Evaluation of Test Methods for Determining the Resistance of Concrete to Chloride-Ion Penetration

by L. Jiang, M. H. Zhang, and V. M. Malhotra

Synopsis:

This paper presents results of a study that compared ASTM C1202 test, a steady-state migration test, a conductivity test, and a non-steady-state diffusion test for determining the chloride-ion penetrability of control portland cement concrete and concretes incorporating fly ash, ground granulated blast-furnace slag, silica fume, metakaolin, and rice-husk ash.

The water-to-cement ratios of the control portland cement concretes ranged from 0.31 to 0.60. The content of fly ash and slag was 20, 40, or 60% by mass of total cementitious materials as cement replacement. Silica fume, metakaolin, and rice-husk ash was used as 8% cement replacement. Most of the concrete mixtures were made from normal-weight aggregate except for two concrete mixtures that were made from lightweight aggregate.

In general, the results from the four test methods led to similar conclusions regarding the penetration of chloride ions into concrete. Therefore, ASTM C 1202 test method can be used for evaluating the resistance to chloride-ion penetration for concrete with or without supplementary cementing materials in spite of its short comings. The conductivity test is another rapid and convenient method, and has potential for wide acceptance by the construction industry for determining ingress of chloride ions into concrete.

Keywords: chloride; diffusion; fly ash; lightweight aggregate; metakaolin; migration; rice husk ash; silica fume; slag; test method

Linhua Jiang is a professor and head of the Department of Materials Science and Engineering, Hohai University, China. He obtained his PhD from the same university. His research interests include durability of concrete, high-performance concrete, concrete repair, and use of waste materials in concrete.

Min-Hong Zhang, FACI, is Associate Professor with Department of Civil Engineering, National University of Singapore. Her research interests include high-strength high-performance lightweight concrete, durability of concrete, impact resistance of high-strength composites, and microstructure of concrete.

ACI Honorary Member V. Mohan Malhotra is Scientist Emeritus, International Centre for Sustainable Development of Cement and Concrete (ICON), CANMET, Natural Resources Canada, Ottawa, Canada. He is a former member of the ACI Board of Direction and has served on numerous ACI committees. He is a prolific author, editor, and researcher, and has received many awards and honors from ACI and other institutions throughout the world.

INTRODUCTION

Corrosion of steel reinforcement in concrete is a serious problem worldwide. One of the primary causes of this corrosion is the penetration of chloride ions, that destroys the passive state of steel in the high alkaline environment in concrete [1]. Most design codes have strict limitations on the total content of chlorides in concrete that are from concrete ingredients such as chemical admixtures and mixing water. The chlorides that cause reinforcement corrosion of structures are often from external sources during the service life of the structures such as sea water or de-icing salts. There is a great need, therefore, to develop methods for evaluating the resistance of concrete against chloride-ion penetration, and to find economical and durable concrete mixtures for applications in severe environment.

There are many test methods for evaluating the resistance of concrete to chloride-ion penetration [2-16], each of them has some advantages and shortcomings. To offer guidelines for the selection of an appropriate test method, some valuable comparisons have been made, though the range of concrete mixtures was limited [5,17-20]. However, there is not much information available for concrete incorporating supplementary cementing material.

This paper presents results of a study that compared ASTM C1202 test, a steady-state migration test, a conductivity test, and a non-steady-state diffusion test for determining the chloride-ion penetrability of control portland cement concrete and concrete incorporating fly ash, ground granulated blast-furnace slag, silica fume, metakaolin, and rice-husk ash.

BACKGROUND

Diffusion Test Methods

Diffusion testing is a common means for the evaluation of the chloride-ion diffusivity into concrete, because this type of method simulates a natural diffusion process. Based on the nature of the measurement, the diffusion test methods can be divided into the steady-state and the non- steady-state methods.

Steady-state diffusion test method--For steady state method, a thin specimen is placed in between two cells. One cell is filled with a chloride solution, e.g. NaCl solution (chloride source cell), while the other may be filled with a chloride free, saturated $Ca(OH)_2$ solution (chloride collecting cell). During the testing, the chloride-ion concentration in the chloride collecting cell is monitored, and the relationship between the chloride concentration and time is established. When steady state is reached, the diffusion coefficient D can be calculated by Fick=s First Law [2].

