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# Effect of acids and sulphates on the durability of self-compacting concretes

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## Abstract

*The deterioration of self-compacting concretes (SCC) in acid and sulphate media is a major problem in the evaluation of structural durability. The aim of our work is to study this effect and to do this, a test protocol was used to evaluate the effect of sulphate and acidic media on the mechanical properties and microstructure of SCCs. Two types of cement were used CEMIII-A-42.5 cement (60% slag) and cement CEMI-52.5 and three water / binder ratios ( $E / L = 0.32-0.38-0.44$ ). The SCC specimens were stored in all three media, water (control), 5%  $H_2SO_4$  and 5%  $Na_2SO_4$ . The measured properties were: The compressive strength of cubic test pieces at 30, 90 and 180 days and X-ray diffraction (XRD) analysis. These results show that high furnace slag improves the durability of SCCs.*

**Keywords:** Durability, sulfuric acid, sodium sulfate, SCC

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## 1. Introduction

Concrete structures are regularly subject to natural environmental stress conditions and industrial chemicals. Sulfuric acid ( $H_2SO_4$ ) is one of the most detrimental to concrete structures because of its presence in groundwater, industrial waste and sewage systems [1]. The interaction between concrete and sulfuric acid causes damage and damage. Although sulfuric acid is still dangerous for cementitious materials [2], the type and content of cement are important factors affecting performance in environments containing sulfuric acid [3]. On the other hand, external sulphate attack on cementitious materials has been a major sustainability problem and a subject of extensive research for many decades [4]. Contradictory results on this type of attack

and the underlying mechanisms have led some authors to revise the subject several times [5-6].

## 2. Experimental investigations

### 2.1 Materials

Two types of cement were used in this study. A CEM I 52.5 N cement produced by LAFARGE at the Le Havre plant was selected. Given its regular use in SCC applications. CEMIII-A-42.5N cement from Le Havre was considered to be in the evolution of current construction practices (limiting the amount of clinker) and to limit the variation of properties (class, clinker). The chemical composition and the physical properties of the cement are presented in Table 1. The fine aggregate was 0-3 mm, its equivalent and equal to 80. The

coarse aggregate was of granular class 8/12 mm their grain size curve is mentioned in Figure 1. The superplasticizer used is from the family of polycarboxylates. It is produced by CHRYSO (OPTIMA 220) and is particularly suitable for self-placing applications. The adjuvant used in this study was a superplasticizer with a density of 1.05, a chloride ion content of less than 0.1% and solids content of 21.6%. The dosage can vary from 0.2 to 3% depending on the fluidity and the desired performance.

Three self-compacting concretes for each type of cement were used in this research, with water / binder ratios ( $E / L = 0.32-0.38-0.44$ ). The compositions of the BAPs adopted in this study were estimated using the Okamura method. The coarse aggregate was limited to 12 mm, the ratio of coarse aggregate to fine aggregate ( $GG / GF$ ) was about 1, the binder content was between 527 and 624 kg / m<sup>3</sup> depending on the  $E / L$  ratio. The total amount of aggregates ranged from 1414 to 1427 kg / m<sup>3</sup>. The amount of superplasticizer has been optimized to improve the workability of the mixture. Mixing proportions of BAP are shown in Table 2.

