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**FLY ASH,
SILICA FUME,
SLAG, AND NATURAL
POZZOLANS IN
CONCRETE**

**CENDRES VOLANTES,
FUMÉES DE SILICE,
LAITIERS ET POZZOLANES
NATURELLES DANS
LE BÉTON**

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FRONT COVER PHOTO: A view of the first high-volume fly ash concrete pavement in India.
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Eighth CANMET/ACI International Conference on Fly Ash, Silica Fume, Slag and Natural Pozzolans in Concrete

Editor

V. Mohan Malhotra



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PREFACE

To conserve both resources and energy, and to reduce CO₂ emissions, the Canadian Centre for Mineral and Energy Technology (CANMET) of Natural Resources Canada, Ottawa, has played a significant role in Canada for over 35 years in research on fly ashes, ferrous and nonferrous slags, and silica fumes. In July-August 1983, CANMET, in association with the American Concrete Institute and the U.S. Corps of Engineers, sponsored a five-day international conference at Montebello, Quebec, Canada, on the Use of Fly Ash, Silica Fume, Slag and Other Mineral By-Products in Concrete. The conference brought together representatives from industries, universities, and government agencies to present the latest information on these materials and to explore new areas of needed research. The two-volume proceedings of the conference containing 62 papers from 15 countries were published as ACI Special Publication SP-79.

In 1986, CANMET, in association with the American Concrete Institute, the Canadian Society for Civil Engineering, and a number of organizations in Spain, sponsored the Second International Conference on Fly Ash, Silica Fume, Slag, and Natural Pozzolans in Concrete. The conference was held April 21-25, 1986, in Madrid, Spain. The two-volume proceedings of the conference containing 72 refereed papers from more than 20 countries were published as ACI Special Publication SP-91.

In 1989, CANMET, in association with the American Concrete Institute, Norwegian Institute of Technology, and several other organizations in Canada and Norway, sponsored the Third International Conference on this subject. The conference was held June 18-23, 1989, in Trondheim, Norway. The two-volume proceedings of the conference containing 83 refereed papers from more than 25 countries were published as ACI Special Publication SP-114.

In 1992, CANMET, in association with the American Concrete Institute, Electric Power Research Institute, U.S.A., and several other organizations in Canada and Turkey, sponsored the Fourth International Conference on the subject. The conference was held May 3-8, 1992, in Istanbul, Turkey. More than 130 papers from 32 countries were received and reviewed in accordance with the policies of the American Concrete Institute; 89 refereed papers were accepted for publication as ACI Special Publications SP-132.

In 1995, CANMET, in association with the American Concrete Institute, Electric Power Research Institute, U.S.A., Canadian Electrical Association, Montreal, and several other organizations in Canada and the United States, sponsored the Fifth International Conference on the subject. The conference was held June 4-9, 1995, in Milwaukee, U.S.A. The two-volume proceedings of the conference containing 62 refereed papers from 23 countries were published as ACI Special Publication SP-153.

In 1998, CANMET, in association with the American Concrete Institute, U.S.A. and Electric Power Research Institute, U.S.A., and several other organizations in Canada and Thailand, sponsored the Sixth CANMET/ACI International Conference on the subject. The conference was held May 31-June 5, 1998, in Bangkok, Thailand. The two-volume proceedings of the conference containing 59 refereed papers from 26 countries were published as ACI Special Publication SP-178.

In 2001, CANMET, in association with the American Concrete Institute, the Electric

Power Research Institute, U.S.A., and several other organizations in Canada and India sponsored the Seventh CANMET/ACI International Conference on Fly Ash, Silica Fume, Slag and Natural Pozzolans in Concrete. The Conference was held July 22-27, 2001, in Chennai (Madras), India. The two-volume proceedings of the conference, containing 53 refereed papers from more than 20 countries were published as ACI Special Publication SP-199.

In 2004, CANMET in association with the American Concrete Institute, Farmington Hills, MI, the Electric Power Research Institute, Palo Alto, CA, UWM Center for By-Products Utilization, Milwaukee, WI, and several other organizations in Canada, sponsored the Eighth CANMET/ACI International Conference on Fly Ash, Silica Fume, Slag and Natural Pozzolans in Concrete. The conference was held in Las Vegas, Nevada, U.S.A., May 23-29, 2004. The proceedings of the conference containing 56 refereed papers from more than 20 countries were published as ACI Special Publication SP-221.

To all those whose submissions could not be included in the conference proceedings, the Institute and the Conference Organizing Committee extend their appreciation for their interest and hard work. In addition to the papers which have been published in the proceedings, a large number of other papers were presented. Most of these papers were published as supplementary papers, and the authors have been encouraged to publish them in technical journals of their choice.

Thanks are extended to the members of the “Technical Paper Review Panel” that met at Sorrento, Italy, Nov. 1-5, 2003, to review the papers. Without their dedicated effort, it would not have been possible to publish the proceedings for distribution at the conference. The cooperation of the authors in accepting reviewers’ suggestions and revising their manuscripts accordingly is greatly appreciated.

The help and assistance of Mr. H. S. Wilson, Consultant, Ottawa, Gordon D. Brearley and Maria Venturino of CANMET, and Dr. A. K. Kuriakose of Ottawa are gratefully acknowledged in the administrative work associated with the conference, and in processing of the manuscripts both for the ACI proceedings and the supplementary volume. Thanks are also extended to A. Bilodeau (Chair) and Messrs. B. Fournier and R. Chevrier (Members) of the Audio-visual Review Panel for their services to ensure that the visuals met the CANMET/ACI criteria.

V.M. Malhotra, Editor

Chair, Eighth CANMET/ACI International Conference on Fly Ash, Silica Fume, Slag and Natural Pozzolans in Concrete

Las Vegas, Nevada, U.S.A.

May 2004

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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 shortcomings. 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

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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 $\text{Ca}(\text{OH})_2$ 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 Molloy [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 diffusivity 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 m²/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% SiO₂, 3.8% SO₃, and 13.0% MgO. The specific gravity of the slag was 2.99, and the percentage of the particles retained on the 45- μ m 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 uncompact silica fume from the production of silicon metal was used. It contained 93.7% SiO₂, and had a specific surface of 26.1 m²/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 aluminosilicate [21], and its physical properties and chemical composition are given in Table 1. It consisted primarily of SiO₂ (51.3%) and Al₂O₃ (42.0%). The material had a specific surface of 16.8 m²/g and a median particle size of approximately 1.3 Φ m, that is smaller than that of ordinary portland cement (approximately 10 Φ m) but larger than that of silica fume (approximately 0.1 Φ m). 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 SiO₂ (87.2 %), and was also high in loss on ignition (8.6 %). The ash also had a relatively high K₂O 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 Φ m. The RHA, however, had an extremely high specific surface of 38.9 m²/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/m³. For the lightweight concrete, the slump was 70 mm, and the density ranged from 1787 to 1844 kg/m³. 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 Gjrv [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).

$$D = \beta \alpha \, dc/dt \quad (1)$$

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 $2.62 \times 10^{-8} \text{ M/s}$, respectively. So,

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

$$\beta = 1.46 \times 10^{-4}$$

$$D = 1.46 \times 10^{-4} \times 799.77 \times 2.62 \times 10^{-8} = 3.06 \times 10^{-9} \text{ (cm}^2/\text{s)}$$

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).

