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LOW CO_2 BINDER: A SOLUTION FOR PRECAST INDUSTRY

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Abstract: *The industry of concrete is faced with the evolution of cements because of limitations in CO_2 emissions (protocol of Kyoto, 1990). Indeed, the current tendency is to decrease the content of clinker in cements (1 ton of clinker = 1 ton of CO_2) by preferentially using mineral additions. This context is of major concern for the precast industry since the resulting cements are generally not very reactive at early ages. Then, the combination between blended cements and specific mineral additions has to be investigated so that both significant reactivity at early age and an optimal performance at 28-day age are gathered.*
This paper deals with the combination between a cement composed of slag (CEM II-A S according to the European Standard EN 197-1) and metakaolin (MK). In steam cured condition, results on mortars showed that there was an increase in compressive strength (39% at 1 day and 8% at 28 days) when an efficient cement (CEM I 52.5 R) was substituted by a binder composed of CEM II-A S 52.5 N and MK. To understand the mechanical results, microstructural analysis on cement paste was undertaken. In particular, X Ray Diffraction qualified the hydration products and thermal analysis (TGA and DTA) quantified the reactivity of original blends (clinker, slag, MK) to evaluate the extent of the pozzolanic reaction due to MK incorporation. These are promising results for decreasing the CO_2 outburst in the atmosphere in the precast industry.

1. INTRODUCTION

Precast concrete products must present mechanical performances so that the pretensionned strands can be relaxed as soon as one day of age and the material quality can be checked at 28-day age. For that purpose, CEMI-52.5R cement according to NF EN 197-1 are used because they combine a high clinker content (at least 95% by weight), a large reactivity at early age and 28-day minimum compressive strength of 52.5MPa measured on normalized mortars (NF EN 196-1). In addition, the maturation of such products and the development of mechanical properties at younger age are enhanced under high temperature curing. However, the heat treatment adversely affects the strength at later ages[1].
In the precast context, an interesting alternative to the use of CEMI-52.5R cements involving high CO_2 release into the atmosphere during their product process (1t clinker = 1t CO_2) consists in studying the behavior of the combination between a composed cement (CEMII-52.5N type) and a mineral addition like metakaolin (MK). Metakaolin, obtained from the calcination of kaolinite clay at 600-700°C (Eq.1), is a promising product. First, the global deshydroxylation reaction of kaolin does not produce CO_2, as described by Eq.1 [2]. The CO_2 emissions during MK production come from the process only (extraction of raw materials, kiln, etc.).

$$Al_2O_3, 2SiO_2, 2H_2O \rightarrow Al_2O_3, 2SiO_2 + 2H_2O \quad (1)$$

Second, MK presents a pozzolanic effect on hydration[3]. During cement hydration, the siliceous and aluminous components issued from the dissolution of MK react with the calcium hydroxide to produce a mixture of C-S-H, C_4AH_{13}, C_3AH_6, C_2ASH_8… . Interests of this addition are multiple toward environmental and performential aspects (mechanical and durability performances improvement[4,5].
This study gives some answers to the progressive replacement of CEMI-52.5R by cement with low clinker content such as CEMII/A-S-52.5N. The use of CEMI-52.5R and CEMII-52.5N cements blended with MK is considered. The objective is to quantify the compressive strength of mortars incorporating such binders in steam-cured conditions and to compare their performances with that of mortars containing cement only. Mechanical results are next explained at the cement paste scale through chemical and physical investigations.

2. EXPERIMENTAL PROGRAM

2.1 Constituents

1) % by weight	C1	C2	MK	Wt %	C1	C2	MK
Type	CEMI 52.5R	CEMII/A-S 52.5N	/	CaO	64.0	60.6	1.2
Density	3.15	3.12	/	SiO_2	20.4	23.1	58.1
Fineness (cm^2/g)	4322	4241	/	Al_2O_3	4.9	6.0	35.1
Clinker proportion 1)	99	82	/	Fe_2O_3	2.3	2.0	1.2
Addition proportion 1)	1 limestone	18 slag (BBFS)	/	SO_3	3.5	2.6	0.3
Passing 10µm 1)	/	/	50	MgO	1.6	2.8	0.2
Surface area (m^2/g)	/	/	18	K_2O	0.9	0.8	1.1
Gypsum	5.5	3.5	/	Na_2O	0.2	0.2	0.1

Table 1: Composition and properties of cements and MK used

Two cements (CEMI-52.5R, CEMII-A/S-52.5N) were used, coming from the same production site but differing in the clinker content : 18% of clinker by weight was replaced by BBFS in CEMII-52.5N. A MK usually employed in the concrete industry was also used. The main chemical and physical properties of the cements and MK are presented in Table 1. Mechanical tests were performed on mortars, which are more representative of concrete than cement pastes but easier to handle than concrete in large experimental programs. All mortars incorporated a standardized quartz sand complying with NF EN 196-1.

