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INFLUENCE OF VOLTAGE ON CHLORIDE DIFFUSION COEFFICIENTS FROM CHLORIDE MIGRATION TESTS

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ABSTRACT

A chloride migration test method is described and test results are given for concrete subjected to a range of potential gradients. A method for setting the potential across the sample length using reference electrodes and Luggin capillaries is described. Apparent and effective diffusion coefficients were calculated from chloride break-through time and steady state chloride flux respectively at each potential. Accounting for polarization and iR drop losses is significant particularly at lower applied potentials.

Background

Due to an increased interest in producing concretes that are resistant to chloride induced corrosion of embedded reinforcing steel, there has been much work directed toward obtaining chloride diffusion coefficients. However, obtaining diffusion coefficients by steady state diffusion cells (1) can be quite slow, especially for high performance concretes. As a result, research in accelerating the movement of chloride ions into hardened concrete by means of electrical conduction or "migration" has been reported in several recent publications (2-9). In the typical test configuration, a DC potential is applied across anodic and cathodic electrodes placed in electrolyte chambers on either side of the test specimen. The chloride ion is conducted into or through the sample from the cathode electrolyte. In these research investigations some measure of chloride "penetrability" is determined either from the steady state chloride flux (3,4,6,7), the conduction current, (8) or the initial non-steady state chloride penetration (4,9).

For the non-steady state case of diffusion plus conduction, the Nernst Planck or modified Fick's second law has been used to describe chloride ion transport in the accelerated chloride conduction tests (5).

$$\frac{dC}{dt} = -\frac{dJ}{dx} = D\left(\frac{d^2C}{dx^2} - \frac{zF\Delta V}{RTl} \cdot \frac{dC}{dx}\right) \tag{1}$$

The exact analytical solution for Equation 1 is (5):

$$C = \frac{C_0}{2}\left[e^{\alpha x} \cdot erfc\left(\frac{x + aDt}{2\sqrt{Dt}}\right) + erfc\left(\frac{x - aDt}{2\sqrt{Dt}}\right)\right] \tag{2}$$

where:

$$a = \frac{zF\Delta V}{RTl}$$

and z = ion valence, F = Faraday's constant, ΔV is the potential drop across the sample, R = gas constant, T = temperature in Kelvin, l = the sample length, C = pore solution concentration at any depth and time t, and C_0 is the pore solution concentration at the surface.

For the case of a steady state conduction flux where the diffusion component is small, Equation (1) simplifies to:

$$J = D\frac{zF\Delta VC}{RTl} \tag{3}$$

Equations 1 and 3 are not likely to stand up to rigorous electrochemical and mathematical evaluation in concentrated polyelectrolyte systems together with complex chemical binding reactions such as exist in concrete. However, they may provide a quasi-scientific method of quantifying results from accelerated migration tests.

The D value from Equation 3 is analogous to an effective diffusion coefficient in a steady state diffusion test in that it relates the pore solution concentration gradient to the flux based on the total sample cross section area and it is assumed that chemical reaction sites have been filled i.e. steady-state conditions. If a break-through time technique (9) is used to solve Equation 2 then the D value is related to pore solution concentrations and porous area fractions and a correction factor for porous area fraction would need to be made to make comparisons with Equation 3. Furthermore, chemical binding reactions are likely to slow down the break-through time thus reducing D.

In these equations the rate of conduction is a function of the potential gradient across the sample. A substantial potential drop exists across the electrode/electrolyte interface necessary to drive the electrochemical reaction at the electrode surface. It is therefore important to set the potential across the length of the specimen itself rather than between the leads to the electrodes. Until recently, information was given in only one paper (8) on setting cell potential across the sample itself, however no details were provided. Recently, a similar concept for setting cell potential was published (10) in a resistivity type test. This contribution describes a method of setting the potential using two reference electrodes and provides data as to the magnitude of potential losses for a range of applied voltages. Further, the data are used to check the validity of equations used to calculate diffusion coefficients in chloride migration tests.

