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The effect of silane-based hydrophobic admixture on corrosion of reinforcing steel in concrete

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A B S T R A C T

The influence of a hydrophobic admixture based on silane on the corrosion resistance of steel reinforcement in concrete was studied. Sound or deliberately pre-cracked concrete specimens were manufactured with w/c of 0.45 and 0.80, both in the presence and in the absence of silane. The specimens were fully immersed in a 3.5% NaCl aqueous solution.

The results, in terms of electrochemical measurements, visual observations, and weight loss measurements of steel reinforcement, show that silane blocked corrosion process in uncracked concrete specimens. On the other hand, in cracked concrete specimens, corrosion of steel reinforcements was unexpectedly more severe in hydrophobic specimens rather than in the corresponding not hydrophobic ones. It is believed that oxygen, which is needed to feed the corrosion process, diffuses faster in a gaseous phase through the open concrete porosity in the hydrophobic concrete, whereas in concrete without silane, oxygen diffuses much more slowly through the water filling the pores of the saturated concrete.

1. Introduction

The protection provided by concrete to reinforcing bars may be reduced and even cancelled by high concrete porosity or the presence of cracks. In both cases, there is rapid penetration of 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 [1].

However, steel corrosion would not occur if water, which acts as a carrier for the diffusion of chloride ions and is the medium where corrosion reactions develop, is permanently prevented from wetting the porous structure of the concrete.

The water in contact with a porous hydrophilic material, such as concrete, penetrates the material by means of capillary forces following the Washburn equation, $p=(2\ \gamma/r_c)\cos\sigma$, where γ represents the liquid surface tension, r_c is the capillary pore radius, and σ is the contact angle. A water droplet, on a hydrophilic solid, wets the solid surface by spreading itself and by absorption through the solid porosity. The contact angle becomes less than 90°, p becomes positive and the liquid fills the pore spontaneously. However, the molecular attraction between water and the concrete pore walls can be lowered by surface treatment using impregnation with hydrophobic agents, such as those based on alkyl-alkoxy-silane [2–18]. In this case, the contact angle becomes higher than 90°, the water droplet keeps itself spherical, and an external pressure p (in this case negative) is necessary to allow the liquid to penetrate the solid porosity. Their alkoxylic groups are chemically bound to the hydrated silicates in the concrete by a condensation reaction, while their hydrophobic alkylic groups come out on the pores surface [19]. Hydrophobic treatments, differ from waterproofing ones, only covering the pore walls by leaving pores practically empty. Capillary pore size in concrete mainly varies from 100 Å to 10,000 Å. Acrylic agents and epoxy resins, due to their large molecular size, can only film the surface by waterproofing it. On the contrary, silanes can penetrate concrete since their molecular size varies from 10 Å to 20 Å [7].

Hydrophobic treatments hinder liquid water to penetrate the structure when pressure is not excessively high. However, differently from waterproofing treatments, they allow water vapour permeation, and in general gas permeation, leading to water leakage from the structure.

The effectiveness of mortar surface treatments with alkyl-alkoxy-silane against water penetration has been demonstrated [15,19,20]. But, their efficiency with time depends on the alkali resistance of the applied compounds, their penetration depth, their resistance to atmospheric agents, and the integrity of the structure [20–24]. Therefore, hydrophobic agents have been recently added in the concrete mixture directly in order to make both the surface and the whole concrete bulk hydrophobic [25–30]. In this way, bulk hydrophobization could cancel the detrimental effect of concrete cover cracking. Therefore, the use of hydrophobic concretes, containing silane admixture, is potentially interesting, from a practical point of view, in reducing the corrosion risk of steel reinforcement.

