MODEL OF A CORROSION PIT WITH MOVEMENT OF ACTIVE BOUNDARIES

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ABSTRACT

Pitting is one of the most destructive types of localized corrosion. This paper presents the mathematical model of the early stages of pitting corrosion after its initiation stage, using a commercial finite element program. In view of the chemical and electrochemical reactions inside a single pit in steel, a two dimensional model that allows the prediction of movement of boundaries of a pit is developed.

KEYWORDS*: Pitting; corrosion; model; steel, simulation*

1.0 INTRODUCTION

Corrosion is a very destructive process of metal loss due to its reaction with the environment. There are many types of corrosion and pitting is one of many types of highly localized corrosion where small holes or cavities are formed on a metal surface but the bulk of the surface remains unattacked. Pitting has a tendency to undercut the metal surface and is usually covered by corrosion product. Therefore, it can be difficult to detect. Pitting can be very destructive due to the fact that pits can cause perforation to the metal. Pits can occur in isolated locations or be so concentrated that it looks like uniform attack (Fontana, 1987; Shreir et al., 2000; Shreir et al., 2000; Perez, 2004; Ahmad, 2006). Studies have found that pitting is induced by the presence of aqueous solution and halides, such as chlorides or bromides (Cui et al., 2001). It is also found that pitting often occurs in situations where general corrosion is prevented by passive oxide film formed on the surface of metal (Cheng & Luo, 2000). The oxide film can break down and is able to self-repair. However, sites that are not able to repair itself are liable for localized

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corrosion to happen. With the presence of halides, rigorous corrosion occurs and it is established that the pH inside a pit drops to a value way below that of the bulk solution (Salleh & Stevens, 2012). It is also established that there are three stages of pitting (Burstein et al., 1993; Laycock & White, 2001; Perez, 2004; Ahmad, 2006): (i.) initiation of pits, (ii) formation of metastable pits and (iii) stable pitting.

The propagation of pitting is not fully understood, even though there is a great body of literature on pitting corrosion of iron. The present paper describes a modelling approach to illustrate stable pitting, which is the evolution of a single, stable pit in steel after the initiation stage. The objective of this study is to look at the corrosion activities inside a pit at different potentials and pH values. A commercial finite element program, called COMSOL Multiphysics, is used as a tool.

2.0 METHODOLOGY

This model is developed for the evolution of single corrosion pit in carbon steel material in aqueous sodium chloride solution. As stated by Sharland (Sharland et al., 1989), to construct a basic corrosion model of iron, six aqueous chemical species must be considered: Fe^{2+}, H^+, O^{H-}, C^{l-}, Na^+ and $FeOH^+$. Pickering (Pickering, 1984) and Al-Khamis and Pickering (Al-Khamis & Pickering, 2001) have reported experimental evidence of hydrogen gas, H_2, formation inside propagating pits. This is also included in the model of crevice corrosion done by Vuillemin et al. (Vuillemin et al., 2007). According to Pourbaix diagram of iron, more ionic species are included, namely $Fe^{3+,}$ FeO_2- and $HFeO_2$-. The model applies the chemical reactions as stated below (Turnbull & Thomas, 1982; Sharland, 1988; Sharland & Tasker, 1988):

$$Fe^{2+} + H_2O \rightarrow FeOH^+ + H^+ \tag{1}$$

$$H_2O \rightarrow H^+ + OH^- \tag{2}$$

In the case of active walls, the metal dissolution (anodic) process is given by (Sharland, 1988):

$$Fe \rightarrow Fe^{2+} + 2e^- \tag{3}$$

The occurrence of gaseous hydrogen formation is considered through the simultaneous occurrence of proton reduction (cathodic) process, which is given by:

$$\mathrm{H}^{+} + e^{-} \rightarrow \frac{1}{2}\mathrm{H}_2 \qquad (4)$$

As mentioned earlier, the model studies a system in sodium chloride solution. However, sodium ions, Na^+, are not involved in the corrosion reaction, but are involved in maintaining the electroneutrality across the mouth of pit. The reason for adding $FeCl^+$ is to accurately model situations in which the bulk chloride concentration is large and ion pairing is likely to be significant. Furthermore, $FeCl^+$ is a stable species in standard conditions (Sharland & Tasker, 1988; Cottis *et al.*, 2004, Salleh & Stevens, 2012).

$$i_1 = i_{01}\exp\left[a_1 F\frac{(V_m - V)}{RT}\right] \qquad (5)$$

$$i_2 = i_{02}\left[\mathrm{H}^{+}\right]\exp\left[a_2 F\frac{(V_m - V)}{RT}\right] \qquad (6)$$

where V_m is the metal potential, V is the electrostatic potential in solution.

