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MONITORING CHLORIDE CONCENTRATIONS IN HARDENED CEMENT PASTES USING ION SELECTIVE ELECTRODES

C.P. Atkins*, J.D. Scantlebury*, P.J. Nedwell⁺, S.P. Blatch*
*Corrosion and Protection Centre, UMIST, U.K.
⁺Department of Civil Engineering, UMIST, U.K.

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ABSTRACT

In a previous paper (1) it has been shown that silver/silver chloride ion selective electrodes are stable in a simulated pore solution and that the potential of these electrodes is a function of chloride ion activity.This has now been compared with chloride concentrations in the pore water, found using a pressure extraction technique, with chlorides added as sodium chloride to the mix water in concentrations ranging from 0.046Mdm^{-3} to 0.46Mdm^{-3} to ordinary portland cement pastes with a water cement ratio of 0.45. The results show good correlation between concentration added and activity calculated from electromotive force data, with an activity coefficient of 0.46 ± 0.07, which agrees with values calculated in the previous paper.

Introduction

Under normal circumstances steel reinforcement in concrete is in a passive condition due to the high pH environment provided by the hydration of cement. One of the causes of the break down of this passivity is attack by chloride ion (2). Currently common methods of finding the level of chlorides in a structure involve destructive techniques.

The potential of silver\silver chloride electrodes depends mainly on the chloride ion activity in the surrounding electrolyte, and therefore it should be possible to use these electrodes as a non destructive method of obtaining the chloride ion activity in cement and concrete structures.

Pore water extraction is reported to be the only reliable method of determining the free chloride ion concentration in concrete (3) and has been used widely for determining the concentrations of ions in solution in concrete, for examples see references (4), (5) and (6), and therefore this was chosen to check the suitability of ion selective electrodes for use in chloride monitoring in cement pastes.

Method

Silver/silver chloride electrodes were prepared in a manner similar to that described in Ives and Janz (7). 25mm long sections of 99.99% pure, 1mm diameter silver wire supplied by Goodfellow Metals were taken and soldered onto screened cables. Heat shrink tubing was cut to an

TABLE 1

Bogue Composition of the Cement Used

Compounds	C_3S	C_2S	C_3A	C_4AF
% in cement	53.8	18.0	11.7	6.5

appropriate length and applied to cover the connection between the silver and the cable. These electrodes were then wiped with acetone to degrease them and anodised in 0.1N HCl at a current density of $0.4mAcm^{-2}$ for approximately 30 to 40 minutes. The electrodes were then stored in dilute HCL solution in the dark until required.

Since free chloride is reported to vary linearly when the chloride ion is added as sodium chloride to the mix water it was decided to use this as the source of the chloride ion. Masses of sodium chloride from 0.3g to 3g were added to 112.5g of water. Each mix was stirred thoroughly until all the sodium chloride dissolved and the solution was then mixed with 250g of ordinary portland cement supplied by Blue Circle Hope Works and poured into 65cc plastic bottles. For Bogue compositions of the cement used see table 1.

2mm diameter holes were drilled in the lids to allow the electrode leads to pass through and the electrodes were rinsed in deionised water and placed in the cement paste. The lids were sealed in place use a non corrosive silicon rubber. The cement was left to cure in the lab until pore water extraction was possible. Each quantity of chloride ion was repeated in triplicate.

Pore water extraction was carried out on an Amsler compression testing machine, using the pore water extractor shown in figure 1. The loading rate used was that recommended by Barneyback, i.e. $2.8Nmm^{-2}s^{-1}$, up to a value of 400kN, which corresponded to 40% of range 2 in 130s on the test rig used. Prior to extraction the bottles were cut open and the potential of each silver\silver chloride electrode was measured using an electronic digital volt meter (Isotech, IDM96) in conjunction with a saturated calomel electrode that had been rinsed in deionised water at between 10 and 20 locations on the surface of the blocks. The leads to the electrodes were then removed and the inside of the pore water extractor was coated in a spray on mould release fluid. The samples were then placed into the extractor and the load applied. The extract was collected using a syringe and placed into individual bottles, which were then sealed using 'Nescofilm'. The extract was diluted by taking a known quantity, measured using a graduated pipette with a least count of 10μl and adding $25cm^3$ of deionised water to this. Again the solution produced was placed into fresh bottles sealed with Nescofilm. The diluted solutions were then analysed for chloride concentrations using a Corning chloride analyser, model number 926.

