

Potential Use of Local Materials as Synthesizing One Part Geopolymer Cement

Areej Almalkawi, Sameer Hamadna, Parviz Soroushian, Nalin Darsana

Abstract—The work on indigenous binders in this paper focused on the following indigenous raw materials: red clay, red lava and pumice (as primary aluminosilicate precursors), wood ash and gypsum (as supplementary minerals), and sodium sulfate and lime (as alkali activators). The experimental methods used for evaluation of these indigenous raw materials included laser granulometry, x-ray fluorescence (XRF) spectroscopy, and chemical reactivity. Formulations were devised for transforming these raw materials into alkali aluminosilicate-based hydraulic cements. These formulations were processed into hydraulic cements via simple heating and milling actions to render thermal activation, mechanochemical and size reduction effects. The resulting hydraulic cements were subjected to laser granulometry, heat of hydration and reactivity tests. These cements were also used to prepare mortar mixtures, which were evaluated via performance of compressive strength tests. The measured values of strength were correlated with the reactivity, size distribution and microstructural features of raw materials. Some of the indigenous hydraulic cements produced in this reporting period yielded viable levels of compressive strength. The correlation trends established in this work are being evaluated for development of simple and thorough methods of qualifying indigenous raw materials for use in production of indigenous hydraulic cements.

Keywords—One-part geopolymer cement, aluminosilicate precursors, thermal activation, mechanochemical.

I. INTRODUCTION

CLAY is a commonly available material; it can be a mixture of different clay and associated minerals, which are strongly affected by the nature of parent rocks [1], [2]. Heat treatment of clay can significantly enhance its chemical activity [3]. The heat treatment temperature range from 500 °C to 800 °C, and generally cause dihydroxylation [4]. At such temperatures, which can be conveniently generated using indigenous furnaces, the octahedral sheets lose water and decompose into a disordered metastable state [5], [6]. This metastate state has reactivity attributes which qualify the resultant activated clay as a pozzolan [7], [8]. Firing to higher temperatures results in the formation of new unreactive phases such as spinel and mullite [9], [10]. In summary, heat treatment (calcination) of clay at moderate temperatures can activate the material to take part in geopolymerization reactions [11]. Thermal activation of clay enhances the sediment reactivity in the dissolution and polycondensation steps of geopolymerization [12].

A recent study [13] has shown that the reactive phase content under alkali activation conditions in a series of aluminosilicates is equivalent to the amount of material that

dissolved in a 1% (v/v) HF solution. The reactive $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio of these materials could be quantified by ICP analysis of the resulting leachates. The methodology proposed in that work, and the findings described above has formed the basis for conducting the investigations presented here.

The formation of geopolymers involves a chemical reaction between an aluminosilicate material and activator solution in a highly alkaline environment. Geopolymerization is believed to consist of three main stages: (1) surface dissolution of Al and Si in a highly alkaline solution, and diffusion of the dissolved species through the solution; (2) polycondensation of the Al and Si complexes with the solution, and gel formation; and (3) hardening of the gel that yields the final geopolymer binder [14]. The dissolution stage can be studied quantitatively. For this reason, the leaching behavior of the calcined sediments in alkaline solution was investigated. Many papers have been published on the dissolution of aluminosilicate compounds, especially in the geochemical literature [15]-[18].

II. A BRIEF REVIEW OF THE CLAY CHEMISTRY AND MINERALOGY

Clay minerals constitute a well-known class of natural inorganic materials with well-known structural, adsorption, rheological and thermal properties. These materials have a hydrophilic character due to the existence of surface hydroxyl (-OH) groups [19]. Applications of clay materials are mostly governed by their surface properties, including surface charges and charge density, adsorption capacities, specific surface area, hydroxyl groups on edges, types of exchangeable cations, silanol groups of the crystalline defects or broken surfaces, and Lewis and Brønsted acidity [20]. Phyllosilicate surfaces are of two basic types: siloxane and hydroxyl. The group of clay mineral referred to as 2:1 (e.g., smectite) has only siloxane surface; the 1:1 group of clay minerals (Fig. 1), including kaolinite, has both types of surfaces (Fig. 1). The hydroxyl surfaces (e.g., Al-octahedral surface in kaolinite) are perfect sites for implanting since the surface hydroxyls can combine by condensation action with alkoxy groups and/or the hydroxyls in hydrolyzed silane. Owing to the high ratio of the terminal surface area of the basal surface, hydroxyl groups situated at broken edges play a crucial role in the silane grafting reaction. However, influential differences of the “grafting” mechanism and nucleus sites prevail among different clay minerals due to the variation of the structure and properties of phyllosilicates.