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

- 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 $1.65 \times 10^{-5} \text{ cm}^2/\text{s}^{20}$, respectively. For specimen C06-19, the I_0 and L are 302 mA and 5.20 cm, respectively. Therefore,

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

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.

Relationship between the charge passed and the initial current--The ASTM C 1202 test is the most commonly used method in North America for determining the resistance of concrete to chloride-ion penetration. Criticisms and doubts have been expressed over the years with regard to this test. Feldman et al. [20, 23] and Zhao et al. [24] investigated the relationship between the charge passed and the initial electrical current, and found that there was a good correlation between the charge passed and the initial current. However, the data were limited.

The results from the present study are shown in Fig. 1, and it seems that there is a good correlation between the charge passed and the initial current, but the relationship was not linear in the entire range of the concretes tested. The relationship was linear up to approximately 2000 coulombs in terms of the charge passed. This is consistent with the data reported by Feldman et al [20, 23]. The reason why there is not a linear relationship between these two parameters in the whole range is that there are significant changes in the electric current during the test for concrete with high initial currents (porous concrete) and relatively small changes for concrete with low initial currents (dense concrete). For durable concrete, one is dealing with low w/c concrete that has low porosity, thus both methods can give satisfactory results.

Diffusion Coefficients of Chloride-Ion Determined by Different Test Methods

Diffusion coefficient D_s determined by the steady-state migration test--The results of the diffusion coefficient determined by the steady-state migration test seem to show similar trend as obtained by the ASTM C 1202 test with some exceptions. However, due to the very nature of the test method, the variation of the test results appeared to be high. Also, the duration of the test is much longer than that of the ASTM test, particularly for dense concrete. For extremely dense concrete a steady-state migration of chloride cannot be reached within a meaningful time, and thus no diffusion coefficient can be calculated. For example, for concrete test specimens cast from the mixture C19 and cured for 91 days, even after 3 months of testing, the chloride-ion penetration through the concrete was negligible.

Diffusion coefficient D_c determined by the conductivity test--The results of the diffusion coefficient determined by the conductivity test appear to show similar trend as that by the charge passed in coulombs in ASTM C 1202 test.

Chloride profiles in concrete after 91 days of the ponding test and the diffusion coefficient D_p determination--Figures 2 to 6 show the effect of w/c, type of supplementary cementing materials, and the type of coarse aggregate on the chloride profile in concrete after 91 days of the ponding test, respectively. The data presented are the averages from three concrete slabs.

As expected, the lower the w/c, the less the penetration of the chloride ions

(Fig. 2). The incorporation of 40 and 60% of the fly ash reduced the chloride-ion penetration even though the chloride-ion content near the surface for concrete incorporating 40% fly ash was somewhat higher than that of the control portland cement concrete (Fig. 3). The chloride profile of the concrete incorporating 20% fly ash was similar to that of the control concrete.

The trend for the concrete incorporating slag was similar to that of fly ash. The incorporation of 40 and 60% of the slag reduced the chloride penetration, whereas the chloride profile of the concrete incorporating 20% slag was similar to that of the control concrete (Fig. 4).

The incorporation of silica fume, metakaolin, or rice-husk ash significantly reduced the chloride-ion penetration (Fig. 5). It seems that the incorporation of 60% slag was as effective as the incorporation of 8% silica fume, metakaolin, or rice husk ash in reducing the penetration of chloride ions. However, the incorporation of 60% fly ash was less effective, and this was due to the nature of the mixture proportion used.

Figure 5 also showed that the chloride-ion penetration into the control concrete with a w/c of 0.3 was very low even compared with that of the SF concrete. This was reflected also from the steady state migration test. However, the results from the ASTM C 1202 test and the conductivity test indicated that the former had higher chloride-ion penetrability than the latter. This maybe attributed to the fact that the pore solution chemistry had more effect on the electric parameters measured in the ASTM test and the conductivity test at 60 V.

The control concrete made with the lightweight aggregate had lower chloride-ion penetrability than that made with the normal-weight aggregate due to the improved interfacial zone between the lightweight aggregate and the mortar matrix (Fig. 6). The results are consistent with those reported in literature [25-27]. This may be explained by the fact that in concrete made with normal-weight aggregate, the interfacial zone between the coarse aggregate and the mortar matrix has higher water-to-cement ratio, and is relatively porous compared with the mortar matrix [28]. However, for concrete made with lightweight aggregate, due to the water absorption by the aggregate, the interfacial zone between the aggregate and the mortar matrix is denser [29]. However, the type of coarse aggregate did not have significant effect on the chloride profile for the concrete incorporating silica fume as the silica fume had improved the interfacial zone between the normal-weight aggregate and the mortar matrix.

The results of the diffusion coefficient determined by the ponding test (Table 7) showed similar trend as that of ASTM C 1202 with some exceptions. However, the diffusion coefficient determined by the ponding test was one order of magnitude higher than that determined by the steady-state migration test or the conductivity test. This may be partly attributed to the fact that the chloride-ion content determined in this test included free, physically absorbed, and chemically bound chlorides. The type of coarse aggregate seems to have great effect on the diffusion coefficient D_p , and this again maybe related to the

nature of the interface zone between the coarse aggregate and the cement paste. It appears that the more porous the cement paste, the more difference there is in the D_p between the lightweight aggregate concrete and the normal-weight concrete.

Relationships between the charge passed and the diffusion coefficients of chloride ions--The relationships between the charge passed according to the ASTM test and the diffusion coefficients obtained by the steady-state migration test, the conductivity test, and the non-steady state diffusion test are shown in Figs. 7 to 9. It can be seen that there are relationships between the charge passed and the diffusion coefficients obtained by these tests. From Figs. 7, 8, 9 and ASTM C 1202, the chloride-ion penetrability of the concrete evaluated by the aforementioned methods is shown in Table 8. Although there are some shortcomings of ASTM C 1202 method and it is theoretically not correct to use the charge passed to evaluate the chloride-ion penetrability of concrete, the test results did indicate that in general these four test methods led to similar conclusions regarding the relative quality of the concrete. However, compared with the steady-state migration test or the non steady-state diffusion test, ASTM C 1202 test method and the conductivity test are much easy to perform and the result can be obtained within short periods of time. In fact, the conductivity test is the most rapid and convenient test method developed to date, and therefore appears to have great potential.

CONCLUSIONS

1. In general, the results obtained by using ASTM C 1202 test method, the steady state migration test, the conductivity test, and the non steady-state diffusion test 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.
2. 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.

