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THE INFLUENCE OF CARBONATION ON THE
CORROSION OF STEEL IN REINFORCED CONCRETE

Mario Collepardi, Romeo Pratesi, Giacomo Moriconi, Marco Pauri
Department of Sciences of Materials and Earth
Faculty of Engineering
University of Ancona, Italy

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Department of Materials and Earth Sciences
Faculty of Engineering
University of Ancona - Italy

ABSTRACT

The changes in electrochemical potential of reinforcing bars do not appear to be in a unique relation with the carbonation process. Furthermore, the data of the present paper indicate that carbonation is a necessary process but not a sufficient one for the steel corrosion, since the humidity into the concrete is also a determining factor in the corrosion process.

1. INTRODUCTION

For long, it was of common opinion that reinforced concrete constituted a material of practically illimited durability. Such view is also supported by the particular protective action of the concrete in consequence of the formation of an adherent and passive oxide film in the high basicity conditions created by the hydration of the cement.

Unfortunately, a poor design and an improperly design execution of structures in reinforced concrete have provided evidence of the limited service life of the structures. Failures of structures are often attributed to reinforcement corrosion processes in aggressive environments. In such specific case, the aggressive phenomena are 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.

It has become of common opinion, since then, that the carbonation process, though inevitable, might be one of the main causes of the phenomenon of deterioration of structures, if not, in some cases, the only responsible one, even when degradation appears rapidly since the beginning of the structures operative life. The aim of the present work is to evaluate the objective responsibility of the carbonation process in reinforcement corrosion phenomena and to verify, if differently, it does not constitute an alibi to the quality and curing deficiency of the concrete and to an insufficiency of the cover thickness.

2. EXPERIMENTAL PART

The carbonation process has with time an evolution measurable in years. To acquire experimental data in a reasonably short time, the corrosion process was carried out, besides in natural

conditions, in an accelerated carbonated atmosphere, that is in an artificially carbon dioxide enriched environment.

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

Finally, to avoid any contamination by factors, other than carbonation, particular attention was taken to prevent the contact of the reinforcement with chlorides. Were casted concretes with different water/cement ratio ($w/c = 0.35 - 0.50 - 0.65 - 0.80$). 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 of $10 \times 10 \times 10$ cm, without rebars, were casted for the determination of the electrical resistivity and of the penetration depth of the carbon dioxide. Moreover, prismatic reinforced specimens of $40 \times 15 \times 10$ 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 and of diameter 8 mm. They were 16 rebars symmetrically positioned with concrete covers varying from 2 to 5 cm. During the casting, 6 graphite bars as counterelectrodes were inserted at equal distances from the steel bars. The graphite counterelectrodes were connected to brass for electrical contact with the testing instrument.

The specimens were cured for seven days in saturated vapour atmosphere. Before their exposure either to the natural atmosphere (carbon dioxide equal to 0.03%) or 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% to accelerate the carbonation process [2].

The following parameters were measured after different time of exposure in carbon dioxide atmosphere:

1. the penetration depth of carbon dioxide by means of phenolphthalein test: an hydroalcoholic solution of 2% phenolphthalein was sprayed on the transversely splitted section of the samples;
2. the electrical resistivity by means of the slopes of the characteristics curves; the measurements were performed on cubic samples on whose parallel faces two aluminium plates were affixed; a high conductive gelatinous substance was used to improve electrical contact; potentials of known values were imposed between the parallel faces of the cube and the current densities were registered;
3. the corrosion electrochemical potential of the reinforcement with respect to mercurous sulphate (SSE) reference electrode by means of a differential electrometer with high input impedance, according to ASTM [3];
4. the polarization resistance of the rebars [4,5,6]], 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], demonstrating an increase in the permeability to carbon dioxide with the increase of water/cement ratio, that is with the porosity of the concrete.

