

Study on Reactivity of Circulating Fluidized Bed Combustion Fly Ashes in the Presence of Water

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Abstract: A study on reactivity of four different Circulating Fluidized Bed Combustion (CFBC) fly ashes has been realized in the presence of water. Paste of each ash was prepared and analyzed for its setting time, expansion and strength. The products of hydration, and their evolutions over a period of time were identified by X-ray diffraction and differential thermal analysis. The results of this study show that the reactivity of the CFBC fly ashes is strongly related to their chemical composition, essentially to their quantity of silica, alumina, lime and sulfate, which promote principally the formation of ettringite, gypsum and C-S-H. It is further noted that the intensity and the proportion of these phases determine the hydration behavior of the CFBC fly ashes.

Keywords: CFBC fly ashes, setting time, expansion, strength, X-ray diffraction, thermal analysis

Introduction

Circulating Fluidized Bed Combustion (CFBC) is one of the *clean* technologies for burning high sulfur combustibles in order to reduce the atmospheric pollution. This technology is particularly interesting because of its capacity to burn low quality and different kind of combustibles and also to reduce SO₂ and NO_x production [1,2]. However, the addition of SO₂ removing sorbents and the use of a lower combustion temperature (850-900°C) produce great quantity and different kind of ash compared to conventional coal combustion systems and creates future management problem, related to the change of regulation concerning the treatment of this kind of industrial waste. In fact, the regulation of non-inert waste is more and more tight and the cost needed for the treatment is more and more expensive.

The properties of CFBC ashes vary according to the nature and the quality of the coal burnt in the power plant [3-7]. Generally, their specific gravity and specific surface are higher than fly ashes produced from pulverized coal power plants that are usually used in the field of civil engineering. Due to desulphurising process in the power plant boiler, CFBC ashes contain more free CaO and SO₃ so that they are generally outside of the ASTM C-618 specification [8]. Furthermore, there are fewer glass particles in this type of ash, which can be attributed to the lower combustion temperature used in this technology.

These conditions render their characteristics quite different from those of ashes obtained from coal pulverized power plants.

This study is a preliminary research for valorizing CFBC fly ashes in the field of civil engineering in order to reduce environmental problem. The principal objective of this present study is to investigate the reactivity of various CFBC fly ashes in the presence of water. The results of this study could be used to determine some strategies for the future use of this kind of fly ash.

The characteristics of the materials studied are firstly described. Then the results drawn of the experimental study carried out by hydrating plain paste of CFBC fly ashes are presented and discussed.

Materials and Experimental Method

Four samples of CFBC fly ashes collected from French power plant have been used for experimental studies that were realized at URG-Structures laboratory, INSA de Lyon in France. These fly ashes were obtained from different type of combustible. Table 1 shows the type of combustible burned in the power plant that gave those four samples, while Tables 2 and 3 give some physical and chemical properties of them. The X-ray diffraction (XRD) diagram of these anhydrous materials which gives their principal existing phases is presented in Figure 1.

Considering calcium oxide (CaO) content, fly ashes are categorized as: (1) low (<10% CaO), (2) medium (10-20% CaO), and (3) high (>20% CaO) calcium fly ash. Furthermore, depending upon the relative amounts of the major chemical constituents, fly ash may be classified as Class C and Class F. Fly ash

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containing more than 50% but less than 70% of silicon, aluminum and iron oxides ($\text{SiO}_2 + \text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3$) are classified as Class C. If the sum of these three oxides exceeds 70% then the fly ash is classified as Class F according to ASTM C618 [8]. Thus, the medium and high calcium fly ashes are considered as Class C fly ash.

