Flash metakaolin/slag/cement binder: An environmental and performantial alternative for steam-cured mortar for precast use

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Paper prepared for presentation

at the Lowering the Carbon Footprint of Concrete Session

of the 2010 Annual Conference of the
Transportation Association of Canada
Halifax, Nova Scotia

Abstract : To limit environmental impact related to the cement production process (CO_2 release into the atmosphere and energy consumption), the current trend is to decrease the clinker content in cement through the use of mineral admixtures. For precast applications, an alternative solution is to use ternary binders such as cement/blast furnace slag/flash metakaolin. In this study, different proportions of slag and flash metakaolin are considered in order to investigate the mechanical (flexural and compressive strength) and durability (porosity, water absorption and permeability) characteristics of steam-cured mortars. The main properties of such binders should have high reactivity at an early age (1 day), optimal performance at 28 days, and enhanced long-term durability. The results show that ternary binder mortars have similar or ever better properties than the control mortar, which uses only cement. Moreover, mortars with binders with 25% flash metakaolin show better performance than the control mortar, particularly in terms of mechanical properties. From an environmental standpoint, saving up to 40% of clinker (with the ternary binder) is a promising approach that reduces energy consumption (-23%) and the amount of CO_2 released into the atmosphere (-34%).

Keywords: Precast applications, flash metakaolin/slag/cement binder, environmental approach

Acknowledgements: The authors are very grateful to SEAC-Gf enterprise and the Association Nationale de la Recherche Technique (ANRT) for supporting the present research.

1. Introduction

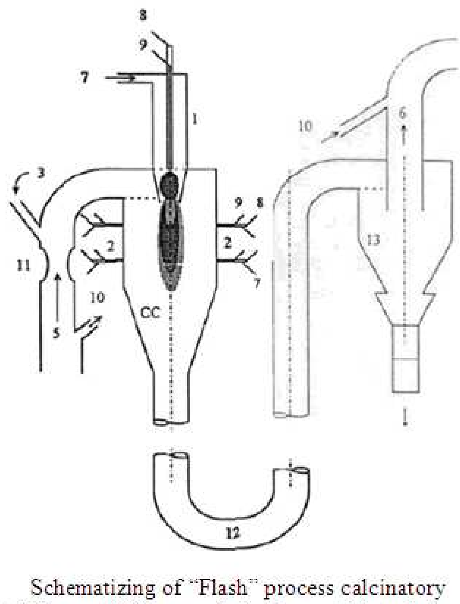
Precast concrete products must present certain mechanical properties so that the pre-tensioned strands can be released as early as one day of age and the material quality can be checked at 28 days. For that purpose, CEMI-52.5R cements (equivalent to GU cement in Canadian standard) are used because they combine a high clinker content (at least 95% by weight), a large reactivity at early age and a 28-day minimum compressive strength of 52.5MPa measured on normalized mortars *[1]*. In addition, the maturation of such products and the development of mechanical properties at a younger age are enhanced under high temperature curing. However, the heat treatment adversely affects the strength at later ages *[2]*.

In the precast context, an interesting alternative to the use of CEMI-52.5R cements, which release high levels of CO_2 during production (1t clinker = 1t CO_2), is to study the behavior of the combination of a binary cement (CEMII-52.5N type) and a mineral addition like flash metakaolin (MK). Metakaolin, obtained from the calcination of kaolinite clay at 600-700°C (Eq.1), shows promise as an effective product with a lower environmental impact *[3]*.

$$Al_2O_3, 2SiO_2, 2H_2O \rightarrow Al_2O_3, 2SiO_2 + 2H_2O \qquad \text{Eq.1}$$

To obtain this artificial pozzolana, the industrial process involves "suspension" or "flash" heat exchanges (Figure 1) *[4]*. Flash calcination parameters (high temperatures for a short duration) are different than traditional calcination (minimum 10 minutes duration), but they nevertheless enables to establish a thermo-chemical model that simulates the transformation. The flash process leads to a special mineralogy and structure of calcined clay with flat and round particles (Figure 2).

