Effect of thermal treatment on the pozzolanic activity of natural clay from selected Kenyan wetlands

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Abstract The use of cement in construction is costly and degrades the environment. Therefore, affordable and easily available alternatives are needed. This study evaluated the effect of thermal treatment on the pozzolanic activity of clay soils. Three wetland clays collected from three sub-counties of Murang'a County, Kenya (Kahuro, Kiharu and Maragua Sub-Counties) were studied after thermal activation. Thermal treatment (calcination) was carried out in an electronic muffle furnace (Advantec KL-420) at 600, 700, and 800°C for a duration of 2 hours. The chemical oxide composition was evaluated using X-ray fluorescence (XRF). Three methods (electrical conductivity, Frattini test, and compressive strength test method) were used to assess the pozzolanic activity of clay. A decrease in the electrical conductivity of the lime-clay solution was observed over a 24 hour period. Results of the Frattini test showed that clay calcined at 600°C and 700°C reacted with Ordinary Portland Cement (OPC) - CEM-I and reduced CaO and OH^- concentrations to levels below the solubility curve of $Ca(OH)_2$. Calcination of clay from Kahuro and Maragua sub-counties, at 600°C and 800°C, respectively, increased the strength activity index of cement blocks from less than 0.75 to about 1 after 28 days of curing. Therefore, a temperature range of 600-800°C was considered effective for calcination. We conclude that thermal treatment increases the pozzolanic activity of natural clay for use as a replacement for cement. Therefore use of blended cement may be a sustainable alternative to the use of cement alone.

Keywords: calcined clay, pozzolanic activity, thermal treatment, pozzolana, cement.

1. Introduction

Conventional building materials in most developing countries are unaffordable to a majority of the population. In addition to the construction cost, there are rising environmental concerns due to the extensive exploitation of natural resources for general construction and other housing development activities [1]. The most commonly used type of cement in Kenya is Portland cement with an estimated consumption of 3.4 million tonnes in 2011 [2]. This material is made by inter-grinding calcareous and argillaceous materials that are then clinkered in a rotary furnace at a temperature exceeding 1300°C, fuelled by petroleum oil or coal. This process is quite expensive, particularly due to the massive demand of raw materials

and energy [3]. The resultant Portland cement is therefore expensive and unaffordable to low-income citizens. In Kenya, counties such as Murang'a reported that around 60% of the housing units have earthen floors [4]. This poor housing quality represents a threat as earthen floors are non-hygienic and can cause serious conditions such as Tungiasis [5]. On the other hand, cement production also results in emissions of approximately 866 kg CO_2/t of clinker [6]. Furthermore, cement produced and consumed globally equals 4.2 Bt per year [7]. This makes the cement industry accounts for 5-8% of global anthropogenic CO_2 emissions, thus majorly responsible for global warming and climate change [8]. Hence, searching for cheap and eco-friendly materials to replace cement is considered one

of the most effective ways to mitigate the environmental impact of the cement industry, lower the construction cost while improving housing quality, especially in developing countries.

According to ASTM C125, a pozzolanic material is referred to as a siliceous and aluminous material which, in itself, possesses little to no cementitious value, but will, in a finely divided form and in the presence of moisture, chemically react with calcium hydroxide $(Ca(OH)_2)$ at ordinary temperatures to generate compounds possessing cementitious properties [7], [9]. It is known that the use of pozzolanic materials in large quantities is important. This ensures that the cement industry remains sustainable and economical, not only in terms of energy efficiency and environment considerations, but also with respect to the durability and life-cycle cost of the resulting concrete structures [10]. On the other hand, other benefits include the increase in strength, low permeability, as well as high sulphate resistance [7]. The amount of pozzolans introduced varies from 5 to 40% of cement [1],[11], [12],[13],[14],[15]. Various high quality reactive pozzolana such as silica fume, fly ash [15], ground granulated blast furnace slag, bagasse ash, industrial by-products [11], and rice husk ash have been introduced as supplementary cementitious materials (SCMs) and are being used completely [9]. Nevertheless there is a shift in interest to search for alternative SCM sources due to supply-and-demand concerns in the future. One of the most promising alternative sources is clay. This material is abundant and widespread, which can lower the transportation cost [6], [12]. Extensive studies have reported that kaolin deposits [16], [17], uncalcined termite clay [18], fired rejected clay bricks [8], burnt clay waste [19], [20], excavated waste clay [21] could be used as SCMs. The clay deposits were found to contain a number of different types of clay minerals like kaolinite, illite, montmorillonite, palygorskite, etc [12]. In addition to reducing the significant carbon dioxide emissions from cement production, these pozzolanic materials have showed to improve the mechanical properties and durability of concretes [1], [6], [20], [22]. However, the extremely slow reaction rate of raw clays at ambient temperature usually leads to low strength which urges the need for thermal treatment.

Thermal treatment of clay produces a state of structural disorder that is a metastable state. Thus, Metakaolin refers to the kaolinite that has been calcined and shows an amorphous reactive structure [23]. Pozzolans contain amorphous and glassy silica which consist of alumino-silicate $((Al_2O_3)_2(SiO_2)$ and $(Al_2O_3)_4(SiO_2))$ [24]. These amorphous phases react with $Ca(OH)_2$ in the presence of water producing cementing compounds like calcium silicate hydrate (C-S-H) along with some alumina-hydrated phases [12], [23]. A study [21] reported that the dehydroxylation of kaolinite happened between 350°C and 600°C, while montmorillonite and illite dehydroxylation took place between 600°C and 950°C. A number of authors have also reported that clays could be transformed into SCMs when they are calcined between 600-900°C [6], [17], [21], [23], [25], and that their pozzolanic activity depended on the dehydroxylation degree and the available surface for reaction. These were affected by calcination conditions such as residence time, temperature, and heating regime [26].

The pozzolanic activity of supplementary cementitious materials is evaluated using direct and indirect methods [7], [14]. Direct methods evaluate the pozzolanic activity by measuring the concentration of Ca^{2+} and OH^- in a solution containing the pozzolanic material and saturated lime (saturated lime test); or a solution containing the pozzolanic material and Ordinary Portland Cement (OPC) - CEM-I (Frattini test) [14]. On the other hand, indirect methods monitor a physical property (strength activity index or electrical conductivity) allowing to measure the material's pozzolanicity. However, direct and indirect methods do not always correlate with each other [1], [7], [12], [14]. Furthermore, the roadmap for identifying if a material can be used as a pozzolanic material is very complex, and some indicators used for this characterization fail. Thus, a study [14] recommended using a combination of these tests to provide a robust evaluation of the pozzolanic activity. However, a roadmap was suggested to evaluate the suitability of industrial by-products for use as SCMs [11]. This roadmap suggested that the most basic test methods to start the analysis are associated with material physical and chemical analysis. The chemical composition requires that the sum of Al_2O_3, SiO_2, Fe_2O_3, as per ASTM C618, be >70% (for class F fly ash). If the chemical composition falls between the requirements and the fineness is characterized, the Frattini test should be conducted. In the making of cement blocks, a 20% by weight replacement of cement with fly ash should be sufficient to achieve a strength activity index (SAI) of at least 0.75 at 7 and 28 days of curing [11].

Based on the background above, it is evident that extensive studies pointed out that natural clays could be used as supplementary cementitious materials after

thermal treatment. However, the pozzolanic activity of clay extracted from wetlands, and the mechanisms of their pozzolanic reactions are yet to be established. Therefore, the aim of this research was to determine the effect of thermal treatment on the pozzolanic activity of wetland clay.

