

# Experimental study of transport properties and natural carbonation of Self compacting concrete incorporating supplementary cementitious materials (SCMs)

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*RÉSUMÉ. La durabilité du béton est l'un des facteurs les plus importants pour la conception des nouvelles structures dans les environnements agressifs. Il est bien connu que les propriétés de transport du béton (la perméabilité, diffusion des ions chlorures) sont d'importants indicateurs de durabilité. L'objectif de cette contribution est d'étudier l'influence des additions minérales sur les propriétés de transport et de la profondeur de carbonatation dans les bétons autoplaçants (BAP). La résistance aux ions chlorures est déterminée par l'essai de migration des chlorures sous champs électrique, la perméabilité sera quant à elle mesurée à l'aide du gaz hélium et d'un perméamètre à charge constante. L'approche Klinkenberg est utilisée pour la détermination de la perméabilité intrinsèque. La profondeur de la carbonatation naturelle des échantillons sera déterminée par l'usage de la phénolphthaléine après 600 jours de séchage de béton. Les résultats montrent que, l'utilisation des additions minérales augmente la résistance des BAP à la pénétration des ions chlorures et réduit leur perméabilité, ils révèlent aussi une profondeur de carbonatation plus élevée que celle du BAP de référence.*

*ABSTRACT. Concrete durability is one of the most important considerations in the design of new structures in aggressive environments. It is now common knowledge that the transport properties of a concrete, i.e; permeability and chloride diffusion coefficient are important indicators of its durability. The main objective of the study presented in this paper is to investigate the influence of supplementary cementitious materials (SCMs) on transport properties and carbonation depth of self compacting concrete (SCC). The chloride resistance of SCCs is measured using a chloride migration test accelerated by an external applied electrical field. Intrinsic permeability is measured using the helium gas and one permeameter at constant load. Klinkenberg approach is used for the determination of the intrinsic permeability. The natural carbonation depth of the specimens was determined by the phenolphthalein after 600 days. Based on the findings of this study, the use of mineral admixtures increases the resistance of SCC to chloride ingress and reduces their permeability but they show a higher carbonation depth compared to reference SCC.*

*MOTS-CLÉS : durabilité, propriétés de transport, béton autoplaçant, additions minérale, carbonatation.*

*KEY WORDS: durability, transport properties, self compacting concrete, supplementary cementitious materials, carbonation.*

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## 1. Introduction

Concrete is an important versatile construction material, used in wide variety of situations. So it is very important to consider its durability as it has indirect effect on economy, serviceability and maintenance.

Self-compacting concretes (SCC) represent a move toward a sustainable material since they encourage the use of mineral admixtures. The high volume of very fine powder necessary to achieve deformability and passing ability properties, in fact, permits SCC to consume large amount of fine particles. Moreover SCC turns out to be materials with an extended durability with respect to conventional concretes.

Indeed concretes technologists have long recognized the significant benefit of incorporating supplementary cementitious materials (SCMs) such as fly-ash, ground granulated blast-furnace slag, silica fume and metakaolin in concrete to extend the life of reinforced concrete structures in severe environments. The SCMs, in the long run, have very significant benefits in reducing the permeability of concrete [SHI 85]. These materials react in a secondary reaction called the pozzolanic reaction. The siliceous portions of the SCMs react with the calcium hydroxide (CH), a hydration product of Portland cement, and produces calcium silicate hydrates (C-S-H) which renders the concrete less porous [ACI 95]. The use of SCMs affects the rate of diffusion at early ages in different ways depending on the reactivity of the material used.

The present publication is mainly based on evaluate the durability and transport properties such as gas permeability, chloride diffusivity on steady state and natural carbonation depth in the four SCCs mixtures incorporating supplementary cementitious materials (SCMs). The total binder material content of the SCC mixtures was kept at 570 kg/m<sup>3</sup> with the water-to-binder material ratio is 0.368. The fresh properties of SCC, including the initial slump flow, the blocking ratio, the segregation ratio and the setting times of cement pastes, were tested.

## 2. Experimental investigation

### 2.1. Materials

A granular class 0/4 sand (S) with a density of 2.6 t/m<sup>3</sup> and limestone gravel (G) with 6.3/10 granular class, 2.66 t/m<sup>3</sup> of density were used in this study. Three cements according to European standard EN 197-1: CEM I 52.5N (Portland cement), CEM III/A 52.5L (slag cement) and CEM V 42.5N (blended cement containing slag and fly ash); limestone filler (LF) and metakaolin (MK) were tested.

