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# Reinforcing steel passivation in mortar and pore solution

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## Abstract

Under field conditions, steel is embedded in concrete for a long period of time before chlorides penetrate. In studying the corrosion behaviour of steel in concrete, mortar or in simulated pore solution, it is essential to allow enough time for the steel to create a passive layer which is the subject of this study. This time is given to steel in chloride free concrete, naturally; while it should be provided to steel in synthetic pore solution, before adding chloride to the solution. For determining this time, samples were made with steel with different surface conditions: as-received with mill scales and sand-blasted. One set of steel bars (as-received and sand-blasted) were embedded in mortar and one set were immersed in synthetic pore solution. Corrosion of each steel bar was monitored every hour by LPR technique for total time of 300 h. Also, half-cell potential of steel bars was measured during that time. Results show that steel needs to be kept at least three days in synthetic pore solution and seven days in mortar to be passivated.

*Keywords:* Corrosion; Mortar; Passivation time; Pore solution

## 1. Introduction

Portland cement concrete pore solution is mainly consisted of saturated $Ca(OH)_2$ (pH = 12.6), but presence of NaOH and KOH increases the pH to more than 13 [1]. Under normal field conditions, in which reinforcing steel is embedded in the concrete for many years before chlorides penetrate the cover, this high alkalinity allows the steel to develop a stable passive film. In laboratory studies, however, the steel is not generally given much time to passivate. Indeed, there are many studies (including some by the current authors) in which steel is embedded in concrete with admixed chlorides or exposed to synthetic pores solution containing chlorides and, therefore, never has a chance to passivate. While, there are many studies concerning the nature and the composition of the passive film in pore solution and concrete [1,2], there does not appear to have been any investigation of the time required for steel to be passivated in concrete or in pore solution. This is particularly critical when the study is being done in pore solution and there is an increasing tendency for such studies in order to obtain results in shorter period of time. In a number of these studies [3–6], it appears that insufficient time was provided for passivation before the steel was exposed to chlorides and, in some cases the chloride was added to the pore solution at the beginning of the experiment. Because of these unrealistic conditions, the application of such results, for example, to the prediction of the corrosion behaviour of steel in structures may be misleading.

In this paper, the time required for deformed black steel reinforcing bar (rebar) to be passivated in mortar and in synthetic pore solution has been determined. The passivation time was measured for specimens in the as-received condition (with the mill scale intact) and specimens of the same bar after removal of the mill scale by sandblasting. Potentiostatic linear polarization resistance

Table 1
Mortar mixture

| Material | Volume |
|---|---|
| Cement, type 10 Portland, kg | 250 |
| Sand | 750 |
| w/c ratio | 0.45 |

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Table 2
Composition of synthetic pore solution, type 10

| Material | Volume |
|---|---|
| NaOH, g | 9.17 |
| KOH, g | 31.4 |
| $CaSO_4 \cdot 2H_2O$, g | 0.96 |
| $Ca(OH)_2$, g | 4.2 |
| Water, l | 1.75 |

(LPR) and half-cell potential techniques were used for determining the time required for passivation. The surface condition of the steel bars, after immersion in pore solution, was studied by Raman spectroscopy.

## 2. Experimental

For this experiment, two sets of samples have been made:

a) Steel bars with two different surface conditions (as-received with mill scale and sand-blasted) embedded in mortar.
b) Steel bars with two different surface conditions (as-received with mill scale and sand-blasted) in synthetic pore solution.

The mortar proportions and the pore solution composition are given in Tables 1 and 2, respectively.

Three sand-blasted and three as-received steel bars were used in each setup as illustrated in Figs. 1 and 2. All samples were

