Use of low grade kaolinitic clays in development of a pozzolan-cement binder system

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ABSTRACT: The use of calcined, kaolinite-rich clays as pozzolanic components in blended cements has gained a great deal of attention in recent years. This reflects its impact on reducing the total embedded carbon dioxide associated with concrete made from such binders. Reduction of CO_2 is two-fold: the clays are calcined at a lower temperature than Portland cement and also replace some of the clinker in the binder phase. Pure kaolinite clay is relatively expensive however, as it is used in other industrial applications.

This work studies the potential utilization of low-grade (less pure) kaolinitic clay as a supplementary cementitious material in mortar formulations. Examination by XRD revealed the presence of kaolinite, illite and quartz as the main clay minerals present in the materials. The clay samples were dried and calcined at 600 ºC and the effect of heat treatment on the physical, mineralogical and microstructural properties studied.

The calcined clay was uniformly blended with ordinary Portland cement at replacement levels of 10%, 20% and 30% by weight and their mechanical properties determined after 7 and 28 days. Blended cements containing 10 wt.% and 20 wt.% calcined clay were seen to have compressive strength results comparable to the reference cement at 28 days.

KEY WORDS: Pozzolan; Kaolinitic clays; Microstructural properties; Calcined clay; Compressive strength; Portland cement.

1 INTRODUCTION

The incorporation of supplementary cementitious materials (SCMs) as a partial replacement of Portland cement for construction applications has been reported as the most effective approach towards the reduction of greenhouse gases from the construction industry [1].

Industrial and agricultural by-products such as pulverised fly ash, ground granulated blast-furnace slag (GGBS), silica fume and rice husk ashes are the most common SCMs. Aside their contribution to the mitigation of solid waste management problems, SCMs also present several technical advantages in concrete including improved compressive strength, durability and impermeability [2].

Notwithstanding these benefits, the accessibility of conventional SCMs from industrial and agricultural sources has its own challenges due to the over dependence on the few industries for a worldwide supply [3]. Again, most of the waste generated by these industries, which can be used as SCMs are of low quality compared to the standard [4]. It has become therefore essential to explore other materials, which possess the quality and are available in quantities that can meet the construction industry's demand.

Kaolinitic clays have been described as the most suitable alternative to replace fly ash and other industrial by-products due to their properties and availability. Clays in their natural form may not have the desired reactivity because of their crystalline structure. However, after heat-treatment, their crystalline structures are transformed into amorphous, thereby improving their pozzolanic reactivity [4]. Furthermore, the temperatures required for clay calcination (usually between 600-900 ºC) are much lower than that of Portland cement [5]. This, in a way, decreases the amount of energy and carbon footprints related to the concrete industry. Even so, clays containing high levels of kaolinite are most preferable because of their appreciable reactivity. High-grade kaolinitic clays are, however, not easily accessible since they are found in only specific places and can also be expensive due to their use in the paper and ceramic industries [6].

Several researchers [7] have extensively studied the use of pure calcined kaolinitic clays for concrete applications and reported improved mechanical and durability properties due to its high reactivity. This research studies the influence of low-grade kaolinitic clay, calcined at 600 ºC, on the thermal, mineralogical and mechanical properties of mortar.

2 MATERIALS AND METHODS

Portland cement (CEM I 52.5 N), manufactured by Hanson, was used as the main binder in this research. Brick clay was obtained from a local brick manufacturer in Bellingdon, England. The raw clay was dried in an oven at a temperature of 120 ºC.

The clay was crushed, pulverized using a hammer mill and oven-dried at 50 ºC for 24 hours. It was then calcined in a Nabertherm Muffle Furnace at a temperature of 600 ºC at a heating rate of 10 ºC/min. The calcined clay, after cooling on a laboratory bench, was milled into fine powder.