Areej Malkawi is with the Michigan State University, United States (e-mail: almalkaw@msu.edu).

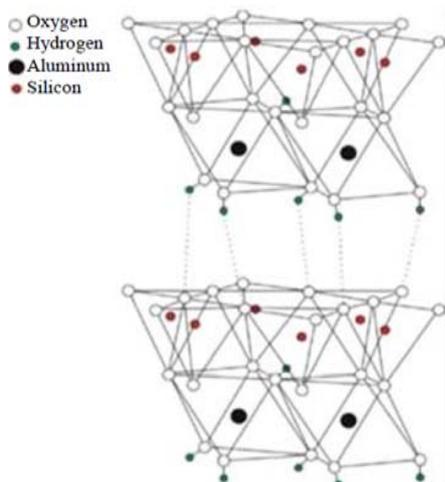


Fig. 1 The structure of 1:1 clay mineral [19]

III. EXPERIMENTAL PROGRAM

A. Selections of Raw Materials, and Their Processing into Hydraulic Cement

The (red) clay used in this reporting period (Fig. 2) was collected from Stockbridge, Georgia. The indigenous alkali used for activation of this red clay included different combinations of natron, lime, quick lime or wood ash (considering that wood ash contributes more than just alkalis to the process). The clay was thermally treated at two different temperatures (400 °C or 750 °C) for 2 hours. This calcination process was performed in a barrel (Fig. 3) where wood was used as fuel. The temperature time-history inside the barrel was monitored using a temperature sensor connected to a data acquisition system. Fig. 4 shows this temperature time-history where a peak temperature exceeding 500 °C was reached after about 1 hour.



Fig. 2 Red clay used as aluminosilicate precursor in synthesizing the indigenous binder



Fig. 3 Indigenous (barrel) furnace used for activation of clay through combustion of wood

The activated clay was milled together with other raw materials using the ball-milling parameters of Table I. The raw materials formulations which were milled together are presented in Table II. Combined milling of the raw materials led to production of indigenous hydraulic cements via mechanochemical reactions, activations and size reduction phenomena.

Most mortar mixtures evaluated in this reporting period had a natural sand-to-indigenous hydraulic cement ratio of 2.5, and water/cement ratio of 0.5 (for achieving desired workability).

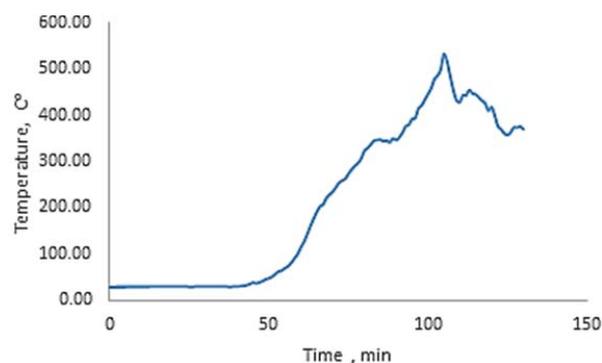


Fig. 4 Temperature time-history within the indigenous (barrel) furnace

TABLE I
MILLING CONDITIONS OF THE THERMALLY TREATED BLENDS OF INDIGENOUS MATERIALS (THE THREE SIZES OF STEEL BALLS WERE USED IN EQUAL WEIGHTS)

Diameter of Steel Balls (mm)			Steel Ball-to-Material Weight Ratio	Milling Duration (hr)
Large	Medium	Small	10: 1	3
76.2	25.4	12.7		

TABLE II
HYDRAULIC CEMENT FORMULATIONS CONSIDERED FOR PRODUCTION OF GEOPOLYMER-BASED HYDRAULIC CEMENT BINDERS WITH (WEIGHT FRACTIONS)

