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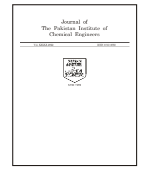

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Synthesis and Characterization of Geopolymeric Refractory Bricks using Blends of Indigenous Fly Ash and Metakaolin

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Abstract

High sintering temperature, is required for the production of refractory bricks which is an energy-intensive operation and utilizes expensive raw material. Geopolymerization is a chemical process that produces a class of inorganic binders of geopolymers. This technique is an energy efficient technique for the geopolymer refractory bricks (GPRB) synthesis because it utilizes low sintering temperature and uses raw material such as fly ash (FA) and metakaolin (MK) which is more economical as compared to conventional raw materials for refractory bricks. As the FA has a high thermal resistance and is available as abundant waste while the metakaoline possesses high compressive strength compared to the FA. In the current study, GPRB were prepared through geopolymerization by blending FA and metakaolin in different weight percent's. The six samples have been designed and prepared with various compositions of FA and metakaoline. The compressive strength and thermal conductivity for pure metakaoline based GPRB were 24.15 MPa and 0.78 W/mK, respectively at 28 days, while these were 3.06 MPa and 0.54 W/mK for pure FA based at room temperature. By increasing the amount of FA in the samples increases the thermal resistance, however, it reduces the compressive strength of the samples. The optimum blending ratio can be selected for different applications according to the minimum mechanical strength requirements with the desired thermal resistance considering the synthesis of specific refractory.

Keywords: Geopolymerization, GPRB, Fly ash, Metakaolin, Geopolymer, Thermal conductivity

1. Introduction:

Refractory bricks are ceramic blocks used in fireplaces, kilns, and furnaces, among other things. For usage under intense mechanical, chemical, and thermal loads, a refractory brick should be able to endure high temperatures and have a high density. The refractory brick should also have low thermal conductivity for greater energy efficiency [1]. Moreover, the refractories are needed to have good mechanical properties and having good heat resistance to withstand the rapid temperature change, corrosion, and erosion by molten metal, glass, slag, and hot gas. The refractory bricks produced for commercial purposes are very costly, energy-intensive due to very high sintering temperatures over 1300 °C which consequently produces CO_2 [2][3]. Porous ceramics has a new class known as Geopolymers and these polymers are alkali-bonded. Furthermore, they have good mechanical strength, chemical and thermal properties. Due to these desired properties, they have received very good responses from researchers ——[4][6]. A French scientist called Davidovits used the word geopolymer to describe the 3D structure of aluminosilicates formed by activating pozzolona material with high alkalis hydroxides.

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Geopolymerization is a step-by-step procedure that begins with the preparation of the alkaline activator, which is then combined with the source material to create an amorphous or semi-crystalline paste. Finally, the paste is molded into the appropriate shape before being cured at temperatures ranging from ambient temperature to 70 degrees Celsius. Consequently, the heterogeneous reaction is completed and the desired structure is obtained.

Natural alumino-silicate refractory bricks have major constituents i.e, clays, diaspore, kyanites, and bauxites. Fire clay bricks have less than 50 percent alumino oxide (Al_2O_3). On the other hand, breaks having Al_2O_3 more than 50 percent are known as High alumina bricks. Previously researchers have used various constituents for the synthesis of refractory bricks such as for the synthesis of mullite refractory, grounded mullite was mixed with 20-50 % of clay (plasticizer), and for the required product heat treatment (1700° C) was applied [2][7][8].

Table 1 Kyanite composition [2]

Compound	Percent
Aluminium oxide (Al_2O_3)	63.45
Silicon dioxide (SiO_2)	31.0
Iron(III) oxide (Fe_2O_3)	3.21
Calcium oxide (CaO)	1.29
Magnesium oxide (MgO)	0.1

***Table 2** Bauxite composition [2]*

Compound	Percent
Aluminium oxide(Al_2O_3)	56.00
Silicon dioxide (SiO_2)	9.50
Water	25.50

The researcher has also investigated FA refractory bricks and different source material (kaolin) and different types of activators are utilized depending on availability and pricing in their respective region. Different ingredients have also been added to achieve specific material properties ——[9][14]. Cao et al. has previously investigated thermally resistant GPRB made with NaOH and Na_2SiO_2 as activators, with raw material FA having low calcium and as well as sand [8]. and the composition is shown in Table 2 [13]. The FA-based refractory bricks provide low thermal conductivity with low compressive strength although the metakaolin-based refractory bricks provide good compressive strength but the thermal conductivity also increases.

