Current Distributions and Dissolution Mechanisms During Localized Corrosion of Steels In Alkaline Environments

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ABSTRACT

In situ corrosion investigations of iron were carried out in alkaline environments to determine the stages of corrosion that may be encountered with steels in concrete. The electrochemical and chemical processes taking place on Fe have been studied using x-ray absorption, current density mapping of the iron surface and artificial pits. The x-ray absorption near edge spectroscopy was used to observe the conversion of Fe to oxide in hydroxide solutions. The oxide formed was electrochemically active and changes in valence states between 2+ and 3+ were observed during electrochemical cycling between the passive state and hydrogen evolution. The oxide continued to thicken during the cycling with very little dissolution or any conversion back to the metallic state. Current density mapping in chloride/hydroxide solution showed that corrosion took place in highly localized areas confined by the formation of a corrosion product shell. The activity within the shell decayed on removing a supporting cathodic area limiting but reactivated on its replacement. Artificial pits were used to study the anodic processes taking place within the region confined by the corrosion product shell. The local pH and anodic behavior were similar to that observed in neutral or slightly acid bulk solutions. The

dissolution within the artificial pits in alkaline bulk solutions was found to be sensitive to the presence of small quantities of nitrite.

INTRODUCTION

The corrosion of steels in concrete initially takes place in crevices with highly alkaline environments that are present between the concrete and the steel. In order to define the role of inhibitors a study has been made of the behavior of pure iron in alkaline solutions and solutions with chlorides and nitrites. Under most conditions corrosion of steel initiates at inclusions (1) and takes place by the undermining of the passive layer (2,3) as a consequence of an aggressive environment that prevents repassivation of the steel. Inhibitors may act by changing the nature of the passive film and prevent its breakdown or by preventing the buildup of the aggressive environment that is maintained during active dissolution under the passive layer.

EXPERIMENTAL

The samples were of pure (99.985%) Fe. For the x-ray absorption experiments evaporated Fe layers were deposited on Mylar sheets coated with a layer of titanium that acted as a current collector. The Fe layer was kept as thin as possible so that changes in the

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chemistry of the Fe due to the formation of the passive oxide was a significant fraction of the total amount of Fe present. Most Fe films were of the order of 10 nm thick. The plastic sheet was used to form a window of a cell with the metal layer in contact with the solution. The monochromatic x-ray beam passed through the plastic and metal. The fluorescence of the Fe as a function of x-ray energy was measured and was directly proportional to the absorption by the Fe. Specific details of the technique are given in a number of publications.(4,5)

Current density mapping was carried out on the cross section of insulated Fe rods 3 mm in diameter. The surface was abraded silicon carbide paper down to 600#. A vibrating probe that converts the Ohmic potential gradients (or IR drops) from a dc to an ac signal, was used to measure the local current density above the metal surface in a 1.0 M NaCl, 0.1 M NaOH solution following methods and cells used previously.(6,7)

Pencil or wire-type artificial pits were used to investigate the dissolution characteristics during localized corrosion.(3,8,9) Wires of the Fe, 1 mm in diameter were imbedded in epoxy and the cross-section of the abraded wire was dissolved back to produce a pit. When additions of NaNO_2 were made to bulk solutions the concentrations given are final values after the addition.

Potentials are referred to the reference electrodes used in the experiments. The mercury sulfate electrode has a potential 0.4 V more positive than the saturated calomel electrode.

