EFFECT OF TEMPERATURE ON OXYGEN TRANSPORT THROUGH SUBMERGED CONCRETE

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ABSTRACT

Experiments have been undertaken in order to study the effect of temperature on the rate of oxygen reduction at steel embedded in concrete. In the experiments reported the steel was polarized at -850 mV(SCE) and the concrete cover was 50 mm. With a temperature increase from 1 °C to 30 °C the current density of oxygen reduction increased from 0.5 mA/m² to 1.2 mA/m². The over-all process of oxygen transport through concrete and electrochemical reduction at embedded steel has been found to be controlled by diffusion.

Key Words: Concrete structures, Steel corrosion, Oxygen transport

1.   INTRODUCTION

On concrete structures exposed to sea water two types of corrosion may occur, corrosion of steel embedded in concrete and corrosion of steel components exposed to sea water.

In both cases the main controlling factor for steel corrosion is the reduction of oxygen at the embedded steel surface. At the steel surface oxygen is consumed by the cathodic reaction which is necessary for the corrosion process to proceed.

When external steel is cathodically protected - which normally is the case for e.g. offshore concrete structures - the oxygen reduction at embedded steel causes a current drainage which may account for the main output of the protection system.

Oxygen transport values through concrete are scarce in the literature. Oxygen flux values for wet concrete have earlier been reported ranging between 1.9 and $14,8*10^{-13}$ mole/cm²sec /1/, depending on concrete quality and thickness. These values correspond to current density values for oxygen reduction of 0.73 and 5.7 mA/m². For concrete with a water/cement ratio of 0.5 and thickness 50 mm the flux value ($5.0*10^{-13}$ mole/cm²sec) corresponds to a current density of 1.93 mA/m², while the effective diffusion(diffusivity) constant is $6.2*10^{-8}$ cm²/sec. Tuutti has studied the diffusion through concrete of different water/cement

ratios and relative humidities /2/. For concretes with 100% RH the reported diffusivities are in the range of 3 to $10*10^{-6}$ cm^2/sec. Page and Lambert report diffusivities for cement pastes between 1 and 3 $*10^{-8}$ cm^2/sec /3/. All the above data are based on oxygen flux measurements through bulk concrete with no oxygen reduction at embedded steel involved.

Several authors have discussed current requirements for cathodic protection of embedded steel /5, 6, 7/. The requirements cited vary between 0.4 and 4 mA/m^2 depending mainly on the concrete quality.

Arup has reported current densities in long term polarization test of steel embedded in concrete piles /4/. The scattering of values is great but at a polarization potential of -850 mV (SCE) a typical value of 1 mA/m^2 is obtained for steel in concrete piles in wet soil and sea water.

Miller et al /8/ have measured the galvanic current between embedded steel and corroding exposed steel to be about 25 mA/m^2 for an area ratio of 10^6 between embedded and exposed steel.

2.   EXPERIMENTAL

2.1.   Principle

The measurements are based on the principle that when a negative potential (within certain limits) is applied to steel embedded in concrete the only cathodic reaction taking place[1] is reduction of oxygen at the steel surface:

$$1/2 \; O_2 + H_2O + 2e - OH^-$$ (1)

Therefore, by applying a constant negative potential to an embedded steel plate the oxygen transport (or rather the rate of oxygen reduction at the steel plate) through the concrete may be recorded as an electrical current. By applying Faradays' law the mass transport per unit time(Flux) and - according to Fick's 1. law - the diffusion constant can be calculated:

$$J - \frac{I_{steadystate}}{nxF}$$ (2)

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[1]Reduction of chromates or other cations present in the concrete is not considered

$$J = -D\frac{dC}{dx} \qquad (3)$$

where:

J = Flux   (mole/cm^{2}s)
D = Diffusion constant (cm^2/s)
C = Concentration   (mole/cm^3)
x = Distance   (cm)
n = Valence   (2)
I = Current density   (A/cm^2)

2.2   Test specimen

The test specimen used is shown in FIG. 1. The specimens were produced by embedding a circular mild steel plate with diameter 90 mm and thickness 1 mm in the center of a concrete cylinder with diameter 110 mm and height 80 mm. An insulated copper wire was connected to the steel plate by means of a copper nail.