This work is aimed to investigate the effect of a hydrophobic admixture on the corrosion behaviour of reinforcements in concrete,

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Table 1
Concrete mixture proportions and relative mechanical strength

Ingredient	Weight (Kg/m^3)			
	w/c=0.45		w/c=0.80	
Cement	350		260	
Water	158		208	
Sand	775		830	
Gravel	1160		1090	
Superplasticizer	3.5		–	
Compressive strength (MPa) at	Without silane	With silane	Without silane	With silane
1 day	16.8	14.8	6.1	4.6
7 days	43.0	37.8	20.5	16.1
28 days	54.5	45.3	26.7	22.3

in the presence as well as in the absence of concrete cracks, reaching the reinforcements, in order to assess the opportunity of using hydrophobic concrete as a potential method for preventing corrosion of rebars in concrete.

2. Experimental

2.1. Materials

Concrete mixtures with water to cement ratio (w/c) of 0.45 and 0.80 were manufactured by using a commercial portland-limestone blended cement type CEM II/A-L 32.5 R according to EN-197/1, with and without silane as a hydrophobic admixture (Table 1). Crushed stone (25 mm maximum size) and natural sand (2 mm maximum size) were used as aggregates. A 40% aqueous solution of naphtalene-based admixture was used to make the concrete with w/c=0.45 as flowable as the concrete with w/c=0.80. The silane admixture was used in form of a 45% aqueous emulsion of an alkyl-triethoxy-silane at a dosage rate of 2% of active ingredient by mass of cement. Table 1 shows the compressive strength at 1, 7, and 28 days for reference and silane-treated concretes. In the presence of silane admixture, a compressive strength reduction of about 10 to 20% was recorded with respect to the reference mixture.

2.2. Specimens

Twenty four prismatic concrete specimens (100×100×400 mm) were produced (Fig. 1).

Half of the specimens, kept uncracked to allow reinforcing steel embedded in them to act as cathode for the short-circuit current measurements, were reinforced with single steel plate (70×1×360 mm) embedded at mid depth (Fig. 1). The rest of the specimens were cracked and reinforced with two steel plates not in contact with each other. The two steel plates (70×1×360 mm and 70×1×120 mm) were placed at 70 mm and 30 mm, respectively, from the specimen side containing a preformed notch, whose function was to initiate a crack reaching the smaller plate under flexural loading. This smaller plate acted as the anode for the short-circuit current measurements, while the larger steel plate was used to facilitate the specimen cracking avoiding its splitting and to control the crack width.

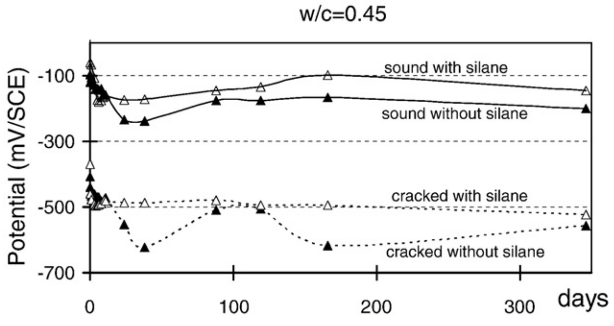


Fig. 2. Corrosion potential of the steel plates embedded in concrete specimens with w/c=0.45, as a function of the test time.

An electric cable, isolated with a PVC sheath, was connected by means of spot welding to the steel plates embedded in uncracked specimens and to the smaller plates embedded in cracked specimens. The weld was protected by epoxy resin before casting the concrete mixture.

Steel plates, instead of usual rebars, were embedded in the prismatic concrete specimens in order to enhance the corrosion process by increasing the cathodic to anodic area ratio, as well as to obtain larger corroded areas to observe and analyze, and to facilitate the specimen cracking with a pre-determined crack width.

All the specimens were kept for 48 h at 100% R.H. and, after demoulding, they were air dried for 1 month at room temperature. After curing, half of all the specimens were stressed by bending, by loading the specimen surface opposite the notch to initiate the development of a crack. Crack width of 1 mm was obtained with sufficient accuracy by slowly varying the applied load. In order to make the water penetration unidirectional and perpendicularly directed to the steel plate through the concrete cover, all the specimen sides not intended to be involved in the water penetration process were epoxy coated.