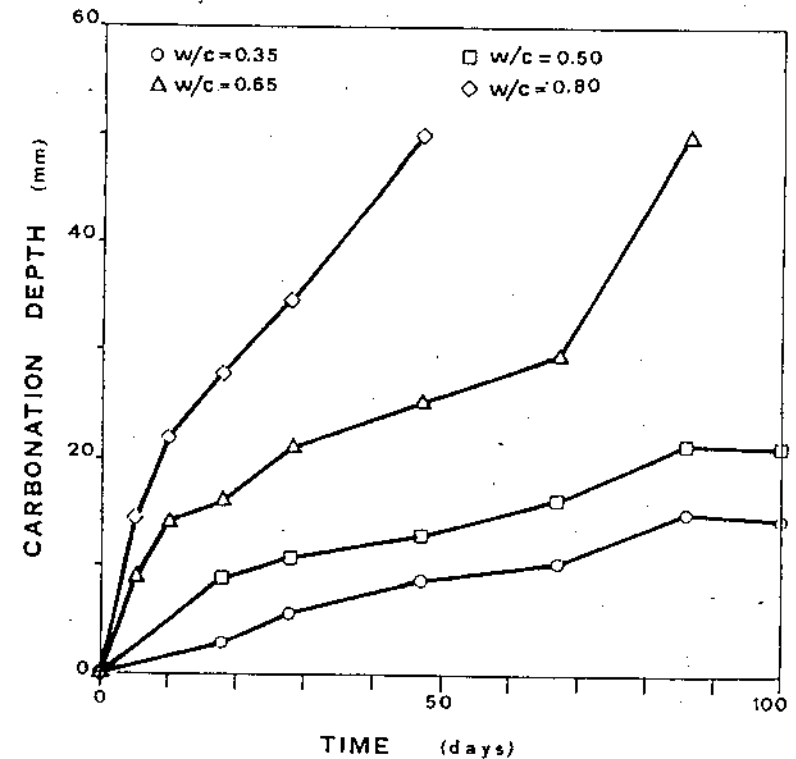


Fig. 1 - The influence of exposure time and water/cement ratio on the carbonation depth in Portland cement concretes in carbon dioxide enriched atmosphere (R.H. = 75%).

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].

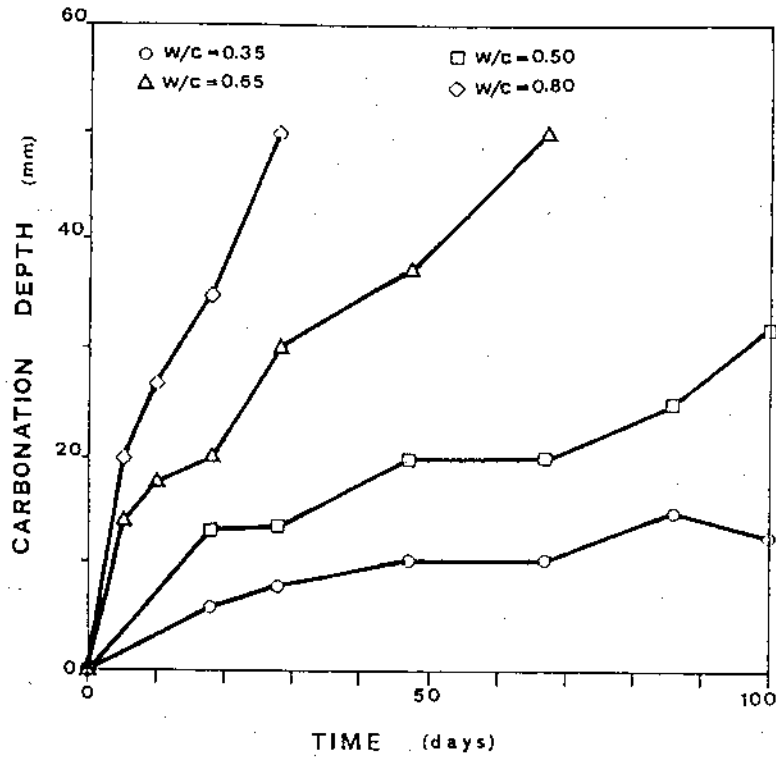


Fig. 2 - The influence of exposure time and water/cement ratio on the carbonation depth in pozzolanic cement concretes in carbon dioxide enriched atmosphere (R.H. = 75%).

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).

