Chapter-5

Preparation and characterization of semi-silica insulation refractory by utilizing lignite fly ash waste materials

5.1 Introduction

Semi-silica refractories are one kind of refractory with a minimum of 72 % silica content as determined by chemical analysis. It is familiar that these bricks have lower refractoriness and significant porosity than either fireclay or silica bricks or superior TSR (thermal shock resistance) than silica (SiO_2) bricks but are poorer than fireclay bricks. These bricks are employed in pillars and walls in soaking pits and roofs, walls, and arches in reheating furnaces. This kind of refractory is usually made of low purity silica or from ground fireclays and siliceous fireclays [156].

Shaped and unshaped, both refractories can provide thermal insulation. Insulating refractories are permanently tailored as a backup liner due to their high porosity, low strength, and low abrasion resistance. Various types of insulating materials exhibit different qualities and purposes. According to the ASTM C155-97 standard, different types of insulating refractories are divided into distinct classes, as shown in **Table 5.1** [157]. The reheat change of the bricks and bulk density are used to classify it [158].

Table 5.1 ASTM classification of insulation refractories.

Group No	Reheat change < 2% when treated at (°C)	Bulk density not greater than (gm/cc)
16	845	0.54
20	1065	0.64
23	1230	0.77
26	1400	0.86
28	1510	0.96
30	1620	1.09
32	1730	1.52

Nowadays, energy conservation plays a pivotal parameter for high energy-consuming industries such as cement, ferrous and non-ferrous. Therefore, cement, ferrous and non-ferrous industries need high thermal efficient insulating refractory to save energy from heat losses and global warming. These refractories are lightweight, highly porous, with low TC and high specific heat capacity than the other types of refractories. Insulating refractories are primarily produced from natural sources such as kaolin, calcium silicate, fireclay, diatomite, vermiculite, alumina, perlite, lightweight refractory aggregates, and quartz via traditional process [47,53,159]. To generate porosity, different type of combustible material is generally added to the raw mix. The highly combustible substance burns out during firing, leaving a substantial percentage of pores within the burnt body. Sawdust, polystyrene foam, fine coke, organic binders, and foams, as well as granular materials such as hollow microspheres, are commonly used as pore former. Extensive use of these natural raw materials renders scarcity of natural resources. Lignite fly ash waste material has the potential to develop an alternative source to solve this problem. Various authors have studied the application of lignite fly ash waste materials such as ceramic fibers [101], refractories, including insulating materials [66–68], and so on.

The rapid growth of the world's population and economic expansion has resulted in an enhancement in energy demand. Coal reserves are the most reliable and accessible fossil energy source on the planet. On the other hand, the enormous utilization of coal as an energy source in coal-fired thermal power plants results in vast volumes of waste material produced in the form of fly ash. These most complex and ample anthropogenic materials that need to dispose of with proper protocol; otherwise, they can cause environmental pollution to interrupt the eco-system [11]. Fly ash is being researched more extensively over the world in order to use and convert it into useful products [13,22,160]. Major electricity is produced in India from coal-fired thermal power plants using low-grade coal, which generally contains an ash content of 30–45 wt.%. Therefore, the Central Electricity Authority (CEA), Government of India, reports that in the years 2019–20, approximately 226.13 MT of fly ash were produced, of which 187.81 MT is utilized [10]. The unutilized fly ash is considered a waste material that needs special attention for dumping [11,12].

Table 5.2 Chemical composition of fly ash used by some researchers.

Composition (wt%)	**Renukoot, India** [70]	**Andhra Pradesh, India** [66]	**Asturias, Spain**[67]	**Candiota, Brazil** [68]
SiO_2	69.35	57.37	53	68.48
Al_2O_3	26.32	29.78	28	20.21
CaO	0.07	8.41	1.6	1.27
Fe_2O_3	1.16	1.83	6.1	6.70
Na_2O	–	0.54	0.6	0.41
K_2O	–	0.32	3.9	1.59
P_2O_5	1.13	–	–	0.05
MgO	0.25	0.68	1.6	0.56
TiO_2	–	1.07	–	0.61
S	0.36	–	–	–

Therefore, the reuse of fly ash as a raw material for semi-silica insulation refractories is one of the potential recycling techniques that have yet to be seriously researched. FA contains substantial quantities of alumina (Al_2O_3), silica (SiO_2), iron oxide (Fe_2O_3), and calcia (CaO), along with other oxides. They are being used as a low-cost material in various industries. Thus, many researchers have been motivated to find out the different applications of fly ash. As a result, numerous authors have investigated suitable application of fly ash such as, zeolites [97], high volume FA concrete [161], geopolymer [72], glass–ceramics [20], ceramic tiles [18], ceramic membrane [162], catalysts [163], agriculture application [164], construction bricks, paving blocks, etc. [165,166]. Some researchers have used fly ash from different sources to produce refractory, and their chemical composition is shown in Table 2.

The main objective of this study is to produce semi-silica insulation refractory by exploring the chemical constituents of FA. The fly ash contains 67.20% SiO_2, 23.89% Al_2O_3, 5.53% Fe_2O_3 is used as potential raw materials. Ball clay and sawdust were used to produce semi-silica insulation refractory by using fly ash, which was an eco-friendly and low-cost material. Five different batches were formulated by incorporating fly ash, ball clay, and sawdust, as shown in **Table 3**. In each batch, ball clay content has been varied with respect to fly ash in different weight percent and sawdust kept fixed. All the compositions were mixed using a pot mill for 10 minutes at 300 rpm before being hydraulically pressed at 130 MPa pressure with 10 wt.% PVA solution as well as a few ml of water addition. The bricks were dried for 24 hours in air prior to the drying at 110 °C for overnight. The samples were fired at the rate of 2.5°C/min up to 500°C for 1 hour and then fired at 1000, 1100, and 1200 °C for 2 hours with a heating rate of 10 °C.

Table 5.3 Batch composition of different samples.

Samples	Fly Ash (wt.%)	Ball Clay (wt.%)	Sawdust (wt.%)
FC00S	90	0	10
FC10S	80	10	10
FC20S	70	20	10
FC30S	60	30	10
FC40S	50	40	10

5.2 Results and discussions

5.2.1 Raw material characterization

The lignite FA waste materials contain alumina and silica as the major constituent shown in **Table 5.4**. The chemical analysis shows alumina content is above 20% while the content of silica is approximately 67% which can be classified as alumino-silicate ashes. It is also can be categorized as class F FA originating from sub-bituminous or lignite coals and possessing a minimum of 70% (alumina, silica and iron oxide), as per the ASTM categorization of FAs.

Table 5.4 Chemical composition of fly ash, ball clay, and sawdust.

Compound (wt. %)	Fly ash	Ball Clay	Sawdust
SiO_2	67.18	59.95	84.5
Al_2O_3	23.91	25.06	3.00
Fe_2O_3	5.50	0.80	1.50
CaO	1.0	0.13	3.50
TiO_2	0.92	2.21	--
Na_2O	0.61	0.12	0.04
MgO	0.29	0.17	0.60
K_2O	0.18	0.61	--
SO_3	0.08	--	--
P_2O_5	0.07	0.07	--
LOI	--	10.85	--

The X-ray diffraction spectra of FA waste material are shown in **Fig. 5.1(a)**. It was observed from the graph that lignite fly ash comprises of crystalline and glassy phases at 2θ range 20-30°. The primary crystalline phases were identified as quartz (089-8945) and mullite (079-1456). **Fig. 5.1(b)** exhibits the XRD spectra of ball clay which is consists of major crystalline phases such as kaolinite (001-0527), quartz (089-8945), and illite (043-0685). The spectrum also indicates that there were some glassy phases in the ball clay.

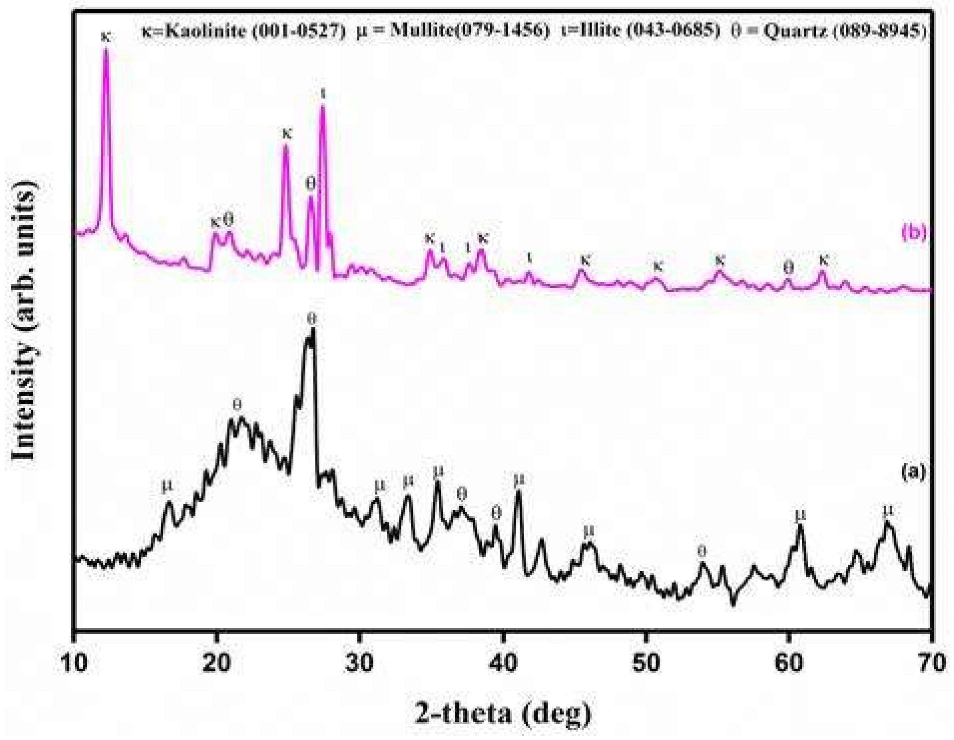

Fig. 5.1: XRD curve of (a) fly ash and (b) ball clay.

