

# Effect of temperature on the behavior of self-compacting concretes and their durability

M. Salhi<sup>\*1,2,3</sup>, A. Li<sup>2a</sup>, M. Ghrici<sup>3b</sup> and C. Bliard<sup>4c</sup>

<sup>1</sup>Department of Civil Engineering, University of Relizane, Bourmadia, Algeria

<sup>2</sup>Laboratory of Civil Engineering, University of Reims Champagne Ardennes, Reims, France

<sup>3</sup>Geomaterials Laboratory, Hassiba Benbouali University of Chlef, P.O. Box 151, Chlef 02000, Algeria

<sup>4</sup>CNRS UMR 7312 ICMR Université de Reims, France

(Received January 16, 2019, Revised April 18, 2019, Accepted April 23, 2019)

**Abstract.** The formulation of self-compacting concretes (SCC) and the study of their properties at the laboratory level were currently well mastered. The aim of this work is to characterize SCC under hot climatic conditions and their effects on the properties of fresh and hardened SCC. Particularly, the effect of the initial wet curing time on the mechanical behavior such as the compressive strength and the durability of the SCCs (acid and sulfate attack) as well as the microstructure of SCCs mixtures. In this study, we used two types of cement, Portland cement and slag cement, three water/binder (W/B) ratio (0.32, 0.38 and 0.44) and five curing modes. The obtained results shows that the compressive strength is strongly influenced by the curing methods, 7-days of curing in the water and then followed by a maturing in a hot climate was the optimal duration for the development of a better compressive strength, regardless of the type of binder and the W/B ratio.

**Keywords:** self-compacting concrete; hot climate; initial curing time; compressive strength; acid attack; microstructure; XRD

## 1. Introduction

The use of self-compacting concrete (SCC) has increased significantly in recent years. SCC was originally developed in Japan when they encounter problems working on construction industry after the Kobe earthquake and it was also developed in Europe soon after. Some examples are column beam joints, bridges and foundations. Because of its flow and flowing capacity, SCC does not need external device for compaction and thus minimizes noise pollution on construction sites compared to conventionally vibrated concrete (CVC). For increase the fluidity and decreased segregation of SCC two distinct forms are possible, the first is to increase the volume of paste (increase in the powder content). This is the addition of fines (using only mineral additions), in which the water/powder ratio was between 0.8 and 1.0 (EFNARC 2005), the second is to use an viscosity modifying agent (VMA); incorporation of mineral and chemical additives with an optimal water/powder ratio between 0.3 and 0.4 depending on the optimal chemical assays.

SCC with less than 30% fly ash, blast furnace slag and silica fume with water ratio 0.35 powder would be the optimal combination of fresh products and mechanical properties was studied (Older and Abdul-Maula 1986).

The influence of different environmental conditions, especially temperature, on the process of hardening SCC has been studied by several authors (Reinhardt 2006, Ortiz *et al.* 2008, Zhao *et al.* 2012). The influence of curing temperature on the mechanical properties of cement materials is widely known. High temperatures affect the behavior of the SCCs, the compressive strength increases more rapidly in the first period but in the long term reaches lower values than that of the hardening at 20°C. Nevertheless, it is also important to analyze how the conditions of initial hardening assign the properties of microstructural SCC. The effect of the curing temperature on the products of hydration has been studied by several researchers (Older and Abdul-Maula 1986, Andersen *et al.* 2004, Friedemann *et al.* 2006, Elkhadiri and Puertas 2008). In these studies, it was found that the high temperatures change the structure of C-S-H. These microstructural studies have been carried out on cement pastes or mortars, but not in SCC. SCC is the most viable option for sites with difficult access conditions such as forced locations or congested reinforcements.

On the other hand, the compressive strength variations according to the maturity and compactness of the fresh concrete matrix highlighted the positive effect of the incorporation of limestone filler on the strength development of SCC under elevated mixing and curing temperature (Ana Cecilia *et al.* 2018). In addition, Bu *et al.* (2014) have found that the curing at 50°C accelerated the

\*Corresponding author, Assistant Professor

E-mail: salhi8@yahoo.fr

<sup>a</sup>Professor

E-mail: alex.li@univ-reims.fr

<sup>b</sup>Professor

E-mail: m.ghrici@univ-chlef.dz

<sup>c</sup>Professor

E-mail: christophe.bliard@univ-reims.fr

hydration reaction. However, when the samples were stored in lime water, the microstructure formed at the higher temperature showed an increase in total porosity, chloride diffusion coefficient, and permeability.

Al-Abduljabbar (2008) was shown that the adverse effect of a high initial temperature of the concrete (35°C - 40°C) on the workability measured immediately after mixing (slump flow, V-funnel flow time, filling ratio in the L-box) and up to 30 min after mixing was more significant for compositions (OPC+fly ash) made with low Gravel/Sand (G/S) ratio by mass (0.55) than compositions developed with G/S close to 1. However, the results were inconsistent at 28 days of age and appeared to depend on design parameters (cement type) and experimental setting: no variations (Weisheit *et al.* 2010) or slight decreases could be observed (Al-Martini 2010).

Other authors have reported an increase in compressive strength, regardless of the combination of Portland cement, fly ash, slag and silica fume, even if the samples were subjected to alternate temperatures (46°C during the day, 24°C during the night) (El-Chabib and Ibrahim 2013).

Khan *et al.* (2015b) found an optimal slag content of 40% for the mix design of high strength concrete. Furthermore, according to Chithra *et al.* (2016) the incorporation of 2% colloidal nano-silica in combination with 40% slag has improved the mechanical properties of high performance concrete.

The durability of concrete is strongly affected by chemicals in aggressive environments (sulphate and acid attacks). In fact, magnesium or sodium sulphates react with the Portlandite of the cement paste and give rise to expensive products (gypsum and secondary ettringite), resulting in the appearance of cracks as well as the deterioration of the cement matrix. Sulfuric, nitric or hydrochloric acid solutions are the most harmful to concrete. Their negative effects on building structures are faster due to sulfates attacks. Portlandite is known to be the most vulnerable component of acid attack (Makhloufi *et al.* 2018). The addition of cement-based materials seems appropriate, as they consume calcium hydroxide and densify the cement matrix, thereby reinforcing resistance to external sulfated and acid attacks (Senhadji *et al.* 2014, Oueslati and Duchesne 2012, Tennich *et al.* 2017).

Tiejun *et al.* (2018) confirmed that compressive strength and dynamic modulus of elasticity are strongly influenced by sulfate attack.

The objective of this research is to study the influence of the hot climate (high temperature 50°C) on the properties of SCCs in the hardened state. The characterization tests of SCC in the fresh state are: slump flow, T500, V-funnel, L-Box and sieve segregation, in the cured state, compressive strength, thermogravimetric analysis (TGA), resistance to sulphate attack, particularly sodium sulphate and sulfuric acid attack of Portland cement (PC) and slag cement (SC) based SCC specimens and visual examination at 180 days. As well as, X-ray diffractograms (XRDs) on SCC samples preserved in different attack environments.