Formulation	Aluminosilicate Precursor	Supplementary Material	Activator	Clay Treatment Condition
1	0.3 Clay	0.3 wood ash	0.4 CaO	Calcination at 900°C for 4 hr
2	0.6 Clay		0.3 Na ₂ SO ₄ & 0.1 CaO	Calcination at 750°C for 4 hrs
3	0.80 Clay		0.15 Na ₂ SO ₄ & 0.05 CaO	Calcination at 750°C for 4 hrs
4	0.6 Clay		0.3 Na ₂ CO ₃ & 0.1 CaO	Calcination at 750°C for 4 hrs
5	0.3 Clay	0.3 Gypsum	0.3 Na ₂ CO ₃ & 0.1 CaO	Calcination at 750°C for 4 hrs

B. Methods

The indigenous hydraulic cement was mixed with water in a mortar mixer for one minute to produce a homogenous paste. Natural sand was then added, and mixing was continued for two more minutes. Fresh mortar mixtures were placed and consolidated in 50mm cube molds, which were kept in sealed condition for 24 hours. They were then demolded, and stored at 90% relative humidity and room temperature until the test age of 7 days. The compressive strength of cube specimens was measured using a LLOYD EZ20 universal testing machine at a crosshead speed of 0.1 mm/min. Ten replicate specimens prepared from each mix were tested in compression, and the mean values are reported as compressive strength.

Chemical composition of the clay was determined using XRF spectroscopy. The FTIR spectroscopy was conducted in the 4000–400 cm⁻¹ range on the as-received and calcined clay in order to assess their chemical environments (bond structures). Particle size distributions of clay and the resultant hydraulic cement were evaluated using a laser granulometer (Horiba 920, shown in Fig. 5).



Fig. 5 Particle size analyzer

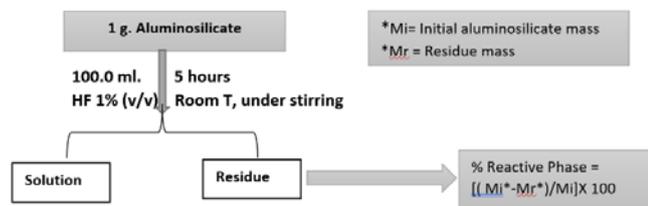


Fig. 6 Outline of the experimental procedure followed to quantify the wt.% of the potential reactive phases of the starting aluminosilicate precursor

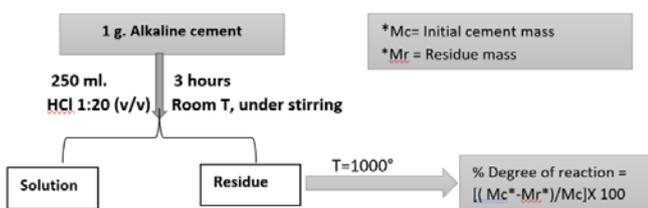


Fig. 7 Outline of the experimental procedure followed for quantifying the degree of reaction

The fraction of reactive phase and the reactive SiO₂/Al₂O₃ ratio of the starting materials were found out by means of selective chemical attack using a 1% (v/v) HF solution as outlined in Fig. 1. Acid attack was carried out by subjecting

1.0 g of each aluminosilicate precursor to 100 ml of a 1.0 vol.% hydrofluoric acid solution for 5 h under stirring action. After the chemical attack proceeded, the solid residue and the solution were separated by filtering using a Sigma Aldrich® ash-less filter paper (% ash < 0.01) for retention of particles under 2 μm. The filtered residue was washed with distilled water until a neutral pH was reached from the funnel. After the residue was completely dry, it was calcined together with the filter paper at 1000 °C in a crucible for 1 h. The percentage of reactive phase was quantified by subtracting the final mass of the residue from the initial mass of the aluminosilicate (Fig. 6).

The percentage of reaction products generated during alkali activation of red clay and volcanic tuff (black lava and Pumice) were measured using selective chemical attack procedure. This approach, outlined in Fig. 7, uses a 1:20 (v/v) HCl solution [21]. Selective chemical attack involved subjecting 1.0 g of each hydraulic cement to 250.0 ml of a 1:20 (v/v) HCl solution for 3 h at room temperature under continuous stirring. After chemical attack, the solid residue and the solution were separated by filtering (as described for the previous procedure). The resulting residue was washed with distilled water until neutral pH was achieved from the funnel. Subsequently, after the residue was completely dry, it was calcined together with the filter paper at 1000°C in a platinum crucible for 1 h. The percentage of reaction products was quantified by subtracting the final mass of the residue from the initial mass of the hydraulic cement.

