

Effect of surface condition on the chloride-induced depassivation of rebar in concrete

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Abstract:

Rebar in concrete is protected against corrosion by a passive film that is stable due to the high alkalinity of the pore solution. Corrosion may start once the protective passive film on the rebar surface breaks down (depassivation) due to the ingress of external ions such as chlorides or processes such as carbonation. The main goal of this investigation is to characterize the effect of surface conditions, specifically the presence of mill scale, on chloride-induced depassivation of rebar in concrete pore solution using electrochemical and microscopy techniques. To achieve this goal, linear polarization tests were conducted on black steel rebar with and without mill scale in a special corrosion cell that is designed to simulate in-service conditions. Both electrochemical and microscopic observations suggest that enhanced corrosion of as-received rebar in concrete occurs in crevices at the interface between the underlying steel surface and the mill scale which are linked to the free surface.

1. Introduction:

Corrosion of reinforcing steel (rebar) in concrete is a well-known durability problem, especially where de-icing or seawater salts come into contact with structures. The corrosion of rebar in concrete may initiate because of pH-reducing reactions (e.g. carbonation) or because of aggressive ions such as chloride. Once corrosion starts, the concrete structure will be gradually damaged because of factors such as the reduction of the cross sectional area of the steel, the cracking and spalling of the concrete cover, and the loss of bond between the steel and surrounding concrete [1].

Within the highly alkaline environment provided by concrete ($\text{pH} > 12.5$), rebar is generally well protected against corrosion by a passive film that reduces the rate of metal loss. The partial or complete loss of the passive layer, known as depassivation, may lead to excessive rates of metal loss/corrosion. Because depassivation of steel dictates when and how the corrosion will start, as well as how it will progress, it is important for civil engineers to understand the mechanism of the depassivation process. It is known that rebar can depassivate if chloride concentrations at the surface are above a threshold value. However, the

thresholds that have been reported in the literature cover a wide range and have large uncertainties [2,3]. For instance, different rebar in similar concrete types and under the same environmental conditions have been reported to depassivate at different chloride thresholds. So far, no widely accepted explanation of this variability of chloride threshold has been provided.

The main hypothesis of this paper is that the variability associated with the chloride threshold values is because of the surface condition of the rebar. Depassivation is known to depend on local surface characteristics. Research has shown that removing the mill scale and polishing the rebar surface before passivation increases the resistance of the passive film against chloride attack [4-6]. However, the underlying mechanism of this effect is not well understood.

In this study, linear polarization was used to investigate the effect of mill scale and polishing on the breakdown of passive films formed on rebar in simulated concrete pore solutions. Scanning electron microscopy (SEM) and optical microscopy were also used to explain the electrochemical observations.

2. Experimental plan:

Black steel rebar samples (Size #10M) with two different surface conditions have been investigated (Fig.1): (a) as-received rebar, with mill scale and deformities; (b) polished rebar, with the mill scale and deformities removed by machining to a depth of ~1mm and then polishing with 600-grit silicon-carbide paper. The rebar was cut to 30-mm lengths and both ends of each piece were covered with a plastic cap in order to avoid exposure of the ends to the test solution. The caps were tightly screwed to the sample to mitigate crevice corrosion at the interface between the steel and the plastic. Three replicate samples were prepared for each surface condition. A simulated concrete pore solution was prepared by dissolving calcium hydroxide ($\text{Ca}(\text{OH})_2$), sodium hydroxide ($\text{Na}(\text{OH})$), potassium hydroxide ($\text{K}(\text{OH})$) and calcium sulfate ($\text{Ca}(\text{SO}_4)$) in distilled water. The concentrations of the ions in the solution are presented in Table 1.

