Pozzolanic Reactivity of Siliceous Wastes

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Abstract

The properties of concrete are governed by cement hydration. The latter can be modified through the incorporation of siliceous additions, which leads to the densification of the concrete's matrix.
In order to better understand the pozzolanic effect of the siliceous additions in Portland cement pastes, X-ray diffraction (XRD) analysis of lime pastes containing three additions (condensed silica fume, blast-furnace slag, and finely ground dune sand) was carried out.
This analysis is a simplified approach to that of cement pastes for which the principal reaction is the fixing of lime, resulting from cement hydration, by additions in the form of second-generation C-S-H (pozzolanic reaction).
Our study shows that the pozzolanic reactivity of a siliceous addition is related to its fineness, but especially to its degree of vitrification.

Key words: X-ray diffraction; siliceous addition; pozzolanic reactivity; C-S-H, amorphous structure

1. Introduction

This research is included within a larger program on the formulation of a very high performance or reactive powder concrete (RPC). The RPC should be dense and compact. The compactness of cement paste can be improved by the formation of second-generation calcium silicate hydrates (C-S-H). The latter are obtained through the introduction of fine siliceous particles having a pozzolanic role that contributes to increase strength and durability of concrete [1,2].

To this end, X-ray diffraction was used to analyze the evolution of the hydration of Portland cement pastes containing three additions: condensed silica fume (SF), blast furnace slag (S), and finely ground dune sand (DS).

In order to better characterize the pozzolanic effect of these additions in Portland cement pastes, the hydration of the (Lime + additions) mixtures was monitored using X-ray diffraction. This study is a simplified approach to that used with cement pastes for which the principal reaction is the fixing of lime, resulting from cement hydrati on, through the additions (pozzolanic reaction).

2. Materials used

The materials used in this study are:

- Lime [$Ca(OH)_2$];
- Dune sand (DS) from the Algerian south, ground to a fineness of 6600cm ^{2} / g [Blaine] with a specific gravity of 2.4;
- A granulated slag (S) of Algerian origin (blast-furnace of El-Hadjar) ground to a fineness of 5000 cm ^{2} / g [Blaine] with a specific gravity of 2.8;
- A condensed silica fume (SF) of Canadian origin with a fineness of 20 m ^{2} /g [BET] and a specific gravity of 2.2;
- Cement CEM II/A originating from an Algerian cement factory with a fineness of 3600 cm ^{2} / g [Blaine] and a specific gravity of 3.1.

Chemical analyses of these three additions are represented in Table 1

Table 1: Chemical analyses of the additions used

Proportioned elements	Dune sands	SF	Slag
SiO_2	86.95	96.00	40.53
Al_2O_3	1.92	0.25	8.16
Fe_2O_3	0.90	0.6	0.75
SO_3	0.44	0.45	2.00
CaO	6.33	1.58	39.89
MgO	0.53	0.2	1.33
LOI	2.81	-	3.00

Of all the additions, slag has the lowest SiO_2 content .

To highlight the mineralogical nature of these additions, an XRD analysis was conducted and is reported in Figures 1, 2, and 3.

X-ray diffraction patterns presented in these figures show that the finely ground dune sand has a crystallized siliceous structure of the *low-quartz* type, whereas slag and condensed silica fume present an amorphous structure. The SF is characterized by a significant centered halation with 4.04 A° corresponding to the principal line of *cristobalite,* which is the nearest form to silica glass from a thermodynamic point of view. [3]

The slag is characterized by a significant centered halation corresponding to the principal line of melilite (C_3MS_2-C_2AS).

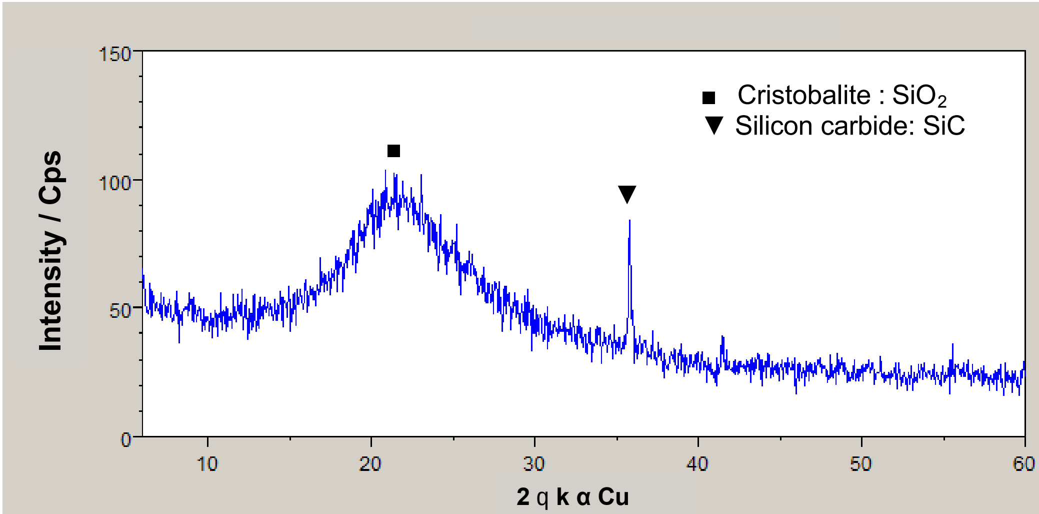

Figure 1 - X-ray diffraction pattern of silica fume (SF)

