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Impedance spectroscopy analysis of the influence of superplasticizers on steel corrosion in OPC mortars

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The influence of commercial superplasticizers on the mechanism of corrosion of steel reinforcements embedded in concrete has been investigated by the impedance spectroscopy technique using Portland cement mortars with and without added chloride. Significant differences in spectra in the range 0.03–65 kHz are shown to occur as a function of composition and moist cure duration up to 240 days. The impedance spectra in the early stages indicate surface layer formation, attributed to superplasticizer adsorption to the surface of reinforcing rods. The adsorbed surface layer persists only within the initial 90 day cure. At longer ages, the superplasticizer layer breaks down. However, calcium lignosulphonate gives markedly lowered corrosion rates in the presence of chloride; the other plasticizers corrode at essentially the same rate as the control without plasticizer.

1. Introduction

A variety of organic admixtures are employed in concrete practice, typically as air-entrainment agents, set-time regulators and plasticizers [1]. In general, the primary function of admixtures has a secondary affect on the kinetics of specific chemical reactions occurring during the course of cement hydration [2]. However, in relatively few cases, admixtures (including superplasticizers) are known to operate by direct adsorption on to the surface of hydrating cement grains [3].

Under normal conditions in well-made concretes, the high pH and low permeability of cement paste results in development of a passivating layer on embedded steel and this protects the steel against corrosion [4]. However, no detailed mechanistic study of the effect of organic plasticizers on steel reinforcement protection and corrosion appears to have been carried out. It is possible that plasticizers could influence the chemical and electrochemical processes associated with the steel: concrete interface.

The normal passivating layer has been suggested to be within the γFe_2O_3–Fe_3O_4 solid-solution range [5]. The effectiveness of the passivating layer depends largely on maintaining conditions for its thermodynamic stability which favoured its formation in the first instance. Uptake of atmospheric CO_2, of CO_3^{2-} and Cl^- ions from marine and underground waters, and loss of concrete alkalinity through leaching of alkali and alkali-earth ions remain the principal sources of irreversible change in paste chemistry which lead to destabilization of the passive layer on embedded steel.

Corrosion inhibition admixtures are widely marketed: presumably one mode of action is to enhance the stability of the oxide layer. However, the impact on corrosion of cement additives used to control other aspects of concrete behaviour, e.g. superplasticizers, which control mix rheology, is not known. The conventional view is that they remain inert during the electrochemical processes that control passive layer formation.

The non-destructive techniques available to monitor changes in passivating layer characteristics are, however, limited. Impedance spectroscopy has emerged as an effective method to distinguish fundamental processes occurring during corrosion [6–8]. Corrosion kinetics and the effect of cure conditions on corrosion rates in reinforced concrete systems have been successfully monitored by this technique, as has the influence of organic compounds on the corrosion behaviour of carbon steel in chloride solutions [9].

The effect of commercial superplasticizers on the corrosion process of embedded steel rods in chlorine-bearing mortars are evaluated using both impedance spectroscopy and the linear polarization method.

2. Experimental procedure

Ordinary Portland cement (OPC), made to BS 12, and fine sand were used for a mortar mix, at a fixed ratio of 0.5:1:3 for water:cement:sand, respectively; the superplasticizers were added to the mix water in concentrations based on the manufacturer's (Cormix) recommended dosage as follows: 1.5%, 0.75% and 0.40% expressed as vol % by weight of cement, for sulphonated melamine formaldehyde (SMF, Cormix SP5), sulphonated naphthalene formaldehyde (SNF, Cormix SP1), and calcium lignosulphonate (CaLS, Cormix P4), respectively. The chloride-doped mixes

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contained a fixed chloride concentration of 862 mmol l^{-1}, equivalent to 2.5% NaCl by weight of cement.

Electrical wire leads were soldered on to one end of 6 mm diameter mild steel rods (composition shown in Table I); the rods were mechanically polished using fine emery paper, degreased in acetone and epoxy masked at both ends leaving an exposed area of 1.32×10^{-3} m^2 and mounted in the configuration shown in Fig. 1, to give three rods cast in each specimen. A minimum of two casts per mix formulation were made: these were cured at 20 °C/100% RH for 3 days prior to subsequent ageing in humidity cabinets at 40 °C/100% RH. These mildly accelerated conditions were chosen to enhance reinforcement corrosion. However, all measurements were made at room temperature.