Experimental

Figure 1 shows a chloride migration apparatus currently being utilized at the University of Toronto. The anode chamber contains 0.6 L of 0.3 mol/L NaOH. The volume of the anode chamber is kept small to allow early detection of chloride break-through from the sample, but still large enough to avoid significant electrolyte concentration changes. The cathode chamber contains 1.5 L of 0.5 mol/L NaCl and 0.3 mol/L NaOH. The cathode chamber is kept large to prevent buildup of the OH^- and the depletion of Cl^-. The experiment creates a near constant concentration of migrating anions (Cl^- and OH^-) at concentrations somewhat representative of real
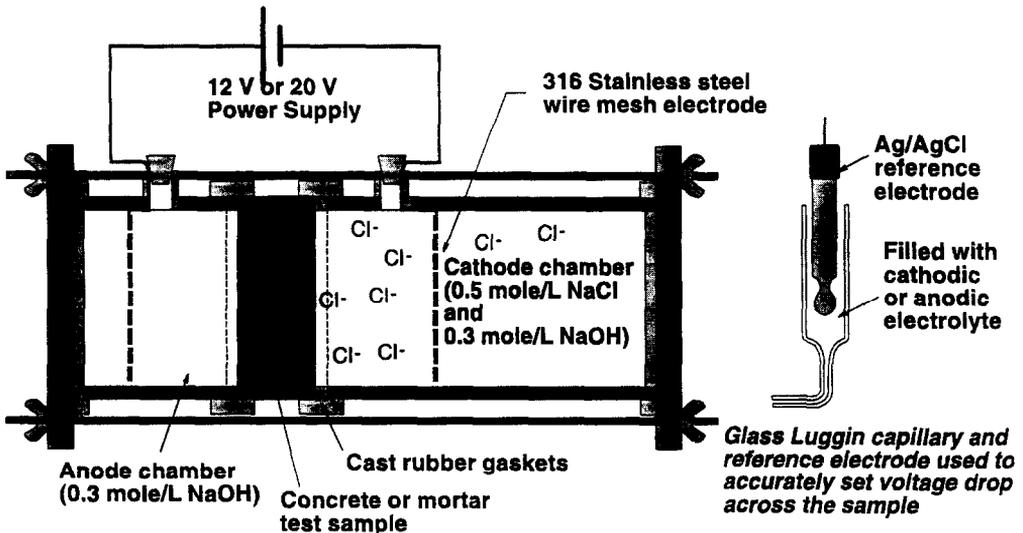
FIG. 1.
Chloride conduction cell and luggin capillary with reference electrode.

cement pore solution. Temperature change due to current flow was not significant even at 30 volts.

A 50 mm gap between the specimen face and the 316 stainless steel wire mesh electrodes allows for the insertion of the reference electrode assembly (right side of Figure 1) through the two openings (normally corked) in the tops of the compartments on either side of the specimen The reference electrode assembly consists of a commercially available double junction Ag/AgCl electrode placed inside a Luggin capillary tube. Both the outer chamber of the double junction electrode and the Luggin capillary tube are filled with the same electrolyte solution as the chloride conduction cell chamber into which they will be inserted. This is done to eliminate contamination of the anode chamber with chloride from the reference electrodes and to reduce liquid junction potentials. The Luggin capillary tube acts to minimize disruption of the electric field. The voltage across the two reference electrodes can then be adjusted to the desired driving potential for the test set up.

The concrete used for the study had a water to cement ratio of 0.49, containing ordinary Portland cement (CSA Type 10), 10 mm crushed limestone, and concrete sand of glacial origin. Concrete was cast into blocks of dimensions 500 × 400 × 100 mm and stored under water until age 1 year at which time 100 mm cores were extracted for another study (11). Some of the cores were left under water at 23 °C for another 2 years, at which time the ends were trimmed to make 30 mm long cylinders for this test.

Results and Discussion

Figure 2 shows the results of chloride conduction tests conducted on concrete from the same batch but on individual core samples in companion cells. Table 1 shows potential differences measured between various locations in the test set up. The data shown in Table 1 was measured
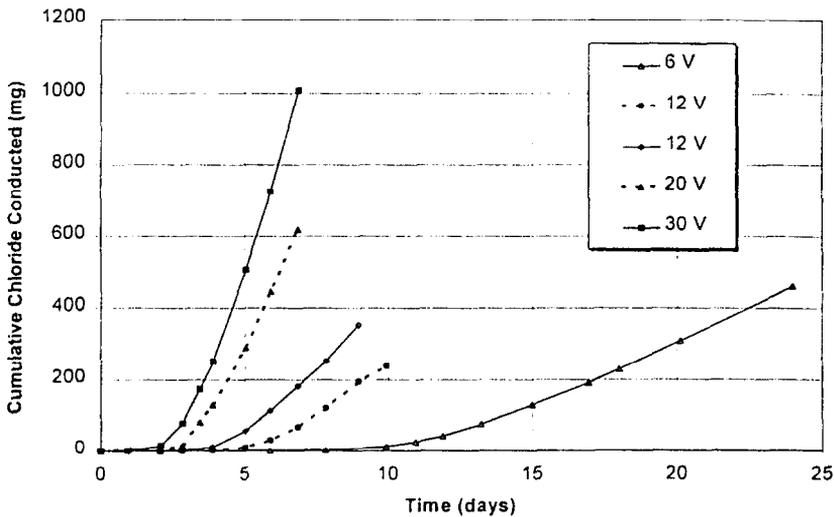
FIG. 2.
Influence of applied voltage on chloride conduction through concrete samples from the same batch (W/C = 0.49).

