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Cement substitution by a combination of metakaolin and limestone

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ABSTRACT

This study investigates the coupled substitution of metakaolin and limestone in Portland cement (PC). The mechanical properties were studied in mortars and the microstructural development in pastes by X-ray diffraction, thermogravimetry analysis, mercury intrusion porosimetry and isothermal calorimetry. We show that 45% of substitution by 30% of metakaolin and 15% of limestone gives better mechanical properties at 7 and 28 days than the 100% PC reference. Our results show that calcium carbonate reacts with alumina from the metakaolin, forming supplementary AFm phases and stabilizing ettringite. Using simple mass balance calculations derived from thermogravimetry results, we also present the thermodynamic simulation for the system, which agrees fairly well with the experimental observations.

It is shown that gypsum addition should be carefully balanced when using calcined clays because it considerably influences the early age strength by controlling the very rapid reaction of aluminates.

1. Introduction

Supplementary cementitious materials (SCM's) are now commonly used to reduce the clinker factor of cements. However above a threshold substitution of about 30%, these materials reduce the mechanical properties, particularly at early age. The availability of commonly used industrial by-products such as fly ash and blast-furnace slags is locally imbalanced and the amounts produced are much less than the worldwide production of cement. Consequently, alternative sources of SCM's such as calcined clays are of interest. Kaolinitic clays are widely available in the earth's crust, and a heat treatment between 600 and 800 °C of such clays leads to the dehydroxylation of the crystalline structure of kaolinite to give metakaolin [1,2]. Metakaolin demonstrates excellent pozzolanic properties [3–6]. The reactivity of metakaolin has been linked to its content of penta-coordinated aluminium ions that are formed during the dehydroxylation process [4,7,8].

Fine limestone is also commonly added to cement and it is established that limestone additions up to around 5% can react with cement and enhance most properties [9–11]. Calcium monocarboaluminate and hemicarboaluminate are formed instead of monosulfoaluminate, which leaves more sulfate to form ettringite. Damidot, et al. have also shown in a recent paper [12] with thermodynamic calculations that the increase in solid volume in a ternary blend cement-limestone–pozzolan when replacing limestone by pozzolan can be related to the reactive aluminous content of the pozzolan. In this sense, the use of metakaolin is interesting because of its high reactive aluminate content.

In this study we investigate the properties of blends with coupled additions of metakaolin and limestone, with the idea that the extra alumina provided by the metakaolin will react with more limestone, allowing good properties to be maintained to higher levels of substitution. There are already reports of such an approach for ternary PC limestone blends with blast furnace slag, fly ash and natural pozzolans [13–17], some improvement of mechanical properties and durability were observed at 28 or 90 days, but none of these studies explained the chemistry underlying these results. More recently De Weert et al. [18] and Moesgaard et al. [19] report a synergetic increase of the mechanical properties of fly ash and limestone to Portland cement and similarly for calcium aluminosilicate glass powder and limestone to Portland cement. They related this synergy to the formation of carboaluminates phases, they found hemicarboaluminate from early age that is progressively converted into monocarboaluminate after 90 days.

2. Experimental procedure

The stoichiometric formation of monocarboaluminate hydrate (MC) was considered: 1 mol of metakaolin reacts with 1 mol of calcium carbonate in the presence of excess calcium ions in aqueous solution to give 1 mol of MC (Eq. (1)). This corresponds to an addition with a weight ratio of 2:1 metakaolin:limestone.

$$A + C\bar{C} + 3CH + H \Rightarrow C_3A \cdot C\bar{C} \cdot H_{12} \quad \text{“monocarboaluminate”} \qquad (1)$$

A Portland cement (PC) containing only trace amounts of limestone was used. The limestone powder (LS) was Durcal 15 from Omya, Switzerland. Highly purity Optipozz metakaolin (MK) produced by

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Table 1
Chemical composition of the main components given by X-ray fluorescence, left part and crystalline composition by Rietveld of the cement, on the right.

Oxides	PC	"MK"	"LS"		
SiO_2	21.01	50.62	0.04	C_3S	62.1%
Al_2O_3	4.63	46.91	0.06	C_2S	15.2%
Fe_2O_3	2.60	0.38	0.05	C_3A cubic	3.9%
CaO	64.18	0.02	56.53	C_3A ortho	2.5%
MgO	1.82	0.09	0.10	C_4AF	6.2%
SO_3	2.78	0.08	/	Anhydrite	1.8%
Na_2O	0.20	0.28	0.04	Hemihydrate	2.3%
K_2O	0.94	0.18	0.04	Aphtitalite	0.5%
TiO_2	0.14	1.29	0.03	Syngenite	2.7%
Others	0.44	0.16	0.02	Periclase	0.5%
LOI	1.26	0.00	43.09	Dolomite	1.5%
Total	100.0	100.00	100.00	Calcite	0.5%
				Quartz	0.3%

flash calcination by Burgess (USA) was used. Details of their chemical composition, size distributions and Rietveld refinement composition normalized to the total crystalline content for OPC are given in Table 1 and Fig. 1.

The formulations investigated are given in Table 2. Mortars were cast at a water/binder ratio of 0.5 with standard sand according to EN-197-1 and pastes at a water/binder ratio of 0.4.[1] Coupled substitutions of MK and LS were made in the weight ratio 2:1.

The coupled substitutions – "blends" – were made at a total level of substitution of 15, 30, 45 and 60%. For comparison, substitutions of just limestone at 15% and just metakaolin at 30% were made; corresponding to the amounts of these materials in the 45% blend. Blends with quartz were made at levels of 15, 30, 45 and 60% to provide a comparison with inert filler. The workability was adjusted when necessary using Rheobuild 5500 superplasticizer (up to 3 wt.% of binder for pastes and 2 wt.% for mortars; at these dosages there was no significant impact on the hydration kinetics).

Flexural and compressive strength measurements were carried out on mortars at 1, 7, 28 and 90 days on 3 prisms of 120×40×40 mm and 6 prisms of 40×40 mm section respectively according to EN-197-1. Hydration of paste samples was stopped by immersion of ca. 5 mm thick slices for 7 days or more in isopropanol and further vacuum drying during at least 3 days. Thermogravimetric measurements on paste samples of about 40 mg of pieces crushed in an agate mortar were done with a Mettler-Toledo TGA/SDTA 851 balance using a 10 °C/min ramp from 30 °C to 900 °C under a 30 ml/min flow of N_2. Mercury intrusion porosimetry (MIP) data from mortars were obtained with POROTEC GmbH PASCAL 140 and PASCAL 440 instruments up to a maximum pressure of 400 MPa. X-ray diffraction (XRD) measurements were carried out on pastes with a PANalytical X'Pert Pro MPD diffractometer in a θ–θ configuration using CuKα source (λ = 1.54 Å) with a fixed divergence slit size of 0.5°. Samples were scanned on a rotating stage between 4 and 65 [°2θ] using an X'Celerator detector with a step size of 0.0167°2θ and a time per step of 30 s. Rietveld analysis was carried out on in-situ hydrating samples (pastes with water/binder ratio 0.4) covered with 25 μm Kapton foil and using the external standard method, with Rutile as standard reference.

