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Critical Review of Rapid Chloride Test Methods for Concrete

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ABSTRACT: Chloride environments pose a threat to the durability and service life of reinforced concrete structures. It is therefore, necessary to use rapid chloride test methods to assess a concrete's potential to retard chloride ion diffusion, for design and quality assurance purposes. Four such tests are presented.

The Bulk Diffusion Test is representative of true diffusion behaviour. The Rapid Chloride Permeability Test, Rapid Migration Test and Chloride Conductivity Test are rapid tests which employ an electrical field in order to accelerate the lengthy diffusion process. A critical review of these tests is presented.

It was found that the Bulk Diffusion Test is most representative of true ion diffusion behaviour, however, it is not suited to quality assurance purposes due to its time-consuming nature. The Chloride Conductivity Test is a suitable rapid test, which requires further development in certain areas concerning sample preparation. The Rapid Migration Test is a suitable test for rapid chloride testing of concrete

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The prize for the winning paper at the 3rd Young Engineers, Practitioners & Technologists Conference was awarded to Tom Gardner from the University of Cape Town for his paper titled: "Critical Review of Rapid Chloride Test Methods for Concrete". This paper was reviewed specifically for the conference and the Society has decided to publish it, since it was judged ~~the best by the technical panel.~~ as a worthwhile paper.

Abstract: *Chloride environments pose a threat to the durability and service life of reinforced concrete structures. It is therefore necessary to use rapid chloride test methods to assess a concrete's potential to retard chloride ion diffusion, for design and quality assurance purposes. Four such tests are presented. The bulk diffusion test is a representation of true diffusion behaviour. The Rapid Chloride Permeability Test, Rapid Migration Test and Chloride Conductivity Test are rapid tests which employ an electrical field in order to accelerate the lengthy diffusion process. A critical review of these tests is presented. It was found that the bulk diffusion test is most representative of true ion diffusion behaviour, however, it is not suited to quality assurance purposes due to its time consuming nature. The Chloride Conductivity Test is a suitable rapid test, which requires further development in certain areas concerning sample preparation. The Rapid Migration Test is a suitable test for rapid chloride testing of concrete.*

Introduction

Chloride-induced corrosion of reinforced concrete is of major concern in marine environments, cold climates where de-icing salts are used and in other areas where highchloride levels are found. It is most practical, and economical, to correctly design the concrete mix to combat the ingress of chlorides. This is done by ensuring that the chemical and pore structure properties of the cover zone (and the concrete in its entirety) sufficiently retard the diffusion of chloride ions through the matrix.

In order to correctly specify a concrete mix that will ensure that the service life of the structure is realised, it is necessary to test the chloride transport characteristics of the concrete mix. This aids in design and in quality assurance on site. Numerous rapid chloride test methods have been developed. Four such tests are presented and critically reviewed.

Chloride Corrosion

When chloride ions enter the concrete and reach the reinforcing steel, corrosion occurs once the chloride threshold value has been reached. At this level the passivating layer is compromised and, in the presence of oxygen and water, corrosion sets in [11]. It has been shown that this critical chloride concentration level lies between 0.17 and 2.5% total chlorides by weight of cement [10].

It is therefore necessary to design and produce concretes of sufficient quality such that chloride ion ingress into the concrete can be retarded to the extent that the design life of the structure or structural element is not compromised.

Chloride Transport in Concrete

Chloride ions are predominantly transported through concrete by diffusion [13]. Diffusion is the movement of ions due to a concentration gradient. This is a lengthy process but is sufficiently powerful to allow chloride ions to reach the reinforcing steel and depassivate it – resulting in corrosion. Diffusion behaviour is described by Fick's First Law [13]:

$$J_d = \square\, D \frac{\partial c}{\partial x} \qquad (1)$$

where Jd is the flux of ions moving through a particular depth x from the surface c is the concentration gradient from the surface or face of ingress and depth x Under the application of an electrical field, transport behaviour is described by the Nernst- Plank equation [13]:

$$J_d = \square\, D \frac{zFU}{RT} \frac{\partial c}{\partial x} \qquad (2)$$

where z is the ion valence
F is Faraday's constant (94 480 J/(V.mol))
U is the applied electrical potential difference (volts)
R is the Gas constant (8.314 J/(mol.K))
T is the absolute temperature

These equations are, however, based on ideal assumptions and do not take ion activity (ionion and ion-solvent) or ion-medium interaction into account. Due to the complexity of ionic chemistry and cement chemistry, an effective diffusion coefficient is generally determined in order to take all these factors into account.