**Table 1.** *Composition and physical properties of cements and mineral additions.*

Name	CEM I	CEM III	CEM V	LF	MK
Clinker content (% in mass)	98	36	54	-	-
Slag content (% in mass)	-	62	25	-	-
Fly ash content (% in mass)	-	-	20	-	-
Specific Surface Blaine (cm <sup>2</sup> /g)	3650	4263	4250	4190	170
Specific gravity (g/cm <sup>3</sup> )	3.15	2.98	2.85	2.7	2.4

**Table 2.** *Mix proportions and physical properties at the fresh state.*

Composition (kg/m <sup>3</sup> )	SCC-CEM I	SCC-CEM I/MK	SCC-CEM III	SCC-CEM V
Aggregate 6.3/10	760	760	760	760
Sand 0/4	780	780	780	780
CEM I	330	280.5	330	330
CEM III	-	-	-	-
CEM V	-	-	-	-
Limestone filler	240	240	240	240
Metakaolin	-	49.5	-	-
Water	210	210	210	210
Superplasticizer	2.8	4.4	2	2.5
w/b	0.368	0.368	0.368	0.368

Their composition and properties are given in Table 1. A total of four SCCs mixtures with a constant water-to-binder ratio (w/b) of 0.368 and a total binder content of 570 kg/m<sup>3</sup> were investigated. Designations, mix proportions and physical properties at the fresh state of the different SCCs are given in Table 2.

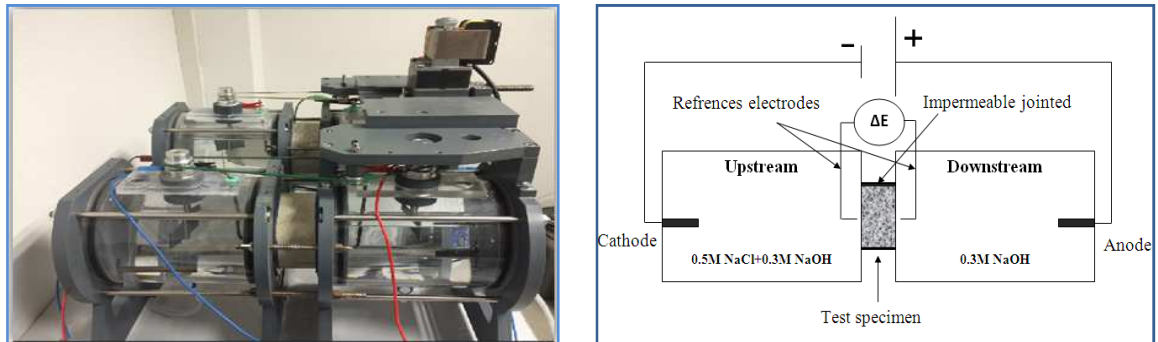
## 2.2. Testing methods

### 2.2.1. Compressive strength

Compressive strength test is performed on cylindrical specimen ( $\Phi 110$  mm x H220 mm). After demoulding, the specimens were cured in water at constant temperatures of  $+20^{\circ}\text{C}$ . The strength was checked after 7, 28, 90 and 360 days curing. The compressive strength of the cylinder specimen is calculated by dividing the maximum load attained during the test procedure by the cross-sectional area of the specimen. The average value from three specimens was taken as the measurement result.

### 2.2.2. Steady state migration test

To perform the steady-state migration tests, a two-compartment cell, as shown schematically in Figure 1, was used. For each SCC, three test specimens ( $\phi = 110$  mm,  $h = 50$  mm) were taken from three cylindrical specimens ( $\phi = 110$  mm,  $h = 220$  mm). The negative side of the cell (compartment 1) was filled with  $0.5\text{mol NaCl} + 0.3\text{mol NaOH}$  solution, where the positive side of the cell (compartment 2) was filled with of a  $0.3\text{mol NaOH}$  solution.