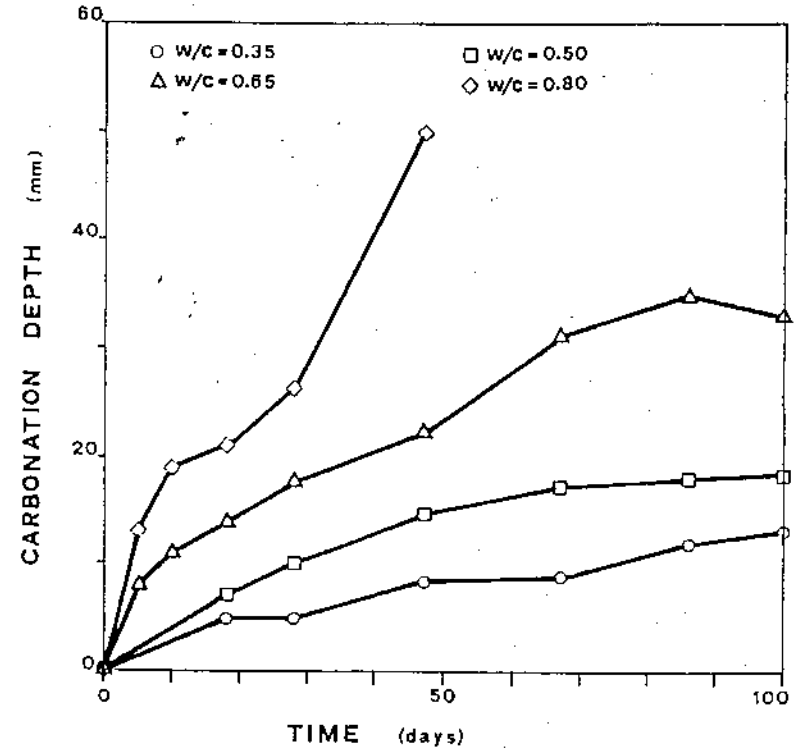


Fig. 3 - The influence of exposure time and water/cement ratio on the carbonation depth in Portland cement concretes with addition of fly ash in carbon dioxide enriched atmosphere (R.H. = 75%).

3.2 Electrical resistivity

As shown in Fig. 4, for a given water/cement ratio, the electrical resistivity of unsaturated Portland cement concrete constantly increases with time. The electrical resistivity also increases with the water/cement ratio [11]. The evolution of resistivity with time is much more evident in carbonated concretes (Fig. 4).

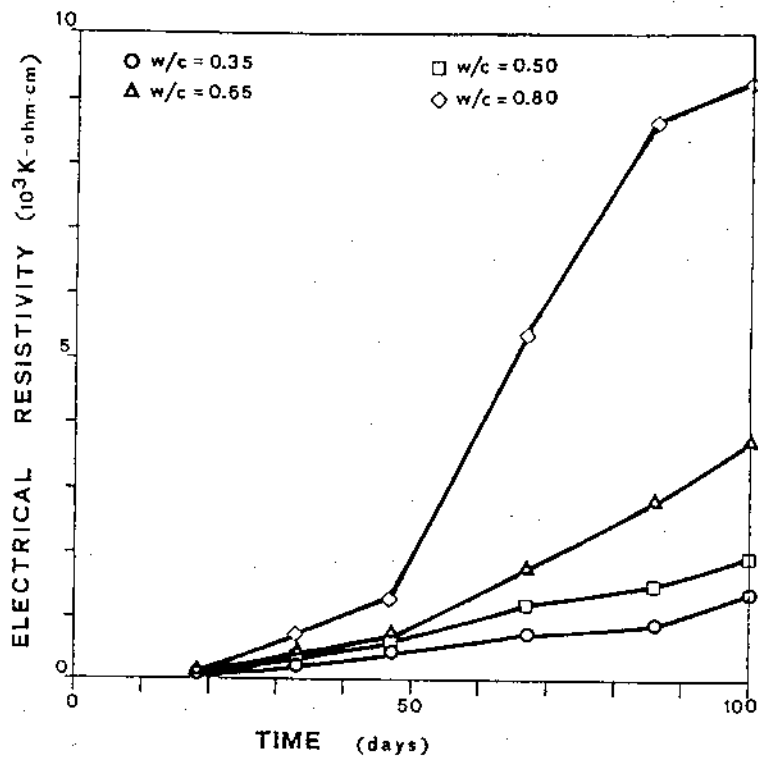


Fig. 4 - The influence of exposure time and water/cement ratio on the electrical resistivity of Portland cement concretes in carbon dioxide enriched atmosphere (R.H. = 75%).

Instead, as reported also in literature [12], a decrease of resistivity with the increase of water/cement ratio is observed in the case of saturated concretes which are in equilibrium with environment of 100% relative humidity, even if the values are in the same order of magnitude (Fig. 5).

Such inversed behaviour is probably due to the conditions of the concrete pore system. In an environment of 75% relative humidity, concretes with higher water/cement ratio have pores which are partially filled with air. Being a dielectric, the air increases the resistivity of the concrete with respect to the same material with water-saturated pores. Such phenomenon is independent of the carbonation depth of the concrete.