Table 1. Type of combustible burned in the power plant giving the CFBC fly ashes

Materials	Type of combustible
Fly ash 1 (A1)	100% grained coal of Gard
Fly ash 2 (A2)	70% grained coal of Gard + 20% coal of Carmaux + 10% coal slurry of Gard
Fly ash 3 (A3)	100% coal of South Africa
Fly ash 4 (A4)	100% lignite of Provence

Table 2. Physical characteristic of CFBC fly ashes

Materials	Specific gravity	Specific surface Blaine (m^2/kg)	Average particle-size diameter (μm)
A1	2.35	1050	11.4
A2	2.56	645	22.9
A3	2.40	710	15.3
A4	2.62	690	37.8

Table 3. Chemical composition of CFBC fly ashes

Materials	Al_2O_3	CaO	SiO_2	Fe_2O_3	SO_3	Free CaO	LOI	Sum of $\text{SiO}_2 + \text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3$
A1 (%)	10.45	7.35	44.14	5.71	4.78	1.58	15.20	60.30
A2 (%)	16.28	15.34	39.36	6.67	7.40	4.98	10.30	62.31
A3 (%)	22.49	18.01	37.40	3.70	6.37	3.20	7.00	63.59
A4 (%)	6.92	41.65	21.27	4.45	18.30	14.41	4.55	32.64

The chemical analysis presented in Table 3 shows that none of the four CFBC fly ashes can be classified as class C or F. This is because the CaO content on CFBC fly ash 1 (A1) is low (7.35%) although the sum of ($\text{SiO}_2 + \text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3$) is 60.30%. For CFBC fly ash 2 and 3 (A2 and A3), their content of sulfur trioxide (SO_3) of 7.40% and 6.37% respectively exceeds the 5% maximum percentage specified in ASTM Standard C 618 [8]. Concerning CFBC fly ash 4 (A4), the sum of ($\text{SiO}_2 + \text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3$) is only 32.64 % and the content of SO_3 is much higher (18.3%) than allowed by ASTM Standard C 618 [8].

For realizing the investigation, plain paste of each ash prepared with a standard consistency according to European standard EN 196-3 [9] was used for its setting time, expansion and strength. The setting time test was realized under water in accordance with European standard EN 196-1 [10] while the stability of the hardened paste is measured by retractometer on the standard 40x40x160 mm prisms.

