9.1 Introduction

Presently, energy conservation is one of the most vital points for the industry. Therefore, the improvement of the thermal efficiency of industrial furnaces used in the ferrous and non-ferrous industries is become essential. The energy losses through the furnaces can be effectively reduced by high performance thermal insulation materials used for lining the inside of furnaces (Katsube *et al*., 2006). This increases the use of insulating and low thermal conductivity materials. On the other hand, new demand of industries is to utilize the industrial waste materials into commercial products. The benefits are saving energy, saving natural resources and reducing waste disposal. Engaged in this thought, use of wastes, will be a way of sinking the cost of ceramic products. A wide variety of waste materials (Dasgupta and Das, 2002; Sutcu and Akkurt, 2009), sludge (Herek *et al*., 2012; Wang *et al*., 2012; Geraldo *et al*., 2017), petroleum coal dust (Rahman *et al*., 2015), coal ash (Yin *et al*., 2016), rice husk ash (Onojah *et al*., 2013; Khoo *et al*., 2013), beverage industry (Eliche-Quesada *et al*., 2011; Fonseca *et al*., 2014), olive (Kadir *et al*., 2013; Bories *et al*., 2015) and wheat (Aouba *et al*., 2015) have been studied for the production of insulation materials such as paper processing residues.

The main objective of the present study was to provide a new route to utilize the fly ash, refractory grog, rice husk ash and rice husk as pore-forming agents in a composition of insulation refractory. The use of these waste materials not only increase the performance but also attractive with respect to environment, sustainability and economy. This technology may be extended for the production of insulation refractory bricks.

9.2 Experimental procedure

In this study six different samples were prepared with different compositions containing FA, RHA, RH, refractory grog and ball clay, as tabulated in Table 9.1. In the compositions, clay was replaced by FA, whereas other ingredients were remaining constant. At the very first stage, all ingredients were crushed and passed through the different sizes of sieves i.e. Grog (≤350 μm), Ball Clay (≤90 μm), Fly Ash (≤90 μm), without heat-treated

RHA (≤150 μm), RH (≤75 μm). Then, all ingredients were weighed according to the batch composition and then mixed by dry milling process for 20 min at 300 rpm in ball mill. After ball milling, least amount of water had been added for semi-dry mixing and the whole mass was mixed for 15 min prior to shaping. Rectangular (40 mm × 10 mm ×2.5 mm) samples were prepared by uniaxial hydraulic press at a pressure of 120 MPa. The pressed samples were dried in an electric air oven at 110°C for 24 h and then firing were done at different temperature from 800 to 1000ºC for 2 h in air atmosphere with heating and cooling rate of 3ºC/min.

Table 9.1 Identification and batch composition of samples.

Samples	Ball Clay (wt.%)	Fly Ash (wt.%)	RHA (wt.%)	Grog (wt.%)	RH (wt.%)
b-1	50	0	30	15	5
b-2	40	10	30	15	5
b-3	30	20	30	15	5
b-4	20	30	30	15	5
b-5	10	40	30	15	5
b-6	0	50	30	15	5

9.3 Results and discussion

Porosity of insulating material has a lot of importance with regards to the performance and applications. Insulating properties (thermal conductivity) of sample depend on the total porosity present in the specimen. The apparent porosity (AP) and bulk density (BD) measurements are done for all sintered samples and mean values are shown in Figure 9.1(a) and (b), respectively. It has been observed that incorporating FA by replacing clay in the composition results in significant changes in AP and BD. Apparent porosity increases from 38% to 53% and bulk density decreases from 1.52 gm/cc to 1.05 gm/cc at 800ºC, similar trends is reported by Otero *et al.* (2004). RH burns through the firing process and forms pores in the structure by releasing CO_2 (Studart *et al*., 2006). When clay is replaced by FA, liquid phase decreases, results formed pores, which cannot be filled completely at 800°C. As a result, densification kinetics is decreased during low temperature firing at 800ºC. The decrease in density may be due to lower weight of FA then ball clay. When temperature is

increased from 800 to 1000ºC, geopolymerisation reaction takes place (Mucsi *et al*., 2018). RHA contains amorphous silica that is more active, this silica starts diffusion reaction with others grains when increasing the firing temperature above 800ºC (Gonzalves and Bergmann, 2007). This diffusion of grains and geopolymerisation reaction are eliminated the pores between grains, aided the decrease of porosity and increase in bulk density with increasing temperature.

