Calcined clays as supplementary cementitious materials

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Summary

In this paper, the use of calcined clays as supplementary cementitious materials (SCMs) is explored. The factors that have led to the increased use of calcined clays such as availability and high substitution rate of clinker are explained. The origin and growth of the use of ternary blends is discussed along with the combined use of calcined clays and limestone with Portland cement. In addition, some key factors to consider when creating a calcined clay limestone cement (CCLC) binder are also considered. We do note that it is important to have the right kaolinite amount, check the efficiency of calcination, consider grinding concerns as well as to ensure the right sulfate and alkali quantities. The workability concerns that have been echoed about calcined clays are illustrated and the fact that we may still need more superplasticizer quantities for CCLC blends is discussed. In addition, the hydration, mechanical strength development and durability qualities are also dwelt upon. The aim of the manuscript is to provide a practical overview of the state of the art in the use of calcined clays as SCMs.

Keywords: Calcined clay limestone cement, Calcined clay, Ternary blends

Abstract

The use of blended cements has increasingly gained attention with the effort to cut down on carbon footprint. This potential has led to the use of different supplementary cementitious materials (SCMs) such calcined clay, fly ash, pozzolans etc to cut down on clinker content in cement. In comparison with other SCMs, calcined clays are available around the world in quantities that can match the production of cement. Most importantly, when used together with limestone in cement binders, calcined clays can produce mechanical properties comparable to OPC at only 50 wt.% of clinker. This has led to an increased interest in calcined clay limestone cement (CCLC). In this paper, an overview of the use of calcined clays as SCMs is explored.

Keywords: Supplementary cementitious materials, Calcined clay, Cement

1 Introduction

Portland cement has been used for more than 200 years for construction throughout different applications. Hence until today Portland cement-based concrete is the most used man-made material in the world. Despite many changes that happened to the production process and the applications of cement, its robustness and versatility were ensured by an unchanged basic chemistry [1].

However, due to its vast annual production environmental concerns concerning global warming put pressure on the cement and concrete industry. With an estimated share of 8% of the global CO_2 emissions, the cement industry had to come up with new pathways to reduce its carbon footprint. Currently the most promising direction is the use of supplementary cementitious materials (SCMs) to reduce the clinker factor in cement. Of the common widely used SCMs, only calcined clays are available in quantities able to support the initiative across the globe for a long time. In this paper we look at the state-of-the-art in the use of calcined clays as SCMs.

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2 Ternary binders

By the early 2000s clinker substitution in cement had reached a plateau and it appeared impossible to further increase the used SCMs such as ground granulated blast-furnace slag (GGBS), fly ash and limestone without loss in strength to unacceptable extends [2,3]. Additionally, the supply of SCMs such as GGBS and fly ash is limited and large quantities will not be available anymore in the near future. Hence ternary binders based on limestone were considered for their advantage of synergy between the SCMs [4].

Many ternary blends have been considered in the past, with the main SCMs being GGBS and fly ash, fly ash and limestone and, recently, calcined clay and limestone. In calcined clay limestone cement (CCLC) the combination of calcined clay and limestone with clinker and gypsum allows to leverage the traditional pozzolanic reaction between silica from calcined clay and portlandite resulting from Portland cement hydration. In addition, alumina provided by the dissolving clays reacts with the excess carbonate from limestone and portlandite and forms carboaluminate phases. As a consequence, ettringite is stabilised and strength synergies are observed due to the additional reduction of capillary porosity [5,6].

The calcined clay does not need to be of high quality in terms of kaolinite content in the raw clay. Raw kaolinitic clays with as low as 40 wt.% kaolinite can reach the same strength after 28 d as OPC [7,8]. Thus, a whole range of low-grade clays unwanted by other industries is available for CCLC.

Following a sourcing of the appropriate clay, it is calcined at temperatures about 800 ºC by calcination in a rotary kiln and somewhat higher temperatures for flash calcination [9,10]. The combination of a properly calcined clay and limestone can substitute up to 45 % of clinker. It has also been reported that clinker substitutions of up to 60 wt.% can be carried out with good performance [1].

Limestone has been widely used in the cement and concrete industry for a long time due to its high availibility, ease of grinding and low price. Due its good grindability, limestone can be used to adjust the particle size distribution of cement and to adjust the rheology and workability of fresh products. In addition to providing nucleation sites for reaction of clinker phases, it also reacts with C_3A to produce hemi- or monocarboaluminate.