In this research work, the geopolymer refractory bricks will be synthesized and studied by mixing the different compositions of FA and metakaolin to obtain brick with low thermal conductivity and good compressive strength. NaOH (10 M) and water solution was made, then combined with Na_2SiO_3 in a ratio of 1.5, and then mixed with the base binder material which is FA, metakaolin in ratio 20/80% (S_3), 40/60% (S_4), 60/40% (S_5), 80/20% (S_6) as well as with 100 % (S_1) FA and 100 % (S_2) metakaolin. FA is a coal combustion product made up of particles that are ejected from coal-fired boilers, along with flue gases with a composition: Silicon dioxide (SiO_2) =46 percent., Aluminium oxide (Al_2O_3) =25 percent., Iron(III) oxide (Fe_2O_3) =2.97 percent., with thermal conductivity (1.254 W/m K), and Kaolin having composition Silicon dioxide (SiO_2)=46 wt%, Aluminium oxide(Al_2O_3) =19 wt%; Sodium oxide (Na_2O) =0.29 wt%; Potassium oxide (K2O) =0.95 wt%, and Iron(III) oxide (Fe_2O_3)=4.27 wt% with thermal conductivity (2·9 W/ (m K) (Lee et al., 2012))——[10][12]. As the raw material are inexpensive and a low sintering temperature is required for geopolymer material synthesis [8][9][15], thus making it suitable for the synthesis of refractory bricks.

2. Experimentation:

2.1. Materials

The sources material was low calcium FA class (F) from the ICI Ash factory in Pakistan and Nowshera, KPK, Pakistan provided the Kaolin clay. Na_2SiO_3 was added to the 10M NaOH solution to prepare the alkaline activator to activate the source material. The NaOH utilized was of technical grade, with a specific gravity of 212.14 g/mol, and Na_2SiO_3 solution with 14.7% of Na_2O, SiO_2=29.4%, and 55.9 % water by mass was acquired from Sigma-Aldrich, Austria.

2.2 Method:

Class-F FA was dried for 2 hours at 105 °C. To convert the kaolin to metakaolin, the clay was calcined at in a muffle furnace (T=850°C, t= 3 hours). The particle size of FA and kaolin were maintained below 80 µm and 800 µm (0.8 mm), respectively bypassing these through a sieve shaker as reported in a previous study for high compressive strength ——[15]. In deionized water, a 10M solution of NaOH (NaOH) was made, and then Na_2SiO_3 was mixed with NaOH solution and stirred for 24 hours to get the alkaline activator solution. The NaOH to Na_2SiO_3 ratio was used 1.5 throughout this research work. Six different samples i.e. S_1 to S_6 were prepared. S_1 is pure FA, while S_2 is pure metakaolin. The remaining samples are the mixtures of FA and metakaolin in different percentages by mass as shown in Table 3. During this study, it is hypothesized to achieve the low thermal conductivity and good compressive strength of the geopolymer refractory bricks by mixing the various compositions of FA and metakaolin (Table 3). The various combinations of the composition of FA and metakaolin are tuned for each sample to investigate the individual and combined effect of fly ash and metakaolin on the performance parameter for geopolymer refractory bricks. The source material was mixed with the alkaline activator in a ratio of 1.5 and the ratio was kept constant throughout the work.

Table 3: Mixing ratio of FA and metakaolin

Samples	***S_1***	***S_2***	***S_3***	***S_4***	***S_5***	***S_6***
FA: Metakaolin (Mass%)	*100:0*	*0:100*	*80:20*	*60:40*	*40:60*	*20:80*

The samples were then cast in the mold sizing 40*40*160 mm (EU standard for Cementous prism) and curing was done in the oven for a total of 3 hours at 70 °C. The material was then de moulded and put for further curing for 7 and 28 days at room temperature to achieve the desired compressive strength. The prepared samples were then characterized for different properties.

