Testing the Chloride Penetration Resistance of Concrete: A Literature Review

by

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1.0 INTRODUCTION

Reinforced concrete structures are exposed to harsh environments yet are often expected to last with little or no repair or maintenance for long periods of time (often 100 years or more). To do this, a durable structure needs to be produced. For reinforced concrete bridges, one of the major forms of environmental attack is chloride ingress, which leads to corrosion of the reinforcing steel and a subsequent reduction in the strength, serviceability, and aesthetics of the structure. This may lead to early repair or premature replacement of the structure. A common method of preventing such deterioration is to prevent chlorides from penetrating the structure to the level of the reinforcing steel bar by using relatively impenetrable concrete. The ability of chloride ions to penetrate the concrete must then be known for design as well as quality control purposes. The penetration of the concrete by chloride ions, however, is a slow process. It cannot be determined directly in a time frame that would be useful as a quality control measure. Therefore, in order to assess chloride penetration, a test method that accelerates the process is needed, to allow the determination of diffusion values in a reasonable time.

2.0 OBJECTIVES AND SCOPE

In this document, a review of the current common methods for determining chloride penetrability of concrete is presented. First, some theoretical background of what influences the penetration of chlorides into concrete is presented in Section 3. The different mechanisms of chloride penetration are presented, followed by a further elaboration of the chloride diffusion theory. The influence of basic properties of concrete on its chloride penetrability is also discussed. In Section 4, individual test procedures are presented. First, the existing long-term procedures are discussed, namely the salt ponding (AASHTO T259) test and the Nordtest (NTBuild 443) bulk diffusion test. The existing short-term tests are then presented. For each test, the procedure, the theoretical basis, and any advantages and disadvantages are presented.

Also included in this document as an appendix is a glossary of some of the common terms related to chloride ingress testing and measurement.

3.0 THEORETICAL BACKGROUND

3.1 Mechanisms of Chloride Ion Transport

Capillary absorption, hydrostatic pressure, and diffusion are the means by which chloride ions can penetrate concrete. The most familiar method is diffusion, the movement of chloride ions under a concentration gradient. For this to occur, the concrete must have a continuous liquid phase and there must be a chloride ion concentration gradient.

A second mechanism for chloride ingress is permeation, driven by pressure gradients. If there is an applied hydraulic head on one face of the concrete and chlorides are present, they may permeate into the concrete. A situation where a hydraulic head is maintained on a highway structure is rare, however.

A more common transport method is absorption. As a concrete surface is exposed to the environment, it will undergo wetting and drying cycles. When water (possibly containing chlorides) encounters a dry surface, it will be drawn into the pore structure though capillary suction. Absorption is driven by moisture gradients. Typically, the depth of drying is small, however, and this transport mechanism will not, by itself, bring chlorides to the level of the reinforcing steel unless the concrete is of extremely poor quality and the reinforcing steel is shallow. It does serve to quickly bring chlorides to some depth in the concrete and reduce the distance that they must diffuse to reach the rebar [Thomas, et al., 1995].

Of the three transport mechanisms described above that can bring chlorides into the concrete to the level of the rebar, the principal method is that of diffusion. It is rare for a significant hydraulic head to be exerted on the structure, and the effect of absorption is typically limited to a shallow cover region. In the bulk of the concrete, the pores remain saturated and chloride ion movement is controlled by concentration gradients. A fuller review of the theory of diffusion is presented in the following section.

3.2 Chloride Diffusion: A Brief Review of the Underlying Theory

Chloride diffusion into concrete, like any diffusion process, is controlled by Fick's First Law, which, in the one-dimensional situation normally considered, states:

$$J = -D_{eff} \frac{dC}{dx} \tag{1}$$

where J is the flux of chloride ions, D_{eff} is the effective diffusion coefficient (see below), C is the concentration of chloride ions and x is a position variable. In practical terms, this equation is only useful after steady-state conditions have been reached, i.e. there is no change in concentration with time. It can be used, however, to derive the relevant equation for non-steady conditions (when concentrations are changing), often referred to as Fick's Second Law:

$$\frac{\partial C}{\partial t} = D_{eff} \frac{\partial^2 C}{\partial x^2} \tag{2}$$

which includes the effect of changing concentration with time (t). This has been solved using the boundary condition $C_{(x=0, t>0)} = C_0$ (the surface concentration is constant at C_0), the initial condition $C_{(x>0, t=0)} = 0$ (the initial concentration in the concrete is 0) and the infinite point condition $C_{(x=\infty, t>0)} = 0$ (far enough away from the surface, the concentration will always be 0).

The solution is:

$$\frac{C(x,t)}{C_0} = 1 - \text{erf}\left(\frac{x}{\sqrt{4D_{eff}t}}\right)$$ (3)

where erf(y) is the error function, a mathematical construct found in math tables or as a function in common computer spreadsheets.

For concrete, there are some factors that interfere with simple interpretation of diffusion data. First of all, the chloride ions are not diffusing through a homogeneous solution. Concrete is a porous matrix that has both solid and liquid components. The diffusion through the solid portion of the matrix is negligible when compared to the rate of diffusion through the pore structure. The rate of diffusion is thus controlled not only by the diffusion coefficient through the pore solution but by the physical characteristics of the capillary pore structure. This effect is normally considered implicitly, however, and the effective diffusion coefficient of the chlorides into the concrete as a whole is considered, called here D_{eff}. Other influences are discussed below.

3.3 Properties of the Concrete that Affect the Chloride Penetration Rate

The rate of ingress of chlorides into concrete depends on the pore structure of the concrete, which is affected by factors including materials, construction practices, and age. The penetrability of concrete is obviously related to the pore structure of the cement paste matrix. This will be influenced by the water-cement ratio of the concrete, the inclusion of supplementary cementing materials which serve to subdivide the pore structure [McGrath, 1996], and the degree of hydration of the concrete. The older the concrete, the greater amount of hydration that has occurred and thus the more highly developed will be the pore structure. This is especially true for concrete containing slower reacting supplementary cementing materials such as fly ash that require a longer time to hydrate [Tang and Nilsson, 1992; Bamforth, 1995].

Another influence on the pore structure is the temperature that is experienced at the time of casting. High-temperature curing accelerates the curing process so that at young concrete ages, a high-temperature cured concrete will be more mature and thus have a better resistance to chloride ion penetration than a normally-cured, otherwise identical, concrete at the same at age. However, at later ages when the normally-cured concrete has a chance to hydrate more fully, it will have a lower chloride ion diffusion coefficient than the high-temperature-cured concrete [Detwiler, et al., 1991; Cao and Detwiler, 1996]. This finding has been attributed to the coarse initial structure that is developed in the high-temperature-cured concrete due to its initial rapid rate of hydration as well as the possible development of ~~initial~~ internal microcracking.

The rate of chloride penetration into concrete is affected by the chloride binding capacity of the concrete. Concrete is not inert relative to the chlorides in the pore solution. A portion of the chloride ions reacts with the concrete matrix becoming either chemically or physically bound, and this binding

reduces the rate of diffusion. However, if the diffusion coefficient is measured after steady-state conditions have been reached, then all the binding can be presumed to have taken place and this effect will not then be observed. If a steady state condition has not been reached, then not all the binding will have occurred and this will affect the results. The chloride binding capacity is controlled by the cementing materials used in the concrete. The inclusion of supplementary cementing materials affects binding, though the exact influence is unclear [Byfors, 1986; Rasheeduzafar, et al., 1992; Sandberg and Larrson, 1993; Thomas, et al., 1995]. Also, the C_3A content of the cement influences its binding capacity, with increased C_3A content leading to increased binding [Holden, et al., 1983; Midgely and Illston, 1984; Hansson and Sorenson, 1990].