The SEM micrograph of FA waste material is shown in **Fig. 5.2(a)**. The majority of the ash is made up of porous glassy particles with a lamellar type of structure. Also, some flaky particles of varying sizes with an uneven and angular morphology can be seen. These alumino-silicates can be used in the production of refractories as raw materials. Basic characterization of FA was already discussed in our earlier research [167,168]. XRF analysis was applied and found that the ball clay mainly consists of silica (SiO_2) and alumina (Al_2O_3) is represented in **Table 5.4**. The structure of clay is defined as calcareous when lime (CaO) content in the clay is greater than 6%. Whereas the clay is known as high refractive when the potassium oxide (K_2O), titania (TiO_2), iron oxide (Fe_2O_3), lime (CaO), and magnesia (MgO) content in the clay are lesser than 9% [169]. Therefore, in this study, the used ball clay is non-calcareous with high refractory properties. Due to the presence of hydroxides and organic materials in the clay, a significant loss of ignition (LOI) was found. The structural features of the ball were observed using SEM and represented in **Fig. 5.2(b)**. It shows a glassy matrix with sheet type of structures. **Table 5.4** represents that silica is the major component of FA, clay, and sawdust.

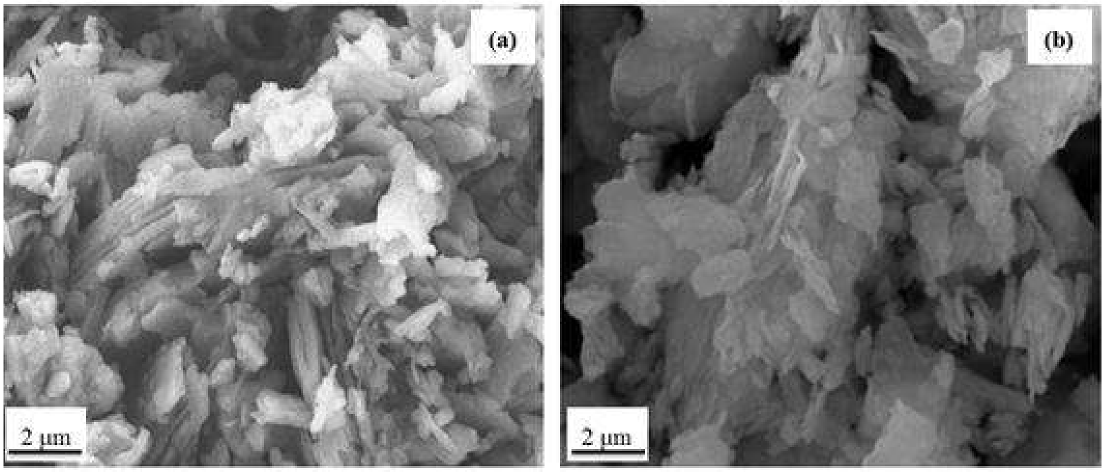

Fig. 5.2: SEM image of (a) fly ash and (b) ball clay.

The phenomena that happened during heat treatment of fly ash up to 1100 °C were checked by the differential thermal analysis technique and shown in **Fig. 5.3(b)**. The endothermic peak on the diagram at around 120 °C is for the evaporation of water molecules. The second small exothermic peak at approximately 575 °C in the DTA thermograms was because of the polymorphic phase transformation of SiO_2 (quartz). The exothermic hump at about 763 °C is responsible for the oxidation of unburned coal, organic matter, and decomposition of $CaCO_3$ [170–172]. There was no fusion of the sample observed till 1100 °C, so it could be used in high-temperature applications as a raw material.

Fig. 5.3(a) exhibits the DTA curve of ball clay up to 1100 °C in the air atmosphere. The endothermic peak at 110 °C was because of the vaporization of surface moisture in the ball clay. The transformation of ball clay into meta-kaolin was

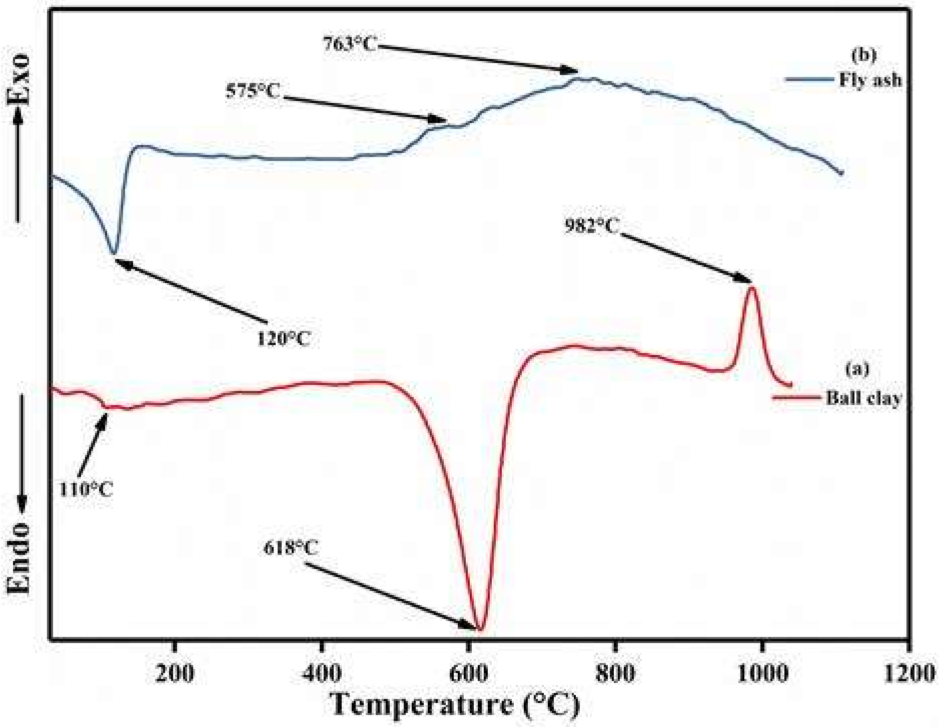

Fig. 5.3: DTA curve of raw material (a) ball clay and (b) fly ash.

responsible for the endothermic peak at 618 °C [173]. Whereas the exothermic peak at higher temperature (982 °C) indicates that the meta-kaolin phase transforms into mullite and amorphous silica (glass) [141,174,175]. The kaolin to mullite phase transformation can be represented by the following reactions (1), (2), and (3), respectively [176,177].

$$Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O \text{ (kaolin)} \xrightarrow{618\ °C\ (endo)} Al_2O_3 \cdot 2SiO_2 \text{ (metakaolin)} + H_2O \quad (5.1)$$

$$Al_2O_3 \cdot 2SiO_2 \xrightarrow{982\ °C\ (exo)} Si_3Al_4O_{12}\text{, Al-Si spinel} + SiO_2 \text{ (amorphous)} \quad (5.2)$$

$$Si_3Al_4O_{12}\text{, Al-Si spinel} + SiO_2 \xrightarrow{1050\ °C} 3Al_2O_3 \cdot 2SiO_2 + SiO_2 \text{ (amorphous)} \quad (5.3)$$

Fig. 5.4(a-e) shows the DTA curve of the raw mix of the brick sample up to 1100 °C in an air atmosphere. Two exothermic peaks appeared between 200 and 530 °C due to the combustion of organic compounds in the raw mix. For compositions FC10S to