$[H^+]$ is the concentration of H^+, a_1 and a_2 are rate constants. The metal dissolution rate and the hydrogen ions reduction rate follow Fick's First Law of Diffusion (Smith & Hashemi, 2006) which stated that the kinetics in Equations and produce their respective fluxes (Turnbull, 1987), as stated below:

$$\text{Flux of metal ions } \mathrm{Fe}^{2+} \text{ (dissolution rate), } J_{diss} = \frac{i_1}{2F} = \frac{0.25\times i_{01}}{F}\exp\left[a_1 F\frac{(V_m - V)}{RT}\right] \qquad (7)$$

$$\text{Flux of hydrogen ions } \mathrm{H}^{+} \text{ (reduction rate), } J_{H^+} = -\frac{i_2}{F} = \frac{i_{02}\times\left[\mathrm{H}^{+}\right]}{F}\exp\left[a_2 F\frac{(V_m - V)}{RT}\right] \qquad (8)$$

where $i_{01} = 2.7\times 10^{1}\ \mathrm{A\,m^{2}}$, $i_{02} = 2\times 10^{7}\ \mathrm{A\,m\,mol^{1}}$, $a_1 = 1$ and $a_2 = 0.5$ (Vuillemin et al., 2007).

The chemical reactions mentioned above apply the equilibrium constants at 25°C obtained from the HSC Chemistry program, which is a chemical reaction and equilibrium software with extensive thermochemical databases.

Since the dissolution of metal occurs at the active region, the rate of corrosion at that region can be calculated. This is done by incorporating the equation *Corrosion*, as below (Laycock & White, 2001):

$$Corrosion = \frac{J_{diss} NAtomic}{\rho n} \tag{9}$$

where

$NAtomic$ - relative molar mass of iron (0.056 kg mol^{-1})
ρ - density of iron (7800 kg m^{-3}).
n - number of electron in iron oxidation reaction (2).

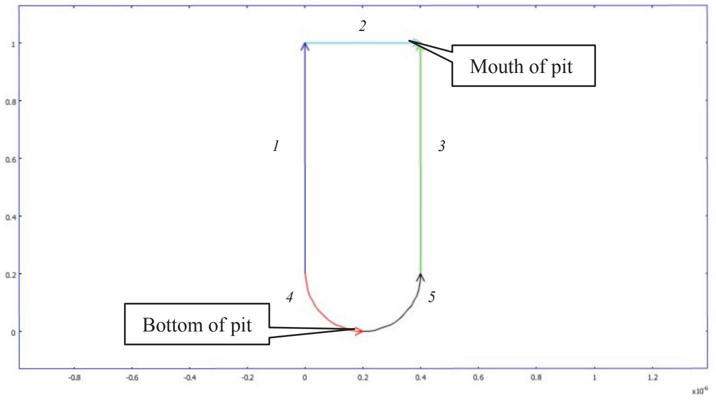


Figure 1. Geometry representing a single pit with a curved bottom

The initial gometry to represent a pit is specified as in Fig. 1. Region *1* and *3* represent the passive walls, region *2* represent the mouth of the pit and regions *4* and *5* are the active bottom of the pit where metal dissolution is expected to be observed. This was mentioned in previous work (Salleh & Stevens, 2012). The model applies the neutral environment of pH 7 and takes the initial chloride concentration to be 1000 mol per cubic meter. It is solved using the Nernst-Planck resolution for the range of potential between -1.5 and 1 volt.