Table 1: Properties of the simulated concrete pore solution

Added compounds (mol/l)				Measured ions (mg/l)				pH
$\text{Ca}(\text{OH})_2$	$\text{Na}(\text{OH})$	$\text{K}(\text{OH})$	CaSO_4	Ca^{2+}	Na^+	K^+	SO_4^{2-}	
0.1	0.1	0.2	0.003	3	2232	8059	277	13.3

The rebar samples were immersed in the simulated pore solution for 8 days to allow the formation of a passive film on the steel surface [7]. Then, sodium chloride (NaCl) was added incrementally at two-week intervals, and linear polarization tests were conducted at the following chloride concentrations: 0,

0.03, 0.05, 0.15, 0.3, 0.5 and 1 M for as-received samples; 0, 0.01, 0.45, 1.25, 2 and 3 M for the polished samples. The two-week time interval between chloride addition and subsequent linear polarization measurement was chosen to give the chloride time to react with the passive film.

A corrosion cell with a co-axial platinum counter electrode was used to carry out the linear polarization tests. Further details about the test cell and the instruments used in this study can be obtained from Ghods et al. [7]. The measurements were started 15 mV below the free corrosion potential, which varied with chloride concentration, and were completed 15 mV above, using a scan rate of 0.166 mV/s as prescribed in ASTM G5 [8].

The cross-sections of oxides on as-received and polished samples were examined with a SEM and an optical microscope before passivation, and after exposure to simulated pore solution (see Table 1) plus 0.45 M NaCl.

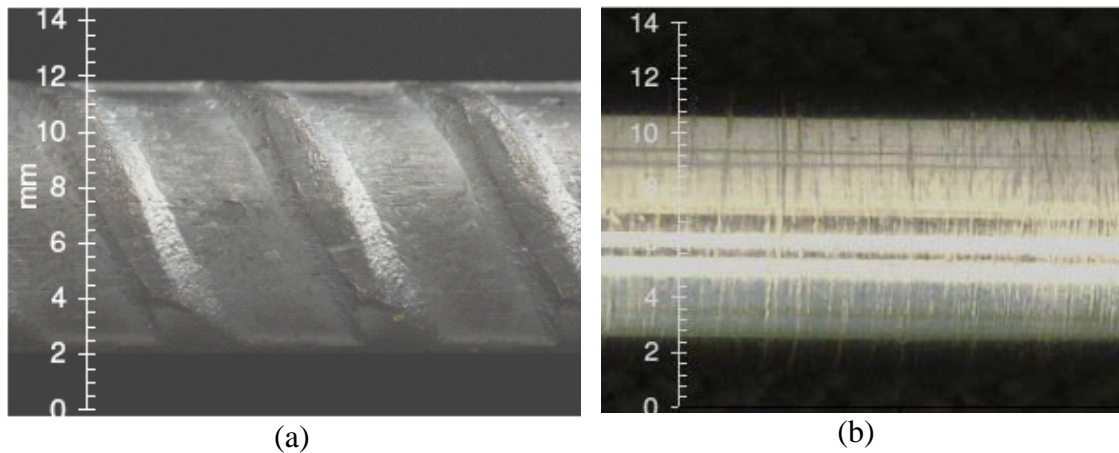


Figure 1: Optical images of rebar samples with two different surface conditions: a) as-received with mill scale and deformities; b) as-received with the mill scale and deformities removed, and the surface polished.

3. Results and discussion:

3.1. Linear polarization test:

The polarization resistance of rebar determined by averaging the results of linear polarization measurements of replicate samples is shown in Fig.2 for as-received and polished surfaces. The determined polarization resistances appear to be more variable for the as-received rebar than for the polished rebar. For both surface conditions, there appears to be a threshold chloride concentration above which there is a dramatic decrease in polarization resistance. This indicates chloride-induced passive film breakdown. The chloride threshold of as-received rebar in the simulated concrete pore solution is approximately 0.1 M, while for polished rebar it is 2 M. Thus, rebar with mill scale has reduced resistance to chloride-

induced corrosion when compared to polished rebar without mill scale. These observations are consistent with reports by other researchers [4-6].