2.3. Tests

After the curing period, all the specimens, sound or cracked, were completely submerged in a 3.5% NaCl aqueous solution, making sure to maintain constant atmospheric oxygen saturation through adequate recycling.

The corrosion probability of the different steel plates was monitored by measuring their corrosion potential with respect to a reference saturated calomel electrode (SCE). Moreover, the kinetics of

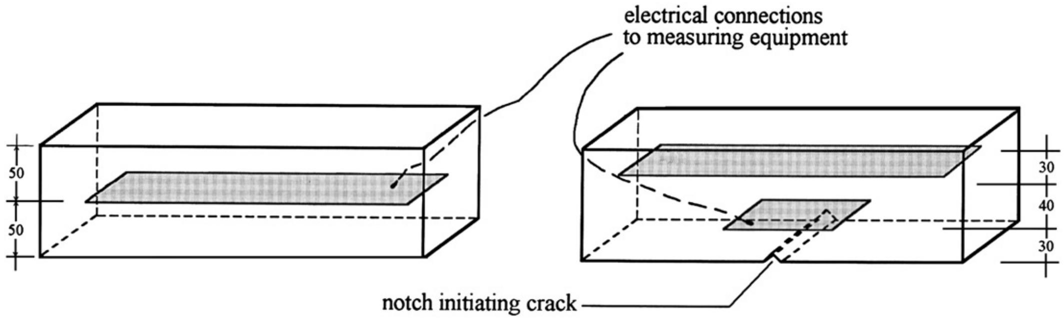


Fig. 1. Prismatic reinforced concrete specimens.

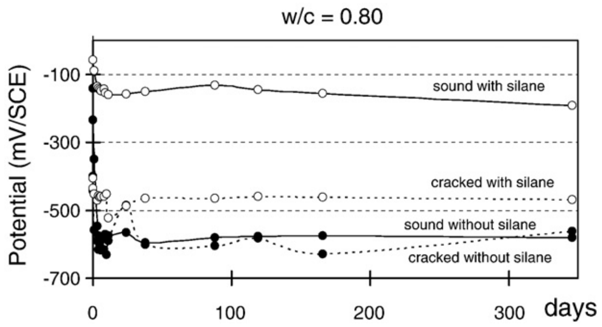


Fig. 3. Corrosion potential of the steel plates embedded in concrete specimens with w/c = 0.80, as a function of the test time.

the corrosion process was monitored by means of the short-circuit current measurements carried out between the smallest plate (anode), embedded in the cracked specimen and reached by the crack tip, and the steel plate (cathode) placed in the corresponding sound specimen. The reported values are the averages of the measurements carried out on three specimens of each type. Some specimens were periodically split to assess the reinforcement corrosion by visual observation and weight loss measurements of the corroded area after pickling.

3. Results and discussion

Figs. 2 and 3 show corrosion potential, as a function of the test time, of the steel plates embedded in sound and cracked concrete specimens with w/c = 0.45 and w/c = 0.80, respectively, both in the presence and in the absence of the hydrophobic admixture.

By assuming that potential values lower than −450 mV/SCE indicate a relatively high corrosion risk of the steel reinforcement, steel plates embedded in concretes with the lowest w/c ratio (Fig. 2) show greater corrosion risk only in the presence of concrete cracks, regardless of the presence of the hydrophobic admixture, due to the low porosity of the cement matrix. Therefore, at w/c = 0.45, a slight benefit could turn out from silane treatment.

On the other hand, in sound concretes manufactured with the highest w/c ratio (Fig. 3), the hydrophobic admixture is able to preserve reinforcement from corrosion even in bad quality concrete, since the corrosion potential of reinforcement was lowered to about −200 mV/SCE with silane from −600 mV/SCE without silane. Furthermore, again, in the presence of cracked concrete, steel plates show greater corrosion risk both in the presence and in the absence of the hydrophobic admixture. Therefore, differently from w/c = 0.45, the corrosion potentials at w/c = 0.80 show benefit of silane treatment at least in the sound concrete.