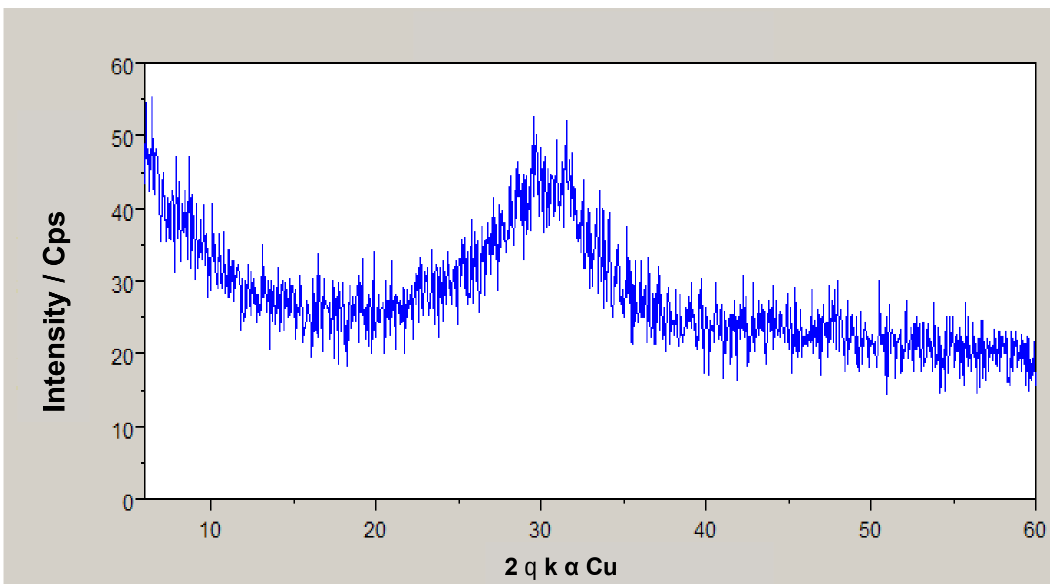

Figure 2 - X-ray diffraction pattern of slag (S)

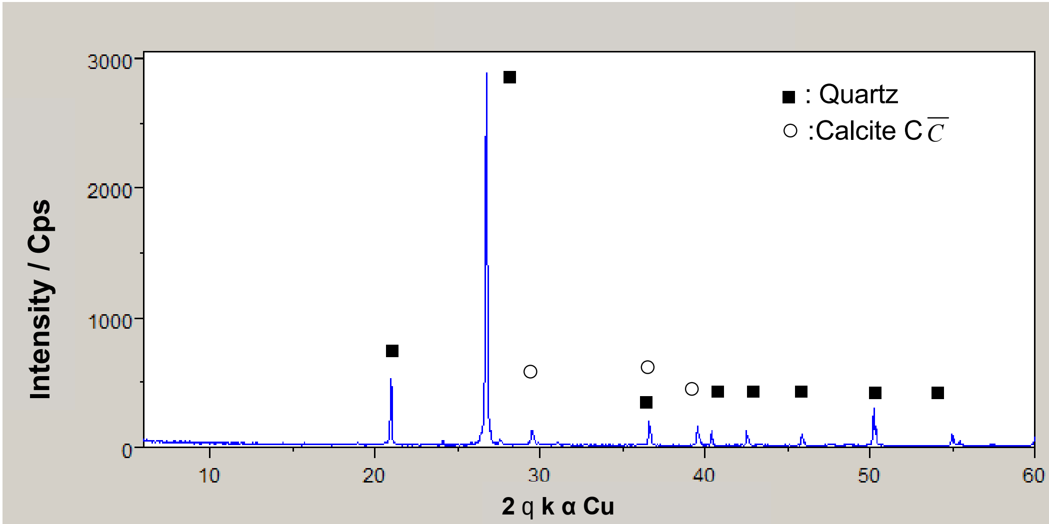

Figure 3 - X-ray diffraction pattern of dune sand (DS)

3. Study of the pozzolanic reactivity of the additions

The evolution of the pozzolanic reaction over time of these additions has been studied using XRD on pastes containing 50% pure lime + 50% addition.

Results of these analyses are presented in Figures 4, 5, and 6.

