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Corrosion Behavior of Steel Bar in Chloride Contaminated Mortars with Fly Ash

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ABSTRACT

In this study, the corrosion behavior of steel in mortars with fly ash was investigated. Electrochemical measurements including the half-cell potential, current density, anodic polarization and cathodic polarization were performed. The test results showed that corrosion current densities in chloride contaminated fly ash mortars with longer curing are within the passivity limit. Also, from the anodic polarization curves, the passivity grades in chloride contaminated fly ash mortars with longer curing were the same as Ordinary Portland Cement (OPC) mortars which indicates that mortars with this binder can provide passivity to steel bars as effective as OPC mortars. Moreover, by cathodic polarization test, fly ash mortars exhibited the ability to reduce oxygen availability which leads to enhancement in corrosion performance.

1. INTRODUCTION

Portland cement concrete has been widely used as a general construction material because of its very good mechanical strength and suitability for use in many types of structures. Moreover, under ideal conditions, it provides an excellent protective environment for the reinforcing steel bars embedded in reinforced structures. This is due to the high alkalinity of concrete (pH$\approx$ 13) that paves way for the formation of a thin iron oxide layer which provides passivity on the surface of the steel. Passivity refers to the loss of chemical reactivity experienced by certain metals and alloys under particular environmental conditions. The insoluble oxide film prevents oxygen from reaching the steel thereby effectively inhibiting the electro-chemical process of corrosion (Richardson, [1]). However, this passive film can be destroyed by aggressive elements

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such as chlorides, and consequently corrosion is instigated. The products of the corrosion process can occupy large volumes to as high as 600 percent of the original metal. This causes tremendous internal pressure that leads to high tensile forces and eventually cracking and spalling of the concrete cover (Mehta and Monteiro, [2]). When this happens, the corrosion process is greatly accelerated and eventually the service life of the structure is put to a halt.

Besides Portland cement, available alternative materials have been used in the concrete industry not only to reduce the overall cost of construction materials but also to support the environmental sector. Among the many available alternative materials, fly ash has been commonly used over the past few years. The fly ash particles slowly react with the available calcium hydroxide thus producing the more stable calcium silicate hydrates (CSH). The formation of more CSH increases the capacity of concrete to resist the diffusion of deleterious elements. However, the performance of fly ash as replacement material in concrete can be effectively developed only when given adequate curing. In a report by Malhotra and Ramezanianpour [3], fly ash concretes that underwent increased curing periods became considerably less permeable to water and oxygen.

Given the enhancing capability of fly ash when used as a replacement material in concrete, it is therefore important that its performance in terms of providing corrosion resistance for the reinforcing steel be investigated. In connection with this, the study was conducted to investigate the corrosion behavior of steel in chloride-contaminated mortars with fly ash.

2. EXPERIMENTAL PROCEDURE

2.1. Materials

Ordinary Portland cement and Class F - fly ash were used as binding materials. The physical properties and chemical compositions of the materials are shown in Table I. Saturated surface dry (SSD) sand with a specific gravity of 2.64 was used to prepare the mortars.

Material	Physical Property		Chemical Composition, %						
	Specific Gravity	Blaine (m^2/kg)	SiO_2	Al2O$_3$	Fe2O$_3$	CaO	MgO	SO_3	Loss on Ignition
Ordinary Portland Cement	3.14	327	21.8	5.10	3.0	63.8	1.70	2.0	0.90
Fly ash	2.33	455	51.9	24.8	5.0	7.9	2.4	0.6	1.8

Table I. Physical Properties and Chemical Compositions of Ordinary Portland Cement (OPC) and Fly Ash (FA)

The mortar mix prepared with Ordinary Portland Cement and cured for 7 days was designated as OPC. The mixes that utilized 15% and 30% fly ash replacement and cured for 7 days were designated as FA15 and FA30 respectively while the mixes that utilized 15% and 30% fly ash replacement but cured until 28 days were designated as FA15-LC and FA30-LC respectively. For designation purposes, the contaminated specimens can be easily identified using the suffix Cl. In this study, the chloride contaminated mortars were prepared in the same manner as the chloride free mortars except that the former were dosed with 2% (by weight of binder) of sodium chloride during the mixing process. A water / binder ratio (W/B) of 0.55 was used for all cases. The composition of different mortars studied is shown in Table II.