Figure 1. Production of metakaolin by flash process (Fumel, France)



Site around the clay/sand carrier

Schematizing of "Flash" process calcinatory — The "flash process" tower

(1) Axial burner (2) Six perpendicular burners (3) Introduction of Kaolin particle (4) Recovery of calcined powder (5) Secondary air inlet (6) hot gas-activated material trap (7) Primary air inlet (8) Pulverized air inlet (9) fuel (10) Parallel air inlet (11) Venturi (12) Refrigeration pipe (13) Cyclone separator (CC) Combustion chamber.

First, the global deshydroxylation reaction of kaolin does not produce CO_2, as described by Eq.1. During MK production, CO_2 emissions only come from the production process (extraction of raw materials, kiln, etc.). Second, MK presents a pozzolanic effect on hydration *[5]*. 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, etc. *[6]*. This addition has multiple effects on environmental and performantial aspects due to mechanical and durability performance improvements *[5,7]*).

This study examines the progressive replacement of CEMI-52.5R by a cement with low clinker content such as CEMII 52.5N (binary slag cement). The use of CEMI-52.5R and CEMII-52.5N cements blended with flash MK is considered. The objective is to quantify the mechanical properties (flexural and compressive strength) and durability properties (porosity and water absorption) of mortars incorporating such binders in steam-cured condition and to compare their performances with that of mortars containing cement only.

2. Experimental program

2.1 Raw materials

To ensure satisfactory early age performance of concrete as well as at long term, the cement C1 with CEM I 52.5R designation *[1]* was used due to its significant great fineness, good Bogue's composition (C_3A=62%, C_2S=10%, C_3A=8%, C_4AF=8%, Gypsum=5%)[1], and large amount of clinker (97% and 3% limestone filler by weight). The cement C2, a binary cement with CEM II 52.R designation *[1]* was also used. It came from the same production site but differed in clinker content; 18% of clinker by weight was replaced by blast furnace slag (GGBS). The main properties of cements (C1 and C2), and slag (GGBF) are shown in Table 1.

Table 1. Physical properties and chemical composition of raw materials

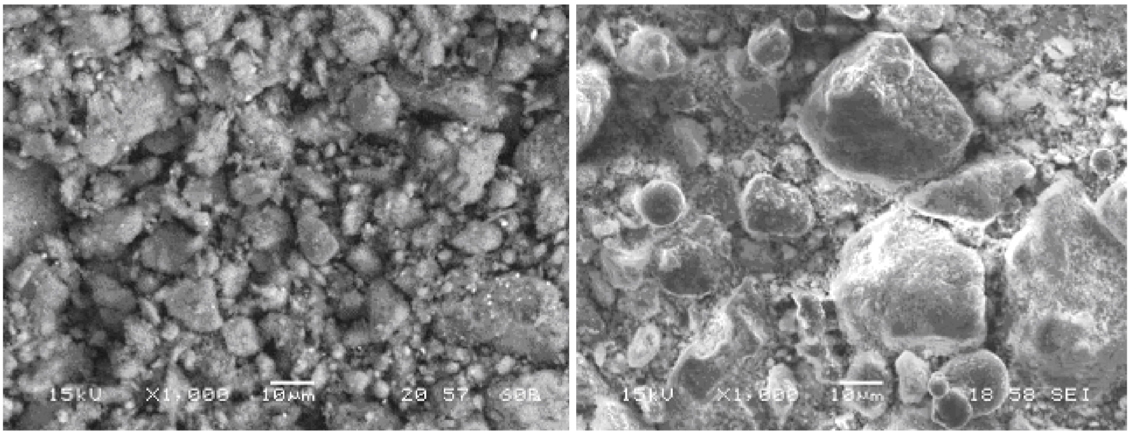
Physical properties									
	Specific gravity (kg/m^3)			Fineness (cm^2/g)			D$_{50}$ (µm)		
C1	3150			4322*			14.0		
C2	3120			4241*			17.0		
GGBS	2900			4700*			/		
MK	2500			187000**			11.5		
*Chemical compositions****									
	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	K_2O	NaO_2	SO_3	LoI
C1	20.4	4.9	2.3	64.0	1.6	0.9	0.2	3.5	0.9
C2	23.2	6.00	2.0	60.6	2.8	0.8	0.2	2.6	0.7
GGBS	37.8	10.6	0.4	41.5	8.6	0.2	/	/	tr
MK	56.2	37.2	1.4	1.2	0.2	1.2	/	/	2.1

