INDUSTRY/FRD COLLABORATIVE RESEARCH PROGRAMME: ACHIEVING DURABLE AND ECONOMIC CONCRETE CONSTRUCTION IN THE SOUTH AFRICAN CONTEXT

SERIES OF RESEARCH MONOGRAPHS

The work reported in this monograph, and others in the series, has arisen chiefly from a research programme into how to achieve durable and economic concrete construction in the South African context. The present programme has been in operation since 1997, and continues the good work achieved in a previous programme under the Foundation for Research Development. The programme is a joint collaborative effort between research students and staff at the Universities of Cape Town and the Witwatersrand. The work of the research students, in particular, is acknowledged. The monographs are essentially compilations of research papers and reports that have emanated from the programme over the past several years.

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M G Alexander, (UCT); Y Ballim (Wits), J R Mackechnie (UCT), March 1999

See inside back cover for a list of monographs in this series

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RESEARCH MONOGRAPH NO. 3

RAPID CHLORIDE CONDUCTIVITY TESTING OF CONCRETE

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INTRODUCTION

Corrosion of reinforcement in concrete structures is probably the greatest problem currently facing the concrete construction industry and its clients. In many countries with developed infrastructures, more than 50% of the construction budget is now expended on repair and maintenance of reinforced concrete structures. Service life prediction, and strategies for life extension of existing structures, have become important areas for research and practical application.

Reinforcing steel in concrete can corrode due to a number of mechanisms, but essentially corrosion results when the protective passive film usually present due to the alkaline nature of concrete is disrupted or destroyed. The mechanism of interest in this monograph is that of chloride attack on the steel surface. This phenomenon arises in situations where chlorides can penetrate the concrete and migrate to the steel, thus causing corrosion. Marine environments as well as the use of de-icing salts in cold climates; give rise to these conditions. Once sufficient chlorides have penetrated the concrete cover layer, corrosion of embedded steel is virtually a self-sustaining process provided sufficient oxygen and moisture is present. Considering the vast scale of this problem locally and world-wide, it is clear that attempts to improve the quality of concrete construction, and in particular the quality of the surface layer of concrete, should be taken seriously.

However, in order to improve the quality of concrete to better resist chloride penetration, it is necessary to have suitable test methods to *characterise* the nature of the as-cast cover layer material. The purpose of this monograph, the third in a series resulting from on-going marine concrete research at the University of Cape Town,(1) is to describe the development of a rapid chloride test method that can assist both designers and constructors to achieve quality concrete construction in the marine environment.

PHILOSOPHY OF THE CONDUCTIVITY TEST METHOD AND ITS USE

The chloride test measures the *conductivity* of the concrete. Conductivity is related to diffusivity, which is the material property governing the rate of penetration of chloride ions. The purpose of measuring conductivity is, firstly, that it is a relevant durability parameter, and secondly that it can be thought of as an *"index" which characterises the intrinsic potential of* *the material to resist chloride penetration*. Such a measurable and unambiguous index of quality, linked to the transport mechanism causing deterioration, allows the characterisation of the concrete at a relatively early age, and can be regarded as a reproducible engineering measure of microstructure and properties of importance to concrete durability.

Measured indexes allow the material to be placed in an overall matrix of possible material performance, these values depending on important material and environmental factors. Thus, it should be possible to produce concretes of required durability by a number of different routes: additional curing, lower w/c ratio, choice of a different cement or extender, etc.

Furthermore, such an indexing approach can ultimately be used as follows:

- as a means of *controlling* a particular property of concrete, or the quality of a particular zone of a concrete element, for example the surface layer. (This control would be typically reflected by a suitable construction specification, in which limits to index values at 28 days are specified).
- as a means of *assessing* the quality of construction for compliance with a set of criteria
- as a basis for *fair payment* for the achievement of concrete quality
- as a means of *predicting* the performance of concrete in the design environment, on an empirical basis.

CRITIQUE OF EXISTING TESTS FOR RESISTANCE TO CHLORIDE PENETRATION OF CONCRETE

"Classical" tests to measure the diffusivity of concrete, while theoretically sound, are generally of too long a duration to be of any practical value. Consequently, voltage-accelerated tests have been developed, most of which are empirical. Such rapid chloride tests have been used to compare the resistance of different concretes to chloride ingress, and to assist in finding economical mixes for high durability applications.

Three types of rapid chloride tests have been developed to date, in which 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(2) test, developed by Whiting(3), 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. This test is in common use particularly in North America. The second type of test is that developed by Dhir et al,(4) who related the steady state chloride flux under a 10 V potential difference empirically to the chloride diffusion coefficient D of the concrete. The third type of test is that of Tang and Nilsson,(5) in which the depth of chloride penetration under a 30 V potential after eight hours is measured, and fundamental electrochemical theory is used to calculate D.

It is important to understand that the electric potential does not accelerate the mechanism of diffusion. The increased flux of ions is caused almost solely by conduction. These tests increase the ionic flux up to 100 times and therefore they are essentially conduction tests with negligible diffusion. Feldman et al(6) 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.

A further problem with the AASHTO test is that it is influenced by differences in the pore water conductivity of various concretes.(7) These differences result in the index obtained not necessarily being proportional to the steady state diffusion coefficient. Cement types such as silica fume blends have very low pore water conductivities, and hence low chloride indexes, which do not necessarily reflect the true resistance of these concretes to chloride ingress. The AASHTO test is the most widely used simply because it is so rapid. However, it can 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.

Objectives of such a test are that it should:

- estimate the steady state diffusivity (physical resistance to chloride ingress) of concrete accurately and have a sound theoretical basis;
- be rapid, efficient and simple to perform;
- be sensitive to the measured property in terms of important material and environmental factors;
- be repeatable and reproducible;
- be of low cost.

Based on electrochemical theory, a very rapid chloride conductivity test has been developed at the University of Cape Town. The test is essentially independent of the concrete pore solution conductivity by virtue of using a high conductivity (5 M) NaCl saturating solution. The test therefore primarily assesses the physical resistance of the concrete microstructure to chloride penetration, and is able clearly to distinguish between different types and grades of concrete. A theoretically sound approach has also been proposed to determine the steady state diffusion coefficient of concrete using this new test. The test has been found to be a useful tool in the accurate prediction of chloride ingress into structures.(1)

This monograph deals with the following topics:

- electrochemical background to the test method;
- details of test method and equipment;
- influence of governing factors;
- use of the chloride test and typical results.

ELECTROCHEMICAL BACKGROUND TO THE TEST METHOD

The new chloride test is based on the ionic distribution that pertains during steady state conduction. With diffusion tests, a period of a year or more is needed before steady state conditions are achieved in concrete specimens of suitable thickness. For voltage-accelerated tests, steady state conduction conditions are achieved much earlier, typically within a week. However, the ionic distribution during steady state conditions differs for the two types of tests. With steady state diffusion the concentration gradient is the driving force and has a constant slope (see Figure 1). For conduction the driving force is the electric field. 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 at the start on one side only, chloride ions move through the concrete in a well-defined front.(5) Steady state conditions occur when the front has passed through the concrete sample, and the chloride concentration in the pore solution is then uniform (see Figure 3). It is this fact that has been exploited to develop a very rapid chloride test, since the same condition can be achieved in a much shorter time by vacuum-saturating a concrete sample with a chloride solution. This permits steady state conditions to pertain from the start.

