

Hydration of combustion ashes-A chemical and physical study

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INTRODUCTION

While a vast amount of work has been devoted over the years to the hydration chemistry of cement, relatively little is yet known about hydration of combustion ashes. However, their use as cement substitutes or additives is developing and their behavior during curing processes is of great interest.

The purposes of the present study are:

- Establish the possibility of using ash blends in mortars as only binder.
- Identify the crystalline hydrates formed and characterize the amorphous hydrates formed during curing.
- Try to correlate the composition of the binder and the hydrates formed during the curing process with the physical properties of the cured material.
- Obtain criteria for the preparation of ash blends in order to insure development of satisfactory mechanical properties of the cured material.
- Consider the retention of certain trace elements during leaching.

SAMPLES

The samples studied were mortars prepared with 3/4 sand as inert material and 1/4 ash blend as only binder.

Only mortars having resisted prolonged immersion without disintegration were considered. The ashes utilized were:

SAPFA: silico-aluminous fly ash from classical pulverized coal burnt at the Emile Huchet power plant located at Carling (Lorraine, France).

GARDANEX: sulphocalcic fly ash from the 600 MWe pulverized coal unit at Gardanne (Provence, France), pre-hydrated by the CERCHAR process¹.

CFBC: representative mixing of bed ash and fly ash from the CFBC unit at Gardanne.

CFBC-H: as above, pre-hydrated by the CERCHAR process.

The typical composition of these ashes and of the sand are given in Table 1.

Table 1

Component	SAPFA	GARDANEX	CFBC	CFBC-H	Sand
SiO ₂	52.00	17.00	12.00	11.57	88.42
Al ₂ O ₃	23.00	8.00	6.00	5.78	7.23
Fe ₂ O ₃	9.00	4.00	5.00	4.82	1.17
CaO	3.00	57.00	48.00	46.26	0.88
MgO	1.76	1.00	0.80	0.77	Trace
Na ₂ O	0.29	0.10	0.10	0.10	0.30
K ₂ O	3.23	0.50	0.30	0.29	2.00
P ₂ O ₅	0.21	0.40	0.70	0.67	n.a.
TiO ₂	0.58	0.20	0.20	0.19	n.a.
LOI	8.00	0.50	1.80	5.45	0.00
SO ₃	0.50	12.0	25.00	24.09	0.00
SUM	101.57	100.70	99.9	100.00	100.00
Free lime	0.00	18.76	12.00	10.00	0.00

Ten formulations of mortar were made. Beams (4x4x16 cm) were prepared and kept in curing conditions. Curing time varied for the different samples from 896 to 1114 days (2.5 to 3.1 years). For the first 9 formulations, the binders were in each case a blend of two different types of ashes. The last formulation, of common use in roads, was included as a reference. The water/binder ratio varied between 0.5 and 0.65. Two curing conditions were used: 1) immersed in water at 20° C; swelling was measured in these samples, which are referenced with the letter G (from French: *gonflement*), and 2) maintained in a saturated moist atmosphere at 20 C; shrinkage was measured in these samples, referenced with the letter R (French: *retrait*). All tests were performed in triplicate.

Table 2 - Formulations of ash blends (figures indicate %)

Samples	SAPFA	GARDANEX	CFBC	CFBC-H
G33/R34	40	60	B	--
G26/R27	50	50	--	--
G40/R41	60	40	B	--
G137/R136	50	--	50	--
G147/R146	70	--	30	--

G157/R156	85	--	15	-
G197/R196	50	--	--	50
G207/R206	70	--	--	30
G217/R216	85	--	--	15
	SAPFA	Slaked lime	Gypsum	--
G227/R226	75	15	10	--

The composition of the various blends was calculated from the analysis of mortars, referred to ignited weight and subtracting the sand contribution. They checked favorably with the estimates obtained from the compositions of Table 1, for ashes mixed as indicated in Table 2.