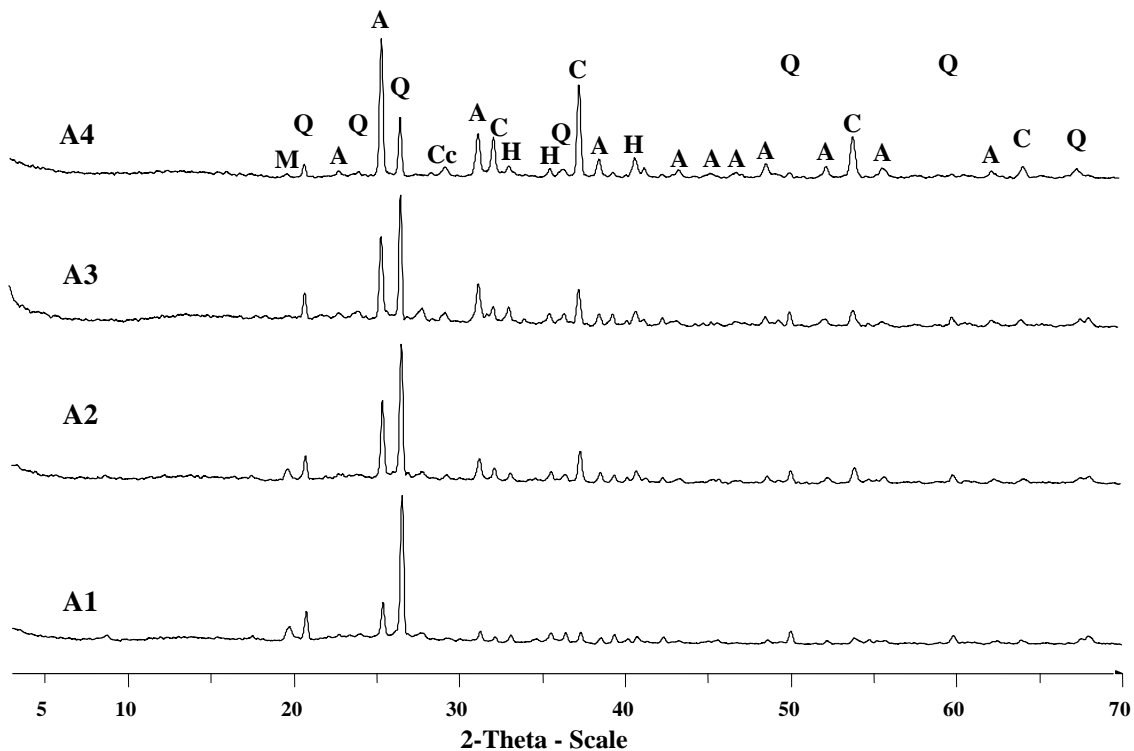


Figure 1. XRD diagram of anhydrous CFBC fly ashes
 A : Anhydrite, C : Free lime, Cc : Calcite, H : Hematite, M : Muscovite, Q : Quartz

As for the strength, three 40x40x160 mm prisms were used to measure flexural and compressive strength at 28, 90 and 180 days of hydration in accordance with European standard EN 196-1 [10]. These prisms were kept first in molds at 20°C and 100% RH for 7 days, then cured in water at 20°C until used for the strength test. This kind of curing was used in order to observe the expansive phenomenon, which often occurs when the paste of CFBC ash is hydrated under water [11]. The same method of curing was used for realizing the expansion measurement by retractometer.

The hydration products and the relative comparison of their progress over time were identified by XRD and Differential Thermal Analysis (DTA) after 1 and 7 days of hydration as well as after hydration and cured in water 28, 90, 180 days. The samples used for these analyses were taken from the central zone of the specimens, dried at 25°C for about 12 hours and then crushed less than 100 µm.

Results

Setting

Table 4 shows the results of setting test for each ash. During the hydration, it is noted that the paste of A2, A3 and A4 can harden, but only after a long period. As for the example, the initial and the final setting of sample A2 can reach respectively 40 and 182 hours. On the other hand, the paste of A1 does not set and harden completely.

Table 4. Setting time of the CFBC fly ashes paste

Materials	Initial setting (hours)	Final setting (hours)
A1	56	-
A2	40	182
A3	15	48
A4	0.7	72

Expansion

Table 5 presents the result of expansion tests after 180 days of hydration realized by retractometer. The measurement of expansion on the sample A1 can not be realized due to the incomplete setting and hardening process of their paste.

This result shows generally that the paste of CFBC fly ash produces an expansion during the hydration. However, it is noted that the paste of A4 develops more expansion in the long term than the others.

Table 5. Expansion of CFBC fly ashes paste after 180 days

Materials	Expansion after 180 days (%)
A1	-
A2	1.0
A3	≈ 0.0
A4	> 60

Mechanical Strength

With the curing time, the majority of CFBC fly ashes paste does not give interesting strength, except for the paste of A2 and A3, as presented in Table 6. It is noted that these two ashes can harden and produce only a small expansion during their hydration as given by retractometer measurement (Table 5).

The absence of the strength in the paste of A1 is related to its incomplete setting and hardening process while the continuous expansion on the paste of A4 leads it to swell and lose totally the strength produced on the 28 days of hydration.

Table 6. Flexural and compressive strength of CFBC fly ashes paste as a function of time

Materials	Flexural strength (MPa)			Compressive strength (MPa)		
	28 d	90 d	180 d	28 d	90 d	180 d
A1	≈ 0	≈ 0	≈ 0	≈ 0	≈ 0	≈ 0
A2	0.98	1.41	1.52	4.33	7.67	7.83
A3	2.68	2.58	4.84	17.2	20.0	21.2
A4	1.33	≈ 0	≈ 0	2.03	≈ 0	≈ 0

Mineralogy

X-Ray Diffraction

The results of XRD analysis indicate a quite similar phenomenon for all the samples. An evolution of certain phases (anhydrite, lime, ettringite, gypsum, and calcite) is observed, while quartz and hematite are almost constant before and after hydration.

Figure 2 shows the evolution of the principal phases, identified by XRD, obtained by tracing the relative intensities of each phase in function of the hydration time: 0, 1, 7, 28, 90 and 180 days. It is clearly noted that the anhydrite and the lime content in the ashes disappear quickly with the curing time. This is generally followed by the formation of ettringite. After 7 days of hydration, it is also identified the formation of gypsum in the paste of each sample except within the paste of A3. In the long period, the ettringite and gypsum become the principal phases observed by XRD.

