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An assessment on the mill scale effects on the electrochemical characteristics of steel bars in concrete under DC-polarization

E. Mahallati *, M. Saremi

Metallurgy and Materials Engineering Department, Faculty of Engineering, University of Tehran, Tehran, Iran

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Abstract

The effects of mill scale on formation and stability of passive film on rebars in chloride-bearing concrete is investigated. Studies were carried out on some electrochemical parameters such as repassivation potential, E_{rep}, and passive current density, i_{pass}, using cyclic potentiodynamic polarization. The superficial mill scale on the rebars was naturally produced during hot-working of steel. The experiments were performed in the concrete samples with a cement/sand/water ratio 1:3:0.6. The results demonstrated that the presence of mill scale on the rebars in chloride-free concrete causes a decrease in electrical resistance of the passive film and its reparability. However in presence of chloride ions because of the severity of corrosion the effect of mill scale on corrosion of rebars is less manifested.

Keywords: Corrosion; Concrete; Mill scale; Passivation; Chloride

1. Introduction

Steel bars embedded in reinforced concrete are traditionally protected due to the presence of passive film that is formed on the surface of reinforcing bar in alkaline condition. Nevertheless, chloride-induced corrosion of steel bar is the most common cause of failure in concrete structures [1–5].

Studies on corrosion of rebars in concrete have most frequently been concentrated on polished steel surface prepared in laboratory works [6–8]. However the natural oxides, which are formed on the steel bar during fabrication or exposure to the atmosphere, may affect the corrosion behavior of rebar in concrete. These superficial ferrous oxides are generally known as "mill scale" and are composed of FeO, Fe_2O_3 and Fe_3O_4. The mechanism whereby mill scale is formed is generally considered to be of dynamic nature so that alternate formation and reduction of higher oxides of iron are occurred. The final result is a scale composed of layers rich in oxygen at the scale surface and rich in iron at the metal surface [9].

Gonzales et al. [10] reported that passivation is fully inhibited or considerably delayed, if reinforcements are appreciably pre-rusted. The effect of superficial coverage with different iron oxide on the corrosion resistance of steel bar in concrete was also investigated [11]. The results showed that in presence of chloride ions, the passivity deteriorated differently depending on the type of oxide present on the surface.

In these studies, polarization resistance measurements and corrosion potentials are often used in attempts to determine the

Table 1
Test program

Sample no.	Condition of concrete samples		Surface condition of rebars		Exposure time (month)
	Without Cl^-	With Cl^-	Polished	Mill scale	
1	*		*		1
2	*		*		3
3	*		*		17
4	*			*	1
5	*			*	3
6	*			*	17
7		*	*		1
8		*	*		3
9		*	*		17
10		*		*	1
11		*		*	3
12		*		*	17

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* Corresponding author.
E-mail address: mahalehs@yahoo.com (E. Mahallati).

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Table 2
Composition of the OPC cement (wt.%)

CaO	SiO_2	Al_2O_3	Fe_2O_3	MgO	SO_3	Insoluble residue	Ignition loss
65.12	20.60	4.97	2.68	1.50	2.62	0.20	1.30

Table 3
Chemical composition of mild steel bars (wt. %)

C	Si	Mn	P	S	Cr	Ni	Cu
0.12	0.02	0.41	0.018	0.04	0.12	0.6	0.14

corrosion rate and the corrosion state of the rebar, respectively, though they can not provide mechanistic information or may be misinterpreted [12].

The aim of this research work is to study the effect of mill scale on the chloride-induced corrosion of rebar in concrete using cyclic potentio-dynamic polarization tests. This technique can provide information about corrosion status of rebar in concrete, the risk of pit initiation (from E_{pit}), and the tendency for pit repassivation (from the size of the hysteresis loop in the reverse pitting scans).

2. Experimental

2.1. Concrete samples

The test programs for all samples are presented in Table 1. The concrete samples with and without chloride additions were prepared using Ordinary Portland Cement (OPC), whose analysis is shown in Table 2. Chloride was added as analytical grade NaCl in a value of 7% by weight of dry cement. All samples with a cement/sand/water ratio of 1:3:0.6 were cast in Perspex moulds as shown in Fig. 1, in which there was a centrally embedded, machined or as received (mill scale-covered), steel bar having the composition given in Table 3. The steel bars (machined and mill scale-covered) were degreased in alcohol after which the machined bars were polished using a series of silicon carbide emery papers of grade 800, 1000, and 1200. Their top and bottom ends were masked with epoxy resin to give an exposed area of 16 cm^2.