Concrete is not inert to reaction with chloride ions. Due to the presence of aluminates, chemical binding of chloride ions may occur. Surface forces (Van Der Waal) cause a significant portion of chloride ions to become physically bound to the pore walls. Chloride binding (physical and chemical) removes a large portion of chloride ions from the pore solution - up to 60% has been reported [14] - slowing the diffusion process.

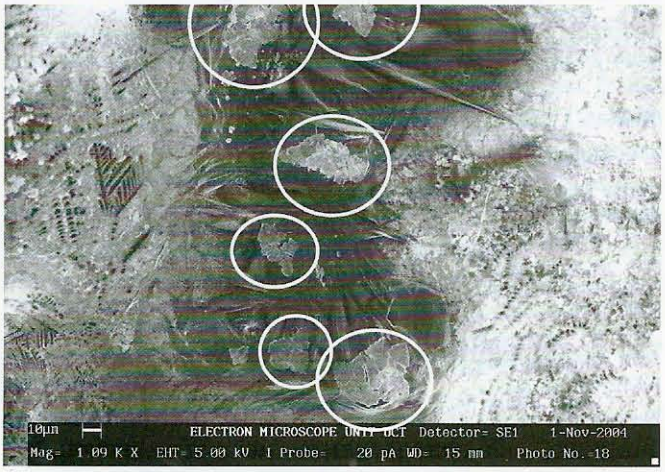

Figure 1: Secondary electron image of Friedel's Salt formation in an OPC mortar

It is common knowledge that supplementary cementitious materials should be used in chloride environments. These materials have the potential to alter the pore- and chemicalstructure of the matrix - retarding chloride ingress by lowering permeability or increasing chloride binding capacity. Figures 1 and 2 show Scanning Electron Micrographs of Friedel's Salt crystals found in an Ordinary Portland Cement (OPC) mortar. These are formed when chloride ions being transported through the matrix react with aluminate deposits – becoming chemically bound.

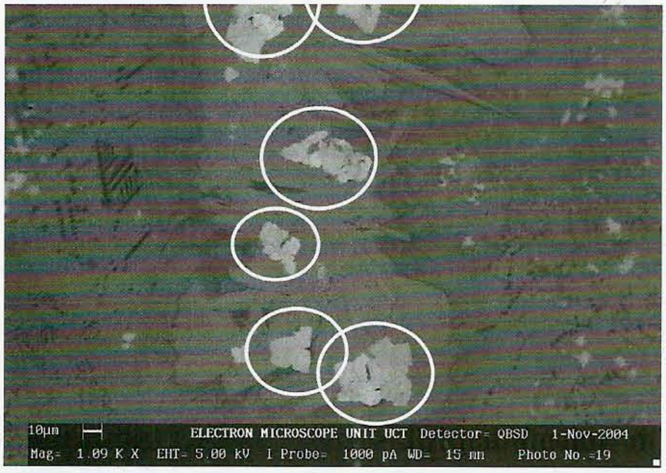

Figure 2: Backscatter Electron image of Friedel's Salt formation in an OPC mortar

