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The effect of the electrochemical chloride extraction treatment on steel-reinforced mortar
Part I: Electrochemical measurements

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Abstract

A study has been made of the effectiveness of electrochemical chloride extraction in reducing chloride-induced corrosion of rebar embedded in steel with chlorides added with the mixing water, ingressed by ponding with a NaCl solution, or both. After exposure for 1 year, specimens with and without chlorides were subjected to an electrochemical chloride extraction treatment. Corrosion measurements taken before and after extraction showed that the treatment halted chloride-induced pitting in those specimens that were under attack. However, the extraction treatment increased the overall corrosion rate for all specimens studied due to reduction of the passive film and significant changes in pore solution and cement chemistry adjacent to the rebar. © 1999 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Steel-reinforced concrete is an extensively used structural material because of its low cost, ease of construction, and durability. With exposure to chlorides either from the use of deicing salts or exposure to marine environments, the steel embedded in concrete may corrode and form expansive products at the steel/concrete interface, which crack and spall the concrete. There are only two rehabilitation methods currently available that are capable of stopping corrosion once it has been initiated: the conventional treatment of cathodic protection and the emerging method of electrochemical chloride extraction. Both techniques normally use an impressed current that transforms the corroding steel from a collection of anodic and cathodic sites to a cathode with the addition of an external electrode and power supply to the surface of the concrete. (For cathodic protection in practice, however, the potential rather than the current may be controlled to ensure that hydrogen is not evolved at the surface of the steel, in which case the corrosion rate may be drastically reduced rather than the steel being made cathodic.) The resultant electrical field gradient repulses the chloride ions (and other anions) from the reinforcing steel. In cathodic protection, a current density of 1 mA/m^2 of concrete surface is typically applied for the remaining lifetime of the contaminated structure. Electrochemical chloride extraction, however, uses higher current densities over shorter time periods, typically 1 A/m^2 of concrete surface for 6 to 8 weeks; the external anode is placed in a liquid electrolyte rather than shotcrete. The resulting effect is that chlorides are removed from the concrete rather than migrating only a short distance away from the reinforcing steel, as is the case with cathodic protection [1]. The primary advantage of electrochemical chloride extraction is that it reduces the long-term personnel and maintenance costs associated with cathodic protection.

Previous research in this area has focussed primarily on the reduction in the chloride contents [2–5], with less work on the subsequent electrochemical behaviour of the system and very little reported work on the microstructural characterization of treated concrete [6], although macrostructural observations of the steel/concrete interface have been reported [7–9]. It is the intention of the present work to integrate electrochemical measurements presented here and microstructural characterization of steel-reinforced mortar reported in Part II of this work [10], so that a more detailed understanding of the future durability of treated structures can be achieved.

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2. Theoretical considerations

2.1. Electrochemical reactions

Corrosion of the reinforcing steel can be represented by two electrochemical reactions: the anodic dissolution of iron, shown in Eq. (1):

$$2\ Fe_{(s)} \rightarrow 2\ Fe^{2+}{}_{(aq)} + 4\ e^{-} \tag{1}$$

and the corresponding oxygen reduction at the cathode that uses the electrons generated by the metal dissolution in its reaction, shown in Eq. (2):

$$O_{2,(g)} + 2\ H_2O_{(l)} + 4\ e^{-} \rightarrow 4\ OH^{-}{}_{(aq)} \tag{2}$$

Prior to the application of the extraction treatment, both of these reactions occur on the surface of the steel, resulting in the formation of corrosion pits that deepen as the rate of corrosion increases and an accumulation of corrosion products.

The application of the extraction treatment uses a direct current (DC) power supply and external anodes to generate a constant current or potential, schematically illustrated in Fig. 1. During the extraction treatment, any corrosion products are electrochemically reduced at the reinforcing steel (cathode) in addition to the reaction represented by Eq. (2). Furthermore, hydrogen gas is evolved at the reinforcing steel because of the low cathodic potential that is induced by the high current density, as in Eq. (3).