* Blaine Method, ** BET Method, *** % weight, LoI = Loss of Ignition, tr = trace.

[1] *In cement chemistry*: C=CaO, S=SiO_2, A=Al_2O_3, F=Fe_2O_3, H=H_2O

The flash metakaolin (MK) was obtained by using a rapid calcination of ground kaolin by the flash process. Table 1 presents the characteristics of the MK. It should be noted that the silicon dioxide/aluminium oxide ratio by mass (S/A) is very high (2.67) in comparison with the one usually observed for pure metakaolin (close to 2). This difference is explained by the high impurity content of the product (47% by weight, including 43% quartz). Flat and round particles are visible in scanning electron microscopy (SEM) observations, as shown in Figure 2. The flat particles are attributed to the intrinsic structure of clay (sheet structure), while the round particles occur due to the rapid calcination process, which transforms a crystallised, organised phase (kaolinite) into a disorganised phase (metakaolin) through crystal lattice failure.

Figure 2. SEM observations of (a) flat and (b) rounded particles of flash MK (×1000 – SEI)



a) b)

2.2 Compositions, mixing and placing procedure

The control mix (containing no flash MK) and all mixes containing flash MK are presented in Table 2. The cement replacement by flash MK is expressed as the mass fraction of cement in the control mix (12.5% and 25% replacement rates). For a given composition, a batch was prepared using a Controlab mixer with 2L maximum capacity. The mixing sequence complied with EN 196-1 *[1]*. Next, the mixture was placed in 4×4×16cm^3 molds using vibration (48Hz, 1.6g).

Table 2. Mix designs of one batch of mortar Mi (g)

Designation	C_i (C1,C2)	Flash MK	Sand	Water
M_i-0%	450.00	0.00	1350	225
M_i-12,5%	393.75	56.25	1350	225
M_i-25%	337.50	112.50	1350	225

2.3 Steam-cured maturation

Immediately after placing, the mortar prisms were exposed to a simulated steam curing cycle with a maximum temperature of 55°C and a total duration of 17.8 h. The test included 2.83 h of pre-setting at 30°C, followed by 2 h of heating at 10°C, with a temperature increase every hour up to 55°C, 12.5 h of exposure at 55°C, and a 2h cooling down period. This cycle corresponds to an average of different steam curing cycles practiced in a factory setting *[8]*. After de-moulding, the mortar and cement paste samples were exposed for long-term curing in water at room temperature (20°C ± 1°C).

2.4 Tests

The various binders (combination of clinker/GGBS/MK) are tested on steam cured mortars at the hardened state on mechanical and durability criterions.

Mechanical performances. At ages of 1, 7 and 28 days, flexural and compressive strength tests were performed strictly in accordance with European Standards *[1]*. For each composition, an average strength was calculated from three flexural measurements on 4×4×16cm^3 prisms and five compressive measurements on 4×4×8 cm^3 half prisms.