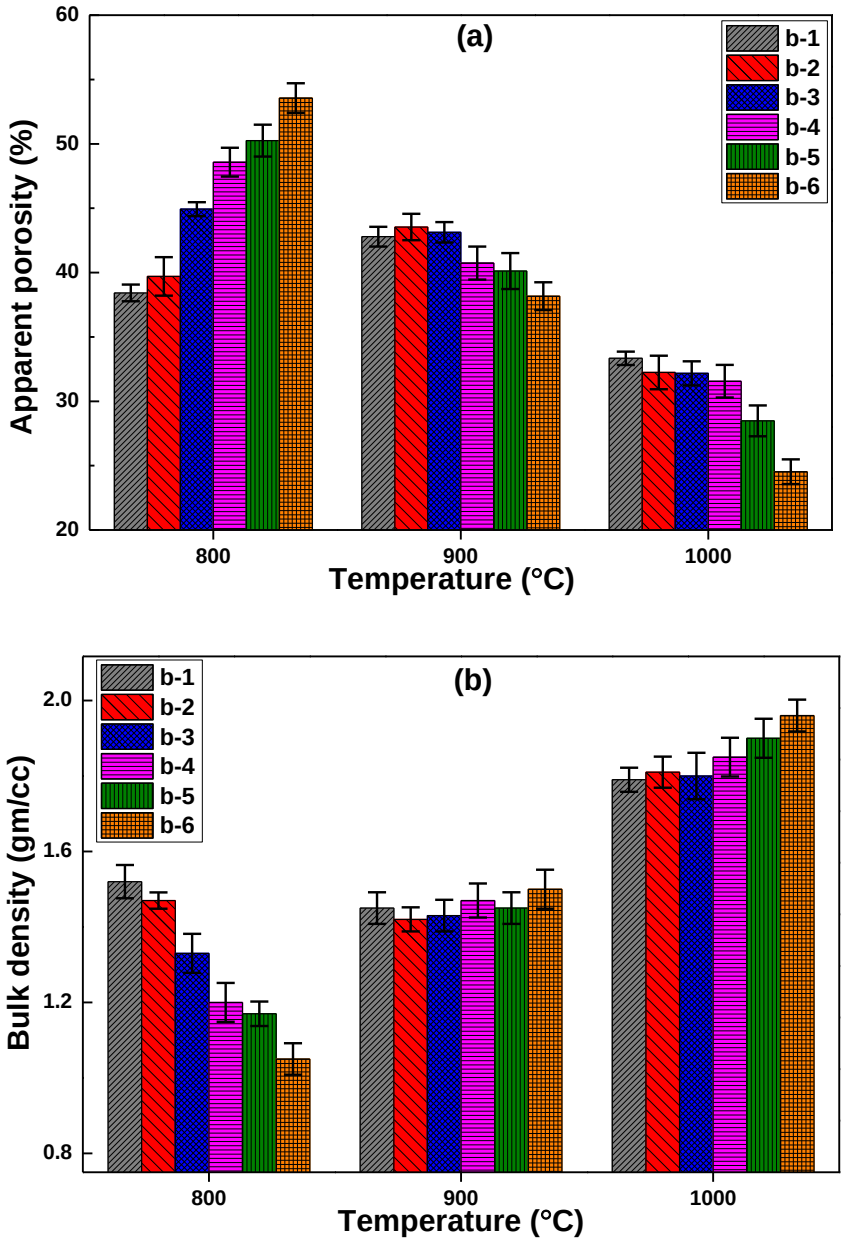


Figure 9.1 (a) Apparent porosity and (b) bulk density of fired refractory samples.

The typical X-ray diffraction patterns of fired samples are shown in Figure 9.2. It is indicated that the samples are mixed of polycrystalline and amorphous broad band.

Comparing the XRD patterns, we may observe that the intensity of crystallinity has increased significantly with increasing firing temperature from 800°C to 1000°C. JCPDS data are used to determine the various phases, i.e., quartz (SiO_2), mullite ($3Al_2O_3{\cdot}2SiO_2$) and anorthite ($CaO{\cdot}Al_2O_3{\cdot}2SiO_2$) developed after firing. However, all samples consist of crystalline silica (SiO_2) as the major phase and with enhancement of FA content in the composition mullite phases intensities are increased.