**Figure 1.** Photo and schema of migration cells

The stainless steel mesh electrodes were connected with a power supply in such a way that the voltage across the concrete specimen  $\Delta E$  was fixed at  $20$  V ( $4\text{V/cm}$ ). During the test, the chloride ion concentration was determined from the solution in the anode cell, titrated with the  $\text{AgNO}_3$  solution by the potentiometric titration method. The chloride flux,  $J$  (steady state), through the specimen is measured by the slope of the linear increase in the chloride concentration in compartment 2 ( $\text{NaOH}$  solution),  $\Delta\text{Ccl}$ , with increasing time,  $\Delta t$ . As the flux becomes constant, Nernst-Planck's relation allows to deduce the value of the diffusion coefficient, as seen in Equation (1):

$$J(x, t) = -D_e \frac{\partial C}{\partial x} + D_e \frac{zF}{RT} \frac{\partial E}{\partial x} C(x, t) \longrightarrow D_e = \frac{JRTL}{zFC\Delta E} \quad [1]$$

Where  $D_e$  is the diffusion coefficient of concrete ( $\text{m}^2/\text{s}$ ),  $c$  is the chloride concentration of the upstream compartment ( $\text{mol}/\text{m}^3$ ) assumed to be constant,  $J(x)$  is the flux of chloride ions ( $\text{mol}/(\text{m}^2 \text{ s})$ ),  $z$  is the chloride ion valency ( $z=1$ ),  $F$  is the Faraday constant ( $F=96,480 \text{ J}/(\text{V}\cdot\text{mol})$ ),  $E$  is the actual potential drop between the surfaces of specimen (V),  $R$  is the gas constant ( $R=8.3144 \text{ J}/(\text{mol}\cdot\text{K})$ ),  $T$  is the absolute temperature (K) and  $v(x)$  is the velocity of the solute ( $\text{m}/\text{s}$ ).

### 2.2.3. Gas permeability

The gas used in this study is helium. Apparent permeability was measured using a Cembureau constant head permeameter showing in Figure 2. Permeability measurements were made in an air-conditioned room ( $20 \pm 1^{\circ}\text{C}$  and  $\text{RH } 50 \pm 2\%$ ). Three concretes cylindrical samples of  $50$  mm thickness were cut from the central portion of each cylinder for testing and placed in a triaxial cell and injection pressure in these tests was applied on below. The setup to perform gas permeability measurements was designed to work as a constant head permeameter under different gas pressures, with the possibility to change the head value and measure the gas inflow and outflow. Each disc was tested with five differential pressures:  $0.1$ ,  $0.2$ ,  $0.3$ ,  $0.4$  and  $0.5$  MPa. After initiating the percolation of helium through a specimen at a given applied pressure, sufficient time (varying from  $30$  min to several hours) is provided for the establishment of steady state flow before an actual measurement is taken. This condition is verified by taking two measurements separated by a  $15$  min time interval. If the two values differ by less than  $3\%$ , a steady state flow condition is assumed to be achieved. For each differential pressure, the apparent

coefficient of permeability  $K_A$  (m<sup>2</sup>) was calculated from the Hagen–Poiseuille relationship, laminar flow of a compressible viscous fluid through a porous body, using the following well-known Equation (2):

$$K_A = \frac{2Q\mu LP_{atm}}{A(P_i^2 - P_{atm}^2)} \quad [2]$$

Where L is the thickness of the sample (m), A is the cross-sectional area (m<sup>2</sup>), Q is the measured gas flow (m<sup>3</sup>/s),  $\mu$  is the coefficient of viscosity (1.96×10<sup>-5</sup> Pa s for helium gas at 20°C),  $P_i$  is the inlet pressure, (i.e. applied absolute pressure) (Pa), and  $P_{atm}$  is the atmospheric pressure (Pa).



Cylindrical specimen Ø110 mm x H50 mm

**Figure 2.** Experimental device used for measuring the gas permeability

Laminar and slip flow in concrete: The method used for determining the intrinsic permeability coefficient ( $K_i$ ), consists of measuring  $K_A$  at different pressures and plotting it against the inverse of the mean pressure. The intrinsic permeability value can be a better parameter for characterization of a concrete for durability compared to the traditional Darcy's coefficient of permeability, as it is independent of the fluid properties and the applied pressure gradient. The most widely used is the relation proposed by Klinkenberg Equation (3) introducing the concept of an intrinsic coefficient of permeability  $K_i$ , relative to viscous flow only:

$$K_A = K_{int} \left( 1 + \frac{\beta}{P_m} \right) \quad [3]$$

Where  $P_m$  is mean gas pressure,  $P_m = (P_i + P_{atm})/2$ ,  $\beta$  is the Klinkenberg coefficient (Pa) which is a function of the porous body and the infiltrated gas, and  $K_v$  is the limiting value of gas permeability when the mean pressure  $P_m$  tends towards infinity. The method of determination of  $K_{int}$  consists in measuring  $K_A$  at different pressures ( $P_i$ ) and plotting it against the inverse of the mean pressure ( $1/P_m$ ). The slope of the line leads to the empirical Klinkenberg coefficient  $\beta$  and the origin leads to the intrinsic permeability.