3. Results

3.1. Mechanical strength

Compressive strength values are given in Fig. 2 and relative compressive strengths compared to PC and quartz references are given in Fig. 3. The 15% blend B15 has higher strength than the 100% PC reference at all ages. The other blends have lower strengths at 1 day, but the 30% and 45% blends show higher strength with respect to PC at 7 and 28 days. Even the 60% blend has 93% of the PC strength at 28 days (330% of the 60% reference with inert filler).

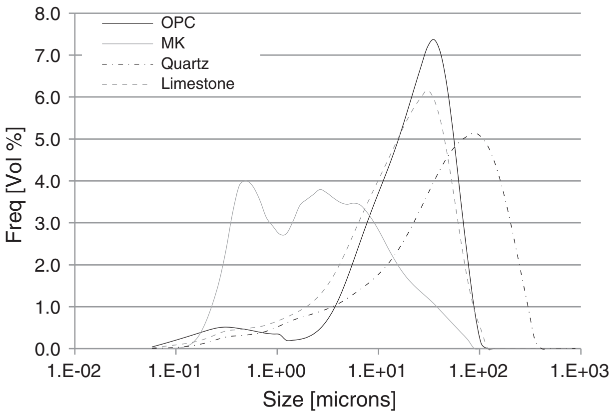

Fig. 1. Particle size distribution of the raw materials measured by laser granulometry.

Flexural strengths (not shown) globally follow the same trends as compressive strengths. All blends, including the 60% blend, show higher or similar bending strength with respect to the pure PC at 7, 28 and 90 days.

3.2. Characterization of pozzolanic reaction by thermogravimetric analysis

The evolution of calcium hydroxide for all blends and references is shown in Fig. 4. The tangent method was used to quantify portlandite from the dehydration peak between 450 and 600 °C and expressed per unit weight of original anhydrous cement as proposed by Marsh and Day [20]. There is no sign of any pozzolanic activity for the limestone blend (L15) and the quartz references. In fact all these samples show a higher amount of portlandite relative to the pure PC samples at the same age due to the so-called "filler" effect where the degree of reaction of the clinker phases is enhanced due to the extra space available for the hydrates [21]. The system with 30% metakaolin and all the blends of MK and LS, show significant reduction in the amount of calcium hydroxide even as early as 1 day. The higher the substitution rate, the stronger is the relative decrease in CH content. In the 60% blend there is nearly total consumption of CH after only 7 days, which might be expected to limit later strength development in this blend. It is also interesting to compare B45 with the MK30 blend containing the same amount of metakaolin. The B45 system shows much stronger consumption of calcium hydroxide after 1 day than MK30.

Fig. 5 shows the derivative of the mass loss as a function of temperature by TGA for all samples at 90 days. The total consumption of portlandite by pozzolanic reaction is confirmed for MK30, B45 and B60. With curing time, there is also a growing peak with maximum

Table 2
Formulations of the blends "B" as well as the quartz references "Ref".

	Cement [%]	Limestone [%]	Metakaolin [%]	Quartz [%]
PC	100	0	0	0
Ref15	85	0	0	15
Ref30	70	0	0	30
Ref45	55	0	0	45
Ref60	40	0	0	60
LS15	85	15	0	0
MK30	70	0	30	0
B15	85	5	10	0
B30	70	10	20	0
B45	55	15	30	0
B60	40	20	40	0

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[1] Due to the higher porosity in the interfacial transition zone around aggregate particles; a w/c ratio of 0.4 in paste is roughly equivalent to the paste phase of concrete with w/c = 0.5.

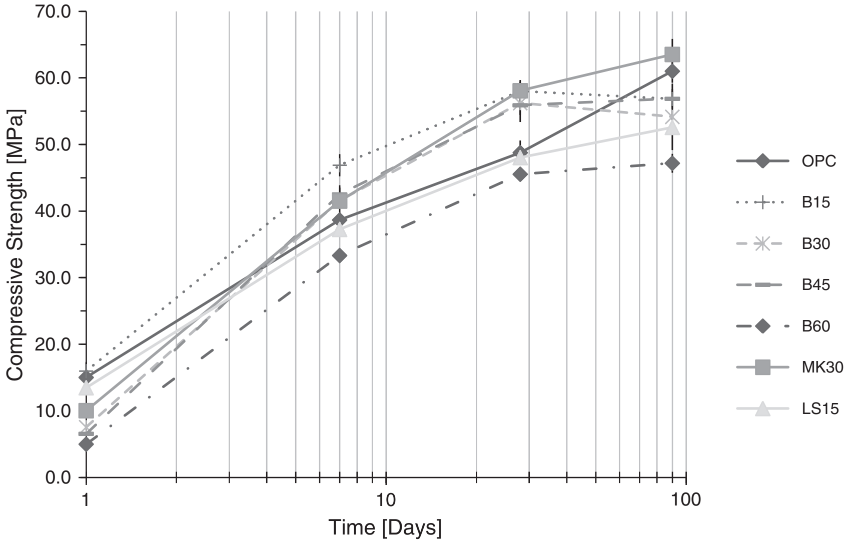

Fig. 2. Compressive strength of blends mortars at 1, 7, 28 and 90 days.