## 2. Experimental investigations

Table 1 Chemical and mineralogical properties of cement

Notation	CEMI-52.5N	CEMIII-A-42.5N
Density (g/cm <sup>3</sup> )	3.16	2.98
Finesse Blain(cm <sup>2</sup> /g)/	4200	5150
Median Diameter (μm)	12	10
Clinker content%	97	37
Limestone content %	0	0
Slag content%	0	62
Secondary component	3	1
Composition of the clinker		
C <sub>3</sub> S	53.7	53.7
C <sub>2</sub> S	19.8	19.8
C <sub>3</sub> A	9.4	9.4
C <sub>4</sub> AF	10.1	10.1
Chemical Characteristics		
Na <sub>2</sub> O active (%)	0.76	0.61
Fire loss 950°C	1.74	2.64
SO <sub>3</sub>	3.39	2.61
Cl <sup>-</sup>	0.06	0.21
S <sup>2-</sup>	0.01	0.47
Residual insoluble	0.26	0.48

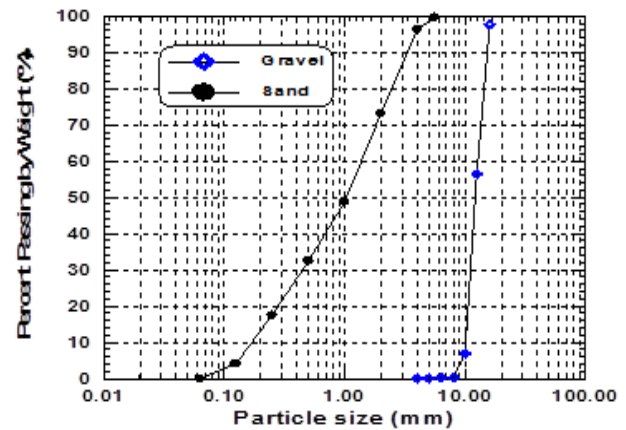


Fig. 1 Particle size distribution of aggregates

### 2.1 Materials

In this study, two types of cement were used: Portland cement (CEMI-52.5N) and slag cement (CEMIII-A-42.5N). The chemical composition and physical properties of the cement were presented in Table 1. The fine aggregate was of 0-3 mm. The coarse aggregate was granular 8/12 mm (Fig. 1). The superplasticizer used in this study has a density of 1.06, a content of chloride ions less than 0.1% and dry extracts between 28 and 31%. The dosage of superplasticizer varied from 0.2 to 3% according to the fluidity and the desired performance.

### 2.2 Mixture proportions

Three self-compacting concretes were used in this work. The water/binder (W/B) ratios varies from 0.32, 0.38 to 0.44. Compositions of the SCC adopted in this study were estimated by using Japanese method (Okamura and Ouchi 2003). The coarse aggregate was limited to 12 mm, the coarse aggregates/fine aggregates (CA/FA) ratio was approximately 1. The content of binder was between 527 and 624 kg/m<sup>3</sup> following the W/B ratio. The total quantity

Table 2 Mix design ingredients

Materials (kg/m <sup>3</sup> )	CEMI-52.5			CEMIII-A-42.5		
	SCC-P32	SCC-P38	SCC-P44	SCC-S32	SCC-S38	SCC-S44
W/B	0.32	0.38	0.44	0.32	0.38	0.44
Cement (C)	624.4	572.2	527.8	624.4	572.2	527.8
Fine Aggregates	757.7	722.2	694.5	757.7	722.2	694.5
Coarse aggregates	770.0	700.0	722.2	770.0	700.0	722.2
Water	199.8	215.7	232.2	199.8	215.7	232.2
Superplasticizer	14.2	7.8	5.0	14.2	7.8	5.0

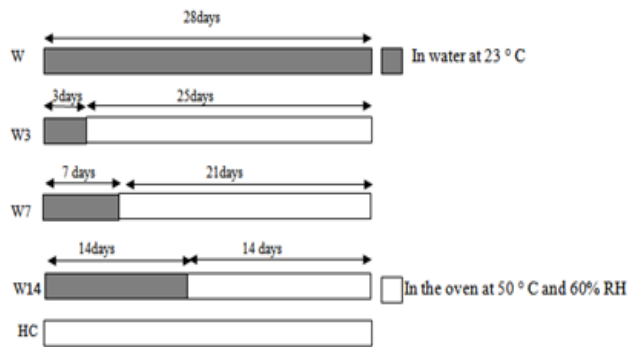


Fig. 2 Curing method

of aggregates varied from 1414 to 1427 kg/m<sup>3</sup>. The quantity of superplasticizer was used to improve the workability of the mix. The SCC mix proportions were shown in Table 2.

### 2.3 Specimens and measurement method

The cubic specimens 15×15×15 cm were kept in five groups in order to study the effect of the different curing methods on the SCC properties. The five curing methods are described in Fig. 2.

#### 2.3.1 Fresh SCC

The slump flow test of fresh SCC was conducted according to the (EFNARC 2005). The L-box test allows to characterize the mobility in a confined environment dynamic segregation. The V-funnel test provides a qualitative assessment of self-compacting concrete (EFNARC 2005). It characterizes the ability of the concrete to pass through an orifice. The test consists of measuring the regularity of the concrete passing through the funnel and measuring the total flow time when the flap is free. The sieve stability test was used to qualify the SCC against the risk of segregation.

#### 2.3.2 Tests on hardened SCC

The compressive test was carried out on cubic specimens 15×15×15 cm according to the EN 206-1 2004 norm

TGA allows to quantify the free and bound water in material as well as the Portlandite and calcium carbonate amounts. It consists of recording continuously the mass variations of a sample subjected to a temperature rise from room temperature up to 950 °C.

#### 2.3.3 Acid attack

Table 3 Durability test

Test	Solution	Test parameter	Specimen size	Immersing time
Sulfate attack	Sodium sulfate (5% Na <sub>2</sub> SO <sub>4</sub> )	Compressive strength	15×15×15 cm	30, 90, 180 days
		XRD		30days
Acid attack	Sulfuric acid (5% H <sub>2</sub> SO <sub>4</sub> )	Compressive strength	15×15×15 cm	30, 90, 180 days
		XRD		30days

The test pieces obtained after 28 days hardening period were immersed in 5% H<sub>2</sub>SO<sub>4</sub> sulfuric acid solution for various time spans to study their behavior in an aggressive acid environment (Table 3).

The cubic specimens of 15 cm were used to evaluate the properties of the SCC specimens held in the acid solution. The specimens were extracted from the solution weekly, rinsed three times with tap water to remove loose reaction products, blotted with a paper towel and left to dry under 23°C and for 30 min before weighing and visual inspection.

#### 2.3.4 Sulfate attack

The sulfate weathering solution was prepared from demineralized water, to which is added sodium sulfate 5%. The volume of the sodium sulfate solution placed in the storage container was 4 times the volume of the studied SCC test pieces. The temperature of the solution is maintained at 23°C. According to ASTM C1012, the pH of the sulfate solution must be between 6 and 8 and the solution must be renewed weekly.

#### 2.3.5 X-ray diffraction (XRD)

Typically, XRD was carried out on 2 g of powdered aliquots obtained by milling the studied samples pieces in an agate mortar to a size of 80 μm. After the crushing tests of the SCC specimens stored in the various attack media, surface pieces were taken and powdered for the XRD analysis.

## 3. Results and discussion

### 3.1 Fresh properties of SCC

In the present study, the spread was measured just after the concrete mixing and an adjustment of the superplasticizer dosage was done in order to achieve the spread required by the (EFNARC 2005). Table 4 summarizes the results of the various characterization tests of the SCCs studied. Each rheological test was performed three times for a given composition and the result represents the average of three values.

The results obtained through the spreading tests show that the spreading of concrete incorporating slag cement for the three SCCs (SCC-S32, SCC-S38 and SCC-S44) and SCC-P38 meets the SF2 class (660-750 mm) according to (EFNARC 2005). As well as, SCC-P32 is in accordance with the SF1 class (550-650 mm), on the other hand, the SCC-P44 meets the SF3 class. It is noted that all

Table 4 Properties of SCC at fresh state

Fresh state properties		CEMI			CEMIII-A			Criteria
W/B		0.32	0.38	0.44	0.32	0.38	0.44	EFNARC 2005
Slump flow	Diameter (mm)	650	670	760	660	680	715	SF1: 550-650 SF2: 660-750 SF3: 760-850
	T500 (s)	6.0	4.0	3.0	4.0	3.0	2.0	2-5 s
L-Box	H <sub>2</sub> /H <sub>1</sub> (%)	81.5	84.2	94	87	86.1	80.5	≥ 80%
V-Funnel	T <sub>0</sub> (sec)	4.0	3.0	1.9	4.0	3.0	2.0	6-12 s
Sieve segregation	%	6	10	15	10	14	16	≤ 20%
Density	Kg/m <sup>3</sup>	2360	2350	2345	2395	2375	2350	-

SCC mixtures incorporating slag cement showed a slightly higher spread than SCC mixtures based on Portland cement, while the opposite case was observed for SCC-44. According to Uysal and Sumer (2011), water demand and workability are controlled by particle shape, particle size and softness of particle surface texture, spreading test results (Slump Flow) mixtures containing limestone filler (LF), marble powder (MP) and basalt

powder (BP). The results show that with a constant amount of water for all mixtures, an optimal 20% LF content leads to higher spreading than other mineral additions (PM, PB). This could be explained by the greater specific surface area of BP and PM particles, which requires a significant amount of water compared to that of LF (Şahmaran *et al.* 2006).