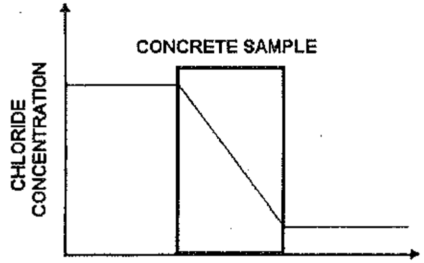


Figure 1: Steady state diffusion

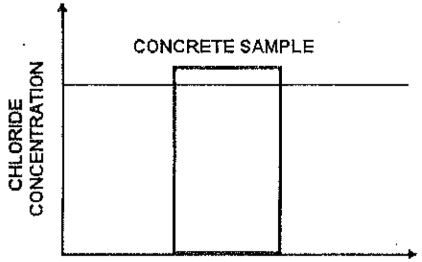


Figure 2: Steady state conduction

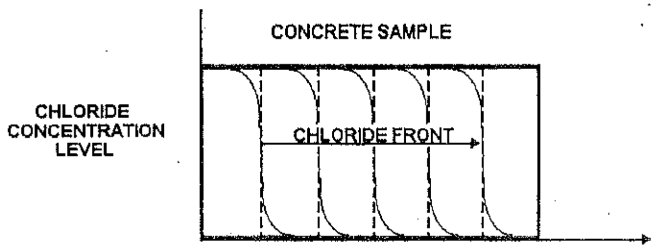


Figure 3: Chloride front in conduction tests

To avoid dilution of the chloride solution inside the concrete, samples require drying prior to saturation. The test is further simplified by measuring the electric current(3,8) instead of the chloride flux.(4) A conductivity value can easily be calculated from the current measurement.

(Further details on the electrochemical background to the test method, and the diffusibility relationship, are given in the Appendix).

TEST METHOD AND ARRANGEMENT

The conductivity test apparatus consists of two 500 ml cells adjacent to a central section containing the concrete sample (see Figure 4 and Plates 1 (a) and (b)). 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 (salt) solution. By holding the apparatus alternately in a vertical position each cell can be removed without spilling the cell solution. See Figure 5.

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 (Luggin capillaries) 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. The voltmeter and the ammeter are arranged as shown when the readings are taken.

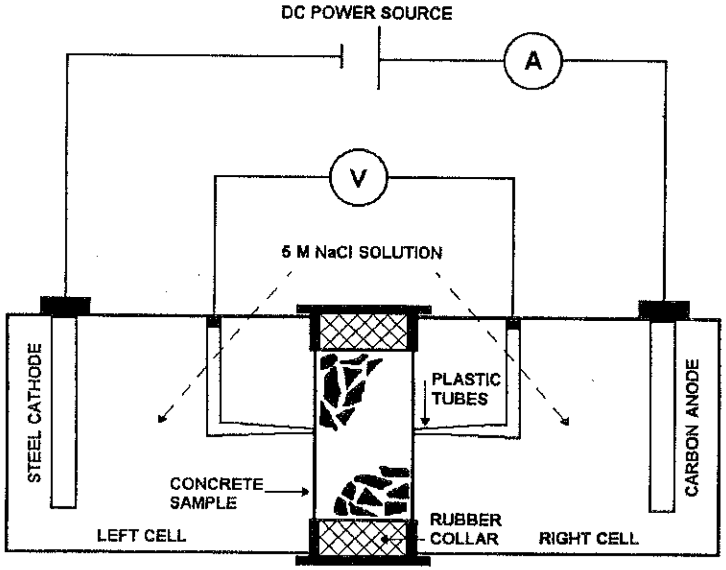


Figure 4: Schematic diagram of conductivity apparatus

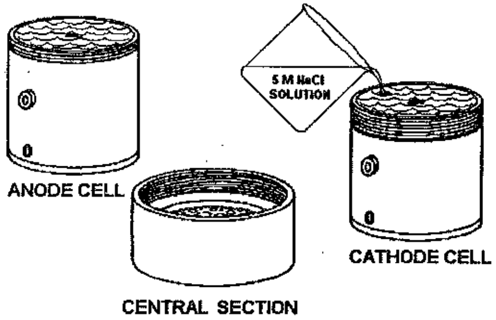


Figure 5: Filling of cells with salt solution

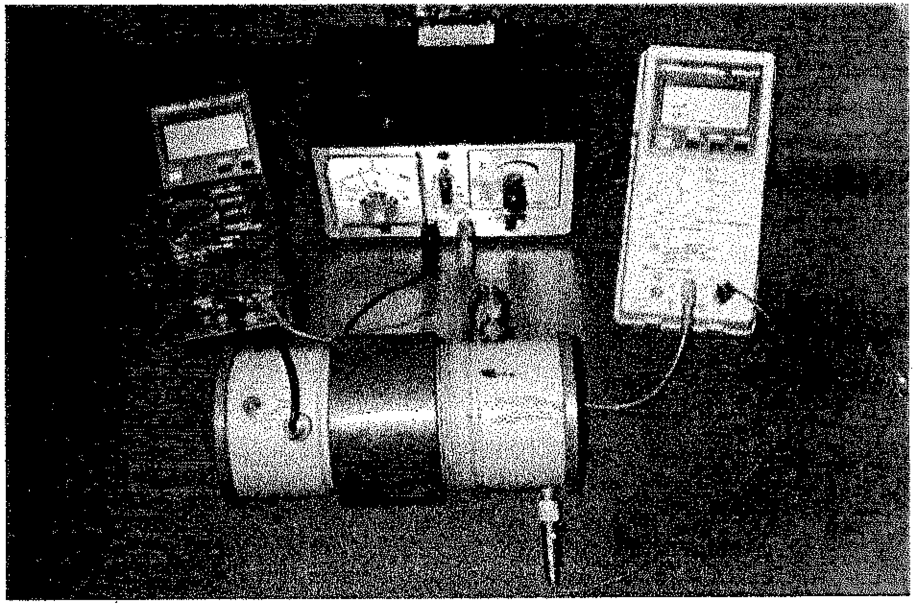
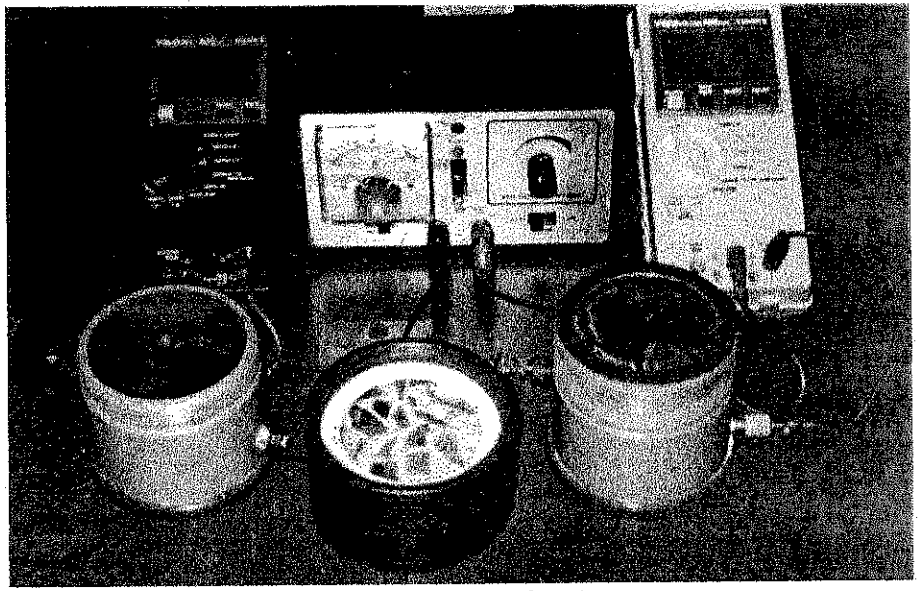