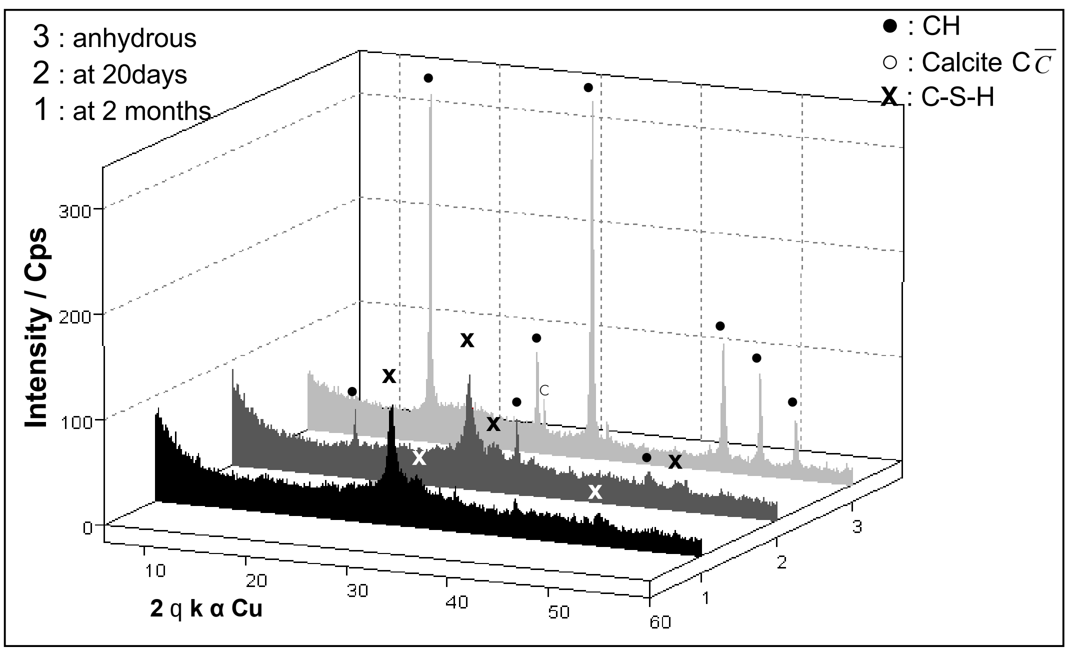

Figure 4 - Hydration of « Lime + SF » pastes at different ages

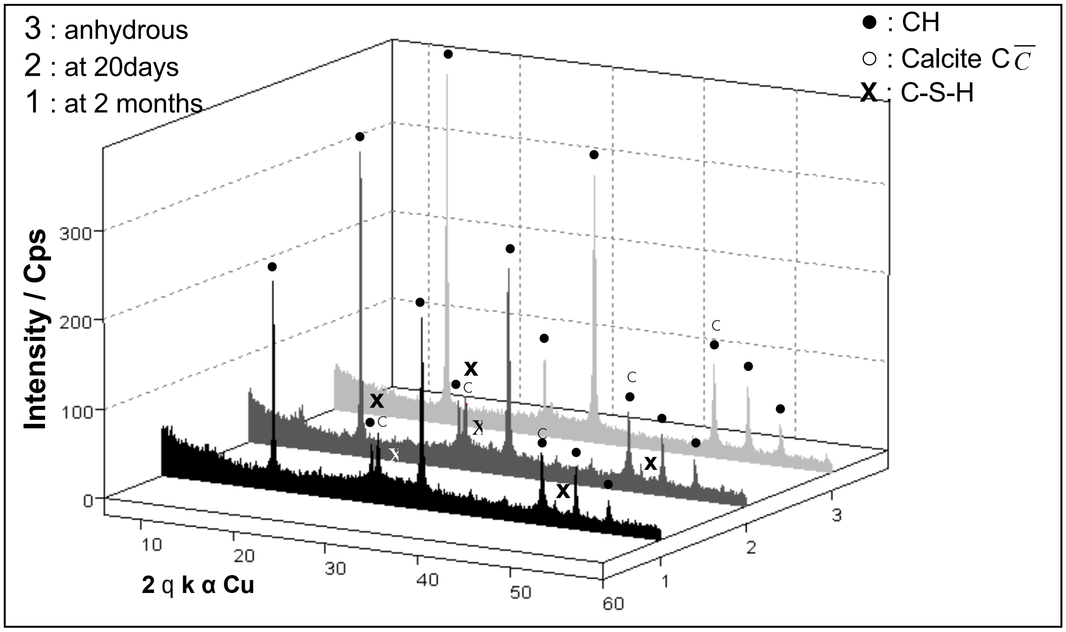

Figure 5- Hydration of « Lime+ Slag » pastes at different ages

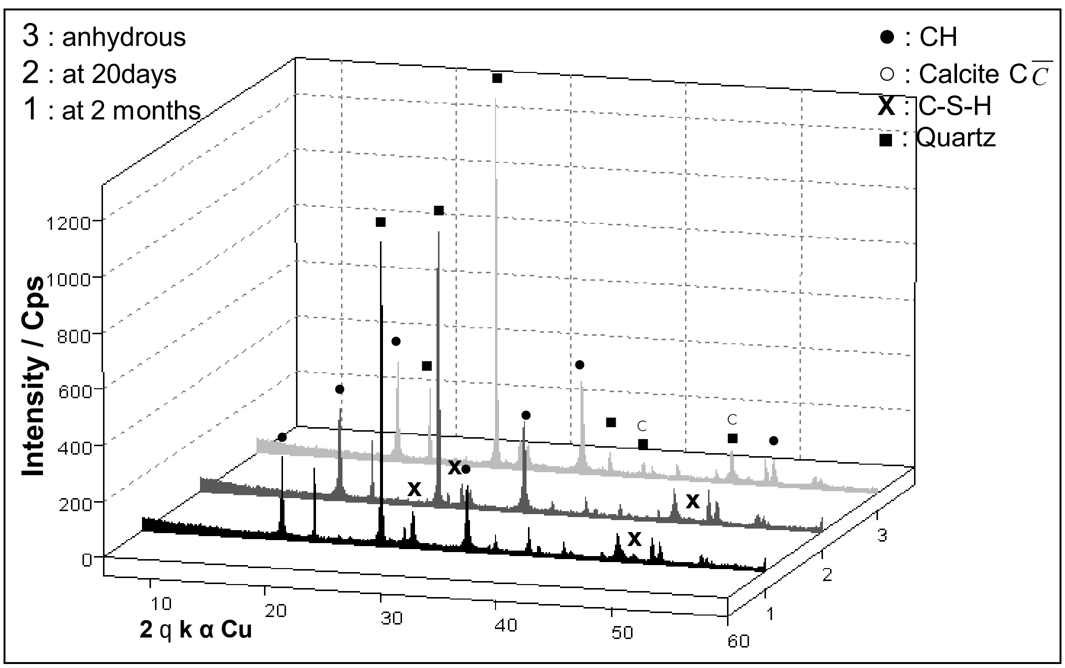

Figure 6- Hydration of « Lime + DS » pastes at different ages