Thus, the LF needs less water and results in higher spreading. Generally, blends that contain mineral additions have shown better performance than the no-mix blend with respect to Abrams cone spreading.

The use of mineral additions in SCCs aims to increase the distribution of powder skeleton particles, and thus reduce friction between particles. Belaidi *et al.* (2012) studied the effect of natural pozzolan (NP) and marble powder (MP) on the rheological properties of binary and ternary self-compacting mortars (SCM). Their results show that mixtures of greater than 15% NP in the binary mixtures gave poor spreading values, indicating that the high level of pozzolan substituted for SCM significantly reduces the spreading diameter.

According to Boukendakdji *et al.* (2009) with water/powder ratio and constant superplasticizer content, an increase in spreading was observed up to 20% slag with a 15% optimum, but at higher slag content both segregation and viscosity increased. On the other hand, with a high content of substitution (slag), the segregation and the

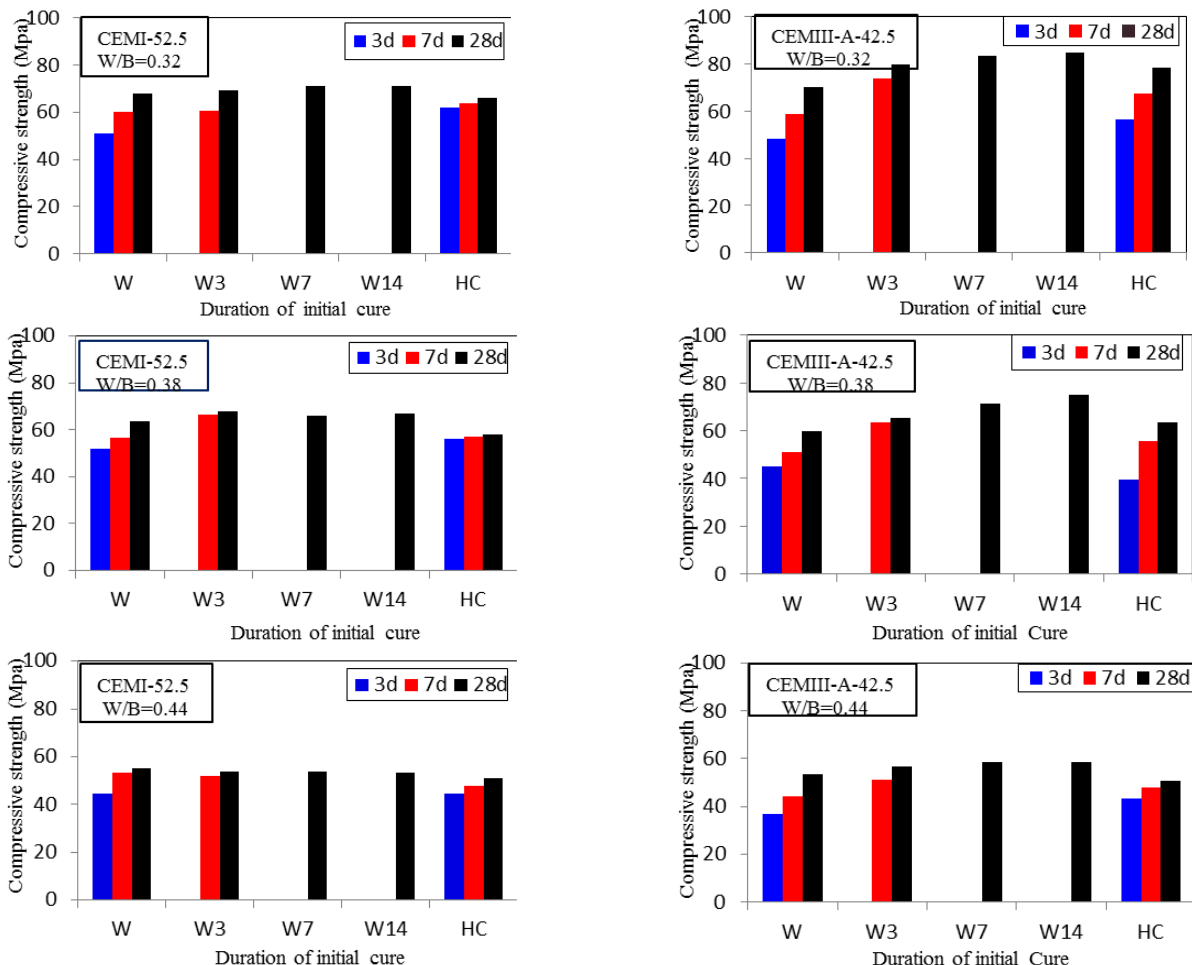


Fig. 3 Effect of the duration and the curing methods on the compressive strength

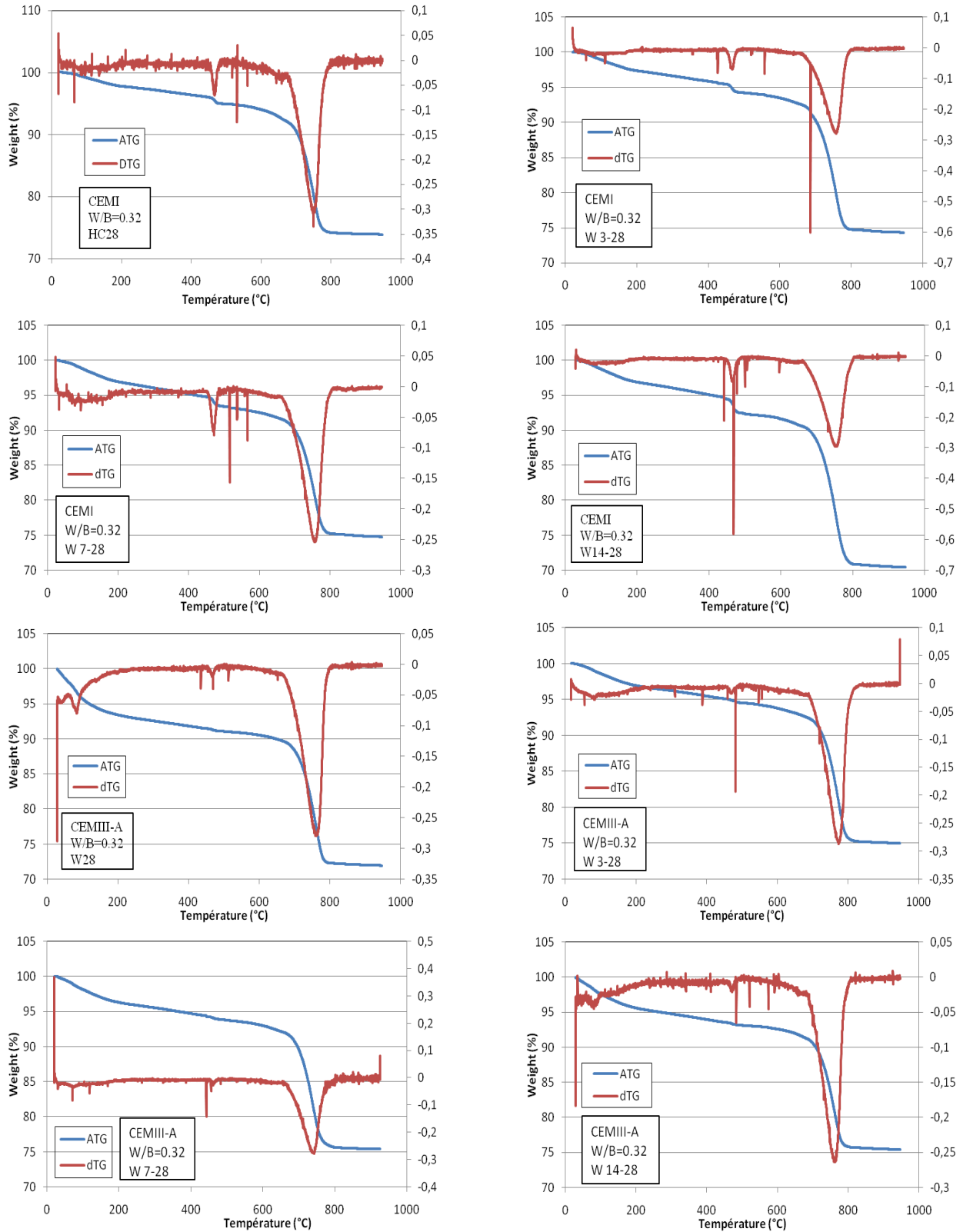


Fig. 4 TGA and DTG curves of SCC

viscosity increase. Other researchers Yahiaoui *et al.* (2017) have studied the effect of slag on the rheology of SCC, they found that the incorporation of the slag improves the workability of SCC and causes a decrease in the shear threshold, moreover, plastic viscosity decreased with

increasing slag content.

