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Strength and Durability of Cement-Based Materials Incorporated with Low Grade Kaolinitic Calcined Clay

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ABSTRACT

Existing literature has shown that high grade kaolin can be processed into metakaolin to replace portions of Portland cement without compromising the properties of cement-based materials. However, , there is limited literature pertaining to the use of clays with low content of kaolinite as a pozzolanic materials, even though lower grade kaolin exists abundantly on the earth crust and in almost every country. This work analyzed clay obtained from Ghana. The clay material was calcined at temperatures ranging from 600^{o}C to 1000^{o}C. The raw clay characterization was determined based on geotechnical properties and the use of solid state ^{27}Al Magic angle spinning nuclear magnetic resonance (MAS NMR). Strength activity index prescribed by the American Society for the Testing of Materials (ASTM) was used as a method of determining the appropriate temperature for clay calcination. Sorptivity analysis was determined as a way of checking the durability of cement and calcined clay mixtures. The results of the test confirmed that the clay material used was a low grade kaolinitic type. The most suitable temperature that yielded maximum strength from the mortar mixtures between cement and calcined clays was at 800^{o}C. The sorptivity test also showed that the incorporation of calcined clay in cement based products refined the pore structure which may enhance durability. The refinement of the pore structure was determined by studying the sorptivity coefficient values which showed that the material resisted the ingress of ions. The study recommended the use of low grade calcined kaolinitic clay as a suitable pozzolanic material.

INTRODUCTION

The use of calcined clays as Portland cement replacement material to formulate blended cementitious binders appears to be increasing in many developing countries including South American countries, Asian, and many African countries (Tironi et al, 2014; Escalera et al, 2014; Chakchouk et al, 2006). The prospects of using calcined clays are reported by several researchers who indicate that, not only does the calcined material improve the mechanical properties of cement-based materials such as concrete, mortar and paste, but also provides reduce cost of cement used in projects containing concrete or mortar. The reduced cement usage also translates to minimize carbon dioxide emissions in the environment (Bediako et al, 2012; Mitrović and Zdujić 2014; Alujas et al, 2015). The demand for Portland cement worldwide has been rising yearly and is estimated to hit about 5 billion tonnes by 2030 which will translates to more carbon dioxide emissions (Potgieter 2012). Lothenbach et al, (2011) reported that a more sustainable approach to cut down the increasing demand of cement in the near future would be the increased use of supplementary cementitious materials that includes calcined clays and shales and other industrial by-products like fly-ash, silica fumes, and slags. The calcination temperatures suitable to produce a good cement replacement material have been reported to be between 500°C and 900°C depending on the nature and type of clay (Tironi et al. 2012; Shvarzman et al. 2003).

Clays from different origins have different properties however the basic building blocks of tetrahedral and octahedral units are the same (Zhou and Keeling 2013). The reactivity of calcined clay with cement is influenced by its kaolinite content and the presence of impurities found in the clay. The impurities that are commonly found in clays include quartz, anatase, rutile, pyrite, siderite, feldspar, etc (Mitrović and Zdujić 2014). Clays with high kaolinite content (≥65%) are classified as high purity clay whereas those with kaolinite content between 40% and 65% are classified as medium quality clay (Aras et al. 2007). Alujas et al. (2015) classified low grade kaolinitic clays as having kaolinite below 40%. The earth crust has abundance of clay, however pure or high grade kaolinitic clays occur less abundantly and therefore processed high grade kaolinitic clays appear to be very expensive as a supplementary cementitious material (Alujas et al. 2015). Today a lot of efforts have been channeled into the development of clay such as montmorillonite, illitic which belongs to a 2:1 clay type and even low grade kaolinitic clays (i.e 1:1 clay type) as pozzolans because of its geographical advantage (Fernández et al. 2011; He et al, 1994; Maia et al. 2014).

Low grade kaolinitic clays occur naturally in the earth crust with associated non clay minerals. The content of kaolinites as well as non-clay minerals influence the quality and reactivity of calcined clays (Tironi et al. 2013). The origin and the geographical location of clay also have direct influence on the content of clay and non-clay material. This therefore suggests that clay from different areas or countries may contain different clay minerals. Alujas et al. (2015) have reported that there is a growing interest on the development of low grade kaolinitic clays as a pozzolanic material. Much literature exists on high grade kaolinitic clays but not on low grade ones (Maia et al. 2014; Bich et al. 2009). This therefore calls for the need to develop a lot of literature on the use of low grade kaolinitic clays as a supplementary cementitious material because of the material's geographical advantage. As almost all cement in Western Africa is imported, the ability to utilize a locally-available material presents an opportunity to reduce the carbon footprint of concrete works, but also improving the local economic situation. This study seeks to investigate the strength performance and durability of blended cements between calcined low grade kaolinitic clays and Portland cement.

