

A model of chromate leaching from inhibited primers

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Abstract: We present a model of the production, transport and reaction of various ionic species involved in the process of leaching of chromate ions from primer layers on metal substrates. The polymer primer layers contain a range of filler particles, some of which are inert, while others are “active”, in the sense that they act to inhibit the onset and progression of corrosion in bare metal, in a situation where the primer layer is breached. A key active corrosion inhibitor is chromate ions, usually provided by strontium chromate (SrCrO_4) particles in the primer. The chromate ions are formed by dissolution in water, which needs to penetrate the primer layer for this to occur. The ions then leach out to the damage site and react with the metal surface to inhibit corrosion. Unfortunately chromate is carcinogenic and therefore is now banned in various parts of the world. More acceptable alternatives for chromate are being keenly sought. A valuable aspect of chromate ions in their inhibitor role is their ability to relatively rapidly leach out after damage initiation, which is not true of many other inhibitors. However, aspects of the mechanism of chromate leaching through primer layers are not well understood.

Some experimental studies have been conducted in order to elucidate aspects of the chromate leaching, but the interpretation of the experiments is difficult because it involves a range of physical and chemical processes occurring simultaneously. These include water infiltration, dissolution, chemical reaction and ion transport through a composite matrix. A model that incorporates key aspects of these processes is a useful tool for interpretation of experiments as well as explaining the key phenomena. We have developed such a model, which results in a set of coupled partial and ordinary differential equations for the concentration of ionic species both within a primer layer and the solution in which the layer is immersed during experiments. The model incorporates SrCrO_4 particle dissolution into its ionic components, the dimerisation reaction for chromate ions converting to dichromate ions, the dissociation of water and the transport of ions via diffusion through pores as well as through charge separation effects. The model calculates the time variation of the concentration of various ionic species, (CrO_4^{2-} , $\text{Cr}_2\text{O}_7^{2-}$, Sr^{2+} , H^+ , OH^- , Na^+ and Cl^-) in a solution due to the leaching of these ions from a primer layer on a metal substrate, which is immersed in the solution. It also calculates the variation with time, through the thickness of the primer layer, of each ionic species. The results of the model show behaviour similar in most aspects to the experimental work. They explain why the experimental solution constituents vary as observed, and show how the pH is affected by the chemical reactions. However, a key feature of the experimental work is the observation that the transport of the chromate ions appears non-Fickian, in the sense that the release rate is not proportional to the square root of time. Our model also produces a non-Fickian release rate, but it is of a different form to that observed in experiments.

In addition to a description of the chromate leaching model equations, numerical solution and sample results, we present hypotheses that might help to explain the discrepancy between our model results and the observed non-Fickian transport. These hypotheses are the subject of on-going investigation.

Keywords: *Chromate leaching, corrosion inhibitors, dissolution, dimerisation, diffusion*

1. INTRODUCTION

In recent years there have been a series of studies of the transport, via leaching, of a range of additives from organic coatings (Nazarov *et al*, 2005, Prozek & Thierry, 2004, Scholes *et al*, 2006, Furman *et al*, 2006). These studies are primarily motivated by the search for an alternative to chromate, which has been widely used as a pigment and corrosion inhibitor, but is known to be carcinogenic. A key feature of the use of chromate, in addition to its effectiveness as a corrosion inhibitor, is its ability to leach out of a breach in a primer layer in a reasonably fast time, thus providing an effective protection. Any alternative inhibitor material would desirably have both inhibitor and transport properties that are comparable with chromate.

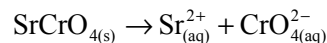
The leaching profiles obtained in experimental studies have found that the leaching rate follows a non-Fickian release rate, that is, the rate is not proportional to $t^{1/2}$, where t is the elapsed time. The non-Fickian behaviour has been associated with the infiltration of water into the layer, the process of releasing chromate from the pigment particles and interaction with the coating matrix.