### 3.2 Compressive strength

The variation of the compressive strength of the SCCs

following the initial curing period is presented in Fig. 3. It has been clearly shown that the curing period plays an important role in the development of mechanical strengths. At a young age, the compressive strength of the SCCs kept in a temperature of 50°C and 60% RH hot climate (HC) is higher than those conserved in water (W) regardless of the W/B ratio and the type of binder. In addition, we see in Fig. 3 that an initial curing period of 7 days is optimal to develop maximum strengths in compression, in comparison with that of the specimens preserved following other periods of cure. We note in Fig. 3 that SCCs with a ratio  $W/B=0.44$  stored in the HC have low compressive strength in the long term regardless of age. According to Knut *et al.* (1991) showed that insufficient diffusion time of hydration products and resulting large pores are responsible for reducing the strength of hardened concretes at high temperatures. They examined the developmental microstructure of hydrated cement pastes at 5-50°C. The study shows that low curing temperatures result in even distribution of hydration products, while high temperatures result in a coarser porous structure. On the other hand, the variation of the composition of the C-S-H gel, main product of hydration of Portland cement, cured at various temperatures, was studied by scanning electron microscopy with energy dispersive X-ray spectroscopy. Samples of two cement pastes were isothermally treated under water at 10, 30 and 60°C for one year. For the C-S-H inner product gel of the two cement pastes, an increased hardening temperature decreased the Ca/Si and Al/Ca ratios, but increased the S/Ca ratio. The Al/S and (Al+Fe)/S ratios decrease with increasing curing temperature. Sulfur, probably in the form of sulfate ions, could adsorb by the C-S-H gel at higher temperatures (José *et al.* 2004).

### 3.3 Thermogravimetric analysis (TGA)

Thermogravimetric analysis TGA provides information on the loss of H<sub>2</sub>O of Portlandite and the loss from the decomposition of CaCO<sub>3</sub> upon heating and quantifies these levels. The TGA/DTG spectra of the samples hydrated for 28 days following the five modes of hardening are presented in Fig. 4. Three different endothermic zones can be distinguished, the first peak between 20 to 350 °C corresponds to the loss of water chemically bound as hydrates, the peak between 350 to 550 °C, corresponds to the process of dehydration of Portlandite according to the reaction balance:

$\text{Ca(OH)}_2 \longrightarrow \text{CaO} + \text{H}_2\text{O}$  (vapor) and the peak from 550 to 800°C corresponds to the decomposition of calcite which is the last significant loss of mass observed in an TGA test. The reaction is the following

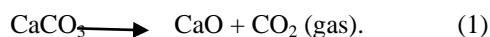


Table 5 shows the variation of percentage of Portlandite and calcite obtained by using TGA.

The amount of Portlandite for SCC at the slag cement base at 28 days is lower compared to that of SCC mixtures incorporating Portland cement and this regardless of the initial curing period.

In addition, this phenomenon is attributed to the consumption of Portlandite following the pozzolanic

Table 5 TGA results and the derived quantities of carbonated products

Type of cement	W/B-Curing	28 days	
		Ca(OH) <sub>2</sub> %	CaCO <sub>3</sub> %
SCC-CEMI	0.32-HC	8.74	45.45
	0.32-W3-28	9.27	43.67
	0.32-W7-28	10.79	40.29
	0.32-W14-28	14.33	48.12
SCC-CEMIII-A	0.32-W7-28	6.83	40.48
	0.32-W14-28	5.82	38.92
	0.32-W28	5.53	42.13
	0.32-W3-28	6.63	42.03

reaction, several studies (Kokubu *et al.* 1989, Escalante *et al.* 2001, Maruyawa *et al.* 2005) have shown that the amount of Portlandite contained in slag-based cement slurries decreases with the increase in the proportion of slag in the binder. For very high substitution rates, no amount of available Portlandite is found in the pulp and this indicates a consumption of Portlandite by hydration of the slag, whereas the carbonate product does not present any major differences.

### 3.4 Acid attack

Fig. 5 shows the evolution of resistance to compression of mixtures of SCCs on the basis of two binders (Portland cement, slag cement) with three water to binder ratio ( $W/B=0.32, 0.38$  and  $0.44$ ) immersed in the two environments of conservation ( $T$ : fresh water, 5% H<sub>2</sub>SO<sub>4</sub>). It can be seen that the evolution of resistance to compression as a function of the age of all the SCCs used retained in fresh water increases steadily with age and presents no fall until the age of 6 months. By contrast, the cubes SCCs test pieces weathered in the acid solution show a decrease in the resistance to compression with the age and this regardless of the type of binder and the report W/B. At the young age, mixtures of SCCs to base of the Portland cement retained in the sulfuric acid have shown a compressive strength is slightly higher than that of mixtures with a basis of slag cement and this regardless of the report W/B. In contrast, in the long run, the opposite case was observed. Beyond 3 months of conservation SCC mixtures containing blast furnace slag exhibited a slightly higher resistance than SCCs without slag. The different trend of the effect of the content of blast furnace slag on the loss of resistance to compression due to the attack to the sulfuric acid can be attributed to the pozzolanic reaction. It is recognized that the beneficial effect of the pozzolanic reaction takes place in the long term (90 days).

The conversion of the Portlandite Ca(OH)<sub>2</sub> in gel C-S-H as a result of the pozzolanic reaction contributes to an increase in the resistance and the reduction of the porosity (Turk and Yazicioglu 2007, Rizwan and Bier 2011).

The attacking process of H<sub>2</sub>SO<sub>4</sub> could be illustrated by equation 2 and method of crushing specimens by (Fig. 6).





