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THE BEHAVIOUR OF PRE-RUSTED STEEL IN CONCRETE

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ABSTRACT

This paper explores the possibility of an effective protection for precorroded steel by effect of the high alkalinity of the encasing mortar (by itself or in combination with the action of sodium nitrite). Application of a waterproof coating on the mortar surface was evaluated for this purpose. The behaviour of clean steel electrodes and in three different pre-corrosion grades was characterized from periodic measurements of the corrosion potential (E_{corr}) and polarization resistance (R_p). Neither mortar alkalinity alone nor in combination with the effect of nitrite ions was found to passivate the reinforcements in the two higher corrosion grades over 2 years of exposure in an atmosphere of a high relative humidity. Also, immersion of the specimens in a 5% $NaNO_2$ solution was found not to passivate steel undergoing active corrosion. The effectiveness of the waterproofing treatment for diminishing reinforcement corrosion was found to rely heavily on timely application.

1. Introduction

Steel in reinforced concrete (RC) has traditionally been assumed to be in a passive state, free from corrosion (1,2) thanks to a passivating, self-renewing, very thin (*ca.* 10 nm) film that is formed at the steel/concrete interface (3). The protective action of the passivating layer is of essentially electrochemical nature and is guaranteed by the high alkalinity of concrete and an appropriate electrochemical potential (4).

As a result, while corrosion of bare steel usually poses serious maintenance problems in wet environments, corrosion of concrete-embedded steel is restricted to a few essential instances that are always related to depassivation, whether local or generalized. In practice, the primary initiating factors for depassivation are believed to be local breakage of the passivating film by effect of chloride ions and its destruction throughout the surface affected by the carbonation front.

Provided passivity is maintained, structures can be expected to last indefinitely. The fact that many RC structures remain in perfect condition after decades of service is the strongest support for this widespread assumption.

While steel corrosion in reinforced concrete makes the exception rather than the rule, it eventually gives rise to severe problems. By way of example, a recent estimate of the repair costs for damaged (corroded) bridge decks in USA was set at \$20 billion and is increasing at a yearly rate of \$0.5 billion (5,6).

The technical and economic significance of corrosion of reinforced steel has urged researchers to find a way of stopping corrosion after it has started. The problem, however, has scarcely been addressed so far except for a few reports on the effect of surface oxides on the corrosion of steel reinforcements embedded in concrete (7), inhibition treatments for corroding steel in chloride-contaminated concrete (5,8,9) and the potential effectiveness of waterproofing coatings for concrete (10,11).

Leaving cathodic protection aside as it has proved to be an effective means for stopping corrosion in reinforced concrete structures (12,13), in this work we sought an answer to the following questions:

(*a*) Can concrete passivate highly rusted reinforcements embedded within?
(*b*) If concrete alkalinity cannot passivate moderately or highly rusted reinforcements, can the addition of nitrite ions —the most effective inhibitor of reinforcement corrosion (9) — to the concrete restore the passive state?
(*c*) Is the external application of nitrite solutions on pre-rusted structures as effective as other, more expensive proven solutions used in current practice?
(*d*) Can a waterproofing treatment substantially decrease the corrosion rate of steel in chloride-contaminated concrete through gradual depletion of dissolved oxygen in the aqueous phase of concrete pores?

2. Experimental

In order to answer these questions, reinforcements that were previously corroded in sea water to add up the effect of surface contamination by chloride and the rust layer were used. Two batches of mortar specimens of 7 × 6 × 6 cm in a cement/sand/water ratio of 1:3:0.5 were prepared. One batch contained no inhibitor while the other was supplied with 1% $NaNO_2$, which was enough to maintain an NO_2^-/Cl^- ratio above unity and hence the passive state in non-corroded reinforcements (14,15). The specimens with no nitrite added were used to simultaneously ascertain whether the highly alkaline pH of mortar by itself sufficed to passivate the surface of pre-rusted reinforcements.

Clean (freshly etched) and corroded reinforcements containing rust layers of 253, 239 and 116 g/m^2 of rust were tested. These rust layers had been formed by exposure to sea water and its chloride concentrations were 3.31, 2.58 and 1.61 g/m^2, respectively, as measured with a Cl^- ion-selective electrode.

