

THE USE OF SUPERPLASTICIZERS AS STEEL CORROSION REDUCERS IN REINFORCED CONCRETE

M. COLLEPARDI, R. FRATESI and G. MORICONI
Department of Sciences of Materials and Earth, University of Ancona, Italy
S. BIAGINI
MAC-MBT, R&D Laboratories, Treviso, Italy

Abstract

The data of the present paper indicate that carbonation is a necessary process but not a sufficient one for the steel corrosion in reinforced concrete. The porous structure of concrete and the environmental relative humidity appear, instead, to be the determining factors in the corrosion process, since their increase causes capillary water to come into contact with steel reinforcement. So, superplasticizers can reduce steel corrosion as they allow a reduction of the water/cement ratio at the same concrete workability, and, at last, a reduction in the water content and the permeability to water of the concrete.

Key-words: Carbonation, Steel corrosion, Superplasticizers.

1 Introduction

Concrete is considered to have a particular protective action on the reinforcing steel bars in consequence of the formation of an adherent and passive oxide film in the high basicity conditions created by the hydration of the cement.

However, failures of structures are often attributed to reinforcement corrosion processes in aggressive environments. Aggressive phenomena are generally ascribed to the intrusion of either chloride ions, able to destroy the passive film, or carbon dioxide, which neutralises the alkalinity of the aqueous solution present in the concrete pores and thus removes the favourable passivation conditions.

The aim of the present work is, after firstly evaluating the real influence of the carbonation process in reinforcement corrosion phenomena, to verify if the use of superplasticizers as water reducers can reduce steel corrosion in reinforced concrete.

2. Experimental part

To acquire experimental data in a reasonably short time, the carbonation process was carried out in an accelerated way by

artificially enriching in carbon dioxide the test environment.

Furthermore, experiments were performed on concretes, rather than mortars, as previously used by other Authors (1), in order to obtain results corresponding to real situation.

Finally, to avoid any contamination by factors, other than carbonation, particular attention was taken to prevent the contact of the reinforcement with chlorides.

Concretes with different water/cement ratio ($w/c = 0.35 - 0.50 - 0.65 - 0.80$) were casted. The binder was Portland cement type I, used separately or in combination with fly ash, an artificial pozzolan. The fly ash substituted partially (20%) the Portland cement or was added with no diminution of the Portland cement. In the case of partial substitution, a pozzolanic cement is, in fact, used.

Cubic concrete specimens (10 cm side) without rebars, were manufactured for the determination of the electrical resistivity and of the penetration depth of the carbon dioxide. Moreover, prismatic reinforced specimens (40x15x10 cm) were prepared for the determination of the corrosion electrochemical potential and the polarization resistance of the rebars. The rebars were of common manufacturing steel (8 mm diameter) and they were symmetrically positioned with concrete covers varying from 2 to 5 cm. During the casting, graphite bars as counterelectrodes were inserted at equal distances from the steel bars.

The specimens were cured for seven days in a saturated vapour atmosphere. Before their exposure to the artificially carbon dioxide enriched environment (carbon dioxide equal to 30%), kept at atmospheric pressure, the sides of the specimen perpendicular to the bars and the surfaces of the emerging bars were coated with epoxy resin. The relative humidity of the environment enriched in carbon dioxide was kept constant at a value of 75% in order to obtain the maximum carbonation velocity (2).

The penetration depth of carbon dioxide was measured after different times of exposure by means of the phenolphthalein test: an hydroalcoholic solution of 2% phenolphthalein was sprayed on the transversely split section of the cubic specimens.

The corrosion electrochemical potential of the reinforcement was measured with respect to mercurous sulphate (SSE) reference electrode by means of a differential electrometer with high input impedance, according to ASTM (3).

The polarization resistance measurements of the rebars (4-6) were carried out galvanodynamically, by polarizing the working electrode by means of the graphite counterelectrode, while the reference electrode was fixed on the external surface of the specimen; a wet sponge of sodium nitrate solution was placed between the reference electrode and the external surface of the specimen to improve surface contact; at last, the ohmic drop due to the concrete thickness

between the reference and the working electrode was compensated (7).