All the concrete samples were initially cured for 14 days in sealed plastic sheets at about 30 °C and then stored in laboratory atmosphere for a week. After the curing period these samples were subjected to alternate wet and dry cycles, soaking in aerated water for 3 days and drying in laboratory air for 4 days. For each condition of concrete sample, rebar surface and exposure time, three identical specimens were tested.

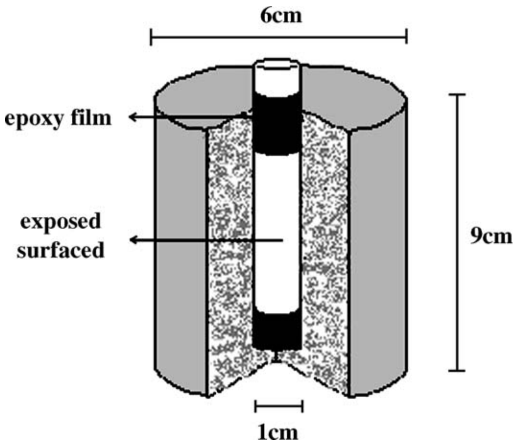

Fig. 1. Schematic illustration of the reinforcing bar embedded in concrete sample.

2.2. Electrochemical measurements

Cyclic potentiodynamic polarization and AC-impedance technique were carried out using an EG and G Model 273A potentiostat/galvanostat and a Frequency Response Analyser Model SI 1255 of Solarton. The impedance measurements were performed in the 100 kHz to 4 mHz frequency range and an alternating potential with signal amplitude of 5 mv.

The samples were kept in the solution for 30 min in order to establish a stable Open Circuit Potential (OCP) at which the cyclic polarization measurements were initiated.

Since the experimental parameters of cyclic potentiodynamic polarization, particularly scan rate, will affect both E_{pit} and E_{rep} [13–15], the cyclic polarization tests were carried out at a constant scan rate of 2 mV s^{-1}. IR compensation was applied using current interrupted method and noise reduction was carried out by the provided software.

3. Results and discussion

The schematic diagram of a typical cyclic potentio-dynamic polarization curve of steel bar in concrete sample is shown in Fig. 2. The potential scanned from 100 mV more negative to the OCP of each specimen toward E_{pit}, then extended approximately 100 mV above E_{pit}, and finally the potential was reversed to intersect the forward polarization curve.

This technique is often used to evaluate pitting susceptibility in electrochemical studies. Two informative potentials, namely pitting potential, E_{pit}, and repassivation potential, E_{rep}, are of interest in cyclic polarization. E_{pit} is the potential at which depassivation occurs and probably pitting starts. On reversal of

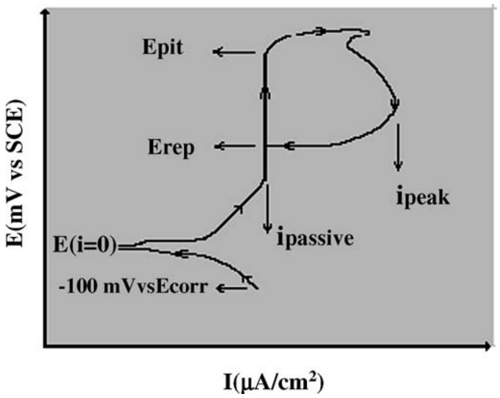

Fig. 2. Schematic diagram of cyclic potentio-dynamic polarization for mild steel in SCP solution.

