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The Influence of Hydrophobized Concrete on the Corrosion of Rebars

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Synopsis: The influence of silane-based hydrophobic products - used as concrete chemical admixtures - on the corrosion of steel rebars was studied. Reinforced concrete specimens with and without a silane admixture were exposed to seawater or to aqueous solutions of de-icing salts containing chlorides. Sound and uncracked or deliberately pre-cracked concrete specimens were manufactured and cured before the exposure to aggressive environments. In the pre-cracked specimens the concrete crack tip was in contact with the steel reinforcement. The results - in terms of corrosion electrochemical potential, short circuit electric current and visual corrosion observed on the steel reinforcement - were compared with those obtained on the corresponding uncracked specimens.

In uncracked specimens any corrosion process was completely blocked independently of the water to cement ratio and concrete cover provided that hydrophobized concrete was used. This effect was due to lack of water penetration, and then of the chloride ingress, through the pores of the hydrophobized cement matrix. In uncracked specimens without the silane admixture, there was corrosion risk when high water to cement ratio and/or thin concrete cover were adopted.

On the other hand, corrosion of steel rebars was surprisingly more severe in cracked specimens manufactured by hydrophobized concrete rather than in the corresponding reference concrete specimens without the hydrophobic admixture. These results can be interpreted by admitting that oxygen diffusion - which is needed to feed the corrosion process - can occur directly as a gaseous phase through the open concrete voids in hydrophobized concrete, whereas in concrete without silane oxygen can diffuse much more slowly only through the water filled concrete voids.

Keywords: Admixtures; corrosion, cover; cracking (fracturing); reinforcing steels

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INTRODUCTION

The protection provided by concrete on reinforcing bars may be reduced and even cancelled by high concrete porosity or the presence of cracks. In both cases, there is a rapid penetration of the chloride ions (which can destroy the passive oxide film protecting the rebars from corrosion) or carbon dioxide (which neutralizes the alkalinity of the aqueous solution in the concrete pores assuring the stability of the passive oxide film). However, steel corrosion would not occur if water - which acts as a carrier for the diffusion of chloride ions - is permanently prevented from permeating the concrete porous structure. Therefore, the use of hydrophobized concretes, i.e. containing silane admixtures, is potentially interesting, from a practical point of view, in reducing the corrosion risk of steel reinforcement.

To prevent corrosion promoted by chloride penetration, various methods are generally adopted. These methods include the reduction of the water to cement ratio (w/c) to decrease porosity and permeability in the cement matrix, the adoption of pozzolan additions to reduce the chloride diffusion, the use of corrosion inhibitors, the surface protective treatment of the steel reinforcements, and the cathodic protection of the rebars. However, when concrete is cracked for some reasons, the adoption of most of the above methods can fail particularly when the crack tip reaches the rebars.

The influence of concrete cracks on corrosion of rebars, which has been for a long time underestimated in the scientific literature, has recently received particular attention (1-5). The purpose of the present work was to investigate the corrosion behaviour of rebars in the presence as well as in the absence of

cracks reaching the rebars. This should improve the understanding of the role played by concrete permeability and cracking in the corrosion process of rebars. Furthermore, it should be possible to assess the opportunity of using hydrophobized concrete as a potential method for preventing corrosion of rebars.

EXPERIMENTAL

Concrete mixtures at w/c of 0.45, 0.50 and 0.80 were manufactured by using portland cement (type I 42.5 R according to the European norms) with and without silane as hydrophobic admixture (Table 1). The silane admixture was used in form of a 30% aqueous emulsion of butyl-ethoxy-silane at a dosage rate of 2% of active ingredient by mass of cement. Table 1 shows the compressive strength at 1-7-28 days for reference and silane-treated concrete: in the presence of silane admixture a compressive strength reduction of about 10-20% was recorded with respect to the reference mixture.

Thirty-six prism specimens (100 x 100 x 400 mm) and 12 cylinder specimens (250 mm in diameter and 300-mm high) were produced. The concrete with the w/c of 0.45 was used only for the prism specimens; the mixtures with w/c of 0.50 and 0.80 were used for the cylinder specimens. Each cylinder specimen (Fig. 1-a) was reinforced with six deformed steel bars (diameter 12 mm). The bars were placed on circular rims with different concrete cover thickness (20, 50 or 80 mm) and kept in vertical position by a perforated PVC anular plate on which they were sealed by epoxy resin. An electric cable, isolated with a PVC sheath, was connected to each steel bar by means of braze welding. The weld was protected by epoxy resin before casting the concrete mixture.

Part of the prism specimens (Fig. 1-b) were reinforced with a single steel plate (60 x 360 x 1 mm) embedded 30 mm from the specimen side containing a preformed notch (10-mm deep and 14-mm wide). This notch was obtained by placing a wooden stick on the bottom surface into the mould. Other prism specimens were reinforced with two steel plates which were not in contact with each other. The two steel plates (60 x 360 x 1 mm and 60 x 90 x 1 mm) were placed at 70 mm and 30 mm respectively from the specimen notched side (Fig. 1-c). An electric cable, isolated with a PVC sheath, was connected to each steel plate by means of spot-welding. Even in this case the weld was protected by epoxy resin before casting the concrete mixture. Steel plates instead of usual rebars were used in prism specimens in order to produce cracked specimens with a pre-determined crack width.

