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Development of fireclay aluminosilicate refractory from lithomargic clay deposits

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Abstract

Lithomargic clay until now has not been utilised to produce refractory bodies due to its low plasticity. In this work, the development and evaluation of fireclay refractory material produced from lithomargic clay deposit has been studied by addition of clay binder. Three formulations were prepared by mixing, semi-dry moulding, drying and firing at temperatures ranging from 1200 to 1400 °C. The fired samples were investigated to determine their physical properties such as bulk density, apparent porosity, linear firing shrinkage, and cold crushing strength. The chemical and mineralogical compositions were also determined. The results show that the linear firing shrinkage values were within limits acceptable for refractory clays. The cold crushing strength increases as temperature increased to 1400 °C. Cold crushing strength increased with increasing binder content. The increase of the highly refractory phases (cristobalite and mullite) and the densification of the bricks due to the presence of fluxing agents were responsible for the high cold crushing strength values. The investigated properties indicate that lithomargic clay underlying bauxite deposits could be used to produce fire clay aluminosilicate refractories.

Keywords: E.Refractory; Fireclay; Lithomargic clay; Cold crushing strength

1. Introduction

Aluminosilicate refractories are manufactured using refractory clays. They mainly are composed of kaolinite clay mineral ($Al_2O_3 \cdot 2SiO_2 \cdot 2\ H_2O$). The fireclay subgroup is that having alumina content of between 25 to 45% [15,5,3,14]. According to the Al_2O_3–SiO_2 phase diagram [1] the fireclay subgroup occurs with an eutectic point (T_e) at 5.5 percent Al_2O_3 and eutectic temperature of about 1595 °C whereas the eutectic point of high alumina refractory subgroup exists at 78 percent Al_2O_3 and eutectic temperature of about 1840 °C. Thus, the refractory quality of high-alumina is usually higher than that of fireclay-bearing refractories. Nevertheless, fireclay refractories are still widely used due to their ease of fabrication, resistance to chemical attack and low cost. Applications for fireclay refractory brick include insulation behind hot-face materials, furnace linings, and specialty applications such as laboratory crucibles and setters.

Refractory clays are usually contaminated with limited amounts of impurity oxides, including TiO_2, Fe_2O_3, CaO, MgO and alkali oxides which act as fluxing agents at high temperatures. These fluxing agents decrease the eutectic temperature of aluminosilicate refractories. However, the amount of fluxes is kept at minimal to minimize their effect on the development of liquid phase at higher temperatures [15,5,3,14,1,6]. Lithomargic clay underlying bauxite deposits in Ghana result from incomplete bauxitisation process. The chemical and mineralogical characteristics indicate that lithomargic clay consist mainly of kaolinite and gibbsite [11]. The SiO_2 (mainly from the kaolinite) and Al_2O_3 contents varies between 27–52% and 31–45%, respectively. The impurities include Fe_2O_3, TiO_2, K_2O, CaO, MgO and Na_2O. The chemical composition suggests

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that lithomargic clays could be used as fireclay aluminosilicate refractories. However, production of refractory ceramic bodies from this clay has not been successful due to its low plasticity. To make this material usable, there is the need to add a binder to produce a mass which could be moulded into bricks to retain their shape during subsequent drying and firing. A local clay deposit (Mfensi clay) has been investigated and found to possess good properties—about 41% clay and 47% free quartz; it has adequate plasticity (PI = 33%) and good workability. It has been used to produce pottery wares such as water coolers, grinding bowls and bricks [2,13]. This clay therefore could be used as a binder to improve the plasticity of lithomargic clay to enable the use of this material. A mixture of Mfensi clay with lithomargic clay could result in materials of varying properties useful for fireclay refractory products. This work is therefore aimed at developing densed fireclay refractory bricks from lithomargic clay deposits using Mfensi clay as a binder.