The concrete was embedded within a plastic cylinder with thickness 5 mm serving both as mould during casting and insulation during the test. The casting was made by half filling the plastic mould with concrete, vibrating on a vibrating table until a smooth surface was obtained, positioning the steel plate, filling up with concrete and vibrating again.
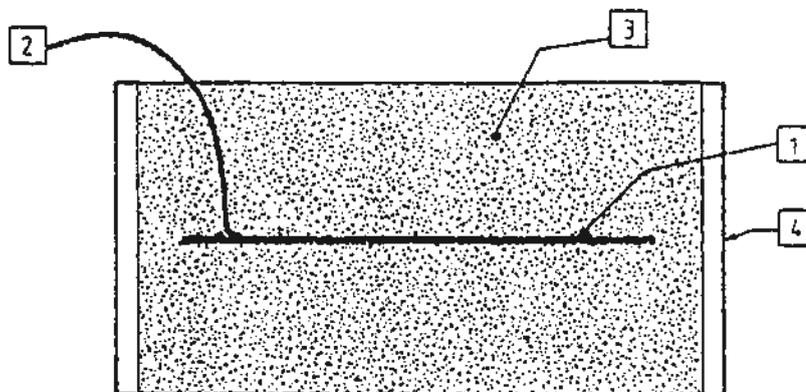
(1) Steel plate   (3) Concrete

(2) Copper lead   (4) Plastic ring

FIG. 1. Test specimen

The concrete was mixed in a 50 liter Ehrlich Mixer using a concrete volume of about 40 liter. The mix design was 1 : 0.5 : 1.67 : 2.56 for cement, water, small aggregate (0 - 4 mm) and coarse aggregate(4 - 12 mm), respectively.

After casting the specimens were cured for 24 hours in 100% RH and water cured for two months.

2.3. Procedure

The experimental set-up is shown i FIG. 2. During the experiments ten specimens were used. The test specimens, stainless steel counter electrode, salt bridge connected to the reference electrode and glass sinter tube for air bubbling were placed in a water-filled plastic container within an environmental chamber. The embedded steels were coupled to a potentiostat and a constant potential of -850 mV vs a saturated calomel electrode was applied.

The oxygen reduction current from each specimen was recorded by measuring the potential drop across a 10 ohm resistor.
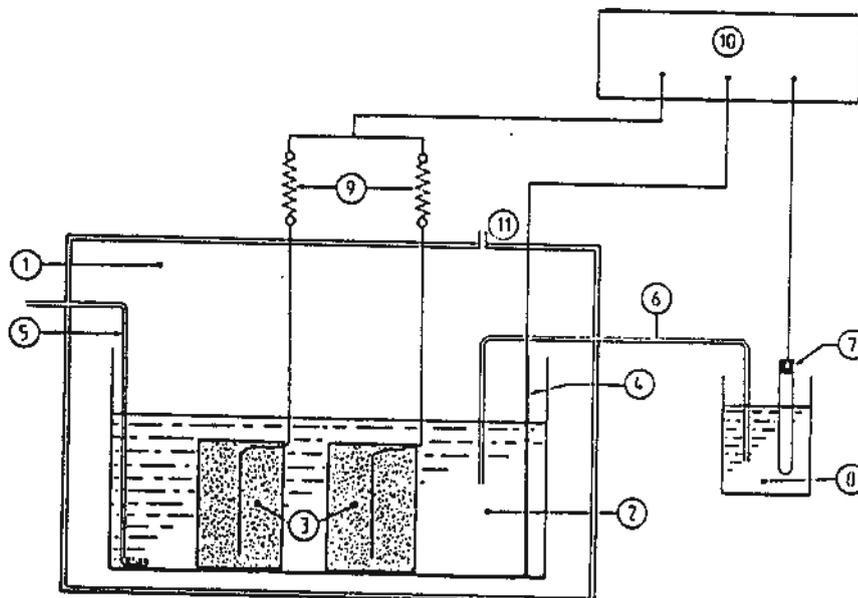
(1) Constant temperature chamber	7) Saturated calomel electrode
(2) Water	(8) Saturated potassium chloride solution
(3) Test specimens	(9) 10 ohm resistor
(4) Counter electrode	(10) Potentiostat
(5) Air inlet	(11) Air inlet
(6) Salt bridge	

FIG. 2. Experimental set-up for measuring oxygen transport through concrete

3. RESULTS AND DISCUSSION

The test results are presented as current densities in Table 1. The values are based on the area of embedded steel which is somewhat smaller than the concrete area. Each value represents the mean of ten recordings.

Table 1. Current densities for oxygen reduction at different temperatures

Temperature (°C)	Current density (mA/m^2)
1	0.507
10	0.690
20	0.882
30	1.170

The current density values vary between 0.5 and 1.2 mA/m^2 as shown in Table 1. These values fit very well with values reported for current demand on cathodically protected offshore structures /9/.

In Table 2 the results are presented both as oxygen flux values and diffusion constants. The calculations are based on equation (2) and (3).

Table 2. Flux values and diffusion constants for oxygen reduction at different temperatures

Temperature (°C)	Flux $*10^{-13}$(mole/cm^{2}s)	D $*10^{-8}$(cm^2/s)
1	1.31	1.19
10	1.86	2.12
20	2.28	3.20
30	3.03	5.10

For calculation of the diffusion constants it is assumed that the oxygen concentration gradient through the concrete is linear and that the oxygen concentration at the steel/concrete interface equals zero. The oxygen concentrations needed for the calculations are given by H. H. Uhlig /10/.