2.3 Analysis:

X-ray Fluorescence analysis (XRF) was performed on the material to know its elemental composition. The conversion of kaolin to metakaolin through phase identification was analyzed through X-ray Diffractometer [Machine Model: Bruker D8 Advance, Voltage: 40kV, Current: 30mA, X-Rays: Cu K alpha, 2Theta-Range: 10 to 80°. The compressive strength of samples cured for 7 and 28 days in room condition was measured by a Toniversal Compressive Machine (TONITEKNIC, Serial no #1130/34) with range/resolution: 0 to 600 KN/0.01 KN. Thermogravimetric analysis (TGA, thermobalance TA Instruments SDT 2960) was carried out at a heating rate of 10 °C/min under the nitrogen atmosphere in a temperature range of 20 °C-900 ℃ [16]. Thermal conductivity analysis was conducted via Thermal Constant Analyzer. The efficiency of geopolymerization reaction was analyzed through FTIR by observing the hydroxyl group in the produced geopolymeric products. Fourier transform infrared spectroscopy was performed through the attenuated total reflectance (ATR) technique (Vector 22, Bruker) with a spectral range and a resolution of 4000–500 cm^{-1} and 2 cm^{-1} respectively.

3. Result and Discussion:

3.1. X-ray Fluorescence Analysis:

The source material's chemical composition was studied through XRF analysis. The results of the XRF analysis of the FA (Model: XRF-1800, Manufacturer: Shimadzu) are shown in Table 4. The ratio of silica to alumina in the source material has a significant effect on the mechanical properties of geopolymers. The compressive strength of geopolymers with high silica to alumina ratio is good. The source material has a silica to alumina ratio of 2, which is regarded as the optimal ratio for high compressive strength. According to the literature, the ideal silica to alumina ratio is 2.

Table 4: XRF analysis of source material

Compound	SiO_2	Al_2O_3	Fe_2O_3	*CaO*	Na_2O	K_2O	SO_3	*MgO*	*Sum of Conc*	*LOI*
FA	47.72	23.78	9.13	3.52	0.72	1.33	2.02	1.02	89.22	10.78
Kaolin Clay	43.24	22.40	3.10	2.88	0.22	0.17	0.07	0.17	72.25	27.75
Metakaolin	47.48	24.03	3.53	2.85	0.22	0.18	0.09	0.26	78.64	21.36

3.2 X-ray Diffraction Analysis:

Figure 1 shows X-ray Diffraction analysis XRD analysis after thermal activation of kaolin clay for checking the phase change of kaolin clay metakaolin. The amorphous structure of metakaolin was ascribed to a large dispersion peak located between 18 and 25 in the XRD pattern of metakaolin. Metakaolin's microstructure was mostly hypocrystalline and amorphous save from quartz crystals [17].

