Cement & Concrete Composites 39 (2013) 93–103

Contents lists available at SciVerse ScienceDirect

Cement & Concrete Composites

journal homepage: www.elsevier.com/locate/cemconcomp

Hydration and strength development in ternary portland cement blends containing limestone and fly ash or metakaolin

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ARTICLE INFO

Article history:
Received 13 October 2012
Received in revised form 22 March 2013
Accepted 30 March 2013
Available online 8 April 2013

Keywords:
Limestone
Metakaolin
Fly ash
Isothermal calorimetry
Carboaluminates

ABSTRACT

This paper reports the influence of limestone particle size and the type of (partial) cement replacement material on hydration and the mechanical properties of cement pastes. Limestone powders having median particle sizes of 0.7, 3, and 15 μm, at OPC replacement levels between 0% and 20% (volume basis), and two other replacement materials of differing reactivity (i.e., Class F fly ash or metakaolin) at replacement levels between 0% and 10% (volume basis), are used to proportion ternary binder formulations. Fine limestone accelerates early-age hydration, resulting in comparable or better 1-day compressive strengths, and increased calcium hydroxide (CH) contents as compared to pure cement pastes. The incorporation of metakaolin in conjunction with limestone powder alters the heat release (i.e., kinetic) response significantly. A ternary blend of this nature, with 20% total cement replacement demonstrates the highest 1-day strength and lowest CH content. Thermal analysis reveals distinct peaks corresponding to the formation of the carboaluminate phases after 28 days in the limestone–metakaolin modified pastes, whereas the incorporation of similar levels of fly ash does not change the response markedly. It is shown that the synergistic effects of limestone and metakaolin incorporation results in improved properties at early ages, while maintaining later age properties similar to that of traditional OPC systems.

1. Introduction

The rapid rate of infrastructure development in many parts of the world has resulted in an enormous demand for portland cement. In order to reduce its environmental impact, both in terms of CO_2 emissions (5% of global output) [1,2] and energy consumption (4600 MJ/ton) [3] it is imperative that the clinker factor of cement be reduced. A number of strategies predominantly based on the use of high volumes of cement replacement materials such as fly ash and blast furnace slag have been practiced by the concrete industry to reduce cement use in concrete.

In recent years there has been increased interest in the use of limestone powder as a partial cement replacement material. Limestone has the advantages of being abundant, inexpensive, and without the environmental costs associated with portland cement. Portland limestone cements have been in extensive use in Europe and Canada since the 1990s. ASTM standards historically allowed only up to 5% limestone (mass basis) in cement, and it has been shown that such low replacement levels can result in comparable or better properties as compared to plain cements [4,5]. Recently ASTM C 595-12 has defined a Type IL cement that can include up to 15% of limestone powder as a cement replacement material [6].

The incorporation of limestone powder modifies the hydration process in low water-to-cement ratio (*w*/*c*) cement systems where a substantial fraction of the cement remains unhydrated [7,8]. The use of appropriate size ranges of limestone powder as a filler material has been reported to result in similar/better fresh properties in self-consolidating concretes, inspite of reduced cement contents [9]. The use of fine limestone powder (finer than OPC) provides nucleation sites and thus accelerates C_3S hydration [7,10,11], while participating to a limited extent in the cement hydration reactions [12]. For this reason, fine limestone powder has been used to limit delays in setting in high volume fly ash mixtures [13]. The use of limestone powder has been shown to slightly increase compressive strength [4], while contrary results have also been reported [5,14,15]. The likely cause of these discrepancies is the use of limestone powders of different fineness, the dosage of limestone powder, water-to-powder ratios, and the type/fineness of cement used. Fine fillers have been shown to decrease the capillary porosity of the paste, which may account for some of the strength gain reported [8]. It has been shown that by increasing the fineness of portland cement or decreasing the water-to-solids ratio (*w*/*s*), some of the strength loss associated with limestone additions can be mitigated [4,7,16].

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http://dx.doi.org/10.1016/j.cemconcomp.2013.03.028

Limestone powder has been shown to chemically interact with the aluminate phases in cement [17] to stabilize a carboaluminate phase at the expense of monosulfoaluminate [18]. This action can, within limits, increase the quantity of ettringite formed which leads to an increase in solid volume, and thus slightly improved mechanical properties. In pure C_3A systems, it has been shown that a significant portion of the carbonate will be consumed after 24 h [19]. In the case of OPC pastes, limestone is expected to react with the aluminous clinker phases [20], ensuring that, at low replacement levels (<5%, mass basis) much if not all of the calcite will be consumed through the course of hydration [18].

The synergy between fly ash and limestone powder has recently been elucidated [21] to show that composite cements containing a low amount of limestone powder (5%) and high amounts of fly ash (30%) perform similarly to a cement containing no limestone powder. However, a common issue with high levels of fly ash incorporation is the delay in setting observed in these systems [22–24]. The use of small amounts of a more reactive cement replacement material with appropriate chemical characteristics could facilitate the use of higher levels of limestone powder without attendant property loss. However, a systematic investigation of the effects of limestone fineness on the behavior of binders containing supplementary cementing materials (SCMs) is missing. This study develops a more detailed understanding of the influence of limestone fineness and additions on the behavior of ternary binder systems (i.e., cement + limestone + SCM), containing SCMs of differing chemical reactivity. As such, these investigations are focused on clarifying the role of limestone fineness and the type of cement replacement material (i.e., metakaolin or a Class F fly ash) on early- and later-age behavior to understand the possibility to proportion ternary binder formulations that display properties similar to traditional OPC systems.

2. Experimental program

2.1. Materials and mixture proportions

The materials used in this study include: a commercially available Type I/II ordinary portland cement (OPC) conforming to ASTM C 150, a Class F fly ash and metakaolin conforming to ASTM C 618, and limestone powder conforming to ASTM C 568. Limestone powders with three different nominal median particle sizes – 0.7 μm, 3 μm, and 15 μm were used. The particle size distributions of the cement, limestone, fly ash, and metakaolin are shown in Fig. 1 and their chemical composition in Table 1. Cement was replaced by volume percentages of limestone powder varying between 0% and 40% in increments of 10% (increments of 5%, up to a total replacement of 10% for the 0.7 μm limestone), and metakaolin and fly ash between 0% and 10% in increments of 5%. In the remainder of this paper, the percentages of limestone or other cement replacement materials reported are all on a volumetric basis, unless otherwise noted. The volumetric water-to-solids ratio $(w/s)_V$ used for the mixtures is 1.10; however since replacement was done by volume and all of the replacement materials are less dense than portland cement, the effective mass-based water to powder ratio of the blended mixtures varies between 0.35 and 0.38. Ternary blends comprising combinations of limestone and metakaolin or fly ash were also proportioned. Fly ash and metakaolin are used as OPC replacement materials because the aluminous nature of these materials favors the formation of the carboaluminate phases [18]. OPC replacement levels of up to 20% by limestone and up to 10% by fly ash or metakaolin were attempted. These selections were made to attain a 28-day compressive strength within 10% of the reference (i.e., plain cement) system. Overall, 42 different paste mixtures were proportioned and evaluated as part of this study.

2.2. Experimental methods

Isothermal calorimetry was carried out as per ASTM C 1702. The pastes were mixed externally as described in ASTM C305 prior to being loaded into the calorimeter. The time elapsed between the instant water was added to the powder(s) and the paste loaded into the calorimeter was approximately 2 min. Isothermal calorimetry was performed over a period of 48–72 h. The powders were dry-blended using a hand mixer at low speed prior to adding water.

