

Fig. 8--Comparison between compressive strengths of the reference and silica fume concretes at 7 days



Fig. 9--Comparison between compressive strengths of the reference and silica fume concretes at 28 days

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Fig. 10--Compressive strength development of concrete with a W/(C+F) of 0.60 $\,$

Electrochemical Behaviour of Steel in Dense Silica-Cement Mortar

By Carolyn M. Preece, Hans Arup, and Thomas Frølund

Synopsis: A study has been made of the ability of a highly dense silica-cement mortar to protect steel reinforcement from corrosion. Corrosion of the steel is an electrochemical process in which the cement pore water acts as the electrolyte. The cement must, therefore, allow (i) passage of electrical current, (ii) diffusion of oxygen and other species from the environment to the steel and (iii) transport of the corrosion products away from the steel. The properties of the cement which are of interest are, thus, its electrical resistivity, its porosity and the chemistry of the pore water, particularly the pH. However, it is the combination of these properties which determines the corrosion rate and, as yet, not enough information is available to allow a direct prediction of the corrosion rate. Consequently, electrochemical polarization measurements have been made in order to determine the actual corrosion behaviour.

In the electrochemical experiments, a steel rod embedded in the mortar is held at a constant potential with respect to a reference electrode and the current flowing between the embedded rod and an external steel electrode is measured. By repeating the process for different values of the potential, it is possible to extrapolate the data to the corrosion potential, thereby giving a direct estimate of the free corrosion rate. These experiments have been carried out in different environments (anaerobic solutions, NaCl solutions, H_2CO_3 solutions, etc.) and the results are discussed in terms of the properties of the silica-cement mortar. Despite the Pozzolanic reaction in the cement, it appears to provide excellent protection to steel reinforcement.

<u>Keywords:</u> <u>cement pastes;</u> corrosion; <u>electrical properties;</u> <u>electrical resistance; mortars (material);</u> porosity; <u>reinforcing</u> <u>steels; silica</u>.

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INTRODUCTION

Good quality concrete provides a highly protective environment for embedded steel, both physically and chemically. The physical presence of the concrete provides some protection by limiting the rate of diffusion and permeation to the steel of species necessary for corrosion, for example 0_2 and water, and the diffusion away from the steel surface of the corrosion products. From the chemical viewpoint, cement contains an aqueous solution of sodium, potassium and calcium hydroxides with a pH typically of the order of 13.5. Moreover, there is a large reserve of undissolved calcium hydroxide which, in the event of any reaction involving the alkalis, buffers the solution to a pH of 12.6. At these high pH values, steel forms a passive film which reduces its corrosion rate to negligible levels. Thus, steel in good quality concrete has a corrosion rate corresponding to $\sim 0.1 \, \mu\text{m/yr}$. which is negligible in terms of the planned lifetime of most concrete structures.

Unfortunately, however, not all concrete is "good" and there are several external factors which destroy the passivity of the steel or the protective quality of the cement. The most common of these are chloride ions, either from chloride-containing ingredients in the original cement mix or penetrating from sea water or from deicing salts in the environment. The effect of the chloride ions is to break down the passivity of the steel even at high pH values, thereby allowing the steel to corrode at rates several orders of magnitude higher than the passive corrosion rate.

Another common cause of corrosion is carbonation of the concrete, in which atmospheric carbon dioxide reacts with the calcium hydroxide and alkali hydroxides in the cement to form carbonates and, in so doing, reduces the pll of the pore solution to below the level necessary for passivation. The rate of carbonation is, however, limited and is, therefore, only a major problem for reinforcements with shallow concrete covers. The corrosion has two effects. Firstly, it reduces the reinforcing capability of the steel. Secondly, the corrosion products cause stresses in the concrete which can result in cracking and spalling of the cover.

The present project has been concerned with the behaviour of reinforcing steel in a mortar or concrete made with a highly dense silica-cement paste, DSP*. This paste is a blend of Portland cement and "microsilica", a condensed silica fume with an average diameter of $^{\circ}$ 0.1 μ m. The high strength of this paste ¹, its good adhesive properties ¹, its low porosity ² and high electrical resistivity ³, etc., recommend its use in structures or applications with higher than normal requirements. However, while one might predict that it has good corrosion protection properties based on its dense structure, there is also the possibility that the Pozzolanic reaction between the silica and cement could reduce the pH of the pore solution to below the level necessary for passivation. The results of thermogravimetric analysis (TGA) and differential thermal analysis (DTA) of DSP paste with a water/cement + silica ratio (w/p) of 0.15, are given in Table I and indicate that a Pozzolanic reaction does take place in this silica cement paste. The amount of free $Ca(OH)_2$ (which can be as high as 20% in hydrated OPC) decreased significantly during the first month after casting, whereas the degree of hydration (as measured by the amount of chemically bound water) was effectively constant after the first ten days. The analyses were not continued for longer periods because the sensitivity of the method did not allow detection of hydroxides in lower concentrations.

