THE ASSESSMENT OF THE ELECTROCHEMICAL BEHAVIOUR OF FLYASH-CONTAINING CONCRETE BY IMPEDANCE SPECTROSCOPY

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The use of flyash in concrete, in partial substitution of Portland cement, has become common practice in recent years. Like cement, flyash also reacts with calcium hydroxide, in the presence of water producing compounds which decrease the porosity of concrete and the ingress of aggressive species into the concrete. However, very few studies have been concerned with the effect of flyash addition on the resistance of the reinforcement towards corrosion. In this paper, the corrosion behaviour of steel reinforcement in concrete with different flyash contents ( 0%, 15%, 30%, 50% w/w ) in partial substitution of Portland cement, was followed by electrochemical impedance spectroscopy (EIS).

The concrete blocks, with a w/c ratio = 0.6, were cured during one week in a saturated humidity chamber before starting the experiments. In each concrete block two steel bars ($\phi = 1$ cm ) were embedded, the distance between them being 6 cm. The dimensions of the blocks were 10x10 cm, and 16 cm height.

Impedance measurements were made between the two steel bars of each concrete block using a *1255 Solartron FRA* and a *1286 Electrochemical Interface*. A set of experiments was made for samples immersed in a 3% NaCl solution and another set was made for samples immersed in 3% NaCl during one year / dried in air 4 months / reimmersed in distilled water.

Fig. 1 shows the Bode plots for a block without flyash for different immersion times in 3% NaCl. In the $|Z|$ plot, the low frequency region is a straight line with slope -1. The double layer capacitance calculated at $\log \omega = 0$ is about 10 $\mu F/cm^2$ which is typical of a pure capacitor, revealing a passive state. The constant impedance at the high frequencies can be interpreted as the ohmic resistance, i.e., the resistence of the concrete, which increases with the time of immersion. This increase was observed for all blocks having different flyash amount and is due to the evolution of the hydration processes of cement and flyash (pozzolanic reactions) which fill the pores of concrete decreasing its porosity and increasing its resistivity. The phase angle has a maximum which becomes shifted to lower frequencies and lower angles, as a consequence of the increasing resistance.

In the case of the 50% block the evolution both concerning the maximum in the phase angle and the ohmic resistance is in the same direction, but the ohmic resistance increases by two orders of magnitude.

Fig.2 shows the impedance spectra for blocks having different flyash content after 10 days of immersion. A state of passivity is observed, with identical values of ohmic resistance and double layer capacitance ( 10 $\mu F/cm^2$ at log $\omega = 0$), except for the 50% block. This unexpected result is a consequence of a delay in the initiation of the hydration processes due to the high flyash content. During the initial stages concrete works as a compact mixing where chloride penetration is promoted causing steel depassivation and initiation of corrosion. One way to overcome this problem is by an increase in the curing time. After some weeks, the slope of the |Z| plot has decreased from -1 to -2/3 approximately, whereas the ohmic resistance has become larger for all the blocks, and especially for those with a higher flyash content. The evolution of the resistance for all blocks is more intense during the first weeks of immersion, assimptotically growing to a steady value. The resistivity of the concrete can be obtained by dividing the ohmic resistance by the concrete thickness. After 6 months of immersion, the concrete resistivity is stable and increases exponentially with the flyash content (fig.3).

For blocks immersed in 3% NaCl / dried / reimmersed three different situations can be identified in the absolute impedance plots (fig.4): passivity on the first days of immersion, with a slope of -1; weak localized corrosion in the form of one or two pits after long immersion times (more than 8 months ), with slopes of about -2/3; and severe corrosion attack, under conditions of natural aeration, with a slope of -1 / 2. This last value reveals a Warburg in the equivalent circuit, which means that the corrosion process occurs under diffusion control. In the phase angle plot the Warburg appears as a maximum at very low frequencies ( < 5 mHz ).