2. Methodology

2.1. Materials

Lithomargic clay was taken from Awaso near Sefwi-Bekwai in the Ashanti region of Ghana. Mfensi clay which was used as a binder was taken from Mfensi village near Kumasi in the Ashanti region. Clay samples were dried in an oven at a temperature of 105 °C for 24 h. Samples were pulverised in a vibratory mill for 30 min. The chemical compositions of the samples were determined using X-ray fluorescence spectroscopy (XRF-Spectro X-LAB 2000). Table 1 shows the chemical composition of the lithomargic and Mfensi clay samples. SiO_2 and Al_2O_3 are the major constituents forming over 70% of the total chemical composition. The minor constituents are Fe_2O_3, MgO, CaO, MnO, Na_2O, K_2O and TiO_2. The level of the sum of these oxides is less than 5% and can therefore be used for the production of aluminosilicate refractories [15,5,3,14]. Mfensi clay is a semi-acid clay with SiO_2 content of 65.6% with a corresponding Al_2O_3 content of 19.5%. The organic matter content of the Mfensi clay (10.9%) was higher than that of the lithomargic clay (3.9%).

Mineralogical compositions were analysed using X-ray diffractometer (Siemens D5000), operating at 40 kV and 40 mA and using Cu Kα radiation. Samples were scanned at 10–50° (2θ) and step size of 0.02°. Fig. 1 shows the XRD pattern of the starting clay minerals. The mineralogical composition of Mfensi clay consists mainly of quartz with minor kaolinite content. The proportion of kaolinite content appears less than what previous studies revealed [13]. The lithomargic clay was composed mainly of kaolinite with minor fractions of gibbsite.

The specific gravities of Mfensi and lithomargic clays were determined using ASTM D854-93 and were found to be 2.56 and 2.38 g/cm^3, respectively. The relatively low density of lithomargic clay makes it suitable for the production of lightweight fireclay refractories. Plasticity index (PI) of Mfensi clay was determined according to ASTM D4318-05 and was found to be 21.9%. Severe shrinkage during drying and firing of refractory bricks are not desirable and therefore PI of Mfensi clay is within acceptable limits.

2.2. Experimental procedure

Three lithomargic–Mfensi clay formulations were prepared by wet mechanical agitation at varying proportions by weight as shown in Table 2. Fireclay refractories of dimension 5.2 cm × 5.2 cm × 5.2 cm were produced from the corresponding batches by mixing, semi-dry pressing and drying. They then were fired in a muffle furnace for 1 h

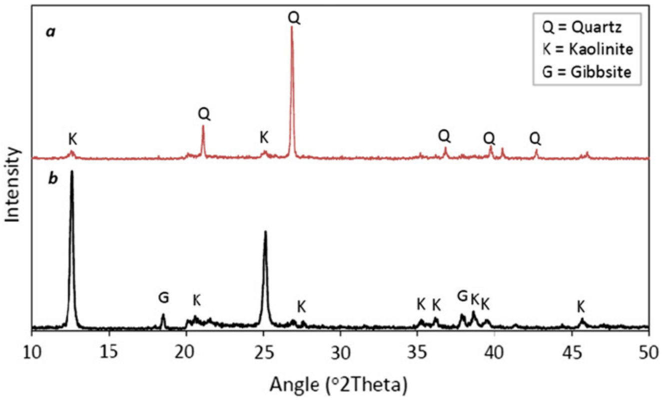

Fig. 1. XRD spectra of Mfensi (a) and lithomargic (b) clay samples before firing.

Table 2
Proportions (wt %) of various formulations investigated.

Sample	Lithomarge (L)	Mfensi (M)
A10	90	10
B15	85	15
C20	80	20

Table 1
Chemical composition of lithomargic (L) and Mfensi (M) clays.

Material	SiO_2	Al_2O_3	Fe_2O_3	MgO	CaO	MnO	Na_2O	K_2O	TiO_2	LOI
M	65.6	19.5	0.8	0.4	0.2	0.2	0.9	0.9	0.6	10.9
L	50.3	42.2	0.4	0.4	0.2	0.3	0.4	0.5	1.4	3.9

at temperatures that ranged from 1200 to 1400 °C. Densification parameters were determined from linear firing shrinkage (ASTM C326-09), apparent porosity and bulk density using the water displacement (Archimedes) method according to ASTM C134. The phase composition of the aluminosilicate bricks were determined using X-ray diffractometry (XRD). The cold crushing strengths of the fired bricks were also determined. For each formulation, five bricks were tested and the average value taken.

