

Use of clay from a local source for calcination and subsequent preparation of the mixed cement

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Abstract: This paper deals with the use of calcinated clay and micronized limestone as supplementary cementitious materials (SMCs) for preparation of blended Portland cement CEM II/B-M (Q-LL). Clay used in this study was calcinated at 700°C and pozzolanic activity after calcination was assessed using accelerated R3 pozzolanic test and modified Chapelle test. The influence of calcinated clay and limestone addition on mechanical properties and hydration process was investigated and an optimal ratio for 35% clinker replacement was found. Initial decrease of mechanical strength at early ages, caused by SCM addition, was almost compensated during maturation of the binder.

1. Introduction

Portland cement, with annual production of 4.1 billion tons worldwide, is responsible for 5–7% of total anthropogenic CO₂ emissions and 7% of total energy consumption. Increasing environmental concerns and focus on sustainable development have created considerable pressure on cement industry [1, 2]. One way of reducing the environmental impact is a partial replacement of clinker by supplementary cementitious materials (SMCs). Conventional SMCs include mainly pozzolanic materials. Most commonly used SMCs are granulated blast furnace slag and fly ash from coal power plants. However, due to high price and relatively low amount of blast furnace slag and decreasing supply of fly ash tied to decommissioning of coal power plants, alternative SMCs are required in order to satisfy the demand for these materials [3].

Clays are highly abundant and accessible worldwide. Calcination of clays between 550–900°C leads to dehydroxylation of clay minerals and the formation of partially disordered silica and alumina rich phases, making them a suitable candidate for use as SMC. Furthermore, compared to conventional SMCs, they can be supplied locally and independently on other industrial sectors. This eliminates the long-distance transport, commonly required with the use of i.e. blast furnace slag and provides long term stability of supply required for the sustainability of production [4]. A positive effect of calcinated clays on hydration process is caused mainly by filler effect in early stages and pozzolanic reaction later [5].

Addition of limestone powder to cement mixture influences hydration process via multitude of effects. Due to particles being smaller than cement particles, it has a filler effect causing a decrease of porosity and an increase in compressive strength [6]. Limestone particles also act as nucleation centres, accelerating hydration of C₃S and increasing the amount of hydration products at early ages. The reported chemical effect of limestone on hydration is limited in Portland cement due to the limited amount of aluminate phases in the clinker. However, it becomes more pronounced in combination with



SMCs containing active alumina and includes interaction with aluminate phases, stabilization of ettringite and formation of mono and hemicarbonates phases [7].

In this study, cement mixtures containing different calcinated clay to limestone ratios were prepared and characterized, with the aim of investigating the influence of calcinated clay and limestone addition on hydration process and strength development of cement mixtures.

2. Materials and methods

Portland cement (Českomoravský cement a.s., plant Mokrá, Czech Republic) with resulted specific surface area 391 m²/kg (determined via Blaine method EN 196-6), gypsum (commercially purchased, pure; Penta, Czech Republic), used as setting regulator, clay calcinated at 700°C (Poštorná, Czech Republic), limestone (LB Cemix, s.r.o., plant Kotouč Štramberk, Czech Republic) sieved under 63 μm, coarse aggregate (Filtlační písky, spol. s r.o., Czech Republic), finely ground quartz sand (Sklopísek Střeleč a.s., Czech Republic) and deionised water were used for cement preparation. The cement composition is summarized in Table 1.

Table 1. Composition (g) of measured samples.

Sample	Cement	Calcined clay	Limestone	Finely ground sand	Gypsum
1	100.0	0.0	0.0	0.0	0.0
2	66.6	30.0	0.0	1.5	1.9
3	66.6	25.0	5.0	1.5	1.9
4	66.6	20.0	10.0	1.5	1.9
5	66.6	15.0	15.0	1.5	1.9

Samples intended for mechanical testing were prepared according to standard ČSN EN 196-1. The homogenized mixture was placed into moulds with the dimensions 4 × 4 × 16 cm. After 24 hours, the experimental specimens were demoulded and water curing conditions were applied under the controlled temperature of 20°C. Mechanical tests were performed after 2, 7 and 28 days.