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Table 1 - Physical properties and chemical analysis of the cement, fly ashes, silica fume, and slag used

	ASTM Type I Cement	ASTM Class F fly ash	Blast- furnace Slag	Silica Fume	Meta- kaolin	Rice- husk ash
Physical Tests						
Specific gravity	3.09	2.47	2.99	2.16	2.50	2.06
Fineness						
-retained on 45 Φ m, %	6.9	20.2	3.1	2.1	0.2	1.0
-specific surface, Blaine, m ² /kg	402	264	449	-	-	-
-nitrogen absorption, m ² /g	-	-	-	26.1	16.8	38.9
Compressive strength of 51 mm cubes, MPa						
-7-day	33.0	-	-	-	-	-
-28-day	40.8	-	-	-	-	-
Water requirement, %	-	95.0	97.1	111.6	-	-
Strength Activity Index, %						
-7-day	-	86.3	77.6	128.8	-	-
-28-day	-	91.3	102.8	-	-	-
Chemical Analyses, %						
Silicon dioxide (SiO ₂)	21.07	56.96	36.6	93.7	51.34	87.2
Aluminum oxide (Al ₂ O ₃)	4.61	29.72	9.8	0.2	41.95	0.15
Ferric oxide (Fe ₂ O ₃)	3.29	5.95	0.5	0.3	0.52	0.16
Calcium oxide (CaO)	64.46	1.44	35.1	0.4	0.34	0.55
Magnesium oxide (MgO)	2.69	1.01	13.0	0.5	0.03	0.35
Sodium oxide (Na ₂ O)	0.28	0.26	0.4	0.2	0.34	1.12
Potassium oxide (K ₂ O)	0.94	2.32	0.5	1.2	0.11	3.68
Equivalent alkali (Na ₂ O+0.658K ₂ O)	0.90	1.79	0.7	1.0	-	-
Phosphorous oxide (P ₂ O ₅)	0.22	0.22	-	0.1	0.28	0.50
Titanium oxide (TiO ₂)	0.16	1.55	-	0.01	1.74	0.01
Sulphur trioxide (SO ₃)	4.69	0.46	3.8	0.3	0.07	0.24
Loss on ignition	1.79	0.72	1.4	2.7	0.72	8.55
<u>Bogue Potential Compound Composition</u>						
Tricalcium silicate C ₃ S	53					
Dicalcium silicate C ₂ S	20					
Tricalcium aluminate C ₃ A	7					
Tetracalcium aluminoferrite C ₄ AF	10					

Table 2 - Grading of the aggregates

Coarse aggregate			Fine aggregate	
Sieve size (mm)	Normal weight	Lightweight		
	Cumulative percentage retained	Cumulative percentage retained	Sieve size (mm)	Cumulative percentage retained
19.0	0	0	4.75	2.9
12.7	35	6.3	2.36	12.4
9.5	60	46.2	1.18	23.3
4.75	100	95.3	0.60	47.7
2.36	100	97.6	0.30	83.4
			0.15	96.0

Table 3 - Physical properties of the aggregates

	Coarse aggregate		Fine aggregate***
	Normal weight*	Lightweight**	
Specific gravity (SSD)	2.70	1.56	2.70
Water absorption, %	0.6	5.2	0.8

* Limestone

** Expanded shale

*** Natural sand

Table 4 - Mixture proportions of concrete

Mix No.	Type of SCM [†]	SCM content, %	Type of coarse agg.	W/CM	W/C	Quantities (kg/m ³)						A.E.A. ^{***} (mL/m ³)
						Water [*]	Cement	SCM	Fine agg.	Coarse agg.	SP ^{**}	
C06	-	-	limestone	0.60	0.60	152	253	0	758	1133	0	46
C05				0.50	0.50	156	312	0	746	1118	0	80
C04				0.40	0.40	153	381	0	708	1063	0.6	119
C12				0.31	0.31	139	445	0	700	1047	8.9	494
C07	Fly ash	20		0.40	0.50	155	309	77	713	1069	0.9	100
C08		40		0.40	0.67	155	232	155	707	1058	1.0	109
C11		60		0.40	1.00	156	155	233	701	1049	1.0	147
C09	Slag	20		0.41	0.51	156	307	77	711	1066	3.5	138
C10		40		0.41	0.68	158	232	155	715	1072	5.4	151
C17		60		0.40	1.00	156	155	233	715	1070	1.2	170
C13	Silica fume	8		0.41	0.44	156	351	31	702	1053	5.4	218
C14	Metakaolin	8		0.41	0.44	156	352	31	707	1059	4.0	219
C15	Rice husk ash	8	0.41	0.44	156	353	31	705	1058	4.0	518	
C18	-	0	expanded shale	0.40	0.40	154	384	0	713	620	1.2	92
C19	Silica fume	8		0.41	0.44	154	349	31	700	606	3.4	189

† supplementary cementing materials

* including water in the superplasticizer

** superplasticizer

*** air-entraining admixture

Table 5 - Properties of fresh concrete

Mix No.	Type of SCM*	SCM content, %	Type of coarse agg.	w/cm	w/c	Temperature, °C	Density, Kg/m ³	Slump, mm	Air content, %
C06			limestone	0.60	0.60	19.5	2275	135	6.7
C05	-	-		0.50	0.50	20.0	2346	95	5.5
C04				0.40	0.40	19.0	2289	95	7.0
C12				0.31	0.31	16.0	2338	195	7.1
C07		20		0.40	0.50	19.5	2331	115	5.5
C08	fly ash	40		0.40	0.67	19.0	2303	160	5.4
C11		60		0.40	1.00	15.0	2296	195	5.2
C09		20		0.41	0.51	19.5	2317	200	6.2
C10	slag	40		0.41	0.68	15.0	2338	145	5.2
C17		60		0.40	1.00	25.0	2327	90	5.3
C13	silica fume	8		0.41	0.44	15.5	2296	190	6.7
C14	Metakaoli	8	expanded shale	0.41	0.44	15.0	2296	135	6.6
C15	rice husk	8		0.41	0.44	15.0	2310	190	6.4
C18	-	0		0.40	0.40	26.5	1844	70	6.2
C19	silica fume	8		0.41	0.44	26.0	1787	70	7.3

