMax
762         Pw(i) = U((i-1)*5 + 3)
763         Pz(i) = U((i-1)*5 + 5)
764         Z(i) = U((i-1)*5 + 4)
765         Mf = M0
766         MfOld = M0
767         DO i = 1, 3
768             Mf = Mf - U(NoPoints * 5 + i)
769           MfOld = MfOld - UOld(NoPoints * 5 + i)
770         END DO
771         Mfm = (Mf + MfOld) / 2
772         DO i = 2, NoPoints
773             Pf(i) = P0 + Z(i) - Pw(i) - Pz(i)
774         END DO
775         Pf(1) = P0S - Pw(1) - Pz(1) - U(NoPoints * NPDE + 3)
776         Mpm = (U(NoPoints * NPDE + 3) + UOld(NoPoints*NPDE + 3))/2
777         Mwm = (U(NoPoints * NPDE + 1) + UOld(NoPoints*NPDE + 1))/2
778         Mum = (U(NoPoints * NPDE + 2) + UOld(NoPoints*NPDE + 2))/2
779         T1 = r1 * U(2) / W0 * (1 - Alpha * Mpm / M0) * Mfm    !Mw
780         T2 = r2 * Mwm
781         T3 = r3 * U(1) / U0 * (1 - Alpha * Mpm / M0) * Mfm    !Mu
782         T4 = r4 * Mum
783         T5 = r5 * Pf(1) / PS0 * Mfm                !Mp
784         T6 = r6 * Mpm
785         T7 = r7 * (U(4) + UOld(4)) / 2 / Z0 * Pf(1)       !Pz
786         T8 = r8 * (U(5) + UOld(5)) / 2
787         T9 = r9 * U(2) / W0 * Pf(1)              !Pw
788         T10 = r10 * U(3)
789         DEMw = (U(5*NoPoints+1) - UOld(5*NoPoints+1))/DTime    !dMw/dt
790         DEMu = (U(5*NoPoints+2) - UOld(5*NoPoints+2))/DTime    !dMu/dt
791         DEMp = (U(5*NoPoints+3) - UOld(5*NoPoints+3))/DTime    !dMp/dt
792         DEZc = (U(5*NoPoints+4) - UOld(5*NoPoints+4))/DTime    !dZc/dt
793         DEPw = (U(3) - UOld(3))/DTime              !dPw/dt
794         DEZ = (U(4) - UOld(4))/DTime              !dz/dt
795         DEPz = (U(5) - UOld(5))/DTime              !dPz/dt
796         write(6,*)
797         write(6,'(4(1pe16.9))',advance='no') U(1)/U0,U(2)/W0,
798        $       Mfm/M0, Pf(1)/PS0
799         write(6,*)
800         write(6,'(4(1pe16.9))',advance='no') U(4)/Z0, DEZ,
801        $       U(5*NoPoints+4)/Z0, DEZc
802         write(6,*)
803         write(6,'(4(1pe16.9))',advance='no') Mwm/M0,DEMw, T1, T2
804         write(6,*)
805         write(6,'(4(1pe16.9))',advance='no') Mum/M0,DEMu, T3, T4
806         write(6,*)
807         write(6,'(4(1pe16.9))',advance='no') Mpm/M0,DEMp, T5, T6
808         write(6,*)
809         write(6,'(4(1pe16.9))',advance='no') Pz(1)/P0S,DEPz, T7, T8
810         write(6,*)
811         write(6,'(4(1pe16.9))',advance='no') Pw(1)/P0S,DEPw, T9, T10
812         write(6,*)
```

```
813    c
814    c        write output to disk file run*.txt
815    c
816          write(20,'(8(1pe16.8))',advance='no') U(1)/U0,U(2)/W0,
817      $        Mfm/M0, Pf(1)/PS0, U(4)/Z0, DEZ,
818      $        U(5*NoPoints+4)/Z0, DEZc
819          write(20,'(4(1pe16.8))',advance='no') Mwm/M0, DEMw, T1, T2
820    write(20,'(4(1pe16.8))',advance='no') Mum/M0, DEMu, T3, T4
821    write(20,'(4(1pe16.8))',advance='no') Mpm/M0, DEMp, T5, T6
822    write(20,'(4(1pe16.8))',advance='no') Pz(1)/P0S, DEPz, T7, T8
823    write(20,'(4(1pe16.8))',advance='no') Pw(1)/P0S, DEPw, T9, T10
824          write(20,*)
825    c    write(6,*)
826    c    DO j = 1, 5
827    c      WRITE(6,*)
828    c      WRITE(6,*)
829    c      WRITE(6,'(5(1X,1pe14.7))')(U((i-1)*NPDE + j),i=1, NoPoints)
830    c    END DO
831    c    do j = 3, 5
832    c      write(20,'(1x,1pd18.10)',advance='no')U(j)
833    c    end do
834    c    WRITE(6,*)
835    c    WRITE(6,*)' **** Pf ****'
836    c    WRITE(6,'(5(1pe14.7))')(Pf(i),i=1, NoPoints)
837    c    WRITE(20,'(1X,1pd18.10)')Pf(1)
838    c    WRITE(6,*)
839    c    WRITE(6,'(5(1X,E14.8))')(U(NoPoints*NPDE + i)/M0,i=1, 4), Mf /M0
840    c    WRITE(6,'(5(1X,E14.8))')(UOld(NoPoints*NPDE + i)/M0,i=1, 4),
841    c  $    MfOld / M0
842    c    WRITE(6,'(5(1X,E14.8))')(((U(NoPoints*NPDE + i) +
843    c  $    UOld(NoPoints*NPDE + i))/ (2 * M0)),
844    c  $    i = 1, 4), (Mf + MfOld) / (2 * M0)
845    c    WRITE(20,'(3(1X,1pd18.10))',advance='no')
846    c  $    (U(NoPoints*NPDE + i)/M0,i=1, 3)
847    c    write(20,'(1x,1pd18.10)') Mf / M0
848    c    WRITE(20,'(5(1X,E14.8))')(UOld(NoPoints*NPDE + i)/M0,i=1, 4),
849    c  $    MfOld / M0
850    c    WRITE(20,'(5(1X,E14.8))')(((U(NoPoints*NPDE + i) +
851    c  $    UOld(NoPoints*NPDE + i))/ (2 * M0)),
852    c  $    i = 1, 4), (Mf + MfOld) / (2 * M0)
853          If(U(NoPoints*NPDE+4) .GT. 0.0D0) Then
854          Suspend = 1
855          Else
856          Suspend = 0
857          End If
858          RETURN
859          END




860          DOUBLE PRECISION FUNCTION WRHS(T)
861          DOUBLE PRECISION T
862          DOUBLE PRECISION PS0, M0, W0, U0, Z0, Zc0, P0, P0S
863          COMMON /SCALE/ PS0, M0, W0, U0, Z0, ZC0, P0, P0S
864          WRHS = W0      !prev W0
865          RETURN
866          END
```