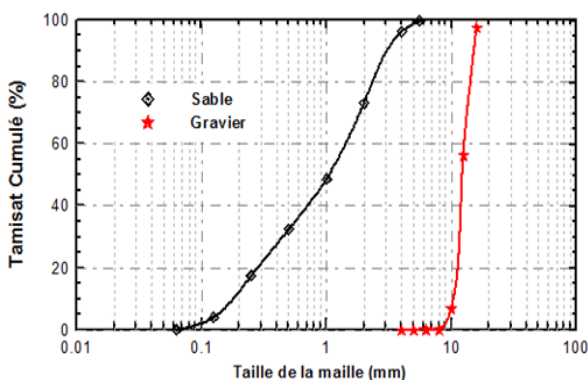


Figure 1: Granulometric distribution of aggregates

Table 2: Composition of SCC

Matériels (kg/m <sup>3</sup> )	CEMI-52.5			CEMIII-A-42.5		
	BAP-32	BAP-38	BAP-44	BAP-32	BAP-38	BAP-44
E/L	0.32	0.38	0.44	0.32	0.38	0.44
Ciment (C)	624.4	572.2	527.8	624.4	572.2	527.8
Sable	757.7	722.2	694.5	757.7	722.2	694.5
Gravier	770.0	700.0	722.2	770.0	700.0	722.2
Eau	199.8	215.7	232.2	199.8	215.7	232.2
Superplastifiant	14.2	7.8	5.0	14.2	7.8	5.0

### 2.3 Specimens and measurement method

15 × 15 × 15 cm<sup>3</sup> cubic molds were used to determine the compressive strength of self-placing concrete specimens preserved in acidic and sulphate media as well as x-ray diffraction (XRD) at 30, 90 and 180 days immersion in different environments. A total of 180 cubes designed to study the effect of attack media on the durability of SCCs.

After mixing, the spreading test, the T500 test, the "funnel" test, L-Box and the sieve stability were performed to characterize the workability of the fresh concrete. After obtaining a SCC, the concrete was molded into 15 × 15 × 15 cm<sup>3</sup> cubes, covered with plastic, allowed to cure for 24 hours, and then stored in water for 28 days. The specimens were then stored in three groups to study the effect of sulfuric acid, sodium sulfate and control medium (water) for comparison.

#### 2.3.1 SCC in the fresh state

The fresh SCC spreading test was carried out in accordance with recommendations [6]. For the L-box test, this test characterizes mobility in a confined environment of dynamic segregation. For the funnel V test, this test allows a qualitative evaluation of self-placing concrete [6]. It characterizes the ability of concrete to pass through an orifice. The test consists of observing the flow of the concrete through a V-shaped funnel and measuring the flow time when the orifice is free. The sieve stability test was used to qualify the SCC against the risk of segregation.

#### 2.3.2 Tests in the hardened state

- *Compressive strength*

After the preparation of 15 × 15 × 15 cm<sup>3</sup> BAP samples, the compression test was performed in accordance with EN 206-1 2004.

- *Attack acid*

After storage of the test pieces for 28 days in water, the

test pieces are immersed in the 5% sulfuric acid solution of  $H_2SO_4$ . High concentrations of 5%  $H_2SO_4$  are used to accelerate the deterioration.  $15 \times 15 \times 15$  cm<sup>3</sup> cubic specimens were used to evaluate the strength of the specimens of self-contained concrete held in the attack media. The initial pH (0.9) of the solution increased rapidly and was then controlled to a maximum threshold value of 2.5 by adding concentrated sulfuric acid which is renewed every month. The samples were removed from the solution weekly, rinsed three times with tap water to remove the loose reaction products, dried with a paper towel and allowed to dry at 23 °C for 30 minutes prior to weighing and drying. 'visual inspection.

- *Sulphate attack*

The sodium sulphate solution is prepared from deionized water to which 5% sodium sulphate is added. The solution is homogenized. To obtain a liter of 5%  $Na_2SO_4$ , the sodium sulphate  $Na_2SO_4$  in powder form was dissolved with stirring at the rate of 70 g per liter of distilled water. The volume of the sodium sulfate solution placed in the storage container is equal to 4 times the volume of the SCC samples tested. Once the sodium sulphate solution is prepared the same day, it is placed in the containers while checking its pH (which is equal to 6). The SCC samples are then introduced into the bins. The temperature of the solution is maintained at 23 °C. According to ASTM C1012, the pH of the sulphate solution must be between 6 and 8 and the solution must be renewed every week. This renewal of solution requires considerable amounts of sodium sulphate. For this we resorted to the method of correction of the solution by adding a quantity of sulfuric acid ( $H_2SO_4$ .3N) twice a week, maintaining the pH between 6 and 8 using pH paper.