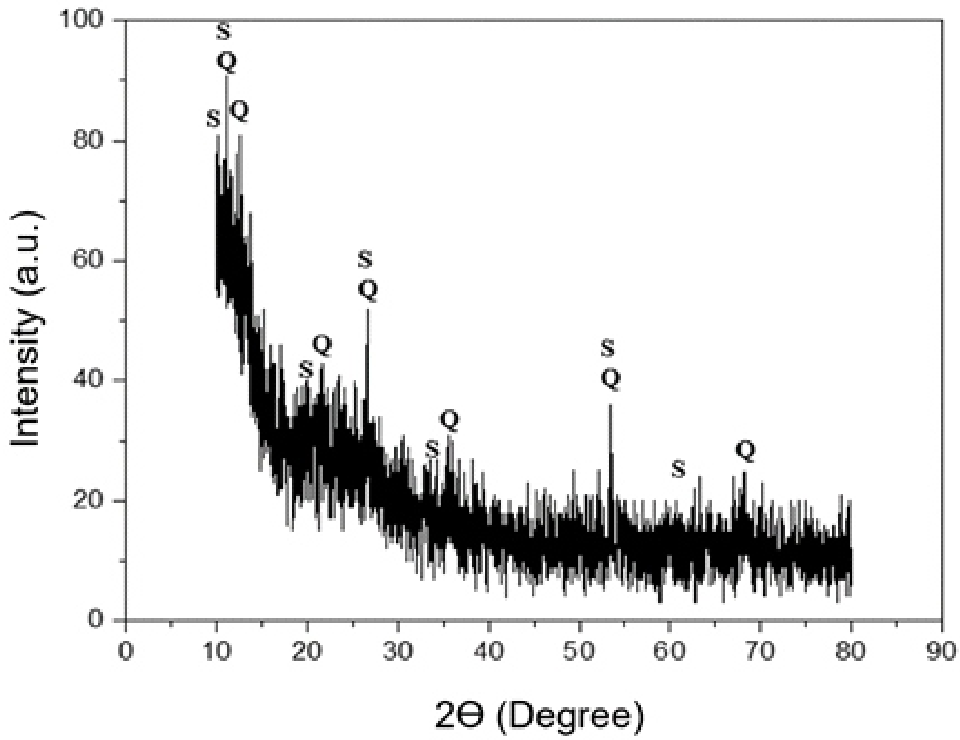

Figure 1: XRD patterns of Activated Kaolin at 650 °C

3.3 FTIR Analysis:

FTIR analysis indicates that there was no hydroxyl present in the material and confirms the occurrence of reactions. From Figure 2, it can be seen that as the metakaolin amount increase, the stretching of the peaks decreases, which shows that metakaolin based refractory bricks are more stable and as the amount of metakaolin the sample becomes more stable. The broad absorption band in the region of 3100-3700 cm^{-1} is attributed to –OH stretching vibration, indicating the availability of –OH in the sample. The peak at 810 cm^{-1} is due to the presence of Al-O, while the peak present at 991 cm^{-1} is due to the Si-O-Al group. The Si-O-Si peak can also be seen at 1400 cm^{-1} which shows the reaction of CO_2 with alkali metal hydroxide as shown in Figure 2

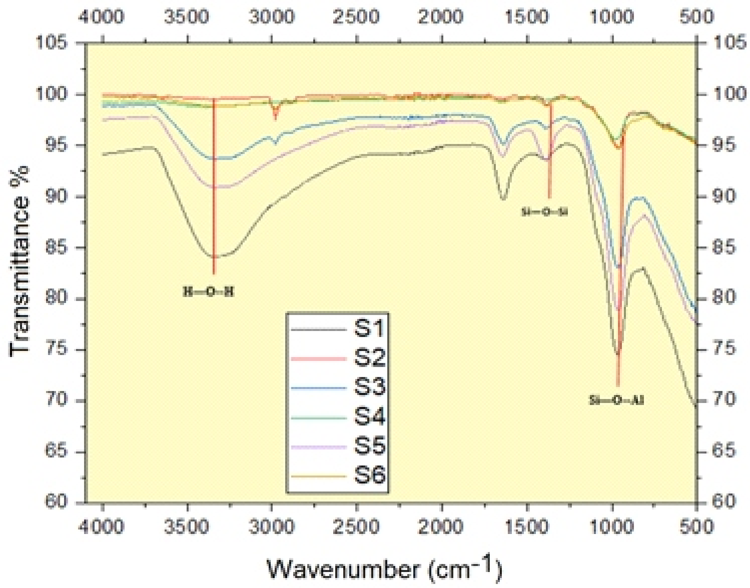

Figure 2: FTIR analysis of the refractory bricks

3.4 Thermogravimetric Analysis (TGA):

TGA was performed for all the synthesized samples as seen in Figure 3. The FA based sample S_1 shows weight loss up to 851 °C then the sample gets stable and the weight loss recorded was 24 %. The graphs show that as the amount of metakaolin increases in the samples, the thermal stability of the samples also increases as S_2 indicates low loss i.e., 18 %, and gets stable at a temperature of 611 °C. These observations indicate that Metakaolin has good reaction value than FA based. The samples S_3, S_4, S_5, and S_6 show less weight loss and high thermal stability due to the presence of metakaolin.