4.0 EXISTING TEST METHODS

4.1 AASHTO T259: Standard Method of Test for Resistance of Concrete to Chloride Ion Penetration (Salt Ponding Test)

The AASHTO T259 test (commonly referred to as the salt ponding test) is a long- term test for measuring the penetration of chloride into concrete. The test requires three slabs at least 75 mm thick and having a surface area of 300 mm square. These slabs are moist cured for 14 days then stored in a drying room at 50 percent relative humidity for 28 days. The sides of the slabs are sealed but the bottom and top face are not. After the conditioning period, a 3 percent NaCl solution is ponded on the top surface for 90 days, while the bottom face is left exposed to the drying environment (see Figure 1). At the end of this time the slabs are removed from the drying environment and the chloride
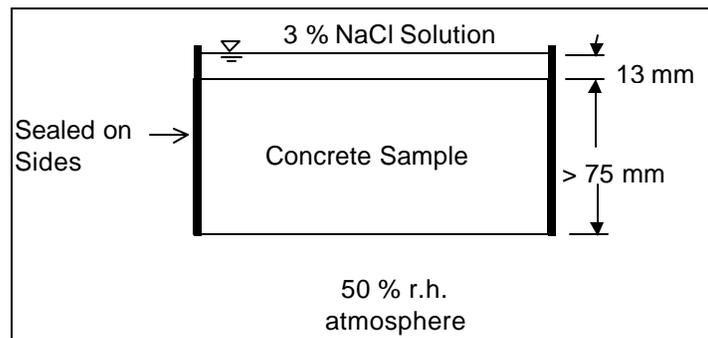

Figure 1. AASHTO T259 (salt ponding) test setup

concentration of 0.5-inch thick slices is then determined [AASHTO T259]. Typically, 2 or 3 are taken at progressive depths. There is difficulty, however, in determining what the results mean. Part of this is due to the complicated testing conditions, discussed in the following paragraph, but part is also due to the crudeness of the evaluation. Little information is being gathered about the chloride profile. Only the average chloride concentration in each 0.5-inch slice is determined, not the actual variation of the chloride concentration over that 0.5-inch. A situation could be envisioned where there are two concretes with the same average chloride concentration in their outer 0.5-inch slice. One concrete has an approximately uniform chloride concentration, while the other has a higher concentration near the

surface and is lower further in. Obviously the first situation will result in a critical chloride concentration reached at some depth sooner than the second situation, yet this distinction would not be detected.

The salt ponding test does provide a crude one-dimensional chloride ingress profile, but this profile is not just a function of chloride diffusion. Since the specimens have been left to dry for 28 days, there is an initial sorption effect when the slabs are first exposed to the solution. Salt solution is drawn quickly in to the pores of the concrete. Also, the exposure of the bottom face to a 50 percent relative humidity environment during the test causes chlorides to be drawn into the concrete through a mechanism other than pure diffusion. There is vapor transmission from the wet front in the concrete to the drier atmosphere at the external face, causing more water to be drawn into the concrete and bringing chloride ions with it. This effect is called wicking.

While all these transport mechanisms may be present in a structure, the relative importance of each is not necessarily reflected by this test procedure. The test overemphasizes the importance of sorption, and to a lesser extent wicking. The relative amount of chloride pulled into the concrete by capillary absorption to the amount entering by diffusion will be greater when the test is only 90 days than when compared to the relative quantities entering during the lifetime of a structure. Also, if wicking is occurring in the concrete element of interest, the relative humidity gradient will likely be less, at least for part of the time, than that which is set up during the test.

For some higher quality concretes, there has also been difficulty in developing a sufficient chloride profile. Insufficient chloride may penetrate in the 90-day duration for a meaningful profile to develop. This has resulted in a need to extend this duration to allow the evaluation of higher quality concretes.

4.2 Bulk Diffusion Test (NordTest NTBuild 443)

A bulk diffusion test has been developed to overcome some of the deficiencies of the salt ponding test to measure diffusion. Though not the first similar test developed, the NordTest is the first formally standardized version of the bulk diffusion test. The first difference in test procedure from the salt ponding test is the sample's initial moisture condition. Instead of being dried for 28 days as with the salt ponding test, the test specimen is saturated with limewater. This prevents any initial sorption effects when the chloride solution is introduced. Also, instead of coating just the sides of the sample and leaving one face exposed to air, the only face left uncovered is the one exposed to a 2.8 M NaCl solution, (Figure 2). It is left this way for a minimum of 35 days before evaluation [NordTest, NTBuild 443-94].

To evaluate the sample, the chloride profile of the concrete is determined by mounting the sample in either a mill or lathe with a diamond tipped bit. The sample is level so that the axis of advance of the bit is perpendicular to the surface of the sample. A pass is made at each depth to grind the concrete sample into dust, which is then collected. This is repeated at greater and greater depths, at depth increments on the order of 0.5 mm. The chloride content of the powder
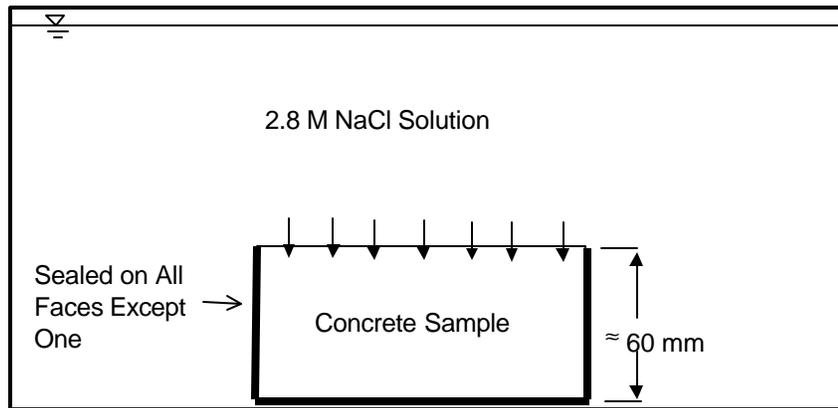
Figure 2. Nordtest setup.

is then determined according to AASHTO T260. The error function solution of Fick's Second Law is then fit to the curve and a diffusion value and surface chloride concentration is determined.

While the Nordtest is capable of modelling chloride diffusion into concrete, it is still a long-term test. For low quality concretes, the minimum exposure period is 35 days. For higher quality concretes, however, this period must be extended to 90 days or longer, just as for the salt ponding test.

4.3 AASHTO T277: Electrical Indication of Concrete's Ability to Resist Chloride Ion Penetration (Rapid Chloride Permeability Test)

In the AASHTO T277 (ASTM C1202) test, a water-saturated, 50-mm thick, 100-mm diameter concrete specimen is subjected to a 60 V applied DC voltage for 6 hours using the apparatus shown in Figure 3. In one reservoir is a 3.0 % NaCl solution and in the other reservoir is a 0.3 M NaOH solution. The total charge passed is determined and this is used to rate the concrete according to the criteria included as Table 1. This test, originally developed by Whiting [1981], is commonly (though inaccurately) referred to as the "Rapid Chloride Permeability Test" (RCPT). This name is inaccurate as it is not the permeability that is being measured but ionic movement. In addition, the movement of *all* ions, not just chloride ions, affects the test result (the total charge passed).

There have been a number of criticisms of this technique, although this test has been adopted as a standard test, is widely used in the literature [Saito and Ishimoiri, 1995; Goodspeed at al., 1995; Thomas and Jones, 1996; Samaha and Hover, 1996] and has been used to limit permeability in at least one standard [CSA/S413-94]. The main criticisms are: (i) the current passed is related to all ions in the pore solution not just chloride ions, (ii) the measurements are made before steady-state migration is achieved, and (iii) the high voltage applied leads to an increase in temperature,
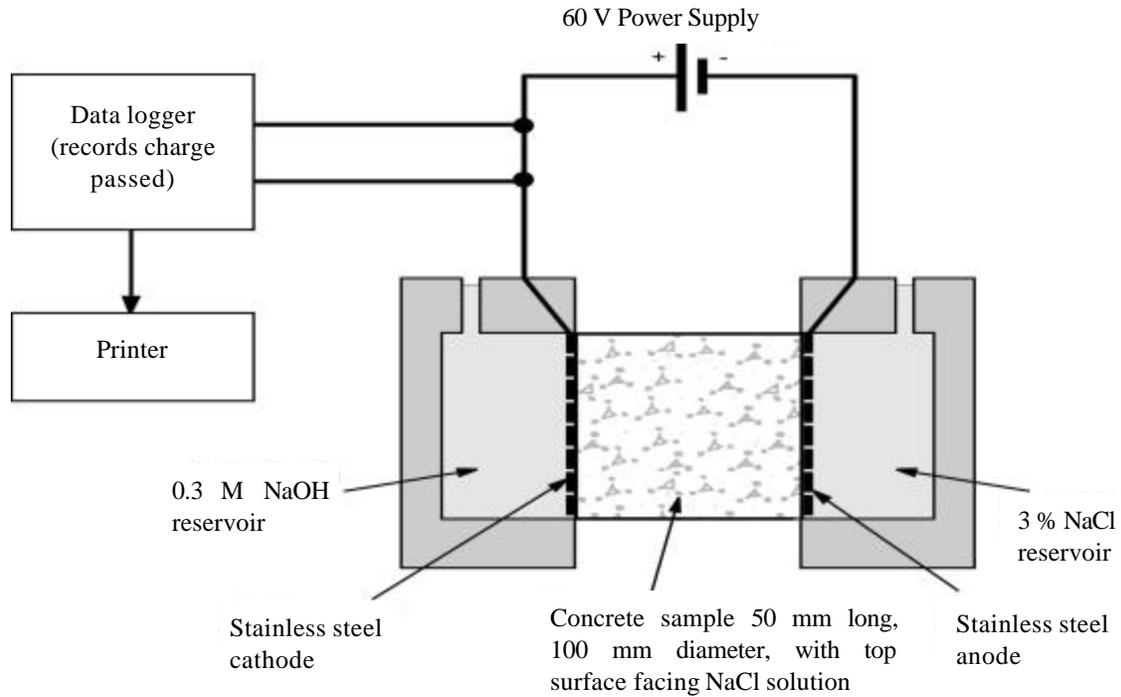
Figure 3. AASHTO T277 (ASTM C1202) test setup.