The particle size of used raw materials was assessed by laser diffractometry (Helos KR, Sympatec) and is shown in Figure 1–Figure 2. Hydration process was analysed by isothermal calorimeter TAM air (TA Instruments) at isothermal temperature 25°C. Analysed samples (5g) were prepared according to standard ČSN EN 196-11. Measurements were performed with a reference sample. Chemical composition was evaluated using X-ray Fluorescence (XRF) analyser Vanta. The instrument analyses elements from magnesium to uranium. Elements lighter than magnesium in silicate materials are defined as a loss on ignition (LOI). X-ray Diffraction (XRD) was used to characterize formed crystalline phases. Phase composition analysis was carried out on Bruker D8 Advance diffractometer with Cu anode ($\lambda K\alpha=1,54184$ Å) and variable divergence apertures at Θ - Θ reflective Bragg-Brentano parafocusing geometry. Determination of amorphous phase content was carried out using 20 wt. % CaF₂ addition as a standard.

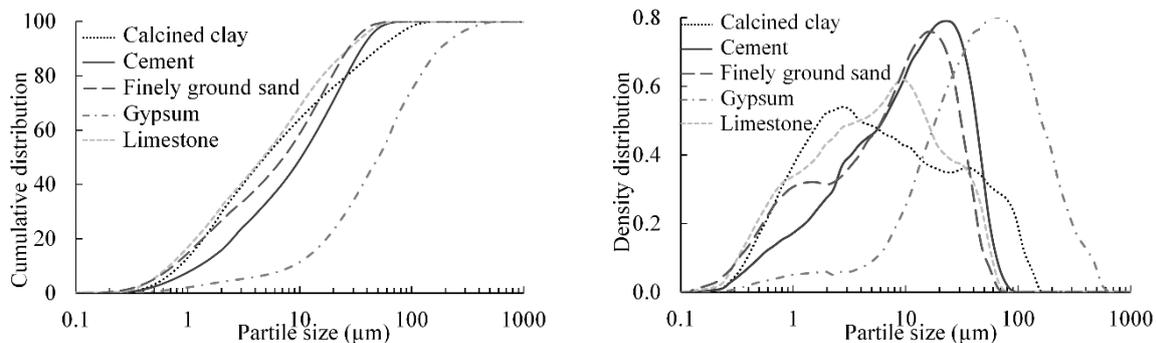


Figure 1. Particle size distribution of raw materials.

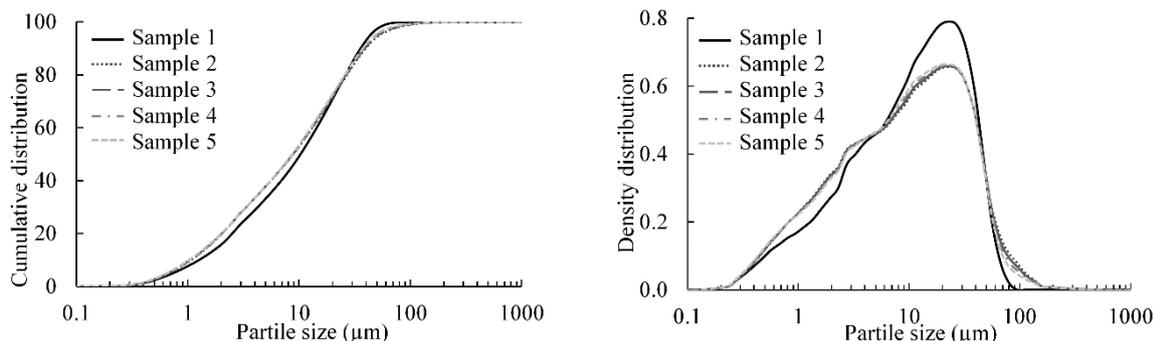


Figure 2. Particle size distribution of measured samples.

The pozzolanic activity of calcined clay was determined using two methods. The first method was the accelerated R^3 test [8]. A solid part of the used mixture contained 1 g calcined clay and 3 g $\text{Ca}(\text{OH})_2$. Water to solid ratio of the used mixture was 1.2. Evolved heat from the sample was measured using isothermal calorimeter TAM air (TA Instruments) at isothermal temperature 25°C . Heat flow was measured for 168 hours. The first hour of the measurement was used for temperature calibration and CaO reaction, and the pozzolanic activity of the clay was determined from the heat evolved during 140 hours. The time of measurement was adjusted to account for the temperature difference, according to hydration heat of microsilica at 20°C and 25°C .