The impedance measurements were carried out in the frequency range of 0.03–65 kHz using a Solartron 1250/1286 frequency response analyser (FRA) interfaced to a BBC computer for data logging. The linear polarization measurement was carried out on a Thompson Ministat with electronic *IR* (ohmic potential drop) compensation, using a saturated calomel reference electrode and a graphite rod auxiliary electrode. An applied potential of 20 mV was used in all measurements.

3. Results and discussion

Fig. 2 shows the impedance plots for OPC mix formulations, cured at 40 °C for 28, 90 and 240 days. The observed arc in Fig. 2 is characteristic of electrode polarization and indicates a barrier to charge transfer; it is associated with the formation of a passivating spinel-structured iron oxide film on the rod surface. The results further indicate that reinforcement passivation is maintained even under conditions of moderately high temperatures, i.e. 40 °C, in the absence of Cl^- ions or carbonation penetrating to the steel–cement paste interface.

TABLE I Minor element chemical composition (wt %) of mild steel electrodes

C	Si	S	Mn	P	Cu	Cr	Ni	Sn
0.12	0.02	0.04	0.41	0.018	0.14	0.12	0.06	0.01

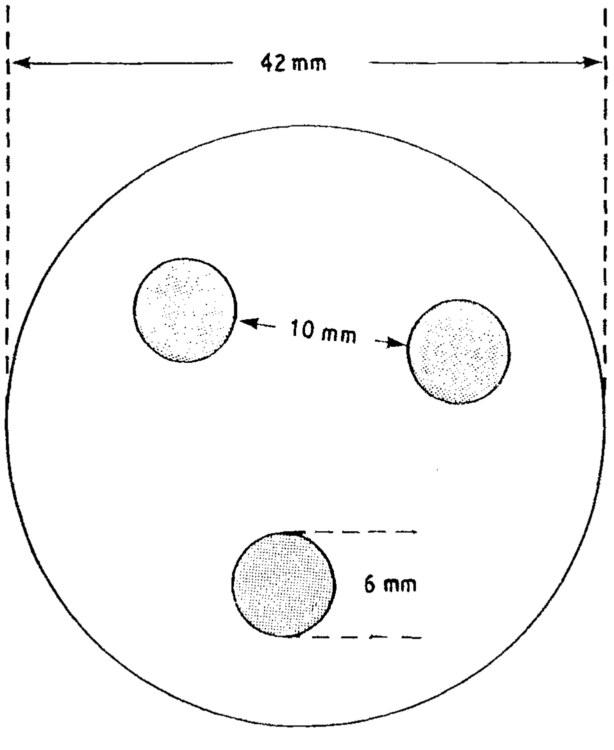

Figure 1 Schematic cross-section view of cast OPC mortar specimen showing embedded steel configuration.

The influence of Cl^- ions on electrochemical processes at the steel:mortar boundary are inferred from the impedance plots shown in Fig. 3 for the chloride bearing specimens cured at 40 °C for up to 240 days. Although only partially complete and somewhat depressed semi-circles are obtained, their impedance characteristics can be determined by fitting semi-circles to the arcs as shown by the broken lines in Fig. 3.

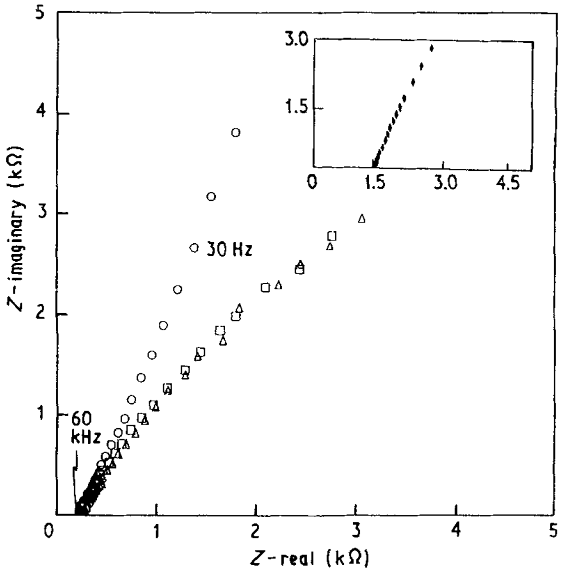

Figure 2 Impedance plots for reinforcing steel embedded in OPC paste for (inset) 28, (○) 90, (□) 180 and (△) 240 days.

