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Synthesis and characterization of new class of geopolymer hybrid composite materials from industrial wastes

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Abstract

Geopolymer belongs to a new class of emerging materials for a number of applications owing to the advantages such as low cost; higher compressive strength; improved fire & acid resistance as well as reduced greenhouse gas emission. In this work, we explore the effective utilization of marble waste as a reactive filler and binder for the development of fly ash based geopolymer hybrid composite materials using extrusion process. The effect of marble waste content on the physico–chemical and mechanical characteristics of prepared hybrid materials was studied through various characterization techniques. The geopolymerization was conducted at two different molarities of

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sodium hydroxide in which the effects of materials properties were studied. The results indicate that the materials prepared at higher molarity exhibits better performance in terms of compressive strength (4.61- 6.52 MPa) (2- 4M). The silicon dioxide present in fly ash reacts with calcium hydroxide present in marble waste forming calcium silicate hydrate network and possibly contributes to the increment in the interfacial bonding in marble waste infiltrated geopolymer matrix. Overall, this improved interfacial adhesion yielded an increase in compressive strength and bulk density but also decreased the water absorption of the developed material. The results of this study not only indicate an effective utilization of marble waste for the production of geopolymer hybrid composite materials via an eco–friendly route but also provide an economical and sustainable route for management of marble waste currently generated in various countries of the world.

Keywords

Geopolymer; Hybrid materials; Marble waste; XRD; SEM; TGA; Mechanical characterization

Introduction

Geopolymers are silico-aluminate inorganic polymers first reported in 1979. From materials science perspective, this relatively new class of polymers is very interesting due to impressive physico-chemical and mechanical properties (Maiti et al., 2018; Zhang et al., 2018). Furthermore, these materials require significantly less energy input to produce which makes them cost effective suitable candidates for a wide spectrum of engineering applications. Any material that contains aluminosilicate and silica in considerable amounts can act as potential precursor for geopolymerization. Fly ash is an industrial waste that has garnered considerable research (Ahmed

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et al., 2014; Alzeer and MacKenzie, 2018; Guo et al., 2018; Pappu and Thakur, 2017; Tian et al., 2018) towards geopolymeric materials preparation due to the presence of notable minerals such as mullite ($Al_6Si_2O_{13}$) and quartz (SiO_2). Considerable research has been done to utilize fly ash waste to prepare geopolymerization based different construction and building materials. Ferone et al. (2011) investigated the mechanical properties of geopolymer bricks prepared using weathered coal fly ash. The samples were prepared using sodium silicate and sodium hydroxide (NaOH) solutions and were cured for 8 days according to four different schemes. The results indicated that samples with only 24 hours curing at 60 °C also showed a remarkable improvement in mechanical strength. Liu et al. (2016) prepared permeable and floatable geopolymer blocks using fly ash. Their work showed that geopolymer block samples can be manufactured using oleic acid and hydrogen peroxide (H_2O_2) solution. The block samples were cured at 80 °C for 10 hours. Although a very low density (0.37 g cm^{-3}) material was obtained, the compressive strength was rather low, only 0.55 ± 0.08 MPa. In a more recent work, Okoye et al. (2017) prepared fly ash based geopolymer concrete in the presence of silica fumes to further improve the durability. The authors tested the compressive strength of the samples that were immersed in sulphuric acid and sodium chloride solution for certain 90 days. The results of the sample were found to be significantly improved along with mechanical properties due to decrease in porosity. The information regarding the usage of marble waste in geopolymer bricks is scarce. Tekin (2016) prepared NaOH activated geopolymer paste using marble, travertine and volcanic tuff wastes. Different molarities (1M, 5M and 10M) of NaOH and different curing temperatures (20, 45 and 75 °C) for 24 hours were the variables in this extensive work. Although the exact amount of marble waste is not clear, at 80% BSW (Bayburt Stone Waste) and 20% TW (Travertine Wastes), the maximum compressive strength was found to be 46 MPa at 10M NaOH.

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In India, about 16 million tons of marble waste has been generated every year and Rajasthan alone produced about 12 million tons annually. Approximately 85% of marble production occurs in Rajasthan state ((Pappu et al., 2007; Thakur et al., 2018). During its mining, processing and post processing, a huge amount of marble waste is generated. Fly ash is another industrial waste which is generated in India on large scale due to dependence on coal combustion based power generation (Pappu and Thakur, 2017). In India, about 230 million tons of coal ash was generated from thermal power stations in the year 2013-2014. Out of this, approximately 108 million tons was utilized for various applications, leaving behind about 40% unutilized fly ash.

In an effort towards development of value addition product utilizing aforementioned industrial waste mitigating the serious environmental impact, this research work aim to develop and prepare durable hybrid composite brick material in an economically sustainable manner. To the best of our knowledge, preparation of hybrid composite materials utilizing both fly ash and marble waste via geopolymerization has not been reported so far (Thakur et al., 2018; Zhang et al., 2016). While incorporation of inexpensive precursors is anticipated to bring down the cost, extrusion technique has been employed to simplify and speed up the process. The effects of varied loading levels of marble waste on the properties of obtained materials have been presented while seeking an optimum amount of marble content without compromising the performance of the material.

Experimental Section

Materials

Fly ash employed in this experiment is of class F (ASTM C618 – 17) and was obtained from Satpura thermal power plant located at Sarni town in the state of Madhya Pradesh of India. The fly ash was dried in oven at 60 ^{o}C for 4 hours before use. The marble waste was received in sun-

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dried powder form of marble waste slurry released by marble processing industry in Udaipur district of Rajasthan state of India. The physical and chemical properties of fly ash and marble waste are reported in **Table 1** and **Table 2** respectively. Sodium hydroxide (NaOH) (97%) pellets and sodium metasilicate (97%) were obtained from Central Drug House (P) Ltd. India. Distilled water was used in all formulations.

Table 1. Physical properties of raw materials.

	Fly ash	**Marble waste**
Specific gravity	2.17	2.39
Bulk density	1.16 g /cm^3	1.77 g/cm^3
Porosity	62.13%	56.36%
Median size	2.26 µm	64.58 µm
Mean Size	17.56 µm	65.59 µm
Mode Size	2.04 µm	63.51 µm
D10	1.30 µm	41.32 µm
D90	51.26 µm	94.12 µm

D10: Diameter at which 10% of the sample mass is comprised of particles with a diameter less than 10 µm

D90: Diameter at which 90% of the sample mass is comprised of particles with a diameter less than 90 µm.

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Table 2. Chemical composition of fly ash and marble waste obtained using X-Ray Fluorescence spectroscopy.

Constituents	Chemical composition (%)	
	Fly ash	**Marble waste**
Silicon dioxide (SiO_2)	62.12	34.66
Aluminium oxide (Al_2O_3)	21.30	3.32
Iron oxide (Fe_2O_3)	5.55	13.12
Titanium oxide (TiO_2)	1.38	-
Magnesium oxide (MgO)	1.58	7.21
Calcium oxide (CaO)	0.53	38.02
Potassium oxide (K_2O)	4.24	2.54
LOI	3.30	1.13

Manufacturing of hybrid geopolymer composite materials

A custom made lab extrusion machine was used for manufacturing of rectangular hybrid geopolymer composite samples. The auger of the extruder was 100 mm in diameter and rotational speed was set at 60-70 revolutions per minute. The dimensions of the die were 36 mm x 36 mm. The extruded material coming out of the die was cut into 76 mm length using a wire cutter, affording samples of dimensions (76 mm x 36 mm x 36 mm). In a typical preparation, pre-