Pozzolanic activity of calcined clay was also assessed by modified Chapelle test according to NF P18-513 standard, Annex A. This test allows quantification of $\text{Ca}(\text{OH})_2$ fixed by 0.4 g of calcined clay when mixed with 0.8 g of CaO and 100 ml of distilled CO_2 free water. The suspension was continuously stirred in an Erlenmeyer flask at $85 \pm 5^\circ\text{C}$ for 16 hours. Erlenmeyer flask was then cooled to ambient temperature with tap water, 24 g of sucrose were added and the suspension was stirred with a magnetic bar for an additional 15 min and filtered. 10 ml of filtrate was titrated with HCl 0.15 M. Blank samples without calcined clay were prepared using the same method [9].

Formed hydration products were analysed using TG-DTA analysis (SDT650, TA Instruments). Samples, used in evolved heat measurement using an isothermal calorimeter, were crushed to 1–2 mm pieces. Hydration process was stopped by washing the samples $2 \times$ with isopropanol and $2 \times$ with diethylether and drying the samples at 45°C . Measurement was carried out up to 1000°C with heating rate $20^\circ\text{C}/\text{min}$ under dried air atmosphere and sample size 40–50 mg.

3. Results and discussion

3.1. Characterization of clay particle

The chemical composition of calcinated clay can be seen in Table 2. Oxides contained in the clay in major quantities are silica and alumina. Other elements are only present in minor quantities. Silica to alumina ratio is of great importance in the use of calcinated clay in blended cements. The amount of silica influences the amount and type of formed hydration products. Alumina rich calcinated clay increases the Al-uptake in C-S-H and the aluminate containing hydrates [10]. The loss on ignition value indicates that clay has lower carbonaceous matter and higher mineral matter contents. This confirms the chemical analysis of clay, where there is little MgO , CaO . The mineralogical composition of used clay can be seen in Table 3. The main identified minerals were quartz, illite, kaolinite and feldspars. The clay sample also contained over 30 % of an amorphous phase.

Table 2. Chemical analysis of clay (XRF).

Chemical composition	MgO	CaO	Al_2O_3	SiO_2	K_2O	TiO_2	Fe_2O_3	LOI (900°C)
Weight (%)	0.9	0.5	19.9	61.8	2.0	1.1	4.2	9.5

Table 3. Chemical analysis of clay (XRD).

Mineral	Quartz	Chlorite	Biotite	Kaolinite	Illite	Albite	Orthoclase	Amorphous
Weight (%)	21.2	7.3	2.4	6.9	15.1	4.5	10.2	32.3

Pozzolanic activity values of clay calcinated at 700°C determined using accelerated R³ test and modified Chapelle test according to standard NF P18-513 are shown in table 4, together with the pozzolanic activity of commonly used pozzolanic materials determined using the same methods. XRD analysis of clay showed the absence of limestone in clay. Therefore, correction of pozzolanic activity due to CaO formed during calcination was not needed.

Table 4. Pozzolanic activity of calcinated clay and commonly used pozzolans.

Raw materials	Quartz - blank	Metakaolin - Elkem	Silicafume - Imeta4	Slag - Štramberg	Calcined clay - Poštorná
R ³ (J/g)	17	222	193	109	202
Chapelle test (mg _{Ca(OH)₂} /g _{pozzolanic})	127	1243	878	489	654

3.2. Isothermal calorimetry

The heat flow curve during hydration is shown in Figure 3, and the main kinetic events related to hydration reactions are highlighted. Portland cement's typical heat flow curve (sample 1) is compared with samples containing calcined clay and limestone in different ratios. The main hydration peak occurs after the end of the induction period. It is associated with the fast dissolution of alite and precipitation of C-S-H and C-(A)-S-H. Ettringite is also continuously precipitating during this time, and sulfate ions are adsorbed in C-(A)-S-H [11].

The presence of active alumina from calcined clay caused an increase in heat flow during the induction period. In samples 2–5, the maximum at the main hydration peak was reached faster. The presence of calcined clay and limestone accelerates the hydration of clinker phases due to filler effect [12]. This is caused by additional surface available for nucleation and growth of hydration products [13, 14]. According to Berodier and Scrivener, limestone also contributes to hydration of cementitious systems via the release of additional Ca²⁺ ions. Calcium ions accelerate the hydration of the clinker phases and shorten the induction time [15]. However, the height of the main hydration (first) peak in samples with calcined clay decreased by 20–25% compared to sample 1 serving as a reference sample.