X-ray diffraction patterns of these figures show that the intensity of the lime rays decrease with time in the presence of the additions, which is due to the fixing of lime by silica particles (pozzolanic reaction) to form C-S-H.

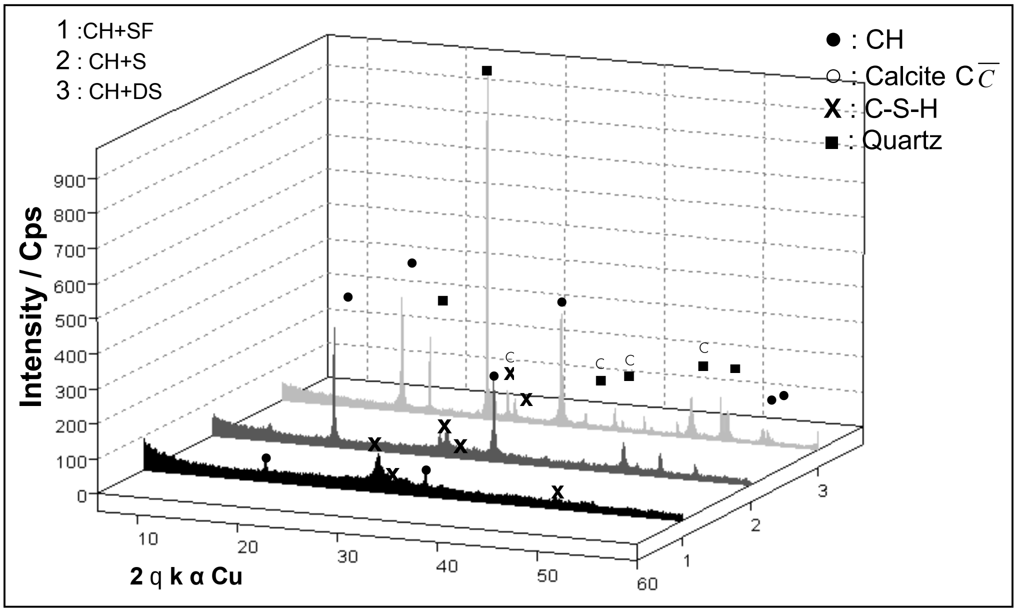

Figure 7 - Comparison of the pozzolanic reactivity of the different additions at 20 days of hydration

