Low CO_2/energy binder for precast industry

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0. Abstract

To limit CO_2 emissions related to the cement production process, the use of cements blended with metakaolin (MK) in precast concrete is considered. The main properties of such binders should combine high reactivity at an early age (1 day) and optimal performance at 28 days. In steam cured conditions, results on mortars show, relative to the reference: i) an increase in compressive strength (+35%) when 25% by weight of efficient cement (CEM I 52.5 R) is substituted by metakaolin, ii) similar performance when CEM I is replaced with a binder composed of CEM II 52.5 N and MK, and iii) a beneficial effect on new blended materials at 28-days brought about by a decrease in the maximum temperature during heat treatment. Saving up to 40% of clinker (with the binder of CEM II and MK) and limiting the energy to be supplied for their maturation are encouraging results for limiting the CO_2 given out into the atmosphere.

1. Introduction: Study context and bibliography

Time delays are a major concern in the precast industry because of their effect on profitability. Accordingly, the concrete used to make building parts (beams and slabs) must have good mechanical characteristics both early and in the long term. Heat treatment is applied to the concrete pieces to accelerate the rate of hydration. This allows sufficient maturity at early ages for the prestressing elements to set in a tensile state. However, such curing conditions can have an adverse effect on the hardened properties [1,2,3,4]. Type CEM I 52.5R cements complying with NF EN 197-1 are generally used in the precasting context. They ensure good reactivity at early age and a minimum of 52.5 MPa is guaranteed for the compressive strength of standardized mortars (NF EN 196-1). But this type of cement contains a minimum of 95% clinker by mass [5] which is linked to high CO_2 release into the atmosphere. For example, during the decarbonation of raw materials, the alite phase (Ca_3SiO_5, i.e. C_3S) produces large quantities of CO_2, as shown by the following basic equation (mass proportions in italics):

$$3CaCO_3 + SiO_2 \xrightarrow{1350°C} Ca_3SiO_5 + 3CO_2 \quad \text{Eq.1}$$
$$300 + 60 \rightarrow 228 + 132$$
Calcium carbonate + silica → C_3S (Alite) + carbon dioxide gas

Eq. 1 deserves some comment:
- irrespective of the type and efficiency of the calcination process, every ton of C_3S produced releases 579 kg of CO_2 and generates a minimum thermal energy of about 1.83 GJ at 20°C;
- the reaction cannot proceed at temperatures lower than about 1250°C, even if a catalyst is used. In practice, it is necessary to bring the raw material temperature to 1400°C so that the reaction rate is high enough to be cost-effective [6,7].

Since cement manufacturing generates increasingly high energy costs together with additional levies related to the treaty of Kyoto (1990), low-CO_2/energy binders are currently of interest to cement makers. In such materials, a part of the clinker is replaced by a mineral addition (limestone filler, siliceous filler, slag, etc.). Metakaolin is a promising addition because of its pozzolanic effect [8, 9, 10, 11]. It is obtained from the calcination of clay at 600-700°C. The dehydroxylation reaction to obtain MK does not produce CO_2 (see Eq.2). The CO_2 emissions during MK production come only from the process (extraction, kiln, etc.).

$$Al_2O_3, 2SiO_2, 2H_2O \rightarrow Al_2O_3, 2SiO_2 + 2H_2O \quad \text{Eq.2}$$

Finally, the total CO_2 released is estimated at 175±25 kg for 1 ton of MK.
Some studies have demonstrated that, when clinker is substituted by MK, the mechanical properties and durability characteristics improve [12,13,14] and creep and shrinkage are reduced [15].
Here, the use of cements blended with MK is considered in the precast context. Hence the objective is to quantify the compressive strength of mortars incorporating such binders in steam-cured conditions and to compare their performance with that of mortars containing cement only.

2. Experimental program

2.1. Constituents

Three cements differing in nature and coming from distinct production sites were used. Each cement was received in a single batch and stored in plastic bags until its use in the test program. A metakaolin (MK) usually employed in the concrete industry was also used. The main properties of the cements and MK are presented in Table 1 and Table 2.
The tests were performed on mortars, which are more representative of concrete than cement pastes but easier to handle than concrete in large

experimental programs. Mortars incorporated a standardized quartz sand (NF EN 196-1) with particle sizes ranging between 0.08 and 2 mm.