We present a model of the chromate leaching process that includes the dissolution of strontium chromate particles, the transport of ionic species through the primer into solution, the conversion of chromate ions to dichromate ions in solution and the dissociation of water. The model can predict the amounts of chromate (and other products) released into solution, as well as the time and spatial variation of the concentrations of chromate and other products within the layer itself. It also predicts aspects of the chemistry associated with the leaching, in particular the variation of the solution pH. We compare model predictions with experimental results, in order to explain some aspects of the results, as well as indicate areas for further development.

2. MODEL DESCRIPTION

Consider a volume V of solution which is exposed to the surface area A of a layer of primer of thickness L attached to a metal substrate. Let the porosity of the layer be ε . At time t after the commencement of an experiment assume there is a molar concentration of $\Phi_i(t)$ and $\phi_i(x, t)$ for some ionic species i in the solution and in the primer respectively. Here, x is the distance through the primer thickness. The primer layer is assumed to contain a large number of (spherical) SrCrO_4 particles, each initially having the same radius, which reduces as dissolution occurs.

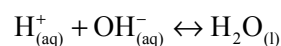
Dissolution of the SrCrO_4 in the primer is modelled by consideration of the chemical process:



This reaction has an associated solubility constant of (Masterton & Hurley, 2005)

$$K_{sp} = [\text{Sr}^{2+}][\text{CrO}_4^{2-}] = 3.6 \times 10^{-5} \text{ (mol/l)}^2$$

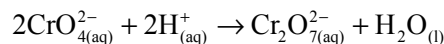
Dissociation of water is represented by the reaction



with the dissociation constant

$$K_d = [\text{H}^+][\text{OH}^-] = 10^{-14} \text{ (mol/l)}^2$$

Chromate ions in acidic solution are known to dimerise to form dichromate ions. This conversion process will affect both the dissolution and transport of chromate ions. The reaction:



is strongly dependent on pH. The equilibrium constant for this reaction is (Michel & Machiroux, 1983)

$$K_{eq} = \frac{[\text{Cr}_2\text{O}_7^{2-}]}{[\text{CrO}_4^{2-}]^2 [\text{H}^+]^2} = 5.888 \times 10^{13} \text{ (mol/l)}^{-3}$$

Other species, such as bichromate (HCrO_4^-) and chromic acid (H_2CrO_4) may also exist, but their equilibrium concentrations are small in the presence of solid SrCrO_4 , so they are not included in the model. In total, the model determines the concentrations of 7 ionic species, being CrO_4^{2-} (concentration ϕ_c), $\text{Cr}_2\text{O}_7^{2-}$ (ϕ_d), Sr^{2+} (ϕ_s), H^+ (ϕ_h), OH^- (ϕ_o), Na^+ (ϕ_n) and Cl^- (ϕ_l). The last two species, Na^+ and Cl^- , are

included because of the potential effect of charge separation as different species diffuse at different rates, but play no other part in the model.

The key equations for the model are based on mass conservation equations for each of the ionic species within the primer layer, as

$$\begin{aligned}
 \varepsilon \frac{\partial \phi_c}{\partial t} + \frac{\partial J_c}{\partial x} &= n4\pi R^2 \sigma (K_{sp} - \phi_c \phi_s) && -\beta(\phi_c^2 \phi_h^2 - \frac{\phi_d}{K_{eq}}) \\
 \varepsilon \frac{\partial \phi_d}{\partial t} + \frac{\partial J_d}{\partial x} &= && \frac{\beta}{2}(\phi_c^2 \phi_h^2 - \frac{\phi_d}{K_{eq}}) \\
 \varepsilon \frac{\partial \phi_s}{\partial t} + \frac{\partial J_s}{\partial x} &= n4\pi R^2 \sigma (K_{sp} - \phi_c \phi_s) \\
 \varepsilon \frac{\partial \phi_h}{\partial t} + \frac{\partial J_h}{\partial x} &= \gamma(K_d - \phi_h \phi_o) && -\beta(\phi_c^2 \phi_h^2 - \frac{\phi_d}{K_{eq}}) \\
 \varepsilon \frac{\partial \phi_o}{\partial t} + \frac{\partial J_o}{\partial x} &= \gamma(K_d - \phi_h \phi_o) \\
 \varepsilon \frac{\partial \phi_n}{\partial t} + \frac{\partial J_n}{\partial x} &= 0 \\
 \varepsilon \frac{\partial \phi_l}{\partial t} + \frac{\partial J_l}{\partial x} &= 0
 \end{aligned}$$