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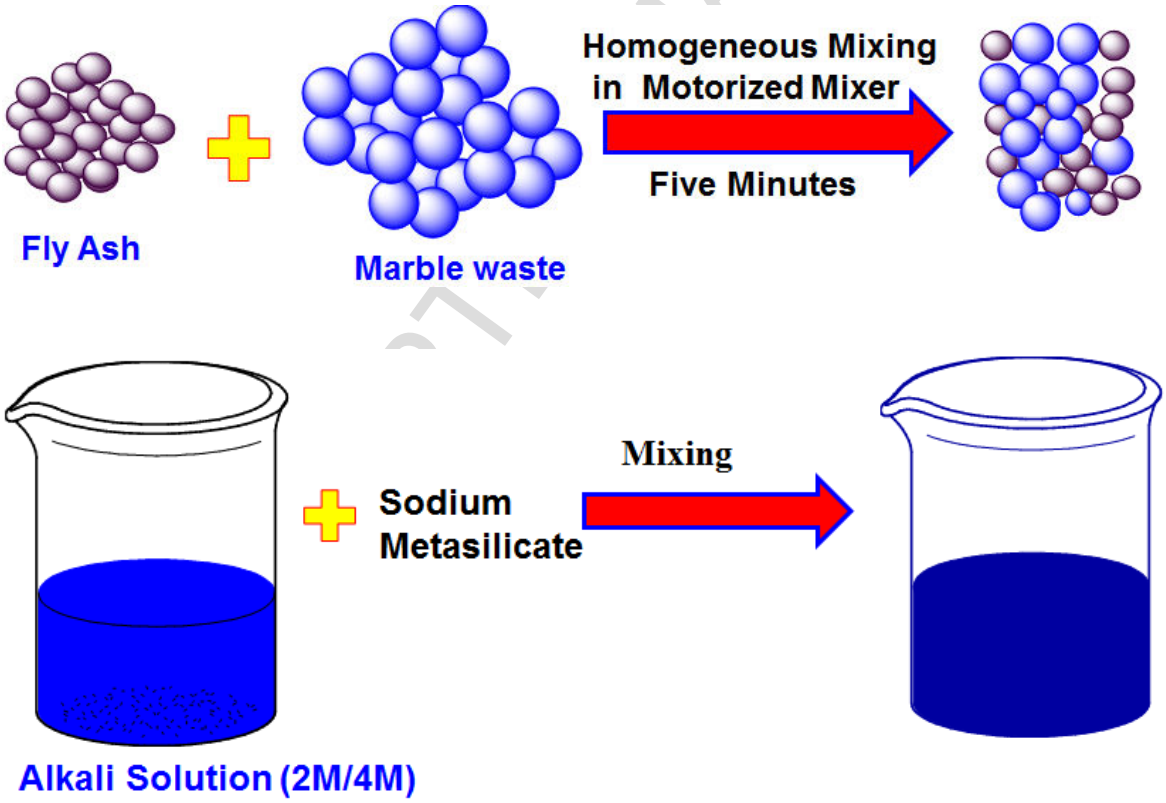
calculated quantities of fly ash and marble waste were homogeneously mixed in a motorized mixer for 5 minutes (**Figure 1**). Simultaneously, solution of NaOH at certain molarity (2M or 4M) and sodium metasilicate in equivalent amount was prepared in boiling water. The use of heated water was to facilitate rapid dissolution and mixing (**Figure 1**). The above solution was then added to the fly ash/marble waste mixture and mixing was continued for further 5 minutes (**Figure 1**). The homogenized mixture was then fed to the extruder and the material coming out of die was cut into predefined length (**Figure 1**). The obtained samples were subsequently cured at 70 °C for 24 hours and afterwards stored in air tight bags for a period of 7 days, prior to various characterizations. The detailed mix design of hybrid geopolymer composite mixes are given in **Table 3**. Sixteen composite mixes were designed for both molarities (2M and 4M) containing 10, 20, 30, 40, 50, 60, 70 and 80% marble waste.



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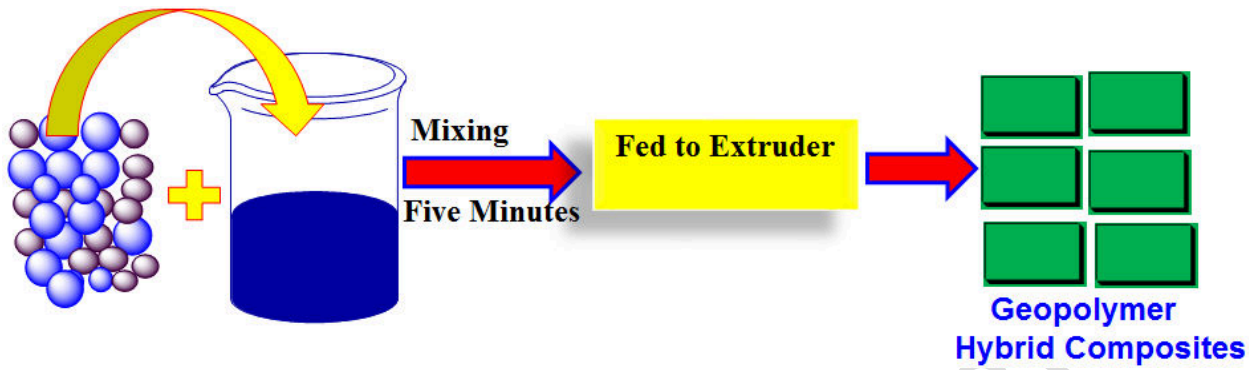

Figure 1. Manufacturing of hybrid geopolymer composite materials.

Table 3. Mix proportion of hybrid geopolymeric composites.

Mix No.	Solid Materials (Wt. %)		NaOH (Molar)	Amount (g)				Alkaline activators/ Precursors
	Fly ash	Marble waste		Marble waste	Fly ash	NaOH	Na_2SiO_3	
2M-10	90	10	2	400	3600	104	104	0.22
2M-20	80	20	2	800	3200	104	104	0.22
2M-30	70	30	2	1200	2800	104	104	0.25
2M-40	60	40	2	1600	2400	104	104	0.25
2M-50	50	50	2	2000	2000	104	104	0.27

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2M-60	40	60	2	2400	1600	104	104	0.27
2M-70	30	70	2	2800	1200	104	104	0.30
2M-80	20	80	2	3200	800	104	104	0.30
4M-10	90	10	4	400	3600	208	208	0.22
4M-20	80	20	4	800	3200	208	208	0.22
4M-30	70	30	4	1200	2800	208	208	0.25
4M-40	60	40	4	1600	2400	208	208	0.25
4M-50	50	50	4	2000	2000	208	208	0.27
4M-60	40	60	4	2400	1600	208	208	0.27
4M-70	30	70	4	2800	1200	208	208	0.30
4M-80	20	80	4	3200	800	208	208	0.30

Characterization of hybrid geopolymer composite materials

X-ray diffraction (XRD)

X- Ray diffractometer (DB advanced model, Bruker, Germany) was used for the analysis of mineral phases of the fly ash and marble waste. X-ray diffraction patterns were recorded using copper tube radiation source at 40 mA current and 40 kV voltage. The patterns were obtained within a 10 to 90° 2θ angular interval with 0.5° step and scan speed of 1.2° per minute.

Particle size analysis

Particle size analysis was performed using Horiba partica laser scattering particle size distribution analyzer LA-950V2. Ethanol was used as a dispersion medium. The refractive indices used for ethanol, fly ash, and marble waste are 1.360, 1.670 and 1.560 respectively.

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Scanning electron microscopy (SEM)

SEM imagery of the fly ash and marble waste were performed using Nova NanoSEM 430 (IE synergy 250) at 5 kV operating voltage. All samples were sputter coated with gold prior to image acquistion.

Thermogravimetric analysis (TGA)

Thermogravimetric analysis was conducted using a Mettler Toledo thermogravimetric analyzer TGA/DSC 1 (Germany).The samples were heated from room temperature to 800 ºC at a heating rate of 10 °C per minute under inert atmosphere of nitrogen.