The change in linear dimension, which has happened in the test sample before and after firing, is called linear shrinkage or expansion. Figure 9.3 shows the mean values of linear shrinkage for the ceramic samples fired at 800, 900 and 1000°C. It has been seen that the total shrinkage in the all-inclusive refractory samples are quite less, i.e., 1.5 to 5.5%. These results can be imposed to the fired raw materials incorporated in the composition (50 to 95%) and rice husk addition, which leads to decrease in the total linear shrinkage. However, increase of firing temperature causes of enhancement in the linear shrinkage of refractory samples. With increasing temperature, may be low melting oxides in the clay mineral increase the melted products in the structure and increase the shrinkage values as well. Based on the results in Figure 9.3, reduction of clay amount in the composition decreases the total linear shrinkage at 800°C. Significant linear shrinkage is observed when temperature rises at 1000°C for all the samples. It may be explained as a result of removal of pores and inter-granular spaces during the firing.

Figure 9.4 exhibits the surface morphology of the fractured cross sectional surface of fired sample. SEM analyses indicate a typical foamy structure with open and close pores at 800°C. There is no preferential orientation or shape of pores. It is seen that FA content has the mark influences on the pore structure, pore size, and pore distribution of insulation refractory (Li *et al*., 2016). Porous structures are also formed by the burning of RH, which contents ~ 80% of organic matter (Sarangi *et al*., 2009). With increasing firing temperature, sintering neck is grown and the pores are shrunk. Accordingly, the pore size is decreased and

densification level increases (Vu *et al*., 2011). The EDS analyses are performed to find out the elemental composition of the samples. Figure 9.5 show the EDX analysis of 0 and 50 wt.% of FA content sample fired at 800°C.

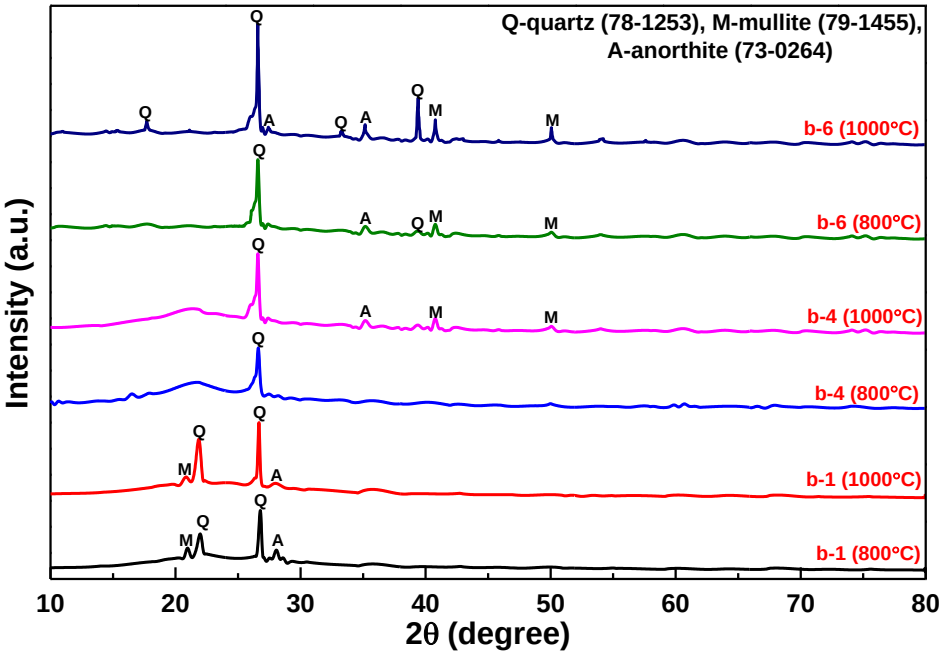


Figure 9.2 XRD analyses of fired refractory samples at 800 and 1000°C.