where the J_i are the fluxes of each ionic species within the layer, which we define as

$$J_i = - \left(D_i \frac{\partial \phi_i}{\partial x} - z_i \phi_i \frac{\sum_{k=1}^n D_k z_k \frac{\partial \phi_k}{\partial x}}{\sum_{k=1}^n D_k z_k^2 \phi_k} \right)$$

and z_k is the charge of ionic species k . The first term in the flux is due to diffusive transport, while the second term is due to the effect of charge separation. The particular form of this term is defined by an assumption that there is no net current in the layer caused by the movement of charge. The coefficients β and γ are set to large values in order to enforce the chemical equilibrium for the reactions. The model assumes that the layer is already fully saturated with water.

We used a shrinking core model of the dissolution of the SrCrO_4 particles, which have radius R and number density n , which means that the rate of dissolution of the particle depends on the particle surface area, as well as on the departure from equilibrium,

$$\frac{dR}{dt} = -\frac{M\sigma}{\rho} (K_{sp} - \phi_c \phi_s)$$

where M is the molecular weight of SrCrO_4 , ρ its density and σ is a rate constant. Given that particles are distributed uniformly throughout the primer layer, we can generalise the equation for R to assume that $R(x, t)$ represents the radius of a particle at position x and time t .

We also develop mass balances for each ion species in the solution, which are

$$\begin{aligned}
 V \frac{d\Phi_c}{dt} &= -AJ_c |_{x=0} && -\beta(\Phi_c^2 \Phi_h^2 - \frac{\Phi_d}{K_{eq}}) \\
 V \frac{d\Phi_d}{dt} &= -AJ_d |_{x=0} && +\frac{\beta}{2}(\Phi_c^2 \Phi_h^2 - \frac{\Phi_d}{K_{eq}}) \\
 V \frac{d\Phi_s}{dt} &= -AJ_s |_{x=0} \\
 V \frac{d\Phi_h}{dt} &= -AJ_h |_{x=0} + \gamma(K_d - \Phi_h \Phi_o) && -\beta(\Phi_c^2 \Phi_h^2 - \frac{\Phi_d}{K_{eq}}) \\
 V \frac{d\Phi_o}{dt} &= -AJ_o |_{x=0} + \gamma(K_d - \Phi_h \Phi_o) \\
 V \frac{d\Phi_n}{dt} &= -AJ_n |_{x=0} \\
 V \frac{d\Phi_l}{dt} &= -AJ_l |_{x=0}
 \end{aligned}$$

where $x = 0$ represents the surface of the primer layer in contact with the solution. The above 2 sets of equations are coupled via continuity and flux conditions at the layer surface. There is a no flux boundary condition at $x = L$, the interface of the primer layer with the metal substrate, and initial conditions are that hydrogen, hydroxide, chloride and sodium ion concentrations are specified for given pH and molar concentration of NaCl. The initial concentrations of chromate, dichromate and strontium ions are set to zero. The partial differential equations were scaled in an appropriate way, then approximated by an implicit in time, centred in space finite difference scheme which yields a tridiagonal matrix problem to be solved. The ordinary differential equations were approximated by a forward in time Euler scheme. This simple but potentially numerically unstable approach allowed a solution to be obtained, provided that sufficiently small timesteps are used.

3. RESULTS

The model equations have been solved numerically for a situation similar to the PR143 primer experiments of Scholes *et al*, 2006, where a sheet of PR143 coated aluminium was placed into a beaker containing a solution having pH of 1,3,5 or 7.

Figure 1 shows a graph of the total chromium released into the solution as a function of time for the 4 different initial pH values of the solution. In each case, the amount of chromium in solution increases until a maximum value is reached, when all the SrCrO_4 particles have dissolved and the whole system is in equilibrium. For the higher pH values, it takes almost 17 days for this situation to be reached, but for pH 3 it takes about 5 days and for pH 1 about 1 day. The key reason for the difference in timing is that, as the pH is reduced, more of the chromate ions that are released by dissolution are converted to dichromate ions. This in turn increases the rate of dissolution and consequently the amount of chromium that is released into solution. That is, the rate of release of chromium into solution is most significantly affected by the combination of the dissolution and dimerisation, rather than by the diffusive transport.