Mortar type	Binder	Sand / binder ratio	W/B ratio
OPC	Ordinary portland cement	2.5	0.55
FA15	85% OPC + 15% Class F -fly ash	2.5	0.55
FA30	70 % OPC + 30% Class F -fly ash	2.5	0.55
OPC- Cl	Ordinary portland cement	2.5	0.55
FA15-Cl	85% OPC + 15% Class F -fly ash	2.5	0.55
FA30-Cl	70 % OPC + 30% Class F -fly ash	2.5	0.55

Table II. Composition of the Mortars

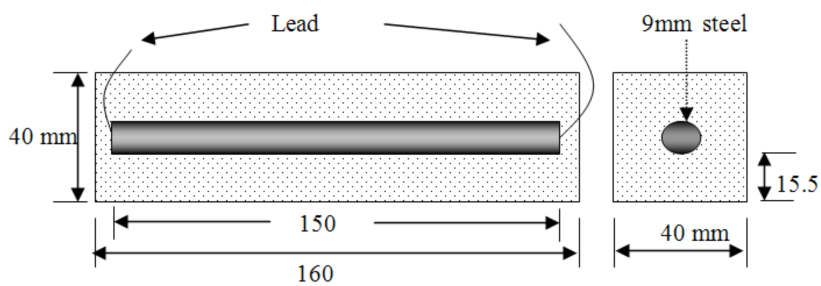

Figure 1. Detail of the Reinforced Mortar Specimen

Type	% composition by weight						
	Fe	C	Si	Mn	P	S	Cu
JIS-SR235	98.88	0.12	0.17	0.50	0.019	0.03	0.18

Table III. Chemical Composition of the Steel

2.2. Specimen Preparation

Prismatic reinforced mortar specimens were prepared as shown in Figure 1. Polished plain steel bars with 9 mm diameter were set up on the center of the prism. The chemical composition of the steel is shown in Table III. After mixing and casting, the specimens were cured in a water bath at different periods of duration. For the OPC specimens, 7-day curing was done. On the other hand, for the FA15 and FA 30 specimens, 7-day and 28-day curing were done. Thereafter, a series of prismatic unreinforced mortar specimens measuring 40 × 40 × 160 mm (prepared and flowability tested in parallel with the reinforced mortar prisms) were subjected to compression test to determine the 7-day and 28-day strengths.

After the curing process of the reinforced mortar prisms, epoxy resin was used to cover all surfaces except for one surface whose area is parallel to the steel. It is on this surface where the diffusion of oxygen will be concentrated. Prior to any measurements, all the reinforced specimens were then kept inside an environmental chamber at a constant temperature of 20 degrees centigrade and relative humidity of 75%.

2.3. Electrochemical Measurements

Electrochemical measurements are important and widely used because they permit the study of reaction mechanisms and the kinetics of corrosion phenomena. The electrochemical measurement methods considered in this study are briefly described in the following subsections.

2.4. Half-cell Potential and Current Density

The corrosion potential was measured using a portable corrosion monitor with an Ag/AgCl half-cell electrode. The corrosion current density was measured using the AC impedance method. The measurement setup is illustrated in Figure 2. The amplitude of the excitation voltage was 50mV, the low frequency was set at 10 mHz and the high frequency at 10 KHz. To obtain the current density, the polarization resistance reading was substituted in Equation 1.

$$I_{corr} = \frac{B}{R_P} \times 10^6 \tag{1}$$

where I_{corr} is the corrosion current density (μA/cm^2), B = 0.026 V and R_P is the polarization resistance measured in $\Omega\cdot$cm^2. The corrosion potential and current density were both measured after 60 and 120 days inside the environment controlled chamber.

