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Early-age activation of cement pastes and mortars containing ground perlite as a pozzolan

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ABSTRACT

Perlite is a natural pozzolan abundant in several countries which are major producers of cement. This makes perlite attractive for producing sustainable concretes. Strength development and heat evolution of perlite-containing mixtures, and the influence of chemical and thermal activation on their early and later age properties were investigated using five activator chemicals and four curing temperature-duration combinations. Chemical activation could increase the 1-day, or 3-day compressive strengths of 25% perlite mortars to above the cement-only control but was not very beneficial to 50% perlite mixtures. Thermal activation could increase strength at ages up to 28 days, and even above the room-temperature control at 1 day. Perlite content affects the maximum value of the isothermal calorimetry heat evolution rate but not its time of occurrence. Chemical and thermal activation influence both the height of the rate peak and its timing, which are linearly correlated for activated or non-activated pastes with a given perlite content.

1. Introduction

The use of natural pozzolans in portland cement-based mixtures dates back more than two millennia [1]. Mielenz et al. [2] wrote “When selected, processed, and used properly, pozzolans can reduce costs, improve quality of concrete, protect concrete against effects of reaction between aggregate and cement alkalis, and inhibit attack by aggressive waters.” Proper selection of a pozzolan requires knowledge of its chemical composition and its reactivity with portland cement. Although several types of “natural” pozzolans, such as diatomaceous earth, and volcanic ashes or tuffs, can be named, each of these types shows variability with respect to reactivity. It is therefore difficult to relate results in the literature obtained by using a particular natural pozzolan from a specific location, to one’s own pozzolan. For this reason, it can be useful to determine the behavior of natural pozzolans which show limited variability and are also abundant and widely available. One such material is perlite.

Perlite is a volcanic glass which contains 2–6% chemically combined water. It has the interesting property that, upon heating to ~900 °C, this water is lost, expanding it to a cellular material of very low bulk density. Consequently, expanded perlite has been widely used by the construction industry as an aggregate in the production of lightweight concretes, insulation products, etc., in addition to its use in other areas like horticulture and pharmaceuticals [3]. Although much-less known, due to its glassy nature and high SiO_2 (70–75%) and Al_2O_3 (12–15%) content, finely-ground unexpanded perlite also possesses pozzolanic properties, as demonstrated in a recent study [4]. Erdem et al. [5] used ground perlite to produce blended cements and mortars, concluding that the grinding of perlite is less energy-intensive than portland cement clinkers. They found that perlite-containing mixtures conformed to standard limitations on setting time, soundness, and compressive strength. The term “perlite-containing mixture” is used in this text to mean that a fraction of the cement in a paste or mortar has been replaced with ground perlite. Uzal et al. [6] reported normal consistency water contents similar to that of a portland cement-only control and that ground perlite-containing concretes had very low permeability after a few weeks. The strengths were low compared to the control mixture, at all ages up to 91 days. Turanlı et al. [7] reported significant decreases in early-age compressive strength for high volume replacement, compared to a portland-cement only concrete mixture. No studies have yet reported heat of hydration of mixtures containing ground perlite as a pozzolan.

Chemical and thermal activation of mixtures containing high volumes of pozzolans have been suggested to improve particularly their early-age strengths. Sodium sulfate (Na_2SO_4) has been shown to be effective in increasing early-strength and sulfate resistance [8]. Wu and Naik [9] used several chemical activators in mixtures containing high volumes of coal ash and also reported that Na_2SO_4 was one of the most effective and economical chemicals in improving early-age strength. Shi and Day [10] concluded that calcium

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chloride dihydrate ($CaCl_2{\cdot}2H_2O$) was very effective in increasing the pozzolanic reaction rate of lime-natural pozzolan mixtures and that thermal activation increased early strength while decreasing ultimate strength. Allahverdi and Ghorbani [11] reported that sodium hydroxide (NaOH) accelerated the setting of lime-natural pozzolan mixtures. Hydrochloric acid (HCl) treatment of pozzolans to increase reactivity has also been suggested [12,13]. Chemical and thermal activation of mixtures containing only a natural or an artificial pozzolan instead of portland cement, though not new, has also been gaining popularity [14–16]. Sodium silicate has been shown to be an effective activator for activation of ground blast furnace slags [17]. Activation of perlite–portland cement mixtures has not been reported.

With a known total worldwide reserve base over 7 billion tons and reserves exceeding 700 million tons [18], perlite is also quite abundant. The “reserve base” is the inplace demonstrated (measured plus indicated) resource from which reserves are estimated. “Reserves” are defined as the part of the reserve base which could be economically extracted or produced at the time of determination [19]. Turkey, China, Japan, the US, Greece, and Italy share a majority of the reserves. As some of these countries are major producers (and some major users) of portland cement, relatively small increases in the fraction of perlite used in concrete, while still meeting desired strength and durability requirements, can result in significant environmental and economical savings, as well as technical benefits. Perlite lacks the waste reuse advantage of artificial pozzolans while being burdened by the resource depletion disadvantage. However, some regions or countries (such as the eastern part of Turkey) may be rich in natural pozzolans but not generate substantial amounts of artificial pozzolans [20–22]. The amounts of the major oxides in perlite vary less than a few percentage points from one source to another and even less within the same pit, much less than the oxides in artificial pozzolans from a single source do [23,24]. This may greatly improve repeatability and facilitate the widespread adoption of the findings of studies using perlite. Chemical activation of artificial pozzolans using the same chemicals report different “ideal” proportions of activators. It is expected that the results shown in this study will have high repeatability, any variation resulting mainly from differences in the portland cements used. This paper presents results of experimental investigations of the effectiveness of chemical and thermal activation in increasing the early- and late-age strengths of portland cement mortars containing medium and high volumes of unexpanded, ground perlite. The effect of chemical and thermal activation on the heat evolution behavior of pastes is also presented.

2. Experimental

2.1. Materials

A CEM I 42.5R portland cement and perlite from a quarry in Erzincan, Turkey were used as cementitious materials in this study. The cement met the requirements of the relevant standard [25]. Table 1 provides the chemical compositions of the portland cement and perlite used, determined by a private research lab, using X-ray fluorescence (XRF). Fig. 1 shows the Cu Kα X-ray diffractogram for the ground, unexpanded perlite.

The uncertainty of major oxide contents determined by XRF is reported to usually be within 0.5–1% [26]. The Portland cement had a Blaine fineness of 3370 cm^2/g. The perlite was ground alone in a laboratory ball mill to a Blaine fineness of 4580 cm^2/g. The specific gravities of the cement and ground perlite were determined as 3.09 and 2.43, respectively. CEN Standard sand [27] and distilled water were used in preparing the mortars. Five chemicals were used for activation: NaOH, sodium silicate (simply referred to as Na_2SiO_3), Na_2SO_4, $CaCl_2$, and HCl. The NaOH, Na_2SO_4, and $CaCl_2$ were in solid form with >97%, >90%, and 84% purity, respectively. The 38.5% solids Na_2SiO_3 (actual SiO_2:Na_2O $\sim$ 3.0) and 37% HCl were used as solutions. The use of NaOH gave low strengths for the mortars containing 25% perlite and was abandoned for the remainder of the tests.

Table 1
Oxide analysis of the powder materials used (%).

