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A CHLORIDE CONDUCTION TEST FOR CONCRETE

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ABSTRACT

The paper describes the development of a very rapid test that measures the permeability of concrete to chloride ions. Once sample conditioning has been done, up to 20 concrete samples can be tested in an hour using a single conductivity cell. The test involves saturating a concrete sample with a 5 M NaCl solution, before measuring the conductivity of the sample. By saturating samples with a highly conductive solution, they have virtually the same pore water conductivity. Different concrete samples yield different conductivities primarily because of differences in their pore structure. The measured conductivity is related to the diffusibility ratio as well as to the chloride diffusivity of the concrete.

Introduction

Rapid chloride tests have been used to compare the resistance of different concretes to chloride ingress. This has proved very useful in finding economical mixes for high durability applications, and has also helped in understanding the factors that improve the resistance of concrete to chloride ingress.

Three types of rapid chloride tests have been developed to date. In all three, a concrete sample is placed adjacent to a chloride solution on the one face, and a chloride-free solution on the other. A potential difference is then applied to draw chloride ions through the concrete. The first type of rapid test is represented by the AASHTO T277 (1) test, developed by Whiting (2), in which the total charge passed through a sample during a six hour period under a 60 V potential difference is measured, and the value used as a chloride permeability index. The second type of test is that developed by Dhir et al (3), who related the steady state chloride flux under a 10 V potential difference empirically to the chloride diffusion D of the concrete. The third type of test is represented by the developments of Tang and Nilsson (4), in whose test the depth of chloride penetration under a 30 V potential after 8 hours is measured, and fundamental electrochemical theory is used to calculate D.

The electric potential does not accelerate the mechanism of diffusion. The increased flux of ions is caused almost solely by the mechanism of conduction. Since these tests increase the ionic flux up to a 100 times, they are essentially conduction tests with negligible diffusion. Feldman et al (5) have shown that a simple conduction test on "virgin" concrete gives the same ranking as Whiting's test and proposed the replacement of AASHTO T 277 with a resistivity (conductivity) test.

Both Whiting's test and the proposed resistivity test of Feldman et al are influenced by the variability of the pore water conductivity of various concretes (6). This variability results in the index obtained not necessarily being proportional to the steady state diffusion coefficient. Cement types such as silica fume blends give very low pore water conductivities. Using these tests to evaluate the relative performance of different cement blends would therefore be doubtful. Although the tests of Dhir et al and Tang and Nilsson obviate this problem, the AASHTO test is still the most widely used because it is so rapid. The AASHTO test can also be criticised on the grounds that the temperature changes significantly during the test, and that there is no theoretical correlation between diffusivity and the test result.

There is therefore a need for a chloride test that is theoretically sound, and that is as rapid or more rapid than the AASHTO test.

Based on electrochemical theory, a very rapid chloride conduction test has been developed at the University of Cape Town. The test is virtually independent of the concrete pore solution conductivity. A theoretically sound approach has also been proposed to determine the steady state diffusion coefficient of concrete using this new test. This, together with a better understanding of the additional factors affecting chloride ingress in real structures (non-steady state) such as chloride binding and absorption of chloride-containing water, will in future aid the accurate prediction of chloride ingress into structures.

This paper deals with the electrochemical principles that led to the development of the new test. It also describes the test method, and the procedure used to determine diffusivity from conductivity measurements.

Development of Method

The development of the new chloride test was based on the ionic distribution that pertains during steady state conduction. Diffusivity and conductivity are most easily measured and calculated under steady state conditions. With pure diffusion tests, a period of a year or more is needed before steady state conditions are achieved in concrete specimens of suitable thickness. With Dhir et al's conduction test (3), steady state conditions are achieved after about 7 days. The fact is not always appreciated that the ionic distribution during steady state conditions differs for the two types of test.

The ionic concentration gradient is the driving force behind diffusion, and a steeper gradient increases the rate of diffusion. With steady state diffusion the concentration gradient has a constant slope (see Figure 1).