For further interpretation, it is interesting to note the theoretical relative proportions of sulphate and free lime contents provided by each binder. In a first calculation, the influence of the pre-hydration treatment of calcic ashes was ignored. Actually the pre-hydration treatment increased LOI as 1 mole of H₂O is consumed by mole of CaO (quick lime), reducing relative contents of the other components.

On the basis of the elemental chemical composition of the ash blends, two chemical indices were defined, whose relevance and use will be discussed below. These were:

$$I(1) = (\text{SiO}_2 + \text{Al}_2\text{O}_3) / (\text{CaO} + \text{SO}_3)$$

$$I(2) = \text{FL} / \text{SO}_3$$

where the formulas of the element oxides represent their % in the ash blend and FL stands for "free lime" (CaO in pre-hydrated ash). I(1) obviously gives a measure of the ratio of silicoaluminous to sulphocalcic components. I(2) relates the available lime to the sulphate present in the sample.

	G33/R34	G26/R27	G40/R41	G137/G197 R136/R196	G147/G207 R146/R206	G157/G217 R156/G216	G227/R22 6
SO ₃ (%)	6.95	5.88	4.8	12.75	7.85	4.18	4.65
Free lime (FL)	11,25	9.38	7.5	6.0	3.6	1.8	11.25
I(1)	1.13	1.72	2.26	1.56	2.68	5.88	3.37
I(2)	1.62	1.60	1.56	0.47	0.46	0.43	2.42

Table 3 - Sulphate, free lime and indices

CHEMICAL CHARACTERIZATION

In the use of mortars, the large excess of inert material (sand) prevents an efficient application of XRD to detect hydrated compounds: spectra become completely dominated by the quartz and feldspar peaks. Therefore, in order to obtain representative samples of the original ash blends, separations by density were performed on the cured samples. For this purpose, the mortar was ground in acetone, dried at room temperature under N₂, suspended in an organic liquid of density 2500 kg/m³ and centrifuged. The density of sand components (mainly silica and feldspars) is

higher and that of most hydrates formed during curing is lower than the chosen density. The light fraction was then used for XRD and other analyses. The separation is not strictly quantitative; therefore the lighter fraction, if large enough, was submitted to a second separation. The obtained light fractions were washed in acetone, dried at room temperature under N₂ and their weight % was determined. These fractions were then used for various analysis.

The analytical techniques employed on a selection of samples included:

- Elemental analysis by X-ray fluorescence (XRF)
- Elemental analysis (trace elements) by induced coupled plasma (ICP)
- Analysis of sulphur by LECO furnace and infrared absorption, and carbonate and sulphate by wet chemistry
- Determination of total alkalinity by treatment with excess of 1M HCl followed by back titration with NaOH.
- X-ray diffraction (XRD)
- Thermogravimetry (TGA) and differential scanning calorimetry (DSC)
- Scanning electron microscope (SEM) of fracture surfaces and energy dispersive X-ray microsonde (EDX) for quantitative elemental analysis of amorphous hydrate (C-S-H)

PHYSICAL TESTS

The following tests were performed on the cured beams:

- Resistance to flexion (kN).
- Resistance to compression (MPa)
- Swelling (G samples) or shrinkage (R samples) (µm/m)
- Weight variation (%)
- Porosity: apparent density, real particles density, open porosity (%)

The results (except porosity) are collected in Table 4.