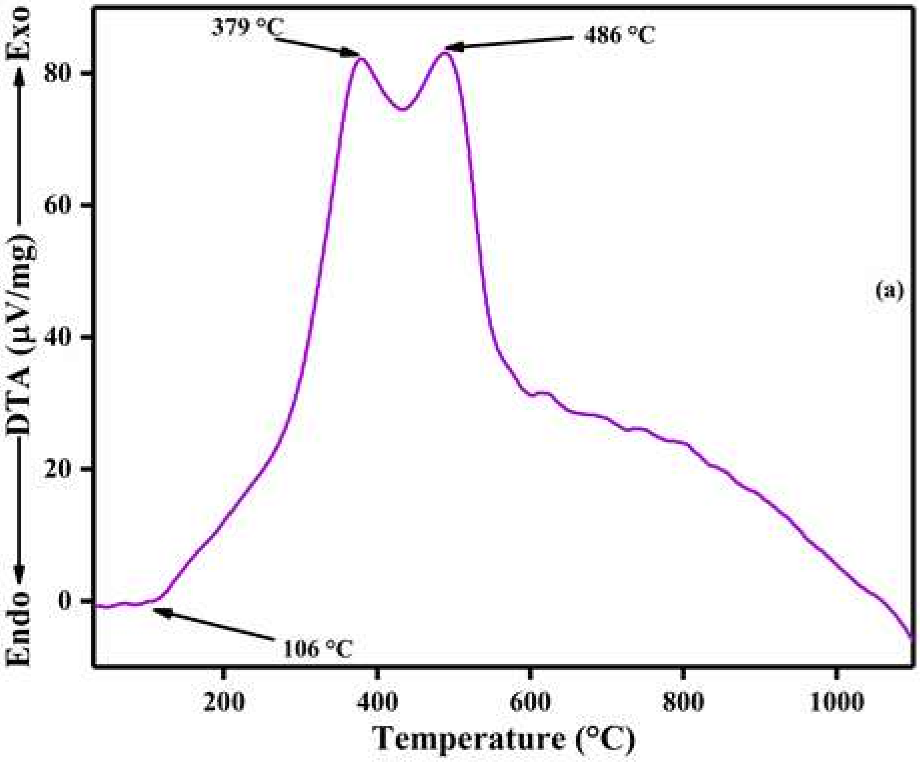

Fig. 5.4(a): DTA curve of raw mix of composition FC00S.

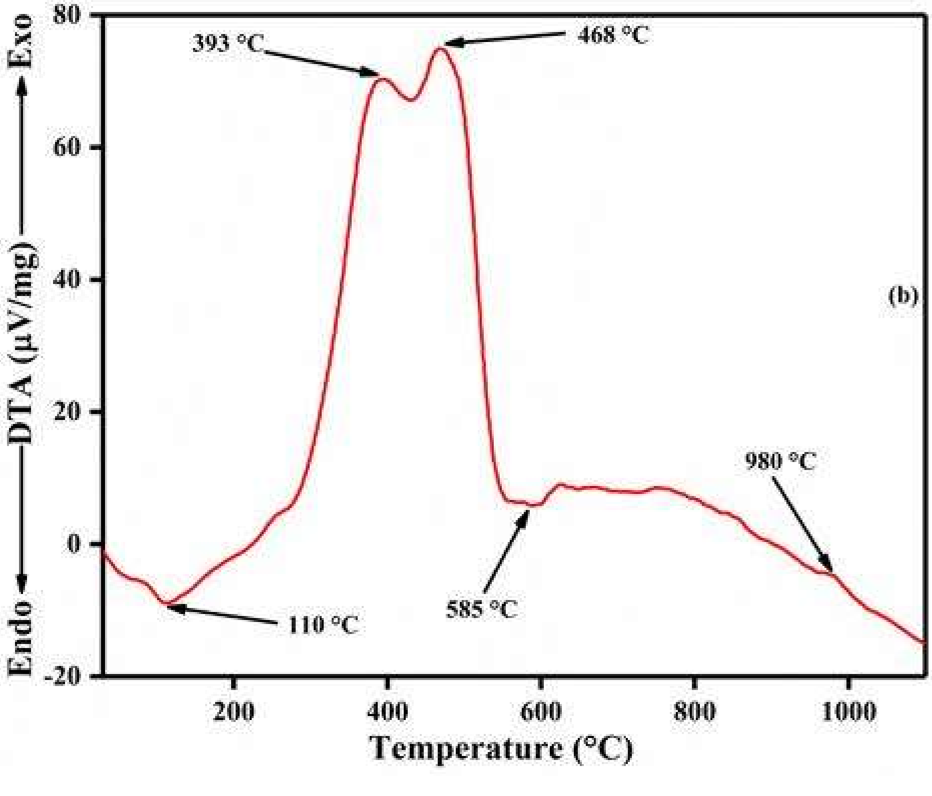

Fig. 5.4(b): DTA curve of raw mix of composition FC10S.

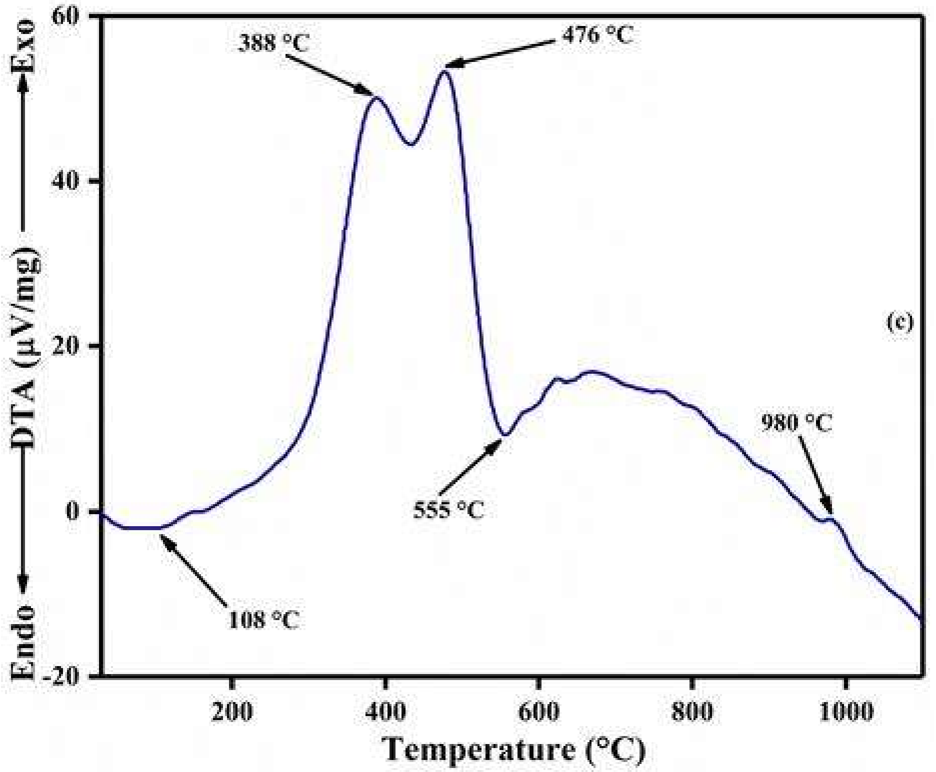

Fig. 5.4(c): DTA curve of raw mix of composition FC20S.

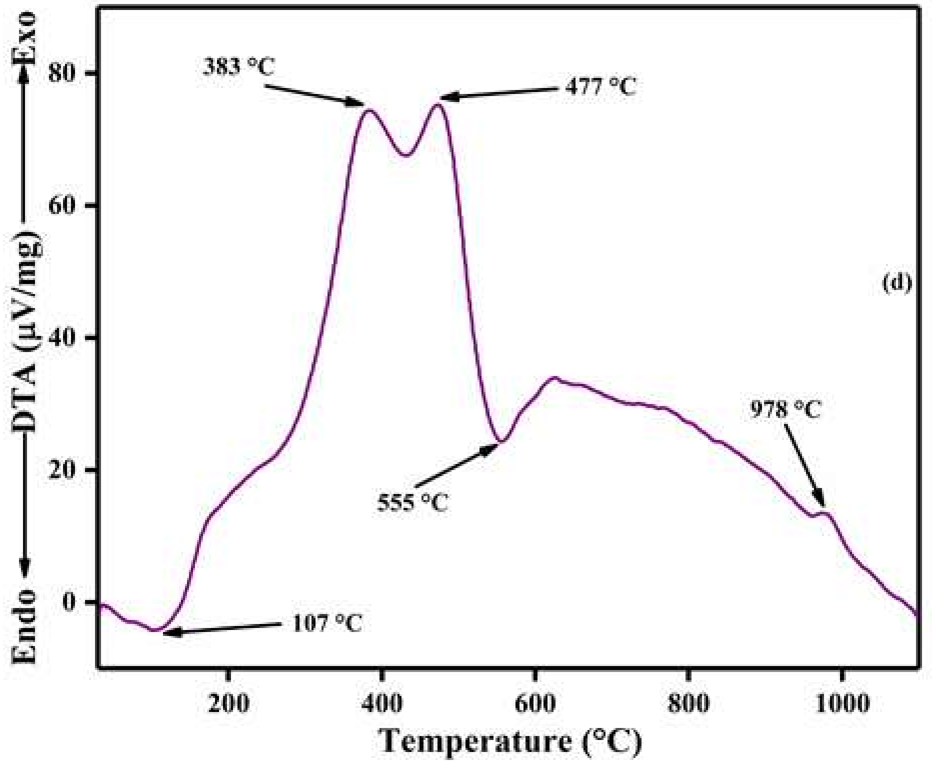

Fig. 5.4(d): DTA curve of raw mix of composition FC30S.