2.2 Compositions, mixing and placing procedures

Mortars: The reference mix containing no MK and all mixes with MK are described in Table 2. The cement replacement by MK was expressed as the mass fraction of cement in the control mix (12.5% and 25% replacement rates). For a given composition, a six-liter batch was prepared using a Controlab mixer with 10L maximum capacity. The mixing sequence complied with NF EN 196-1. Next, the mixture was placed in 4×4×16cm^3 molds using vibration (48Hz, 1.6g).
Cement pastes: A Perrier mixer with 2L maximum capacity was employed to make cement pastes whose compositions are given in Table 2. Each mixture was placed in cylindrical moulds (Ø30mm, h=50mm) with the same vibration as the one applied on mortars.

<table>
<tr><th>Blended</th><th>Designation</th><th>C1</th><th>C2</th><th>MK</th><th>Standardized Sand</th><th>Water</th></tr>
<tr><td rowspan="6">Mortars</td><td>MI-0%</td><td>450.00</td><td>/</td><td>/</td><td rowspan="6">1350</td><td rowspan="6">225</td></tr>
<tr><td>MI-12.5%</td><td>393.75</td><td>/</td><td>56.25</td></tr>
<tr><td>MI-25%</td><td>337.50</td><td>/</td><td>112.50</td></tr>
<tr><td>MII-0%</td><td>/</td><td>450.00</td><td>/</td></tr>
<tr><td>MII-12.5%</td><td>/</td><td>393.75</td><td>56.25</td></tr>
<tr><td>MII-25%</td><td>/</td><td>337.50</td><td>112.50</td></tr>
<tr><td rowspan="4">Cement pastes</td><td>PI-0%</td><td>500</td><td>/</td><td>/</td><td rowspan="4">/</td><td rowspan="4">175</td></tr>
<tr><td>PI-25%</td><td>375</td><td>/</td><td>125</td></tr>
<tr><td>PII-0%</td><td>/</td><td>500</td><td>/</td></tr>
<tr><td>PII-25%</td><td>/</td><td>375</td><td>125</td></tr>
</table>

Table 2: Mixture proportion for a quantity of 0.8L (g)

2.3 Heat treatment

Immediately after placing, the mortar prisms or paste cylinders were exposed to a simulated steam curing cycle with a maximum temperature of 55°C and a total length of 17.8h. It included 2.83h of pre-setting at 30°C, followed by 2h of heating at 10°C temperature increase per hour up to 55°C, 12.5h of exposure at 55°C and a 2h cooling down period. This cycle corresponds to an average from different steam curing cycles practiced in factory. After de-moulding, the mortar and cement paste samples were exposed for long-term curing at room temperature (20°C ± 1°C) in water.

2.4 Tests

Mechanical tests. At ages of 1 and 28 days, compressive strength tests were performed strictly in accordance with NF EN 196-1 (average strength from 5 measurements on 4×4×8cm^3 prisms).

Microstructural tests. Microstructural analysis was undertaken on cement pastes to explain the evolutions of mechanical performances observed on mortars containing MK or not. The reactivity of the resulting blends was also analysed (1day), compared to the initial reactivity of each cement studied.

Stopping of hydration. Because a lot of mixtures were simultaneously to be studied, it was necessary to stop the hydration, especially at early ages. Freeze-drying technique was chosen in this study.

X-Ray Diffraction. XRD technique qualifies crystallised hydrated and anhydrous phases in paste.

Differential thermal analysis (DTA) and thermogravimetric analysis (TGA). Such thermal analysis is useful to observe the evolution of the hydration and especially to estimate the process of the pozzolanic reaction. DTA locates the ranges corresponding to thermal decompositions of different phases in paste, while TGA simultaneously measures the weight loss due to the decompositions. TGA coupled with DTA makes then possible the hydration reactions to be qualitatively and quantitatively followed [6-7]. Further informations on the microstructural tests are gathered in Table 3. Thermograms (section 3-2) are presented up to 600 and 650°C for DTA and TGA respectively because beyond these temperatures, there is no useful information for the study (absence of calcium carbonate).