2. Materials and methods

2.1. Materials

Natural clays (collected in triplicates) were obtained from Gathima wetland in Gatundu village, Kahuro sub-county; Murari wetland in Murang'a town, Kiharu sub-county; and Kaingiro wetland in Gakoigo town, Maragua sub-county (Fig. 1). In each site, the three replicates were randomly sampled at a depth of 60 cm. The samples were coded as GT1, GT2, and GT3, for Gatundu; MU1, MU2, and MU3 for Murang'a Town; and GK1, GK2, and GK3 for Gakoigo. Undesirable components such as roots, leaves of trees and plants were removed from the samples before use. The samples were then dried at 105°C to a constant weight using an EYELA windy oven (Model WFO – 1000ND, Rikakikai Co. Ltd, Tokyo, Japan). The samples were then crushed using a ball mill and sieved through a 75 microns sieve size [27].
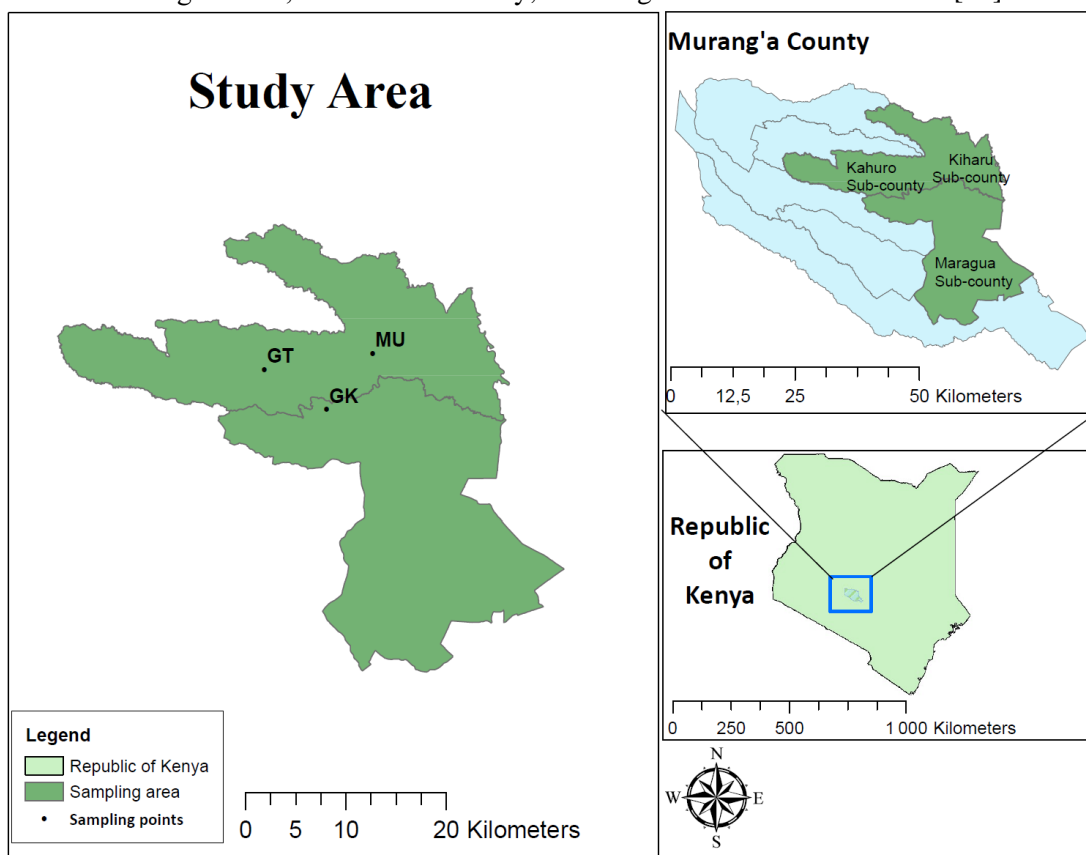
Fig. 1. Map of study area showing the sampling sites GT (Gatundu), MU (Murang'a Town), and GK (Gakoigo)

2.2. Characterization of raw clay

2.2.1. Determination of loss on ignition (LOI)

This test was intended to estimate the amount of organic matter which reduces the pozzolanic activity if present in amounts higher than 10% [28]. To determine the loss on ignition (LOI), 1 g of the sample was oven dried at 105°C for 24 hours. Next, the sample was weighed to determine the moisture content and then calcined at 500°C for 24 hours using an electronic muffle furnace (Advantec KL-420, Japan) [29], [30]. The analysis was done in triplicates for each sample. The LOI value was calculated using equation (1):

$$LOI \% = \left(\frac{A}{B}\right) \times 100 \qquad (1)$$

Where A is the loss in mass between 105°C and 500°C, B is the mass of moisture-free sample. Calculations were made to the nearest 0.01%.

2.2.2. Determination of chemical oxide composition

The chemical analysis was conducted using X-ray Fluorescence using a handheld XRF analyser (S1 TITAN Handheld XRF Analyser – Bruker) [16], [22], [31]. The analysis was conducted at the Mines and Geology Department, at the ministry of Petroleum and Mining, Nairobi, Kenya. Each analysis was done in 3 replicates.

2.3. Clay calcination

The calcination was carried out to transform clay into an amorphous material [28]. Crushed clay was sieved through a 75 microns sieve. An electronic muffle furnace was used for calcination. Clays were calcined at 600°C, 700°C and 800°C [32]. The heating rate was 25°C per minute and the time of residence at maximum temperature was fixed at 2 hours. Samples without thermal treatment were referred to as raw clay. The calcined clays were allowed to cool down to room temperature in the furnace overnight. After calcination, the material was gently ground by hand using a mortar and a pestle.

2.4. Evaluation of pozzolanic activity

The pozzolanic activity of clay was measured using the electrical conductivity test, Frattini test and the compressive strength test.

2.4.1. Electrical conductivity test

The electrical conductivity test was conducted following the procedure described in [33] and [34]. This test assessed the pozzolanic activity by monitoring, at regular interval of times, the electrical conductivity of a saturated solution of $Ca(OH)_2$ at $40 \pm 1°C$ after the addition of clay [1]. 200 cm^3 of distilled water was heated on a hot magnetic plate (Polymix PX-MST) at $40 \pm 1°C$. Some 0.54 g of $Ca(OH)_2$ powder was mixed with distilled water, while stirring, to make a saturated solution. The initial electrical conductivity of the solution was determined using a conductivity meter (SIBATA Model SC-17 A).

Some 5.0 g of clay was added to the solution at $40 \pm 1°C$, and the mixture was continuously stirred using a magnetic stirrer for two minutes. The electrical conductivity of the resulting solution was measured at 0.033 (2 minutes), 0.5, 1, 2, 4, 22, and 24 hours. The EC value gradually decreases with time when the added material is reactive due to the consumption of Ca^{2+} ions by the pozzolanic reaction [1]. The process was repeated three times.

2.4.2. Frattini test

The Frattini test evaluated the amount of dissolved Ca^{2+} and OH^- in a solution containing OPC CEM-I and the pozzolanic material after curing for 8 and 15 days [14]. The procedure specified in EN 196-5 was used. Portland cement, OPC-CEM-I, (16 g) and the clay (4g) were mixed with 100 ml of distilled water. The chemical composition of Portland cement is presented in Table 1. After mixing the three components, samples were left for 8 and 15 days in sealed plastic bottles in a water bath at 40°C. After curing, the samples were vacuum filtered through a 2.5 µm nominal pore size filter paper (Whatman No. 42) and allowed to cool down to ambient temperature in sealed Buchner funnels. The filtrate was analysed for $[OH^-]$ and $[Ca^{2+}]$ by titration against dilute HCl (0.1 mol/l) and Ethylenediaminetetraacetic acid (0.03 mol/l) (EDTA), respectively [34]. Results were presented as a graph showing CaO (mmol/l) on the y-axis against $[OH^-]$ (mmol/l) on the x-axis. Test results below the Portlandite saturation curve indicate the removal of Ca^{2+} from the aqueous solution (the solution becomes unsaturated in Portlandite), which is then attributed to the pozzolanic activity of the material added to cement. Results lying on the line indicate zero pozzolanic activity, while the results above the line correspond to no pozzolanic activity. It should be noted that this procedure assumes that no other source of calcium is present in the system, since leaching would invalidate this approach [13].

Table 1: Chemical composition of the Ordinary Portland Cement (OPC) CEM-I used

Oxides	SiO₂ (%)	Al₂O₃ (%)	Fe₂O₃ (%)	CaO (%)	SO₃ (%)	K₂O (%)	TiO₂ (%)	Others (%)
Composition	25.38	4.75	2.91	63.00	2.32	0.79	0.25	0.6

2.4.3. Compressive strength test

This test involved the determination of the strength developed by mortar specimens following the procedure described in [14]. Cement mortars containing clay

replacing OPC CEM-I at 20% were tested. The control sample was prepared using 450 g of OPC CEM-I, 1350 g of graded sand and 225 ml of water. The test mixture was prepared with 360 g of OPC, 90 g of pozzolanic material, and 1350 g of graded sand. The water-to-cement ratio was

maintained at 0.5 to eliminate it as a variable [31]. 40 mm ×40 mm ×160 mm square prisms were cast and kept in the moulds for 24 hours. Then the prisms were demoulded and cured in saturated lime water for 7, 14, and 28 days. After the respective curing time, the square prims were removed from lime saturated water, surface-dried in an oven and cut using a concrete cutting machine to obtain 40 mm cubes. The uniaxial compressive strength was measured using a compressive strength testing machine (MATEST S.p.A TREVIOLO 24048 ITALY). The results were plotted from the average of three specimens. The strength activity index (SAI) was evaluated using equation (2) [35]:

$$SAI = \frac{CS_1}{CS_2} \qquad (2)$$

Where CS_1 is the compressive strength of cement block made with blended cement (MPa), and CS_2 is the compressive strength of cement block made with cement alone (control sample) (MPa).