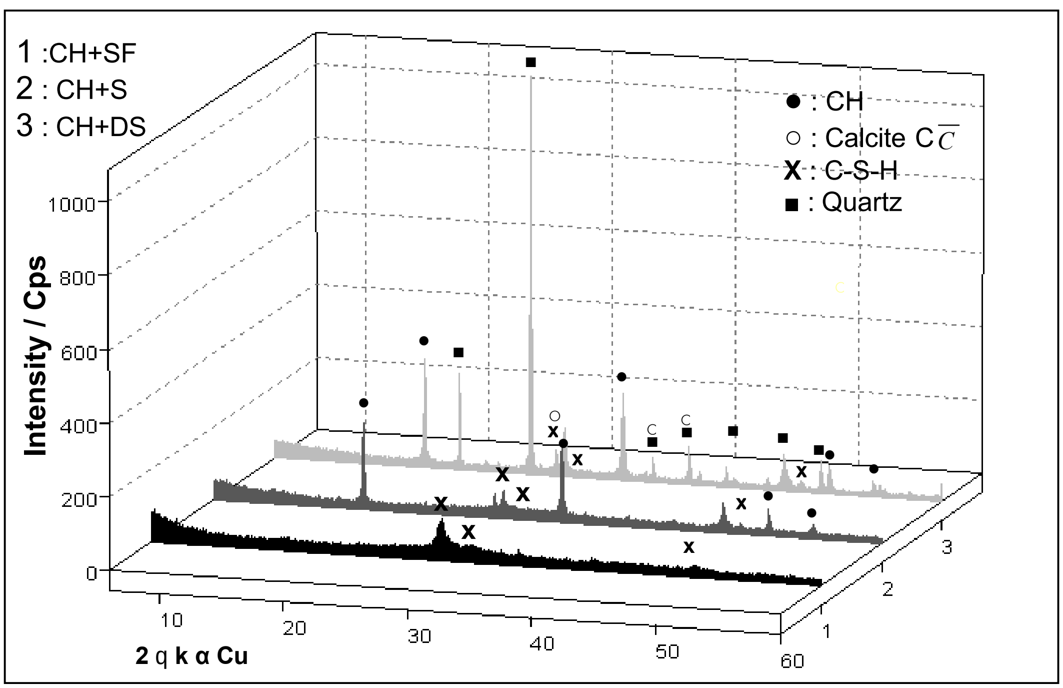

Figure 8 - Comparison of the pozzolanic reactivity of the different additions at 2 months of hydration

- Figure 7 shows that at 20 days of hydration, the intensity of the lime rays is more significant in the presence of dune sand compared to the mixtures containing slag or SF.
- Figure 8 shows the total absence of lime in the « Lime + SF » mixture at 2 months of hydration, which explains the strong pozzolanic reactivity of SF due to its very high fineness and amorphous state.
- Despite its crystalline form, dune sand displays pozzolanic reactivity that is in agreement with Benezet and Benhassaine [12].
- The pozzolanic reactivity of dune sand is partial and less significant than that of ground slag, since the latter has an amorphous structure, unlike ground dune sand, which is crystallized.

It can be concluded that amorphous silica is able to fix significant quantities of lime in a ratio of $CaO/SiO_2 > 1$. This has been confirmed by the low silica content of the slag.

Considering the high reactivity of the SF used, due to its high fineness and the amorphous structure of the silica it contains, and in order to specify the semi-crystallized structure of the C-S-H obtained at 20 ^{0} C, it has been thought that would be useful to represent X-ray diffraction patterns of the « CH + SF » mixture at 2 months of hydration (Figure 9), since they do not present additional diffraction rays corresponding to the reflections h.k.o as: 3.06 A° (220), 2.80 A° (400), and 1.83 A° (040) (which is in agreement with H.F.W. Taylor and R. Sierra) [4, 5, 6].