$$H_2O_{(l)} + 2\ e^{-} \rightarrow 2\ OH^{-}{}_{(aq)} + H_{2,(g)} \tag{3}$$

The electrochemical reactions occurring at the external anode are represented by Eq. (4) and Eq. (5):

$$2\ H_2O_{(l)} \rightarrow 4\ H^{+}{}_{(aq)} + O_{2,(g)} + 4\ e^{-} \tag{4}$$

$$2\ Cl^{-}{}_{(aq)} \rightarrow Cl_{2,(g)} + 2\ e^{-} \tag{5}$$

The reaction represented by Eq. (5) can be suppressed by keeping the pH of the electrolyte sufficiently high, above approximately 9. An alkaline electrolyte capable as acting as a buffer solution (e.g., 0.1 M sodium borate, Na_3BO_3) is often used for this purpose. The electrolyte also counteracts the acidification of the surface of the concrete from the reduction of pH by the hydrogen ions formed by the reaction in Eq. (4).

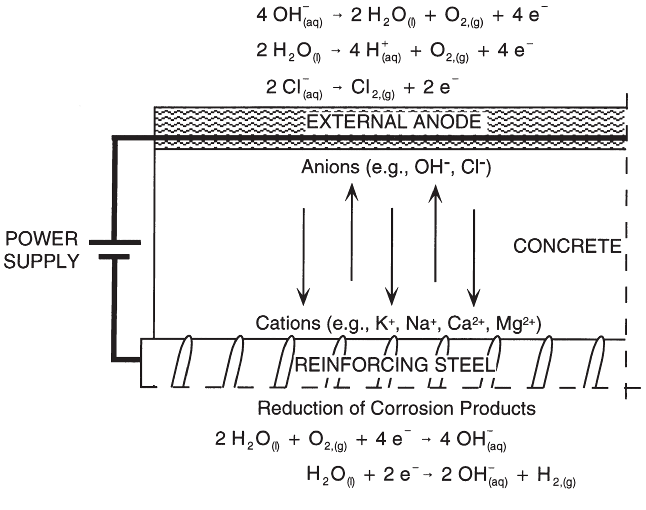

Fig. 1. Schematic illustration of the application of the electrochemical chloride extraction treatment to a corroding reinforced concrete structure.

2.2. Effect of electrochemical chloride extraction on corrosion rates

Using linear polarization resistance techniques, Green et al. [11] observed that prior to the application of the extraction treatment, the corrosion rates were 80 to 350 mA/m^2, whereas immediately after the treatment, the corrosion rate was 3.2 A/m^2 and dropped to 80 mA/m^2 after 21 days. They concluded that the extraction treatment did not significantly reduce the corrosion rate in the period up to 21 days after the treatment was halted.

To explain these results, Green et al. [11] concluded that the treatment induced a local oxygen depletion and increased the pH because of oxygen reduction and water hydrolysis, respectively. These effects would increase the corrosion rate relative to the passive corrosion rate but would be considerably lower than active corrosion due to chlorides. Hansson [12], using deaerated samples produced by prolonged cathodic polarization, showed that the corrosion rate of bare steel is significantly higher than the original passive corrosion rate, but values of the magnitude observed by Green et al. are unlikely to be due to the depletion of oxygen alone. It is most likely that the increased pH due to the cathodic polarization of the steel resulted in alkaline attack of the steel, which generates $HFeO_2$-ions as illustrated by the high pH, low potential region of the E/pH diagram in Fig. 2. The exact mechanism of this attack is unclear but Odden [4] and Buenfeld and Broomfield [6] found black-brown rust on the surface of the steel, which they attributed to the extraction treatment. From the oxygen and water deficiency imposed by the extraction treatment, magnetite (Fe_3O_4) was probably the corrosion product formed. In consideration of these factors, Green et al. [11] concluded that corrosion rate measurements taken shortly after the treatment ended were likely to have overestimated the equilibrium corrosion rate. The effect of oxygen replenishment and the reestablishment of the equilibrium pH in the pore solution at the steel/concrete interface were suggested as topics for future work.