```
867          SUBROUTINE  StepInTime(Matrix, Row, Col, Y, YOld, N, DX, DT,
868       $    Time, IFAIL)
869          IMPLICIT NONE
870          DOUBLE PRECISION Matrix(*), Y(*), YOLD(*), DX, DT, F(500), Time
871          INTEGER Row(*), Col(*), N, M, NZ, ierr, i, KOUNT, Kyrlov, IFAIL
872    C
873    C     If no ALLOCATE statement then uncomment the next 11 lines
874    C
875    c     INTEGER MaxPoints, MaxM
876    c     PARAMETER (MaxPoints = 50)
877    c     PARAMETER (MaxM = 2*(50 + MaxPoints*20))
878    c     DOUBLE PRECISION alu(2*MaxM), wu(2*(5*MaxPoints+4)),
879    c  $     wl(2*(5*MaxPoints+4)), VV(2*(5*MaxPoints+4)*I0),
880    c  $     , YD(2*(5*MaxPoints+4))
881    c     INTEGER jlu(2*MaxM), ju(2*(5*MaxPoints+4)),
882    c  $    jr(2*(5*MaxPoints+4)), jwu(2*(5*MaxPoints+4))
883    c  $    , jwl(2*(5*MaxPoints+4))
884    C
885    C     And remove the next 2 lines
886    C
887          DOUBLE PRECISION, DIMENSION(:), ALLOCATABLE ::alu, wu, wl, VV,
888       $    YD
889          INTEGER, DIMENSION(:), ALLOCATABLE ::jlu, ju, jr, jwu, jwl
890          DOUBLE PRECISION PS0, M0, W0, U0, Z0, Zc0, P0, P0S
891          COMMON /SCALE/ PS0, M0, W0, U0, Z0, ZC0, P0, P0S
892          INTEGER ITest, IGOOD, Aitest(20), Suspend, IMax
893          DOUBLE PRECISION Atest(20)
894          LOGICAL ILambda, PrecipitationBegun
895          COMMON /FLAG/ILambda, PrecipitationBegun, ITest, Suspend, IMax
896          DOUBLE PRECISION TEST, Tol, VecMax
897          Kyrlov = 15
898          TOL = 1.0D-09
899          TEST = 1.0D0
900          M = 2*(50 + N*20)
901    c     WRITE(6,*)' Allocating space M=',M
902    C
903    C     If not using allocate statement remove next 4 lines
904    C
905          ALLOCATE(ALU(2*M), jlu(2*M), ju(2*(5*N+4)), jr(2*(5*N+4)),
906       $    jwu(2*(5*N+4)),
907       $    jwl(2*(5*N+4)), wu(2*(5*N+5)), wl(2*(5*N+4)),
908       $    VV(2*(5*N+4)*Kyrlov),YD(2*(5*N+4)))
909    C
910          KOUNT = 0
911          DO WHILE((TEST .GT. TOL).AND.(KOUNT.LT.30))
912              CALL SetUpMatrix(Y, DX, DT, N, M, Matrix, Row, Col, NZ)
913              CALL CalculateF(Y, YOld, DX, DT, N, M, F, Time, IGOOD)
914              IF(IGOOD .NE. 0) THEN
915             WRITE(6,fmt='(i1)',advance='no') IGOOD
916    c          WRITE(6,fmt='(i1)') IGOOD
917                IFAIL = -1
918                DEALLOCATE(ALU, jlu, ju, jr, jwu, jwl, wu, wl, VV, YD)
919                RETURN
920              END IF
921    c     IF(KOUNT.EQ.1) THEN
922    c         CALL pltmtps (5*N+4,5*N+4,0,Col,Row,",",",0 , 66)
923    c         CALL PrintMatrix(Matrix, Row, Col, NZ, 5*N+4)
924    C     END IF
925    C     WRITE(6,*)'*** F ***',(F(i),i=1,5*N+4)
926          CALL ilut(5*N+4, Matrix, Col, Row, 20, 1.0D-5, alu,
```

```
927        $      jlu, ju, 2*M, wu, wl, jr, jwl, jwu, ierr)
928               IF(ierr .ne.0) THEN
929                 write(6,*)' ilut ierr =',ierr
930                 IF(ierr .GT. 0) THEN
931               WRITE(6,'(10i4)')(Col(i),i=Row(ierr),Row(ierr+1)-1)
932               WRITE(6,'(6G12.4)')(Matrix(i),i=Row(ierr),Row(ierr+1)-1)
933                 END IF
934                 IFAIL = -1
935                 RETURN
936               END IF
937               YD = 0.0D0
938               CALL pgmres(5*N+4, Kyrlov, F, YD, VV, 1.D-6, 100, -1, Matrix,
939        $      Col, Row, alu, jlu, ju, ierr)
940               IF(ierr .ne.0) THEN
941                 write(6,*)' pgmres ierr =',ierr
942                 IF(ierr .GT. 0) THEN
943                   WRITE(6,'(10i4)')(Col(i),i=Row(i),Row(i+1)-1)
944                   WRITE(6,'(6G12.4)')(Matrix(i),i=Row(i),Row(i+1)-1)
945                 END IF
946                 IFAIL = -1
947               END IF
948               TEST = VecMax(YD,Y,5*N+4)
949               DO i = 1, 5*N + 4
950                 Y(i) = Y(i) - YD(i)
951               END DO
952               Kount = Kount + 1
953            Aitest(Kount) = itest
954            Atest(Kount) = test
955     c        WRITE(6,'(a,2i4,4d12.4)')'TEST =',Kount,itest,TEST,Y(5*N+3),
956     c   $       M0, TOL
957          END DO
958          IF(KOUNT.GE.29) THEN
959                 IFAIL = -1
960     c      DO i = 1, 10
961     c        WRITE(6,'(i4,e13.6)')Aitest(i), Atest(i), Tol
962     c      END DO
963     c      WRITE(6,*)' ***** Analytic Jacobian ******'
964     c      CALL PrintMatrix(Matrix, Row, Col, NZ, N*5+4)
965     c      CALL CalculateJ(Y, YOld, DX, DT, N, 5*N+4, F, Time,
966     c   $       Matrix, Row, Col, NZ)
967     c      WRITE(6,*)' ***** Numerical Jacobian ******'
968     c      CALL PrintMatrix(Matrix, Row, Col, NZ, 5*N+4)
969     c      WRITE(6,'(a,2i4,3d12.4)')'TEST =',Kount,itest,TEST, Y(5*N+3),M0
970          ELSE
971                 IFAIL = KOUNT
972          END IF
973     C
974     C    Remove following statement if not using allocate
975     C
976          DEALLOCATE(ALU, jlu, ju, jr, jwu, jwl, wu, wl,VV,YD)
977          RETURN
978          END
979     c-------------------------------------------------------------------c
980     c                    S P A R S K I T                    c
981     c-------------------------------------------------------------------c
982     c                ITERATIVE SOLVERS MODULE                      c
983     c-------------------------------------------------------------------c
984     c contents: (May 7, 1990)                          c
985     c----------                                   c
986     c                                          c
```

```
987    c pgmres : preconditioned GMRES solver                           c
988    c ilut   : incomplete LU factorization with dual truncation strategy c
989    c ilu0   : simple ILU(0) preconditioning                         c
990    c milu0  : MILU(0) preconditioning                               c
991    c ope    : routine for matrix-by-vector product                  c
992    c lusol0 : forward followed by backward triangular solve (Precond.) c
993    c bsort2 : bubble sort routine used by ilut.                      c
994    c                                   c
995    c Note: all preconditioners are preprocessors to pgmres.           c
996    c usage: call preconditioner then call pgmres.                    c
997    c                                   c
998    c-------------------------------------------------------------c
```

