Chapter 8

Porous Ceramic Composite using Industrial and Agricultural Waste via Sacrificial Fugitive Technique

8.1 Introduction

The preceding chapters, have successfully engineered porous composites and foams by utilizing Coal overburden waste (MW) through the Alumina dissolution process and Sucrose dehydration process, showcasing their remarkable high porosity range. However, in light of the expansive spectrum of applications for porous ceramic composites, the necessity arises for composites with narrower porosity ranges that possess distinctive features such as nano and micro pores, closed pores, and enhanced mechanical strength. The selection of the appropriate porous structure exhibiting such advantages depends on the specific requirements dictated by various applications. Although the prior techniques, as elucidated in earlier chapters, predominantly yielded porous structures with porosity levels surpassing 60%, comprising both open and closed cells, there exists a compelling need to engineer structures with lower porosities, yet augmented strength, preferably with minimized or absent open cells. These novel porous composites find extensive utility, particularly in the realm of refractory applications, while also extending their potential to diverse fields including biomaterials, catalyst support systems, and adsorption materials. Additionally, as stated in the objective section, this study concurrently endeavors to address the realm of "Waste Valorization" and ascertain the efficacy of employing the sacrificial fugitive method to fabricate such porous structures.

Bio wastes like sawdust, rice husk, and coke fines are commonly used as fugitive materials, contributing to the porosity of the samples and offering a solution to the disposal issues associated with bio-generated waste [185–187]. RH, a byproduct generated during the rice extraction process, poses significant environmental concerns as it is considered an agricultural waste. With global rice production reaching millions of tons annually, the literature indicates that approximately 200 kg of RH is produced per metric ton of rice [188]. Disposing of RH presents a considerable challenge due to its large surface area and carbon content, leading to potential pollution risks. Efforts have been made to find suitable ways to utilize RH effectively while minimizing its impact on the environment. Researchers have explored different methods of utilizing RH, including direct reinforcement with other components or utilizing its high silica content by converting it into ash [189]. Rice husk is primarily composed of hydrated silicon, cellulose, and lignin [190]. Several approaches, such as chemical and thermal treatments, have been employed to extract silica from RH, with thermal treatment being the preferred method. The resulting silica particles exhibit a high reactivity, requiring minimal grinding, which is a significant advantage of this process. The carbonaceous constituents present in rice husk provide the necessary energy for pyrolysis, leading to the production of highly porous silica with a substantial surface area[191]. Throughout this process, approximately 20% of the rice husk remains as burnt-out residue, of which 95% comprises silica. Exploiting the removal of over 80% of RH content and utilizing the inorganic material (silica) as the burnt-out residue, researchers have successfully employed RH as a fugitive material to fabricate porous composites [120].

In this section, Rice Husk (RH) is employed as a fugitive material to create porous composites and precisely control their porosity. The fabrication of samples is carried out using a powder processing route and the cold pressing method. Initially, the samples are prepared using an appropriate binder and subjected to testing. However, the successful molding of green samples using MW presents challenges due to its limited binding capability and plasticity. Moreover, the sintering process for MW products requires high energy consumption, resulting in elevated production costs due to the high aluminosilicate content. Therefore, the incorporation of additives becomes crucial to enhance moldability and reduce the sintering temperature. One such additive is Red Mud (RM), which exhibits favourable binding and plasticity properties, making it widely used in the ceramic industry [192]. RM, a solid waste generated during the aluminum refining process from bauxite ore, poses a significant environmental challenge. The global annual production of RM amounts to approximately 120 million tons, with around 1.5 tons of RM generated per ton of aluminum produced [193–195]. RM primarily consists of iron, silicon, alumina oxides, as well as trace amounts of heavy metals and other potential pollutants. Disposing of RM is a major concern due to its high alkalinity, which can lead to the leaching of pollutants into soil and water [196]. By incorporating RM into MW, the moldability of the mixture is improved, and the sintering temperature can be reduced. The effects of incorporating RM on the fabrication process and the resulting physical and thermomechanical properties are also analyzed. In addition to providing binding ability to MW powders and serving as a sintering additive, the utilization of RM aligns with the goal of valorizing waste materials.

In an effort to address the detrimental environmental effects of industrial and agricultural waste, the present study focuses on the utilization of these wastes to manufacture insulation bricks. The main constituents of these bricks are Coal overburden waste (MW), while Rice Husk (RH) serves as a pore-forming agent and Red Mud (RM) used as binding and sintering additive. The study involves the preparation of different mixture ratios of RM and MW, and the physical and mechanical properties of each composition are thoroughly examined and compared. By incorporating varying weight percentages of RH into the compositions, a range of porosities is achieved, and the insulation properties of the bricks are measured accordingly. The resulting porous bricks are meticulously evaluated to determine their viability as advanced insulation materials.

This research presents a viable and cost-effective approach to produce insulation bricks, offering a sustainable solution for the conversion of RM and MW waste on a large scale. By minimizing the adverse environmental impact of these wastes and providing a low-cost product with broad applications, the study contributes to waste reduction and promotes efficient resource utilization.

8.2 Materials and Method

8.2.1 Materials

MW is the primary ingredient used for manufacturing insulation brick and obtained from NCL, Singraulli, India. MW was initially ball-milled to get finer particle and was sieved through 250-355 and <180-micron sized sieve for uniformity. The RH used as fugitive material was collected from the local agricultural land near Varanasi, India. The RH was initially washed to remove any dust particle from it and then milled and sieved through 63-120 and 355-420-micron sized sieve to achieve consistent porosity of the bricks with different pore sizes. RM of size below 63 microns was used as an additive and obtained from Hindalco Industries-Renukoot, India. Two different sizes of MW and RH were used to study the effect of particle size of both raw material and fugitive material on physical and mechanical properties of insulating brick. Sucrose solution prepared with Sucrose: Water: 6:4 has been used as binder.

8.2.2 Preparation of Insulation brick

Various mixer compositions were prepared using two different particle sizes MW (< 180 micron; 250-355 micron) and RH (<180 micron; 320-420 micron) with varying proportion of RH (5, 10, 15, and 20 wt%) to fabricate insulating refractory. Optimized amount of sucrose solution (15 wt% of each composition; 9 wt% on dry weight basis) was used as binder through proper mixing in a mortar and pestle. The addition of sucrose solution provides the necessary plasticity for moulding. Further, to investigate the effect of RM addition, fine powder of RM (<63 micron) was added in three different proportions (MW: RM:2:1; 1:1; and 1:2) with varying amount of RH. All compositions were denoted with a general formula $^{x}MW\_^{y}RH_{z}$ and $^{x}MW_{a}\_RM_{b}\_^{y}RH_{z}$, where ‘x’, and ‘y’, represents particle size of MW and RH being used to fabricate brick; ‘z’, represents weight percentage of RH in each composition and, ‘a’, and ‘b’ represents MW and RM proportion w.r.t to each other. In this formula, ‘x’ and ‘y’ represents size in µm and 'z' represents RH content in wt%. Green compacts of cylindrical shape with a diameter of 10 mm and a thickness of 20 mm were prepared using a steel die and pressing dry mixture uniaxially at 100 MPa. 14 compositions were selected from numerous trials for successful dry pressing into green compacts, followed by drying at 130°C for 12 hours. The compacts were then consolidated and sintered at 1000-1500°C to produce a high-quality final product.

8.2.3 Characterization of raw materials and Insulation brick

Initially, raw MW and RM were physiochemically characterised quantitatively and qualitatively through various techniques. An X-ray Fluorescence (XRF) device was used to detect the presence of oxides in raw MW and RM (S8 Tiger, Bruker model). With a step size of 0.02° and a 2 range of 5-80°, the XRD (Rigaku Miniflex 600 Desktop X-Ray Diffractometer) data of raw MW and RM and sintered insulation brick are studied. The present study investigates the thermal stability of RH by examining their thermal degradation and loss on ignition through TGA (Simultaneous Thermal Analyzers, Model Labsus, Setaram, Caluire, France) under air up to 600°C. In order to determine the physical properties of sintered bricks, such as bulk density and apparent porosity, established test protocols are utilized, including the Archimedes' displacement method and water immersion, following the guidelines set out in the ASTM C20-00 (2010) and ASTM C373 (2014) standards. Additionally, the cold crushing strength (CCS) of thoroughly prepared sintered brick samples are tested on the Universal Testing Machine (INSTRON), using the ASTM C133-97 (2008) standard at a crosshead speed of 0.2 mm/min. The heat conductivity of insulation brick is determined using a TPS-500 Hot Disk equipment (Goteborg, Sweden). The surface morphology and microstructure of the samples are analyzed by a Scanning Electron Microscope (SEM) (ZEISS, Jena, Germany, EVO 18–2045), providing information on pore size, shape, and connectivity. Leaching behaviour of alkali metal ions through the sintered brick is evaluated using a digital pH and conductivity meter. The leaching solutions are prepared by mixing the crushed and powdered sintered brick with distilled water at a constant concentration of 1 g/L. All experiments are performed at a constant temperature of 28℃ with a leaching duration of 48 hours. The mobility of heavy metals in the sintered insulation brick was investigated by assessing their leaching behaviour using the toxicity characteristic leaching method (TCLP). Raw MW was found to have a pH below 5 after being diluted with 1N HCL solution, hence the TCLP test was performed with extraction solution 1 (pH = 4.93 0.05), a solid-to-liquid ratio of 1:20.