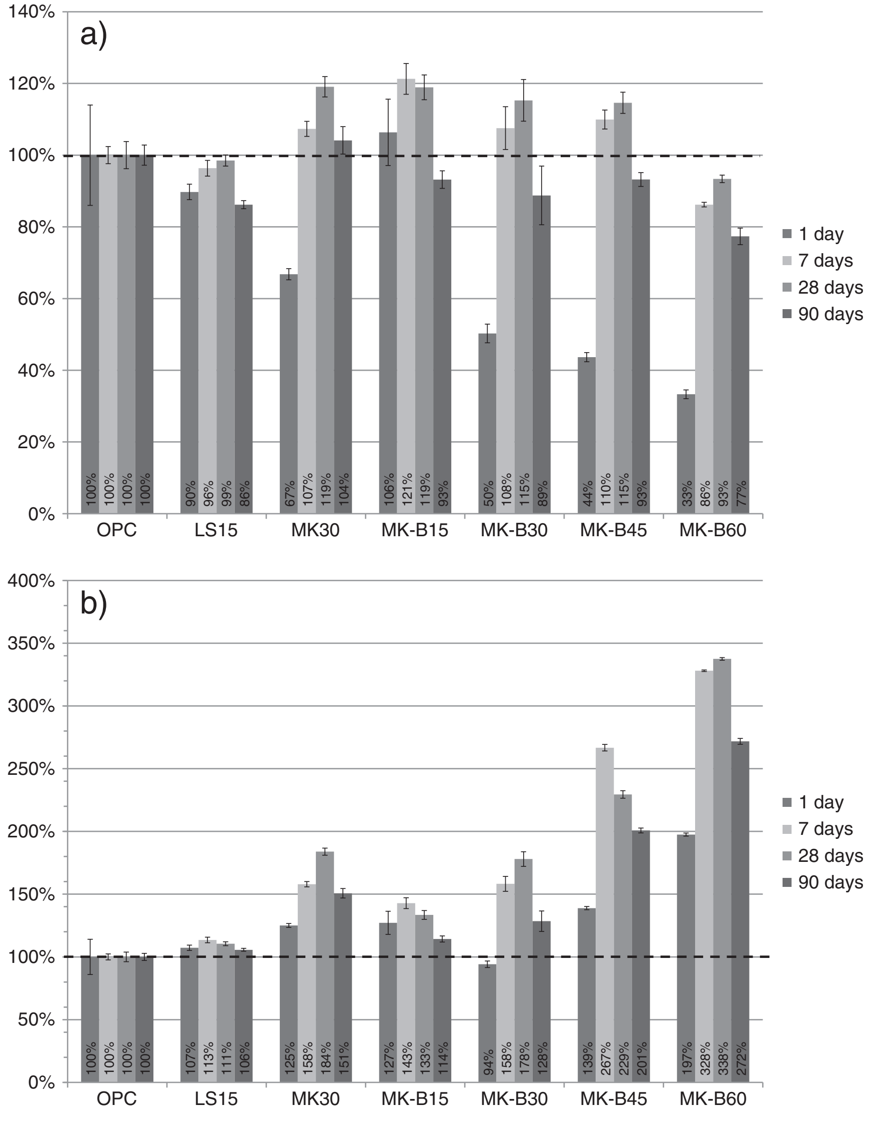

Fig. 3. a) and b): Compressive strength of blends normalized to the strength of pure PC (a) and to the quartz reference (b) mortars at 1, 7, 28 and 90 days.

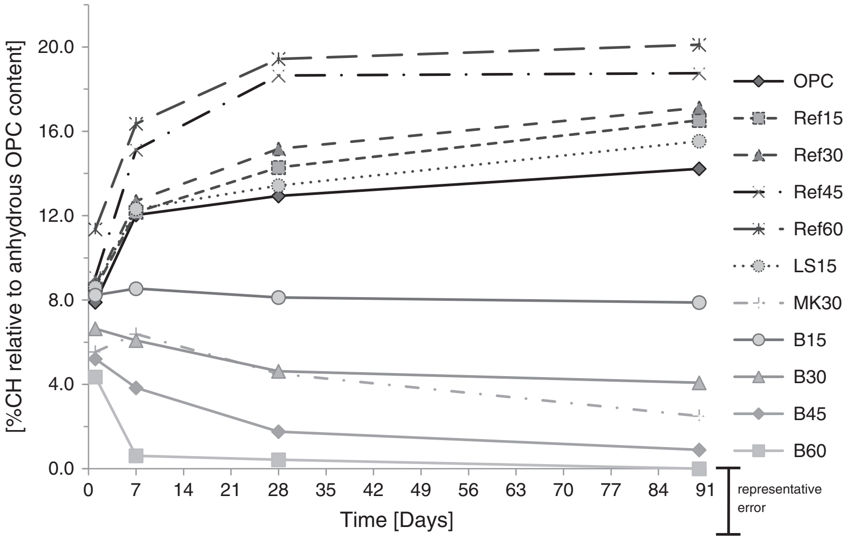

Fig. 4. Evolution of the CH content (determined from TGA mass loss) normalized to the PC content in the paste.

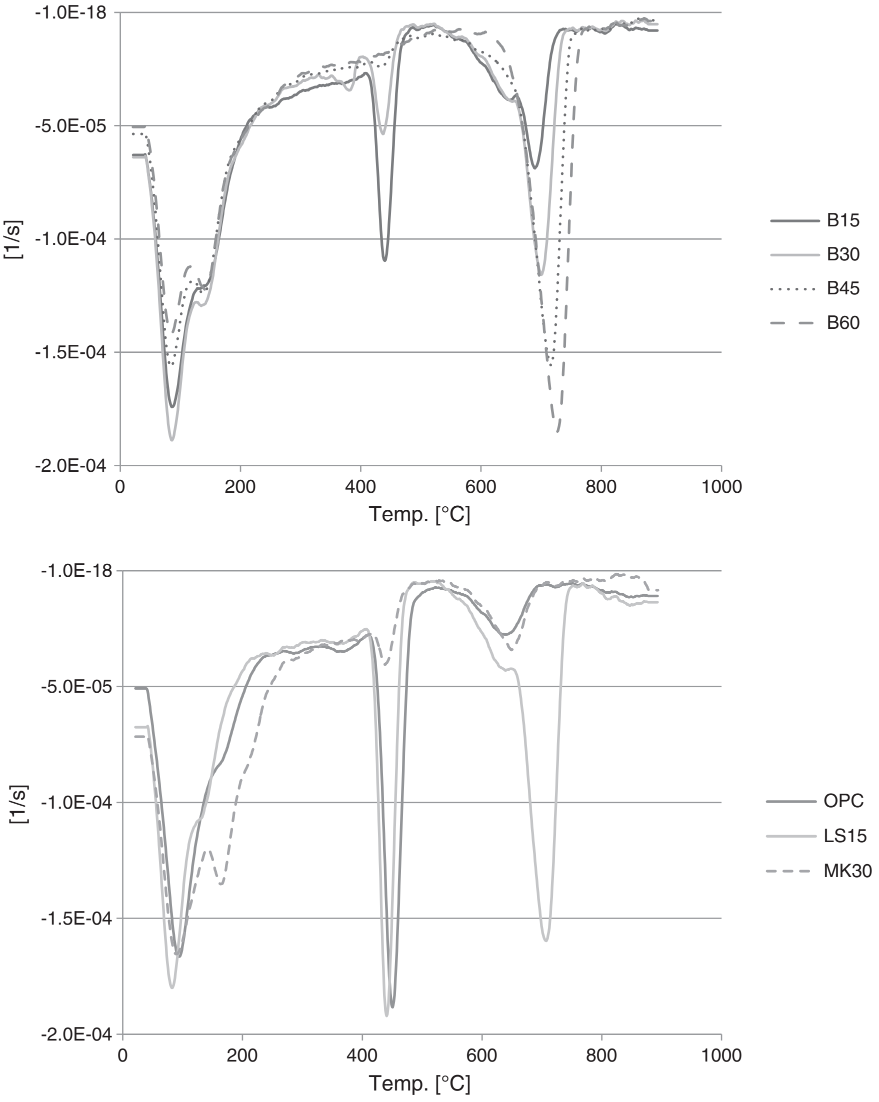

Fig. 5. Time derivative of the mass loss as a function of the increasing temperature obtained by TGA analysis of samples at 90 days.

around 140 °C for B45 and 180 °C for MK30 respectively. It is possible to assign these peaks to the presence of carboaluminates and strätlingite respectively. The peaks above 600 °C are due to decarbonation, mainly from the non-reacted calcite in the case of LS15 and the blends but also to some carbonation by atmospheric CO_2 as well as reaction of isopropanol with C–S–H, as reported by Beaudoin et al. [22].