	G33	G26	G40	G137	G147	G157	G197	G207	G217	G227
Age of testing (days)	896	896	896	1106	1106	1106	1003	1003	1003	954
Flexion (kN)	3,66	3,45	2,92	2,05	1,96	1,31	2,1	2,05	1,08	1,84
Compression (MPa)	56,1	47,4	47,7	22,45	16,05	9,17	35,4	23,4	6,1	15,05
Swelling (µm/m)	5320	3453	2623	5903	1717	419	6773	3527	2110	2083
Weight variation (%)	8,02	8,1	6,89	8,16	6,88	6,86	5,82	5,84	6,97	4,76

	R34	R27	R41	R136	R146	R156	R196	R206	R216	R226
Age of testing (days)	905	905	905	1114	1114	1114	1009	1009	953	961
Flexion (kN)	2,66	2,46	1,99	1,43	1,11	0,94	1,66	1,37	0,84	0,73
Compression (MPa)	36,8	32,1	22,4	8,7	6,25	3,6	14,35	9,4	4,3	2,5
Shrinkage (µm/m)	-1447	-683	-471	-873	-600	-570	-1650	n.a.	-483	133
Weight variation (%)	1,59	1,7	0,31	-1,09	-2,44	-3,46	-1,86	-2,17	-4,06	-8,53

Table 4 : Mechanical performance of the old sample beams

RESULTS AND DISCUSSION

For reasons of brevity, a selection of the most significant features is presented, rather than a detailed account of results.

A) Degree of hydration and mechanical strength.

Several results can be used as indicators of the "degree of hydration" of the binder, after a curing period : 1) the loss on ignition, after subtracting the CO₂ corresponding to carbonate, indicates the amount of water incorporated by chemical hydration of the ash components; 2) the percentage of light fraction (density <2500 kg/m³) obtained by a standardized procedure of density separation; 3) the water loss % during gravimetric analysis, at temperatures below decomposition of calcite, i.e., below the region of 500 to 600 C. Fig. 1 shows the second of these properties, plotted against resistance to compression. It is evident that there is a strong correlation between the resistance to compression and each of this hydration indicators. A similar result is obtained with any of the other two properties.

B) Identification of hydrated phases

XRD, TGA and DSC allow one to identify the main crystalline hydrates present in the cured samples. XRD also permits detection of minor peaks corresponding to hydrated Ca-Al silicates. Amorphous hydrated Ca-Al silicates were studied in a number of samples by EDX. Quantitative XRD performed on 4 light fractions of mortar samples (G26, R27, G197 and G22) indicated between 46 and 76% of the samples as being crystalline, the rest consisting of "cement gel" C-S-H (or rather C-S-A-H, since Al content is comparable to that of Si).

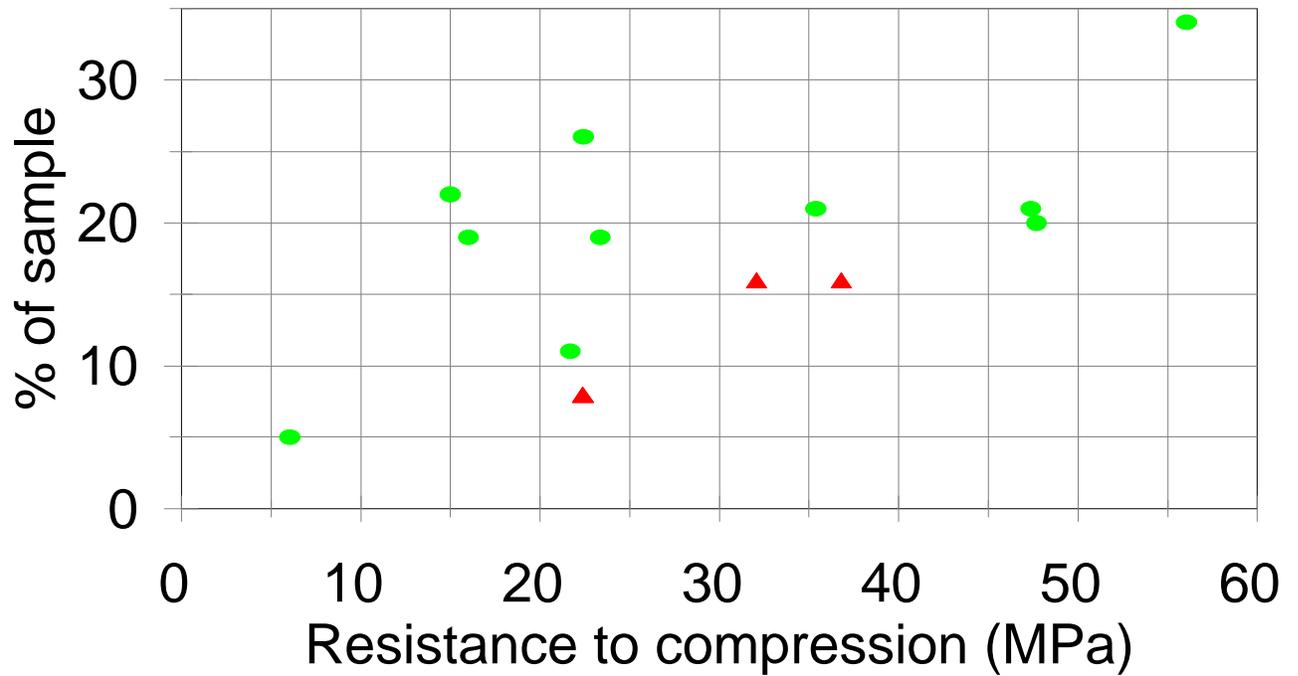
Regarding the crystalline hydrates, the results indicate the following conclusions for the mortars that have stood the curing process without disintegration due to dimensional instability.