8.3 Results and Discussion

8.3.1 Physical-chemical characterization of raw materials

The primary constituent of insulating refractory brick is MW. The detailed characterization of raw MW can be found in Chapter 6. RH is used as fugitive material. The thermogravimetric analysis of rice husk shows decomposition of RH in three stages. The weight loss in the first stage is associated with adsorbed water in the temperature range of 40-90°C and is around 4.5% which is followed by weight loss of around 42% due to burnout of volatile organic component (220°C-380°C). Finally, the remaining burnout of carbon in RH contributes to weight loss of approximatively 50% (380°C-1000°C). The weight loss was constant after 1000° and residue known as RHA. Studies have shown that major part of this residue is silica. Chemical composition of RM was identified and quantified using XRF (Table 1). The higher concentration of SiO_2 and Al_2O_3 approves the dominance of aluminosilicate type minerals in RM. Apart from aluminosilicate mineral, significance presence of Iron oxide was also seen in RM. Presence of lower fraction of oxide of Titanium, Potassium, Magnesium, Sodium and Calcium are also evident in RM. However, concentration of Sodium oxide and titanium oxide is comparatively high in RM. The reports shown by other studies also represent similar concentration of major oxides in RM. XRD results shown for raw RM reveals that it consists of Quartz (79-1906), Anatase (84-1285), Rutile (78-1510), Aluminium Iron Oxide (84-2154), Magnesium silicate (74-1684), and Sodium Aluminium Silicate (80-1561) phases with Hematite (79-0007) as most evident phase.

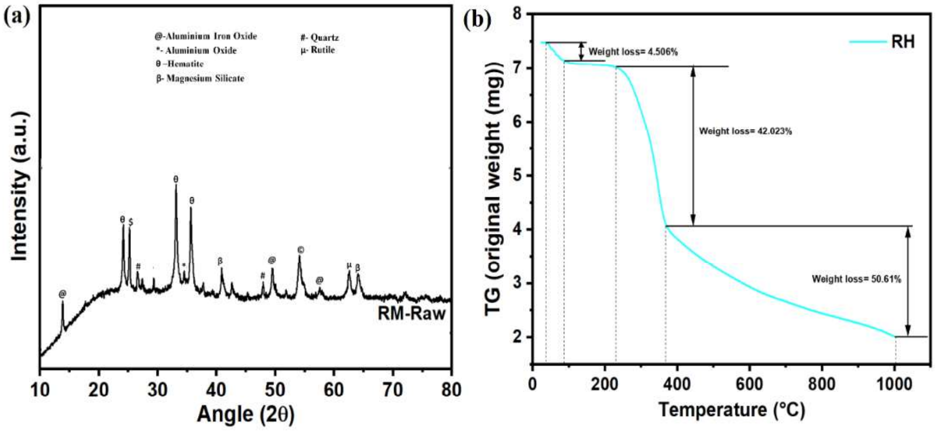


Fig. 8.1 (a) XRD of raw RM, (b) TGA of RH

Table 8.1 XRF analysis of RM.

Oxides	Content (%)
SiO_2	10.81
Al_2O_3	20.59
Fe_2O_3	25.58
K_2O	0.15
MgO	0.18
Na_2O	7.72
TiO_2	11.87
CaO	2.05
BaO	NA
P_2O_5	0.47
ZrO_2	0.11
MnO	0.03
V_2O_5	NA
Cr_2O_3	0.13
CuO	0.02
ZrO_2	0.11

8.3.2 Physical, Mechanical and Thermal Properties of Insulation brick:

Insulating materials are evaluated based on several fundamental properties to determine their suitability for specific applications. These properties include Bulk density, Apparent porosity, Cold crushing strength, and thermal conductivity. In adherence to the Indian standard for insulating bricks (IS 2042: 2006), a comprehensive classification system has been established, correlating the range of various grades of insulating bricks with these primary parameters. This classification framework facilitates the selection of insulating bricks that align with specific thermal resistance requirements, thereby promoting efficient and effective insulation practices (Table 2).

Table 8.2 Physical properties of Insulating Bricks (IS 2042: 2006)

Characteristic	Requirement		
	Grade A	Grade B	Grade C
Bulk density, g/cm^3, Maximum	1.00	0.90	0.75
Apparent porosity, (%), Minimum	60	60	65
Cold crushing strength, MPa, Minimum	2	1.5	0.7
Thermal conductivity at 600°C W/mK at hot face, Maximum	0.52	0.35	0.28

8.3.3 Effect of firing temperature, RH content and particle size on Porosity of Insulating brick:

Porosity is one of the most important factors that is used to characterize insulation brick. Properties like bulk density, cold crushing strength and thermal conductivity are greatly influenced by porosity of the structure. Variables that effect the porosity in any structure includes composition of material, additive and fugitive materials, particle size of raw material and fugitive material and finally consolidation temperature. The apparent porosity (AP) possessed by as fabricated insulation brick are in the range of 8.1-66.3%. Fig. 8.2 shows the variation of AP of fired brick as a function of sintering temperature, RH content and particle size of RH and MW.

AP decreases constantly with increase in firing temperature irrespective of compositions and particle size (Fig. 2 (a-f)). During sintering process high temperature transforms particles into a viscous liquid or increases atomic mobility which further helps in chemical reaction and grain growth within the system and finally consolidates the particles thereby decreasing AP. Also, the presence of alkali, alkaline earth, and minor iron quantities, combined with the significant presence of siliceous material in raw MW, facilitates the formation of a glassy phase with a low melting point. Sintering, in turn, diminishes surface tension, enabling particle consolidation and further decreasing porosity. This process contributes to the reduction in porosity of the bricks after firing.

Addition of RH enhances the porosity to the fired samples. The RH works as fugitive material and escapes out during firing, thus providing space to the structure. The RH mostly consists of organic matters (around 70%) and during the sintering process the organic content of RH is removed as suggested by TGA study of RH and thus providing space to the structure which ultimately enhances the porosity of the fired bricks. More the RH content in the green samples more will be porosity in fired bricks. Growth in AP % is linear with increase in RH content for each temperature group samples as shown in Fig.8.2 (a-f).