especially for low quality concretes, which further increases the charge passed [Andrade, 1993; Zhang and Gjorv, 1991; Malek and Roy, 1996; Roy, 1989; Geiker, et al., 1990]. Lower quality concretes heat more as the temperature rise is related to the product of the current and the voltage. The lower the quality of concrete, the greater the current at a given voltage and thus the greater heat energy produced. This heating leads to a further increase in the charge passed, over what would be experienced if the temperature remained constant. Thus, poor quality concrete looks even worse than it would otherwise.

Table 1. RCPT ratings (per ASTM C1202)

Charge Passed (coulombs)	Chloride Ion Penetrability
> 4,000	High
2,000-4,000	Moderate
1,000-2,000	Low
100-1,000	Very Low
< 100	Negligible

These objections all lead to a loss of confidence in this technique for measuring chloride ion penetrability. In addition, they also lead to a loss of precision. The ASTM C1202 statement on precision, based upon work by Mobasher and Mitchell [1988], states that the single operator coefficient of variation of a single test has been found to 12.3 %, and thus two properly conducted tests should vary by no more than 35 % if done by one person. The between-laboratory measurement is naturally less precise and a single test result will have a coefficient of variation of 18.0 %. To minimize the variation, three samples are generally tested and the average value reported. However, a precision statement is also given for this type of test and it is stated that the average of three samples should not differ by more than 29 % between two separate laboratories [ASTM C1202].

Another difficulty with the RCPT test is that it depends upon the conductivity of the concrete being in some way related to the chloride ion penetrability. Thus, any conducting material present in the concrete sample will bias the results, causing them to be too high. This would be the case if any reinforcing steel is present, if conductive fibers are used (e.g. carbon or steel), or if a highly ionic conductive pore solution is present [ASTM C1202]. This pore solution effect may be noticed if calcium nitrite is included as a corrosion inhibiting admixture, and other admixtures may also have this effect [ASTM C1202]. Because these conductors all influence the results so that a higher coulomb value than would otherwise be recorded is determined, the method still could serve as a quality control test. It can qualify a mix, but not necessarily disqualify it [Ozyildirim, 1994]. If an acceptably low rating is achieved, it is known that the concrete is not worse than that, at least within the precision of the test method.

Despite these drawbacks and limitations, attempts have been made to correlate RCPT values with diffusion coefficients from other tests [Thomas and Jones, 1996; Berke and Hicks, 1992].

4.4 Electrical Migration Techniques

Often the movement of chlorides is accelerated through the use of an electrical field that is of a lower intensity than that used in the RCPT. The data can also be collected differently to better evaluate the actual movement of chloride ions (as opposed to simply measuring the charge passed).

The movement of ions in a solution under an electrical field is governed by the Nernst-Planck equation [Andrade, 1993]:

$$-J_i = D_i \frac{\partial C_i(x)}{\partial x} + \frac{z_i F}{RT} DC_i \frac{\partial E(x)}{\partial x} + C_i v_i(x) \tag{4}$$

where J_i is the flux of the ionic species i, D_i is the diffusion coefficient of the ionic species i, $C_i(x)$ is the concentration of ionic species i as a function of location x, z_i is the valence of ionic species i, F is Faraday's constant, R is the universal gas constant, T is the temperature, E(x) is the applied electrical potential as a function of x and $v_i(x)$ is the convection velocity of i.

Conceptually, this can be broken down to [Andrade, 1993]:

$$\text{Flux} = \text{pure diffusion} + \text{electrical migration} + \text{convection} \tag{5}$$

Now, considering the situation where there is no convection (i.e. no pressure or moisture gradients) and assuming that the pure diffusion portion is negligible compared to the effect of electrical migration, which is reasonable for a sufficiently strong applied voltage (at least 10-15 V) [Andrade, 1993], Equation 4 becomes:

$$J = \frac{z_i FDC_i}{RT}\frac{\partial E(x)}{\partial x} \tag{6}$$

This allows the solution for D once the chloride ion flux is determined if it is also assumed that the voltage drop across the cell is linear. Also, it must be assumed that the chloride concentration is constant in the upstream cell, that steady state conditions have been reached and that heating of the solution and concrete is negligible [Andrade, 1993].

Another method of determining D is to apply the Nernst-Einstein equation [Lu, 1997]. The Nernst-Einstein equation states:

$$D_i = \frac{RT\sigma_i}{z_i^2 F^2 C_i} \tag{7}$$

where σ_i is the specific conductivity, and the other terms are as defined before. Once the specific conductivity is known, then the diffusion coefficient can be determined. To determine σ_i, know that:

$$\sigma_i = t_i \sigma \tag{8}$$

where σ is the total conductivity and:

$$t_i = \frac{Q_i}{Q} = \frac{I_i}{I} \tag{9}$$

where t_i is called the transfer number and relates the electric quantity (Q) or current (I) carried by species i to the total electric quantity or current. It has been suggested to take the value of t as 1 as a simple and proper approach, though it is admitted that this is not correct [Lu, 1997].

Electrical migration tests are performed in a two-chamber cell with the concrete sample as the division between the two chambers, as shown in Figure 4. The concrete sample can be of any size, but is usually a disk of 100 mm diameter and length about 15 to 50 mm. The thickness of the disk will affect the duration of the test, but a sufficient size is required to avoid aggregate interface influences. If the size of the aggregate is comparable to the thickness of the specimen,
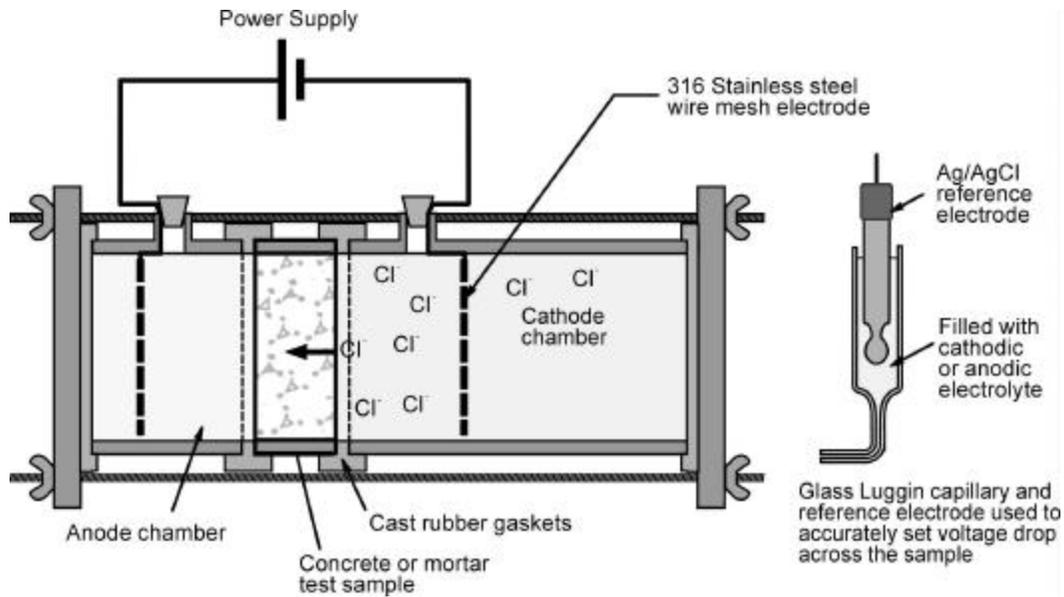
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Figure 4. Typical chloride migration cell.

then there may exist a weak transition zone around the aggregate that extends most of the way through the sample. This will provide a faster path to the movement of chloride ions than would exist in the bulk concrete. To avoid this, the thickness of the sample must be larger than the maximum aggregate size [McGrath, 1996]. Initially, the cathode chamber contains chloride ions, but the anode chamber is chloride-free. The host solution varies, but is typically either distilled water or limewater. A voltage is then applied to drive the chloride ions through the concrete while the chloride concentration of the downstream (anode chamber) solution is monitored, typically by periodically removing small aquilots and determined the chloride concentration of these samples. The change of chloride concentration with time allows the calculation of diffusion coefficients.