Durability indicators. Durability criteria such as water porosity, water absorption and oxygen permeability are described in the AFPC-AFREM recommendations *[9]*. Both tests were done at 35 days of age. For porosity (p_w), which is characterized by the global volume of void in the material, the mortar specimens (4-cm cubic specimens) were weighed in hydrostatic, humid and dry conditions (20°C) after void saturation. The water absorption test measures the mass increase due to water introduced by capillarity pore. With this test, absorption after 24h of immersion (Ab_{24h}) and sorptivity or absorption velocity (S) can be used to characterize the capillary pore network. Analysis of durability results (p_w, Ab_{24h} and S) is associated with Washburn's theory on impregnation dynamics *[10]*.

For the permeability test, oxygen gas was used as the permeating fluid because it does not interact with the cementitious matrix. Measurements were made with a constant head permeameter developed by Cembureau *[9]*. Permeability measurements were made on dried cylindrical samples (Ø30mm×15 mm) to avoid the influence of water content on the permeability coefficient. The apparent permeability coefficient was calculated at three pressure values: 0.10, 0.25 and 0.40 MPa. Results analysis (intrinsic permeability k_{int} and Klinkemberg coefficient β) is associated with the Klinkemberg theory on flow of percolating fluid in porous networks *[11]*.

3. Results and discussion

3.1 Mechanical considerations

Strength results of mortars at 1, 7 and 28 days are shown in Table 3.

Table 3. Results of flexural and compressive strength for the various steam cured mortars

	M1-0%	M1-12.5%	M1-25%	M2-0%	M2-12.5%	M2-25%
Flexural strength						
1 d	**5.60** (±043)	5.36 (±0.25)	5.72 (±0.39)	5.89 (±0.60)	4.97 (±0.21)	6.18 (±0.03)
7 d	**5.94** (±0.46)	5.89 (±0.35)	5.92 (±0.29)	6.08 (±0.26)	6.40 (±0.28)	7.32 (±0.49)
28 d	**7.56** (±0.05)	6.42 (±0.46)	6.60 (±0.39)	6.86 (±0.70)	6.87 (±0.30)	8.40 (±0.57)
Compressive strength						
1 d	**33.9** (±0.96)	27.5 (±0.75)	37.4 (±0.23)	38.4 (±1.02)	31.8 (±0.94)	35.5 (±0.47)
7 d	**38.4** (±1.15)	34.6 (±0.88)	40.1 (±0.69)	43.2 (±0.96)	37.5 (±1.06)	37.8 (±0.57)
28 d	**47.6** (±1.21)	42.5 (±1.41)	47.6 (±1.59)	51.8 (±1.58)	45.5 (±1.01)	47.0 (±0.94)