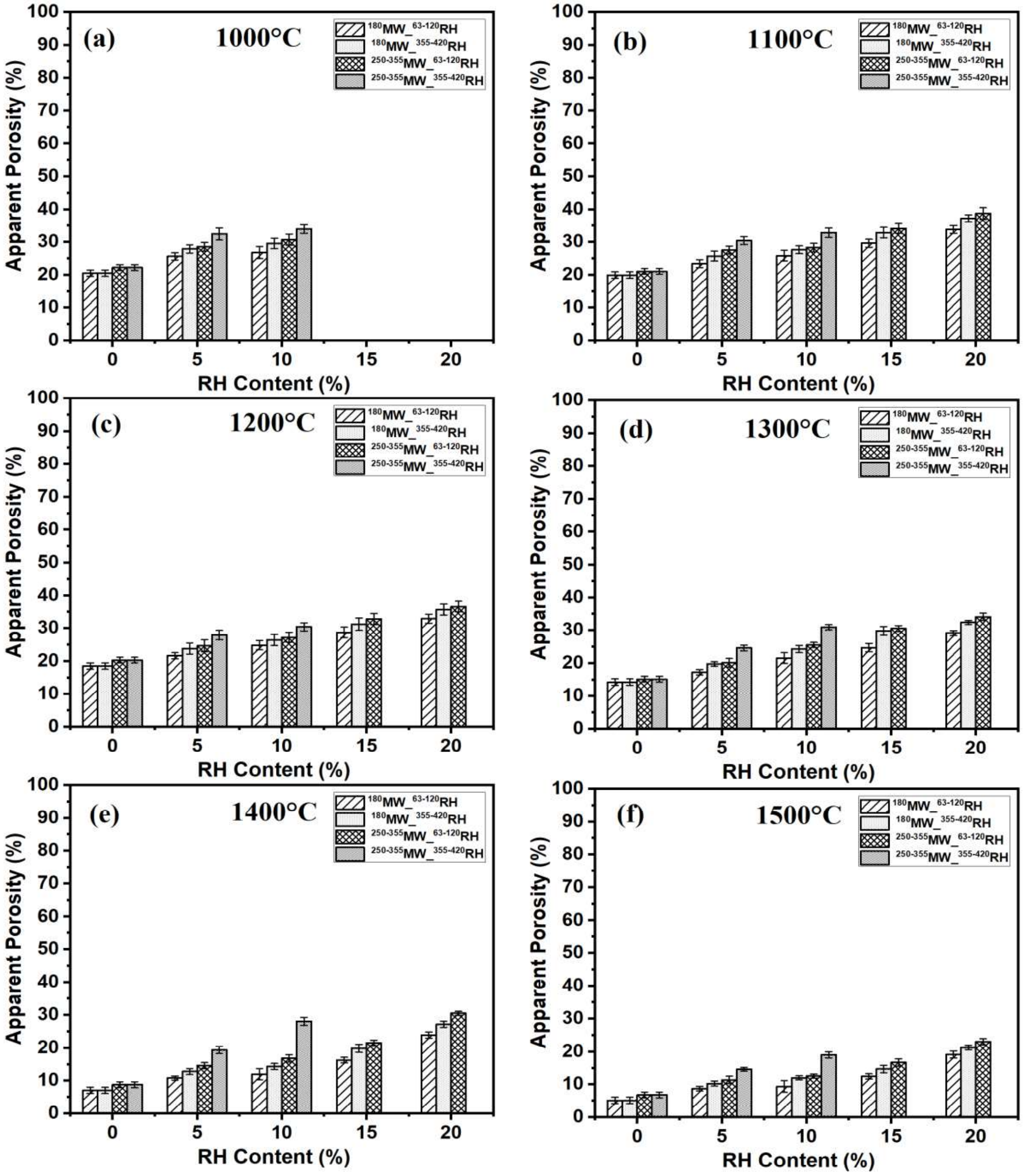


Fig. 8.2 Variation of Apparent Porosity of fired bricks with RH content prepared with different particle size of RH and MW and sintered at different temperatures (a)- 1000°C (b)- 1100°C (c)- 1200°C (d)- 1300°C (e)- 1400°C (f)- 1500°C

Similarly, the augmentation in particle dimensions of MW and RH exhibits a notable amplification in the AP. This phenomenon is clearly demonstrated in the graph, where each composition, including various RH contents and temperatures, manifests an upsurge in porosity when the particle size of RH is enlarged while keeping the MW particle size constant Fig.8.2 (a-f). This trend is also observed when the particle size of MW is altered. The escalation in porosity resulting from the utilization of larger-sized RH can be attributed to the increased space provided by the larger RH particles after combustion. Similarly, the enhancement in porosity due to larger particle size of MW is attributed to the relatively larger voids created by these particles during the rearrangement process that occurs during the formation of the green MW samples. The gaps between particles become more pronounced during the rearrangement of particles in samples during the palletization of green samples. Consequently, the enlargement in particle size for both MW and RH leads to the formation of a more porous structure.

Figure 8.6 presents a graphical illustration that depicts the mechanism of pore formation and the ability to tailor porosity using particles of varying sizes of RH and MW. This depiction provides a clear visual representation of the process by which pores can be created and controlled, offering insights into the mechanisms that govern the formation of porous insulation brick. According to IS:2042 standards an insulation brick must have AP at least 60%. Out of 78 compositions, 6 follows the IS:2042 standards of AP for insulation bricks.

8.3.4 Effect of firing temperature, RH content and particle size on Bulk Density of Insulating brick:

Bulk density serves as a significant parameter in characterizing insulating materials. Typically, the compaction of initial green samples intensifies as firing temperatures rise. This phenomenon occurs due to the processes of shrinkage, vitrification, and sintering, which lead to the occupation of pores through atomic diffusion and partial melting of particles within the samples. Consequently, particle consolidation and grain growth contribute to the densification of the samples. Figure 8.3 illustrates the variation in bulk density of the insulation brick with the addition of Rice Husk (RH), sintering temperature, and varying particle sizes of both mining waste (MW) and RH. The graph clearly demonstrates the substantial influence of firing temperature on the bulk density of the brick. Higher firing temperatures result in an increase in bulk density. This can be attributed to the enhanced sintering of the samples, as well as the formation and growth of grains at elevated temperatures, effectively eliminating any gaps between the grains and leading to more efficient densification. Among all the compositions and particle sizes of MW and RH used, the samples sintered at 1500°C exhibit the highest bulk density, while the samples sintered at 1000°C display the lowest bulk density.

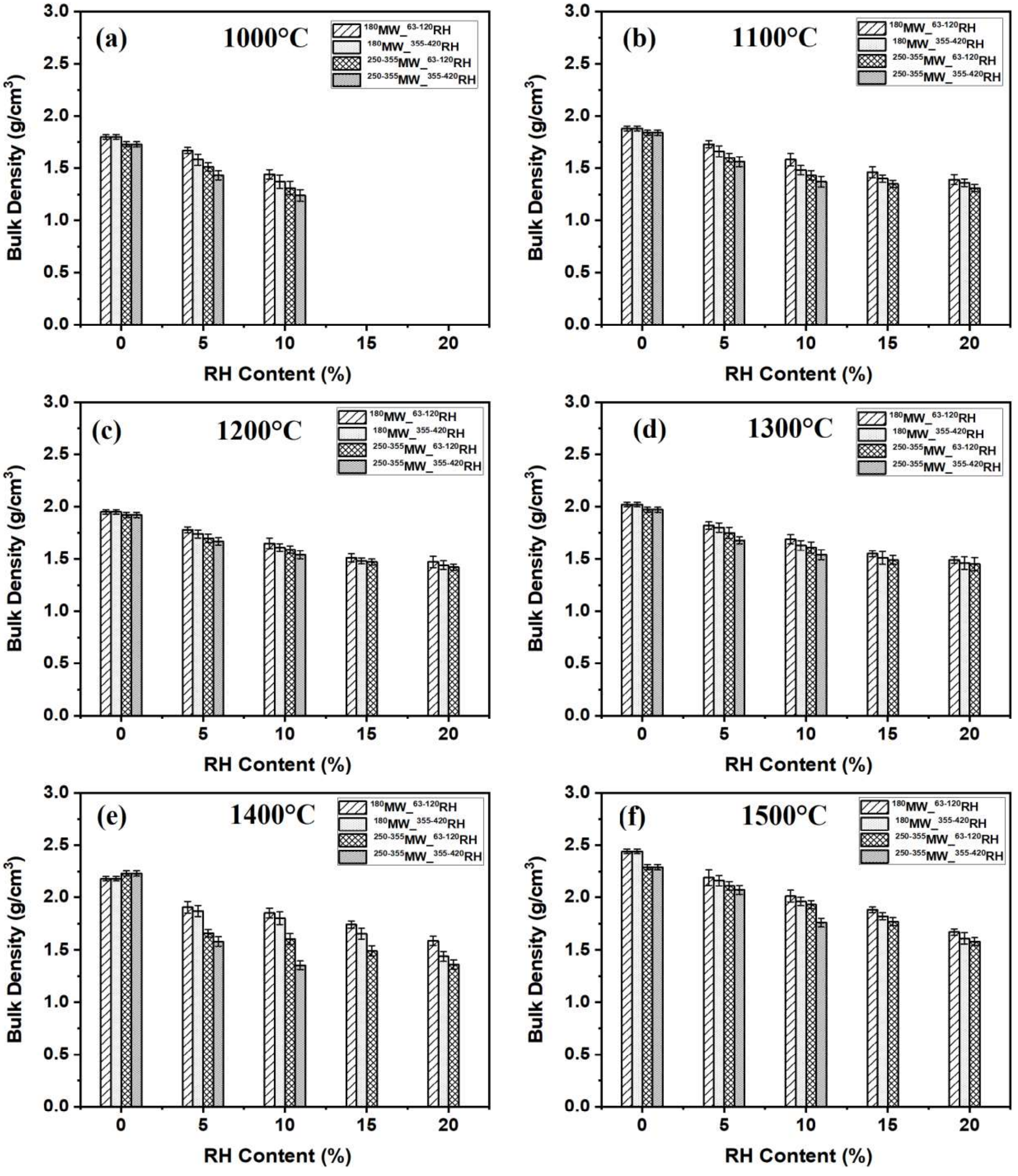


Fig. 8.3 Variation of Apparent Porosity of fired bricks with RH content prepared with different particle size of RH and MW and sintered at different temperatures (a)- 1000°C (b)- 1100°C (c)- 1200°C (d)- 1300°C (e)- 1400°C (f)- 1500°C

The inclusion of Rice Husk (RH) in the composition leads to a linear decrease in bulk density across various compositions and firing temperature ranges. The weight content of RH plays a significant role in influencing the bulk density of the fired samples. Observations indicate that for every 5% increase in RH content, there is an approximate 1-20% decrease in bulk density.

This reduction in bulk density becomes more pronounced as the concentration of RH increases. The decrease in bulk density attributed to the incorporation of RH can be attributed to the increased space provided by the RH particles after burnout. This additional space reduces the densification of the samples, resulting in a lower bulk density. Consequently, a higher amount of RH in the composition leads to the presence of more voids and therefore a lower bulk density in the samples.