Furthermore, Green et al. [11] averaged the corrosion rates determined using the linear polarization resistance technique over the total area of steel in their specimens, whereas the corrosion of rebar normally produced by chlorides is localized and, in the present authors' experience of this type of specimen and exposure, typically less than 10% of the total steel area. Consequently, the actual corrosion rates in the pitted area prior to extraction would have been significantly higher than the values reported, while the values determined after extraction would have been correct be-

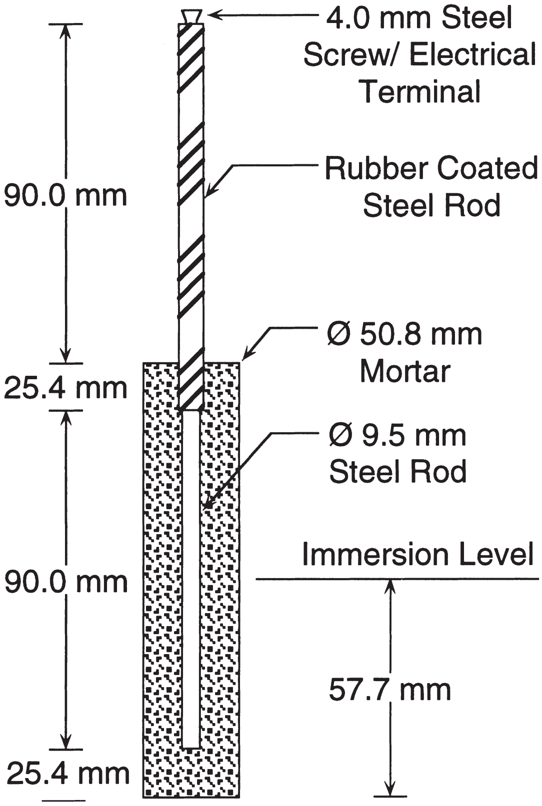

Fig. 2. Detailed drawing of cylindrical mortar specimens.

cause of the general nature of corrosion. Therefore, the true effect of extraction on corrosion rates is still unclear.

3. Experimental procedures

Cylindrical mortar specimens of the mixture proportions given in Table 1 were cast with a centrally embedded steel rod, as illustrated in Fig. 2. These specimens were used to investigate any difference between the effect of chlorides admixed in the fresh mortar and those chlorides that ingressed into the hardened mortar from an external solution. For the admixed chlorides, 2.0% chlorides by mass of cement were added as NaCl to the mixing water. All specimens were demoulded after 24 h and were cured for 28 days at approximately 25°C and 100% relative humidity. Half of the specimens were immersed in a 1 M NaCl solution that was saturated with calcium hydroxide, while the remainder were only immersed in a saturated calcium chloride solution. In total, four different situations were investigated and their mixture proportions and exposure regimes are included in Table 1.

Table 1
Mixture proportions and exposure regimes of the cylindrical mortar specimens

Component	Mix 1	Mix 2	Mix 3	Mix 4
Type I cement	1	1	1	1
Sand	3	3	3	3
Water	0.5	0.5	0.5	0.5
Admixed chloride ion content (percentage by mass of cement)	0	2	0	2
Ingressed chloride ion content (mol/L of immersion solution)	0	0	1	1

After approximately 10 months, linear polarization resistance and full potentiodynamic polarization measurements were performed on those specimens that were to undergo the extraction treatment. The remaining untreated specimens were used as controls. The extraction treatment was performed using a current density of 1 A/m^2 of mortar surface (approximately 8.37 A/m^2 of steel surface) for 8 weeks with 0.1 M Na_3BO_3 as the electrolyte and platinized titanium mesh as the external anode. At the conclusion of the treatment, the specimens were again immersed in a saturated calcium hydroxide solution. After 31 days had elapsed, the linear polarization resistance and full potentiodynamic polarization measurements were repeated on the treated specimens. One untreated and one treated specimen for each type of chloride exposure were sectioned lengthwise and the steel rods were prised from the mortar. The remaining treated specimens were undisturbed to allow their long-term corrosion activity to be monitored. The interior of each specimen was photographed immediately after sectioning to record and visually assess the macroscopic appearance of the steel and the surrounding mortar. Approximately 30 mm of both the steel rod and its mortar cover were further sectioned at the centre of the immersion level of the specimens, indicated in Fig. 2. Triplicate mortar chloride analyses were performed using potentiometric titration on representative samples of the mortar, and the steel and the mortar adjacent to the steel were studied using an environmental scanning electron microscope coupled with energy dispersive X-ray spectroscopy. These results are reported in Part II of this work [10]. Total porosity measurements and pore size distribution measurements were also performed on triplicate mortar sections and were reported in a previous publication [13].