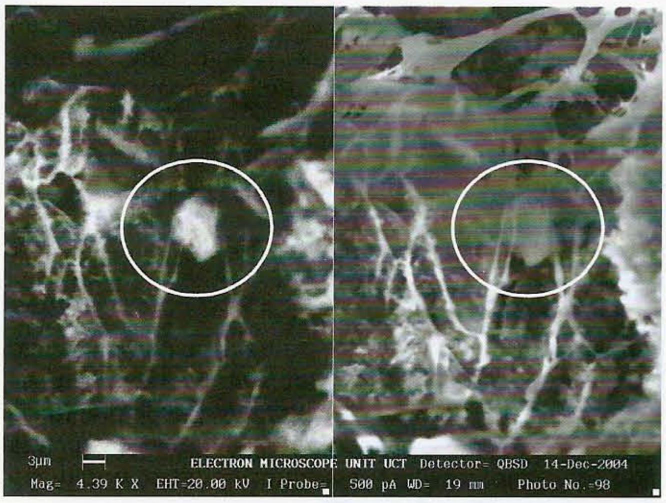

Figure 3: Friedel's Salt found in a Corex slag mortar (Backscatter electron image - left, Secondary electron image – right)

Figure 3 shows a distinctly different type of Friedel's Salt formation to that which occurs in OPC. This Ground Granulated Corex Slag (GGCS) cementitious matrix also has a distinctly different morphology. It is these significant differences that require categorisation before an engineer is able to successfully employ supplementary materials in a chloride environment. Chloride tests must be used for this purpose. Mix design decisions should be supported by trial tests or prior research to establish optimum blend ratios and water-binder ratios – which generally differ significantly to those required purely for strength.

It is also possible to physically retard the transport of chloride ions. As the ions can only move through the pore structure, limiting or decreasing the porosity and permeability of the matrix can combat chloride ion ingress.

Changes in the chemical or physical nature of the concrete matrix, therefore, decreases the effective diffusion coefficient of the concrete matrix. It is this parameter that rapid chloride tests attempt to measure, either directly or indirectly (through resistivity or conductivity measurements).

Bulk Diffusion Test (Nordtest NTBuild 443)

In this Scandinavian test samples are saturated with limewater and then sealed on all sides except the top face, and submerged in a 2.8 M NaCl solution (Figure 4), for a minimum of 35 days. After this time chloride profiling is done, by grinding off 0.5mm portions of the sample, to evaluate the specimen. The total chloride content is thus obtained.

The chloride concentration profile is then used to determine the diffusion value and surface concentration[1].

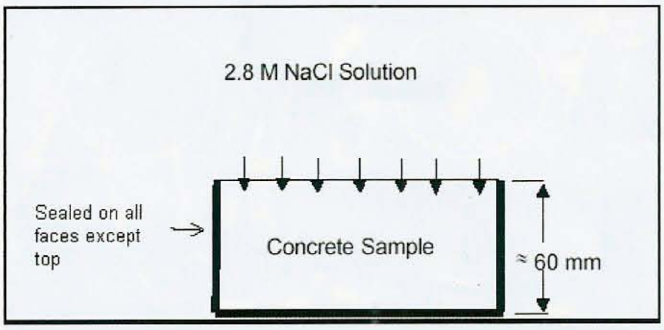

Figure 4: NordTest Setup [7]

A primary advantage of the Bulk Diffusion Test (BDT) is that it is a good reflection of true diffusion behaviour.

The large sample sizes prescribed (100mm diameter cylinders with a depth greater than 75mm) allows a variety of aggregate sizes and a large, representative concrete sample to be tested.

Chloride binding impacts on the depth of penetration and the concentration gradient. This will, therefore, be reflected in the resulting penetration profile.

Samples are water cured in saturated limewater, and are not required to be dried. Thus, the test does not require any sample preparation that may damage the sample's pore structure. Profiling of the samples does, however, require suitable grinding equipment with tolerances to grind 0.5mm layers. 25mm saw cuts can be used on low grade samples due to increased penetration depth. This is not recommended as sawing requires the use of water which may remove a significant amount of chlorides during the cutting process.