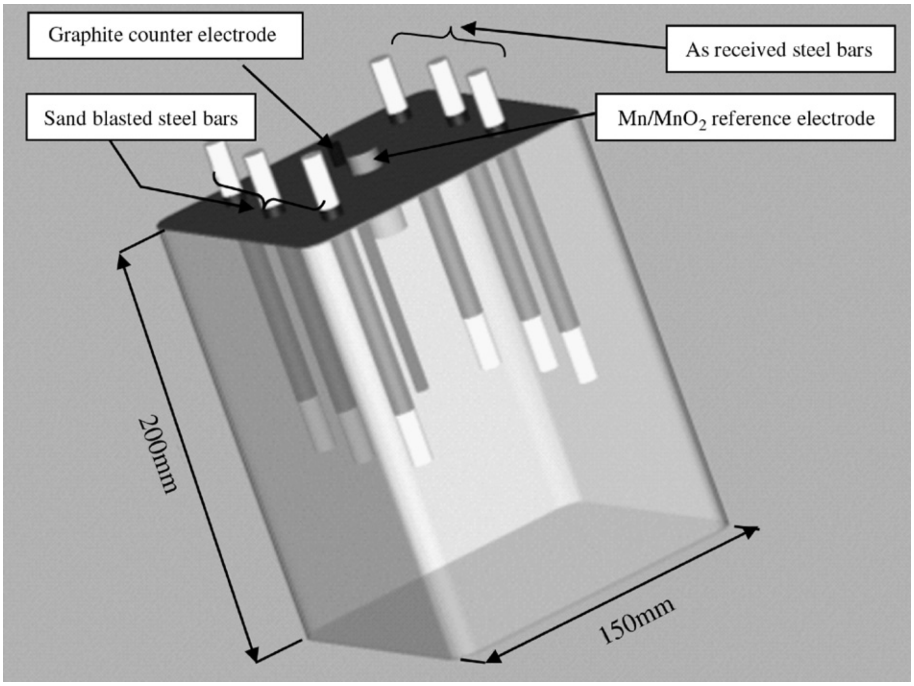

Fig. 1. Schematic plan of the immerse steel bars in synthetic pore solution.

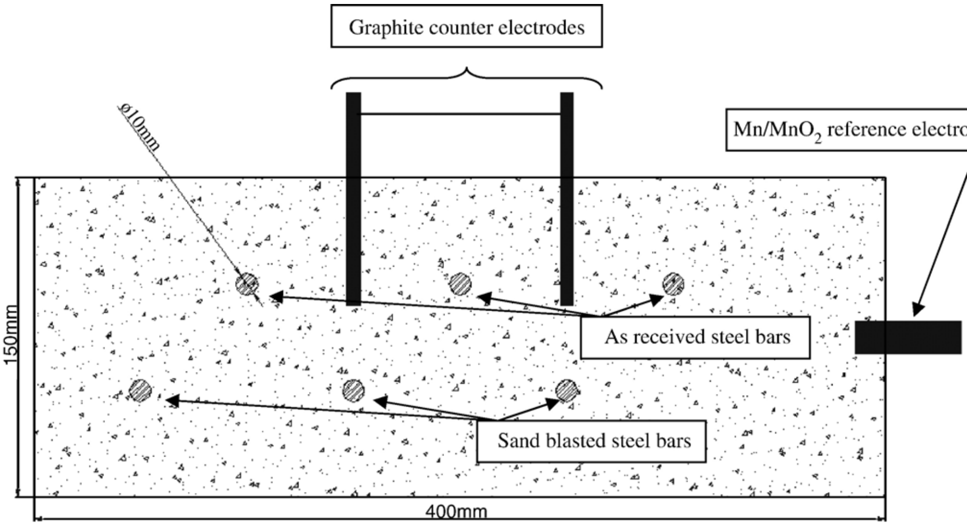

Fig. 2. Schematic plan of the mortar sample with embedded steel bars.

Table 3
Samples used in the experiment

| Passivation time | |
|---|---|
| Pore solution | 3 sand-blasted steel bars<br>3 as-received bars |
| Mortar | 3 sand-blasted steel bars<br>3 as-received bars |

connected to automatic data acquisition system, developed at the University of Waterloo. This enabled the authors to monitor the corrosion current density, by using potentiostatic LPR, and half-cell potential of each steel bar, every hour. A $Mn/MnO_2$ electrode was used as a reference electrode and graphite rods were used as counter electrodes in both setups. In addition to electrochemical measurements, the surface condition of the steel bars, after immersion in pore solution for two months, was studied with Raman spectroscopy technique and the results were compared to the Raman spectra taken from a steel bar which had not been exposed to the solution.

Number of the samples and their explanations are summarised in Table 3.