The most obvious and important difference that may arise between different testing methods is the voltage that is applied. This directly affects the time required to perform the test. A voltage low enough to avoid heating of the sample while high enough to ensure a sufficiently short-test duration is required. While a wide variety of voltages are reported in the literature, they commonly are in the 10-12 V range [Streicher and Alexander, 1995; Zhang and Gjorv, 1991; Andrade and Sanjuan, 1994; Delagrave, et al., 1996; Detwiler, et al., 1991; Jacobsen, et al., 1996; McGrath and Hooton, 1996]. While this voltage range avoids the problem of heating the sample, it generally results in long test durations, unless an unacceptably thin sample is used, of the order of 5 mm.

It may not be necessary to use such a low voltage to avoid the problem of heating, however. A study was conducted by El-Belbol and Buenfeld [1989] where the temperature rise was monitored for a variety of voltages in an apparatus similar to that currently used for the RCPT. They found for a 0.5 w/cm mortar, while there was a temperature rise of 18°C for a voltage of 60 V, there was what they

called a negligible rise for an applied voltage of 40 V. Their test lasted approximately 4 days at this voltage for their concrete. Other problems that may be encountered with high voltage (excessive hydrogen gas production, rapid degradation of the electrodes) were not discussed.

The other drawbacks of the AASHTO T277 test previously discussed can be dealt with in an electrical migration cell not by modifying the testing apparatus or conditions relative to the RCPT, but by altering how the test is evaluated. The chloride ion concentration of the downstream solution must be periodically monitored to ensure that only the movement of chloride ions will be used to evaluate the diffusion coefficient, D. The downstream chloride ion concentrations are then plotted as a function of time, yielding a plot such as the one shown in Figure 5. As illustrated in Figure 5, there is usually some small initial concentration of chlorides, attributable to background chlorides present in the concrete.
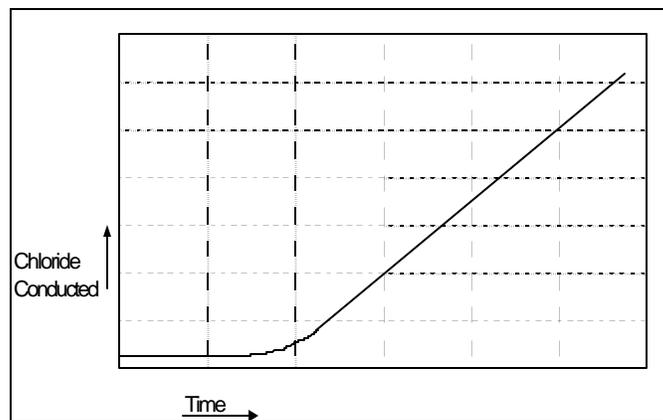

Figure 5. A typical migration plot (downstream chloride concentration versus time).

This concentration will not change, however, until a certain time has passed, called the breakthrough time. At breakthrough, chlorides from the upstream solution have reached the downstream solution and steady-state conditions have been achieved. The chloride concentration information can be used in a variety of ways to evaluate diffusion coefficients. First, as steady-state conditions have been achieved, the change in concentration of the chlorides in the downstream cell is equivalent to the chloride flux, J, and is constant. It is then simple to apply the Nernst-Planck equation (equation 4). This is the most common technique to determine diffusion coefficients in migration experiments [Detwiler, et al. 1991; McGrath and Hooton, 1996; Dhir, et al., 1990; Andrade, 1993; Zhang and Gjorv, 1994].

Another technique is to consider non-steady-state diffusion. This is not used as often as it involves solely the time to breakthrough and this can be difficult to determine. Sometimes it is considered when the chloride conducted into the downstream cell reaches a certain level, say 25 mg, and sometimes it is the point of intersection of the initial constant portion of the curve and the linear portion of the constant flux or steady-state portion of the curve. These values can differ and this can have an influence on the diffusion coefficients calculated [McGrath, 1996]. There is also greater numerical complexity in

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calculating diffusion coefficients in this manner. It has been used successfully by some researchers, however [Tang and Nilsson, 1991; Hooton and McGrath, 1995; Halamickova, et al., 1995].

While capable of addressing the criticisms of the RCPT about temperature rise and ability to consider what is occurring in the migration of chlorides, there is still a significant drawback to the use of an electrical migration type test. Inclusion of conductive materials, e.g. metal or carbon, will short-circuit the cell with the current being carried by the conductor rather than the ions in pore solution. In the case of an electrolyte, i.e. calcium nitrite, instead of the current being carried by the chloride ions, the current will be carried by the more highly ionically mobile nitrite ions. Thus, the chloride ions would effectively experience a lower potential gradient, reducing the distance they would travel in a given time. This effect may be minor in the concentrations of nitrite ions found in practice.

4.5 The Rapid Migration Test (CTH Test)

Tang and Nilsson [1991] proposed a variation on the conventional migration cell unique enough to be mentioned separately. A migration cell is set up with a specimen 50 mm thick and 100 mm in diameter, and an applied voltage of 30 V, as shown in Figure 6. The experiment

Figure 6. Tang and Nilsson migration cell

proceeds as usual for an electrical migration test, except that the chloride concentration of the downstream solution is not monitored. Instead, after a specified duration (Tang and Nilsson used 8 hrs.) the samples are removed and split, and the depth of chloride penetration is determined in one half of the specimen using a colorimetric technique in which a silver nitrate solution is used as a colorimetric

indicator. When a silver nitrate solution is sprayed on a concrete containing chloride ions, a chemical reaction occurs. The chlorides bind with the silver to produce silver chloride, a whitish substance. In the absence of chlorides, the silver instead bonds with the hydroxides present in the concrete, creating a brownish color. This method was first investigated by Collepardi, et al. [1970]. Work done by Otsuki, et al. [1992] to determine the optimum concentration of silver nitrate solution to be used indicates that a 0.1 N solution is suitable and that the color change border corresponds to the location of a soluble chloride concentration of 0.15 % by weight of cement.

The work done by Otsuki, et al. [1992] examined the total chloride contents as well as the soluble chloride percentage and found that this varied depending upon whether the chlorides came from an external source or were present at initial mixing, the w/c ratio of the concrete, and whether a concrete, mortar or paste were used. The soluble chloride percentages were found to remain constant.

This depth of penetration can be used to determine a chloride ion diffusion coefficient. Using the following equation derived from the Nernst-Einstein equation [Tang and Nilsson, 1991]:

$$D = \frac{RT}{zFE} * \frac{x_f}{t} \tag{10}$$

where x_f is the inflection point of the chloride ion profiles that needs to be related to the depth given by the colorimetric technique. The depth of penetration itself may also be a useful parameter.

Similar to the more usual migration cell, the CTH test is capable of addressing the criticisms of the RCPT related to examination of actual chloride ion movement and temperature rise.   However, as in the case of a typical migration test, inclusion of conductive materials, such as metal or carbon, could short-circuit the CTH cell, with the current being carried by the conductor rather than the ions in pore solution. If the conductor does not short-circuit the cell (i.e. if a piece of steel is parallel to the surface), there is the possibility of it reacting with the chloride ions and affecting ion movement in that manner. However, if the chloride ions do not penetrate to the depth of the steel, this would not be a problem. Also, if a conductive ionic species, i.e. calcium nitrite, is present, the current will be carried by the more highly ionically mobile nitrite ions instead of the chloride ions. The chloride ions would effectively experience a lower potential gradient, reducing the distance they would travel. This effect may be minor in the concentrations of nitrite ions found in practice.