The particle size of both mining waste (MW) and Rice Husk (RH) also has a significant impact on the bulk density (BD), similar to the effect on Apparent Porosity (AP), but in the opposite direction. The size of RH particles has a notable influence on the bulk density of the fired samples. Increasing the particle size of RH from 63-120 µm to 355-420 µm results in a decrease in bulk density ranging from 1-25%. This behavior can be attributed to the larger space provided by the larger RH particles after the burnout stage, which leads to a lower bulk density. Similarly, bricks prepared using larger-sized MW particles exhibit lower bulk density across all compositions of RH and sintering temperatures. Once again, the presence of more voids in larger-sized particles serves as the primary factor behind this phenomenon. A decrease in bulk density ranging from 7-32% was observed when the MW particle size transitioned from <180 µm to 250-355 µm. It was also observed that the effect of MW particle size on bulk density is more significant compared to the influence of RH particle size. This can be understood by considering the fact that the intragranular pores resulting from the rearrangement of MW particles are more substantial compared to the space provided by the burnout of RH particles.

The prepared insulation brick possesses bulk density in the range of 0.85-2.15 g/cm^3 (Fig. 8.3(a-f)). As per the IS:2042 standards the maximum allowable density that insulation brick should possess is 1 g/cm^3. Out of total 78 compositions of fired samples, 22 samples satisfy the IS:2042 standards criterion of Bulk density for insulation bricks.

8.3.5 Effect of firing temperature, RH content and particle size on Cold Crushing Strength of Insulating brick:

The cold crushing strength (CCS) of an insulation brick is a critical parameter that qualitatively defines its characteristics and indicates the strength of the connecting particles or grains within the brick system. According to IS:2042 standards, an insulation brick must have a CCS in the range of 0.69-2 MPa, whereas the prepared insulation brick in this study exhibited CCS values ranging from 6.06-35 MPa. Figure 8.4 shows the relationship among the mean CCS values of the various compositions of insulation bricks with sintering temperature, RH content and particle size. The BD and AP properties of fired bricks directly reflects the CCS behaviour. The increase in RH content lowers the CCS, for all compositions and sintering temperatures ranges and can be attributed to more pores due to addition of as explained in AP and BD section.

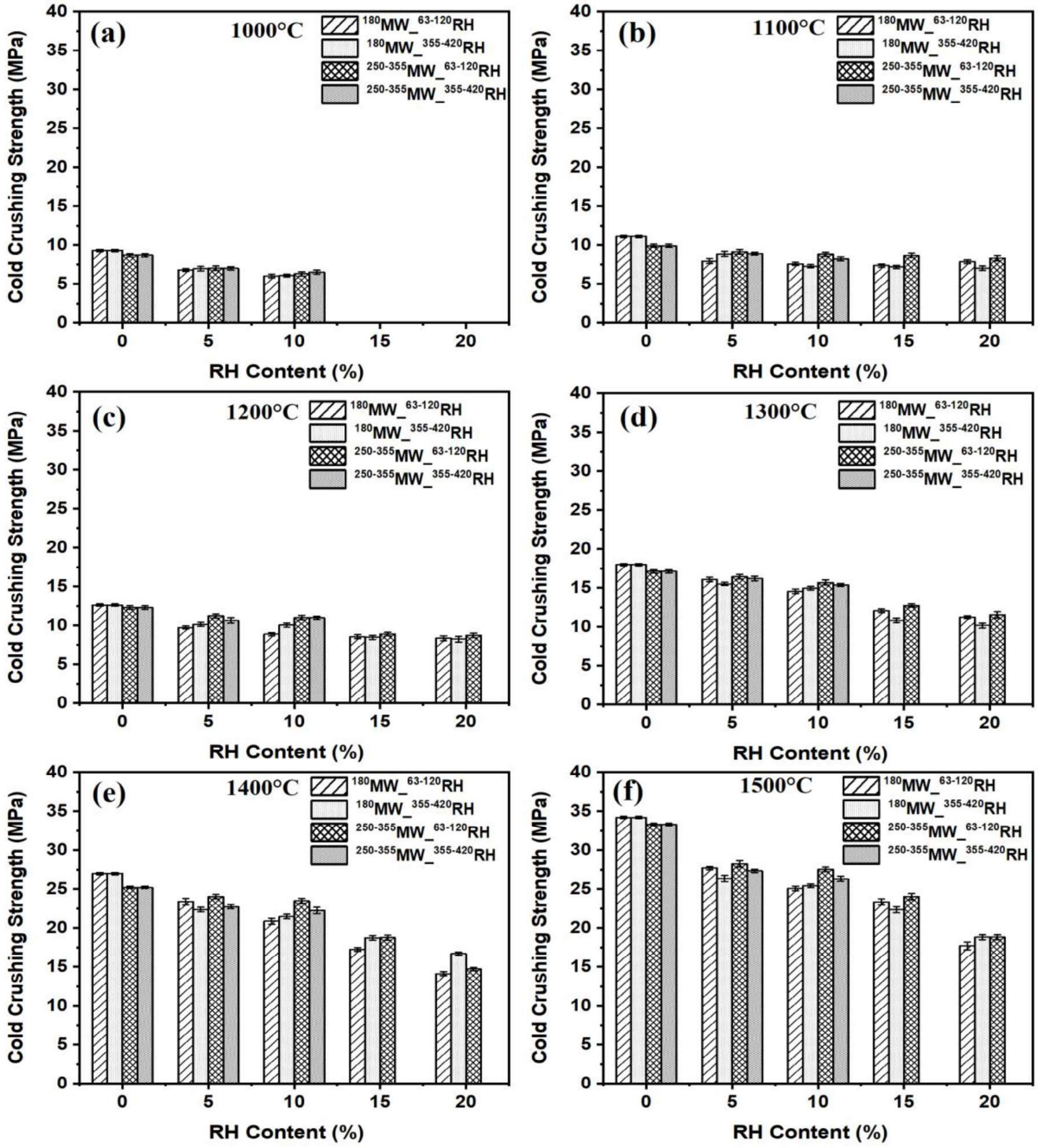


Fig. 8.4 Variation of CCS of fired bricks with RH content prepared with different particle size of RH and MW and sintered at different temperatures (a)- 1000°C (b)- 1100°C (c)- 1200°C (d)- 1300°C (e)- 1400°C (f)- 1500°C

The findings revealed a positive correlation between the sintering temperature and the Cold Crushing Strength (CCS) values across all specimens. This can be explained by the vitrification process of low melting fluxes and their accumulation in the pore structure, thereby enhancing the mechanical strength of the samples. Additionally, the presence of aluminosilicate at high temperatures forms various phases, which further enhances CCS properties, while the formation of a needle-like mullite structure strengthens the brick.

Interestingly, the effect of the particle size of rice husk (RH) and mine waste (MW) on CCS was quite different from that on apparent porosity (AP) and bulk density (BD). Increasing the RH particle size increased the AP and decreased CCS, whereas increasing the MW particle size enhanced CCS irrespective of an increase in AP. This phenomenon could be attributed to the better strength exhibited by larger MW particles than smaller ones. However, an increase in MW size also led to an increase in AP due to more spaces present during compaction, where intergranular spaces are more pronounced due to irregular rearrangement of bigger particles. The experimental results confirmed that the CCS values of all samples met the IS:2042 standards for insulation bricks, and their strength was well-matched with commercially available products.

8.3.6 Effect of firing temperature, RH content and particle size on Thermal Conductivity of Insulating brick

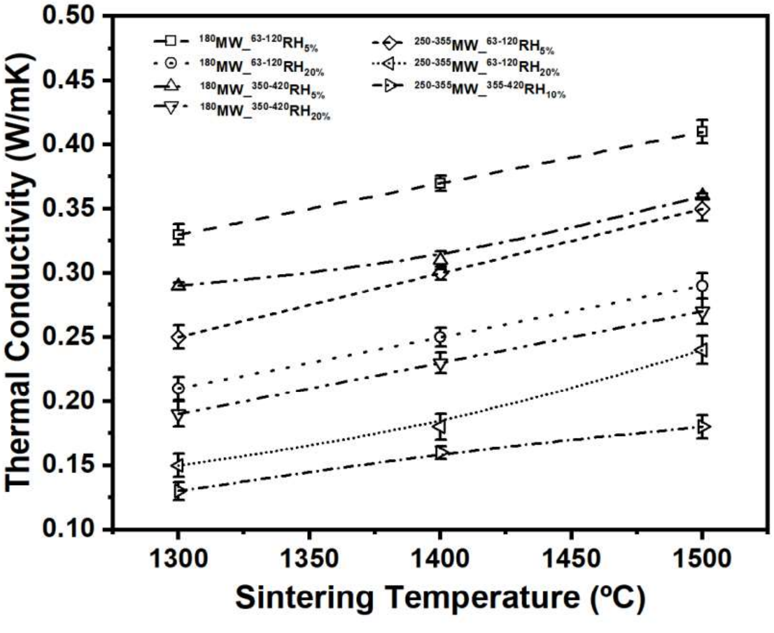


Fig. 8.5 Thermal conductivity variation of fired refractory with sintering temperature