```
999              subroutine pgmres (n, im, rhs, sol, vv, eps, maxits, iout,
1000       *              aa, ja, ia, alu, jlu, ju, ierr)
1001   c--------------------------------------------------------------
1002          implicit real*8 (a-h,o-z)
1003          integer n, im, maxits, iout, ierr, ja(*), ia(n+1), jlu(*), ju(n)
1004          real*8 vv(n,*), rhs(n), sol(n), aa(*), alu(*), eps
1005   c---------------------------------------------------------------*
1006   c                                             *
1007   c              *** ILUT - Preconditioned GMRES ***             *
1008   c                                             *
1009   c---------------------------------------------------------------*
1010   c This is a simple version of the ILUT preconditioned GMRES algorithm. *
1011   c The ILUT preconditioner uses a dual strategy for dropping elements  *
1012   c instead of the usual level of-fill-in approach. See details in ILUT *
1013   c subroutine documentation. PGMRES uses the L and U matrices generated *
1014   c from the subroutine ILUT to precondition the GMRES algorithm.       *
1015   c The preconditioning is applied to the right. The stopping criterion *
1016   c utilized is based simply on reducing the residual norm by epsilon.  *
1017   c This preconditioning is more reliable than ilu0 but requires more   *
1018   c storage. It seems to be much less prone to difficulties related to  *
1019   c strong nonsymmetries in the matrix. We recommend using a nonzero tol *
1020   c (tol=.005 or .001 usually give good results) in ILUT. Use a large   *
1021   c lfil whenever possible (e.g. lfil = 5 to 10). The higher lfil the   *
1022   c more reliable the code is. Efficiency may also be much improved.    *
1023   c Note that lfil=n and tol=0.0 in ILUT will yield the same factors as *
1024   c Gaussian elimination without pivoting.                      *
1025   c                                             *
1026   c ILU(0) and MILU(0) are also provided for comparison purposes       *
1027   c USAGE: first call ILUT or ILU0 or MILU0 to set up preconditioner and *
1028   c then call pgmres.                            *
1029   c---------------------------------------------------------------*
1030   c Coded by Y. Saad - This version dated May, 7, 1990.         *
1031   c---------------------------------------------------------------*
1032   c parameters                                  *
1033   c-----------                                  *
1034   c on entry:                                   *
1035   c=========                                    *
1036   c                                             *
1037   c n     == integer. The dimension of the matrix.            *
1038   c im    == size of krylov subspace: should not exceed 50 in this  *
1039   c          version (can be reset by changing parameter command for  *
1040   c          kmax below)                         *
1041   c rhs   == real vector of length n containing the right hand side.  *
1042   c          Destroyed on return.                *
```

```
1043   c sol   == real vector of length n containing an initial guess to the  *
1044   c         solution on input. approximate solution on output          *
1045   c eps   == tolerance for stopping criterion. process is stopped      *
1046   c         as soon as ( ||.|| is the euclidean norm):                 *
1047   c         || current residual||/||initial residual|| <= eps          *
1048   c maxits== maximum number of iterations allowed                      *
1049   c iout  == output unit number number for printing intermediate results *
1050   c         if (iout .le. 0) nothing is printed out.                    *
1051   c                                                                     *
1052   c aa, ja,                                                             *
1053   c ia    == the input matrix in compressed sparse row format:         *
1054   c         aa(1:nnz) = nonzero elements of A stored row-wise in order  *
1055   c         ja(1:nnz) = corresponding column indices.                  *
1056   c         ia(1:n+1) = pointer to beginning of each row in aa and ja.  *
1057   c         here nnz = number of nonzero elements in A = ia(n+1)-ia(1)  *
1058   c                                                                     *
1059   c alu,jlu== A matrix stored in Modified Sparse Row format containing  *
1060   c          the L and U factors, as computed by subroutine ilut.       *
1061   c                                                                     *
1062   c ju    == integer array of length n containing the pointers to      *
1063   c         the beginning of each row of U in alu, jlu as computed      *
1064   c         by subroutine ILUT.                                        *
1065   c                                                                     *
1066   c on return:                                                          *
1067   c==========                                                          *
1068   c sol   == contains an approximate solution (upon successful return). *
1069   c ierr  == integer. Error message with the following meaning.        *
1070   c         ierr = 0 --> successful return.                            *
1071   c         ierr = 1 --> convergence not achieved in itmax iterations.  *
1072   c         ierr =-1 --> the initial guess seems to be the exact        *
1073   c                     solution (initial residual computed was zero)   *
1074   c                                                                     *
1075   c-----------------------------------------------------------------*
1076   c                                                                     *
1077   c work arrays:                                                        *
1078   c============                                                        *
1079   c vv    == work array of length  n x (im+ 1) (used to store the Arnoli *
1080   c         basis)                                                      *
1081   c-----------------------------------------------------------------*
1082   c subroutines called :                                                *
1083   c ope   : matrix by vector multiplication delivers y=ax, given x     *
1084   c lusol0 : combined forward and backward solves (Preconditioning ope.) *
1085   c BLAS2  routines.                                                    *
1086   c-----------------------------------------------------------------*
1087         parameter (kmax=50)
1088         real*8 hh(kmax+1,kmax), c(kmax), s(kmax), rs(kmax+1),t
1089   c------------------------------------------------------------
1090   c arnoldi size should not exceed kmax=50 in this version..
1091   c to reset modify paramter kmax accordingly.
1092   c------------------------------------------------------------
1093         data epsmac/1.d-16/
1094         n1 = n + 1
1095         its = 0
1096   c------------------------------------------------------------
1097   c outer loop starts here..
1098   c-------------- compute initial residual vector --------------
1099         call ope (n, sol, vv, aa, ja, ia)
1100         do 21 j=1,n
1101              vv(j, 1) = rhs(j) - vv(j,1)
1102    21    continue
```

```
1103      c------------------------------------------------------------
1104      20   ro = sqrt( ddot(n, vv, 1, vv, 1) )
1105           if (iout .gt. 0 .and. its .eq. 0)
1106       *      write(iout, 199) its, ro
1107           if (ro .eq. 0.0d0) goto 999
1108           t = 1.0d0/ ro
1109           do 210 j=1, n
1110                vv(j,1) = vv(j,1)*t
1111      210  continue
1112           if (its .eq. 0) eps1=eps*ro
1113      c    ** initialize 1-st term  of rhs of hessenberg system..
1114           rs(1) = ro
1115           i = 0
1116      4    i=i+1
1117           its = its + 1
1118           i1 = i + 1
1119           call lusol0 (n, vv(1,i), rhs, alu, jlu, ju)
1120           call ope (n, rhs, vv(1,i1), aa, ja, ia)
1121      c----------------------------------------
1122      c    modified gram - schmidt...
1123      c----------------------------------------
1124           do 55 j=1, i
1125                t = ddot(n, vv(1,j),1,vv(1,i1),1)
1126                hh(j,i) = t
1127                call daxpy(n, -t, vv(1,j), 1, vv(1,i1), 1)
1128      55   continue
1129           t = sqrt(ddot(n, vv(1,i1), 1, vv(1,i1), 1))
1130           hh(i1,i) = t
1131           if ( t .eq. 0.0d0) goto 58
1132           t = 1.0d0/t
1133           do 57  k=1,n
1134                vv(k,i1) = vv(k,i1)*t
1135      57   continue
1136      c
1137      c    done with modified gram schimd and arnoldi step..
1138      c    now  update factorization of hh
1139      c
1140      58   if (i .eq. 1) goto 121
1141      c--------perform previous transformations  on i-th column of h
1142           do 66 k=2,i
1143                k1 = k-1
1144                t = hh(k1,i)
1145                hh(k1,i) = c(k1)*t + s(k1)*hh(k,i)
1146                hh(k,i) = -s(k1)*t + c(k1)*hh(k,i)
1147      66   continue
1148      121  gam = sqrt(hh(i,i)**2 + hh(i1,i)**2)
1149      c
1150      c    if gamma is zero then any small value will do...
1151      c    will affect only residual estimate
1152      c
1153           if (gam .eq. 0.0d0) gam = epsmac
1154      c
1155      c    get  next plane rotation
1156      c
1157           c(i) = hh(i,i)/gam
1158           s(i) = hh(i1,i)/gam
1159           rs(i1) = -s(i)*rs(i)
1160           rs(i) =  c(i)*rs(i)
1161      c
1162      c    determine residual norm and test for convergence-
```

