

# AEA TECHNOLOGY

## The Initiation of Pitting Corrosion in Metals.

Note for European Study Group with Industry,

Bristol University, April 1992

S.M.Sharland,

Theoretical Studies Department,

AEA Decommissioning & Radwaste.

### Corrosion Processes.

Aqueous corrosion of metals takes many forms, the simplest and best characterised of which is *uniform corrosion*. This is associated with a progressive and evenly distributed dissolution of the metal. Under certain chemical and electrochemical conditions, the process leads to the deposition of an oxide film on the metal. Generally, the rate of corrosion of the metal in this *passive* state is less than that of a bare, *active* metal surface. However, 'flaws' in this film can lead to exposure of small parts of the metal surface to the corrosive environment. In some cases, the passive film can re-form over this area. However, under certain conditions, the bare sites can activate and corrode at a faster rate than the surrounding metal, leading to *pitting corrosion* (a form of *localised corrosion*).

### Electrochemical Reactions in Corrosion.

A simple corrosion cell for a metal in an oxygenated environment is illustrated in figure 1. This shows the generation and consumption of electrons by anodic and cathodic reactions. The rate at which a metal corrodes (related to the corrosion current density,  $i_a$ ) is determined by the kinetics of these reactions, which depend on the chemical environment of the metal and the electrostatic potentials in the system. The dependence of reaction rate on electrode potential,  $E$ , is commonly illustrated using an Evans diagram. (figure 2).

The potential and corrosion current density of the system,  $E_{\text{corr}}$  and  $i_{\text{corr}}$ , are marked by the intersection of the anodic and cathodic reaction curves. At this point, the total number of electrons generated by the metal dissolution balances exactly the number consumed by the cathodic reduction process. The sites of the reactions may be less than a millimetre apart, as in uniform corrosion, or may be separated, as in localised corrosion. In the latter case, the resistance of the solution to the flow of charge from the site of the anodic reaction to that of the cathodic reaction contributes to the overall determination of the corrosion rate at the active site.

### Passivation of Metal Surfaces.

The formation of a passive film on a metal surface affects the kinetics of the anodic dissolution reaction. A simplified view of the situation is illustrated in the Evans diagram in Figure 3. As the potential is increased, the current density reaches a maximum at the point where an oxide film precipitates. For a range of increasing potential, the metal is then 'screened' from the solution by the film, and the current density is effectively independent of metal potential. Above a certain value of the potential, the metal is susceptible to localised corrosion.

There are a number of parameters used commonly in discussion of the initiation of localised corrosion:

- 1) The pitting potential,  $E_p$ , i.e. the electrical potential of the metal above which pitting corrosion can be sustained (although below this, unstable pits may form).
- 2) The passivation potential,  $E_{\text{pass}}$ , i.e. the potential at which the passive film forms.
- 3) The activation potential,  $E_{\text{act}}$ , i.e. the potential at which the passive film disappears.

These are illustrated in figure 3. The potential is the effective potential driving the corrosion reaction. For localised corrosion, the inside of the pit will be in the active state i.e.  $E < E_{act}$ , whereas the metal outside the pit will be in a passive state, i.e.  $E > E_{pass}$ .

### **The Initiation of Localised Corrosion.**

The initiation of pitting corrosion in many metals is regarded generally as a random event. Many of the dynamic measures of the process, such as the corrosion current, exhibit apparently random fluctuations. For example, many investigators of stainless steel behaviour in chloride solutions have observed the occurrence of anodic current transients below the pitting potential. These transients have been shown to be caused by the nucleation, temporary growth and repassivation of individual micropits. Such dynamical behaviour make the physical and chemical mechanisms controlling the process extremely difficult to resolve. A number of studies using time-series analysis techniques on the measured corrosion currents have been performed to investigate the underlying dynamics of the pit-initiation process. These have suggested that the dynamics are chaotic and controlled by a small number of variables.

### Mechanistic Interpretation.

Despite the seemingly complex dynamics, a number of clear stages can be recognised in the pit initiation process:

- 1) The metal surface is covered by an oxide film, and the charge generated by the metal dissolution reaction is consumed by the cathodic reactions (for example, oxygen reduction).

- 2) A small area of the surface activates, and the local potential driving the corrosion reactions drops. A current flows between this active site and the surrounding passive surface. (Chloride ions play an important role in film breakdown, although the microscopic mechanisms are not well understood).
- 3) Either processes act to prevent repassivation of the exposed patch, and a localised corrosion site is established (stable pitting), or the area re-passivates, and the potential increases (unstable pitting).

Two types of experiments have been carried out to investigate the initiation phase through the time series. In the first, the metal is kept under potentiostatic control (i.e. kept at a constant potential) and current oscillations are measured, and in the second, the total current passing from the metal is kept constant and the potential is measured (galvanostatic control). The two are clearly related; the former has been studied more widely, but it may be easier to derive a mechanistic model of the second system.

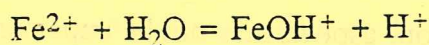
#### Potentiostatic System.

Figure 4 shows a typical time series associated with unstable pitting events, in 304 stainless steel, polarised to 200 mV (vs saturated calomel electrode(SCE)) and exposed to a solution containing 1000 ppm  $\text{Cl}^-$ . The time series is characterised by a series of increases in current, relating to a local activation of the metal surface, followed by a repassivation corresponding to the decrease in current. Occasionally, the rise in current is quite large, before the repassivation occurs. In some cases, the peaks and troughs are superimposed, suggesting that several sites on the metal surface are become active simultaneously. It is thought that these initiation sites may be associated with inclusions in the metal, i.e. points where the passive film is weaker.

The dynamics of pit initiation (at a single site) may be regarded as having a fixed point in some phase space, and some perturbation to the system leads to the growth of the passive current. This would perhaps correspond to a linear instability of the fixed point, and may be considered a local problem, if we assume that the pits are independent. The next stage seems to be where the current 'saturates' and then decreases. Finally, the surface repassivates completely and the pit 'dies'. This may be a local process similar to the birth stage.

Some of the important processes and assumptions that may be necessary to derive a representation of this system are as follows:

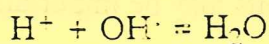
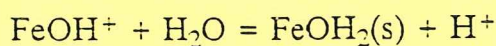
- 1) The pits behave independently.
- 2) A detailed mechanistic description of the film breakdown process is not necessary.
- 3) Solution chemistry may be important, for example, if we assume equilibrium for the reaction,



then

$$\frac{[\text{FeOH}^+][\text{H}^+]}{[\text{Fe}^{2+}]} = K$$

Other chemical reactions in the system include,



plus chromium hydrolysis reactions for stainless steel.

- 4) For active corrosion, the corrosion current density depends on the exponential of the potential and an ohmic resistance in solution.

- 5) Transport of aqueous species away from the metal surface, by diffusion, may be important, since this will affect the local potential in solution.

The paper by Talbot, Oriani and DiCarlo investigates the stability of a number of models of the passivation and activation of metal surfaces, based on some of the processes in 3) - 5). Although, these are not directed at pitting corrosion, the approach may be relevant.