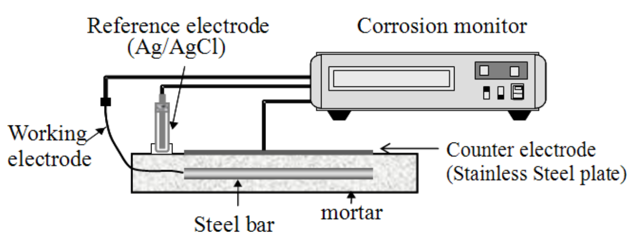

Figure 2. Measurement Setup for Corrosion Potential and Current Density

2.5. Anodic Polarization Curve

In order to obtain the anodic polarization curve, the natural potential of the steel bar was gradually shifted to +1 V at a scanning speed of 1mV per second and the corresponding anodic current was measured. The plot of the anodic current for each scanned potential gives the anodic polarization curve. The measurement setup for the anodic polarization is shown in Figure 3. A stainless steel plate was used as a counter electrode and an Ag/AgCl as reference electrode.

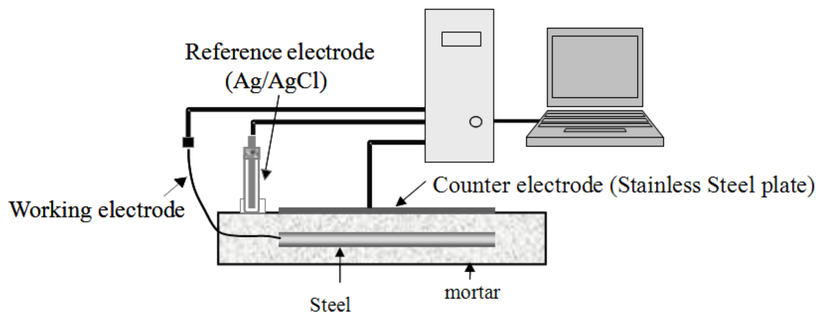

Figure 3. Setup for Anodic Polarization Test

2.6. Cathodic Polarization Curve

The measurement setup for the cathodic polarization test is the same as the setup shown in Figure 3. A stainless steel plate was also used as counter electrode and an Ag/AgCl as reference electrode. However for this measurement technique, the natural potential of the steel bar was gradually shifted to -1.4 V at a scanning speed of 1mV per second and the corresponding cathodic current was measured.

3. RESULTS AND DISCUSSION

3.1. Properties of Fresh and Hardened Mortars

The flowability and compressive strength at the age of 7 and 28 days are shown in Table IV. For each mortar type, six specimens were tested. The 7 and 28-day compressive strengths for the fly ash specimens are lower than the OPC specimens. This result is generally accepted since fly ash has less contribution to strength when normal curing is done at ages less than or equal to 28 days.

Mortar type	Flowability (cm)	Compressive strength (MPa)	
		7 days	28 days
OPC	10.1	28.0	45.1
FA15	10.3	22.5	38.0
FA30	11.2	19.0	31.6

Table IV. Properties of Mortar

3.2. Half-cell Potential and Current Density

The result of the corrosion potential monitoring is shown in Figure 4. For each mortar type, three specimens were monitored. Half cell potential monitoring results show more negative values in the chloride contaminated mortars with fly ash where curing was done for only 7 days indicating that there is more corrosion susceptibility or there is a higher probability of corrosion. However, the potentials of the fly ash mortars that were cured for longer period were almost the same as the OPC mortars. This may indicate that the probability of corrosion was lowered in fly ash mortars that underwent longer curing. But potential values only show a qualitative indication that there is a certain level of corrosion activity and as such, a quantitative means, which is more reliable and recommendable, was done by monitoring the corrosion current density.