MATERIALS AND METHODS

Materials. The materials that were used for the study were Portland cement meeting both ASTM C150 Type I and Type II classifications, clay material, graded sand, a chemical admixture and potable water. The Portland cement was obtained from Ash grove, Chanute, Kansas in the United States. Table 1 presents the properties of the cement. The clay material was obtained from Ghana in the Ashanti region area of the country. Table 2 presents the geotechnical properties of the clay.

The clay is classified as silty clay with an actual clay content of 28.4%. Graded sand which conformed to ASTM C778 was used for mortar specimens. Mixtures also included a polycarboxylate type high range water reducing (HRWR) admixture. Mixture water was potable municipal water from the University of Missouri- Kansas City (UMKC).

Table 1. Properties of Portland cement

Property	ASTM Type I/II cement
Physical	
Fineness (m^2/kg)	401.7
Specific gravity	3.13
Chemical	
SiO_2 (%)	20.49
Al_2O_3 (%)	4.26
Fe_2O_3	3.14
CaO (%)	63.48
MgO (%)	2.11
SO_3 (%)	2.90
Na_2O+K_2O (%)	0.49
LOI (%)	2.20
Mineralogy	
C_3S (%)	56
C_2S (%)	15
C_3A (%)	6
C_4AF (%)	9

Table 2. Some geotechnical properties of the clay

Particle Size Distribution (%)				Soil type
Clay	Silt	Sand	Gravel	Silty clay
28.4	19.5	52	0.1	

Methods

Clay characterization. The raw clay was characterized based on its geotechnical properties and these properties included clay, silt and sand content. Aluminum structure of the clay was probed to determine if the clay was a 1:1 or 1:2 type using nuclear magnetic resonance (NMR). The NMR was a Tecmag Apollo Console (Houston, TX) with 8.45 T magnet and custom, single channel, 4 mm wide-bore NMR probe which evaluated ^{27}Al. About 90 mg of sample was taken for the analysis and signals were represented as chemical shift value; δ: ppm. The ^{27}Al frequency was 93.074 MHz. ^{27}Al spectrum was acquired with MAS spinning frequency, last delay and 90º pulse length of 8 KHz, 1s and 2.5 µs, respectively. Aluminum nitrate [Al(NO_3)] was used as the reference compound for ^{27}Al. This experiment was performed at ambient temperature without any corrections for sample heating.

Clay calcination. The clay material was air-dried for about 72 hours and ground into fine particles. Ground air-dried clay material were placed in a ceramic bowl and placed in an electric furnace. The clay material was calcined at each temperatures of 600˚C, 700˚C, 800˚C, 900˚C, and 1000˚C in the furnace for 3 hours. After the calcination period, the furnace was switched off and the ceramic bowl and its content allowed to cool down in the furnace for about 24 hours. The calcined clay material was sieved through a 75µm sieve using a sieve shaker.

Strength determination. The strength activity index described in ASTM C311 was used for the strength determination of the mixtures between the calcined clays and Portland cement. The standard specifies a replacement value of 20% of Portland cement. The determination of strength activity index is given as:

$$SAI = \frac{A}{B} \times 100\% \quad (1)$$

Where SAI= strength activity index
A= compressive strength of blended cement containing the calcined clay
B= compressive strength of the control

Mortar for the determination of strength performance was prepared in accordance with ASTM C305. The clay material calcined at the various temperatures was used to prepare different batches of mortars. Table 3 shows the mortar mixture proportions used for the SAI determination. The flow of the mortars were maintained using the HRWR, shown in Table 3 as weight of cementitious materials. Flow of the mortar was determined according to ASTM C1437. In addition to the 20% replacement used to determine the ASTM C311 SAI, mixtures were also prepared with 10%, 30%, and 40% cement replacement using the calcining temperature with the highest strength, which was 800°C (Table 4). Samples were cured for 3, 7, or 28 days according to ASTM C192 in lime water. Compressive strength of the cube samples were performed according to ASTM C109.