## 3. Results and discussion

Figs. 3 and 4 show the corrosion current densities measured over a period of 300 h by LPR for the samples embedded in mortar and immersed in synthetic pore solution, respectively. These results show that the corrosion current density for both surface treatments drops to the expected value for passive state ($10^{-3}$ to $10^{-4}$ A/$m^2$) [7] and stabilised after about 160 h (~7 days) in mortar and 70 h (~3 days) in synthetic pore solution. This difference may be attributed to the fact that the pH of the synthetic pore solution was high (~13.5) when the bars were immersed, whereas the pH of the mortar mixing water was initially neutral and

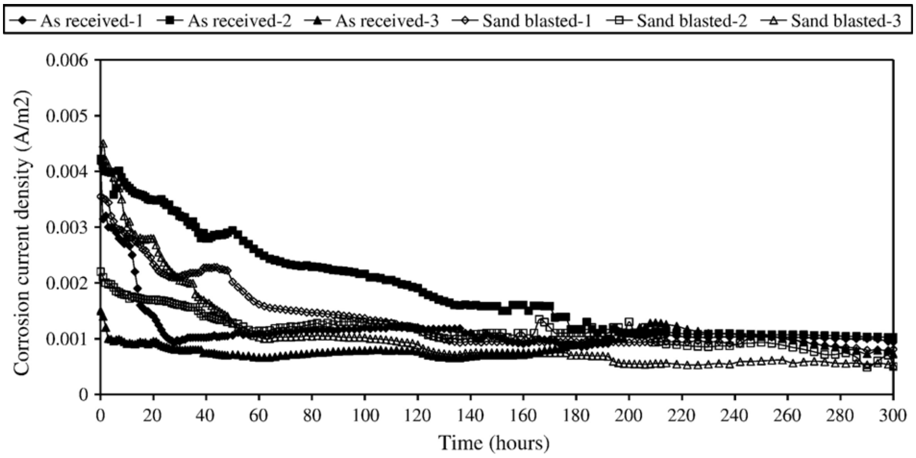

Fig. 3. Corrosion current density of steel embedded in mortar for 300 h.

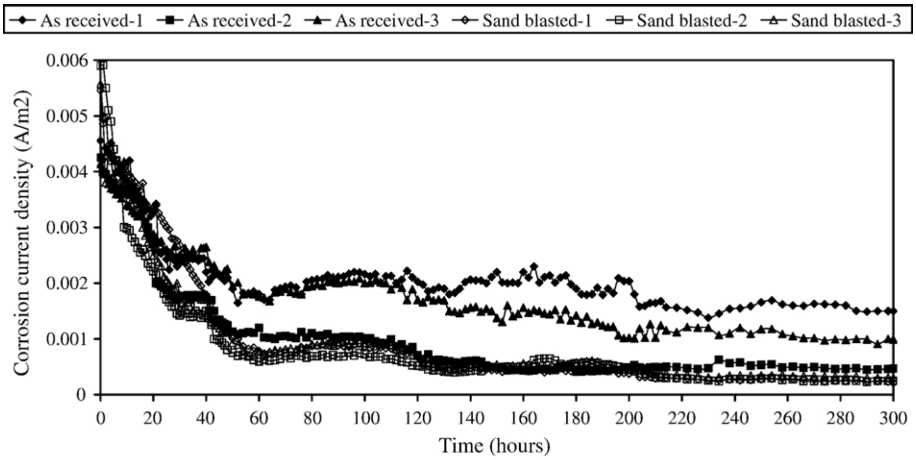

Fig. 4. Corrosion current density of steel in synthetic pore solution for 300 h.