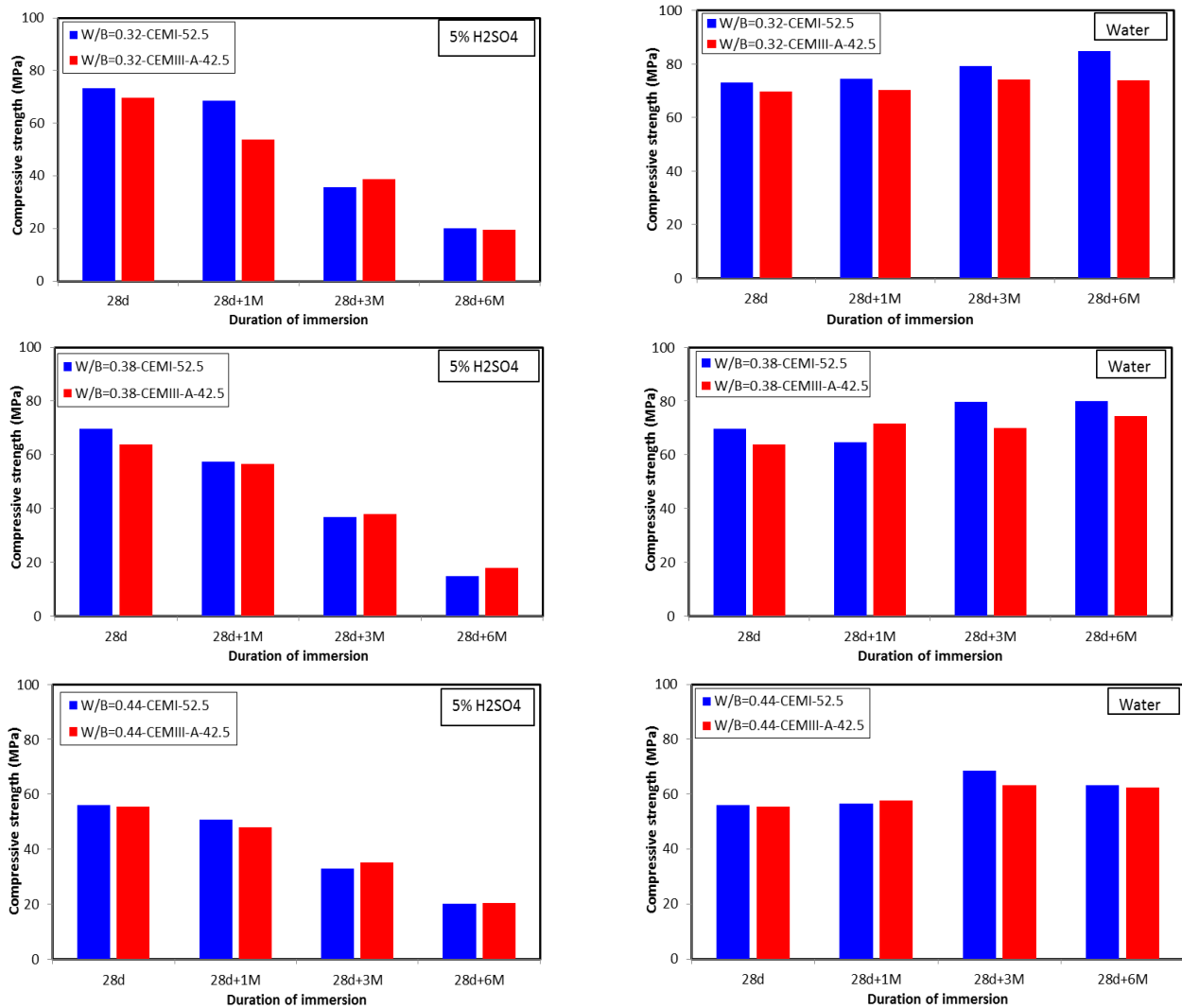
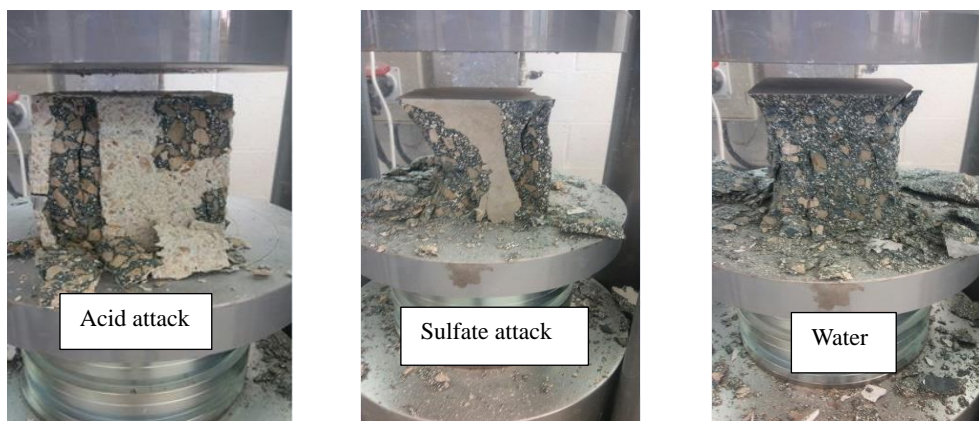
Fig. 5 Compressive strength of specimen immersed in 5% H<sub>2</sub>SO<sub>4</sub> and Water

Fig. 6 Breaking mode

### 3.5 Sulfate attack

The development of the resistance to compression of the SCCs specimens immersed in the 5% Na<sub>2</sub>SO<sub>4</sub> sulfate solution is presented in Fig. 7. It can be observed that the resistance to compression of all mixtures of SCC does not show a similar trend.

For the SCCs with W/B ratios 0.38 and 0.44, it increases in the initial phase, reaches a maximum value, and then tends to decrease. According to (Aye *et al.* 2010, Brown and Badger 2000, Santhanam *et al.* 2003), this variation depends mainly on the crystallization of the continuous salt and generation of gypsum and ettringite in the pores or micro cracks of concrete. At the initial stage,

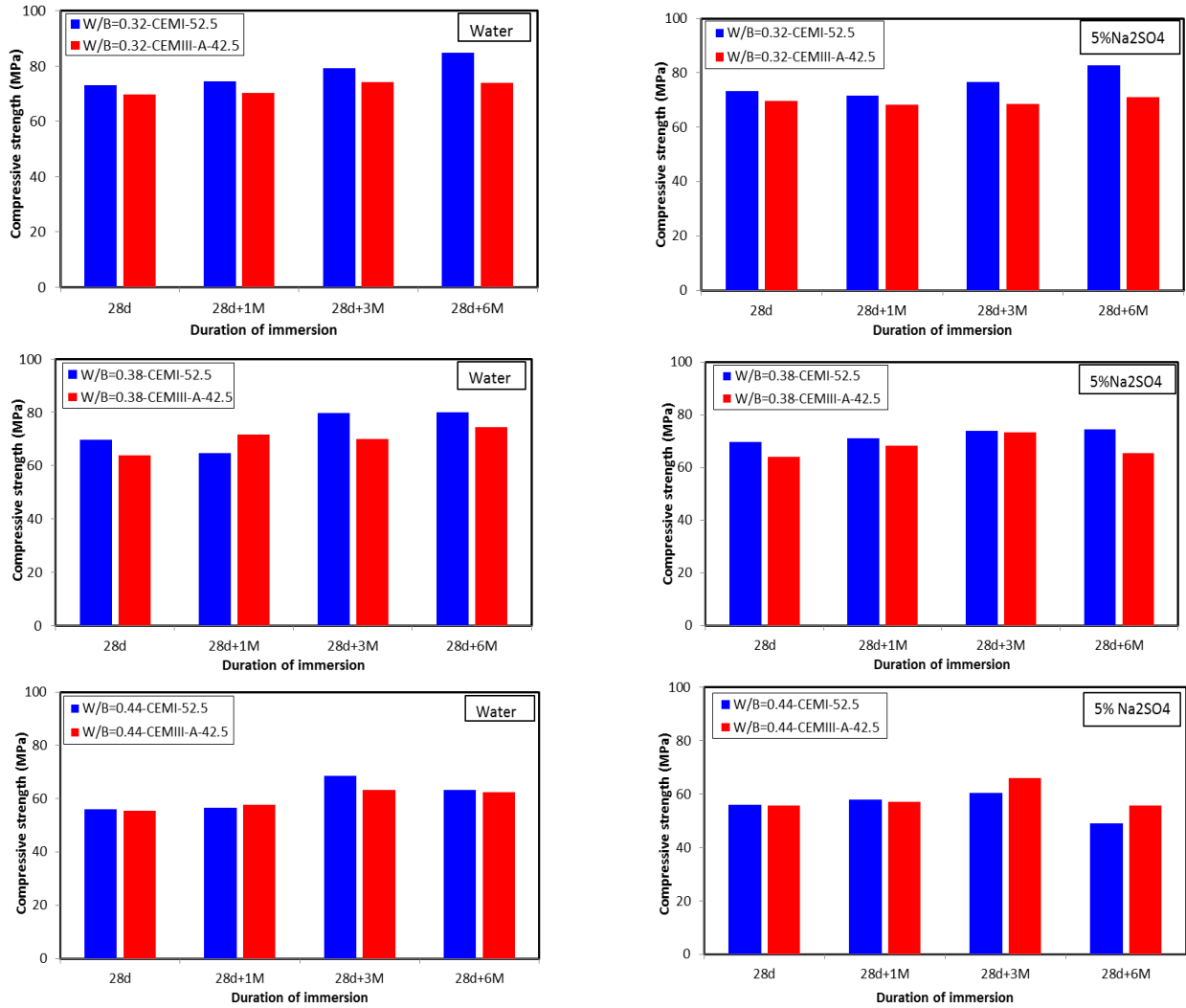
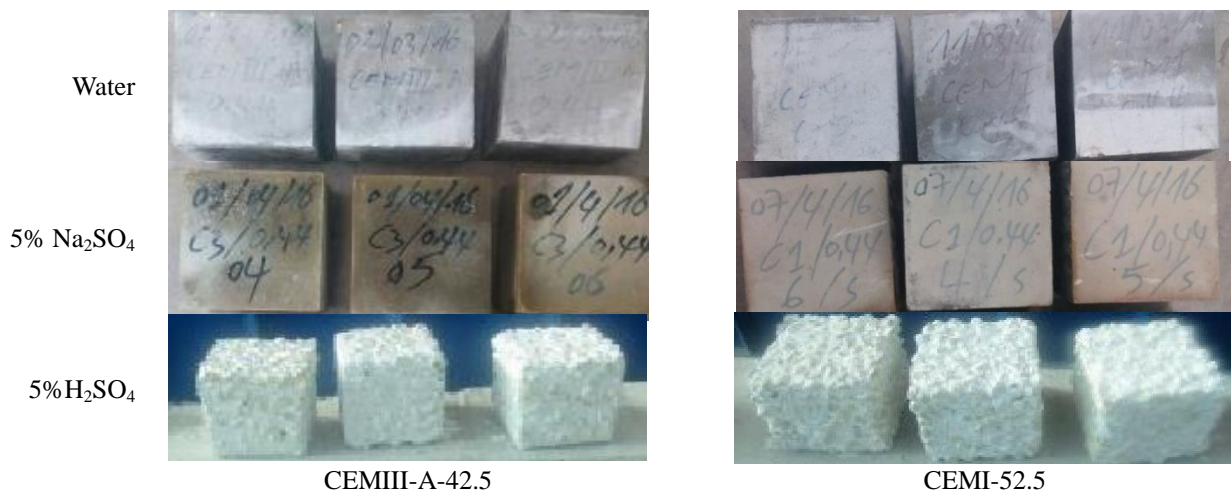