Fourier transform infra-red spectroscopy (FTIR)

The FTIR spectra were obtained for marble waste and fly ash samples at room temperature using Thermo Scientific Nicolet iS50 spectrometer equipped with diamond crystal ATR accessory. The total number of scans were 64 at a scan resolution of 4 cm^{-1}.

Compression test

The compression tests were performed using an Instron 8801 universal testing machine at a constant loading rate of 14 N mm^{-2} per minute, in accordance to IS 3495 (Part 1): 1992 protocol. The compression strength was calculated using the equation:

$$\text{Compressive strength (MPa)} = \frac{\text{Maximum load at failure (N)}}{\text{Average area of the bed faces (mm}^2\text{)}}$$

Water absorption

The water absorption tests were conducted in accordance with ASTM C67-07 method.Water absorption percentage was calculated using the equation:

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$$\text{Water absorption (\%)} = \frac{(\mathrm{W} - \mathrm{D})}{\mathrm{D}} X\ 100$$

where D is the dry weight of the sample and W is the weight of the sample after 24 hour soaking in water.

Bulk density

The bulk density of the hybrid geopolymeric composite samples was determined in accordance with ASTM C830-00 method. The average value was calculated from three samples. Bulk density was calculated using the equation:

$$\text{Bulk density}\ (\mathrm{g\ cm^{-3}}) = \frac{\mathrm{D}}{\mathrm{V}}$$

where D and V are the dry weight and volume of the sample respectively.

Dimensional stability

The linear shrinkage of the hybrid geopolymeric composite samples was determined in accordance with ASTM C356-10 method. Linear shrinkage was calculated using the equation:

$$\text{Linear shrinkage (\%)} = \frac{(\mathrm{L_1} - \mathrm{L_2})}{\mathrm{L_1}} X\ 100$$

where L_1 is average length, width or thickness of sample without soaking heat and L_2 is average length, width or thickness of sample after soaking heat.

Change in weight

The change in weight of hybrid geopolymeric composite was determined in accordance to ASTM C356-10 method and was calculated using equation:

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$$\text{Change in weight (\%)} = \frac{(W_1 - W_2)}{W_1} X\ 100$$

where W_1 is the weight of the sample before soaking heat and W_2 is the weight of sample after soaking heat.

Results and discussion

Raw materials properties and characterization

The FESEM micrographs obtained for fly ash and marble waste are shown in **Figure 2**. depicting their respective morphologies. Fly ash primarily consist of spherical particles with smooth surface. These smooth spherical aluminosilicate particles are formed due to thermochemical conversion of mineral particles during coal combustion. These aluminosilicate particles are also known as cenospheres (Nyale et al., 2013). The images also reveal an apparent wide size distribution with diameters of cenospheres varying from 0.9 µm to 40 µm. In stark contrast, the marble waste seems to have coarse aggregate with irregular shape and rough surface. Furthermore some of these aggregates further agglomerated to form even bigger particles. Like fly ash, marble waste also seems to have wide particle size distribution with average size varying between 5 µm to 115 µm.

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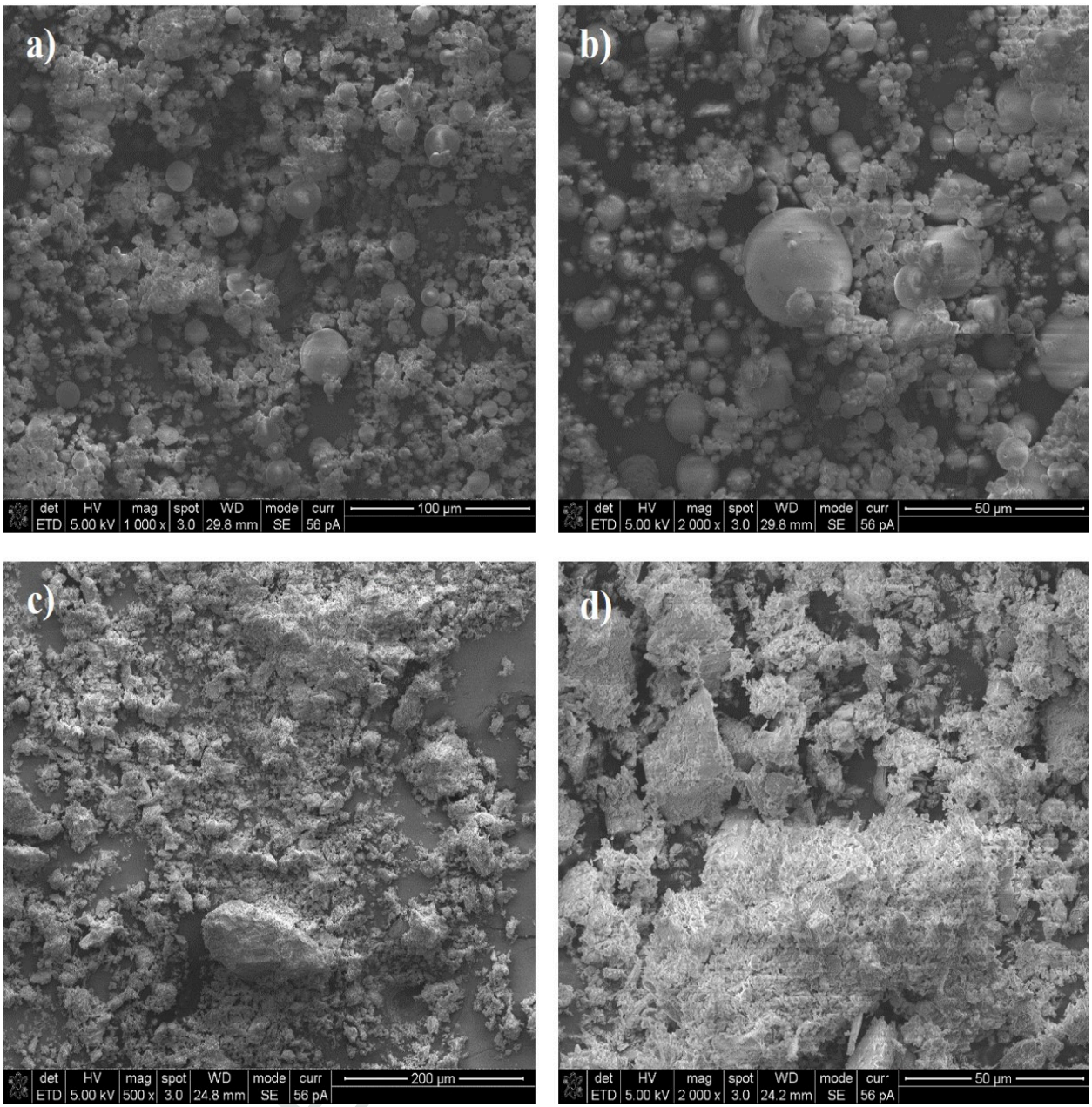

Figure 2. FESEM images obatined (a,b) fly ash and (c, d) marble waste.

The XRD spectra of the fly ash and marble waste are shown in **Figure 3**. The detailed analysis of studied fly ash diffractogram reveals the presence of mainly three crystalline mineral phases: quartz (SiO_2), mullite ($3Al_2O_32SiO_2$) and lime (CaO). The diffractogram of marble shows the presence of mainly calcite ($CaCO_3$), dolomite ($CaMg\ (CO_3)_2$) and quartz (SiO_2).