4.6 Resistivity Techniques

Resistivity techniques are another method of assessing the ability of chlorides to penetrate concrete. Resistivity is the electrical resistance of a substance, normalized to a unit cross-section and length, and conductivity is the inverse of resistivity. The conductivity of a saturated porous medium is primarily determined by the conductivity of the pore solution [Kyi and Batchelor, 1994; Streicher and Alexander, 1995]. A number called the Formation Factor (FF) can be then constructed which is:

$$FF = \sigma/\sigma_0 \tag{11}$$

where σ is the conductivity of the porous material and σ_0 is the conductivity of the pore solution. Now, both the conductivity and the diffusivity in a porous medium are related to the same factors, the tortousity, constrictivity, pore size and connectivity. Thus it can also be stated that:

$$FF = D/D_0 \tag{12}$$

where D is the diffusivity of the porous medium (the factor of interest) and D_0 is the diffusivity of chloride in the pore solution. This final value can be determined from physical and chemical tables of constants [Streicher and Alexander, 1995].

There are two main types of tests that can be done to determine a resistivity value, involving either direct current (DC) or alternating current (AC) [Monfore, 1968]. Alternating current resistivity is measured by placing a test specimen between two electrodes and applying an alternating voltage between them and monitoring the current to determine a resistance value. Direct current resistivity can be measured by applying a voltage between two electrodes with the concrete sandwiched between them, as shown in Figure 7. However, because concrete conducts electricity as an electrolyte, there is a polarization developed. This causes the actual voltage causing current to be reduced by an unknown amount. If it is assumed that this polarization effect is constant at different applied voltages, this effect can be accounted for by taking current measurements at two voltages. The determination of DC resistance is thus from the equation [Monfore, 1968]:

$$R = \frac{E_{a1}I_2 - E_{a2}I_1}{I_1 - I_2} \tag{13}$$

where R is the resistance, E_{a1} and E_{a2} are the two applied voltages and I_1 and I_2 are the relevant currents. This can be then converted to a resistivity using the equation:

$$\rho = R\frac{A}{L} \tag{14}$$

where ρ is the resistivity, A is the cross-sectional area and L is the length of the specimen.
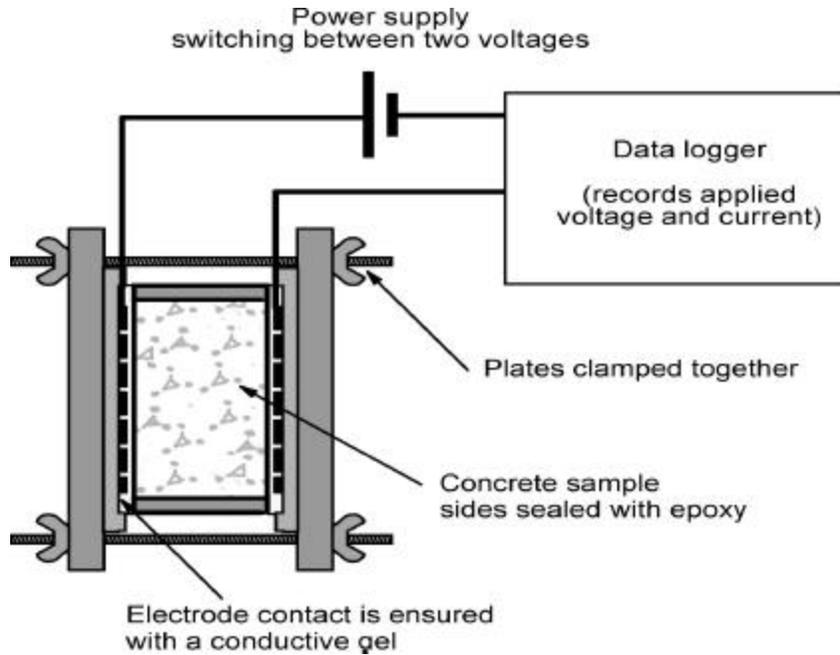
Figure 7. DC Resistivity measuring device.

The Wenner array probe is a technique for determining resistivity on concrete in situ, without removing cores to place between plates. It consists of a set of four points, each a constant distance apart, a. The two outer points are where the current is applied, while the inner two points measure the potential, see Figure 8. This has the advantage of eliminating the influence of polarization as the actual potential is measured across an inner region. For a semi-infinite region (where the thickness is much greater than the distance between the points) the resistivity can be calculated as [Morris, et al., 1996]:

$$\rho = 2\pi a \frac{P}{I} \tag{15}$$

where ρ is the resistivity, a is the distance between points, P is the measured potential, and I is the applied current. If the thickness is not much greater than the distance between two points, then correction factors must be applied, and have been developed by Morris, et al [1996].

Resistivity techniques have the advantage of speed and deal with a test method already familiar to many concrete researchers. These techniques also provide a value that may be useful when determining corrosion rates in concrete, namely the resistivity of the concrete. Resistivity tests avoid heating of the concrete as the voltage can be low, usually in the range of 10 V or lower [Streicher and Alexander, 1995], and is only applied for short times. There are some major difficulties that may arise when it comes to determining the conductivity of the pore solution, however. Either pore solution must be removed from the concrete to allow the determination of
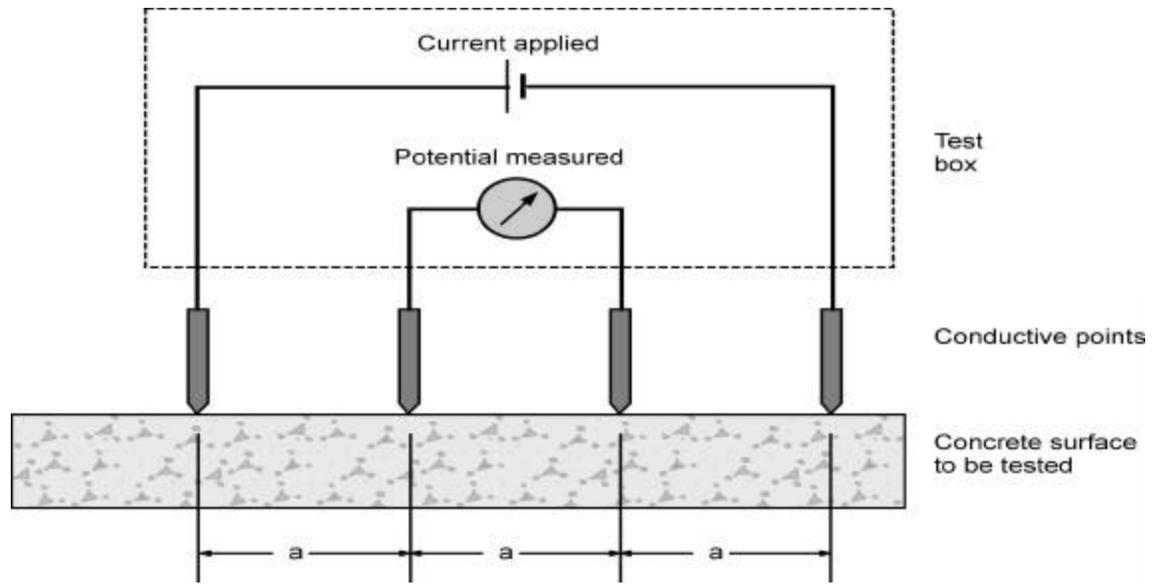
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Figure 8. Wenner Array Probe.

its resistivity or the concrete must be pre-saturated with a solution of known conductivity. Each of these techniques has drawbacks.

Pre-saturation of the concrete with a solution of known conductivity first requires that the sample be dried. This will prevent dilution of the saturating solution [Streicher and Alexander, 1995]. Depending on the concrete and drying technique, drying can lead to damage of the pore structure due to microcracking and can thus cause an increase in diffusivity [Neville, 1981]. It also may be difficult to get the solution into the concrete uniformly. Vacuum saturation techniques are normally used, but even vacuum saturation may not completely saturate the concrete for high quality, thick concrete samples (more investigation of this is needed). This technique also assumes that the solution is identical before and after it has entered the concrete, which may not be the case. The pore solution of concrete normally contains a wide range of ions (mainly alkali hydroxides), some of which will precipitate when the concrete is dried. When a solution enters the concrete, the precipitated ions will then return to solution and thus affect its conductivity. The magnitude of this effect is currently unknown, however, and may be insignificant if the solution introduced into the pore structure is of sufficiently high conductivity. Therefore, a highly conductive solution is normally used, for example 5 M NaCl [Streicher and Alexander, 1995]. This technique does have the advantage of ensuring steady state conditions are achieved from the start of the testing procedure.