- The main product is generally ettringite, or to be more precise, AFt. In 4 of the samples, whose light fractions were analyzed by QXRD (G26, R27, G197, G227), AFt represented between 18 and 25% of the light fraction. However, it was missing in 5 out of 17 samples, for which the mortars developed lower resistance to compression.
- Gypsum is generally present in lower concentration, and missed in 5 out of 17 samples.
- Portlandite had practically disappeared (R156 was an exception).
- Numerous compounds of the system CaO-SiO₂-Al₂O₃-H₂O were detected by XRD in very small peaks. For instance, many samples revealed either CAS4H6 (cement notation) or CAS10H7, or both. Most of these compounds had ratios Si/Ca of 2 to 10 and Al/Ca of 2.
- In some samples, small peaks of very unstable hydrates were detected by TGA in the mortar, decomposing below 100°C (G26, R27, G147). These hydrates disappeared in the treatment for density separation; they were not identified.

Regarding the amorphous hydrated component, its presence in abundant proportions is made evident by the thermogravimetric recordings. Between the peak due to AFt and that of carbonate, i.e., between 200 and 600°C, a substantial and gradual loss of water occurs, that must be attributed

Fig.1-Light fraction

All double separations



▲ Shrinkage ● Swelling

to it. For instance, the TGA of the light fraction of sample G26 shows a water loss of 10.5% (corresponding to 28% ettringite) in a peak of the differential recording centered at 110°C, but also a gradual loss of 7.4% between 200 and 600 C. This is illustrated in Fig. 2.

The composition of this amorphous component was investigated in some of the samples by EDX. For instance, data for 30 points selected in mortar G40 suggested the following average elemental composition (not considering oxygen or hydrogen): $\text{CaSi}_{0.63}\text{Al}_{0.35}\text{S}_{0.21}\text{Fe}_{0.07}\text{Mg}_{0.05}$. This indicates considerable substitution of Si by Al and S.

These results suggest an amorphous component with undefined variable composition amounting to as much as one quarter to a half of the sample (in light fractions). Within this mass, small amounts of crystalline Ca-Al hydrated silicates develop sufficiently to give detectable peaks in XRD; these hydrates have variable compositions, all with high Si/Ca ratios.

C) Relation between ash blend composition and mechanical strength developed

The chemical composition of the ash blends used as binders in the mortars can be characterized by the two indices I(1) and I(2) defined before. It appears that there is a clear correlation between I(1) and the resistance to compression. It must be kept in mind that only the successful formulations have been evaluated; other formulations led to excessive swelling and disintegration. The correlation indicated is clearly shown in Fig. 3.