### Galvanostatic System.

The potential oscillations from the galvanostatic experiments are fairly different in nature. A singular value decomposition analysis of this time series suggests that the attractor does not have such a clear fixed point.

Some of the important processes and assumptions that may be necessary to derive a representation of this system are as follows:

- 1) The spatial (i.e. diffusion) aspects may not be important in this problem, but the pits interact electrically.
- 2) The total current flow in the system remains fixed, but the local current density will change, both as parts of the surface activate, and area of active surface increases as micropits grow.
- 3) The shape of the growing pits may be important. In the experiments, they are observed to start as hemispherical.

A simple representation of the problem which may provide the basis for a fuller description of the process is as follows:

The metal surface acts as a capacitor, and assuming a low value for the potential initially, as the current is applied, the potential rises until it reaches a high enough value for a pit to nucleate. The pit nucleates and draws a current  $I_{\text{pit}}$  ( $< I_{\text{applied}}$  initially), which must increase to keep the pit stable. The potential increase slows down and turns over when all the current is drawn by the pit.

$$\frac{dE}{dt} = C (I_{\text{applied}} - I_{\text{pit}})$$

where  $C$  is a capacitance term. The potential driving the pit growth is also related to the local current density.

$$E - E_0 = A \log (i_{\text{pit}}/i_0) + B a i_{\text{pit}}$$

where  $a$  is the pit depth and  $A$  and  $B$  are constants. It may be possible to ignore the first term on the right hand side and assume ohmic control. The current density is dependent on the rate of change in size of the pit, so

$$M \frac{da}{dt} = i_{\text{pit}}$$

The pit will repassivate when the product  $a i_{\text{pit}}$  drops below a critical value, and the potential will rise linearly again, as the capacitor recharges.

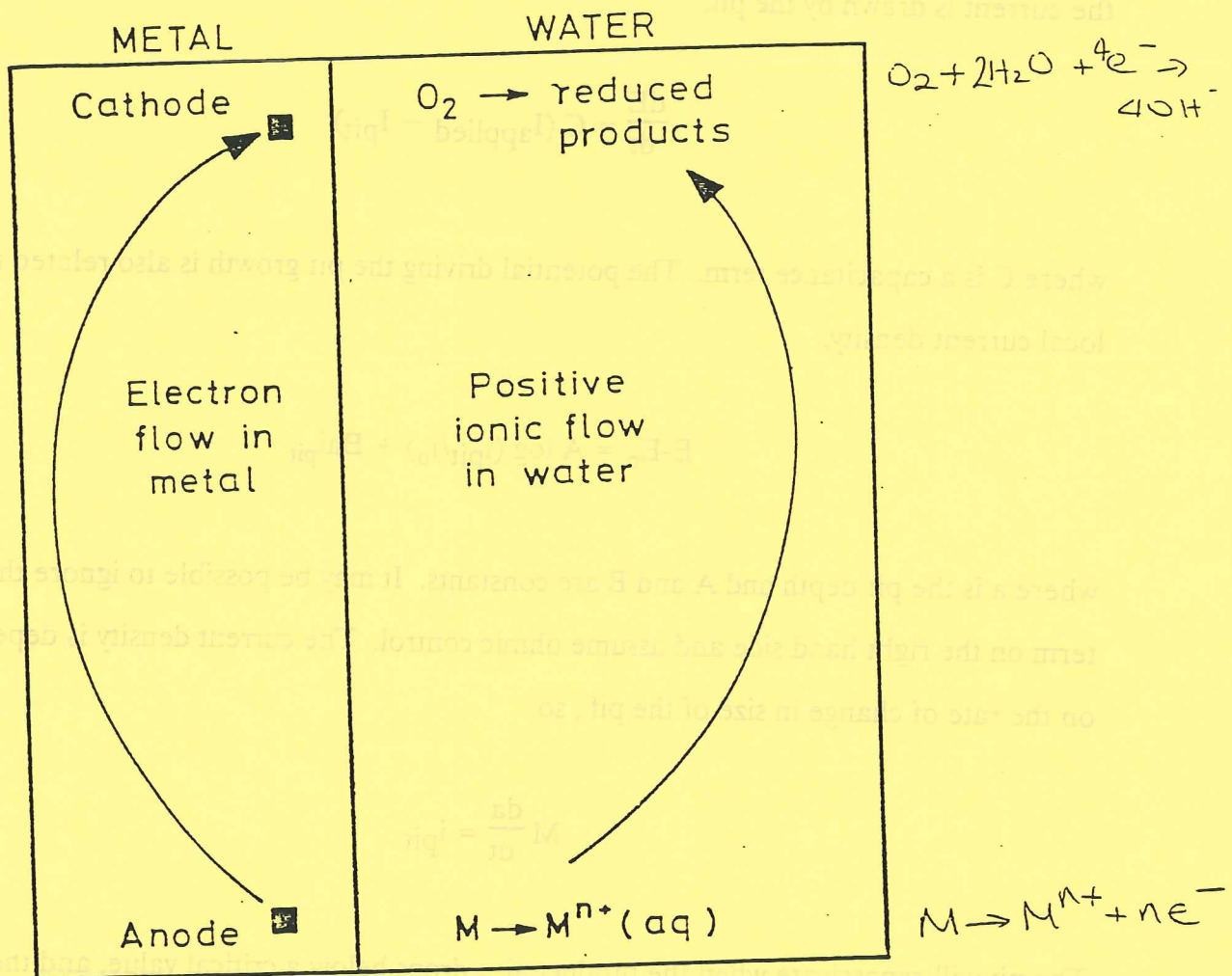


Figure 1 Schematic illustration of charge flow during aqueous corrosion.