RESULTS AND DISCUSSION

Figure 1 shows XANES measurements at $-0.2 \text{ V}_{\text{msc}}$ ($+0.2 \text{ V}_{\text{acc}}$) during repeated stepping cycles between -0.2 and $-1.6 \text{ V}_{\text{msc}}$. It shows the behavior

of the passive film on Fe in alkaline solutions, in the absence of chloride. Little if any Fe dissolved and the thickness of the oxide present increased in thickness with potential stepping. The conversion of metal resulted in the progressive shift in the edge to higher energies with cycling. A small loss of about 15% of Fe originally present was determined from a drop in height of the absorbance step (measured at 7300 eV, well above the edge) which sums the contribution from all Fe species present. The loss occurred during the 15 cycles and set the maximum value for Fe dissolution or other causes, such as flaking of the deposit. The fraction of un-converted Fe metal remaining after the 15 cycles was estimated from the first knee at lower energies which was dominantly from the spectrum of Fe metal. It had dropped by about 55% indicating approximately half the iron still remained. XANES measurements at $-1.6 \text{ V}_{\text{msc}}$ were in agreement with earlier work (4) where the reduced oxide was composed of divalent Fe. A comparison of the changes observed with XANES can be made with polarization measurements. Figure 2 shows the first and fifth repeated voltammetry cyclic at 10 mV/s with an inset of five cycles. Current peaks increased in size indicating that the oxide was thickening with each cycle. From the XANES results this was caused by a thickening oxide and was not due to other causes for example an increased surface area of metal with each oxidation/ reduction cycle.

Scanning vibrating probe measurements of the corrosion behavior of pure Fe in 0.1 M NaOH/ 1.0 M NaCl solutions were carried out with 3 mm diameter rods i.e. 0.07 cm^2 . Corrosion was initiated by connecting a Pt wire to increase the potential. A finger of corrosion product formed starting from the edge of the sample and stopped when the Pt was disconnected. Figure 3A shows the sample when the Pt was disconnected. Figure 3B shows the distribution of the normal component of the current density above the surface.

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High anodic currents were observed over the corrosion product with the highest currents above the tip of the finger. On disconnecting the Pt the currents dropped dramatically and then slowly decayed away with the surrounding passive surface acting as the cathode. The changes can be seen from Figure 2C, and 2D. The corrosion re-initiated when the Pt was reconnected and the corrosion product spread from the side of the finger.

In order to investigate the effects of inhibitors on dissolution within the corrosion covered volume, artificial wire type pits were used. Figure 4 shows one set of results where the potential was cycled from -0.7 to 2.0 V_{sce}. Corrosion initiated at -0.2 V_{sce} during the first cycle. Each subsequent cycle involved active dissolution of Fe producing the maximum current when supersaturation of the dissolved products lead to precipitation of a salt layer and a minimum of current, on increasing the potential. The salt layer remained throughout the remaining part of the cycle until the potential decreased to -0.25 V_{sce}. At about this potential the current dropped and the salt layer dissolved. The open circuit potential in the pit was about -0.5 V_{sce}. With increased depth of the pit the currents decreased because of increased diffusion path. The behavior was similar to that in neutral or acid chloride solutions except for the precipitation of the dissolution products at the mouth of the pit which further inhibited diffusion. With high, 1.0 M concentrations of nitrite, added on the 10th cycle, the current dropped and the pit surface repassivated. Details of the effect is shown inset in Figure 4. Also shown in Figure 5, when small additions of 0.005 M NaNO₂ were made distinct decreases in current were observed for the artificial pits held at a fixed potential.

ACKNOWLEDGMENTS

This research was performed under the auspices of the U.S. Department of Energy, Division of Materials Science, Office of Basic Energy

Sciences under Contract No. DE-AC02-76CH00016.

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Figure 1. XANES measurements of an Fe film in 0.1 M NaOH measured at -0.2 V(mse) during steps between -1.6 V and -0.2 V (MSE).

Figure 2. Cyclic voltammetry at 10 mV/s for Fe in 0.1 M NaOH. The inset shows all 5 cycles

Figure 4. Cyclic voltammetry at 5 mV/s for a wire-type pit electrode in 1.0 M NaCl with 0.1 M NaOH. On the 10th cycle $NaNO_2$ was added to give a 1.0 M concentration. The inset shows the behavior of the current after the nitrite was added.

Figure 5. Changes in current for a wire-type pit in 1.0 M NaCl with 0.1 M NaOH solution showing decreases on addition of $NaNO_2$.