The exothermic heat of hydration of the indigenous hydraulic cements produced in the project was measured using a calorimeter (TAM Air Isothermal Calorimeter manufactured by TA Instruments). In this test, about 25g of freshly mixed paste was weighed into a flask, which was then capped and placed in the calorimeter. Heat generation was monitored over 24 hours.

IV. TEST RESULTS AND DISCUSSION

A. Chemical Composition of the Indigenous Raw Materials

Table III presents the chemical composition (and loss on ignition) of the clay used in this reporting period. Chemical composition of the clay was generated via XRF spectroscopy. This clay is observed to be rich in Si and Al, which are essential to the geopolymerization process; it also incorporates a minor content of potassium.

TABLE III
THE ELEMENTAL COMPOSITION AND LOSS ON IGNITION (LOI) OF CLAY

	Si	Al	Fe	Ti	K	LOI
Clay	28.6	15.2	0.66	0.30	0.382	7.07

B. Measurement of the pH of Clay and an Indigenous Hydraulic Cement

The measured values of pH are presented in Fig. 8 for the red clay used in this investigation and also for a hydraulic cement with a formulation comprising activated clay: sodium sulfate: quick lime at 60: 30: 10 weight ratios. The hydraulic cement, as expected, produces a high pH value. This high pH

value is required for dissolution of aluminosilicate compounds, to be followed by formation of hydrates with binding effective (C-A-S-H and N,C-A-S-H) [22].

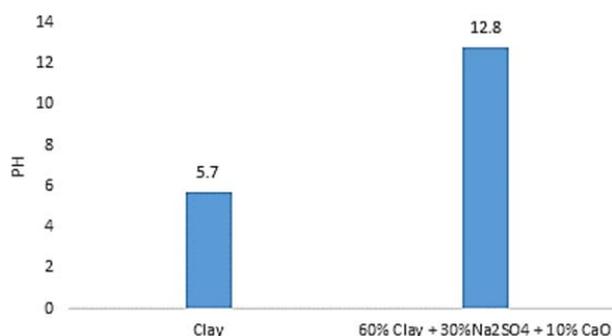


Fig. 8 Measured values of pH for the as-received red clay and the resultant hydraulic cement after thermal activation of clay and its mechanochemical processing with alkalis

C. Compressive Strength of Mortars with Indigenous Binders

The 7-day compressive strength test results for the indigenous hydraulic cements with formulations of Table II are summarized in Fig. 9. The indigenous hydraulic cement Formulation 2 comprising clay: sodium sulfate: quick lime at 0.6: 0.3: 0.1 weight ratios produced the highest 7-day compressive strength which exceeded 7 MPa. The second highest 7-day compressive strength of about 5 MPa was provided by the indigenous hydraulic cement Formulation 4 comprising clay: sodium carbonate: quick lime at 0.6: 0.3: 0.1 weight ratios. These are viable levels of early-age compressive strength which point at the success of the approach comprising simple heat treatment of clay followed by its milling together with other indigenous materials to produce indigenous hydraulic cements with desired binding qualities.

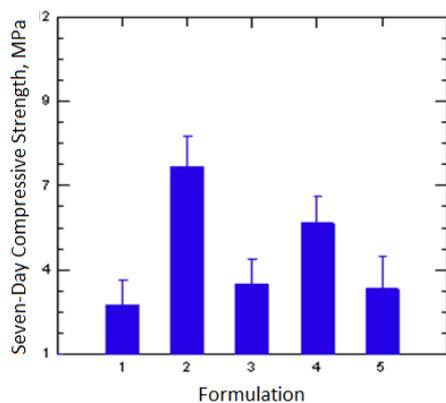


Fig. 9 Compressive strengths at 7 days of age obtained with indigenous hydraulic cements.