Table 1 : Composition and properties of cements used

	C1	C2	C3
Type	CEM I[a)]	CEM I[b)]	CEM II[b)]
Class	52.5	52.5	52.5
Reactivity of younger age	R	R	N
Density	3.15	3.15	3.12
Fineness (cm^2/g)	4200	4322	4241
Clinker proportion ([c)])	97[a)]	99[b)]	82[b)]
Addition proportion ([c)])	3 (limestone)	1 (limestone)	18 (slag)
Bogue composition of clinker			
C_3S ([c)])	62.0	58.9	58.9
C_2S ([c)])	10.2	14.2	14.2
C_3A ([c)])	8.1	9.3	9.3
C_4AF ([c)])	8.4	6.9	6.9
Gypsum ([c)])	5.0	5.5	3.5

[a)] clinker 1, [b)] clinker 2, [c)] % by weight

Table 2 : Chemical composition and physical properties of the metakaolin used

Oxides	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO
Percent by weight	58.1	35.1	1.2	1.2	0.2
Oxides	Na_2O	K_2O	SO_3	LOI	
Percent by weight	0.1	1.1	0.3	1.9	

Passing 10µm (% by weight) = 50
Passing 2µm (% by weight) = 12
Surface area (m^2/g) = 18

2.2. Compositions, mixing and placing

A batch for the reference mix without MK, designed according to French standard NF EN 196-1, was composed of three parts by mass of sand, one part of cement and a half part of water. All mixes with MK involved the same proportions of sand, powder (cement + mineral admixture) and water as the reference mix. The cement replacement by MK was expressed as the mass fraction of cement in the control mix. Replacement rates were 12.5% and 25%. Beyond 25% replacement, preliminary studies showed that the workability and placing of mortars was impaired due to the water demand of MK [16]. Table 3 gives the denominations and compositions used in this study.

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 $4 \times 4 \times 16 cm^3$ molds using vibration (48Hz, 1.6g).

Table 3 : Mixture proportion for a 0.8-L batch (g)

Designation	C1	C2	C3	MK	Standardized Sand	Water
M1-0%	450.00	/	/	/		
M1-12.5%	393.75	/	/	56.25		
M1-25%	337.50	/	/	112.50		
M2-0%	/	450.00	/	/		
M2-12.5%	/	393.75	/	56.25	1350	225
M2-25%	/	337.50	/	112.50		
M3-0%	/	/	450.00	/		
M3-12.5%	/	/	393.75	56.25		
M3-25%	/	/	337.50	112.50		

2.3. Steam curing

Immediately after placing, the mortar prisms were exposed to a simulated steam curing cycle with a maximum temperature of 55°C. It included 2.83 h of pre-setting at 30°C, followed by 2 h of heating at 10°C temperature increase per hour up to 55°C, 12.5 h of exposure at 55°C and a 2 h cooling down period. The total length of the simulated steam curing cycle was 17.8 h. After de-molding, the mortar bars were exposed for long-term curing at room temperature (20°C±1°C) immersed in water up to the time of tests.

2.4. Mechanical tests

At ages of 1 and 28 days, compressive strength tests were performed strictly in accordance with French Standard NF EN 196-1. For each composition, an average strength was calculated from 5 measurements on half prisms 4×4×8 cm^3.