- *X-Ray Diffraction (XRD)*

The XRD was carried out on powder samples of the order of 2 g which were ground with an agate mortar up to 80 microns. On the other hand, the fact of reducing to powder a solid sample like in XRD, can subject it to an accelerated

degradation (reaction of the Portlandite exposed to the  $CO_2$  which gives the calcite, and evaporation of the free water) so in the case of the preparing a large number of mature samples always poses the question of conservation. After crushing the SCC samples stored in the different attack media, surface pieces were removed and ground for XRD.

### 3. Results and discussion

#### 3.1 Properties of fresh SCCs

In the present study, the spreading was measured just after concrete mixing and a superplasticizer adjustment was made to achieve the values required by [6]. Table 2 summarizes the results of the various characterization tests of the SCCs studied. The results obtained from the spreading tests show that the spreading of cement-containing concrete CEMIII-A (dairy cement) for the three SCCs (SCC-L32-SCC-L38-SCC-L44) and SCC-38 corresponds to the class SF2 (660-750mm) according to [6]. Similarly, for the CEMI (CPA) SCC cement (SCC-32) conforming to the SF1 class (550-650mm), on the other hand, the SCC (SCC-44) meets the SF3 class. It should be noted that all SCC mixtures containing CEMIII-A cement had a slightly higher spread compared to CEMI cement-based SCC mixtures, whereas the opposite case was observed for SCC-44. According to [7], water demand and handling are controlled by particle shape, particle size and particle texture, Slump Flow test results, marble powder (PM) and basalt powder (PB). [7] show that with a constant amount of water for all mixtures, an optimal 20% filler (FC) content leads to greater spreading than other mineral additions (PM, PB). This could be explained by the greater surface area of BP and PM particles, which requires a significant amount of water compared to that of (FC) [8]. As a result, the CF needs less water and translates into greater spread. Generally, mixtures that contain mineral additions have shown better performance than the unmixed blend with respect to Abrams cone spreading. Other researchers [9] have studied the effect of slag on the rheology of SCCs, they found that the incorporation of slag improves the workability

of the SCC and causes a decrease in the shear threshold. Viscosity decreases with increasing slag content.

**Table 2 :** Properties of fresh SCCs

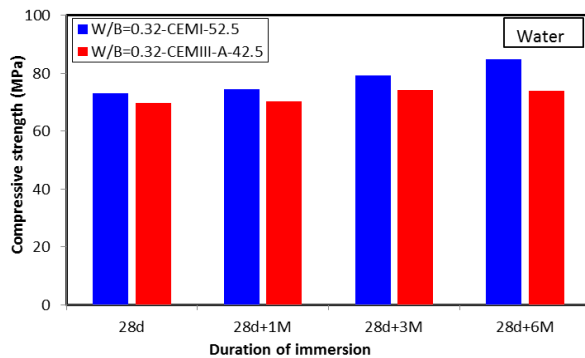
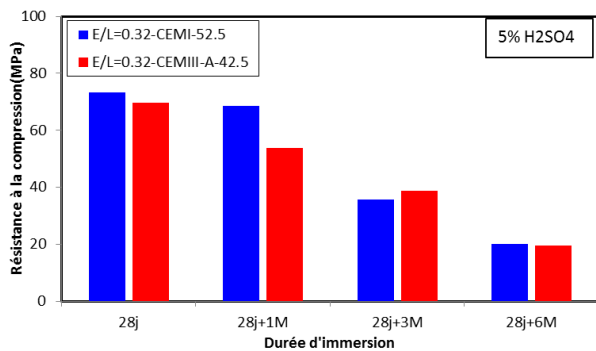
Propriétés à l'état frais		CEMI-52.5			CEMIII-A-42.5			Recommandations EFNARC 2005
E/L		0.32	0.38	0.44	0.32	0.38	0.44	
Etalement	Diamètre (mm)	650	670	760	660	680	715	SF1: 550-650 SF2: 660-750 SF3: 760-850
	T500 (s)	6.0	4.0	3.0	4.0	3.0	2.0	2-5 s
L-Box	H <sub>2</sub> /H <sub>1</sub> (%)	81.5	84.2	94	87	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
Laitance	%	6	10	15	10	14	16	≤ 20%
Masse volumique	Kg/m <sup>3</sup>	2360	2350	2345	2395	2375	2350	-