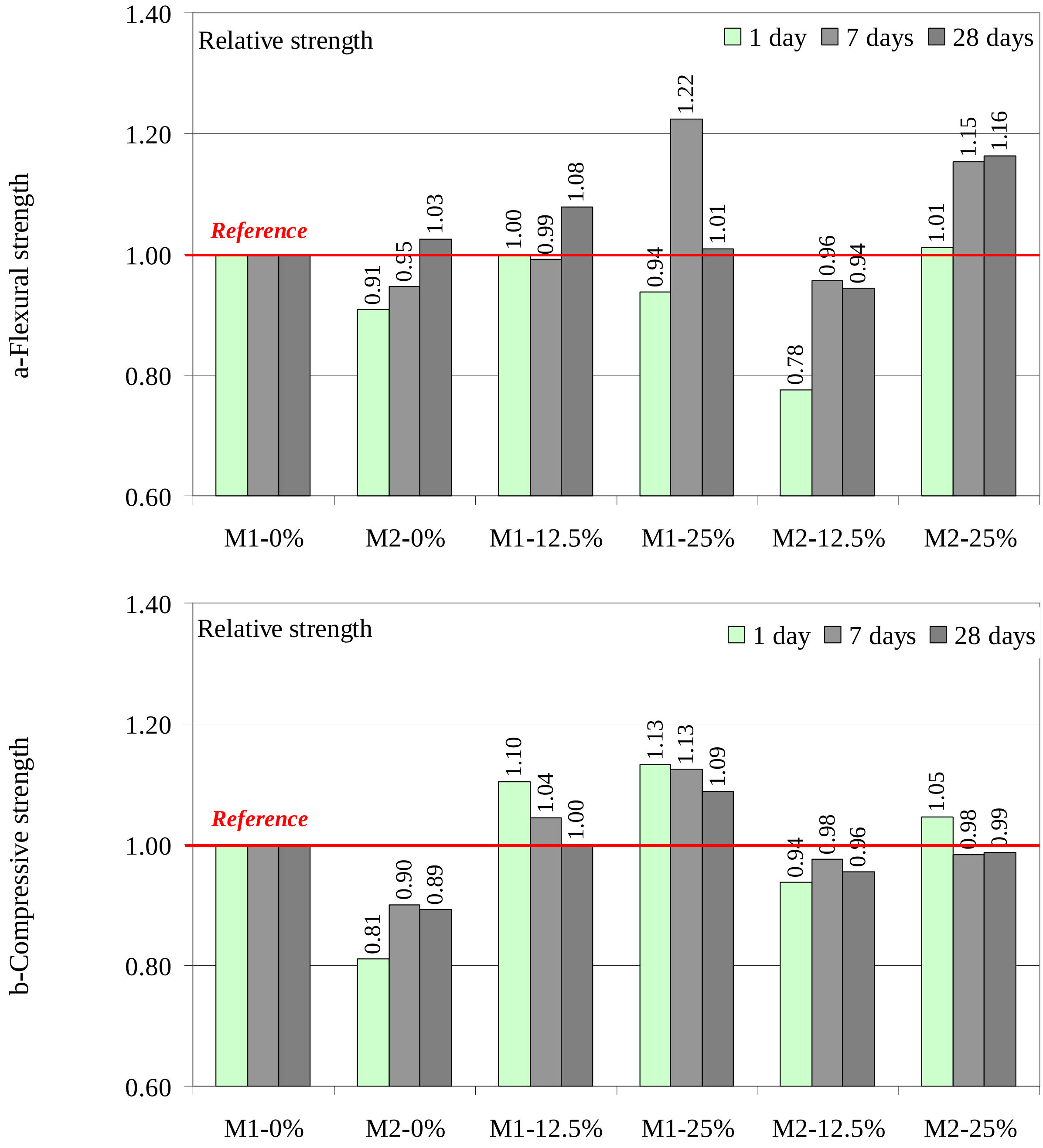
In order to easily assess the performance of any cement/MK combination, figure 3 shows strength relative to the reference strength. Eq. 2 introduces relative strength noted RSi (d). The reference strength values correspond to the average value of M1-0% (bold type in Table 3).

$$RSi(d) = \frac{Rci(d)}{Rc_{Reference}(d)} \quad \text{Eq.2}$$

RSi(d): relative strength of tested binder i in comparison with reference binder at d days
Rci(d): strength of tested binder i at d days (MPa)
$Rc_{Reference}(d)$: strength of reference blend at d days (MPa)

Figures 3 show flexural and compressive 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 3. Relative strength for various steam cured binders: a-Flexural b-Compressive



Flexural strength. Several observations and comments can be made about the flexural performance (a in Figure 3). Lower performance was observed for C2 than for C1 (comparison between M1-0% and M2-0%). At early age and at 7 days, this level of performance can be explained by the clinker dilution by slag (18% replacement rate). Accordingly, C2 appears to be unsuitable for some precast applications. Nevertheless, in comparison with control mortars (M1-0% and M2-0%), performance was improved when flash MK was incorporated up to a substitution rate of 25%, regardless what cement was used. It is important to note that a better long-term performance was achieved in the case of a binary cement (comparison between reference strength and M2-25%, cement C2). Hence, it is possible to substitute up to 25% of cement with flash MK in steam-cured materials and obtain mechanical properties that are very similar (1 day) or significantly higher than the reference samples (28 days). In terms of flexural considerations, this promising result encourages the use of a ternary binder (cement + slag + flash MK) as a component of concrete mix designs for the precast industry.