Part of the prism specimens were deliberately cracked by flexural stress so that a crack width of 1 mm was produced in the preformed notch area. The remaining uncracked sound prism specimens were used as reference to determine the influence of cracking on the mechanism of corrosion. The letter *C* or *S* indicates whether cracked or sound specimens were used, whereas the

letter *R* or *H* indicates whether reference or hydrophobized concrete was used. For instance, the code *H-C* indicates hydrophobized (*H*) and cracked (*C*) concrete specimens.

The cylinder specimens were cured 1 month at room temperature and then immersed in natural sea water.

The prism specimens were exposed to a 3.3% CaCl_2 aqueous solution ($\text{pH} = 8$) after 1 month of curing time at room temperature. Some specimens were permanently exposed to the aggressive environment up to about 1 year. Other specimens were first immersed in the aggressive aqueous solution (3 hours) and then exposed to air (21 hours) for each 1-day cycle up to about 1 year.

Both the corrosion potential of the rebars (Fig. 1-a and -b) with respect to a reference saturated calomel electrode (SCE) and the short circuit currents between the two steel plates (Fig. 1-c) were measured.

Some specimens (Fig. 1-b) were autopsied to assess the corrosion by visual observation, the morphology of the corrosion products, the pH in the corroded area just after splitting the reinforced specimens, the mass loss and the surface of the corroded area after pickling.

RESULTS

Sea water corrosion tests

Cylinder specimens (Fig. 1-a) were used for the sea water corrosion tests. For both reference and hydrophobized mixtures, two *w/c* (0.50 and 0.80) and three concrete covers (20, 50 and 80 mm) were adopted.

Figures 2 and 3 show the free corrosion potential in mV SCE of each of the six rebars, embedded in the reference and the hydrophobized concrete respectively, as a function of the immersion time of cylinder specimens in sea water. It is assumed that when the potential of rebars is lower than -500 mV SCE the corrosion risk of the steel reinforcement is relatively high (6).

The corrosion potential of rebars embedded in the reference mixture (Fig. 2) was in the range -100 mV SCE to -300 mV SCE (then corresponding to a very low corrosion risk level) only when low *w/c* (0.50) and thick cover (≥ 50 mm) were adopted. With a *w/c* of 0.50 and a concrete cover as low as 20 mm, the corrosion behavior - in terms of SCE potential of the embedded bars - was erratic: only for two of the six bars the corrosion potential did not drop to level as low as -400 or -500 mV SCE.

The corrosion risk became relatively high when the rebars were embedded in the reference concrete mixture with a *w/c* as high as 0.80: the corrosion potential dropped to -500 mV SCE for almost all the six embedded rebars of each specimen in less than 4 months of sea water exposure. The drop was quicker with lower concrete cover thickness.

On the other hand, the corrosion potential of rebars embedded in the hydrophobized concrete mixture (Fig. 3), did not show any drop and remained at a level as high as -100 mV SCE except for some rebars embedded in the specimen with the higher w/c (0.80) and the lower cover thickness (20 mm). However, even in this case, the lowest potential in three of the six rebars did not attain to the corrosion risk level of -500 mV SCE.

De-icing salts corrosion tests

Sound and pre-cracked prism specimens, with one or two steel plate reinforcements, were used to study the corrosion behavior of rebars embedded in the reference or hydrophobized concrete mixture, both with a water-cement ratio of 0.45 (Table 1).

Figure 4 shows the free corrosion potential of the steel plate embedded in the prism specimens (Fig. 1-b), which were continuously immersed in the CaCl_2 aqueous solution up to about 1 year. Similar results for the corrosion potential - not shown here for the sake of brevity - were obtained when the specimens were immersed (3 hr) in the aggressive solution and then dried (21 hr) in the air. For each of the four test types (*R-S*, *R-C*, *H-S*, and *H-C*) two or three prism specimens were studied. The interruption of some curves on Fig. 4 corresponds to the time when the specimens were autopsied in order to assess by visual observation the corrosion of the embedded steel plate. The corrosion potential of the reinforcement in the sound specimens as a function of the time was always as high as about -200 mV SCE for the reference mixture (*R-S*) and about -100 mV SCE for hydrophobized concrete (*H-S*). This excellent corrosion behavior for the uncracked specimens is substantially related with the low w/c (0.45) and then with the low porosity of the cement matrix.

In the cracked specimens, just after the immersion in the CaCl_2 aqueous solution, there was an immediate decrease of the corrosion potential at about -600 mV SCE for the reference mixture (*R-C*) and at about -500 mV SCE for the hydrophobized concrete (*H-C*). Therefore, both *R-C* and *H-C* specimens were at about the same level of corrosion risk. However, at 1 year, through visual observation of the autopsied specimens, the corrosion appeared to be much more remarkable in the steel plate embedded in the hydrophobized concrete than in that of the reference mixture (Fig. 5). Surprisingly, the steel plates of the *H-C* specimens were completely perforated in the corroded area close to the crack tip even if the corrosion potential of the *H-C* specimens indicated a corrosion risk a little lower with respect to the *R-C* ones (-500 mV SCE versus -600 mV SCE).