Plate 1: Chloride conductivity apparatus (a) Assembled



(b) Component parts of equipment

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. With experience, it is possible to test up to 20 samples per hour. During the short duration of the test, relatively few ions migrate and small volume cells can therefore be used.

Test method

Full details of the test, in the form of a Draft Standard Test Method, are supplied in Monograph 4 in this series (*Concrete durability index testing manual*). The appendix contains a full review of the electrochemical theory behind the test, and of the work done in developing and proving the test method. The following sections summarise the essential aspects of the test, and the influence of important factors.

Sample preparation

The test apparatus was designed for mortar or concrete samples of 68 mm diameter, and thicknesses of between 10 and 40 mm. (Similar apparatus can be designed for other sample diameters). Usually mortar and concrete samples 25 mm thick are tested. The sample is cored with a diamond tipped core barrel. The core size is suitable for samples to be retrieved either from laboratory specimens, or from actual structures; for the latter, a hand-held coring machine may be used. The core is then sliced using a diamond saw. The average thickness of each disc is measured with a vernier calliper.

The sample size and test method makes the test very suitable for studying environmental and other influences such as type and duration of curing, use of different cementitious materials, effects of site compaction, and so on.

Conditioning of sample

The concrete discs are placed in an oven at 50°C for seven 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.

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. Although less water will be removed at 50°C compared with drying at 100°C, trials in our laboratory using samples dried at the two temperatures showed that the difference was insignificant. In any event, conductivity is relatively insensitive to small changes in concentration at high concentrations (see Figure 6).

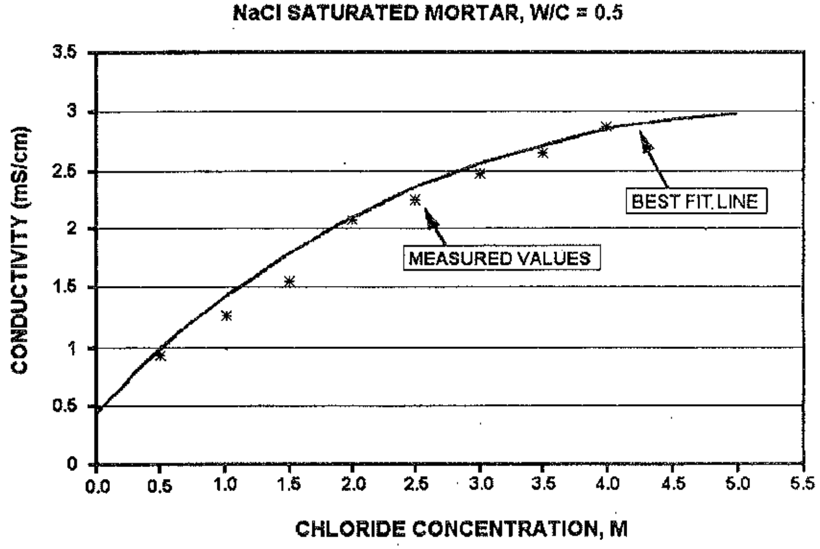


Figure 6: Conductivity of mortars saturated with chloride solutions of different concentrations

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.

The period of vacuum saturation depends on the sample thickness, and five hours (plus fifteen hours soaking) has been found to be more than adequate for 25 mm thick samples. Samples of 25 mm thickness generally 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.

The purpose of using the high concentration 5 M NaCl solution is to ensure that the test assesses the resistance of the concrete microstructure to the passage of chloride ions, rather than the inherent conductivity of the pore solution. A simple resistivity test would measure the latter, but may not properly represent the chloride resistance of the material. Presaturation with a 5 M solution minimises these problems.

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 in Figure 4, 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.

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

$$\sigma = \frac{i\,t}{VA} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots (1)$$

where σ - conductivity of sample [mS/cm]
i - electric current [mA]
V - potential difference [V]
t - thickness of sample [cm]
A - cross-sectional area of sample [cm^2]

The appendix contains details of the development of the test, and of a ruggedness test carried out to determine the sensitivity of the test to various factors. In terms of the sample preparation the only factors found to be critical in terms of control were the vacuum saturation time, and the subsequent soaking period before testing. Thus, these parameters are restricted to 5 + 0,5 hours, and 18 ± 1 hours respectively. In all other respects, the test was shown to be sufficiently rugged for use in different laboratories.

Regarding the influence of materials and environmental factors, typical results are shown in Figure 7.(1) It is clear that:

- Concrete grade and, more importantly, cement type have profound influences. Thus, higher concrete grades are more resistant to chloride ingress, as would be expected, with the lower to intermediate strength grades showing larger improvements with strength.

  The use of blended cements – in this case fly ash and ggbs (slag) – can result in very substantial improvements in chloride resistance. This also means that lower strength grades might be used for these mixes while still retaining adequate chloride resistance.
- The influence of initial curing is also important, particularly for lower grade concretes. Thus, there is both engineering and economic sense in ensuring that adequate curing is carried out on site.

(Care should be taken when interpreting results of this test when it is used on surface treated concretes. For this reason, it is good practice to slice off the surface 5 mm of core samples before cutting them to the required 25 mm thickness.)

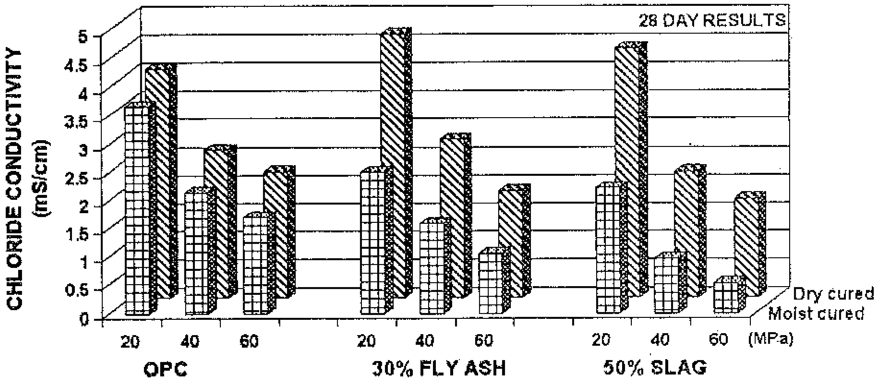


Figure 7: Conductivity as a function of cement type and curing

PRACTICAL USE OF THE RAPID CHLORIDE TEST

As confidence in use of the UCT rapid chloride test grows, so other applications in both research and construction will be found. The following uses are suggested, for which limited experience is already available.

a) Development of chloride resistant concretes

The ease with which the test is carried out readily allows optimisation of mix designs and choice of materials for chloride resistant concretes. In addition to the examples shown in Figure 7, work has been carried out in the laboratory to examine other cementitious materials, and choice of mix proportions.