**3.2 Acid attack**

Fig. 2 shows the evolution of the compressive strength of BAP mixtures incorporating two binders (CEMI, CEMIII-A) with three ratios E / L = (0.32, 0.38 and 0.44) immersed in the two conservation media [T: fresh water, 5% H<sub>2</sub>SO<sub>4</sub>]. We observe that the evolution of the compressive strength as a function of age of all BAPs preserved in freshwater increases regularly with age and shows no decrease until the

age of 6 months. On the other hand, the SCC specimens preserved in the acid solution show a decrease in compressive strength with age, irrespective of the type of binder and the W/B ratio. BAP CEMI-based cement preserved in sulfuric acid showed a slightly higher compressive strength than cement-based CEMIII-A mixtures regardless of the W /B ratio. On the other hand, in the long term beyond 3 months of storage, the opposite case was observed, that is to say that blast furnace slag SCC blends has slightly higher resistances than SCC blast furnaces. cement base without addition. The different trend of the effect of blast furnace slag content on the loss of compressive strength due to the attack of sulfuric acid can be attributed to the pozzolanic reaction. It is recognized that the beneficial effect of the pozzolanic reaction is long-term (90 days). The conversion of Portlandite Ca(OH)<sub>2</sub> in the C-S-H gel as a result of the pozzolanic reaction contributes to an increase in resistance and reduction of porosity [10-11].

The H<sub>2</sub>SO<sub>4</sub> etching process can be illustrated by the following equation.