Non-steady state diffusion test methods--For non-steady-state methods (ponding or immersion tests), one surface of a specimen is usually in contact with a chloride solution in order to ensure a one-dimensional diffusion. After a certain period of time, the chloride-ion content of concrete at different depths from the exposure surface is determined, and the chloride-ion profile of the concrete specimen is established. The diffusion coefficient D then is calculated from the chloride-ion profile by Fick=s Second Law [3, 4]. However, it is well documented that the rate of chloride ingress into concrete decreases with time [5], thus the diffusion coefficient obtained by this method is not a constant, but a time-dependent parameter. To take the time-dependent factor into consideration when calculating the diffusion coefficient, a power function of time has been assumed by Mangat and Molly [6].

In general, both diffusion tests aforementioned are time consuming and are only suitable for laboratory investigations, and therefore, are not practical for rapid determination of the resistance of concrete to chloride-ion ingress on on-going construction jobs.

Migration Test Methods

To determine the resistance of concrete to chloride-ion ingress more rapidly, a test method (so-called Rapid Chloride Permeability test) was developed by Whiting [7] and has gained considerable acceptance in the U.S.A. (AASHTO and since then several other test methods have been developed [9-13]. The principle of the migration tests is the accelerated movement of the chloride ions by the use of an externally applied electrical field.

Non-steady-state migration test methods--
ASTM C1202 - Electrical indication of concrete's ability to resist chloride ion penetration ASTM C1202 test method measures the amount of electric charge that has passed through a saturated concrete disk specimen. The chloride source cell is filled with a 3% NaCl solution and the chloride collecting cell is filled with a 0.3 N NaOH solution. A potential difference of 60V direct current (DC) is maintained across the specimen for 6 hours. The total charge passed, in coulombs, is calculated and used to evaluate the resistance of concrete to the penetration of chloride ions. The main shortcomings of this method [17,18] are: (1), It is sensitive to difference in the chemistry of pore solution, and therefore may exaggerate the effectiveness of supplementary cementing materials on the reduction of penetrability; (2), There is no direct correlation between the accumulated charge passed through the specimen and the chloride transportation behavior: and (3), A constantly applied voltage of 60 V may produce a varying amount of heat inside the specimen and thus affect the test results. However, the test is reasonably reproducible and rapid.

Nordtest Method NT Build 492 This test was based on the method originally developed by Tang and Nilsson [9]. A concrete specimen is exposed to a concentrated sodium chloride solution on one side and a sodium hydroxide solution on the other side. An external potential from 10 to 60 V is applied across the specimen for varying periods of time from 6 to 96 hours. The strength of the external potential and the duration of the test time depend on the quality of concrete. After the test, the specimen is split into two pieces along its axis. The depth of chloride-ion penetration and the chloride-ion content of the concrete at different depths are determined. Based on the depth of chloride-ion penetration and the Nernst-Plank equation, the chloride diffusivity can be calculated [12, 13]. This type method has a sound theoretical basis and good accuracy. The test duration is relatively short. However, the method also have some disadvantages such as: (1), the chemically bound chloride-ions may affect the penetration profile of the chlorides inside the specimen; (2), the chloride-ion concentration at source, at distance x, and at the penetration front represents different media; and (3), the measurement of the penetration depth may induce some extra errors, e.g. the difference in profiles at different cross sections.

Steady-state migration test method--The test arrangement is similar to that used in ASTM C1202. However, the applied external potential is reduced from 60 V to approximately 10 to 15 V. During the testing, the chloride-ion concentration in the chloride collecting cell is monitored until a steady state is reached, and the relationship between the chloride-ion concentration and time can be established. Based on the steady-state migration tests and the relevant theoretical basis such as the Einstein relation, the Nernst-Einstein equation, or the simplified Nernst-Plank equation, the chloride-ion diffusion coefficient can be calculated [9-11].

The steady state migration test method has certain advantages over the non-steady-state migration tests. However, there are still practical disadvantages for this type of method and these are: (1), the duration of the test cannot be predicted, making scheduling of a test program difficult in some cases. For high-performance concrete with low w/cm and incorporating supplementary cementing materials (SCM), the test may take several months before the steady state is reached. This increases the real age of the concrete and makes relative comparison difficult; (2), the concentration of the chloride ions in the collecting cell needs to be measured, and the transference number of this ion needs to be known in order to calculate the diffusion coefficient; and (3), the concentration of the chloride-ions in the source solution changes with time and maintaining a constant chloride source concentration during a test over several months is difficult.