Insulation bricks are distinguished primarily by their poor heat conductivity. Insulating property of a porous material depends on their porosity, pore architecture, density, and chemical composition. The prepared insulating brick possesses thermal conductivity in the range of 0.37-

0.67 W/mK. Despite the significant thermal conductivity possessed by mullite (5.2 W/(mK)) and silica (1.5 W/(mK)), the developed brick exhibits a low thermal conductivity which can be attributed to closed and open pores found in the structure of brick. The air trapped within the pores has a relatively low thermal conductivity, which helps in lowering heat transfer. Figure 8.5 shows thermal resisting properties and its variation of the fabricated insulation refractory with sintering temperature and varying compositions. It is observed that the thermal conductivity decreases evidently with the addition of RH due to increase in porosity. In contrast, the thermal conductivity of bricks rises as a function of sintering temperature and composition due to consolidation of structures at higher temperatures which eventually enhances radiation through the solid crystalline phase. Moreover, increase in particle size of both MW and RH, further decrease in the thermal conductivity was seen due to the decrease in porosity. The IS:2042 standard specifies that the thermal conductivity of an insulation brick should fall within the range of 0.28-0.52 W/mK. The present study indicates that most of the insulation prepared bricks meet this criterion for thermal conductivity. However, it should be noted that the selection of a particular brick from among the Type A, B, or C categories of IS:2042:2006 is based on whether it satisfies all the relevant parameters, including AP, BD, CCS, and thermal conductivity.

8.3.7 XRD, Microstructural and Leaching Analysis of Insulation Brick

8.3.7.1 XRD Analysis

Fig. 8.7 (a) shows the XRD plot of sintered insulating refractories with various compositions and particle size of MW and RH sintered at different temperatures. Due to the intricate mineral composition of raw MW, insulation refractories experience many transitions of different mineralogical phases at high sintering temperatures, which also have a substantial impact on the microstructure of the brick. The findings of the mineralogical analysis indicated that the majority of the aluminosilicate minerals in raw MW go through phase change and are primarily in the mullite phase (79-1454), which gives the bricks considerable strength. However, samples sintered at higher sintering temperature demonstrate improved mullitization with a high proportion of mullite phase. Additionally, silica with various phases is the second most prevalent component in the sintered samples due to relatively high concentration of silicate minerals. Due to conversion of quartz to tridymite (71-0261) and cristobalite (77-1317) phase and subsequent mullitization, the amount of quartz (78-1252) is diminished in higher sintered samples. Thermal decomposition of Iron sulphide and formation of Iron oxide and Iron silicate at higher temperatures is observed to lessen or diminish Iron sulphide, which is believed to be primary factor of acid drainage. Magnesium (Pyrope) and calcium (Titanite) complexes with silicates are also found in trace amounts.

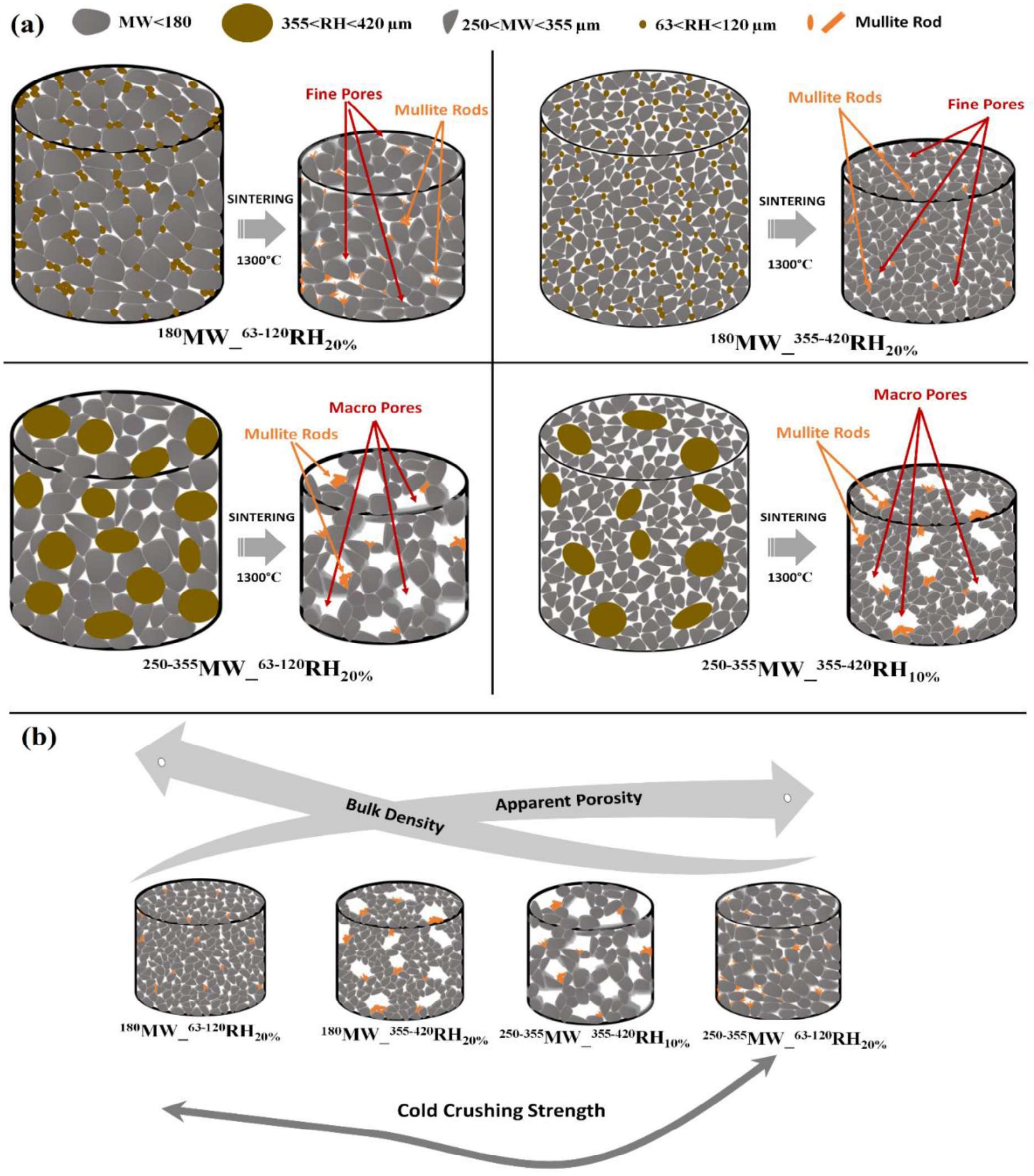


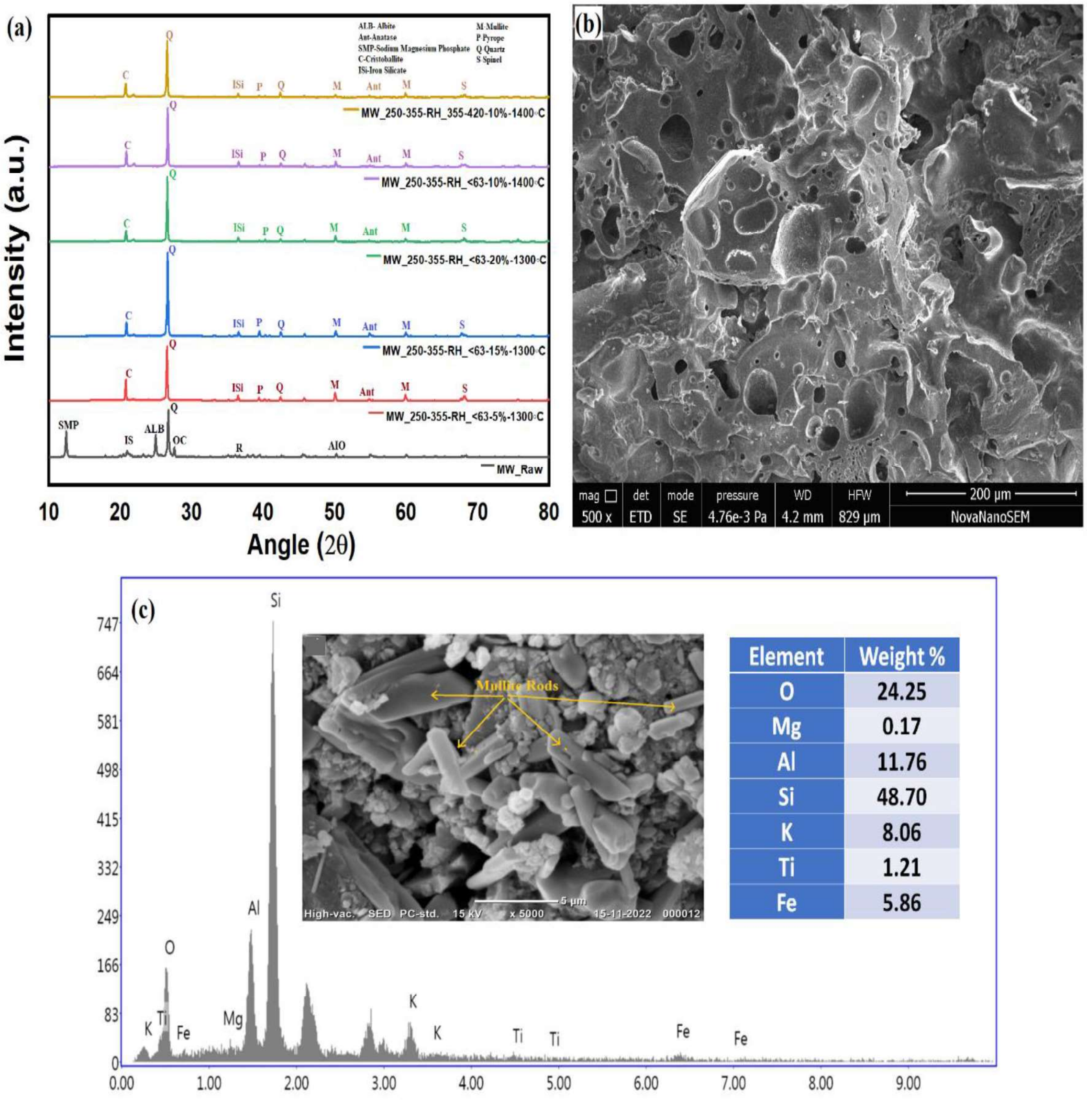
Fig. 8.6 (a) Pictorial representation of pore formation mechanism and effect of MW and RH size on porosity, (b) Physical properties variation of fired refractories of various compositions