Compressive strength. In regards to compressive performance (b in Figure 3), several observations and comments can be made. First, in the case of CEM I cements (C1), compressive strength increases with the increase in MK substitution rate. However, in the near future, cement containing large amounts of clinker like CEM I will progressively disappear in order to limit CO_2 emissions. Second, when compared to C1 (CEM I types), the binary cement C2 presents the weakest characteristics at all ages (see compressive strength or relative strength results of corresponding standardized mortars M1-0% and M2-0% in Table 3 or in Figure 3). 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 (1 day) and in the long term (28 days). Conversely, when a part of C2 is replaced with flash MK, the reactivity of the resulting binder is significantly improved at 1 day and 28 days. These observations are accurate for 12.5% and 25% substitution rate. In terms of compressive strength, binary cement (C2), a less reactive cement than CEM I cement (C1), could be a promising product when partially replaced with flash MK. When compared with CEM I cements in steam-cured conditions, replacing 25% by mass of a CEM II with flash MK saves 40% of clinker, yields improved mechanical performance at early ages, and has similar mechanical performances in the long term.

3.2 Durability considerations

Porosity, absorption and permeability are the primary parameters for characterizing durability properties. Table 4 presents the results of durability indicators like water porosity (p_w), water absorption after 24 hours of immersion (Ab_{24h}) and sorptivity (S) traducing the absorption velocity, intrinsic oxygen permeability (k_{int}) and Klinkemberg coefficient (β).

Table 4. Durability indicators *[9]*

Designation	M1-0%	M1-12.5%	M1-25%	M2-0%	M2-12.5%	M2-25%
Water porosity						
p_w (%)	16.3±0.12	15.7±0.35	17.6±0.09	17.7±0.19	17.4±0.11	17.9±0.23
Absorption test						
Ab_{24h} (kg/m^2)	3.90	4.49	5.12	4.29	6.64	4.90
Sorptivity S (kg.m^2/√h)	0.88	0.99	1.17	0.90	1.39	0.99
Oxygen permeability						
Intrinsic perm. k_{int} (m^2)	8.4	62.6	24.8	11.6	27.4	14.1
Klinkemberg coef. β	0.45	0.26	0.83	0.29	0.27	0.25

Water porosity. Irrespective of the cement (C1 or C2), the porosity (p_w) of flash MK-based mortar in steam-cured conditions increases (M1-X% and M2-X%) in comparison with reference material made with CEM I only (M1-0%). The porosity increases with the increase in MK substitution ratio. The water porosity is slightly increased when flash MK is incorporated (+1.1 to 1.6%). The low variation of porosity values (from 15.7 to 17.9%) shows that the porous volume is not significantly modified.

Water absorption. The water absorption coefficient after 24h immersion (Ab_{24h}) is higher for the control mortar (M1-0%) than for mortars incorporating flash MK (Mi-X%). Furthermore, the sorptivity (S), which is relative to water absorption kinetics, is slower in the control mortar (M1-0%) than in the MK-based material. However, it is important to note that these different increases do not fundamentally affect the durability properties of mortars with flash MK. These variations can explain a change in the porous network with the increase of average pore size when flash MK is incorporated.

Oxygen permeability. Intrinsic permeability values (k_{int}) are equivalent for all the mortars studied. Indeed, they only begin to differ with a 10 or 100 factor. For the Klinkemberg coefficient (β), traducing the connectivity and tortuosity of porous network, permeability can be observed at a low evolution. It is well known that permeability is controlled by the percolation path resulting from the connectivity and tortuosity of the porous network. However, based on the measurements, there is no indication to show that pore connectivity and tortuosity have changed. It is only possible to conclude that the incorporation of MK does not significantly modify the oxygen permeability.