3. Results and discussion

Fig. 2 shows the influence of firing temperature on the bulk density and apparent porosity of the various formulations. The bulk density increased as firing temperature increased from 1200 to 1400 °C for all formulations. The bulk densities increased sharply from 1200 to 1300 °C due to the formation of high viscosity siliceous phase [9] which facilitates precipitation of primary mullite [7]. The fraction of this liquid phase depends on batch composition and firing temperature. Within the temperature range investigated, C20 with the highest binder content recorded the highest bulk density followed by B15 and A10, respectively. Above 1300 °C most of the Al_2O_3/SiO_2 have transformed into mullite therefore slight change in densities were observe. The samples attained highest densities at 1400 °C, where complete mullitilisation has occurred. The C20 samples recorded the highest bulk density (3.69 g/cm^3) followed by B15 (3.65 g/cm^3) and A10 (3.53 g/cm^3), respectively. The formation of a glassy phase caused by the presence of fluxing agents and alkali oxides (CaO, MgO, Na_2O, K_2O) helped improved densification of the fired bricks.

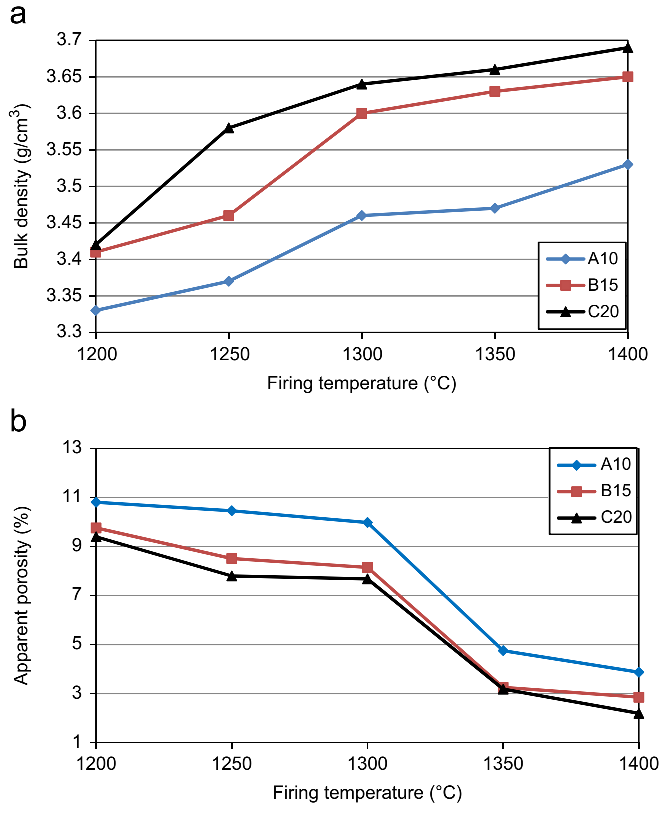

Fig. 2. Effect of firing temperature on bulk density (a) and apparent porosity (b).

The apparent porosity decreased for all formulations over the firing temperature range. It decreases gradually from 1200 to 1300 °C due to shrinkage and pore removal by vitrification and chemical reactions (conversion of meta-kaolinite to mullite, glass formation). Between 1300 to 1350 °C, the apparent porosity decreased sharply. This is mainly attributed to the expansion that accompanies the quartz to cristobalite polymorphic transformations that occur on firing at such high temperatures closing the pores respectively [15,5,3,14]. The decrease in porosity reduces the volume of the bricks whilst improving the mechanical properties [9].

Fig. 3 shows the effect of firing temperature on linear firing shrinkage for the various formulations. The linear firing shrinkage could be used as direct measure of extent of densification. The linear firing shrinkage increased gradually from 1200 to 1250 °C, increased sharply from 1250 to 1300 °C and then increased again gradually from 1300 to 1400 °C for all formulations. That is, three stages of densification could be observed. The first stage (1200 to 1250 °C) was due to pore removal by vitrification and conversion of meta-kaolinite to mullite as confirmed by the XRD measurement shown in Fig. 4. The second stage (1250 to 1300 °C) was due to the volume expansion that accompanies quartz to cristobalite phase transformation which resulted in pore closure [15,5,3,14]. At the final stage of densification (1300 to 1400 °C) grains grow as full density was reached [7]. The final vitrified body was densed and containing primary mullite that was formed during vitrification, secondary mullite that was formed by precipitation of the liquid during cooling, solidified cristobalite and filler quartz from the binder material (Fig. 4). It can be observed that there were no marked difference in the linear firing shrinkage values at 1350 °C and 1400 °C. The linear firing shrinkage values were slightly higher for the C20 sample followed by B15 and A10, respectively. This is mainly attributed to the higher binder content