```
1163    c
1164          hh(i,i) = c(i)*hh(i,i) + s(i)*hh(i1,i)
1165          ro = abs(rs(i1))
1166    c 131   format(1h ,2e14.4)
1167          if (iout .gt. 0)
1168       *      write(iout, 199) its, ro
1169          if (i .lt. im .and. (ro .gt. eps1)) goto 4
1170    c
1171    c     now compute solution. first solve upper triangular system.
1172    c
1173          rs(i) = rs(i)/hh(i,i)
1174          do 30 ii=2,i
1175              k=i-ii+1
1176              k1 = k+1
1177              t=rs(k)
1178              do 40 j=k1,i
1179                 t = t-hh(k,j)*rs(j)
1180    40      continue
1181              rs(k) = t/hh(k,k)
1182    30    continue
1183    c
1184    c     form linear combination of v(*,i)'s to get solution
1185    c
1186          t = rs(1)
1187          do 15 k=1, n
1188              rhs(k) = vv(k,1)*t
1189    15    continue
1190          do 16 j=2, i
1191              t = rs(j)
1192              do 161 k=1, n
1193                 rhs(k) = rhs(k)+t*vv(k,j)
1194    161     continue
1195    16    continue
1196    c
1197    c     call preconditioner.
1198    c
1199          call lusol0 (n, rhs, rhs, alu, jlu, ju)
1200          do 17 k=1, n
1201              sol(k) = sol(k) + rhs(k)
1202    17    continue
1203    c
1204    c     restart outer loop  when necessary
1205    c
1206          if (ro .le. eps1) goto 990
1207          if (its .gt. maxits) goto 991
1208    c
1209    c     else compute residual vector and continue..
1210    c
1211          do 24 j=1,i
1212              jj = i1-j+1
1213              rs(jj-1) = -s(jj-1)*rs(jj)
1214              rs(jj) = c(jj-1)*rs(jj)
1215    24    continue
1216          do 25 j=1,i1
1217              t = rs(j)
1218              if (j .eq. 1) t = t-1.0d0
1219              call daxpy (n, t, vv(1,j), 1, vv, 1)
1220    25    continue
1221    199   format('   its =', i4, ' res. norm =', d20.6)
1222    c     restart outer loop.
```

```
1223          goto 20
1224    990   ierr = 0
1225          return
1226    991   ierr = 1
1227          return
1228    999   continue
1229          ierr = -1
1230          return
1231    c-----------------end of pgmres --------------------------------------
1232    c-------------------------------------------------------------------------
1233          end
1234    c-------------------------------------------------------------------------
```

```
1235          subroutine ilut (n,a,ja,ia,lfil,tol,alu,jlu,ju,iwk,
1236         *              wu,wl,jr,jwl,jwu,ierr)
1237    c-------------------------------------------------------------------------
1238          implicit real*8 (a-h,o-z)
1239          real*8 a(*), alu(*), wu(*), wl(*), tol
1240          integer ja(*),ia(*),jlu(*),ju(*),jr(*), jwu(*),
1241         *    jwl(*), n, lfil, iwk, ierr
1242    c-------------------------------------------------------------------------*
1243    c                *** ILUT preconditioner ***              *
1244    c                --------------------------              *
1245    c     incomplete LU factorization with dual truncation mechanism    *
1246    c     VERSION 2 : sorting  done for both L and U.              *
1247    c                                            *
1248    c-------------------------------------------------------------------------*
1249    c---- coded by Youcef Saad May, 5, 1990. ---------------------------*
1250    c---- Dual drop-off strategy works as follows.            *
1251    c                                        *
1252    c     1) Theresholding in L and U as set by tol. Any element whose size*
1253    c        is less than some tolerance (relative to the norm of current  *
1254    c        row in u) is dropped.                         *
1255    c                                          *
1256    c     2) Keeping only the largest lenl0+lfil elements in L and the   *
1257    c        largest lenu0+lfil elements in U, where lenl0=initial number  *
1258    c        of nonzero elements in a given row of lower part of A      *
1259    c        and lenlu0 is similarly defined.                  *
1260    c                                        *
1261    c Flexibility: one can use tol=0 to get a strategy based on keeping the*
1262    c largest elements in each row of L and U. Taking tol .ne. 0 but lfil=n*
1263    c will give the usual threshold strategy (however, fill-in is then    *
1264    c impredictible).                               *
1265    c                                          *
1266    c-------------------------------------------------------------------------*
1267    c PARAMETERS
1268    c-----------
1269    c
1270    c on entry:
1271    c==========
1272    c n      = integer. The dimension of the matrix A.
1273    c
1274    c a,ja,ia = matrix stored in Compressed Sparse Row format.
1275    c
1276    c lfil   = integer. The fill-in parameter. Each row of L and
1277    c          each row of U will have a maximum of lfil elements
1278    c          in addition to the original number of nonzero elements.
```

```
1279    c        Thus storage can be determined beforehand.
1280    c        lfil must be .ge. 0.
1281    c
1282    c iwk     = integer. The minimum length of arrays alu and jlu
1283    c
1284    c On return:
1285    c==========
1286    c
1287    c alu,jlu = matrix stored in Modified Sparse Row (MSR) format containing
1288    c        the L and U factors together. The diagonal (stored in
1289    c        alu(1:n) ) is inverted. Each i-th row of the alu,jlu matrix
1290    c        contains the i-th row of L (excluding the diagonal entry=1)
1291    c        followed by the i-th row of U.
1292    c
1293    c ju      = integer array of length n containing the pointers to
1294    c        the beginning of each row of U in the matrix alu,jlu.
1295    c
1296    c ierr    = integer. Error message with the following meaning.
1297    c        ierr  = 0    --> successful return.
1298    c        ierr .gt. 0  --> zero pivot encountered at step number ierr.
1299    c        ierr  = -1   --> Error. input matrix may be wrong.
1300    c                        (The elimination process has generated a
1301    c                        row in L or U whose length is .gt.  n.)
1302    c        ierr  = -2   --> The matrix L overflows the array al.
1303    c        ierr  = -3   --> The matrix U overflows the array alu.
1304    c        ierr  = -4   --> Illegal value for lfil.
1305    c        ierr  = -5   --> zero pivot encountered.
1306    c
1307    c work arrays:
1308    c=============
1309    c jr,jwu,jwl   = integer work arrays of length n.
1310    c wu, wl       = real work arrays of length n+1, and n resp.
1311    c
1312    c Notes:
1313    c ------
1314    c A must have all nonzero diagonal elements.
1315    c-----------------------------------------------------------------------
1316            if (lfil .lt. 0) goto 998
1317    c-------------------------------
1318    c initialize ju0 (points to next element to be added to alu,jlu)
1319    c and pointer.
1320    c
1321            ju0 = n+2
1322            jlu(1) = ju0
1323    c
1324    c  integer double pointer array.
1325    c
1326            do 1 j=1, n
1327               jr(j)  = 0
1328    1       continue
1329    c-----------------------------------------------------------------------
1330    c beginning of main loop.
1331    c-----------------------------------------------------------------------
1332            do 500 ii = 1, n
1333            j1 = ia(ii)
1334            j2 = ia(ii+1) - 1
1335            lenu = 0
1336            lenl = 0
1337            tnorm = 0.0d0
1338            do 501 k=j1,j2
```