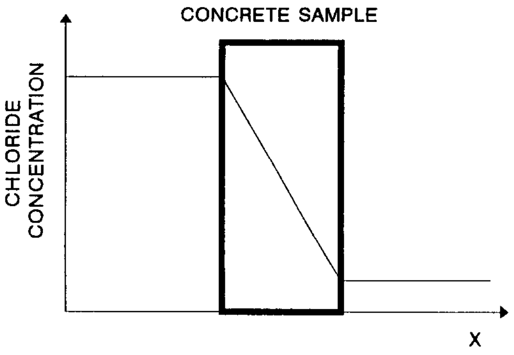


FIG. 1
Steady state diffusion

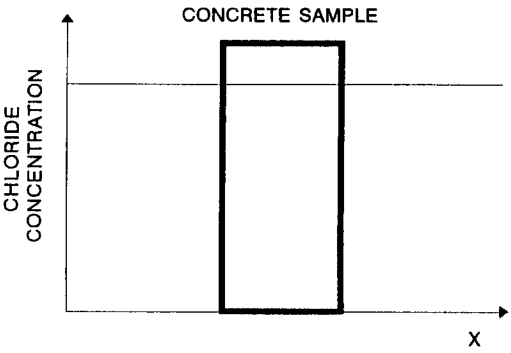


FIG. 2
Steady state conduction

With conduction the driving force is the electric field. In the same electric field each charge would experience the same force. Thus, in steady state conduction the electric field is constant, and the charged ions are uniformly distributed (see Figure 2).

In a conduction test, with a chloride solution on one side only, at the start, the chloride ions move through the concrete in a well defined front (4). Steady state conditions are achieved when the front has passed through the concrete sample. The chloride concentration in the pore solution of the concrete is then uniform (see Figure 3). This can be exploited to permit a very rapid chloride test, since virtually the same condition can be achieved in a much shorter time by vacuum-saturating a concrete sample with a chloride solution.

With Dhir et al's test the condition required for steady state conduction is achieved after several days by electrically pulling a chloride front through a water saturated concrete. By initially saturating the samples in a chloride solution steady state conditions pertain from the start.

To avoid dilution of the chloride solution inside the concrete, samples require drying prior to immersion. The test is further simplified by measuring the electric current (2,7) instead of measuring the chloride flux (3). The current measurement is readily converted into a conductivity value. Later in this paper a theoretical approach is proposed to determine the chloride diffusivity (D) from conductivity (current) measurements.

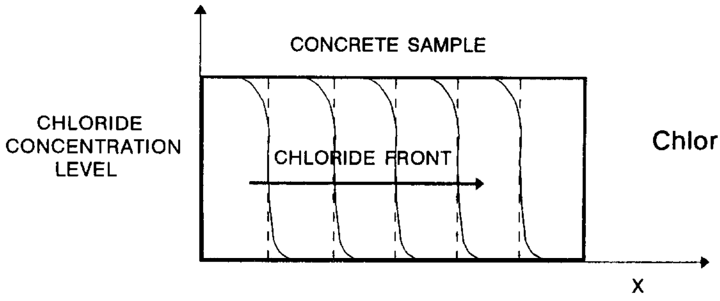


FIG. 3
Chloride front in conduction tests

Test Arrangement

The characteristics of the new test determined the design of the test apparatus. Since the test involves a single current reading, the apparatus can be used consecutively on a series of samples. The time taken to set up the apparatus for each test determines the rate at which samples can be tested. During the short duration of the test relatively few ions migrate and small cells can therefore be used.

The conduction test apparatus consists of two 500 ml cells adjacent to a central section containing the concrete sample (see Figure 4). Both cells screw on to the central section, thus compressing the silicone rubber collar and clamping the sample. Each cell contains a 5 M NaCl solution. By holding the apparatus in a vertical position each cell can be removed without spilling the cell solution. The potential difference is applied to a carbon anode and a stainless steel cathode by a 0 - 20 V (0 - 3 A) DC power source. Two copper/copper sulphate halfcells and a voltmeter are used to measure the potential difference between the solutions accurately. Two plastic tubes lead from the halfcells to the sample surfaces to accurately measure the potential applied across the sample only. The current measured has been shown to be independent of the conductivity of the cell solutions because of this detail. Both the voltmeter and the ammeter are arranged as shown when the readings are taken.

Test Method

Sample preparation

The test apparatus was designed for mortar or concrete samples of 68 mm diameter, and thicknesses of between 5 and 40 mm. (Similar apparatus can be designed for other sample diameters). Usually mortar samples of 10 mm and concrete samples of 25 mm are tested. The concrete or mortar is cored with a diamond tipped core barrel fixed to a suitable drill. The core is then sliced using a diamond saw. The average thickness of each disc is measured using a vernier calliper.