	CEM I 42,5R	Perlite
SiO_2	19.6	71.1
Al_2O_3	5.0	13.0
Fe_2O_3	3.7	1.6
CaO	64.5	1.6
MgO	1.6	0.5
SO_3	2.4	1.6
K_2O	0.7	3.8
Na_2O	0.8	4.2
Loss on ignition	2.9	2.9

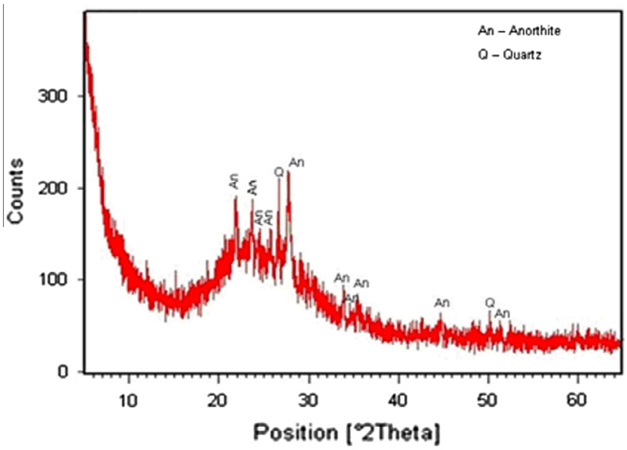

Fig. 1. X-ray diffractogram for the unexpanded perlite used.

2.2. Mixture proportions and experimental methods

The study attempted the chemical and thermal activation of pastes and mortars with 25%, 50%, or 75% (by mass) of the portland cement replaced with perlite. The strength development of mortars and hydration heat evolution behavior of the pastes were investigated. Three different amounts of chemicals, 2%, 4%, and 6% by mass of the total cementitious materials (cement + perlite) were used. Based on the initial findings, the 50% and 75% perlite mortars were subjected to 2% chemical activator and thermal activation. Thermal activation involved steam curing at 55 °C or 85 °C for 3 or 10 h. Strength development of mortars with no activation, only chemical activation, and both chemical and thermal activation were compared with each other and with the control mixture containing only portland cement and sand. Table 2 presents the mixture proportions used in the different categories of mortars for which test results are presented.

In accordance with the findings of Uzal et al. [6], the consistency of the mortars did not change noticeably with the addition of perlite and the water-to-cementitious materials ratio for all mixtures was set to 0.485. The sand-to-cementitious material ratio for all mixtures was 2.7. Mortars were mixed at room temperature, following the durations and order of mixing described in [28]. Three $4 * 4 * 16$ cm mortar prisms were cast for each test age. The prisms were first tested under three point bending and then the six halves

Table 2
Proportions of materials used for the pastes and mortars.

Mixture designation	Cement (mass % of total cement and perlite)	Perlite (mass % of total cement and perlite)	Activator (mass % of total cement and perlite)	Chemical activator used	Curing temperature for thermal activation (°C)	Duration of thermal activation
Control	100	0	None	None	23	-
P25	75	25	None/2, 4, 6	NaOH or Na_2SiO_3 or Na_2SO_4 or $CaCl_2$ or HCl	23	-
P50	50	50	None/2, 4, 6	Na_2SiO_3 or Na_2SO_4 or $CaCl_2$ or HCl	None/55/85	3 h/10 h
P75	25	75	2	$CaCl_2$	85	10 h

were each tested in compression. Specimens to be thermally activated were placed in a humid oven immediately after casting.

The heat evolution of the pastes was measured using isothermal calorimetry, at 23 °C and at 55 °C. The pastes had a water-to-cementitious powder material ratio (W/Cm) of 0.40 and a mass of ~10 g. This W/Cm was chosen to maintain paste uniformity and prevent bleeding. The recorded heat flow (in mW) and evolved heat were normalized by the total powder mass. The pastes were prepared ex-situ and then placed in the calorimeter which disturbs the heat equilibrium in the measurement chamber. Contribution of the reactions to the recorded heat flow cannot be distinguished from this disturbance until the chamber regains equilibrium (after ~30 min) and the data is not dependable up to this point. Consequently, the heat peak typically seen in the first few minutes due to rapid dissolution of some cement constituents cannot be distinguished from the peak caused by the chamber disturbance.

3. Results and discussion

3.1. Strength development

The efficiency of the activation attempts was judged by comparing the early-age and later-age strengths of the mortars with those of the non-activated, perlite-incorporating mortars and the cement-only control. Although it could be expected that high amounts of perlite addition could affect setting time, or that the use of some of the chemical activators could influence durability negatively, the goal was to eliminate some of the chemicals and chemical/thermal activation combinations before investigating a broader range of properties on successful mixtures. The mortar prisms were tested in three-point bending and the two halves from each were tested in uniaxial compression. The flexural strengths of the mortars were ~15–25% of the compressive strengths, in all cases, and only the results of compressive strength are presented. The coefficient of variation of compressive strength corresponding to a certain age (average of six measurements) mostly lies between 2% and 5% but was as high as 10% for a few of the data points. The strength results are shown with 5% vertical error bars to allow more meaningful comparison of the measured differences.

3.1.1. Mortars containing 25% perlite

3.1.1.1. Influence of chemical activator content. The effect of increasing the activating chemical content from 2% to 6%, on the 1-, 3-, 7-, and 28-day strengths of room temperature-cured P25 mortars (incorporating 25% perlite) is shown in Fig. 2.

It is seen in Fig. 2 that increasing the chemical activator content from 2% to 4% or 6% generally decreases strength. At 1 day, the mixtures activated with Na_2SiO_3, Na_2SO_4, and $CaCl_2$ appear to be exceptions to this, however the difference between the strength of the mixtures with higher and lower chemical activator content is not large. This strength reduction caused by increasing chemical activator content appears to become greater at later ages. At 28 days, the strengths of the mixtures with 6% activator are 5–42% lower than the strengths of those containing 2% activator, for the various chemicals. Since the use of lower amounts of chemicals is also economically and environmentally preferable, only strength results obtained using 2% chemical activator are discussed in the following sections.

3.1.1.2. Influence of chemical activator type. The mean compressive strengths of P25 mortars with different activators and no heat curing, normalized against the control mixture are shown in Fig. 3. A value greater than 1.0 indicates that the strength of that mixture exceeds that of the control mortar at that particular age. The compressive strength development of the control mortar, and the unactivated P25, and P50 mortars at room temperature are provided in Fig. 4.

The P25 mixtures without any chemical or thermal activation show an expected strength loss compared to the control at very early ages. However, the pozzolanic reaction appears to increase strength to within 5% of the control at 3 days and surpass the control between 28 and 56 days, for the non-activated mortar. Although such rapid strength gain at a replacement level of 25% is unusual, the total evolved heat of P25 pastes (shown in later sections) also exceed that of the control at 1–2 days. Of the chemically activated mixtures, $CaCl_2$ and HCl give the highest ultimate strengths while NaOH appears detrimental and gives the lowest strengths of all mixtures beyond 1 day. The mixtures activated with Na_2SO_4 and $CaCl_2$ possess 30–40% higher strength than the unactivated P25 mixture at 1 day. At 3 days, the strengths of these mixtures exceed even that of the control mixture, by ~3% and ~20%. In effect, there is a net increase over the non-activated mortar. Despite its high ultimate strength the mortar activated with HCl possesses a 1-day strength about 65% and 43% of the non-activated P25 and control mixtures, respectively. Na_2SO_4 also improves early-strength but slightly decreases strength after 28 days. Thus, without any thermal activation, and to overcome the drawback of early strength loss for the P25 mixtures, $CaCl_2$ and Na_2SO_4 appear to be most effective and a choice may be based on expected exposure conditions and whether the concrete will be reinforced or plain. It is apparent that perlite is an effective pozzolan at this replacement level, even without thermal activation.