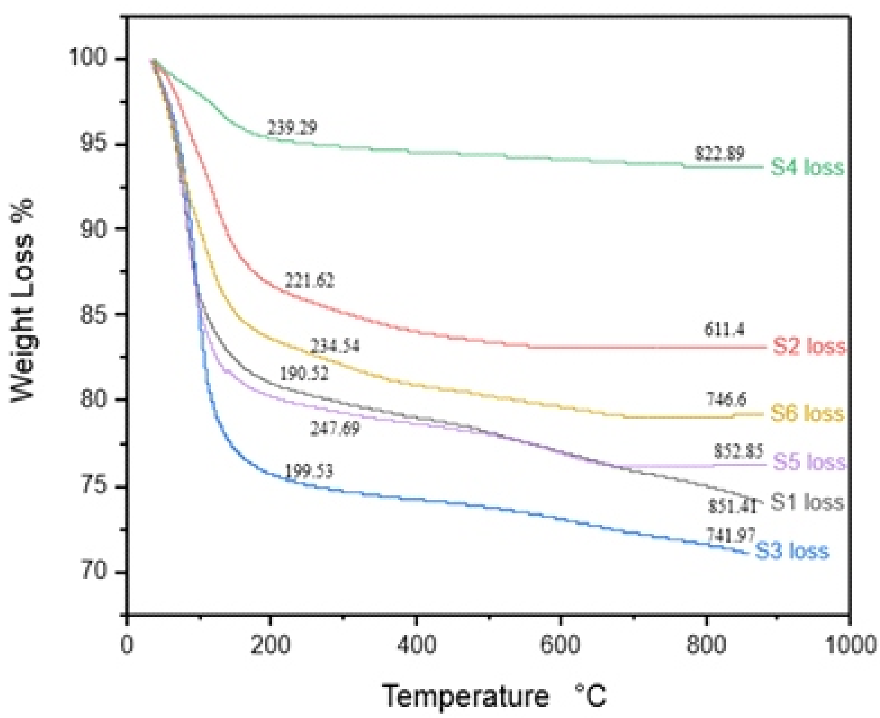

Figure 3: TGA curves of Geopolymeric refractory bricks for all samples

3.5 Compressive Strength:

The mechanical properties of all the samples were studied by performing the compressive strength test on the samples (Figure 4). It has been observed that when pure metakolin is used for geopolymer refractory bricks achieve a maximum compressive strength of 19.08 MPa, on the other hand, FA geopolymer showed the lowest strength of 2.24 MPa. Increasing the amount of metakaolin in samples, the compressive strength of the geopolymers also increases for S_3 (2.98 MPa). For S_4, the increasing ratio 40 % of metakaolin, the compressive strength became 3.58 MPa, while it increased to 7.16 MPa for S_5 and for S_6, it becomes 10.21 MPa. The compressive strengths of these samples were examined after being cured for 7 days. After 28 days The compressive strength was also investigated as can be seen in Figure 4, The compressive strength of all the samples has improved with the passage of time which concludes that by providing more curing time, the compressive strength of the geopolymers gets

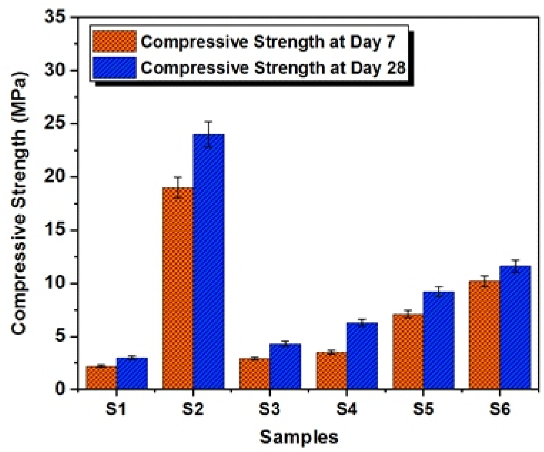

Figure 4: Compressive strength compression for all the samples of days 7 to 28

3.6 Thermal Conductivity(TC):

The thermal conductivity of all the samples was also investigated (Figure 5). When we increase the amount of metakaolin in the samples, the compressive strength increases while an increasing amount of FA decreased the TC of the prepared samples. S_1 exhibits the lowest TC of 0.7837 W/mK, while S_2 TC was 0.54 W/mK at room temperature. S3 having 20% amount of flyash TC recorded for S3 was 0.3344 W/mK. The TC results show that as the amount of metakaolin is increased in the samples TC increase and decreases when the amount of