Conductivity Method

The conductivity method is based on the ionic distribution that pertains during steady-state conduction [15]. Conductivity and diffusivity are most easily measured and calculated under steady-state conditions. To shorten the test period and to reduce the effect of the chemistry of the pore solution, specimens are saturated with a concentrated chloride solution in this method so that the steady-state condition can be obtained from the beginning. The specimen is mounted in a cell filled with the chloride solution, and the current passing through the specimen under a given external voltage is measured. The conductivity of the specimen then can be calculated from the current, external voltage and specimen size. By the conductivity of the specimen and the conductivity of its pore fluid, diffusibility ratio is obtained. The diffusibility is a "material" constant, and is defined as the ratio between the diffusivity of an ion in a porous material to that of the same ion in the pore solution. By multiplying this number with the diffusivity of chloride ions in the pore solution, the chloride diffusivity of the porous medium can be obtained [15, 16]. There may be two shortcomings of this method: (1), the pore solution may still have some effect on the results, because the transference number is not equal to 1.0; and (2), according to Debye-Huckel theory, the diffucivity may be affected by the chloride-ion concentration.

INVESTIGATIONS AT CANMET

CONCRETE MIXTURE PROPORTIONS AND PROPERTIES

Materials

Cement--ASTM Type I normal portland cement was used, and its physical properties and chemical composition are given in Table 1.

Fly ash--The fly ash used was from Belews Creek Generating Station, Duke Power, North Carolina, U.S.A. Its physical properties and chemical composition are given also in Table 1. The fly ash was ASTM Class F type with a CaO content of 1.4%, and the specific surface (Blaine) of the fly ash was 264 m^2/kg.

Ground granulated blast-furnace slag--The chemical composition and physical properties of the slag are given in Table 1. The slag contained 35.1% CaO, 36.6% SiO_2, 3.8% SO_3, and 13.0% MgO. The specific gravity of the slag was 2.99, and the percentage of the particles retained on the 45-μm sieve was 3.1%. The slag activity indices at 7 and 28 days were 77.6 and 102.8%, respectively, thus the slag meets the requirements of Grade 100 of ASTM C 989.

Silica fume--A dry uncompacted silica fume from the production of silicon metal was used. It contained 93.7% SiO_2, and had a specific surface of 26.1 m^2/g determined by the nitrogen adsorption method. The detailed chemical composition and physical properties of the silica fume are given in Table 1.

Metakaolin--Metakaolin (MK) is thermally activated alumino-silicate [21], and its physical properties and chemical composition are given in Table 1. It consisted primarily of SiO_2 (51.3%) and Al_2O_3 (42.0%). The material had a specific surface of 16.8 m^2/g and a median particle size of approximately 1.3 Φm, that is smaller than that of ordinary portland cement (approximately 10 Φm) but larger than that of silica fume (approximately 0.1 Φm). The specific gravity of the material was 2.5.

Rice-husk ash--The rice-husk ash (RHA) used was a processed waste material incinerated at a controlled temperature and atmosphere [22]. The chemical composition and physical properties of the RHA are given in Table 1. Its carbon content was 5.91 %, and thus was black in colour. The chemical analysis indicated that the material was principally composed of SiO_2 (87.2 %), and was also high in loss on ignition (8.6 %). The ash also had a relatively high K_2O content of 3.68%, that probably originated primarily from the use of fertilizers in the growing of rice. The RHA had a specific gravity of 2.06, and a median particle size of approximately 7 Φm. The RHA, however, had an extremely high specific surface of 38.9 m^2/g determined by nitrogen absorption, and the value was almost 1.5 times of that for silica fume. Its high specific surface is due to its open pore structure [22].

Aggregates--The coarse aggregate used was crushed limestone or expanded shale, both with a maximum nominal size of 19 mm. The fine aggregate used was natural sand from the Ottawa region. The limestone coarse aggregate was separated into different size fractions, and then recombined to a specified gradation shown in Table 2. The expanded shale coarse aggregate and the natural sand were used as received, and their gradings are given also in Table 2. The specific gravity of the limestone coarse aggregate and fine aggregate were 2.70, and the corresponding values for the water absorption were 0.6 and 0.8 percent, respectively (Table 3). The specific gravity of the expanded shale aggregate was 1.56, and the 24-hour water absorption was 5.2%.