3.1.1.2.1. Influence of Na_2SO_4. Many investigations have concluded that the addition of Na_2SO_4 leads to high early strengths due to increased ettringite formation. Formation of ettringite results in a much greater volume increase than when calcium silicate hydrate (C-S-H) or other products are formed (~164% vs. ~17%). The increased solid volume results in increased early strength [9,29]. As calcium hydroxide (CH) is formed through hydration of the cement, part of the Na_2SO_4 reacts with it to form gypsum and NaOH. This increases the paste pH which in turn increases the rate of pozzolanic reaction at early ages, which results in a further increase in strength [30]. As pH surpasses ~12.5, the dissolution of the SiO_2 in perlite and solubility of CH formed during hydration increase. Shi and Day [29] also suggested that the presence of Al (as is the case for perlite) increases the dissolution of natural pozzolans due to

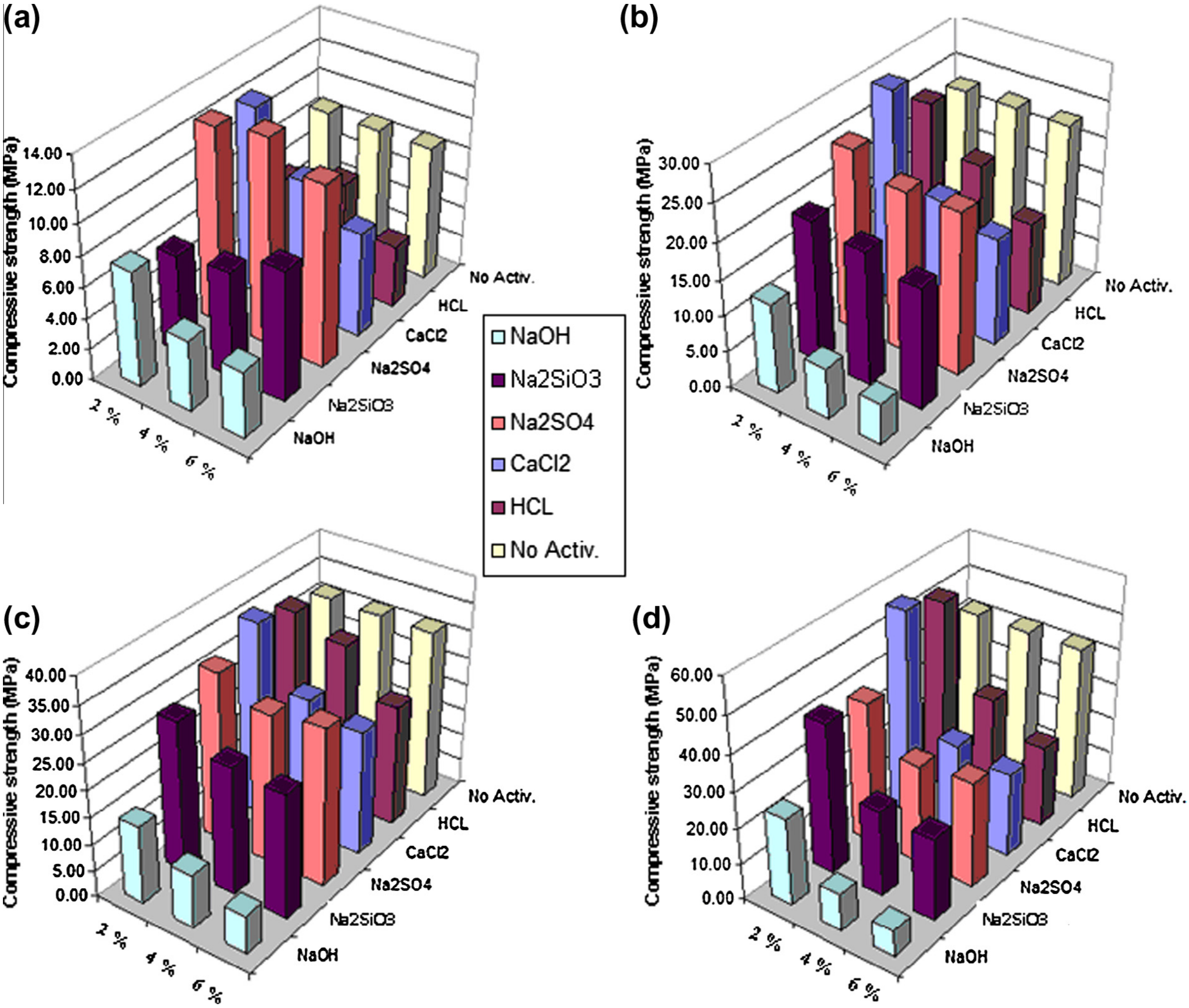

Fig. 2. Influence of increasing chemical activator content on strength of room-temperature cured P25 mortars at: (a) 1 day; (b) 3 days; (c) 7 days; and (d) 28 days.

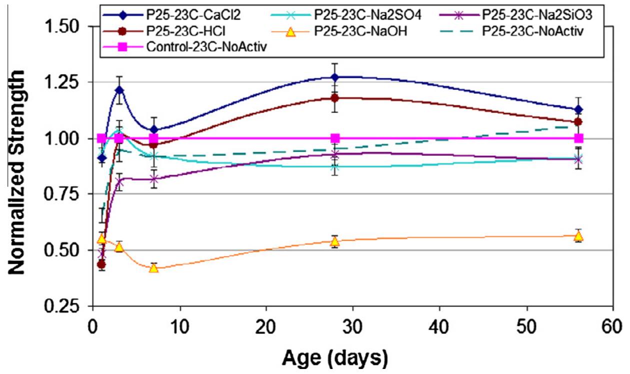

Fig. 3. Compressive strengths of chemically-activated P25 mortars normalized against the pure cement control mortar strengths.

the lower bonding energy of Al–O bonds compared to the Si–O bond. The formation of NaOH could also possibly explain the lower 28-day strength measured.

3.1.1.2.2. Influence of $CaCl_2$. The addition of $CaCl_2$, however, results in decreased pH, which reduces the dissolution of perlite and slightly delays the pozzolanic reaction. The Ca^{2+} concentration increases but the amount of dissolved monosilicate and aluminate species is decreased. Shi and Day [29], working with $CaCl_2$-activated lime-pozzolan pastes reported that $C_3A \cdot CaCl_2 \cdot 10H_2O$ and $C_3A \cdot Ca(OH)_2 \cdot 12H_2O$ form quickly but not much C-S-H forms. In the perlite–cement mortars, the former is likelier to form, at least at early ages. Formation of $C_3A \cdot CaCl_2 \cdot 10H_2O$ increases solid volume more than C-S-H formation, which increases density and after some time, increases strength.

3.1.1.2.3. Influence of Na_2SiO_3. When sodium silicates with high silica moduli (as in this study) which are less alkaline are used, the initial pH is lower and it takes longer for it to rise to the initial pH of the control. Brykov et al. [31] used such a sodium silicate and reported that sodium silicate allows hydration to continue even when the solution becomes supersaturated with Ca^{2+} and pH stabilizes at a value higher than in the control. This is supported by the wider, longer-lasting heat evolution peak for sodium silicate-activated pastes (shown in later sections). The concentration of OH^- can also affect the formation of ettringite crystals. In more alkaline pore solutions, even with low CH concentration, smaller ettringite crystals form.