Once prepared, the specimens were stored in a highly wet environment. Steel corrosion rates were estimated from periodic measurements of the polarization resistance, as described in previous papers (16–18).

Another specimen batch made in the same cement/sand/water proportion but containing clean electrodes was coated with waterproof epoxy resin paint in order to check its effect on the corrosion rate. The mortar specimens contained no additive, 2% Cl^- or 2% Cl^- + 3% NO_2^-. The additives were added relative to cement weight (Cl^- as $CaCl_2$ and NO_2^- as $NaNO_2$). The epoxy paint was applied at two different times, *viz.* 24 h after preparation of the specimens (at cast-off) and 28–30 days later (at the end of curing in a highly wet environment).

Finally, changes in the corrosion rate of clean and pre-rusted electrodes immersed in a saturated $Ca(OH)_2$ solution containing no chloride were also monitored. The electrodes were pre-rusted in a chamber at room temperature and 100% relative humidity, containing SO_2, for 30 days in order to allow a rust layer of *ca.* 395 g/m^2 to be formed. These are the ideal conditions for electrode passivation as the high alkalinity of concrete is preserved while avoiding the countless crevices resulting from the multiphasic nature of concrete.

3. Results

3.1. The Behaviour of Pre-Rusted Steel. Figure 1 shows the high significance of the rust layer to reinforcement passivation. Thus, clean surfaces were rapidly passivated by effect of the high pH of mortar. On the other hand, the reinforcements that were pre-rusted to the higher grades maintained corrosion currents of *ca.* 1 µA/cm^2 after nearly 1000 days of testing, which suggests that, at least part of their surface, had not yet reach the passive state. The reinforcements that were pre-rusted to the lowest grade exhibited much lower i_{corr} values which, however, clearly exceeded those for the reinforcements where corrosion products were removed by etching prior to preparation of the mortar specimens.

Passivation of clean steel caused i_{corr} to gradually decrease —at least during the first 200 days of testing—; on the other hand, pre-rusted surfaces seemingly reached a near-steady state after the first 100 hours. Figures 2 and 3 show the results obtained for the clean and pre-rusted electrodes embedded in mortar with and without an inhibitor at 1, 8, 30, 150, 350 and 720 days. As can be seen:

(*1*) The response of clean and rusted surfaces could be markedly different with the presence or absence of nitrite ions;

(*2*) i_{corr} rapidly levelled off for pre-rusted surface, except for the least rusted reinforcements in the presence of NO_2^-; and

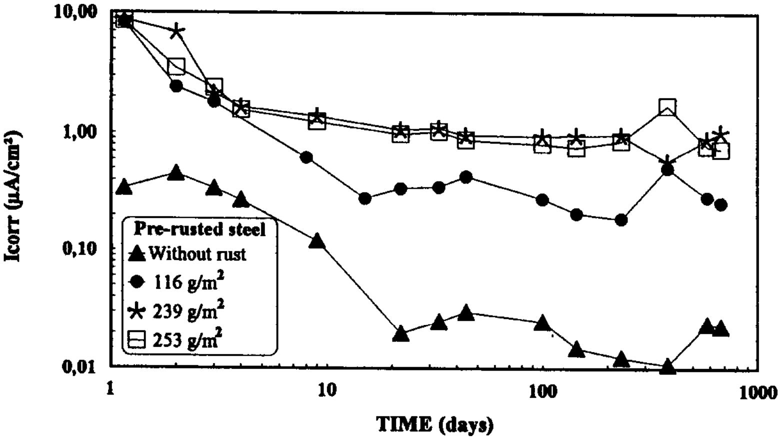

FIG. 1.

Variation of i_{corr} with time in mortar specimens containing no inhibitor. The passive state is reached only in steel without rust.

