

Phase and microstructure evolution during hydrothermal solidification of clay–quartz mixture with marble dust source of reactive lime

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Abstract

Marble dust (200 μm size), air and water polluting waste, generated by the marble cutting industries has been used as cheap source of lime for hydrothermal solidification of clay–quartz mixtures at different saturated steam pressure (0.525–1.225 MPa). Marble dust was calcined at two different temperatures (900 and 1000 °C) and then added to the clay–quartz mixture, with clay/(clay + quartz) ratio 0.9, at two different amounts. The hydrothermally solidified samples were characterized by bulk density, apparent porosity, flexural strength, porosimetric study, phase and microstructural analysis and the results were compared against similarly treated chemical grade CaCO_3 containing compositions. Tobermorite [$\text{Ca}_5(\text{Si}_6\text{O}_{18}\text{H}_2)\cdot 4\text{H}_2\text{O}$] and hydrogarnet [$\text{Ca}_3\text{Al}_2(\text{SiO}_4)(\text{OH})_8$] were the major phases formed in the treated samples, which are responsible for the strength development. Microstructural study supports the generation of these hydrated phases. Porosimetric study reveals that higher exposed area of the chemical grade CaCO_3 containing composition results higher extent of hydrothermal reaction and higher strength. Though marble dust containing compositions showed relatively lower strength values, the combined properties of the hydrated products are suitable as new building material where such mesopore containing products with inherent micron range pore size distribution are important parameters.

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1. Introduction

Process of hydrothermal treatment for strength development in lime bearing systems is known for long but research on hydrothermal reactions and solidification behavior in the system $\text{CaO-SiO}_2\text{-H}_2\text{O}$ system has started late^{1–4} and most of the works were based on high purity raw materials. Now as the acquisition of purer variety of raw materials is becoming increasingly difficult due to gradual depletion of good quality earthy minerals and higher cost, the need to recycle and reuse of various waste materials is felt. Again utilization of various waste materials for large volume consuming products is the demand of the society to clean up the environment.

Research^{5–10} on the subject of hydrothermally treated products was based on the synthesis of typical calcium silicate hydrate (C–S–H) materials (namely, tobermorite, xonotolite, etc.). Effects of addition of some impurities in the pure system were also studied in many works. Kondo et al.⁸ studied the effect of clayey materials like kaolinite, sericite, etc. Asaga et al.¹¹ have described the effects of alkalis and starting raw materials on the quartz–lime system. Mitsuda and his co-workers studied^{12,13} the effect of substitution of silicon ion by aluminium ion in the formed tobermorite of the $\text{CaO-SiO}_2\text{-H}_2\text{O}$ system. Studying on the crystal chemistry of calcium silicate hydrates Kalousek reported¹⁴ the formation of hydrogarnet for ratios of $\text{Al}/(\text{Si} + \text{Al})$ in the range of 0.12–0.50 when kaolinite is used as the source of aluminium. In a detailed study, Laosa Thompsor and Grutzeck¹⁵ described the effects of starting materials, composition and hydrothermal treatment time and temperature on the structure and composition of re-

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action products like calcium silicate hydrates, tobermorite, hydrogarnet, etc. for the $\text{CaO-SiO}_2\text{-Al}_2\text{O}_3\text{-H}_2\text{O}$ system.

Ishida¹⁶ described the development of hydrothermally solidified (at 150 °C) lime containing earth ceramics tiles, consuming only about one-sixth of energy in comparison to presently produced fired ceramic tiles. As reported, use of such hydrothermally solidified tiles will help to maintain sustainable development in construction of a recirculation based society as against the consumption based social and economic system and also can reduce the energy consumption by about 19% for individual dwelling units. Maenami et al.¹⁷ studied the mechanism of strength development in hydrothermally solidified kaolinite–quartz–lime systems with Al/(Si + Al) atomic ratio 0–0.5 and Ca/(Si + Al) ratio between 0.23 and 0.25. They reported strength development due to formation of tobermorite [$\text{Ca}_5(\text{Si}_6\text{O}_{18}\text{H}_2)\cdot 4\text{H}_2\text{O}$] for compositions with Al/(Si + Al) less than 0.05 and due to the formation of mesopore on the generation of reaction product hydrogarnet [$\text{Ca}_3\text{Al}_2(\text{SiO}_4)(\text{OH})_8$] for compositions with Al/(Si + Al) greater than 0.05. Ishida¹⁸ reported highest strength obtained for Al/(Si + Al) ratio <0.05 with hydrothermal treatment period of 2 h. Filling of pores by tobermorite results densification and strength improvement but prolong treatment caused pore coalescence and strength degradation. For ratios >0.24, improvement in strength was due to the formation of hydrogarnet phases without reducing the total pore volume or pore size. He also described that in situ formation and dispersion of ultrafine hydrogarnet particles from surface of kaolinite towards interior, results bonding of kaolinite and improves strength.