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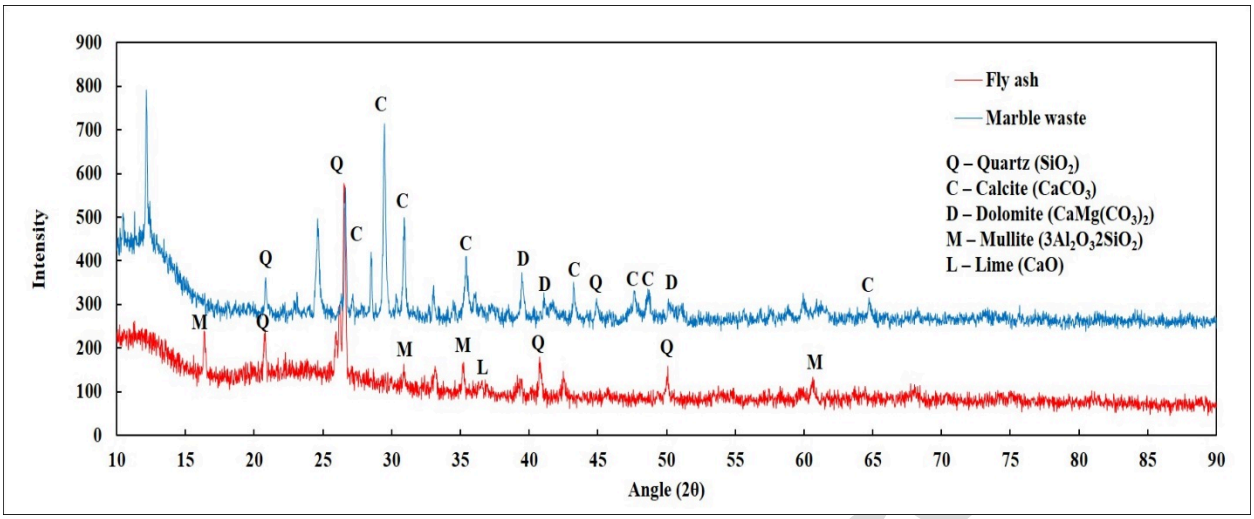

Figure 3. XRD diffractograms obtained for fly ash and marble waste.

The particle size distribution of the marble waste and fly ash is shown in **Figure 4**. The average particle size of fly ash, as can be observed, spanned over a large scale (0.7 – 310 µm). The size of major population of fly ash particles varied between 1 – 10 µm. The size values greater than 100 microns observed for fly ash are probably due to agglomeration of two or more particles, such particles were also observed in SEM images. The marble waste powder, on the other hand, showed two well separated size populations of particles. The first population size range spanned between 0.6 and 4.5 µm. The cumulative percentage of this population however was very low, less than 0.25%. The second population present in significantly high proportions spanned between 30 and 250 µm. The approximate size of particles having highest cumulative percentage in this population found to be 67.5 microns. The statistical values for diameter obtained for both marble waste powder and fly ash are given in **Table 1**.

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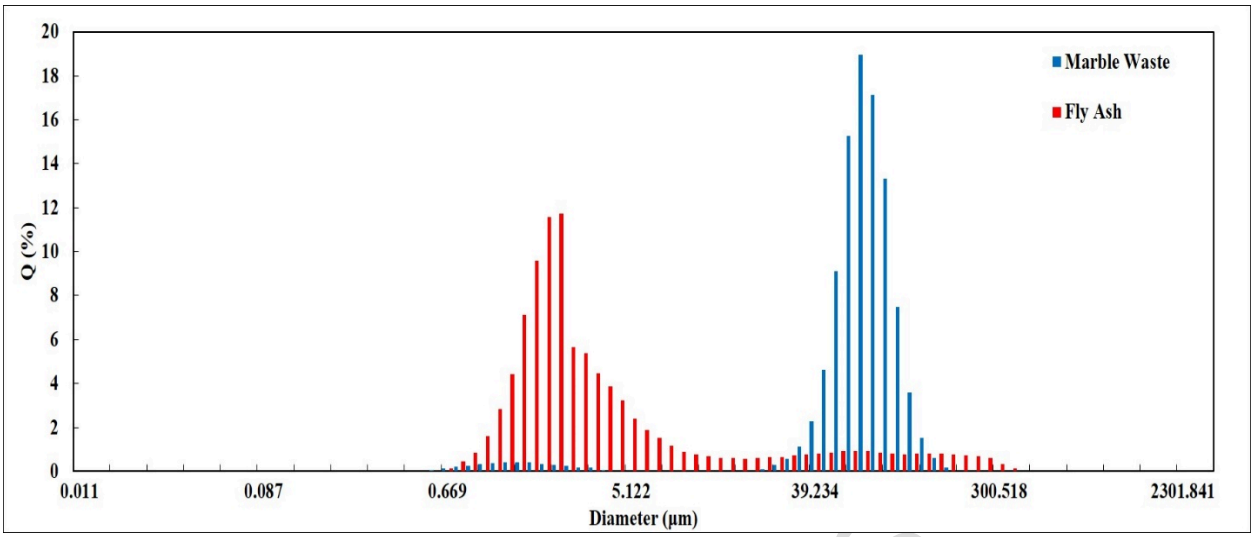

Figure 4. Particle size distribution of fly ash and marble waste.

In **Figure 5**, FTIR spectra obtained for marble waste and fly ash are presented. In case of fly ash, the bands at 776 cm^{-1}, 1031 cm^{-1} and 422 cm^{-1} represent the anti-symmetric stretching vibration of Si–O–Si, while the band at 422 cm^{-1} arise due to bending vibration of O-Si-O bonds. The band at 541 cm^{-1} represents the stretching vibration of Al–O bond. These four bands indicated the existence of mullite and quartz in fly ash (Criado et al., 2016; Ismail et al., 2014; Wang et al., 2019). In case of marble waste, the stretching bands at 1432 cm^{-1} and 876 cm^{-1} are assigned to C-O bond arising from calcium carbonate. An interesting aspect of this marble waste is the presence of strong bands at 985 cm^{-1}, 776 cm^{-1}, 641 cm^{-1} and 444 cm^{-1} (Chouhan et al., 2018; Kore and Vyas, 2016) that indicates significant presence of quartz in the system that can take part in geopolymerization reactions making marble waste as active filler.

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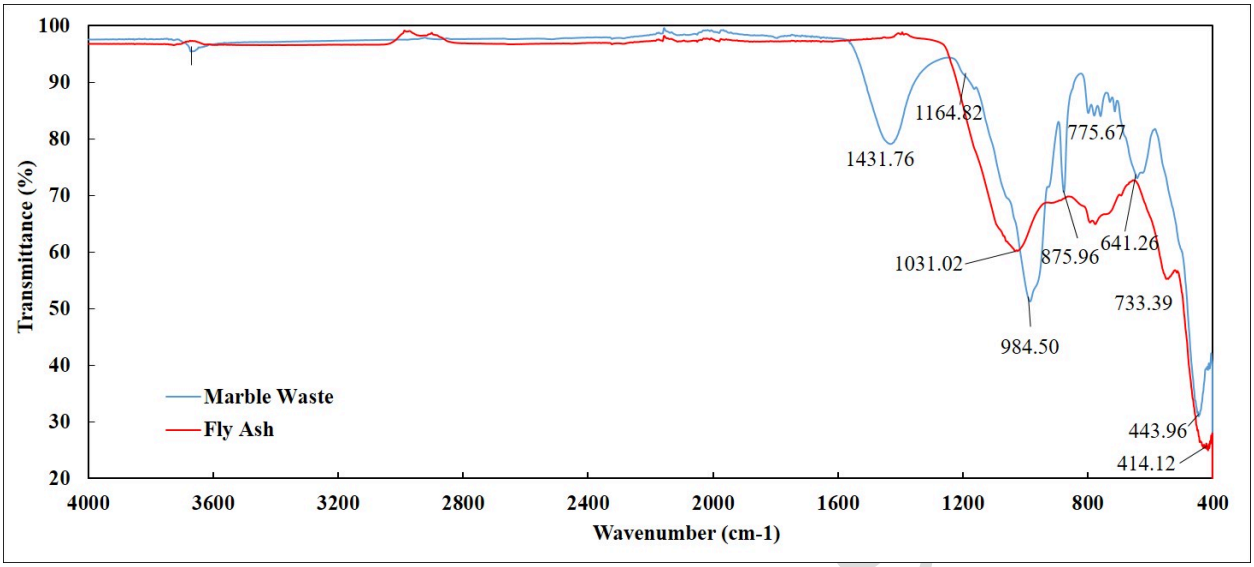

Figure 5. FTIR spectra of fly ash and marble waste.