Determining the conductivity of the pore solution after the fact also has drawbacks. First of all, steady-state conditions are unlikely to be achieved, requiring a more complicated analysis described by Andrade, et al. [1993]. Also, for high quality concretes it may be difficult to extract pore solution from

a sample. A theoretical method has been presented for estimating the conductivity of the pore solution [Andrade, et al., 1993], but given the inhomogeneous nature of concrete it cannot be recommended.

Finally, resistivity techniques are still based on electrical measurements and as such the inclusion of conductive materials will remain a problem just as for the electrical migration cells and the RCPT.

4.7 Pressure Penetration Techniques

Another method to accelerate the flow of chloride ions into concrete is by exposing one face of the concrete to a solution containing chloride that is under pressure. This will serve to drive the chlorides into the concrete under both convection and diffusion. This will be governed by the equation [Freeze and Cherry, 1979]:

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} - \overline{v} \frac{\partial C}{\partial x} \tag{16}$$

where $\overline{v}$ is the average linear rate of flow which is [Freeze and Cherry, 1979]:

$$\overline{v} = -\frac{k}{n} \frac{\partial h}{\partial x} \tag{17}$$

and k is the hydraulic permeability, n is the porosity and h is the applied pressure head. The solution to this differential equation is [Freeze and Cherry, 1979]:

$$\frac{C_{x,t}}{C_s} = 0.5 \left[\text{erfc}\left(\frac{x - \overline{v}t}{2\sqrt{Dt}} \right) + \exp\left(\frac{\overline{v}x}{D} \right) \text{erfc}\left(\frac{x + \overline{v}t}{2\sqrt{Dt}} \right) \right] \tag{18}$$

This allows the determination of chloride diffusion coefficients, if a chloride profile is known at a specific time.

The testing of concrete for chloride penetrability using a pressure penetration method is similar to determining water permeability using a pressure cell (Figure 9). The concrete sample is pre-saturated with water and placed in a permeability cell. Care is taken to ensure an adequate seal around the sides of the cell to avoid leakage. A chloride-containing solution is introduced to one face of the concrete and a pressure is applied. This pressure is maintained for a given period of time after which the concrete sample is removed from the cell and tested for chlorides as described below.

This method can be used in two ways. First, the solution to the differential equation can be fitted to a chloride profile. This concept has the disadvantage of requiring chloride profile grinding and great numerical complexity. An alternative is to determine the depth of penetration of a known concentration of chloride at a specific time. This depth can be used to rate
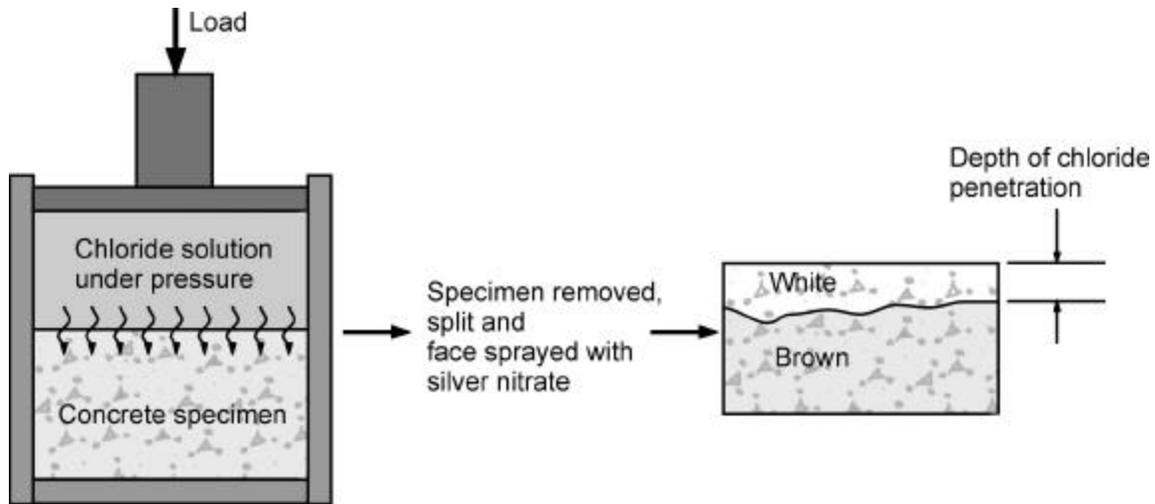
Figure 9. Pressure Penetration Test Procedure.

differentconcretes tested under identical conditions. The depth to a known chloride concentration can be conveniently determined using a colorimetric technique such as the silver nitrate spray procedure described previously in Section 4.5. This value can also be used to determine water permeability using the Valenta equation [Valenta, 1969]:

$$k = \frac{nlx_d}{th} \qquad (19)$$

where k is the hydraulic conductivity, n is the porosity, l is the length of the specimen, x_d is the depth of chloride penetration, t is the time over which pressure was applied and h is the applied head.

4.8 Indirect Measurement Techniques

The permeability of concrete has been a property of interest for a long time. There have been many methods used to evaluate both water and gas permeability. Most of these are based upon Darcy flow considerations.

Liquid permeability (normally water) is generally measured in one of two ways: the depth of penetration in a given time, or the rate of inflow or outflow. The variation of the rate of inflow or outflow with time can also be measured. This information allows the calculation of coefficients of permeability, using either the Darcy equation (using inflow or outflow) or the Valenta equation (depth of penetration). The calculated permeability depends upon the viscosity of the fluid that is used to measure it, though formulations are available that consider the effect of viscosity [Bamforth, 1994].

Measuring the permeability of concrete to gases uses a similar technique, though the actual formula to calculate it, though analogous, also includes the effect of pressure. The permeability of a gas is strongly dependent on the pressure at which it is measured [Bamforth, 1994].

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Though many techniques have been developed that are capable of measuring the permeability of concrete to gas or liquids, these techniques are not suitable for evaluating the ability of concrete to resist chloride ingress. Armaghani and Bloomquist [1993] at the Florida Department of Transportation have assessed the relationship between water permeability and chloride ion permeability (RCPT test results). To do this, they examined the correlation between different grades of concrete as rated by the RCPT and the water permeability in the lab as measured by a constant pressure, steady state flow permeameter. They have also developed a field permeability test which is reported to take only 2 to 3 hours [Armaghani and Bloomquist 1993]. No correlation between the results of the field permeability test and the RCPT is provided, though the field permeability test has been correlated to the laboratory permeability measurements [Meletiou, et al., 1992]. For the lab technique developed in Florida, the time frame is too long to provide an acceptable rapid test, though the field permeability test would be acceptable. In addition, the output given is not directly theoretically related to the chloride ion penetration but to an empirical correlation to the RCPT. The property measured has little relationship to how chlorides penetrate a concrete structure.

4.9 Sorptivity

The sorptivity of concrete is a quantity that measures the unsaturated flow of fluids into the concrete [Hall, 1989]. Sorptivity is a measure of the capillary forces exerted by the pore structure causing fluids to be drawn in to the body of the material. While theoretically possible to consider the flow in any geometry, it is too mathematically complex to be of any practical use except where there are one dimensional flow conditions.
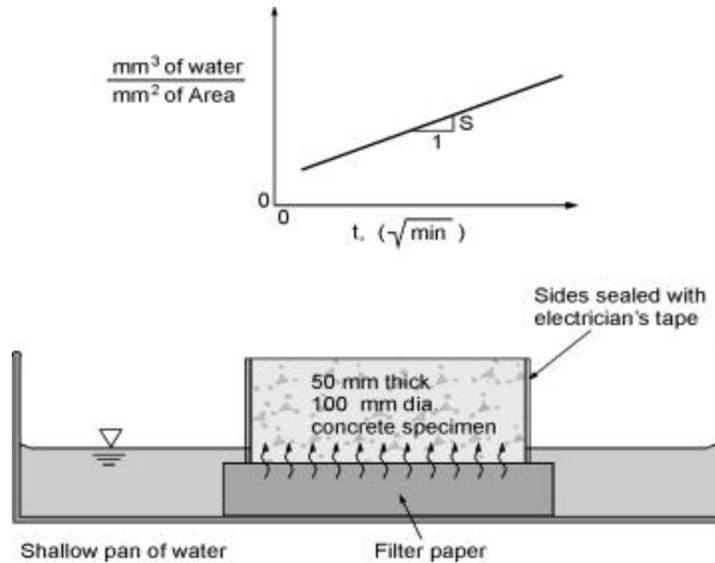
For one dimensional flow, it can be stated that [Hall, 1989]:

$$i = St^{1/2} \qquad\qquad (20)$$

where i is the cumulative water absorption per unit area of inflow surface, S is the sorptivity and t is the elapsed time. In a lab situation where the concrete sample can be dried consistently and the flow conditions can be well defined, is it relatively easy to get a good fit line using least squares regression when plotting i vs. the square root of time. A field sorptivity test has also been developed [DeSouza, et al., 1995].