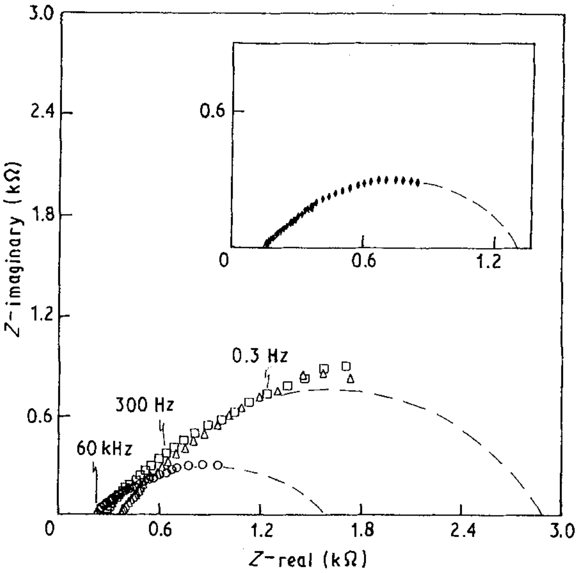

Figure 3 Impedance plots for reinforcing steel embedded in OPC paste with 2.5% NaCl for (inset) 28, (○) 90, (□) 180 and (△) 240 days.

Non-uniformity of the rod surface, probably resulting from pitting, may be responsible for the depressed impedance arcs. The mean capacitance, C, of the plots in Fig. 3 determined from the frequency, F, and charge transfer resistance, R_{ct}, values using the relation $C = (2\pi F R_{ct})^{-1}$, falls within the range 350–800 mF m^{-2} which is typical of a double-layer capacitance. The charge transfer resistance, R_{ct}, is of the order of 2.0 Ωm^2, and shows very little variation over the 240 day cure cycle. This illustrates probable attainment of steady-state conditions in the corrosion process. When the plots of Fig. 3 are compared to those of Fig. 2, obtained from chloride-free specimens, it is clear that a significant change in the fundamental kinetic processes has occurred at the steel:mortar interface boundary. This change is attributed to the presence of Cl^- ions; a transition from the passivated state characteristic of the control plots in Fig. 2 to charge transfer kinetics is evident. The exact mechanism by which Cl^- ions accelerate corrosion under conditions of high alkalinity, as occur in cement paste, remain unclear, although several theories have been proposed to explain the action of Cl^- in acidic and neutral media [10].

In the presence of Cl^- ions, superplasticizers in mix formulations significantly alter both high- and low-frequency impedance response. To facilitate comparison, representative impedance plots obtained from the three superplasticizers, namely SMF, SNF and CaLS, are shown in Figs 4–6, respectively; the results will be discussed collectively. In each figure, the 28 day exposure plots are presented separately, as an inset, to encompass differences in scale.

3.1. Bulk conductivity

Bulk conductivity behaviour of the paste matrix has been determined from the high-frequency regime in the impedance plots. The mean matrix resistance for SMF superplasticizer, shown in Fig. 4, is of the order of 1.25 ± 0.08 Ωm^2 at 28 days, decreasing to 0.25 ± 0.05 Ωm^2 after a 90 day cure, with no discernible change thereafter up to 240 days. The five-fold higher resistivity observed at 28 days, in comparison to the longer curing times, is consistent with expectations; the higher resistivity is attributed to the residual concentrations of the poorly conducting high molecular weight superplasticizer in the cement pore fluid. In non-superplasticized and chloride free pastes, resistivity increases as water is withdrawn into hydrates. These hydrates block pores and thereby reduce the connectivity of the remaining water; hence the interconnected porosity and electrolyte migration is retarded. The presence of chloride alters this situation; ions present in solution act as the main conducting species but chloride and OH^- ions differ in mobility. Their mobilities, and hence contributions to the conductivity, are apparently impeded by the polymeric chains of the superplasticizers during the early stages of cement hydration. This is not surprising given that the size of the polymer units is comparable to the mean conduction path length. Higher conductivity values are obtained at later stages, because partial removal of superplasticizer occurs: it is precipitated irreversibly and becomes adsorbed into the paste matrix during the course of cement hydration [11]. Chloride may also affect the microstructure, giving rise to a more open hydrate morphology.