3. Results and discussion

Table 4 : Average Compressive strength results and corresponding standard deviation

	Values of reference	M1-0%	M2-0%	M3-0%
1 day	39.3	40.2 (±0.78)	33.6 (±0.96)	27.5 (± 0.75)
28 days	54.1	55.5 (±0.69)	47.6 (±1.21)	42.5 (± 1.41)

	M1-12.5%	M1-25%	M2-12.5%	M2-25%	M3-12.5%	M3-25%
1 day	48.9 (±1.02)	50.5 (±0.88)	44.7 (±1.16)	47.1 (±0.56)	41.3 (± 1.67)	44.3 (± 0.73)
28 days	54.4 (±0.98)	57.5 (±0.97)	48.3 (±1.43)	51.0 (±0.31)	47.1 (± 1.13)	48.3 (± 1.78)

The compressive strength results are shown in Table 4. Reference strength refers to the average performance of standardized mortars, calculated from 3 precast sites where CEM I 52.5R is traditionally used in some applications. In order to easily assess the performance of any cement/MK combination, results are expressed in terms of strength relative to the reference strength.

3.1. CEM I 52.5 R / MK binder

Fig.1 : Relative strength for C1 and C2 binders

C1 mortars

C2 mortars

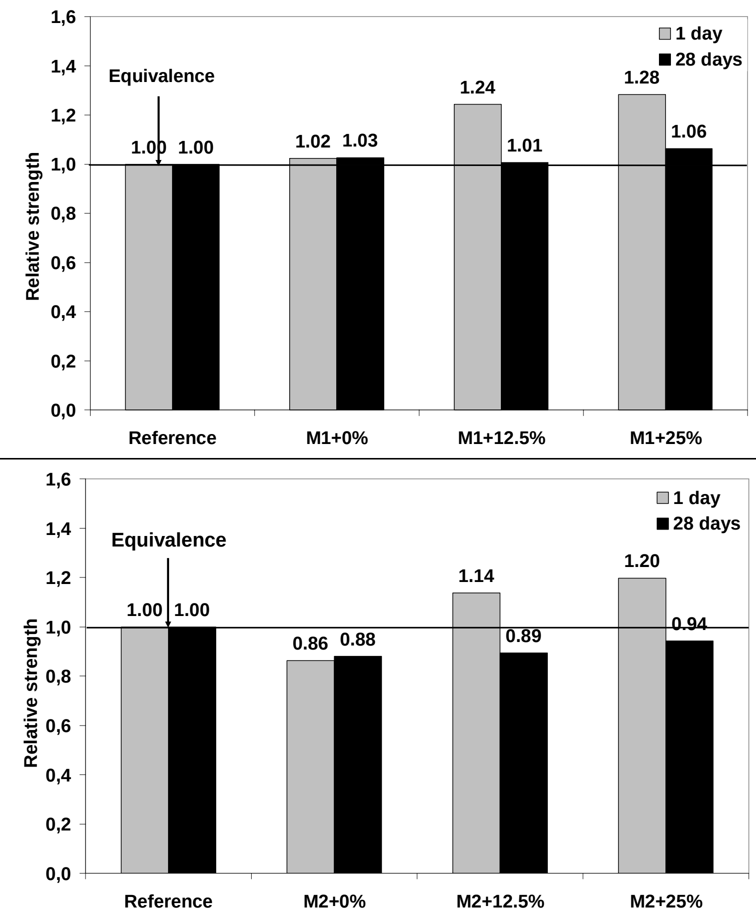


Fig.1 presents relative strength values obtained from cements C1 and C2 respectively, according to the levels of their replacement with MK.

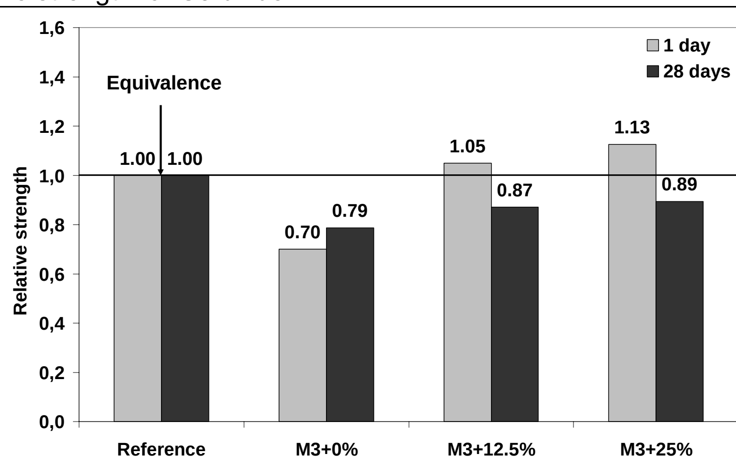
Several observations and comments can be made. Despite similar fineness and density (Table 1), and regardless of the age of test, lower performance is observed for C2 than for C1 (comparison between M1-0% and M2-0%). At early ages, this can be explained by a higher C_3S/C_2S ratio in C1 than in C2. Accordingly, C2 appears to be unsuitable for some precast applications.