Compressive strengths were determined in accordance with ASTM C109 on 50 mm cubes stored in saturated limewater until the age of testing. Simultaneous thermal analysis (thermogravimetric analysis (TGA) and differential thermal analysis (DTA)) was carried out on selected pastes at ages of 1, 7, and 28 days to determine the calcium hydroxide (CH) and calcium carbonate (CC) contents. The tests were carried out in a pure nitrogen environment, at a flow rate of 20 ml/s. A heating rate of 10 °C/min was employed and the pastes were heated from ambient to 950 °C. The non-evaporable water content (w_n) was calculated as

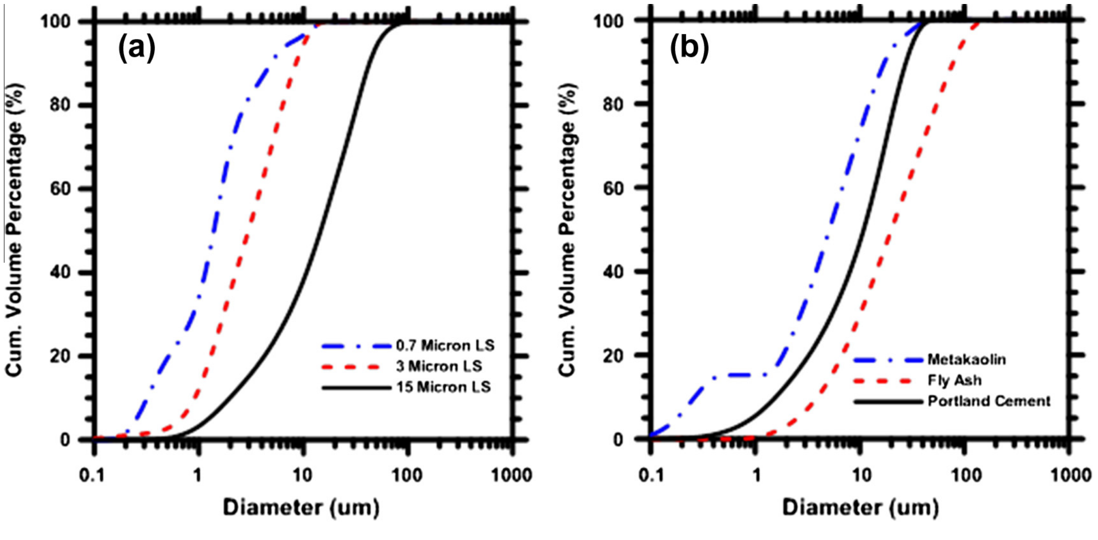

Fig. 1. Particle size distributions of: (a) limestone powders and (b) cement, fly ash, and metakaolin.

Table 1
Chemical composition of the component materials.

Component (%)	Cement	Fly ash	Metakaolin
SiO_2	21.0	58.4	51.7
Al_2O_3	3.61	23.8	43.2
Fe_2O_3	3.47	4.19	0.5
CaO	63.0	7.32	–
MgO	3.26	1.11	–
SO_3	3.04	0.44	–
Na_2O	0.16	1.43	–
K_2O	0.36	1.02	–
LOI	2.13	0.50	0.16

Limestone powder contains 95–97% $CaCO_3$ as per the manufacturer.

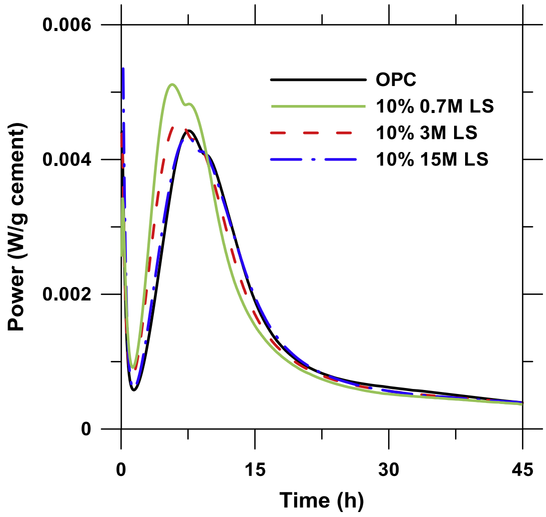

Fig. 2. Influence of limestone fineness on the heat release rate. Representative heat flow curves are shown. The uncertainty in the heat flow is less than 2% based on measurements on triplicate specimens.

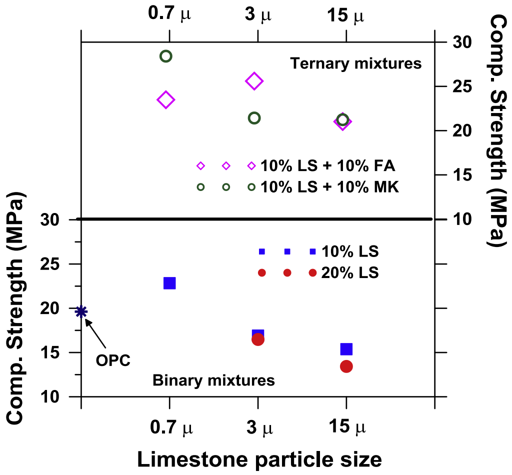

Fig. 3. 1-Day compressive strengths of binary and ternary blends of limestone and fly ash/metakaolin.

the difference between the mass measurements at 950 °C and 105 °C, normalized by the mass at 950 °C, and corrected for the loss on ignition of the cement powder (based on its mass fraction in the paste) and the calcium carbonate content (650–800 °). This value was found to be very similar to the mass fraction of the paste remaining after heating to 600 °C. The CH contents were determined based on the mass change measured between temperatures in the DTA curve corresponding to the CH peak [25].

3. Results and discussions

3.1. Early-age behavior of binary and ternary cementitious pastes

Isothermal calorimetry was carried out on binary and ternary paste blends containing several dosages of limestone powder of different particle sizes. The following sections provide insights into the influence of limestone fineness, dosage, and the synergistic effects of limestone powder and metakaolin or fly ash on the calorimetric response. The timing of the primary and secondary hydration peaks, their amplitudes, and the slopes of the acceleration and deceleration regimes are used to describe the influence of blend composition on the calorimetric response. Since a large set of mixtures is evaluated, a computer program was developed to extract these parameters from the calorimetric curves to expedite analysis. To keep the discussions succinct, the data reported is limited to OPC replacements levels of 10% and 20% by limestone and 10% by fly ash or metakaolin.

3.1.1. Effect of limestone fineness and dosage on the progress of reactions

Fig. 2 depicts the heat release curves of the plain cement paste as well as those modified using 10% limestone powder, for three different median particle sizes. It is immediately evident that finer limestone powders accelerate reactions; increasing the magnitude of the heat release peak and shifting the peaks to earlier times. For example, for the finest limestone powder, i.e., 0.7 μm, the main hydration peak is 15% higher than that of the OPC paste, it appears 25% sooner, and the slopes of the acceleration and deceleration regions are about 40% higher. The calorimetric response of the paste incorporating fine limestone also demonstrates a more pronounced shoulder on the main hydration peak. These effects are attributable to the limestone powder accelerating hydration [11,26] by enhancing the number of nucleation sites for the hydration products, as described in [27]. With increasing coarseness of limestone powder, the heat release curve begins to mimic that of the plain paste. The differences in surface areas of the particles has implications in their dissolution rates, which reflect in the changes in the heat release response as observed. The effects of limestone size-dependent acceleration are supported by 1-day compressive strength datasets (Fig. 3) which show that the mixture containing finer limestone powder has a higher 1 day strength than the OPC paste. Previous studies have reported that up to 5% limestone powder (by mass) can be used without compromising early age strength [11,14]. However, with increasing limestone coarseness and dosage, the compressive strength is noted to reduce due to effects including increasing porosity and a progressively reducing mineral acceleration effect.

The influence of limestone dosage for varying particle sizes on the calorimetric response is shown in Fig. 4a–c. For the 0.7 μm and 3 μm size powders, an increase in the limestone content is found to significantly influence early reactions, with a larger peak amplitude, earlier occurrence of the peak, and increase in the slope of the acceleration and deceleration regions being noted in comparison to the plain cement paste [28]. However, the calorimetric signatures are not substantially influenced by the presence of coarser limestone powders, irrespective of their contents in the paste. It is additionally noted that pastes proportioned at different water contents (dilution) to mimic water content increase with cement replacement show overlapping curves (Fig. 5). Notwithstanding the changes in *w*/*c*, the heat response curves are largely identical, suggesting that the reaction kinetics at early ages is largely a filler effect rather than an influence of a change in the effective *w*/*c* [10].