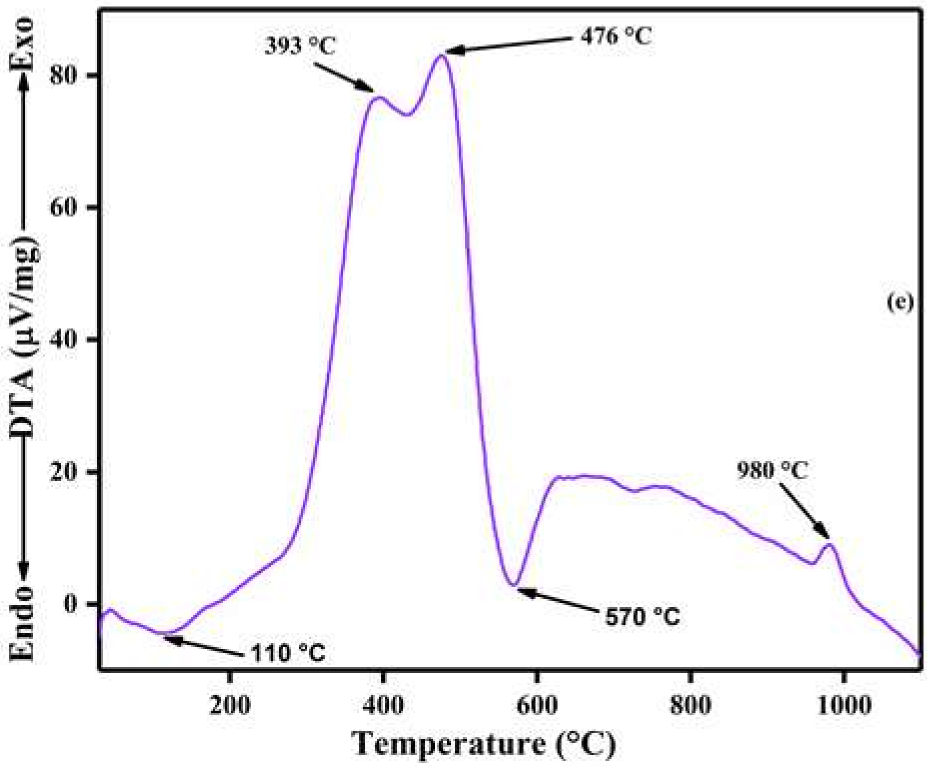

Fig. 5.4(e): DTA curve of raw mix of composition FC40S.

FC40S, upon increasing the clay content, the endothermic peak between 530-630 °C gradually increases because of the dehydroxylation of ball clay and polymorphic phase conversion of quartz. Upon increasing the temperature, the meta-kaolin transforms into mullite and free silica, and therefore the exothermic peak at 982 °C has appeared. The intensity of the exothermic peak increased with the ball clay content in the compositions.

5.2.2 Characterization of fired semi-silica insulation bricks

The qualities of alumino-silicate fired refractory bricks depend on the chemical composition, pore formers or density, and firing temperature. The chemical composition of different fired refractory bricks has been analyzed by X-ray Fluorescence (XRF) and is shown in **Table 5.5**. It has been observed that the incorporation of up to 40 wt.% clay content is the primary reason for the changes of silica content in the compositions of fired refractory bricks. Variation of clay content from 0-40 wt.% in the composition results in changes of SiO_2 content from 77-73 wt.% in the fired brick composition. The SiO_2 content was found to be 76.75, 76.05, 75.10, 74.15, and 73.20 for the compositions FC00S, FC10S, FC20S, FC30S, and FC40S, respectively. These refractories are within the semi-silica refractory range (minimum SiO_2 content 72%) as per ASTM C27-98 [46]. The most important characteristics of semi-silica refractory are the resistance to the thermal spalling ability to load resistance against high-temperature deformation and the development of protective glaze coating during application [156].

Table 5.5 Chemical analysis of different fired refractory bricks.

Compound (wt.%)	FC00S	FC10S	FC20S	FC30S	FC40S
SiO_2	76.75	76.05	75.10	74.15	73.20
Al_2O_3	18.31	18.66	19.26	19.75	20.30
Fe_2O_3	2.09	2.01	1.94	1.86	1.78
CaO	1.02	0.81	0.98	1.16	1.33
TiO_2	0.63	1.15	1.28	1.41	1.54
Na_2O	0.48	0.52	0.56	0.59	0.63
MgO	0.23	0.31	0.28	0.31	0.33
K_2O	0.23	0.26	0.38	0.46	0.53
ZrO_2	0.05	0.05	0.05	0.05	0.05
P_2O_5	0.02	0.04	0.04	0.05	0.05
BaO	--	0.03	0.03	0.04	0.04
SO3	0.02	0.03	0.03	0.04	0.04
SrO	0.02	--	--	--	--
CeO_2	0.03	--	--	--	--

The X-ray diffraction (XRD) spectra of all the samples fired at 1000, 1100, and 1200 °C for 2 hours are represented in **Fig. 5.5(a-c)**, respectively. It can be observed from **Fig. 5.5(a)** that the primary crystalline phase was SiO_2 (quartz) (01-078-1252) along with minor phases mullite (01-079-1450) and cristobalite (027-0605). When the

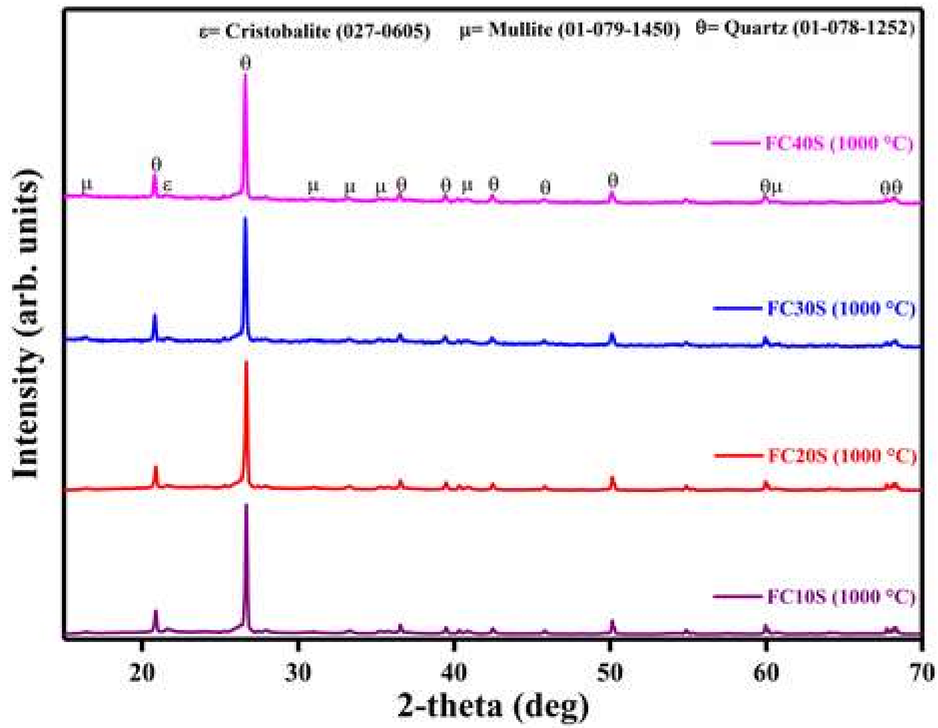

Fig. 5.5(a): XRD curve of the sawdust incorporated different samples fired at 1000°C.

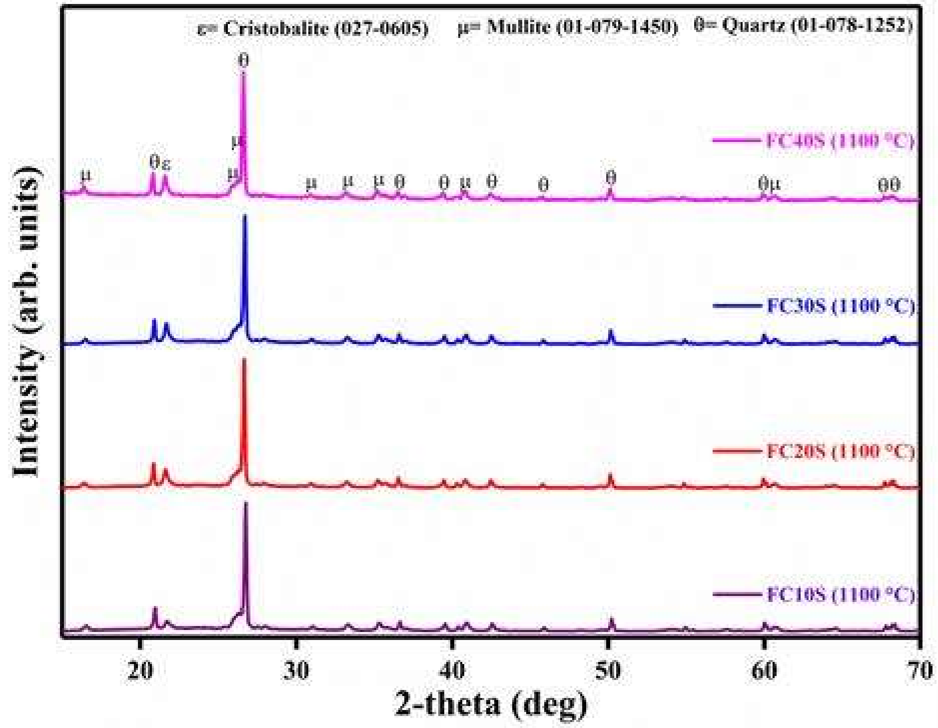

Fig. 5.5(b): XRD curve of the sawdust incorporated different samples fired at

1100°C.