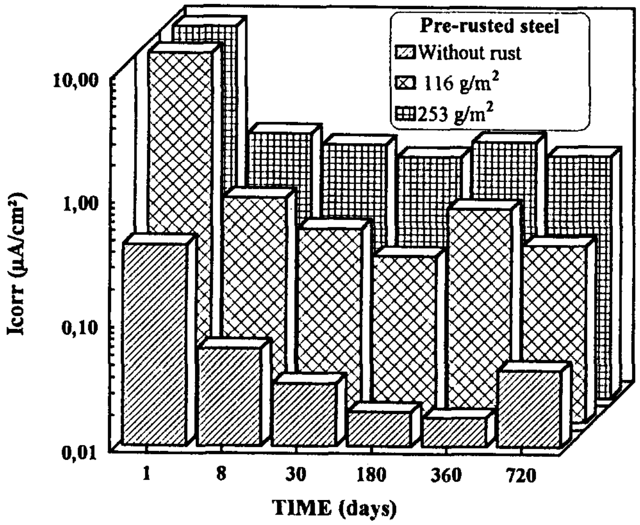

FIG. 2.

Comparison of initial i_{corr} values and the estimated ones after 8, 30, 150, 350 and 720 days of exposure in mortar with no nitrite added.

(*3*) Within 1 week, i_{corr} for clean surfaces decreased below 0.1 μA/cm², thus confirming effective passivation, which, however, was subsequently improved (i_{corr} decreased to *ca.* 0.01 μA/cm²).

Whether nitrite was added or not during preparation of the mortar had no significant effect, except on the samples rusted to the lowest grade where addition of 1% NO_2^- ensured passivation (Fig. 3). The amount of nitrite added was always more than adequate to ensure an NO_2^-/Cl^- ratio well above the accepted threshold for preserving the passivity of clean surfaces.[15] For the more extensively rusted surfaces, i_{corr} continued to be *ca.* 1 μA/cm² after 2 years of exposure —whether or not an inhibitor was added—, which is too high a value for the steel/concrete system.

If the inhibitor added to the mixing water cannot passivate highly rusted surfaces, any inhibitor penetrating the concrete from a solution (used to irrigate or immerse it) will less likely reduce corrosion to an adequate extent for practical purposes. Figure 4, which illustrates the behaviour of mortar specimens with embedded active electrodes on immersion in solutions containing a high NO_2^- concentration, confirm this assumption. In fact, after months of immersion, the corrosion rate remained quite high.

3.2. Effect of Waterproofing Coatings. Concrete waterproofing coatings are frequently used to avoid penetration of aggressive substances from the environment. They were applied to deliberately chloride containing mortar with embedded steel reinforcements in an active corrosion state in order to determine whether depletion of dissolved oxygen would stop corrosion.

Figure 5 shows changes in i_{corr} on application of a waterproofing coating of epoxy resin applied at the end of mortar curing (30 days) in a wet chamber. Figure 6 shows the same

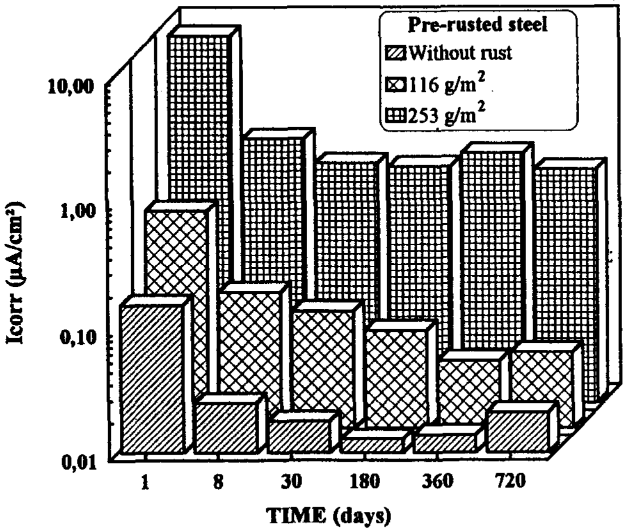

FIG. 3.
Comparison of initial i_{corr} values and the estimated ones after 8, 30, 150, 350 and 720 days of exposure in mortar containing 1% NO_2^-.

information for specimens encapsulated in epoxy resin 24 h after fabrication of the mortar (*i.e.* at cast-off).