It can be seen from the log-log plot that, for high and moderate initial pH values, the curves have 3 distinct parts: in the first part the amount of Cr released increases roughly proportional to t , in the second part it increases roughly proportional to $t^{1/2}$ and in the final part it remains constant.

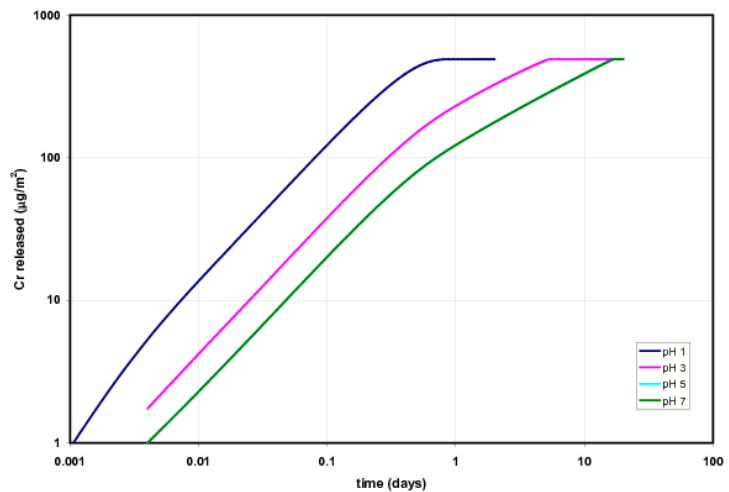


Figure 1. Graphs showing the cumulative amount of chromium released into solution for 4 different experiments, each having a different initial pH, as shown in the legend. Note the curves for pH 5 and pH 7 virtually overlap, so only one is visible.

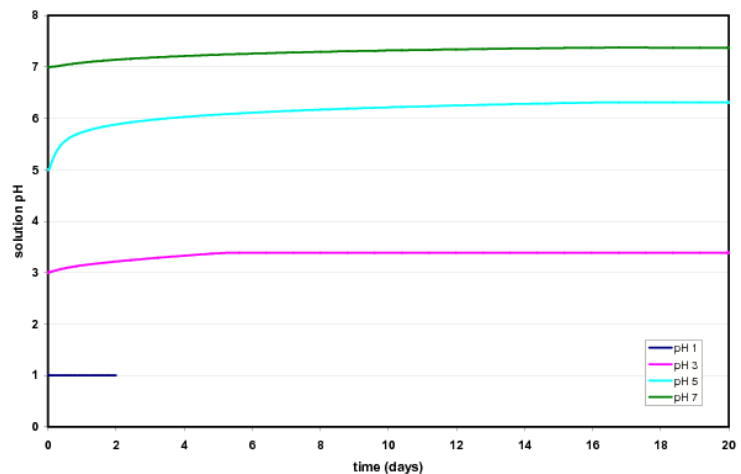


Figure 2. Graph showing the calculated variation of the solution pH with time for 4 different experiments, each having a different initial pH, as shown in the legend.

Figure 2 shows the variation in the solution pH with time for the 4 different initial pH values of the solution. For pH 1, there is virtually no change in pH with time, because, even though most of the chromate ions are converted to dichromate ions, the amount of hydrogen ions required to achieve the conversion is very small compared to the initial number of hydrogen ions. At pH 3 and pH 5, there is a closer match between the amount of available hydrogen ions and the amount of chromate ions released, so there is a more noticeable change in pH. At pH 7, however, there are few available hydrogen ions compared to the amount of chromate ions, so minimal dimerisation occurs and consequently the pH changes only marginally.