Mechanical and physical properties of prepared hybrid geopolymer composite materials

Compressive strength

In construction material applications, compressive strength is one of the important parameter which is used to meet the engineering quality (Görhan and Şimşek, 2013). Therefore, the effect of marble powder on the compressive strength of prepared hybrid geopolymeric composite was determined and the mean values are shown in **Figure 6**. In the present case, the compressive strength of the geopolymer composite depends upon the strength of geopolymer gel and the interfacial bonding between geopolymer gel and marble waste particles. The results show that 7 days compressive strength for the bricks prepared at 4M, varied between 3.38 to 6.52 MPa, while for those at 2M varied between 1.82 to 4.61 MPa. For both cases (2M and 4M), compressive strength increased upto 60% marble waste content reaching 4.61 MPa and 6.52 MPa respectively. However, beyond 60% marble content, the strength gradually decreased reaching 4.43 MPa (4M)

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and 3.38 MPa (2M) at 80% marble waste content. The increase in compressive strength can be attributed to the presence of high amount of silicon dioxide (SiO_2) in marble waste as evidenced by XRF and FTIR analyses. This silica takes part in the reaction forming interfacial bonds between marble waste particles and fly ash matrix thereby increasing strength. The strong interfacial covalent bonding faciliates an effective distribution of applied load onto the geopolymer matrix. The dissolution of solid aluminosilicate source into silicate and aluminate monomers which then undergo further condensation reactions to produce geopolymer gel is the first and critical step in the geopolymerization process . The increase in calcium content has been reported to be involved in facilitating the dissolution step of aluminosilicate by raising the pH in local environments which in turn increases the extent of geopolymerization and thus geopolymer frame work (Chen et al., 2011; Duxson et al., 2007; Khale and Chaudhary, 2007; Panagiotopoulou et al., 2007; van Deventer et al., 2007). In secondary role, calcium has been observed to be incorporated into the geopolymer pore structure as a counter balancing cation instead of alkali cation which causes decrease in unit cell size of the geopolymer. Considering above with respect to the current study, we postulate that calcium ions emanating from marble waste play the same two important roles during geopolymerization. Probably for the very same reasons, despite high fly ash content (90%) low strength was observed due to low amount of calcium causing lower extent of dissolution (Lee and van Deventer, 2002; Mikuni et al., 2007; O'Connor et al., 2010; Temuujin et al., 2009; van Deventer et al., 2007; Yip et al., 2008). With increase in marble waste content, the amount of calcium increased while the total silica and alumina decreased reaching an optimum ratio (Si/Ca, Si/Al, Al/Ca) imparting maximum strength (Omar et al., 2012; Ulubeyli and Artir, 2015). Beyond 60% marble waste, the decrease in compressive strength may be attributed to the decrease in overall silica and alumina (contribution from fly ash) content in the system leading to reduced Si-

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O-Al bonds especially between marble waste particles and fly ash. The lower strength observed for hybrid geopolymeric composite samples prepared at low molarity (2M) can be attributed to lower quantity of NaOH used, which in turn led to lower extent of geopolymerization as well as crosslinking.

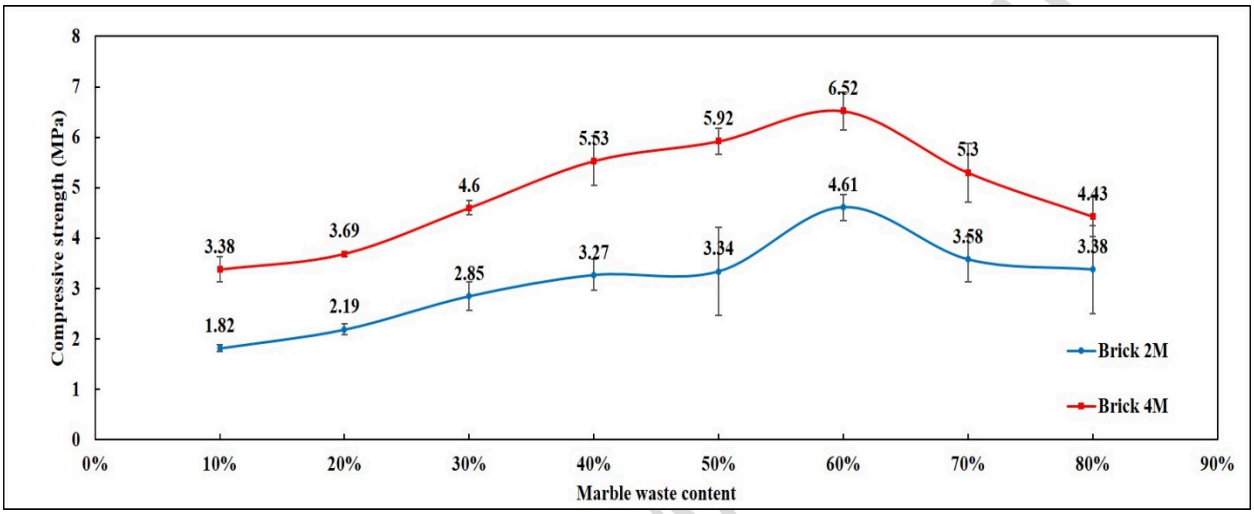

Figure 6. Compressive strength of hybrid geopolymeric composite samples prepared at different molarities and marble waste content.

According to national building code, the minimum strength for hybrid composite bricks used in partition wall should not be less than 3.5 MPa, while the Indian standard code IS 1077: 1992 stipulates that, the value should be between 3.5 and 35 MPa. Based on our results, it can be stated that the hybrid geopolymeric composite bricks made at both molarities satisfied the above criteria while utilizing a high amount of marble waste (60%).

Water absorption rate

The water absorption rate of a material including hybrid geopolymeric composite bricks depends on its chemical nature, structural morphology and pore volume. A high degree of

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geopolymerization in geopolymer bricks can lead to a denser (less porous) and less permeable matrix structure. The results of water absorption of prepared samples are shown in **Figure 7**.

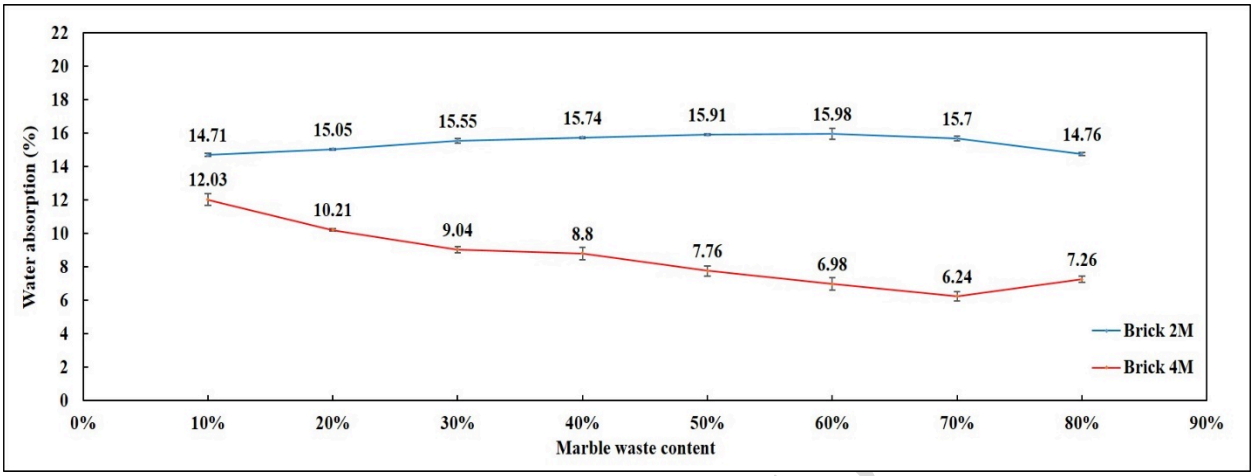

Figure 7. Water absorption percentage of hybrid geopolymeric composite samples prepared at different molarities and marble waste content.