The difference in the corrosion behaviour of steel plates embedded in *R-C* and *H-C* concretes - as determined by visual observation of autopsied specimens (Fig. 5) - was confirmed by short circuit current measurements in the two steel plate specimens shown in Fig. 1-c. Figure 6 shows this current as a function of the time in three different specimens of *R-C* and *H-C* type permanently immersed in the CaCl_2 aqueous solution. The short circuit current is

proportional to the diffused oxygen (7, 8) consumption rate in the cathodic area and to the corrosion of the anodic area on the steel plate close to the crack tip. This was immediately in contact with Cl^- ions just after the immersion of the specimens in the chloride aqueous solution. Therefore it was immediately depassivated and acted as anode:



On the other hand, the upper steel plate of the specimen shown in Fig. 1-c, far away from the cracked notched area, acted as cathode for the reduction of the diffused oxygen:



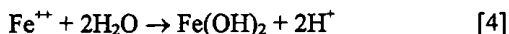
The electrochemical processes [1] and [2] were active until Cl^- ions penetrated the concrete cover (30 mm) of the upper steel plate and then cancelled any potential difference between the two steel plates.

In the *R-C* specimens the short circuit current (Fig. 6) - which is related to the corrosion rate - increased up to 5-6 μA and then decreased to a negligible current level. The initial increase in the current was related with the amount of oxygen available into the air-cured concrete before the immersion in the CaCl_2 aqueous solution. The subsequent decrease in the current was caused by the lower oxygen diffusion rate through the water-filled pores after the immersion in the aqueous solution. Moreover, in some *R-C* specimens, the short circuit current (Fig. 6) and the related corrosion rate dropped to zero since no potential difference between the two steel plates was recorded when Cl^- ions diffused up to the upper steel plate (Fig. 1-c) initially acting as the cathode.

The mass loss of the anodic steel plate directly measured in the autopsied *R-C* specimen was higher than the amount of corroded steel theoretically calculated through the integrated current-time curve on Fig. 6. This difference should be related with an additional acidic corrosion caused by the attack of H^+ ions on the steel reinforcement close to the crack tip (9):



The relatively high H^+ ions concentration on the anodic steel plate close to the crack tip - confirmed by pH measurements (4+5) - was produced by the hydrolysis process of Fe^{++} ions generated by the anodic reaction [1]:



In the hydrophobized concrete cracked specimens the short circuit current between the two steel plates (Fig. 1-c) was more erratic (*H-C* in Fig. 6).

Nevertheless, it was 10 to 100 times higher than that of the corresponding reference concrete specimens (*R-C* in Fig. 6) permanently immersed in the CaCl_2 aqueous solution. This behavior - which confirms the visual observation of the corroded anodic steel plate in the autopsied specimens (Fig. 5) - should be related with a higher diffusion rate of the oxygen molecules through the partly or totally empty pores of the hydrophobized concrete up to the upper steel plate acting as cathod. In other words, the corrosion rate of the steel reinforcement close to the crack tip, and then in direct contact with Cl^- ions (anodic area), is higher just because of the hydrophobic character of the cement paste. This reduces the water saturation of the pores and therefore favors the diffusion of the gaseous oxygen to steel reinforcement protected by the hydrophobized concrete cover (cathodic area).

The higher oxygen diffusion rate through the pores of the hydrophobized concrete accelerates the oxygen consumption in the CaCl_2 aqueous solution and this, on its turn, accelerates the oxygen transfer from the air to the liquid phase in contact with the cracked hydrophobized concrete specimens.

The above corrosion mechanism is confirmed by the short circuit current measurements in the *R-C* and *H-C* specimens exposed to the CaCl_2 aqueous solution (for 3 hours) alternated to the dry air exposure (for 21 hours). Figures 7 and 8 show the potential difference between the two steel plates (Fig. 1-c) as a function of the short circuit current for *R-C* and *H-C* specimens respectively. Figure 7 indicates that in the reference concrete cracked specimens, for a given potential difference between the two steel reinforcements, the current is much higher in the dry-wet exposure than in the permanent immersion under the Cl^- aqueous solution. This is related to the higher oxygen diffusion rate through the reference concrete when the cracked specimens are exposed to dry-wet cycles with respect to the permanent immersion in the liquid phase. On the other hand, in the hydrophobized concrete cracked specimens (Fig. 8), the current does not significantly depend on the type of exposure to Cl^- ions (wet-dry cycles or permanent immersion). This behavior is related to the approximately same oxygen diffusion through the hydrophobized concrete cracked specimens when exposed either to dry-wet cycles or to permanent immersion in the liquid phase.

CONCLUSIONS

In sound and uncracked concrete specimens, exposed to sea water after an air curing of 1 month, the use of silane, as hydrophobizing chemical admixture, blocked the corrosion of steel rebars even in mixtures with w/c as high as 0.80 provided that a cover of at least 50 mm is adopted. With w/c as low as 0.50, the corrosion of rebars in hydrophobized concrete specimens exposed to sea water is blocked even with cover as thin as 20 mm.