Nevertheless, in comparison with control mortars (M1-0% and M2-0%), whatever the cement used, performance was improved when MK was incorporated: the higher the substitution rate, the better the performance at 1 day and 28 days of age. It is important to note that long-term performance is almost achieved in the case of a lower quality cement (comparison between reference strength and M2-25%, cement C2). 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 (1 day) or very similar to the reference ones (28 days). This is a promising result which encourages the use of a CEM I 52.5R / MK binder as a component of concrete mix designs for the precast industry.

3.2. Replacement of a CEM I by a CEMII / MK binder

Fig.2 presents the relative strength values obtained from cement C3, according to the levels of its replacement with MK. Compared to C1 and C2 (CEM I types), the blended cement C3 presents the weakest characteristics at all ages (see compressive strength or relative strength results of corresponding standardized mortars M1-0%, M2-0% and M3-0% in Table 4 or in Figs.1, 2). In precast conditions, it is not possible to achieve the expected results with this type of cement, i.e. guaranteed strength both at early ages and in the long term. Conversely, when a part of C3 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 C2/MK binder.

Fig.2 : Relative strength for C3 binder

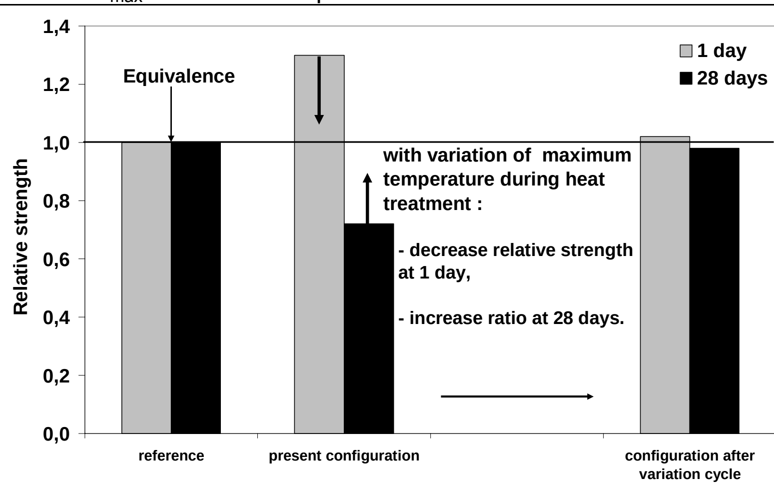


As already noted in the case of CEM I cements, strength increases with the increase in the substitution rate. In the near future, cements containing a large amount of clinker like CEM I will progressively vanish in order to limit CO_2 releases. Accordingly, a less reactive cement than CEM I could be a promising product when it is partially replaced with MK. Here, in comparison with CEM I cements in steam-cured conditions, the replacement of 25% by mass of a CEM II by MK, saving 40% of clinker, yields improved mechanical performance at early ages and correctly approaches the reference in the long term.

3.3. High temperature decrease of thermal treatment

It is a well-known fact that heat treatment increases performance at early ages and decreases it at later ages.
Regardless of the cement or the cement/MK combinations, this is clearly confirmed here (sections 3.1 and 3.2) in steam curing conditions. The through-solution mechanism is accelerated in the first stages of hydration with the rise in temperature, and it seems that the incorporation of MK enhances this acceleration, as shown by Figs.1, 2. At later ages, the hydration reactions are essentially of a topochemical nature and as such take place mostly on the surface of the reacting materials [17]. High curing temperature conditions such as those applied in this study rapidly increase the occurrence of topochemical reactions. Accordingly, the hydration products are not evenly distributed [1,2,3,4], which weakens the whole material. The adverse effect of temperature on performance seems to be reduced with the use of MK (Figs.1, 2). At this step, the question arises as to whether the maximum curing temperature may be lowered in order to optimize the performance of cement/MK binders, i.e. to diminish the too-beneficial effect on strength at 1-day age and to limit the drop in strength at 28-day age (Fig.3).