The composites samples prepared at 2M showed a minimum water absorption of 14.71% while maximum of 15.98% at 10% and 60% marble waste content respectively. On the other hand, samples prepared at 4M showed a minimum water absorption of 6.24% while maximum of 12.03% at 70% and 10% marble waste content respectively. However, the corresponding compressive strength has increased from 1.82 MPa to 4.61 MPa respectively. In case of 4M, the absorption of water decreased considerably with the increase in marble waste content. Further, for a given marble content value, the bricks prepared at 2M exhibited higher water absorption as compared to 4M. In case of 2M bricks, the water absorption increases very slightly as the marble waste content increased, which may be due to higher porosity in the sample and due to lower bonding between marble waste and geopolymer gel. For 4M bricks, the absorption decreased as the marble waste increased, which may be due to high density and low porosity of sample and increased bonding between marble waste particles and geopolymer gel.

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Bulk density

The quality of hybrid geopolymeric composite bricks can be further assessed by their bulk densities. Usually the bulk density values of clay bricks lies in the range of 1.8 to 2.0 g cm^{-3} (Lin, 2006). Density of fly ash based geopolymeric bricks lie between 1.57 – 1.61 g cm^{-3} (Görhan and Kürklü, 2014). The bulk density values of brick samples containing different marble waste content are shown in **Figure 8**.

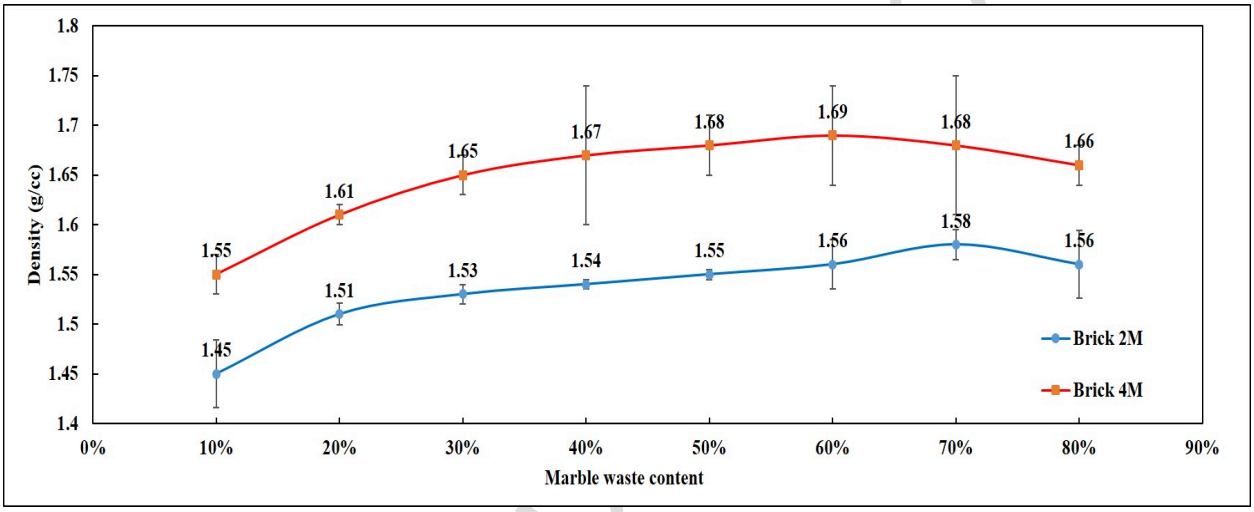

Figure 8. Bulk densities of hybrid composite hybrid geopolymeric composite samples prepared at different molarities and marble waste content.

The results indicate that increasing the content of marble waste increased the overall bulk density of the bricks. This is non-surprising given the fact that the density of marble waste is 2.69 g cm^{-3}. It can be further observed that in both cases (2M and 4M) the density increases upto 50% of marble content after which it attains a stable plateau. Compairing the composite bricks prepared at two molarities, an increase of 6 to 8% in density was observed from 2M to 4M. This is an expected result as increasing the amount of NaOH will increase the extent of geopolymerization as well as the formation of bonds between marble waste particles and the geopolymer matrix. The reaction

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between the matrix and marble particles can be attributed to latter's binding property arising due to hydration of calcite during brick preparation. The result is an overall increase in the crosslink density leading to reduction in pore size and increase in density of the material.

Dimensional stability

The dimensional stability aspect of a geopolymer composite brick is an another parameter to define its quality often reported in terms of shrinkage. **Figure 9** shows the amount of shrinkage observed in the bricks after being kept at 120 °C for 24 hours.

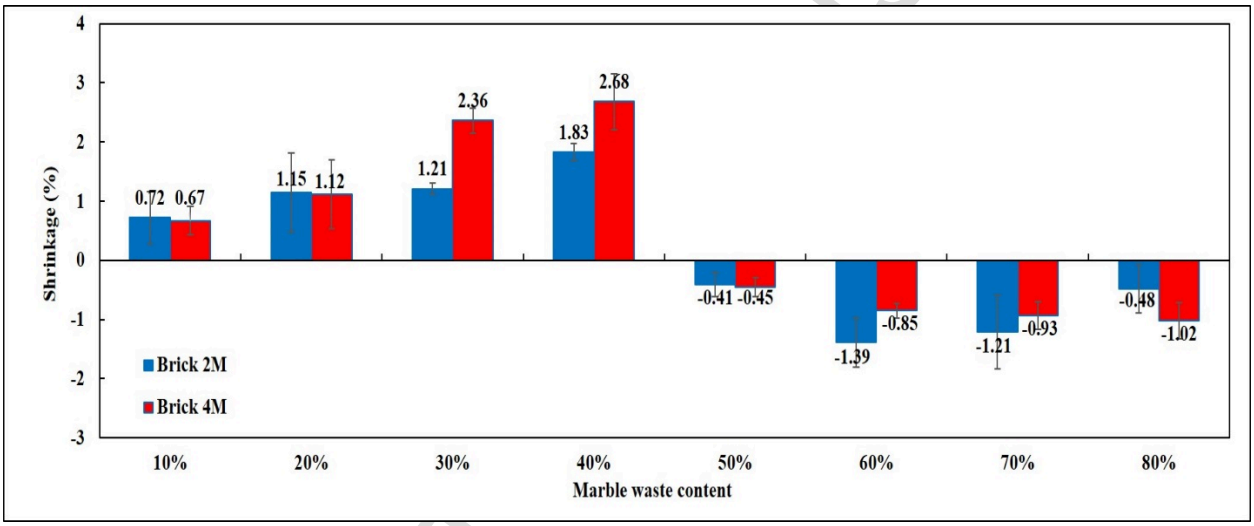

Figure 9. Dimensional stability of hybrid geopolymeric composite samples prepared at different molarities and marble waste content.