For this last condition, oxygen depletion was seemingly effective to halt corrosion provided the amount of corrosion products formed was not too large, since i_{corr} for the coated specimen

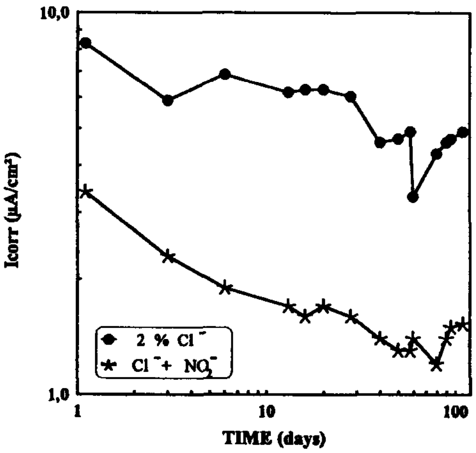

FIG. 4.
Behaviour of active reinforcements embedded in mortar specimens on immersion in a 5% NO_2^- solution.

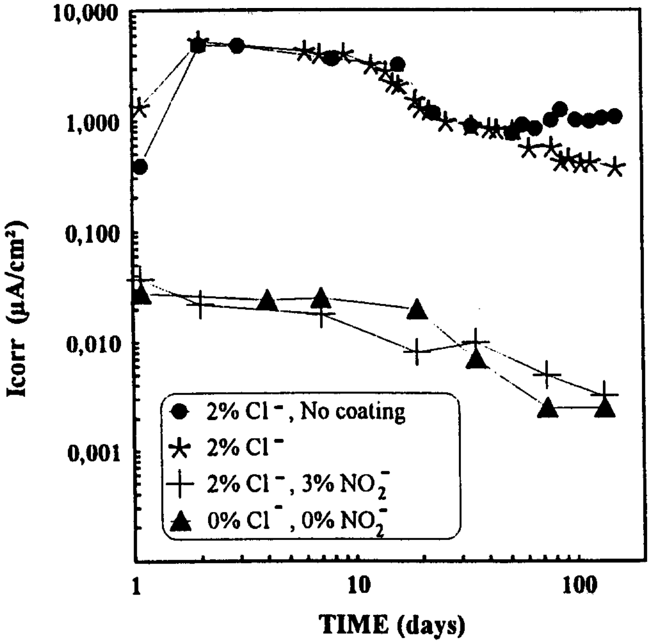

FIG. 5.

Variation of i_{corr} for chloride-containing mortar specimens encapsulated in epoxy resin at the end of curing.

containing 2% Cl$^-$ was always much lower than that for its uncoated counterpart. The differences after 100 days exceeded one order of magnitude.

On the other hand, coatings applied 30 days after fabrication (at the end of curing) resulted in no significant improvement by effect of oxygen depletion (Fig. 5). This suggests that the partial cathodic process involved may be other than the reduction of dissolved oxygen in the aqueous phase of concrete pores.

The specimens containing no chloride and those to which 2% Cl$^-$ + 3% NO_2^- was added (supposedly with sufficient inhibitor to preserve the passive state with no waterproofing) seemingly did not benefit from application of the waterproof coating.

Finally, as can be seen in Fig. 7, highly rusted steel surfaces (*ca.* 395 g/m^2) also hindered rapid passivation in $Ca(OH)_2$ saturated solutions; the corrosion rate differed by two orders of magnitude, approximately, from that for clean electrodes.

4. Discussion

4.1. Protection of Pre-Rusted Surfaces. The results shown in Figs 1–3 allow one to draw several revealing conclusions, namely:

(*i*) Extensive pre-rusting of steel reinforcements severely hinders passivation, even at the highly alkaline pH of concrete (Figs. 1 and 2).