3.0 RESULT AND DISCUSSION

By applying a current, corrosion rates of a metal can be measured and a polarization curve can be produced. The polarization curve is the degree of potential change as a function of the amount of current applied. The degree of polarization is a measure how the rates of the anodic and the cathodic reactions are affected by various environmental conditions.

Fig. 2 shows that, the corrosion potential is about -0.86 volt. As potential increases, the current density, log i, increases and this indicates active dissolution of metal.

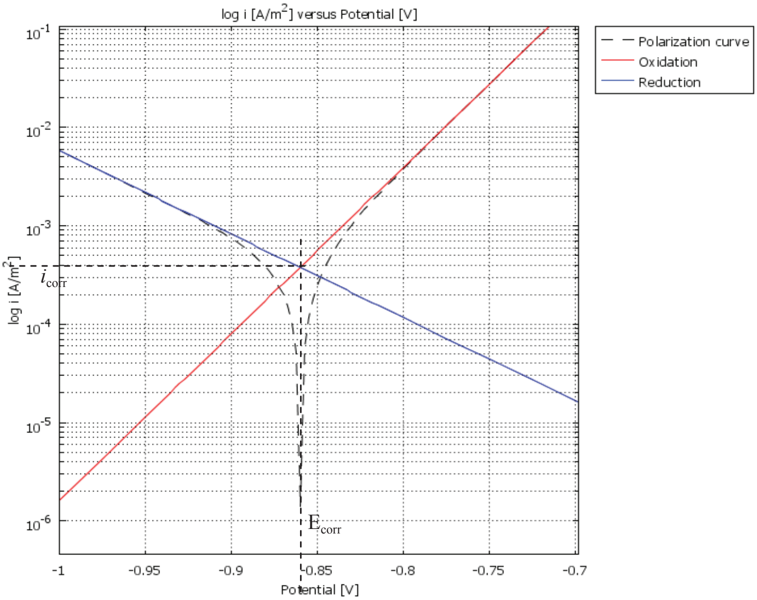
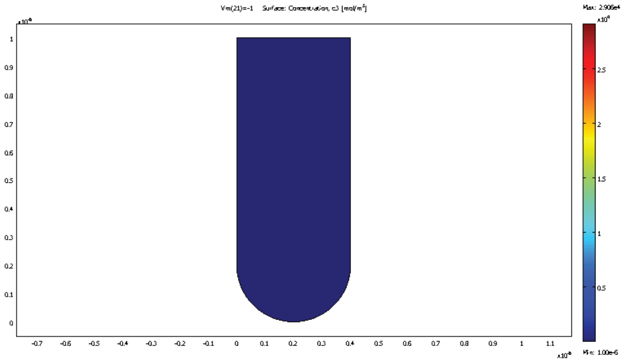


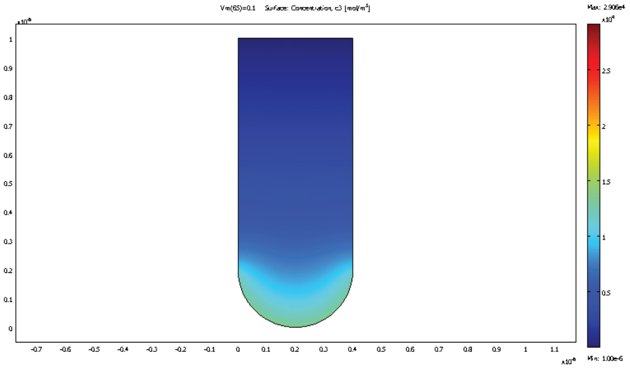
Figure 2. Graph showing the polarization curve at the bottom of pit

Further down the pit, the pH is expected to be lower than the pH at the mouth. The higher the concentration of H^+, the lower the pH is going to be. As the potential increases, hydrogen ions gradually accumulate at the bottom of the pit. This is shown in the experiment done by Lee (Lee et al., 1981) and shown in the model by Salleh (Salleh & Stevens, 2012) where the pH inside the pit drops to 4.7.