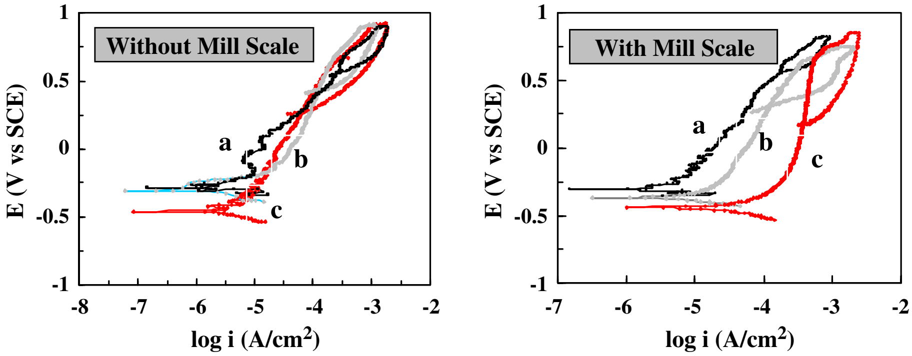

Fig. 3. Cyclic polarization curve of steel bar embedded in chloride-free concrete: (a) 1 months, (b) 3 months, (c) 17 months.

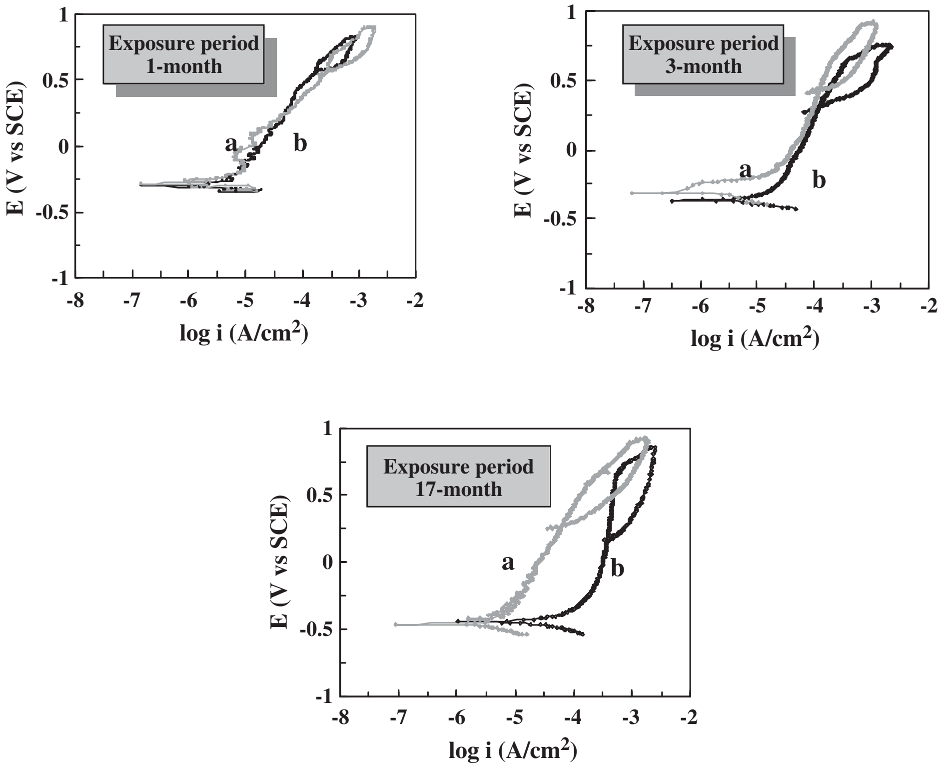

Fig. 4. Cyclic polarization curves of steel bars for three exposure periods in chloride-free concrete samples; (a) without mill scale, (b) with mill scale.

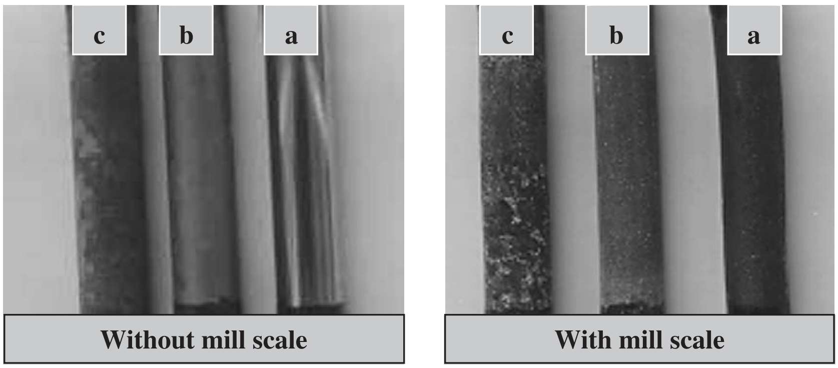

Fig. 5. Photograph of rebars with and without mill scale embedded in concrete samples. From right to left (a) reference, (b) in absence of Cl$^-$, (c) in presence of Cl$^-$.