The influence of pre-existing cracks (1 mm wide) on the corrosion of steel reinforcements in plain or hydrophobized concrete was studied by exposing

sound and cracked specimens to CaCl_2 -based deicing salts. In sound specimens - with w/c of 0.45 and cover of 20 mm - there was no significant difference in the corrosion behavior between the reference mixture and the hydrophobized concrete. On the other hand, in cracked specimens the reference concrete surprisingly performed better than the hydrophobized one in protecting the steel reinforcement close to the crack tip. This different behavior was explained by admitting that the gaseous oxygen diffuses better through the open pores of the hydrophobized concrete with respect to the water saturated pores of the reference mixture. A more rapid oxygen diffusion through the concrete pores is capable of feeding a more severe corrosion of rebars close to the crack tip, since oxygen consumption is required for the related cathodic process on the steel reinforcement embedded in the uncracked area of the specimens.

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TABLE 1 — COMPOSITION AND PROPERTIES OF CONCRETE MIXTURES AT EQUAL SLUMP LEVEL (220-240 mm)

INGREDIENT:	Batching amounts (Kg/m ³) in concrete mixtures with w/c of:					
	0.45	0.50		0.80		
Portland cement	350	335	260			
Water	158	168	208			
Sand (F. m. = 2.6)	775	780	830			
Gravel (5-25 mm)	1160	1150	1090			
Superplasticizer(*)	3.5	3.35	-			
Compressive strength (MPa) at:	without silane	with silane(**)	without silane	with silane(**)	without silane	with silane(**)
	16.8	14.8	14.5	12.0	6.1	4.6
1 day	43.0	37.8	40.1	35.9	20.5	16.1
7 days	54.5	45.3	47.9	42.4	26.7	22.3
28 days						

(*) 40% aqueous solution of naphthalene-based admixture

(**) 2% by mass of cement

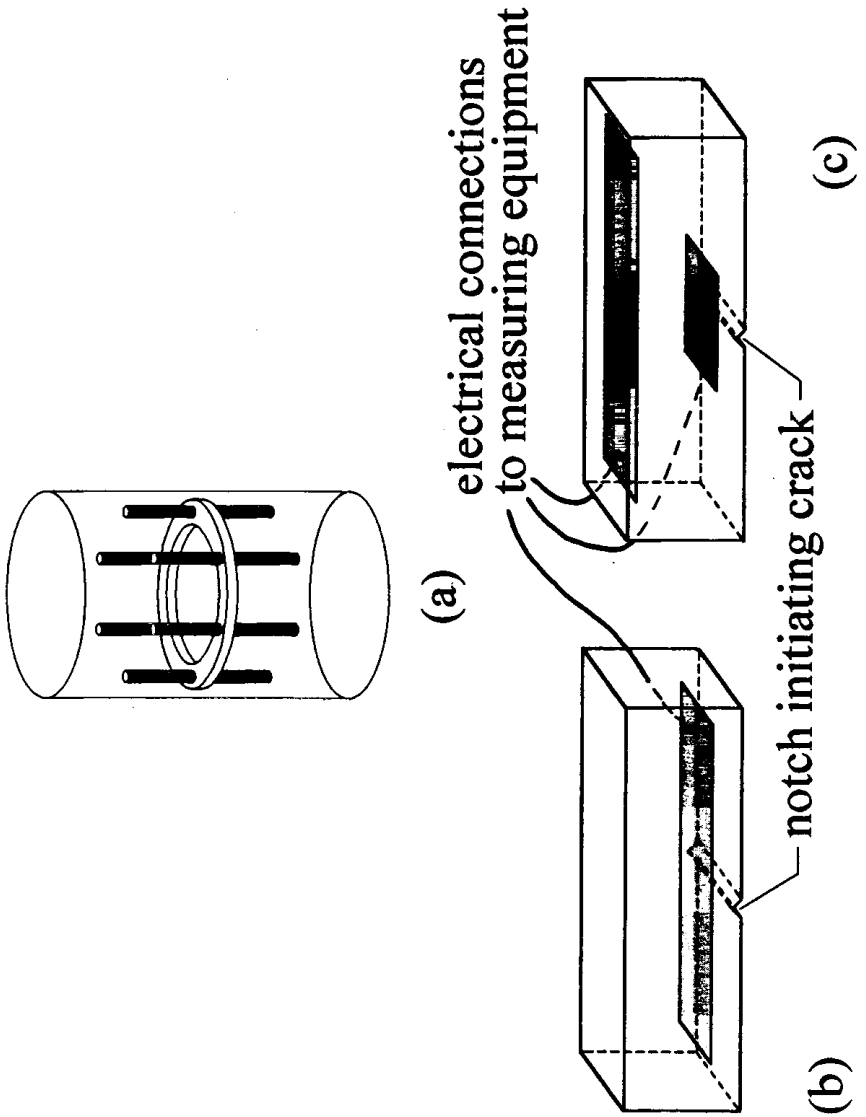


Fig. 1—Schematic view of cylinder specimen (a) and prism specimens with one (b) and two (c) reinforcing steel plates