A primary criticism of this test is the length and variability of test duration. Depending on the quality of the concrete the test may be extended up to 90 days (excluding the initial 28 day curing time). This is not only unsuitable for quality control but significant microstructural change will occur during that time. This will include the formation of more hydration products and a decrease in porosity. Of primary concern is the increase in C_2S hydration during this time and the increase in AF_m phase as both these phenomena will influence the chloride binding potential of the concrete.

The determination of total chloride concentration using digestion by acid solution may yield erroneous results. The amount of chlorides extracted increases with nitric acid concentration as well as temperature. It has been shown that even aggressive conditions such as boiling nitric acid may lead to less than 90% of the actual chloride content being ascertained [6]. Others have attempted to address the chloride binding phenomena by isolating the free chloride ions. It is generally accepted to assess bound versus free chlorides by performing pore expression and analysing the expressed fluid as being representative of the pore solution. Again, this maybe incorrect and misleading. The disruption of the matrix during crushing (increasing of surface area), as well as the release of loosely bound chlorides [6], may result in erroneous representations. Measured free chloride concentrations may be up to 20% higher than the actual pore solution concentration [6].

The Rapid Migration Test

Tang and Nilsson [14] developed the Rapid Migration Test (RMT). This test employs an electrical current and visual analysis. A 50mm thick 100mm diameter sample is placed in a typical migration cell (Figure 5). A 30 V potential difference is applied across the specimen for 18 hours. The specimen is then split and a 0.1 M silver nitrate solution applied as a colorimetric indicator.

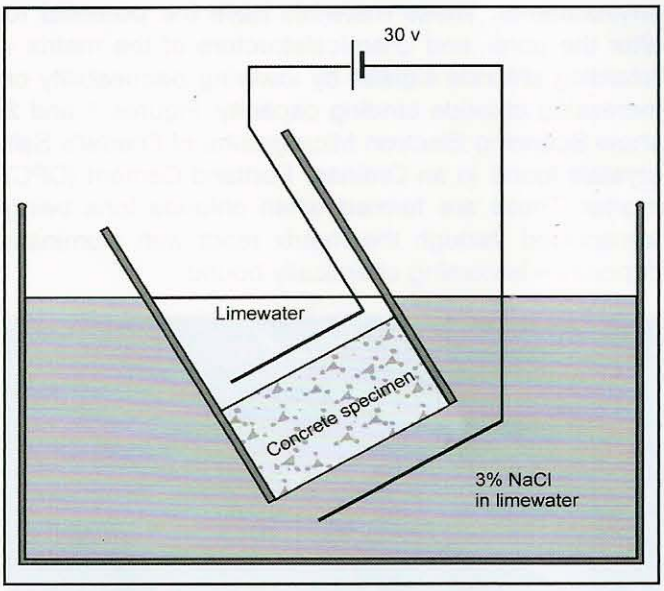

Figure 5: Rapid migration test setup [7]

In the presence of chlorides, the solution reacts to become white silver chloride. In the absence of chlorides, the solution turns a brown colour. The colour change boundary, when using a 0.1 M silver nitrate solution, corresponds to a soluble chloride concentration of 0.15% by weight of cement [7].

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[1] The detailed test method, apparatus and results analysis guidance can be found in: NTBUILD 202, 2nd Edition. Approved 1984-05. Concrete, Hardened: Chloride Content

The depth of penetration is then used to determine a chloride ion diffusion coefficient.[2]

The application of an electric field accelerates the diffusion process by applying more energy to the ions. This energy would affect the binding potential by causing changes in ion-ion, ionsolution and ion-medium interaction. The impact of an electrical field on both transport and binding mechanisms is not sufficiently established. Castelotte et al [4] showed that electrical fields do impact on binding behaviour, suppressing it at low concentrations (< 2.7 M) and increasing binding capacity at concentrations greater than 2.7 M. Therefore, the application of an electrical field in order to drive the chlorides into the concrete may affect the results obtained.