Beyond 90 day cure duration, the high-frequency plots of Fig. 4 remain unchanged indicating that steady-state conditions prevail; this steady state is attained at 40 °C between 28 and 90 days. This time scale, inferred from the time-dependent changes observed in impedance measurements, accords with the results of periodic chemical analysis of superplasticizer concentration in pore fluids extracted from OPC pastes showing that most of the reaction between cement and superplasticizer occurs within the first 28 days [12]. The observed decrease in matrix resistivity after 28 days, shown in Fig. 4 for SMF, is also observed in comparable plots for SNF and CaLS, shown in Figs 5

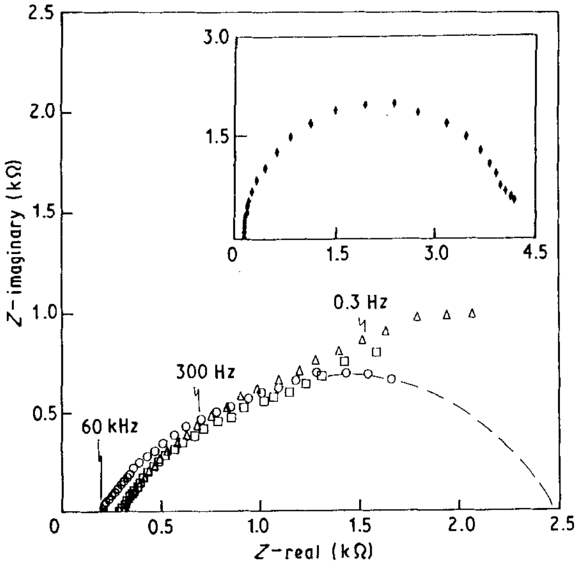

Figure 4 Impedance plots for reinforcing steel embedded in OPC paste containing SMF superplasticizer for (inset) 28, (○) 90, (□) 180 and (△) 240 days.

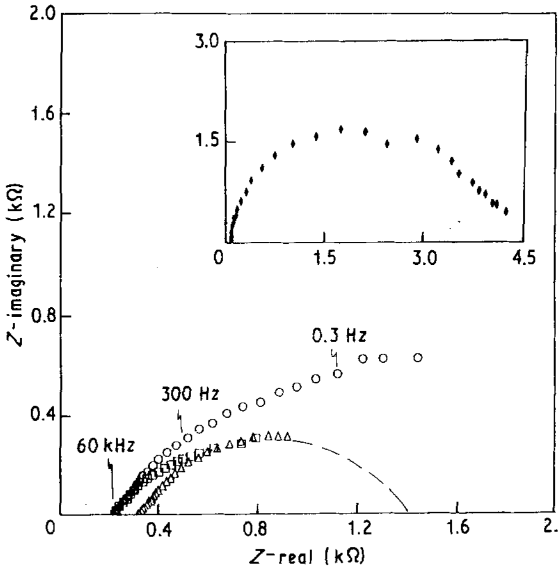

Figure 5 Impedance plots for reinforcing steel embedded in concrete containing SNF superplasticizer for (inset) 28, (○) 90, (□) 180 and (△) 240 days.

and 6, respectively. Most significantly, the lowered matrix resistance, ~ 0.25 ± 0.05 Ωm^2, is characteristic of all chloride-bearing matrices after prolonged cure and occurs irrespective of the presence or absence of superplasticizers.