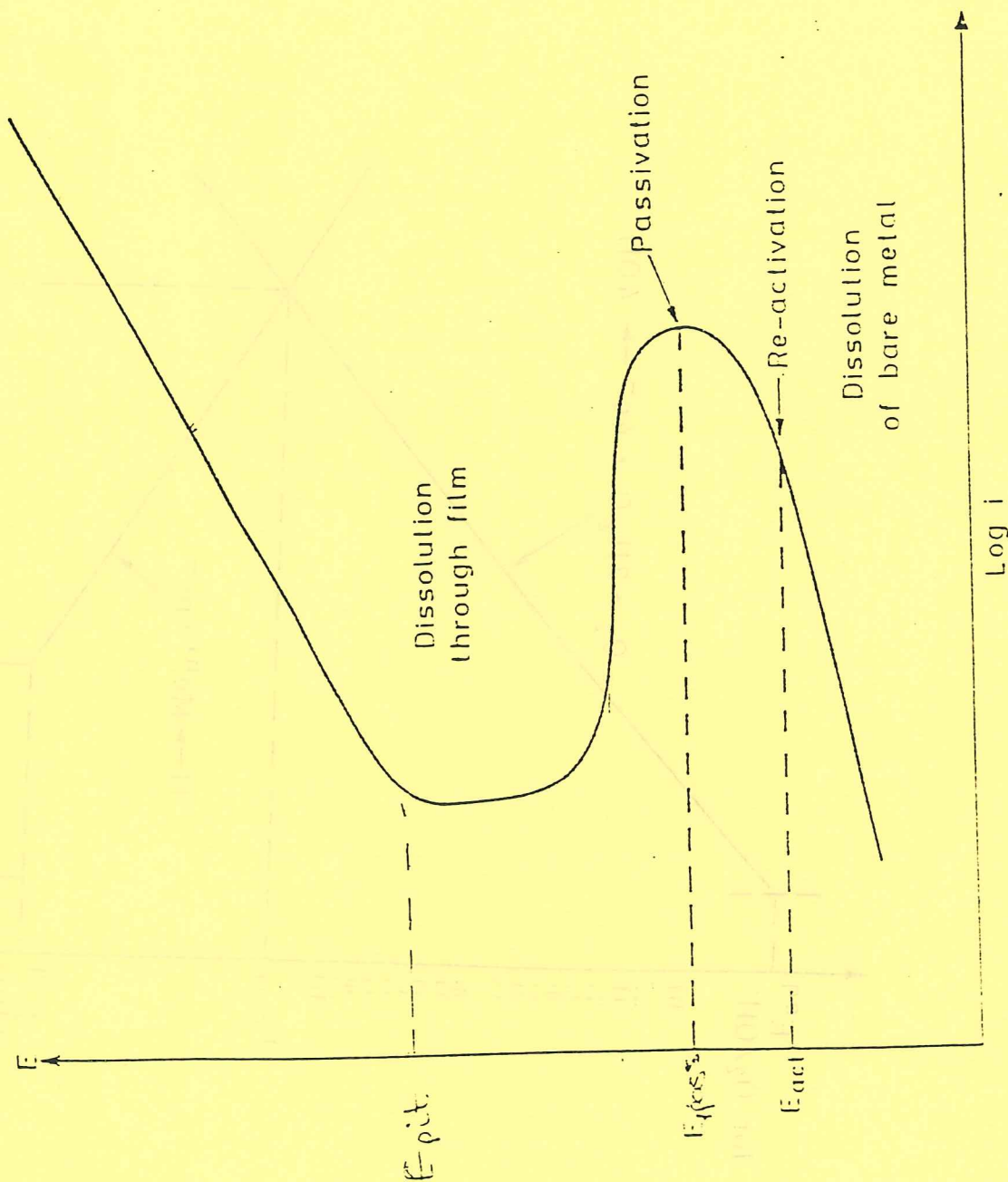


Figure 3 Schematic anodic polarisation curve.

Figure 3. Representative electrochemical characteristics

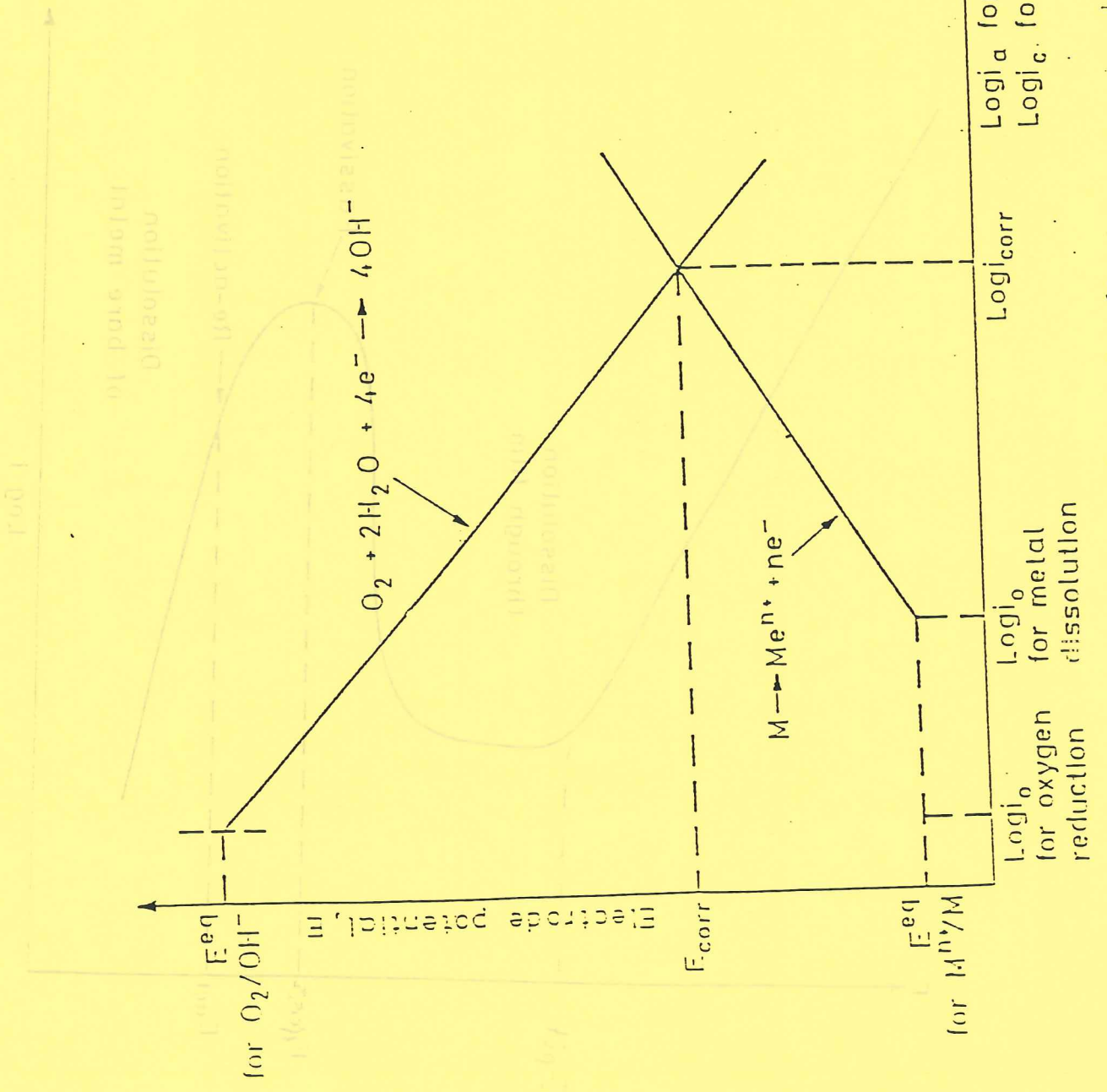


Figure 2. A typical Evans diagram for corrosion of iron.