3.3. X-ray diffraction

The XRD patterns (Fig. 6) for the PC system show the formation of ettringite, monosulfoaluminate and a growing quantity of portlandite. In the MK30 system (containing only metakaolin) there are ettringite and strätlingite at 7, 28 days and 90 days as well as monosulfoaluminate, along with less portlandite. The limestone-PC blend (LS15) shows the formation of hemicarboaluminate from 7 days and monocarboaluminate from 28 days instead of monosulfoaluminate. In the B45 blend, which contains 15% of LS and 30% of MK, the formation of ettringite is enhanced in a similar manner, but there is a larger and increasing amount of hemicarboaluminate from 1 day throughout the period of study.

XRD data show also the development of the main crystalline alumina containing hydrate phases for all the blends. In the pure PC the amount of monosulfoaluminate grows over time. Some appears in the blends at 1 day but later on disappears. With increasing blending there is the formation of increasing amounts of hemicarboaluminate and ettringite at all ages. Ettringite increases with time for all blends, but seems to level off around 7 days. Hemicarboaluminate increases with time, for B30 and B45, while for B15 and B60 it seems to plateau at 28 days (however, due to the possibility of preferential orientation for these phases, these trends are only qualitative). Monocarboaluminate only starts to increase significantly after 28 days in the LS15 system, in the blends there is a low amount of this phase even at 90 days. It is interesting to note the

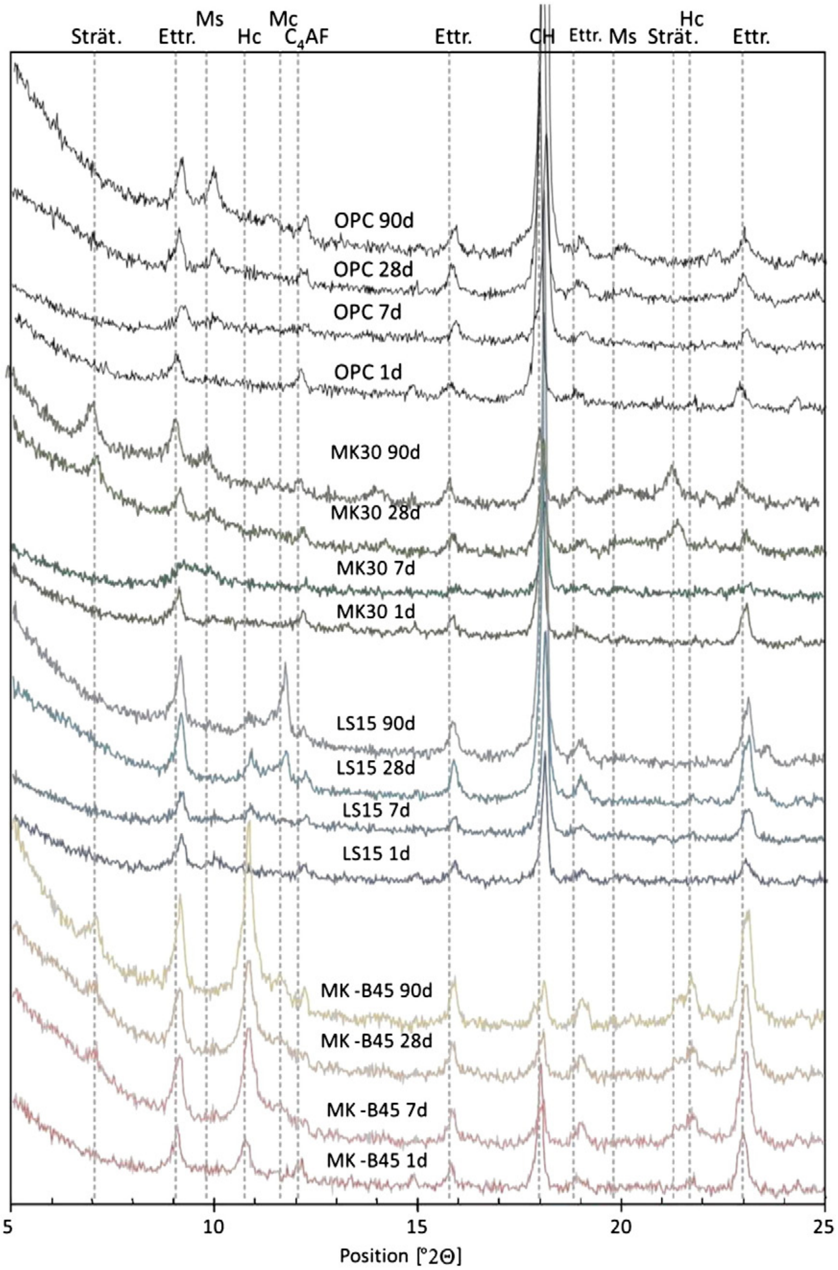

Fig. 6. XRD patterns for PC, MK30, LS15, and MK-B45 at 1, 7, 28 and 90 days. While in PC ettringite and monosulfoaluminate (Ms) hydrate form, MK addition leads to the formation of strätlingite (Strät) and reduction of the portlandite peak (CH). With limestone addition in both LS15 and blend systems, formation of hemicarboaluminate (Hc) and later on monocarboaluminate (Mc) are observed.

persistent presence of the metastable hemicarboaluminate, while a significant quantity of unreacted calcite remains in the blends. Strätlingite is detected in both MK30 and B45 from 28 to 7 days respectively.

3.4. Estimation of degree of reaction of MK by mass balance calculations

To estimate the degree of reaction of the metakaolin simplified mass balance calculations were made based on portlandite consumption by thermogravimetric analysis. For the metakaolin substituted sample, the difference between the portlandite present in the equivalent quartz reference (to take account of the filler effect) and the blend was considered to have reacted with metakaolin to produce C–A–S–H gel. For the blends, metakaolin was assumed to react with calcium carbonate and portlandite to form hemicarboaluminate AFm and C–A–S–H gel.

Fig. 8 shows the EDS microanalyses plotted as Al/Ca ratio against of Si/Ca (atomic %) ratio for B45 and OPC aged 300 days. due to the high level of intermixing with strätlingite, ettringite and metakaolin, it was difficult to determine the composition of the C–A–S–H gel for the calculations. This was taken as ($C_{1.67}A_{0.27}SiH_x$) as indicated in the figure The figure also indicates a shift in the composition of the C–S–H between the plain OPC system and the systems containing additions, similar to that widely observed in systems containing pozzolanic materials [21]. This indicates that some calcium for the reaction may come from the C–S–H. However, given the approximate nature of the calculation, the number of assumptions already made and the uncertainty of the EDS analyses, it was decided not to include this in the calculations.

The formula taken for the reaction of metakaolin (AS_2) is:

$$0.24C\overline{C} + 5.02CH + AS2 + (0.74 + 2x)H => 0.48C3A(C\overline{C})0.5H12 + 2C1.67A0.27SHx$$

The main error in this calculation (Table 3 and Fig. 9) is the fact that strätlingite formation was ignored. Strätlingite was observed by XRD in blends B30, B45, and B60 after 7 or 28 days and remained present even after 300 days. This means that the degree of reaction of the metakaolin is underestimated as strätlingite formation only consumes 3.7 mol of calcium hydroxide per mole of metakaolin as opposed to 5–6 mol for the formation of C–A–S–H and hemicarboaluminate. Other errors may be introduced by the fact that metakaolin has a finer particle size than the quartz filler, so the extra portlandite produced by filler effect may be underestimated, although the effect of filler size has been found to be minor after 3 days [23] and by the assumption that only hemicarboaluminate is formed, as monocarboaluminate consumes more calcite. Although a decrease in the peak from decomposition of calcite was also observed, this could not be quantified reliably, due to variations in the small degrees of carbonation of the pastes and the storage in isopropanol.