```
1339                tnorm = tnorm+abs(a(k))
1340     501        continue
1341                tnorm = tnorm/real(j2-j1+1)
1342  c
1343  c--- unpack L-part and U-part of row of A in arrays wl, wu --
1344  c
1345           do 170  j = j1, j2
1346              k = ja(j)
1347              t = a(j)
1348  c       if (abs(t) .lt. tol*tnorm) goto 170
1349              if (abs(t) .lt. tol*tnorm .and. k .ne. ii) goto 170
1350              if (k .lt. ii) then
1351                 lenl = lenl+1
1352                 jwl(lenl) = k
1353                 wl(lenl) = t
1354                 jr(k) = lenl
1355              else
1356                 lenu = lenu+1
1357                 jwu(lenu) = k
1358                 wu(lenu) = t
1359                 jr(k) = lenu
1360              endif
1361     170   continue
1362  c      tnorm = 0.0d0
1363  c      do 171 k=j1,j2
1364  c         tnorm = tnorm + abs(a(k))
1365  c 171   continue
1366  c
1367  c      tnorm = tnorm/real(j2-j1+1)
1368              lenl0 = lenl
1369              lenu0 = lenu
1370              jj = 0
1371              nl = 0
1372  c----------------------------------------------------------------
1373  c--------------------- eliminate previous rows --------------------
1374  c----------------------------------------------------------------
1375     150   jj = jj+1
1376              if (jj .gt. lenl) goto 160
1377  c----------------------------------------------------------------
1378  c in order to do the elimination in the correct order we need to
1379  c exchange the current row number with the one that has
1380  c smallest column number, among jj,jj+1,...,lenl.
1381  c----------------------------------------------------------------
1382              jrow = jwl(jj)
1383              k = jj
1384  c
1385  c determine smallest column index
1386  c
1387              do 151 j=jj+1,lenl
1388                 if (jwl(j) .lt. jrow) then
1389                    jrow = jwl(j)
1390                    k = j
1391                 endif
1392     151   continue
1393  c
1394  c exchange in jwl
1395  c
1396              j = jwl(jj)
1397              jwl(jj) = jrow
1398              jwl(k) = j
```

```
1399    c
1400    c exchange in jr
1401    c
1402            jr(jrow) = jj
1403            jr(j) = k
1404    c
1405    c exchange in wl
1406    c
1407            s = wl(k)
1408            wl(k) = wl(jj)
1409            wl(jj) = s
1410    c
1411            if (jrow .ge. ii) goto 160
1412    c---------get the multiplier for row to be eliminated: jrow
1413            fact = wl(jj)*alu(jrow)
1414            jr(jrow) = 0
1415            if (abs(fact)*wu(n+2-jrow) .le. tol*tnorm) goto 150
1416    c------------------------------------------------------------------
1417    c------------ combine current row and row jrow ---------------------
1418    c------------------------------------------------------------------
1419            do 203 k = ju(jrow), jlu(jrow+1)-1
1420             s = fact*alu(k)
1421             j = jlu(k)
1422             jpos = jr(j)
1423    c
1424    c if fill-in element and small disregard:
1425    c
1426             if (abs(s) .lt. tol*tnorm .and. jpos .eq. 0) goto 203
1427             if (j .ge. ii) then
1428    c
1429    c    dealing with upper part.
1430    c
1431                if (jpos .eq. 0) then
1432    c    this is a fill-in element
1433                   lenu = lenu+1
1434                   if (lenu .gt. n) goto 995
1435                   jwu(lenu) = j
1436                   jr(j) = lenu
1437                   wu(lenu) = - s
1438                else
1439    c    no fill-in element --
1440                   wu(jpos) = wu(jpos) - s
1441                endif
1442             else
1443    c
1444    c    dealing with lower part.
1445    c
1446                if (jpos .eq. 0) then
1447    c    this is a fill-in element
1448                   lenl = lenl+1
1449                   if (lenl .gt. n) goto 995
1450                   jwl(lenl) = j
1451                   jr(j) = lenl
1452                   wl(lenl) = - s
1453                else
1454    c    no fill-in element --
1455                   wl(jpos) = wl(jpos) - s
1456                endif
1457             endif
1458     203    continue
```

```
1459              nl = nl+l
1460              wl(nl) = fact
1461              jwl(nl)  = jrow
1462              goto 150
1463     c----------------------------------------------------------
1464     c------------ update l-matrix ----------------------------
1465     c----------------------------------------------------------
1466     160   len = min0(nl,lenl0+lfil)
1467              call bsort2 (wl,jwl,nl,len)
1468     c
1469              do 204 k=1, len
1470                if (ju0 .gt. iwk) goto 996
1471                alu(ju0) =  wl(k)
1472                jlu(ju0) =  jwl(k)
1473                ju0 = ju0+l
1474     204     continue
1475     c
1476     c  save pointer to beginning of row ii of U
1477     c
1478              ju(ii) = ju0
1479     c
1480     c  reset double-pointer jr to zero (L-part - except first
1481     c  jj-1 elements which have already been reset)
1482     c
1483              do 306 k= jj, lenl
1484                jr(jwl(k)) = 0
1485     306     continue
1486     c
1487     c
1488     c be sure that the diagonal element is first in w, jw
1489     c
1490              idiag = 0
1491              idiag = jr(ii)
1492              if (idiag .eq. 0) goto 900
1493     c
1494              if (idiag .ne. 1) then
1495                s = wu(1)
1496                wu(j) = wu(idiag)
1497                wu(idiag) = s
1498     c
1499                j = jwu(1)
1500                jwu(1) = jwu(idiag)
1501                jwu(idiag) = j
1502     c
1503              endif
1504     c
1505              len = min0(lenu,lenu0+lfil)
1506              call bsort2 (wu(2), jwu(2), lenu-1,len)
1507     c----------------------------------------------------------
1508     c------------ update u-matrix ----------------------------
1509     c----------------------------------------------------------
1510              t = 0.0d0
1511              do 302 k=2, len
1512                if (ju0 .gt. iwk) goto 997
1513                jlu(ju0) = jwu(k)
1514                alu(ju0)  = wu(k)
1515                t = t+ abs(wu(k) )
1516                ju0 = ju0+l
1517     302     continue
1518     c
```