* supplementary cementing materials

Table 6 - Compressive strength of concrete

Mix No.	Type of SCM*	SCM content, %	Type of coarse aggregate	w/cm	Density, kg/m ³	Compressive strength (MPa)		
						7d	28d	91d
C06	-	-	limestone	0.60	2328	19.3	23.8	27.3
C05	-	-		0.50	2356	29.5	36.7	40.3
C04	-	-		0.40	2327	33.1	38.9	42.7
C12	-	-		0.31	2373	49.7	58.8	62.6
C07	fly ash	20		0.40	2355	32.3	39.2	50.1
C08		40		0.40	2332	22.5	32.6	42.9
C11		60		0.40	2326	10.6	19.9	33.1
C09	slag	20		0.41	2360	32.1	41.9	48.3
C10		40		0.41	2395	34.3	53.2	55.5
C17		60		0.40	2355	26.4	38.4	44.2
C13	silica fume	8		0.41	2317	38.8	52.0	53.1
C14	meta-kaolin	8		0.41	2341	44.4	53.4	57.2
C15	rice husk ash	8	expanded shale	0.41	2345	38.1	48.1	52.7
C18	-	0		0.40	1880	30.5	36.1	41.3
C19	silica fume	8		0.41	1806	35.7	46.1	49.5

* supplementary cementing materials

Table 7 - Resistance of concrete to chloride-ion penetration

Mix No.	Type of SCM	SCM content, %	Type of coarse aggregate	w/cm	ASTM C1202 (Coulomb)		D (10^{-8} cm ² /s)			
					28d	91d	28d*	91d*	91d**	42d***
C06	-	-	limestone	0.60	3878	3796	2.70	2.65	3.59	17.4
C05				0.50	3367	2782	1.55	1.62	1.87	13.7
C04				0.40	2424	2257	0.65	0.78	1.54	11.3
C12				0.31	1396	914	0.06	0.06	0.62	3.9
C07	fly ash	20		0.40	2044	726	0.67	0.20	0.76	11.4
C08		40		0.40	1386	457	0.33	0.27	0.75	6.7
C11		60		0.40	1670	401	0.71	0.14	0.68	8.0
C09	slag	20		0.41	1688	1266	0.19	0.25	0.99	7.7
C10		40		0.41	840	504	0.03	0.05	0.53	4.4
C17		60		0.40	601	408	0.04	0.07	0.33	0.6
C13	silica fume	8		0.41	405	269	0.07	0.10	0.26	2.4
C14	meta-kaolin	8		0.41	404	379	0.05	0.04	0.38	2.2
C15	rice husk ash	8		0.41	1187	475	0.07	0.09	0.41	3.0
C18	-	-	expanded shale	0.40	2239	1909	0.85	0.74	1.11	2.6
C19	silica fume	8		0.41	316	313	0.15	H	0.26	0.7

* by steady-state migration test [9], Ds

** by conductivity test [15], Dc

*** determined according to AASHTO ponding test results (based on total chloride), Dp

H Negligible amount of chloride ion penetrated through the concrete after 3 months, and no diffusion coefficient can be calculated.

Table 8 - Evaluation of concrete resistance to chloride penetration

Chloride-ion penetrability	Charge passed (Coulombs) per ASTM C1202	Diffusion coefficient ($10^{-8} \text{ cm}^2/\text{s}$)		
		Steady-state migration test, Ds	Conductivity test, Dc	Non-steady diffusion test, Dp
High	>4000	>3.0	>4.0	>18
Moderate	2000-4000	0.7-3.0	1.3-4.0	8-18
Low	1000-2000	0.2-0.7	0.8-1.3	5-8
Very low	100-1000	<0.2	<0.8	<5
Negligible	<100			

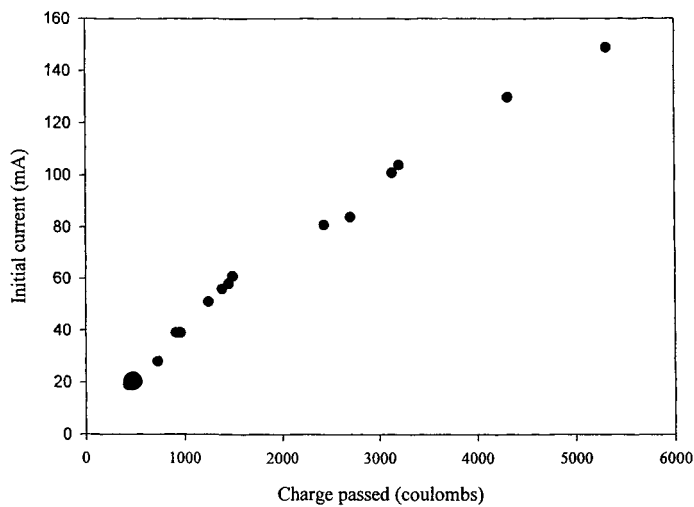


Fig. 1 - Relationship between the charge passed according to ASTM C 1202 and the initial current.

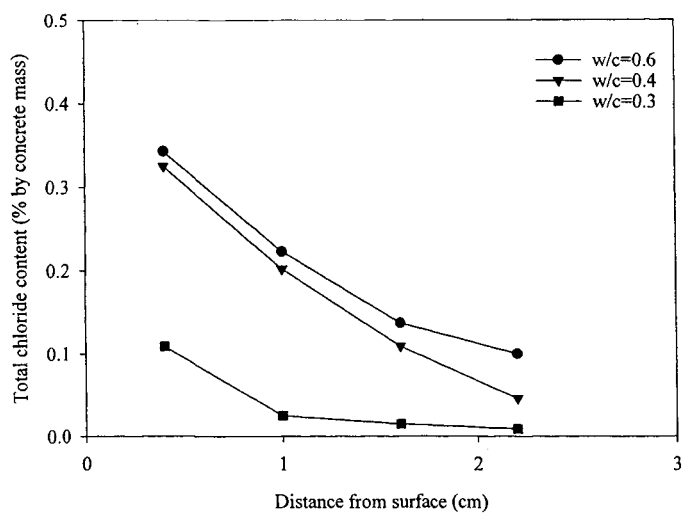


Fig. 2 - Chloride profiles of the control portland cement concrete.

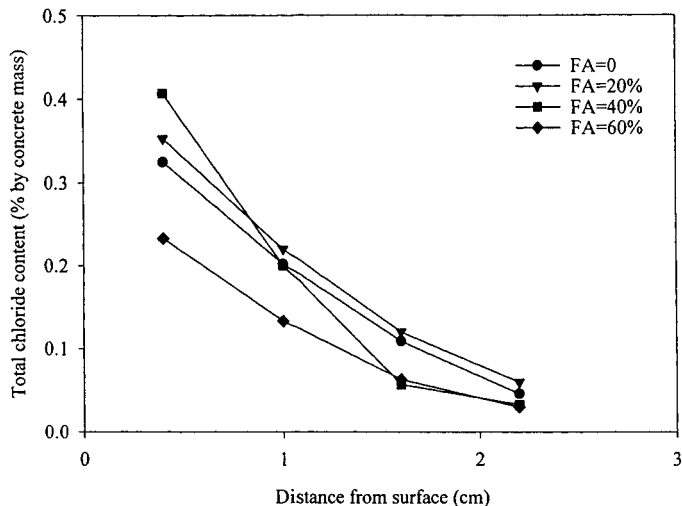


Fig. 3 - Chloride profiles of the fly ash concrete.