Various comments can be made on this representation:

- Immersion curing (G samples) give higher resistance than curing at 100% RH (R samples) of the same ash blend composition (see pairs G26-R27, G33-R34, G40-R41, G147-R146, G197-R198, G217-R216, G227-R226).
- Resistance to compression decreases with increasing index. When no pre-hydration of the ash lime was performed, none of the specimens survived to immersion if their index values exceeded about 2.5.
- The influence of the index I(1) is made clear by series of samples like G40-G26-G33 and R41-R27-R34, which only differ in the ratio of the two ashes mixed in the blend (cf. Table 2). The variation in this ratio generally results in a corresponding variation of the resistance to compression.
- At equivalent I(1), the index I(2) shows a strong influence on resistance. Thus, I(2)=1.6 for the series G33-G26-G40, while I(2)=0.5 for G197-G147, with lower resistance.

It is also significant to relate the resistance to compression of the cured mortar with the water loss measured by TGA between 200 and 600°C, which can be taken as a measure of the amount of C-S-H (cf. Fig.2). A clear correlation is found, which points to the important role of the amorphous component in the development of mechanical strength.

D) Retention of certain trace elements during leaching

Heavy metals were analysed by ICP in the mortar beams. It was possible, from the concentrations in the mortar samples, to estimate the concentration of these elements in the original ash blends,