2.5. Data analysis

The design used in this study was a full factorial design. Factors included the clay type varied at 3 levels, calcination temperature (Raw, 600°C, 700°C, and 800°C) and time. The results were subjected to a graphical representation of the mean and the standard deviation. The data on pozzolanic activity were further subjected to an analysis of variance to evaluate the association between independent variables and their interactions on the pozzolanic activity using R-software. Results for strength activity index at 7, 14 and 28 days were subjected to a comparison with ASTM C618 standards. Frattini test results were compared to the solubility curve of $Ca(OH)_2$ based on the EN 196-5 standards.

3. Results and discussion

3.1. Characteristics of raw clay

It was observed that all raw clay samples conformed to the ASTM C618 chemical requirements for natural pozzolans (Table 2) meaning that $SiO_2+Al_2O_3+Fe_2O_3 > 70\%$, $SO_3 < 4\%$, and $MgO < 4\%$ [11], [28]. The large presence of pozzolanic oxides suggests that clay is likely to positively influence the strength development of cement blocks. SO_3 was present in trace quantities, suggesting a positive volumetric stability and hydration kinetics when clay replaces cement [36]. On the other hand, MgO which in excess of 4% would make the pozzolana unsound, was not detected [28]. In contrast, LOI was higher than the 10% minimum required, suggesting a high content of unburnt carbon. This indicated that the adsorption of air entraining agents could be higher, which could inhibit the pozzolanic activity of raw clay [28], [36]. Thus, it was necessary to calcine the clay before its use as a replacement for cement.

Table 2: Chemical composition and loss on ignition of raw clay samples

Sample	Parameters										
	SiO_2 (%)	Al_2O_3 (%)	Fe_2O_3 (%)	CaO (%)	MgO (%)	K_2O (%)	TiO_2 (%)	SO_3 (%)	Others (%)	SiO_2 $+Al_2O_3$ $+Fe_2O_3$ (%)	LOI (%)
GT1	44.57	30.38	19.63	0.38	undetected	0.25	4.17	Undetected	0.61	94.59	14.11
GT2	45.26	28.50	20.12	0.55	undetected	0.32	4.69	Undetected	0.56	93.88	11.76
GT3	41.11	34.11	19.31	0.24	undetected	0.18	4.23	Undetected	0.83	94.52	13.03
MU1	52.77	26.53	15.63	0.86	undetected	0.41	2.43	Undetected	1.37	94.93	14.40
MU2	50.47	29.26	15.18	0.72	undetected	0.76	2.32	Undetected	1.27	94.92	12.33
MU3	48.57	30.36	15.42	0.93	undetected	1.06	2.44	Undetected	1.22	94.35	13.45
GK1	43.91	33.91	17.20	0.44	undetected	0.25	3.15	Undetected	1.14	95.02	12.84
GK2	44.06	34.36	16.99	0.33	undetected	0.24	3.26	Undetected	0.76	95.41	13.97
GK3	44.06	33.86	17.28	0.41	undetected	0.28	3.23	Undetected	0.88	95.21	13.84

3.2. Evaluation of the pozzolanic activity based on electrical conductivity

This test evaluated the reactivity of clay with calcium hydroxide. The results show the variation of the electrical conductivity (EC) of the lime-water solution after the addition of clay, as a function of calcination temperature and time (Fig. 2, Fig. 3 and Fig. 4). In the first 0.033 hour (2 minutes) following the reaction of the saturated solution of $Ca(OH)_2$ and clay, a drastic drop of the electrical conductivity was observed (Fig. 2, Fig. 3 and Fig. 4). A similar decrease in EC, evaluated at 3 and 10% per hour during the first 5 hours, was reported by Walker and Pavía [37] on calcined clay, rice husk ash, and micro-silica. This significant drop in the initial stage was owed to the high reduction rate of Ca^{2+} and OH^- ions, attributed to a fast fixation of the dissolved $Ca(OH)_2$ by calcined clay particles [12]. As similarly reported elsewhere, the EC later decreased slowly indicating a reduction in the content of chemically active components [1], [37].

The drop in electrical conductivity of clay calcined at 600°C (Fig. 2a, Fig. 3a, and Fig. 4a) was greater than 700°C (Fig. 2b, Fig. 3b, and Fig. 4b) and 800°C (Fig. 2c, Fig. 3c, and Fig. 4c). The highest decrease in EC was observed in Gakoigo (GK) clay calcined at 600°C, from an initial value of 6.54 S/m down to 4.34 S/m and 1.099 S/m at 0.033 and 24 hours, respectively (Fig. 4a). The maximum drop for raw clay was 3.9 S/m after 24 hours for both Gatundu (GT) and Murang'a town (MU) clays (Fig. 2a and Fig. 3a), compared to 3.6 S/m for GK clay (Fig. 4a). However, after calcination, GK reactivity significantly increased with EC drops of 5.44, 5.07, and 3.95 S/m for clay calcined at 600°C (Fig. 4a), 700°C (Fig. 4b), and 800°C (Fig. 4c), respectively, compared to 5.26, 5.48, 4.9 S/m (Fig. 2a, Fig. 2b, Fig. 2c, respectively), and 4.5, 3.56 and 3.33 S/m (Fig. 3a, Fig. 3b, Fig. 3c, respectively) for GT and MU, respectively, after 24 hours. This indicated that clays calcined at 600°C possess better pozzolanic reactivity, due to the presence of amorphous silica, which consumes the Portlandite phases to form additional C-S-H phases [24], [38]. The low reactivity observed at 800°C could be explained by a recrystallization of mineral phases, oxidation of iron oxides and its transformation into hematite, which ultimately led to a decrease in the amorphous phases when the heating temperature increases to 800°C [38].

Results from the analysis of variance (confidence level of 95%) showed that both clay type and calcination temperature had a significant effect on the electrical conductivity with p-values of 2.25e-05 and $< 2e-16$, respectively. Moreover, an interaction between the clay type and the calcination temperature (p-value = 8.05e-13) was also observed. This could be due to the differences in chemical and mineralogical compositions which affected the dehydroxylation degree of the clays. The individual comparison showed that there was no substantial difference between EC values for raw clay and clay calcined at 700°C (Fig. 2.b, Fig. 3.b, and Fig. 4.b), and raw clay and clay calcined at 800°C (Fig. 2.c, Fig. 3.c, and Fig. 4.c) at later ages. This closeness of the EC results showed the absence of a substantial effect when the calcination temperature excessively increases beyond 600°C [38]. However, a significant difference was observed between raw clay and clay calcined at 600°C. The results above suggested that the highest dehydroxylation degree was achieved at a calcination temperature of 600°C.

Based on this test, calcined clay from Gakoigo showed higher reactivity compared to clay from Gatundu village and Murang'a town. A study [37] reported that the pozzolanic reaction is governed by the amount of active silica and alumina ($SiO_2 + Al_2O_3$), and the specific surface. From the chemical composition results above, it is apparent that there was no major difference between the alumina and silica contents ($SiO_2 + Al_2O_3 \approx 78\%$) for the three investigated clays. Hence, the chemical composition could not be instrumental to explain the higher reactivity of Gakoigo clay as compared to the other analysed clays. However, not all the fraction of the clay structure is activated in the same degree and the dehydroxylated material contains amorphous, polycrystalline and crystalline fractions. In this study, the higher reactivity could be due to the amorphous fraction ($SiO_2^{r-} + Al_2O_3^{r-}$) which could be more predominant in the Gakoigo clay than in the Gatundu and Murang'a town clays [39]. This suggested that the amorphousness achieved after calcination determines the pozzolanic activity to a much greater extent than other pozzolan properties such as silica content [37].

Pozzolanic reaction leads to a reduction of free Ca^{2+} and OH^- ions, which should lead to a decrease in electrical conductivity [13]. A study [7] reported that when the variation of the electrical conductivity within the first 2 minutes exceeds 0.12 S/m, the material can be classified pozzolanic. This suggested that calcined clay possesses some pozzolanic properties. Similar observations were reported in [1] on the pozzolanic activity of clays calcined at different temperatures. In contrast, Jurić, Carević, Serdar and Štirmer [13] reported an increase in electrical

conductivity with time for wood biomass fly ashes. The authors [13] concluded that this method was not fully reliable for assessing the pozzolanic activity of fly ash due to the high content of soluble salts in the chemical composition, mostly Na_2SO_4, K_2SO_4 and $CaSO_4$, which increase the conductivity. In the present study, the chemical composition reported no presence of CaO, MgO, Na_2O, and SO_3 in all clay samples. Thus, we might assume that there was no interference of soluble salts in the electrical conductivity values reported.