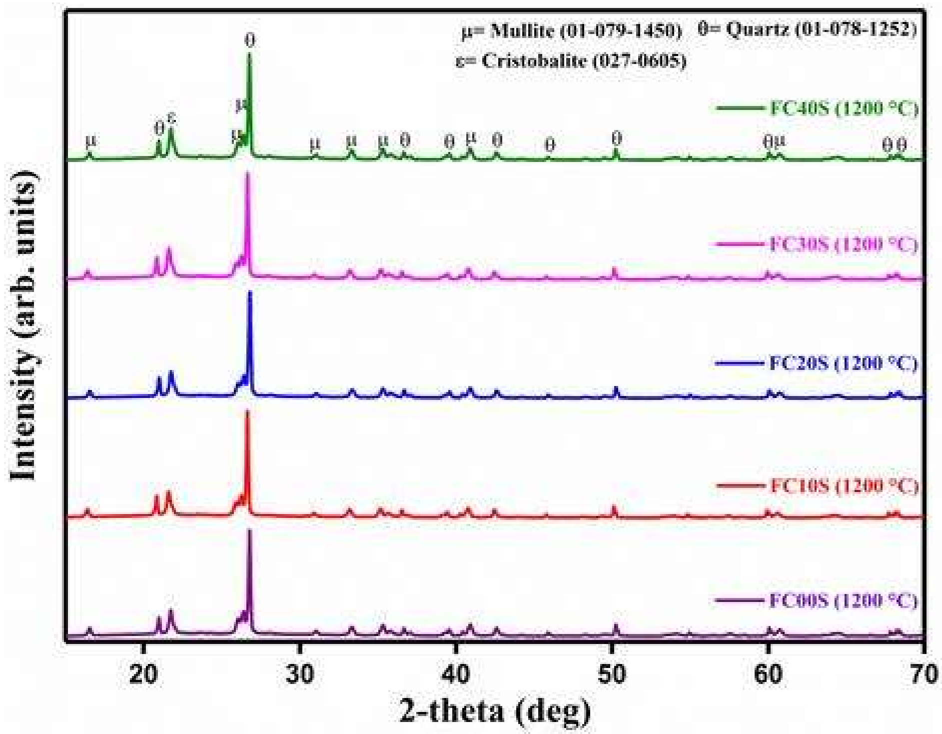

Fig. 5.5(c): XRD curve of the sawdust incorporated different samples fired at 1200°C.

firing temperature is raised to 1100 and 1200 °C for 2 hours, the intensity of mullite and cristobalite peaks increases and are shown in **Fig. 5.5(b)** and **(c)**, respectively. The primary reason is the higher amount of ball clay and their higher firing temperature, which resulted in mullite and cristobalite phase formation. This mullite and cristobalite will enhance the high-temperature strength of the refractory.

The surface morphology of different samples sintered at 1100 °C is shown in **Fig. 5.6**. **Fig. 5.6(a)** shows that grains are loosely bonded due to low clay content, and large numbers of pores are present in the structure. With increasing the clay content decreasing trend in porosity was observed for other compositions. For composition, FC20S intergranular pores can be seen from **Fig. 5.6(b)**, whereas in **Fig. 5.6(c)**, interconnected channel pores are observed. On the other hand, in composition, FC40S pores are irregular, large and fused type grains were observed due to higher clay content. The EDX analysis of composition FC40S has shown in **Fig. 5.7**. The in-situ mullite whisker formation is shown in **Fig. 5.8**.

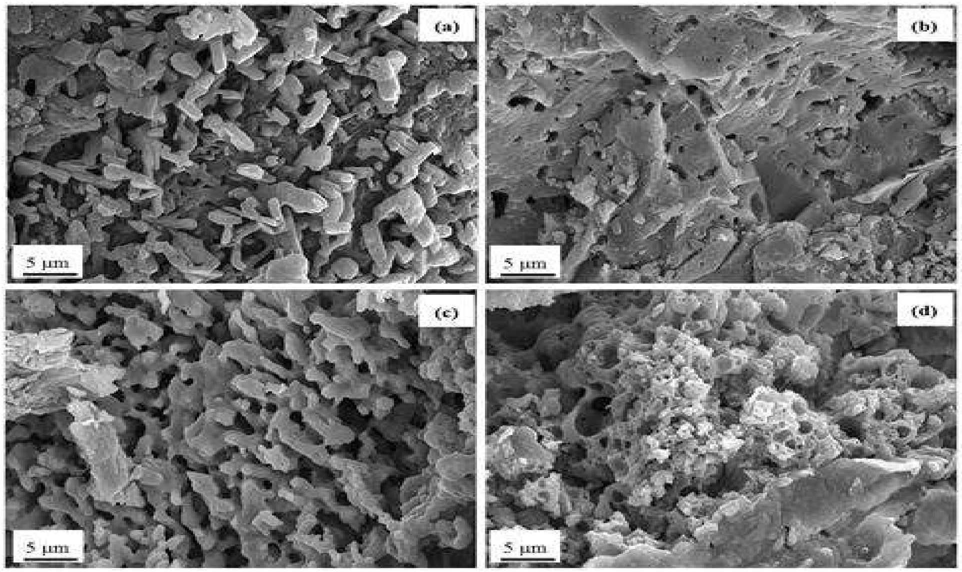

Fig.5.6: Surface morphology of the sawdust incorporated samples (a) FC10S, (b) FC20S, (c) FC30S, and (d) FC40S fired at 1100 °C.

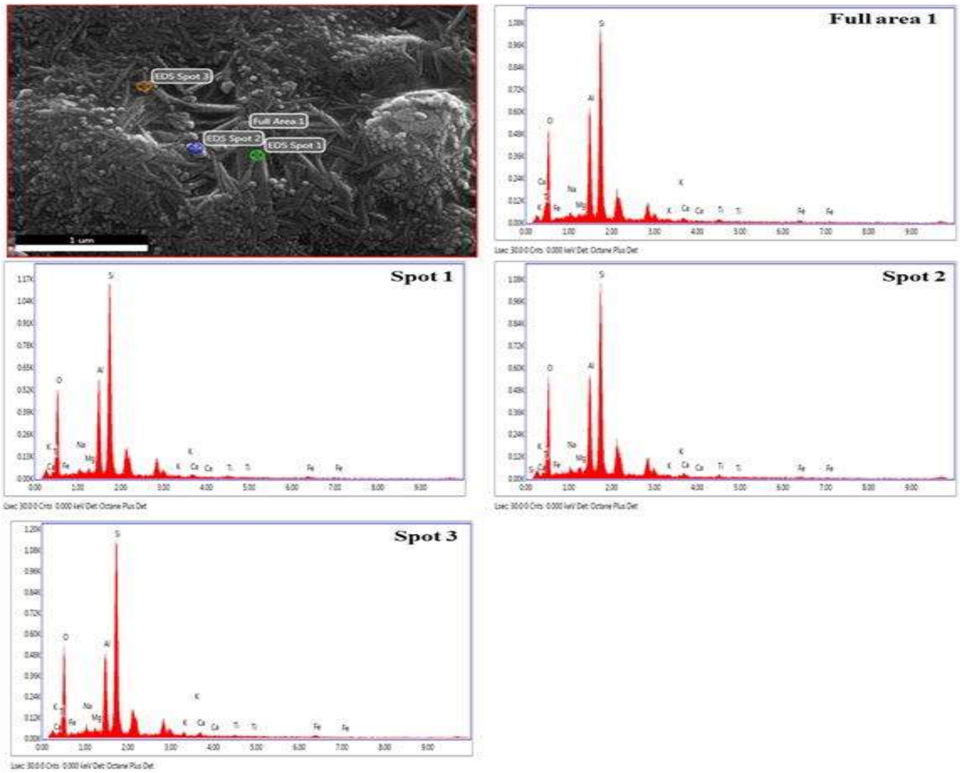

Fig. 5.7: EDS image of composition FC40S fired at 1100 °C.