Fig. 7 Compressive strength of specimen in water and 5% Na<sub>2</sub>SO<sub>4</sub>



CEMIII-A-42.5

CEMI-52.5

Fig. 8 Visual inspection after 6 Months of immersion

the expansion induced by the crystallization and new products (i.e., gypsum and ettringite) can fill the pores and micro-cracks, and increase the compactness of the concrete, which leads to an increase in the resistance to compression at the level of macro pores (Escalante *et al.* 2001).

At the advanced stage, however, with a supplementary crystallization of salt and the formation of gypsum ettringite, the pores or micro-cracks in the concrete cannot accommodate a new expansion. Of new cracks begin to appear and to develop when the constraint of expansion



exceeds the resistance to traction. Therefore, the resistance to compression of the concrete has a tendency to decrease. The visual inspection of the specimens preserved in the three solutions are shown in (Fig. 8)

### 3.6 X-ray diffraction (XRD)

#### 3.6.1 XRD analysis (acid attack)

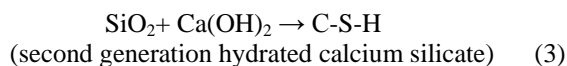
The X-ray diffraction analyzes were carried out both before the acid etching and after 1 month of immersion in  $H_2SO_4$  solution. Fig. 9 shows the XRD spectra for each type of study concrete sample. The matrix of the outer surface of the samples was analyzed.

The superposition of the two spectra of the samples immersed in water (control medium) and those immersed in the attack medium, shows the effect of  $H_2SO_4$  acid etching on the external surfaces of the studied concretes. The results of the XRD analysis confirm those of the mechanical study. The presence of a large amount of gypsum (G) can be noted for all the concretes subjected to the attack of acid of  $H_2SO_4$ , which explains the great degradation of the surface in contact with this type of acid.

For SCCs made from Portland cement (Fig. 9) a strong signal at the angle  $2\theta=18.1749$  which characterizes the presence of a large amount of quartz is found, due to the sands used in the mix. The superposition of the 2 different spectra (control medium and sulfuric acid) shows the disappearance and appearance of new hydrated phases. For example: At the lines  $2\theta=18.1749$ ,  $2\theta=34.2176$  the peak intensity of Portlandite (P:  $Ca(OH)_2$ ) for the samples of SCC prepared by a Portland cement (Water/Binder= 0.32) preserved in water (control) is visible (average signal), whereas for the acidic medium the intensity of this peak is almost nil this is due to the consumption of the Portlandite following the reaction of  $Ca(OH)_2$  with the acid ( $H_2SO_4$ ).

In fact, in contact with sulfuric acid, calcium hydroxide (Portlandite) reacts to form calcium sulphate, which is deposited as gypsum (Eq. (1)). In addition, the calcium sulphate constituted by this first reaction will react with the calcium aluminate phase in the cement to form hydrated calcium trisulfoaluminate (ettringite).

For slag cement (Fig. 9) with W/B ratio=0.32 (rich in slag 60%) the peak intensity of  $Ca(OH)_2$  is minimal in the control medium following the pozzolanic reaction according to Eq. (2) because this type of cement is rich in silica.



In addition, the intensity of the Portlandite peaks for the three W/B ratios (0.32, 0.38 and 0.44) are almost similar.

- The peaks identifying the gypsum (G:  $CaSO_4 \cdot 2H_2O$ ) are at  $2\theta=20.9766$ ,  $2\theta=36.0982$  and  $2\theta=43.3136$ , the intensity of the gypsum is greater for the SCCs prepared by Portland cement comparison of that of the SCCs made by cement with dairy.

- The most intense peak is always at slot  $2\theta=29.5353$ , which characterizes the presence of a large quantity of quartz (Q), due to the sands used and also the blast furnace slag.

- His intensity of the quartz peaks in self-compacting

concretes made by slag cement are significantly higher compared to that of SCC made by Portland cement.

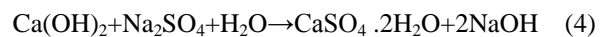
- A small ettringite peak (E) at the line  $2\theta=10.7292$ , this minimum intensity is due to the short immersion time in sulfuric acid (1 month).

- A small peak is detected at line 39.5524, which characterizes the presence of calcite (C:  $CaCO_3$ ).

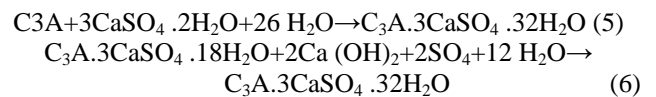
#### 3.6.2 XRD analysis (sulfate attack)

X-ray diffraction mineralogical analyzes were performed on SCC samples after one month immersion in the 5% sodium sulphate solution and the control medium (water).

In the presence of sodium sulphate calcium hydroxide reacts to form gypsum according to the following equation:



The gypsum formed by this reaction participates in the formation of secondary ettringite from residual anhydrous  $C_3A$  or hydrated aluminates (monosulfoaluminates), according to the following two equations:



The DRX spectra of the various studied concretes confirm the formation of gypsum and ettringite following the  $Na_2SO_4$  sulphate attack. The density of the gypsum peaks is greater compared to that of the ettringite. The peaks identifying the gypsum (G:  $CaSO_4 \cdot 2H_2O$ ) are at  $2\theta=(20.9766, 36.0982, 43.3136, 48.6484)$ . The peak identifying the ettringite (E:  $C_3A \cdot 3CaSO_4 \cdot 32H_2O$ ) are at  $2\theta=10.7292$  and  $2\theta=40.8189$ , the peak intensity is important for the SCCs made by slag cement compared to that of the SCCs manufactured by Portland cement.