D. FTIR Spectra of Raw and Calcined Clay

FTIR spectroscopy was conducted in order to gain insight the chemical environment in clay as it undergoes dehydration via heat treatment. The FTIR spectra produced for the red clay before and after calcination are presented in Fig. 10. The band at 1045 cm^{-1} is associated with quartz and silicate minerals

(feldspar, phyllosilicates), but it can be also related to the stretching of Al-O and Si-O bonds in the amorphous aluminosilicate structure. This band got more pronounced and sharper after calcination. One could attribute this to the formation of an amorphous structure with an abundance of Al-O and Si-O bonds after calcination. At 3,400 cm^{-1} , the position of the broad absorption band of water is observed clearly for raw clay. This band was eliminated for calcined clay, which can be attributed to the loss of water (dehydration) upon calcination. Two infrared bands are observed at 1550 cm^{-1} and 1677 cm^{-1} in the raw clay, which can be assigned to the bending mode of the H-O-H bond in water. These bands were eliminated after calcination of clay which again points at dehydration of clay upon calcination. Hydroxyl stretching in calcined clay could also generate bands in this region, which is not pronounced in this case. The band at 3430 cm^{-1} corresponds to strongly hydrogen bonded water, whereas bands at 1550 cm^{-1} and 1677 cm^{-1} are attributed to less strongly hydrogen bonded water and corresponds to the position of the water bending mode of liquid water [23].

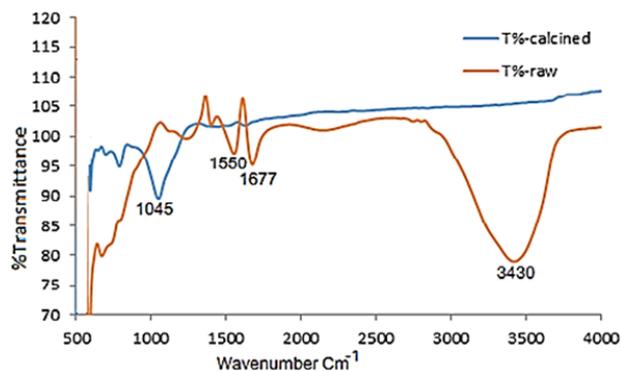


Fig. 10 FTIR spectra of clay prior to and after heat treatment for 3 hours at 700 °C

E. Correlation of the Reactivity of Aluminosilicates Material with the Resultant Compressive Strength

Table IV presents the potentially reactive phase contents of three indigenous aluminosilicate precursors (clay, pumice and red lava). Clay and pumice (but not red lava) are observed to offer high reactivity generally defined as having more than 50 wt.% reactive phase contents [24]. The degree of reaction test data presented in Table V confirm that high reactive phase contents in aluminosilicate precursors translate into high degrees of reaction of the resultant indigenous hydraulic cements. The 28-day compressive strength test results obtained with each indigenous hydraulic cement are presented in Fig. 11, together with the potentially reactive phase contents of the aluminosilicate precursors of these hydraulic cements. The results presented in Fig. 11 indicate that there is a correlation between the compressive strength provided by the resultant indigenous hydraulic cement and the potentially reactive phase content of the indigenous aluminosilicate precursor used in preparation of the hydraulic cement. In other words, the simple test on the simple test for measurement of the potentially reactive phase content can be an effective

means of qualifying indigenous aluminosilicate precursors for production of indigenous hydraulic cements. It should also be noted the 28-day compressive strengths generated by indigenous hydraulic cements made with red clay and pumice as aluminosilicate precursors are highly desirable.

TABLE IV
POTENTIALLY REACTIVE PHASE CONTENTS OF INDIGENOUS ALUMINOSILICATES PRECURSORS

Indigenous Aluminosilicate Precursor	Reactive Phase, wt.% (selective chemical attack – 1 vol.% HF)
Clay	75.5
Pumice	92.9
Red Lava	33.4

TABLE V
DEGREES OF REACTION OF INDIGENOUS HYDRAULIC CEMENTS MADE WITH DIFFERENT ALUMINOSILICATE PRECURSORS

Aluminosilicate Precursor for Indigenous Hydraulic Cement	Degree of reaction % (selective chemical attack – 1:20 v/v HCl)
Clay	22.3
Pumice	21.76
Red Lava	9.4

F. Particle Size Distribution of Clay

Fig. 12 presents the particle size distributions of the red clay used in this investigation (obtained via sieve analysis per ASTM D6913), and that of an indigenous hydraulic cement formulated with red clay and subjected to simple processing techniques described earlier (obtained via laser granulometry). While the raw clay is relatively coarse (with a mean particle size of 1000 μm), the resultant hydraulic cement (with mean particle size of 9.34 μm) has a particle size distribution that is not dissimilar to that of normal Portland cement. Table VI presents data on particle size distribution of the indigenous hydraulic cement extracted from Fig. 12.