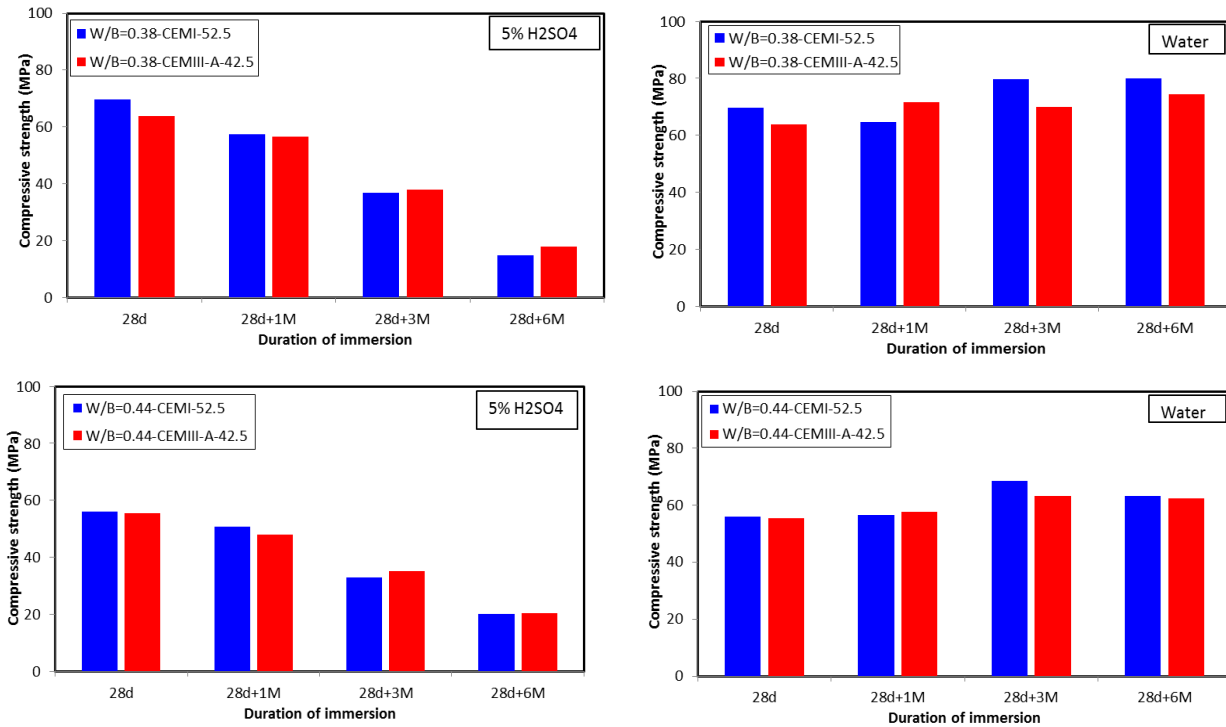


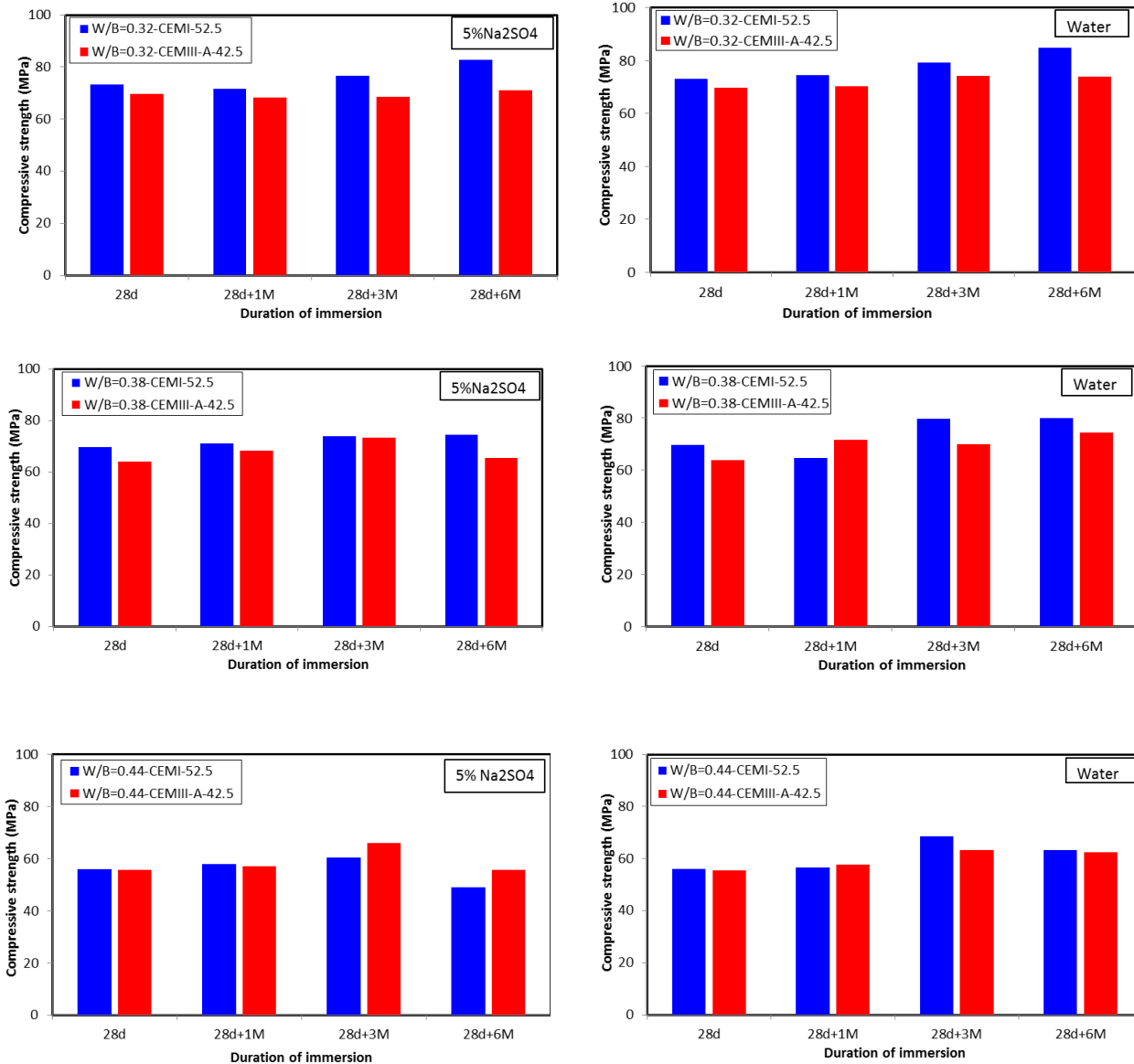
Figure 2 : Compressive strength of SCCs stored in 5% H<sub>2</sub>SO<sub>4</sub> solution and in water