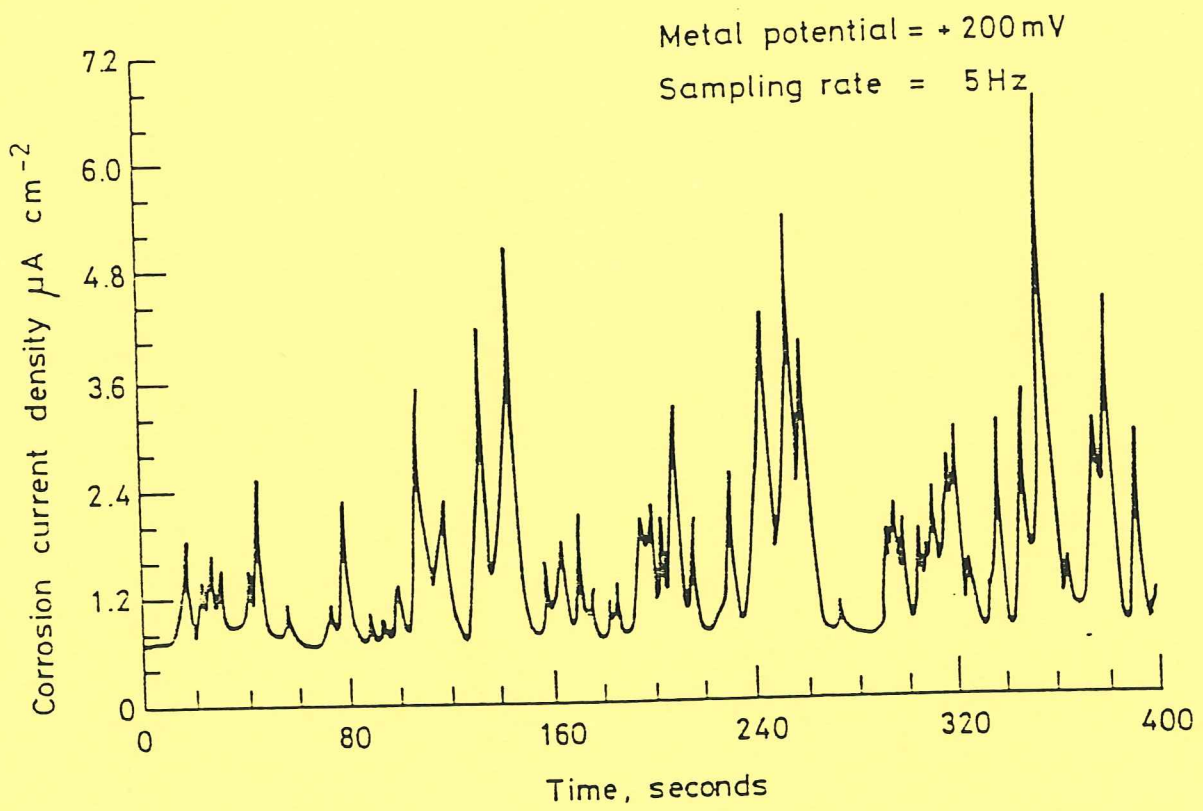


FIG. 4

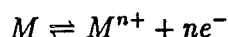


# Pitting Corrosion in Metals

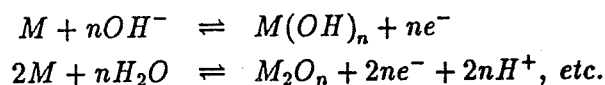
September 24, 1992

## 1 Introduction

The problem brought to the Study Group by AEA is to develop a model or mechanistic explanation of the chaotic oscillations observed in the current/voltage during pitting corrosion of a stainless-steel anode immersed in an electrolyte. At low anode potentials the anode undergoes rapid 'active' corrosion with metal ions passing into solution according to



At larger anode potentials the solution is unable to absorb the large flux of  $M^{n+}$  ions and various precipitation reactions cause the formation of a protective 'passive' layer of oxide or hydroxide, which greatly reduces the rate of corrosion. Possible reactions in this regime are



It should be noted that passivation is favoured by basic conditions and activation is favoured by acidic conditions. At still larger anode potentials and in the presence of aggressive ions (such as  $Cl^{-}$ ) the corrosion becomes concentrated in anodic pits in which an acidic environment maintains active corrosion, while the rest of the electrode is passive, more basic and cathodic. The oscillations which AEA observed in this regime suggest that an active pit is unstable, either nucleating, growing and dying, or flipping between active and passive states according to some dynamical process.

From Figure 4 of AEA's report, it estimated that the oscillations on a  $5 \text{ cm}^2$  electrode have a typical magnitude of  $1 \mu A \text{ cm}^{-2}$  and duration 1 s. Thus each oscillation corresponds to a charge transfer  $Q = 5 \mu C$ . If this charge represents oscillation of an  $n$ -valent metal of density  $\rho$  and molecular weight  $M$  then a volume  $QM/nF\rho$  is corroded from the anode, where  $F$  is Faraday's constant. For  $Fe \rightarrow Fe^{2+}$  this volume is  $1.5 \times 10^{-10} \text{ cm}^3$  or  $150 \mu m^3$ , which represents a good-sized pit!

This calculation suggests the questions: (1) Is each current peak associated with only one pit? (2) Do consecutive peaks correspond to different pits and if so what links the passivation of one pit to the activation of another in the potentiostatic case? (3) What would be observed on a larger electrode (more pits) or a smaller electrode (perhaps with only one pit possible)?

Two follow-up calculations are recommended: (1) A more careful look at the time-series to get a better estimate of the time-scale and magnitude of current fluctuations; (2) Comparison with results for anodes of different sizes. In particular, the fluctuation/background current ratio contains information about the relative importance of pit and leakage processes.

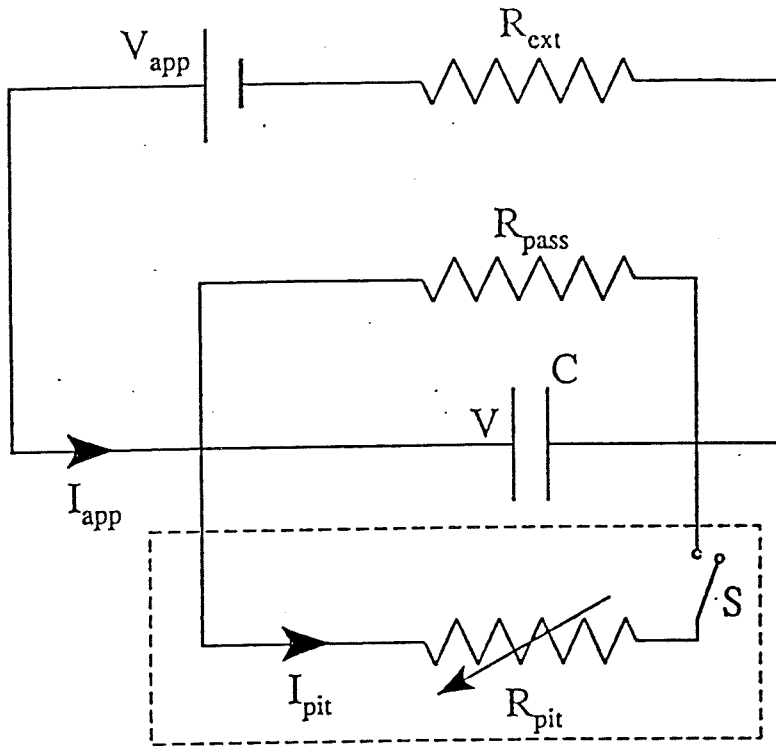


Figure 1: An electrical representation of the anode and the external circuitry. The single pit (dashed box) may be repeated many times in parallel for multiple pits

## 2 The 'Newman' model

A simple representation of the electric circuit is shown in Figure 1. Either the applied voltage  $V_{app}$  (potentiostatic control) or the applied current  $I_{app}$  (galvanostatic control) is fixed at a value of order  $0.2V$  or  $10\mu A$ .  $R_{ext}$  represents the resistance of the external circuit (about  $10\Omega$ , chiefly from the electrolyte) and  $R_{pass}$  the large resistance of the passive area of the anode. The double layer on the anode has capacitance  $C$  and potential  $V$ . A single active/passive pit corresponds to the switch  $S$  and variable nonlinear resistor  $R_{pit}$  (dashed box); in practice, there will be a number of such pits in parallel.