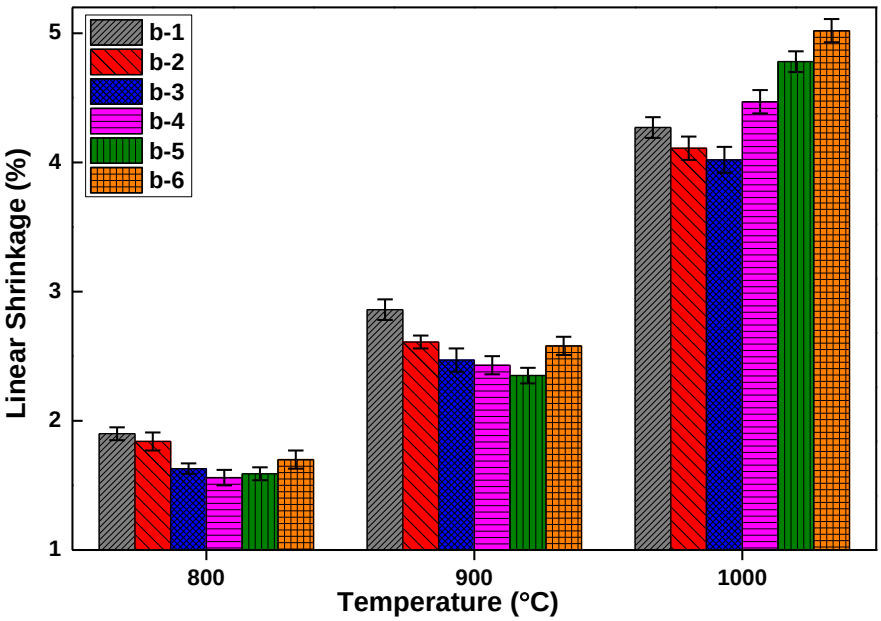


Figure 9.3 Linear shrinkage of fired refractory samples.

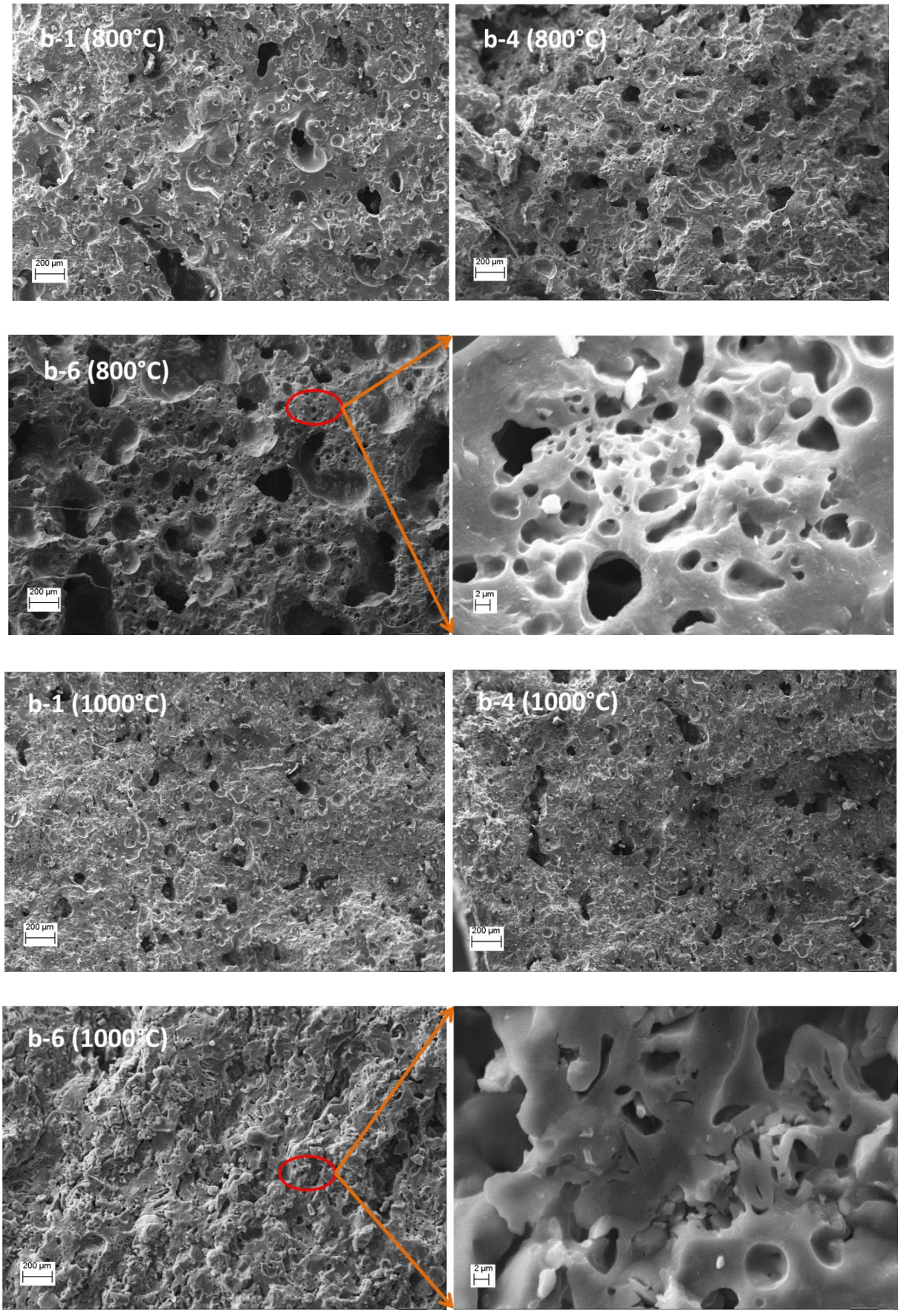
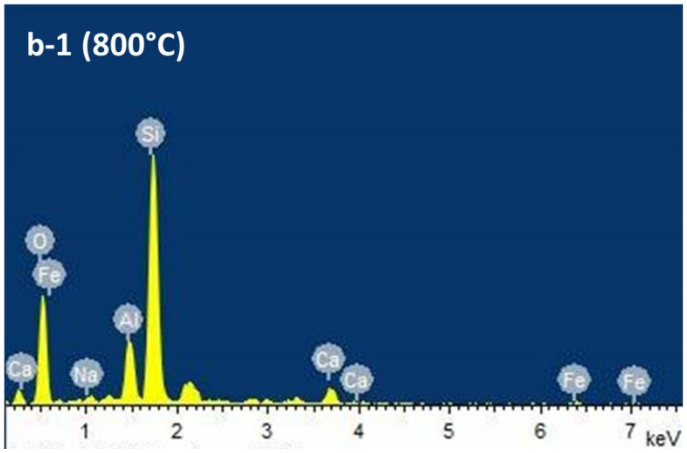
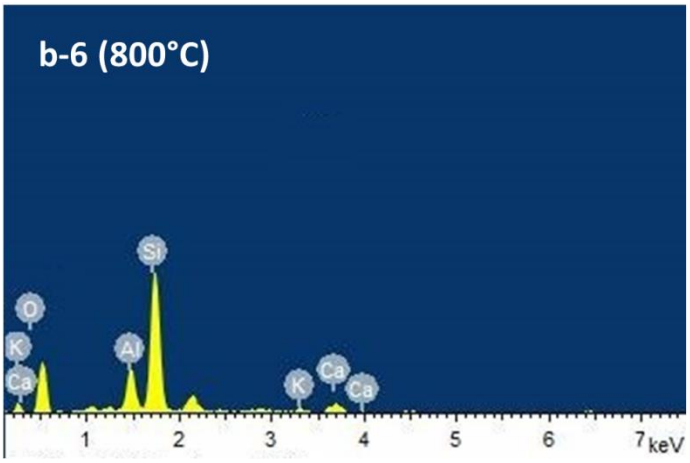