4. Results and discussion

4.1. A comparison of the linear polarization resistance measurements, before and after extraction

The corrosion current densities of the selected specimens before extraction and 31 days after the conclusion of the treatment are compared in Fig. 3. If one assumes the criterion described by Andrade et al. [14] that corrosion rates lower than 1 mA/m^2 represent passive conditions, then it might be concluded that none of the chloride-containing specimens were corroding prior to the application of the extraction treatment. However, when these measured corrosion currents were corrected to take into account the observation that corrosion occurred on only about 5% of the polarized surface area of the steel, all specimens containing chlorides could be considered as actively corroding. Consequently, for those specimens that were observed to be corroding when the steel was prised from its mortar, values for the corrosion current densities averaged both over the whole steel surface and over 5% of the surface are given in Fig. 3, together with the post-treatment corrosion rates averaged over the whole bar. It is clear from these data that the post-treatment corrosion rates are significant, even 1 month after conclusion of the treatment. This is due to two factors. First, the treatment reduced any passive film along with any existing corrosion products on the surface of the steel leaving it susceptible to active general corrosion over the whole steel area. It also electrochemically reduced any dissolved oxygen in the local concrete pore solution, thereby eliminating any possibility of repassivation. Second, the treatment produces large amounts of OH^- ions at the steel surface, increasing the pH to very high levels and putting the steel in the alkaline corrosion region of the E/pH diagram given in Fig. 4.

The possibility of an alkaline attack is supported by the presence of the black-brown areas observed on the surface of the steel after extraction, which is described in Section 4.3. At the cathodic potentials measured during the course of the extraction treatment and immediately afterwards (approximately −1.2 V SCE), the locally high pH would induce the formation of $HFeO_2^-$ and FeO_2^{2-} ions, the only dominant species stable in the limited high pH corrosion regions shown in Fig. 4 [15].

Similarly treated samples had corrosion current densities of the same order of magnitude and potentials more negative than −375 mV SCE 1 year after completion of the extraction treatment. This can be attributed to the fact that the specimens remained immersed in the $Ca(OH)_2$ solution and, therefore, little oxygen that would allow repassivation could diffuse to the reinforcing steel. If the specimens were exposed to the atmosphere, it is likely that these corrosion rates would have been lower.

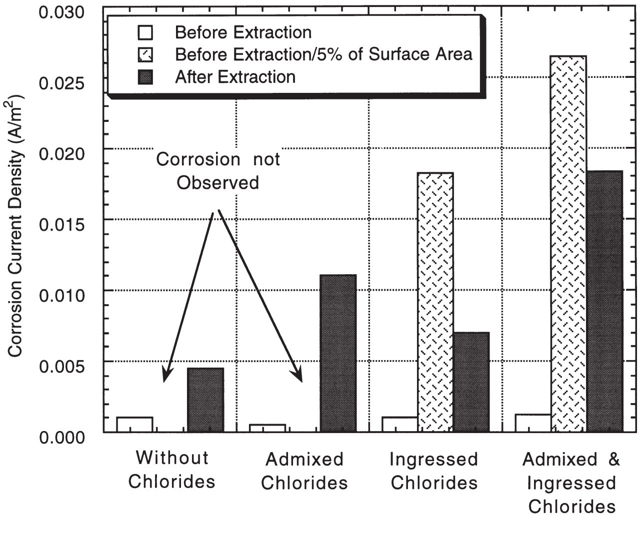

Fig. 3. A comparison of the mean linear polarization resistance measurements taken before (five specimens) and 31 days after (three specimens) an extraction treatment.