3 Factors to consider in binder formulation

3.1 Choice of raw clay

The geological selection of a raw clay involves several steps stretching back to the choice of the quarry. Transportation costs and size of quarry are two major considerations. After that, as stated earlier, any kaolinitic clay with over 40 wt.% of kaolinite is suitable for use in CCLC. Thus, after a clay has been mined and dried, it needs to be prepared for characterization. The most important characterization techniques are thermogravimetric analysis (TGA) and Xray diffraction (XRD). With TGA the kaolinite content can be determined and with XRD a full phase composition including kaolinite content can be determined.

3.2 Efficient calcination

Following calcination using either static or flash calcination, it is necessary to check whether the calcination was effective. This can be done by carrying out a thermogravimetric analysis (TGA) as shown in Figure 1. A mass loss of less than 1.0%, of the reference mass at 200 ºC, may be considered to indicate efficient calcination. Fig. 2 shows the difference in temperature loss between raw and calcined clays as measured by TGA. Alternatively, a simple oven test may be carried out by first drying the sample at 200 °C for at least 24 hours then recalcining the sample for 1 hour at the calcination temperature of 850 °C. Afterwards weigh and record the sample mass; the difference must not exceed 0.5% [11].

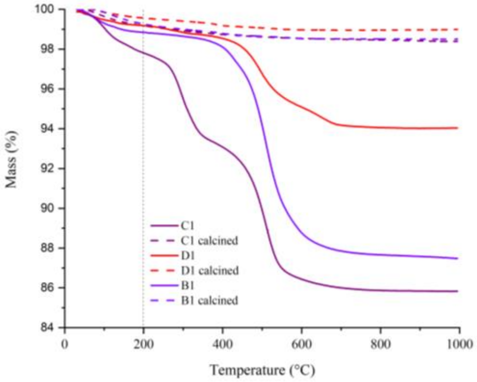

Figure 1 TGA mass loss before and after calcination.

3.3 Grinding of components

A proper particle size distribution is necessary to ensure good reactivity of any cement. In the case of CCLC there are 3 main components: clinker, which is hard to grind, and limestone and calcined clay, which are easy to grind. This gives rise to a problem that when the components are ground together, they tend to interact and affect each other's grinding. If intergrinding is carried out for CCLC then clinker tends to concentrate in the coarse fraction while the limestone and calcined clay are finely ground. This limits the reactivity of the clinker and thus the whole binder. Therefore, separate grinding works more effectively.

3.4 Sulfate optimisation

Sulfate optimisation is essential for each binder and highly reactive SCMs used [12–14]. In the case of OPC, sulfate is added based on aluminate content. CCLC may significantly impact the hydration kinetics, which leads to the necessity of adding more gypsum to balance the system as shown in Figure 2. As can be seen both at high metakaolin clay and low metakaolin clay are requiring almost the same amount of gypsum to show that total aluminium content is not sufficient to compute the optimal sulfate content. Without proper adjustment, both the silicate and aluminate peak occur together, thus limiting the reaction of the silicate phase. Sulfate optimization may be done using calorimetry by varying the gypsum/anhydrite content then observing the peak occurrences. Ideally, there should be a clear separation between the silicate (first) and aluminate (second) peak. Compressive strength measurement between 2 up to 28 d is the other reliable and simple way of doing sulfate optimization.

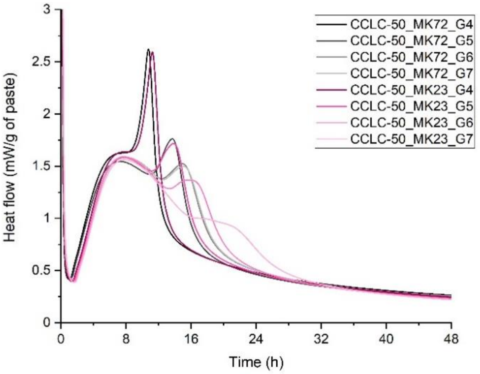

Figure 2 Sulfate adjustment for CCLC-50 blends with MK72 and MK23 clays.