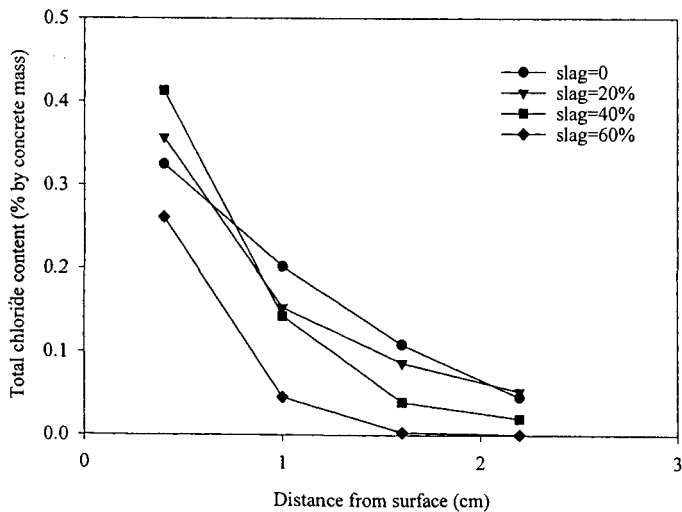


Fig. 4 - Chloride profiles of the slag concrete.

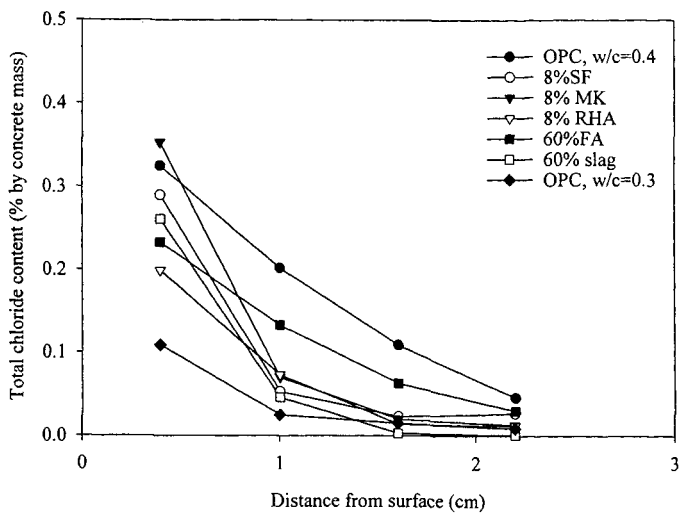


Fig. 5 - Chloride profiles of the concrete incorporating various supplementary cementing materials.

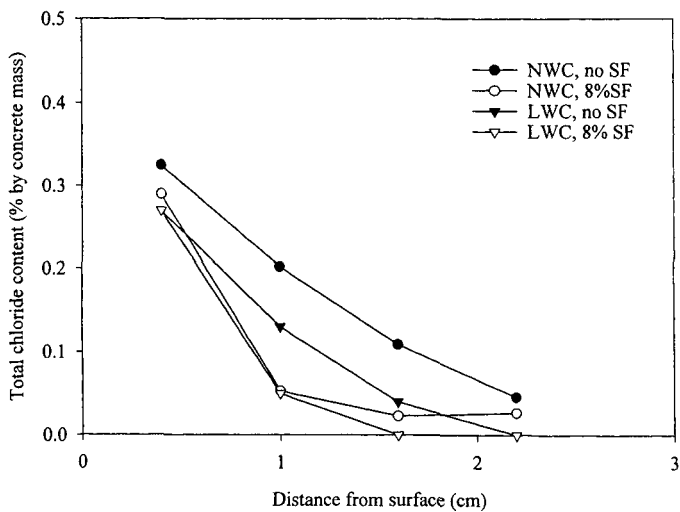


Fig. 6 - Chloride profiles of the lightweight concrete in comparison with those of the normal weight concrete.

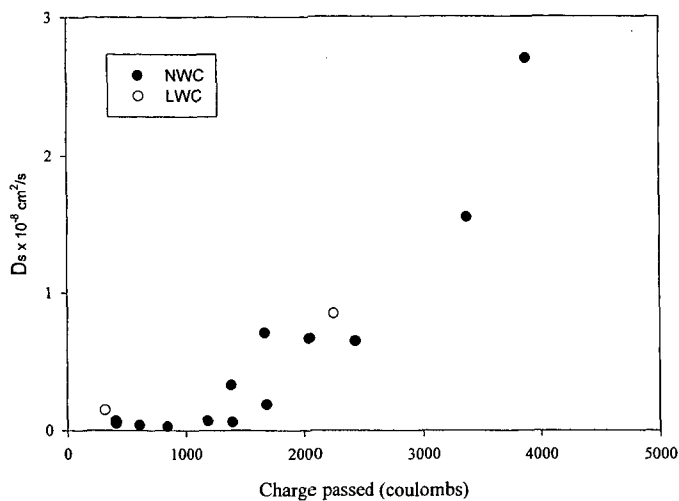


Fig. 7 - Relationship between the charge passed and the diffusion coefficient of chloride determined by the steady state migration test (concrete cured for 28 days)

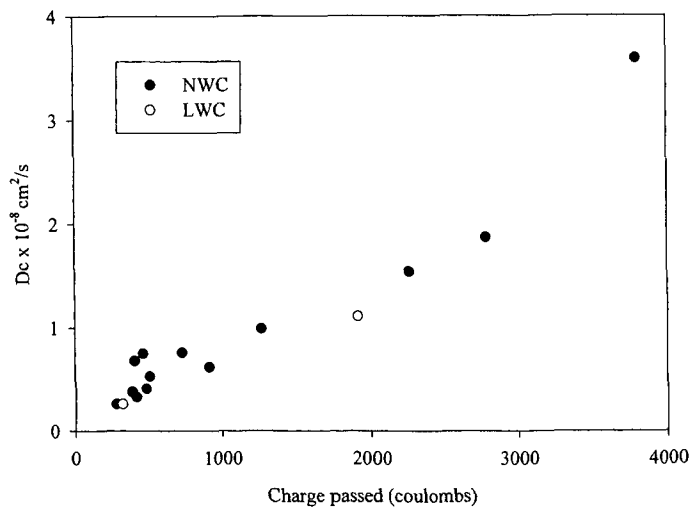


Fig. 8 - Relationship between the charge passed and the diffusion coefficient of chloride determined by the conductivity test (concrete cured for 91 days)