3.2. Interface reaction

The surface coverage of reinforcing steel is governed mainly by competition between cement hydration products and superplasticizer: it is known from microscopy [5] of ordinary pastes, i.e. pastes formulated without superplasticizers, that surface coverage of steel by cement hydration product is rather incomplete. This interpretation is supported by the impedance plots. The 28 day impedance semi-circles, Figs 4–6, have associated capacitance values of the order of 7.0 ± 1.5 $\mu F m^2$, a significantly lower value with respect to the normal value associated with double-layer capacitance (100–800 $mF m^2$). Thus this loop is attributed to a surface phenomena, such as an adsorbed superplasticizer layer on the steel surface. A physical adsorption is envisaged, with poor surface coverage of the steel, as evinced by the extremely low capacitive values. Moreover, the presence of a loop due to an adsorbed layer is short lived; it disappears after about 90 days cure which strongly suggests a temporary interaction between the superplasticizer species and its substrate. It is not entirely clear why the superplasticizer:substrate steel interaction should be temporary. However, conversion of initially soluble superplasticizer to an insoluble form is associated with changes in molecular structure. Presumably these changes, which result in its insolubility, also affect the stability and strength of the adsorbed layer. Chloride penetration through the adsorbed superplasticizer layer, with subsequent pitting action, may also lead to its physical disruption but this mechanism is speculative. For whatever reason, the potential inhibitive action of the superplasticizers due to sorption appears to be short lived.

The absence of the surface film loop in the impedance plots for superplasticized samples cured beyond 90 days is particularly noteworthy. Thus the 90 day impedance plots indicate that a time-dependent transition point in the nature of reaction processes occurring at the interface boundary has been reached. This transition occurs over approximately the same period as changes in mortar resistivity, referred to earlier, and is attributed to the attainment of steady state conditions within the system. The 90 day impedance response, shown in Figs 4–6, is characteristic of charge transfer-controlled kinetics, with capacitance values ranging between 200 and 600 $mF m^2$ in contrast to the much lower capacitance shown in the 28 day plots. These capacitance values have been calculated by fitting semicircles to the respective arcs (shown by broken lines in the figures). The capacitance values thus obtained are comparable to corresponding values calculated for the chloride-bearing but superplasticizer-free specimens shown in Fig. 3, which gave capacitance values between 400 and 600 $mF m^2$ after curing for 28 days or more. These values are also consistent with the results of several published studies, notably John *et al.*'s [7] measurements which involved impedance measurements on several samples exposed under a variety of cure conditions.

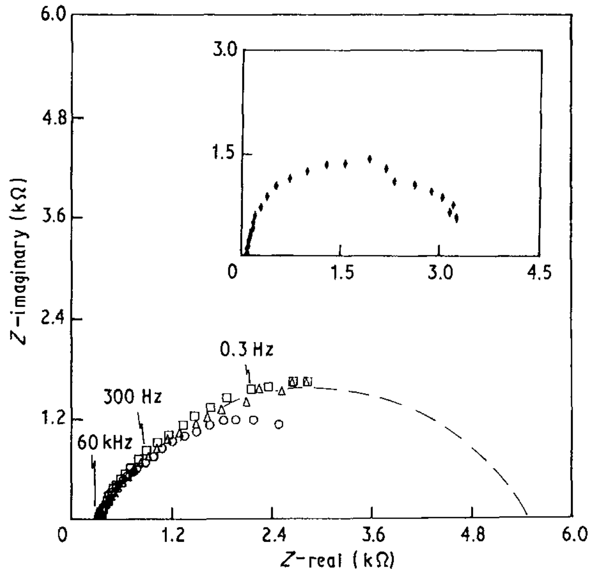

Figure 6 Impedance plots for reinforcing steel embedded in concrete containing CaLS superplasticizer for (inset) 28, (○) 90, (□) 180 and (△) 240 days.