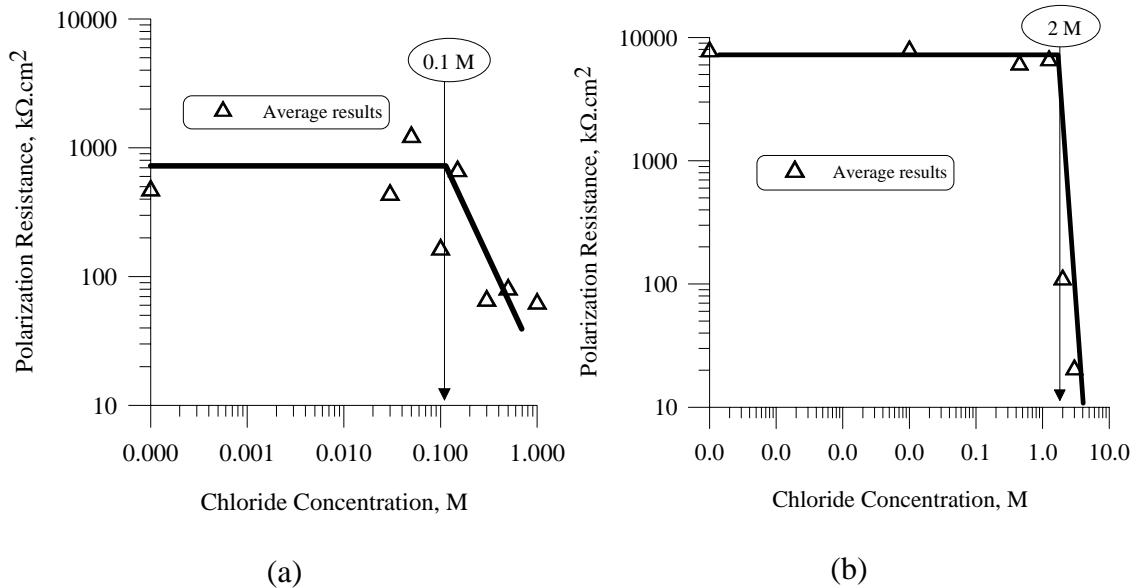


Figure 2: Polarization resistance of a) as-received rebar samples b) polished rebar samples

3.2. Microscopy:

The SEM images of as-received rebar with mill scale before immersion in the simulated concrete pore solution are shown in Fig.3. The average thickness of mill scale on the rebar surface was found to be 20-40 μm (Fig.3(a)). Higher magnification SEM images of the mill scale (Fig.3(b)) revealed that the interface region between the underlying steel and the mill scale was filled with voids and pores. In some locations, there were also cracks inside the mill scale that linked the voids and pores to the free-surface. Hence, these cracks are pathways for the concrete pore solution to penetrate into the voids and pores. Energy Dispersive X-ray Spectroscopy (EDS) analysis of the mill scale is presented in Fig.3(c). The results show that the mill scale generally consists of iron oxide components, as expected [9].

Optical images are shown in Fig.4 of representative oxide cross-sections taken from as-received rebar with mill scale after immersion in the simulated concrete pore solution plus 0.45 M NaCl. The images show that the corrosion primarily initiates in crevice sites beneath the mill scale. In locations where the mill scale does not exist, there is no evidence that the rebar is corroding. Thus, for as-received rebar samples, voids and pores at the interface between the underlying steel and the mill scale provide sites for crevice corrosion.

Figure 5 shows SEM images of an oxide cross-section of polished rebar before passivation. In contrast to the as-received rebar, there was no visible layer of iron oxide on the steel surface, as expected because the mill scale was removed; the

steel surface was clean and quite uniform. No sign of corrosion was observed in optical microscope images of cross-sections taken from polished samples after exposure to the simulated concrete pore solution with 0.45 M NaCl added. However, when the chloride concentration was increased beyond the threshold value (2 M), it was observed that crevice corrosion initiated where the cap was attached to the rebar sample (See Fig. 6). This re-iterates the importance of crevices.