A second factor that could contribute to the possibility of reinforcement corrosion in DSP materials is their higher than normal tendency to shrinkage cracking, resulting from the very low w/c ¹ ratio . It was, therefore, deemed essential that the actual behaviour of the cement with respects to corrosion of embedded steel be determined.

* This material has been developed by Aalborg Portland Cement Fabrik A/S, Denmark, and is marketed in certain countries under the trade name DENSIT.

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ELECTROCHEMICAL MEASUREMENTS OF STEEL IN CONCRETE

The corrosion of steel is an electrochemical process in which the cement pore water acts as the electrolyte. For corrosion to occur, the cement must allow (i) passage of electrical current, (ii) diffusion of oxygen and other species from the environment to the steel surface and (iii) transport of the corrosion products away from the steel. The properties of the cement which determine its protective capabilities are, thus, its electrical resistivity, its porosity and the chemistry of the pore water, particularly the pH. However, it is the combination of these properties which determines the corrosion rates and, as yet, not enough information is available to allow a direct prediction of the corrosion from independent measurements of these other properties. Moreover, under normal circumstances under which the embedded steel is passive, it is not possible to obtain an accurate measure of corrosion rates from visual inspection or weight loss measurements. Electrochemical techniques, on the other hand, are sufficiently sensitive to permit the detection of corrosion rates as low as 0.01 µm per year.

The electrochemical reaction of corrosion of steel in high pH solutions can be considered of consisting of two half cell reactions: an anodic oxidation of iron, most probably to magnetite:

$$3 \text{ Fe} + 4 \text{ H}_20 \rightarrow \text{Fe}_30_4 + 8 \text{ H}^+ + 8\text{e}^-$$
 Eq. 1

and a cathodic reduction of oxygen:

$$2 H_2O + O_2 + 4e^{-} \rightarrow 4 OH^{-}$$
 Eq. 2

During actual corrosion, the rate of emission of electrons by the iron is exactly equal to the rate of consumption of electrons by the oxygen and, therefore, there is no measurable net current. In order to obtain an estimate of the current, it is necessary to shift the potential away from the equilibrium, measure the resultant net current and extrapolate the data to the equilibrium potential.

Experimentally, this is accomplished as illustrated schematically in Fig. 1. A steel rod is embedded in cement, mortar or concrete, and is immersed in water and held at a constant electrochemical potential with respect to a reference electrode. The current flowing between the embedded steel (the working electrode) and an external steel plate (the counter electrode) is measured. The process is then repeated for different values of applied potential.

SPECIMEN PREPARATION

The composition of the cement and the proportions of the mortar used in this investigation are given in Tables II and III. A mortar of the base cement, a sulphate resistant Portland cement (SRPC) of the proportions given in Table III, was used as a control for comparative purposes. This mortar was made with as low a w/c ratio as possible. Cylindrical 4.5 cm ϕ x 16 cm, specimens were cast with an embedded steel rod as illustrated in Fig. 2. The rod had press-fit plastic end-pieces giving an exposed area of 30 cm² and plastic end-plates were glued to the cement using epoxy resin. After casting, the specimens were subjected to vibration to minimize the entrapped bubbles and were kept at 100% RH for 24-48 hrs. before demoulding. They were then kept in Ca(OH)₂ saturated water at ambient temperature for 13 weeks prior to testing.

ELECTROCHEMICAL TESTING

Four samples of SRPC mortar and 4 samples of each of the DSP mixes were placed in each of two tanks and immersed in water saturated with calcium hydroxide to prevent leaching of the hydroxide from the cement. In order to obtain a standard starting point for the experiments, the oxygen was removed from the system by bubbling nitrogen continously through the tank solution and by impressing a cathodic potential (-900 mV vs. standard calomel reference electrode (SCE)) on the samples. The impressed potential results in the reduction of the oxygen dissolved in the cement pore water by the reaction given by Eq. 2.

The samples were held in this condition for four weeks, by which time the current had become anodic indicating that the corrosion potential (the potential existing at the steel surface in the absence of external control) had fallen to below -900 mV SCE. This is indicative of complete absence of oxygen, including the reduction of the passive film. Such conditions have been observed in practise only in concrete deeply submerged in the sea or underground for 6 months or longer $^{4-6}$.

After this standardization process, potentiostatic polarization curves for each sample were obtained as follows. The potential of the embedded electrodes was held constant with respect to the reference electrode for 24 hrs. and the current flowing between each specimen and the counter electrode was measured. This procedure was repeated for potentials ranging from -1000 mV SCE to +450 mV SCE and the data are plotted in Figs. 3 and 4.

After obtaining the polarization curves, NaCl was added to one tank to give a 1 N solution and, in the second tank, the Ca(OII)₂ solution was replaced with deaerated water and the N₂ gas was replaced with deaerated CO₂.

All the samples were held at a constant anodic potential (+100 mV SCE) and the current between the samples and the counter electrode was monitored daily in order to detect the onset of any corrosion. After approximately three weeks, the SRPC samples in the NaCl solution began to corrode and the polarization procedure described above was repeated to obtain the curves given in Figs. 5 and 6.