Testing	Sample/weight	Testing characteristics
Hydration stop	cement paste cylinder	liquid nitrogen (-196°C) during 5min , freeze-dryer : 1 day, temperature -40°C, vacuum 13.3Pa
XRD	powder passing on a 40µm sieve	Co Kα radiation (λ=1.789Å), 40kV, 30mA, 4°<2Θ<70°, recorded step : 0.04°, counting time : 10s
DTA	40µm powder / [1.0-1.1] g	constant temperature increase : 5.8°C/min maximal temperature : 950°C
TGA	40µm powder / [0.2-0.22] mg	constant temperature increase : 7.5°C/min maximal temperature : 700°C

Table 3: Microstructural tests details

3. RESULTS AND DISCUSSION

3.1 Mechanical performances of steam cured binders

	Values of reference or MI-0%		MII-0%	
1 day	33.9 (±0.96)		27.5 (±0.75)	
28 days	47.6 (±1.21)		42.5 (±1.41)	
	MI-12.5%	MI-25%	MII-12.5%	MII-25%
1 day	44.7 (±1.16)	47.1 (±0.56)	41.3 (±1.67)	44.3 (±0.73)
28 days	48.3 (±1.43)	51.0 (±0.31)	47.1 (±1.13)	48.3 (±1.78)

Table 4: Average Compressive strength results and corresponding standard deviation

The compressive strength results at 1 and 28 days on mortars are shown in Table 4. In order to easily assess the performance of any cement/MK combination, figures are presented in terms of strength relative to the reference strength. Eq.2 introduces relative strength noted $RS_j(i)$. The reference strength values correspond to the average value of MI-0%.

$$RS_j(i) = \frac{R_{c\,j}(i)}{R_{c\,Reference}(i)} \tag{2}$$

$RS_j(i)$ = relative strength of tested binder j in comparison with reference binder at i days
$R_{c\,j}(i)$ = compressive strength of tested binder j at i days (MPa)
$R_{c\,Reference}(i)$ = compressive strength of reference blend at i days (MPa)

Figures 1 and 2 show the relative strength values (RS) obtained from cements C1 and C2 respectively, according to the levels of their replacement with MK, from 0% to 25%.

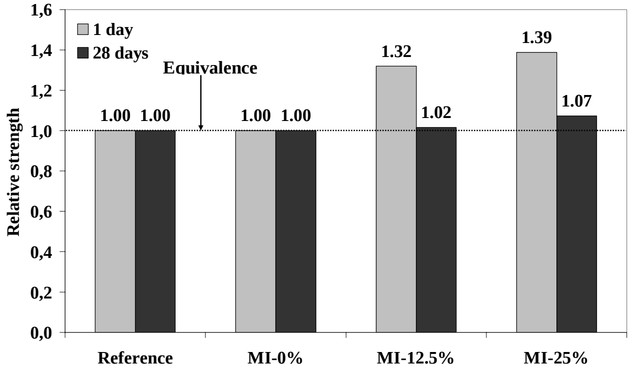

Figure 1: Relative strength of mortars : C1 and C1/MK binder

<u>CEMI 52.5R mortars</u> (Figure 1). At early age (1d), in comparison with control mortars (MI-0% or reference), performance was improved when MK was incorporated: the higher the substitution rate, the better the performance. Hence, it is possible to substitute up to 25% of cement by MK in steam-cured materials and obtain mechanical properties that are significantly increased.
At long term (28d), compared to control mortars (MI-0%) performance was slightly increased when MK was incorporated at a substitution rate of 25%.

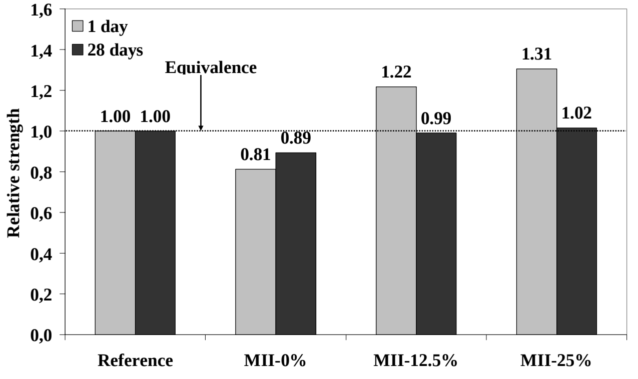

Figure 2: Relative strength of mortars : C2 and C2/MK binder

<u>CEMII 52.5N mortars</u> (Figure 2). Compared to MI-0% mortars, MII-0% presents weaker characteristics at all ages. In precast conditions, it is not possible to achieve the expected performances with this type of cement, i.e. guaranteed strength both at early ages and in the long term. Conversely, when a part of C2 is replaced with MK, the reactivity of the resulting binder is significantly improved at 1 day and 28 days. It is even close to that obtained with C1/MK binder.