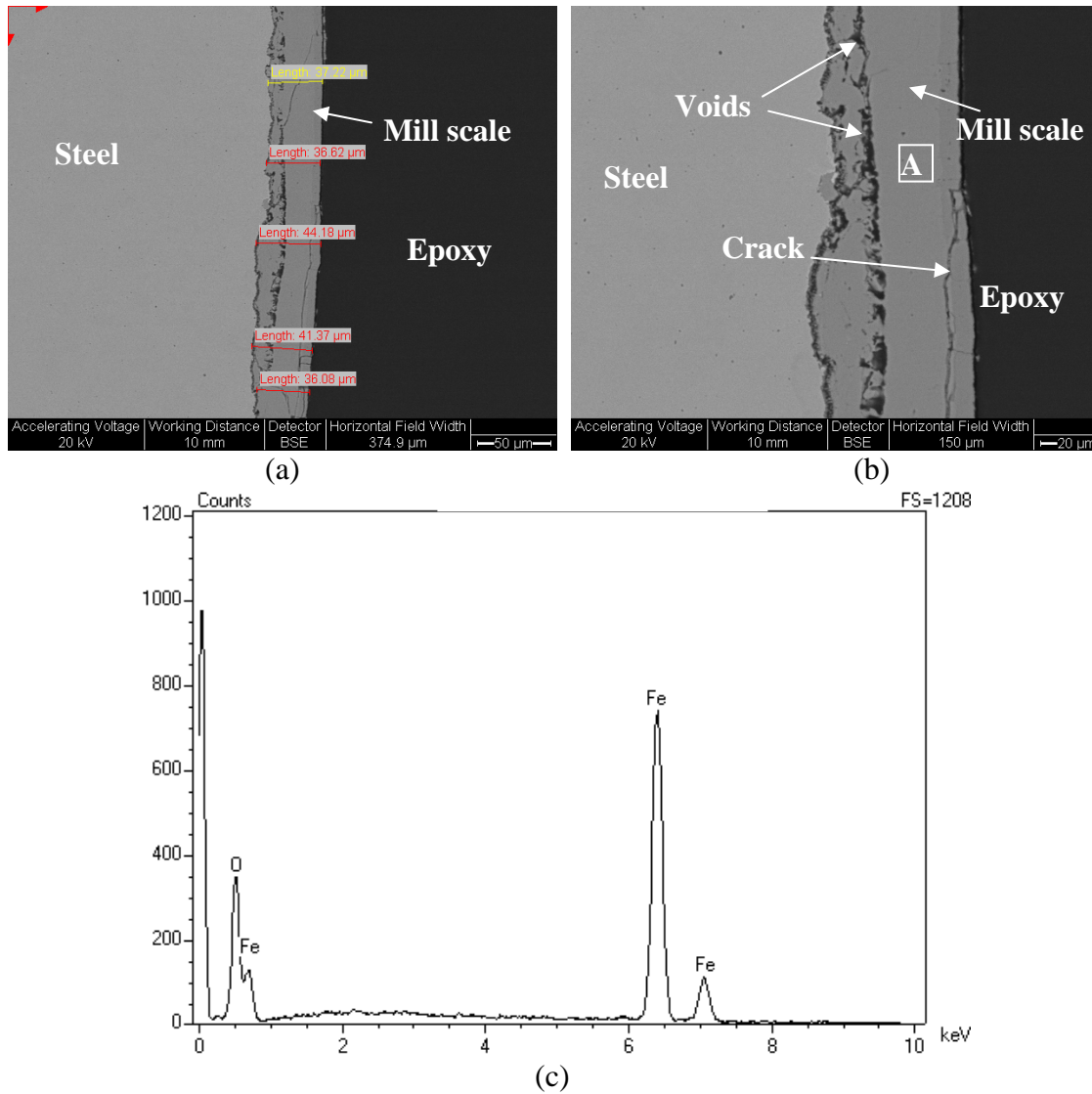


Figure 3: SEM images of as-received rebar samples before exposure: a) higher magnification image; b) lower magnification image and c) EDS analysis of area "A" marked in Fig. 3(b)

The results of this work suggest that the variability of rebar in-service might be attributable, at least in part, to crevice corrosion at the steel/mill-scale interface. Compared to the polished rebar, the as-received rebar has greater variability in polarization resistance, and lower chloride depassivation threshold. In addition,

as-received rebar has pores and voids at the steel/mill-scale interface that are connected by cracks to the free surface. These observations are all consistent with the optical-microscope observations that corrosion of as-received rebar primarily initiates in crevice sites beneath the mill scale. Thus, the observed variability in the chloride threshold values of as-received rebar in service could be linked to crevice corrosion at the steel/mill-scale interface, because of the variability in how mill scale is formed in production. Further electrochemical and microscopic studies are required to support this conclusion.