Fig.3 : Variation of T_{max} and its consequences



Figs.4 to 6 present the relative strength values obtained for mortars incorporating 25% by mass of MK, i.e., M1-25%, M2-25%, M3-25% respectively, according to the maximum curing temperature (55°C as defined in the standard cycle, 50°C and 45°C).

Irrespective of the type of cement, the decrease in the maximum temperature of the curing cycle was accompanied by a decrease in the strength at early ages, as expected. However, although performance was maintained at 45°C for cements CEM I (C1 and C2), this was not the case for CEM II (C3).

For CEM II, 50°C is a threshold value below which performance cannot be guaranteed. At 28 days of age, the adverse effect of thermal treatment on strength is not counteracted by decreasing the maximum temperature to 45°C but the performance level is kept constant for all binders tested.

Fig.4 : Variation of T_{max} for M1-25%

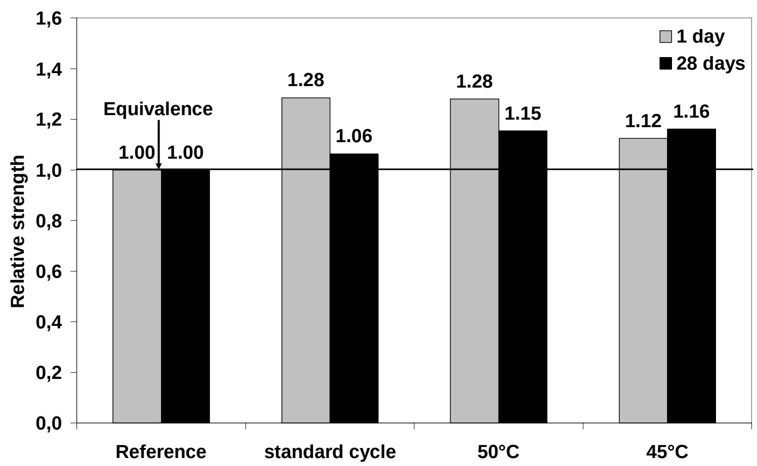


Fig.5 : Variation of T_{max} for M2-25%

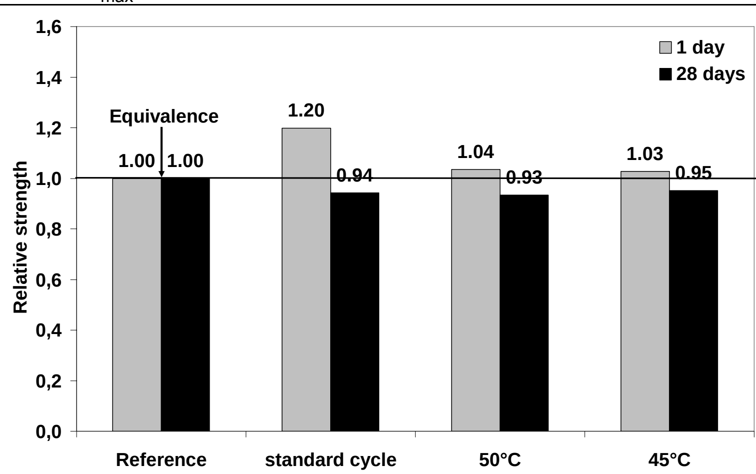
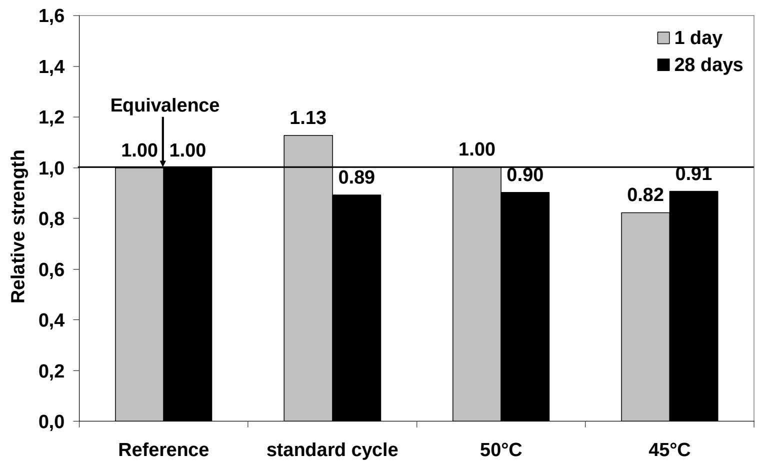