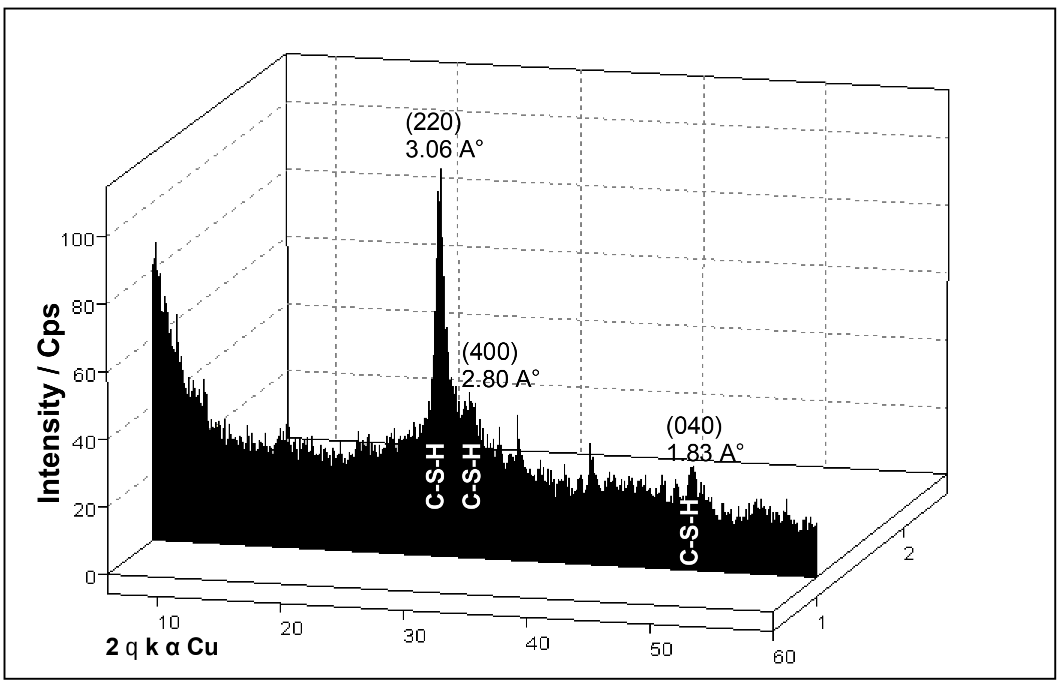

Figure 9 - Pozzolanic reactivity of the SF at 2 months of hydration

4. Hydration of cement in presence of additions

The tests previously carried out on lime pastes have highlighted the kinetics of fixing of lime by the additions. In the same manner, a comparative study using XRD on the evolution of Portland cement hydration in the presence of 15% of these additions (SD, L, SF as cement substitution) has been carried out.

Figures 10, 11, and 12 show that:
- At 20 days of hydration, the rays of lime and C-S-H appear and the intensities of the C_3S and C_2S rays decrease, which explains the hydration of calcium silicates.
- In the presence of dune sand at 20 days of hydration, the intensities of the quartz rays decrease compared to those of the anhydrous mixture, showing the pozzolanic reaction of dune sand, as confirmed by previous results with lime).
- At 2 months of hydration, the intensities of the lime and cement minerals rays (even those of quartz) decrease significantly, which shows the pozzolanic effect of these additions.

In the presence of SF, the reduction in lime is more significant. This can be explained by the high pozzolanic reactivity of SF, which confirms hydration results with lime [3, 4, 7].