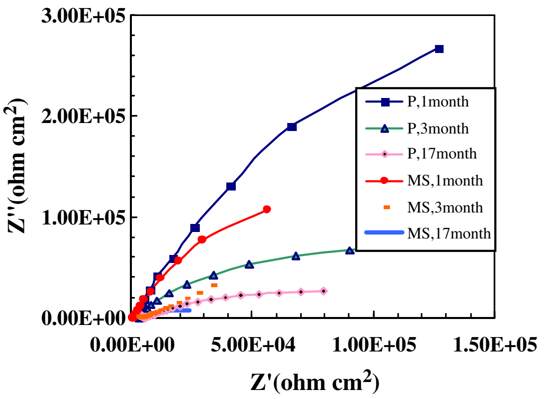

Fig. 6. Nyquist plot of steel bar in chloride-free concrete samples. P = Polished bar, MS = Mill scale-covered bar [18].

the anodic polarization curve upon reducing potential the destructed passive film may be repaired. In this case, the reverse scan intersects the forward scan at E_{rep} below which pitting cannot occur. If pitting is not present, there is minimal hysteresis loop between the forward and reverse scans. Therefore the existence of the hysteresis is usually an indication of pitting, while the size of the loop is often related to the amount of pitting.

3.1. Chloride-free concrete samples

The cyclic polarization curves of polished (without mill scale) steel rebars embedded in chloride-free concrete samples and subjected to an alternate wet and dry cycles for 1, 3, and 17 month are shown in Fig. 3(a). There is no significant difference between the curves except in their repassivation potentials, E_{rep}, which are shifted to less positive values over the time. This may be an indication of the formation of a less repairable passive film on steel bars in concrete, as have been discussed in other research works [16,17].

The cyclic polarization of mill scale-covered bars in similar concrete samples for three exposure periods is depicted in Fig. 3(b). In these plots a considerable rise in i_{pass} is observed with a fall in the E_{rep} with time, which is significant after 17 months of immersion period. The increase of i_{pass}, which is a criterion of anodic dissolution of metal in passive state, can be attributed to the reduction of electrical resistance of the passive film, R_{pass}, during the exposure time. In this regard, R_{pass} corresponds to the formation and thickening of a tight passive film, whose protectiveness depends on outward transport of cations (M^{n+}) and its combination with O^{2-} or OH^- ions at the film/solution interface. As a result, the superficial mill scale working as a barrier, can prohibit the ions O^{2-} and OH^- to reach the cations M^{n+}, and hence hinders or markedly delays the passivity even in high alkaline solutions.

Therefore, the role of mill scale on promotion or prevention of passivity can be shown by comparing the electrochemical behavior of bare and mill scale-covered embedded steel under the same exposure conditions. These are comparatively presented for three interval tests of 1, 3 and 17 months in Fig. 4. It is observed that for each stage of exposure time, the presence of mill scale on the rebars causes a decrease in electrical resistance of the passive film, which is demonstrated on cyclic curves by an increase in i_{pass}. For example, the i_{pass} value of sample no. 6 having 17 months of exposure time was increased ten times due to the presence of mill scale. Furthermore, the mill scale leads to a decrease in E_{rep} value of steel bars in concrete too. These behaviors indicate that mill scale diminishes protection properties of passive film formed on rebars.

In chloride-free samples (Fig. 3) the reverse scans intercept the forward polarization curve at high potentials indicating high E_{rep} or better reparability of the passive layer. There were no sign of localized or general corrosion on rebars surface as shown in Fig. 5. However, in mill scaled samples, subjecting to wet and dry cycles, a decrease of 40, 89 and 95 mV are observed in E_{rep}, in comparison with the polished rebars, on the cyclic curves after 1, 3 and 17 months of immersion, respectively (Fig. 4). This change is ascribed to a decrease in passive film reparability due to presence of superficial mill scale.