A positive shrinkage value indicates a contraction in the dimensions of the material as per the equation defined in the experimental section. The results indicate that upto 40% marble waste content, a contraction in the dimensions of the brick samples occurred (1.83% for 2M and 2.68% for 4M respectively). Samples prepared at 4M exhibited higher contraction as compared to those prepared at 2M. Further increasing the amount of marble content resulted in negative shrinkage values indicating an expansion in the overall dimension of the bricks. At 80 % marble waste

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content, samples prepared at 2M and 4M showed an expansion of 0.48% and 1.02% respectively. Overall the results indicate a very low degree of dimensional change (contraction and expansion) occurence in hybrid geopolymeric composite samples irrespective of molarity change as well as increase in marble waste content. It can be interpolated that at 50 % marble waste content, the hybrid geopolymeric composite sample should have minimal or near zero dimensional change in terms of expansion or contraction. We hypothesise that the contraction observed upto 40 % marble waste content is the result of the shrinkage caused by the release of pore water from the gel, also known as 'capillary strain' exceeding the inherent thermal expansion factor of the main fly ash geopolymer matrix. However, at higher marble content, this capillary strain is much less pronounced due to lower water binding capacity of marble particles as well as high degree of crosslinking despite a reduction in proportion of main aluminosilicate gel.

Weight loss on ignition of hybrid geopolymeric composites

Weight loss occurence in monolithic materials such as hybrid geopolymeric composite brick is related to their densification and development of pores in them. The weight loss values determined for the brick samples after soaking heat at 120 °C for 24 hours are shown in **Figure 10**. It can be observed that in case of both molarities, the weight loss increased upto 40 % marble waste content after which it attain a stable plateau irrespective of increase in content of marble waste. A maximum of 4.12 % and 7.34 % weight loss was recorded at 40% marble waste containing brick sample prepared at 2M and 4M molarities respectively. Compairing the samples at two molarities, it can be stated that samples at 4M experienced more weight loss, as high as 231% at 10% marble waste content. The observed greater weight loss can be attributed to higher amount of geopolymer gel formation at higher molarity that can hold higher amount of water. The weight loss stabilization

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beyond 40% marble waste content is attained probably due to increasing amount of marble particles having lower water binding capacity as compare to alumina silicate geopolymer gel that is now reduced as minority component.

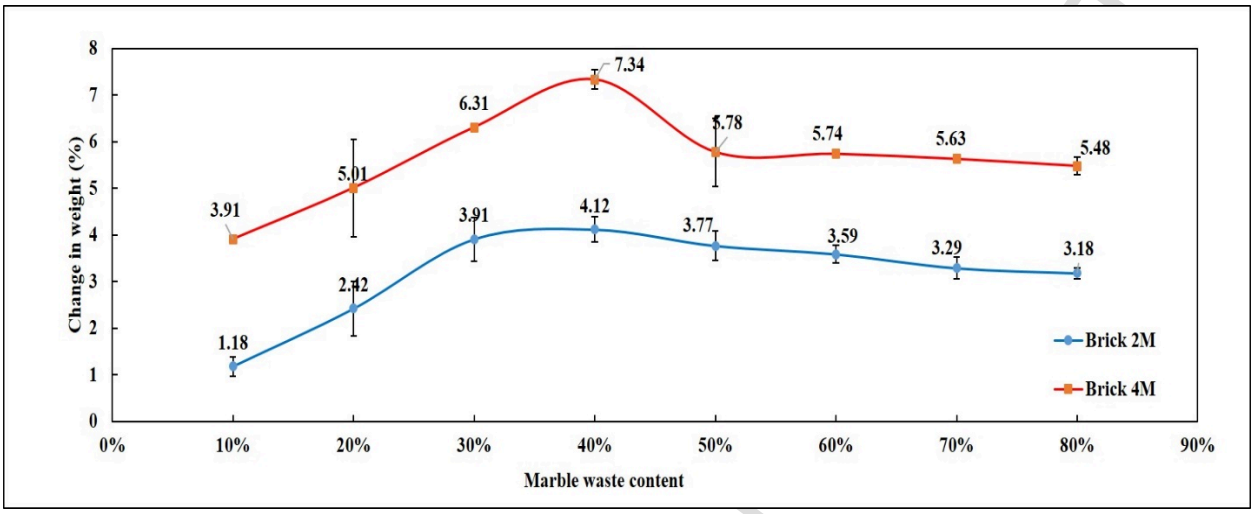

Figure 10. Water loss percentage of hybrid geopolymeric composite samples prepared at different molarities and marble waste content.

XRD analysis

X- ray diffraction pattern for fly ash, marble waste, 2M and 4M hybrid geopolymeric composite bricks (60% marble waste) are shown in **Figure 11**. In the prepared hybrid geopolymeric composite, their is no indication for the formation of new crystalline phases. In both the cases (2M and 4M) diffractogram showed the presence of mainly quartz and calcite crystalline mineral phases, coming from fly ash and marble waste respectively. In marble waste, peaks for calcite & dolomite can be observed which are also the major constituents. In fly ash, the foremost constituents appears to be quartz as indicated by crystalline peak. It can be observed from the diffractograms of prepared hybrid geopolymeric composites (2M & 4M) that the peaks for calcite & dolomite have noticeably reduced intensity indicating their consumption in the geopolymerization process.

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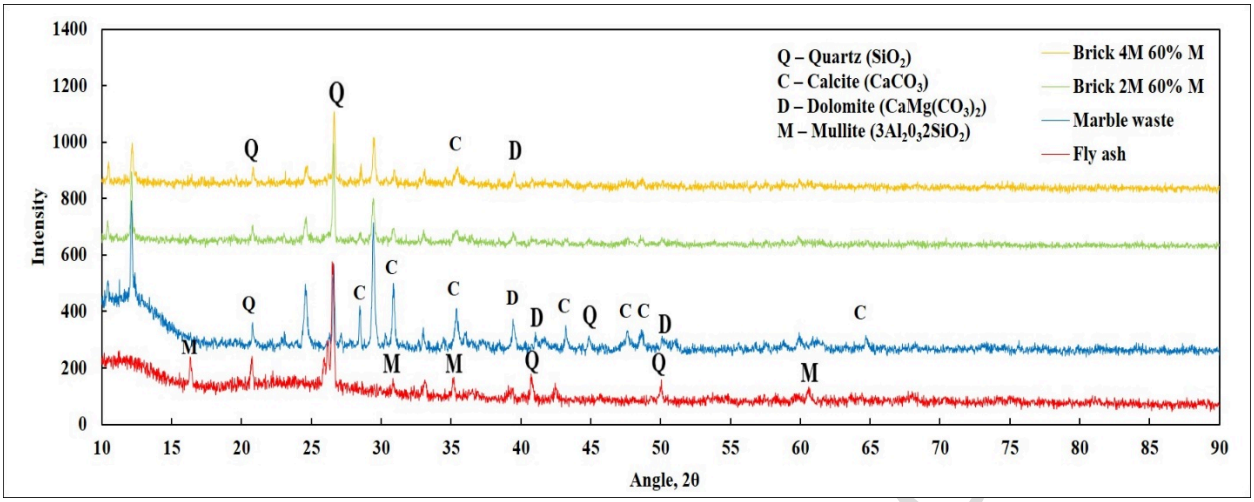

Figure 11. XRD diffractograms obtained for hybrid geopolymeric composite samples prepared at different molarities and 60% marble waste content.