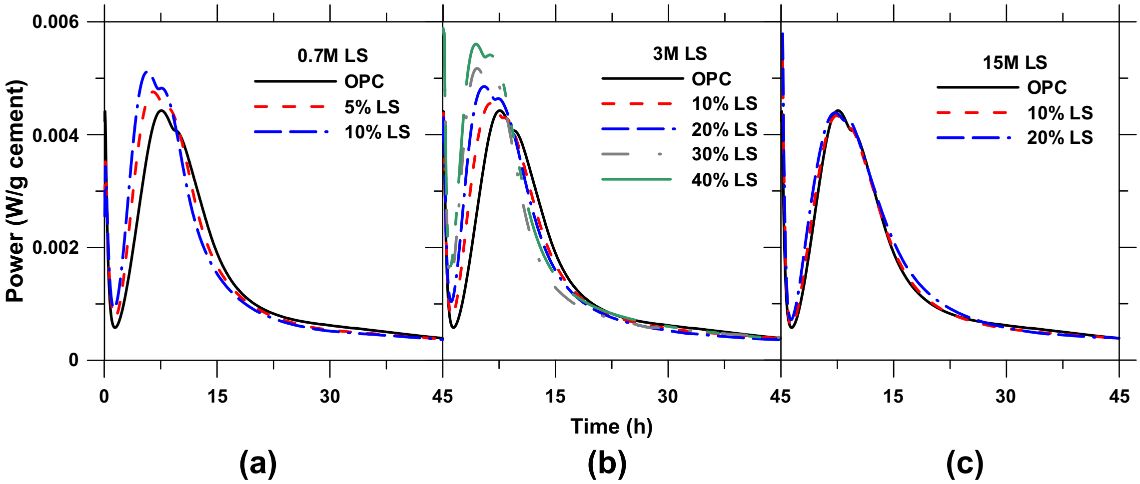

Fig. 4. Influence of limestone dosage on heat release rates for pastes containing: (a) 0.7 μm limestone powder, (b) 3 μm limestone powder, and (c) 15 μm limestone powder. Representative heat flow curves are shown. The uncertainty in the heat flow is less than 2% based on measurements on triplicate specimens.

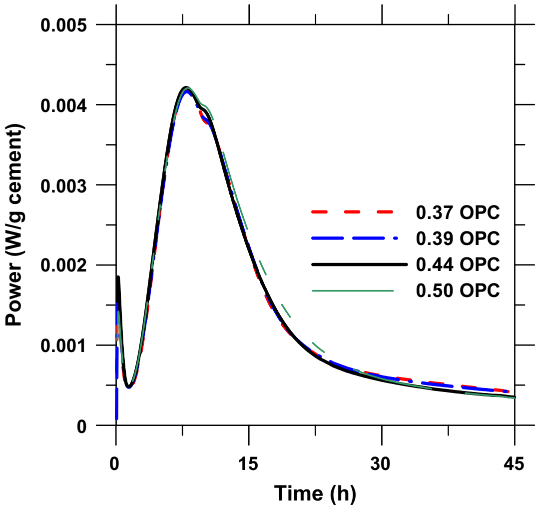

Fig. 5. Influence of *w*/*c* ratio on the calorimetric response of OPC pastes. Representative heat flow curves are shown. The uncertainty in the heat flow is less than 2% based on measurements on triplicate specimens.

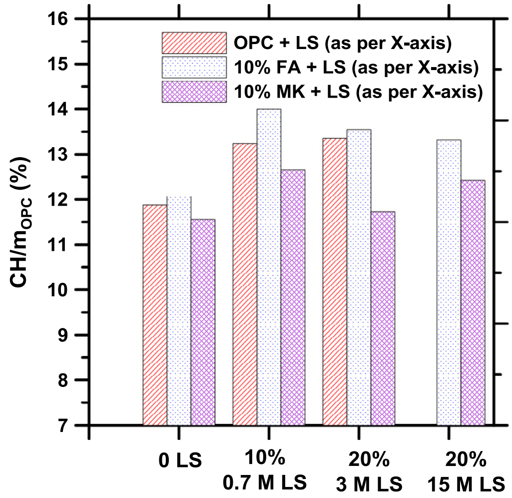

Fig. 6. 1 Day CH contents for selected binary and ternary pastes.

Fig. 6 shows 1-day CH contents of selected pastes normalized by the mass fraction of OPC in the pastes. The normalized 1-day CH contents are higher for the 0.7 μm and 3 μm limestone containing pastes, consistent with the acceleration effects noted in Fig. 4a and b. For the paste containing 15 μm limestone powder, the normalized CH is similar to that of the plain paste (not shown in graph) indicating no acceleration effects as supported by Fig. 4c.

3.1.2. Influence of fly ash and metakaolin replacements on the progress of reactions

It is instructive to examine the influence of aluminous cement replacement materials such as fly ash and metakaolin (bulk Al_2O_3 contents of 24% and 43% respectively, mass basis) on the early-age heat release response of pastes containing limestone powder. Fig. 7a and b shows heat release for binary pastes containing 5% or 10% of fly ash or metakaolin as the only cement replacement materials. The calorimetric response of fly ash modified pastes is very similar to that of the OPC paste (total heat released after 48 h of 233 J/g cement compared to 236 J/g for OPC). In this regard, fly ash performs similarly to the coarser limestone powder (15 μm). This is unsurprising, as the fly ash is not expected to react substantially at early times. However, in the presence of metakaolin, the amplitude of the peak and the slope of the curve during the acceleration region increases with an increase in the metakaolin content, similar to results reported in [29]. In addition, increasing the metakaolin dosage is also found to result in a more pronounced shoulder in the heat release response.

An analysis of the response of pastes containing fly ash or metakaolin requires considerations of their particle sizes and reactivity. Fly ash has a median particle size similar to the coarsest limestone powder whereas the median particle size of metakaolin is much smaller (5 μm). When the heat release parameters for the 10% metakaolin modified paste are compared to those of the OPC paste with 10% of 3 μm limestone powder, they are quite similar, demonstrating the influence of particle size. The peak amplitude is slightly higher for the metakaolin modified paste, but the peaks appear at virtually the same time. The normalized CH contents of the fly ash and metakaolin modified pastes are similar to that of the OPC paste at age of 1 day as observed from Fig. 6, suggesting that at early times, their hydration behavior is rather similar. For example, the 10% fly ash modified paste (7.5% by mass) produces a 7% reduction in the 1-day actual (unnormalized) CH content, whereas for the 10% metakaolin modified paste (7.9% by mass), the reduction in CH is about 11%. In other words, the reduction