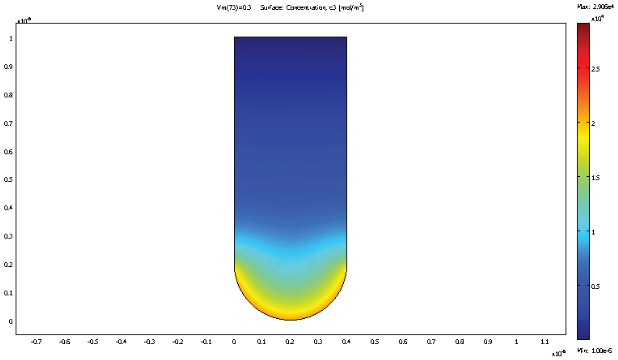
From Fig. 3, the concentration of Fe^{2+} at the bottom of the pit is indicated to be slightly higher than that at the side of the pit where the active region meets the passive region. Accumulation of metal ions, Fe^{2+}, occurs gradually at the bottom of the pit and this is the region where the model is set to be active. The concentration of Fe^{2+} at the bottom of the pit increases along with potential and this indicates that the metal dissolution is occurring continuously. Furthermore, Fe^{2+} is also observed starting to accumulate higher up the pit. This agrees with the theory of diffusion where species move under the action of concentration gradient where species move from high to low concentration until even concentration is achieved for all species. In this case, the concentration of Fe^{2+} has reached a limit where the metal ions diffuse to the area where the concentration of Fe^{2+} is lower. It is expected that Fe^{2+} will diffuse out of the pit, as stated by Grimm and Landolt (Grimm 1994), and hence, promotes dissolution of metal, forming general corrosion to the metal surface.



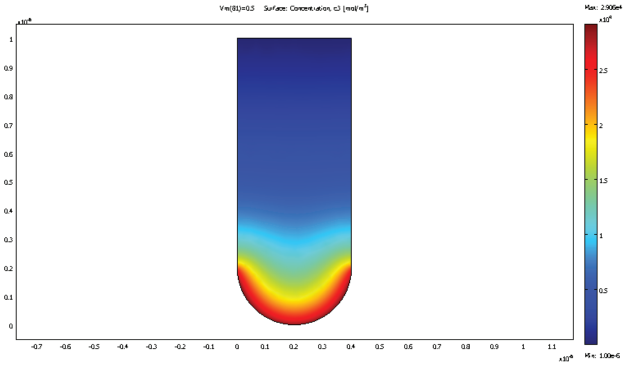
(i)



(ii)



(iii)



(iv)

Figure 3. Figure (i)-(iv) show the stages with respect to potential, where accumulation of Fe^{2+} occurs at the bottom of the pit

With the accumulation of Fe^{2+} inside the pit, this gives a positively charged environment inside the pit. This phenomenon attracts negatively charged chloride ions, into the pit through the process of migration. With increasing concentration of Cl^- inside the pit, this in turn gives a negatively charged environment inside the pit and thus, attracts the H^+ ions through the dissociation of water in the bulk solution. Accumulation of H^+ occurs inside the pit (Salleh & Stevens, 2012).

The presence of a solution of H^+ and Cl^- ions form a solution which is acidic and corrosive. The acidic environment further promotes metal dissolution and this process continues (Lee et al., 1981; Yuan et al., 2010). This can be seen when the expression corrosion is plotted against metal potential, as in Fig.4. The corrosion rate is plotted and it increases as potential increases. The rate is observed to be lower at the bottom of the pit compared to that at the side of the pit.