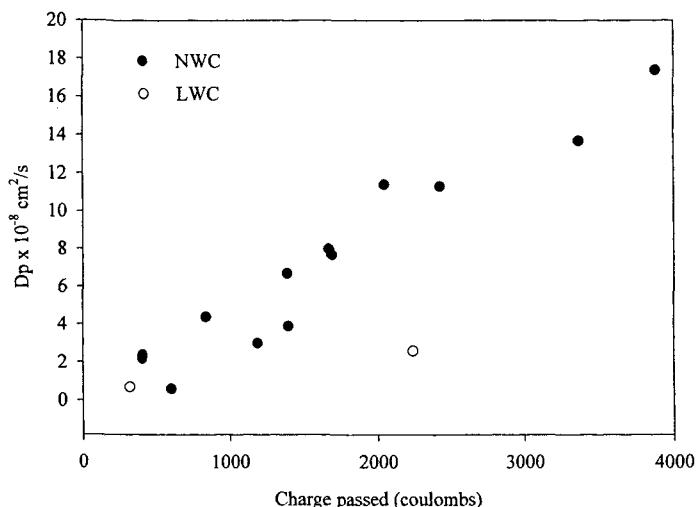


Fig. 9 - Relationship between the charge passed and the diffusion coefficient of chloride ions determined by the non-steady-state diffusion test. Charge passed was determined for concrete cured for 28 days, but D_p was determined according to AASHTO 259 of which the concrete was cured for 42 days (14 day moist curing + 28 day in lab air) followed by 91 days ponding with chloride solution.

Sustainable Development and Durability of Self-Compacting Concretes

by L. Coppola, T. Cerulli, and D. Salvioni

Synopsis:

Self-compacting concretes (SCC) represent a move toward a sustainable material since they encourage the use of waste and recycled materials. The high volume of very fine powder necessary to achieve deformability and passing ability properties, in fact, permits SCC to consume large amount of fly-ash, very fine particles generated by the recycling of demolished concrete structures, and huge amount of calcareous filler available from the marble quarries. Moreover SCC turn out to be materials with an extended durability with respect to conventional concretes. Since fresh properties of self-compacting concretes (SCC) are significantly different from those of conventional concretes (CC) durability can be significantly improved when a SCC is used due to a modification of the microstructure of the interfacial transition zone between aggregates and cement matrix.

This paper presents results of an experimental study carried out to evaluate changes in microstructure of interfacial transition zone (itz) and of bulk paste for both SCC and CC. Data on the influence of the calcareous filler, a fundamental ingredients to achieve self-compactability, on the hydration process of cement are also presented.

Data indicate that the decrease in internal bleeding, when self-compacting concrete is used, seems to favour the formation of a stronger transition zone characterized by a less porous structure and with a limited amount of microcracking responsible for higher compressive strength values for SCC with respect CC. No differences were detected by EDAX analysis in the chemical nature of itz with respect the bulk matrix both for SCC and CC.

Finally, observations of the cement hydration by analysis of the temperature profile vs time seem to indicate the calcareous grains promote formation of heterogeneous nucleation responsible for the increased crystallinity of ettringite, for a shorter normally dormant period and, hence, for higher strength values at early ages, when the calcareous filler is used.

Keywords: bond strength; calcareous filler; chloride diffusion; durability; gas permeability; interfacial transition zone; plastic settlement; plastic shrinkage; self-compacting concretes; sustainable development

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INTRODUCTION

According to a study that has been carried out recently [1], in Europe innovation in construction is concentrated in 4 main directions, which can be defined simplistically as follows:

- to build in a sustainable manner;
- to schedule appropriate building maintenance;
- to build safe and comfortable buildings;
- to build well and efficiently.

Of these directions, the first two ones are prevalent and are destined to represent the “new construction ideology” of this millennium, at least for the next 30-50 years. In particular, to build in a sustainable manner means to focus great attention on the following features:

- physical, environmental and technological resources;
- problems related to human health;
- energy conservation of new and existing buildings;
- control of construction technologies and methods.

Moreover, sustainability requires is to consider a building “life-cycle” extended over the useful life-time. This includes consideration of the building maintenance, demolition and recycling. This means that in our country, and generally speaking in “our ancient continent”, to build sustainably imposes dramatic changes to our construction methods and a

need to avoid provoking any “destabilizing” impact on our environment. Therefore, this request for sustainability requires a change of our thousand year-old European and Italian philosophy of construction buildings as:

- monolithic;
- realized by means of irreversible assemblies;
- based on rigid connections;
- based on “non-renewable resources”.

As a matter of fact, reinforced concrete structures represent the real antithesis of sustainable development since they are:

- monolithic;
- based on irreversible reinforced concrete conjunctions;
- based on portland cement concrete, the production of which demands consumption of large amount of natural resources (such as clay, limestone and, generally, stony materials from quarries or riverbeds).

Taking into account the above mentioned features the question is: “What direction must the concrete industry follow to satisfy the need for sustainability in constructions?” *By optimizing the composition of new concretes using different ingredients from those utilized in traditional concretes, capable of assuring sustainability on the basis of “innovation”.*

Innovation in concrete construction means:

- production of precast reinforced concrete elements based on hydraulic materials using renewable or recycled ingredients;
- to increase performance in service of reinforced concrete elements in order to reduce cross-sections and, hence, volume of concrete produced;
- to increase durability of concrete structures to prolong the maintenance time reducing the amount of deteriorated concrete to be recycled and consumption of special repair materials based on non-renewable resources.

Precast Concrete

In the near future the concrete industry is destined to serve the precast element plants, more than placement on job-sites. In this way the realization of elements that can be assembled in the job-site will allow the realization of components that can be mounted easily and, at the same time, can be replaced and recycled in a very simple manner.

The production of these reinforced or prestressed concrete elements will be located close to urban areas, in order to meet prevalent methodology of the construction works in the next 20-30 years (Table 1), which will be made up of dispersed small projects, in form of buildings for commercial use and

which will be in the centres of the towns subjected to a strong urban renewal. This methodology of building works will encourage the production of precast elements located close to urban areas requiring a small impact on the environment. From this point of view, self-compacting concretes can satisfy sustainability since they can drastically reduce acoustic environmental pollution, due to the possibility of casting precast elements without vibration.

Self-compacting concretes (SCC) also provide a significant opportunity for the use of waste and recycled materials. The higher volume with respect to conventional concrete (CC) of very fine powder necessary to achieve deformability and passing ability capacities permits them to incorporate high volumes, for instance, of fly-ash [2]. This will represent a key-point since the amount of fly-ash available in the near future will increase. In fact, some governments (i.e. Italy, USA, etc.) will build new carbon-based thermoelectric power generation plants to resolve problems related to the increasing demand of energy. These demands partially caused the black-outs in Italy and USA during the summer of 2003.

Finally, SCC are also “large volume consumers” of very fine particles generated by the recycling of demolished concrete structures not easily usable in traditional mixtures [3, 4, 5] and the huge amount of calcareous fillers available from the marble quarries. From this point of view SCC represent the “most voracious Dea Khali” as Metha defined in sustainable concretes [6].