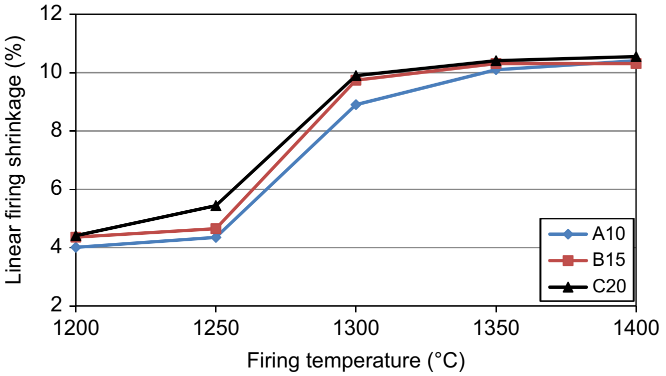

Fig. 3. Effect of firing temperature on linear shrinkage.

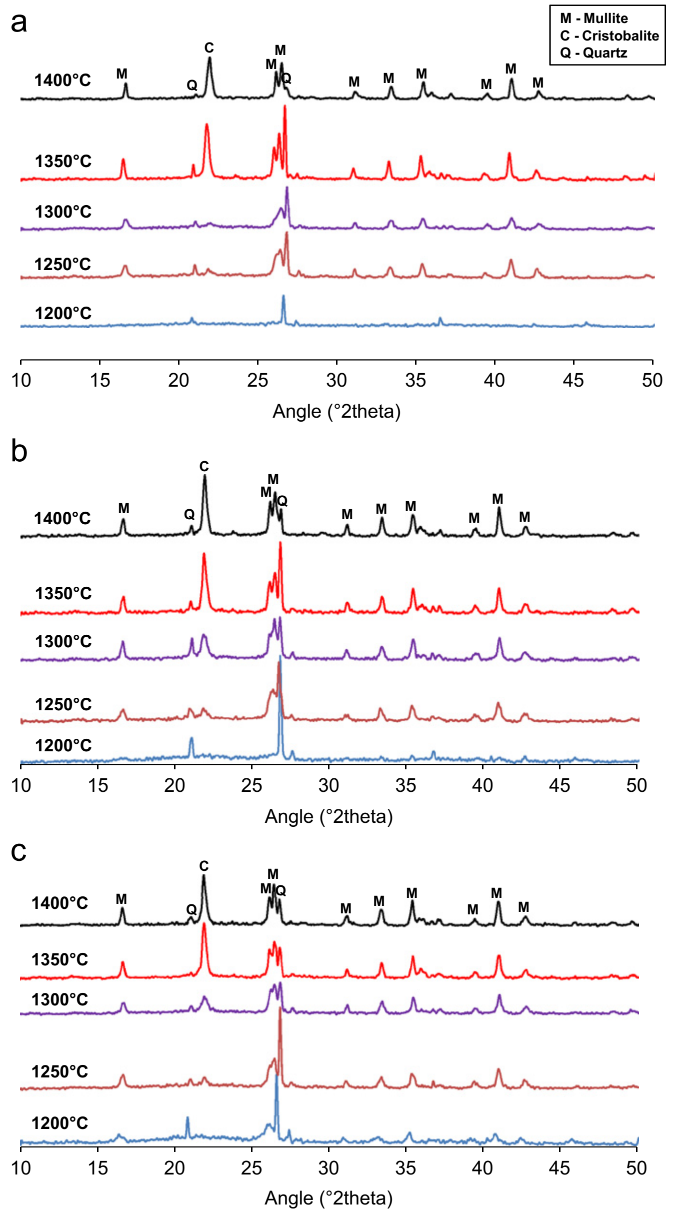

Fig. 4. XRD patterns of fired bricks at various temperatures (a) A10 (b) B15 and (c) C20 formulations.