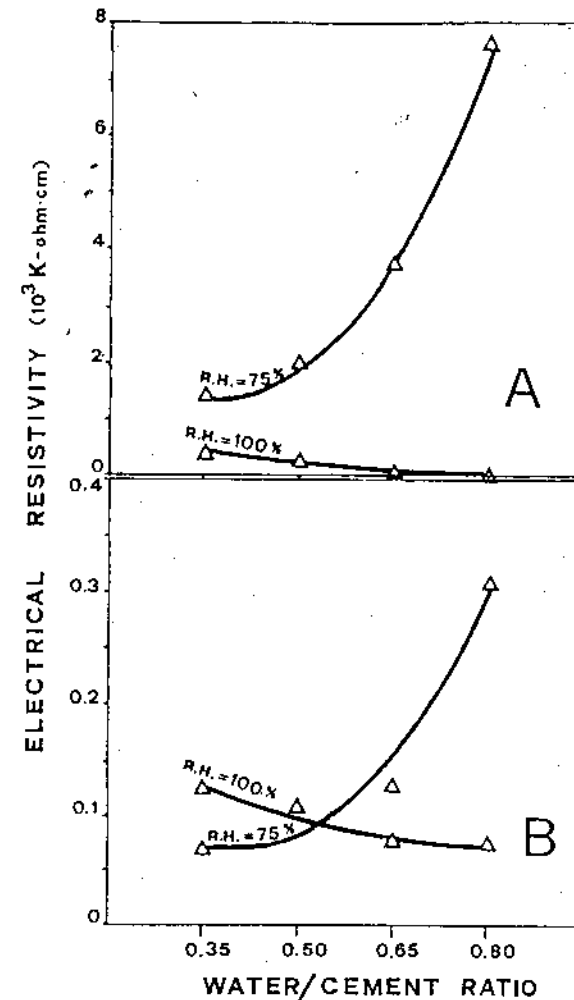


Fig. 5 - The influence of water/cement ratio and relative humidity on the electrical resistivity of carbonated (A) and non-carbonated (B) Portland cement concretes after 100 days curing time.

The addition of fly ash, however, does not significantly modify the above-described behaviours nor the resistivity values.

3.3 Electrochemical potential

The electrochemical potentials of the bars embedded in concrete were measured during their exposure in natural and artificially carbon dioxide enriched atmospheres.

3.3.1 Electrochemical potential in natural environment

The electrochemical potentials of the rebars (in any case not reached by the carbonation front) exposed to natural carbonation always maintain their values in the range between -370 mV and -580 mV SSE, values which are indicative of the reinforcement passive state and which do not seem, during the test, to be influenced by the concrete water/cement ratio.

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 [13,14,15,16] at pH 8.3, measured on the concrete aqueous extract. These results confirm that the non-carbonated concretes constitute a passive environment for the rebars. The changes in potential registered are essentially dependent on the thermo-hygrometric changes of the atmospheric conditions.

3.3.2 Electrochemical potential in carbon dioxide enriched environment

The potential of reinforcements subjected to accelerated carbonation shows significant changes with exposure time, as indicated in Fig. 6. However, since the evolution of the potentials was not modified by the carbonation front (point C on curves in Fig. 6), 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. 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.