```
1519    c    save norm in wu (backwards). Norm is in fact average abs value
1520    c
1521            wu(n+2-ii) = t / real(len+1)
1522    c
1523    c    store inverse of diagonal element of u
1524    c
1525            if (wu(1) .eq. 0.0) goto 999
1526    c
1527            alu(ii) = 1.0d0/ wu(1)
1528    c
1529    c    update pointer to beginning of next row of U.
1530    c
1531            jlu(ii+1) = ju0
1532    c
1533    c    reset double-pointer jr to zero (U-part)
1534    c
1535            do 308 k=1, lenu
1536            jr(jwu(k)) = 0
1537    308    continue
1538    c-------------------------------------------------------------------
1539    c    end main loop
1540    c-------------------------------------------------------------------
1541    500  continue
1542            ierr = 0
1543            return
1544    c
1545    c    zero pivot :
1546    c
1547    900    ierr = ii
1548            return
1549    c
1550    c    incomprehensible error. Matrix must be wrong.
1551    c
1552    995    ierr = -1
1553            return
1554    c
1555    c    insufficient storage in L.
1556    c
1557    996    ierr = -2
1558            return
1559    c
1560    c    insufficient storage in U.
1561    c
1562    997    ierr = -3
1563            return
1564    c
1565    c    illegal lfil entered.
1566    c
1567    998    ierr = -4
1568            return
1569    c
1570    c    zero pivot encountered
1571    c
1572    999    ierr = -5
1573            return
1574    c---------------- end of ilut ---------------------------------------
1575    c-------------------------------------------------------------------
1576            end
1577    c-------------------------------------------------------------------
```

```
1578            subroutine ilu0 (n, a, ja, ia, alu, jlu, ju, iw, ierr)
1579            implicit real*8 (a-h,o-z)
1580            real*8 a(*), alu(*)
1581            integer ja(*), ia(*), ju(*), jlu(*), iw(*)
1582    c----------------- right preconditioner ----------------------------*
1583    c              ***   ilu(0) preconditioner.  ***          *
1584    c-------------------------------------------------------------------*
1585    c Note that this has been coded in such a way that it can be used
1586    c with pgmres. Normally, since the data structure of a, ja, ia is
1587    c the same as that of a, ja, ia, savings can be made. In fact with
1588    c some definitions (not correct for general sparse matrices) all we
1589    c need in addition to a, ja, ia is an additional diagonal.
1590    c Ilu0 is not recommended for serious problems. It is only provided
1591    c here for comparison purposes.
1592    c-----------------------------------------------------------------------
1593    c
1594    c on entry:
1595    c----------
1596    c n      = dimension of matrix
1597    c a, ja,
1598    c ia     = original matrix in compressed sparse row storage.
1599    c
1600    c on return:
1601    c-----------
1602    c alu,jlu = matrix stored in Modified Sparse Row (MSR) format containing
1603    c          the L and U factors together. The diagonal (stored in
1604    c          alu(1:n) ) is inverted. Each i-th row of the alu,jlu matrix
1605    c          contains the i-th row of L (excluding the diagonal entry=1)
1606    c          followed by the i-th row of U.
1607    c
1608    c ju     = pointer to the diagonal elements in alu, jlu.
1609    c
1610    c ierr   = integer indicating error code on return
1611    c          ierr = 0 --> normal return
1612    c          ierr = k --> code encountered a zero pivot at step k.
1613    c work arrays:
1614    c--------------
1615    c iw     = integer work array of length n.
1616    c-------------
1617    c IMPORTANT
1618    c-----------
1619    c it is assumed that the the elements in the input matrix are stored
1620    c    in such a way that in each row the lower part comes first and
1621    c    then the upper part. To get the correct ILU factorization, it is
1622    c    also necessary to have the elements of L sorted by increasing
1623    c    column number. It may therefore be necessary to sort the
1624    c    elements of a, ja, ia prior to calling ilu0. This can be
1625    c    achieved by transposing the matrix twice using csrcsc.
1626    c
1627    c-------------------------------------------------------------------
1628            ju0 = n+2
1629            jlu(1) = ju0
1630    c
1631    c initialize work vector to zero's
1632    c
1633            do 31 i=1, n
1634               iw(i) = 0
1635    31     continue
1636    c
1637    c main loop
```

```
1638    c
1639            do 500 ii = 1, n
1640                js = ju0
1641    c
1642    c generating row number ii of L and U.
1643    c
1644                do 100 j=ia(ii),ia(ii+1)-1
1645    c
1646    c    copy row ii of a, ja, ia into row ii of alu, jlu (L/U) matrix.
1647    c
1648                    jcol = ja(j)
1649                    if (jcol .eq. ii) then
1650                        alu(ii) = a(j)
1651                        iw(jcol) = ii
1652                        ju(ii)  = ju0
1653                    else
1654                        alu(ju0) = a(j)
1655                        jlu(ju0) = ja(j)
1656                        iw(jcol) = ju0
1657                        ju0 = ju0+1
1658                    endif
1659    100     continue
1660                jlu(ii+1) = ju0
1661                jf = ju0-1
1662                jm = ju(ii)-1
1663    c
1664    c exit if diagonal element is reached.
1665    c
1666                do 150 j=js, jm
1667                    jrow = jlu(j)
1668                    tl = alu(j)*alu(jrow)
1669                    alu(j) = tl
1670    c
1671    c perform  linear combination
1672    c
1673                    do 140 jj = ju(jrow), jlu(jrow+1)-1
1674                        jw = iw(jlu(jj))
1675                        if (jw .ne. 0) alu(jw) = alu(jw) - tl*alu(jj)
1676    140         continue
1677    150     continue
1678    c
1679    c    invert and store diagonal element.
1680    c
1681                if (alu(ii) .eq. 0.0d0) goto 600
1682                alu(ii) = 1.0d0/alu(ii)
1683    c
1684    c    reset pointer iw to zero
1685    c
1686                iw(ii) = 0
1687                do i = js, jf
1688                iw(jlu(i)) = 0
1689                end do
1690    500     continue
1691                ierr = 0
1692                return
1693    c
1694    c    zero pivot :
1695    c
1696    600     ierr = ii
1697    c
```

```
1698            return
1699   c------- end of ilu0 -------------------------------------------------
1700   c----------------------------------------------------------------------
1701            end
1702   c----------------------------------------------------------------------
```

```
1703            subroutine milu0 (n, a, ja, ia, alu, jlu, ju, iw, ierr)
1704            implicit real*8 (a-h,o-z)
1705            real*8 a(*), alu(*)
1706            integer ja(*), ia(*), ju(*), jlu(*), iw(*)
1707   c----------------------------------------------------------------------*
1708   c            *** simple milu(0) preconditioner. ***            *
1709   c----------------------------------------------------------------------*
1710   c Note that this has been coded in such a way that it can be used
1711   c with pgmres. Normally, since the data structure of a, ja, ia is
1712   c the same as that of a, ja, ia, savings can be made. In fact with
1713   c some definitions (not correct for general sparse matrices) all we
1714   c need in addition to a, ja, ia is an additional diagonal.
1715   c Ilu0 is not recommended for serious problems. It is only provided
1716   c here for comparison purposes.
1717   c----------------------------------------------------------------------
1718   c
1719   c on entry:
1720   c----------
1721   c n      = dimension of matrix
1722   c a, ja,
1723   c ia     = original matrix in compressed sparse row storage.
1724   c
1725   c on return:
1726   c----------
1727   c alu,jlu = matrix stored in Modified Sparse Row (MSR) format containing
1728   c         the L and U factors together. The diagonal (stored in
1729   c         alu(1:n) ) is inverted. Each i-th row of the alu,jlu matrix
1730   c         contains the i-th row of L (excluding the diagonal entry=1)
1731   c         followed by the i-th row of U.
1732   c
1733   c ju     = pointer to the diagonal elements in alu, jlu.
1734   c
1735   c ierr   = integer indicating error code on return
1736   c          ierr = 0 --> normal return
1737   c          ierr = k --> code encountered a zero pivot at step k.
1738   c work arrays:
1739   c-------------
1740   c iw     = integer work array of length n.
1741   c------------
1742   c Note (IMPORTANT):
1743   c-----------
1744   C it is assumed that the the elements in the input matrix are ordered
1745   c    in such a way that in each row the lower part comes first and
1746   c    then the upper part. To get the correct ILU factorization, it is
1747   c    also necessary to have the elements of L ordered by increasing
1748   c    column number. It may therefore be necessary to sort the
1749   c    elements of a, ja, ia prior to calling milu0. This can be
1750   c    achieved by transposing the matrix twice using csrcsc.
1751   c--------------------------------------------------------------
1752            ju0 = n+2
1753            jlu(1) = ju0
```