3.5 Alkali adjustment

The alkali content of the clinker affects hydration reactions, mechanical properties and durability properties of concrete significantly. While it leads to a reduction of strength at later ages, alkalis tend to accelerate early hydration and give high early-age strength but lower late-age strength [15]. Additionally, alkalinity is also known to favour pozzolanic reaction. Hence, alkali adjustment can be done using for example Na_2SO_4 or K_2SO_4 to improve early strength [15, 21]. The results obtained by Hanpongpun [16] show that it is difficult to obtain comparable strength between CCLC and OPC at 28 d when using a low-alkali cement. Hence, when a low alkali clinker is used, it may be beneficial to perform an alkali adjustment and the optimal adjustment may easily be determined using calorimetry or strength measurements.

4 Rheology and workability and the use of superplasticizers

One of the main differences between CCLC and OPC is the rheology/workability. As noted by Ferraris et al. [22], rheological properties of concrete need to be carefully balanced to achieve specific goals such as limiting segregation, producing a good surface finish, minimizing pumping pressure, or controlling formwork pressure. Hence, thorough understanding of the rheological properties of CCLC is required.

Figure 3a shows the difference in onset and growth of rheological properties of OPC and different CCLC binders. The increase in SCM substitution leads to an increase in static yield stress (SYS, i.e. the shear stress required to initiate flow). Figure 3b compares the influence of limestone and that of calcined clay and as can be seen the sharp increase in yield stress observed in Figure 3a is due to the influence of calcined clay. Interestingly in Figure 3b we can also see the synergistic effect of the combination of calcined clay and limestone reflected in the increase in yield stress after just 1 hour of hydration.

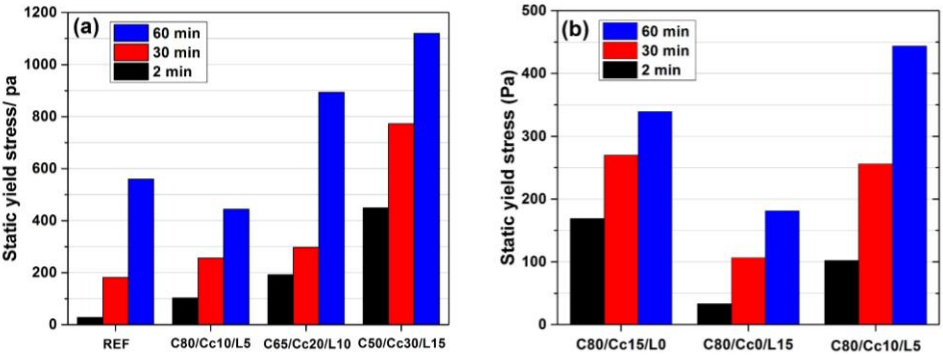

Figure _ The variation of SYS with resting time, and comparison of the effect of limestone and calcined clay on SYS at (b) 80wt.% substitution [17].

As stated earlier, one of the advantages of the use of limestone is its adjustment of workability or at the very least comparable initial rheological properties to those of OPC before hydration begins to strongly influence rheology. Therefore, it is no surprise that Figure 3b shows that only calcined clay can be responsible for the observed increase in yield stress with increased SCM substitution. In another study Hou et al. [18] showed that one of the factors leading to the high-water demand of calcined clay compared to limestone was the negative surface charge of calcined clays (Figure 4). Additionally, by using ^{1}H NMR and µCT techniques they showed that this negative surface charge led to flocculation within the CCLC systems that left less water available to contribute to fluidity and that hydration did not have as much an effect, as least within the first hour, as it does in an OPC due to a lower clinker factor. These observations have since been echoed in other recent studies [19,20].

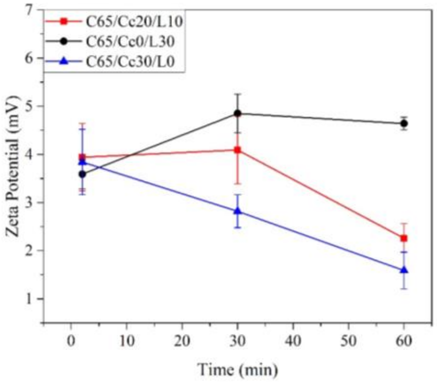

Figure 4 Variation of zeta potential at 60 wt.% substitution [18].