Figure 9.4 SEM images of fired refractory samples.



Element	Weight %	Atomic %
O K	54.55	68.36
Na K	1.41	1.23
Al K	7.40	5.50
Si K	31.80	22.70
Ca K	3.34	1.67
Fe K	1.50	0.54
Total	100	100



Element	Weight %	Atomic %
O K	52.41	66.79
Al K	11.30	9.42
Si K	30.61	20.05
K K	1.67	0.92
Ca K	5.38	2.82
Total	100	100

Figure 9.5 EDX analyses of fired (800°C) b-1 and b-6 refractory samples.

Mean values of bending strength of the fired samples is shown in Table 9.2 and Figure 9.6 shows the maximum displacement at the elastic curve of some selective fired samples at room temperature. Flexural strength is decreased with increasing ratio of FA in the composition, especially when firing temperature is 800°C. The values of flexural strength are decreased from 10.28 to 4.84 MPa due to increase of porosity and pore size, as shown in SEM image (Figure 9.4). Therefore, crack concentration in the non-ductile body is increased; as a result less value of stress is required for breaking (Kazmi *et al.*, 2016). However, strength is increased with temperature due to the higher sintering degree of the samples and the development of crystalline phases by the reaction of FA and RHA silica. As understood from this study waste concentration in the body and firing temperatures of refractories have significant effects on the strength of refractory.

Table 9.2 Bending strength and CCS of fired sample at different temperatures.

Samples	Bending strength (MPa)						CCS (MPa)					
	800°C		900°C		1000°C		800°C		900°C		1000°C	
	Mean	s.d.	Mean	s.d.	Mean	s.d.	Mean	s.d.	Mean	s.d.	Mean	s.d.
b-1	10.28	0.2	8.13	0.3	12.86	0.34	22.56	0.42	19.73	0.24	24.22	0.35
b-2	9.35	0.2	7.46	0.2	13.28	0.19	21.82	0.37	18.96	0.36	24.56	0.24
b-3	8.72	0.25	7.83	0.26	13.89	0.34	18.45	0.28	19.35	0.42	24.80	0.19
b-4	6.02	0.16	9.64	0.34	14.06	0.21	16.83	0.30	20.72	0.37	25.93	0.51
b-5	5.76	0.24	10.12	0.17	15.54	0.27	15.32	0.45	21.46	0.36	27.38	0.45
b-6	4.84	0.27	11.89	0.28	17.11	0.24	14.45	0.24	22.42	0.27	31.54	0.37