On the other hand, it is observed that a certain quantity of anhydrite still remains in the sample of A1 and A3, even after 180 days of hydration, which can be related to the presence of anhydrite insoluble in these ashes. This phenomenon was also observed by other studies [12]. The formation of calcite due to carbonation of the remaining lime can also be noted in each sample.

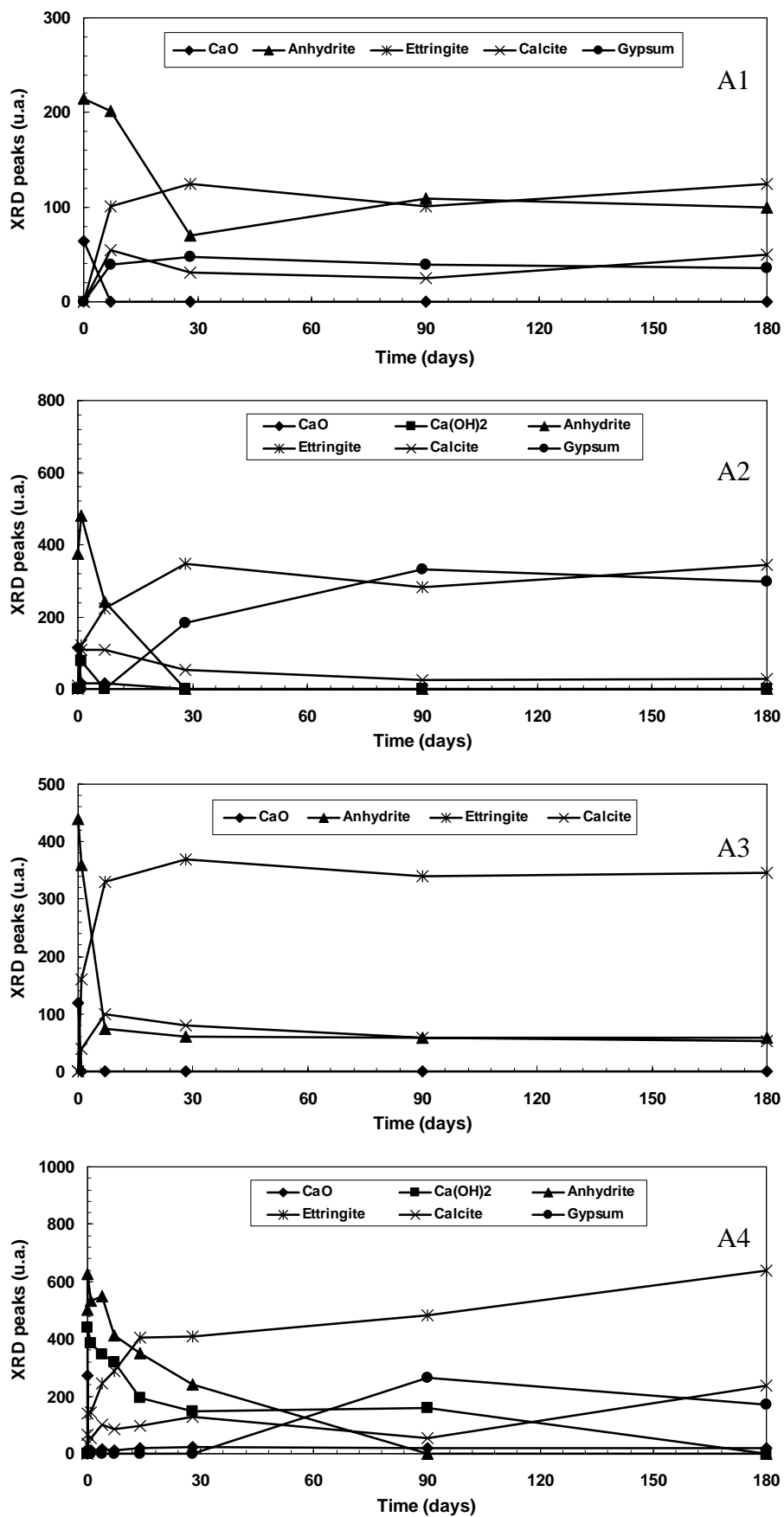


Figure 2. Evolution of several phases identified by XRD on hydrated CFBC fly ashes paste as a function of time