Increased Performance

Use of large amounts of pozzolanic materials and limestone, together with the acrylic-based admixtures, is more effective in reducing the mixing water with respect traditional naphthalene-based superplasticizers and allows the manufacture of high performance self-compacting concretes. The greater concrete homogeneity in the job-site and the smaller dependence of the structural performances on the workmanship quality will allow in the future to design self-compacting concrete structures, with a lower partial safety coefficient of the material. This will mean inevitably a reduction of the structure cross sections and consequently of the amount of the concrete used. Moreover, self-compacting concretes can be made easily and, thanks to their rheological properties, they may be used not only precast elements, but also in concrete cast on the job-site, with the respect for both the workers' health (because of the absence of vibration) and for the environment (because of the drastic reduction of the acoustic noise).

Improved Durability

Finally, self-compacting concretes turn out to be materials for the realization of building structures and components, with a much durability than the one of the standard concretes. The greater durability of self-compacting concretes satisfies the request for sustainability, because it will be possible to delay the maintenance and, therefore, limit the volumes of deteriorated concrete to be disposed of and lower use of repair mortars based on special mixtures big consumers of non-renewable resources.

Extension of durability of self-compacting concrete structures and elements is due to:

the improved durability of self-compacting concretes themselves, as direct consequence of the better quality of the interfacial transition zone and of the lower tendency to crack in comparison with the standard concrete mixtures; a better quality of the concrete in the job-site, due to the reduced dependency on the procedures of casting and compaction.

2. PARAMETERS AFFECTING DURABILITY

Many factors influence physical and mechanical properties of concrete, such as water/cement, type of cement, use of materials having pozzolanic activity, type and particle size distribution of aggregates, type and dosage of admixtures. But even other important parameters may have a strong influence on the microstructure and, hence, on elastic and mechanical properties of concrete. These factors, less generally focused on, are related to the fresh state of concrete and concern rheological properties (cohesion and plastic viscosity), transportation, handling and placing of fresh concrete, segregation and bleeding, plastic settlement and curing. Rheological properties, in fact, can significantly modify nature and structure of the concrete interfacial transition zone (itz), between aggregate and concrete paste, which is responsible for the mechanical properties, watertightness, fire resistance and durability of prestressed and reinforced concrete structures [7].

Since fresh properties of self-compacting concrete (SCC) are significantly different from those of conventional concrete (CC), formation, nature and microstructure of itz can change significantly when a SCC is used instead of CC. For these reasons properties of hardened SCC can dramatically differ from those of CC even for the same water/cement ratio, type of cement, type and maximum size of the aggregates.

This paper presents results of an experimental program carried out to evaluate the main changes of the itz in SCC with respect that of CC.

3. INTERFACIAL TRANSITION ZONE

In freshly conventional compacted concrete, due to the presence of coarse aggregate, water films, initiated by vibration, tend to accumulate close to the aggregate surface. These films determine an increase in the w/c next to the aggregate compared to the bulk mortar [8]. As a consequence of the higher water/cement, the crystalline hydration products ettringite and calcium hydroxide (CH) in the vicinity of the coarse aggregate consist of larger crystals and therefore they form a more porous structure than in the bulk mortar matrix [9]. For these reasons, even for low w/cm, amount and size of voids in the transition zone will be larger than in bulk mortar. Moreover, CH crystals tend to locate themselves with the c-axis perpendicular to the aggregate surface. This results in a less adhesion capacity both for the lower surface area, and consequently weaker Van der Waals forces, and also because of preferred failure sites for the oriented structure [10].

In addition to larger amount and size of voids, the presence of microcracking is the major reason for the weakness of itz. Extension of microcracking depends on many factors, but the most important is related to concrete tendency to segregate which, in turn, is related to the aggregate size and grading, cement factor, type and dosage of admixtures, amount of water, workability, method of placing and compaction. For instance, a poorly graded aggregate can favour segregation; the larger the maximum size of the aggregate, the higher the internal bleeding. Moreover, for the same workability, the higher the amount of water the weaker the itz.

Due to the presence of microcracks, the transition zone significantly influences the durability of concrete, since it is more permeable than the bulk mortar. This means that concrete durability cannot be exclusively related to the w/c, type of cement and pozzolanic material, but should be attributed even to parameters, such as size and grading of aggregate, cohesion, etc, that can influence properties of itz.

Self-compacting concretes with high content of very fine particles (size lower than 0.150 mm), a lower volume and maximum size of coarse aggregates with respect those of conventional concrete, a more stable conveyor phase, improved rheological properties due to effective high-range water reducers and viscosity modifying agents, are expected to affect in a positive manner the itz, promoting a less porous microstructure.

In order to investigate these effects on itz, microstructure of self-compacting concretes and conventional concretes were analyzed by using the environmental Scanning Electron Microscope.

4. EXPERIMENTAL INVESTIGATION

Two conventional concretes, two self-compacting concretes with limestone filler (av.size = 30 μm) and two SCC containing pulverized fly-ash were manufactured. Mixture compositions are given in Table 2.

Water/cement was kept constant for CC and SCC: 0.40 for the first set of mixtures and 0.60 for the second one, respectively. Mixtures proportions were approximately the same: the cement content and the amount of water were constant. Dosage of superplasticizer, content of viscosity modifying agent, and the amount of coarse aggregate were adjusted to achieve self-compactability properties.

Concrete specimens were manufactured both to study microstructure and to determine compressive strength at early and long ages (cured at $T = 20^\circ\text{C}$; R.H. = 95%).

Figures 1-4 show micrographs of self-compacting concretes and conventional concrete with a w/c of 0.60. Figure 1 highlights presence of a very porous microstructure in itz of conventional concrete as confirmed by the large dark area. On the contrary a more homogeneous and less porous structure of itz was detected for SCC containing both FA and CaCO_3 .

Figure 2 indicates the presence of microcracks in itz and the matrix not well-bonded to the aggregate surface, for the CC. On the other hand absence of evident microcracks and a matrix well-bonded to the aggregate were found in SCC containing both FA and CaCO_3 . The denser microstructure of SCC was confirmed by analysis of Figure 3, where the porosity of itz in CC concrete is significantly higher with respect that of SCC.

The higher porosity and the presence of microcracks in itz were responsible (Fig. 4) for the larger crystals of hydration products in CC with respect those of SCC [11].

These results seem to confirm the beneficial effect of a more stable paste in self-compacting concretes that is capable of decreasing internal bleeding and, hence, porosity of itz. This effect was independent of the type of filler: in SCC both with limestone and fly-ash, porosity was consistently lower than that in conventional concrete. Reduction in microcracking and in porosity of itz with respect CC were more pronounced in self-compacting concrete with w/c equal to 0.60: in conventional concrete, in fact, the higher w/c, the higher tendency of the mixture to segregate. Same results, not shown, were obtained for concrete with w/c equal to 0.40, even though

differences were not as evident as detected in mixtures with w/c equal to 0.60.