Most of the above research works on the hydrothermally treated products are based on purer materials. To make such products commercially viable, use of wastes as cheaper raw materials is important. But, only a few works are available that uses such waste materials. Use of ceramic tiles wastes for hydrothermally treated products is available in literature.^{19,20} Watanabe et al.²¹ studied the feasibility of low grade silica sand (67% purity) for hydrothermal solidification at 140–180 °C with 20% lime content. They reported hydrogarnet and calcium silicate hydrates as initial reaction products whose amount was reduced with the progress of reaction and amount of tobermorite was increased. Strength was reported to be dependent on the amount of reaction products and strength increases with increasing temperature and time of hydrothermal treatment.

Marble is one of the most popular aesthetic rock used in huge quantities and is commonly available in nature. Many countries like China, Italy, Spain, Greece, India, Portugal, etc. are making a good worldwide business out of it. But marble slurry, generated as a by-product during cutting of marble stones is a serious threat to the marble generating industries. Total waste generation from mining to finished product is about 50% of mineral mined and the dried slurry product is quiet fine. Ninety percent of the particles are below 200 μm . Air borne fine marble dust causes dust/air pollution, occupies vast fertile land, affects the land productivity, causes

occupational health problem and can block flow regime of aquifer thus affecting underground water availability.²² This marble dust is planned to use as the active source of lime for hydrothermal treatment of clay–quartz mixture in the present study.

The present investigation describes a study of hydrothermal treatment of clay–quartz–lime mixture with clay/(clay + quartz) weight ratio 0.9 under 0.525–1.225 MPa saturated steam pressure. This particular clay/(clay + quartz) ratio of 0.9 was selected from the results of an earlier study of the present authors where chemical grade calcium carbonate was used as a source of CaO for hydrothermal treatment of clay–quartz mixture.^{23,24} Product tiles were characterized with respect to their physico-mechanical, porosimetric, phase and microstructural properties and the results were compared with the one of the similarly treated chemical grade CaCO_3 incorporated clay–quartz mixture.

2. Experimental

The raw materials used in the study are quartz powder (West Bengal, India), clay (Rajmahal, Bihar, India), marble dust (Bihar, India) and chemical grade calcium carbonate (S.D. Fines Chem Ltd., India). First the raw materials were chemically analyzed (process described later) and tested for phases present by X-ray diffraction method. Then chemical grade CaCO_3 was calcined at 900 °C for 1 h soaking time and marble dust was calcined at 900 and 1000 °C with 1 h soaking time. Calcined marble dust was again characterized for different properties. Calcined lime obtained from both the processes was then added to the clay–quartz mixture to prepare five batches as provided in Table 1.

All these batches were slaked with excess water to complete the slaking of lime. Slaked mixture was air dried (60% relative humidity at a temperature of 30 °C) for 2 days and then oven dried at 110 ± 10 °C for 1 day. Dried powders were loosely de-agglomerated and then uniaxially pressed at 50 MPa specific pressure with 6–8% moisture addition to obtain bars of dimension 60 mm \times 6 mm \times 6 mm. Bars were then hydrothermally treated under saturated steam pressure in an autoclave. Saturated steam pressure was varied from 0.525 to 1.225 MPa with 2 h holding time. Autoclaved products were then air dried for 1 day (60% relative humidity at a temperature of 30 °C) and oven dried at 110 ± 10 °C for 1 day. Dried bars were then tested for bulk density, apparent porosity and flexural strength. The results reported here are the average of six samples with a standard deviation of 0.65–0.70.

Composition showing better characteristics was further characterized for phase analysis, microstructural evolution and mercury intrusion porosimetry, up to 420 MPa (60,000 psi) mercury pressure.

For chemical analysis gravimetric method was utilized to determine SiO_2 and Al_2O_3 , whereas Fe_2O_3 , CaO and MgO were estimated volumetrically.²⁵ Alkalis were determined by

Table 1
Batch composition (wt.%)