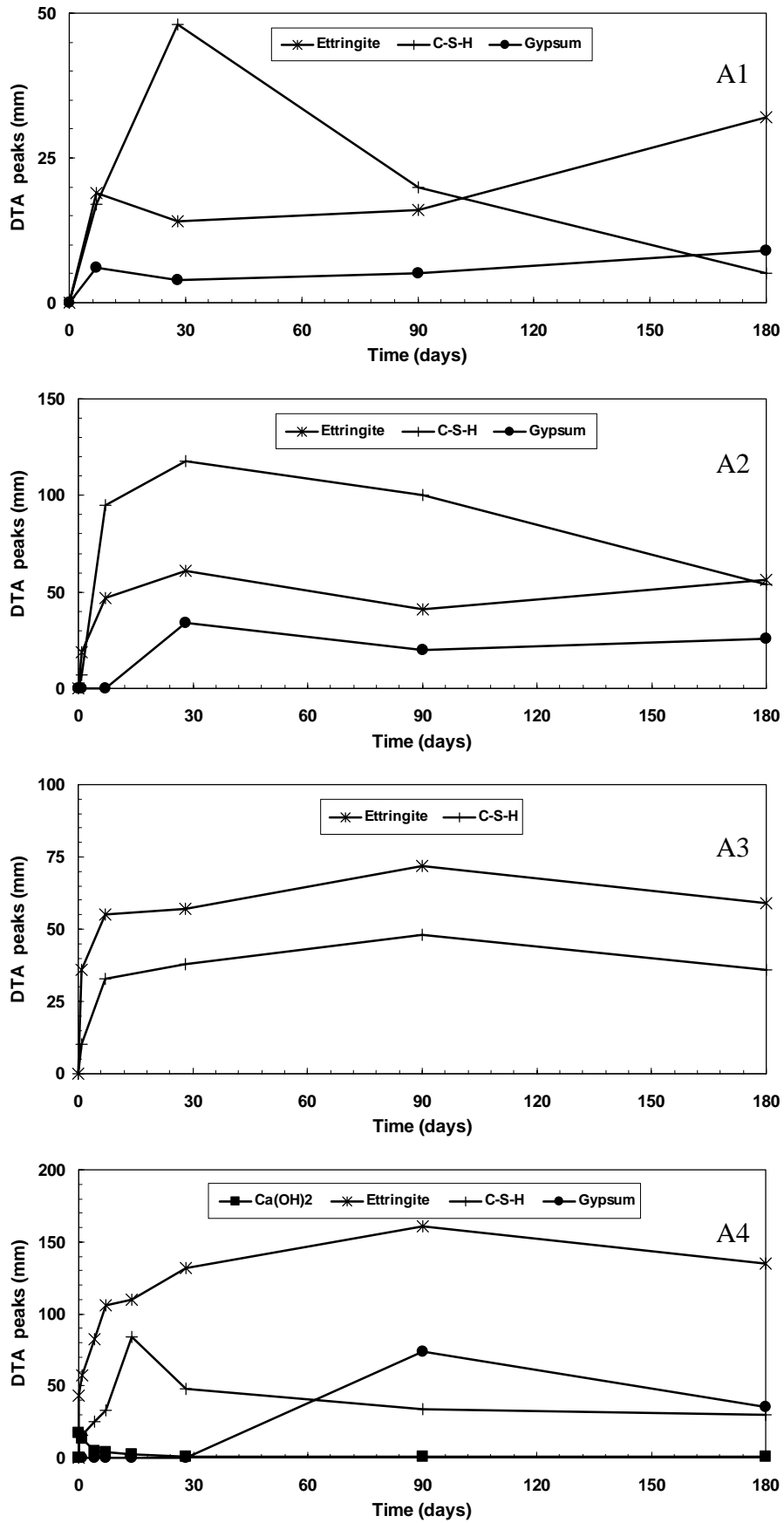


Figure 3. Evolution of several phases identified by DTA on hydrated CFBC fly ashes paste as a function of time