3.1.1.2.4. Influence of NaOH. The influence of NaOH and Na_2SiO_3 on hydration are somewhat related. NaOH addition has been reported to increase reaction rate at 1 day [32] and result in fewer smaller pores [33], leading to a preferential formation of a denser C-S-H gel and a heterogeneous structure. Higher available alkalis make C-S-H coarser [34], platy, and crystalline [35]. The structure created is acicular, less dense and its mechanical properties are

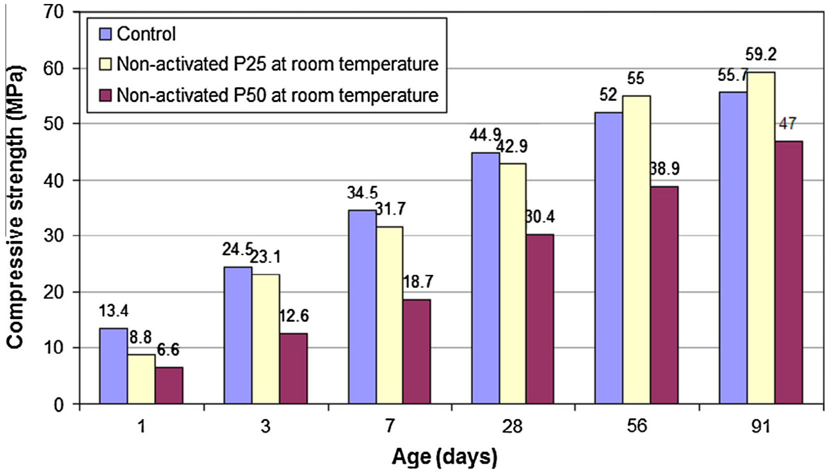

Fig. 4. Compressive strength development of the unactivated control (100% cement), P25, and P50 mortars at room temperature.

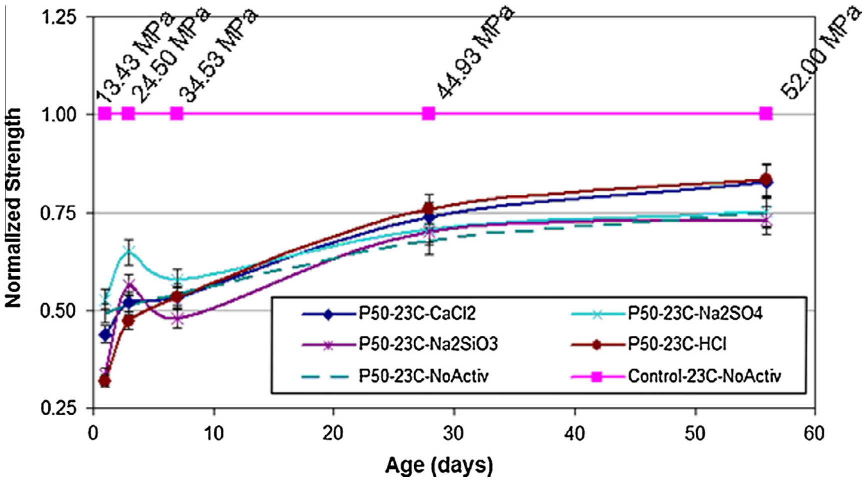

Fig. 5. Compressive strengths of chemically activated P50 mortars normalized against the control mortar strengths.

decreased [36,37]. The influence of alkalis on cement hydration is complex and can also depend on the mineralogical composition of the cement and sulfate levels of the system, impacting not just reaction rates but also products [38].

3.1.1.2.5. Influence of HCl. In HCl-activated mixtures, like with $CaCl_2$ activation, it is possible that the pH decreases and Cl^- ions become available to form new products with increased volume and a denser microstructure. The reactivity of the perlite itself can be enhanced as well. Alexander [12] reported increased reactivity of pozzolans with HCl addition and attributed the increase to the formation of reactive silica gel. Acid treatment increases the reactivity of low-Ca pozzolans (like perlite) but in high-Ca pozzolans, calcium is dissolved and reactivity is reduced.

3.1.2. Mortars containing 50% perlite

The compressive strengths of the P50 mixtures, with different activators and no heat-curing, are compared to the non-activated P50 mortar in Fig. 5, again normalized against the cement-only control mortar strength (given in Fig. 4) at each age.

The P50 mixture without any chemical or thermal activation has about half the strength of the control mixture until 7 days, after which this difference diminishes. The strength did not reach that of the control during the testing period (but was within 10% after 3 months, reinforcing the effectiveness of perlite even at a cement replacement of 50%). The early-age strengths of all activated P50 mixtures were much lower than the control, similar to the unactivated case. In fact none of the chemical activators appeared satisfactory at later ages with the highest strength achieved using HCl or $CaCl_2$ being only ~10% higher than the unactivated mixture. The early strength improvement provided by addition of Na_2SO_4 was minor, about 10% over the non-activated mortar strength. As discussed earlier, this difference is not too significant considering the uncertainty attached to the strength measurements. Similarly, the strengths at 7 and 28 days are not significantly different than each other.

While so effective with the P25 mixtures, the ineffectiveness of $CaCl_2$ and Na_2SO_4 in activating the P50 mixtures may be due to the reduced amount of high-volume product forming phases in the system. Increasing the perlite content results in decreased cement content, which results in a decrease in the amount of phases like C_3A and $CaSO_4$. Similar to the P25 mortars, HCl caused reduced early strength despite achieving the highest ultimate strength. Nevertheless all room temperature-cured P50 mixtures had sufficient ultimate strengths for structural use. It appears that for the 50% cement replacement case, thermal activation may be needed, to overcome losses in early-age strength. The actual values of the strength of the P50 mortars can easily be calculated using the normalized strengths in Fig. 5 and the control mortar strengths in Fig. 4.

3.1.2.1. Influence of thermal activation duration and temperature. Two different temperatures, 55 °C and 85 °C, and two different durations, 3 h and 10 h, were used for thermal activation of the P50 mixtures, as explained in Table 2. The intention was to investigate the effect of temperature-curing duration combinations from medium temperature-medium duration, to high temperature-long duration.

Fig. 6 shows the compressive strengths of the 50% perlite mixtures incorporating the various chemical activators, thermally activated according to each of the four temperature-duration combinations, and normalized against the room-temperature cured control mortar. For comparison, the strength development of the non-activated P50 mortar is given in Fig. 4 and shown as "P50 No Activ" in Fig. 6.

The "medium temperature-medium curing duration" and the "high temperature-high curing duration" combinations gave, with a few exceptions, the minimum and maximum strengths, respectively, for a set of mortars activated using the same chemical.

3.1.2.1.1. Curing at 55 °C. Curing at 55 °C for 3 h improves the 1-day strength of mortars activated with $CaCl_2$ (~5%) or Na_2SO_4 (~50%), compared to the non-activated P50 mortar, but not those containing Na_2SiO_3 or HCl. Even with this increase, the early-age strengths of the chemically and thermally activated P50 mortars are only 50–75% of the control. The strengths on the following days, however, are nearly the same as those of the non-activated sample. Increasing curing temperature to above 50 °C can result in the conversion of AFt in Na_2SO_4-activated pastes to AFm resulting in a volume decrease [29] hence the lower ultimate strength of these mortars in Fig. 6. HCl activation greatly reduced the 1-day strength. This heat-curing regimen does not provide great benefits and thermal activation at higher temperatures and/or for longer time periods may be needed.