If another conductive ionic species is present, such as calcium nitrite (found in some admixtures), it is possible that this may carry the majority of the current, increasing the conductivity of the pore solution [9]. This would lower the impact of the electrical field on the chloride ions specifically and deem the results incomparable to those of concrete not containing such admixtures. Although the concentration of such ions in practice is generally low, they are commonly found in anodic inhibiting admixtures. The presence of longitudinal reinforcing steel deems the use of this test impossible as it would short circuit the system. This test would also be sensitive to alkalinity affects as an increase in hydroxide ions would result in a similar effect on the current carrying capacity of the chlorides. Condensed Silica Fume would bias results due to its impact on the alkalinity of the pore solution and, hence, the conductivity.

The test duration and potential difference used are not single, prescribed values. Depending on the concrete grade, varying durations or potential differences may be employed in order to obtain a more pronounced penetration depth. This aids in measurement - generally done with a steel rule to the nearest millimetre. Mackechnie and Alexander [9] found that these values vary from 20V for 12 hrs for low grade concretes to 60 V for 48 hrs for high strength concretes. These are based on the initial current passed - guidelines are given in certain standards [7].

Mackechnie and Alexander [9] also noted that slower reacting materials such as Fly Ash (FA) would be inherently disadvantaged by such a test due to their slow reacting characteristics. Testing at 56 or 90 days is preferable for such mixes, even though it is impractical for quality control purposes. Slow reacting extenders and slow developing hydration products generally reach significant maturity after approximately 180 days but generally not before 28 days age. Rapid tests would, therefore, be a reflection of a substantially immature microstructure in terms of chemical composition and pore structure. Note: This point is true of all rapid chloride test methods conducted at 28 days age. Mackechnie and Alexander [9] support the use of this test (as well as other rapid tests), suggesting that the results be corrected for long term microstructural effects.

As is true of the BDT, the impact of chloride binding would slow the penetration rate and concentration levels. This would be reflected in the test results. However, the affect of the electrical field on the binding behaviour is uncertain.

Rapid Chloride Permeability Test

The North American Rapid Chloride Permeability Test (RCPT) involves placing a water saturated 50mm thick 100mm diameter sample in a migration cell and applying a 60 V DC current for 6 hours (Figure 6). One cell of the migration device is filled with 3.0% NaCl solution and the other with 0.3 M NaOH solution. The total charge passed is then monitored over the 6 hour duration and used to give a concrete rating.

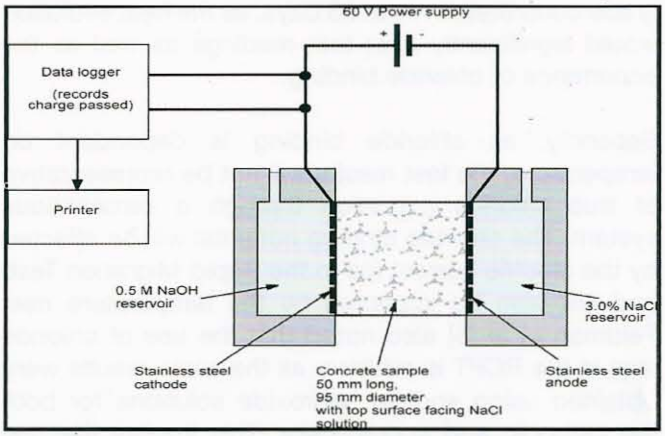

Figure 6: RCPT setup [7]

[3]ASTM C1202 - 97 [3] clearly states in the opening clause that: "This test method is applicable to types of concrete where correlations have been established

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[2] The detailed test method, apparatus and results analysis guidance can be found in: Tang, L. and Nilsson, L-O. (1992) Rapid Determination of Chloride Diffusivity in Concrete by Applying an Electrical Field. ACI Materials Journal, Vol. 89, No. 1, pp. 49 – 53. ACI, USA.

[3] The detailed test method, apparatus and results analysis guidance can be found in: ASTM C 1202 - 97. Standard Test Method for Electrical Indication of Concrete's Ability to Resist Chloride Ion Penetration. ASTM, USA.

between this test procedure and long term chloride ponding procedures such as those described in AASHTO T 259."