8.3.7.2 Leaching analysis

The evaluation of heavy metal mobility in the fired bricks was conducted using the toxicity characteristic leaching procedure. The mobility of heavy metals is influenced by several factors, including the firing temperature, mineralogy composition, and pH of the leach solution. After undergoing the heat treatment process, all samples demonstrated a significant reduction in the mobility of heavy metal elements. The mobility levels were found to be within the limits set by the US-EPA for non-hazardous waste. The results of heavy metal mobility are presented in Table 3. The ability of the prepared bricks to fix metals depends on the type of crystal system present within their structure. Samples with well-formed crystal structures exhibited greater strength and chemical stability. Metals such as Arsenic (As), Copper (Cu), Cadmium (Cd), Zinc (Zn), Lead (Pb), and Chromium (Cr) reacted with the aluminum and silicon present in the raw tailings materials, forming corresponding spinel, silicate, and aluminosilicate structures. X-ray diffraction (XRD) analysis revealed that the sintering process resulted in the formation of new heavy metal crystal structures, including Albite, Iron silicate, Pyrope, and Spinel, which were not present in the initial samples. The high sintering temperature played a crucial role in immobilizing the heavy metals within these structures, securely fixing them within the system. This fixation effect of spinel or silicate frameworks during sintering led to a significant decrease in metal leaching [197]. The formation of these complexes helped in mitigating the leaching of heavy elements and other elements present in the leachates.

8.3.7.3 Microstructural Analysis

Fig. 7 (b) shows microstructure of inner section of a fractured sintered brick prepared using 10% RH with a particle size of 180 µm and 355-420 µm of MW and RH respectively, sintered at 1400°C. Homogenous distribution of fine spherical pores clearly visible through the SEM micrograph are due to eradication of RH particles during firing process. Most of the pores are closed one and are due to consolidation of particles at high sintering temperature. Generally porous composites prepared using RH as fugitive material have random pore shapes and distributions. However, the as fabricated insulating brick encompass spherical pores which could be attributed to selection of uniform size RH particles. The dense matrix shown in SEM micrograph is due to consolidation of various silicate phases, imparting strength to the porous brick. Moreover, presence of high amount of aluminosilicate phases and higher sintering temperature causes formation of mullite phase. Mullite rods embedded within silicate phases are clearly seen in Fig. 7 (c). The dimensions of rods are characterized by an average diameter and length that fall within the range of 0.1-0.05µm and 0.1-0.5µm, respectively. The EDS analysis results demonstrate the presence of all potential components in the prepared refractory, are also attached with the SEM image. EDS results are in accordance with XRD results, showing the presence of Fe, Al, Si, O, Ti, Mg and K elements, which confirms the existence of aluminosilicate, heavy metal-based oxides and mullite phase in MW based insulation bricks. The higher content of Al, Si and O elements confirms the formation of mullite phase and presence of silicate phase.



Element	Weight %
O	24.25
Mg	0.17
Al	11.76
Si	48.70
K	8.06
Ti	1.21
Fe	5.86

Fig. 8.7 (a)XRD pattern of fired refractory sintered at different temperatures, (b) SEM image of inner cross-section of fired refractory showing closed and open pores, (c) EDS analysis showing elemental proportions in the fired refractory with SEM image showing existence of Mullite rods

While insulation bricks produced solely using MW and RH generally meet the requirements outlined in the IS:2042:2006 standard, there remains room for enhancing their properties, particularly in terms of achieving higher cold crushing strength (CCS). This improvement can be attained through the incorporation of appropriate additive materials. Further investigation highlights the importance of incorporating RM to realize this gap, as elucidated in the subsequent section. By exploring the potential benefits and effects of RM, it is possible to unveil promising avenues for enhancing CCS and overall brick performance.

Table 8.3 Environmental and durability properties of selected fired insulating brick (TCLP test).

Samples/Ele-ments	As μgL^{-1}	Ba μgL^{-1}	Cd μgL^{-1}	Cr μgL^{-1}	Cu μgL^{-1}	Mo μgL^{-1}	Pb μgL^{-1}	Sulfates μgL^{-1}	Zn μgL^{-1}
Raw MW	371	141	3.2	24.7	89	16.6	69.54	319.5	1054
Insulating Brick	48	28	0.09	6.32	48	5.39	11.64	79.61	220

8.3.8 Effect of RM Addition on Physico-Mechanical and Thermal Properties of Insulation Brick

Table 8.4 Weight % of major oxides of various mixture composition of MW and RM (Based on XRF data- Table 1)

Oxides	MW: RM: 2:1	MW: RM: 1:1	MW: RM: 1:2
SiO_2	36.54	30.11	23.67
Al_2O_3	23.40	22.7	22.1
Fe_2O_3	10.82	14.51	18.2
K_2O	1.69	1.31	0.92
MgO	1.23	0.97	0.71
Na_2O	3.29	4.4	5.50
TiO_2	4.7	6.5	8.28
CaO	1.35	1.53	1.7

Table 8.4 data demonstrates that an increase in the RM content in the raw mixture leads to a corresponding increase in the percentages of Iron oxide, Titanium oxide, and Sodium oxide, while the Silica content is reduced. The percentages of the other oxides remain nearly constant. Upon being combined with RH and heat-treated, the resulting compositions form various aluminosilicate phases, as indicated by the XRD data in Fig. 8, which displays the peaks of

different phases with varying intensities. Notably, the intensity of quartz decreases with the addition of RM, indicating the conversion of free silica into various alkali-metal and other aluminosilicate minerals. Iron oxide converts primarily into an iron silicate structure, while the remaining oxide transforms into Pseudobrookite with a small portion of free Iron oxide. Titania transforms into either Pseudobrookite or remains in the form of Rutile. Alkali metals form minerals with aluminosilicates and exist in the form of Sanidine, Forsterite, Kyanite, Anorthite, and Albite, as indicated in the XRD plot. The addition of RM to MW, followed by thermal treatment, results in the localized fusion of bricks, which eventually reduces their porosity and insulation properties. It was observed that the addition of RM enhances the BD of brick, which is attributed to the Iron content of RM. The BD graph shows that insulation brick with a higher ratio of RM has higher BD for all compositions and temperatures, with a sharp increase observed up to 50% of RM addition (Fig. 8.9). Further addition of RM leads to steady growth in BD, which was found to be in the range of 0.9-1.4 g/cm^3 with the addition of RM. The apparent porosity of the samples also decreases with the addition of RM. The pattern for the increase or decrease in AP and BD due to the change in particle size of MW and RH and sintering temperature is unchanged with RM addition (Fig. 8.10). However, the effect of RM addition on CCS is quite different. Up to 50% addition of RM, CCS follows the pattern of AP and BD, i.e., with increasing RM content, CCS initially increases. This can be attributed to the higher content of Iron oxide in RM, which combines with the free silica and forms iron silicate and iron aluminosilicate compounds, imparting more strength to the brick system. However, at higher RM content, the MW content drops significantly, and the availability of free silica for the formation of respective silicates is lowered, resulting in a decrease in CCS beyond 50% RM addition, regardless of higher BD and lower AP (Fig. 8.11). The data for thermal conductivity of $^{250-355}$MW_$^{63-120}$RH$_{20\%}$ also corroborates the result of AB and BD due to addition of RM. Thermal conductivity is observed to be increased due to addition of RM (Fig. 12). The data suggests that the optimum range for RM addition lies within 30-50%, providing considerable AP and BD as needed for brick specification with better mechanical strength. According to IS:2042 standards, only two compositions with RM content are found to be suitable for class C type insulation brick. Alkali immobilization characteristic of the sintered insulation bricks is assessed through the availability of free alkali ions in their leachates. The leachates of raw RM, DI and insulation bricks sintered at different temperatures were tested for ion conductivity and pH (Table 5). The pH and conductivity values of raw RM were used as a reference and found to be highly basic (pH=11.01) with high ion conductivity (608.12 µS/cm), indicating a higher concentration of soluble alkali in raw RM leachates. However, the pH and conductivity values of the sintered insulation brick were significantly reduced, approaching those of natural water, suggesting that the alkali ions were trapped in aluminosilicate during the sintering process. This can be attributed to the formation of albite and anorthite-like phases, which successfully trapped the alkali metal ions within aluminosilicate frameworks, thereby reducing their mobility [198].