The mass balance calculations in Table 3 and Fig. 9 show the degree of reaction of metakaolin, increases with time, reaching a maximum value of 52% for B15 at 90 days. The degree of reaction increases with blending at 1 day but decreases at all later ages, although this is thought to be misleading due to the important amount of strätlingite formed in the blends with higher levels of substitution. The combined addition of limestone in B45 shows a similar degree of reaction of metakaolin to MK30 at 1 day, then enhanced metakaolin reactivity at 7 and 28 days. The MK30 and the blend have similar degrees of reaction at 90 days, when the strätlingite error is considered. The low degree of reaction in the B60 blend suggests a limitation to the reaction due to portlandite exhaustion.

3.5. Thermodynamic modelling

Thermodynamic modelling was carried out using the Gibbs free energy minimization programme GEMS [24]. The effect of increasing cement substitution by blending at the chosen 2:1 weight ratio metakaolin:limestone was studied. The C–S–H composition was amended to take account of the calcium to silica ratio and aluminium incorporation measured by EDS analysis as described above. Si-hydrogarnet, goethite and hematite were excluded because they do not precipitate for kinetic reasons at 20 °C. The exact chemical compositions of the raw materials used (Table 1) was taken as input in the GEMS program. The C–A–S–H gel molar volume in GEMS is taken from the work of Kulik et al. [25], the value does not include gel porosity and was not adjusted for the aluminium incorporation as there is no data available to account for it. The data are shown as volumes relative to the total volume considered (for 100 g of blend) to take account of the different densities of the components. The plot, Fig. 10a, assumes the degree of reaction of cement as 80%, and the degree of reaction of metakaolin and limestone calculated (Table 3). The phase assemblages agree qualitatively with the experimental observations, except for the absence of strätlingite which is not predicted to form in the thermodynamic calculation.

For comparison, a scenario is shown (Fig. 10b) where the degree of reaction of the cement is 100% and that of metakaolin is kept constant at 50%. Limestone is allowed to react freely. This version shows the

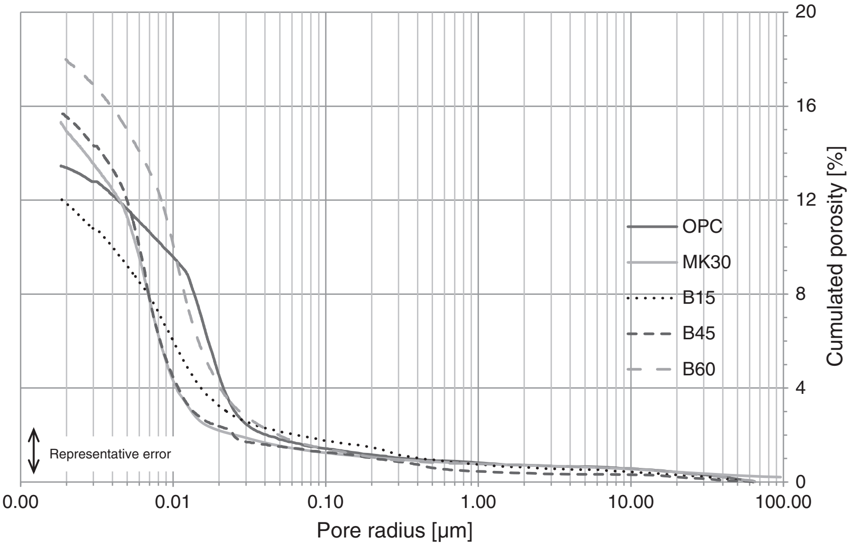

Fig. 7. Cumulated porosity as a function of pore entry radius at 28 days obtained by mercury intrusion porosimetry.

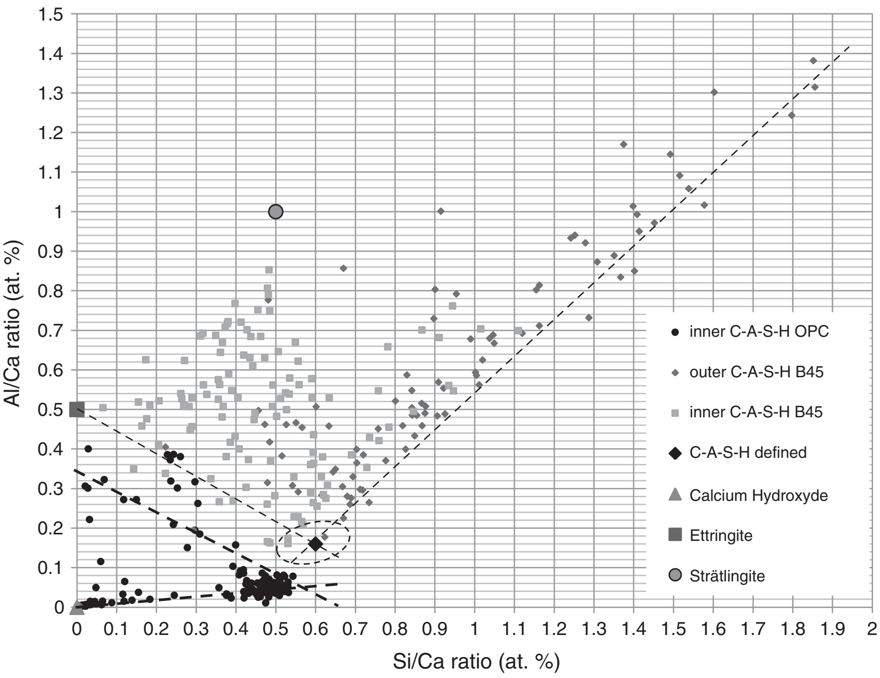

Fig. 8. Graphical treatment of EDS points analysis obtained on a B45 300 d old paste, Al/Ca ratio is plotted as a function of Si/Ca ratio (in atomic percentage). X-ray volume of interaction at the used acceleration voltage (15 kV) is about 1 μm, resulting in intermixing of C–A–S–H with ettringite, strätlingite and non-reacted metakaolin. The dotted lines join C–A–S–H with ettringite and with ettringite and form the lower limits in term of Al/Ca ratio of the cloud of measured points. The C–A–S–H composition in the blend lies within the dotted circle but cannot be precisely defined. The chosen C–A–S–H composition for mass balance calculations is represented. For comparison inner C–A–S–H of OPC is given, where intermixing with portlandite and AFm/AFt is observable.

appearance of strätlingite from 40% blending and the disappearance of portlandite above 30% blending. This suggests that the degree of reaction of the metakaolin may indeed be underestimated. This second version shows only monocarboaluminate in contrast to hemi and monocarboaluminate in the first graph.