Edax analysis indicated that no differences exist in terms of chemical structures between crystal phases in itz with respect hydration products in the bulk matrix for CC or SCC. In particular, data did not reveal any differences of the amount of sulfur in itz compared with the bulk matrix for CC or SCC. These results seem to be not in agreement with some experimental data available in literature [10, 12] which indicated in CC, near to itz, elongated needle-like crystal phases with high amounts of sulfur.

Data on microstructure seem to be in agreement with compressive strength values (Table 3). Independent of the nature of the very fine material, the compressive strength of SCC is higher than that of CC. In particular, compressive strength of SCC containing large amount of calcareous filler was higher than the corresponding value measured for both CC and SCC with fly ash, independent of the w/c and the age. At age of 90 days the gap in compressive strength value is partially bridged in SCC with fly-ash due to the pozzolanic reaction. Data confirm the positive role exerted by a stable and cohesive paste in SCC in reducing internal bleeding. This limits microcracks formation and reduces porosity of itz increasing compressive strength values of SCC with respect CC. Same results on the influence of SCC and limestone filler on properties of itz and, consequently, on compressive strength of concrete are reported in [11, 12, 13]: data available in literature seem to confirm that, at the same w/cm, SCC will produce higher compressive strength than CC [14]. In particular, when limestone filler is used higher compressive strength values were detected even at early age [15, 16]. Finally, data seems to indicate that limestone filler affects cement hydration process. In order to investigate this effect, if any, the temperature profile of the hydration process of cement pastes with and without calcareous filler was studied. Three different pastes were manufactured by using a CE I 52 R portland cement according to EN 197/1, two types of calcareous fillers with different granulometry (30 μm and 150 μm the average size for CF1 and CF2, respectively) and a siliceous filler with the same average size of CF1. The water/cement and the cement/filler were kept constant and equal to 0.35 and 0.30 respectively.

Figure 5 shows the instantaneous peaks in the temperature profiles for the three different pastes as a consequence of the hydration of the alumina phases. Figure 5 seems to indicate that the paste containing the finer (CF1) calcareous filler is characterized by a lower maximum temperature compared with that of cement pastes with the coarser limestone filler or the siliceous filler. Moreover, as clearly indicated in Fig. 6, the cement paste with the finer limestone filler is responsible for a shorter dormant period with respect to those of the other cement pastes studied. This means that the

finer limestone filler is capable to accelerate the hydration process of the silicate phases.

The changes in temperature profile of hydration process of paste containing the finer CaCO_3 filler seems to indicate an increased crystallinity of ettringite due to the presence of the calcareous grains acting as nucleation site responsible for the lower temperature of the instantaneous peak. Formation of sites of heterogeneous nucleation is responsible for the shorter dormant period, the acceleration of the hydration process and, hence, for the higher strength values at early ages (Table 3).

This hypothesis on calcareous grains acting as nucleation sites is also reported in a paper by Kadri et.al. [17].

Several authors mention that the presence of calcareous filler reduces the normal dormant period and accelerates the hydration process [18-21].

These data on the effect of limestone filler seem to be in agreement with the results of adiabatic hydration tests [22]: the maximum temperature rise was systematically higher for self-compacting concrete containing calcareous filler with respect CC.

5. PLASTIC SETTLEMENT

The beneficial effect in reducing internal bleeding is confirmed by the reduction of plastic settlement in SCC with respect to conventional concrete. Sonebi et al [23] found that SCC exhibit greater stability than the traditional concretes: at about the same w/c (0.68 and 0.71 for CC and SCC, respectively) plastic settlement was 0.24% and 0.21% for CC and SCC respectively. Same results were obtained by Khayat [24, 25].

These data are in agreement with the bond strength between deformed steel bar and concrete matrix: at 28 days $\tau_{\max}$ of SCC [23] was about 16-40% higher than the conventional mixture. Higher bond strength in SCC, in fact, should be related to a more stable paste capable of reducing the water film beneath the reinforcement and, consequently, to improve the itz mechanical properties.

6. PLASTIC SHRINKAGE

Absence of internal and external bleeding in SCC, however, is one of the causes for their higher plastic shrinkage with respect conventional mixtures. Turcry et al [26] found that, for the same loss of water, plastic shrinkage of SCC is at least 2 times higher than that of CC. The lower water/fine material

and the finer capillary pore structure are responsible for a faster development of the negative pressure causing plastic shrinkage. Even with a delay in the setting time of SCC, due to the higher dosage of superplasticizer, the higher plastic shrinkage of SCC occurs with respect CC. This means that, in order to gain beneficial effect on strength and durability due to the improvement in properties of itz, in real structures curing of fresh SCC surface requires great care.

7. GAS PERMEABILITY, RESISTANCE TO FREEZING AND THAWING AND CHLORIDE DIFFUSION

The positive role of SCC in decreasing microcracking and porosity of itz is also responsible for a more durable concrete. Trägårdh [13] found a decrease in the gas diffusion coefficient for a self-compacting concrete ($9.8 \cdot 10^{-18} \text{ m}^2/\text{s}$) with respect a conventional concrete ($13.6 \cdot 10^{-18} \text{ m}^2/\text{s}$) with the same w/cm (0.40).

Results obtained by Assiè et al. [27] reveal that SCC (w/cm = 0.53) shows lower permeability to oxygen ($0.6 \cdot 10^{-16} \text{ m}^2$) than CC ($1.5 \cdot 10^{-16} \text{ m}^2$) with about the same w/c (0.50).

Similar results were obtained by De Schutter et al. [28]: for the same w/cm, gas permeability of SCC was from $\frac{1}{2}$ to $\frac{1}{6}$ of the corresponding value for CC whereas water permeability was somewhat lower for SCC ($1.44 \cdot 10^{-11} \text{ m/s}$ and $1.66 \cdot 10^{-11} \text{ m/s}$ for SCC and CC, respectively).

Resistance to freezing and thawing in the presence of deicing salts is essentially the same for SCC and CC [15, 28]. This means that in order to prevent concrete deterioration a water/cement lower than 0.50, blastfurnace slag cement (CE III/B according to EN 197/1) and air entraining admixtures must be used [29, 30].

Chloride diffusion coefficient of SCC ($16.1 \cdot 10^{-12} \text{ m}^2/\text{s}$) was found lower (13) than that ($19.2 \cdot 10^{-12} \text{ m}^2/\text{s}$) of CC with the same w/c (0.40). Audenaert et al. (31) found that for the same w/c chloride diffusion coefficient was slightly lower for SCC with respect CC. However, type of cement (blastfurnace slag cement replacing ordinary Portland cement) and use of fly-ash seems to have more influence than self-compactability on the reduction of chloride diffusion. This means that the capacity of hydration products in the presence of pozzolanic addition to absorb free chloride ions is more important in slowing down chloride penetration than the beneficial effect exerted by SCC on properties of itz.

Capillary suction is significantly lower in SCC with respect CC: Audenaert et al. (31) found a penetration height in CC almost twice as high as that for