As already noted in the case of CEMI cements, strength increases with the increase in the substitution rate. In the near future, cements containing a large amount of clinker like CEMI will progressively vanish in order to limit CO_2 releases. Accordingly, a less reactive cement than CEMI could be a promising product when it is partially replaced with MK. Here, in comparison with CEMI cements in steam-cured conditions, the replacement of 25% by mass of a CEMII by MK, saving 33% of clinker, yields improved mechanical performance at early ages and correctly approaches the reference in the long term.

3.2 Discussion of the cement/MK binder performance related to the paste microstructural properties

Mechanical tests gave promising results which encourage the use of a CEMII-A/S-52.5N/MK binder as a component of concrete mix designs for the precast industry. A microstructural study was undertaken to clarify the positive effect of MK on strength. The microstructural investigations were carried out at 1 day of age only because the increase in strength was signifiant at 1 day of age.

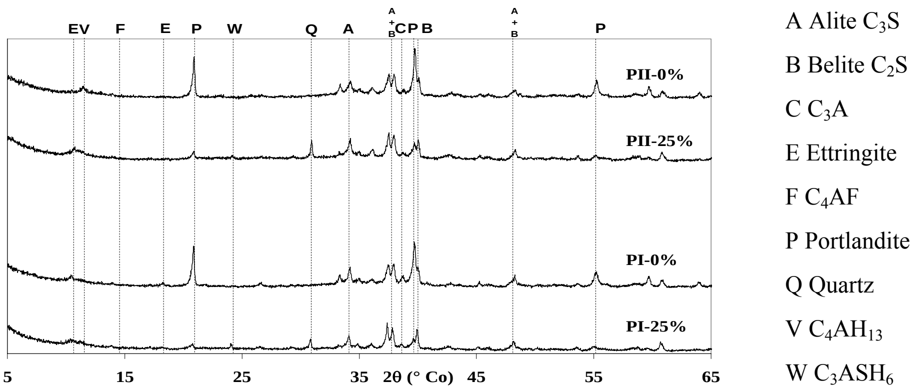

Figure 3: XRD diagram at 1 day

XRD analysis. Figure 3 presents the X-ray diffraction patterns of pure pastes (PI-0%, PII-0%) and pastes blended with MK (PI-25%, PII-25%).

i) The evolution of consumption of calcium hydroxide (noted P on Figure 3) relative to pozzolanic reaction can be assessed by considering the two main diffraction peak (primary $2\Theta=39.7°$ and secondary $2\Theta=20.9°$).

ii) The diffraction peak at about $2\Theta=12.1°$ corresponds to the C_4AH_{13} hydrate. It is an isostructural of Portlandite with hexagonal structure of little leaf belonging to AFm family and obtained by substitution of calcium with aluminium. The peak is weakly perceptible in the case of PI-0% and PII-0%, implying no or only a little C_4AH_{13} formation in these pastes. The diffraction peak becomes very obvious concerning PI-25% and PII-25%,

iii) Hydrogarnet (C_3ASH_6) is noted in cement/MK blend (PI-25% and PII-25%) as indicated by diffraction peak at about $2\Theta=23.9°$.

iv) Whatever the binder tested, ettringite is visible according to the diffraction peak at about $2\Theta=10.6°$.

To complete the information available from XRD technique, quantitative data must be sought for about the amorphous hydrated phases like C-S-H.

DT analysis. In Figure 4, specific hydrated phases resulting from pozzolanic reaction can be distinguished by DT analysis.