Figure 8 shows results(9) for a series of laboratory concretes using Western Cape materials (other than the cement extenders), in which

- w/binder ratio varied from 0,49 to 0,66;
- portland cement, ggbs and csf were used as binders, in the ratios 100% pc, 50/50 pc/ggbs, 90/10 pc/csf, and 50/40/10 pc/ggbs/csf;

- curing comprised full water curing for 28 d, or 3 days of water curing followed by 25 d of air curing at 55% R.H. (all at 22°C).

The use of cement extender materials greatly reduces the chloride conductivity of the concrete. In our experience, it is virtually impossible to produce a chloride-resistant concrete without the use of a cement extender. Both ggbs and csf (and, of course, fly ash) have very beneficial effects on the initial chloride conductivity values. Ggbs has the added benefit of being able to bind chloride ions with time, thus further limiting their ingress into the concrete. The use of blended mixes of ternary pc/ggbs/csf combines the pore refining and microstructural densification properties of csf with the chloride binding properties of ggbs, and gives very low chloride conductivity values.

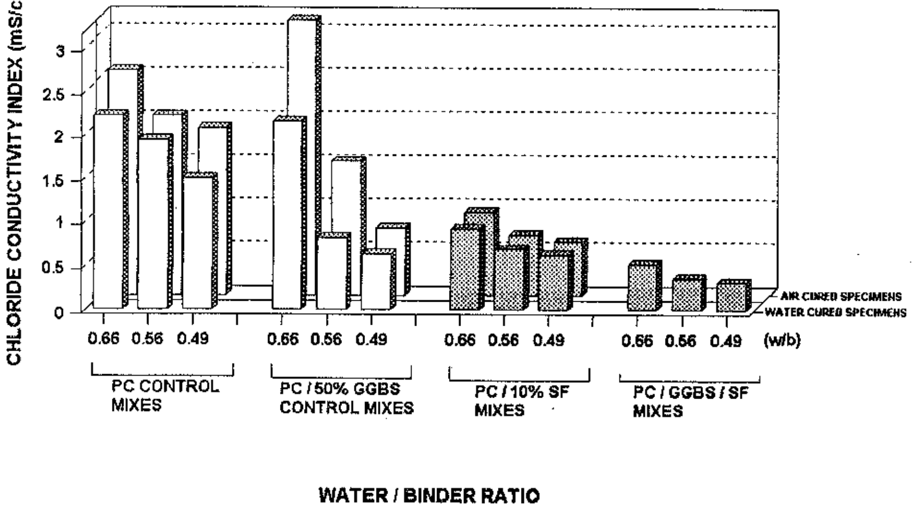


Figure 8: Conductivity for concretes made with Western Cape materials (other than the cement extenders)

b) Control of concrete quality during construction, and performance specifications

The test method is suitable for use as a quality control test on construction projects. Since the property of concern, i.e. chloride resistance, is being measured, it is possible to set limits on acceptable values during routine sampling of site mixes. In this way, it can be ensured that concrete of the required quality and type is being produced. Random sampling of portions of the actual structure by means of small diameter cores could also be used to check on construction quality (e.g. compaction and control on curing).

For this approach to be successful, there are several other requirements:

i. the development of suitable statistical criteria for acceptance or rejection of a test result;
ii. maximum values which a test determination should not exceed;
iii. action to be taken in the event of non-compliance with the above criteria;
iv. a possible basis of payment for the achievement of the required quality, and penalties for non-achievement.

The points raised above are essentially the issues that would need to be incorporated in a performance specification for durability in, say, a marine environment. Although such a specification has not yet been drafted, preliminary suggested limits for chloride conductivity values are given in Table 1.

Table 1: Suggested maximum values for chloride conductivity of concretes for use in marine environments (assuming 50 y design life, 60 mm cover, and moderate moist curing)

Exposure	*Maximum chloride conductivity (mS/cm)*			
	Type of cement			
	OPC	*70/30 OPC/FA*	*50/50 OPC/Slag*	*90/10 OPC/CSF*
Tidal zone and splash zone	0,80	1,50	1,25	0,40
Spray zone	1,25	2,00	1,5	0,50

As an illustration of the application of this approach to site construction, results are given in Figure 9 from the testing of actual structural elements which were cored and tested for chloride conductivity at 28 d after casting.(10)

All concretes used plain OPC as binder, except Site 5 which comprised a 25% fly ash blend. The sites from which the samples were cored for testing were scattered over the Cape Peninsula area, and concretes were cast at different times of the year and subjected to varying site curing regimes. Thus, the results represent the range of conductivity values that can be obtained in typical site conditions. This range is wide, reflecting variable site practices and environmental influences. Nevertheless, it is interesting to note that several site concretes achieved better results than fully cured lab samples comprising similar materials, shown by the dashed line in Figure 9.

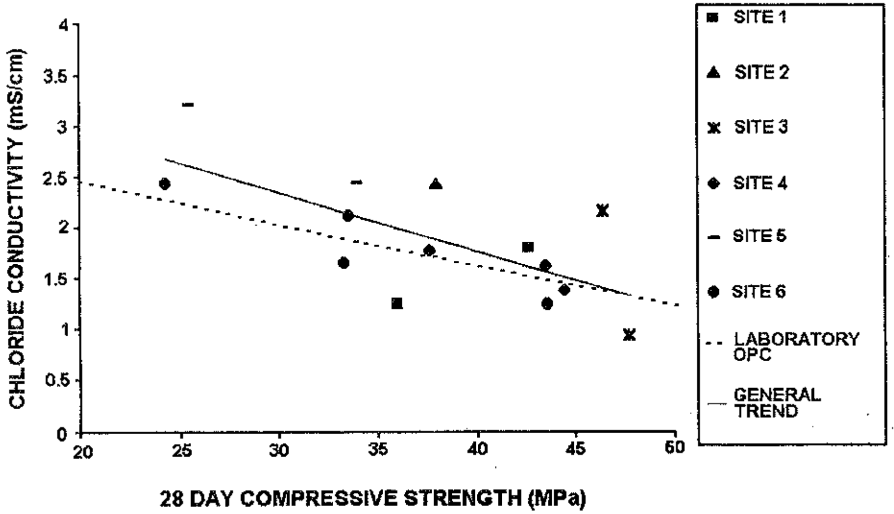


Figure 9: Chloride conductivity of actual structural elements, at 28 d[(10)]

It is the authors' opinion that an approach in which material indexes of site concretes are measured and compared with acceptable values, particularly if coupled with post-construction checks on concrete cover, would result in a vast improvement in concrete durability.

c) Prediction of long-term durability performance

One of the most powerful potential uses of the rapid chloride test is the prediction of long-term durability performance. Since the test is closely related to chloride transport and binding mechanisms occurring in practice, it can be expected that conductivity values should correlate with long-term chloride ingress into concrete structures. The fact that a short term (28 d) measure of conductivity can be used to predict long-term ingress is a very powerful aid in durability design. An example of this approach is given below.