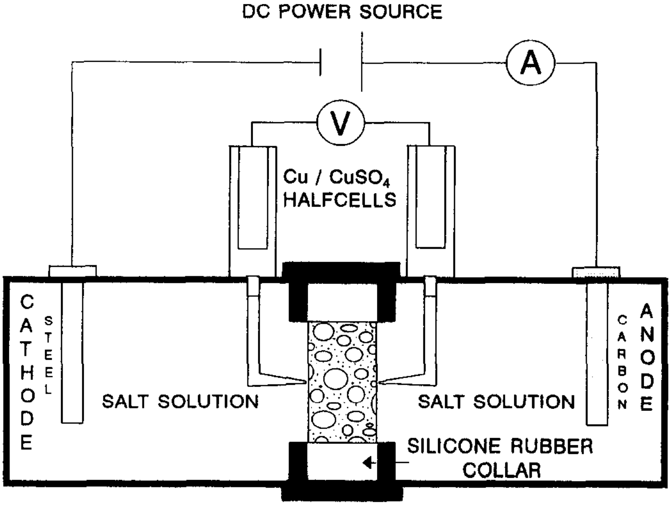
Conditioning of sample

The concrete discs are placed in an oven at 50 °C for 7 days to remove moisture from the concrete pores. The discs are then vacuum saturated in a 5 M NaCl solution for 5 hours, and left to soak in the solution for an additional 18 hours or so.

The drying process is required to ensure uniform saturation with the chloride solution and to prevent the dilution of the saturating solution. The temperature of 50 °C was chosen since much less damage is caused at lower drying temperatures in terms of conductivity compared with 100 °C (8). Although less water will be removed at 50 °C compared with drying at 100 °C, preliminary trials in our laboratory using samples dried at the two temperatures showed that the difference was found to be insignificant. In any event, conductivity is relatively insensitive to small changes in concentration at high concentrations (see Figure 6).

Significant drying damage in terms of conductivity was observed only for mixes with very low w/c (< 0.3) ratios. In hot climates, the on-site drying conditions are often not far removed from those used for the test procedure.

FIG. 4
Conduction test arrangement



The period of vacuum saturation depends on the sample thickness, and 5 hours has been found to be more than adequate for 25 mm thick samples. Samples of 25 mm thickness would reach constant weight within two hours (60 MPa concrete). Tests on samples with thicknesses of 15 mm, 20 mm, 25 mm and 30 mm yielded identical conductivities, proving adequate saturation as well as a uniform chloride distribution.

Testing and output

The cells containing the NaCl salt solutions are screwed onto the central section containing the sample. The circuit is arranged as shown and the current is measured at the applied voltage (2, 5 or 10 V). 10 V is preferred, but 2 or 5 V are used for very permeable or thin samples in order not to exceed the reading limits of the ammeter. Up to 20 samples can be tested in an hour.