### 3.3 Sulphate attack

The development of the compressive strength of the SCCs stored in the 5% Na<sub>2</sub>SO<sub>4</sub> sulphate solution is shown in Figure 3. It is observed that the compressive strength of all SCC mixtures does not show a similar tendency.

SCCs with W / B ratios = 0.38 and 0.44 show an increase in compressive strength in the initial phase, reach a maximum value, and then tend to decrease. According to [12-13], this variation depends mainly on the continuous crystallization of the salt and the generation of gypsum and ettringite in the pores or microcracks of the concrete. In the initial stage, crystallization-induced expansion and new products (ie, gypsum and ettringite) can fill pores and microcracks and increase the compactness of the concrete, resulting in an increase in strength. compression at the

level of macropores [14]. In the advanced stage, however, with additional salt crystallization and the formation of ettringite and gypsum, the pores or microcracks in the concrete can not accommodate further expansion. New cracks begin to appear and develop when the expansion stress exceeds the tensile strength. As a result, the compressive strength of concrete tends to decrease. In addition, the results showed a great loss of compressive strength in concretes with low compressive strength (high W / B ratio) and this loss is more pronounced for cement-based SCCs CEMI. Indeed, when the ratio water / binder decreases, the volume and connectivity of the porous network are reduced, and thus make the penetration of aggressive agents more difficult [15 -16]. [5] and added that the resistance of concrete to sulfate attack increases as the water / binder ratio decreases and as the cement content increases.



**Figure 3 :** Compressive strength of SCCs stored in 5% Na<sub>2</sub>SO<sub>4</sub> solution and water



**Figure 4:** Left solution 5% H<sub>2</sub>SO<sub>4</sub>, right solution 5% Na<sub>2</sub>SO<sub>4</sub>

### 3.4 X-ray diffraction analysis (XRD)

The XRD measurements were made from the surface degradation after crushing of the sample, the

superposition of the spectra confirms the presence of a significant amount of ettringite over the entire surface exposed to sodium sulfate attack and sulfuric acid. Significant gypsum peaks were detected at about  $2\theta = 20.97$  and  $2\theta = 36.09$  for both types of cement. The results of DRX show the presence of a higher amount of ettringite in SCC (CEMI) than in SCC-L (slag cement). In addition, a high intensity of Portlandite peaks was observed in SCCs based on CEMI cement compared to SCCs with SCCs based on slag cement. This explains the