The corrosion currents for both water to cement ratios (Figs. 4 and 5) surprisingly show that the reinforcements corrode more freely on immersion when concrete is treated with silane. In particular, short-circuit currents (Fig. 4) were initially very high due to oxygen trapped in the air cured concrete. However, in the absence of silane after few days of full immersion, the short-circuit currents rapidly decreased to values of few microamperes, as a consequence of the low availability of oxygen when dissolved in water. In the presence of the hydrophobic admixture, the short-circuit currents remained up to two order of magnitude higher than those measured in not hydrophobic concrete. Since oxygen reduction is the reaction generally controlling the kinetics of the corrosion process, it is clear that oxygen flux is higher through the unsaturated pores of the hydrophobic concrete. Moreover, concerning with not hydrophobic concrete, short-circuit currents resulted one order of magnitude higher in concretes manufactured with the lowest w/c ratio with respect to those measured in concretes manufactured with the highest w/c ratio. These results could be explained by a lower saturation degree of less porous concrete. In non-hydrophobic concrete, oxygen diffusion occurs faster through the unsaturated concrete pores.

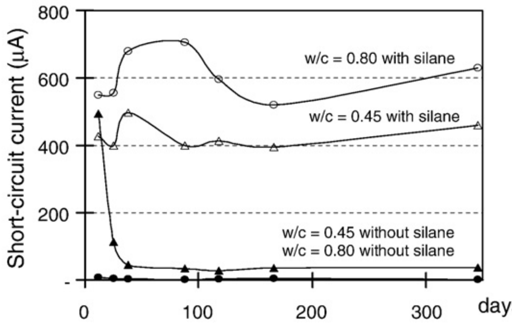


Fig. 4. Short-circuit currents of the steel plates embedded in concrete specimens, as a function of the test time.

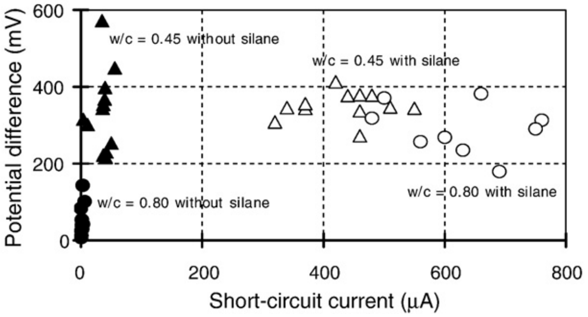
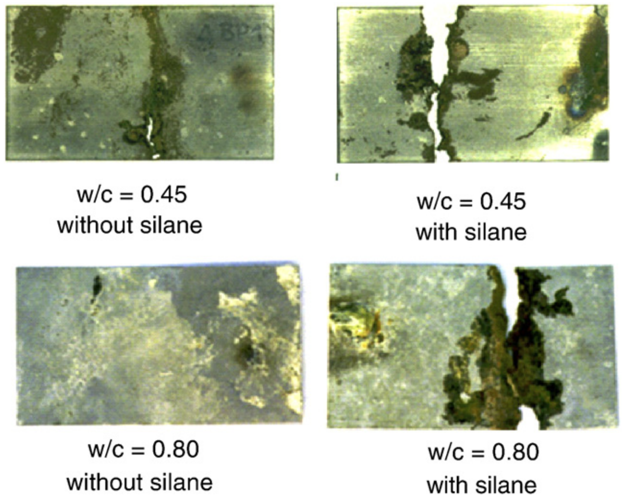


Fig. 5. Potential difference versus short-circuit current.