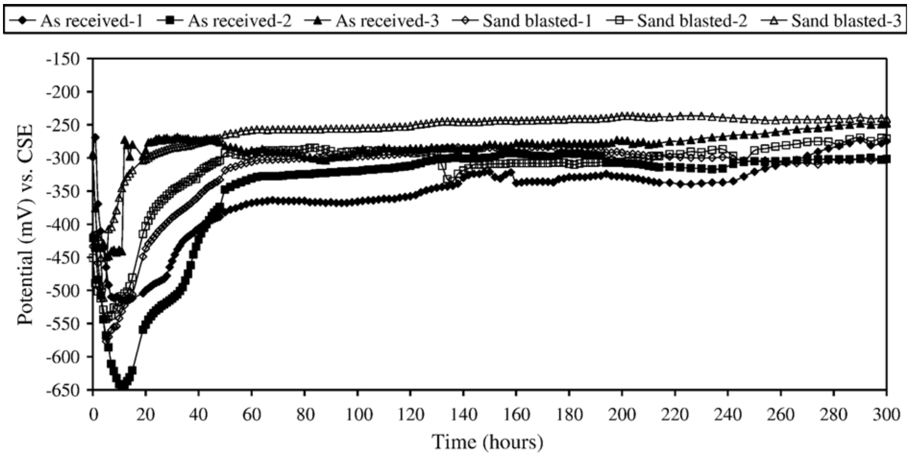

Fig. 5. Half-cell potential values of steel embedded in mortar for 300 h.

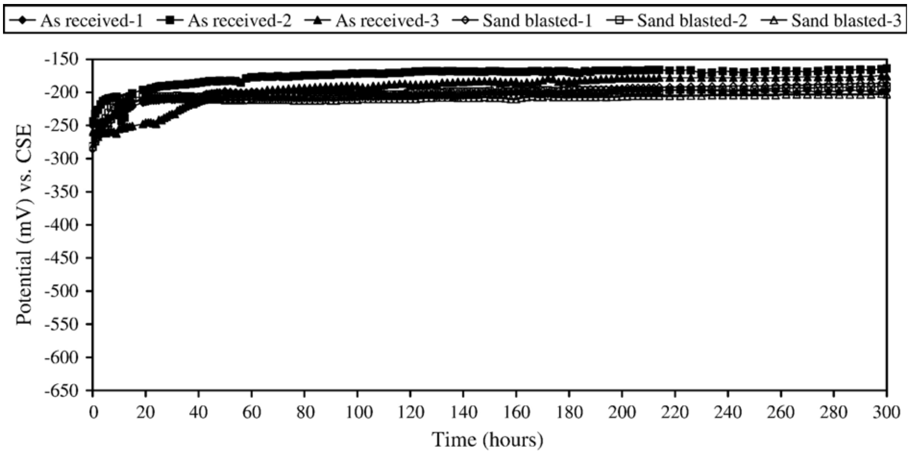

Fig. 6. Half-cell potential values of steel immersed in synthetic pore solution for 300 h.

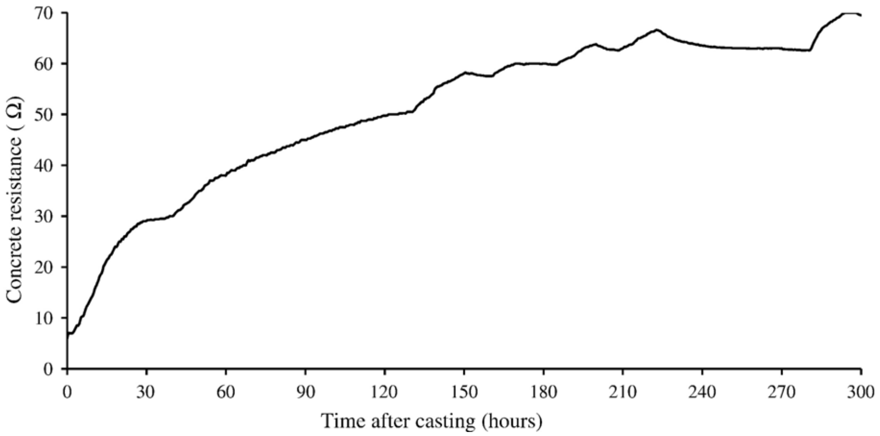

Fig. 7. Mortar resistance, measured every 30 min for 300 h.

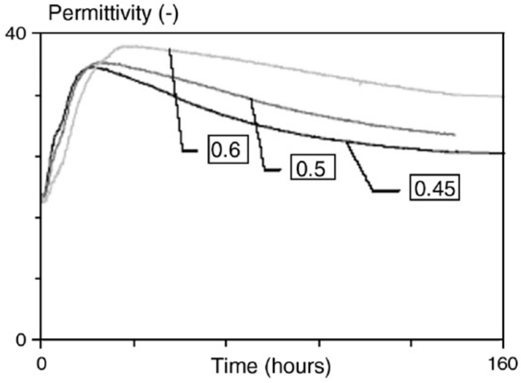

Fig. 8. Permittivity of young concrete with ordinary Portland cement [13].

increased over time as the mortar hydrated. It has been shown that the passivity of steel increases with increasing pH [8] but, as discussed below, research has indicated that the pH in cement paste or mortar reaches a value of 13 very rapidly. A second factor could be the greater mobility of ions in pore solution than mortar.