AEA suggests  $C = 10^{-4} F/cm^2$  (though a parallel-plate model of the passive layer with thickness  $h = 10 nm$  implies a lower value for the capacitance/area given by  $\epsilon/h \simeq 3 \times 10^{-6} F cm^{-2}$ ). The charging time of the double layer is of order  $CV_{app}/I_{app} = 2 s$  for galvanostatic control or  $CR_{ext} = 10^{-3} s$  for potentiostatic control. (The large difference between these times is a little odd and suggests that galvanostatic control needs to be very sensitive in order to control the current through the small resistance  $R_{ext}$ .)

In the galvanostatic case, if  $S$  closes, corresponding to activation of the pit, then the discharge time is of order  $CR_{pit}$ . This is  $1 s$  for a  $1\mu m$  pit using the formula suggested by AEA,  $R_{pit} = B/2\pi a$ , where  $B = 10^{-1} \Omega m$  and  $a$  is the radius of the pit. The discharge current is of order  $V_{app}/R_{pit} \simeq 20 \mu A$ , which may be a bit large due to the neglect of the overpotential in the expression for  $R_{pit}$ . However, this sort of RC-circuit does seem to give the right order-of-magnitude timescale and current fluctuations.

The 'Newman' model is based on these ideas together with the assumptions that: (1) the current through  $R_{pass}$  can be neglected; (2)  $S$  closes when  $V$  increases to a critical value  $V_{act}$ ; (3) the resistance  $R_{pit}$  is represented by the relation

$$V - V_0 = A \log(i_{pit}/i_0) + \frac{BI_{pit}}{2\pi a}$$

where  $i_{pit}$  is the current density and  $A$ ,  $i_0$  and  $B$  are constants; (4) the pit passivates if  $V$  decreases

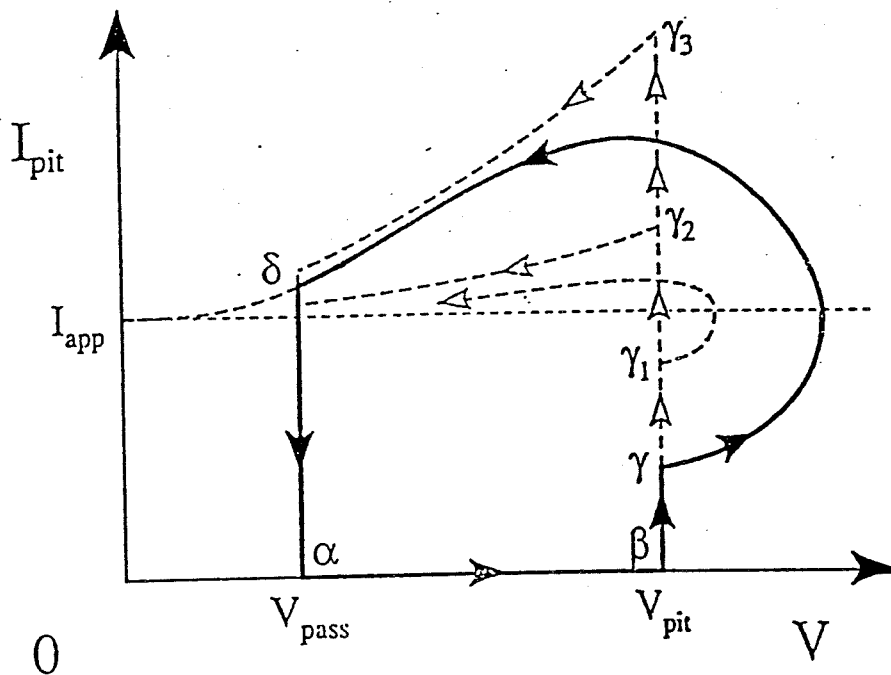


Figure 2: Phase portrait for the Newman model.  $\alpha\beta\gamma\delta$  represents a possible oscillation for a given pit size.

to a critical value  $V_{pass}$ .

With these assumptions we can obtain oscillations in the galvanostatic case, as shown in Figure 2:  $\alpha\beta$  represents the charging of the double layer;  $\beta\gamma$  instantaneous initiation of a pit;  $\gamma\delta$  the growth of the pit and decrease in  $R_{pit}$  that eventually must lead to  $I_{pit} \rightarrow I_{app}$  and a decrease in  $V$ ;  $\delta\alpha$  the instantaneous repassivation of the pit. However, there are serious problems with this model:

1. The point  $\gamma$  and subsequent trajectory  $\gamma\delta$  depend on the initial pit size, which is unknown and cannot be predicted within this model;  $\gamma_1$  to  $\gamma_3$  represent alternative solutions for an increasing range of pit sizes. This is more likely to give random oscillations than chaotic.
2. If the initial pit size is small and  $V$  continues to rise (e.g.  $\gamma\delta$  or  $\gamma_1\delta$ ), why don't other pits also fire?
3. Under potentiostatic control  $V$  would remain close to  $V_{app}$  and, consequently,  $a$  and  $I_{pit}$  would increase monotonically while  $R_{pit}$  decreased monotonically; this provides no mechanism for oscillation.
4. The model provides no mechanistic explanation for activation and repassivation.

We conclude that, while the 'Newman' model may give oscillations, it does not answer the questions posed by AEA.

### 3 A field theory for pit corrosion

This model considers two aspects of the physical problem which were thought to be central to the oscillations that occur in both the galvanostatic and the potentiostatic situations. The two aspects are first the ionization of metal atoms at the metal/electrolyte interface which erodes the metal

surface. The second aspect is the generation of protons by the reaction of the ionized metal atoms and the surrounding water which makes the electrolyte very acidic and diffusion of these protons is required to reduce the acidity to a level where a passive layer can form. The model does not at present consider how the passive layer breaks down, how the passive layer is removed or how it is regrown. We presume all these latter processes can be characterized by some critical level of acidity or electric field and that the processes are so rapid that they play no subsequent part in the dynamics of the oscillations.