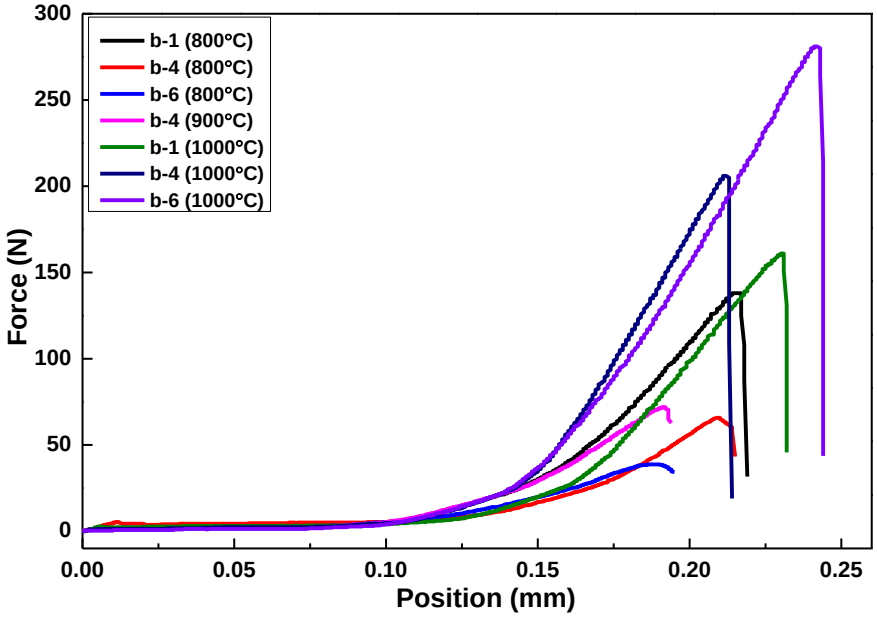


Figure 9.6 The maximum displacement at the elastic curve of fired refractory samples at 800, 900 and 1000°C for b-1, b-4 and b-6.

Cold crushing strength (CCS) is a very important parameter for insulating refractories. CCS of the samples, as shown in Table 9.2, are measured at room temperature after firing at 800, 900 and 1000ºC for 2 h. It is found that these insulating samples have shown good mechanical strength, these results may be attributed to the presence of fired refractory grogs into the composition. Refractory grogs act as a non-shrinkage material that increase the stress resists ability of the samples (Bhardwaj *et al*., 2017). Table 9.2 shows that the CCS of samples is decreased with the increase in fly ash addition. CCS values are decreased to almost 36% for fully replacement of clay with FA, when firing at 800ºC. Due to the presence of higher percent of open pores, it may cause the loss of strong bonding in the structure, results decrease in CCS of specimens (Sutcu *et al*., 2015). CCS values of the samples are remarkably

improved with firing at higher temperature. It has seen that decreases in porosity and increases in bulk density with increasing temperature. As a result, CCS of samples is increased with increasing firing temperature of the insulating refractory. Usually, it is considered that CCS of specimens mostly depends on their density, porosity and pore size distributions (Aouba *et al*., 2016). A linear relationship is observed between CCS and apparent porosity for samples fired at 800°C, as shown in Figure 9.7.