Table 3. Mortar mixture proportions used for SAI determination

Temp (ºC)	Mix name	Mass (g)				w/b	HRWR (%)	Flow (%)
		Cement	Clay	Sand	Water			
Control	Control	500	0	1375	242	0.485	0.0	106
600	20P600	400	100	1375	242	0.485	0.4	111
700	20P700	400	100	1375	242	0.485	0.4	110
800	20P800	400	100	1375	242	0.485	0.4	110
900	20P900	400	100	1375	242	0.485	0.3	115
1000	20P1000	400	100	1375	242	0.485	0.2	116

Table 4. Mortar mixture proportions of cement and various amounts of calcined clay

Mix	Content (%)		w/b	Mass (g)				HRWR (%)	Flow
	Cement	Clay		Cement	Clay	Sand	Water		
Control	100	0	0.485	740	0	2035	359	0.00	107
10P800	90	10	0.485	666	74	2035	359	0.14	107
20P800	80	20	0.485	592	148	2035	359	0.32	114
30P800	70	30	0.485	518	222	2035	359	0.34	105
40P800	60	40	0.485	444	296	2035	359	0.45	107

Durability studies. Since durability-related distresses are a function of water and ion transport through the hydrated cement phase, the durability analysis for this study focused on absorption. Water sorptivity testing was performed in accordance with the ASTM C1585. The theory behind sorptivity states that if a mortar or concrete surface is exposed to wetting by water, then the cumulative water absorption, *i* is proportional, during the initial absorption period, to the square root of elapsed wetting time *t*:

$$i = S\sqrt{t} \tag{2}$$

S is the sorptivity measured in g per mm^2 (of wetted area) per $sec^{1/2}$ and is determined from the slope of the linear part of i versus $t^{1/2}$ curve (Sabir et al., 1998).

RESULTS AND DISCUSSIONS

Clay characterization. Figure 1 shows the solid state ^{27}Al MAS NMR of raw clay. Two resonating points corresponding to 68.30 ppm and -0.76 ppm clearly observed. The two resonances indicate a 1:1 clay type i.e. an octahedral ($Al^{(vi)}$) and a tetrahedral ($Al^{(iv)}$) environment. Clay types having 1:1 structure are usually classified as a kaolinitic type of clay. The resonating point around 68.30 ppm corresponds to a tetrahedral environment whereas the point at -0.76 ppm shows an octahedral environment confirming the studies of Hanna et al. (1995). From Table 2, the clay content that was present in the raw material was approximately 28%. Corroborating the results between Table 2 and Figure 1, it could be stated that the clay is a low grade kaolinitic clay.

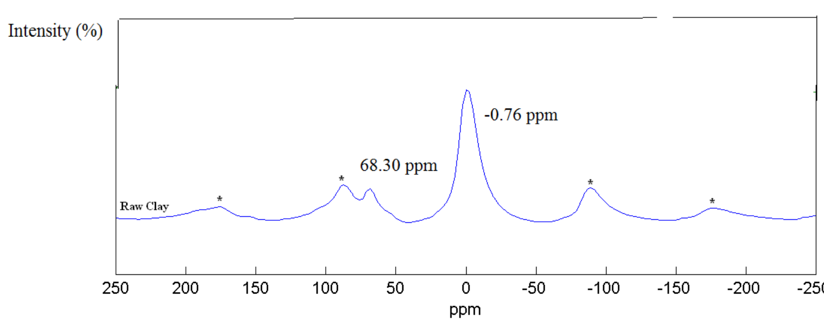

Figure 1. Solid state ^{27}Al MAS NMR of raw clay

Strength performance (SAI). Figure 2 shows the strength activity index (SAI) of mortars containing calcined clay materials from 600-1000^{o}C. The ASTM C618 standard specification recommends that mortars containing 20% pozzolan must attain strength higher than 75% of the control mortar at both 7 and 28 days. All mixtures met the criteria at both ages. The SAI values showed that the mortar which contained calcined clay at 800^{o}C (20P800) had the maximum strengths at 7 and 28 days. The performance of 20P800 indicated that calcination temperature at 800^{o}C was the most suitable temperature to provide more reactive phases in the calcined material.