### 3.1 Mathematical Model

Consider first the problem of the ionization of the metal ions into the electrolyte bath. There is a very narrow electric double layer that forms at the metal/electrolyte interface which we shall idealize by a potential jump from the electrolyte to the metal surface. The metal is taken as a perfect conductor at a uniform potential  $V(t)$ . The electrolyte has many ionized species in it (here we take species  $i = 1$  to  $n$  each with charge  $Z_i$  and concentration  $C_i$ ) and away from the electric double layer the equations governing their motion are first Poisson's equation with charge neutrality

$$0 = \sum_1^n Z_i C_i$$

and a drift diffusion equation for each species

$$\frac{\partial C_i}{\partial t} = D_i \nabla \cdot \left( \nabla C_i + \left( \frac{q}{kT} \right) Z_i C_i \nabla \phi \right)$$

where  $D_i$  is the species diffusivity,  $kT$  is the thermal voltage (about  $0.025V$  at room temperature, and  $\phi$  is the electric potential. In the usual way we can multiply each species equation by  $Z_i$ , sum them and use the Poisson equation to get

$$\nabla^2 \phi = 0 .$$

We shall also make the usual assumption that the species of interest here ( $Fe^{++}$ ) occurs in such small concentration compared to the common salts in the electrolyte that the electric current  $i$  is given by

$$i = -\sigma \nabla \phi$$

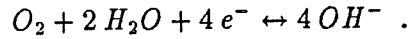
where  $\sigma$ , the conductivity of the solution, can be taken as constant.

The problem to be solved is therefore Laplace's equation in the electrolyte with the potential on the metal specified as  $V(t)$  and the potential at the 2<sup>nd</sup> electrode at 0. To complete the model we must consider the resulting boundary conditions in the electrolyte near at the 2<sup>nd</sup> electrode, the boundary conditions in the electrolyte near the metal surface where there is no passive layer and the boundary conditions near the passive layer. These boundary conditions are determined by the behaviour of any electric double layer near the interface, the reactions required to ionize various species and the dielectric properties of the passive layer. We consider the various situations and start with a discussion of the 2<sup>nd</sup> electrode.

The 2<sup>nd</sup> electrode



At the 2<sup>nd</sup> electrode the main source of current is due to the ionization of the water generating hydroxal ions by the reaction



For the situations of interest we can consider the reaction rate to depend only on the local potential jump across the electric double layer and this dependence is of Arrhenius type. Hence the current  $i$  leaving the 2<sup>nd</sup> electrode can be expressed as

$$i \cdot n = k_e \exp((\phi - 0)/E_e)$$

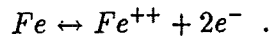
where  $\phi$  is the potential in the electrolyte just away from the electric double layer and  $k_e$  is a rate constant and  $E_e$  an activation energy. This expression excludes the physically observed phenomena that there is a critical potential jump or current below which the reaction does not occur. It may be therefore that the boundary condition should be of the form

$$i \cdot n - i_{H_2O-crit} = k_e \exp((\phi - 0)/E_e)$$

and this is the form used here.

#### The metal surface without a passive layer

At the metal surface where there is no passive layer the main source of current is due to the ionization of the metal by the reaction



For the situations of interest we can again consider the reaction rate to depend only on the local potential jump across the electric double layer and this dependence is of Arrhenius type. Hence the current density leaving the metal surface can be expressed as

$$i \cdot n = k_m \exp((V(t) - \phi)/E_m)$$

where  $\phi$  is the potential in the electrolyte just away from the electric double layer and  $k_m$  is a rate constant and  $E_m$  an activation energy. In a similar way to that mentioned above this condition will actually be considered in the form

$$i \cdot n - i_{Fe-crit} = k_m \exp((V(t) - \phi)/E_m)$$

The various constants in these expression can be determined from the Evans diagram which is valid for the case where the current from the 2<sup>nd</sup> electrode equals that from the metal surface without passive layer and where the two potentials in these expressions are taken equal (equivalent to taking very large conductivity in the electrolyte).

In addition to the electrical boundary condition we also note that because metal atoms are being removed from the surface and put into solution it is necessary to consider conservation of mass. This requires that for every atom that is ionized and put into solution the metal surface will retreat by an atomic spacing. Taking a macroscopic view of the surface this requires the normal velocity of the metal surface,  $v$ , is proportional to the current leaving the surface so that

$$v = -K i \cdot n$$

## The passive layer

At parts of the metal surface where there is a passive layer we must consider two aspects of the behaviour. Firstly there is a transfer of charge from the metal into the passive layer, transport of this charge through the passive layer and transfer of the charge into ionic species in the electrolyte. Secondly the passive layer acts as a very good dielectric and charge can build up within the thin electric double layer. We wish to write boundary conditions relevant to the behaviour of the potential away from the passive layer and the electric double layer that account for these phenomena without the model becoming too complicated. The charge transport is complicated and there is uncertainty as to the role of metal ions in carrying charge across the passive layer. For the purpose of this model the charge transport is taken to be adequately modelled by taking the current proportional to the potential drop from the metal surface to the electrolyte just outside any electric double layer. In practice this relation will be nonlinear but this simplification is used here as is the fact that the passive layer has a very high resistance compared to the electrolyte bath. To model the charge build up within the electric double layer a simple model where the layer acts as a capacitor is adopted. The resulting boundary condition is

$$i \cdot n = \frac{1}{R}(\phi - V(t)) + C \frac{d}{dt}(\phi - V(t))$$

where  $R$  is the layer resistivity and  $C$  is the layer capacitance.

The electrical problem also requires a condition which models the behaviour of the external circuit. The two separate cases usually considered are either

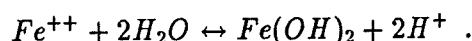
$$\text{Galvanostatic : } \int_S i \cdot n \, dS = I$$

or

$$\text{Potentiostatic : } V(t) = V$$

where  $I$  and  $V$  are constant and  $S$  is the entire surface of the electrode.

When the  $Fe^{++}$  ions go into solution they react with the water (and also hydroxal ions) in the reaction



The interest is then in the diffusion of the protons away as the high acidity appears to create conditions where the passive layer cannot be formed. To keep the model simple a number of sweeping assumptions were made. First the reaction was taken to be sufficiently rapid that the  $Fe^{++}$  leaving the surface created a number flux of protons of twice the size (this will obviously not be strictly valid since the reaction takes time to occur and may actually approach equilibrium, but is adopted here). Secondly the reaction creates  $Fe(OH)_2$  which precipitates from the solution. Experimental evidence indicates this may form a porous shell around the corrosion pit but here we do not consider either the formation, or behaviour of any of this precipitate. Thirdly the high acidity may dissolve some of the passive layer near the pit and since the behaviour of this passive remains relatively unknown we presume it is removed so that as the pit grows the edge of the passive layer retreats with the pit edge (there may be situations where the passive retreats more slowly creating a partially covered pit, as in electrical etching, or perhaps where the passive layer is removed from unpitted parts of the metal surface). Finally we presume that at some critical level of acidity the precipitating  $Fe(OH)_2$  can form a passive layer on the metal surface (this is similar to the critical value of  $a_{pit}$  used in other simulations to determine growth of a passive layer).