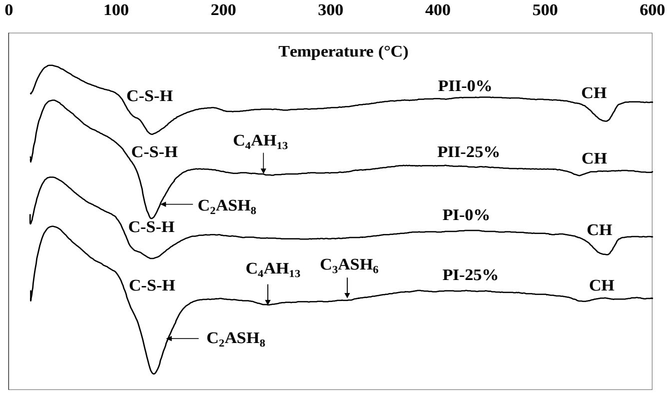

Figure 4: DTA diagram at 1 day

i) As expected from XRD results, a less amount of CH is visible within the temperature range of 520-570°C in pastes with MK than in reference pastes, indicating the consumption of CH by the pozzolanic reaction as soon as 1 day of age.
ii) The pozzolanic reaction can also be seen by observing the decomposition of hydration products within the temperature range of 100-180°C. Indeed, C-S-H phases are identified in both types of pastes but a hydrated calcium silica-aluminate phases are observed in blended pastes only (PI-25% and PII-25%) because of a deep endothermic peak located at 250°C.
iii) the analysis also confirms the presence of hydrated aluminate in cement/MK blinder : C_4AH_{13} located at about 250°C, gehlenite C_2ASH_8, Hydrogarnet C_3ASH_6, located at about 300°C is more visible in CEMI/MK paste (PI-25%) paste than in PII-25% paste.

TG analysis. In Figure 5, TGA quantifies the weight loss due to decomposition of hydrated phases. Dilution effect due to cement substitution by MK was taken into account for this quantitative consideration.

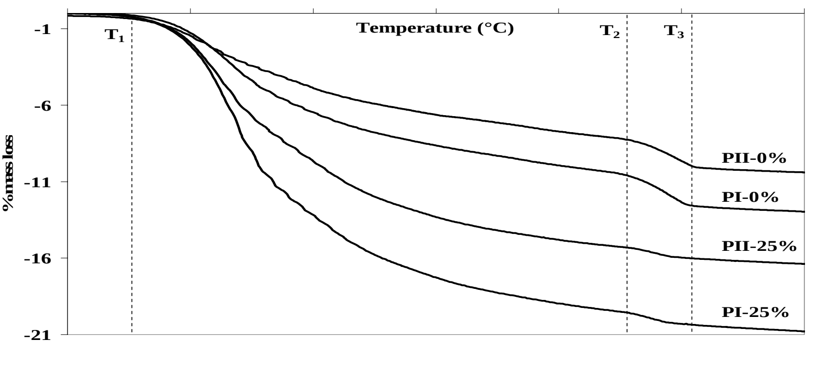

Figure 5: DTG diagram at 1 day

i) The decomposition of calcium hydroxide (CH) was analysed from 520°C to 560°C. Despite the difference in reactivity between C_1 and C_2 cements, the quantities of CH formed in both pastes PI-0% and PII-0% are similar.
ii) When cement (C1 or C2) is substituted by 25% of MK by weight, the reactivity of the resulting binder is improved and the amount of CH is decreased. This is consistent with XRD and DTA results indicating that the pozzolanic reaction, thermo-activated in steam curing conditions, occurs as soon as 1 day of age.
iii) Within the temperature range of 100-175°C, the decomposition of C-S-H and assimilated phases is considered. It can be observed that the weight loss is more important in PI-0% paste than in PII-0% paste, indicating a higher C-S-H quantity in PI-0% than in PII-0%. This explains in some extent the difference in strength between MI-0% and MII-0% (Figures 1 and 2). When MK is incorporated, the amount of C-S-H and hydrated silica calcium aluminates is increased, whatever the cement used. This observation confirms the increase in compressive strength in cement/MK systems.

4. CONCLUSION

- From the point of view of mechanical performance, the replacement of CEMI-52.5R cement by CEMII-A/S-52.5N/MK binder is possible. An increase in the substitution rate of MK corresponds to an increase in the compressive strength on mortar. When 25% of CEMII-A/S-52.5N is replaced by MK, the compressive strength is significantly improved at early age (+31%) and not affected at 28 days age, compared to the incorporation of CEMI-52.5R only.
- Increased mechanical performances of CEMI-52.5R/MK and CEMII-A/S-52.5N/MK can be explained by the pozzolanic reaction, observed through a calcium hydroxide consumption, an increase in the amount of C-S-H and the development of hydrated silica calcium aluminates.
- Environmentally, the use of CEMII/MK binder is positive : [1)] % by weight there is clinker saving (33% in this study) implying a reduction of the CO_2 released into the atmosphere.
- This study is of interest for cement makers and concrete manufacturers because it shows that the prospects for the CEMI cement to be progressively vanished and low-CO_2 binder such as CEMII/MK to be used are possible. Accordingly, increased energy costs issued from the treaty of Kyoto (1990) could be reduced.

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