The study of Nyquist plots resulting from impedance measurements of rebars with or without superficial mill scale in concrete samples shows the presence of two arcs at high and low frequencies. These arcs are due to two-separated time constants of the reactions taking place on steel surface. The high frequency arc is related to the adsorption of OH^- ions on steel surface. The low frequency arc is due to the interfacial reactions comprising two processes with a similar and inseparable time constant. These processes are passive film formation and charge transfer reaction [16].

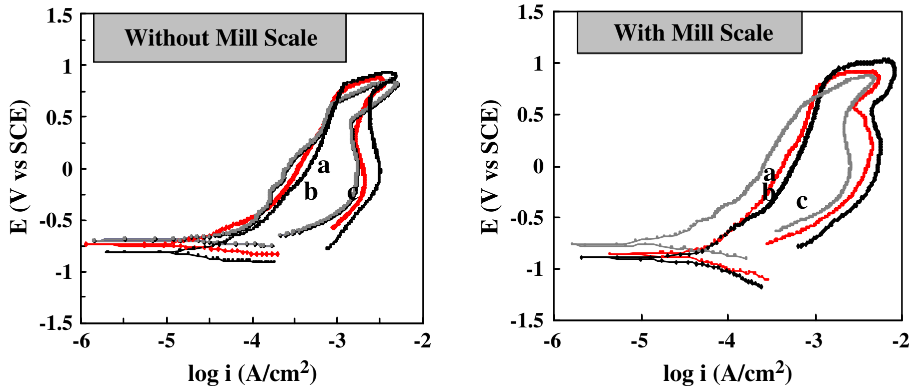

Fig. 7. Cyclic polarization curve of steel bar embedded in chloride-bearing concrete; (a) 1 months, (b) 3 months.

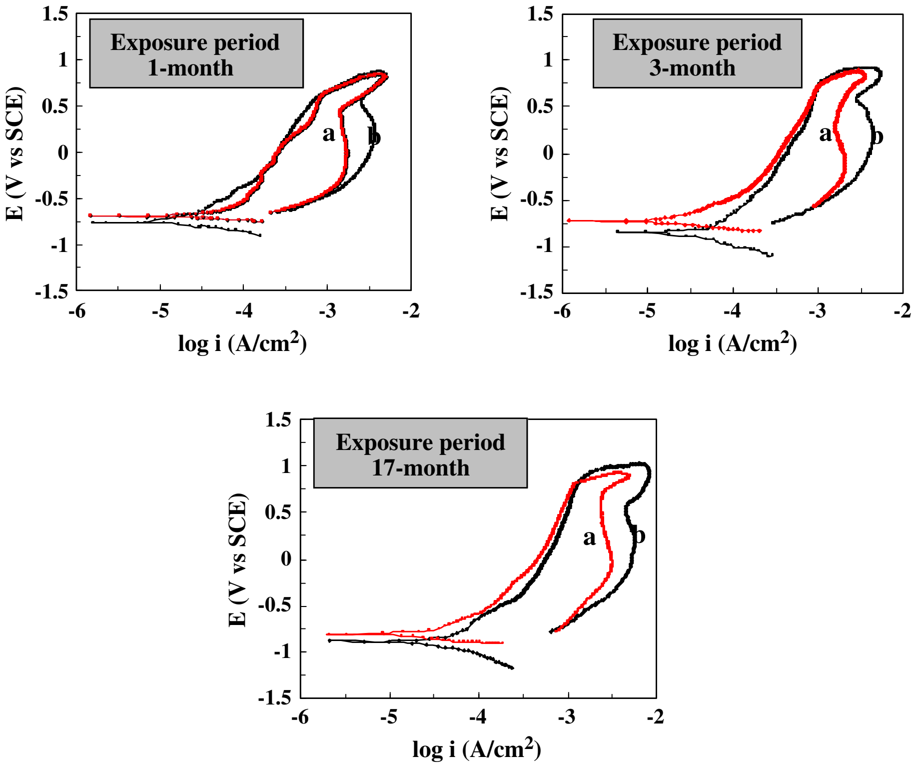

Fig. 8. Cyclic polarization curves of steel bars for three exposure periods in chloride-bearing concrete samples; (a) without mill scale, (b) with mill scale, (c) 17 months.