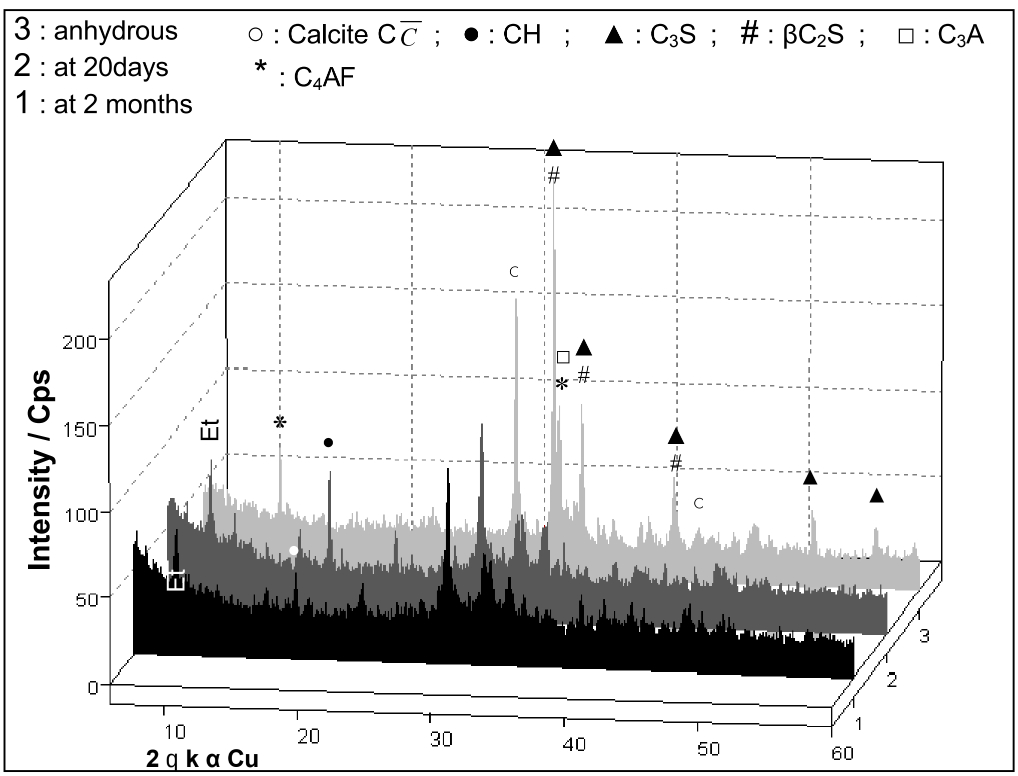

Figure 10 - Hydration of the « CEM II/A + SF» pastes at different ages

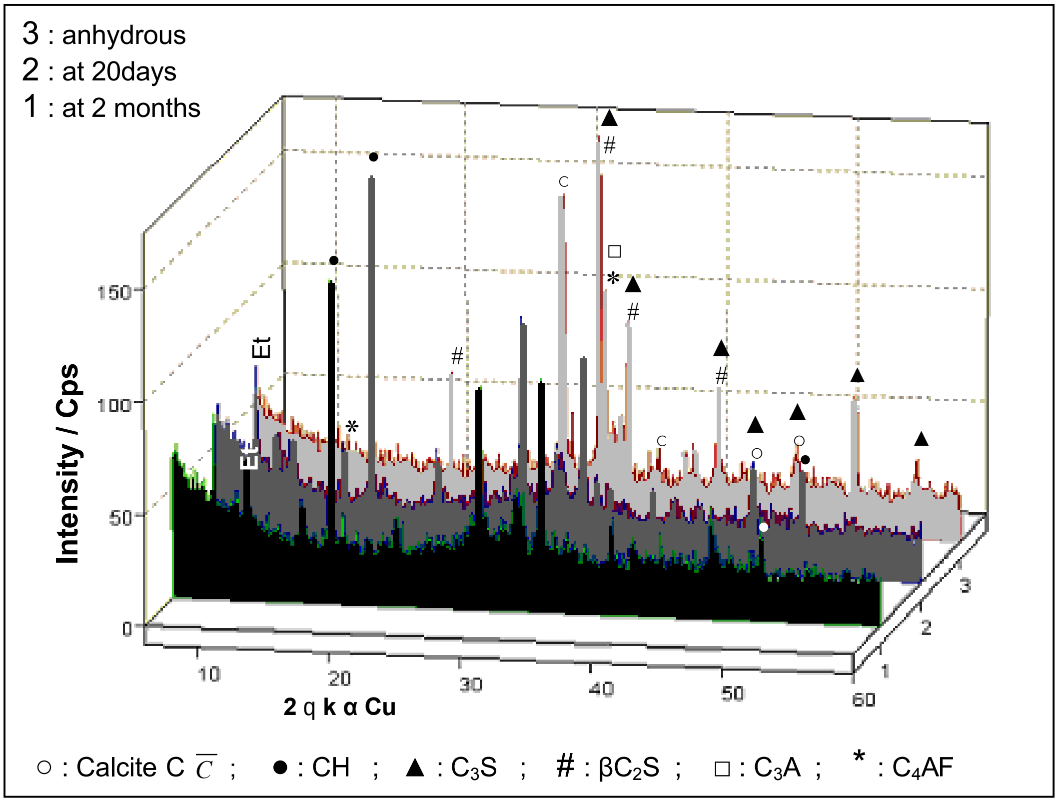

Figure 11 - Hydration of the « CEM II/A + Slag» pastes at different ages

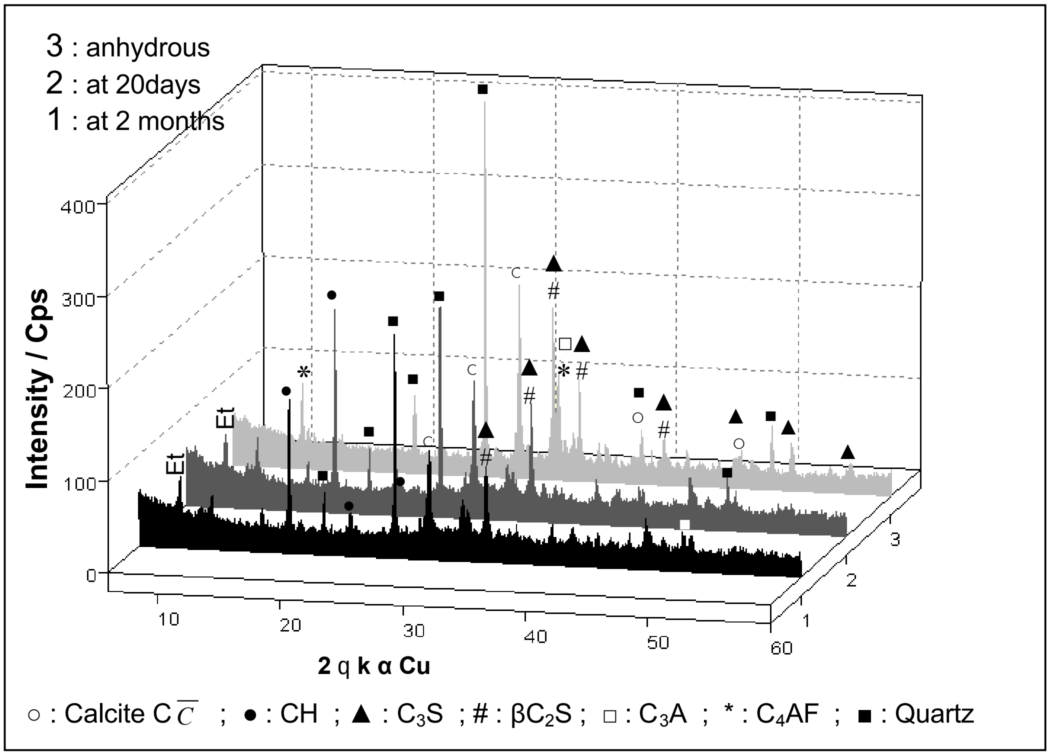

Figure 12 - Hydration of the « CEM II/A + DS » pastes at different ages

5. Pozzolanicity of the additions by mechanical tests

In order to confirm the results obtained by XRD, we determined the pozzolanic activity indices, which represent the relationship between compressive strength of the RPC with additions and those without additions: $\mathbf{I.A = 100} \times S_{cA} / S_{cc}$

The mixtures used are:

- RPC without additions: the flexible paste is made up of cement, water and superplasticizer.