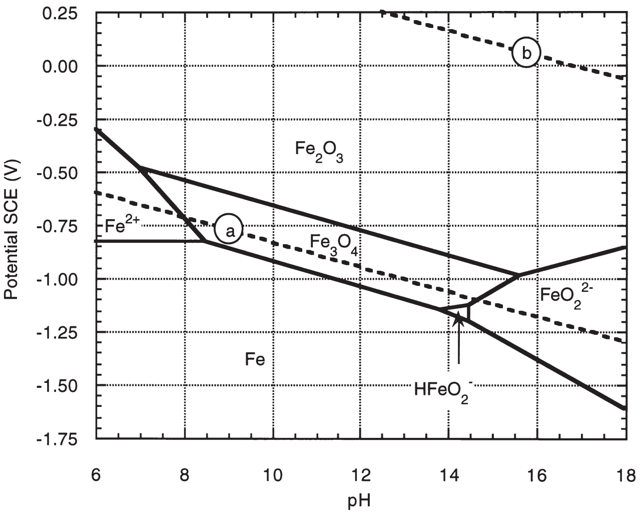

Fig. 4. E-pH diagram of the Fe-H_2O system at 25°C and 101.3 kPa (courtesy of the Facility for the Analysis of Chemical Thermodynamics [15]).

4.2. A comparison of the full polarization curves before and after extraction

Full polarization curves for specimens with both admixed and ingressed chlorides and for specimens without chlorides are given in Figs. 5(a) and (b), respectively. The solid line in Fig. 5(a) represents the behaviour of the steel prior to treatment and the shift to higher currents at a potential of about −100 mV SCE is typical of chloride-induced pitting corrosion. Correcting the measured corrosion current densities to account for an assumed anodic region of approximately 5% would shift the anodic portion of the solid curve to the right but would not change its form. The dashed line, representing the behaviour after the extraction treatment, shows a very different trend: the initial portion of the anodic curve is at a higher current level than the equivalent portion of the pre-treatment curve, representing the general corrosion of the depassivated steel. However, at more positive potentials, it does not increase due to pitting but, instead, decreases due the reformation of the passive film.

In contrast, the solid line in Fig. 5(b) does not exhibit any pitting behaviour (which was expected because the specimen did not contain chlorides) and the post-treatment curve is at higher currents at all potentials. This is again expected because the pre-treatment curve represents the behaviour of passive steel in concrete with a pH of about 13.5, whereas the post-treatment curve represents its behaviour after depassivation and in concrete with a much higher pH. This behaviour was also observed in the post-treatment curves of steel exposed to only admixed or ingressed chlorides. Under these circumstances, it is likely that any chloride-induced corrosion pits were destroyed, but that the steel remained

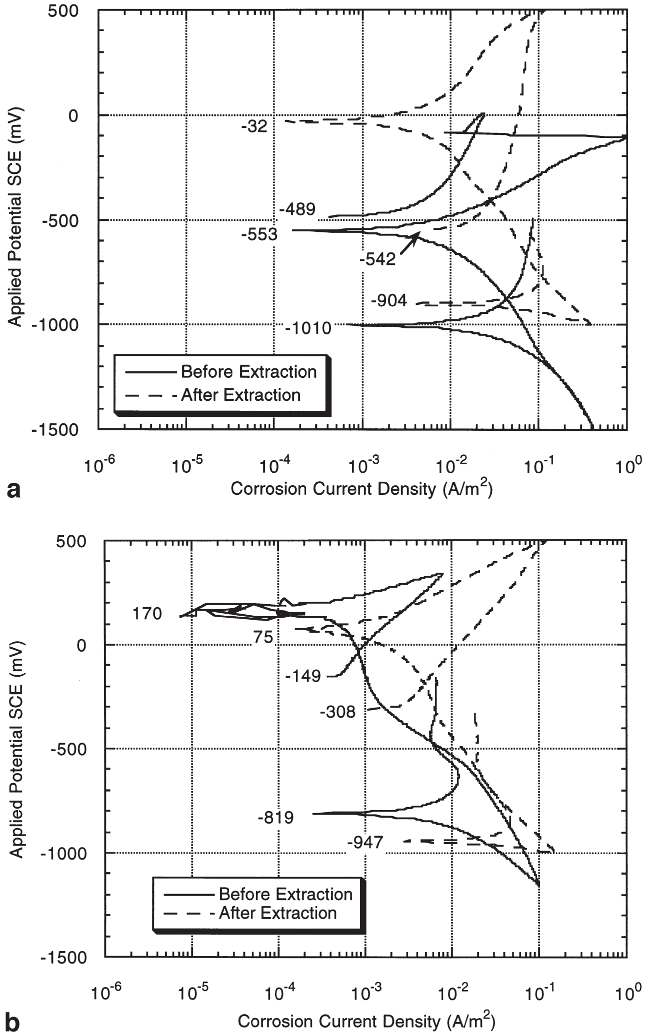

Fig. 5. (a) Full polarization curves for the specimen that contained admixed and ingressed chlorides, before and 31 days after an extraction treatment. (b) Full polarization curves for the specimen that never contained chlorides, before and 31 days after an extraction treatment.

depassivated in an environment with a higher pH, similar to the steel that was never exposed to chlorides.