A series of portland cement-based concretes together with fly ash and slag concretes were cast as 300x300x450 mm blocks.[(11)] Water/binder ratios varied from 0,30 to 0,85, with fly ash replacements varying between 30% and 50%, and ggbs replacements between 50% and 70%. The concretes were wet cured for three days after demoulding before being dry cured at 60% R.H. and 23°C, and then exposed at Simonstown at the age of two months.

Good correlations were found between 28 day chloride conductivity values and diffusion coefficients measured after two years (shown in Figure 10). A similar trend was also found between chloride conductivity and critical chloride depth (shown in Figure 11). (Critical chloride depth is the depth into the concrete at which the total chloride concentration equals 0,4% by mass of binder; the 0,4% limit is regarded as a practical threshold limit for initiation of steel corrosion).

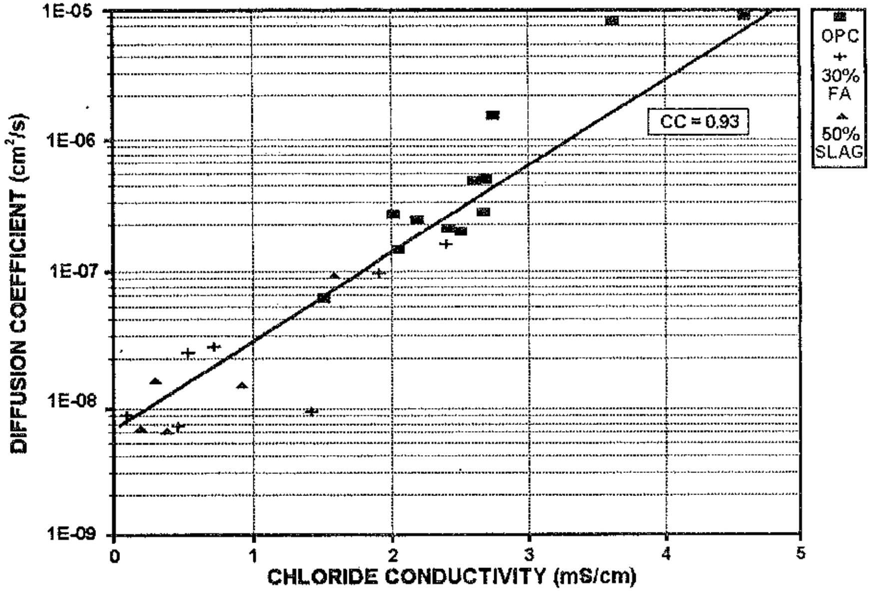


Figure 10: Chloride conductivity versus diffusion coefficient, after two years marine exposure

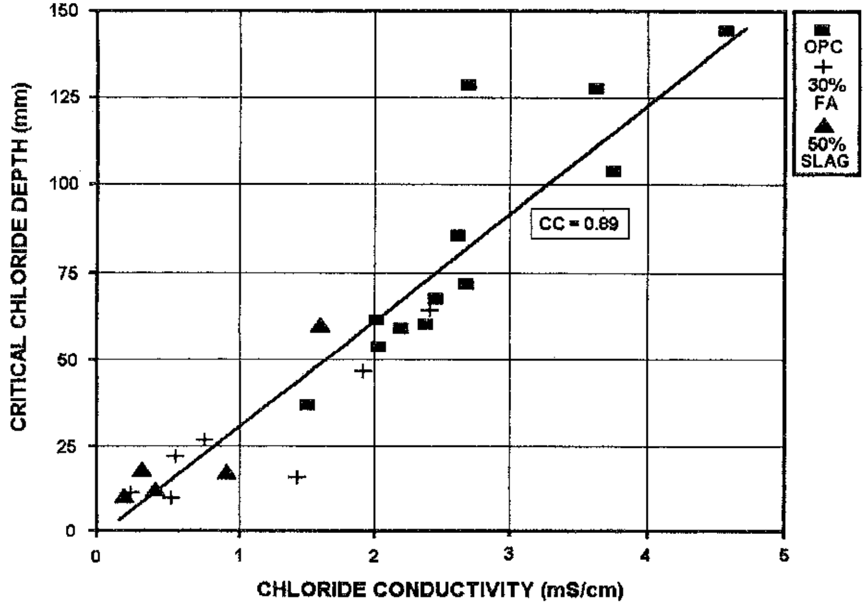


Figure 11: Chloride conductivity versus critical chloride depth, after two years marine exposure

It is clear from the figures that, for this marine exposure site, good correlations were achieved which permit the early age conductivity measurement to be used for predicting long term chloride ingress. This approach is also the basis of the Durability Design Monograph of Mackechnie.(1)

CONCLUSIONS

The new chloride conductivity test has a sound theoretical basis and, as far as can be ascertained, is the most rapid of all chloride tests developed to date. Results indicate it is repeatable and reproducible with the coefficient of variation of the test being generally less than 7%. The test is simple to perform and the apparatus is inexpensive.

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

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

APPENDIX
DEVELOPMENT AND PROVING OF TEST METHOD

A.1 Diffusibility relationship and conductivity of pore solutions

Relationships between diffusivity and conductivity
At low ionic concentrations of a conducting solution, diffusion and conduction are linearly related by Einstein's relationship:

$$\mu = zF\frac{D}{RT} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots (2)$$

where μ - mobility of ion
z - charge of ion
F - Faraday's constant
D - diffusivity of ion
R - gas constant
T - absolute temperature

Other relationships, such as the Nernst-Planck equation involving diffusion and conduction parameters, are usually derived from Einstein's equation and apply only under ideal conditions.(12)

In a saturated porous medium, where the solid phase is a non-conductor such as in concrete, the rate of diffusion and conduction is affected by the tortuosity and constrictivity of the pore structure.(13) 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.(13,14)

$$Q = \frac{D}{D_o} = \frac{\sigma}{\sigma_o} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots (3)$$

where Q - diffusibility of porous material
D - diffusivity of ion through porous material
D_o - diffusivity of ion through pore solution
σ - conductivity of porous material
σ_o - conductivity of the pore solution

The chloride diffusivity of a porous medium can therefore theoretically be obtained from conductivity measurements of the porous medium, and of the pore fluid. Knowing the diffusivity of chloride ions in the pore solution, the chloride diffusivity of the porous medium can be obtained.