By comparing the two spectra of before and after attack, we can see, for all self-compacting concretes, the disappearance of Portlandite (P) after sulphate attack. The latter reacted with  $H_2SO_4$  to form gypsum according to equation 4. The latter participates in the formation of ettringite (Eqs. (5) and (6)). The comparison between the different studied SCCs indicates the differences in properties. It can be noticed that the peaks that characterize the gypsum (G) and the ettringite are more visible and more intense for the SCC (Portland cement) than for the SCC (slag cement). This is directly linked to the high Portlandite content, as seen by the peak intensities observed for the SCCs made by Portland cement. On the other hand, in the slag cement based SCC, the Portlandite is present before the sulphate attack because of its consumption by pozzolanic reaction.

## 4. Conclusions

Based on the results, the following conclusions can be drawn:

- At a young age, SCCs based on Portland cement develop compressive strengths greater than SCCs based on slag cement. On the other hand, in the opposite case, and this has been observed in the long term. In addition,

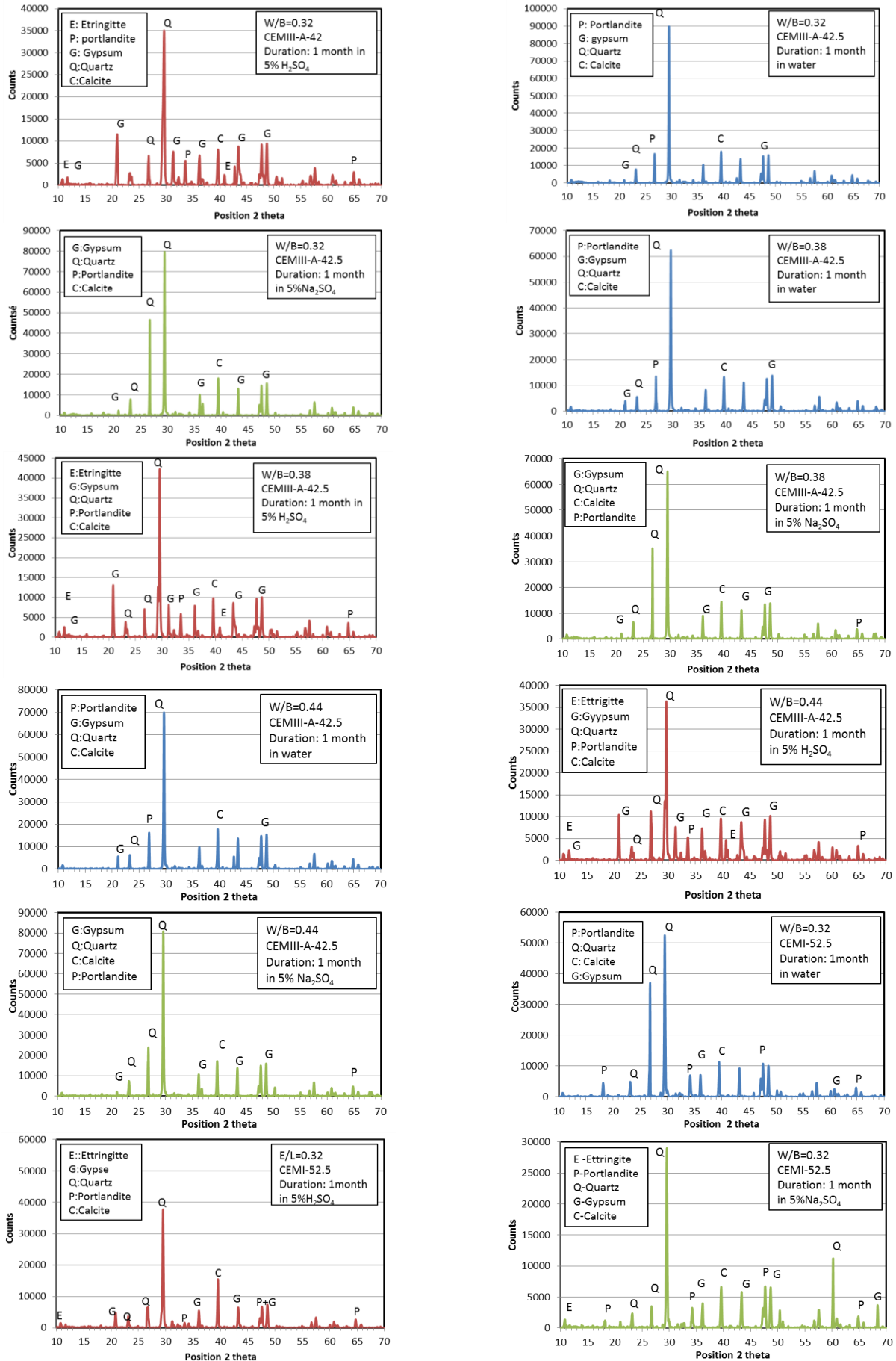


Fig. 9 XRD of self-compacting concretes conserved for 30 days in attacking environments

the compressive strength is strongly influenced by the curing method, seven days of initial curing in water followed by a ripening in a hot climate was the optimal duration for a better development of compressive strength.

- The amount of Portlandite for SCC at the (SC) base at 28 days is lower compared to that of SCC mixtures incorporating (PC) and this regardless of the initial curing period. The different results from compression and diffractogramme tests confirm that concretes formulated from slag cement remain less sensitive to sulfuric attack and external sulphatic attack compared to SCCs formulated with Portland cement and this regardless of the ratio W/B. Concretes made by Portland cement with a high ratio W/B are those that have the most visible signs of acid attack.

- The XRD analyzes confirm that the origin of the degradations of the samples subjected to the immersion in the sulfuric acid can be attributed to a formation of the secondary ettringite following the formation of the gypsum to properties and safety of structural concrete or reinforced concrete members.