Depending on the test conditions, the high frequency arc may not seen in extended frequency spectrum, because high and low impedance networks are in series and the larger impedance controls the plot scaling. Hence the high frequency arc is not particularly observed in the Nyquist plot of rebar in chloride-free concrete having higher impedance arc at low frequencies. It should be noted that the high frequency arc may be seen by admittance plot or by enlarging the high frequency portion of the spectrum.

Fig. 6 shows the Nyquist plot of rebars with or without superficial mill scale in chloride-free concrete samples. This figure demonstrates that in each period of exposure time, the reduction in size of the impedance arcs, induced by mill scale, leads to more surface activation and consequently enhancing charge transfer process.

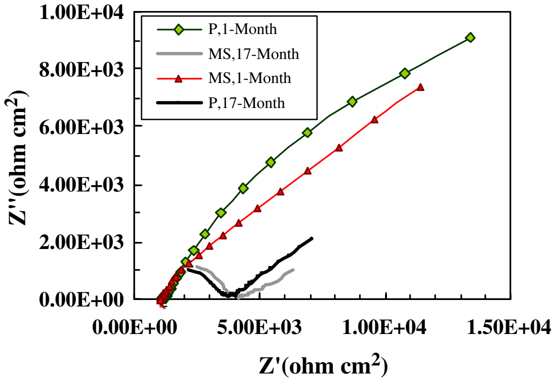

Fig. 9. Nyquist plot of steel bar with and without mill scale in Cl^- bearing concrete. P: Polished rebar, MS: Mill scale-covered rebar [18].

3.2. Chloride-bearing concrete samples

With respect to Figs. 3 and 7 it is observed that in spite of chloride ions addition to concrete samples the E_{pit} of rebars occurs at the same potential. This is due to the fact that the concentration of chloride ions on the rebar surface does not reach to the threshold value needed for passivity breakdown ($[Cl^-]/[OH^-]=0.6–1$). It has already shown that addition of chloride ion to simulated concrete pore solution below the $[Cl^-]/[OH^-]$ ratio of 1 will not affect the pitting potential [16]. In these conditions the breakdown of passive film during anodic polarization may come from other factors such as; oxygen evolution process and/or stress concentration in the passive film due to increase in film thickness. Since, in cyclic potentiodynamic polarization, the pitting potential (E_{pit}) is not a preset parameter therefore during anodic polarization, the potential of rebar is increased to higher potentials (i.e. +0.7 V for rebars in concrete) in which the passive film is destructed and the anodic curve goes to transpassive region.

In presence of chloride ions the reverse polarization curves of steel bars with or without mill scale shows no intercept of forward curve and consequently E_{rep} equals to open circuit potential, E_{ocp}, (Fig. 7). It can be deduced that the repair of destructed passive film is impractical, and as a result, pitting corrosion is inevitable at these sites.

In Fig. 5, it is shown that in Cl^- bearing concrete, the sample with or without mill scale will corrode after a few months of immersion in wet and dry cycles (compare sample C in both figures of 17 month period). It is further shown in polarization diagrams of Fig. 7 that in Cl^- bearing concrete samples the rebars will corrode from the beginning no matter if they have mill scale or not whether they are immersed in short or long term period.

It is realized that the effect of mill scale is overshadowed by the Cl^- induced corrosion, although there are slight differences between the polarization curves by comparing individual curves of various immersion periods (Fig. 8).

The results obtained in this study are in agreement with the earlier investigation of the subject using AC-impedance method [18] and was concluded that in Cl^- bearing concrete samples, the effect of mill scale on rebar activities is negligible (Fig. 9).

4. Conclusion

(1) The presence of mill scale on steel bars in concrete reduces the electrical resistance and reparability of the passive film, consequently reduces its protective characteristics.
(2) Superficial mill scale increases the corrosion of steel bar in concrete, but in presence of Cl^- ions its effect is overshadowed by the high corrosion rate resulted from chloride ions.
(3) Finally it can be concluded that presence of mill scale on rebar in concrete is a detrimental and retarding parameter on the formation and performance of passive film.

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