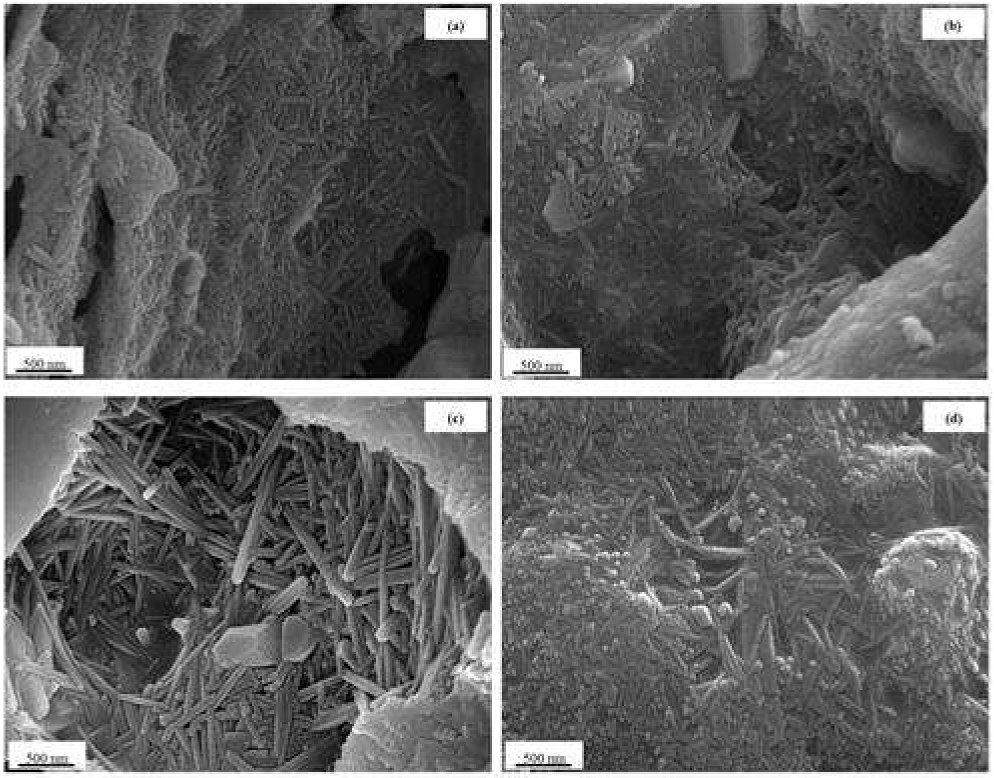

Fig. 5.8: SEM image of mullite whisker for composition (a) FC10S, (b) FC20S, (c) FC30S, and (d) FC40S fired at 1100 °C.

The shrinkage of ceramic samples plays a vital role which depends on sintering temperature. In **Fig. 9**, the mean linear shrinkage values of various burnt refractory brick samples are represented as a function of temperature. The figure exhibits that the total linear shrinkage after firing varied from 1.20% to 4.70% with increasing the firing temperature. The low shrinkage value is due to the use of lignite FA, which is a burnt product of coal-fired thermal power plants. On the other hand, due to the increased amount of ball clay content and thereby the formation of low melting phase upon firing results in the highest linear shrinkage of FC40S compared to the FC10S, FC20S, FC30S composition [169,178].

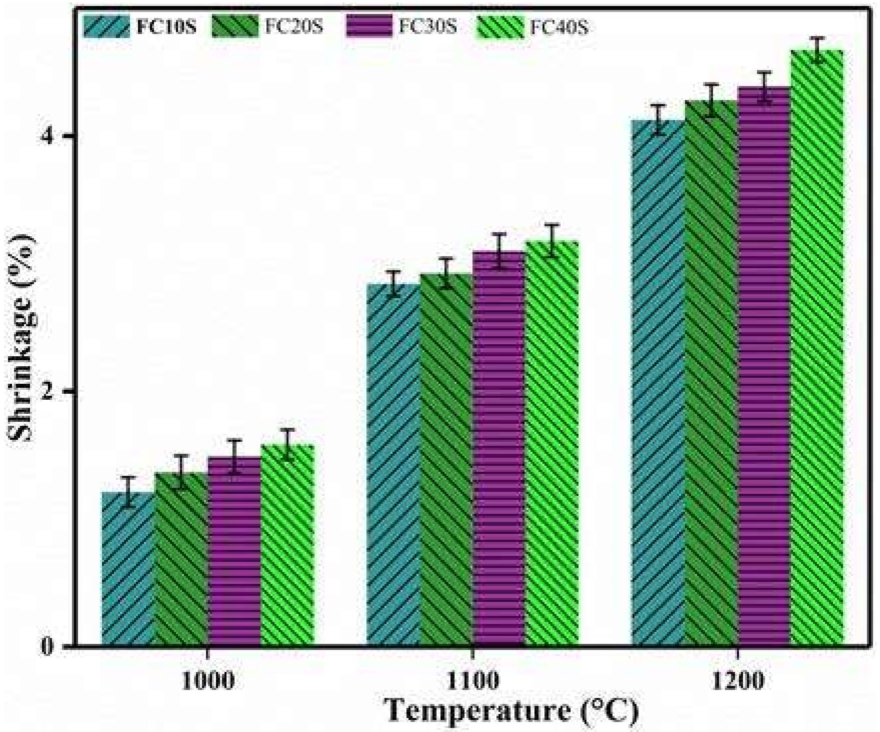

Fig. 5.9: The shrinkage behavior of the sawdust incorporated fired samples as a function of temperature.

For insulation refractory, porosity is an important parameter that needs to be considered. It is influenced by different parameters, such as the firing schedule, particle size, and composition of various raw materials. **Fig. 5.10** shows the AP of the fired sample after sawdust incorporation as a function of clay content and firing temperature. It was found that the 54% AP for FC10S at 1000 °C was decreased significantly to 30% when the firing temperature was 1200 °C for the FC40S. The lignite fly ash contains unburnt coal, and the ball clay also has organic matters which generate pores upon firing in the refractory. Along with that, the incorporated sawdust during firing leaves the void spaces within the matrix, which increases overall porosity in the refractories. The sawdust components such as hemicellulose, cellulose, and lignin gradually decompose with the temperature and leave pore in the structure by releasing CO_2 gas and H_2O vapor [52]. Upon increasing the clay quantity up to 40% and firing

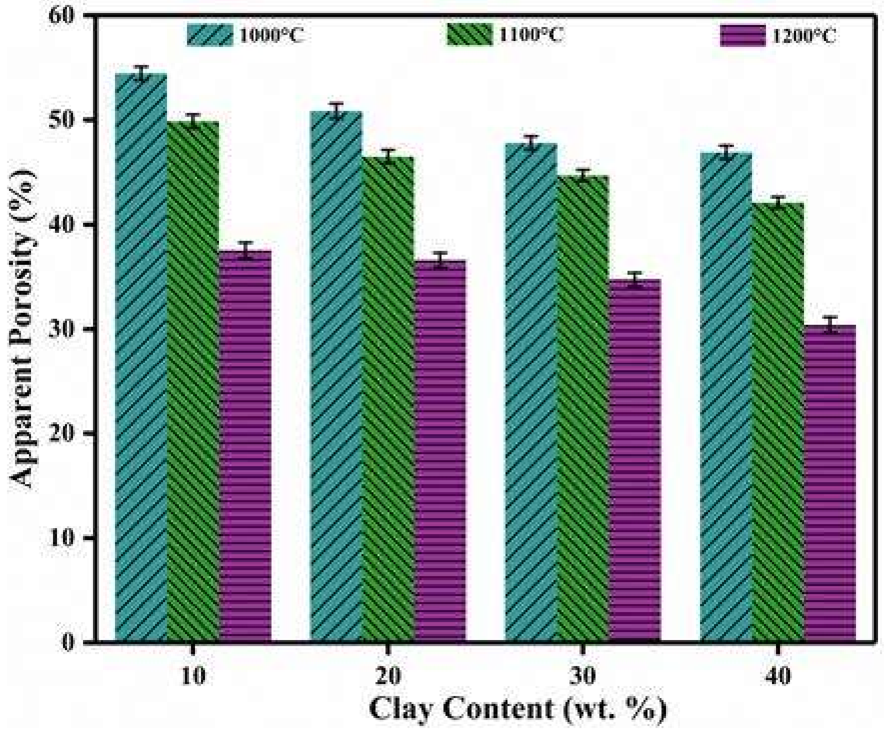

Fig. 5.10: The apparent porosity of the sawdust incorporated different compositions fired at 1000, 1100, and 1200 °C.

temperature, the porosity of the fired samples decreased significantly. These occur because of shrinkage, vitrification, and sintering, which resulted in filling up the pores by atomic diffusion and partial melting in the samples. The alkaline earth and alkaline oxide, which were present in the refractory brick, starts to melt at a low temperature, and some open pores are converted into close pores by low-temperature vitrification [52,179].