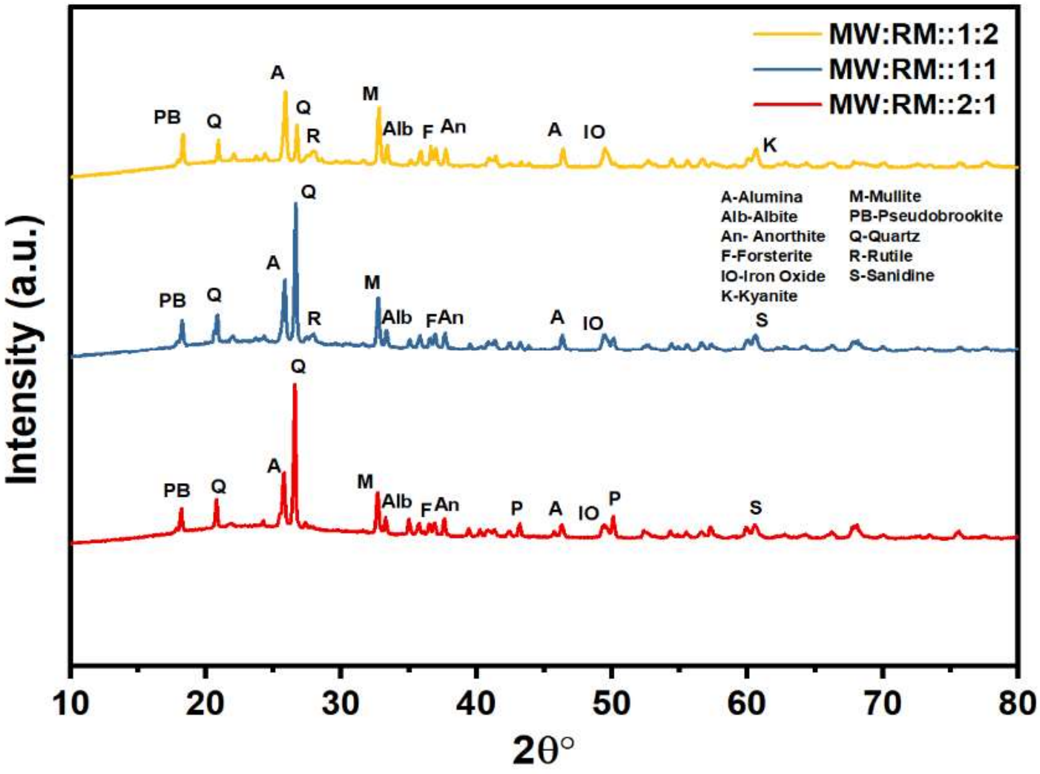


Fig. 8.8 (a) XRD pattern of fired brick with varying RM composition

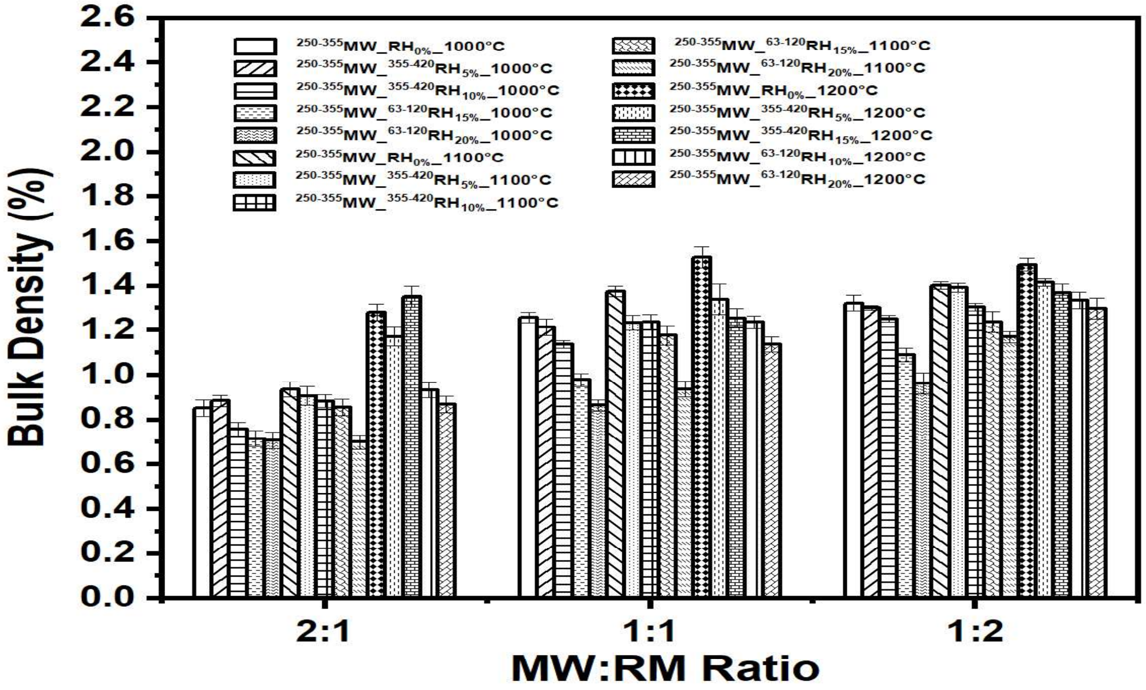


Fig. 8.9 Effect of varying MW:RM weight ratio of fired bricks on Bulk Density

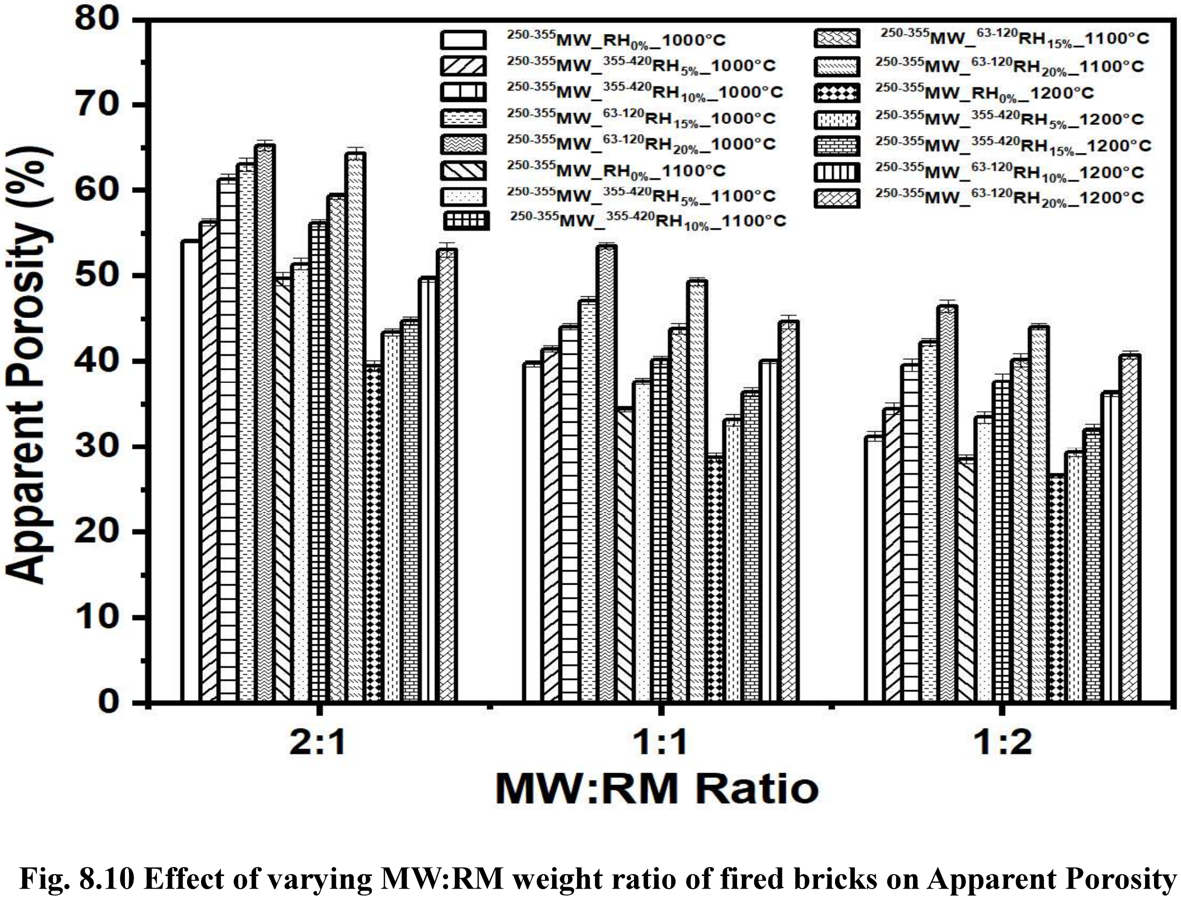


Fig. 8.10 Effect of varying MW:RM weight ratio of fired bricks on Apparent Porosity