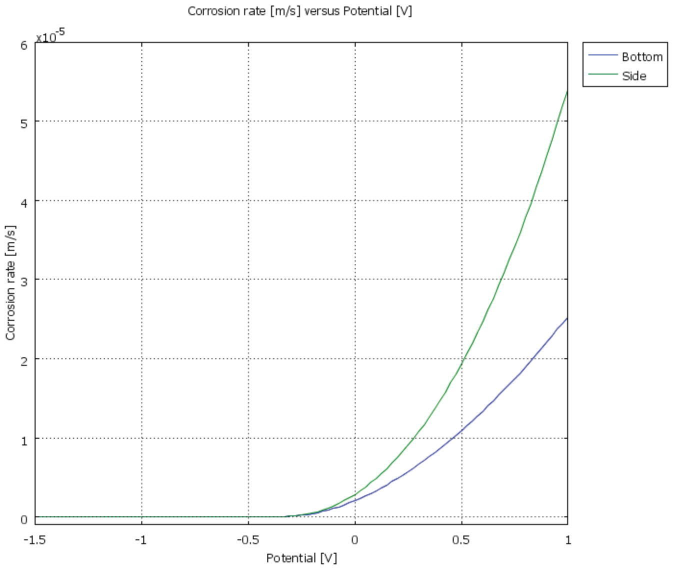
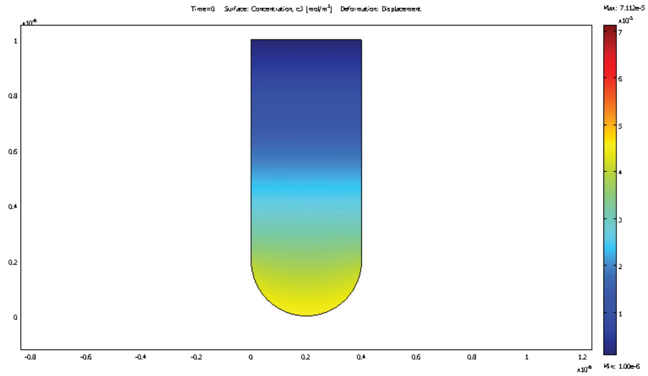


Figure 4. Illustrating of corrosion rate at two points along the pit

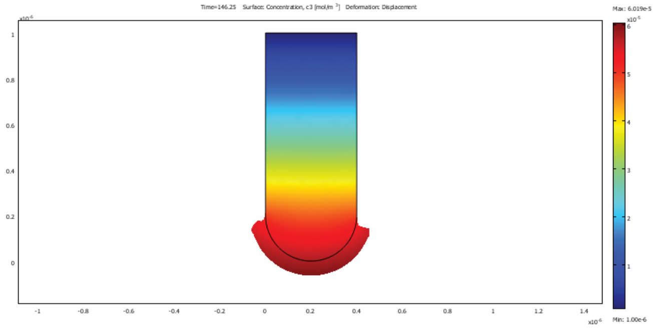
Since the expression *Corrosion* defines the velocity with which the boundaries should move, the expression *Corrosion* can be plotted at the active sites, which are only at the bottom and side of the pit.

From Fig. 4, it is interesting to see that the corrosion rate at the side of the pit is higher than the corrosion rate at the bottom of the pit. Since the rate is lower at the bottom of the pit, this is due to accumulation of certain species that prevents further dissolution of metal, and the differences in potential and current density due to geometric effects. In real life problems, this may be due to formation of rust or iron oxide. To prove this, more equations need to be included in the model as future work. The corrosion rates can also be seen increasing gradually starting from potential -0.3 V. This is because at potential -0.3 V, the pH is found to be around 4.7, as stated by Salleh (Salleh & Stevens, 2012).

Solving the model in the Moving Boundary (ALE) mode allows the graphic presentation that shows the boundary of the active regions are moving outwards, indicating that metal dissolution occurs. Fig. 5(i) shows that at time 0 seconds, corrosion activities occur at the bottom of the pit and this is indicated by the small change in the concentration of metal ion Fe^{2+}. After 146.25 seconds, the concentration of Fe^{2+} at the bottom of the pit increases, as indicated in Fig. 5(ii). The boundary of the active region is seen to be moving outwards, indicating metal dissolution. This, in turn, makes the area at the bottom of the pit increases.



(i) Pit geometry at 0 second



(ii) Pit geometry at 146.25 seconds

Figure 5. Dissolution of metal is shown to occur by the moving boundary at the bottom of pit which is seen to move outwards

4.0 CONCLUSION

The model is constructed as a first step to develop a model that can represent a propagating pit and predict pit shape. It is suggested that salt film formation and passivity are considered in the next stage of modelling. Progressive work is to be carried out by adding more chemical reactions involved in the corrosion processes.

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