A distinct aluminate hydration peak is observed for all samples. However, broadened and delayed aluminate hydration peak was observed in blend limestone and calcined clay. It has been reported that the amount of alumina available for the formation of the carboaluminate phase controls the reactivity of calcite [16, 17]. The studies suggest that other factors, in addition to the aluminate content, could affect the kinetics of calcite dissolution in low clinker factor cements [18]. In measured samples with calcined clay and limestone, the pozzolanic activity was affected, and the depletion of the sulphate content was slowed down [18]. The heat flow after 75 h in the cement with calcined clay was higher due to the ongoing pozzolanic reaction.

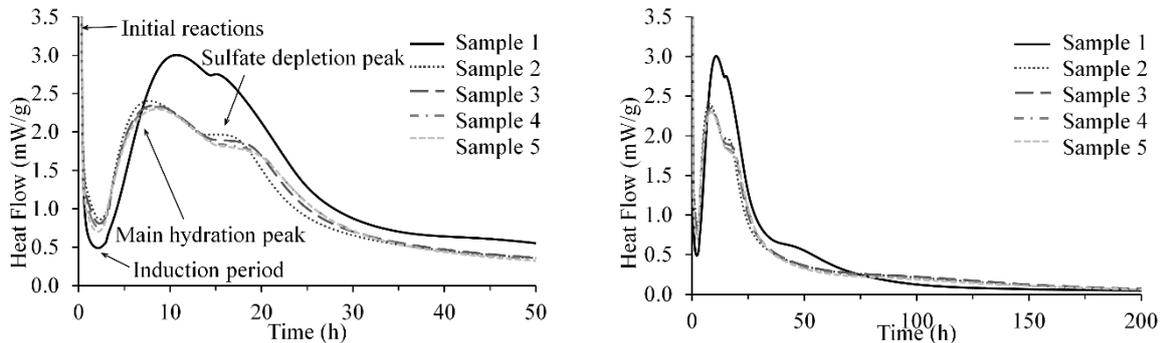


Figure 3. Heat release per gram of solid.

As can be seen from the total hydration heat of prepared samples (Figure 4), the substitution of clinker with calcined clay and limestone significantly influenced the hydration process. Cumulative hydration heat after 48 h, observed for the sample 1 (without calcined clay and limestone), was 259 J/g. The addition of calcined clay and limestone caused a decrease of evolved hydration heat by about 18 % (210–215 J/g). This difference became progressively smaller at later stages of hydration. Total hydration heat after 168 h in sample 1 was 331 J/g and only about 8–14% lower in other samples, which can be attributed to the pozzolanic reaction during later hydration stages. Out of clay containing samples, the highest heat was released by the sample with 5% limestone and 25% calcined clay. These observations are in agreement with other similar studies dealing with calcinated clay and limestone cement mixtures and can be explained by filler effect and pozzolanic reaction [19, 20].

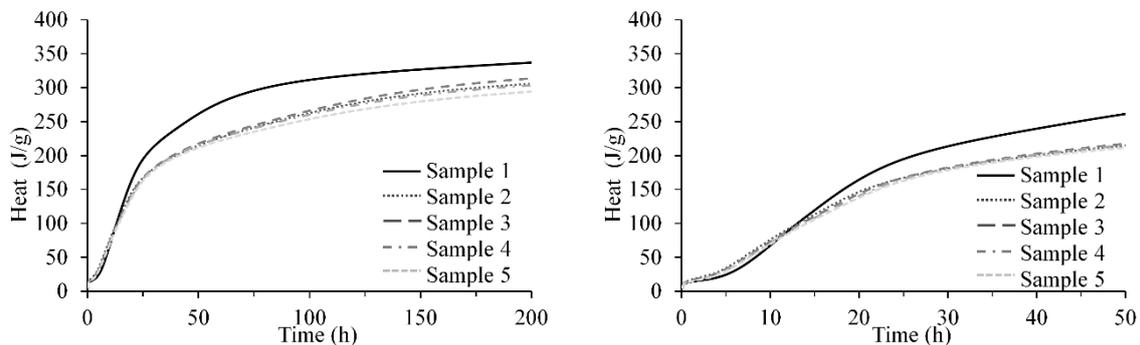


Figure 4. Cumulative heat released per gram of solid.

3.3. Testing of mechanical parameters

Typically, the degree of hydration of Portland cement is about 50% after one day of hydration. After 28 days, the degree of hydration typically increases to around 80%, and most of the unhydrated material is the slow-reacting belite phase and large cement grains [21]. Mechanical parameters of prepared samples with calcined clay and limestone were compared to Portland cement. The resulting compressive and flexural strengths at 1, 7 and 28 days are shown in Figure 5.