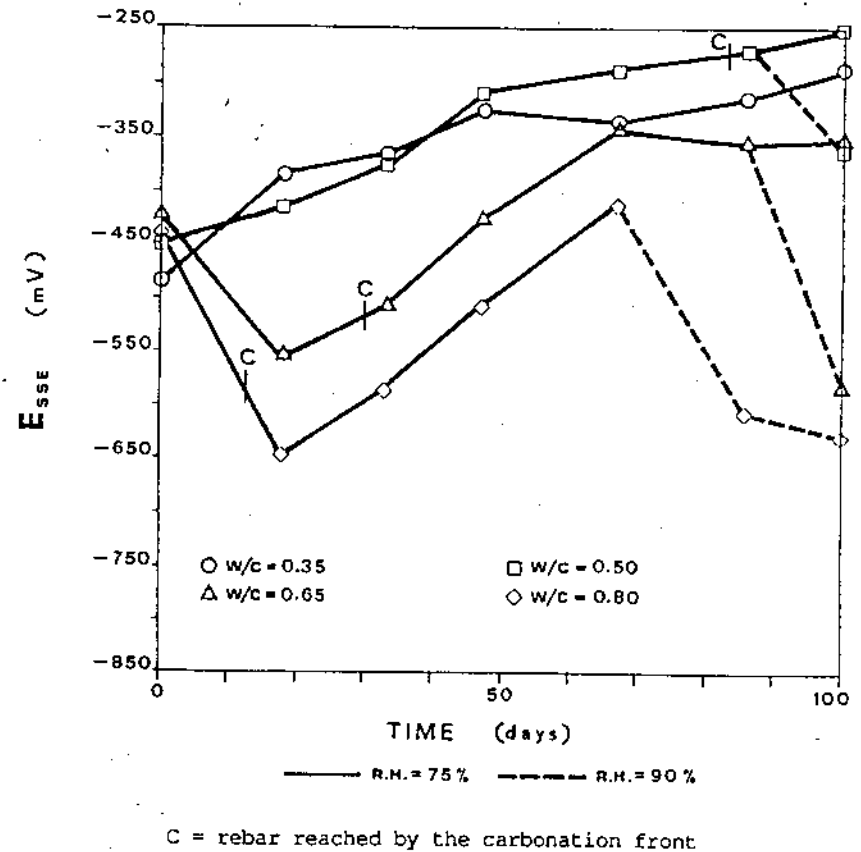
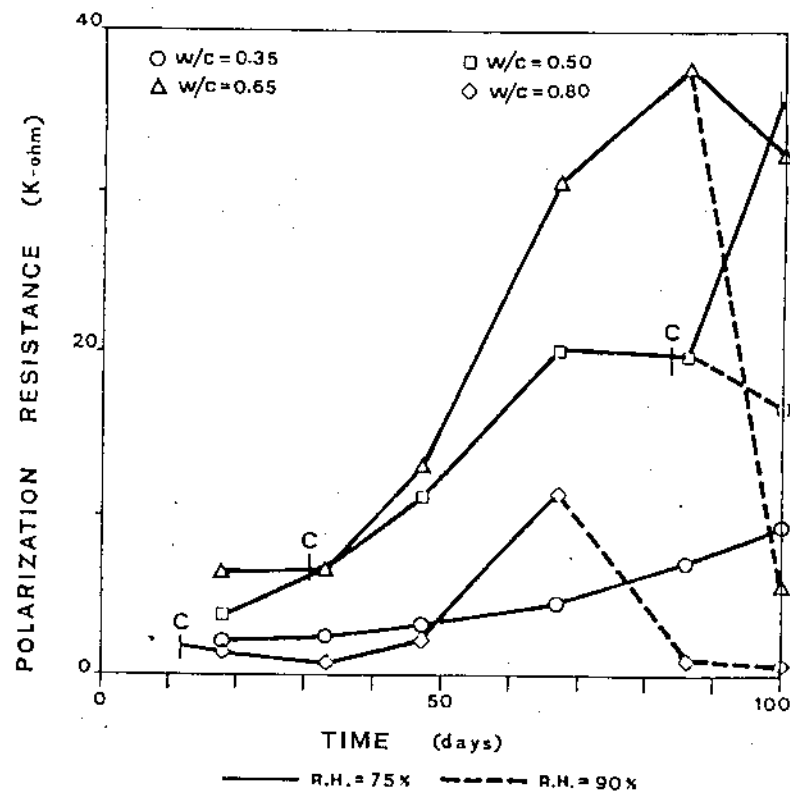


Fig. 6 - The influence of exposure time, water/cement ratio and relative humidity on the electrochemical potential of the rebars in Portland cement concretes with 2 cm concrete cover in carbon dioxide enriched atmosphere.

3.4 Polarization resistance

The polarization resistance values for reinforcements with 2 cm concrete cover, shown in Fig. 7, 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. 7) 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 the low polarization resistance values, which should indicate



C = rebar reached by the carbonation front

Fig. 7 - 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.

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. 7 appears to be in agreement with the model proposed for the interpretation of the electrochemical potential 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:

- 1 - The carbonation depth in concrete strongly depends on the water/cement ratio and increases with the latter.
- 2 - The addition of fly ash without diminution of the cement reduces the penetration depth of carbon dioxide, while the addition of fly ash as a substitution of part of the cement (pozzolanic cement) increases the carbonation depth.
- 3 - The electrical resistivity is higher in carbonated concretes, independently of the presence of fly ash.
- 4 - The electrical resistivity of concrete depends on its water/cement ratio; it increases with the water/cement ratio in unsaturated concretes, while it decreases with the

water/cement ratio in water-saturated concretes, regardless of the presence of fly ash, in any case.

- 5 - The validity of potential readings coupled with polarization resistance measurements to indicate active corrosion state is shown from the direct observation of the rebars: effectively, more negative potential values and low polarization resistance values are indicative of corrosion.
- 6 - Electrochemical potential or polarization resistance measurements, separately performed, cannot be considered reliable for such complex system as reinforced concrete.
- 7 - In the total absence of chlorides, the carbonation process appears a necessary condition but not a sufficient one to initiate corrosion process in reinforced concrete, which seems, instead, to be strongly influenced by the environmental relative humidity and obviously by the availability of oxygen.
- 8 - The presence of fly ash, either in addition or in substitution of the cement, does not modify the corrosion behaviour of the reinforcements with respect to rebars in concretes consisting of Portland cement.

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