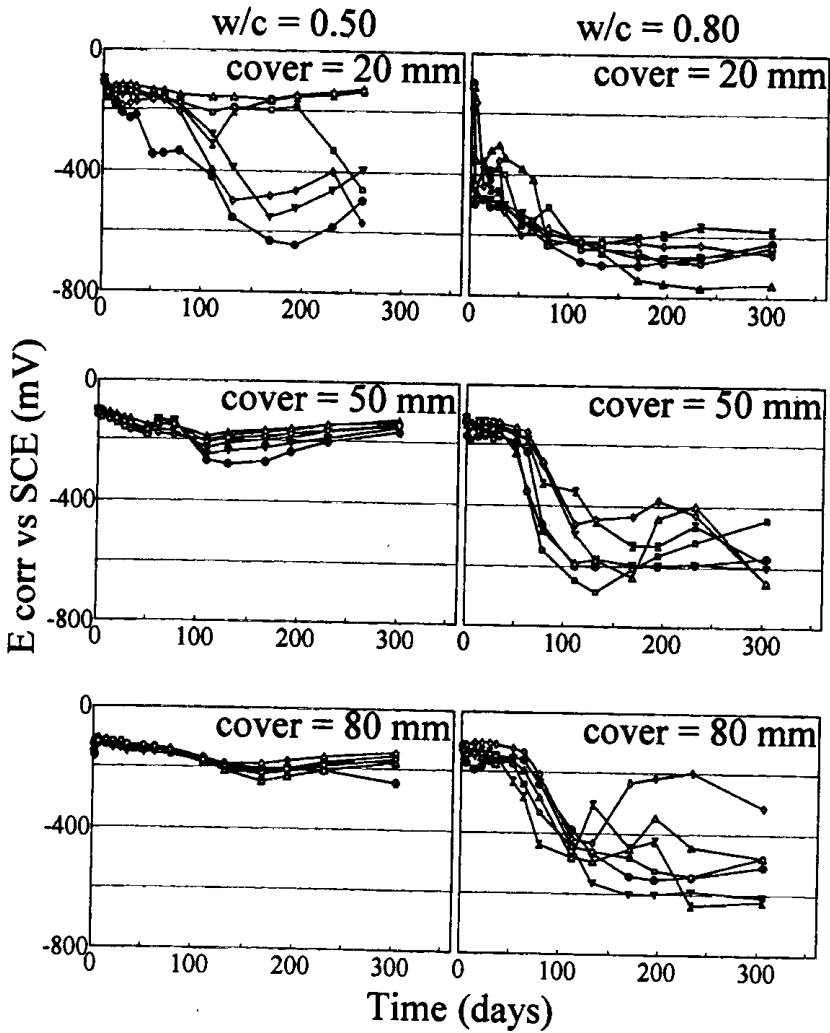


Fig. 2—Corrosion potential of rebars embedded in cylinder specimens manufactured with plain concretes and exposed to sea water

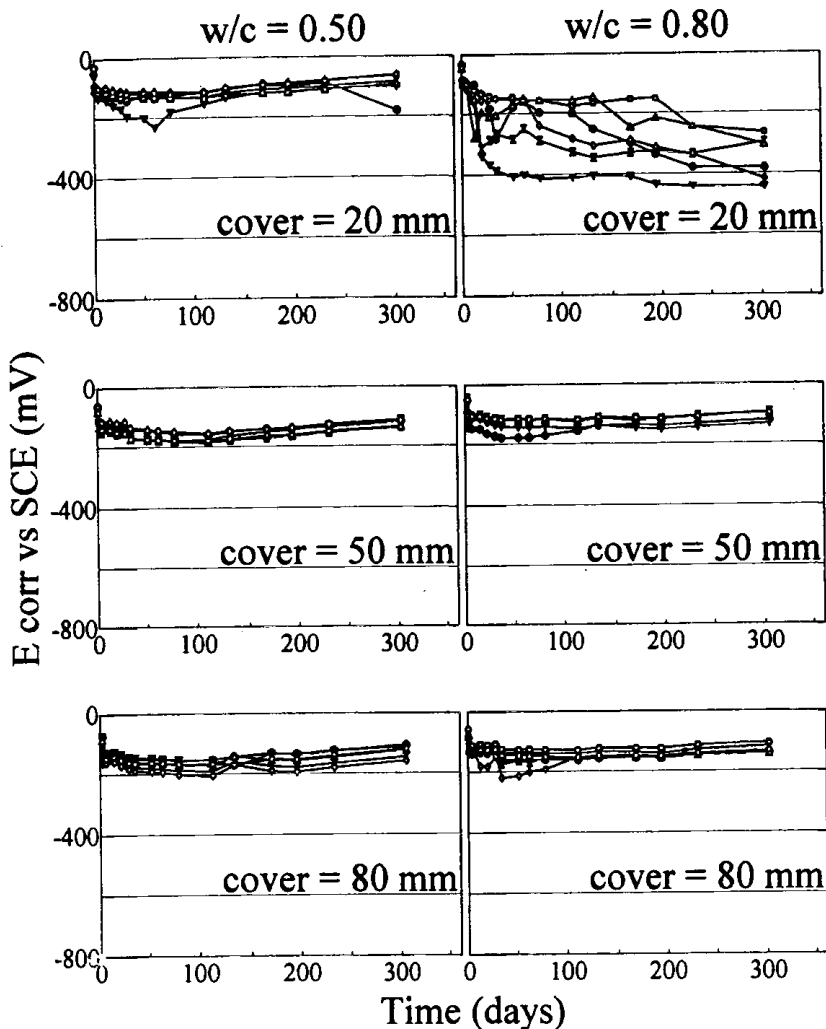


Fig. 3—Corrosion potential of rebars embedded in cylinder specimens manufactured with hydrophobized concretes and exposed to sea water