In the case of curing the samples at 55 °C for 10 h, the effectiveness of $CaCl_2$ increases, with the 1-day strength improvement rising to 36%. HCl activation is also much improved in this lengthened curing regime. No other significant change in strength development is observed.

3.1.2.1.2. Curing at 85 °C. When the samples are cured at 85 °C for 3 h, HCl activation is once again ineffective and 1-day strength is only ~60% of the strength of the non-activated mortar. The strength of this mortar remains the lowest at all ages. Although the early-age strength of Na_2SiO_3 mortars is not improved, they achieve the highest strength of all the mortars beyond ~7 days. Na_2SiO_3 activation studies on slags have shown that there exist optimum curing temperatures and durations that yield higher strengths [17]. Similar temperature-duration combinations probably exist for activation of perlite with various alkaline chemicals.

Thermal activation at 85 °C for 10 h substantially increases the early-age strength of all P50 mortars compared to the non-activated mortar cases. All activated mortars have 1-day strengths equaling or exceeding the 1-day strength of the room-temperature cured control mortar. $CaCl_2$-activated samples once again possess high strength, both at early ages and later ages. The HCl mortars, also similar to its behavior in the other cases, increases in strength between 1 and 3 days, and afterwards. Also common to all activators is that their strengths relative to the control drop beyond 1 day. The lowest relative strength is at around 7 days for nearly all activated mortars with a slight subsequent increase, due probably to continued pozzolanic activity. Nevertheless, strengths of none of the thermally and chemically activated P50 mixtures are noticeably higher than those of only chemically activated mixtures, beyond 28 days. Na_2SiO_3 and Na_2SO_4 mortars have significantly lower later-age strengths than the control and the other activated mixtures. It appears, therefore, that thermal activation at 85 °C for 10 h can overcome problems caused by slow strength gain due to high perlite content. However, ultimate strength is negatively af-

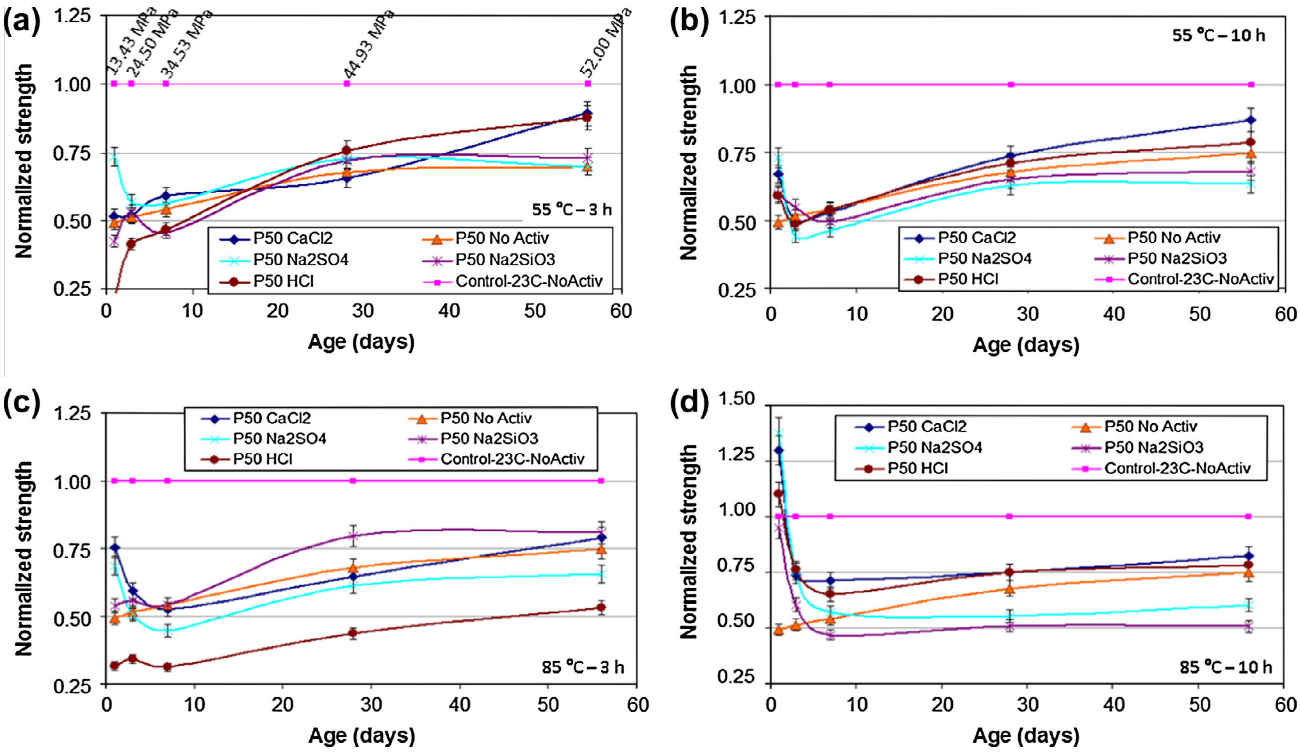

Fig. 6. Compressive strengths of chemically activated P50 mortars cured: (a) at 55 °C for 3 h; (b) at 55 °C for 10 h; (c) at 85 °C for 3 h; and (d) at 85 °C for 10 h, normalized against the pure cement control mortar strengths at room temperature.

fected as is often the case for high-temperature cured portland cement-only mixtures.

Longer curing helps the chloride-containing activators to work better, regardless of curing temperature. This can be related to the strength development of HCl^- or $CaCl_2$-activated P50 mixtures (Fig. 5). Although their 1-day strengths are lower than that of the non-activated mixture, they surpass it after several days, suggesting that the contribution of these activators to the mortar occurs with a delay of several days. The sensitivity of $CaCl_2$-activated P50 mixtures to increased curing temperature is higher than those of Na_2SO_4-activated mixtures but lower than those of HCl-activated mixtures. $CaCl_2$- and HCl-containing pastes are probably affected more positively by increasing curing temperature because increased temperature accelerates the dissolution of perlite and formation of large-volume reaction products [39]. Also, activated mixtures are more sensitive in general to changes in temperature because of their higher apparent activation energies [40]. Na_2SO_4-activated mixtures increase in strength relative to the room temperature mixture with heat curing only up to 3 days but not beyond that. Shi and Day [39] reported similar behavior for a lime-pozzolan blend.

3.1.3. Mortars containing 75% perlite

Since $CaCl_2$ activation at 85 °C for 10 h successfully improved the 1- and 3-day strengths of the 50% perlite mixtures, its effect on a mixture with a higher replacement level of ground perlite was also investigated. Table 3 compares the strength development of mixtures containing 50%, and 75% perlite, activated with 2% $CaCl_2$ at 85 °C for 10 h.

Increasing the cement replacement level to 75% substantially decreases both early- and later-age strengths. The thermally-activated P75 mixture has a 1-day strength comparable to those of non-activated P50 mortars at 1 day. However, the strength does not improve measurably during the following week and only doubles up to 56 days. The upper limit for cement replacement with perlite for structural uses appears to lie between 50% and 75% by mass.

3.2. Heat evolution

The heat evolution vs. time data is presented to loosely parallel the compressive strength development data. First, the behavior of non-activated and chemically-activated P25 pastes at 23 °C is discussed. Then, the effect of increasing perlite content from 0% to 75% is shown for the non-activated pastes at 23 °C. Increasing perlite content affects the chemically-activated pastes similarly at 23 °C and are omitted.