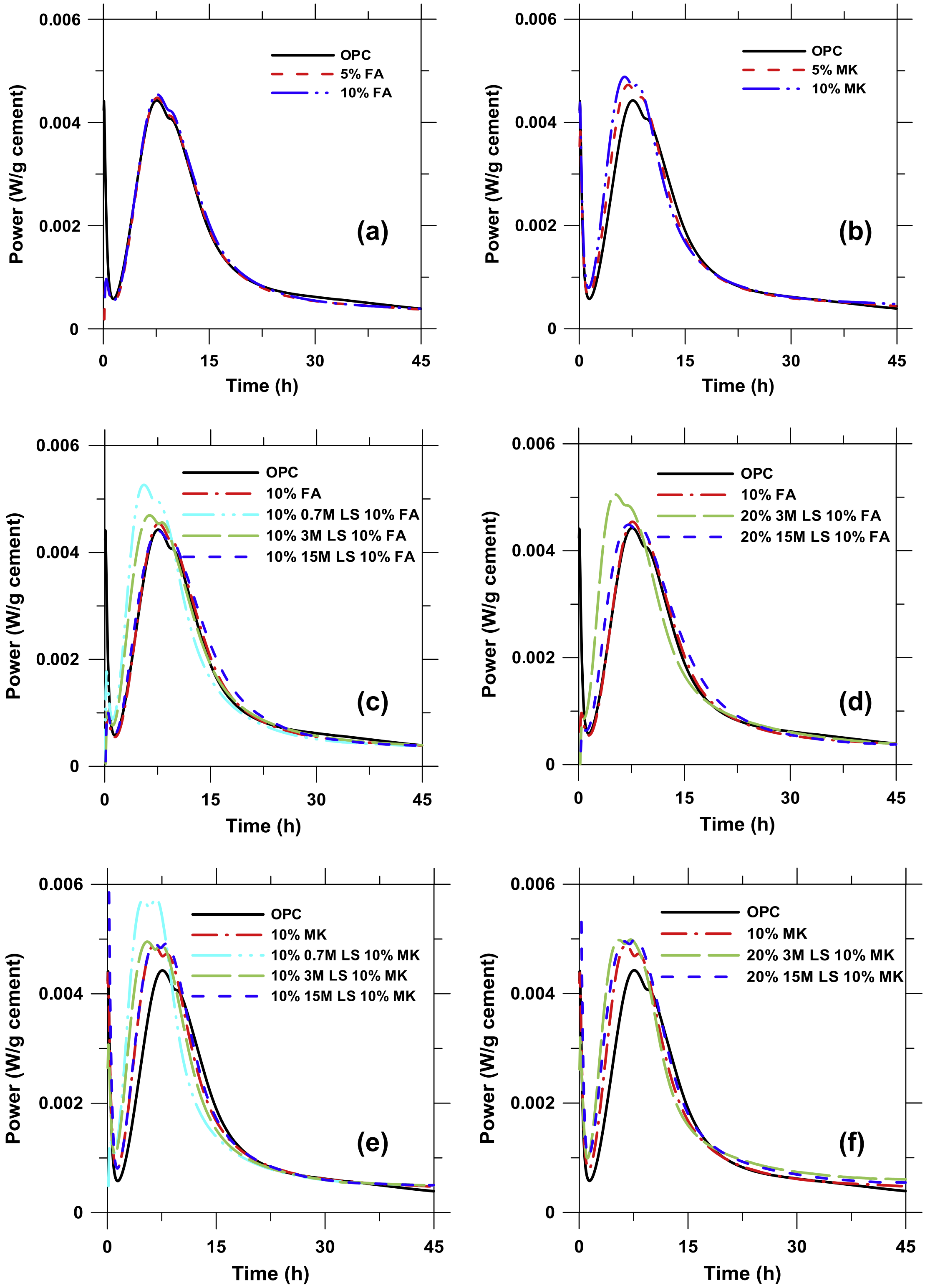

Fig. 7. Calorimetric response of: (a) fly ash modified pastes, (b) metakaolin modified pastes, (c) ternary mixtures of 10% limestone and 10% fly ash, (d) ternary mixtures of 20% limestone and 10% fly ash, (e) ternary mixtures of 10% limestone and 10% metakaolin, and (f) ternary mixtures of 20% limestone and 10% metakaolin. Representative heat flow curves are shown. The uncertainty in the heat flow is less than 2% based on measurements on triplicate specimens.

roughly scales with the OPC replacement level even though metakaolin incorporation results in a slightly higher reduction of CH. Fig. 7a and b shows that, while the incorporation of fly ash does not change the reaction kinetics considerably, the use of metakaolin results in an acceleration of reactions. This is likely due to the early age pozzolanic reactions and CH consumption in metakaolin blended pastes, which are expected to be more reactive than fly ash or silica fume modified pastes [30].

Table 2
Parameters of the calorimetric response for binary and ternary cement pastes.

OPC	FA	MK	LS	LS particle size (μm)	Main hydration peak				Slopes	
					Peak 1		Peak 2		Accel. (W/g h)	Decel. (W/g h)
					Time (h)	P (W/g)	Time (h)	P (W/g)		
100	0	0	0	–	7.5	0.0044	–	–	0.0009	−0.0005
90	0	0	10	0.7	5.7	0.0051	7.6	0.0048	0.0013	−0.0007
				3	6.4	0.0046	8.2	0.0043	0.0010	−0.0005
				15	7.4	0.0044	9.1	0.0041	0.0008	−0.0004
90	10	0	0	–	7.6	0.0046	–	–	0.0009	−0.0004
80	10	0	10	0.7	5.6	0.0053	7.4	0.0050	0.0014	−0.0007
				3	6.3	0.0047	8.1	0.0045	0.0010	−0.0005
				15	7.6	0.0044	9.4	0.0042	0.0009	−0.0004
90	0	10	0	–	6.4	0.0048	8.2	0.0047	0.0011	−0.0006
80	0	10	10	0.7	4.9	0.0057	6.7	0.0057	0.0017	−0.0009
				3	5.5	0.0050	7.4	0.0050	0.0012	−0.0005
				15	6.5	0.0049	8.0	0.0049	0.0011	−0.0006

3.1.3. Progress of reactions in fly ash/metakaolin containing limestone containing pastes

The calorimetric response of ternary blends containing up to 10% of fly ash or metakaolin with different particle sizes/dosages of limestone powder are discussed in this section. Fig. 7c and d represents the effects of a combination of limestone powder and fly ash on the heat release response of cement pastes. Fig. 7c depicts the calorimetric response of systems containing 10% of limestone and fly ash whereas Fig. 7d shows the response of the systems containing 20% limestone powder augmented with 10% fly ash. From both the figures, it can be noticed that the behavior of the ternary systems are different from those containing fly ash as the sole cement replacement material. When the response of the systems containing 10% fly ash and 10% limestone powder of varying sizes shown in Fig. 7c is compared to those containing 10% limestone powder alone (Fig. 2), it is noticed that the early age behavior of limestone powder modified pastes is not significantly modified by the presence of fly ash. To better facilitate these comparisons, Table 2 shows the parameters of the heat release curves of the plain, binary, and ternary mixtures. Comparing the 10% limestone powder modified pastes with and without fly ash, the time of appearance of the main hydration peak and the shoulder, the peak amplitudes, and the slopes of the acceleration and deceleration regions are found to be very similar. While it has been reported that small amounts of limestone powder have an influence on the reaction products and properties of OPC-fly ash blended systems [21,31], these are predominant at later ages as driven by the somewhat slow, time dependent dissolution of fly ash which releases aluminate species into the pore solution [32]. Increasing the limestone content of the ternary blends to 20% as shown in Fig. 7d results in a behavior fairly similar to that of the 20% limestone powder pastes without fly ash; although a small enhancement in the peak amplitude and slightly earlier appearances of the main hydration peak and the shoulder peak are noted.

For the pastes containing limestone powder along with 10% fly ash, Fig. 6 shows that increasing the limestone content increases the normalized CH content as expected. Expectedly, increasing coarseness of the limestone powder and increasing dosage reduces the normalized 1-day CH contents. However, it can be noticed that a further cement reduction of 10% through fly ash incorporation in limestone powder modified concretes does not result in a corresponding change in the normalized CH contents, suggesting that the addition of fly ash does not influence early age behavior. A comparison of the isothermal calorimetry results for limestone powder modified pastes with and without fly ash (Figs. 4 and 7c and d) also indicate that the benefits of low amounts of fly ash addition, in conjunction with limestone powder, up to 20% are not readily observed at early ages. This observation highlights the need to select a more reactive aluminous cement replacement material, metakaolin, to be used in limestone powder modified systems so as to induce changes in early age behavior.

Fig. 7e shows the heat release response of pastes containing 10% limestone and 10% metakaolin as (partial) cement replacement materials while Fig. 7f shows the response of pastes containing 20% limestone powder augmented with 10% metakaolin. The synergistic early age effects of small amounts of metakaolin in conjunction with 10% or 20% cement replacement by limestone powder are evident from these figures. For example: from Fig. 7e, it is noted that limestone powder in combination with metakaolin results in two distinct peaks (corresponding to C_3S and C_3A hydration) of similar magnitudes – indicating that aluminate hydration is potentially enhanced in the presence of metakaolin. These peak heights increase with decreasing median particle size of the limestone powder. The parameters of the heat release peaks of these ternary blends for a limestone replacement level of 10% are shown in Table 2. The acceleration in hydration reaction in the presence of finer limestone powder and metakaolin as compared to limestone alone can be quantified based on the time of appearance of the peaks and the peak amplitudes provided in Table 2. The fact that the secondary peak related to the aluminate reaction is equal in magnitude to the primary peak in the ternary metakaolin blends (note that when limestone or metakaolin alone is used as a cement replacement material – Figs. 4 and 7b – the primary and secondary peak amplitudes are different) suggests that the combination of finer limestone powder and metakaolin enhances the reaction kinetics at early ages in a more direct fashion than any other combination of binary or ternary blends evaluated here.

The normalized 1-day CH contents of metakaolin modified pastes are found to be consistently lower than those of pastes containing only limestone or limestone/fly ash as OPC replacement materials. The reaction of carbonate from limestone with Al from the OPC and metakaolin results in the formation of the mono/hemi-carboaluminate hydrates. Thermodynamic calculations suggest that the formation of the carboaluminates initiates as early as 1 day in limestone containing systems [11,31], a point confirmed by XRD [5,33]. The formation of carboaluminates (specifically, hemicarboaluminate) consumes CH [11,18,19]. While this action partly explains the reduced CH content observed in ternary blends containing metakaolin, an additional contribution of the pozzolanic action of metakaolin at ages as early as 1 day [30,34] may be another factor to consider.