#### 2.2.4. Natural carbonation test

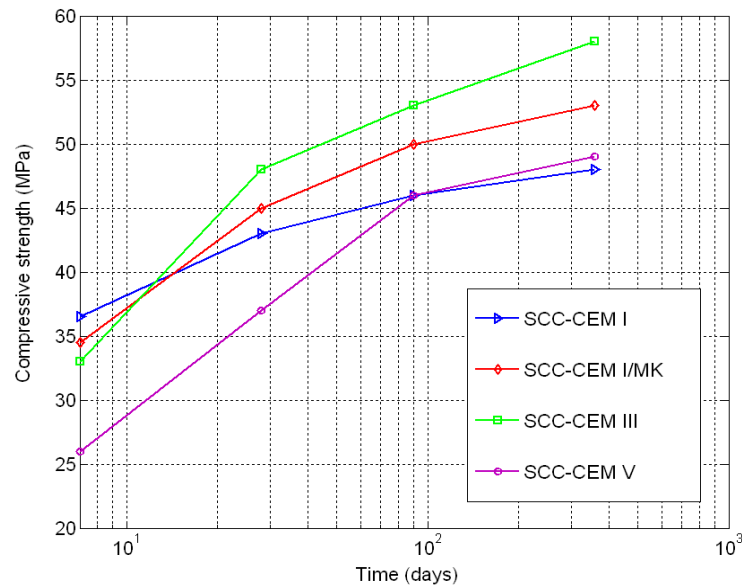
The natural carbonation test is performed on 70 mm x 70 mm x 280 mm specimen. The specimens were placed after demolding in a room temperature regulated to 20 ° C and relative humidity of 50 ± 5% for 600 days. The carbonation depth of the specimens was determined by the phenolphthalein method recommended by RILEM CPC-18.

### 3. Results

#### 3.1. Compressive strength

The compressive strength of the different composites at different ages is shown in Figure 3. As can be expected, the compressive strength of all the studied SCCs composites enhances by their ages. This enhancement is more intense for SCCs composites with mineral admixtures. Compared to the reference SCC, SCCs composites with mineral admixtures exhibit lower compressive strength at very early age. In fact, after one week of aging, the compressive strength of SCC-CEM I/MK, SCC-CEM III and SCC-CEM V composites is

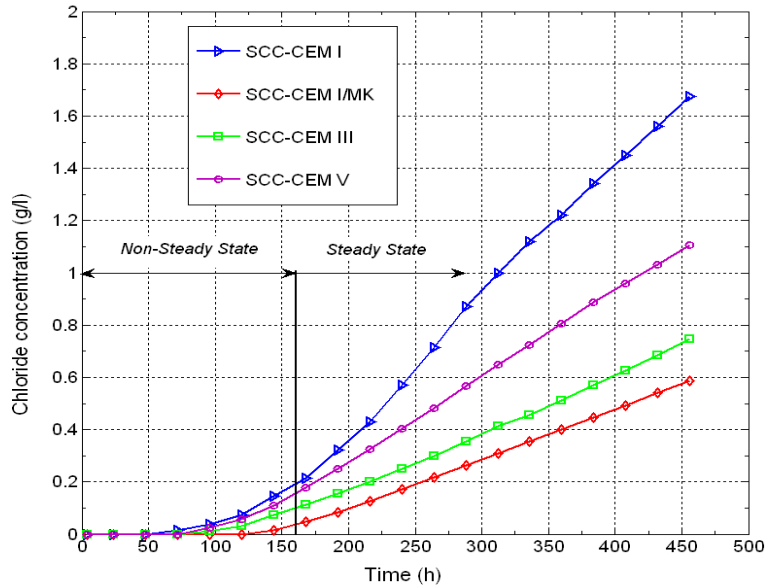
respectively 5.5%, 9.5% and 30% lower than the one of SCC-CEM I composite. At 28 days of aging, the compressive strength of SCC-CEM I/MK and SCC-CEM III composites became higher than the one of the control SCC composite by 5% and 12% respectively, but this increase of compressive strength starts from 90 days for the SCC-CEM V composite. The latter observation is in agreement with the results found in previous studies for ordinary concrete containing metakolin [KHA 05]. However for high performance concrete, MK seems to have more significant influence. The obtained result suggests that MK have an important effect on the development of hydrates even before 28 days of aging probably due to its pozzolanic reactivity and to nucleation sites that it offers [KHA 05]. This remark is consistent with both non-evaporable water content and water porosity experimental results. Compared to SCC composite with MK, SCCs with CEM III and CEM V exhibit lower compressive strength at early ages particularly due to the well-known slow hydration kinetics of slag [ATI 09]. These results are in a good agreement with the experimental results of previous studies performed on SCC based on slag cements [ATI 09]. However, at long term (360 days), the compressive strength of SCCs with mineral admixtures exceeds the one of the reference SCC composite. Particularly, SCC based on CEM III presents the highest compressive strength, 21% higher than the one of the reference SCC at 360 days.