This indirectly implies that the salt ponding test be conducted on all concrete types for correlation purposes. Considering that the Bulk Diffusion Test is an improved test, based on the salt ponding test, the code indirectly states that the BDT is preferable in obtaining a true fundamental representation of chloride ion transport behaviour to the RCPT.

As an electric current is employed, the test is affected by other ionic species present, pore solution alkalinity and the presence of steel reinforcement (as in the Rapid Migration Test, above).

The high voltage applied to the concrete for the required time can lead to a temperature increase within the concrete. This has two major implications. Firstly, the resistance of the concrete is affected. As the test relies on current passed at a constant voltage as a result, a decrease in resistance would affect results and make poor concretes look even worse.

Feldman et al [5] noted that: "In the case of the 1-week old specimen, the sample rapidly became very hot on polarization and the application time had to be reduced to a 3-hr period."

These samples were at a w:b ratio of 0,55. This would imply that the RCPT can not be used to categorise low grade concretes, even at 28 days, as the heat evolution would significantly alter test readings as well as the occurrence of chloride binding.

Secondly, as chloride binding is dependent on temperature, the test results will not be representative of true chloride migration through a cementitious system. The chloride binding potential will be affected by the electric current (as in the Rapid Migration Test) and will also be impacted by the temperature rise. Feldman et al [5] also noted that the use of chloride ions in the RCPT is arbitrary as the same results were obtained using sodium hydroxide solutions for both the cathodic and anodic cells. This implies that the RCPT does not in any way represent chloride binding in cementitious materials and, therefore, cannot give a true representation of the actual behaviour of concretes in a chloride environment.

Warnings have been issued regarding the application of the RCPT to silica fume-containing concretes [8]. It was reported the conventional CEM I concretes may have coulomb values of up to 15 times higher than silica fume or slag containing concretes. This was attributed to the extenders inherently high electrical resistivity and its influence on the conductivity of the pore solution. Ninety day salt ponding tests showed that the actual chloride ingress would only decrease by a factor of one or two.

Mackechnie and Alexander [9] also showed that the RCPT results "fell into two distinct bands, OPC and FA concrete had high results while CSF [Condensed Silica Fume], MK [Metakaolin] and SL [Slag] concretes produced significantly lower results". Mackechnie and Alexander [9] went on to state that Fly Ash (FA) containing concrete is unfairly disadvantaged in the RCPT as FA is a slow reacting extender and that testing on FA containing concretes should be conducted at 56 or 90 days.

Feldman et al [5] made measurements of the initial current or resistivity of the samples prior to the test, at room temperature. Using these measurements, the same ranking could be obtained for the samples, as that obtained from the actual test. Feldman noted that this method could replace the RCPT for those types of concrete. This procedure is similar to that which is employed in the Chloride Conductivity Test (CCT).

Chloride Conductivity Test

This South African test involves the measurement of a sample's conductivity. A 25mm thick, 68mm diameter specimen is dried in an oven at 50°C and pre-saturated via vacuum saturation with a 5 M NaCl solution. A migration cell is used, in which the sample is placed between two cells containing 5 M NaCl solution (Figure 7). A 10 V potential difference is applied across the sample and the corresponding current used to calculate the concrete's conductivity.[4]

Sample drying at 50°C, during preparation, may result in microcracking, which could potentially affect the conductivity and transport properties. This is undergoing further investigation.

Again, the application of an electric current may impede chloride binding and the presence of other ionic species and reinforcing steel may affect the results obtained. Even though the application of the

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[4] The detailed test method, apparatus and results analysis guidance can be found in: Alexander, M.G.; Mackechnie, J.R. and Ballim, Y. (1999). Research Monograph No. 2. Guide to the use of durability indexes for achieving durability in concrete structures. The University of Cape Town and the University of the Witwatersrand, South Africa. Alexander, M.G.; Streicher, P.E. and Mackechnie, J.R. (1999). Research Monograph No. 3. Rapid chloride conductivity testing of concrete. The University of Cape Town and the University of the Witwatersrand, South Africa.

current is relatively instantaneous, the effects of this are unknown and may affect the conductive behaviour of the ions.