Another quantity that is measured in the experiments is the Cr/Sr ratio in the solution. The calculated time variation for this quantity is shown in Figure 3. In all cases, the ratio exceeds unity for the first few hours, but thereafter it becomes unity. According to this model, the reason for the ratio exceeding unity is that the diffusivity of chromate and dichromate ions is assumed to be greater than the diffusivity of the strontium ions. Accordingly, chromium is transported into the solution faster than strontium, even though equal (molar) amounts of chromium and strontium are released during dissolution. Eventually, the ratio must come back to unity, as it is shown to do. The actual time for this to occur will depend on the relative diffusivities.

Figure 4 shows graphs of the calculated variation of the SrCrO_4 particle radius across the primer layer, at different times during the leaching process. There are curves for both pH 5 and pH 1 and they show quite different behaviour. In the pH 5 case, particles near the surface of the layer dissolve faster than those further into the layer. As a result, there is a dissolution front moving through the layer - on the surface side of the front the particles have completely dissolved and on the inner side of the front the particles have hardly

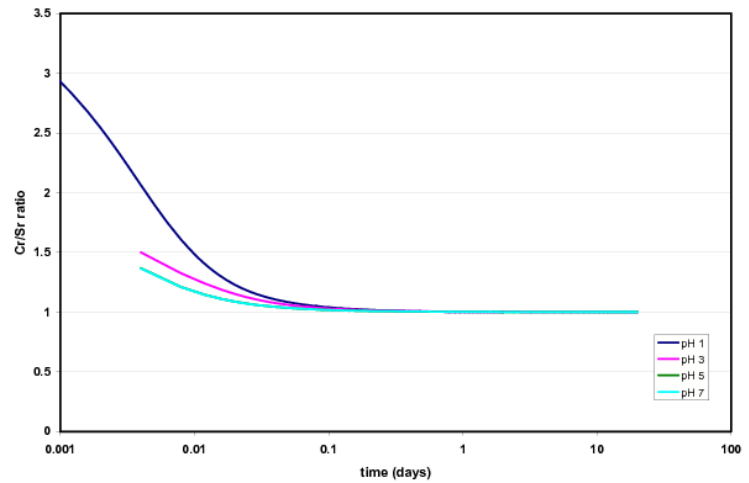
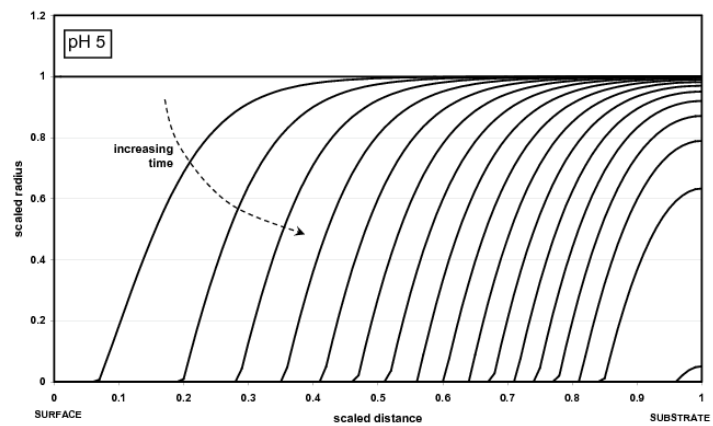
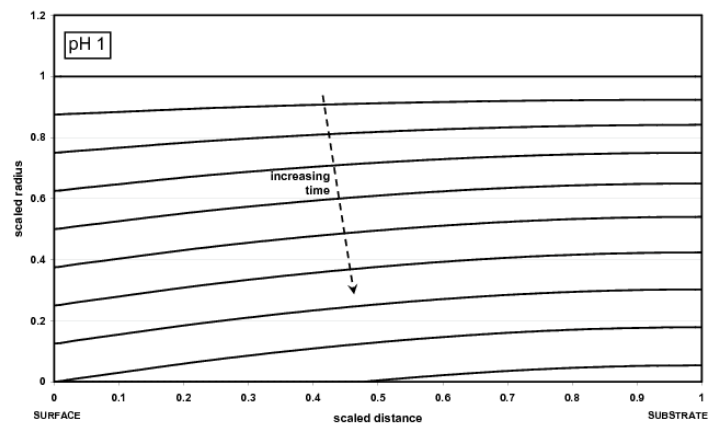


Figure 3. Graph showing the calculated variation of the ratio of chromium to strontium in solution with time for 4 different experiments, each having a different initial pH, as shown in the legend.