**Figure 3.** Evolution of compressive strength of SCCs with age.

### 3.2. Effect of admixtures on chloride diffusion

The effect of mineral admixtures on accumulation of chloride ions in the downstream compartment is shown as a function of time for the five SCCs in Figure 4. The time to penetrate through the specimen ( $T_{Pass}$ ) is the intersection point of the line with the X-axis.  $T_{Pass}$  depends on the porosity of concrete and chloride binding [TRU 00]. The results presented are based on the average obtained from two replicate samples tested for each SCC. The concentration of chloride migration through concrete shows firstly an exponential relationship that called the non-steady-state (chloride ions are in the process of penetrating through saturated pores in specimen and have not reached the anode cell) then increases with the testing time after a different stage that show an approximate linear relationship called steady-state (flux of chloride ions passing through the specimen becomes constant). To compare the resistance of the SCCs based on three kinds of cements against the concentration of chloride migration through concrete, the SCC-CEM III based on blast furnace slag showed a higher resistance to chloride migration relative to SCC-CEM V and SCC-CEM I. The replacing of 15% of Portland cement by metakaolin is significantly improved the chloride migration through concrete compared to reference SCC, SCC-CEM III and SCC-CEM V. The penetration of chloride ions into reference SCC composite based on CEM I was determined after only 50 hours, with a diffusion coefficient of  $3.89 \times 10^{-13} \text{ m}^2/\text{s}$ . The time to penetrate of  $\text{Cl}^-$  is greater for the SCC based on MK (135h), with a decrease of the diffusion coefficient of 76% compared to reference SCC. Regarding the time of penetration ( $T_{Pass}$ ), measuring the duration of the transition phase, the SCC based on CEM III showed a lower  $T_{Pass}$  compared to SCC-CEM I and SCC-CEM V that give a lower effective diffusion coefficient by 65% and 34% respectively. In this investigation is also observed an increase in the time of penetration in the blended mixtures depending on the nature of the additions. However, the time of penetration of chlorides ions is important that showing good resistance to the penetration of  $\text{Cl}^-$ .