3.2. Compressive strength development

The compressive strengths of plain, binary, and ternary cement paste blends up to 28 days of hydration are shown in Fig. 8. The

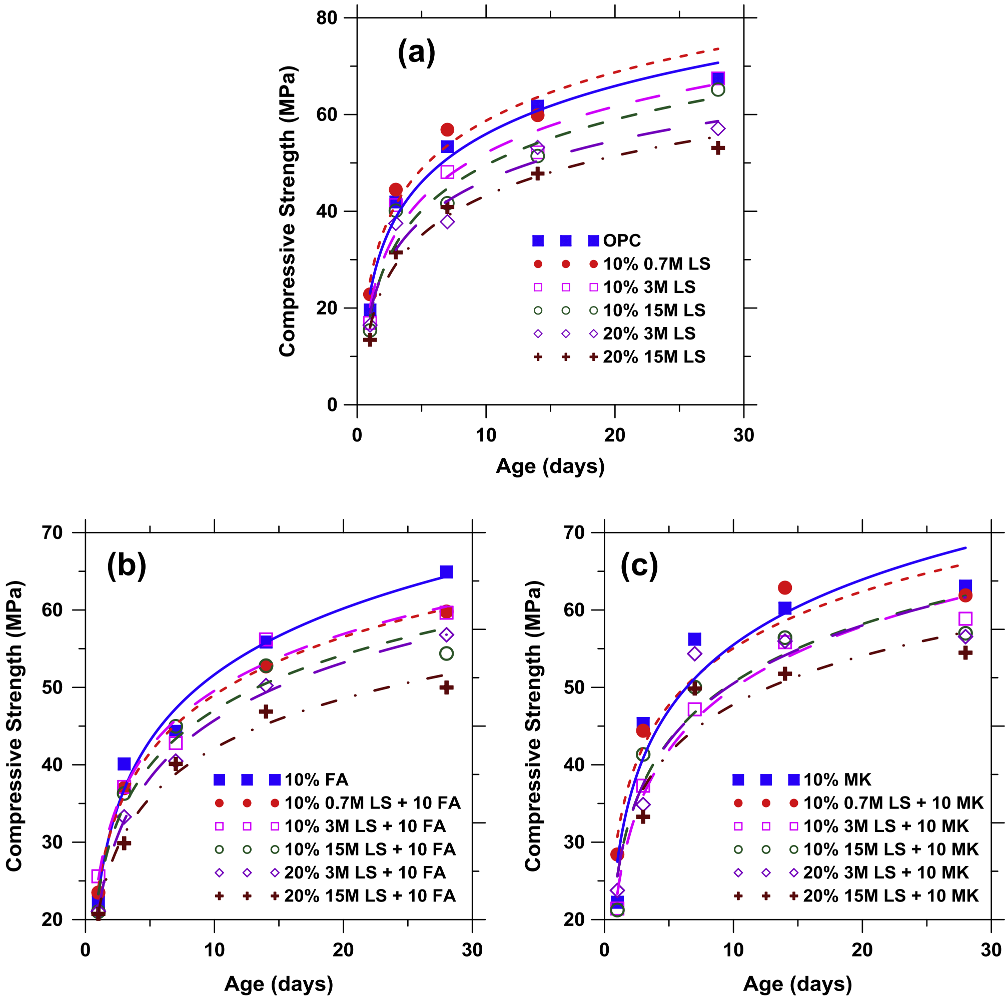

Fig. 8. Compressive strength development of: (a) OPC- limestone pastes, (b) OPC-limestone-fly ash pastes, and (c) OPC-limestone–metakaolin pastes. The standard deviation in compressive strengths ranged from 0.5 MPa at early ages to 4.5 MPa at later ages, but are not shown in the graphs to avoid cluttering.

compressive strengths for the OPC-limestone powder pastes are shown in Fig. 8a. The paste containing 10% of 0.7 μm limestone powder shows the highest strengths until 14 days of age, after which it shows strengths similar to that of the plain paste. The enhancement in cement hydration facilitated by the fine particles of limestone powder is responsible for this effect. Similar results are reported for limestone powder modified cement pastes in [4,5,31]. With increasing limestone content and median particle size, the compressive strengths at all ages are found to reduce, as expected. The reduction is not very prominent at early ages except for the higher replacement levels with the coarser limestone powder, due in part to mineral acceleration effects being able to partially compensate for the effects of OPC replacement. However, for the 15 μm limestone powder modified paste, a 20% replacement of cement by limestone powder results in a 21% strength loss at 28 days, attesting to the effects of OPC by coarse limestone powder on mechanical properties.

The compressive strength development of ternary blends containing fly ash or metakaolin along with limestone powder is provided in Fig. 8b and c respectively. The use of metakaolin with 10% of the finer limestone powder provides compressive strengths similar to or higher than that of 10% metakaolin modified cement pastes at the ages considered. Note that similar or higher strengths are achieved in this case even when the cement replacement level in the ternary blend is double that of the binary blend. However, for a similar paste in which fly ash is used, the compressive strengths are generally substantially lower than the 10% metakaolin modified paste – demonstrating the synergistic effects of the use of fine limestone powder with metakaolin. A comparison of Fig. 8b and c shows that for the same level of cement replacement with limestone powder of a given particle size, mixtures containing metakaolin have marginally higher strengths (of the order of 5%) at all ages than the plain paste. For a given total cement replacement level, the ternary blends (containing fly ash/metakaolin with limestone powder) demonstrate higher 28 day strengths than the corresponding OPC-limestone blends. This can be attributed to the combined effects of: (1) carboaluminate formation and ettringite stabilization and (2) the pozzolanic reactions, which would increase the solid volume of the hydrates and reduce the porosity in the system [11,19,35].

3.3. Thermal analysis of pastes: influence of limestone and fly ash/metakaolin

3.3.1. Analysis of TG and DTG curves

The discussions provided earlier suggest that fine limestone powder in combination with a small amount of metakaolin results in higher heat release and strength as compared to pastes composed with fine limestone and fly ash. Thermogravimetric (TG) and differential thermogravimetric (DTG) curves for the 1 day hydrated systems are provided in Fig. 9a. It is noted that the residual mass fraction at 600 °C is similar for the OPC paste and the 10%