3 Results and discussion

3.1 Carbonation depth

The results of the carbonation depth with exposure time in carbon dioxide atmosphere, for concretes consisting of Portland cement, are shown in Fig. 1. The data are in agreement with those reported in literature (8,9),

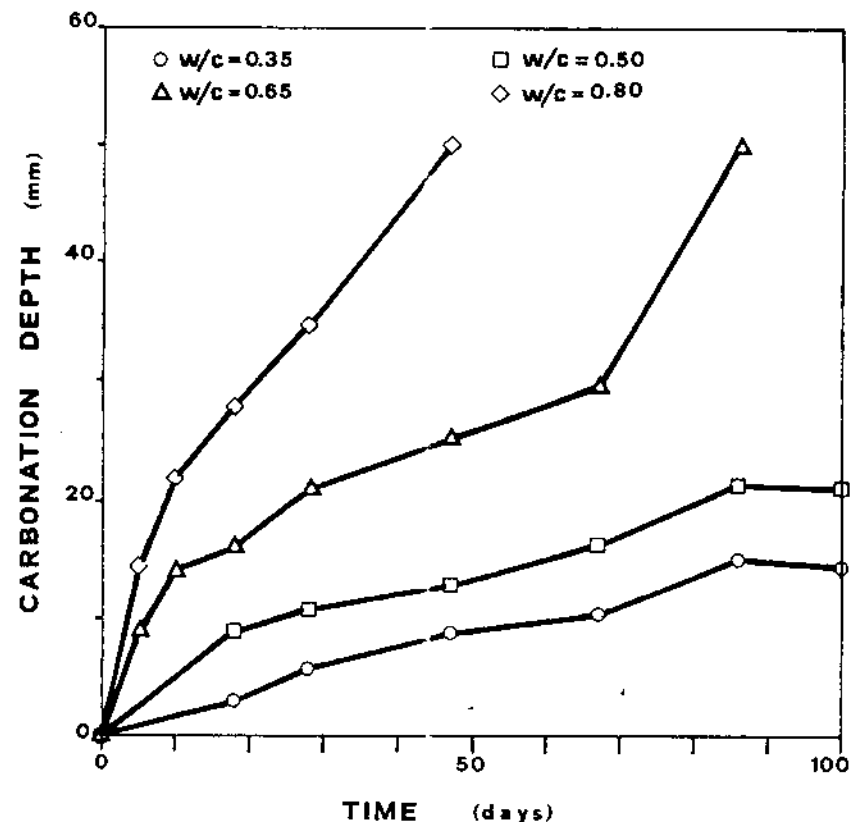


Fig. 1. The influence of exposure time and water/cement ratio on the carbonation depth in Portland cement concretes in carbon dioxide enriched atmosphere (R.H. = 75%).

demonstrating an increase in the permeability to carbon dioxide with the increase of water/cement ratio, that is with the porosity of the concrete.

Using pozzolanic cement with the same water/binder ratio (Fig. 2), the evolution appear similar to that shown in Fig. 1, but a higher penetration depth with the same exposure time is observed, due to a greater initial porosity derived from a higher effective water/cement ratio (10) and a lower amount of hydrolisis lime available (6).

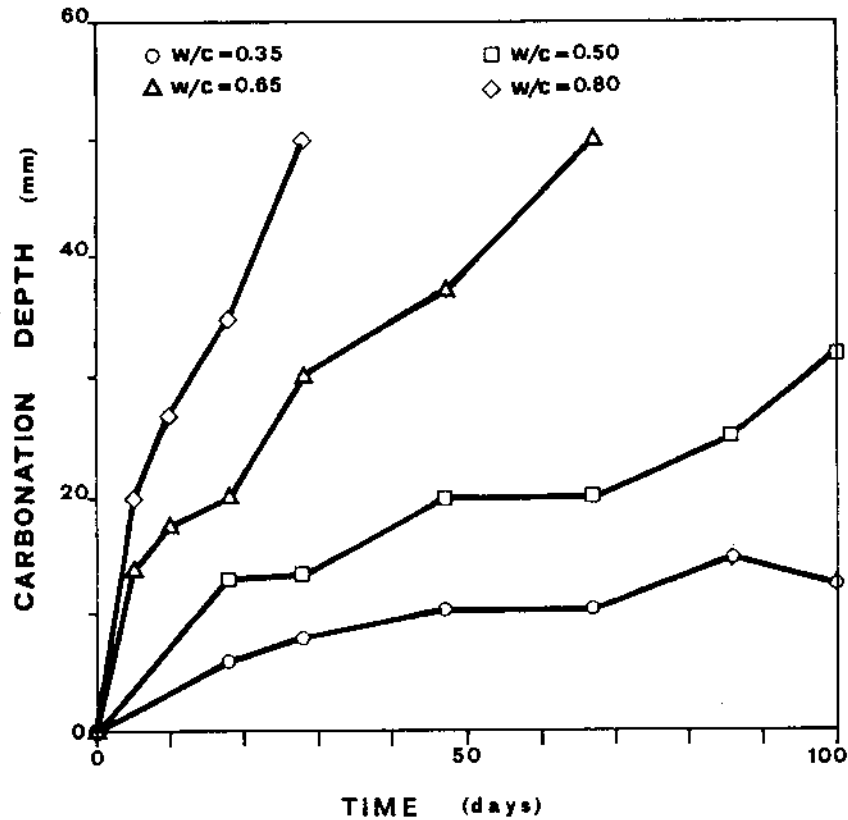


Fig. 2. The influence of exposure time and water/cement ratio on the carbonation depth in pozzolanic cement concretes in carbon dioxide enriched atmosphere (R.H. = 75%).