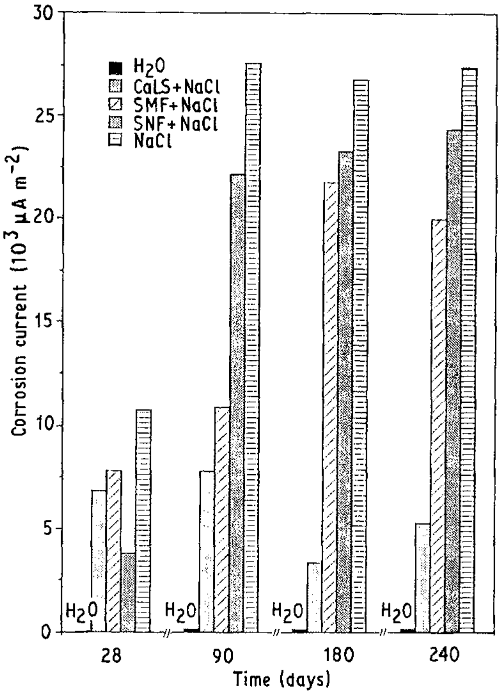

Figure 7 Mean corrosion current versus exposure time plots for superplasticized and control mix formulations.

The extent to which superplasticizers alter steel reinforcement reaction kinetics can be readily seen in the corrosion current versus time plots of Fig. 7. Slightly lower corrosion rates are observed for SMF and SNF in comparison with the chloride-only sample, which suggests a moderate inhibition effect. More significant, however, are the much lower corrosion rates recorded for CaLS, which are five times less than the corresponding rate for the control sample. Previous reports, e.g. Goma *et al.* [13], indicate that superplasticizers are broadly neutral with respect to corrosion rates. In the title study we find that SMF and SNF do not much affect corrosion rates, but that CaLS has a definite inhibiting action, measured over 240 days.

In attempting to explain the origins of superplasticizer inhibition or neutrality to Cl^--induced reinforced concrete corrosion, the present impedance analysis clearly discounts the possibility of stabilizing the passivating film by adsorbed superplasticizer molecules in the long term; an adsorbed surface layer is obtained, but has only a transient existence: by ~ 90 day cure period, it has disappeared. The impedance plots further suggest that partial inhibition by the superplasticizers occurs without a detectable change of the electrochemical controlling process at the steel:mortar interface boundary because all chloride-bearing samples, both superplasticized and non-superplasticized, appear to be governed by a charge transfer process. Thus a chemical reaction between superplasticizers and Cl^- ions appears to be the most likely cause of inhibition. This process may involve chlorination of the superplasticizer. Thus chlorine is converted from soluble, ionic form to covalently bonded, insoluble form as the superplasticizer undergoes denaturation with precipitation/adsorption into the paste matrix. This explanation is supported by pore fluid expression measurements showing that 70% reduction in soluble, ionic chlorine concentration is observed after 180 days, from an initial value of $862\,\mathrm{mmol\,l^{-1}}$ to $260\,\mathrm{mmol\,l^{-1}}$ [12]. Because the chemical constitution of the various superplasticizers differs, it is not surprising that their ability to react with Cl^- at high pH should also differ, with CaLS being the most effective.

It might, therefore, be anticipated that at lower chloride contents, less than the amount required to saturate a superplasticizer used at its recommended dosage, even more substantial chloride removal would occur. The partition functions for chloride between pore fluid and solids (including superplasticizer) are not at present known and require further study, but may lie within concentrations encountered in normal concrete practice and exposure.

4. Conclusions

Impedance spectra indicate that the following events occur in superplasticized cements.

1. An adsorbed superplasticizer layer forms on the surface of reinforcing steel rods embedded in mortar.
2. This layer is broken down or dissipated by a 90 day cure. Thereafter, the surface film impedance spectra is no longer observed as the kinetics at the steel:mortar interface are dominated by charge transfer.
3. Commercial superplasticizers either remain neutral (SMF, SNF) or moderately inhibit (CaLS) chloride-ion induced corrosion of steel reinforcements in mortar containing 2.5 wt % NaCl.
4. The mechanism of Cl-initiated corrosion remains unaffected by superplasticizer additions. It is inferred from the impedance spectra of the superplasticized and control samples that the mode of superplasticizer inhibition involves chemical interaction between superplasticizer and chloride ions, rather than direct stabilization of the passivating iron oxide film through an adsorption reaction.

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