Then, the heat evolution behavior of P50 mixtures at 55 °C is discussed. Since it was shown in Fig. 5 that chemical activation alone did not improve the strengths of P50 mortars much at 23 °C and that thermal activation was needed, the effect of the various activators on the P50 pastes at 55 °C is discussed next. Finally, the influence of increasing perlite content from 0% to 75% is discussed again, this time at 55 °C, for the non-chemically activated pastes and for pastes incorporating 2% $CaCl_2$.

Table 3
Compressive strengths of chemically- and thermally-activated P50 and P75 mortars containing 2% $CaCl_2$, cured at 85 °C for 10 h (MPa).

Designation	Compressive strength (MPa)					
	1 day	3 days	7 days	28 days	56 days	91 days
P50 with 2% $CaCl_2$	17.4	18.1	24.6	33.7	42.9	52.1
P75 with 2% $CaCl_2$	6.6	6.6	6.9	11.7	13.4	14.0

3.2.1. Chemically activated P25 mixtures at room temperature

The heat evolution behaviors of perlite-containing pastes were compared with each other and the control. The influence of chemical activation on the amount and rate of heat evolution at early ages was investigated. Fig. 7 shows the rate of heat evolution vs. time, and the cumulative heat vs. time curves for the non-activated and chemically activated (with 2% activator) P25 mixtures.

The main heat evolution rate-time peak (the peak often associated with the hydration of calcium silicates) of the $CaCl_2$ activated paste forms the earliest and is the most pronounced among all cases. This peak does not have a shoulder or secondary peak (often associated with hydration of C_3A but can also be due to early pozzolanic reaction [41]). All other activated pastes show a secondary peak. It is possible that the main peak engulfs the shoulder peak in the $CaCl_2$-activated paste. The second earliest and highest main peak is that of the Na_2SO_4-activated paste. These results are similar to the compressive strength results given in Fig. 3. The slowest reacting paste was the one containing Na_2SiO_3, which also gave the lowest peak. This paste has a much longer time between its main and secondary peaks than the other pastes (~15 h vs. 4–5 h). Hydration of this paste was slower even than the unactivated paste, again similar to its strength development shown in Fig. 3.

The paste containing $CaCl_2$ gives off the most heat up to about age 17 h, after which the Na_2SO_4 paste overtakes it (Fig. 7b). Despite yielding lower compressive strengths than the others up to a time between 7 and 28 days, the heat evolved by the Na_2SiO_3-activated mixture passes the control at ~2 days. After 20–24 h, the non-activated P25 total heat surpasses the non-activated control. It is seen in Fig. 3 that the strength of the P25 mixture catches up with that of the control before day 3 and then eventually exceeds it. So the time scale for the paste (calorimetry) and the mortar (strength) appear to be different.

3.2.2. Effects of increasing perlite content at room temperature

Fig. 8 shows the influence of increasing the replacement level of cement with perlite on the heat behavior of a non-activated paste.

For the non-activated cases in Fig. 8a, the time to the main peak is not affected by the replacement percentage. This contrasts with a delayed peak reported for increasing fly ash and ground slag contents [42,43]. The height of this peak (the maximum rate of heat evolution), however, is greatly affected. The drop in peak height is related with the decrease in portland cement content of the mixture. However, for each cement replacement level, the peak height is slightly greater than expected based on the percentage of remaining Portland cement (e.g. ~1.9 mW/g instead of ~3 mW/g $*$ [50/100] = 1.5 mW/g for the P50 paste). This can be due to perlite contributing to the reaction at this stage, in a minor capacity. Also, the surface of the fine glassy perlite might be amplifying the hydration. It is also worth noting an increase in the height of the shoulder relative to the height of the main peak, with increasing perlite. This increase is probably due to this peak being a combination of ettringite to monosulfate conversion [44] and simultaneous pozzolanic reaction [41].

Presence of sand, difference in sample size, etc. also cause the paste (calorimetry) time scale to be different than the mortar (strength) time scale. Hence the non-activated P25 exceeds the cumulative heat of the control at 23 °C after 24 h but the strength between 1 and 3 days.

3.2.3. Thermal and chemical activation of P50 mixtures

Fig. 9 shows the heat evolution behavior of activated and non-activated P50 mixtures at a temperature of 55 °C.

A pronounced shoulder peak is immediately noticeable on all P50 curves as well as on the control. Therefore, thermal activation accelerates heat evolution shortly after final set, which happens near the top of the ascending left side of the main peak (at ~3 h

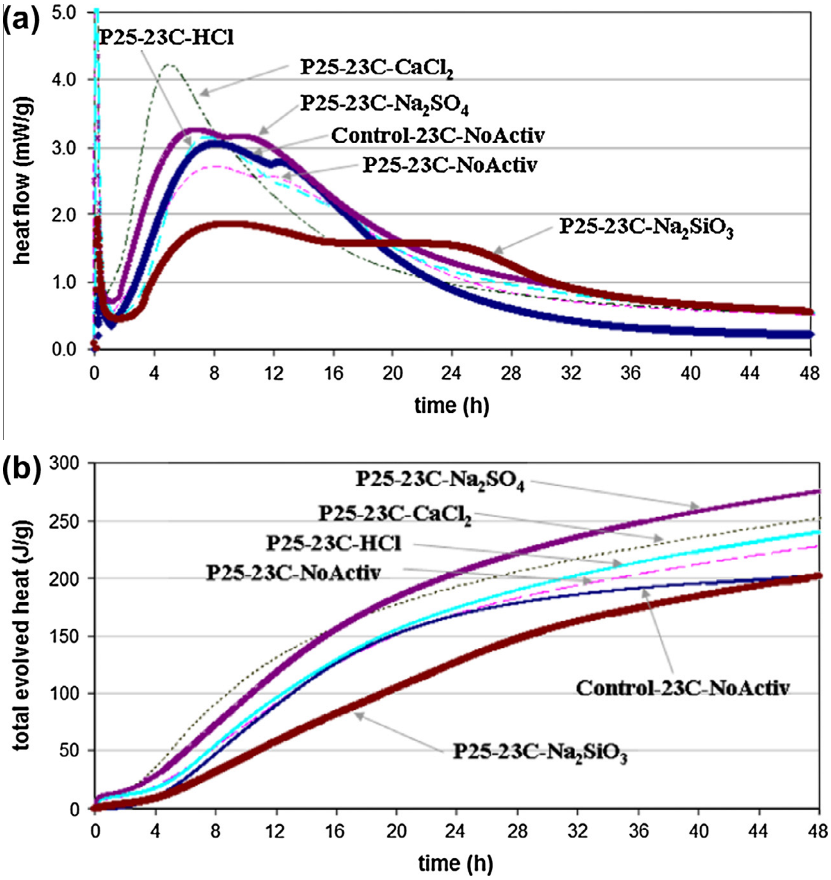

Fig. 7. (a) Rate of heat evolution vs. time; and (b) cumulative heat evolved vs. time for non-activated, and chemically activated P25 pastes, and the cement-only control paste.