The impedance experiments have proved to be a practical method both for comparing the influence of additives on concrete behaviour and for the study of the corrosion process on steel surface. The slope of the | Z | plot changes with the evolution of corrosion, and its value helps to a better understanding of the potential values which are usually the more common way to decide about the steel surface state.

One interesting result from this work was the establishment of a mathematical law (exponential type) which relates the resistivity of concrete with the flyash amount.



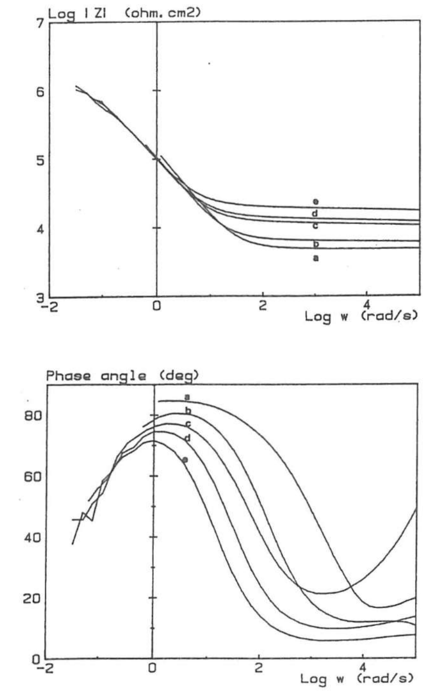


Fig.1 - Bode plots for a concrete block without flyash, in 3% NaCl
a - 1day; b - 12 days;c - 45 days; d - 67 days; e - 117 days.

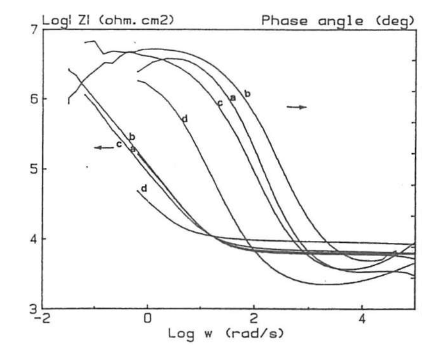


Fig.2 - Bode plots for concrete blocks, having different flyash content after 10 days of immersion in 3% NaCl a - 0%; b - 15%; c - 30% ; d - 50%.

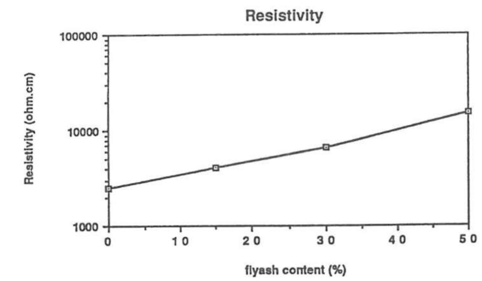


Fig.3 - Concrete resistivity after 6 months in 3% NaCl as a function of flyash content.

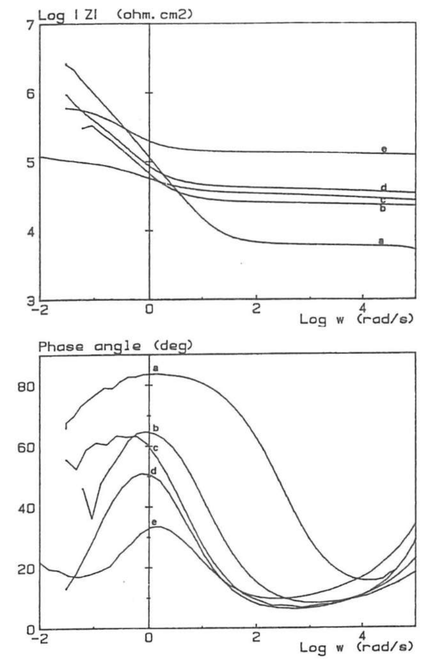


Fig.4 - Bode plots for a block with 15% of flyash in 3% NaCl/air/distilled water.
a-10days(3%NaCl); b-130 days(3%NaCl); c-426 days( distilled water); d-241 days(3% NaCl); e - 390 days (air)