Thermogravimetric analysis

The thermal decomposition curves obtained for marble waste and hybrid geopolymeric composite samples prepared at 2M and 4M, at 60% marble waste content respectively are shown in **Figure 12**. In case of marble waste powder, an approximate 20% single step weight loss was observed. This loss pertains to the decomposition of calcium carbonate starting at 550 ºC and ending at 800 ºC. This decomposition involves the release of CO_2 leaving behind calcium oxide as final product (Gatta et al., 2014). The two samples exhibited first decomposition between 40 to 100 °C which can be attributed to the loss of volatile organic compounds and water. The second decomposition occurring at 175 °C is due to the loss of physically absorbed water molecules. It can also be observed that the 4M sample reported a higher weight loss arising due to higher amount of absorbed water present in it. The third decomposition starts at 400 °C which is 100 °C less than that for marble waste (550 °C). This decomposition (400 to 600 °C) is due to the dehydroxilation of the aluminosilicate frame work in the brick samples. The fourth decomposition between 650 to

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800 °C can be assigned due to the complete decomposition of calcite from marble waste. **Table 4** shows onset, endset temperatures and weight loss % obtained for marble waste and hybrid geopolymer composite samples.

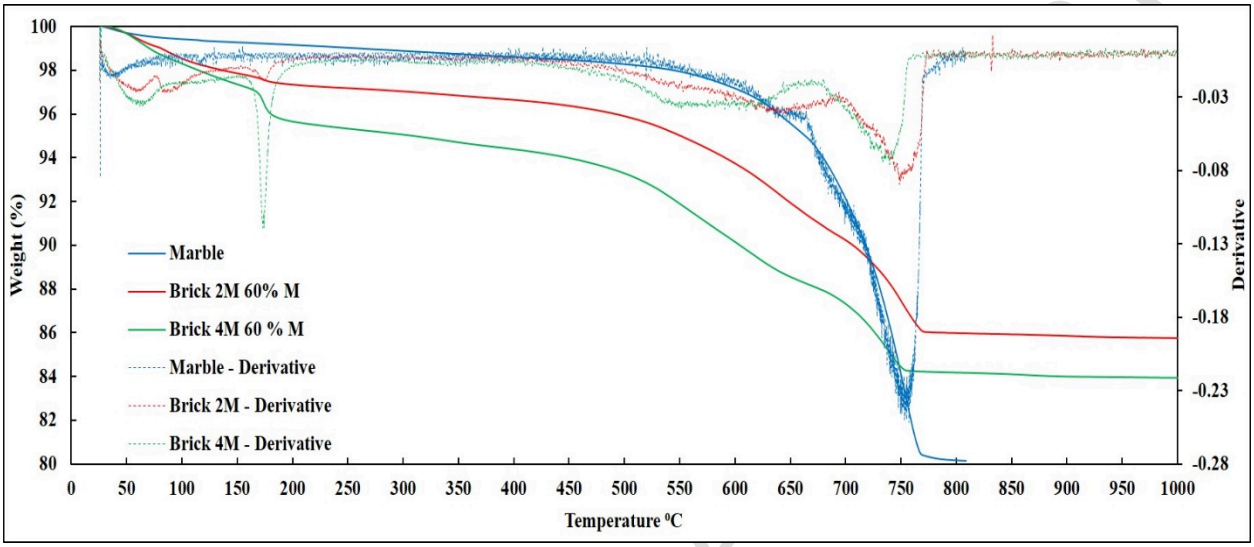

Figure 12. TGA thermal decomposition curves obtained for hybrid geopolymeric composite samples prepared at different molarities and 60% marble waste content.

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Table 4. Onset, endset temperatures and weight loss % obtained for marble waste and geopolymer composite.

Sample	Onset (°C)	Endset (°C)	Weight loss (%)
Marble waste	648.83	755.37	18.20
Brick 2M 60% M	497.42	761.51	10.57
Brick 4M 60% M	483.27	745.27	9.86

Conclusion

In this work, hybrid fly ash matrix based geopolymer composite bricks were prepared via extruson technique using fly ash and marble waste. The amount of marble waste was varied from 10 to 80 % and fly ash content varied from 20 to 90% by weight in the formulation. The results indicated that higher compressive strength and lower water absorption was achieved at higher molarity of NaOH (4M) along with the addition of marble waste. Maximum compressive strength was achieved at 60 % marble waste content; 6.52 MPa at 4 molarity and 4.61 MPa at 2 molarity of NaOH respctively. The water absorption capacity of hybrid composite was found to be lower with increase in marble waste at 4 molarity of NaOH. The minimum water absorption capacity of hybrid composite bricks was 6.24 % with 4 molarity of NaOH. The increase in percentage of marble waste content increased the shrinkage. The shrinkage of hybrid bricks varied between 2.68 and -1.39% and the achieved shrinkage is within the permissible limits as recommend in BIS: 4139- 1989 for use in building applications with the use of 60% marble waste with 40% fly ash, which was found

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to be an intermediate condition.. The increase in compressive strength with the inclusion of marble waste is attributed to the presence of significant amount of silica causing interfacial bonding between fly ash matrix and marble grains while calcium facilitate dissolution of aluminosilicates required for geopolymerization. The extrusion technique in conjunction with geopolymerization process saves a significant amount of time as compared to traditional clay processes. Adopting such process in industrial scale can drastically reduce production cost and increase output due to reduction in composite formation time, energy and manpower. The finding of the present study has shown a potential solution, introducing a new class of high strength composite brick followed by effective utilization of fly ash and marble waste as a major resource materials. Realisation of this research finding in a commercial scale is expected to be major intervention for waste recycling and safe environmental management.

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Disclosure statement

No potential conflict of interest was reported by the author.

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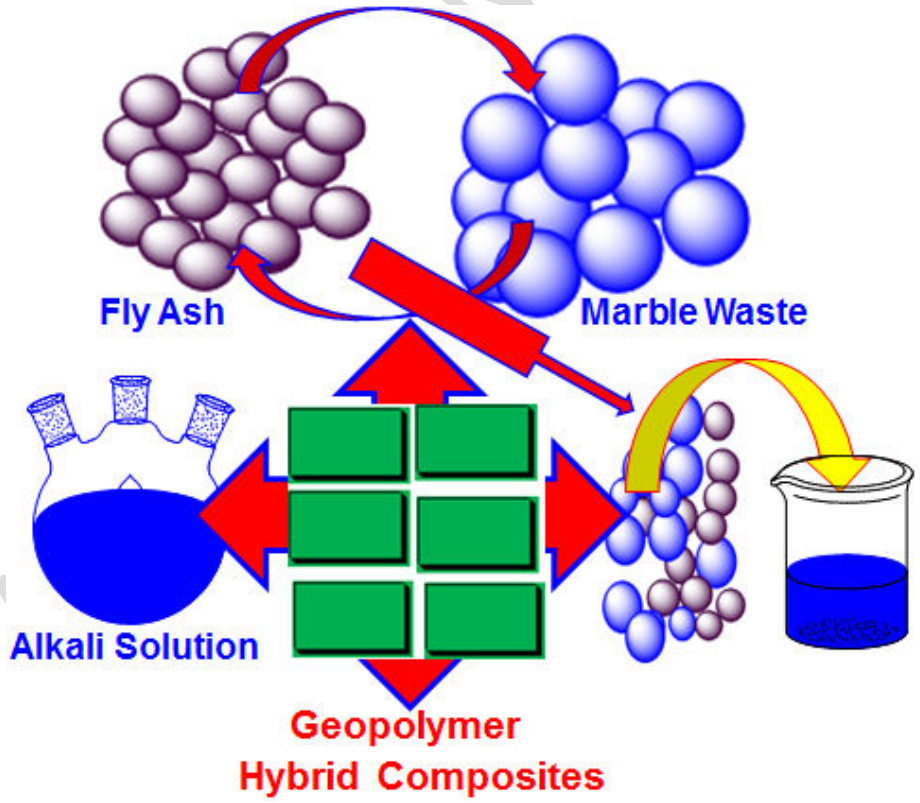
Graphical Abstract



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