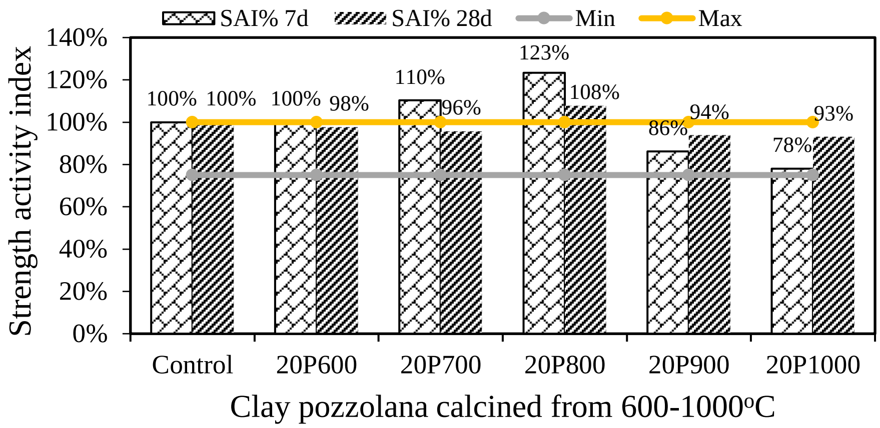

Figure 2. SAI of mortars containing calcined clay from 600-1000^{o}C

Compressive strength. Since 800^{o}C had the highest SAI at the ASTM C311 prescribed 20% replacement, additional replacement levels were also investigated. Table 4 shows the mortar mixture proportions between Portland cement and calcined clay at 800^{o}C. Figure 3 presents the effect of the calcined material on strength of Portland cement. Compressive strength values obtained at 20% (20P800) replacement of Portland cement gave the maximum strength values at 3, 7 and 28 days. Beyond 20% replacement the strength was reduced. The performance of 20P800 indicated that 20% of calcined clay used to replace cement was very adequate to react and form stable compounds with Portland cement. This enhanced the strength performance of 20P800. Beyond 20%, the calcined materials behaved as inactive materials.

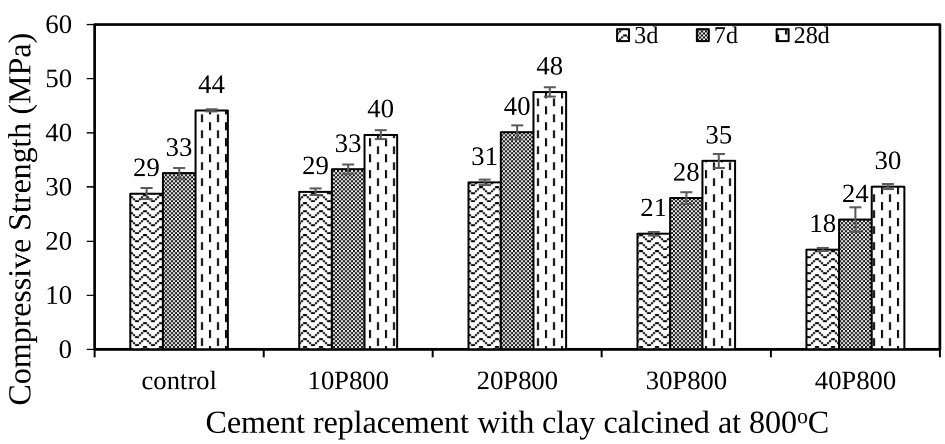

Figure 3. Compressive strength of mortars containing 10-40% calcined clay

Durability test. Figure 4 shows the sorptivity analysis of the control mortar and with 20% replacement for cement with the 800°C calcined clay. Water sorptivity is a form of transport property of water or ions in unsaturated porous surfaces. It characterizes the material's ability to absorb and transmit water or ions through it by capillary suction (Sabir et al., 1998). The work of Siddique (2013) stated that reducing sorptivity is important to decrease ingress of chemical compounds including chlorides and sulfates which can cause serious damage.

Figure 4 shows initial and secondary sorptivity coefficients. The initial and secondary coefficients for the control mortar (CON) were 0.0107 and 0.0017 respectively whereas that of the blended cement mortar (20P) were 0.0028 and 0.0008 respectively. The initial sorptivity values of CON and 20P indicated that the blended mortar resisted ingress of ions more than the control. The trend was the same for the secondary sorptivity values. Generally, the sorptivity trends pointed out the higher resistance of mortar mixture containing 20% calcined clay than the unblended mortar mixture. This could mean that the blended mortar mixture contributed to pore size refinement of the mortar structure. In this case blended materials would be more durable than the unblended cement.