The corresponding half-cell potential values for the steel in mortar and synthetic pore solution are plotted in Figs. 5 and 6, respectively. The values for the specimens embedded in mortar showed dramatic changes within the first ~50 h (~2 days) exhibiting a considerable negative shift in potential during the first ~10 h, after which the potential rapidly became more anodic over the next ~40 h and changed only gradually thereafter. This is in contrast to the corrosion data which exhibited only gradual decrease over a much longer period. It is also in contrast to the variations in half-cell potential values for specimens immersed in synthetic pore solution, which did not exhibit a negative shift but increased rapidly in the first ~20 h and continued with a slow anodic shift thereafter.

Several factors have been considered to explain this difference. First is the pH of the environment which was constant at ~13.5 in the pore solution but increases from neutral water in the mortar. However, studies [9] have shown that the pore solution in concrete reaches values of ~13 within approximately 1 h of mixing the concrete.

Second, the resistivity of the concrete was considered as a factor. Therefore, the electrical resistance of mortar of the same proportions as those in Table 1, was monitored, by electrochemical impedance spectroscopy (EIS), every 30 min for 300 h and the results are shown in Fig. 7. It is clear that the mortar resistance increased with a relatively sharp slope within first ~15 h after casting, after which, the rate of increase decreased. This, by itself, could not explain the half-cell behaviour of the steel in mortar but is probably a contributory factor.

Third, the rise in temperature of the mortar as it hardens was considered as a factor. However, any temperature rise would influence the corrosion rate more than the half-cell potential. Again, temperature alone is not likely to be responsible for the observed changes in potential but, again is probably a contributing factor.

Fourth, NMR studies of cement hydration [10,11], indicate a rapid increase in the formation of C–S–H and a corresponding drop in capillary porosity in the 8–20 hour period after casting.

A parameter which is dependent on all these factors, relative humidity, temperature, polarity of the environment and the mobility of the ions and charges in the medium, is the relative permittivity [12] and the structural and chemical changes monitored by NMR, pH measurements and electrical resistance measurements would result in a change in the permittivity of mortar.

The half-cell potential is a measure of the potential field existing between the reference electrode, charge $q_1$ and the rebar, charge $q_2$. The potential force between these two electrical charges can be calculated from the following equation:

$$F = k\frac{q_1 q_2}{r^2}$$

where $r$ is the distance between two charges (the cover depth) and $k$ is a constant (the coulomb constant). In the present case, it can be assumed that $q_1$, and $r$ are constant and $q_2$ and $k$ are changing during hydration process. $k$ is related to the relative permittivity,

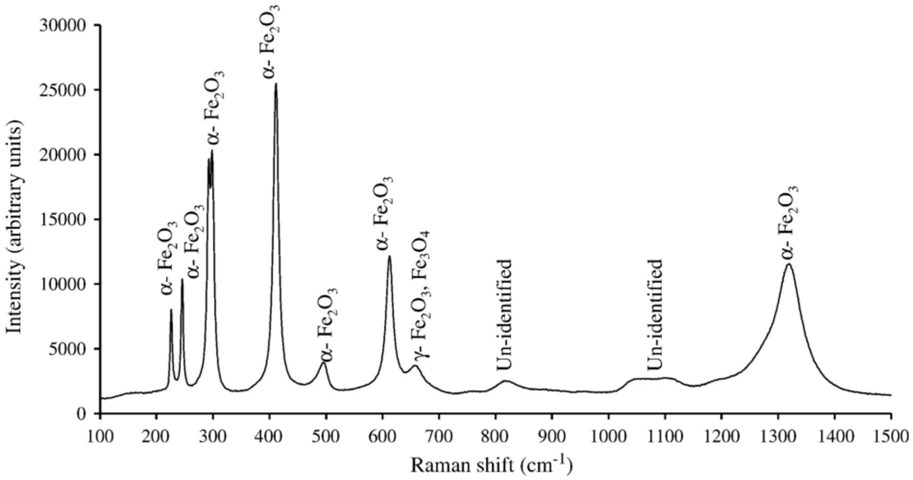

Fig. 9. Raman spectra of steel with mill scale (as-received).