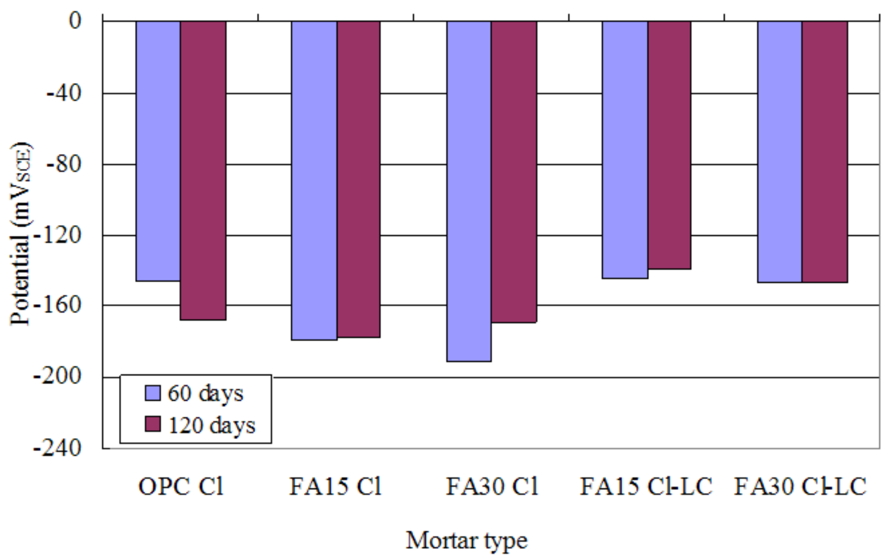

Figure 4. Half-cell Potential

The result of the current density monitoring is shown in Figure 5. For each mortar type, three samples were monitored. The passivity limit is generally defined at a corrosion current density of 0.1 μA/cm^2 (Andrade and Alonso, [4]). In the case of specimens with chloride, the current densities in the fly ash mortars were relatively higher than the OPC mortars. The fly ash mortars cured for 7 days exhibited the highest corrosion rates. The values are even greater than the limit of 0.1 μA/cm^2 which indicates that the rate of corrosion is already outside the passive region. However, for the fly ash specimens that were cured for a longer period of time, the corrosion rate is still within passivity limit. Therefore the corrosion performance of fly ash mortars, that underwent longer period of curing, can be as effective as ordinary Portland cement mortars in terms of keeping the corrosion rate within passivity limit at least during the initial stage.