```
1754    c initialize work vector to zero's
1755            do  i=1, n
1756               iw(i) = 0
1757            end do
1758    c
1759    c-------------- MAIN LOOP ----------------------------------
1760    c
1761            do 500 ii = 1, n
1762               js = ju0
1763    c
1764    c generating row number ii or L and U.
1765    c
1766               do 100 j=ia(ii),ia(ii+1)-1
1767    c
1768    c copy row ii of a, ja, ia into row ii of alu, jlu (L/U) matrix.
1769    c
1770                  jcol = ja(j)
1771                  if (jcol .eq. ii) then
1772                     alu(ii) = a(j)
1773                     iw(jcol) = ii
1774                     ju(ii)  = ju0
1775                  else
1776                     alu(ju0) = a(j)
1777                     jlu(ju0) = ja(j)
1778                     iw(jcol) = ju0
1779                     ju0 = ju0+1
1780                  endif
1781    100      continue
1782               jlu(ii+1) = ju0
1783               jf = ju0-1
1784               jm = ju(ii)-1
1785    c s accumulates fill-in values
1786               s = 0.0d0
1787               do 150 j=js, jm
1788                jrow = jlu(j)
1789                tl = alu(j)*alu(jrow)
1790                alu(j) = tl
1791    c----------------------perform linear combination --------
1792                  do 140 jj = ju(jrow), jlu(jrow+1)-1
1793                     jw = iw(jlu(jj))
1794                     if (jw .ne. 0) then
1795                        alu(jw) = alu(jw) - tl*alu(jj)
1796                     else
1797                        s = s + tl*alu(jj)
1798                     endif
1799    140      continue
1800    150      continue
1801    c---------------------- invert and store diagonal element.
1802               alu(ii) = alu(ii)-s
1803               if (alu(ii) .eq. 0.0d0) goto 600
1804               alu(ii) = 1.0d0/alu(ii)
1805    c---------------------- reset pointer iw to zero
1806               iw(ii) = 0
1807               do i = js, jf
1808                iw(jlu(i)) = 0
1809               end do
1810    500      continue
1811               ierr = 0
1812               return
1813    c    zero pivot :
```

```
1814    600    ierr = ii
1815           return
1816   c------- end of milu0 ------------------------------------------
1817   c-----------------------------------------------------------------
1818           end
1819   c-----------------------------------------------------------------
```

```
1820           subroutine ope (n, x, y, a, ja, ia)
1821           real*8  x(n), y(n), a(*)
1822           integer n, k1, k2, ja(*), ia(n+1)
1823   c-----------------------------------------------------------------
1824   c sparse matrix * vector multiplication
1825   c-----------------------------------------------------------------
1826           do 100 i=1,n
1827             k1 = ia(i)
1828             k2 = ia(i+1) -1
1829             y(i) = 0.0d0
1830             do k=k1, k2
1831                y(i) = y(i) + a(k) * x(ja(k))
1832             end do
1833    100    continue
1834           return
1835   c------------------ end of ope ------------------------------------
1836   c-----------------------------------------------------------------
1837           end
1838   c-----------------------------------------------------------------
```

```
1839           subroutine lusol0 (n, y, x, alu, jlu, ju)
1840           real*8  x(n), y(n), alu(*)
1841           integer n, jlu(*), ju(*)
1842   c-----------------------------------------------------------------
1843   c
1844   c performs a forward followed by a backward solve
1845   c for LU matrix as produced by  ILUT
1846   c
1847   c-----------------------------------------------------------------
1848   c local variables
1849   c
1850           integer i,k
1851   c
1852   c forward solve
1853   c
1854           do 40 i = 1, n
1855             x(i) = y(i)
1856             do 41 k=jlu(i),ju(i)-1
1857                x(i) = x(i) - alu(k)* x(jlu(k))
1858    41       continue
1859    40     continue
1860   c
1861   c   backward solve.
1862   c
1863           do 90 i = n, 1, -1
1864             do 91 k=ju(i),jlu(i+1)-1
```

```
1865                    x(i) = x(i) - alu(k)*x(jlu(k))
1866      91     continue
1867               x(i) = alu(i)*x(i)
1868      90     continue
1869    c
1870           return
1871    c----------------end of lusol0 --------------------------------------
1872    c--------------------------------------------------------------------
1873           end
1874    c--------------------------------------------------------------------



1875           subroutine bsort2 (w, ind, n, ncut)
1876           integer n, ncut, ind(*)
1877           real*8 w(*)
1878    c--------------------------------------------------------------------
1879    c simple bubble sort for getting the ncut largest
1880    c elements in modulus, in array w. ind is sorted accordingly.
1881    c (Ought to be replaced by a more efficient sort especially
1882    c if ncut is not that small).
1883    c--------------------------------------------------------------------
1884    c local variables
1885           logical test
1886           integer i, j, iswp
1887           real*8 wswp
1888    c
1889           i = 1
1890      1    test = .false.
1891           do 2 j = n-1,i,-1
1892               if (abs(w(j+1))  .gt. abs(w(j)) ) then
1893    c---- swap-------------------------------------
1894               wswp = w(j)
1895               w(j) = w(j+1)
1896               w(j+1) = wswp
1897    c---- reorder original ind array accordingly --------
1898               iswp = ind(j)
1899               ind(j) = ind(j+1)
1900               ind(j+1) = iswp
1901    c---- set indicator that sequence is still unsorted--
1902               test = .true.
1903               endif
1904      2    continue
1905           i = i+ 1
1906           if (test .and. i .le. ncut) goto 1
1907    c
1908           return
1909    c----------------end of bsort2 --------------------------------------
1910    c--------------------------------------------------------------------
1911           end



1912           subroutine daxpy(n,t,x,indx,y,indy)
1913           real*8 x(*), y(*), t
1914    c-----------------------------------------------------------------
1915    c does the following operation
```

```
1916      c y <--- y + t * x ,   (replace by the blas routine daxpy )
1917      c indx and indy are supposed to be one here
1918      c------------------------------------------------------------------
1919              do l k=1,n
1920              y(k) = y(k) + x(k)*t
1921      1     continue
1922              return
1923      c-------------- end of daxpy ----------------------------------
1924              end
1925              function ddot(n,x,ix,y,iy)
1926              real*8 ddot, x(*), y(*), t
1927      c------------------------------------------------------------------
1928      c computes the inner product t=(x,y) -- replace by blas routine..
1929      c------------------------------------------------------------------
1930              t = 0.0d0
1931                  do 10 j=1,n
1932                  t = t + x(j)*y(j)
1933      10    continue
1934          ddot=t
1935          return
1936      c******* end of ddot  *****************************************
1937          end
```