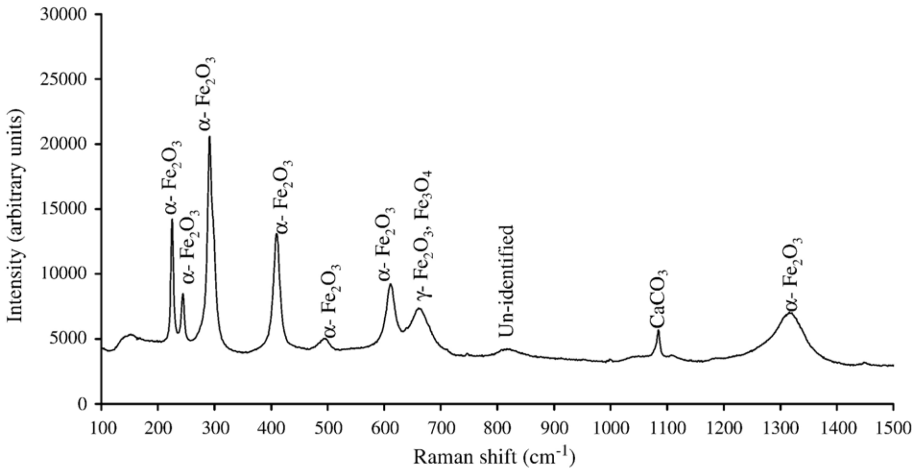

Fig. 10. Raman spectra of steel with mill scale (as-received), immersed in pore solution for 2 months.

$\varepsilon_r$, which describes how an electric field is disturbed by a dielectric medium of the environment according to the following equation:

$$k = \frac{1}{4\pi\varepsilon_r}\cdot$$

For example, $\varepsilon_r$ for water is ~80 and for dry concrete is ~4 [13]. Van Beek et al. [14] measured the permittivity of concrete for 160 h and observed a rapid increase in $\varepsilon_r$ in the first ~16 h after casting for a concrete with w/cm = 0.45, i.e. the same as in the present work. Their results are shown in Fig. 8 in which the maximum in permittivity corresponds to the minimum in potential drop observed in Fig. 5.

During hydration, the steel passivates in the high pH of the mortar resulting in a decrease in the potential charge, $q_2$. However, because a similar decrease in $q_2$ would be expected for steel in synthetic pore solution, which does not exhibit a major change in half-cell potential, it appears that changes in the permittivity with hydration dominate the changes in half-cell potential in mortar, and presumably, also in concrete.

The as-received steel (with the mill scale intact) generally shows a higher corrosion rate than sand-blasted steel but there is no consistency in half-cell potential values. Moreover, all $E_{corr}$ values are between −350 and −200 mV CSE, which is within the range of "uncertainty of active corrosion" according to the ASTM C876 guidelines for interpretation of half-cell potential data [15]. This indicates that the ASTM recommendations are not applicable to potentials in the earliest stages of passivation of the steel, while the passive layer is being developed.

It is also important to note that the half-cell potential values appear to reach "steady state" faster than the values of corrosion current density. However, these "steady state" values are far more negative than those normally considered to represent the passive state of steel in concrete or mortar and indicate that it takes considerably longer for the potential to attain a "true" passive value. This is also the conclusion of observations in the field, where steel has taken more than three months to reach potentials more positive than −200 mV CSE [16]. This implies that it actually takes much longer for the steel to be fully passivated than is suggested by the corrosion rates determined here which, in fact, continued to decrease very slowly even after 300 h in solution or mortar.