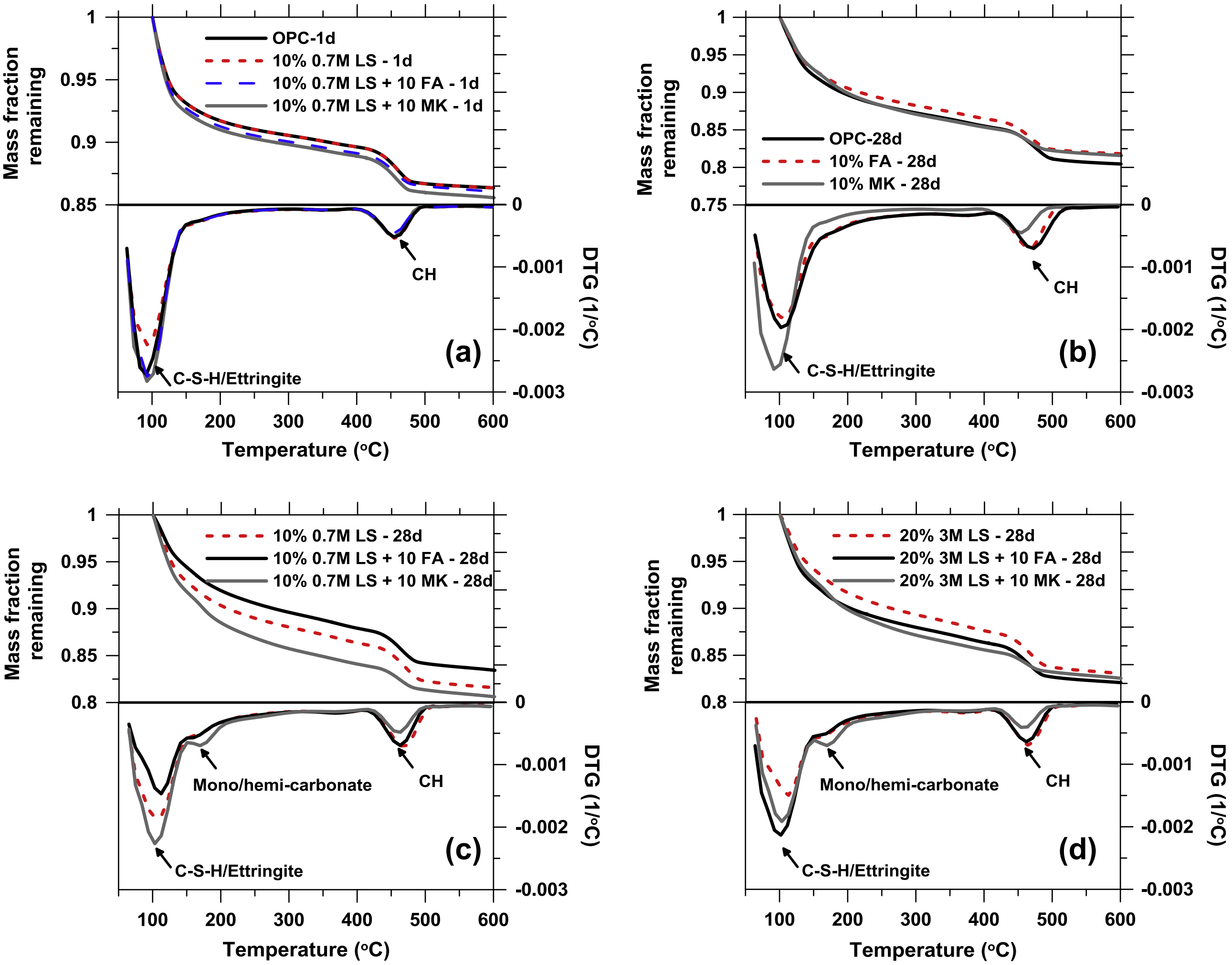

Fig. 9. TG and DTG curves of: (a) 1 day hydrated binary and ternary pastes containing limestone and fly ash/metakaolin, (b) 28 day hydrated pastes containing fly ash/metakaolin, (c) 28 day hydrated ternary blends with 10% 0.7 μm limestone, and (d) 28 day hydrated ternary blends with 20% 3 μm limestone. Representative data is shown. The uncertainty in the mass loss was less than 5% for duplicate measurements made at the same age.

0.7 μm limestone powder modified paste with and without fly ash, indicating similarities in their w_n contents. The w_n is the highest for the ternary blend with metakaolin, indicating the enhanced reactivity of metakaolin + limestone blends at early ages- as also supported by the strength gain response and normalized CH contents.

The peak at about 100 °C, linked to the decomposition of C–S–H and ettringite [21,31] is slightly higher for the ternary blend containing metakaolin, potentially suggesting increased amounts of C–S–H and/or the stabilization of ettringite in the presence of limestone. However, no monocarbonate is observed in the 1 day DTG curves, though slight (if any) formation is only expected at such early ages [5].

The TG and DTG curves of OPC, fly ash, and metakaolin modified pastes cured for 28 days are shown in Fig. 9b. The OPC and fly ash modified pastes show similar behavior at 28 days. The beneficial effects of metakaolin in terms of increasing the C–S–H content and decreasing the CH contents can be clearly seen in this figure. This figure provides context to the TG and DTG analysis of ternary blends shown in Fig. 9c and d. From the DTG curve of the ternary blend of 10% 0.7 μm limestone and metakaolin shown in Fig. 9c, a distinct peak around 180 °C corresponding to the carboaluminate phases [11,31] is observed. The formation of the carboaluminates, in conjunction with the pozzolanic reaction decreases the CH content even though the w_n (and hence anticipated CH production) is the highest among all the three pastes shown in this figure. The formation of carboaluminate phases can be quantified using the residual amounts of $CaCO_3$ in the pastes. Fig. 10 shows the residual mass fraction of $CaCO_3$ in the pastes hydrated for 1 and 28 days, obtained by dividing the mass fraction of $CaCO_3$ from TG analysis by the initial mass fraction of $CaCO_3$ in the paste. It can be readily noticed from this figure that the residual calcium carbonate content is lower for the limestone modified pastes containing metakaolin, confirming the increased consumption of limestone to form carboaluminate phases. For example, in the paste containing 10% 0.7 μm limestone by volume (8.7% by mass), 14% of all the limestone added (or 1.21% by mass of cement) reacts after 28 days. This value increases to 16% (1.4% by mass of cement) and 19% (1.65% by mass of cement) if the binder contains 10% of fly ash or metakaolin by volume respectively in addition to limestone. For the paste containing 20% 3 μm limestone by volume (17.4% by mass), 17% of all the limestone added (3% by mass of cement) is consumed after 28 days whereas this value increases to 17.2% (3.1% by mass of cement) and 18.2% (3.4% by mass of cement) in the presence of additional 10% fly ash or metakaolin by volume. The amounts of limestone reacted are in the general range reported in [20,36].

The TG and DTG results for a larger replacement level of cement with 3 μm limestone powder along with metakaolin or fly ash is shown in Fig. 9d, which also shows a DTG peak corresponding to

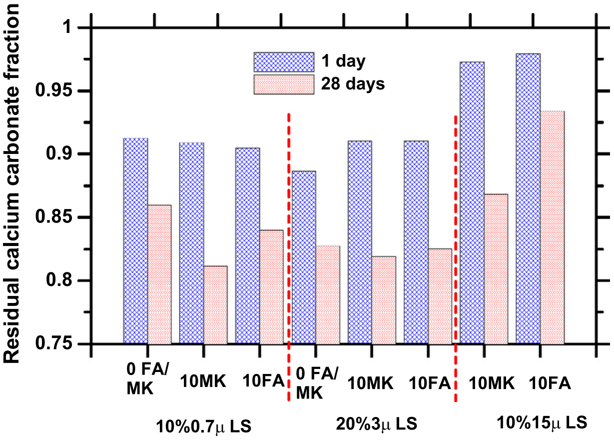

Fig. 10. Residual calcium carbonate contents in the limestone powder modified pastes after 1 and 28 days of hydration. The uncertainty in the residual CC fractions was in the range of 3–5% for duplicate samples tested at the same age.

the presence of carboaluminates. Note that even at higher limestone replacement levels, the intensity of the carboaluminate peak is relatively unchanged as compared to Fig. 9c. This qualitatively shows that a higher replacement level of the 3 μm size limestone powder is able to provide the same effect as a lower replacement level of the 0.7 μm limestone powder as far as carboaluminate formation is concerned. Fig. 10 confirms this observation where the residual carbonate contents in 10% 0.7 μm limestone powder and 20% 3 μm limestone powder are found to be similar. Such an effect was not noticed for the 15 μm size limestone powder as can be noted from Fig. 10.

For the limestone-fly ash ternary blends shown in Fig. 9c and d, only a very small peak is seen in the DTG curve corresponding to carboaluminate phases. In order to clearly distinguish between the effects of fly ash and metakaolin in limestone powder modified pastes, the heat flow corresponding to the thermal decomposition of the pastes is shown in Fig. 11. The thermal signature corresponding to carboaluminates is clearly observed in this figure, with a noticeable minor peak at around 180 °C for the OPC–limestone–metakaolin blend. The minor peak is similar in size and much smaller for the limestone powder modified pastes with and without fly ash, and for the OPC paste. The fly ash content in these pastes is only 10%, which proves insufficient to form a significant volume of carboaluminates. It has been shown in previous publications that a much higher cement replacement level with fly ash (30–35%), which in turn means higher amount of aluminates, coupled with small amounts of limestone (5%) result in a detectable peak in the DTG curves at around 180 °C [21,31]. It was also shown that higher amounts of fly ash in conjunction with smaller amounts of limestone powder can result in later-age (beyond 28 days) properties, comparable to OPC mixtures. However the disadvantage of using such high volumes of fly ash is the lack of early-age property development. In this study, it is shown that the combination of a reactive aluminate source with fine limestone powder can provide 1- and 28-day properties comparable to OPC mixtures for cement replacement levels of 20% (by volume).