The use of superplasticizers can solve the rheology/workability problems and several studies have investigated this key issue. For example, Schmid et al. [23] showed that the dispersing power of zwitterionic superplasticizers was slightly superior to that of that of conventional PCEs when it came to the dispersion of calcined clays or CCLC blends. Akbulut et al. [24] reported that a co-monomer which introduced sulfonic acid groups into the acrylic acid backbone of MPEG PCEs possessing a low polyethylene glycol grafting density enhances its dispersing performance even at high clinker substitution rates, but requires high dosages. Recently Li et al. [25] studied the effectiveness of the dispersive force of different PCE superplasticizers on calcined clay cement with a calcined clay containing ~50 wt.% of metakaolin at 0–40% substitution rate for the clinker. They reported that PCEs which fluidize OPC best also provided optimal performance in CC blended cements, but at much higher dosages. They also noted that of all the PCEs used the methallyl ether (HPEG) polymer produced superior dispersing performance compared to the MPEG-based superplasticizers and that introduction of a cationic group into an MPEG PCE improved its performance as compared to conventional anionic MPEG polymers [25]. In a nutshell, some improvements in the current PCEs could be made but they can work effectively as they are. The only challenge is that we still must use more.

Earlier we compared limestone and calcined clay influence on the rheology of CCLC; a question remains whether different calcined clays could also have variations in rheological behaviour. In a recent study [26], we compared the performance of calcined clays with a wide range of phase compositions. Figure 5a shows the rheological performance of three different industrial clays in CCLC-50 blends with the use of a superplasticizer to increase measuring time. Clearly not all calcined clays perform the same in terms of onset and growth of rheology. In a different study we compared the growth of storage modulus (stiffness) with hydration time in a calcined clay – portlandite – gypsum system (Figure 5b). And again, observed different growth rates over time. A close analysis of the phase compositions and specific surface (SSA) area showed that the iron phases led to higher SSA which increased water demand and early reactivity of the iron-rich calcined clays [26]. An increase in superplasticizer demand was the downside but early age compressive strength was superior.

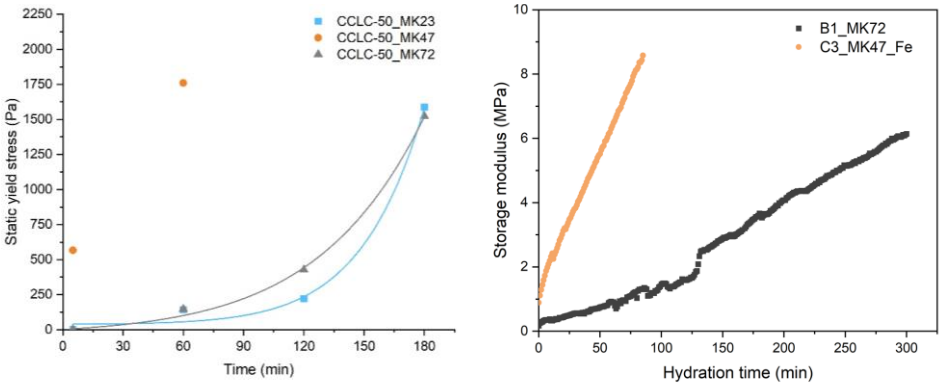

Figure 5 Growth of static yield stress of CCLC blends and storage modulus of the clay-portlandite-gypsum system with hydration time.

5 Hydration and mechanical properties

There are three main reactions that occur in calcined clay limestone cement (CCLC) in addition to the filler effect provided by both SCMs:

1. Pozzolanic reaction between metakaolin from calcined clay and portlandite, to form C-S-H
2. Reaction of the calcite with C_3A to produce hemi- and monocarboaluminate,
3. The synergistic reaction between metakaolin, calcite and portlandite to yield hemi- and monocarboaluminate AFm phases.

These reactions contribute to strength development by forming space filling hydrates (C-S-H and AFm) while reducing low-strength portlandite.

Several techniques are required to quantitatively determine the amount (mass/volume) of hydrates and extent of hydration of certain components. With XRD the degree of hydration of clinker and limestone can be determined. TGA can be used to more reliably quantify portlandite. Determination of the reaction degree of metakaolin is challenging and has been determined to be best done using the mass balance approach [27].

Research [28,29] has shown that parameters such as the composition of clinker, particle size of the individual components, temperature and alkali content affect strength development. It has also been largely reported that the 3-day strength of CCLC is (slightly) lower than that of OPC but higher than that of fly ash or slag cements at comparable clinker factors. Typically, 7 d and 28d strength are comparable or even higher than OPC.