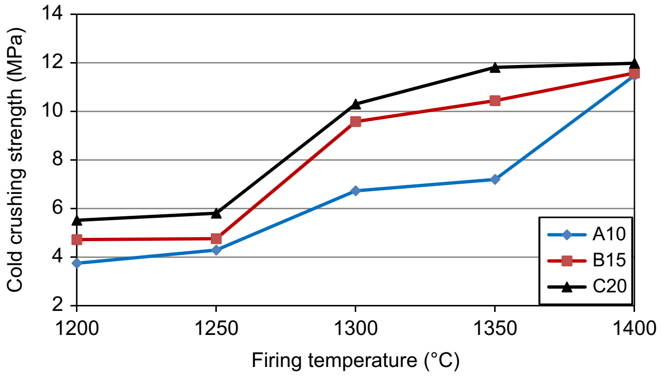

Fig. 5. Effect of temperature on cold crushing strength.

which had higher organic matter and flux agents. The fluxing action of the impurity oxides causes liquid phase to form at higher temperatures.

Fig. 4 shows the phase composition of the fired aluminosilicate bricks at various temperatures. The sum of fluxing oxides is ~4%. Hence, variable amounts of liquid phase are expected to form in the fired bricks from 1200 to 1400 °C as the binder content varies from 10 to 20 wt%. The amount of liquid phase depends on the Al_2O_3/SiO_2 ratio, fluxing oxide content and firing temperature. Therefore, the glassy phase content is expected to be high in the C20 bricks followed by B15 and A10, respectively. It can be observed that at 1200 °C no mullite peaks were identified due to the formation of amorphous silica from kaolinite [4]. Further heating to 1250 °C transforms kaolinite to mullite and also results in crystallisation of the silica to cristobalite. The formation of crystalline mullite started at 1250 °C with complete mullitilisation occurring at 1400 °C for all formulations. It can also be observed that at temperatures up to 1350 °C quartz was still present in relatively high concentrations in the fired bricks. This is mainly attributed to the addition of increased amount of Mfensi clay to the lithomargic clay bricks. The increase in firing temperature leads to the gradual decrease of quartz peak intensity and its complete disappearance in bricks fired at 1400 °C, especially for A10 formulation where SiO_2 content was low. The other samples (B15 and C20) had some residual quartz. Nevertheless, reduction of the amount of free silica (consumed in the formation of mullite) produced at 1400 °C results in increased uses for fireclay bricks at higher temperatures. The bricks fired at 1400 °C mainly are composed of mullite, cristobalite and glassy phase. The quartz mineral is associated with the binder clay. The reactivity of quartz is much less than the SiO_2 liberated from kaolinite structure on firing to 1400 °C. Hence, some of the quartz grains of these brick do not transform to cristobalite but react with Al_2O_3 to form mullite or participate in liquid-phase formation [15,5,3,14,1,6]. The high mullite content in fired bricks improves creep and corrosion resistance [10].

Fig. 5 shows the effect of firing temperature on the cold crushing strength of the various formulations. The results indicate that absolute cold crushing strength values increased strongly with increasing firing temperatures. The cold crushing strengths of the fired bricks are influenced by their phase composition. The fired bricks densified on firing within the temperature range of 1300 to 1400 °C. The increase of the highly refractory phases (cristobalite and mullite) and the densification of the bricks due to the presence of flux agents improved the cold crushing strength of the bricks.

4. Conclusion

It has been possible to produce densed fireclay bricks using lithomargic clay and a clay binder (Mfensi clay). The addition of a clay binder improved the plasticity of the lithomargic clay allowing ceramic bodies to be formed. Good combination of results was obtained by addition of

20 wt% binders and firing temperature of 1400 °C. The linear firing shrinkages observed were less than 11% and therefore make it suitable for refractory material. The apparent porosities were less than 4% for bricks fired at 1400 °C. The bricks fired at 1400 °C show accepted chemical and phase composition as well as densification, and cold crushing strength properties. It can be concluded that there is a possibility of using lithomargic clays as fireclay aluminosilicate refractory materials. The fireclay bricks produced could be used as low to high heat duty applications such as crucibles and kiln linings.

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