The BD of the different specimens with the variation of firing temperature and clay content is represented in **Fig. 5.11**. It was seen that with increasing the clay quantity and sintering temperature, the density of the fired samples decreased significantly from 1.68 to 1.34 gm/cc. The presence of alkali, alkaline earth, and iron combined with the siliceous material during firing produces a low-melting glassy phase and decreases the porosity of the bricks. However, at a high temperature, sufficient atomic mobility or a viscous liquid in the sample is developed to

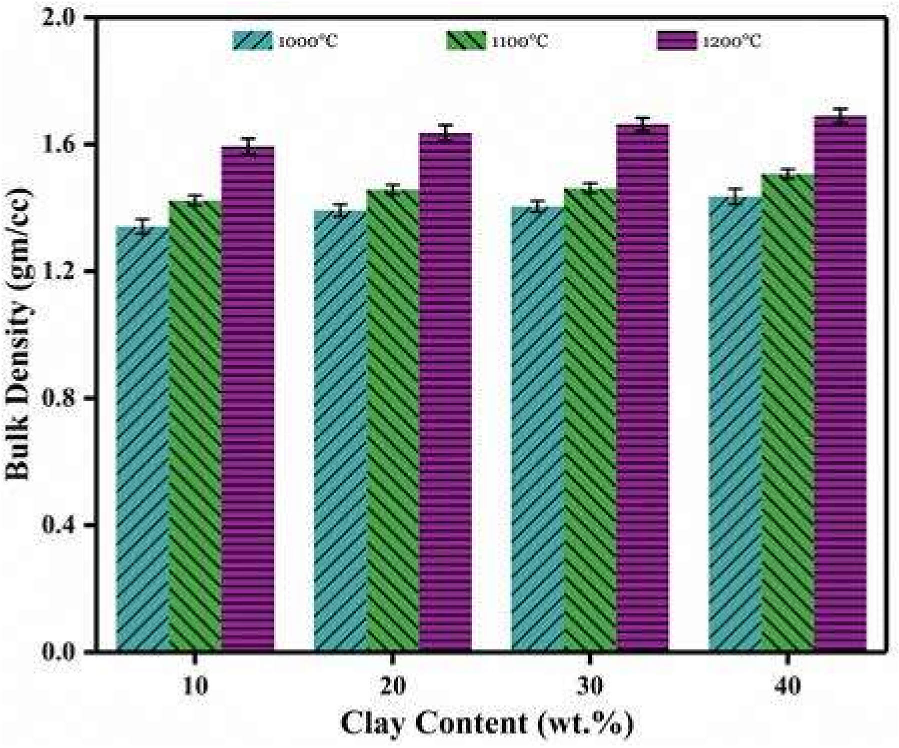

Fig. 5.11: The bulk density of the sawdust incorporated fired samples at different temperatures.

allow chemical reactions, sintering, and grain growth. The sintering phenomenon decreases the surface tension to consolidate the particles and thereby reduces the porosity [180]. The ASTM C155-97 standards state that insulating firebrick should possess density according to the classification shown in **Table 5.1**[157]. In this study, we have found that the densities of the insulating firebricks fall in the group of 32 or 33 (1.52gm/cc).

The cold crushing strength (CCS) plays a significant role in the performance of refractory material in the working atmosphere. **Fig. 5.12** shows the relation between the mean value of the CCS of the different fired specimens and the firing temperatures. The data illustrates that the CCS values increased with the sintering temperature and ball clay content. The vitrification of low melting fluxes and their deposition within

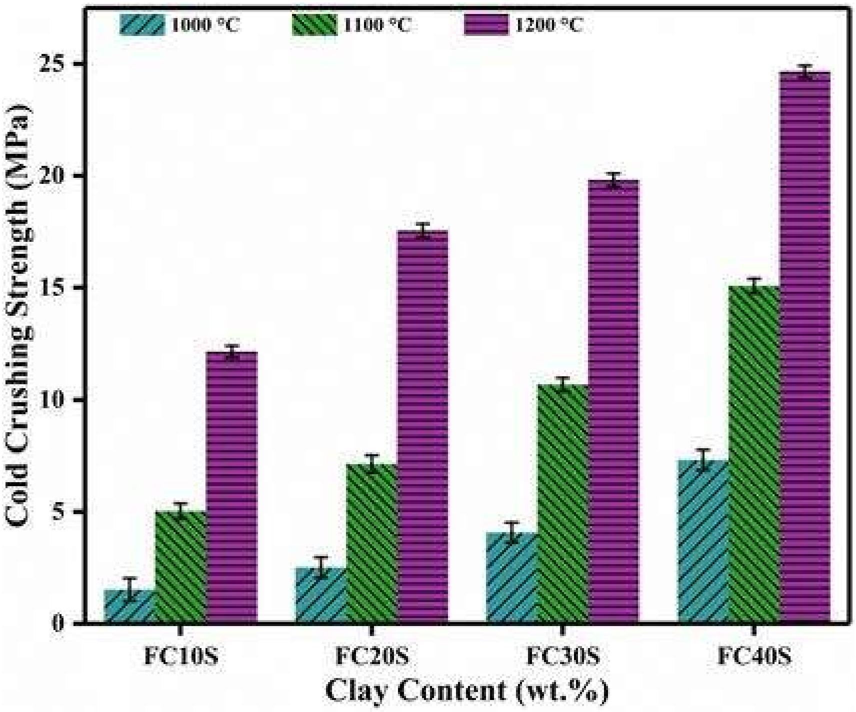

Fig. 5.12: The cold crushing strength of the sawdust incorporated fired samples at different temperatures.

the pore helps in strength improvement. The strength of FC30S was 4.07 MPa for 1000 °C, which increased to 10.69 MPa and 19.82 MPa when fired at 1100 and 1200 °C, respectively. A similar pattern was also found for FC10S, FC20S, and FC40S, where CCS values increased with the firing temperature. The experimental result revealed that the CCS values of FC30S and FC40S are well-matched with ASTM C155-97 [157]. The strength of these samples was almost well-matched with the commercially available products [181].

The cold modulus of rupture (CMOR) of the fired samples at different firing temperatures (1000 to 1200 °C) and clay content are shown in Fig. 5.13. It was observed that with the increase of firing temperature, the CMOR values for all the samples were increased. It is indicative of the strength of the bonding system of the refractory product. The CMOR rose from 0.23 to 6.89 MPa with the firing temperature and raising content of clay (up to 40 wt.%). At high temperatures, the presence of ball clay in fly ash increases the crystalline phase formation, which helps in the improvement of CMOR properties. It is evident from the SEM images (**Fig. 5.8**) that the mullite crystal formation increased with the increasing amount of ball clay content. This needle-like mullite structure is the primary factor for strength enhancement. All the refractory samples fired at 1200 °C and the compositions FC30S and FC40S fired at 1100 °C fall in the range of criteria of semi-silica refractory bricks as per ASTM C27-98 (MOR> 2.07 MPa). The study also showed that the FC30S possesses the MOR values that were well-matched with ASTM C155-97 [157] for the insulation refractory bricks. The obtained MOR values were also well matched to the commercially available products [181].

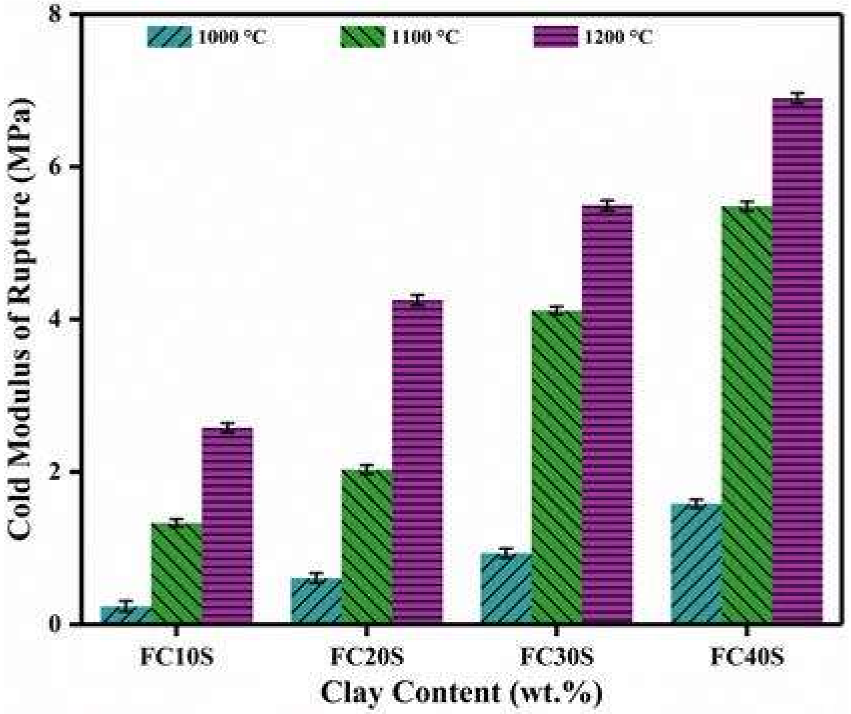

Fig. 5.13: The cold modulus of rupture of the sawdust incorporated fired samples at different temperatures.