Strength development before 3 d is not dependent on the clay grade, that is metakaolin content (Figure 6). Other factors, especially specific surface area seem to have a higher effect as shown in the strength correlation below. And as discussed earlier (section 4), the high specific surface area was due to the presence of iron secondary phases. As hydration progresses from 7 to 28 d the effect of metakaolin becomes apparent. It is important to once again note that by 28 d calcined clays with 40 wt.% of metakaolin normally have comparable strength to OPC. Beyond 28 d little strength gain is observed in general [8]. It has been reported that high grade clays (>80% metakaolin) reach their maximum strength after one month while the low-grade clays (<30%) have probably depleted their metakaolin already at earlier reaction times. High grade clays may continue to slowly react over time, but the depletion of portlandite means that there is little contribution to strength. Therefore, there is no huge advantage in using high grade clays and 40-60% seems to be the best range.

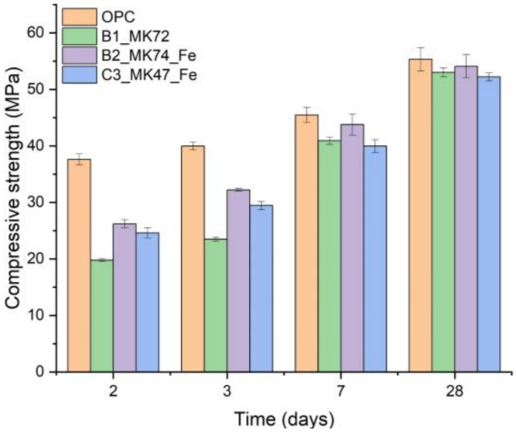

Figure 6 Variation of zeta potential at 60 wt.% substitution.

6 Durability

Calcined clay limestone cement (CCLC) performs better than other blended cements and OPC in most exposure conditions. The main reason for this is that the pore-structure has been reported to be more refined (illustrated, for example, by a smaller critical pore entry radius) than that of OPC and, for example, fly ash blended cements [1,30]. This is due to the hydration reactions described earlier which lead to better space filling and thus a more refined and uniform distribution of pores. Refined porosity leads to lower permeability and thus more durable concrete in many exposure conditions. Chloride resistance is a good illustration of this effect.

Chloride ingress depends on the diffusion of ions through concrete which is mostly governed by the porosity of the concrete, as well as the phase assemblage of the binder [8,30]. The greater the substitution of clinker with calcined clay and limestone (2:1 ratio) the better the resistance to chloride ingress. In addition to the pore refinement, it has been reported that the higher alumina content of CCLC leads to the binding of more chlorides leaving fewer ions available to interact with the reinforcement and that the conversion of monocarboaluminate to Friedel's salt leads to a chemical bonding of the chlorides which reduces the reversibility of the binding [31]. Hence, using CCLC-50 concrete structures in saline environments is expected to improve service life.

CCLC mortars have also been shown to be resistant to Alkali-silica reaction (ASR) expansion even when reactive aggregates were used [32,33]. This has been reported to be due to the low alkalinity in CCLC (slightly lower pore solution pH than OPC) and also the release of alumina in the pore solution from calcined clay which can reduce the rate of aggregate dissolution significantly [33].

Carbonation is known to be generally higher in blended cements concrete, and the same is true for CCLC [34]. The main component binding carbon dioxide from the atmosphere in concrete is calcium oxide. Thus, the reduction of clinker leads to an increase in carbonation rate. Results have shown that prolonged curing before exposure may improve carbonation resistance. Additionally, carbonation is slow at very low and very high humidity which tends to be the condition at locations where CCLC has the highest potential use, such as tropical countries, or in marine structures [8].

7 Outlook

Recent developments have seen the legislation of CCLC largely approved in India. In Europe substitution levels of up to 35% are possible and efforts are being made for CCLC-50 to be approved based on the vast results showing its reliable performance. An increasing number of companies are moving beyond just showing interest in the initiative but rather synthesizing plans for implementation. Thus, we can only predict that the implementation of CCLC is set to grow considerably in the near future.

The target to reach net zero of carbon emissions by 2050 as an industry requires the use of various techniques together and the use of reliable SCMs is a key part of the vision. Calcined clays look set to be more than just a topic of interest in the conversation.

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