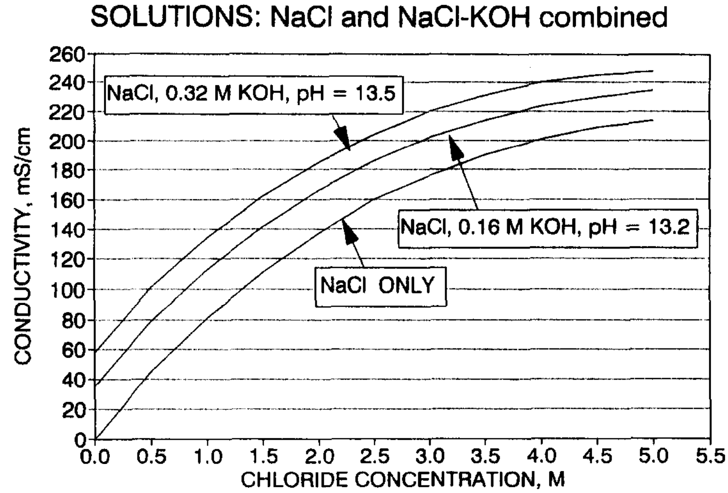


FIG. 5
Conductivities of various chloride and chloride/hydroxide solutions

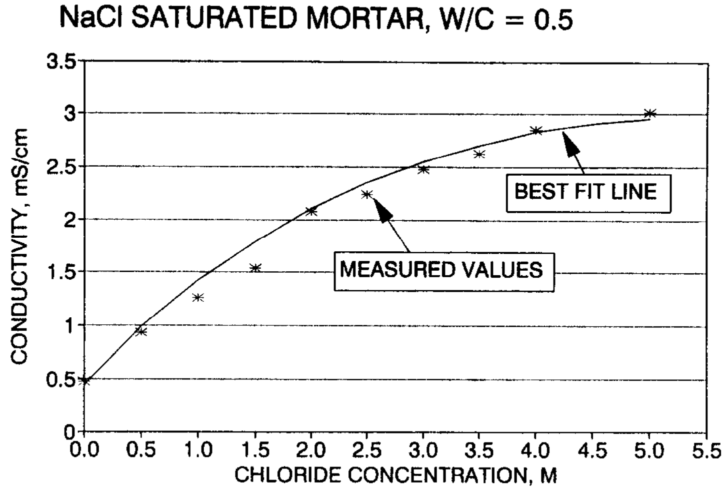


FIG. 6
Conductivities of mortar samples saturated with various chloride solutions

To determine the conductivity of each sample, the measured current, applied voltage and the sample dimensions are substituted in equation 1:

$$\sigma = \frac{i}{V}\,\frac{t}{A} \qquad (1)$$

where σ ... *conductivity of sample* $[\frac{mS}{cm}]$

i ... *electric current* $[mA]$

V ... *potential difference* $[V]$

t ... *thickness of sample* $[cm]$

A ... *cross-sectional area of sample* $[cm^2]$

Relationships between Diffusivity and Conductivity

Although diffusion and conduction are different ionic transport mechanisms, at low ionic concentrations both are linearly related by Einstein's relationship (equation 2).

$$\mu = zF\,\frac{D}{RT} \qquad (2)$$

where μ ... *mobility of ion*

z ... *charge of ion*

F ... *Faraday's constant*

D ... *diffusivity of ion*

R ... *gas constant*

T ... *absolute temperature*

At higher concentrations there are various factors that influence each mechanism differently. Other relationships involving both diffusion and conduction parameters such as the Nernst-Planck equation are usually derived from Einstein's equation and apply only under ideal conditions (9).

In a saturated porous medium, where the solid phase is effectively an insulator, the rate of diffusion and conduction would be affected by the tortuosity and the constrictivity of the pore structure (10). A material constant Q (diffusibility) is defined in Equation (3) as the ratio between the diffusivity of an ion in a porous material to that of the same ion in the pore solution only. This constant is also equal to the ratio between the mobility (or conductivity) of an ion in a porous material to that of the same ion in the pore solution (10,11). (Note that both the diffusivity and mobility coefficients in the porous material are in terms of the average flux per unit area of the medium.)

$$Q = \frac{D}{D_0} = \frac{\sigma}{\sigma_0} \tag{3}$$

where Q ... *diffusibility of porous material*

D ... *diffusivity of ion through porous material*

D_0 ... *diffusivity of ion through pore solution*

σ ... *conductivity of porous material*

σ_0 ... *conductivity of the pore solution*

Theoretically it is therefore possible to determine the chloride diffusivity of a porous medium by conductivity measurements. By measuring the conductivity of the porous medium, and the conductivity of its pore fluid, the diffusibility ratio is obtained. This number is then multiplied by the diffusivity of chloride ions in the pore solution to obtain the chloride diffusivity of the porous medium.

Although the diffusivity of concrete has been determined from conductivity measurements using the Nernst-Planck electrochemical relationship (4,7), the non-ideal nature of the solutions used affect this relationship. Andrade's method (7) also requires the transport number of the chloride ions, ie. what percentage they are contributing to the current. This number varies, and to determine the chloride flux alone would be time consuming. Using the diffusibility ratio eliminates these problems, since both solutions contain the same ions at the same concentrations ie. they have the same chloride transport numbers and the same activity coefficients.

This method is also suited to the proposed conductivity test since the conductivity of the pore solution (σ_0) can be assumed to be very little different from that of the 5 M NaCl saturating solution. This is shown in the next section.

Conductivity of the Concrete Pore Solution

Saturating the concrete samples with a highly conductive solution is aimed at ensuring that all samples have practically the same pore solution conductivity. This assumption was checked as follows:

The conductivity of the saturating salt solution can easily be measured. However mobile ions such as K^+, Na^+ and OH^- are also present in concrete pores, which would increase the conductivity of the pore solution (σ_0). To mechanically express the pore solution of a concrete sample and measure its conductivity is difficult and impractical for routine rapid testing, and hence the value of σ_0 must be assumed.