The addition of calcined clay caused significant decrease of compressive strength especially at early ages. Compressive strength values are relatively similar among samples 2–4. Ever bigger decrease was observable in sample 5. The difference in compressive strength compared to reference sample 1 after 2 days was 32–34% and 42 % for sample 5 containing 15% limestone and 15% calcined clay. After 7 days of the water curing conditions, the difference of compressive strength values decreased to only 26–29%, compared to the reference sample. One exception being sample 5 achieving only 60% of the compressive strength of the reference sample. After 28 days the compressive strength of clay containing samples were comparable to those of the sample 1. This trend is a clear illustration of the effect of ongoing pozzolanic reaction due to the calcined clay addition.

Studies have shown that the amorphous content in cement affects the mechanical properties. The limited amount of amorphous phase also reduces the reaction between calcined clay and limestone to form mono/hemicarboaluminate hydrates. However, the reduction of stable mono/hemicarboaluminate contributes to reduced compressive strength [22].

The lowest values of compressive strength after 28 days were achieved in sample 5, containing 15% calcined clay and the highest values in sample 3 with 25% calcined clay. The effect of pozzolanic activity can be seen here. At a later time was a greater increase in the compressive strength. The contribution of pozzolanic reaction to compressive strength becomes significant mainly at later stages of hydration process. [23].

A similar trend was also observed for the development of flexural strength. However, after 28 days flexural strength of the samples reached values similar to those of the reference sample. Furthermore, flexural strength loss caused by the substitution of cement was fully compensated after 28 days in sample 4, containing 20% of calcined clay and 10% of limestone. 2:1 ratio between calcined clay and limestone was also found as optimal by other similar studies [22].

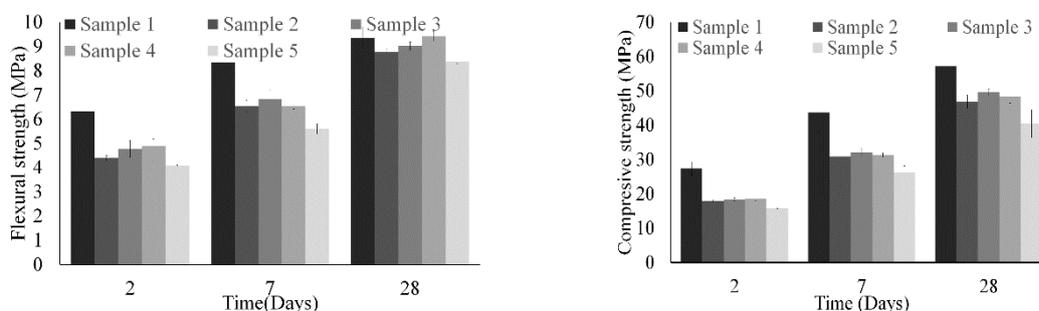


Figure 5. Mechanical parameters of measured samples.

3.4. DTA analysis of hydration products

Figure 6 shows results of TG/DTA analysis and DTG curves for measured samples after 8 days of hydration. TG/DTA curves show 3 main mass loss areas with corresponding endothermic peaks. Peaks in temperature range around 50–160°C are attributed to the decomposition of ettringite (Aft), C-S-H and C-A-S-H phases. Hemicarbonate aluminate hydrate (HC) decomposes at 140–200°C. Characteristic peak of portlandite (CH) decomposition can be seen in the temperature range between 440–530°C. Decomposition of carbonates generally takes place between 625–875°C [24, 25].

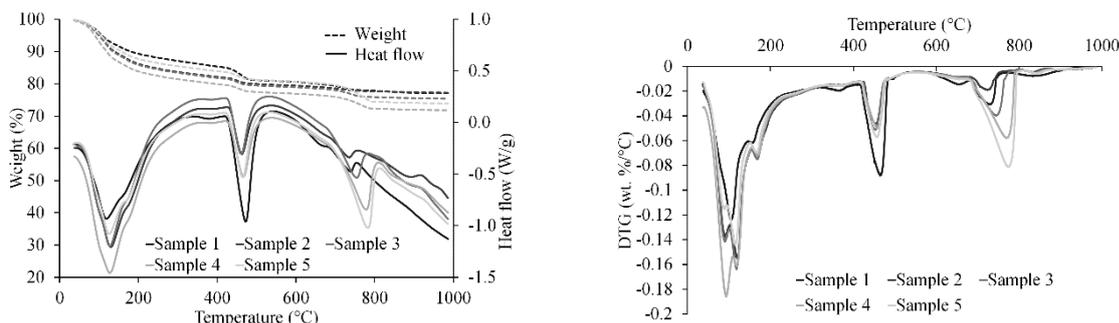


Figure 6. TG/DTA and DTG curves of hydrated cement samples.