3.4 Environmental considerations

Environmentally speaking, flash MK is an interesting product. Table 5 presents the values concerning energy consumption and CO_2 release into the atmosphere. First, flash MK production releases less CO_2 into the atmosphere than cement production; global kaolin dehydroxylation reaction by the flash process does not produce CO_2 (Eq.1). The CO_2 release from MK production (1 ton of flash MK produced = 175 kg of CO_2) only comes from the process (extraction of raw materials, kiln, etc.) and not from the chemical reaction (dehydroxilation). In cement production, this release is due to the decarboxylation of $CaCO_3$ (clinkerization) and the process (1 ton of clinker produced = 1 ton of CO_2).

Second, during production, there is less thermal energy generated for flash MK than for clinker (1 ton of MK produced = 2.95 GJ, calculated from confidential data of an environmental impact assessment, and 1 ton of cement produced = 4.69GJ *[12]*).

Without factoring in the transport of raw materials, Table 5 presents the environmental impact of balance for the various precast concrete binders (C1, C2, flash MK combination) based on energy and CO_2 release. Regardless of the concrete application, replacing cement (C1 or C2) with flash metakaolin gives similar performances on mechanical and durability criteria (Figure 3 and tables 3 and 4), and has a positive effect on the environment because the manufacture of precast elements offers significant energy savings in terms of raw material production (-4.7% to -22.8%) and reduced CO_2 release (-10.3% to -34.1%).

Table 5. Environmental balance of 1 ton of binder based on energy and CO_2 release

Calculus hypothesis on raw materials

	Clinker *[12]*	GGBS *[13]*	MK *[14]*
CO_2 release (kg/t)	1000	0	175
Consumed energy (GJ/t)	4.69	0.00	2.95

Calculus for 1 ton of binder

	CO_2 release (kg/t)	Benefit*	Energetic consumption (GJ/t)	Benefit*
M1-0%	1000	/	4.69	/
M1-12.5%	897	-10.3%	4.47	-4.7%
M1-25%	794	-20.6%	4.26	-9.2%
M2-0%	820	-18.0%	3.85	-17.9%
M2-12.5%	739	-26.1%	3.73	-20.5%
M2-25%	659	-34.1%	3.62	-22.8%

* Benefit corresponding to the decrease of criteria compared with CEM I cement (i.e. M1-0%)

4. Conclusion

To ensure day-to-day profitability, the precast industry regularly employs CEM I 52.5R cement and thermal maturation (steam curing). Both approaches lead to good mechanical performance at early age (1 day) and in the long term (28 days). At present, environmental concerns are leading precast concrete producers to look for alternative solutions that will decrease the high clinker content in concrete design. This paper has investigated the effect of flash MK incorporation in binary cement (clinker + slag) on the mechanical properties (flexural and compressive) and durability properties (porosity, water absorption and oxygen permeability) of steam-cured mortars. The following conclusions can be drawn:

- From a mechanical point of view, the replacement of CEM I-52.5R cement by CEM II 52.5N / flash MK binder is possible. An increase in the substitution rate of flash MK shows equivalent flexural strength in comparison to the control mortar. In terms of compressive strength, when 25% of CEM II 52.5N is replaced by flash MK, strength is improved at early age and not affected at 28 days age, compared to the incorporation of CEM I 52.5R only.
- From a durability point of view, indicators such as water porosity, water absorption and gas permeability are maintained; a variation of the porous network is assumed when MK flash is incorporated into mortars.
- From an environmental perspective, saving up to 40% of clinker (with ternary binder) is a promising approach due to decreased energy consumption (-23%) and reduced CO_2 released into the atmosphere (-34%).

Although flash MK is not well-known, the performance levels of flash MK-based mortar are similar to those of the mortar containing no MK flash. Furthermore, the cement/slag/flash metakaolin combination is a low carbon dioxide/energy binder, currently of interest to cement makers. The results presented in this study are promising for precast concrete manufacturers who are concerned about preserving the environment.

5. References

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