4.3. Macrostructural features of the steel/mortar interface, without and after an extraction treatment

Without an extraction treatment, corrosion pits covering about 5% of the surface area were evident only on those samples that were exposed to ingressed chlorides both with and without admixed chlorides. The steel that was exposed to only admixed chlorides did not have observable corrosion pits, presumably because of its lower chloride exposure most likely due to chloride binding, which reduces the available chlorides in the pore solution for participation in active corrosion. Furthermore, all samples except those that contained admixed and ingressed chlorides were found to have mortar adhering to the surface of the steel.

After the extraction treatment, there was not any observable mortar adhering to the surface of any of the steel samples but, instead, a fine white product was found covering the surface of all steel samples, similar to the product reported in other work [7]. In addition to the powder, all steel samples had large areas (50–100% of the surface area) that were discoloured black-brown. This is probably attributable to the alkaline corrosion process: although $HFeO_2^-$ and FeO_2^{2-} ions are likely to have been formed in the high pH/low potential conditions of the treatment, the steel would become more noble as the effect of the cathodic polarization decreased over time and, with the redistribution of the OH^- ions, magnetite (Fe_3O_4) would become the dominant product formed. This product is black, which concurs with the observed products.

4.4. Mortar chloride measurements

Treated samples that originally contained ingressed chlorides, both with and without admixed chlorides, were found to have lower chloride contents than their untreated counterparts at the steel/mortar interface, as indicated by the bar chart in Fig. 6. The chloride levels in these specimens were reduced to less than 0.1% chlorides by mass of mortar from levels that were as high as 0.38% for the specimens that contained ingressed chlorides. Thus, it is clear that the treatment was more successful in removing chlorides that were ingressed than those that were admixed. This is to be expected as admixed chlorides are more likely to be chemically bound within the hydration products of the cement paste and/or trapped in closed pores.

5. Conclusions

The electrochemical chloride extraction treatment halted chloride-induced corrosion but increased the overall general corrosion rate. These higher corrosion current densities can be explained as follows: (1) the extraction treatment re-

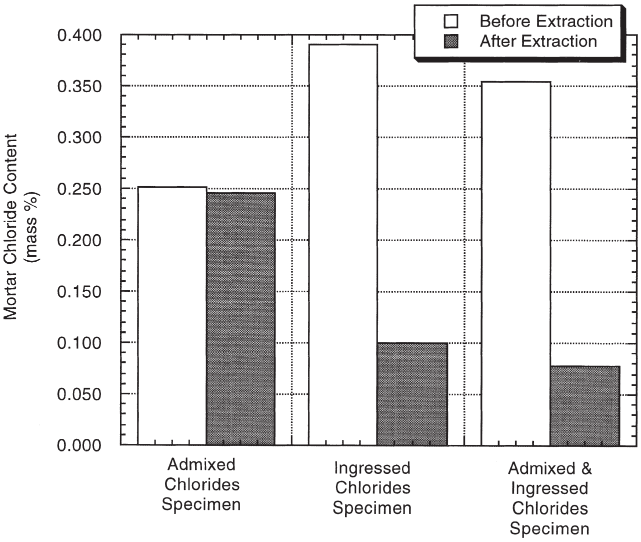

Fig. 6. Mortar chloride analyses of the steel/mortar interface (within 10 mm), without and after an extraction treatment.

sulted from a localized accumulation of hydroxide ions and (2) the electrochemical reduction of oxygen at the steel/mortar interface. The former caused an alkaline attack of the surface of the steel, while the latter inhibits repassivation. Thus, it is probable that general corrosion conditions will persist in treated structures until an internal equilibrium is reestablished at the steel/concrete interface (i.e., diffusion of hydroxide ions throughout the concrete cover and diffusion of oxygen to the surface of the steel). It is only once this stage is reached that a treated structure may truly be considered rehabilitated.

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