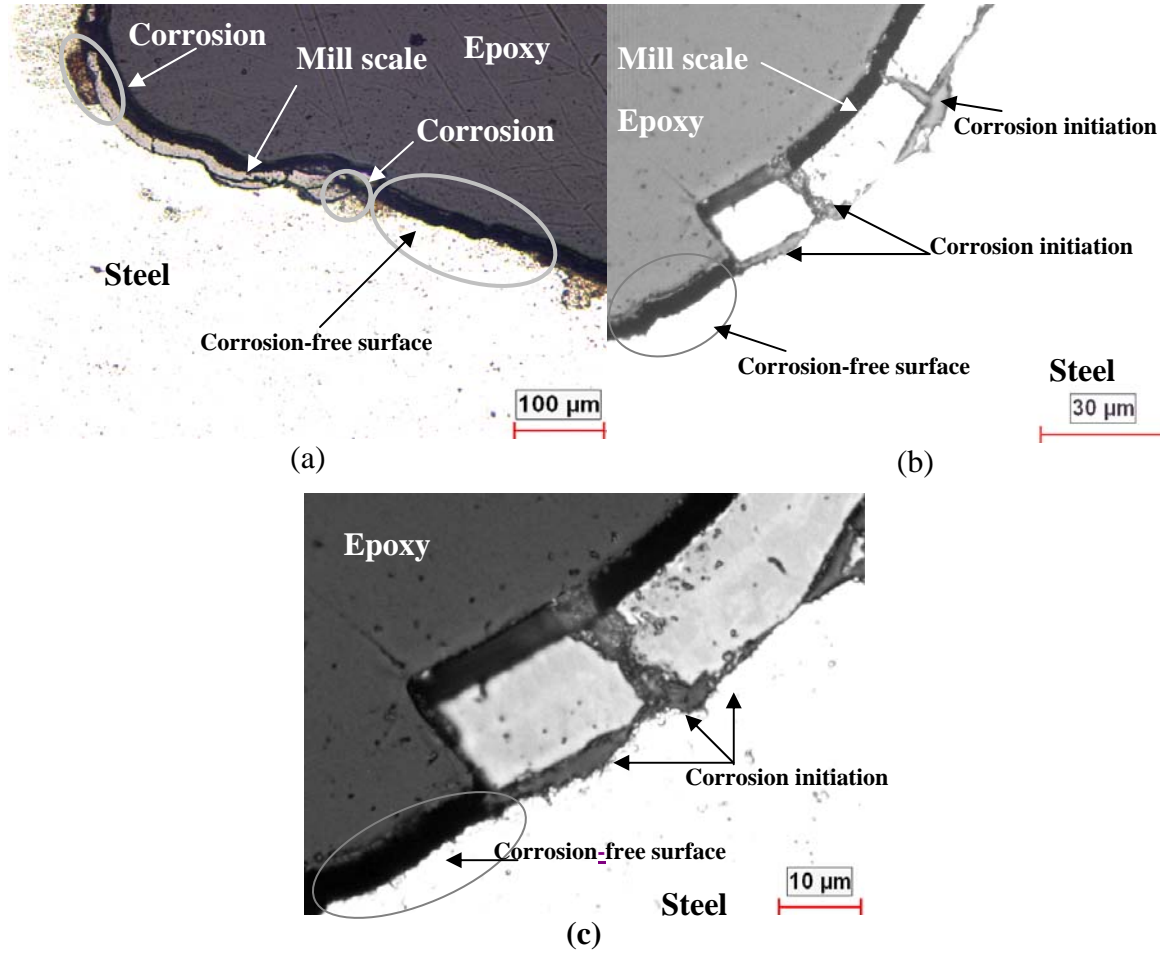


Figure 4: Optical microscope images of as-received rebar samples showing corrosion initiation at different locations.