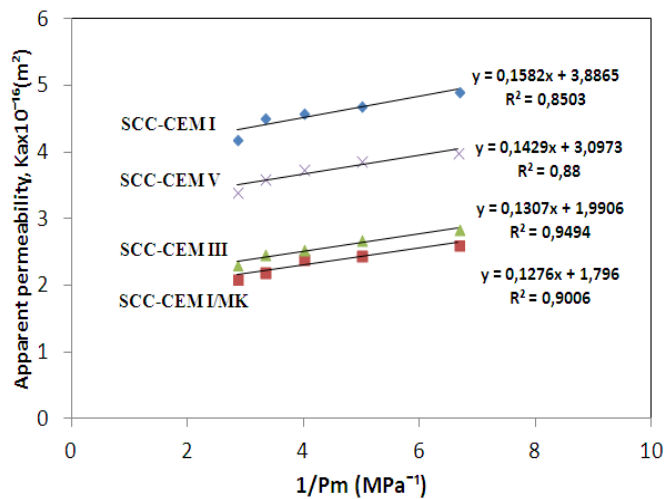


**Figure 4.** Evolution cumulative increase of chloride in downstream cell.

The presence of high amount of  $\text{Ca}(\text{OH})_2$  in the hydrated matrix creates a large volume of continuous pores which is the case for SCC based on Portland cement. Therefore, the consumption of lime by the minerals admixtures during of hydration (pozzolanic reaction) leads to a reduction in volume of the interconnected capillary pores. Previous researchers [MAT 99] and [ALD 99] have reported that the pozzolanic materials with fine particles can fill in the space enclosed by cement hydrates and thus block the capillary pores of concrete. It has been reported that reduction of chloride diffusion is as a result of the pozzolanic reaction. As a result of pozzolanic reaction that occurs in the SCC containing metakaolin, slag and fly ash, the microstructure becomes more dense, tortuous and discontinuous relatively when compared to reference SCC.

### 3.3. Evolution of gas permeability with the different additions

The evolution of intrinsic permeability with the different mineral admixtures is given in Figure 5. These results correspond to two samples of SCCs composite from the same batch of concrete and the same size ( $\phi = 110 \text{ mm}$ ,  $h = 50 \text{ mm}$ ).



References	intrinsic permeability ( $10^{-16}$ )
SCC-CEM I	3.88
SCC-CEM I/MK	1.79
SCC-CEM III	1.99
SCC-CEM V	3.1

**Figure 5.** Evolution of the apparent permeability.

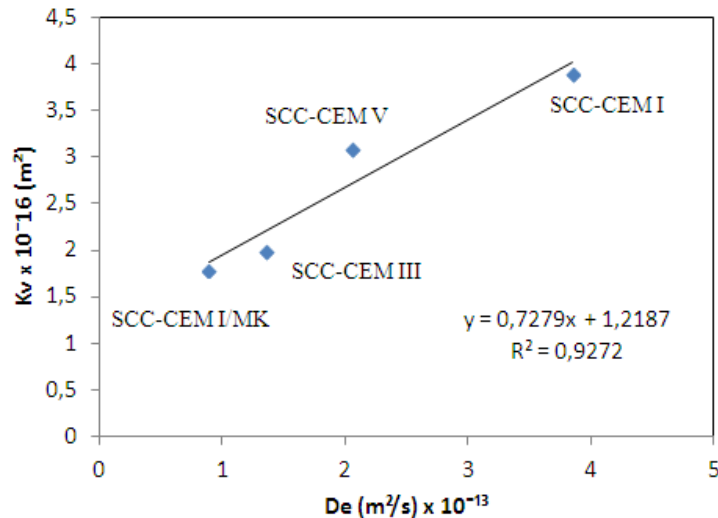
The results show that gas permeability is influenced by the use of mineral admixtures in the SCCs samples. The results put in evidence that the intrinsic permeability coefficient  $K_v$  of reference SCC is higher than the SCCs based on mineral admixtures. It is generally observed that the replacing of 15% of Portland cement by MK lower intrinsic permeability coefficient by 64% than the reference SCC is succeeded. This could be due to the fact that the pores were filled by hydration products, which would result in pore refinement leading to improved



performance of the cementitious composites. Regarding the SCCs manufactured by three types of cement, SCC based on CEM III show a lower intrinsic permeability relative to SCC-CEM I and SCC-CEM V by 48% and 20% respectively. This might be explained by the finer network porosity of SCCs based on mineral admixtures than reference SCC porosity that show a lower gas permeability than reference SCC. Concretes are a capillary porous material and its permeability is closely related to its microstructure [ZAI 00].

### 3.4. Relationship between gas permeability coefficients and chloride diffusion coefficients

Previous studies have already mentioned the existence of a high correlation between gas permeability and chloride ions diffusion [SUG 96]. Figure 6 shows a relationship between the gas permeability coefficients versus the chloride diffusion coefficients of the different SCCs.