## References

- Al-Abduljabbar, A.H (2008), "Effect of time and temperature on workability of SCC", <http://faculty.ksu.edu.sa/28745/DocLib/Hisham.SCC.pdf>.
- Al-Martini, S. and Nehdi, M. (2010), "Effects of heat and mixing time on self-compacting concrete", *Proc. Inst. Civil Eng. Constr. Mater.*, **163**(3), 175-182. <https://doi.org/10.1680/coma.800047>.
- Andersen, M.D., Jakobsen, H.J. and Skibsted, J. (2004), "Characterization of white Portland cement hydration and the CASAH structure in the presence of sodium aluminate by <sup>27</sup>Al and <sup>29</sup>Si MAS NMR spectroscopy", *Cement Concrete Res.*, **34**, 857-868. <https://doi.org/10.1016/j.cemconres.2003.10.009>.
- ASTM C 1012-95a (2000), Standard Test Method for Length Change of Hydraulic-Cement Mortars Exposed to a Sulfate Solution, Annual Book of ASTM Standards, Volume 04.01 Cement, lime, Gypsum.
- Aye, T., Oguchi, C.T. and Takaya, Y. (2010), "Evaluation of sulfate resistance of Portland and high alumina cement mortars using hardness test", *Constr. Build. Mater.*, **24**(6), 1020-1026. <https://doi.org/10.1016/j.conbuildmat.2009.11.016>.
- Belaidi, A.S.E., Azzouz, L., Kadri, E. and Kenai, S. (2012), "Effect of natural pozzolana and marble powder on the properties of self-compacting concrete", *Constr. Build. Mater.*, **31**, 251-257. <https://doi.org/10.1016/j.conbuildmat.2011.12.109>.
- Boukendakdji, O., Kenai, S., Kadri, E.H. and Rouis, F. (2009), "Effect of slag on the rheology of fresh self-compacted concrete", *Constr. Build. Mater.*, **23**(7), 2593-2598. <https://doi.org/10.1016/j.conbuildmat.2009.02.029>.
- Brown, P.W. and Badger, S. (2000), "The distributions of bound sulfates and chlorides in concrete subjected to mixed NaCl, MgSO<sub>4</sub>, Na<sub>2</sub>SO<sub>4</sub> attack", *Cement Concrete Res.*, **30**(10), 1535-1542. [https://doi.org/10.1016/S0008-8846\(00\)00386-0](https://doi.org/10.1016/S0008-8846(00)00386-0).
- Chithra, S., Kumar, S.R.R.S. and Chinnaraju, K. (2016), "The effect of Colloidal Nano-silica on workability, mechanical and durability properties of High Performance Concrete with Copper slag as partial fine aggregate", *Constr. Build. Mater.*, **113**, 794-804. <https://doi.org/10.1016/j.conbuildmat.2016.03.119>.
- EFNARC (2005), The European Guidelines for Self-Compacting Concrete: Specification, Production and Use, The Self-Compacting Concrete European Project Group.
- El-Chabib, H. and Ibrahim, A. (2013), "The performance of high-strength flowable concrete made with binary, ternary, or quaternary binder in hot climate", *Constr. Build. Mater.*, **47**, 245-253. <https://doi.org/10.1016/j.conbuildmat.2013.05.062>.
- Elkhadiri, I. and Puertas, F. (2008), "The effect of curing temperature on sulphate-resistant cement hydration and strength", *Constr. Build. Mater.*, **22**(7), 1331-1341. <https://doi.org/10.1016/j.conbuildmat.2007.04.014>.
- Escalante-Garcia, J.I. and Sharp, J.H. (2004), "Variation in the composition of C-S-H gel in portland cement pastes cured at various temperatures", *J. Am. Ceram. Soc.*, **82**(11), 3227-3241. <https://doi.org/10.1111/j.1151-2916.1999.tb02230.x>.
- Escalante, J.I., Gomez, L.Y., Johal, K.K., Mendoza, G., Mancha, H. and Mendez, J. (2001), "Reactivity of blast-furnace slag in Portland cement blends hydrated under different conditions", *Cement Concrete Res.*, **31**(10), 1403-1409. [https://doi.org/10.1016/S0008-8846\(01\)00587-7](https://doi.org/10.1016/S0008-8846(01)00587-7).
- Friedemann, K., Stallmach, F. and Kärger, J. (2006), "NMR diffusion and relaxation studies during cement hydration a non-destructive approach for clarification of the mechanism of internal post curing of cementitious materials", *Cement Concrete Res.*, **36**(5), 817-826. <https://doi.org/10.1016/j.cemconres.2005.12.007>.
- Khan, R.A., Satyanaryana, A. and Sharma, R. (2015b), "Development of high performance concrete", *UKIERI Concrete Congress-Concrete Research Driving Profit & Sustainability-International Conference*, 1090-1102.
- Kjellsen, K.O., Detwiler, R.J. and Gjörv, O.E. (1991), "Development of microstructures in plain cement pastes hydrated at different temperatures", *Cement Concrete Res.*, **21**(1), 179-189. [https://doi.org/10.1016/0008-8846\(91\)90044-I](https://doi.org/10.1016/0008-8846(91)90044-I).
- Kokubu, K., Takahashi, S. and Anzai, H. (1989), "Effect of curing temperature on the hydration and adiabatic temperature characteristic of Portland cement-blast furnace slag concrete", *American Concrete Institute Concrete Journal*, SP 114-66.
- Liu, T., Qin, S., Zou, D. and Song, W. (2018), "Experimental investigation on the durability performances of concrete using cathode ray tube glass as fine aggregate under chloride ion penetration or sulfate attack", *Constr. Build. Mater.*, **163**, 634-642. <https://doi.org/10.1016/j.conbuildmat.2017.12.135>.
- Makhloufi, Z., Kadri, E.H., Bouhicha, M. and Benaissa, A. (2012), "Resistance of limestone mortars with quaternary binders to sulfuric acid solution", *Constr. Build. Mater.*, **26**(1), 497-504. <https://doi.org/10.1016/j.conbuildmat.2011.06.050>.
- Maruyawa, I., Suzuki, M. and Sato, R. (2005), "Prediction of temperature in ultra-High Strength concrete based on the temperature dependent hydration model", *American Concrete Institute Concrete Journal*, SP 228-75.
- Okamura, H. and Ouchi, M. (2003), "Self-compacting concrete", *J. Adv. Concrete Technol.*, **1**(1), 5-15. <https://doi.org/10.3151/jact.1.5>.
- Older, I., Abdul-Maula, S. and Zhongya, L. (1986), "Effect of hydration temperature on cement paste structure", *MRS Proc.*, **85**, 139-144. <https://doi.org/10.1557/PROC-85-139>.
- Ortiz, J.A., Aguado, A., Agulló, L., García, T. and Zermeño de León, M.E. (2008), "Experimental study of the effect of temperature on the strength of ready-mixed concrete. Theory", *Mater. Constr.*, **58**(291), 7-22. <https://doi.org/10.3989/mc.2008.v58.i291.103>.
- Oueslati, O. and Duchesne, J. (2012), "The effect of SCMs and curing time on resistance of mortars subjected to organic acids", *Cement Concrete Res.*, **42**(1), 205-214. <https://doi.org/10.1016/j.cemconres.2011.09.017>.
- Reinhardt, H.W. and Stegmaier, M. (2006), "Influence of heat curing on the pore structure and compressive strength of self-

- compacting concrete (SCC)", *Cement Concrete Res.*, **36**(5), 879-885. <https://doi.org/10.1016/j.cemconres.2005.12.004>.
- Rizwan, S.A. and Bier, T.A. (2012), "Blends of limestone powder and fly-ash enhance the response of self-compacting mortars", *Constr. Build. Mater.*, **27**(1), 398-403. <https://doi.org/10.1016/j.conbuildmat.2011.07.030>.
- Şahmaran, M., Christianto, H.A. and Yaman, İ.Ö. (2006), "The effect of chemical admixtures and mineral additives on the properties of self-compacting mortars", *Cement Concrete Compos.*, **28**(5), 432-440. <https://doi.org/10.1016/j.cemconcomp.2005.12.003>.
- Santhanam, M., Cohen, M.D. and Olek, J. (2003), "Effects of gypsum formation on the performance of cement mortars during external sulfate attack", *Cement Concrete Res.*, **33**(3), 325-332. [https://doi.org/10.1016/S0008-8846\(02\)00955-9](https://doi.org/10.1016/S0008-8846(02)00955-9).
- Senhadji, Y., Escadeillas, G., Mouli, M. and Khelafi, H. (2014), "Influence of natural pozzolan, silica fume and limestone fine on strength, acid resistance and microstructure of mortar", *Pow. Tech.*, **254**, 314-323. <https://doi.org/10.1016/j.powtec.2014.01.046>.
- Sumer, U.M. (2011), "Performance of self-compacting concrete containing different mineral admixtures", *Constr. Build. Mater.*, **25**(11), 4112-4120. <https://doi.org/10.1016/j.conbuildmat.2011.04.032>.
- Tennich, M., Ben Oueddou, M. and Kallel, A. (2017), "Behavior of self-compacting concrete made with marble and tile wastes exposed to external sulfate attack", *Constr. Build. Mater.*, **135**, 335-342. <https://doi.org/10.1016/j.conbuildmat.2016.12.193>.
- Turk, K., Caliskan, S. and Yazicioglu, S. (2007), "Capillary water absorption of self-compacting concrete under different curing conditions", *Ind. J. Eng. Mater. Sci.*, **14**(5), 365-372.
- Velandia, D.F., Lynsdale, C.J., Provis, J.L. and Ramirez, F. (2018), "Effect of mix design inputs, curing and compressive strength on the durability of Na<sub>2</sub>SO<sub>4</sub>-activated high volume fly ash concretes", *Cement Concrete Compos.*, **91**, 11-20. <https://doi.org/10.1016/j.cemconcomp.2018.03.028>.
- Weisheit, S., Waldmann, D. and Greger, M. (2010), "Influence of environmental conditions for the rheological properties of SCC", *K. Khayat D. Feys 6th International RILEM Symposium on Self-Compacting Concrete and 4th North American Conference on the Design and Use of SCC*, Montreal, Canada.
- Yahiaoui, W., Kenai, S., Menadi, B. and Kadri, E.H. (2017), "Durability of self-compacted concrete containing slag in hot climate", *Adv. Concrete Constr.*, **5**(3), 271-288. : <https://doi.org/10.12989/acc.2017.5.3.271>.
- Zhao, H., Sun, W., Wu, X. and Gao, B. (2012), "Effect of initial water-curing period and curing condition on the properties of self-compacting concrete", *Mater. Des.*, **35**, 194-200. <https://doi.org/10.1016/j.matdes.2011.09.053>.