```
1938          DOUBLE PRECISION FUNCTION VecMax(YD,Y,N)
1939          DOUBLE PRECISION YD(N), Y(N), TEST
1940          INTEGER N, IMax, ITest, Suspend
1941          LOGICAL ILambda, PrecipitationBegun
1942          COMMON /FLAG/ILambda, PrecipitationBegun, ITest, Suspend, IMax
1943          VecMax = 0.0D0
1944          DO i = 1, N
1945              TEST = ABS(YD(I) / MAX(1.D-6, ABS(Y(I))))
1946              IF(VecMax .LT. TEST) THEN
1947                VecMax = TEST
1948                IMax = i
1949              END IF
1950          END DO
1951          RETURN
1952          END
```

```
1953              subroutine pltmtps (nrow,ncol,mode,ja,ia,title,key,type,
1954      1              job, iounit)
1955      c-------------------------------------------------------------------
1956      c this subroutine creates a 'PS' file for plotting the pattern of
1957      c a sparse matrix stored in general sparse format. It can be used
1958      c for inserting matrix plots in a text. The size of the plot can be
1959      c 7in x 7in or 5 in x 5in ..
1960      c
1961      c Adapted from pltmt in module INOUT by Paul Frederickson. March, 1990
1962      c       + slight modifications by Y. Saad.
1963      c-------------------------------------------------------------------
1964      c nrow  = number of rows in matrix
1965      c
1966      c ncol  = number of columns in matrix
```

```
1967    c
1968    c mode  = integer indicating whether the matrix is stored
1969    c        row-wise (mode = 0) or column-wise (mode=1)
1970    c
1971    c ja    = column indices of nonzero elements when matrix is
1972    c         stored rowise. Row indices if stores column-wise.
1973    c ia    = integer array of containing the pointers to the
1974    c         beginning of the columns in arrays a, ja.
1975    c
1976    c title = character*72 = title of matrix test ( character a*72 ).
1977    c key   = character*8  = key of matrix
1978    c type  = character*3  = type of matrix.
1979    c
1980    c job   = integer. tells pltmt whether or not to reduce the plot.
1981    c          if enabled then the standard size of 7in will be
1982    c          replaced by a 5in plot.
1983    c          job =  0 : do not reduce
1984    c          job =  1 : reduce plot to 5 inches.
1985    c
1986    c iounit = logical unit number where to write the matrix into.
1987    c
1988    c----------------------------------------------------------------
1989    c notes: 1) Plots square as well as rectangular matrices.
1990    c        2) Does not writer a caption yet.
1991    c        3) No bounding box put in yet
1992    c----------------------------------------------------------------
1993            integer ja(*), ia(*)
1994            character key*8,title*72,type*3
1995            real delta
1996    c-------
1997            n = ncol
1998            if (mode .eq. 0) n = nrow
1999            nnz = ia(n+1) - ia(1)
2000            maxdim = max0 (nrow, ncol)
2001            m = 1 + maxdim
2002    c keep this test as in old pltmt (for future changes).
2003            if (mod(job,10) .eq. 1) then
2004              delta = 72*5.0/(2.0+maxdim)
2005            else
2006              delta = 72*7.0/(2.0+maxdim)
2007            endif
2008    c-------
2009            write(iounit,'(A)')'%!PS-Aodbe'
2010            write(iounit,'(A)')' gsave 50 -500 translate'
2011            write(iounit,*) delta, delta, ' scale'
2012            write(iounit,*) ' 0.25 setlinewidth'
2013    c-------
2014            if (mod(job,10) .eq. 1) then
2015              write (iounit,*) ' 23 55 translate'
2016            else
2017              write (iounit,*) ' 2 35 translate'
2018            endif
2019    c-------
2020            write(iounit,*) ' newpath'
2021            write(iounit,*) 0,0,' moveto'
2022            write(iounit,*) m,0,' lineto'
2023            write(iounit,*) m,m,' lineto'
2024            write(iounit,*) 0,m,' lineto'
2025            write(iounit,*) ' closepath stroke'
2026            write(iounit,*) ' 1 1 translate'
```

```
2027            write(iounit,*) ' 0.5 setlinewidth'
2028            write(iounit,*) ' /p {moveto 0 -.25 rmoveto '
2029            write(iounit,*) '       0  .50 rlineto stroke} def'
2030    c
2031    c----------- plotting loop ----------------------------------------
2032    c
2033            do 1 ii=1, n
2034               istart = ia(ii)
2035               ilast  = ia(ii+1)-1
2036               if (mode .ne. 0) then
2037                  do 2 k=istart, ilast
2038                     write(iounit,*) ii-1, nrow-ja(k), ' p'
2039    2          continue
2040               else
2041    c          y = xnrow - real(ii)
2042                  do 3 k=istart, ilast
2043    c              x = real(ja(k)-1)
2044                     write(iounit,*) ja(k)-1, nrow-ii, ' p'
2045    3          continue
2046               endif
2047    1       continue
2048    c--------------------------------------------------------------------
2049    c
2050            write(iounit,*)' showpage grestore'
2051            return
2052    c
2053    c quit if caption not desired.
2054    c      if ( (job/10) .ne. 1)  return
2055    c
2056    c      write(iounit,127) key, type, title
2057    c      write(iounit,130) nrow,ncol,nnz
2058    c 127    format('.sp 4'/'.ll 7i'/'.ps 12'/'.po 0.7i'/'.ce 3'/,
2059    c    *    'Matrix: ',a8,',  Type: ',a3,/,a71)
2060      130    format('Dimension: ',i4,' x ',i4,' Nonzero elements: ',i5)
2061    c      return
2062    c---------------- end of pltmt ----------------------------------
2063            end
```

```
2064        SUBROUTINE PrintMatrix(Matrix, Row, Col, NZ, N)
2065        DOUBLE PRECISION Matrix(NZ)
2066        INTEGER Row(*), Col(*)
2067        INTEGER I, J
2068        WRITE(6,'(20I3)')(Row(i),i = 1,N+1)
2069        WRITE(6,'(20I3)')(Col(i),i = 1,NZ)
2070        DO I = 1, N
2071            WRITE(6,'(10(2X,I4,6X))')(Col(J),J=Row(I),Row(I+1)-1),Row(i)
2072            WRITE(6,'(10G12.4)')(Matrix(J),J=Row(I),Row(I+1)-1)
2073        END DO
2074        RETURN
2075        END
```

```
2076        SUBROUTINE CalculateJ(Y, YOld, DX, DT, N, M, F, Time,
2077      $    Matrix, Row, Col, NZ)
2078        INTEGER N, M, ROW(*), COL(*), IGOOD
2079        DOUBLE PRECISION Y(M), YOLD(M), F(M), DX, DT, Time
2080        DOUBLE PRECISION Temp(M), FTemp(M), DFjDxi, Matrix(*)
2081        CALL CalculateF(Y, YOld, DX, DT, N, M, F, Time, IGOOD)
2082        NZ = 0
2083        DO j = 1, M
2084            ROW(j) = NZ + 1
2085            DO i = 1, M
2086              Temp = Y
2087              Temp(i) = Y(i) + 1.D-8
2088          CALL CalculateF(Temp, YOld, DX, DT, N, M, FTemp,Time,IGOOD)
2089              DFjDxi = (FTemp(j) - F(j)) / 1.D-8
2090              IF(DFjDxi .NE. 0.0D0) THEN
2091                Matrix(NZ+1) = DFjDxi
2092                COL(NZ+1) = i
2093                NZ = NZ + 1
2094              END IF
2095            END DO
2096        END DO
2097        RETURN
2098        END
```

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