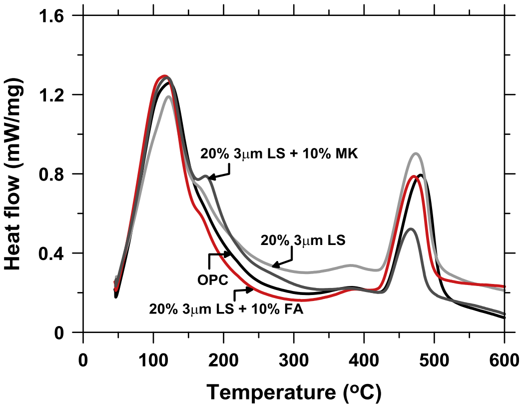

Fig. 11. Heat flow curves for the limestone modified pastes at 28 days of hydration.

3.3.2. Bound water and CH contents

If the total mass loss value at 600 °C (w_n) is assumed indicative of a reasonable measure of the volume of reaction products, then the increased reaction product volume (even at 20% less cement in the paste, and a reduced CH content) can be considered to be contributed by (i) accelerations in hydration facilitated by the filler effect of limestone powder, (ii) higher reactivity of metakaolin to form pozzolanic C–S–H, and (iii) the formation of carboaluminates through the reaction between the aluminates from metakaolin and carbonates from limestone powder. These effects compensate for the reduced cement content in ternary blend with metakaolin (and limestone) to enable a compressive strength similar to that of the OPC paste (Fig. 8).

The non-evaporable water contents (w_n) and the CH contents after 1, 7, and 28 days of hydration, normalized by the mass fractions of cement in the pastes are shown in Fig. 12a and b for selected binary and ternary blend pastes. For all the pastes considered, a major fraction of the water is bound in the first 7 days of hydration. The OPC paste has the lowest normalized w_n at all ages among all the binary pastes considered in Fig. 12a. The 10% 0.7 μm limestone powder and the 20% 3 μm limestone powder modified pastes show higher normalized w_n and normalized CH contents at 1 and 28 days, attesting to the effect of fineness and amount of limestone powder on accelerating cement hydration (Figs. 4 and 8). The 10% fly ash modified paste shows a higher normalized w_n than the OPC paste at 1 day, and similar w_n at later ages. The enhancement in reactivity of cement provided by metakaolin and its own reaction at early ages result in the metakaolin modified paste showing a higher normalized w_n than the OPC paste at all ages. It is also important to note from the lower panel of Fig. 12a that this paste has the lowest normalized CH content, with a significant lowering of CH contents at 28 days as compared to the other pastes. Higher w_n and lower CH contents are indicators of the effective pozzolanic reaction of metakaolin starting at very early ages. For all the other pastes, the CH contents follow trends similar to that of w_n. The normalized w_n and CH contents of the ternary blend pastes are shown in Fig. 12b. Immediately evident from this figure are the higher normalized w_n values for the ternary blends as compared to the binary blends shown in Fig. 12a. The paste with overall 30% cement replacement by volume (20% 3 μm limestone powder and 10% metakaolin or fly ash) show higher normalized w_n at later ages, closely followed by the metakaolin modified 10% 0.7 μm limestone powder paste. The normalized CH content of the limestone–metakaolin blends shown here reduces or remain fairly constant with age while the normalized w_n values for the corresponding pastes are seen to increase. For cement hydration, an increase in w_n generally means an increase in CH. The reduction in CH can be construed as an indication of the change in reaction products, i.e., due to pozzolanic reactions and the formation of the carboaluminate hydrates as shown in Fig. 9 through the TG and DTG curves. Evidence of reaction product modification at 28 days of hydration can be seen in both 0.7 μm and 3 μm size limestone powder pastes containing metakaolin. A total cement replacement of 20% (10% 0.7 μm limestone and 10% metakaolin) results in a much higher 1 day compressive strength and comparable 28 day compressive strength as compared to the OPC paste.

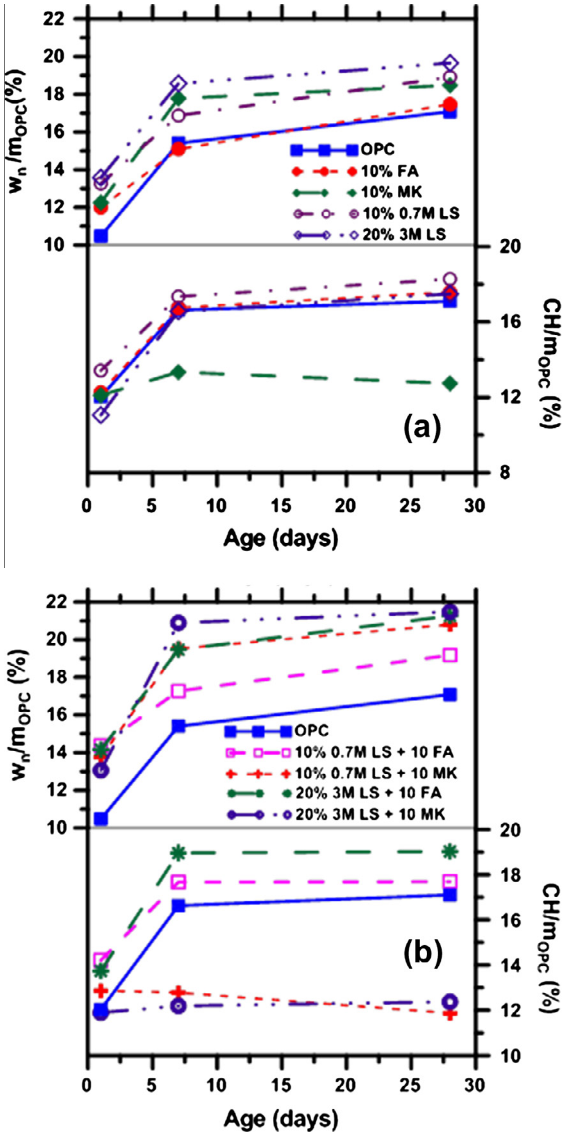

Fig. 12. Non-evaporable water and CH contents of: (a) binary mixtures containing limestone or fly ash/metakaolin, and (b) ternary blends of limestone and fly ash/metakaolin.

Such a beneficial effect is not observed for OPC–limestone–fly ash blends. Even cement replacement at 30% level (20% 3 μm limestone powder, 10% metakaolin), results in only a 15% strength reduction as compared to the plain OPC paste. Small amounts of monocarboaluminate, shown to have a high modulus [37], could also play a role in mitigating strength loss in these mixtures. The incorporation of small amounts of metakaolin is thus found to be beneficial in improving the properties of limestone powder modified systems at ages up to 28 days.

4. Conclusions

This paper describes the influence of limestone fineness and the reactivity of the alumina source on the early-age heat release response, the compressive strength and hydration products formed for cement pastes containing limestone powder of three different median particle sizes or a combination of limestone powder and small amounts (10%) of fly ash or metakaolin. Fine limestone powders (0.7 and 3 μm) were found to accelerate the early-age cement hydration at all the dosages studied. The paste with 10% of 0.7 μm limestone powder was found to have better 1 day strength and increased normalized non-evaporable water (w_n) and CH contents than the OPC paste. Increasing limestone coarseness and dosage reduced the compressive strength as expected. Cement replacement by metakaolin in binary blends resulted in a higher heat release rate while replacement by fly ash did not produce large changes in the calorimetric response.

The calorimetric response of the pastes containing limestone was not considerably modified by the presence of fly ash whereas significant changes in the calorimetric response was observed when metakaolin was used in conjunction with fine limestone powder (0.7 and 3 μm). The enhanced reaction kinetics in ternary blends containing 10% 0.7 μm limestone powder and 10% metakaolin resulted in the highest 1 day compressive strength and the 1-day normalized CH content was among the lowest of all the evaluated pastes. While CH reduction could also be partially attributed to carboaluminate formation, it was not detected in the thermal decomposition signatures of these pastes. It could also be that the enhanced aluminate phase reaction contributed to increased incorporation of Al^{3+} in the C–S–H at early ages rather than forming carboaluminates.

The fine limestone powder (0.7 and 3 μm) modified pastes at 10% cement replacement level showed compressive strengths comparable to those of OPC pastes until 28 days. The ternary blend of metakaolin along with 10% 0.7 μm limestone powder resulted in compressive strengths that were higher than either of the corresponding binary blends, even at a higher overall cement replacement level. Such a response was not observed in the case of fly ash. The normalized w_n at 28 days for the ternary blends of 0.7 and 3 μm limestone powder and metakaolin was higher than that of the OPC paste, the binary blends, and the ternary blends containing fly ash. While the normalized w_n of these pastes increased with age, the normalized CH contents were found to reduce or remain unchanged with age, indicating changes in reaction products. The DTG curves for the 28 day cured ternary pastes with both 0.7 and 3 μm limestone powder confirmed this through the observation of the presence of carboaluminates. Thus, this paper brings out the role of the overall chemical compatibility of cement replacement materials, with a view towards selecting the replacement material (in terms of its physical and chemical characteristics) to produce synergistic effects and optimal OPC replacement efficiency. As such, this work advances approaches to utilize multiple material solutions based on limestone and metakaolin to proportion ternary binders, dedicated to reducing the use of OPC in concrete.