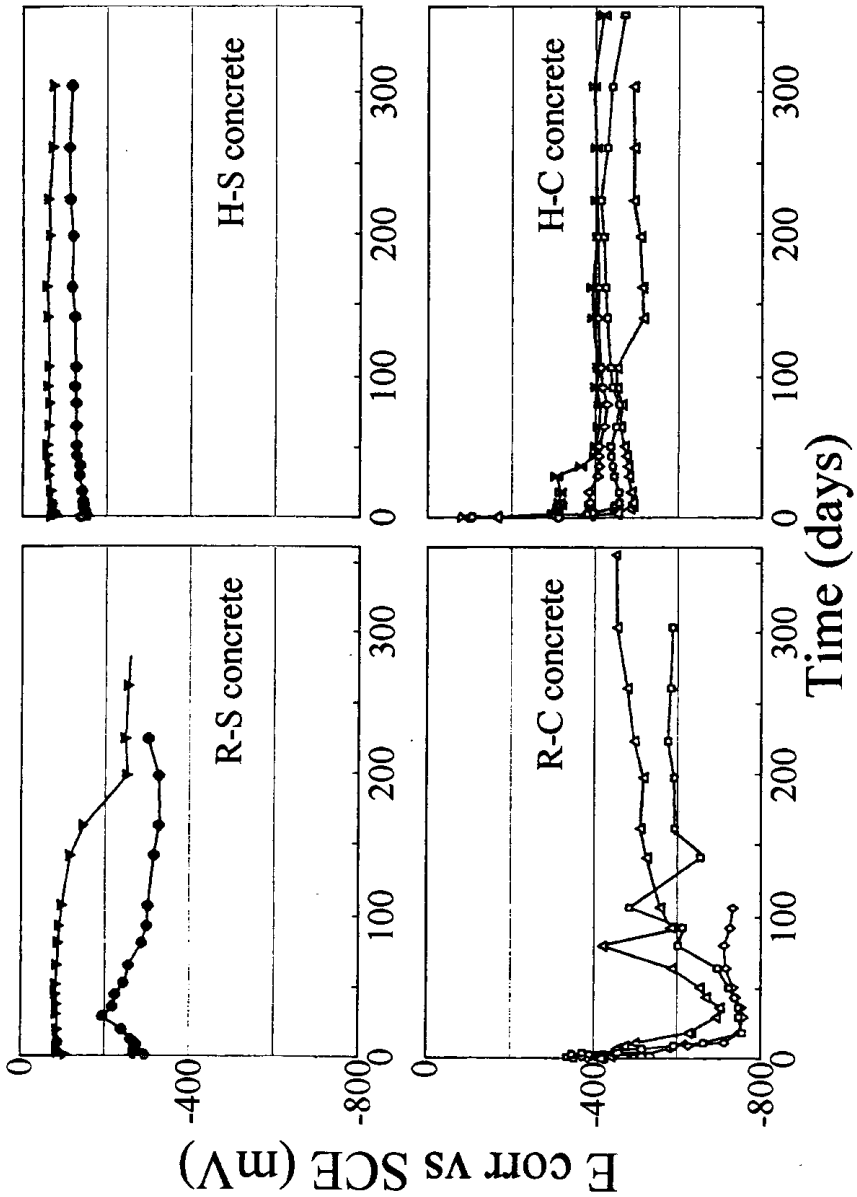


Fig. 4—Corrosion potential of the steel plate in sound (S) or cracked [®] prism specimens manufactured with reference (R) or hydrophobized (H) concrete mixtures, and exposed to the CaCl₂ aqueous solution