Determining the sorptivity of a sample in the lab is a simple, low technology technique illustrated in Figure 10. According to the ASTM draft standard, all that is required is a scale, a stopwatch and a shallow pan of water. The sample is preconditioned to a certain moisture condition, either by drying the sample for 7 days in a 50°C oven or by drying for four days at 50°C and then allowed to cool in a sealed container for three days. The sides of the concrete sample are sealed, typically with electrician's tape. The initial mass of the sample is taken and at

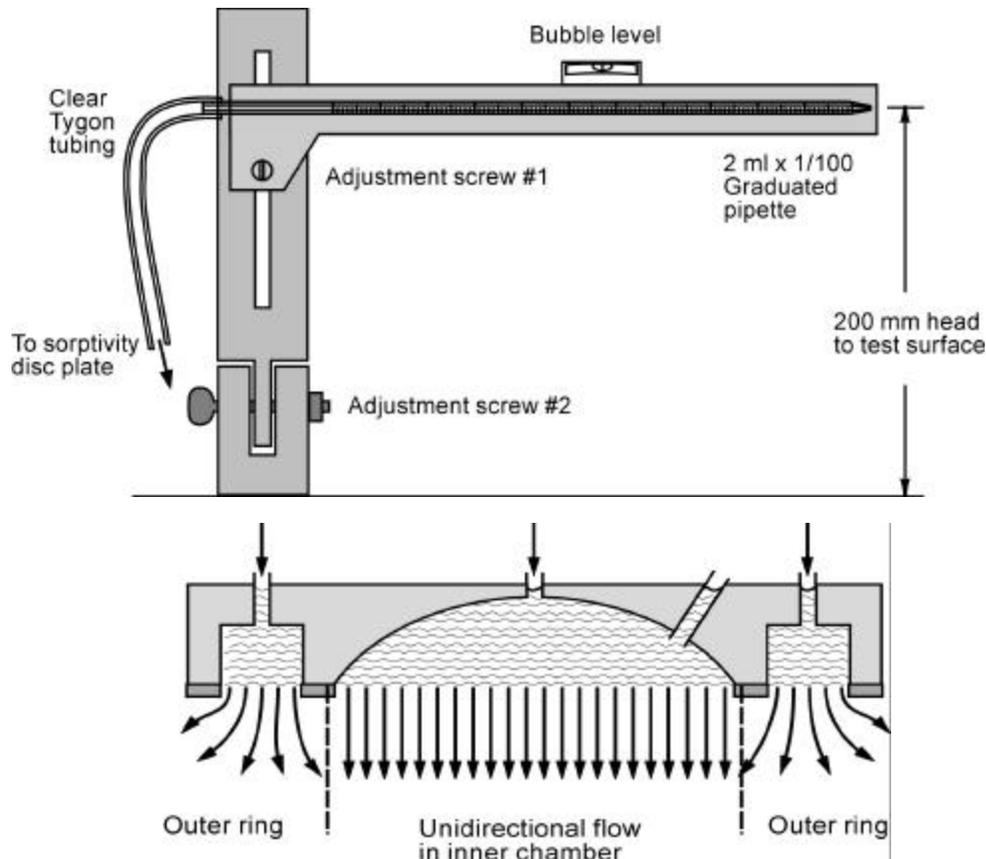**Figure 10.** Lab Sorptivity Technique

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time 0 is immersed to a depth of 5-10 mm in the water. At selected times (typically 1, 2, 3, 4, 5, 9, 12, 16, 20 and 25 minutes) the sample is removed from the water, the stopwatch stopped, excess water blotted off with a damp paper towel and the sample weighed. It is then replaced in the water and the stopwatch started again. The gain in mass per unit area over the density of water is plotted versus the square root of the elapsed time. The slope of the line of best fit of these points (ignoring the origin) is reported as the sorptivity.

A method of determining the sorptivity of concretes in the field has been developed at the University of Toronto [DeSouza, 1996]. The apparatus used is shown in Figure 11. The device consists of an outer guard ring that is clamped on to the surface to be tested by a vacuum. This ring defines a test region and saturates the concrete around the test region to provide unidirectional flow. An interior plate through which water can be supplied is then attached to the concrete (bottom illustration in Figure 11). The amount of water flowing into the concrete is then determined at various time intervals with a graduated pipette (top illustration in Figure 11). The moisture content of the concrete is also determined at the time of testing to allow for an adjustment to a standard condition.

While sorptivity tests avoid many of the difficulties of the RCPT and is able to evaluate concretes containing conductive materials, it does have its limitations. First, it is only able to evaluate the surface of the concrete. The sorptivity of concrete is affected only by the surface conditions, at least in the time frame that is typically considered. Therefore, a sorptivity test will not give any information on the bulk properties of the concrete. Sorptivity test results may be useful if the steel is very shallow, but for typical depths of steel used for high performance, durable structures this is not usually the case.

Another difficulty is the dependence of sorptivity on the moisture content of the sample. This is not a problem in a lab situation, but for a field test the variable moisture content could drastically

Figure 11. Field sorptivity apparatus

Bubble level

Clear Tygon tubing

Adjustment screw #1

2 ml x 1/100 Graduated pipette

200 mm head to test surface

To sorptivity disc plate

Adjustment screw #2

Outer ring | Unidirectional flow in inner chamber | Outer ring

alter results [Hall, 1989]. Also, sorptivity is not a constant property over the long term. When a sample is initially exposed to water, it will absorb water following the above relation with some initial sorptivity, say S_i. After some time, however, there will be a change from this value and then the additional absorption will follow the same relation with another sorptivity, S_f [Martys and Ferraris, 1997]. This change has been attributed to the initial dominance of the larger
capillary pores resulting in a larger sorptivity value until they are filled, after which the smaller gel pores dominate with their lower sorption effects.

The final difficulty is that sorptivity is not a property that is normally dealt with by construction engineers. Permeability, that is movement under pressure through a saturated medium, or diffusion, ion movement, are both more common criteria.

4.10 Other Test Methods

There are two other test methods which have been proposed in the literature for determining the diffusion of chlorides in concrete. Both of these methods use another substance to diffuse into concrete and relate the values achieved to the diffusion of chloride ions.

The first method, proposed by Feldman [1987], uses the diffusion measurement of propan-2-ol into a saturated cement paste. The weight change of an initially water saturated paste submerged in propan-2-ol is monitored. For the specimens used by Feldman (paste, w/c of 0.3 to 1.0, 1.14 mm thick) this

was monitored for 3 to 7 days. Monitoring the weight change allows the determination of the diffusivity of propan-2-ol into the cement paste, which Feldman claims is similar to that of chloride ions. Details of this calculation are contained in the referenced paper.

Sharif, et al. [1997] have proposed relating the diffusion of a gas through concrete to chloride penetration into the concrete. They propose the use of a two-chamber testing rig with a concrete specimen as the dividing wall. One chamber is filled with nitrogen gas while the other chamber is filled with helium gas at some specific pressure. The concentrations of both gases are monitored in each cell and any presence of the other gas in a cell is due to diffusion of the gas through the concrete. The ratio of the porosity of the concrete to the tortuosity of the concrete can be calculated (see the referenced paper for details on the equations). This ratio is considered to be independent of the material passing through the pore structure. Thus, the diffusion of chlorides through the concrete is a function of this ratio and the diffusion of chlorides in water. This is similar to the concept employed when considering resistivity values. The values reported by Sharif, et al. [1997] in their paper comparing the diffusion coefficients determined from chloride ponding and those determined by gas diffusion "reveal an excellent agreement."