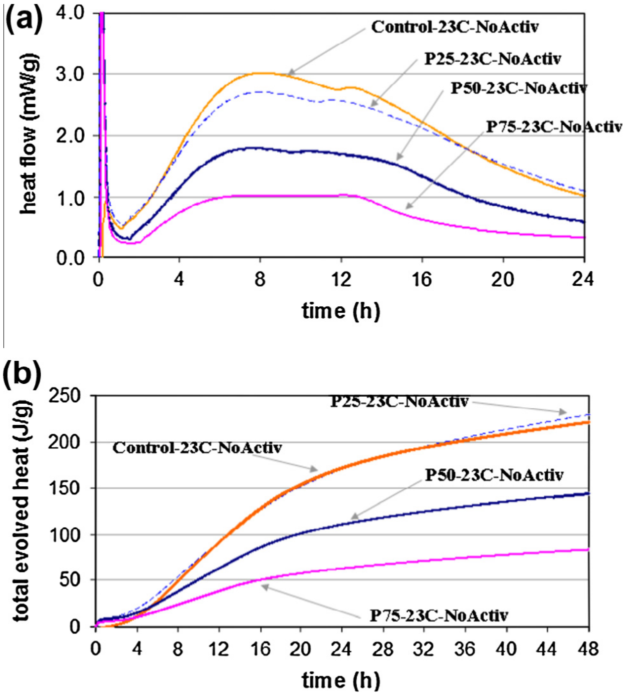

Fig. 8. (a) Rate of heat evolution vs. time; and (b) cumulative heat evolved vs. time for non-activated P25, P50, P75 pastes, and the cement-only control paste, at room temperature.

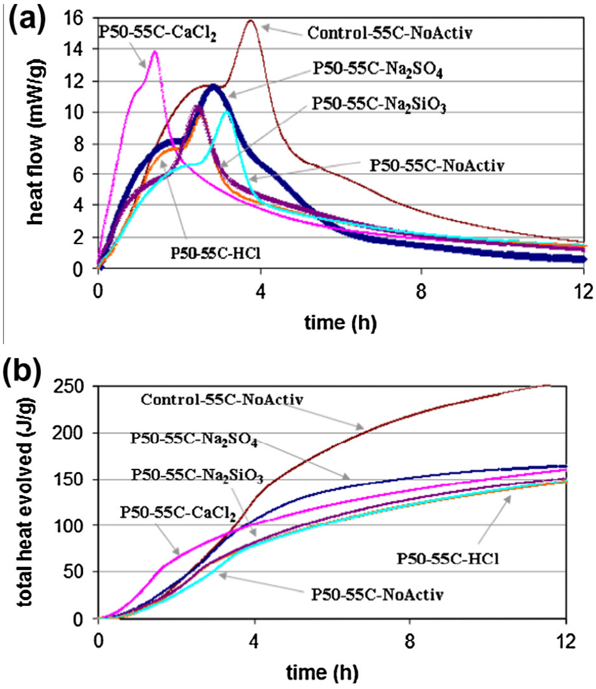

Fig. 9. (a) Rate of heat evolution vs. time; and (b) cumulative heat evolved vs. time for P50 mixtures and the control, at 55 °C.

for the non-activated control in Fig. 9a). The additional heat evolved due to this shoulder is about 20–25% of what would be expected during that same time interval (from 3.1 h to 4.8 h for P100 Control-55C-NoActiv in Fig. 9a) i.e. the area under the rate of heat evolution curve if the shoulder did not exist. This corresponds to about 10–15 J additional heat energy for the different mixtures. Fig. 9b shows that this short-duration acceleration is difficult to see in the cumulative evolved heat vs. time curve and could easily be missed.

3.2.4. Effect of increasing perlite content at 55 °C

Fig. 10 shows the effect of increasing perlite content on the heat evolution behavior of non-activated mixtures at 55 °C, as well as mixtures activated with 2% $CaCl_2$, to represent the activated cases.

Changing perlite content influences the height of the main heat peak more than its time of occurrence, for the 55 °C mixtures (similar to what was observed in Fig. 8). For the non-activated mixtures, the peak occurs slightly earlier as perlite content is increased. This shift, as well as the reduction in peak height is nearly linear with increasing perlite content. The time of the main peak is several hours earlier at 55 °C than at 23 °C. $CaCl_2$-activation also causes earlier peaks.

The total heat evolved for the non-activated and $CaCl_2$-activated cases is similar for all of the P25, P50, P75 cases, and the cement-only control case, after some time. This time span increases with increasing perlite content (~8 h for the control, ~12 h for P25, etc. in Fig. 10b). So the activator is effective only for a short time period after hydration begins.

The peak heights in the 55 °C cases are 5–7 times those at 23 °C. At 55 °C, the shoulder peak is very noticeable for the non-activated mixtures, no matter what the perlite content is. For the activated 55 °C mixtures, the shoulder becomes more prominent with increasing pozzolan content. This may be because the activator affects the cement reactions more than it does the perlite so the dominant shoulder in Control-55C-NoActiv is less dominant in Control-55C-$CaCl_2$. However, beyond the activator affecting the cement, the shoulder grows as perlite content increases. So, temperature increases shoulder height but activator increases cement activity to make the shoulder less dominant, until cement content decreases and the shoulder becomes more dominant again. The height of the shoulder peak relative to the height of the main peak increases with replacement level. Över [45] also reported a shoulder peak exceeding the main peak in height, for pastes incorporating 35% natural pozzolan. However, this was the case only for pozzolanic cements with a Blaine fineness higher than 5000 cm^2/g and not observed with cements ground coarser or containing less pozzolan.

The 2% $CaCl_2$-activated 55 °C P50 mixture peak is still lower than the non-activated 100PC peak. However, for the P25 case, the $CaCl_2$-activated paste gives a higher peak than the non-activated paste. The $CaCl_2$-activated paste main peaks are ~60–80% higher than the non-activated peaks for the control, P25, P50, and P75 mortars. The cumulative heat curve for the $CaCl_2$-activated