Results of Raman spectroscopy are shown in Figs. 9–11 and the main Raman bands of reference iron oxide compounds are

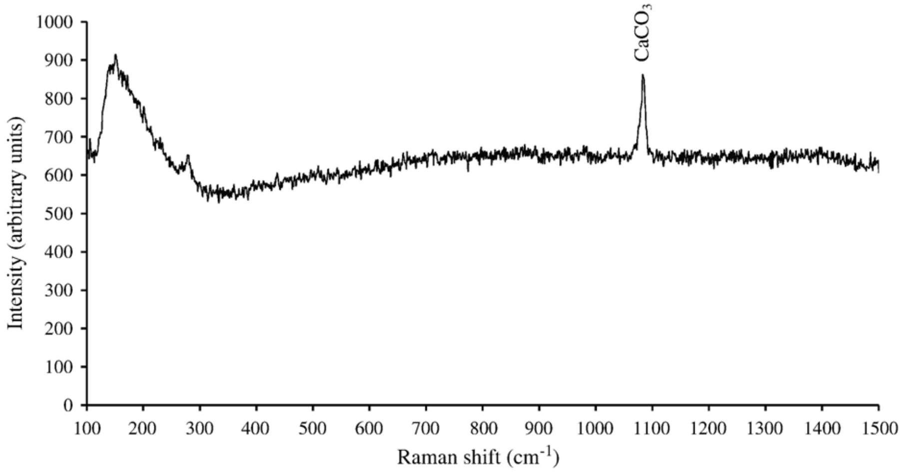

Fig. 11. Raman spectra of sand-blasted steel, immersed in pore solution for 2 months.

Table 4
Main bands of reference iron oxide compounds (in $cm^{-1}$) [13–16]

| Magnetite | Hematite | Maghemite |
|---|---|---|
| $Fe_3O_4$ | $\alpha$-$Fe_2O_3$ | $\gamma$-$Fe_2O_3$ |
| 289 | 225 | 265 |
| 319 | 247 | 300 |
| 418 | 295 | 350 |
| 550 | 412 | 395 |
| 670 | 500 | 505 |
|  | 613 | 660 |

given in Table 4 [17–20]. Comparison between Figs. 9 and 10 and data from Table 4 reveals that, even after two months immersion in synthetic pore solution, the mill scales still exist on the as-received samples, with no apparent change in their composition. As expected, there is no observable iron oxide on the surface of sand-blasted steel bars (Fig. 11) because a passive film is too thin to be detected by this technique. It should be noted that the scale of intensity axis in Figs. 9 and 10 is different from that in Fig. 11.

## 4. Summary and conclusions

- In concrete structures, the steel normally has many years to develop a protective passive film over its surface before chlorides penetrate the concrete cover. This is not the case in laboratory specimens. Nevertheless, results from corrosion measurements show that steel bar in mortar and pore solution does need a significant amount of time for passivation. The time required for the corrosion rate of steel in mortar to drop to a rate typically considered to be passive is approximately 7 days but it continues to decrease slowly for a long period after that. Moreover, the half-cell potential takes even longer time to reach the level normally considered to be indicative of passive behaviour. It is clear from these data that it is inappropriate to conduct laboratory studies of steel in concrete to which chlorides have been added at the time of mixing unless the intention is to study the behaviour of embedded steel in concrete with chloride-contaminated components.
- The anomalous behaviour of the half-cell potentials of steel in mortar during the first 2 days is tentatively attributed to changes in the permittivity of the mortar as it sets and hardens. However, this has yet to be confirmed.
- For steel in pore solution, the corrosion rate took about 3 days to drop to passive levels and, again, continued to decrease very slowly thereafter. The potentials did not mimic those of steel in mortar but increased from ~−275 mV CSE to ~−200 mV CSE over a period of about 3 days. Therefore, for tests of steel in pore solution, it is recommended that steel be kept in the solution for at least a week before adding chloride to the solution.
- Generally, as-received steel bars show a marginally higher corrosion current density than did the sand-blasted ones, but this was neither consistent nor significant. Moreover, there is no such trend in the half-cell potential values. As mentioned before, half-cell potential values are more negative than −200 mV CSE and, therefore, according to the ASTM C876 have a high probability of corrosion. It must be concluded, therefore, that the ASTM criteria cannot be applied to fresh mortar or concrete.
- The passive film which is developed on the sandblasted steel in synthetic pore solution is too thin to be observable by Raman spectroscopy and there is no observable difference in the structure of the surface films of the steel with mill scale before and after exposure to synthetic pore solution for two months.

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