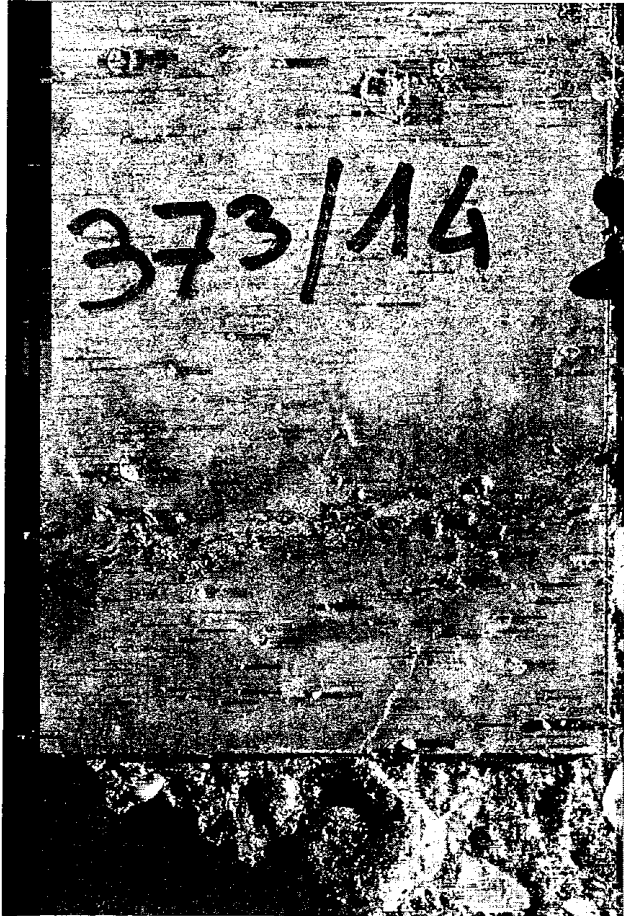


Fig. 5A—Corrosion of the steel plate in autopsied cracked prism specimens manufactured with reference concrete mixture and exposed to the CaCl_2 aqueous solution



Fig. 5B—Corrosion of the steel plate in autopsied cracked prism specimens manufactured with hydrophobized concrete mixture and exposed to the CaCl_2 aqueous solution

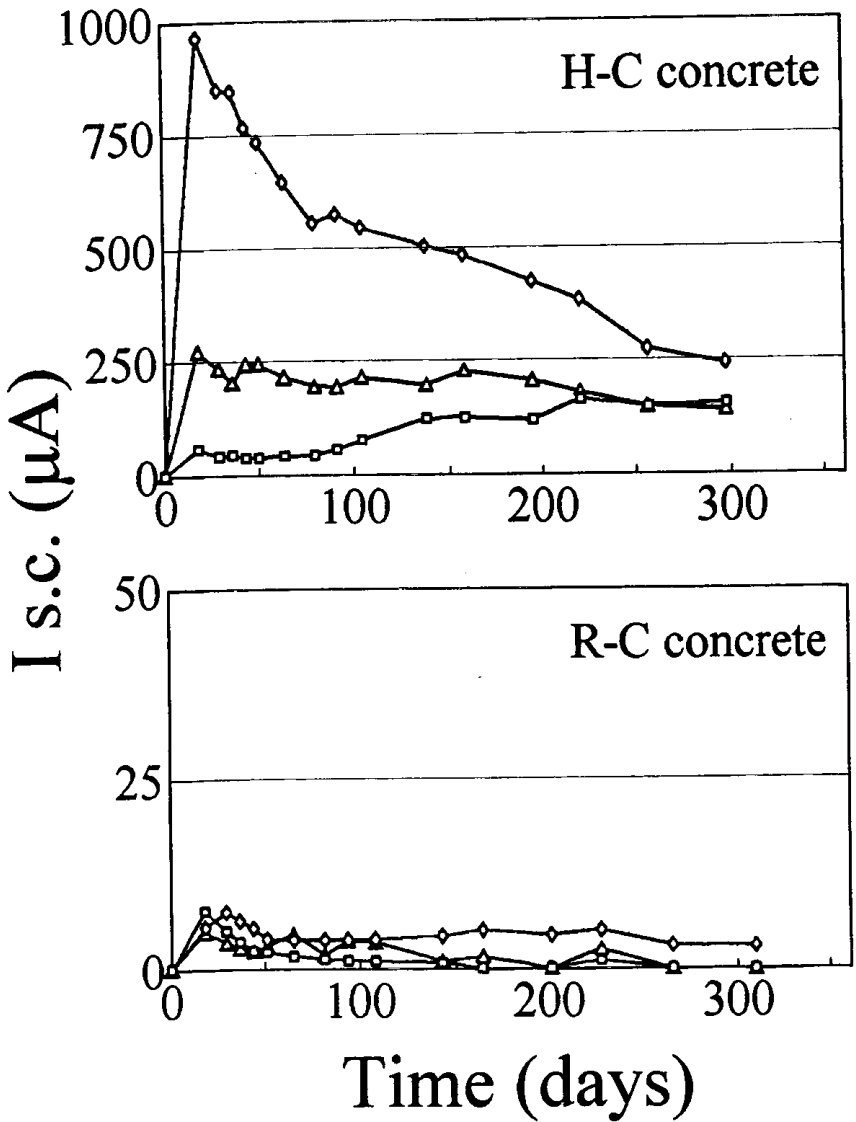


Fig. 6—Short circuit current between the two steel plates of prism specimens (c in figure 1) manufactured with reference (R) or hydrophobized (H) concrete both cracked and exposed to the CaCl₂ aqueous solution