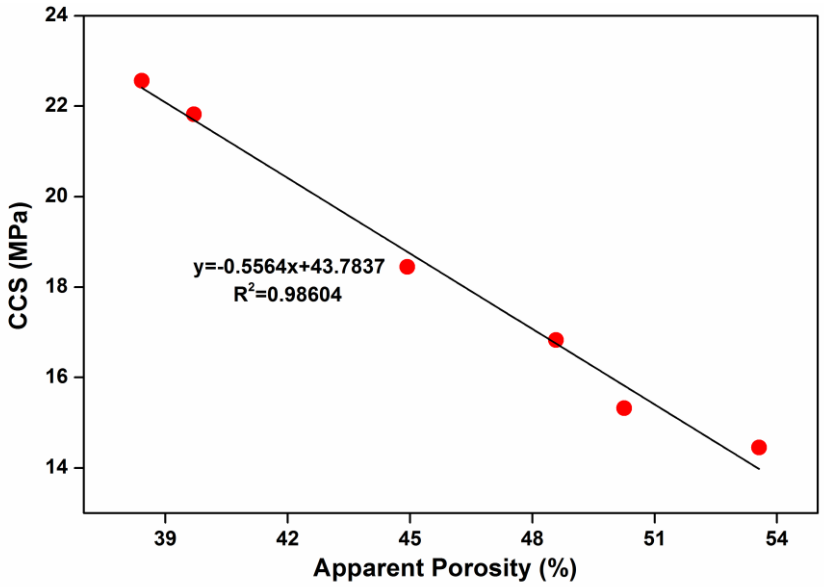
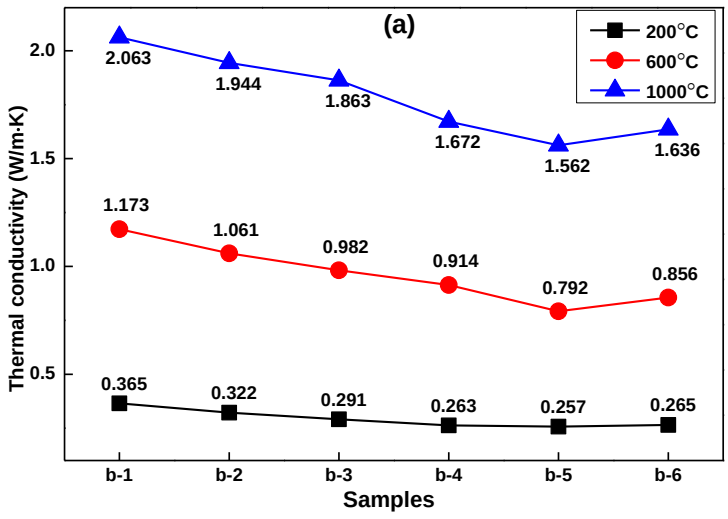


Figure 9.7 Relation between CCS and apparent porosity of 800°C fired specimens.

The thermal conductivity measurement is essential for insulation refractories. Many factors like application temperature, chemical and mineralogical compositions, complexity of structure and defect are affected the thermal conductivity of refractories. Figure 9.8 (a-c) shows the temperature dependence thermal conductivity of fired samples at 800, 900 and 1000°C, respectively. Measurement is performed at temperatures 200ºC, 600ºC and 1000ºC. It is seen that the thermal conductivity co-efficient of all samples are enhanced with the increasing firing temperature of samples. It may be due to decrease in porosity with increasing firing temperature. Thermal conductivity values of the samples decreases with the addition of FA. It may be due to increase of apparent porosity and decreases of densification. This porosity acts as a fence to the flow of heat and as a result thermal conductivity of the samples

drop (Görhan and Simsek, 2013). Figure 9.9 shows the relationship of between thermal conductivity and apparent porosity of fired samples at 800°C. In sample b-6, the conductivity slightly increases due to the effect of pore size. The effects of radiation on pore conductivity are increased with the increasing pore volume. Pores of large size are increased the conductivity, whereas small pores remain a good barrier for radiation effect with increasing temperature (Bragança *et al*., 2008). It is seen that the thermal conductivity values is increased with the increasing measurement temperature of conductivity. Heat transfer through a solid happens via energy transfer between vibrating atoms by phonons, photons, electrons, ions, etc. For refractory materials, phonons and photons are the key media for thermal conductivity, and their contribution depends on the temperature mainly. At low temperatures (<300ºC) energy flow in materials mainly occurs via lattice vibrations (phonons) at speed of sound and significantly decreases to a lower value at higher temperatures, where the photon conductivity (radiation) mainly governs the conductivity. Generally, photon conductivity (radiation) is increased with the increasing temperature in crystalline materials, which is the principal mechanism of energy travel at high temperature through the materials (Pal *et al*., 2012). This mood is a fast sequence of absorptions and emissions, of photons that transfer at the speed of light. This type of conduction is exclusively vital in porous ceramics like above refractory. As a result, thermal conductivity of b-1 samples fired at 800°C is 0.65 W/m·K for 200°C and 2.56 W/m·K for 1000°C.