consumption of Portlandite by the pozzolanic reaction to

form a second generation C-S-H gel

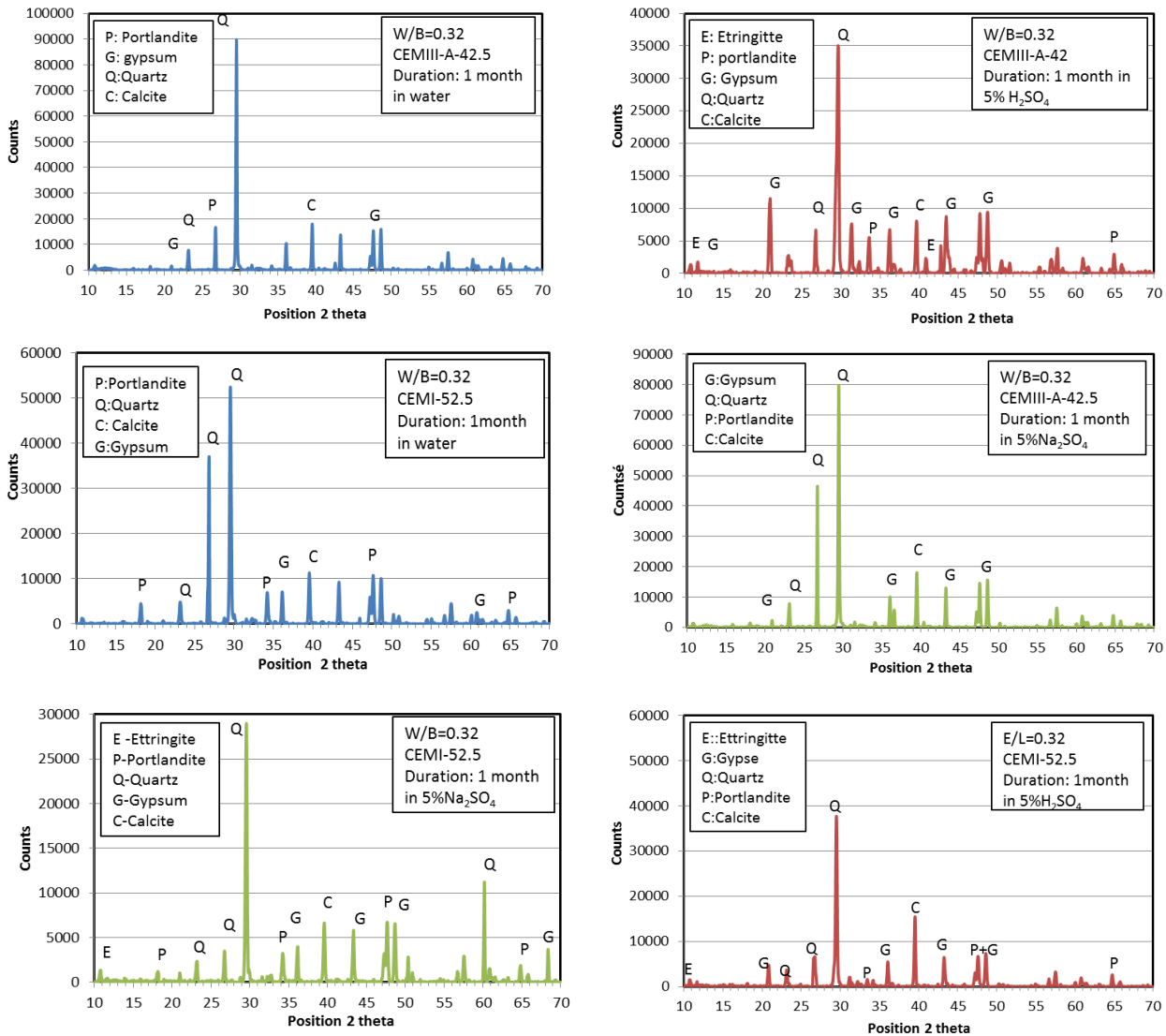


Figure 5 : DRX spectra of SCCs in the three media

4. Conclusion

The various results from compression and X-ray diffractogram tests confirm that concretes formulated from CEM III-A 42.5 remain less sensitive to external sulfuric and sulphatic attack compared to that of SCCs formulated from CEMI-52.5 and this regardless of the

ratio W/B. CEMI-52.5 concretes with a high W/B ratio are those with 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.

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