Tang and Nilsson(5) and Andrade(8) have determined the diffusivity of concrete from conductivity measurements using the Nernst-Planck equation. However, the non-ideal nature of the solutions affect this relationship. Andrade's method also requires the transport number of the chloride ions (i.e. 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, i.e. they have the same chloride transport numbers and the same activity coefficients.

The UCT conductivity test is suited to the method in equation (3) since the conductivity of the pore solution (σ_o) 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 helps ensure that all samples have practically the same pore solution conductivity. The validity of this assumption is explored below.

The conductivity of the saturating salt solution is governed by its ionic strength, and can 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_o). 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_o must be assumed.

The conductivities of NaCl solutions of different concentrations were measured. 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 12.

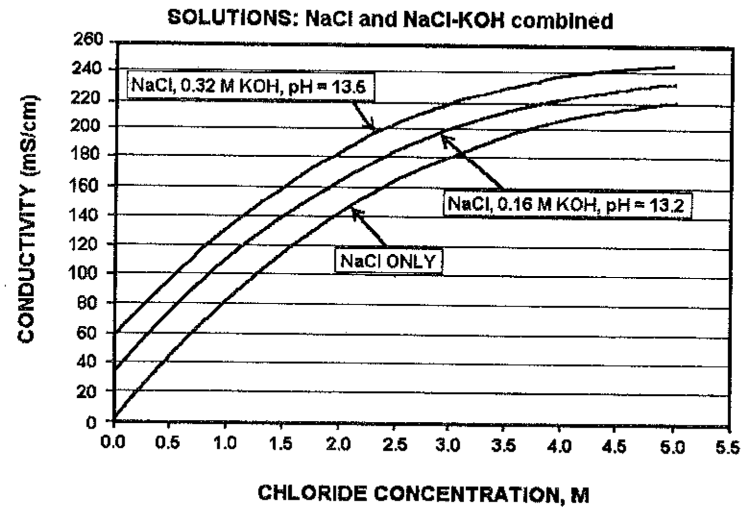


Figure 12: Conductivities of various chloride and chloride/hydroxide solutions

The rate of increase in conductivity reduces at higher concentrations mainly because of the increase in viscosity of the solutions. The presence of NaCl provides the major contribution to conductivity of the solutions 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 mortar samples (all cored from the same specimen) saturated with NaCl solutions of different concentrations were determined using the conductivity test. Results were shown previously in Figure 6. Using the best fit line of Figure 6, the diffusibility ratio (Q) was calculated at different chloride concentrations for the curves of Figure 12. Results are given in Figure 13.

The conductivity part of the diffusibility relationship ($Q = \sigma/\sigma_o$) remains sensibly constant at higher chloride concentrations regardless of the concentration of KOH in the pore solutions. At low NaCl concentrations, the diffusibility ratio is very sensitive to the KOH in the pore solution.

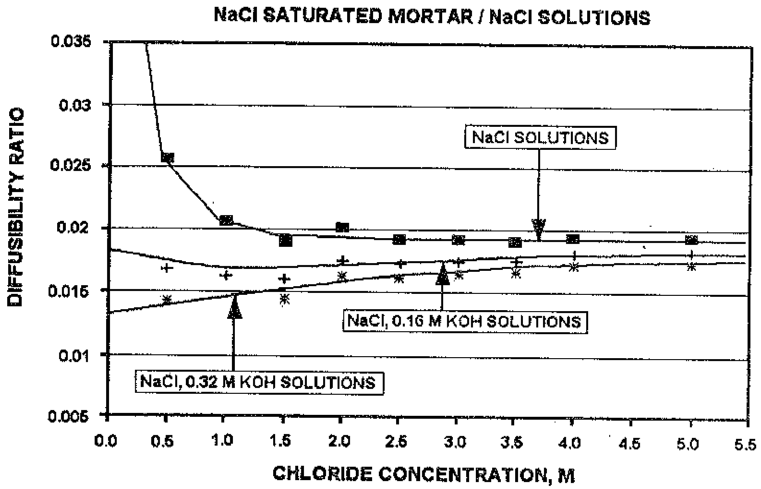


Figure 13: Diffusibility ratios of various solutions

Page and Vennesland(15) have reported the ionic concentrations in the porewater of an ordinary portland cement (OPC) paste and a cement silica fume paste – see Table 2. The cement used had relatively high Na_2O and K_2O contents of 0,41% and 1,18% respectively.

Table 2: Porewater compositions of OPC and silica fume pastes (at 28 days) (after Page and Vennesland(15))

	K^+	Na^+	OH^-	SO_4^{2-}
OPC	0.63 M	0.27 M	0.83 M	0.31 M
80 %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/cm^2/mole. The pore solution conductivity of the OPC paste would therefore be approximately seven times higher than that of the silica fume paste. However, after saturating with a 5M NaCl solution, the conductivity of the OPC pore solution would be only approximately 20% higher (from Figure 12). Thus, the test method would give a better representation of the physical resistance of a concrete matrix to chloride ingress than the AASHTO or similar tests, on the basis that it standardises the pore solution conductivity.

Influence of governing factors

Material and environmental factors

The first requirement for any new test purporting to measure a critical property such as resistance to chloride ingress is that it should be sensitive to the important material and environmental factors known to influence actual performance. These factors are:

- cement type, e.g. OPC, or blends of OPC with supplementary cementitious materials such as fly ash and ground granulated blast furnace slag (ggbs);
- concrete strength, in particular w/c ratio, since this is the primary factor influencing strength;
- curing of the concrete.

Several large test programmes have been conducted over a number of years in the UCT labs, using typical South African materials. The results of all these tests have been used to check the influence of the above factors. Binders for the mixes comprised Ordinary Portland Cement (OPC), OPC/fly ash (70/30), OPC/slag (50/50), and OPC/Condensed Silica Fume (90/10) blends. Target strengths varied from 20 to 60 MPa. 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. Three samples were tested for each mix and curing combination.

The mean results are shown in Figure 14[16] in the form of chloride "isoconductivity" lines which were interpolated between the measured values. The lowest and highest conductivity results differed by an order of magnitude (c. 0,5 mS/cm to c. 5,0 mS/cm), and the mean of all the coefficients of variation was calculated to be about 6%. Clear and consistent trends could therefore be established and the sensitivity of the test to the various factors was demonstrated.