Chemical composition of the raw samples were determined by XRF using Panalytical Axios mAX WDXRF spectrometer. XRD analysis of the powders were also carried out using a 3rd generation Malvern Panalytical Empyrean XRD Diffractometer. TG/DSC analysis was also conducted with the Perkin Elmer DSC 7 analyser. Particle size analysis was performed using the Laser Diffraction method with the Malvern Mastersizer 2000 analyser.

CEM-I cement was partially replaced with the calcined clay in weight percentages of 10 wt.%, 20 wt.% and 30 wt.% to form Portland-calcined clay blended cements. 50 × 50 × 50 mm mortar cubes were prepared according to methods specified by BS EN 196-1:2016, using a cement to sand ratio of 1:3 and water/binder ratio of 0.4. The mortar cubes were cured under water and their respective compressive strengths determined after 7 and 28 days. Setting times and water demand was also determined using the Vicat apparatus as described in BS EN 196-3:2016.

Figure 1. Raw clay

Figure 2. Calcined clay

3 RESULTS AND DISCUSSION

The particle size distributions of the clay, calcined clay and CEM-1 cement are presented in Figure 3. Other physical properties are also shown in Table 1. Specific gravity is observed to decrease with increasing calcined clay content in the mortar. Water needed to form a workable paste, on the other hand, increased with increase in the calcined clay content. The smaller particle size of the calcined clay, possibly increased the surface area of blended cement and therefore required more water [8]. There was also a progressive increase in both initial and final setting times as the pozzolan content increased.

Table 1. Some properties of the reference cement , calcined clay and blended cements

Property	CEM I	CC	10%CC	20%CC	30%CC
Specific gravity	3.15	2.62	3.05	2.96	2.82
water demand, %	28.2	–	32.4	33.3	39
Initial set, min	162	–	180	190	200
Final set, min	250	–	280	295	320

CC – Calcined clay

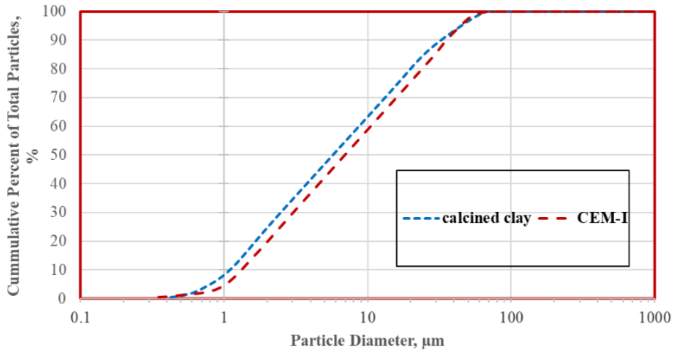

Figure 3. Particle size distribution of calcined clay and the reference cement.

The XRF analysis of the calcined clay and the reference cement are shown in Table 2. The chemical compositions of the raw materials were generally within acceptable limits. The calcined clay contains 40.54% SiO_2, which passes the ASTM C618 minimum requirement of 25% for pozzolans. Also, the sum SiO_2, Al_2O_3 and Fe_2O_3 is higher than the minimum 70% prescribed by ASTM C618 but must, however, be interpreted with caution.

Table 2. Chemical composition of calcined clay and the reference cement.

Material	**Chemical composition, %**								
	SiO_2	**$A1_2O_3$**	**Fe_2O_3**	**MgO**	**CaO**	**Na_2O**	**K_2O**	**SO_3**	**Cl**
CC	**40.54**	**28.75**	**25.42**	**1.40**	**0.25**	**0.20**	**1.07**	**0.19**	**0.01**
CEM-1	**21.0**	**4.4**	**2.7**	**1.6**	**66.7**	**0.6**	**1.99**	**2.27**	**≤0.1**