Sample: UNIVERSITY OF TORONTO G26-L

Method: TGA 10 C°/MIN TO 1000 °C

TGA File: IRIBARNE.188

Run Date: 25-Feb-98 09:34

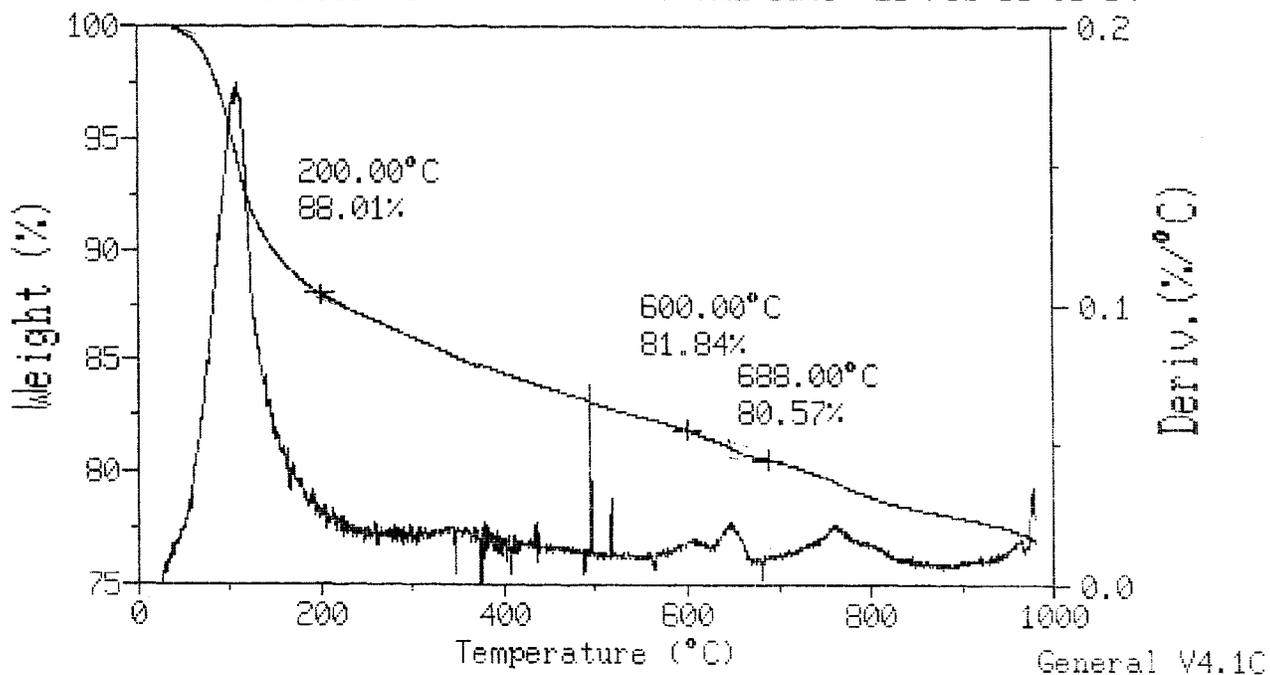
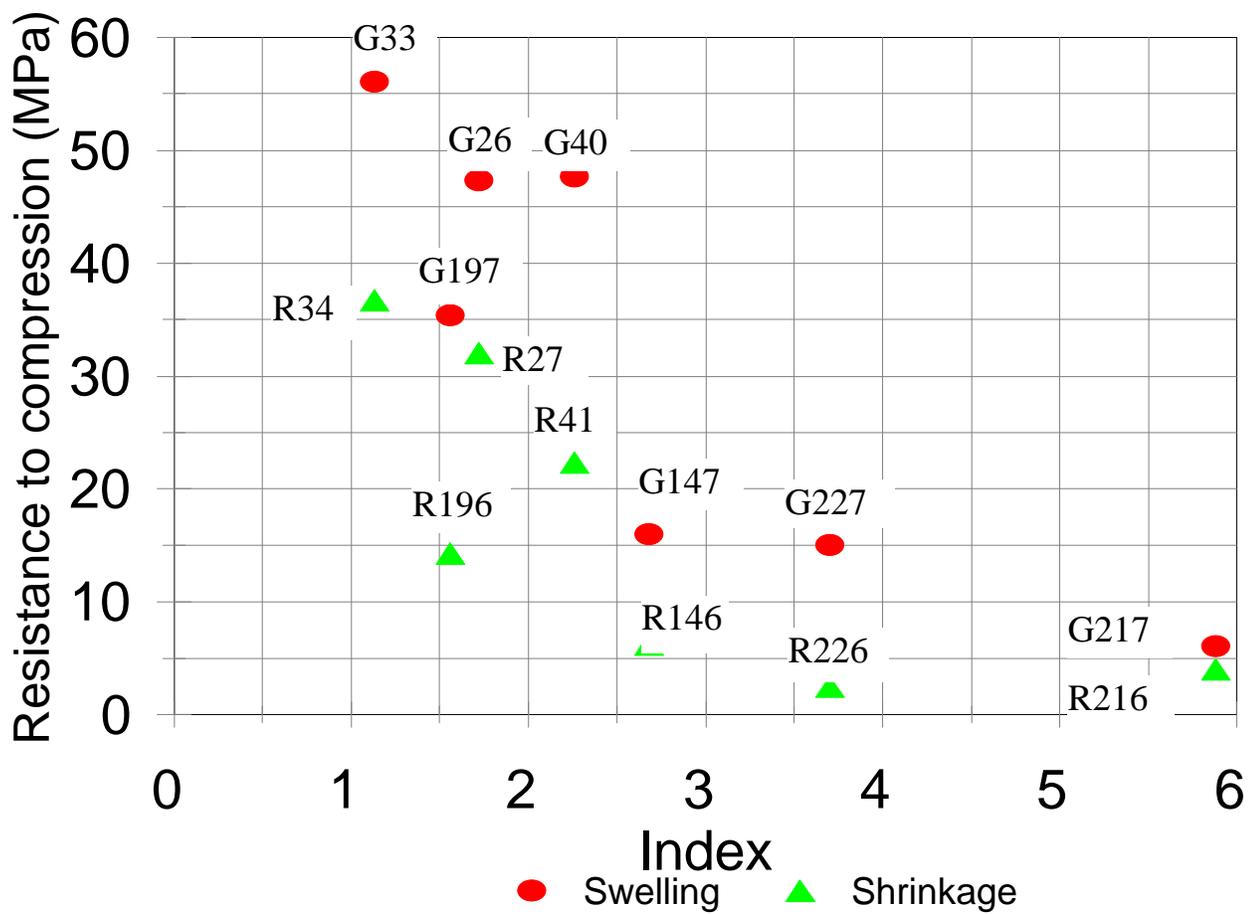