3.3. Evaluation of the pozzolanic activity based on Frattini Test

The results of CaO and OH^- concentrations (mmol/l) from the Frattini test are reported (Fig. 5, Fig. 6, and Fig. 7). Concentration values lying below the Portlandite $(Ca(OH)_2)$ saturation line indicated the removal of Ca^{2+} from the solution which was attributed to pozzolanic activity. Results lying on the line were indicative of zero pozzolanic activity and results above the line corresponded to no pozzolanic activity. Raw clays and clays calcined at 800°C showed no pozzolanic activity at 8 days, suggesting a supersaturation in Portlandite. After 15 days, raw clay fell slightly below the Portlandite saturation line, indicating near zero activity [13]. On the other hand, the CaO and OH^- concentrations for samples calcined at 800°C shifted into the zone of pozzolanic activity at 15 days. This demonstrated the slow reactivity of this particular sample group at later ages. This was also reported in [23] with excavated clay calcined at 550°C for 1 h. The transformation of calcined clay from amorphous to crystalline at excessive calcination temperature could explain the lower pozzolanic activity at 800°C [38].

Clays calcined at 600°C and 700°C showed higher pozzolanic activity than clays calcined at 800°C. At these temperatures, a significant undersaturation was observed with respect to Portlandite [13], [14]. This was due to a presence of large amorphous silica, which consumed the Portlandite phases to form C-S-H phases. A study [40] reported that the temperature range of 600-900°C achieved the highest level of kaolin transformation to Metakaolin. Another study [41] also reported that an almost complete dehydroxylation (0.99) could be achieved in the range of 700°C-800°C for Iranian kaolin. This suggested that the optimum temperature for dehydroxylation varied with clay type. This study found that calcination at 600°C and 700°C achieved better pozzolanic properties irrespective of the clay type. These results were in line with [42] that revealed that alum sludge calcined at 600°C, 700°C, and 800°C showed positive pozzolanic activity at 15 days.

The statistical analysis at 95% confidence level showed that both the clay type (p-value = 0.02725) and the temperature (p-value < 2e-16) influenced the CaO consumption during the Frattini test. No interaction was observed between the clay type and the temperature (p-value = 0.28951) at 95% confidence level.
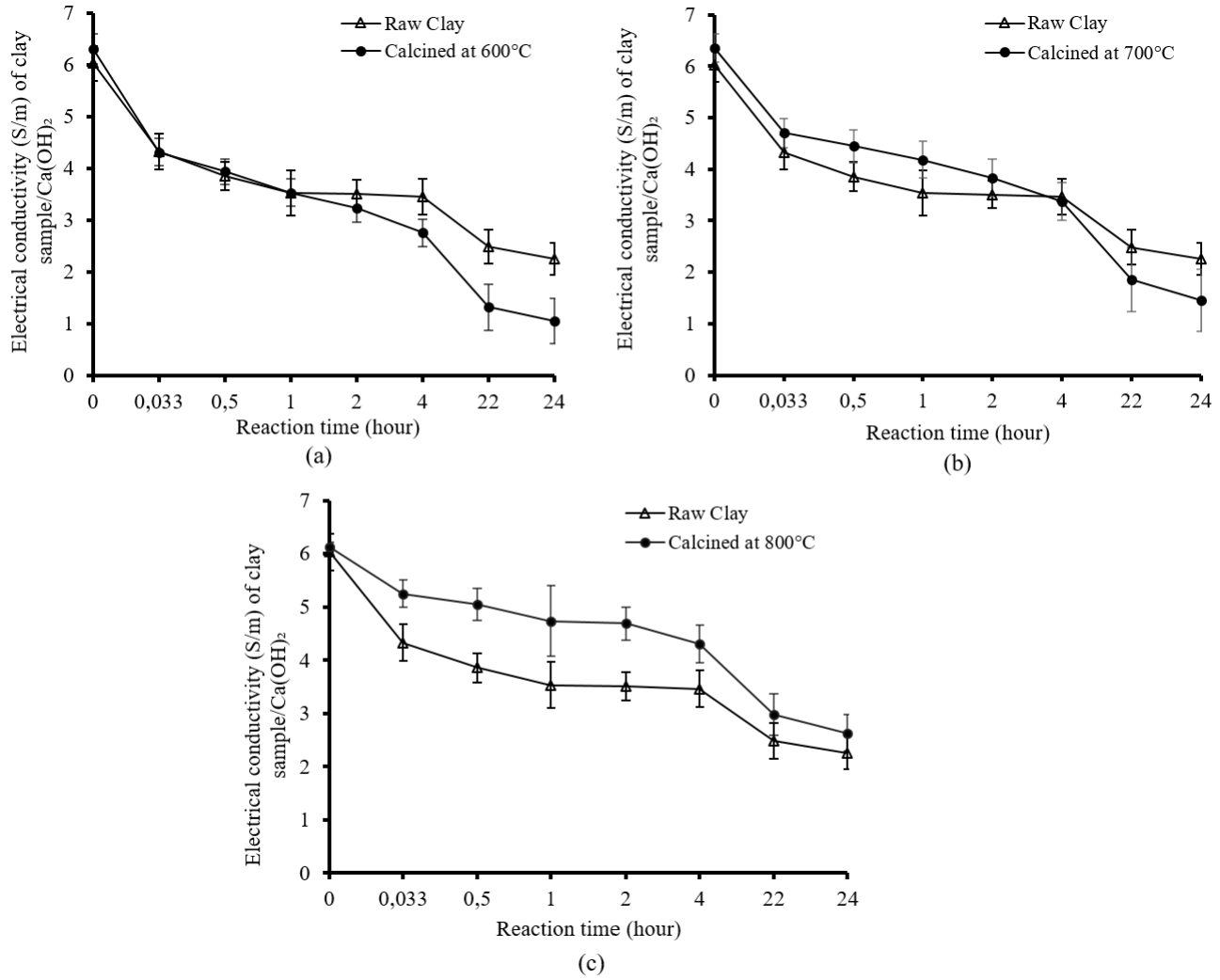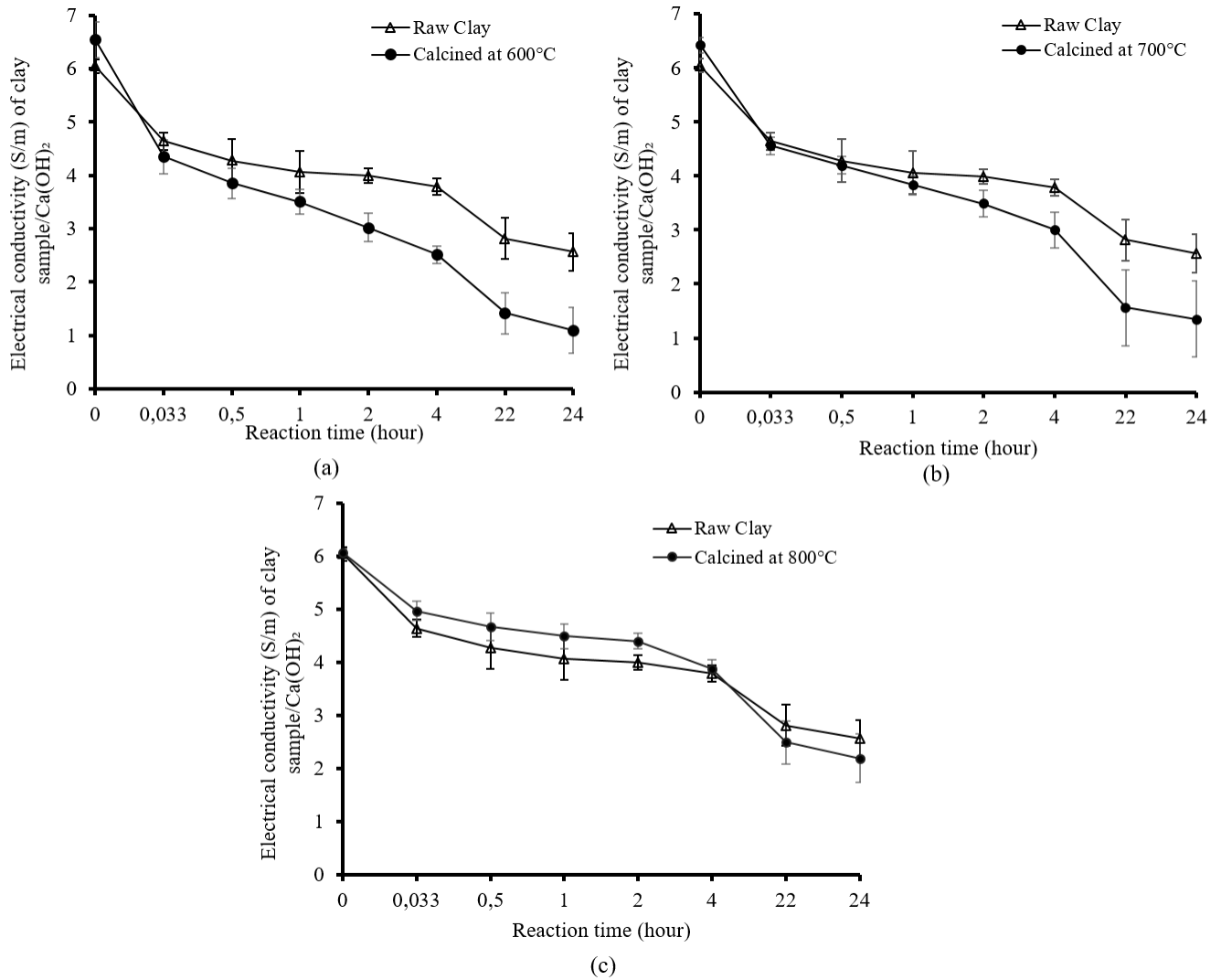
Fig. 2. Electrical conductivity (EC) of aqueous solutions of $Ca(OH)_2$ after the addition of clay from Gatundu (GT): (a) clay calcined at 600°C and raw clay, (b) clay calcined at 700°C and raw clay, (c) clay calcined at 800°C and raw clay.
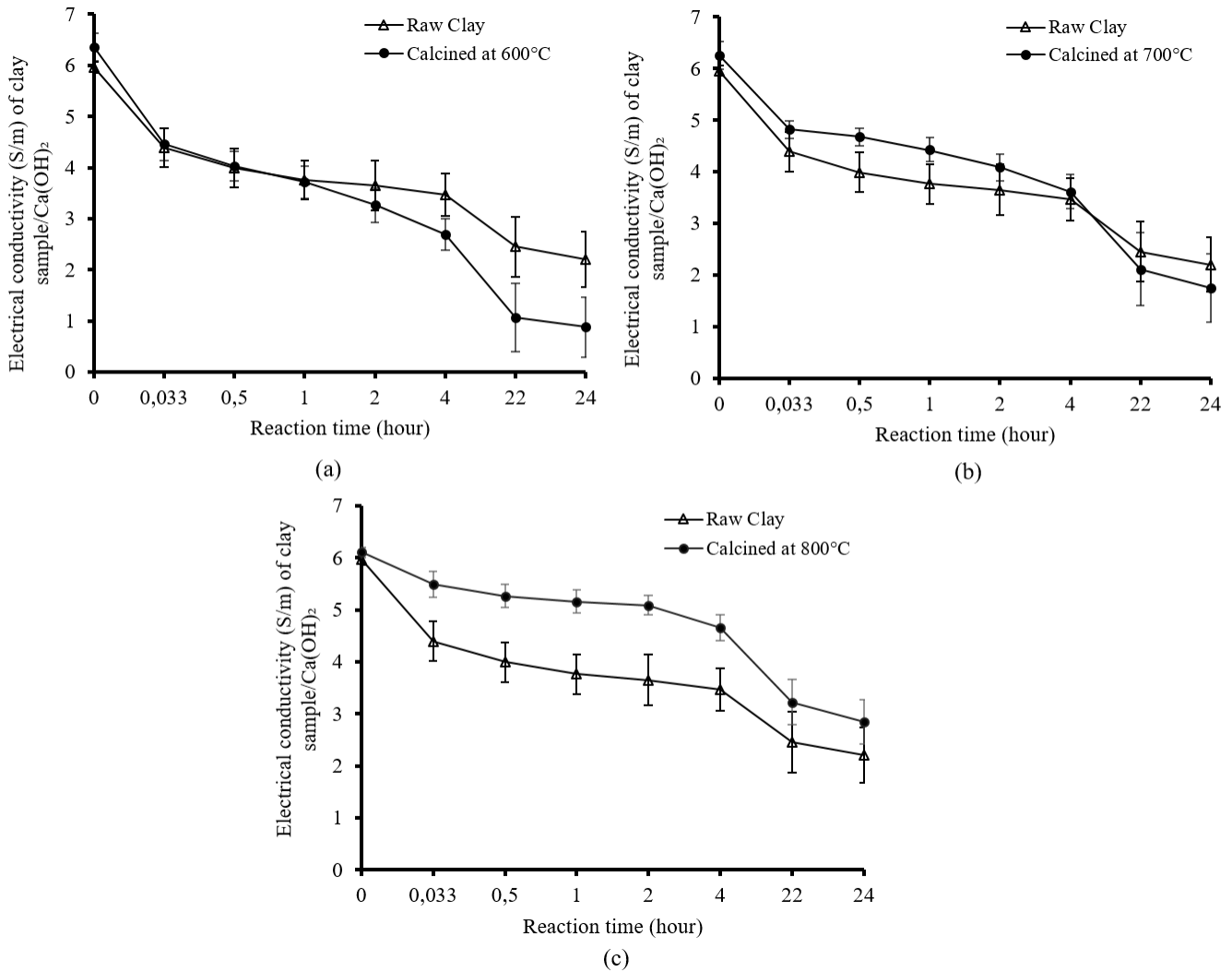
Fig. 3. Electrical conductivity (EC) of aqueous solutions of $Ca(OH)_2$ after the addition of clay from Murang'a town (MU): (a) clay calcined at 600°C and raw clay, (b) clay calcined at 700°C and raw clay, (c) clay calcined at 800°C and raw clay.