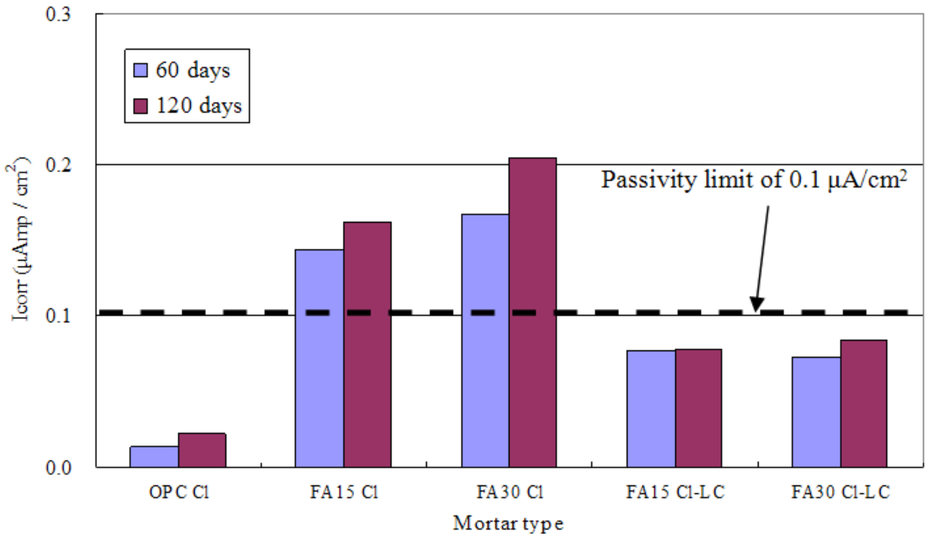

Figure 5. Corrosion Current Density

3.3. Anodic Polarization Curves

The anodic polarization curves (Figs. 6 and 7) were obtained for both the chloride free and chloride contaminated mortar specimens. Figure 6 show that the curves for the fly ash and OPC specimens showed almost the same trend qualitatively indicating that the passivating capacity of fly ash is as effective as OPC in the chloride free specimens even though the curing period was as short as 7 days. The addition of fly ash to ordinary Portland cement did not hamper the ability of the mortars to provide alkaline environment for the steel bars in the absence of chloride.

In the case of chloride contaminated specimens, Figure 7 shows that the anodic behavior of fly ash mortars with only 7 days curing drastically shifted to higher currents relative to the OPC mortars. Nevertheless, when comparison is made with OPC and fly ash mortars with longer curing, the difference in corrosion trend was strikingly compensated. This anodic polarization data confirms that incorporation of fly ash with adequate curing can lead to better integrity of the passivation film around the steel bar even in the presence of chloride.

A more systematic way to evaluate the degree of passivity provided by the OPC and fly ash mortars can be presented by using the grading criteria for passivity presented earlier by Otsuki *et al.* [5]. The criteria were based on the behavior of the anodic polarization curves of steel bar in various solutions. The degrees of passivity of the steel bar were presented as different grades depending on how the current densities behaved between +0.2 V and +0.6 V (versus SCE) potential on the anodic polarization curve. The passivity grading criteria is summarized in Table V. Using the aforementioned grading criteria, the passivity grades of the steel embedded inside the mortar specimens were determined and summarized in Table VI for the purpose of a more systematic qualitative comparison of the anodic polarization curves.

The passivity grade of the steel bars in fly ash mortars went down to passivity grade 3 after