The conductivities of NaCl solutions of different concentrations were determined experimentally. The same solutions, but containing KOH and $Ca(OH)_2$ were tested to determine what effect these ions have on the conductivity of NaCl solutions. The results are shown in Figure 5.

The rate of increase in conductivity is reduced at higher concentrations mainly because of the increase in viscosity of the solutions. With the combined NaCl and KOH solutions the presence of NaCl makes up the major contribution to conductivity at higher NaCl concentrations. For example, at 5 M NaCl and 0.16 M KOH, NaCl contributes about 92 % of the total conductivity. It was found that the addition of $Ca(OH)_2$ had a negligible effect on conductivity.

The conductivities of nominally similar mortar samples (cored from the same specimen) saturated with NaCl solutions of various concentrations were determined using the conductivity test. Results are given in Figure 6.

The diffusibility ratio (Q) was calculated at different chloride concentrations for the NaCl only curve, the NaCl, 0.16 M KOH curve and the NaCl, 0.32 M KOH curve of Figure 6. Results are given in Figure 7.

From the figure it is clear that the conductivity part of the diffusibility relationship ($Q = \sigma/\sigma_0$) remained sensibly constant at higher chloride concentrations regardless of the assumed levels of KOH in the pore solutions. The figure also shows that at low NaCl concentrations, the diffusibility ratio is very sensitive to the assumed KOH content in the pore solution.

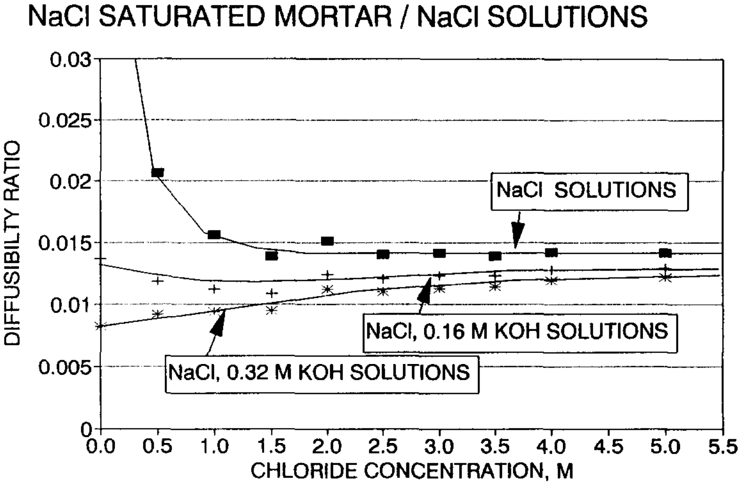


FIG. 7
Diffusibility ratios

The ionic concentrations in the porewater of an ordinary portland cement (OPC) paste and a cement silica fume blend paste were measured by Page and Vennesland (12) and are shown in table 1. The cement used had relatively high Na_2O and K_2O contents of 0.41 % and 1.18 % respectively.

TABLE 1
Porewater Compositions of OPC and Silica Fume Pastes (at 28 days).

@ 28 DAYS	K^+	Na^+	OH^-	SO_4^{2-}
OPC	0.63 M	0.27 M	0.83 M	0.31 M
OPC, 20 % SILICA FUME	0.11 M	0.06 M	0.09 M	0.33 M

The equivalent mobilities of K^+, Na^+ and OH^- are 75, 50 and 200 S/cm²/mole. The pore solution conductivity of the OPC paste would therefore be approximately 7 times higher than that of the silica fume paste. However, after saturating with a 5 M NaCl solution, the conductivity of the OPC pore solution would be only approximately 20 % higher (from figure 5).

Work is in progress to verify that the diffusibility ratio determined from the conduction test is similar to the diffusibility ratio determined from pure diffusion tests. Work is also in progress to correlate the 'theoretical' chloride diffusivity (steady state) with the 'apparent' diffusivity measured in real structures. This would involve other effects such as chloride binding and exposure conditions.