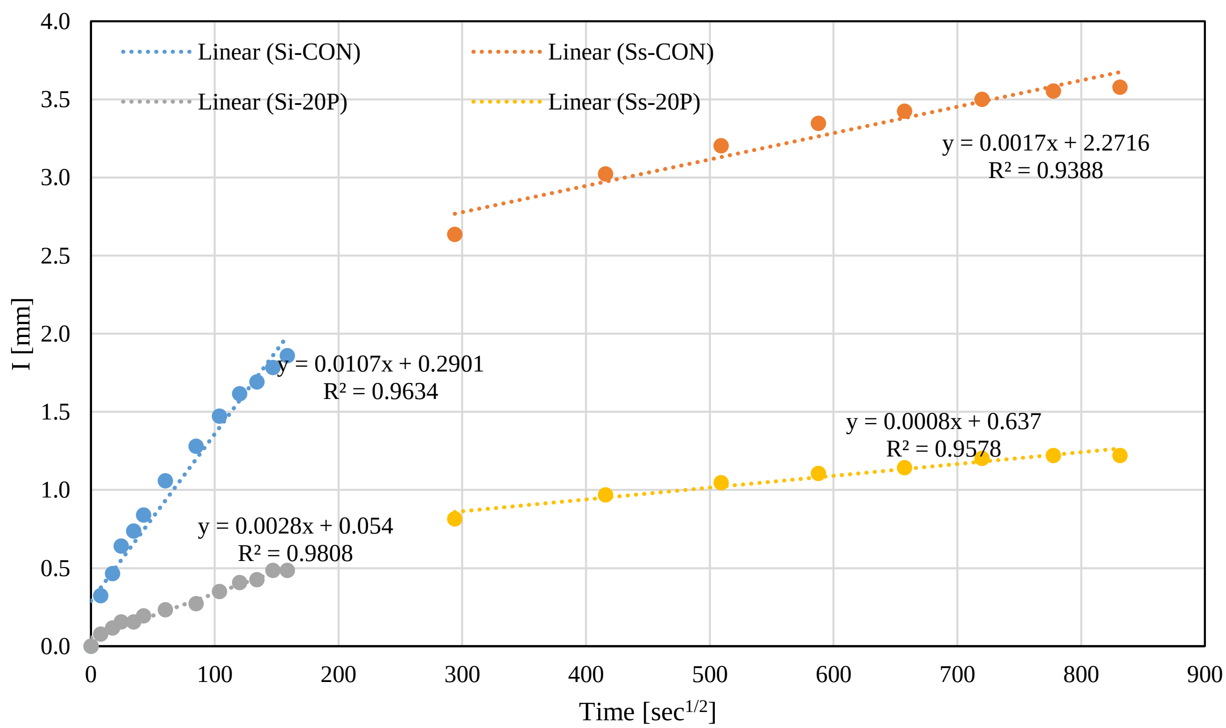

Figure 4. Sorptivity of control and calcined clay mortars

CONCLUSIONS AND RECOMMENDATIONS

Much of the literature supports using calcined high purity kaolin clay for cement replacement. The clay both reduces the carbon footprint of the concrete mixture, but also improves strength and durability. However, where pure kaolin clays are not found, lower purity, local materials have the potential for incorporation into concrete as well. This study investigated a mixed silty clay soil from Ghana calcined at various temperature. The following conclusions were drawn from the study:

1. The clay material characterization showed that the clay was a 1:1 kaolinitic clay type of low kaolinitic grade.
2. The calcination temperature of 800^{o}C was suitable to produce more pozzolanic active phase in the calcined material hence increased the strength activity index
3. Calcined clays at 800^{o}C replacing 20% of Portland cement led to enhancement in strength performance than even the unblended mixtures.
4. The application of 20% calcined clays in Portland cement positively influences pore size refinement of cement-based products, resists the ingress of ions and therefore ultimately improves durability of the material

Calcining this clay in Ghana has the potential to reduce the amount of imported clinker while improving the strength and durability of local concrete. The work suggests further studies are needed on the nature of hydrated compounds formed in the mixture between Portland cement and calcined clays and long-term performance in the field.

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