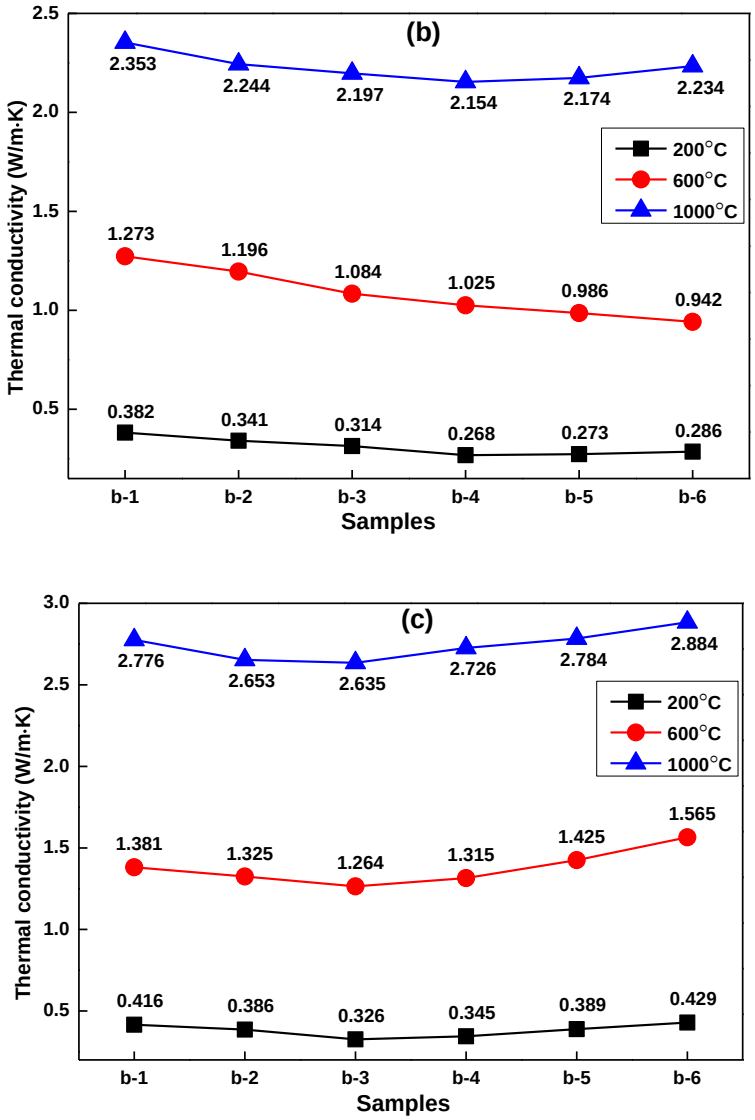


Figure 9.8 Temperature dependent thermal conductivity of different refractory samples fired at (a) 800°C, (b) 900°C and (c) 1000°C.

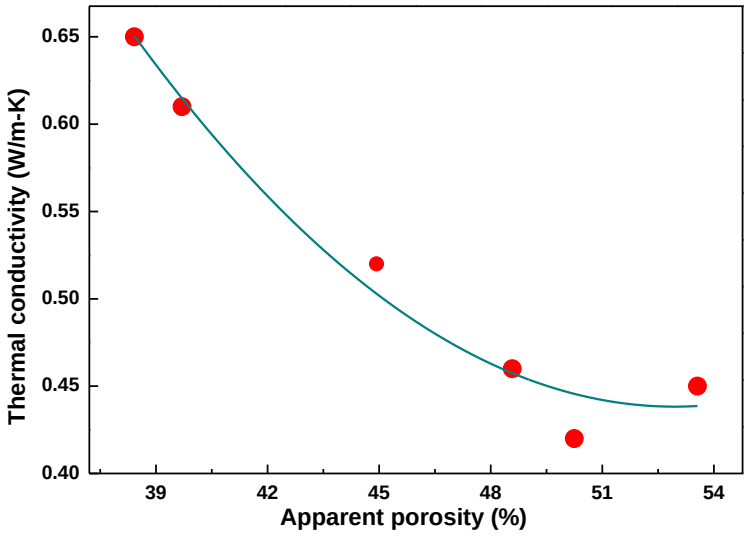


Figure 9.9 Relation between thermal conductivity and apparent porosity of 800°C fired specimens.

9.4 Summary

It is established that substantial amounts of waste materials can be used to fabricate insulation refractory. The properties of insulation samples incorporating fly ash, rice husk ash, rice husk and fired refractory grog are investigated. Use of different wastes as a raw material in fabrication of insulation refractories can be a significant way of recycling. Varying the FA content in mixtures, it is possible to improve the insulation properties of sintered bodies. Results show low thermal conductivity, high porosity, low density, moderate CCS and flexural strength with waste incorporation. Sample b-6 fired at 800°C can be envisaged as a refractory material to be used for insulation purpose. The obtained results show that it would be promising for the large-scale fabrication of insulation refractories.