Fig. 4. Electrical conductivity (EC) of aqueous solutions of $Ca(OH)_2$ after the addition of clay from Gakoigo (GK): (a) clay calcined at 600°C and raw clay, (b) clay calcined at 700°C and raw clay, (c) clay calcined at 800°C and raw clay.
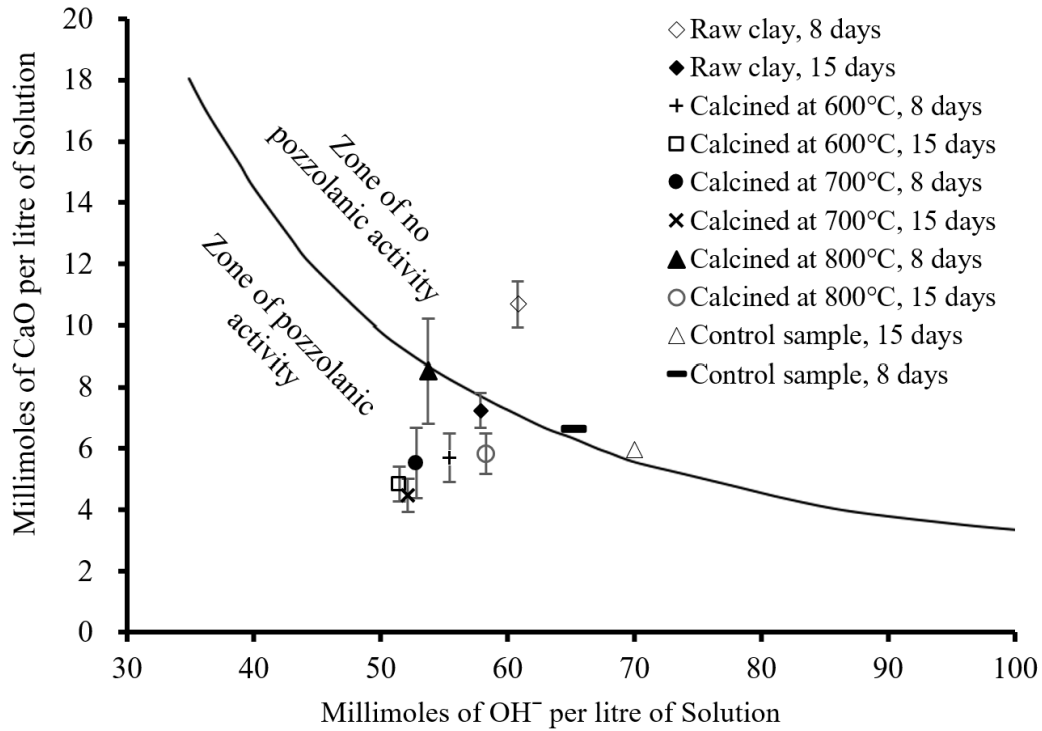
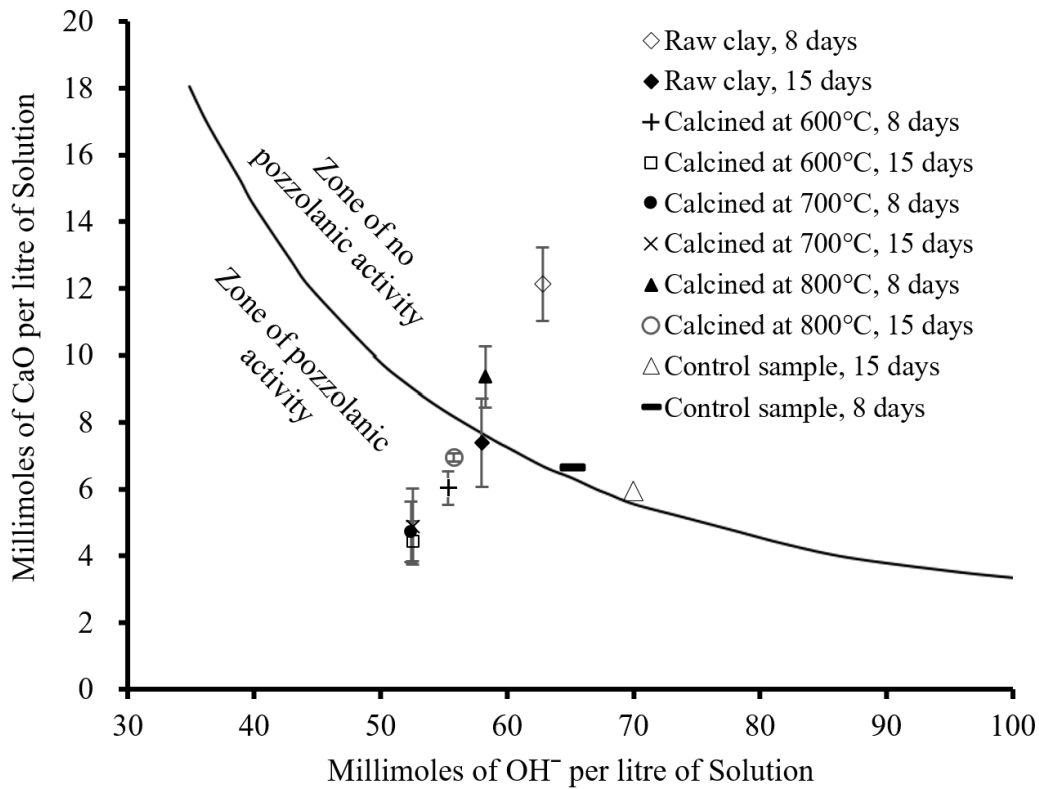**Fig. 5.** Frattini test results for blended cement containing 20% of clay from Gatundu tested after 8 and 15 days.