Superplasticizer--A sulphonated naphthalene formaldehyde condensate based superplasticizer was used in most of the concrete mixtures. The superplasticizer is a dark brown solution containing 42% solids.

Air-entraining admixture--A multi-component synthetic resin type of air-entraining admixture was used in all concrete mixtures.

Mixture Proportions

The proportions for the concrete mixtures are summarized in Table 4. For normal-weight portland cement concrete, the control concrete mixtures had water-to-cement ratios (w/c) of 0.30, 0.40, 0.50, and 0.60. For the other normal-weight concrete mixtures, a water-to-cementitious material ratio (w/cm) of 0.40 was selected. The fly ash and slag were used at 20, 40, and 60% by mass of the total cementitious materials. For concrete mixtures incorporating silica fume, metakaolin, and rice-husk ash the cement replacement level was 8%. Two lightweight concrete mixtures were also made, one was a control lightweight concrete with a w/c of 0.4 and in the other mixture 8% Portland cement by mass was replaced by silica fume.

Properties of Fresh Concrete

The properties of the fresh concrete, i.e. slump, air content, density and temperature were determined, and are given in Table 5. For the normal-weight concrete, the slump ranged from 90 to 200 mm, and the density ranged from 2275 to 2346 kg/m^3. For the lightweight concrete, the slump was 70 mm, and the density ranged from 1787 to 1844 kg/m^3. The air content of the concrete ranged from 5.2 to 7.3%.

Specimen Preparation

For each concrete mixture, twenty 102x203-mm cylinders were cast for determining the compressive strength and the resistance to chloride-ion penetration using ASTM C 1202 test method, conductivity, and steady-state migration tests. Four 300x300x75-mm slabs were also cast for ponding test (non steady-state diffusion test).

All the specimens were cast in two layers, and consolidated on a vibrating table. The slabs were consolidated by roding. After casting, all the specimens were covered with a plastic sheet and wet burlap and left in the casting room for

24 hours. The specimens were then demoulded and transferred to a moist curing room at 20 ± 3 °C and 100% relative humidity until the time of testing.

Compressive Strength of Concrete

The compressive strength test results are given in Table 6. For the control portland cement concrete, the 28-day strength increased from 23.8 to 58.8 MPa for w/c ranging from 0.60 to 0.31. The concrete with 20% fly ash as cement replacement had 7- and 28-day strength similar to that of the control concrete of equivalent w/cm, but had higher strength at 91 days. However, the concrete with 60% fly ash as cement replacement had lower strengths at all three ages as expected. The concrete incorporating 20 or 40% slag as cement replacement had 7-day strength similar to that of the control concrete with equivalent w/cm, but higher strengths at 28 and 91 days. For the concrete with 60% slag, the 28- and 91-day strengths were similar to those of the control concrete, but 7-day strength was somewhat lower. The concrete incorporating 8% silica fume, metakaolin, or rice-husk ash had higher strength at all ages up to 91 days compared with that of the control concrete with equivalent w/cm. The highest strengths were achieved with the concrete containing metakaolin. The strength of lightweight concrete was lower than that of the corresponding normal-weight concrete.

TEST METHODS USED

Non-Steady-State Migration Test - ASTM C 1202

The resistance of the concrete to the chloride ion penetration was determined according to ASTM C 1202 test method at the ages of 28 and 90 days using the top portion of two cylinders at each age.

Steady-State Migration Test

A method developed by Zhang and Gjørv [9] was used to determine the diffusion coefficient of chloride ions at 28 and 90 days. The top portion (51-mm) of three cylinders was used for each concrete at each age. The experimental arrangement and procedure are the same as those used in the ASTM C 1202 test, except that the external potential applied across the concrete specimens was 12 volts. The top portion of each cured cylinder was first cut off, surface dried, and then coated with epoxy on the side surface. Before testing, all the specimens were vacuum saturated. The chloride concentration in the chloride collecting cell was monitored periodically during the test. The experiment continued until a steady-state flux of chloride ions was reached.