Regarding the solid volume, in the first version (calculated degrees of reaction) this remains roughly constant up to about 20% blending and then decreases slowly to about 80% of the pure PC at 60 blending. In the second case (100% PC reaction, 50% MK) it increases up to 3% and then decreases to about 90% at 60% blending.

Fig. 15, shows the strength of the mortars at 90 days against the porosity calculated by GEMS. Although there is a general trend of decreasing strength with increasing porosity, the correlation for this small number of points is not strong and up to 45% level of blending there is almost no decrease in strength despite a significant increase in porosity. It must be noted, that the density used for the C–S–H in the GEMS calculations does not include gel porosity, which is

Table 3
The calculated reacted fractions of metakaolin (top) and calcium carbonate (bottom), based on the hypothesis of formation of hemicarboaluminate and C–A–S–H gel based on the portlandite consumption measured by thermogravimetry analysis.

Metakaolin reacted fraction					
	MK30	MK-B15	MK-B30	MK-B45	MK-B60
1	4.77%	0.99%	3.94%	4.05%	4.65%
7	9.31%	14.46%	16.89%	13.05%	9.43%
28	19.07%	33.80%	26.40%	21.02%	13.43%
90	26.05%	51.88%	34.74%	21.91%	13.94%

$CaCO_3$ reacted fraction				
	MK-B15	MK-B30	MK-B45	MK-B60
1	0.22%	0.85%	0.88%	1.01%
7	3.13%	3.65%	2.82%	2.04%
28	7.31%	5.71%	4.55%	2.91%
90	11.22%	7.51%	4.74%	3.01%

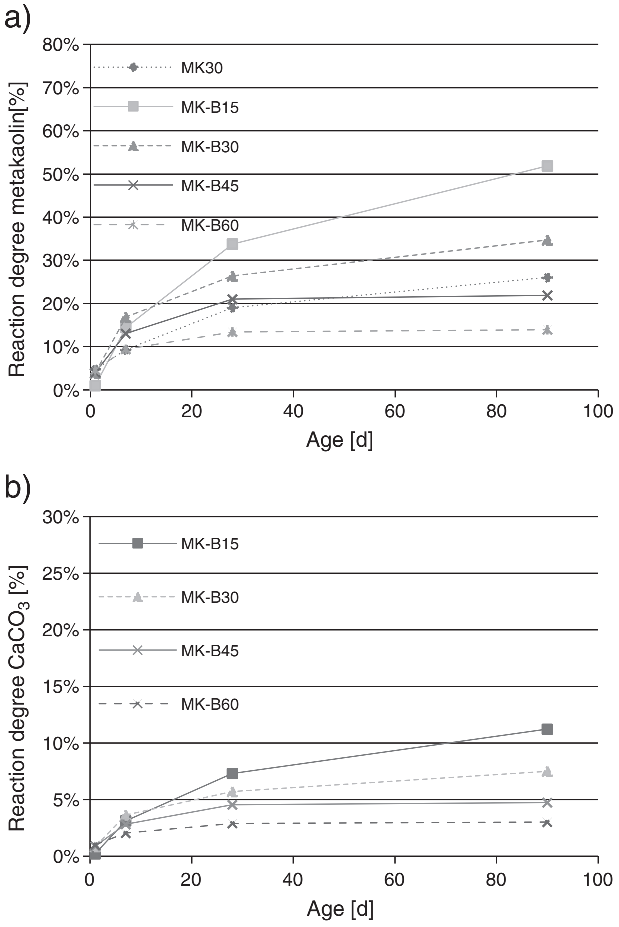

Fig. 9. Metakaolin (a) and limestone (b) reactivities calculated by mass balance.

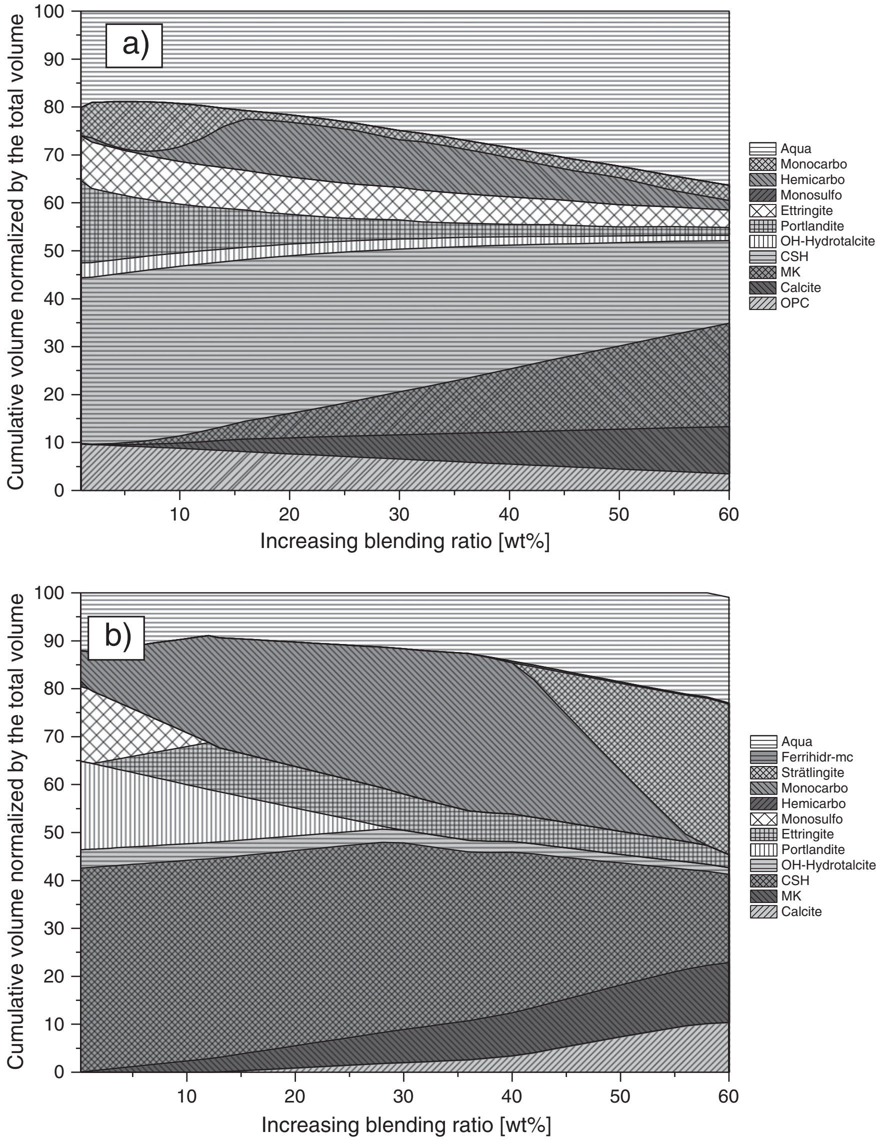

Fig. 10. a) and b): Thermodynamic simulations of the phase assemblage with increasing substitution of cement by our 2:1 metakaolin:limestone blend. The total cumulative volume of solid products is represented as a function of increasing blending percentage. In the first figure the reactivities of limestone and metakaolin obtained from mass balance calculations in the hypothesis of formation of hemicarboaluminate and real $C_{1.67}A_{0.27}SH_x$ are used, while in the second the limestone is let freely reacting and metakaolin fixed at 50% reactivity. PC was supposed to react at 80% in case a) and 100% in case b).

consequently included in the overall porosity, whereas such gel porosity is not usually considered detrimental to strength.