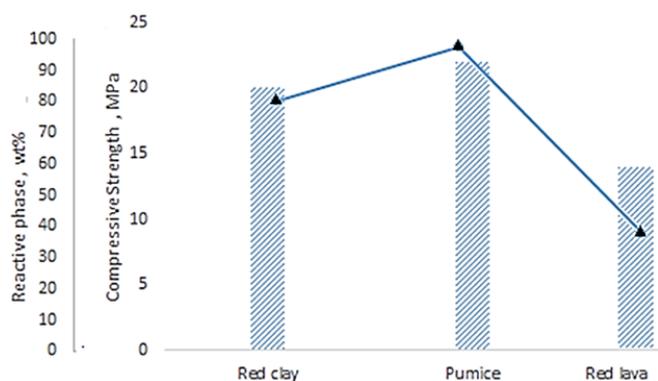


Fig. 11 28-day compressive strengths provided by indigenous hydraulic cements (bars), and the potentially reactive phase contents of the indigenous aluminosilicate precursors used for production of these hydraulic cements (\blacktriangle)

Microscopic investigations of the morphological attributes [25] of indigenous hydraulic cements formulated with clay, pumice and black lava indicated that: (i) the cement based on clay had a relatively large content of coarser particles, which reduced the ability of cement particles to pack densely [26]; (ii) the cement based on pumice provided a more uniform

particle size distribution which enabled the cement particles to pack densely; and (iii) the cement based on black lava was distinguished by the presence of elongated particles.

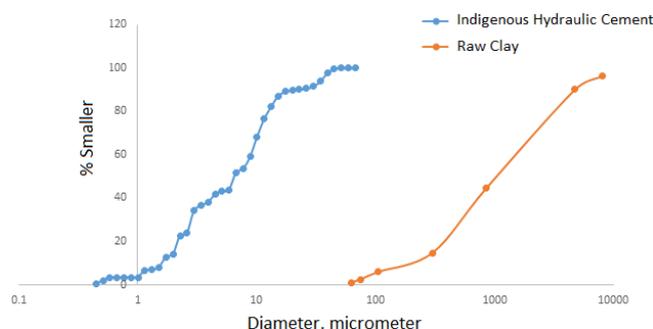


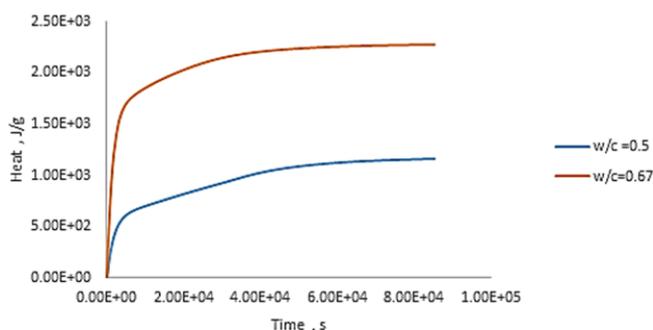
Fig. 12 Particle size distributions of the raw red clay and an indigenous hydraulic cement formulated with the clay.

TABLE VI
STATISTICS PARAMETERS DEFINING THE PARTICLE SIZE DISTRIBUTION OF THE INDIGENOUS HYDRAULIC CEMENT FORMULATED WITH RED CLAY

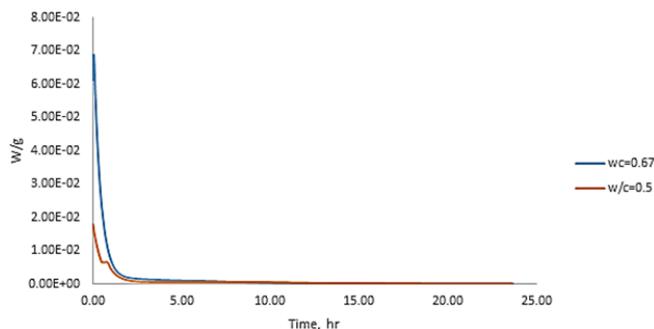
Specific surface area	18350 cm^2/cm^3
Median	6.52 μm
Mean	9.34 μm
S.D.	9.88 μm

G. Heat of Hydration

Fig. 13 (a) presents the cumulative heat of hydration of the indigenous hydraulic cement based on red clay with 0.5 and 0.67 water/cement ratios. The corresponding rates of heat release are shown in Fig. 13 (b). A higher water/cement ratio is observed to produce a rise in the heat of hydration and the rate of heat release of the cement formulated with red clay. Increasing the water/cement ratio provides more space for growth of cement hydrates, with the nucleation sites of red clay boosting the hydration process [27]-[29]. In spite of the chemical complexities of indigenous cements, alkali aluminosilicate hydrates are expected to be prevalent among their hydration products. This chemistry has an accelerated pace of hydration reactions, and generates relatively high exothermic heats of hydration. For this reason, the rate of heat release and the total heat released are higher for the indigenous hydraulic cement considered here when compared with Portland cement.