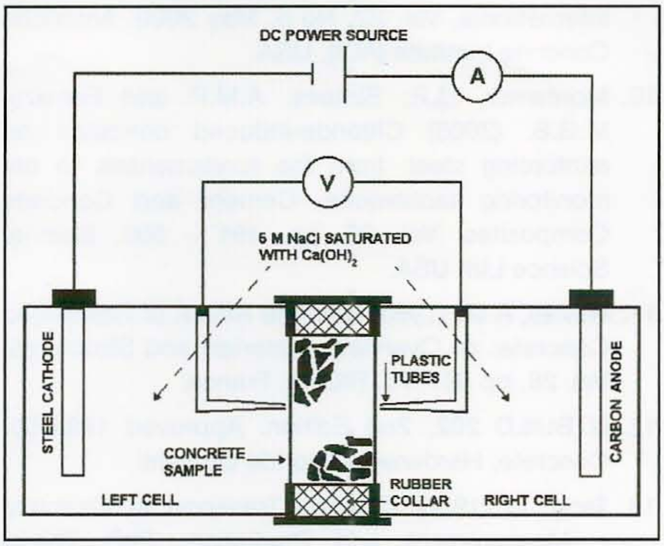

Figure 6: RCPT setup [7]

If the presaturation process was successful, almost all chloride binding would take place prior to the test. This was the aim of the test method, in order to obtain relatively equal solution conductivity throughout the sample and, hence, only measure the sample's conductivity. The test would, therefore, not take chloride binding into account and only be sensitive to porosity and permeability effects. Hence, the test would be an ion permeability test and not account for chloride ion's unique binding behaviour – an important parameter.

However, vacuum saturation of high-grade concretes may be unsuccessful in completely saturating the samples with chloride solution, creating a chloride concentration gradient between the surface zone and the centre of the sample. It has been found that this is so – hence, indirectly taking chloride binding into account. The concentration gradient significantly alters the conductivity of the pore solution, causing this binding effect to be represented in the test results.

Conclusions

Rapid chloride testing in necessary in categorising concretes to be used in chloride environments. Due to the fast paced nature of construction and precast operations, it is imperative that these methods can be conducted over a short period of time (i.e. obtaining results within, say, 40 days of casting).

The Bulk Diffusion Test is the most fundamental test and is not affected by the unknown implications of using an electrical field to accelerate the diffusion process. However, the test is time consuming and is not suitable for quality assurance purposes. The test has, however, been used to calibrate most other test methods. This test is best suited for and should be used in long term research projects.

The RCPT has fallen into disrepute. The many disadvantages of the test procedure results in variable effects on different mixes and samples – affecting results. Improved tests have been developed and should be considered above the RCPT.

The Chloride Conductivity Test is a convenient rapid chloride test. Sample preparation does, however, require the use of an oven able to maintain 50 °C and vacuum saturation equipment. Although sample preparation does affect the microstructure of the samples, the test has been calibrated using the BDT and long term tests on actual structures. Due to its simplicity, it is well suited for quality assurance purposes.

The non-steady state Rapid Migration Test is an improvement of the RCPT and uses a superior analysis technique. Sample preparation does not affect the microstructure of the samples, is not complicated and does not require vacuum saturation equipment. The applied potential difference does not generate excessive temperature gains and the analysis technique is simple to perform. This test is therefore best suited for quality assurance purposes.

A variety of tests are available for categorising concrete's chloride transport properties. It is, however, necessary to have an appreciation for and understand the tests' limitations - before utilising the results to make long term predictions of a concrete's potential service lifespan. It is equally necessary to consider the ease with which the tests can be carried out in testing laboratories – to ensure that consistent results can be obtained.

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