(a)



(b)

Figure 4. Graphs showing the calculated variation in the SrCrO_4 particle radius across the primer layer at different times during the leaching process, for 2 different pH values being (a) pH 5, at 1 day intervals and (b) pH 1 at 0.1 day intervals.

dissolved at all - all of the dissolution is happening in a region near the front. There is no such front evident for the pH 1 case. Instead, particles at all depths in the layer dissolve at roughly the same rate, although it is slightly faster near the surface. The reason that there is no dissolution front for the pH 1 case is that the dissolution rate is higher due to the dimerisation reaction. As chromate ions appear, they are instantly converted to dichromate ions because of the equilibrium condition, and so further dissolution occurs. As a result, the process is dominated by dissolution. In the pH 5 case, there is very little dimerisation, so the process is dominated by the transport of ions - as the ions are created by dissolution, they are transported to the surface where the concentration remains low. This results in faster dissolution at the surface than in the interior of the layer, leading to the dissolution front forming.

The effect of the dissolution front upon the distribution of the ionic species within the layer can be seen in the graphs of Figure 5 which shows profiles of chromate ion concentration at different times during leaching. The profiles show that, for the pH 5 case where a dissolution front occurs, the chromate ion concentration varies linearly on the surface side of the front, and is roughly constant on the inner side of the front.

The linear variation in concentration indicates that there is effectively a steady-state diffusion profile set up because the diffusion is fast compared to the dissolution, and this accounts for the $t^{1/2}$ behaviour in the graphs of Figure 1.

In the pH 1 case, there is no clear linear behaviour because there is no front in this case. Rather, the situation is set up so that there is a rough balance between the rate of dissolution and the diffusion at the surface, so that the flux into the solution is roughly linearly with t . This behaviour also occurs in the very early time of the higher pH experiments, accounting for the linear with time behaviour in the first part of those experiments. It is possible to show how these two different regimes occur by considering a simplified version of the model, which provides an explanation of the time dependence of the leaching rate.

4. DISCUSSION AND CONCLUSIONS

It is instructive to compare the results in terms of the chemistry effects of the experiments and the transport effects. By *chemistry* we mean particularly the variation of the solution pH with time. According to the model, pH variation is due to the effects of the dimerisation reaction. A comparison between Figure 2 and Figure 6 of Scholes *et al*, 2006 shows that, by and large, our model results exhibit the same behaviour for pH variation as measured in the experiments.

In terms of transport, the overall comparison between the model and the experiments depends principally on the assumption used for the nature of the diffusion process assumed in the model. The leaching rate in the