As for the granular skeleton, it is composed of natural state dune sand of which the diameter of the coarsest grain is lower than 0.630 mm.

- RPC with additions: same composition except that part of the cement was replaced by 15% additions (SF, S or DS).

Compressive strengths obtained on test tubes (4 × 4 × 16 cm^3) and the pozzolanic activity index of the RPC tested are given in Table 2 and Figure 13 .

Table 2: Compressive strength and pozzolanic index of activity of the RPC tested

	3 d		7 d		14 d		28 d		90 d	
	S_c MPa	**I.A** %	S_c MPa	**I.A** %	S_c MPa	**I.A** %	S_c MPa	**I.A** %	S_c MPa	**I.A** %
CEMII/A (control) **W/B = 0.20**	32	100	46	100	55	100	86	100	98	100
CEMII/A+15% SF **W/B = 0.17**	56	175	83	180	97	176	120	140	144	147
CEMII/A+15% S **W/B = 0.20**	30	94	44	96	53	96	84	98	106	108
CEMII/A+15% DS **W/B = 0.20**	26	81	36	78	52	95	80	93	105	107

Taking into account the superplasticizing role played by SF, we could reduce the W/B ratio to 0.17 instead of 0.20.

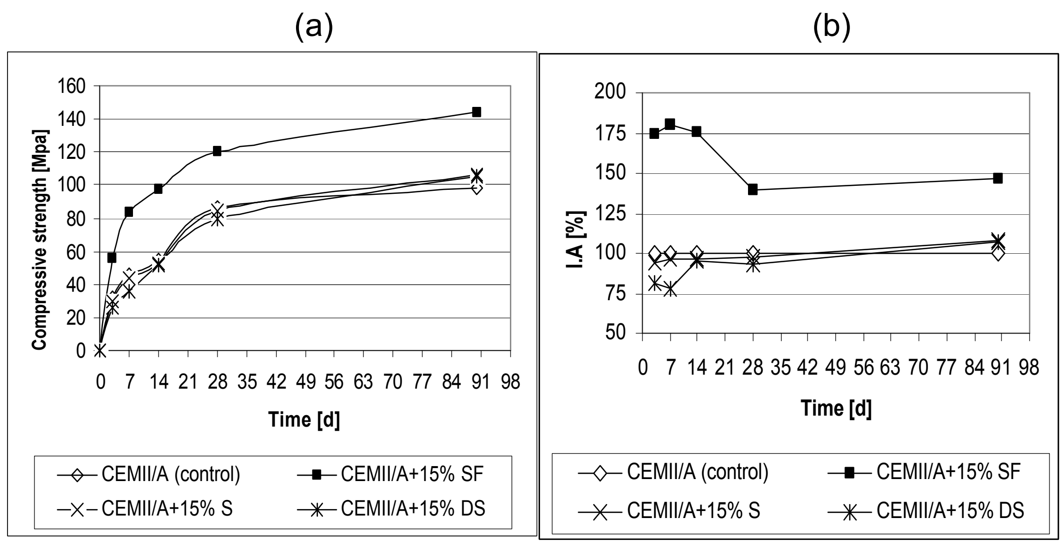

Figure 13 - Variation of compressive strength and pozzolanic activity index of the RPC tested.

Figure 13 (b) shows that the additions play a pozzolanic role from their pozzolanic index higher than 75%.

The pozzolanicity of SF is very high compared to the two other additions.

As for the dune sand, its activity index remains lower than that of slag, despite its specific surface and SiO_2 content being higher than those of slag. This could be explained by the slowness of the pozzolanic reaction.

These results show that pozzolanic reactivity is more significant in materials having an amorphous structure than in those that are crystallized.

A classification of the pozzolanic activity indices can be established as follows:

$$I.A_{SF} \gg I.A_{S} > I.A_{DS}$$

The results obtained consolidate the conclusions found through XRD. They show that a crystallized siliceous material, when it is very finely divided, can be reactive.

6. Conclusion

This study enabled to draw the following conclusions:

Very finely ground dune sand, in spite of its crystalline nature, has a partial pozzolanic reactivity [4, 12].

Ground slag, with a lower fineness than that of dune sand and a low silica content, has a better pozzolanic reactivity than dune sand because it has an amorphous structure, which explains the importance of mineralogical structure on the pozzolanic reaction.

It is acknowledged in the literature that due to its high fineness, SF is suited to the production of high and very high performance concrete, both at early and advanced ages [2, 8, 9, 10]. Indeed, the very fine particles of silica fume can fill spaces between cement particles [11], which render the concrete matrix more compact and thus improve its durability [1, 2, 9]

These results are of great interest for concrete technology, as they enable to improve concrete quality at lower cost through the introduction of siliceous additions available locally in our country (blast-furnace slag and dune sand).

7. References

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