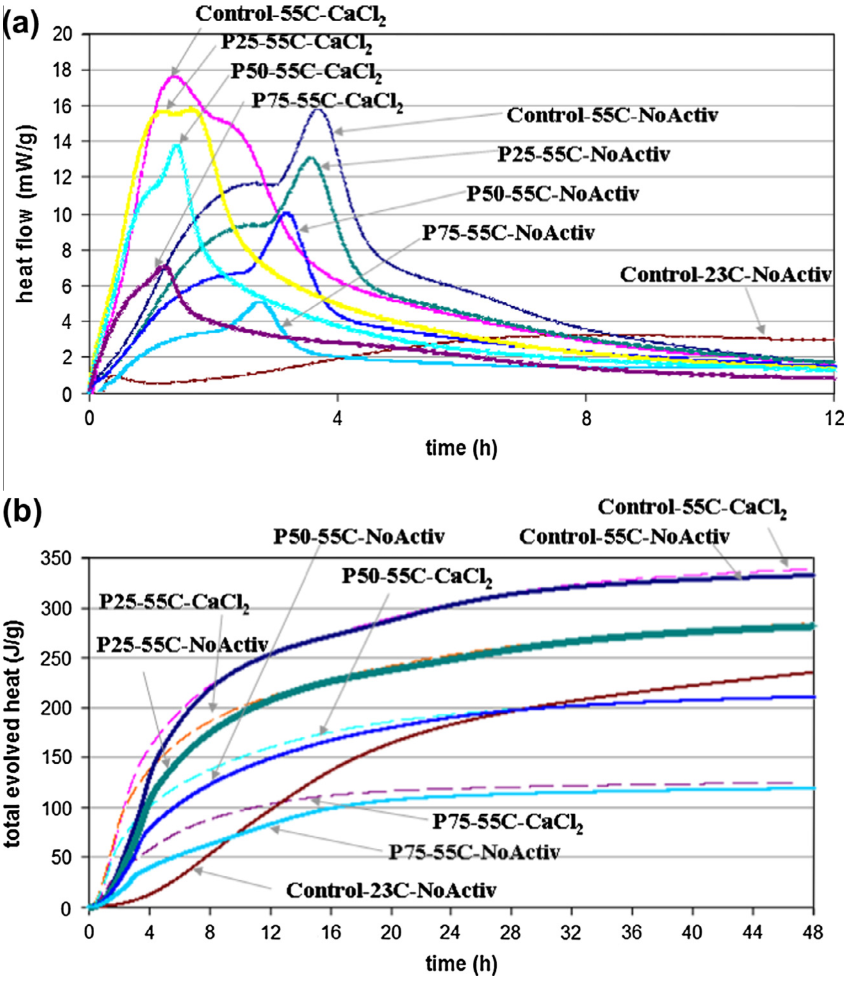

Fig. 10. (a) Rate of heat evolution vs. time; and (b) cumulative heat evolved vs. time for P25, P50, and P75 mixtures activated with $CaCl_2$ or not activated, at 55 °C, and the control.

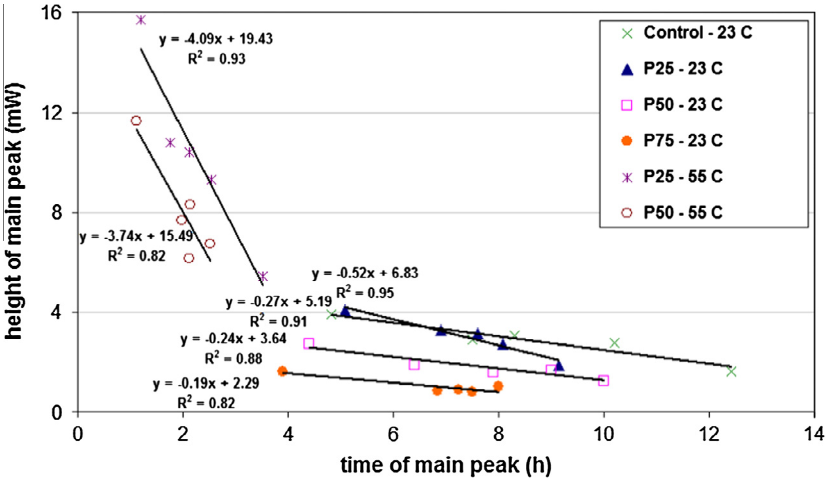

Fig. 11. Relations between the time of occurrence of the main heat evolution peak and its height, for P25, P50, P75, and the control paste at room temperature and at 55 °C.

55 °C P50 is similar to the non-activated 23 °C 100PC control after ~24 h. The strengths are also similar. Therefore this replacement level is the maximum.

3.2.5. Relations between features of the rate of heat evolution vs. time curve

Fig. 11 shows an inverse linear relationship between the height of the heat evolution rate main peak and the time at which it occurs, for samples at room temperature and at 55 °C, with identical cement replacement percentages. The five points in each group represent the four activators and one non-activated case.

Faster reacting mixtures tend to also evolve more early heat and the relationship is quite strong even when various activators are used. The slope of the best-fit line in Fig. 11 increases clearly with increasing temperature for a given perlite content. For a given temperature, increasing perlite content mostly decreases the slope, with the exception of the P25-23 °C samples. For the 55 °C heat curves, the shoulder peak makes the main peak difficult to identify for some pastes (e.g. the P75 mixtures in Fig. 10a). Due to the higher and earlier peaks observed with thermal activation, the slopes of the 55 °C regression lines are much greater. These relations can be useful for predicting changes in the heat evolution of mixtures due to chemical and/or thermal activation.

It is known that strength development can be related to amount of heat evolution [46]. The time and height of the main hydration peak of the non-activated and activated P25 pastes are also linearly related separately to the 3-day and the 7-day compressive strengths of their mortar counterparts (with $r^2 > 0.80$). However, since the data come from paste specimens and mortar specimens, with slightly different W/Cm, and different sizes, and because the relation to the 1-day or 28-day strengths is weak, it is not possible to conclude that the relationship is meaningful.

The combined annual cement production of the six countries listed in the introduction exceeds 2.2 billion metric tons, around two thirds of the worldwide production [47]. Concretes incorporating medium or high volume fractions of ground natural perlite as a pozzolan can provide environmental and economical advantages.

4. Conclusions

The influence of chemical and thermal activation on the strength development and heat evolution behavior of perlite-portland cement mixtures was investigated. The following general conclusions can be drawn:

(a) Perlite is an effective natural pozzolan that can be used to replace 25–50% of portland cement without a significant loss of ultimate strength.

(b) The decrease in the early-age strength of mixtures incorporating 25% perlite can be overcome by using chemical activation with 2% $CaCl_2$ or Na_2SO_4. HCl and Na_2SiO_3 are not effective at very early ages but improve strength later on. NaOH is not an effective activator for perlite-cement mixtures at room temperature.

(c) The early-age strengths of mixtures incorporating 50% perlite cannot be increased sufficiently using chemical activation alone. Adding 2% Na_2SO_4 results in a ~10% strength increase over the non-activated 50% perlite mortar at 1-day and even less at later ages. Effective recovery of the early-age strength of such mixtures requires thermal activation.

(d) Longer curing at higher temperatures increases early-age strength but decreases or does not affect ultimate strength. Curing of samples incorporating 50% perlite at 55 °C for 3 h improves only 1-day strength but not at later ages. Curing 50% perlite-incorporating mortars at 85 °C activated with 2% $CaCl_2$, Na_2SO_4, or HCl for 10 h improves strength up to 7 days. Na_2SiO_3 only improves the 1-day strength. Na_2SiO_3- or Na_2SO_4-incorporating 50% perlite mortars, cured at 85 °C for 10 h have significantly lower ultimate strengths than the pure cement control or the non-activated 50% perlite mortar. The strength of the 75% perlite mortar activated with 2% $CaCl_2$ at 85 °C for 10 h is only half that of the room-temperature control at 1 day, and reaches only one fourth the ultimate strength of the control.

(e) Chemical activation with all activators except Na_2SiO_3 shifts the main rate of heat evolution peak to earlier ages and increases its height. $CaCl_2$ gives the highest and earliest rate peak and Na_2SO_4 evolves the most total heat beyond ~17 h.

(f) Changes in the perlite content of pastes affect only the height of the heat evolution rate peak but not its timing, for a given chemical activator (or no activator) and a given curing temperature.

(g) At room temperature, the prominence of the "shoulder peak" on the descending branch of the C_3S hydration peak increases with increasing perlite content. At 55 °C, this peak is higher than the C_3S peak for all the pastes, even those containing no activator or no perlite. Increasing temperature and use of an activator increases the heights of both peaks. Dilution of cement with perlite decreases the C_3S peak yet still promotes the shoulder peak.

(h) The total heat evolved by $CaCl_2$-activated and non-activated pastes containing the same perlite content and cured at 55 °C are different only up to a certain age, beyond which they are nearly identical. This age becomes greater with increasing perlite content. Chemical activation is thus effective only for a short time when thermal activation is also used.

(i) Changes in the height and time of occurrence of the rate of heat evolution vs. time main peak with the use of various chemical activators appear to be linearly related for the same perlite content and curing temperature. This observation can be useful in developing heat development models for activated pastes.

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