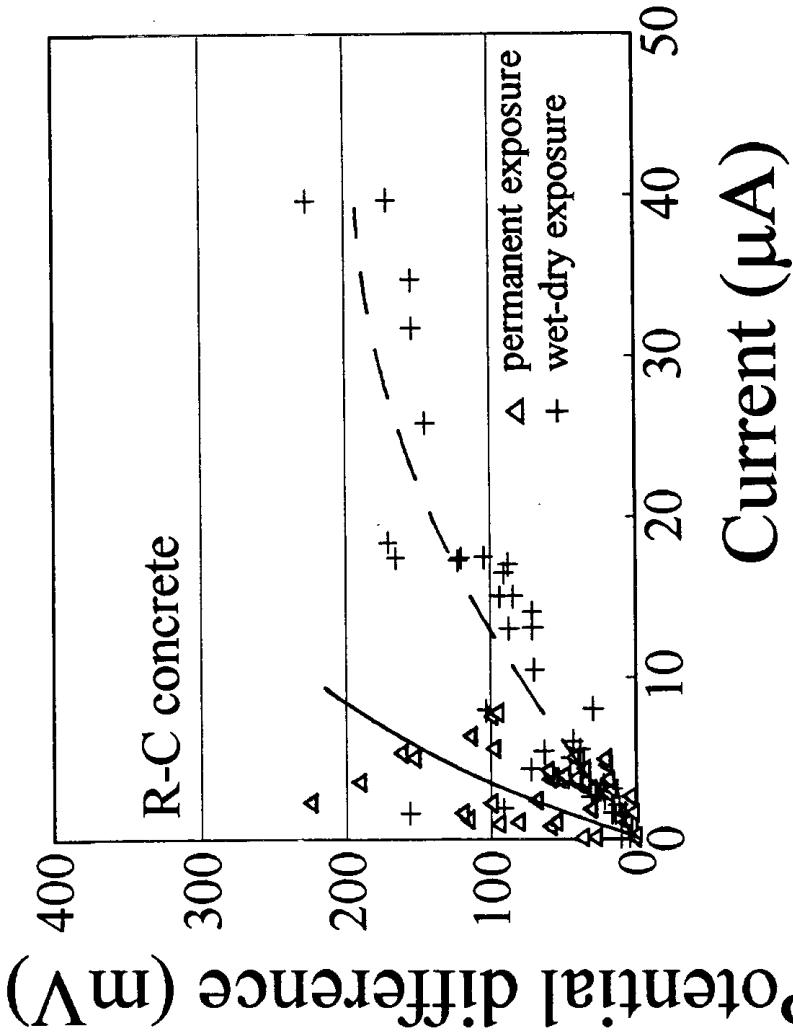


Fig. 7—Potential difference versus current between the two steel plates of cracked prism specimens manufactured with reference concrete and exposed to the CaCl₂ aqueous solution

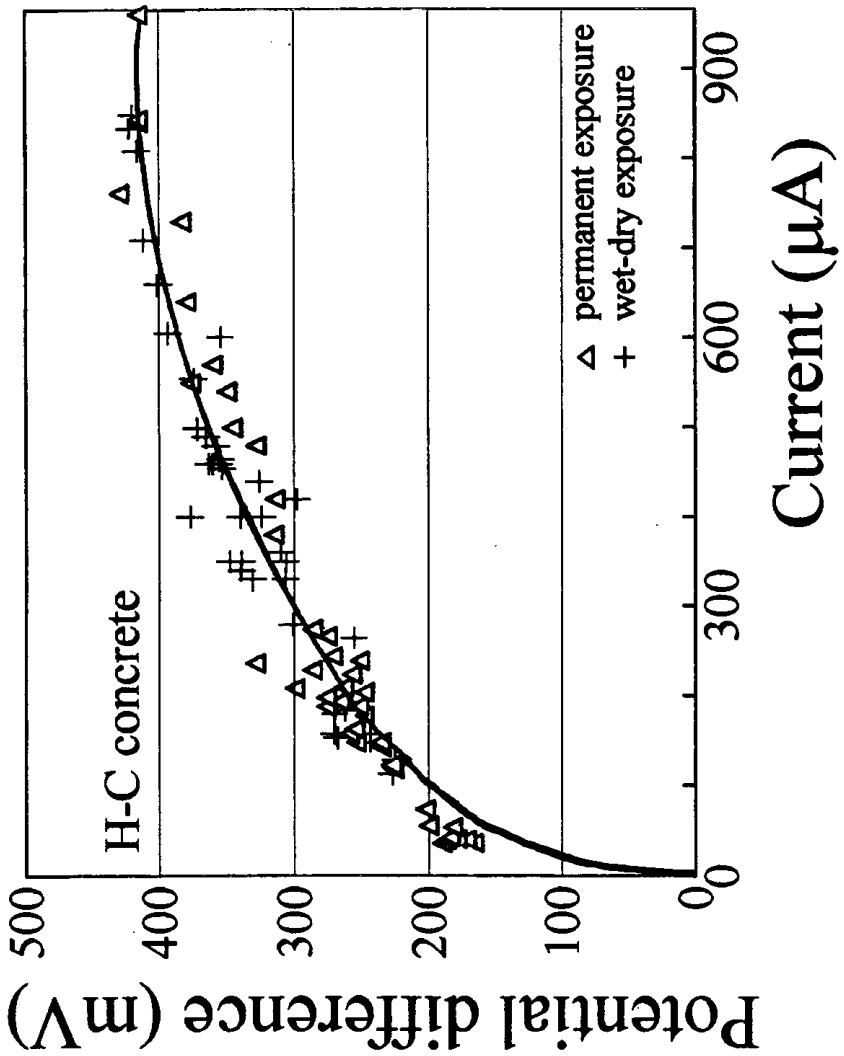


Fig. 8—Potential difference versus current between the two steel plates of cracked prism specimens manufactured with hydrophobized concrete and exposed to the CaCl_2 aqueous solution