Instead, the use of fly ash in substitution to the fine inert, rather than cement, systematically decreases the

depth of penetration of the carbon dioxide (Fig. 3).

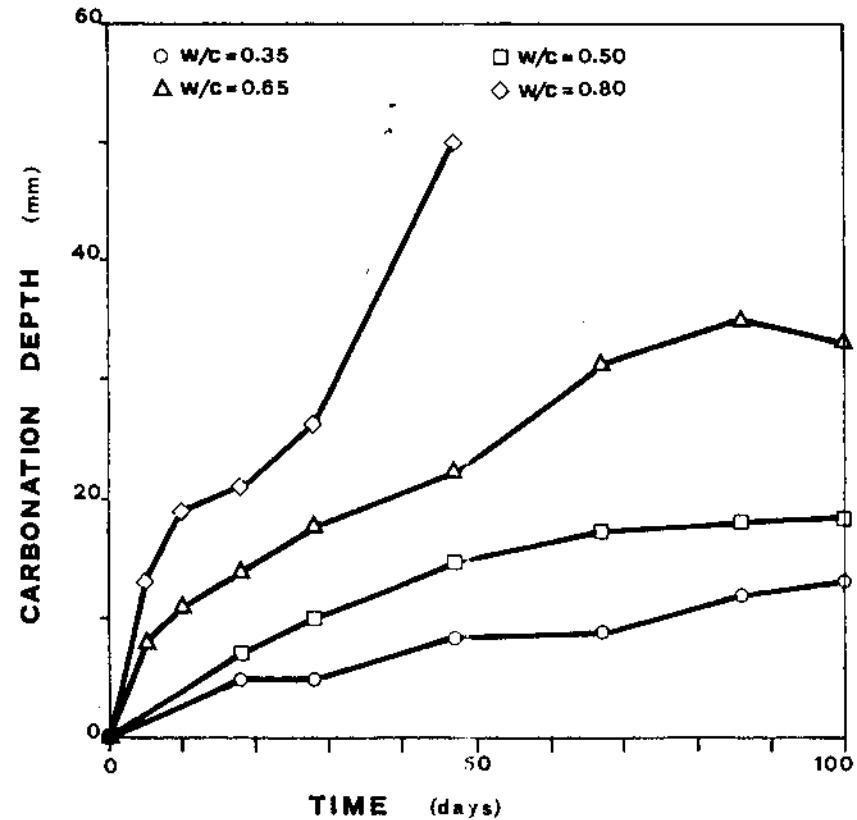


Fig. 3. The influence of exposure time and water/cement ratio on the carbonation depth in Portland cement concretes with addition of fly ash in carbon dioxide enriched atmosphere (R.H. = 75%).

3.2 Electrochemical potential

The potential of reinforcements subjected to accelerated carbonation shows significant changes with exposure time, as indicated in Fig. 4. However, since the evolution of the potentials was not modified by the carbonation front (point C on curves in Fig. 4), these potential variations could not be attributed to the carbonation process.

The potential trend, in carbonated concretes, depends on

the water/cement ratio and for its lower values ($w/c = 0.35$ and $w/c = 0.50$) moves gradually towards less negative values, that is towards representative values of the stability of the protective oxide film. We would like to recall that the potential values of the active state can be considered significant in the range between -600 mV and -1250 mV SSE as can be deduced from Pourbaix's diagram (10-13) at pH 8.3, measured on the concrete aqueous extract. No change in the potential tendency was observed even when the carbonation front had reached the reinforcements. This fact is probably justified by the low water/cement ratio and therefore by the lack of water necessary for the formation of a liquid layer on the rebars.