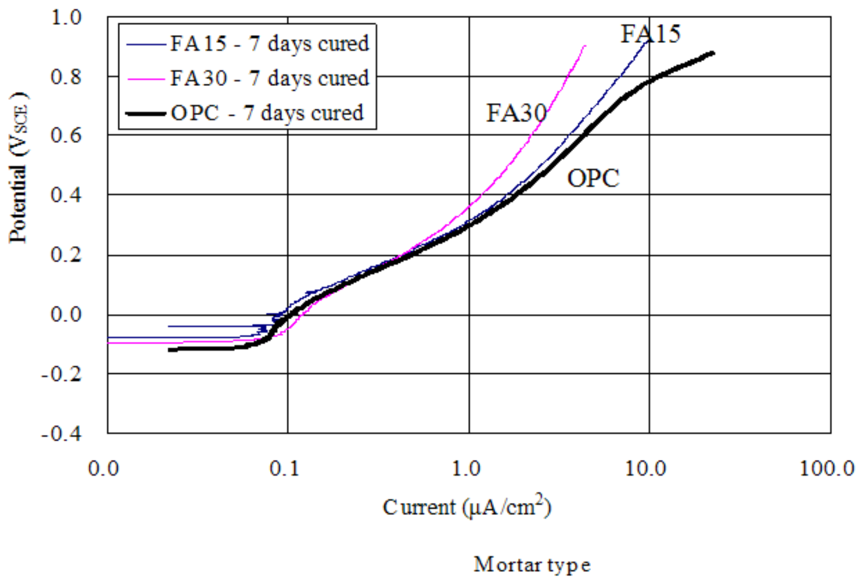

Figure 6. Anodic Polarization Curves of Mortars without Chloride

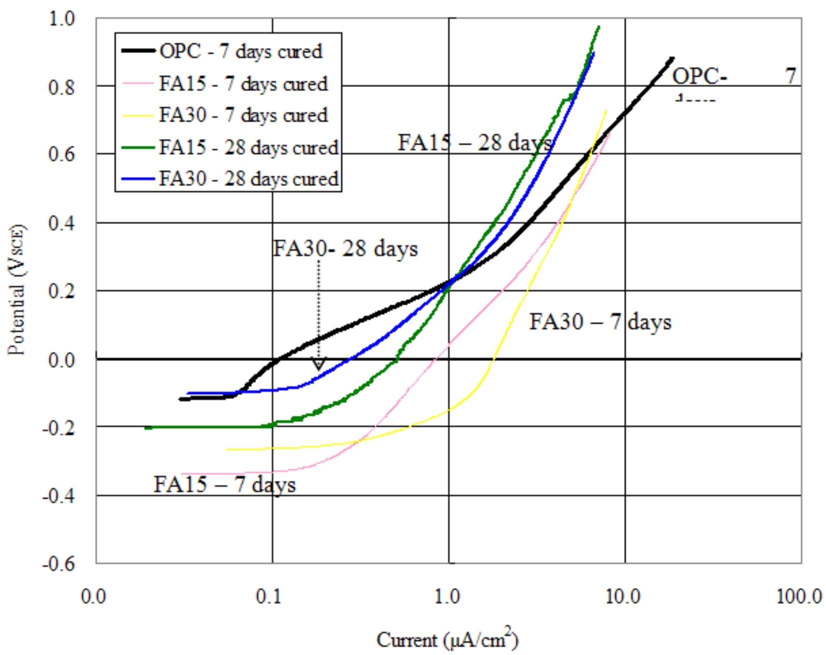

Figure 7. Anodic Polarization Curves of Cl-contaminated Mortars

the contamination of chloride. However, this significant downgrade was not observed when the OPC specimens were compared with the fly ash specimens that were cured in longer periods. Again it can be stressed that fly ash cement can be as effective as OPC in providing corrosion protection for reinforcing steel provided that longer curing is performed.

Passivity Grade	Criteria	Remark
0	When current density I $\geq$ 100 μA/cm^2 in at least one point between +0.2 V and +0.6 V (vs. SCE)	Poor Passivity
1	When 10 $\leq$ I < 100 between +0.2 V and +0.6 V (vs. SCE)	Some degree of passivity which is better than no passivity
2	When I$\geq$ 10μA/cm^2 in at least one point between +0.2 V and +0.6 V (vs. SCE)	Some degree of passivity which is better than passivity grade 1.
3	When 1 $\leq$ I < 10 between +0.2 V and +0.6 V (vs. SCE)	Some degree of passivity which is better than passivity grade 2.
4	When I$\geq$ 1μA/cm^2 in at least one point between +0.2 V and +0.6 V (vs. SCE)	Some degree of passivity which is better than passivity grade 3.
5	When I < 1 between +0.2 V and +0.6 V (vs. SCE)	Excellent passivity

Table V. Passivity Grade Evaluation Criteria

Category	Mortar type	Passivity Grade
Cl free	OPC	4
	FA15	4
	FA30	4
Cl-contaminated	OPC -Cl	4
	FA15-Cl	3
	FA30-Cl	3
	FA15-Cl (long curing)	4
	FA30-Cl (long curing)	4

Table VI. Passivity Grades of the Steel Bars Embedded in Mortars

3.4. Cathodic Polarization

Since the anodic polarization response (Figure 7) is almost the same for OPC mortars and fly ash mortars with increased curing, the significant decrease in current density can be attributed to the performance of the mortars under cathodic polarization, the results of which are shown in Figures 8 and 9. The cathodic polarization curves for the fly ash mortars that underwent increased curing period are generally shifted to reduced current densities over much of the potential range.