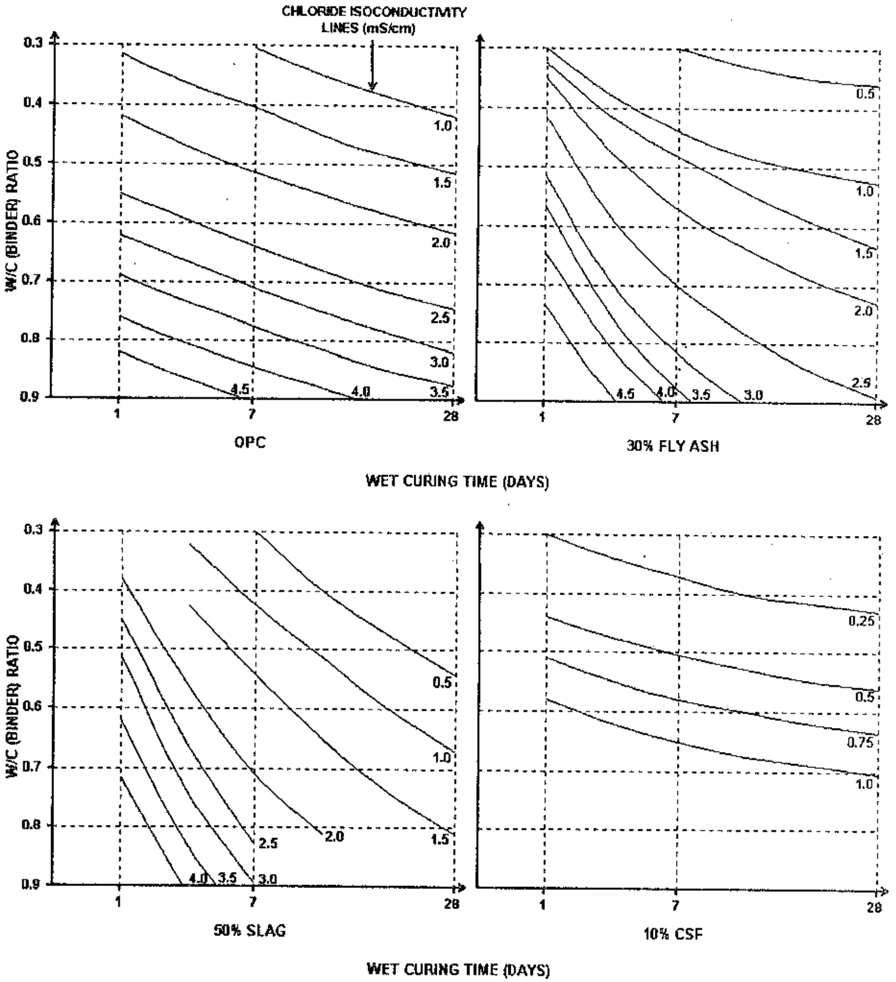


Figure 14: Chloride isoconductivity charts (for different binder types)

From Figure 14, it can be seen that OPC mixes are not as sensitive to curing as are fly ash and slag mixes. All the mixes were less sensitive to curing at higher strengths (lower w/c), and more sensitive to curing at lower strengths (higher w/c). An increase in w/c ratio increased the chloride conductivity of all the OPC mixes. The fly ash and slag mixes moist cured for shorter periods were very sensitive to w/c ratio. The blended mixes cured for longer periods had very low chloride conductivities, in particular the slag mixes. Substantially lower chloride conductivities were obtained using blended mixes with w/c ratios of 0.7 and lower, regardless of curing, and also for all well cured concretes (seven days moist curing and more), regardless of w/c ratio.

Factors involved in the test

Test factors include effects such as sample thickness, nature and concentration of the saturating solution, temperature etc. A full discussion of all of these effects is beyond the scope of this monograph, but is included in ref. 17. The influence of the test factors was examined using a ruggedness test procedure (ASTM E 1169-89),(18) in which a statistically designed series of experiments is carried out to determine whether a measurement process is sufficiently rugged to withstand small changes in operating conditions which may occur if the test is run in different laboratories.

The variables associated with the test were considered to be:

- Variables included in the conductivity relationship (equation 1): applied voltage; measured current; sample thickness; cross-sectional area of sample.
- Variables not reflected in the conductivity relationship: concentration of saturating solution; temperature.
- Factors affecting the assumed conditions of the test: concentration of cell solution; time of oven drying; time of vacuum saturation; time of immersion before test; time of reading after voltage is applied.

The conductivity relationship is a fundamental electrochemical relationship, and as such need not be verified. A separate series of tests in which specimen thicknesses were varied showed that, for thicknesses between 20 and 30 mm, the conductivity relationship governs the test, and this variable is not significant within the given range. These variables were therefore excluded from the ruggedness test. The remaining factors used in the ruggedness test were:

Concentration of saturating solution; temperature. The conductivities of solutions are related to ionic concentration and temperature. In the test method, 'chloride conductivity' is defined as the dc conductivity of an initially dry concrete sample saturated with a 5 M NaCl solution at 25°C. In the ruggedness test, the conductivity range used was 4,5 to 5 M, and the temperature range was 22 to 25°C.

Concentration of cell solution. Ideally the test results should be independent of the conductivity of the cell solutions. (The test apparatus was designed to achieve this by using Luggin capillaries). This variable was included in the ruggedness test to verify that the results were for all practical purposes independent of the cell solution conductivity. Cell solution concentrations varied from 1 to 5 M NaCl solutions.

Oven drying time; Vacuum saturation. The test method assumes that the concrete samples are sufficiently dry after oven drying, and sufficiently saturated after vacuum saturation so as not to affect the test result. Incomplete drying could lead to the dilution of the saturating solution which would reduce the conductivity of the sample. Incomplete saturation could also lead to a decrease in conductivity. Drying and saturation times are dependent on the specimen size and the quality of the concrete. The ruggedness test results therefore apply only for specimens approximately 25 mm in thickness, and of the same quality in terms of microstructure (effectively concretes of strength less than about 60 MPa). Oven drying times varied between 7 and 14 d, and vacuum saturation times between 2 and 5 hours.

Immersion time. The saturated concrete will continue to cure, resulting in a more refined pore structure. Chloride ions will also be bound by the cement, removing them from solution, and affecting the pore structure. These factors will reduce the conductivity of the concrete. Immersion times varied between 0 and 18 hours.

Reading time. The test apparatus is not designed to maintain the steady state conditions for very long (which would require cells with larger volumes, stabilisation of pH in the cell solutions, and control over temperature in the cells). The reading times were accordingly varied between 0 and 2 minutes.

The influence of variation in the above factors was assessed in a carefully designed programme, in which extra care was taken to reduce inherent sample variability, using a 40 MPa OPC concrete. Full details are given in ref. 17. The results of the ruggedness test showed that, at the 95% significance level, only the factors of vacuum saturation time and immersion (soaking) time require controls closer than those given above. In view of this, the specifications chosen for these factors in the standard test method were:

Vacuum saturation time: 5 + 0.5 hours
Immersion time: 18 ± 1 hours

The remaining factors would not require more stringent specifications on a statistical basis. For practical purposes, however, closer limits are prescribed for most of these factors in the standard test method. (See Monograph 4 in this series: *Concrete durability index testing manual).*