Results

The results are presented in figures two and three. Figure two shows the mass of added chloride against calculated activity and concentration. Figure three shows the calculated activity against concentration found using pore water extraction. The line of best fit was calculated using the regression function of Borland Quattro pro™, the rank correlation coefficient for this data was 0.8873 with 27 degrees of freedom, which is acceptable at the 99.95% confidence limits.

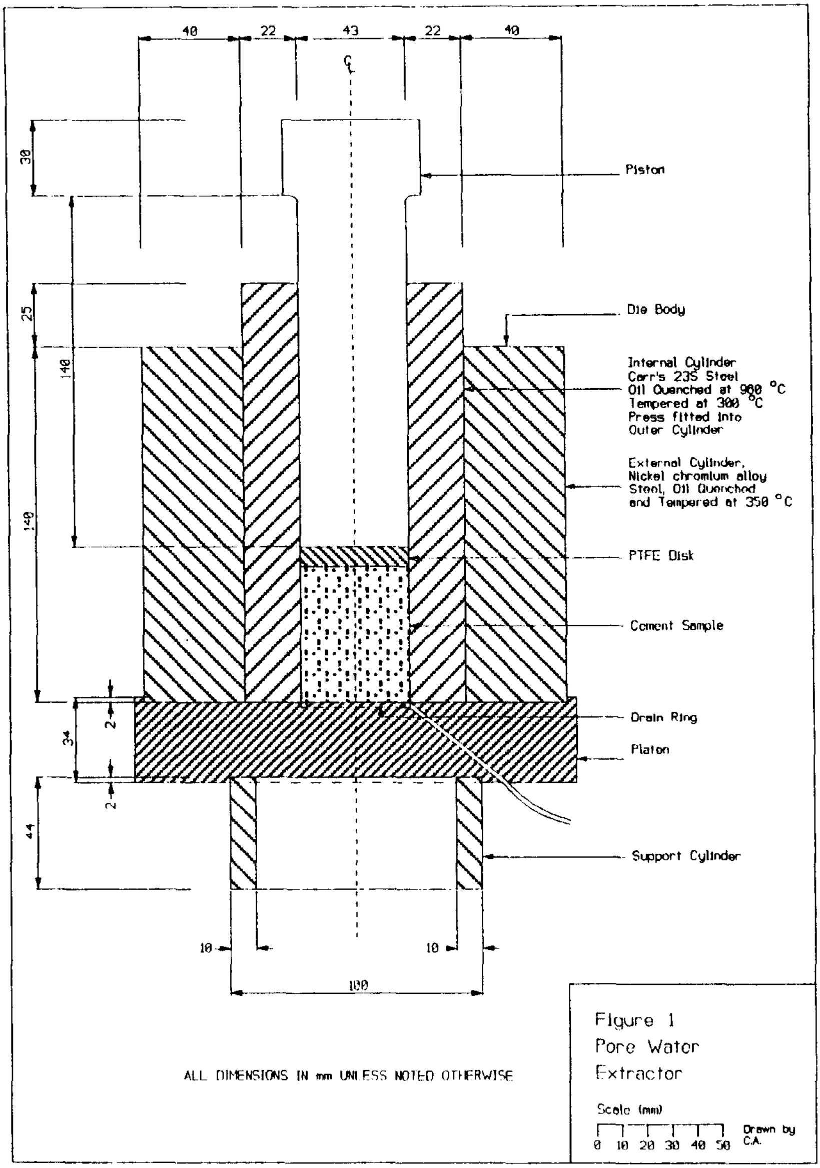

FIG. 1.
Diagram of the pore water extractor used.

Discussion

The activity of the chloride ion can be calculated by straightforward mathematical manipulation of the Nernst (7) equation:

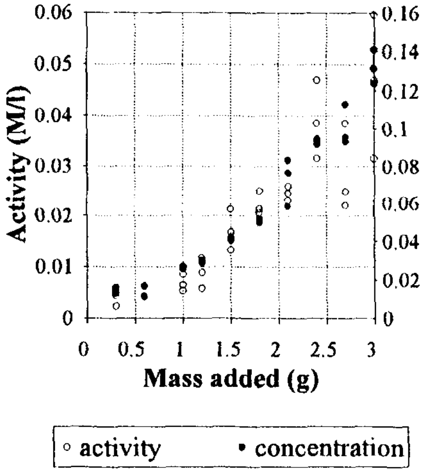

FIG. 2.
Mass of chloride added vs calculated activity/measured concentration.