By comparing (Fig. 5) the short-circuit currents as a function of the potential difference between the steel plates acting as anode (cracked specimen) and cathode (uncracked specimen), respectively, it can be observed that at equal potential difference, which represents the electromotive force of the corrosion process, the highest corrosion currents were monitored in hydrophobic concretes, especially when the higher w/c ratio was used.

The difference in the corrosion behavior of steel plates, as determined by electrochemical measurements, was confirmed by direct visual observation of the steel plates extracted from broken specimens (Fig. 6). After 6 months, corrosion appeared to be much more remarkable in the steel plates embedded in the hydrophobic concretes with respect


w/c = 0.45
without silane

w/c = 0.45
with silane

w/c = 0.80
without silane

w/c = 0.80
with silane

Fig. 6. Visual observation of reinforcements extracted from the specimens after 6 months-immersion in the chloride solution.

Table 2
Measured and calculated weight loss of reinforcement after different immersion times in the chloride solution

Specimen	Exposure time (months)	Measured weight loss (g)	Calculated weight loss (g)
w/c=0.80 with silane	12	6.1	5.2
w/c=0.80 with silane	6	3.8	2.6
w/c=0.45 with silane	6	2.6	1.4
w/c=0.45 with silane	13	4.1	3.8
w/c=0.45 with silane	12	1.5	1.1
w/c=0.45 without silane	12	0.6	0.5
w/c=0.45 without silane	6	0.5	0.4
w/c=0.45 without silane	11	0.6	0.4

to those embedded in the not hydrophobic ones. Surprisingly, all the steel plates embedded in the hydrophobic concrete were completely perforated in the corroded area close to the crack tip. On the other hand, the steel plates embedded in not hydrophobic concrete with w/c=0.80 did not show any corrosive attack.

In Table 2, the measured weight loss of reinforcing steel plates, extracted from the split specimens after different periods of full immersion in the aggressive solution, are compared with the theoretical weight loss calculated by the short-circuit current integration with time as a consequence of the Faraday's law. Weight loss of steel reinforcements embedded in not hydrophobic concretes with w/c of 0.80 is not reported since sign of corrosion was not detected after one year of full immersion. It is evident that the presence of silane causes a much higher weight loss of the reinforcements, due to the corrosive attack, with respect to that observed in reinforcements embedded in not hydrophobic concretes, especially when high w/c ratio was used. It is also evident that the weight loss calculated by the Faraday's law is always lower with respect to that experimentally measured. This was due to acidity (pH=5, as measured) caused by the hydrolysis of the corrosion products, which enhanced the oxidation process because the cathodic reaction was promoted not only by oxygen reduction but also by hydrogen reduction.

4. Conclusions

In sound concrete specimens exposed to chloride solution, the use of silane as hydrophobic admixture prevented the corrosion of reinforcing steel even in concrete mixtures with w/c as high as 0.80. This effect was due to the very low water absorption, and then chloride ingress, through the pores of the hydrophobic matrix.

In cracked specimens, the reference concrete surprisingly performed better than the hydrophobic one in protecting the steel reinforcement from corrosion. This different behaviour can be explained by allowing that oxygen, stripped by the surrounding aqueous chloride solution, can diffuse faster in a gaseous phase through the open concrete porosity in immersed hydrophobic concrete. Whereas in concrete without silane, oxygen diffuses much slower through the water filling the pores of the saturated concrete. Faster oxygen diffusion through the concrete pores is able to drive a more severe corrosion of steel reinforcement close to the crack tip, since oxygen consumption is required for the related cathodic process on the steel reinforcement.

In order to avoid that the reader muddles up admixtures commonly used to protect concrete from reinforcement corrosion, like waterproofing admixtures or corrosion inhibitors as well as superplasticizers in a more wide sense, it should be pointed out that hydrophobic admixtures act in a completely different way. They can be quite promising when properly used, in particular in poor quality concrete, being mainly effective in preventing water ingress in the concrete rather than counteracting specific aspects related to concrete durability.

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