2 days after the power was switched on. The potential drops throughout the cell did not vary extensively as the test progressed (potential drop across the sample reduced by about 1 to 2 % by the end of the test).

The polarization appears to be slightly dependent on the applied voltage but for the most part appears to be a function of the type of electrode reaction and not a function of the rate of charge transfer on the electrode surface. The iR drop in the electrolyte solution was calculated to be negligible for the low current flow through these concretes. In Table 1 the sum of the individual potential drops does not precisely equal the overall cell potential drop. This is believed to be

TABLE 1
Map of Potential Drop in Chloride Conduction Cell

Sample No.	Nominal Voltage	Measured Potential Difference (V)				
		Anode Lead/ Cathode Lead	Anode Reference Electrode/ Cathode Reference Electrode	Anode Lead/ Anode Reference Electrode	Cathode Reference Electrode/ Cathode Lead	Total Polarization and iR Drop (col 2-3)
1	6	7.88	5.97	0.55	1.31	1.91
2	12	14.03	11.95	0.58	1.33	2.08
3	12	14.01	11.94	0.59	1.34	2.07
4	20	22.18	19.98	0.58	1.42	2.20
5	30	32.30	29.94	0.60	1.45	2.36

TABLE 2

Influence of Voltage Determination on Diffusion Coefficients

Sample No.	Nominal Voltage	D (x 10^{-12} m^2/s) non steady state eq (2)			D (x 10^{-12} m^2/s) steady state eq (3)		
		Using Potential Across leads	Using Potential Across Sample	Error (%)	Using Potential Across leads	Using Potential Across Sample	Error (%)
1	6	2.9	3.7	21	3.1	4.1	24
2	12	3.8	4.4	14	2.8	3.3	15
3	12	3.5	4.1	15	3.3	3.9	15
4	20	3.6	3.9	8	5.1	5.7	11
5	30	3.4	3.6	6	5.9	6.3	6

due to the need for use of a high impedance voltmeter to prevent significant current flow through the voltmeter.

The importance of using the correct voltage on the calculation of diffusion coefficients from Equations 2 and 3 is shown numerically in Table 2. Equation 2 was applied using the method described in (9) where break-through time was taken at the first reliable inflection of the anode chamber chloride concentration (at $C/C_o = 0.003$). The D values from Equation 3 are divided by porosity volume fraction as a simple approximation of area fraction.

Using the potential across the cell leads results in errors which increase as the applied voltage decreases. However this error can be quite easily corrected for, at least by initial calibration of the system with the Luggin capillaries.

It is interesting to note the influence of voltage on the calculated D values for the two methods of determination. Equation 2 values appear to be less affected by voltage than do D values determined by Equation 3. The fact that Equation 2 gives nearly the same D value for widely varying test conditions suggests some degree of validation of the derivation of the equation and its underlying assumptions. One such simplifying assumption is that binding is a linear function of concentration (and thus just a scalar modification of D) or that binding is not present. It also may suggest that binding is not strongly dependent on time, at least within the period taken to complete the tests (25 days for the 6 V sample to 7 days for the 30 V sample). It may also be true that binding is not significant in the conduction test where the majority of the chloride is likely to pass through only the coarsest pore fraction, at least up to the time of break-through.

The D value from Equation 3 is more than linearly dependent on voltage. It appears that other significant factors are not being accounted for, such as the influence of voltage on the interaction of the migrating species with the charged surface layers. It is possible that tests at lower voltages had not reached steady state and the test time should have been extended, but this does not seem to be able to account for all the differences between high and low voltage tests.

It may be expected that the steady state flux used in Equation 3 should produce a higher D value as it is not hindered by binding. This effect may be offset by the fact that chloride break-through will be dominated by the very coarsest connected pores and one short circuit would bias the results. For this reason the steady state test may be more appropriate for prediction of chloride penetration into real concrete structures.

Conclusions

Obtaining diffusion coefficients using steady state diffusion cells can be quite slow, especially for high performance concrete. Research into electrical migration methods is now common. The magnitude of polarization across the anode and cathode in this type of experiment can be quite significant particularly if theoretical relationships such as the Nernst-Planck equation are applied to the conduction cell test data in order to calculate diffusion coefficients. The resulting error increases as applied potential decreases. Total polarization was found to range from 1.91 V to 2.36 V for 6 and 30 Volts nominal applied potential with the test configuration described here.

   Calculated diffusion coefficients were reasonably constant over the voltage range tested for the non-steady state migration case but tended to increase with increased voltage for the steady state case.

Acknowledgment

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