Due to the complex nature of hydrated cement pastes and overlap of decomposition temperature ranges of different phases, quantification and identification of emerging phases using TG/DTA analysis can be difficult. In this study, the temperature range 50–400°C was assigned to mass loss caused by dehydration of ettringite, C-S-H, C-A-S-H and carboaluminate phases (AFm), 400–500°C to dehydroxylation of CH and 600–900°C to the decomposition of carbonates. Mass loss in these ranges is reported in Table 5.

Table 5. Mass loss of hydrated cement samples determined by thermal analysis.

Sample	Mass loss (wt. %)		
	Dehydration (C-S-H, C-A-S-H, Aft, Afm)	Dehydroxylation (CH)	Decarbonation (Carbonates)
1	14,1	4,2	3,4
2	17,4	2,2	2,0
3	17,7	2,4	3,4
4	19,2	2,4	5,0
5	15,7	2,7	6,6

With the increasing amount of calcined clay added to the mixture, the amount of CH in hydrated cement decreased. This trend can be partially attributed to the lower amount of cement in the paste and partially to the pozzolanic reaction of calcined clay, as can be seen with the increase of remaining portlandite, with the increasing amount of limestone in the mixture. While DTG curve of the reference PC sample only shows two distinctive peaks within 50–200°C temperature range, with a small shoulder observable on the low temperature range of the first peak, samples with calcined show three distinctive peaks in the temperature range 50–200°C. According to Boháč [25] the low temperature peak found around 90°C can be assigned to dehydration of amorphous C-S-H. This peak becomes most pronounced in sample 4 with calcined clay to limestone ratio 2:1. Temperature shift of C-S-H decomposition to lower temperature compared to Portland cement sample possibly suggests lower crystallinity of pozzolanic reaction products. Peak around 120°C can then be attributed to ettringite decomposition and further dehydration of formed C-S-H [26]. Decomposition peak of formed hemihydrate was observed at 170°C [4, 27]. Higher amount of formed C-S-H and C-A-S-H provides further evidence of good pozzolanic activity of calcined clay and synergistic effect of calcined clay and limestone on cement hydration. These findings are in good agreement with available literature [4–6, 25].

The last significant mass loss was related to the decomposition of carbonate phases. Substitution of cement by SMC caused a significant drop in carbonate content in sample 2. Limestone addition manifested itself by an increase of carbonate content and also shifting the decomposition to higher temperatures in samples 3–5, suggesting different type, structure or crystallinity degree of added limestone. Carbonate peaks observable in samples 1–2 can be likely attributed to decomposition of the micro-filler present in commercially produced cement and carbonation product. The reference sample also showed a small additional peak at around 650°C, barely observable in other samples. This fact suggests the presence of poorly crystalline carbonation products, which generally decompose at this temperature and readily react with calcined clays, forming carboaluminate phases in samples 2–5 [26].

4. Conclusions

Blended Portland cements, to meeting the requirements set by standard EN-197-1 – CEM II/B-M, were successfully prepared by partial substitution of clinker by locally sourced calcined clay and limestone. The optimal calcined clay to limestone ratio, with 30 % clinker substitution, was found to be 2:1. The addition of calcined clay and limestone lead to increased heat flow during the induction period and earlier maximum on the main hydration peak due to active alumina content in the clay and filler effect. Heat flow after 90 h of hydration was higher than Portland cement due to the pozzolanic reaction of calcined clay. The addition of calcined clay and limestone lead to a lower amount of portlandite, increased amount of C-S-H and C-A-S-H and formation of carboaluminate hydrates. A significant increase in the amount of hydration products confirmed via thermal analysis further confirms the synergistic effect of calcined clay and limestone on Portland cement hydration.

Clay and limestone addition caused a decrease of initial compressive and flexural strength. However, after maturation, prepared blended cements reached long term strengths comparable to those of Portland cement.

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