Fig. 6. Frattini test results for blended cement containing 20% of clay from Murang'a town tested after 8 and 15 days.
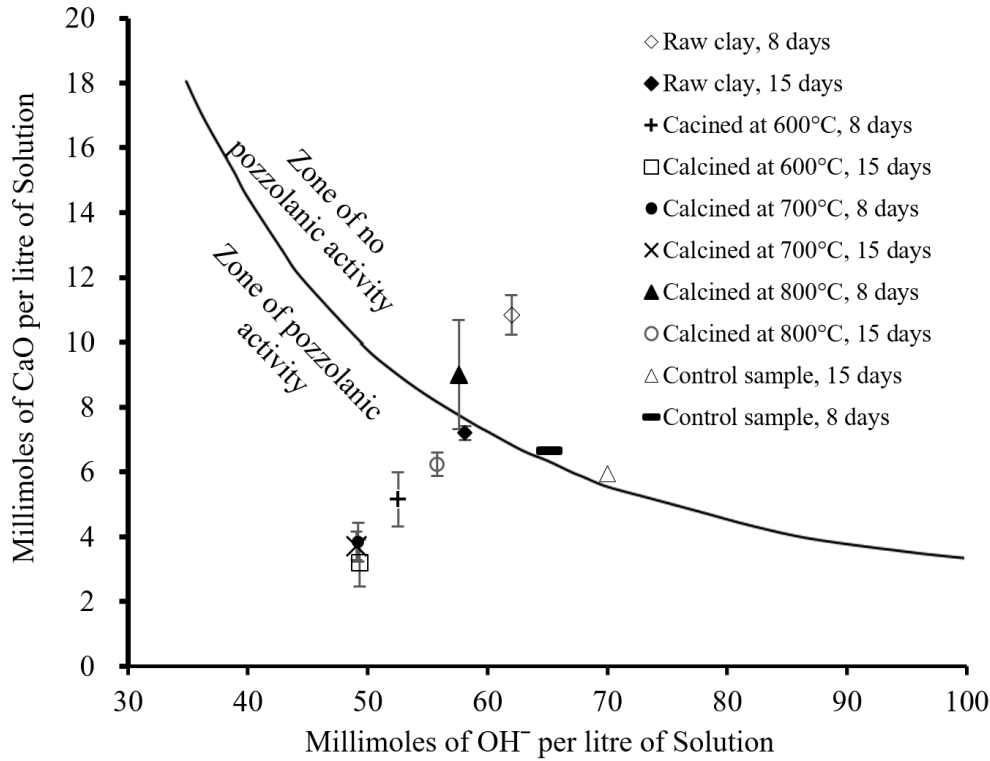
Fig. 7. Frattini test results for blended cement containing 20% of clay from Gakoigo tested after 8 and 15 days.

3.4. Evaluation of the pozzolanic activity based on compressive strength test

The results show the evolution of compressive strength as a function of calcination temperature and curing time. It was generally observed that the compressive strength increased with curing time (Fig. 8, 9, and 10). Clay from Gakoigo (GK), calcined at 800°C, achieved a strength activity index (SAI) of 1.073 after 28 days (Fig. 11c). Similarly, clay from Gatundu (GT), calcined at 600°C, maintained a SAI of 1 after 7 days, and increased to 1.11 after 28 days (Fig. 11a). However, the SAI reduced to 0.90 when the calcination temperature increased to 800°C (Fig. 11a). A study [43] reported that the compressive strength increases with the content of amorphous phases. This could explain the strength activity index achieved by clay from Gakoigo, calcined at 800°C (Fig. 10c and Fig. 11c). However, depending on the clay type, an excessive increase in the calcination temperature may lead to the recrystallization of mineral phases. This causes a decrease in the amorphous phases and the compressive strength. This could explain the lower performance of clay from Gatundu when the temperature increased from 600°C to 800°C (Fig. 11a) [38]. Compared to GK and GT, MU did not perform well at all temperatures.

The analysis of variance at 95% confidence level showed that both temperature and clay type had a significant effect on the compressive strength, with p-values equal to < 2e-16 and 3.09e-10, respectively. An interaction was also observed between the temperature and the clay type (p-value 1.94e-13). The individual comparison between raw and calcined clays (Fig. 8, 9, and 10) showed that there was a significant difference between the compressive strength of the uncalcined and calcined clay at all ages. This study found that the temperature range of 600-800°C achieved a SAI > 0.75 at 7 and 28 days in line with ASTM C618 criteria (Fig. 11).

Other researchers have reported that a 30% replacement rate of cement with clay, calcined at 800°C, achieved a strength activity index of 1.02 (SAI > 0.75) [12]. On the other hand, a study achieved an optimum SAI of 0.9 for wood biomass fly ash at 28 days with a replacement of 15% [13]. In contrast, another study [42] reported a SAI < 0.75 for alum sludge calcined at 600°C after 7 and 28 days, compared to 800°C which achieved a SAI of 1.14 at 28 days. In this study, the optimum temperature was 600°C. The difference with Jurić, Carević, Serdar and Štirmer [13] could be due to the nature and quality of the

clay. These factors affect the dehydroxylation degree and the content of amorphous phases after calcination [1].

Several studies reported the strength performance of various pozzolanic materials. A study [37] reported that the replacement of 50% lime with calcined clay achieved a mechanical index similar to ground granulated blast furnace slag. The strength achieved was 69% higher than rice husk ash and micro-silica, and 89% higher than pulverised fly ash. In opposite, Faleschini et al. [7] reported that a 50% cement replacement with municipal solid waste incinerator bottom ash (MSWI BA) caused about 50% strength loss in cement blocks. However, a 10% replacement lead to a slight strength increase after 28 days of curing. The authors [7] argued that replacing