Acknowledgements

The authors gratefully acknowledge the National Science Foundation for the financial support for this research (CMMI 1068985). The materials were provided by U.S. Concrete, OMYA A.G, Headwaters Resources, and Burgess Pigments, and are acknowledged. The first author also acknowledges the Dean's Fellowship from the Ira A. Fulton Schools of Engineering at Arizona State University (ASU). This research was conducted in the Laboratory for the Science of Sustainable Infrastructural Materials at Arizona State University (ASU) and the Laboratory for the Chemistry of Construction Materials and the Molecular Instrumentation Center at the University of California Los Angeles (UCLA). The authors gratefully acknowledge the support that has made these laboratories possible. The contents of this paper reflect the views of the authors who are responsible for the facts and accuracy of the data presented herein, and do not necessarily reflect the views and policies of the funding agency, nor do the contents constitute a standard, specification, or a regulation.

References

[1] Hendriks CA, Worrell E, De Jager D, Blok K, Riemer P. Emission reduction of greenhouse gases from the cement industry. International Energy Agency (IEA); 2002.

[2] Worrell E, Price L, Martin N, Hendriks C, Meida LO. Carbon dioxide emissions from the global cement industry 1. Annu Rev Energy Environ 2001;26(1):303–29.

[3] Government of Canada NRC. Energy consumption benchmark guide: cement clinker production office of energy efficiency. April 22; 2009.

[4] Tsivilis S, Chaniotakis E, Badogiannis E, Pahoulas G, Ilias A. A study on the parameters affecting the properties of Portland limestone cements. Cem Concr Compos 1999;21(2):107–16.

[5] Voglis N, Kakali G, Chaniotakis E, Tsivilis S. Portland-limestone cements. Their properties and hydration compared to those of other composite cements. Cem Concr Compos 2005;27(2):191–6.

[6] Tennis P, Thomas MDA, Weiss WJ. State-of-the-art report on use of limestone in cements at levels of up to 15%, SN3148. Skokie, Illinois, USA: Portland Cement Association; 2011.

[7] Bonavetti V, Donza H, Menéndez G, Cabrera O, Irassar EF. Limestone filler cement in low w/c concrete: a rational use of energy. Cem Concr Res 2003;33(6):865–71.

[8] Bentz D, Irassar EF, Bucher B, Weiss WJ. Limestone fillers conserve cement Part 1: An analysis based on powers model. Concr Int 2009;31(11):41–6.

[9] Felekoğlu B, Tosun K, Baradan B, Altun A, Uyulgan B. The effect of fly ash and limestone fillers on the viscosity and compressive strength of self-compacting repair mortars. Cem Concr Res 2006;36(9):1719–26.

[10] Oey T, Kumar A, Bullard JW, Neithalath N, Sant G. The filler effect: the influence of filler content and surface area on cementitious reaction rates. Sub J Am Ceram Soc 2012.

[11] Lothenbach B, Le Saout G, Gallucci E, Scrivener K. Influence of limestone on the hydration of Portland cements. Cem Concr Res 2008;38(6):848–60.

[12] Opoczky L. Progress of particle size distribution during the intergrinding of a clinker–limestone mixture. ZEMENT KALK GIPS; 1992. p. 45648–648.

[13] Bentz DP, Ferraris CF. Rheology and setting of high volume fly ash mixtures. Cem Concr Compos 2010;32(4):265–70.

[14] Bentz D, Irassar EF, Bucher B, Weiss WJ. Limestone fillers conserve cement; Part 2: Durability issues and the effects of limestone fineness on mixtures. Concr Int 2009;31(12):35–9.

[15] Dhir RK, Limbachiya MC, McCarthy MJ, Chaipanich A. Evaluation of Portland limestone cements for use in concrete construction. Mater Struct 2007;40(5):459–73.

[16] Cam HT, Neithalath N. Moisture and ionic transport in concretes containing coarse limestone powder. Cem Concr Compos 2010;32(7):486–96.

[17] Ingram K, Poslusny M, Daugherty K, Rowe W, Klieger P, Hooton RD. Carboaluminate reactions as influenced by limestone additions. Proc Carbonate Additions Cem 1990:106414–23.

[18] Matschei T, Lothenbach B, Glasser FP. The role of calcium carbonate in cement hydration. Cem Concr Res 2007;37(4):551–8.

[19] Bonavetti VL, Rahhal VF, Irassar EF. Studies on the carboaluminate formation in limestone filler-blended cements. Cem Concr Res 2001;31(6):853–9.

[20] Kakali G, Tsivilis S, Aggeli E, Bati M. Hydration products of C_3A, C_3S and Portland cement in the presence of $CaCO_3$. Cem Concr Res 2000;30(7):1073–7.

[21] De Weerdt K, Kjellsen KO, Sellevold E, Justnes H. Synergy between fly ash and limestone powder in ternary cements. Cem Concr Compos 2011;33(1):30–8.

[22] Langan BW, Weng K, Ward MA. Effect of silica fume and fly ash on heat of hydration of Portland cement. Cem Concr Res 2002;32(7):1045–51.

[23] Fajun W, Grutzeck MW, Roy DM. The retarding effects of fly ash upon the hydration of cement pastes: the first 24 h. Cem Concr Res 1985;15(1):174–84.

[24] Sakai E, Miyahara S, Ohsawa S, Lee SH, Daimon M. Hydration of fly ash cement. Cem Concr Res 2005;35(6):1135–40.

[25] Dweck J, Buchler PM, Coelho ACV, Cartledge FK. Hydration of a Portland cement blended with calcium carbonate. Thermochim Acta 2000;346(1–2):105–13.

[26] Ramachandran VS. Thermal analyses of cement components hydrated in the presence of calcium carbonate. Thermochim Acta 1988:127385–94.

[27] Soroka I, Setter N. The effect of fillers on strength of cement mortars. Cem Concr Res 1977;7(4):449–56.

[28] Pera J, Husson S, Guilhot B. Influence of finely ground limestone on cement hydration. Cem Concr Compos 1999;21(2):99–105.

[29] Kadri EH, Kenai S, Ezziane K, Siddique R, De Schutter G. Influence of metakaolin and silica fume on the heat of hydration and compressive strength development of mortar. Appl Clay Sci 2011.

[30] Poon CS, Lam L, Kou SC, Wong YL, Wong R. Rate of pozzolanic reaction of metakaolin in high-performance cement pastes. Cem Concr Res 2001;31(9):1301–6.

[31] De Weerdt K, Haha MB, Le Saout G, Kjellsen KO, Justnes H, Lothenbach B. Hydration mechanisms of ternary Portland cements containing limestone powder and fly ash. Cem Concr Res 2011;41(3):279–91.

[32] Deschner F, Winnefeld F, Lothenbach B, Seufert S, Schwesig P, Dittrich S, et al. Hydration of Portland cement with high replacement by siliceous fly ash. Cem Concr Res 2012.

[33] Ipavec A, Gabrovšek R, Vuk T, Kaučič V, Maček J, Meden A. Carboaluminate phases formation during the hydration of calcite-containing Portland cement. J Am Ceram Soc 2011;94(4):1238–42.

[34] Lagier F, Kurtis KE. Influence of Portland cement composition on early age reactions with metakaolin. Cem Concr Res 2007;37(10):1411–7.

[35] Marsh BK, Day RL. Pozzolanic and cementitious reactions of fly ash in blended cement pastes. Cem Concr Res 1988;18(2):301–10.

[36] Taylor HFW. Cement chemistry. Thomas Telford; 1997.

[37] Moon J, Oh JE, Balonis M, Glasser FP, Clark SM, Monteiro PJM. High pressure study of low compressibility tetracalcium aluminum carbonate hydrates $3CaO{\cdot}Al_2O_3{\cdot}CaCO_3{\cdot}11H_2O$. Cem Concr Res 2011.