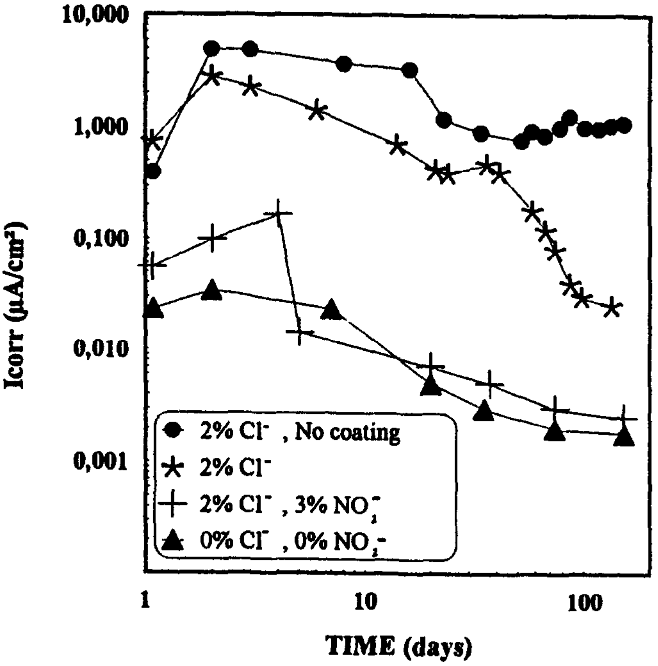

FIG. 6.
Variation of i_{corr} for chloride-containing mortar specimens encapsulated in epoxy resin 24 h after preparation (at demolding).

(*ii*) Nitrite ions have an undeniably favourable effect that ensures passivation of mildly rusted reinforcements (116 g/m^2). However, it cannot guarantee passivation of severely rusted surfaces,which exhibit corrosion currents above 1μA/cm^2 after2 years of exposure (Fig. 3).

(*iii*) Passivation is rapidly achieved with clean surfaces obtained by etching of pre-rusted surfaces, whether or not the mortar is supplied with nitrite.

It should be noted that i_{corr} values of *ca.* 1 μA/cm^2, which are seemingly very low, are indeed very hazardous for reinforced concrete structures, which can develop cracks at very small corrosion penetration depths -occasionally as small as 20 μm (19)-. Therefore, the answer to questions *a* and *b* raised in the Introduction is "no". Nitrites were effective in passivating only moderately rusted steel surfaces.

4.2. The Protective Effect of Externally Applied Nitrite Solutions on Pre-Rusted Structures.

There are occasionally reports on the effectiveness of ponding chloride-contaminated concrete in an inhibitory solution in order to diminish the corrosion rate of corroded reinforcements (5,8). Forced migration of inhibitory cations under an electrical field (reinforcements would act as cathodes) may boost this favourable effect, particularly taking into account that chloride ions may be simultaneously attracted by external anodes by virtue of the same electrical field. However, the efficiency of these methods is quite modest (8) rela-

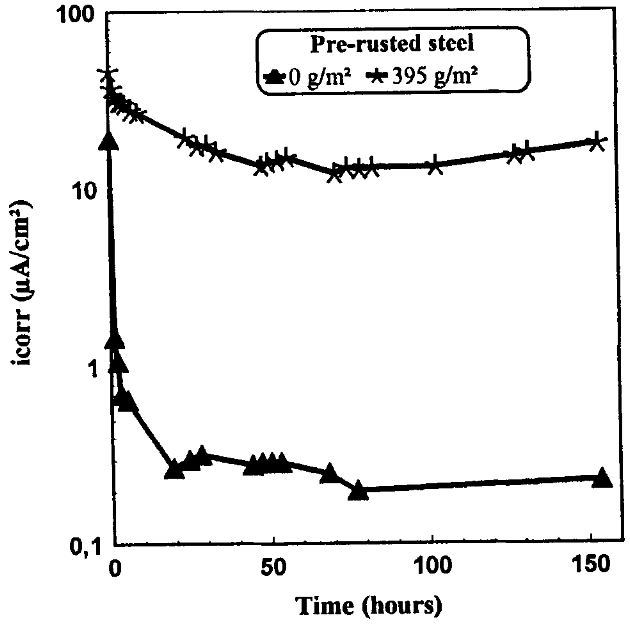

FIG. 7.

Influence of time on i_{corr} for steel, both clean and pre-rusted, in a $Ca(OH)_2$ saturated solution containing no chloride.

tive to that obtained by adding appropriate doses of nitrites during fabrication of chloride-contaminated mortar. In fact, an increase in R_p from 865 to 3525 Ω cm² (75%) with the previous treatment is quite substantial (8), but still inadequate taking into account that the corresponding i_{corr} values are 30 and 7.4 μA/cm², respectively, at an intermediate value of 0.026 V constant B in the Stern–Geary equation, $i_{corr} = B/R_p$ (20).

Consistent with these results, our results show that the typical i_{corr} values for the active state gradually decreases during immersion of mortar specimens in a solution containing 5% NO_2^- (Fig. 4). However, the decrease is so small that the desired transition from the active to the passive state does not take place, not even after 100 days of exposure, which is much longer than the exposure period achieved by repeated *in situ* irrigation with an inhibitory solution.