huge amounts of cement with pozzolanic materials induces severe strength loss due to the weaker nature of the ash. Another study [38] reported that a 20% cement replacement with uncalcined ultrafine volcanic ash could achieve a SAI of 1.02 only after 91 days of curing. Similarly, Jurić et al [13] reported a SAI of 1 for cement blocks containing 15% wood biomass fly ashes after 365 days of curing. In opposite, this study found that calcination of clay increased the strength activity index of cement blocks from less than 0.75 to about 1 after 28 days of curing. Thus, compared to calcined clay, other pozzolanic materials demonstrated a delayed pozzolanic action [38].
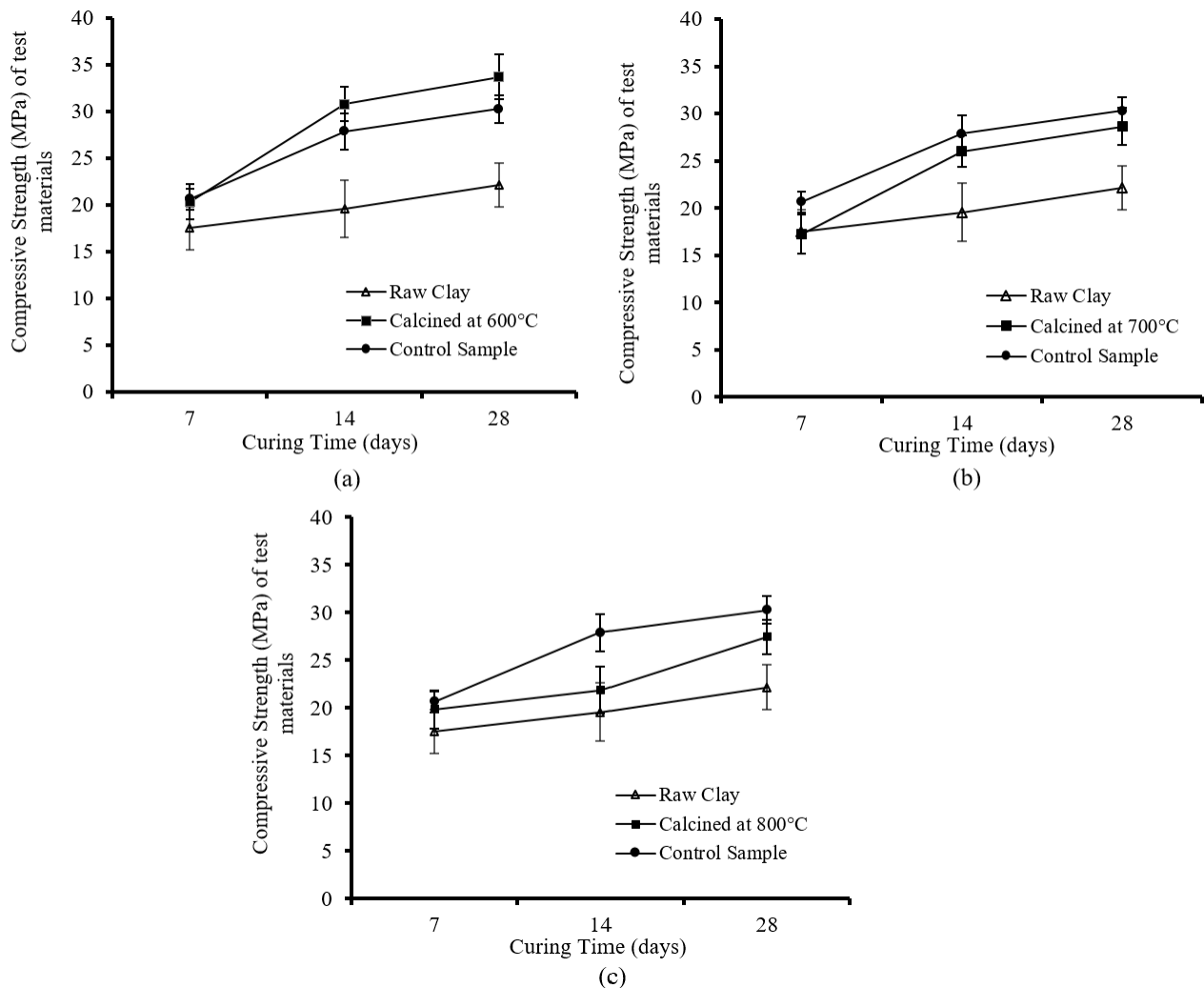
Fig. 8. Compressive strength of blended cement blocks with 80% OPC and 20% clay (GT) after 7, 14, and 28 days: (a) clay calcined at 600°C, raw clay, and control sample, (b) clay calcined at 700°C, raw clay, and control sample, (c) clay calcined at 800°C, raw clay, and control sample.
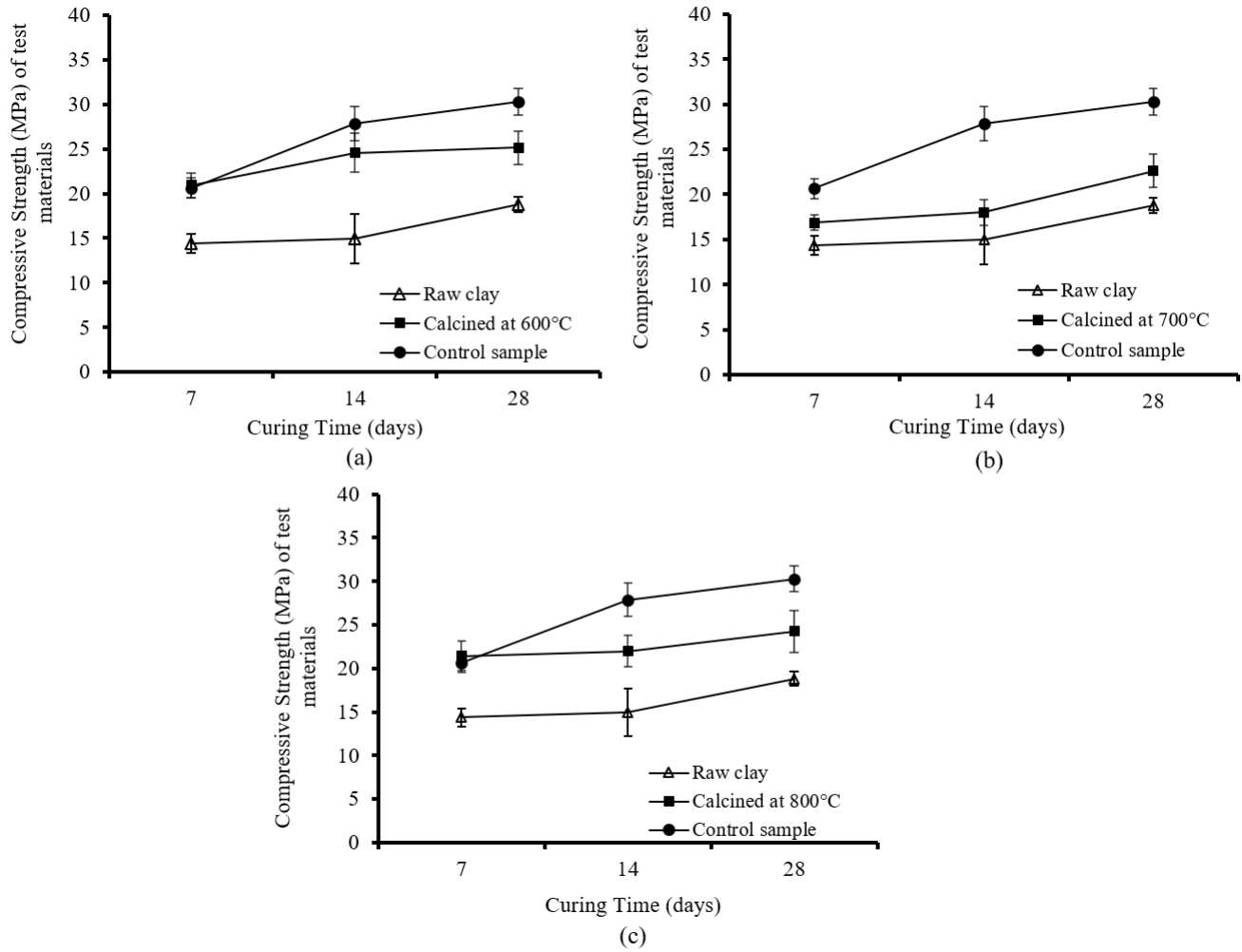
Fig. 9. Compressive strength of cement blocks with 80% OPC and 20% clay (MU) after 7, 14, and 28 days: (a) clay calcined at 600°C, raw clay, and control sample, (b) clay calcined at 700°C, raw clay, and control sample, (c) clay calcined at 800°C, raw clay, and control sample.
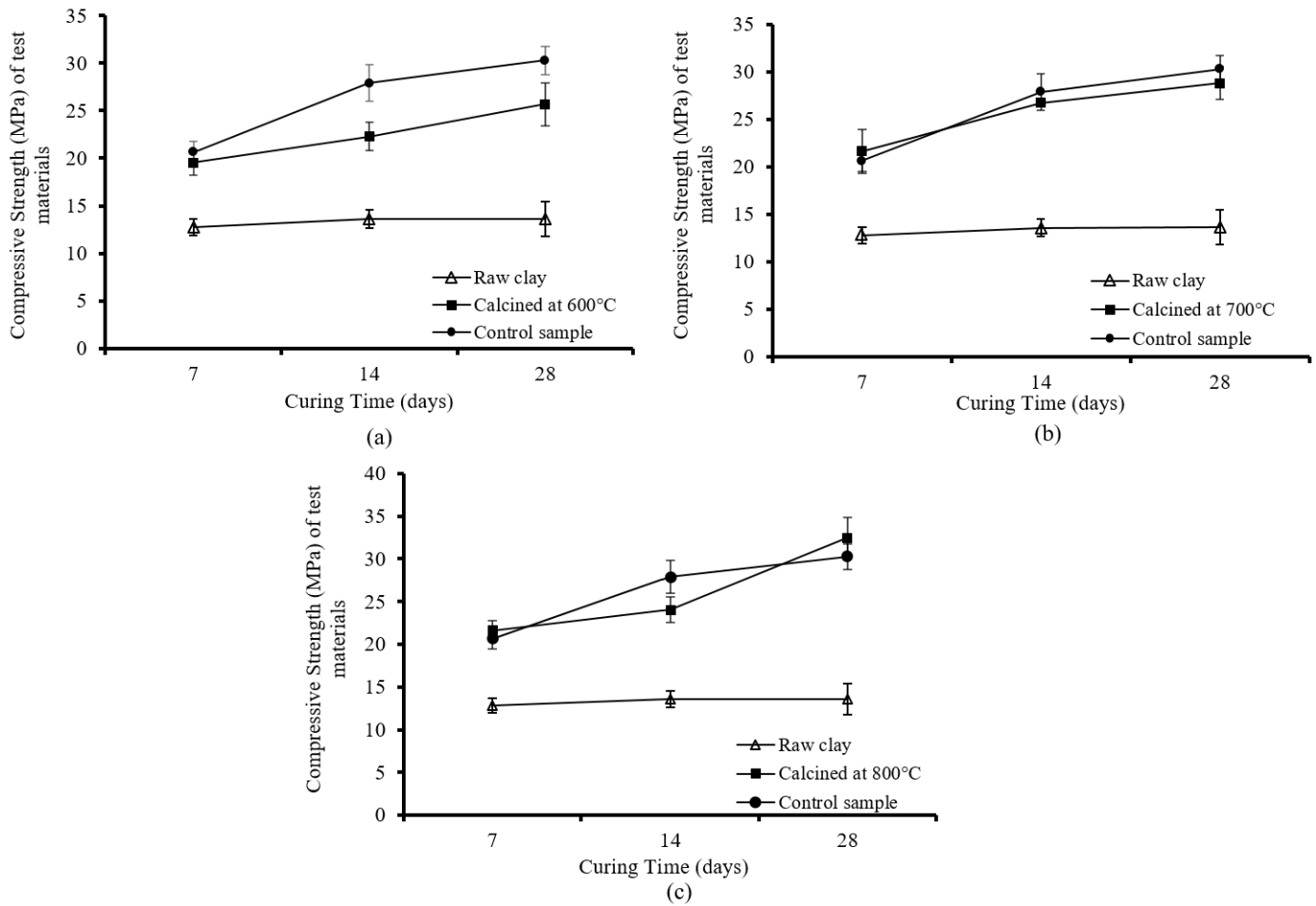
Fig. 10. Compressive strength of cement blocks with 80% OPC and 20% clay (GK) after 7, 14, and 28 days: (a) clay calcined at 600°C, raw clay, and control sample, (b) clay calcined at 700°C, raw clay, and control sample, (c) clay calcined at 800°C, raw clay, and control sample.
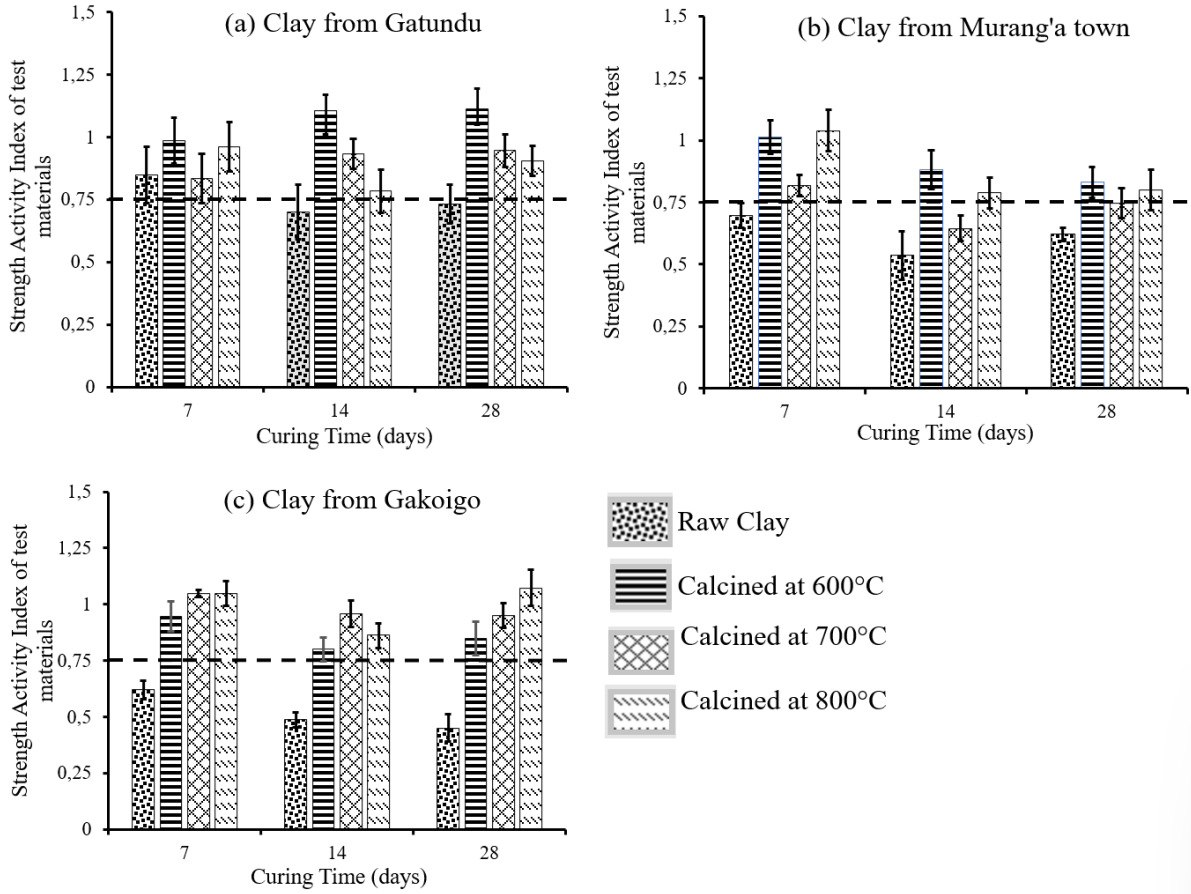
Fig. 11. Strength Activity Index (SAI) of cement blocks after 7, 14, and 28 days.