The low thermal conductivity is a paramount property of insulation refractories. It is dependent on the chemical composition, density, and pore structure of the final products. The temperature-dependent TC of the samples fired at 1000, 1100, and 1200 °C are shown in **Fig. 5.14(a)-(c)**, where measurement was conducted at 600 and 1000 °C. **Fig. 5.14(a)** shows that the lowest and highest value of thermal conductivity is 0.15 and 0.23 W/mK when measured at 600 °C. While thermal conductivity was measured at 1000 °C, the lowest value was 0.26 W/mK for the FC10S (fired at 1000 °C), and the highest value was 0.66 W/mK for FC40S (fired at 1200 °C). The low TC of the semi-silica refractories is because of their low density and presence of a porous network within the structure. The entrapped air within the pore act as an insulator, which results in a reduction in the thermal conductivity [52,182]. On the

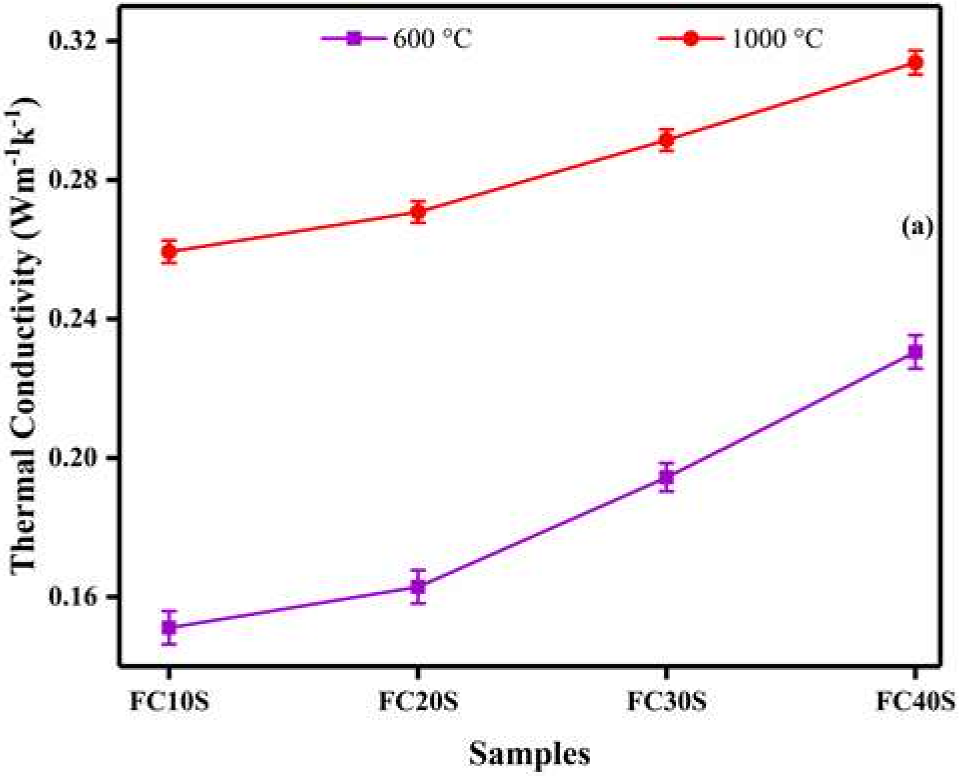

Fig. 5.14(a): Thermal conductivity of the sawdust incorporated different samples fired at 1000 °C.

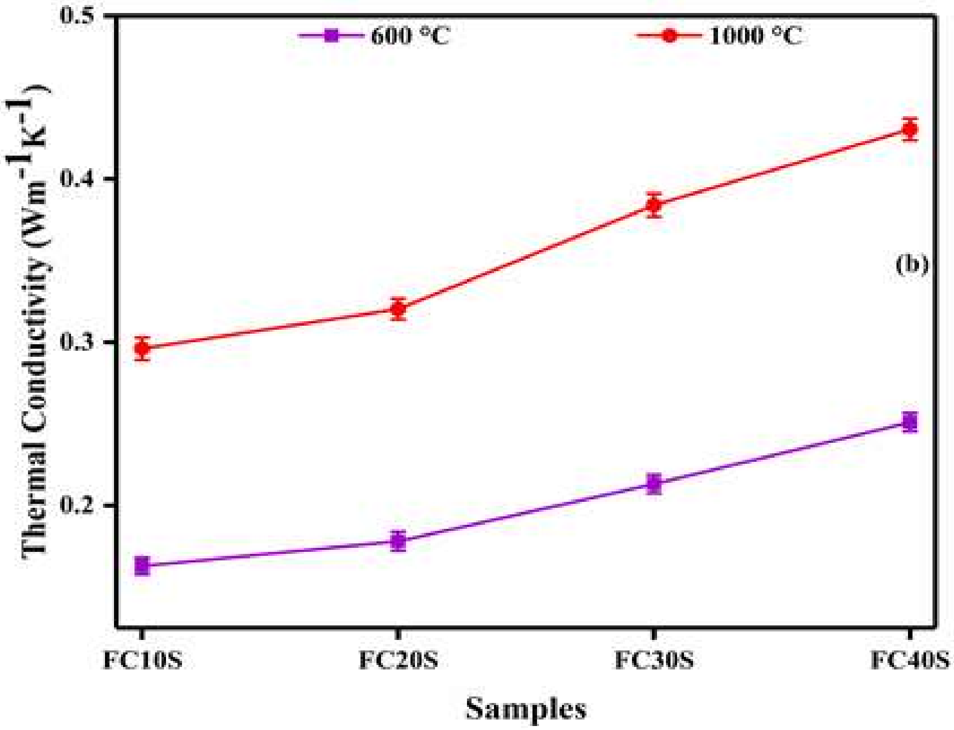

Fig. 5.14(b): Thermal conductivity of the sawdust incorporated different samples fired at 1100 °C.

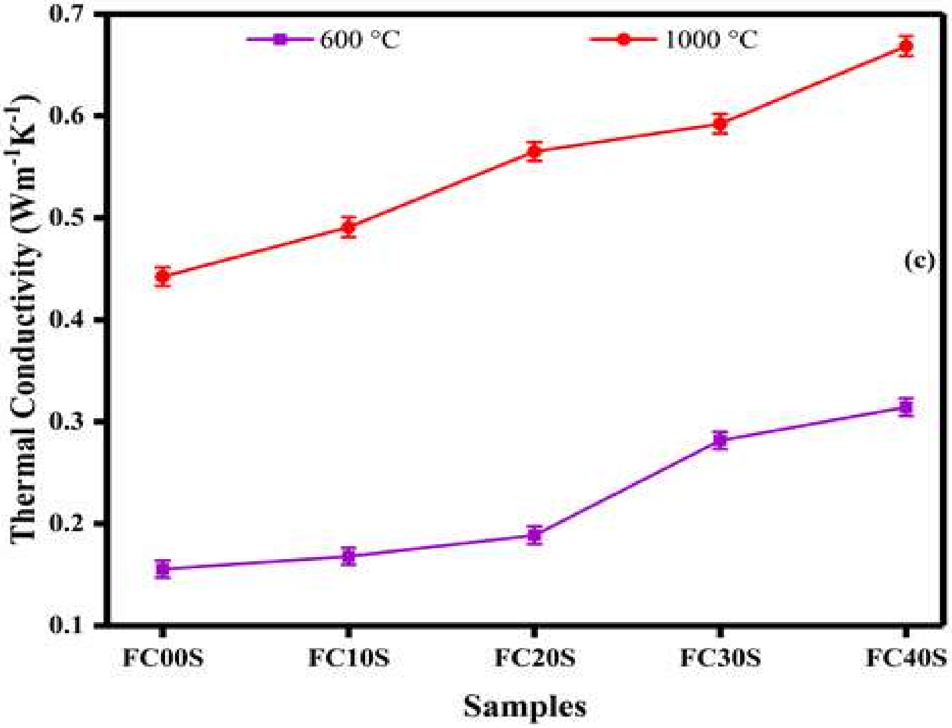

Fig. 5.14(c): Thermal conductivity of the sawdust incorporated different samples fired at 1200 °C.

contrary, the thermal conductivity increases in accordance with the firing temperature and composition because of radiation through the crystalline solid of the refractory compositions [66,183]. However, the thermal conductivity of materials with the same porosity may show different values due to variations in chemical compositions and microstructures [182]. In this study, the FC30S sintered at 1100 °C showed thermal conductivity of 0.38 W/mK (measured at 1000 °C), which was similar to commercial products [181,184].

5.3 Summary of the results

This study successfully shows that the combination of FA, ball clay, and sawdust could produce semi-silica insulation refractory. Here FA has been used primary raw materials with the variation of ball clay content up to 40% and sawdust as pore former. The physicochemical study showed that the fabricated fired brick consisting of 73-78% silica is the semi-silica group of refractories according to ASTM standard. The FA content 50% (FC40S), 60% (FC30S), and 70% (FC20S) fired at 1100 and 1200 °C showed improved CCS, MOR, AP, and thermal insulation properties. Whereas FA content 80% (FC10S) and 90% (FC00S) fired at 1000 °C possess low density, high porosity, and low thermal conductivity. Therefore, FC30S and FC40S fired at 1200 °C can be used as semi-silica refractory, and FC30S fired at 1100 °C can be used as insulation refractory. The results are well-matched with ASTM standards and similar to commercial products. So, the fly ash waste material could be an effective approach to reuse for fabrication of semi-silica insulation refractory to save the environment from hazardous effects.