While some of the data presented using these techniques show that they may produce reasonable values, there are possible difficulties in performing these experiments that have not yet been mentioned. The propan-2-ol replacement technique has only been performed on very thin cement pastes. It may not be possible to perform this technique on representative concrete samples in a realistic period. For the gas diffusion technique, it can be difficult to adequately seal the sides of the concrete. Another difficulty with the gas diffusion technique is that the mathematics involved in determining useful values are complex, and the concept that the cement paste portion of concrete (often referred to as "gel" to indicate its amorphous structure) presents the same porosity–tortuosity values to very different ions (e.g., helium, nitrogen, chloride) is questionable. Finally, neither of these techniques in any way consider the effects of chloride binding.

4.11 Summary

Table 2 provides a summary of the test methods described in the previous sections, grouped into three main categories (long term, short term, and other). A summary of some of the advantages and disadvantages to each testing procedure is provided in the table.

An examination of Table 2 reveals that each test has strengths and weaknesses. For example, the Nordtest (bulk diffusion test) and AASHTO T259 (salt ponding test) each model the actual chloride ingress well, however as long-term tests they are not suitable for use as a quality control test during construction. Other methods, like the RCPT, have a more nebulous relationship with what actually occurs in the concrete, but have the advantage of a short duration. Finally, some tests fall between these two extremes.

Table 2. Summary of Chloride Penetration Test Methods

Test Method		Considers Chloride Ion Movement	At a Constant Temperature	Unaffected by Conductors in the Concrete	Approximate Duration of Test Procedure
Long Term	AASHTO T259 (salt ponding)	Yes	Yes	Yes	90 Day after curing and conditioning
	Bulk Diffusion (Nordtest)	Yes	Yes	Yes	40 - 120 Days after curing and conditioning
Short Term	RCPT (T277)	No	No	No	6 hours
	Electrical Migration	Yes	Yes	No	Depends on Voltage and Concrete
	Rapid Migration (CTH)	Yes	Yes	No	8 hours
	Resistivity	No	Yes	No	30 Minutes
	Pressure Penetration	Yes	Yes	Yes	Depends on Pressure and Concrete (but potentially long)
Other	Sorptivity – Lab	No	Yes	Yes	1 week incl. Conditioning
	Sorptivity-Field	No	Yes	Yes	30 minutes
	Propan-2-ol Counter-diffusion	No	Yes	Yes	14 days with thin paste samples
	Gas Diffusion	No	Yes	Yes	2-3 hrs.

5.0 CONCLUSIONS

As can be seen from the work presented above, the transport of chloride ions into concrete is a complicated, multi-mechanistic phenomenon. It is important to understand some of the basic concepts underlying chloride ingress into concrete to enable the proper consideration of this eventuality when designing with reinforced concrete. A multitude of tests has been proposed and used to test the resistance of concrete to chloride ingress, and Table 2 reveals that each test procedure has advantages and disadvantages. What is immediately obvious, however, is that no one test is a panacea, and different situations may require different tests. A proper understanding of the limitations of each testing procedure as well as what is required for the situation at hand will allow for the correct selection of testing procedure in each case.

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APPENDIX
Glossary of Terms Related to Chloride Penetration and Testing in Concrete

Absorption: drawing in of fluids into unsaturated pores by capillary suction

Accelerators: admixtures to concrete that accelerate concrete setting time and increase early and ultimate strengths, governed by ASTM C494 Type C

Admixtures: chemicals added to concrete as it is being mixed which can affect the fresh concrete properties or the properties of concrete after it has set, governed by ASTM C494

Anolyte: that portion of the electrolyte in the vicinity of the anode, where electrons enter the solution

Catholyte: that portion of the electrolyte in the vicinity of the cathode, where electrons leave the solution

Chloride Binding: the combination of chloride ions with the cement matrix of the concrete either through physical or chemical means. It reduces the effective chloride concentration in the pore solution, called the free chloride concentration.

Conductivity: a material property describing the ease with which electrons or ions can pass through a unit length of that material of a unit cross-section, the inverse of resistivity.

Connectivity: a concept describing the degree to which pores are connected to one another or are separated, for example if two pores have many open paths between them, their is a high connectivity, while if their are few or no paths between them, their is a low connectivity

Constrictivity: a concept describing the degree to which a pore system narrows; for example a concrete with one large pore is not very constricted (has a low constrictivity) while a concrete with many narrow pores is very constricted (has a high constrictivity) even if their porosities are identical

Convection: the movement of a fluid, including the species it may contain, through a porous body

Diffusion Coefficient: the proportionality constant (D) in Fick's Laws governing diffusion

Diffusion: The movement of species, i.e. chloride, under a concentration gradient

Diffusivity: the adverb form of diffusion

Electrolyte: a solution in which current is carried by the movement of ions

Fick's Laws: The theoretical relationships governing diffusion. Fick's First Law states that

$$J = -D\frac{dC}{dx} \ .$$ Fick's Second Law states that $\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial x^2} \ .$

Flux: quantity of material that passes a unit surface area per unit of time

Gradient: the change in value of a quantity per unit distance in a specified direction

Hydration Inhibitors: a chemical admixture which, when dispensed into concrete, prevents hydration for a period of time by forming a barrier around cement particles

Hydraulic Head: the water pressure which is the driving force behind permeability flow. Usually expressed in m of water

Maturity: A concept describing the degree of hydration of a concrete. It considers both the age of the concrete and the curing conditions it experienced. For strength, is defined as the product of the days and the temperature above a certain baseline value, commonly -10°C. For example, if a concrete spent 3 days at 20°C and then 25 days at 10°C, its maturity would be (3 days) x (20°C - (-10°C)) + (25 days) x (10°C - (-10°C)) or 590 days-°C.

Migration: the movement of ions in a solution under an electrical potential gradient. Related to diffusion by the Nernst-Einstein equation, $J = D\frac{zFU}{RTL}c$.

Non-Steady State Conditions: when the situation is changing with time, i.e. a changing flux

Penetrability: a concept describing the ease at which chloride ions may penetrate concrete, under all transport mechanisms.

Permeability (k): The ease of fluid ingress under a pressure gradient, $Q = k\frac{h}{l}A$

Permeability Cell: a device for measuring permeability

Polarization: when an electrical potential is applied to an electrolyte, there is a tendency of ions to separate based upon their charge, this causes a potential of the opposite direction of the applied potential; also called back emf

Porosity: the relative amount of pore space in concrete, expressed as the percent of the entire volume that consists of pores

Potential: the voltage difference between an anode and a cathode

Resistance: a property of a specific item of a specific geometry and material composition that describes the difficulty with which electrons or ions have in passing through that material under an electrical field

Resistivity (r): a material property describing the difficulty with which electrons or ions travel through a unit length of that material of a unit cross-section under an electrical field

Retarders: a chemical admixture which delays setting time, governed by ASTM C494 Type B

Sorptivity: rate of absorption of water into an unsaturated surface of concrete by capillary action

Steady-State Conditions: the situation is not changing with time, i.e. the flux remains constant

Steam Curing: a curing regime where concrete is exposed to high temperatures for a short duration at early ages. In this work, after the initial set, the air temperature surrounding the concrete was increased from 25°C to 65°C at 20C°/hr, this temperature was maintained for 7.5 hours and then the air temperature was reduced to 25°C at 20 C°/hr. The relative humidity was maintained at nominally 100 %.

Superplasticizers (high range water reducing admixtures): an admixture that reduces the quantity of mixing water required to produce concrete of a given consistency by 12 % or greater, governed by ASTM C494 Type F

Supplementary Cementing Materials: minerals that are added in place of cement that exhibit cementitious and/or pozzolanic reactions in the presence of lime, can be either natural or man-made, common ones are slag, fly ash, and silica fume

Tortousity: a concept describing the shape of a pore system, for example a straight pore has a low tortousity while a convoluted, curving pore has a high tortousity

Transport Mechanisms: the different methods which ions can travel from place to place, including, but not necessarily limited to diffusion, permeation, wicking, sorption and migration

Vapor Diffusivity: The rate at which water vapor can travel through the unsaturated pores

Water Reducers: an admixture that reduces the quantity of mixing water required to produce a concrete of a given consistency

Wicking: evaporation of water from pores deposits salt and draws more solution to the evaporation front by absorption. Requires an air-exposed surface. Is dependent on humidity and the vapor diffusivity of concrete