Fig. 2 - Thermogravimetric analysis of sample G26-L

Fig. 3-Resistance to compression-Index

$$\text{Index} = (\text{SiO}_2 + \text{Al}_2\text{O}_3) / (\text{CaO} + \text{SO}_3)$$



after taking into account that they had been mixed with sand (assumed devoid of such elements), mixed with water at a certain w/b ratio and absorbed hydration water during the curing. The concentrations estimated from the R samples (cured in air at 100% R.H.) should correspond to the original ones; those calculated from G samples (cured immersed for several years in water) might indicate the disappearance of these elements by leaching.

From the 5 couples of mortar specimens, the results for arsenic indicated reductions varying between 8 and 114 mg/kg (average value 40 mg/kg, medium value 9 mg/kg) and those for chromium between -22 mg/kg (meaning an increase) and 43 mg/kg (average value 20 mg/kg, medium value 23 mg/kg). Expressed in percentage of specimen weight, reductions of arsenic were higher than those of chromium due to higher average initial values (124 mg/kg of chromium versus 62 mg/kg of arsenic). In spite of the high level of error in these estimates, the results suggest that these elements become trapped in the hydrates so as to reduce considerably, if not quite totally, their leaching. In the case of zinc, analytical difficulties made these comparisons virtually impossible (all differences were negative, between -55 and -207 mg/kg, meaning a significant increase during immersion). In any case, considering that these samples remained immersed for 2 or 3 years, from the second day after casting, so long before achieving hydrate formation, it is reasonable to conclude that in the classic scenario of civil work applications, heavy metals should be expected to remain trapped in the hardened matrix.

CONCLUSIONS

It has been shown that it is possible to obtain good mechanical properties in mortars using ash blends as only binder.

The indices I(1) and I(2) appear as useful indicators to guide formulation of ash blends. However, they must be used with caution, since they have only been applied to the samples described in this study. Also, other properties have not been considered yet (e.g., influence of particle size distribution). The following conclusions can be drawn from the present results.

- It was possible to produce mortars that reached more than 55 MPa of compressive resistance, of the same order of magnitude as with Portland cement. The heat of reaction was 3 or 4 times smaller, but the rates of setting and hardening were lower.
- For blends prepared from similar ashes, there is a clear relation between I(1) decreasing from 6 to 1 (as the ratio of the two ashes vary), with the achieved resistance to compression of the mortar increasing from 5 to 40 Mpa.
- A difference in the index I(2) from 0.5 to 1.6 corresponded to a difference of 20 MPa in the resistance obtained.
- The pre-hydration of the CaO of sulphocalcic ashes was favorable (GARDANEX) or necessary (CFBC-H) to avoid excessive swellings leading to disintegration.
- Concentration of SO₃ should be between 4 and 7% in the blend, in order to obtain 25 MPa of resistance without deleterious expansions in immersed beams (samples G); over 8%, the corresponding swelling measurements will easily exceed 2500 Fm/m, causing a severe risk of irreversible deleterious expansion.

- Heavy metals remain captured in the solid matrix of the mortar.

The main hydration products have been identified, and characterization of the amorphous C-S-H has been obtained for a number of samples.

These studies on hydration are being continued on ash pastes already considered in a previous study².

ACKNOWLEDGMENTS

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