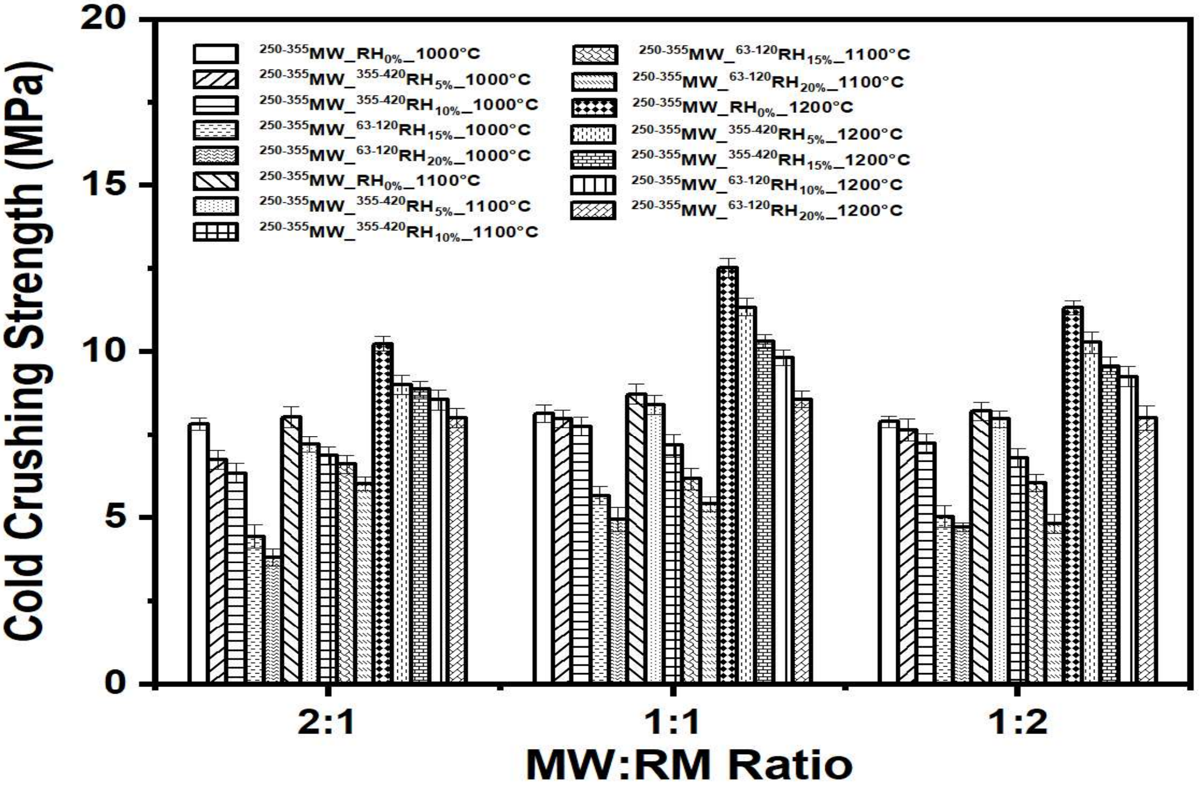


Fig. 8.11 Effect of varying MW:RM weight ratio of fired bricks on Cold Crushing Strength

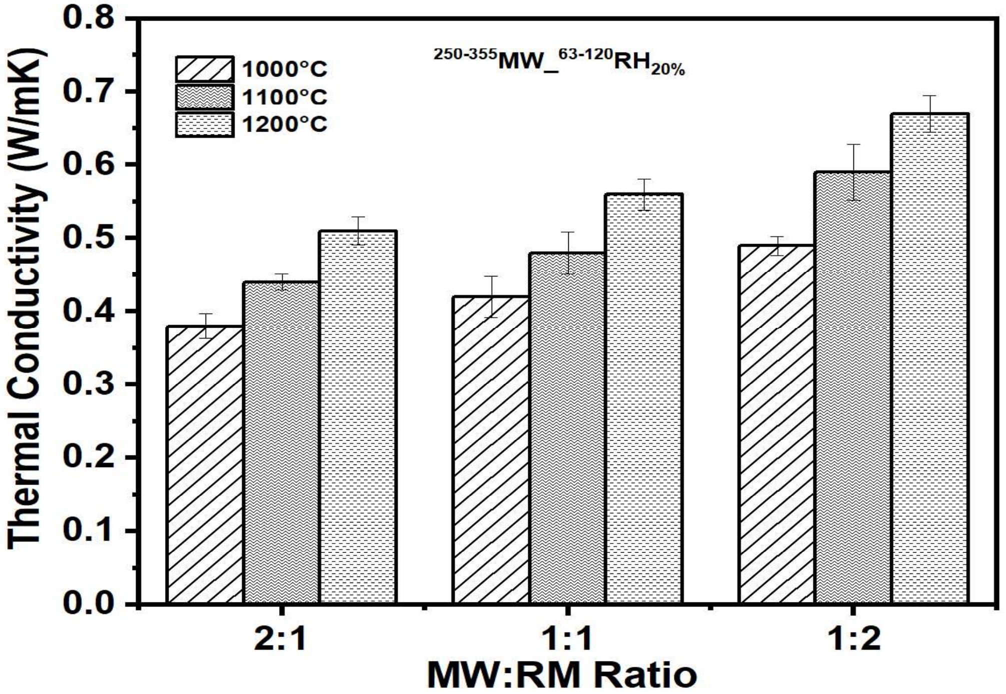


Fig. 8.12 Effect of varying MW:RM weight ratio of fired bricks on Thermal Conductivity

Table 8.5 The conductivity and pH values of leachates of raw RM and MW-RM based insulating brick

Sintering temperature (°C)	pH	Conductivity (µS/cm)
Raw RM	11.01	608.12
Distilled Water	7.00	8.72
$^{250\text{-}355}MW_1\_RM_1\_{}^{63\text{-}120}RH_{20\%}$@1000°C	7.23	10.75
$^{250\text{-}355}MW_1\_RM_1\_{}^{63\text{-}120}RH_{20\%}$@1100°C	7.18	9.12
$^{250\text{-}355}MW_1\_RM_1\_{}^{63\text{-}120}RH_{20\%}$@1200°C	7.11	8.95

8.4 Conclusions

The present study explores the possibility of producing IS standard insulating brick using industrial grade solid wastes and agricultural waste. Coal mine overburden waste was chosen as primary ingredient and Rice husk was used as pore former. Subsequently, effect of Red Mud as an additive on the physical and thermomechanical properties were are also investigated. The developed porous composite possesses apparent porosity, compressive strength and thermal conductivity in the range of 26-54 %, and 6-35 MPa and 0.37-0.67 W/mK respectively. Results show that rice husk can be used as an affordable source of pore former that not only helps to achieve a wide range of porosity, but also its residue in the form of silica facilitates the formation of aluminosilicate and other silicate phases. However, maximum utilization of RH is restricted to 23 wt% due to spring back effect of RH over this wt% thereby generating cracks in the fired samples. As the size of these components increases, the porosity also increases linearly. However, their impact on mechanical property is inverse, as compressive strength decreases with an increase in rice husk size due to a higher porosity rate. Conversely, compressive strength increases with an increase in the size of coal mine overburden waste particles, regardless of porosity rate, as larger particles demonstrate better strength. Moreover, the addition of red mud also improves the brick's strength, but it comes at the cost of lower porosity and higher thermal conductivity. Higher concentrations of red mud (>50%) result in a decrease in strength, along with porosity and thermal conductivity. Ultimately, only two compositions prove suitable for Type C insulation brick with red mud addition. It is worth noting that the presence of mineralogical phases such as silica, alumina, and iron oxide helps form phases like mullite, albite, and spinel at high temperatures. This not only helps strengthen the bricks but also inhibits the mobilization of heavy and alkali metals. In conclusion, the present study has shown that three types of insulation bricks are possible using coal mine overburden waste, red mud, and rice husk, with enhanced mechanical strength.