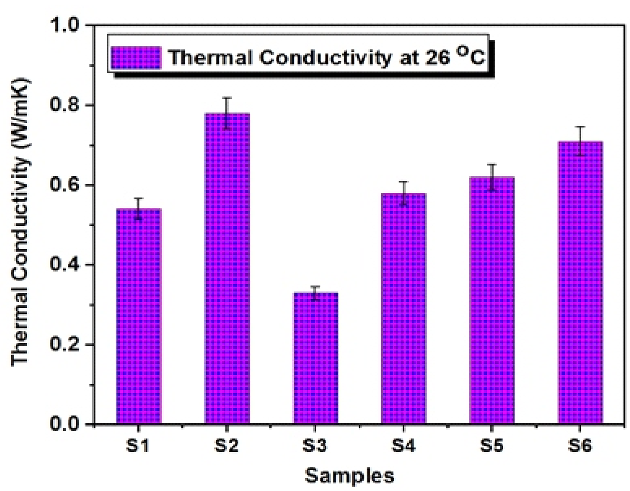

Figure 5: Thermal conductivity of the synthesized samples at room temperature

3.7 Cost and Energy Comparison of Geopolymeric and Alumina Refractory Bricks

Thermal processes for the synthesis of refractories are widely used which require extremely high temperatures (1000-1200 °C) for proper microstructure and high mechanical properties [18], while Geopolymer material requires low sintering temperature. The mixing ratio for FA/ metakaolin to alkali activator and Na_2SiO_3 to NaOH has been designed as 1.5. Geopolymer paste of 530 grams composed of NaOH and Na_2SiO_3 in 10 molar solutions as per design has been calculated as 200 grams. FA amounts of 300 grams were determined by the following equations (1) and (2).

$$g\ Na_2SiO_3 / g\ NaOH = 1.5 \quad (1)$$

$$g\ FA\ /\ g\ AA = 1.5 \quad (2)$$

The density of GPRB is measured by calculating the mass fraction of components (Eq. 3) of GPRB as follows by Eq (4).

Mass fraction of A = Mass of A required / Total mass of geopolymer past (3)

1/?= MF of FA/ ñ of FA + MF of NaOH/ ? of NaOH + MF of Na_2SiO_3/ ñ of Na_2SiO_3+MF o Dist water/ ? of dist water (4)

Scaling of mix design for GPRB having 1 m^2 area and thickness of 0.04 m. Furthermore, the mass required has been calculated through the equation (5) was obtained 50724 grams as for FA/AA, Na_2SiO_3/NaOH, the volume of GPRB (m^3) NaOH (g), Na_2SiO_3(g), FA(g), kaolin clay (g), and H_2O.

The mass required of GPRB = Density of GPRB / Vol of Required GPRB (5)

Man power, ball mill power, and muffle furnace I and II power consumption were calculated in KW with a combined value of 29.973 kW while the heat required to harden $1m^2$ * 40 mm of GPRB has been calculated using equation (6), while C_p was determined by Eq (7) and Eq (8). The values of C_p for NaOH, Na_2SiO_3, FA, Kaolin clay, and water are 1.4875, 0.92, 0.72, 0.878, and 4.184 respectively.

$$Q = mCp\Delta T \quad (6)$$

$$Cp\ mixture = (XNaOH*CpNaOH + XNa_2SiO_3*CpNa_2SiO_3 + XH_2O_2*CpH_2O_2 + XH_20*CpH_2O + XFA*CpFA) \quad (7)$$

$$Cp_{mixture} = \sum_i^n xi \quad Cpi \quad (8)$$

Where

"i"=specific raw material

n=number of raw materials

Cpi=heat capacity

Xi=mass friction

Total friction has been converted to tons by density= mass of material/volume of material obtaining cost for 0.04 m^3 of GPRB of FA 44.42 $ and for metakaolin based GPRB 67.98 $ and the final cost has been compared with available alumina refractories in the market which is 200-600 $.

4. Conclusion:

In conclusion, the inorganic GPRB was synthesized from cost-effective raw materials (i.e. FA and metakaolin) through geopolymerization. A high sintering temperature (1200 °C) is required in the conventional refractory brick's synthesis process while geopolymerization is a sintering-free technique process and has promising features. An inverse relationship has been observed for the compressive strength and Thermal conductivity with the mixing ratio of MK and FA. The results show that increasing the amount of FA reduces the thermal conductivity of the GPRB. FA/metakaolin 20/80 % with a reasonable compressive strength of 19 MPa (day 7), 24 MPa (day 28) were achieved under the appropriate mixing of metakaolin to FA by 8:2 and Na_2SiO_3 to NaOH by 1.5 molar ratios respectively with 10 M concentrated NaOH solution. The observations show the compressive strength of the bricks increases with time, and the bricks possess the highest compressive strength after 28 days. The thermal conductivity of the samples decreased with increasing the amount of FA in the samples. As by adding 20 % FA, value reduction has been noted from 0.5415 W/mK to 0.3344 W/mK. Almost the same trend has been recorded for all the samples. The cost calculated for FA based on the geopolymeric refractory bricks of volume 1m * 1m * 0.04 m /ton was 44.42 US $ and for the same volume/ton of MK based geopolymeric refractory bricks were 67.98 US $ while the commercially available alumina-based refractory cost is 200-600 $. The results indicate that the synthesis of refractory bricks through geopolymerization is an eco-friendly and cost-effective technique.

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