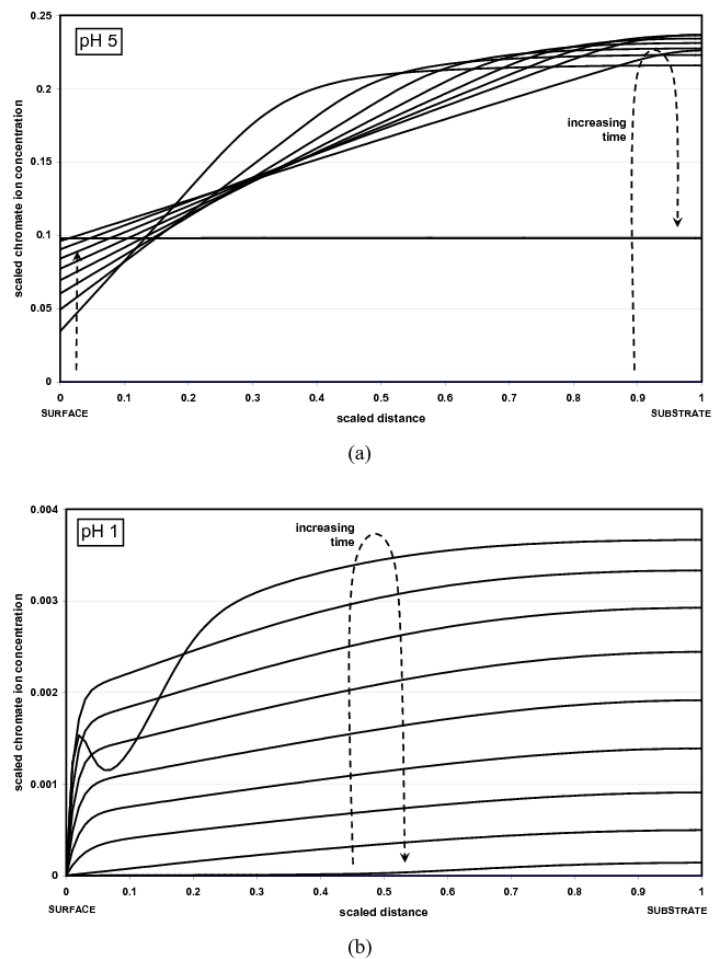


Figure 5. Graphs showing the calculated variation in the chromium ion concentration across the primer layer at different times during the leaching process, for 2 different pH values being (a) pH 5 and (b) pH 1. Note that the profiles are at approximately 1 day intervals in (a) and approximately 0.1 day intervals in (b).

model shows the standard Fickian behaviour for much of the time, producing a rate that is proportional to $t^{\frac{1}{2}}$ whereas in at least some experiments the leaching rate seems to be non-Fickian. The non-Fickian behaviour indicates that there is some effect which causes the diffusivity of the ionic species to vary as the leaching proceeds. Aspects we are considering include blockage of the transport medium or immobilisation of the ions via some interaction with the polymer matrix.

The model does not consider some effects that may have some significance in the leaching process. Firstly, no account has been taken of the infiltration of water into the pore structure of the primer layer. According to some estimates (Prozek & Thierry, 2004, Scholes *et al*, 2006) this takes of the order of minutes to hours. In terms of the leaching experiments considered here, this time is short compared to the total leaching time. However, it may be a significant effect in the rate of leaching in a real situation where a breach in a layer occurs. We developed an unsaturated flow model, which incorporates the effect of capillary pressure upon the rate of infiltration, as well as the effect of the local saturation upon the transport mechanisms. The results indicated that, while the infiltration has a small effect on the leaching rate in the early part (the first few hours) of the experiment, it doesn't change the overall behaviour of the leaching rate curves produced here. Next, our assumption of the SrCrO₄ particles being uniformly sized spheres is unlikely to be true, as these particles are often needle shaped and vary in size. In order to test the effect of different size, we modified the model to consider a bi-modal size distribution, which is the simplest enhancement from our existing model. The results showed that the basic phenomena described here are not changed by the inclusion of the different particle sizes, although the timing is changed somewhat. This is because the shrinking core model of dissolution is sensitive to the surface area to volume ratio of the particles, and this is high for small particles, which thus dissolve more quickly. Hence the same loading of SrCrO₄ will dissolve at different rates depending on both the mean size and distribution of particle sizes. However, there will still be a dissolution-dominated release followed by a transport-dominated release of leachate. Finally, our most basic assumption of the primer layer acting as a porous medium implies that the layer structure contains a system of connected pores that are in contact with the dissolving SrCrO₄ particles, and that within these pores the ionic species move through the solution due to a chemical potential gradient. For this to be a reasonable assumption would require that the dimensions of the pore structures be large compared to the size of the ionic species, which would require pores of the order of around 0.1µm. It is not clear whether such a pore structure occurs in these materials. Moreover, the particle loading in the layer might affect pore connectivity, thus having a significant effect on the leaching behaviour. This is an area of current investigation.

The model presented here provides a valuable resource for understanding the process(es) associated with the transport of corrosion inhibitor additives to primer layers. It appears likely that a mechanism exists which inhibits the transport of the leachate(s) as the leaching process continues, in order to account for the observed non-Fickian behaviour of the leaching. We suggest that such an effect is associated with the interaction of the filler particles (including the leachates) with the primer layer matrix. The nature of the pore structure of the primer layer matrix is not well understood, let alone the interaction between the matrix and the filler particles as leaching occurs. Therefore, our work points to the need for further investigation of this particular aspect of leaching of chromate inhibitors from primer layers.

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