Therefore, the answer to question *c* in the Introduction is also "no".

4.3. Application of Waterproofing Coatings. Active corrosion initiating factors for reinforced concrete structures (carbonation and chloride ions mainly) must penetrate from the outside; therefore, waterproofing coatings may be effective protection provided they are applied timely. Occasionally, they are applied to structures which have already been penetrated by the aggressive agents, on the assumption that depletion of dissolved oxygen in the aqueous phase held in the pore network can stop corrosion, failing the partial cathodic process.

As can be seen from Figs. 5 and 6, encapsulation with epoxy resin did not interfere with the predictable preservation of the passive state of steel in the specimens with no chloride ion and those to which Cl^- and NO_2^- were added, irrespective of the time the resin was applied. Coating the specimens to which only chloride was added -which must corrode in the active state- only decreased i_{corr} to a significant extent if the treatment was applied immediately on preparation of the specimen (Fig. 6). Otherwise, if the attack had progressed to an appreciable extent when the coating was applied, the effect was insubstantial (Fig. 5). In fact, the corrosion rate remained at a high level in the complete or virtually complete absence of oxygen -whereas values about 2–3 orders of magnitude smaller should be expected, based on oxygen permeability data for organic coating films (21)-.

Oxygen diffusion to the reinforcements cannot by itself account for the high corrosion rates observed (above 1 $\mu A/cm^2$), which were maintained for months (Fig. 5). A cathodic reaction other than oxygen reduction must therefore be involved. In this respect, one can rule out the reduction of Na^+, K^+ and Ca^{2+} ions in the aqueous phase of mortar, because they require much more negative potentials than those reached in practice. Nor can the reduction of Fe^{3+} to Fe^{2+}, proposed as an alternative to oxygen reduction (7), significantly offset the anodic half-reaction since no net dissolution of Fe would take place in a de-aerated medium once existing Fe^{3+} ions had been reduced.

The sole plausible explanation is the reduction of protons, which is highly unlikely in such an alkaline medium as mortar. For the reduction to be thermodynamically feasible, there should be strong local acidification in the mortar, which has been demonstrated by some authors (16,17).

Therefore, the answer to question *d* in the Introduction depends on the circumstances. Thus, waterproofing concrete is only effective against corrosion if done timely, *viz.* before chloride ions have penetrated the structure or the concrete has carbonated since corrosion of the reinforcements cannot be stopped once it has started (10).

In a corroded structure, waterproof coatings are much more efficient if the concrete is dried prior to application (10) since the corrosion rate for reinforcements that are attacked in the active state is inversely proportional to the resistivity of concrete (22).

4.4. The Behaviour of Pre-Rusted Steel in a $Ca(OH)_2$ Saturated Solution. The experiments performed in a solution saturated with $Ca(OH)_2$ were intended to simulate the ideal conditions for steel passivation, *viz.* a high pH, the absence of chloride ions and the many crevices that develop in between the mortar and the reinforcement surface in concrete. Even so, highly pre-rusted steel (about 395 g/m^2 of rust) suffices to hinder or considerably delay its passivation (Fig. 7). If oxygen reduction were the rate-determining step in the corrosion process, then, taking into account the diffusion coefficient of oxygen, its water solubility and the thickness of diffusion layers in a quiescent solution, an active electrode should be corroded to an extent about 1000 times greater in a $Ca(OH)_2$ saturated solution than in mortar or concrete. In fact, the diffusion coefficient of oxygen and its water solubility would be roughly identical in the aqueous phase held in mortar pores and in a $Ca(OH)_2$ saturated solution. On the other hand, while the thickness of the diffusion layer (δ) in quiescent solutions is *ca.* 0.1 mm, in mortar specimens with a 1-cm thick cover oxygen would have to diffuse to the steel surface through a thickness roughly 100 times greater, so its diffusion rate would be lower by a similar factor. On the assumption of a mortar porosity of 15%, oxygen flux should be roughly 660 times slower in mortar. However, Figs 1, 2 and 7, and previous results, have shown that the corrosion rate of active mortar- and concrete-embedded reinforcements is similar to that in a solution saturated with $Ca(OH)_2$. In fact, $Ca(OH)_2$ saturated solutions have traditionally been used to simulate the behaviour of passive steel in reinforced concrete and, with some chloride added, that of active reinforcements.