The diffusion coefficient was then calculated by Eq. (1).

$$D = \beta\ \alpha\ dc/dt \tag{1}$$

where

dc/dt = the rate of increase in the chloride concentration in the chloride collecting cell with time when a steady state is reached,

β = correction factor [9],

$$\alpha = \frac{T}{\Delta\psi}\frac{LV}{C_0 A_0}$$

where

T = absolute temperature, in kelvin

$\Delta\psi$ = the applied electrical potential, in volt

L = the specimen thickness, in cm

V = the volume of the chloride collecting cell, in mL

C_0 = the chloride concentration in the chloride source solution, in M

A_0 = the cross sectional area of concrete specimen, in cm^2

For example, in this test, $\Delta\psi$, C_0, and A_0 are 12 V, 0.5M, and 78.5 cm^2, respectively. For specimen C08-7, the T, L, V, and dc/dt are 293.03 K, 5.14cm, 250ml, and $2.62H10^{-8}$M/s, respectively. So,

$$\alpha = \frac{293.03}{12} \times \frac{5.14 \times 250}{0.5 \times 78.5} = 799.77\ (KXcm^2/VXM)$$

$\beta = 1.46H10^{-4}$

$D = 1.46H10^{-4}\ H\ 799.77\ H\ 2.62H10^{-8} = 3.06H10^{-9}\ (cm^2/s)$

Conductivity Test

The conductivity of the samples was measured at the age of 90 days, and the cells used for ASTM C 1202 test was used for this one as well. The top portion of each cured cylinder was first cut off, then surface dried, and coated with epoxy on the side surface. Before testing, all the specimens were vacuum saturated with 2.5M NaCl solution instead of water. During the test, the NaCl solution in the chloride source cell was also 2.5M NaCl solution. The external electric potential applied for the test was 60 volts. The initial current was measured and recorded, and the calculation of the diffusion coefficient of chloride was based on the method developed by Streicher and Alexander [15].

The diffusion coefficient can be calculated using Eq. (2).

$$D = D_0\frac{\sigma}{\sigma_0} = \frac{I_0}{\Delta\psi}\frac{L}{A_0}\frac{D_0}{\sigma_0} \tag{2}$$

where D_0 = diffusivity of ion in pore solution,

σ = conductivity of the solution saturated medium,

σ_0 = conductivity of the pore solution,

I_0 = initial current, in mA,
A_0 = the cross sectional area of concrete specimen, in cm^2

For example, in this study $\Delta\psi$ and A_0 are 60 V and 78.5 cm^2, respectively. The σ_0 and D_0 for 2.5 M NaCl were assumed to be 160 mS/cm[14] and $1.65\text{x}10^{-5}$ cm^2/s[20], respectively. For specimen C06-19, the I_0 and L are 302 mA and 5.20 cm, respectively. Therefore,

$$D = \frac{302}{60} \times \frac{5.20}{78.5} \times \frac{1.65 \times 10^{-5}}{160} = 3.44\text{H}10^{-8} \text{ (cm}^2\text{/s)}$$

Non Steady-State Diffusion Test (AASHTO T 259 Ponding Test)

Ponding test, based on AASHTO T259, was started after an initial moist curing of the concrete slabs for 14 days, followed by 28 days drying in the laboratory air. The test slabs were then continuously ponded with a 3% NaCl solution for 90 days. After that, the total chloride content of the samples at different depths was determined by high-performance ion chromatography (HPIC), and the diffusion coefficient of chloride ions was calculated by Fick's Second Law.

RESULTS AND DISCUSSION

The results of the resistance of concretes to chloride-ion penetration determined by the various tests are summarized in Table 7.

Non Steady-State Migration Test - ASTM C 1202 Test

The chloride penetrability measured in term of the charge passed decreased with the decrease in the w/c, and with the incorporation of supplementary cementing materials such as fly ash, slag, silica fume, metakaolin, or rice-husk ash. At 91 days, the incorporating of 40 or 60% either fly ash or slag approaches the values for concrete incorporating metakaolin or rice husk ash. The lowest value at 91 days was 269 coulombs for concrete incorporating 8% silica fume.

The chloride penetrability of the concrete made with the expanded shale lightweight aggregate was similar to that made with the normal-weight limestone aggregate even though the former had higher total porosity and lower compressive strength than the latter.

The extension of the curing time from 28 to 91 days reduced the chloride-ion penetrability considerably for concrete incorporating fly ash, slag, and rice-husk ash; however, this effect on the control portland cement concrete and concrete incorporating silica fume or metakaolin was limited.