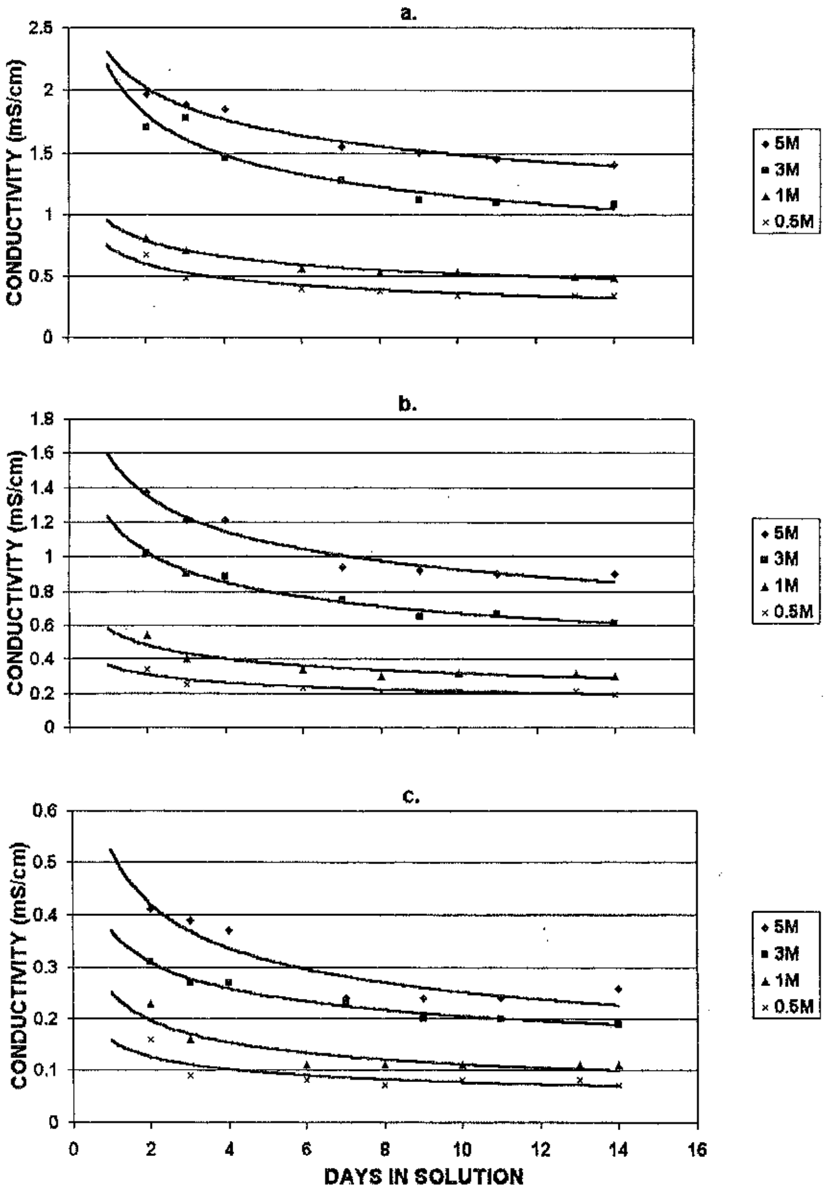


Figure 16: Conductivity reductions with time for concretes with different binders
a. OPC b. 90/10 OPC/CSF c. 50/50 OPC/Slag

In comparison with OPC concretes, slag concretes have substantially lower initial conductivities, and also approach very much lower final conductivities after two weeks of soaking in the chloride solution. This also helps to explain their superior performance in chloride environments.

The mechanics and kinetics of the above processes are still the subject of much research. Nevertheless, it appears that the chloride conductivity test may be useful to assess long-term chloride binding effects over a relatively short test period.

REFERENCES

1. Mackechnie, J. R., 'Predictions of reinforced concrete durability in the marine environment', Research Monograph, University of Cape Town, 1997.
2. Standard Method of Test for Rapid Determination of the Chloride Permeability of Concrete, AASHTO T-277-83, Washington D.C., 1229-1234, 1983.
3. Whiting, D., 'Rapid Determination of the Chloride Ion Permeability of Concrete', Final Report No. FHWA/RD-81/119, Federal Highway Administration, 1981.
4. Dhir, R. K., Jones, M. R., Ahmed, H. E. H., and Seneviratne, A. M. G., 'Rapid estimation of chloride diffusion coefficient in concrete', Magazine of Concrete Research, 42 (152), 1990, pp 177-185.
5. Tang, L., and Nilsson, L. O., 'Rapid determination of the chloride diffusivity in concrete by applying an electrical field', ACI Materials Journal, 89 (1), 1992, pp 49-53.
6. Feldman, R. F., Gordon, W. C., Brousseau, R. J., and Tumidajski, P. J., 'Investigation of the rapid chloride permeability test', ACI Materials Journal, 91 (3), 1994, pp 246-255.
7. Streicher, P. E. and Alexander, M. G., 'A critical evaluation of chloride diffusion test methods for concrete', Proceedings 3rd CANMET/ACI Int. Conference on Concrete Durability, Nice, France, 1994, Supplementary Papers, ACI, Detroit, 1994, pp 517-530.
8. Andrade, C., 'Calculation of chloride diffusion coefficients in concrete from ionic migration measurements', Cement and Concrete Research, 23 (3), 1993, pp 724-742.
9. Magee, B. J., Performance of Silica Fume concrete, Research Report 1/98, Concrete Materials Research Group, University of Cape Town, 1998, 79 pp.
10. Bouwer, S. M., Practical implementation of index tests for assessment and control of potential concrete durability, MEng Thesis, University of Stellenbosch, September 1998.
11. Streicher, P. E., The development of a rapid chloride test for concrete, and its use in engineering practice, PhD Thesis, University of Cape Town, 1997.
12. Bockris, J. O. M., and Reddy, A. K. N., Modern Electrochemistry, London: Macdonald, 1970.
13. Atkinson, A., and Nickerson, A. K., 'The diffusion of ions through water-saturated cement', Journal of Materials Science, 19, 1984, pp 3068-3078.

14. Garboczi, E. J., and Bentz, D. P., 'Computer simulation of the diffusivity of cement-based materials', Journal of Materials Science, 27, 1992, pp 2083-2092.
15. Page, C. L., and Vennesland, O., 'Pure solution composition and chloride blending capacity of silica-fume cement paste', Mat. and Struct., 16 (91), 19-25 (1983).
16. Streicher, P. E., PPC/UCT Research Project: Durability of marine cements. Final Project Report, August 1996, University of Cape Town, 1996.
17. Streicher, P. E. and Alexander, M. G. 'Towards standardisation of a rapid chloride conduction test for concrete', To be published in ASTM Journal: Cement, Concrete and Aggregates, 1999.
18. ASTM E 1169-89, Standard guide for conducting ruggedness tests, Amer. Society for Testing and Materials, 1989.
19. ASTM E 178-80, Standard practice for dealing with outlying observations, Amer. Society for Testing and Materials, 1980.
20. Arya, C., Buenfeld, N.R., and Newman, J. B., ' Factors influencing chloride binding in concrete', Cement and Concrete Research, 20 (2), 1990, pp 291-300.
21. Alexander, M. G. and Streicher, P. E. 'Proposal for a rapid chloride binding test for concrete', Proceedings, Int. Symposium on High-Performance and Reactive Powder Concretes, Sherbrooke, Aug. 1998, Eds. P-C Aitcin and Y. Delagrave, Vol. 2, Univ. of Sherbrooke, 1998, pp 421–437.