Differential Thermal Analysis

This analysis was realized from 20° up to 600°C. Several endothermic peaks have been generally identified for each sample during the analysis. These peaks appear at the temperature ranges: 105-115°C, 120-130°C, 135-150°C, 155-160°C, 180-190°C and 525-550°C. The first peak indicates the dehydration of free water while the second peak is attributed to the water loss of the gel hydrated calcium silicate (C-S-H). The C-S-H peak grows during the curing time until 28 days of hydration and tends to decrease after that.

The third peak corresponds to the dehydration of ettringite. As already observed by XRD analysis, the ettringite peak increases noticeably during the hydration time and essentially in the paste of A4. The next two endothermic peaks in the DTA diagram identify the dehydration of gypsum. As already mentioned by XRD analysis, there is also no gypsum identified by DTA within the paste of A3. The last endothermic peaks corresponds to the dehydration of hydroxide de calcium Ca(OH)_2 whose intensity decreases during the hydration time.

These observations are presented in Figure 3 obtained from relative height of each phase identified by DTA for each sample after 0, 1, 7, 28, 90 and 180 days of hydration.

Discussion

The reactivity of CFBC fly ashes in the presence of water can be related to their chemical composition, essentially the quantity of silica, alumina, lime and sulfate that governs principally the formation of ettringite, gypsum and C-S-H as already identified by XRD and DTA. The intensity and the proportion relative of these three phases depend on the type of ash hydrated and determine the final state of their paste.

A low intensity of C-S-H produced within the paste of A1 prevents its setting and hardening process. This is possibly due to the low quantity of lime present in this ash which is not sufficient to be combined with silica to produce C-S-H. The formation of ettringite and gypsum did not give any improvement in their mechanical performance but otherwise they developed a slight expansion favoring the decomposition of C-S-H. Moreover, the presence of the important quantity of unburned coal (> 15%) perturbs probably the hydration process of this ash.

The presence of more lime in A2 and A3 make them more reactive to produce a binder compound C-S-H. The formation of certain quantity of ettringite

combined with sufficient C-S-H allows the paste of A2 and A3 to harden and to develop certain strength. Moreover, the rapid formation of ettringite and the absent formation of gypsum within the paste of A3 reduce its expansion and give it an advantage for developing its strength, as compared with the paste of A2.

The initial formation of ettringite combined with C-S-H, until 28 days of hydration, gives certain strength on the harden paste of A4. However, the continuous formation of ettringite and the new formation of gypsum after this period strongly increase the expansion within this harden paste. This expansion increases then its porosity and thus favors the water and carbonic attack to the C-S-H compound, which finally leads to its destruction. The important quantity of sulfate and lime in this ash plays an important role to the formation of these expansive phases. In this last case, it is the decomposition of C-S-H, liberating lime, which increases the formation of calcite within their paste.

Conclusions and Further Study

Conclusions

The results of this study give some conclusions as follows:

- The reactivity of CFBC fly ashes in the presence of water is strongly related to their chemical composition, essentially to their quantity of silica, alumina, lime and sulfate, which finally determines their hydration behavior.
- The incomplete setting and hardening process of CFBC fly ash paste is attributed to the presence of low quantity of lime and important quantity of unburned coal.
- The expansive behavior of the paste of CFBC fly ash is directly related to the important formation of ettringite and/or gypsum.
- The sufficient formation of C-S-H combined with the rapid and limited formation of ettringite can give certain strength to the harden paste of CFBC fly ash.

Further Study

Based on the results of this study, it seems that the use of CFBC fly ashes alone as a hydraulic binder is impossible. Other studies to provide a way to valorize this kind of waste, in order to reduce environmental problem, is therefore necessary to be realized. Several future studies are proposed, such as: the use of CFBC fly ashes as partial replacement or as addition of Portland Cement and the use of CFBC fly ashes as an activator of Ground Vitrified Blast Furnace Slag.

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