Typical Results

A series of Ordinary Portland Cement (OPC) mixes and OPC fly ash (70/30) blends with target strengths of 20, 40 and 60 MPa were tested. Mixes were wet cured at 23 °C for either 1, 7 or 28 days. The 1 and 7 day cured samples were further cured at 60 % R.H. and 25 °C until 28 days when all samples were tested. The cement compositions are shown in table 2. Mix details are shown in table 3. Three samples were tested for each mix and curing combination. The mean and coefficient of variation of each set of three measured conductivities were calculated. The mean results are shown in Figure 8. Chloride "isoconductivity" lines were interpolated between the measured values. The lowest and highest conductivity results differed by an order of magnitude (0.44 mS/cm to 4.66 mS/cm), and the mean of all the coefficients of variation was calculated to be 6 %. Clear and consistent trends could therefore be established and the sensitivity of the test was demonstrated.

TABLE 2
Cement Composition

%	SiO_2	Al_2O_3	Fe_2O_3	CaO	SO_3	K_2O	Na_2O
OPC	21.1	3.2	3.6	64.4	2.5	0.4	0.3
OPC/FA BLEND	30	11.9	3.5	47.8	1.7	0.4	0.3

TABLE 3
Mix details

TARGET STRENGTH, MPa	OPC MIXES		FLY ASH MIXES	
	W/C	CEMENT/m³	W/(C+FA)	C+FA/m³
20	0.83	240 kg	0.76	245 kg
40	0.55	360	0.48	380
60	0.34	465	0.30	495

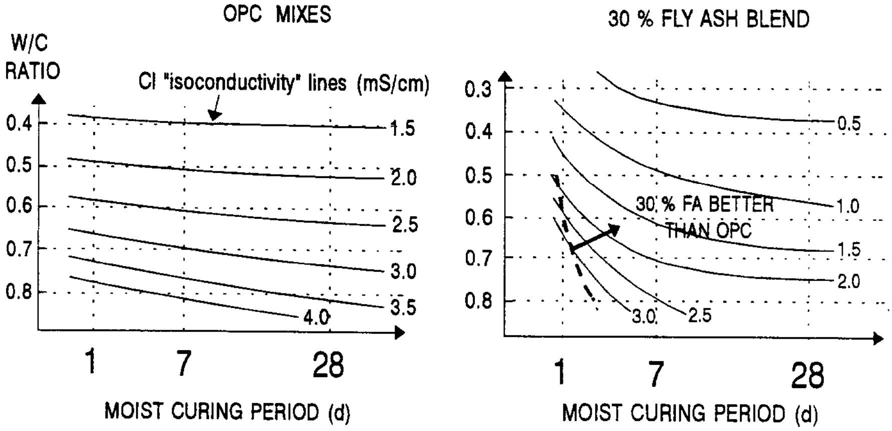


FIG. 8
Chloride 'isoconductivity' graphs for OPC and fly ash mixes

Discussion of results

1) The OPC mixes were not very sensitive to curing in contrast with the fly ash mixes.
2) All the mixes were less sensitive to curing at higher strengths, and more sensitive to curing at lower strengths.
3) An increase in w/c ratio increased the chloride conductivity of all the OPC mixes. The fly ash mixes moist cured for shorter periods were very sensitive to w/c ratio. The fly ash mixes cured for longer periods had very low chloride conductivities and were less sensitive to w/c ratio than the OPC mixes.
4) Substantially lower chloride conductivities were obtained using fly ash mixes with w/c ratios of 0.5 and lower, regardless of curing, and also for all well cured concretes (7 days moist curing and more), regardless of w/c ratio. Only the inadequately cured fly ash mixes with high w/c ratios (1 day moist cured, w/c = 0.8) did not show an improvement over OPC.

Conclusions

The new chloride conduction test has a sound theoretical basis and, as far as can be ascertained, is the most rapid of all chloride tests developed to date. Early results indicate it is repeatable and reproducible. The test is simple to perform and the apparatus is inexpensive. The sample is not altered physically or chemically during the test (instant test) making it possible to test concretes cured for very short periods.

The characteristics of the test make it suitable for various applications.

1) It can be used at the design stage to evaluate different mixes in terms of their potential durability.
2) It can be used as an index test for quality control purposes on concrete structures being built.
3) The effects of different cements and cement blends on chloride diffusivity, as well as other effects such as curing and compaction on the potential durability of concrete can be studied.
4) The effect of chloride binding on chloride diffusivity can also be studied.

Acknowledgements

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