(a) Cumulative heat release



(b) Rate of heat release

Fig. 13 Heat of hydration test results measured at different water/cement ratios for the indigenous hydraulic cement formulated with red clay

V. CONCLUSIONS

The experimental work conducted in this paper for development of indigenous binders, emphasizing the use of red clay as the primary aluminosilicate precursor, yielded the following conclusions.

1. Laser granulometry test data indicated that the raw clay used in this investigation is relatively coarse (with a mean particle size of 1000 μm). The resultant hydraulic cement (with mean particle size of 9.34 μm) had a particle size distribution comparable to that of normal Portland cement.
2. Microscopic investigations of the morphological attributes of indigenous hydraulic cements formulated with clay, pumice and black lava indicated that: (i) the cement based on clay had a relatively large content of coarser particles, which reduced the ability of cement particles to pack densely; (ii) the cement based on pumice provided a more uniform particle size distribution which enabled dense packing of cement particles; and (iii) the cement based on black lava was distinguished by the presence of elongated particles.
3. FTIR spectroscopy was conducted to gain insight the chemical environment in clay as it undergoes dehydration via heat treatment (calcination). The results pointed at possible formation of an amorphous structure with an abundance of Al-O and Si-O bonds after calcination. Water was observed clearly for raw clay but was absent in calcined clay, which can be attributed to dehydration upon calcination. Hydroxyl stretching in calcined clay could also generate bands in this region, which is not pronounced in this case.
4. Test data on the cumulative heat of hydration and the rate of heat release of the hydraulic cement based on red clay with 0.5 and 0.67 water/cement ratios indicated that a higher water/cement ratio produced a rise in the heat of hydration and the rate of heat release of the cement formulated with red clay. Increasing the water/cement ratio provided more space for growth of cement hydrates, with the nucleation sites of red clay boosting the hydration process. In spite of the chemical complexities of indigenous cements, alkali aluminosilicate hydrates are

expected to be prevalent among their hydration products. This chemistry has an accelerated pace of hydration reactions, and generates relatively high exothermic heats of hydration. For this reason, the rate of heat release and the total heat released are higher for the indigenous hydraulic cement when compared with Portland cement.

5. The indigenous hydraulic cement formulation comprising clay: sodium sulfate: quick lime at 0.6: 0.3: 0.1 weight ratios produced the highest 7-day compressive strength which exceeded 7 MPa. The second highest 7-day compressive strength of about 5 MPa was provided by the indigenous hydraulic cement formulation comprising clay: sodium carbonate: quick lime at 0.6: 0.3: 0.1 weight ratios. These are viable levels of early-age compressive strength which point at the success of the approach comprising simple heat treatment of clay followed by its milling together with other indigenous materials to produce indigenous hydraulic cements with desired binding qualities.
6. The potentially reactive phase contents of three indigenous aluminosilicate precursors (clay, pumice and red lava) were measured. Clay and pumice (but not red lava) were found to provide high reactivity, generally defined as having more than 50 wt.% reactive phase contents. Measurements on the degree of reaction indicated that high reactive phase contents in aluminosilicate precursors translate into high degrees of reaction of the resultant indigenous hydraulic cements. The 28-day compressive strength test results obtained with each indigenous binder confirmed that there is a correlation between the compressive strength provided by the resultant indigenous hydraulic cement and the potentially reactive phase content of the indigenous aluminosilicate precursor used in preparation of the hydraulic cement. In other words, the simple test on the simple test for measurement of the potentially reactive phase content can be an effective means of qualifying indigenous aluminosilicate precursors for production of indigenous hydraulic cements. The 28-day compressive strengths generated by indigenous hydraulic cements made with red clay and pumice as aluminosilicate precursors were highly desirable.

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