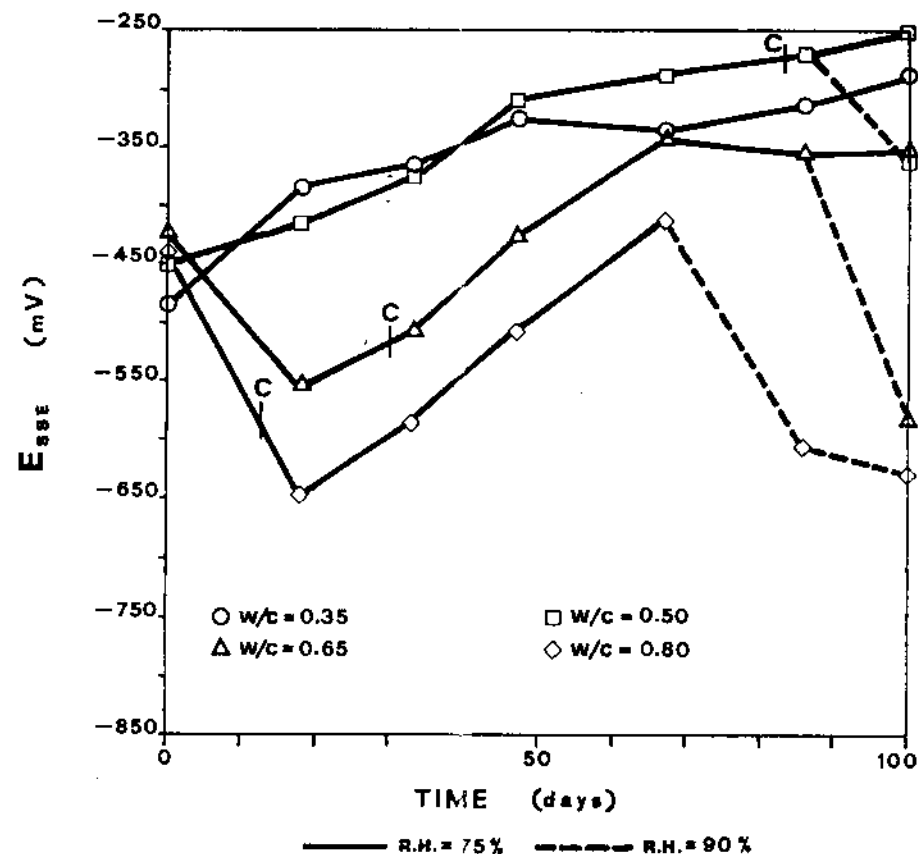
Instead, rebars embedded in concretes of higher water/cement ratio ($w/c = 0.65$ and $w/c = 0.80$) show an initial tendency towards more negative potentials. Such tendency is inverted afterwards and once again it occurs independently of the fact that the reinforcements were reached by the carbonation front. The initial trend is probably due to the growing instability of the protective oxide film, for a simultaneous availability of both water and oxygen in more porous concretes. The successive evolution can be explained by the progressive disappearance of the water layer on the rebars surface, caused by the drying of the porous concretes in an humidity unsaturated environment (R.H. = 75%). Effectively, a net decrease of the potentials is observed when the relative humidity is varied from 75% to 90%, due, probably, to the formation of a new liquid layer on the rebars surface. Such effect increases with water/cement ratio, the capacity of more porous concretes to absorb water being greater.

From the above-mentioned data, it would seem, therefore, that the determining factor for the progressing of corrosion in reinforced concrete is not much the carbonation process, which is of course essential for the dissolution of the protective oxide film, as the formation of a liquid layer on the rebars and obviously the presence of oxygen.

Such conclusions have been confirmed from results, not reported here, concerning reinforcements with concrete covers greater than 2 cm.

3.3 Polarization resistance

The polarization resistance values for reinforcements with 2 cm concrete cover, shown in Fig. 5, increase with time in carbon dioxide enriched environment at 75% relative humidity. An increase in relative humidity from 75% to 90% (dotted curves) causes a sudden drop of the polarization resistance values. The carbonation front (point C on Fig. 5) does not seem to have a direct influence on such evolution. On the contrary, the polarization resistance values for higher concrete covers remain constantly low with time. Such behaviour is actually very difficult to interpret, since