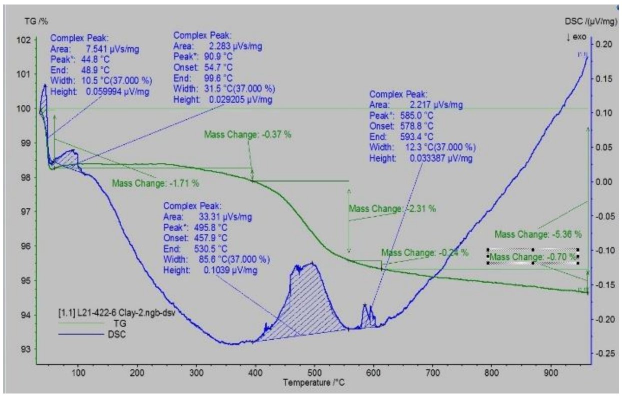

Figure 4. TGA/DSC of the clay.

The XRD patterns of the raw clay, as shown in Figure 5 is generally made up of quartz, kaolinite, illite and other associated minerals. The presence of illite can be associated with K_2O and Na_2O/MgO [13] as seen in the XRF data in Table 2.

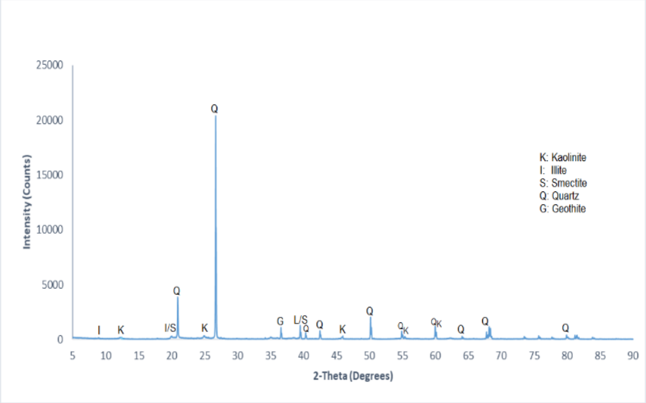

Figure 5. XRD of clay

The 7 and 28 day compressive strength results of the reference and blended cements are presented in Figure 6. The control sample recorded 7 and 28 day strength of 36.6 MPa and 58.5 MPa respectively. These strength values consistently reduced as the calcined clay replacement increased from 10 wt.% to 30 wt.%. The addition of 10% metakaolin decreased strengths to 34.5 MPa and 55.5 MPa respectively, but still satisfied EN 197-1 [17] standard. Considering the percentage reductions, 20 wt.% appears to be the optimum replacement level.

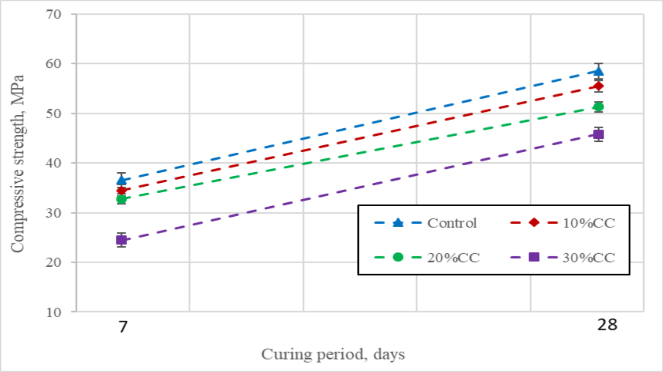

Figure 6. Compressive strength of calcined clay mortar.

4 CONCLUSION

This paper has studied the potential of calcined low-grade kaolinitic clay, calcined at 600 °C, as cement replacement in mortar formulations. The chemical compositions of the reference cement and calcined clay contained all the relevant oxides and were within acceptable limits. TGA/DSC analysis revealed a complete dehydroxylation of kaolinite to form metakaolinite at 600 °C. XRD analysis showed that the clay largely made up of quartz, kaolinite, illite and other associated minerals. The partial replacement of CEM I with the calcined clay caused a decrease in both early and later strengths. At this stage, 20 wt.% is recommended as the optimum replacement, pending further investigations.

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