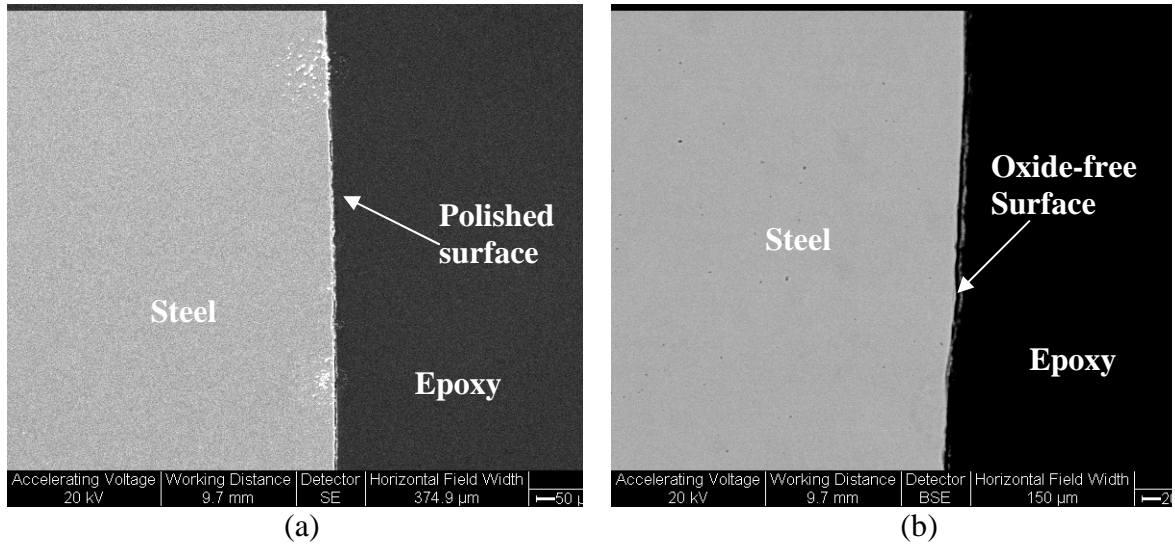


Figure 5: SEM images of polished rebar samples before immersion: a) lower magnification image; b) higher magnification image.

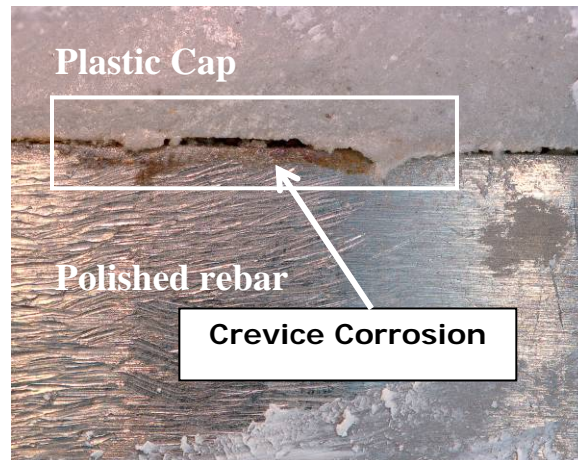


Figure 6: Crevice corrosion at the interface between the polished rebar sample and the plastic cap at chloride concentration in excess of 2 M

4. Conclusion:

Linear polarization resistance tests show that the condition of the surface has a significant impact on the chloride-induced depassivation of rebar in concrete pore solution. As-received rebar with mill scale has much lower polarization resistance and lower chloride depassivation threshold than polished rebar with the mill scale and deformities removed. The microscope studies suggest that local crevice corrosion at the steel/mill-scale interface may be responsible for corrosion initiation in as-received rebar; this needs to be supported by additional

electrochemical and microscopic studies. The implication is that corrosion rates determined from studies with polished samples will under-predict rates in-service.

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