3.6. Porosity

The results of mercury intrusion porosimetry at 28 days are shown in Fig. 7. The total porosity is higher for all the blended systems with the exception of B15. However, there is a refinement of the pore microstructure for all the blended systems compared to the pure PC. These changes in pore size distribution probably also contribute to the lack of good correlation between strength and porosity calculated by GEMS discussed above.

3.7. Gypsum adjustment

Fig. 11 shows the early age isothermal calorimetry results for the blends, normalized with respect to the content of Portland cement. The same amount of plasticizer (2 wt.% of binder) was used in all blends. The slope of the acceleration period increases with the level of addition, suggesting that metakaolin provides extra nucleation sites for C–S–H [21]. The degree of reaction of the Portland cement component during the main peak is also enhanced by the dilution effect.

The use of such calcined clays with high surface area modifies significantly the reactivity of the aluminates phases. The higher the levels of metakaolin in the blend, the stronger and earlier is the aluminate peak corresponding to sulfate depletion. A small and broad shoulder peak is seen in the plain Portland cement with low C_3A content, corresponding to the second formation of ettringite [26,27], with a later peak even lower and broader associated to conversion of ettringite into monosulfate. Nevertheless in presence of metakaolin the first aluminate peak increases in intensity, is narrower and occurs earlier. The second "conversion" peak occurs much earlier in the B45 and is merged together with the first peak in the case of higher blending percentage. It is not yet clear how metakaolin contributes to this peak, it can be supposed that it provides a considerable amount of new surface for heterogeneous nucleation of hydrates. It was not possible to determine whether aluminates originating from the metakaolin also participate in the reaction at this stage.

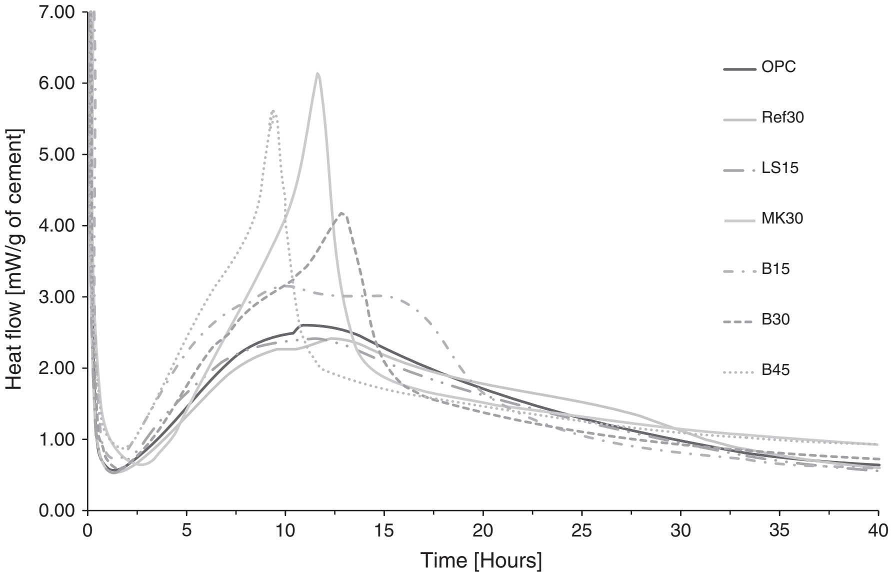

Fig. 11. Isothermal calorimetry curves of the blend pastes (water/binder ratio 0.4) until 40 h. The higher the cement replacement by the blend, the higher the secondary aluminates peak.

For the highest levels of addition the systems appear under sulfated, with the sulfate depletion occurring before the maximum of the peak of the main silicate reaction. Therefore we decided to investigate the impact of adding extra gypsum to the blends. The results of gypsum additions of 1.5 and 3% on the compressive strengths of the B45 blends are shown in Fig. 12 and calorimetry in Fig. 13. With increasing sulfate content the strength at 1 day is considerably improved with 1.5% addition (69% of the reference pure PC compared to 44% without addition) and then slightly decreased to 64% with 3% addition. In the latter case the aluminate peak is not completed by 24 h. At 7 and 28 days, compressive strengths are very similar across the range of gypsum additions.

In-situ XRD measurements with Rietveld refinement confirm the beneficial effect of 1.5 wt.% gypsum addition on the degree of reaction of C_3S at 1 day, which is increased from 47 without addition to 53%. The amount of ettringite also increases ((from 5.9% with no addition to 10.5% with gypsum addition), Fig. 14). For hemicarboaluminate, as there is no structural data available; a model phase derived from the unit cell parameters commonly accepted in the literature [28] has been used to estimate semi quantitatively its variation, which is plotted on a second axis.

The additions of gypsum will not lead to expansion as the total SO_3 content is still well below the threshold of 5 to 6% SO_3, commonly accepted in the literature for expansion [29].

4. Conclusions

This study shows coupled substitutions of metakaolin and limestone for Portland cement can give excellent performance at relatively early ages. Up to 45% of substitution a 2:1 blend of metakaolin and limestone yields better mechanical properties at 7 and 28 days than the 100% Portland cement reference. Even 60% substitution has 93% of the pure Portland reference strength at 28 days. The XRD results show that calcium carbonate reacts with the aluminates in the metakaolin, forming significant amounts of hemicarboaluminate and to a lesser extent monocarboaluminate from as early as 1 day.

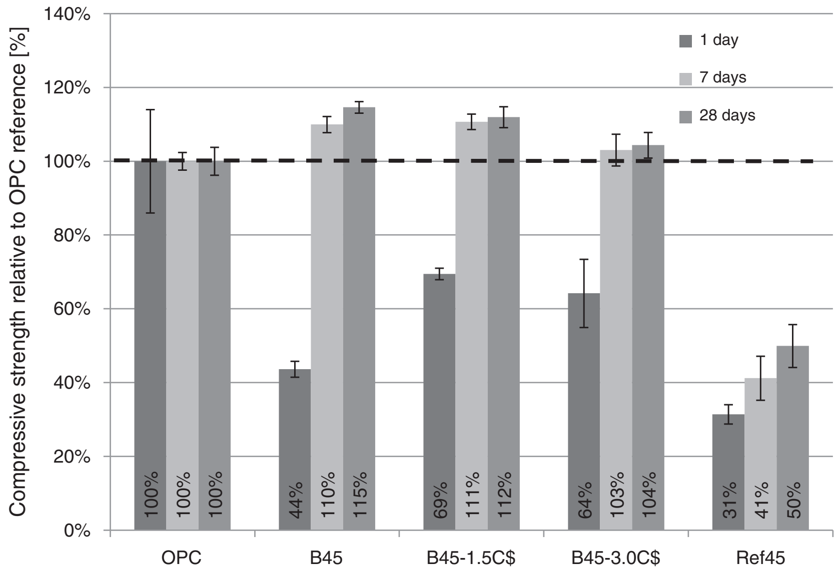

Fig. 12. Evolution of the mechanical strength of blend systems at 45% substitution as a function of the gypsum added at all ages.