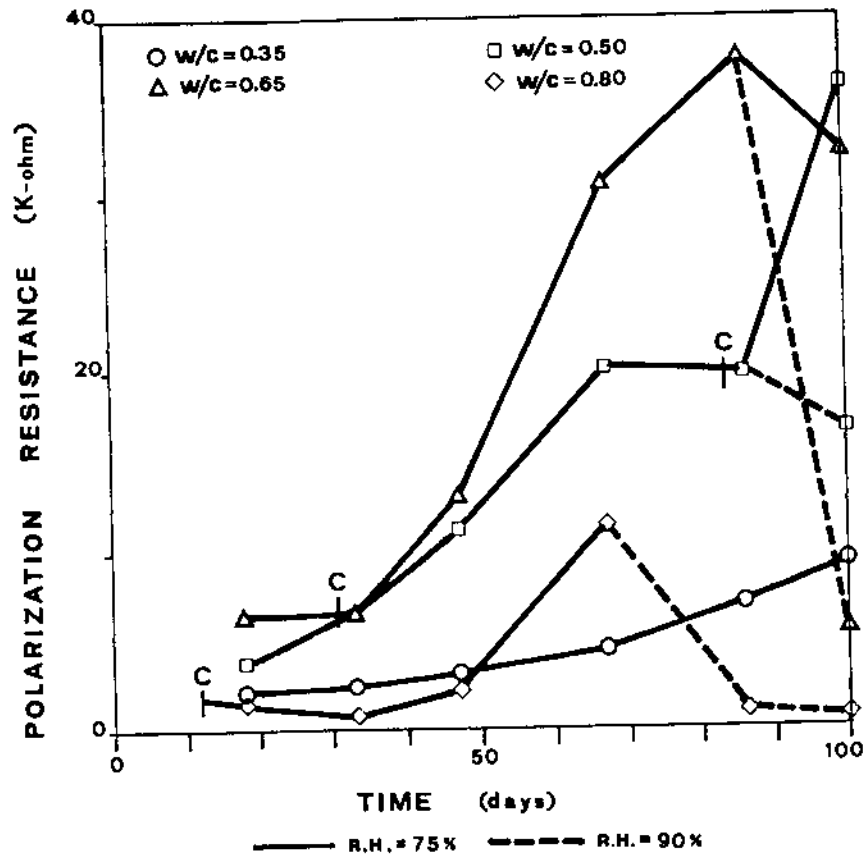


C = rebar reached by the carbonation front

Fig. 4. The influence of exposure time, water/cement ratio and relative humidity on the electrochemical potential of the rebars in Portland cement concretes with 2 cm concrete cover in carbon dioxide enriched atmosphere.

the low polarization resistance values, which should indicate corrosion active state, are not justified by the corresponding electrochemical potential values which, instead, indicate passive state of the rebars.

The evolution of the polarization resistance reported in Fig. 5 appears to be in agreement with the model proposed for the interpretation of the electrochemical potential



C = rebar reached by the carbonation front

Fig. 5. The influence of exposure time, water/cement ratio and relative humidity on the polarization resistance of the rebars in Portland cement concretes with 2 cm concrete cover in carbon dioxide enriched atmosphere.

trends, based on the possibility of formation of a liquid layer on the rebars surface.

Effectively, the polarization resistance increases with time, particularly for rebars embedded in concretes with high water/cement ratio, that is in concretes which are more porous and which dry easily. The anomaly shown by the polarization resistance values (whose trend is, however, consistent with the others) in concrete with 0.80

water/cement ratio is the object of further investigation. Such anomaly might probably be ascribed to the simultaneous complex influence of the various parameters which determine the equilibrium with the environmental relative humidity for the formation of a water liquid layer on the rebars surface. The changes in the potential and polarization resistance values of rebars placed at 2 cm from the concrete surface, with 0.65 water/cement ratio, and exposed to different relative humidities (75% and 90%) do suppose a different surface state of the rebars and have therefore suggested a direct observation of such presumed different surface conditions by splitting the concrete cover. Rebars exposed to 90% relative humidity have put into evidence corrosion traces, while those exposed to 75% relative humidity have shown surfaces covered with the protective oxide film. One can then deduce that low electrochemical potential values coupled with low polarization resistance values should indicate an effective corrosion state.

The visual observation of the corresponding rebars embedded in concrete with 0.35 water/cement ratio and 2 cm concrete cover, with low polarization resistance and high potential values, did not show any corrosion traces.

One can, therefore, conclude that low polarization resistance values indicate an effective corrosion activity if only they are coupled by low electrochemical potential values.

Briefly, the addition of fly ash (not reported in this paper) modifies the kinetics of carbonation but does not change at all the described results for concretes with Portland cement only.

4 Conclusions

The results of the present work show that the carbonation depth in concrete strongly depends on the water/cement ratio, increasing with it. Moreover, the addition of fly ash without diminution of the cement reduces the penetration depth of carbon dioxide.

In other words, the carbonation depth is anyway reduced by lowering the concrete porosity.

On the other hand, in the total absence of chlorides, electrochemical measurements proved the carbonation process to be a necessary condition but not a sufficient one to promote corrosion process in reinforced concrete, which seems, instead, to be strongly influenced by the concrete permeability to water and, obviously, to oxygen.

As a result, every admixture able to allow a reduction in concrete porosity and permeability can be considered a corrosion reducer admixture. By this point of view, superplasticizers are real steel corrosion reducers, when used as water reducers.

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