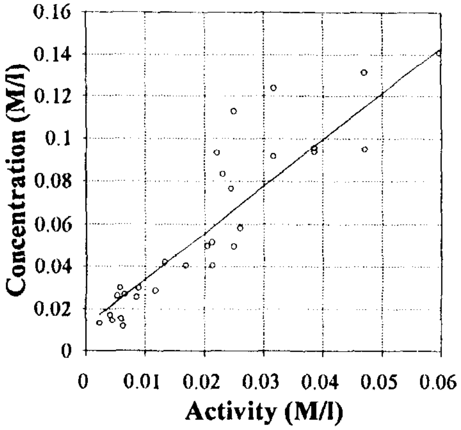

FIG. 3.
Calculated activity vs concentration.

$$E = E^{o} + \frac{RT}{nF}\ln a_{Cl^-} - E_{ref} \qquad (1)$$

where
E = Measured potential (V)
E^{o} = Standard Electrode potential of the silver/silver chloride electrode(V)
R = Gas constant (J mol^{-1} K^{-1})
T = Absolute temperature (K)
n = Number of electrons
F = Faraday constant (C mol^{-1})
E_{ref} = Potential of the reference electrode used (V)
a_{cl^-} = Activity of the chloride ions in solution (mol dm^{-3})

therefore

$$a_{Cl^-} = e^{\frac{nF}{RT}(E_{ref}+E-E^{0})} \qquad (2)$$

The main source of error in this experiment was caused by measuring the potential of the silver/silver chloride electrodes using an external saturated calomel electrode. This technique may well include a contribution from an IR drop, caused by the high and variable resistivity of the concentre. Due to the logarithmic relationship between activity and potential, the higher the activity of chloride in solutions, the higher will be the error, illustrated below using a error of 10mV.

$$a_{Cl^-} = e^{\frac{nF}{RT}(E_{ref}+E-E^{0}\pm 0.01)} \qquad (3)$$

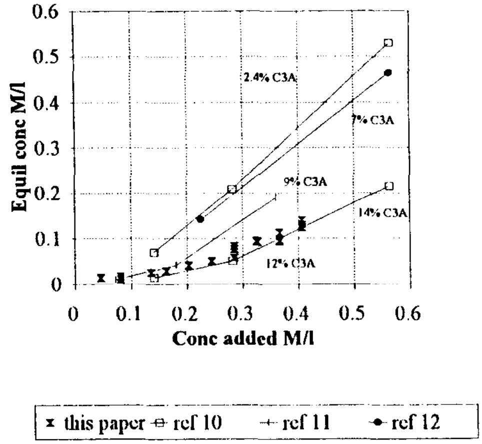

FIG. 4.
Comparison of published data on NaCl binding.

$$i.e. \quad a_{Cl^-} = a_{Cl^-} \times (1.48,\ 0.67) \tag{4}$$

In practice this can be easily avoided by the use of a luggin tubulus containing a solid state electrolyte which effectively moves the tip of the external reference electrode to next to the silver/silver chloride electrode. This procedure was not used in this experiment due to the destructive nature of pore solution extraction. To minimise this error the potential of each electrode was measured in between 10 and 20 positions spiraling down around the external face of each sample. The modal value was then taken and used in the calcuations.

The data produced suggests a ratio of activity to concentration of 0.46 ± 0.07, which agrees with that produced in earlier work (1).

In other, as yet unpublished work carried out by the authors, results suggest that the final concentration of the chloride ion depends on the chloride concentration in the mix water rather than the mass of chloride as expressed as a percentage of mass of cement and as such the graph in figure 4 has been produced comparing previous work (10), (11), (12) with the data produced from pore water extraction in this study. The data shows good agreement with the general trends illustrated in figure 4. From figure 4 it is suggested that chloride binding for sodium chloride depends upon the tricalcium aluminate concentration and on the concentration in the mix water. It has been reported (13) sulphates preferentially react with tricalcium aluminate and so it is expected that the concentration of sulphate ions present in cement will affect the quantity of free chloride found in the pore water. The effect from the tricalcium aluminate is to be expected since the only relevant chloride binding effect for sodium chloride is that caused by the formation of Friedels salt, as according to Lambert et al. (14), the calcium silicate hydrate has no part in the binding of sodium chloride.

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