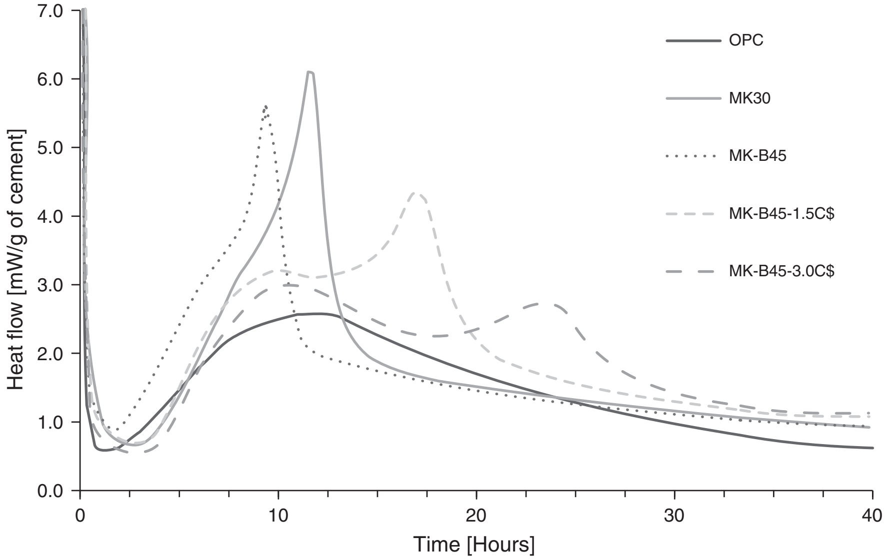

Fig. 13. Isothermal calorimetric curves plotted for blend systems at 45% substitution with different gypsum contents.

Thermodynamic simulations coupled with simplified mass balance generally supported the experimental observations of the phase assemblages formed.

TGA shows that the reactions of metakaolin and limestone consume calcium hydroxide, which may be completely absent in blends with high levels of substitution at late ages. The metakaolin appears

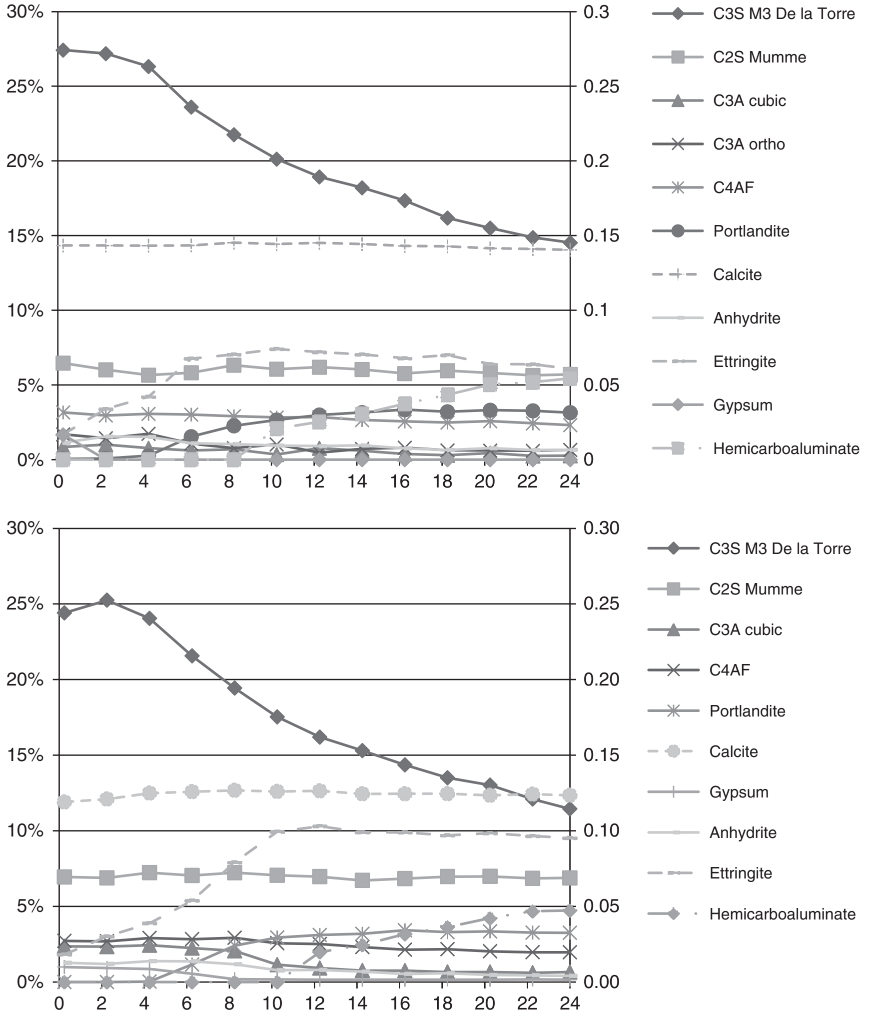

Fig. 14. Evolution of phases obtained by Rietveld refinement of in-situ XRD during the first 24 h of hydration for B45 (top) and B45 + 1.5 wt.% gypsum (bottom). Gypsum addition enhances C_3S hydration as well as ettringite formation.

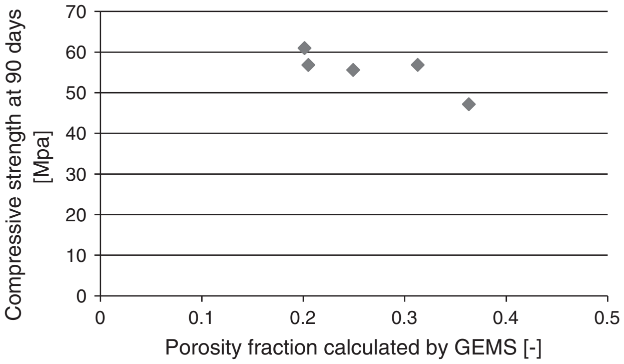

Fig. 15. Compressive strength at 90 days represented as a function of its corresponding porosity calculated by GEMS.

to react faster in the system with limestone than in the binary metakaolin/Portland cement blend. Also, the limestone reacts faster in the system with metakaolin than in the binary limestone/Portland cement blend. These results point to strong synergistic effects with coupled substitutions of this type. Of course the consumption of calcium hydroxide could mean that the high substitution level blends may carbonate more rapidly. This and other aspects of durability are currently being studied.

It was also shown that the level of sulfate addition has an important effect on the early strengths of the blends. In systems containing high volumes of fine calcined clays, the sulfate content must be adjusted in order to prevent undersulfation.

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