Fig.6 : Variation of T_{max} for M3-25%

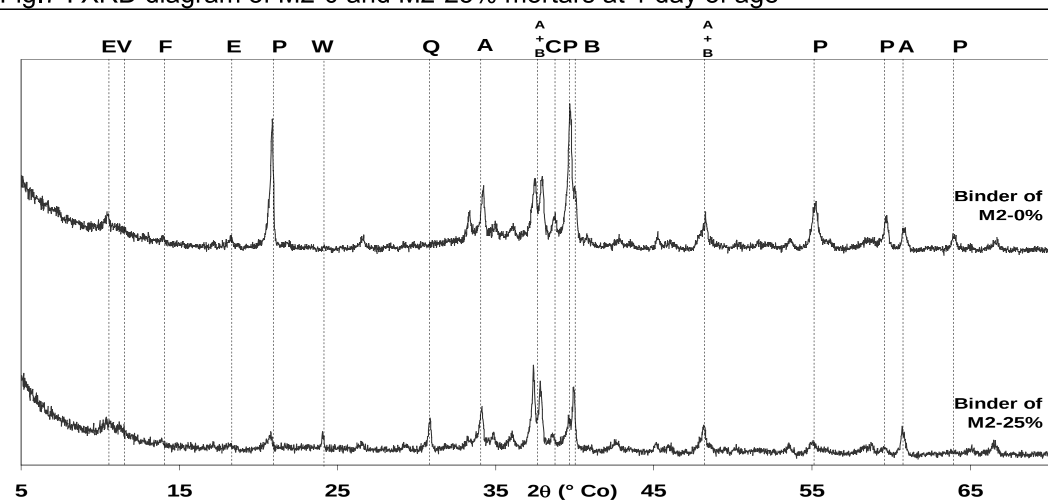


Here, it is possible to conclude that it may be possible to optimize the curing cycle via a reduction in the maximum temperature when cement (CEM I or CEM II) is partially replaced by MK. The energy consumption is then decreased, leading to cost savings for the precast concrete makers and a positive impact on the environment.

3.4. Microstructural investigation to explain the performance evolution with C2 binder

Fig.7 presents XRD patterns of M2-0% and M2-25% mortars, cautiously obtained from 40µm powdered samples and 9h of analysis time.