The equation for the motion of the number density,  $C_H$ , of protons is the same as any other ion

$$\frac{\partial C_H}{\partial t} = D_H \nabla \cdot \left( \nabla C_H + \left( \frac{q}{kT} \right) C_H \nabla \phi \right)$$

and using the assumptions outlined above the boundary conditions are that on the passive layer

$$\left( \nabla C_H + \left( \frac{q}{kT} \right) C_H \nabla \phi \right) \cdot n = 0$$

on the bare metal surface

$$D_H \left( \nabla C_H + \left( \frac{q}{kT} \right) C_H \nabla \phi \right) \cdot n = 2i \cdot n$$

The simple model of the corrosion process is completed by specifying a condition for the start of a pitting event and by making some assumption about the passive layer concerning its properties as it forms. In order to make the model simple very simple criteria were used consisting of a critical field strength within the passive layer creating a pitting event at a point (equivalent to the pitting potential  $E_p$  used elsewhere), and secondly by assuming the passive layer gains its resistive and capacitive properties as soon as it forms. It is also assumed that it is not necessary to consider how the passive layer grows thicker or how its resistive and capacitive properties change if it does grow thicker. This then completes the model.

The problem to be solved is:

$$\nabla^2 \phi = 0 \quad .$$

$$i = -\sigma \nabla \phi$$

$$\frac{\partial C_H}{\partial t} = D_H \nabla \cdot \left( \nabla C_H + \left( \frac{q}{kT} \right) C_H \nabla \phi \right)$$

on the 2<sup>nd</sup> electrode

$$i \cdot n - i_{H_2O-crit} = k_e \exp((\phi - 0)/E_e)$$

$$\left( \nabla C_H + \left( \frac{q}{kT} \right) C_H \nabla \phi \right) \cdot n = 0$$

near the metal surface without a passive layer

$$i \cdot n - i_{Fe-crit} = k_m \exp((V(t) - \phi)/E_m)$$

$$v = -K i \cdot n$$

$$D_H \left( \nabla C_H + \left( \frac{q}{kT} \right) C_H \nabla \phi \right) \cdot n = 2i \cdot n$$

near the metal surface with a passive layer

$$i \cdot n = \frac{1}{R} (\phi - V(t)) + C \frac{d}{dt} (\phi - V(t))$$

$$\left( \nabla C_H + \left( \frac{q}{kT} \right) C_H \nabla \phi \right) \cdot n = 0$$

and either

$$\text{Galvanostatic : } \int_S i \cdot n \, dS = I$$

or

$$\text{Potentiostatic : } V(t) = V$$

The first pit starts at a random position and grows until the proton concentration at the surface within the pit decays to a specified level when the whole surface is then taken to become passive. The surface remains passive until again a new pit forms. It is assumed for simplicity that the next pit forms away from the existing pit since otherwise this would make the geometry awkward for numerical simulation. However, in practice it is expected that the next pit will form near the first pit since that is where the passive layer will be thinnest and most easily broken.

### 3.2 Initial analysis of the model

The model described above can be studied to determine some of the overall characteristics of the solution. In particular it is of interest to determine if the model can give the oscillations seen either in the potential  $V(t)$  during galvanostatic experiments and in the total current  $\int_S i \cdot n \, dS$  during potentiostatic experiments.

As a start to the analysis the electrical problem was considered with no dependence on the resulting proton distribution. The passive layer is taken as initially complete and the charge over it is taken as uniform. A pit is then initiated at a particular point and we seek to describe development. The scale of the problem is the typical pit size (1 micron) so this is the natural scale of the problem. Since the governing equation is Laplace's equation the problem is localized to the pit vicinity. The problem is therefore Laplace's equation in the upper half plane plus the pit. The boundary condition at infinity is that the potential tend to the potential at the electrolyte side of the 2<sup>nd</sup> electrode. The boundary conditions on the passive layer and the active pit are as described above. An inspection of the size of the terms showed that the passive layer resistance was very large, the passive layer capacitance was very small. Hence these currents are only important in determining the potential  $V(T)$  on the electrode since only then must we consider the ratio of the size of the pit to the size of the whole electrode for the galvanostatic case. In the potentiostatic case things are much easier as  $V(t)$  is known. A numerical solution of this moving boundary problem has yet to be performed.

A brief inspection of the problem shows that for short times the pit dimensions grow linearly (we expect it to be hemispherical) with the total flux of ferrous ions from the pit therefore increasing quadratically with time. This fits in well with the expectation that the diffusion of protons away will, at least for these short times, be unable to prevent the acidity level in the pit from rising rapidly. For much longer times the behaviour is less well understood. If there is no dissolution current (ie.  $i_{Fe-crit} = 0$ ) then the pit growth rate might be expected to become like  $(t \ln t)^{1/3}$  which sends the ferrous ion flux to a constant. This behaviour would unfortunately not allow the acidity level to reduce by diffusion. It was therefore seen as essential that the model include the dissolution current since then the ferrous ion flux might tend to zero at large times and the diffusion of protons could then reduce the acidity levels sufficiently for a passive layer to form.

It remains for the model to be solved numerically and for a more careful examination of the implications of the model to be extracted. There has also considerable simplifications made in the model and this may have excluded certain crucial physical mechanisms in the oscillation production.

## 4 Reaction-diffusion models

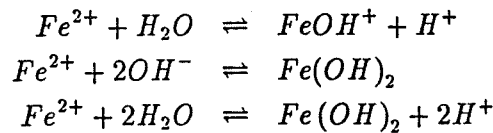
The key observations that stable pits remain active because they are more acidic and that passive layers are formed by insoluble precipitates suggest that we must consider the chemistry and ionic transport. A general formulation for the concentrations  $C_i$  uses

$$\frac{\partial C_i}{\partial t} = D_i \left\{ \nabla^2 C_i + \frac{n_i F}{RT} \nabla(C_i \nabla \phi) \right\} + R_i$$

$$\epsilon \nabla^2 \phi = \sum n_i C_i$$

together with boundary conditions on  $\phi$ , the flux of ions at the electrodes and the total number of ions in solution, and with known reaction terms  $R_i$ .

For the system brought to the Study Group, the electrodes are sources of  $Fe^{2+}$  and  $OH^-$ . Key reactions are



Given the constraint that the well-conducting electrolyte remains electrically neutral, a minimal set of species is likely to be  $Fe^{2+}$ ,  $Cl^-$ ,  $H^+$ ,  $OH^-$ ! (the first two representing, respectively, acidification and precipitation). There is also a danger that, in order to obtain the hysteresis implicit in an active/passive cycle, it will be necessary to include reaction/precipitation kinetics to perturb the system away from marginal solubility. Without these kinetics the system will hover at the active/passive boundary.

## 5 Generalisations of the Newman model

In this section we collect some ideas generated in discussions subsequent to the Study group.

### 5.1 Quasi-static generalisations of the Newman model

Here we are still assuming that all pits are hemispherical. However, it is unsatisfactory to have  $a$ , the pit radius as a dependent variable. In this subsection we restrict ourselves to a single fully developed pit, the size of which changes very slowly on the time scale of the observed oscillations. Then to get interesting dynamics, one has to consider the chemistry more closely. There are many possibilities.

#### 5.1.1 A salt-formation model

This model involves the following three variables: metal ion concentration, chloride ion concentration, and passive surface fraction. We consider the potentiostatic case.