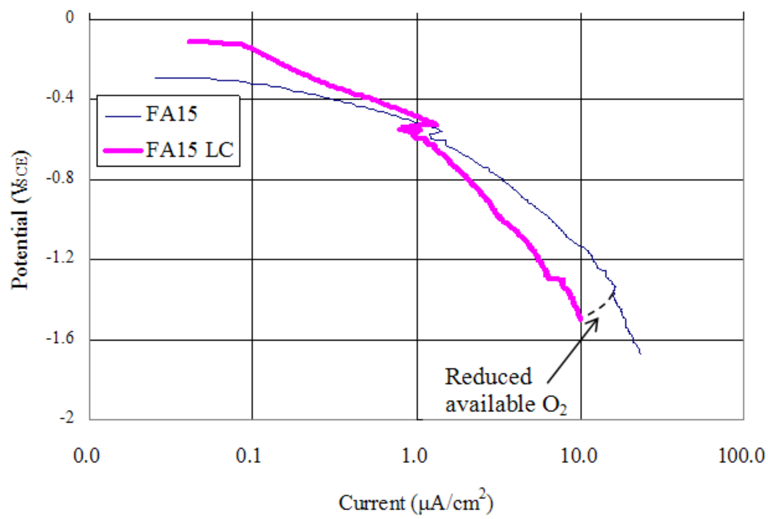

Figure 8. Cathodic Polarization Curves for FA15

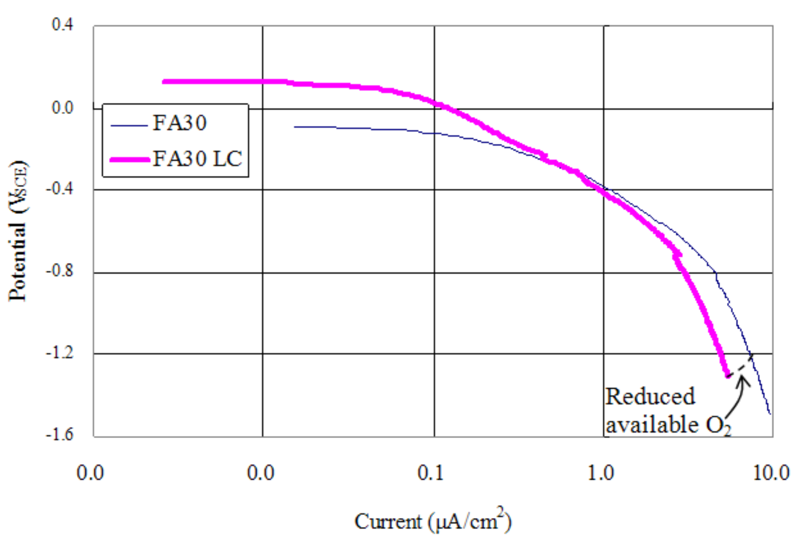

Figure 9. Cathodic Polarization Curves for FA30

When chloride ions reach the embedded steel bar, the passivation is reduced and the corrosion proceeds in the presence of sufficient oxygen and moisture. Theoretical studies about corrosion measurements by Bentur *et al.*(1997) show that the behavior of the cathodic polarization curve is related to the concentration of oxygen in corrosion process, specifically illustrating that reduction in oxygen content shifts the cathodic curve to lower current densities over wide range of potentials. Figures 8 and 9 exactly demonstrate this kind of behavior which indicates that one important factor related to the improvement of the corrosion performance of fly ash mortars that underwent increased curing is attributable to the reduction of available oxygen.

4. CONCLUSIONS

Chloride contaminated mortars blended with fly ash, when given increased curing, can be as effective as OPC mortars in inhibiting the corrosion rates within the passivity limit.

Using the anodic polarization technique, the passivity grades obtained in chloride contaminated fly ash mortars provided with longer curing is the same as OPC mortars.

Through the cathodic polarization test, it was found that the mortars blended with this binder have the ability to reduce the availability of oxygen when adequate curing is provided.

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