Fig.7 : XRD diagram of M2-0 and M2-25% mortars at 1 day of age

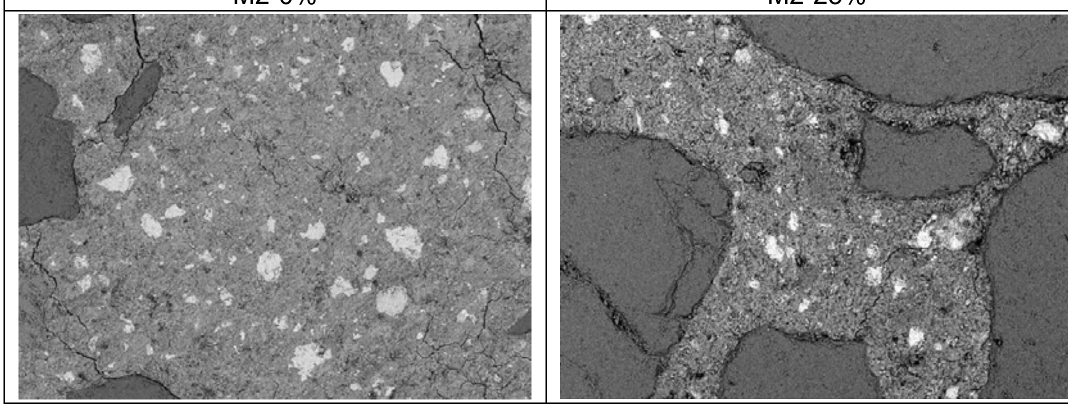


A alite (C_3S)
B belite (C_2S)
C C_3A
E ettringite
F C_4AF
P portlandite (CH)
Q quartz
V C_4AH_{13}
W C_3ASH_6

The improvement of mechanical performance at early age can be explained by a thermo-activation of pozzolanic reaction as well as classical hydration reactions thanks to steam curing. Indeed, at 20°C curing, it is known that pozzolanic reaction proceeds slowly in time [10]. But, according to Fig.7, MK incorporation in cementious matrix coupled with a thermal treatment leads to portlandite consumption (2Θ = 39.7° main peak and 2Θ = 20.9° secondary peak), as already noted [18]. In addition, hydrates neo-formed by pozzolanic reaction rather than hydration reaction only can be observed, such as hydrogarnet C_3ASH_6 (2Θ = 23.9°) and C_4AH_{13} (2Θ = 12.1°).
Figure 8 presents two typical SEM views (BSEI mode) of M2-0% and M2-25% respectively, obtained from polished sections. It can be observed a decrease in the biggest remaining anhydrous phase (white area) with MK incorporation. The total anhydrous phase seems also to be reduced for M2-25% in comparison with M2-0%.

Fig.8 : Images of polished sections of M2 mortars at 28 days of age- SEM, BSEI mode (×200)

M2-0% | M2-25%



3.5. Environmental benefit for almost equivalent performance

By way of illustration and considering that 1 ton of clinker produced generates 1 ton of CO_2 released into the atmosphere, Tab.5 shows the CO_2 reduction when CEM I 52.5R is replaced with CEM I 52.5R/MK or CEM II 52.5N/MK binders in mortar designs.

Table 5 : Emission and reduction of CO_2 for different blends

	Mass CO_2 emission per m^3 mortar (kg)	Reduction CO_2 / M1-0%
M1-0%	496	/
M1-25%	370	-25%
M3-0%	447	-10%
M3-25%	332	-33%

For almost equivalent performance, the CEM II/MK binder (M3-25%) implies a 33% reduction value in CO_2 emission in comparison with CEM I cement (M1-0%). This result needs to be validated at the concrete scale. Studies on concrete designs incorporating such binders are currently underway.

4. Conclusions

Based on measurements of mortar compressive strength, this study provides some answers, in the context of the precast industry, to the need for a progressive decrease in clinker production so as to limit the CO_2 released into the atmosphere.

- It is possible to substitute up to 25% of CEM I 52.5R cement by Metakaolin (MK) in steam-cured materials and obtain mechanical properties that are significantly increased (1-day age) or practically the same as the reference ones incorporating cement only (28-day age). This is a promising result encouraging the upcoming use of a CEM I 52.5R / MK binder as a component of concrete mix designs for the precast industry.
- For the same replacement rate as that applied to CEM I 52.5R, CEM II 52.5N cement becomes an attractive product. The resulting binder saves 40% of clinker and, in comparison with mortars incorporating CEM I cements only, it improves the mechanical performance at early ages and satisfactorily approaches it in the long term.
- The optimization of the curing cycle is possible via a reduction in the maximum temperature when cement (CEM I or CEM II) is partially replaced by MK. The energy consumption is then decreased, giving rise to a cost gain for the precast concrete manufacturers and a positive impact on the environment.

5. Acknowledgements

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