For the metal ion (of concentration  $m$ ) we have:  $dm/dt =$  release from the surface  $-$  leakage out of the pit  $+ salt dissolution - salt precipitation$ . For the chloride ion (of concentration  $c$ ):  $dc/dt =$   $-$  leakage out of the pit  $+ electromigration + salt dissolution - salt precipitation$ . For the passive

portion of the pit surface,  $\theta$ ,  $d\theta/dt$  is positive if  $E_{Flade} < E_{appl}$  and negative if  $E_{Flade} > E_{appl}$ , which is what we retain from the Franck–FitzHugh model. Next we need some instantaneous relations. Below  $k_i$  denote various constants. We assume that both the corrosion current density  $i$  and the Flade potential can be read from the potentiostatic anodic polarization curves, which means that

$$E_{Flade} = E_{Flade}^0 + k_1 \log \frac{c}{c_0},$$

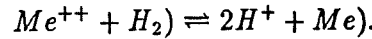
and something like

$$i = k_2 e^{k_3 c},$$

or some other monotone dependence. The release rate of the metal ions is proportional to  $i(1 - \theta)$ . Leakage rates are given by Fick's law. Electromigration rate for chloride is (?) proportional to  $m$ . It is not at all clear how to write the salt formation and dissolution terms. One has to take into account the fact the solutions are very highly concentrated. The correct formulation will have to involve the Becker–Döring formalism.

### 5.1.2 A proton-driven galvanostatic model

Here we use the notation of the paper of Sazou and Pagitsou (Electrochimica Acta, 36(8), 1301-1308 (1991)).  $H(\cdot)$  is the Heaviside step function.  $k_+$  and  $k_-$  denote, respectively, the forward and backward rates of the reaction



If we assume that

- the concentration of the metal ions is proportional to  $ai$ ,
- $E - E^0 = Bai$ , as in the Newman model,

we have the following equations for the variables  $h$  (proton concentration),  $\theta$ , and  $E$  in a single active pit of radius  $a$ :

$$\begin{aligned} \frac{dh}{dt} &= k_+ \frac{E}{B} - k_h - k_d(h - h_0), \\ \frac{d\theta}{dt} &= k_f k_g (\theta + (1 - 2\theta)H(E - E_{Flade}))(E - E_{Flade}), \\ \frac{dE}{dt} &= \frac{1}{C} (I_{appl} - \frac{2\pi a}{B} (1 - \theta)i). \end{aligned}$$

The Flade potential depends on  $h$  according to

$$E_{Flade} = E_{Flade}^0 + \beta \log \frac{h}{h_0}.$$

Thus an increase in current will result in an increase in acidity, which will cause the Flade potential to rise, which causes the active surface fraction to grow, which will cause  $I_{pit}$  to grow, which will cause  $E$  to drop, and thus  $i$  will also fall.

## 5.2 An integro-differential generalization of the Newman model

Another idea is to assume that  $x \equiv a$ , the radius of a hemispherical pit, is an independent variable. That is, we assume that it possible to define a function  $T(x, t)$ , such that  $T(x, t)\delta x$  measures the number of pits of sizes in the interval  $(x, x + \delta x)$  at time  $t$ . The population of pits consists of two sub-populations, of active and passive pits, with densities  $A(x, t)$  and  $P(x, t)$ , respectively. Furthermore, we assume that the instantaneous transition probabilities (activation and passivation probabilities)  $p_A(x, t)$  and  $p_P(x, t)$ , depend on time through their dependence on the overpotential  $\eta(t) = E(t) - E_0$ . We assume that an active pit of size  $x$  grows at a rate  $r(x, t) \equiv r(x, \eta(t))$ .

If we take the size of an average nucleation event to be  $x_n$ , a computation shows that  $A(x, t)$  and  $P(x, t)$  satisfy the following equations:

$$\frac{\partial P}{\partial t} = p_P(x, t)A(x, t) - p_A(x, t)P(x, t) \quad (1)$$

$$\frac{\partial A}{\partial t} = p_A(x, t)P(x, t) - p_P(x, t)A(x, t) - \frac{\partial}{\partial x}(r(x, t)A(x, t)). \quad (2)$$

These equations are to hold for  $x \in (x_n, \infty)$  and are to be supplemented by initial and boundary conditions, an equation for the evolution of  $\eta$  and functional dependencies of various transition probabilities and rates on  $\eta$ . First of all we note that from the Newman model (under pure Ohmic control)  $i(t) = \eta(t)/Bx$ , whence we get that

$$\frac{dx}{dt} = r(x, t) = \frac{\eta(t)}{BMx},$$

so that

$$\frac{d\eta}{dt} = \frac{1}{C}(I_{appl} - \frac{2\pi\eta}{B} \int_{x_n}^{\infty} A(x, t)x dx). \quad (3)$$

In view of (3), it makes sense to look for a solution of (1)–(3), such that  $\eta(t)$  is nonnegative and uniformly bounded for all time and such that

$$\int_{x_n}^{\infty} A(x, t)x dx < \infty. \quad (4)$$

Condition (4) imposes a natural boundary condition at  $x = x_n$ . Since we assume that the increase in the total number of pits is due to nucleation only,

$$\frac{d}{dt} \int_{x_n}^{\infty} T(x, t)x dx = r(x_n, t)A(x_n, t) - \lim_{x \rightarrow \infty} r(x, t)A(x, t),$$

and the second term on the right hand-side goes to zero by our assumption (4), we have that

$$A(x_n, t) = \frac{f(\eta(t))}{r(x_n, t)},$$

where  $f(\eta)$  is the instantaneous nucleation rate. It seems reasonable to impose also the condition

$$P(x_n, t) = 0.$$

The instantaneous nucleation rate and the transition probabilities have to be understood next. Below  $k_s$  denote generic constants.

1. For  $f(\eta)$ , we assume, following Galvele, that there exists a certain “rupture potential,”  $E_r$ . A reasonable form for the nucleation rate is then

$$f(\eta) = k_n H(\eta - E_r),$$

or a mollified version of the above function.

2. For  $p_A$ , physical considerations lead one to try

$$p_A x, t = \frac{k_A H(\eta - E_{pit}) x_n}{x},$$

so that it is harder to activate a larger passive pit.

3. In the spirit of Fleishman’s work, we can also assume that an active larger pit is harder to passivate,

$$p_P x, t = \frac{k_P H(E_{pass} - \eta) x_n}{x}.$$

Of course, one can assume that  $E_{pass}$  and  $E_{pit}$  depend explicitly on  $x$ .

If we take above  $E_{pass} < E_r < E_{pit}$ , we shall retain the hysteresis loop of the Newman model. Note that the above model can be attacked by Monte Carlo methods, and that one does not have to assume that the number of pits is large. In a more sophisticated version of this model one can introduce shape heterogeneity of pits (which is manifested, for example, by differing degrees of pit mouth occlusion). In this case the rate of growth of an active pit stops being a deterministic function, but is given by a probability distribution.

Sections (1, 2, 4) were contributed by J. A. Lister, while section (3) is joint work of J. R. King, A. A. Lacey and C. P. Please. Section (5) is joint work of R. Newman, B. Vainas and M. Grinfeld, who also compiled this report.