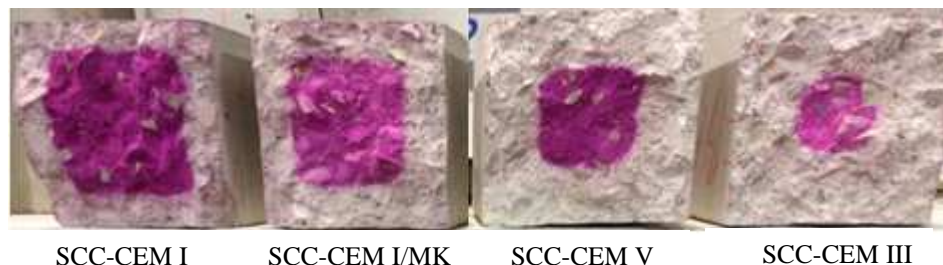


**Figure 6.** Relationship between gas permeability coefficients and chloride diffusion coefficients

It can be seen firstly the gas permeability increases with the diffusion coefficient  $D_e$ . It confirms that there is a close relationship between permeability and diffusion. Into account the type of mineral admixtures in the SCCs, the correlation coefficient is about 0.93. According to Sugiyama et al [SUG 96], the correlation between two physical properties that is the permeability and diffusion coefficients are largely related to the same factor which is the water/binder ratio.

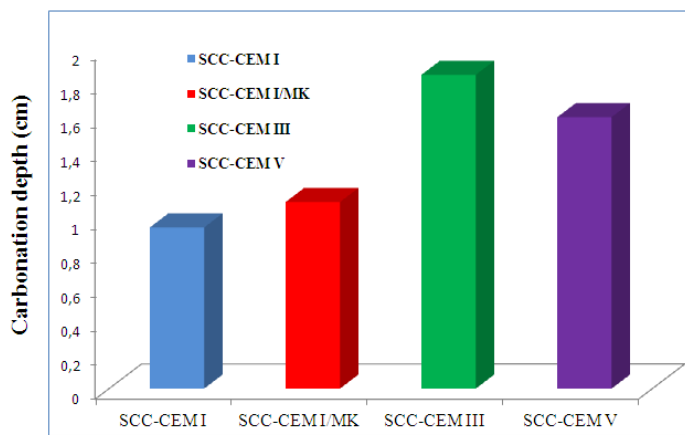
### 3.5 Natural carbonation

The natural carbonation test is performed on three samples  $7 \times 7 \times 28 \text{ cm}^3$  for each SCC mixture that were stored in the air-conditioned room with a temperature of  $20 \pm 2 \text{ }^\circ\text{C}$  and a relative humidity of  $50 \pm 2\%$ . The measure of carbonation depth was carried out after 600 days of aging in the regulated room. Carbonation areas are highlighted by phenolphthalein as showing in Figure 7. The carbonation depths after 600-days are shown in Figure 8.



**Figure 7.** Natural carbonation after 20 months for 4 SCCs studied.

The values of carbonate depths after 600 days for SCCs based on SCMs are between 1.2 and 1.9 cm, while that of the reference SCC show a value of 1.05 cm. This is because that CH content and porosity of the SCC are two key factors controlling carbonation depth of the SCC, the use of minerals admixtures in the SCC lowered the CH content which allows penetrating the  $\text{CO}_2$  gas through concrete.



**Figure 8.** Natural carbonation depth for SCCs

#### 4. Conclusion

- Compared to the reference SCC, SCCs with SCMs exhibit lower compressive strength at very early ages. At long term (360 days), the compressive strength of SCCs with SCMs exceeds the reference SCC. SCC based on slag cement presents the highest compressive strength, 21% higher than the one of the reference SCC. The effect of SCMs on tensile splitting strength is found to be quite similar to that of compressive strength.
- Replacements of Portland cement by CEM III and CEM V increases the resistance of SCCs to chloride ingress and reduces their permeability. This result is related to the binding capacity of chloride that is greater in the blended mixtures than in Portland cement mixture.
- SCCs manufactured with the mineral admixtures (metakaolin, fly ash, slag HF) decreases significantly both the chloride migration coefficient and the intrinsic permeability. After one year of aging, the SCC-CEM I/MK, SCC-CEM III and SCC-CEM V seems to reduce chloride migration coefficient by a factor of 4.2, 2.8 and 1.9 respectively compared to control SCC, and the intrinsic permeability is found lower by a factor of 2.2, 1.9 and 1.3 respectively compared to control SCC.
- A linear correlation is obtained between intrinsic permeability coefficient  $K_v$  and diffusion coefficient  $D_e$ , although both do not correspond to the same transfer mechanisms.
- According to the natural carbonation test results, the SCCs based on mineral admixtures show a higher carbonation depth. This is because a lower CH content in these SCCs which allows penetrating the CO gas through concrete.

#### 5. References

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