As the tables show there is a pronounced effect of temperature on oxygen transport through the concrete. By increasing the temperature from 1 °C to 30 °C the oxygen flux increases from 1.31 to 3.03 $*10^{-13}$ or about 130 % even if the oxygen concentration of the water is reduced from 14.24 to 7.67 ppm.

The effect on the diffusivity is therefore even more pronounced, as reflected in the diffusion constant given in Table 2. By increasing the temperature from 1 to 30 oC the diffusion constant increases 330 %.

The activation energy for the process can be calculated by means of an Arrhenius plot as shown in FIG. 3. The data fit very well to a straight line giving an activation energy of 15.0 kJ/mole.

According to Akita the activation energy for diffusion in pure water is 13.7 kJ/mole /11/. The activation energy for oxygen diffusion through pore water can be calculated to 13.8 kJ/mole taking into account the higher ionic strength of a concrete pore solution.
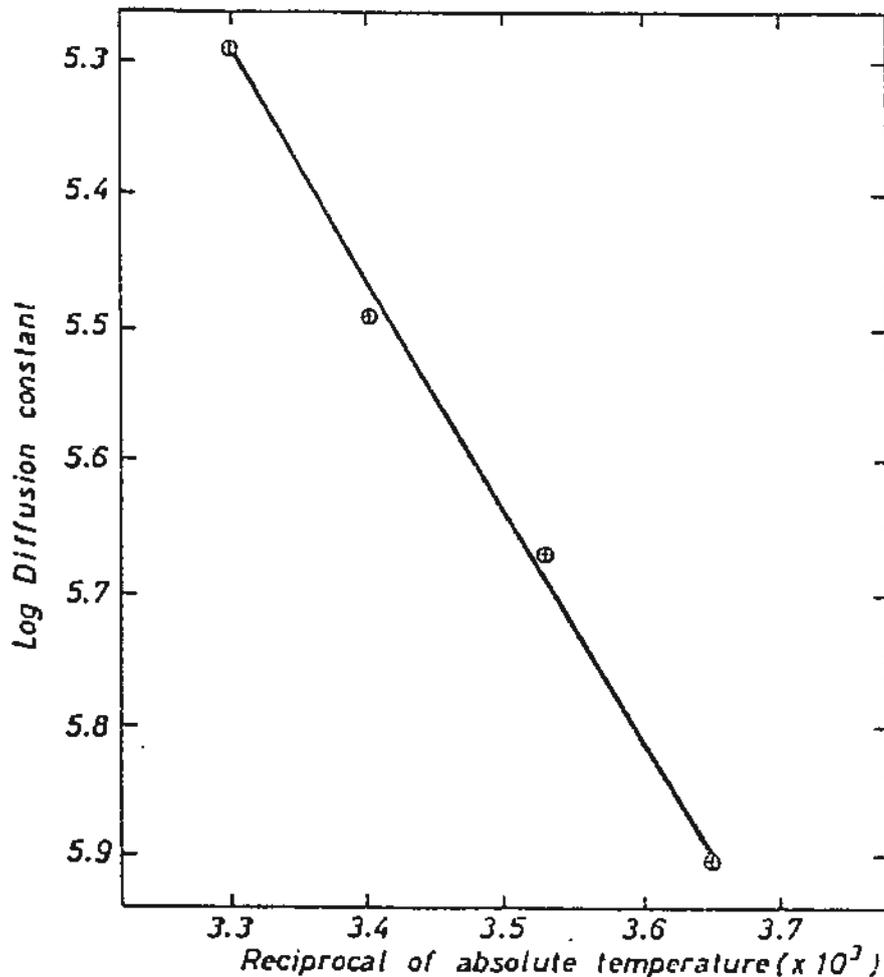

FIG. 3. Arrhenius plot for oxygen diffusion in concrete and reduction at embedded steel

These values fit very well with the activation energy found in the present work for the over-all process of oxygen diffusion through concrete and reduction at the embedded steel plate. This demonstrates that the prosess is controlled by diffusion of oxygen through the concrete and not by electrochemical reduction of oxygen at the steel.

This observation, however, is valid only for situations where the oxygen diffusion is very low. For concretes with lower moisture content the rate determining step might be electro-chemical reduction of oxygen.

The diffusivity values found by Page and Lambert/3/ for cement pastes were about fifty times lower than what has been found for concrete in this work. The activation energies, however, are almost identical: 19.0, 22.0 and 14.9 kJ/mole for the w/c-ratios 0.4, 0.5 and 0.6, respectively. They explain the differences in activation energy by the effect of water/cement ratio on the continuity of pores within the coarsest size-range of the material. Following this argument the present result reflects the well known interface effect of concrete compared to paste of the same water/cement ratio.

4.   CONCLUSION

The temperature has a substantial effect on the oxygen reduction at steel embedded in concrete. A temperature increase from 1 °C to 30 °C causes an increase in current density from the reduction process from 0.5 to 1.2 mA/cm^2. In the present work the rate limiting step in the overall process of oxygen diffusion through wet concrete and electrochemical reduction at embedded steel is diffusion.

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