RESULTS AND DISCUSSION

The data given in Fig. 3 show that there is only a minor effect of water: cement + silica (w/p) ratio on the electrochemical behaviour of steel embedded in DSP mortar within the range of values investigated. The scatter of the data for the four different w/p ratios, in fact, overlapped. Furthermore, Fig. 4 indicates that there is little difference in the potentiostatic response of steel in DSP and SRPC under anaerobic conditions. These observations are, at first sight, rather surprizing in view of the significant differences in those properties of DSP and SRPC which are considered to influence the electrochemical behaviour. A recent model for the corrosion of steel in concrete 7 indicates that the controlling factors are normally the electrical resistivity and pH of the concrete. However, the electrical resistivity of DSP mortar with w/p = 0.15is approximately three orders of magnitude higher than that of SRPC mortar at 100% RH and 22°C. Therefore, it must be concluded that, under these conditions in which the current density in both types of mortar is extremely low and the steel is not actively corroding, the electrical resistivity is not a limiting factor.

Moreover, it has been shown ⁸ that, when ordinary Portland cement is cast, a layer of almost pure Portlandite $(Ca(OII)_2)$ is precipitated on any solid surface in contact with the cement. It is reasonable to assume that the same phenomenon occurs in SRPC and in DSP, although it is likely that the thickness of such a layer will be different for the different cements. If a Portlandite layer is formed on the steel in both cements, then the chemical environment adjacent to the steel in both DSP and SRPC is essentially the same and, at current densities too low to be affected by the electrical resistivity of the cement, the potentiostatic behaviour can be expected to be similar.

Carbon dioxide is known to have the greatest effect in concrete at a relative humidity of $\sim 80\%^9$ and has a much lower effect in dry or completely wet concrete. However, it was thought that CO_2 might enhance the rate of leaching of $Ca(OH)_2$ from the cement and, by so doing, reduce the pH and lead to the initiation of corrosion. However, as illustrated in Fig. 5, this has not been the case within the time span of this experiment. Despite the fact that their environment has a pH of 6, none of the specimens was adversely affected. One interesting aspect of DSP is, however, clear from Fig. 5. Normally, when the potential of steel in concrete is higher than +200 mV SCE, oxygen is evolved by the reverse reaction of Eq. 2. This gives rise to an increase in the measured anodic current at high potentials, such as that exhibited by SRPC specimens in Fig.5. No such an increase was observed in DSP although the potential was increased up to +850 mV SCE.

There is only approximately 7% chemically unbound water in the 0.15 w/p DSP compared with 0.15% in SRPC. Moreover, low temperature microcalorimetry experiments ² have shown that the largest dimension of the pores in DSP are only of the order of 20Å and that there are essentially no capillary pores. The pores are, thus, not likely to form an interconnected system which would allow easy transport of water to the steel surface. It is probable, therefore, that the absence of any noticable oxygen evolution in DSP is due to the lack of available water adjacent to the steel. If this is true, it is a highly desirable situation since corrosion of steel requires the presence of water, as indicated by Eq. 1.

In NaCl solution, there was a marked difference in the potentiostatic response of SRPC and DSP as illustrated in Fig. 6. The steel in SRPC was completely depassivated and corroded at rates up to three orders of magnitude higher than did the steel in DSP. It should be noted, however, that the onset of corrosion in SRPC was considerably more rapid than one would expect under "normal" circumstances because, by holding the steel at an anodic potential, the negatively charged chloride ions were transported to the steel by electrical migration, as well as by diffusion. Moreover, the concentration of chloride ions necessary to initiate corrosion decreases as the potential becomes more anodic.

Grønvold's model of corrosion ⁷ shows that the maximum possible rate of corrosion is determined by the electrical resistivity of the mortar. Thus, even if the DSP samples had begun to corrode, their current should be significantly lower than that of the SRPC.

SUMMARY AND CONCLUSIONS

The highly dense silica-cement paste has been found to provide a high degree of corrosion protection to embedded steel. This protection can be attributed to the very low w/p ratio and the ultra fine pore structure which apparently limits the access of water to the steel surface. Corrosion has not been detected in the DSP samples after several months in environments specifically designed to accelerate corrosion, despite the fact that the silica undergoes a Pozzolanic reaction thereby, possibly, reducing the pH of the pore water in the cement.

There are two factors which could account for this high degree of corrosion protection. Firstly, the lack of available water may prevent corrosion taking place even in the absence of passivity. Secondly, the high electrical resistivity limits the corrosion due to the formation of galvanic cells at flaws such as cracks or voids. The steel exposed to such flaws becomes anodic and the large surrounding areas of protected steel act as the cathode giving a high cathode:anode area ratio. In low resistivity cement, this results in high galvanic currents but, in the DSP material this should not be possible.

It should be noted, however, that the results reported in this paper were obtained on "young" (< 1 yr old) samples. The electrical resistivity measurements³ show that the dense silica cement materials approach equilibrium at a much slower rate than do Ordinary Portland Cement or Sulphate resistant Portland Cement. It is possible, therefore, that the protective qualitities of the dense silica cement might also change with time more than do those of the ordinary cements.

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