To define the pozzolanic activity of calcined clays, various authors [1], [14] recommended the use of a combination of the electrical conductivity, Frattini test, and the compressive strength test. The results obtained were summarized and compared with existing standards to evaluate the suitability of analysed clay for application as a pozzolanic material (Table 3). In this study, only uncalcined clays failed to meet the requirements for application as a replacement for cement. Hence, a thermal treatment 600-800°C produces enough dehydroxylation to transform the clays into supplementary cementitious materials. In particular, clay calcined at 600°C showed better pozzolanic activity for the electrical conductivity test, Frattini test and compressive strength test. This material could therefore serve as a low-cost and low impact alternative to cement, especially for low income communities unable to afford cement. This will reduce the construction cost and the environmental impacts associated with the use of cement.

Table 3: Pozzolanic activity of analysed clays compared with ASTM C618 and EN196-5 criteria

Criteria	Material evaluated											
	Gatundu Clay				Murang'a Town Clay				Gakoigo Clay			
Temperature	Raw	600	700	800	Raw	600	700	800	Raw	600	700	800
XRF	P*	P	P	P	P	P	P	P	P	P	P	P
EC test	P	P	P	P	P	P	P	P	P	P	P	P
Frattini test	F*	P	P	P	F	P	P	P	F	P	P	P
SAI > 0.75	F	P	P	P	F	P	P	P	F	P	P	P

*P: Pass
*F: Fail

4. Conclusion

This work investigated the effect of thermal treatment on the pozzolanic activity of wetland clays. We conclude that clay calcination at 600-800°C provides sufficient pozzolanic activity. The variation in the pozzolanic activity of clay from different wetlands in the study site was not substantial. Use of calcined clay as a pozzolanic material could therefore be more environmentally sustainable compared to the use of cement alone.

Recommendation

This study recommends that calcined clay could be used as a partial replacement of clinker in the manufacturing of blended cement, and possibly limestone calcined clay cement. The pozzolanic material can also partially replace cement in concretes, cement mortars, and earth building. A study is currently underway to evaluate the effect of the blended cement on the strength and water absorption of rammed earth floor for low income housing. It is recommended that a calcination plant be publicly funded by the government or any other agency to produce calcined clay. Furthermore, a quantitative analysis should be undertaken to establish the cost and environmental impacts of the use of calcined clay in construction and cement for possible up-scaling and adoption by cement manufacturers.

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