As in mortar specimens, if reinforcements are appreciably pre-rusted, results show that passivation is fully inhibited or considerably delayed. Everything suggests that the anodic half-reaction controls the corrosion process in concrete structures and in a $Ca(OH)_2$ saturated solution, whether reinforcements are in the active or in the passive state. The cathodic half-reaction takes place to the extent required to offset the anodic oxidation process.

Conclusions

- Mortar alkalinity by itself or that of a $Ca(OH)_2$ saturated solution, which suffices to rapidly passivate a clean steel surface, does not ensure passivation of highly pre-rusted steel.
- The effect of nitrite ions, whether included during mortar fabrication or supplied by immersion in an appropriate solution, is also inadequate for passivating strongly pre-rusted reinforcements.
- The efficiency of waterproofing treatments relies heavily on timeliness. Applied to new structures, they can effectively prevent chloride ions from penetrating concrete. After that, coatings are scarcely effective since oxygen depletion does not stop corrosion.

Acknowledgements

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References

1. C.L. Page and K.W.J. Treadaway, Nature 297, 109(1982).
2. 12-CRC Committee., "Corrosion of reinforcement and prestressing tendons. A state of the art report", Matér. et Const. 9, 187 (1976).
3. J.R. Gancedo, C. Alonso, C. Andrade and M. García, Corrosion (NACE) 45, 976 (1989).
4. K.K. Sagoe-Crentsil and F. P. Glasser., Mag. Concr. Res. 41, 205 (1989).
5. W.D. Collins, R.E. Weyers and I.L. Al-Qadi, Corrosion (NACE) 49, 74 (1993).
6. Strategic Higway Research Program-Research Plans, Final Report, Technical Research Area 43, pp. TRA 4-1-TRA 4-60, May, 1986.
7. J. Avila-Mendoza, J.M. Flores, and U.C. Castillo, Corrosion (NACE) 50, 879 (1994).
8. S. Hettiarachchi and A.T. Gaynor, Mater. Perf. 31 N° 3, 62 (1992).
9. N. S. Berke, Mater. Perf. 28 N° 3, 41 (1989).
10. D.W. Pfeifer and M.J. Scali, "Concrete sealers for protection of bridge structures". National Cooperative Higway Research Program. Report 244. pp. 1-14, Washington D.C., (1981).
11. P.R. Vassie, "Concrete coatings: do they reduce ongoing corrosion of reinforcing steel?", in Corrosion of reinforcement in concrete, pp. 456-470, C.L. Page, K.W.J. Treadaway and P.B. Bamforth Eds., publised for the Society of Chemical Industry by Elsevier, London, 1990.
12. W.R. Schutt, "Cathodic protection for reinforced concrete structures. The U,S.A. experience", in Corrosion of reinforcement in concrete, pp. 507-514, C.L. Page, K.W.J. Treadaway and P.B. Bamforth Eds., publised for the Society of Chemical Industry by Elsevier, London, 1990.
13. J. Bennett, Anti-Corrosion 33 N° 11, 12 (1986).
14. C. Andrade, C. Alonso and J.A. González, Cem. Concr. Aggr. 8, 110 (1986).
15. E. Ramírez, E. Otero and J.A. González; Br. Corros. J. 28, 121 (1993).

16. J.A. González, A. Molina, E. Otero and W. López, Mag. Concr. Res. 42, 23 (1990).
17. J.A. González, E. Otero, S. Feliu and W. López, Cem. Concr. Res. 23, 33 (1993).
18. J.A. González, S. Algaba and C. Andrade, Br. Corros. J. 15, 135 (1980).
19. C. Andrade, C. Alonso and F.J. Molina, Mater. Struct. 26, 453 (1993).
20. M. Stern and A. L. Geary, J. Electrochem. Soc. 104, 56 (1957).
21. F. Rodríguez, "Corrosión inducida por contaminaciones hidrosolubles en la intercara metal/pintura". Tesis Doctoral. Univ. Politécnica de Madrid, ETSII, Madrid, 1994.
22. W. López and J.A. González, Cem. Concr. Res. 23, 368 (1993).