Batch	Clay	Quartz	Marble dust source of lime calcined at		Chemical grade CaCO ₃ source of lime calcined at 900 °C
			900 °C	1000 °C	
D	74.4	8.2	–	–	17.5
D1	74.4	8.2	17.5	–	–
D2	74.4	8.2	–	17.5	–
D3	70.85	7.8	21.4	–	–
D4	70.85	7.8	–	21.4	–

flame photometry and loss on ignition test was carried out on ignition at 1000 °C for 1 h. Phase analysis was done by X-ray diffraction method (Phillips make X-ray diffractometer, model PW 1730) using Cu-K α radiation at a scanning speed of 2°/min in the diffraction range of 10–70°. Calcination of lime source was done in an electrically heated programmable furnace. Pressing was done in a hydraulic press (make Fred S. Carver) of 25 ton capacity. Hydrothermal treatment was done in an autoclave (make Vikram Scientific Instruments) with 20 l capacity. Bulk density and apparent porosity were determined by conventional liquid displacement method using Archimede's principle in xylene medium. Non-aqueous medium was selected to avoid any rapid hydration of unhydrated lime component, may be present in the body. Flexural strength was measured as 3-point bending strength using a universal testing machine (make Instron, model 5500R) for hydro-thermally treated samples of size 60 mm \times 6 mm \times 6 mm (available mold size). Microstructural analysis was done on the fractured surface of the samples in a scanning electron microscope (make Leica model S 430i). Porosimetric study was done in a mercury intrusion porosimeter (make Quantachrome Instruments, USA). The pore tortuosity, pore size, volume of intrusion, etc. data of the samples were automatically measured and calculated by the equipment with the help of software developed by Quantachrome Instruments, USA.

3. Results and discussion

3.1. Raw materials

Chemical analyses of the starting materials are provided in Table 2. Quartz powder is more than 98% pure with only a

Table 2
Chemical analysis, as oxide content in weight percent, of the raw materials

	Quartz fines	Clay	Chemical grade CaCO ₃	Marble dust
SiO ₂	98.11	48.87	–	25.38
Al ₂ O ₃	0.41	34.39	–	3.71
Fe ₂ O ₃	0.22	0.87	–	1.26
TiO ₂	Trace	0.93	–	1.73
CaO	0.68	0.42	55.67	36.44
MgO	Trace	Trace	–	6.99
Alkalis	0.22	0.33	–	2.96
LOI	0.19	13.83	43.67	21.12

Table 3
Some details of the calcined (1000 °C) marble dust

Oxide component	Weight percent
Chemical analysis	
SiO ₂	31.95
Al ₂ O ₃	5.12
Fe ₂ O ₃	2.07
TiO ₂	1.47
CaO	45.88
MgO	8.69
Alkalis	3.66
Physical properties	
Average particle size (μ m)	75
True specific gravity	3.02

little lime, alumina, iron and alkali impurities. Clay contains little excess silica and lime, iron, titania and alkalis as impurities. Chemical grade calcium carbonate is about 99% pure. Marble dust used in the study is found to be highly impure and contains very high amount of silica. Source of marble is associated with source of calcium silicate (wollastonite) containing minerals, which contaminates the lime source. High silica containing lime source, as found in Bihar, India,²⁶ is a waste material being remained unused; planned to use in the study where both lime and silica are required. Some details of the calcined marble dust is provided in Table 3.

X-ray diffraction patterns of the starting materials are provided in Figs. 1–3. Quartz powder (Fig. 1) is found not to be contaminated with other minerals. Clay (Fig. 2) is found to contain little amount of free quartz, which supports the presence of excess silica as found in chemical analysis. Marble dust powder (Fig. 3) mainly consists of calcite (CaCO₃) and also contain some silicate phases namely wollastonite

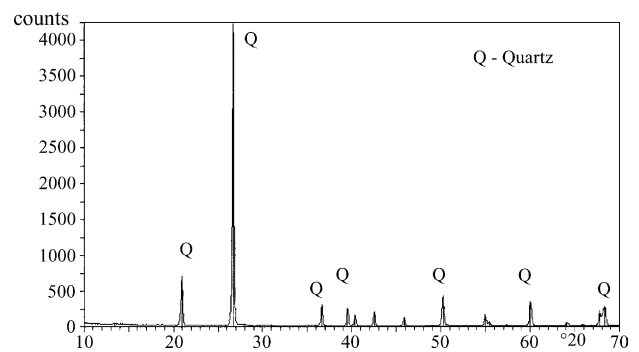


Fig. 1. X-ray diffraction pattern of quartz.

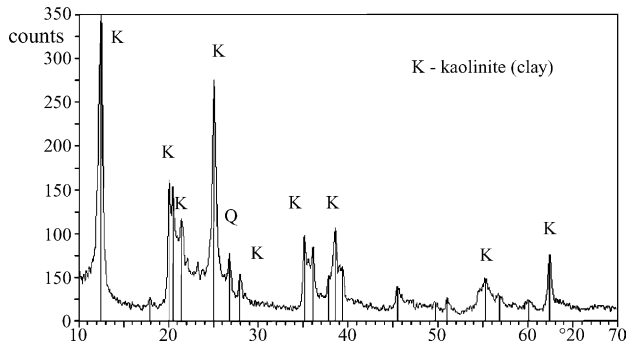


Fig. 2. X-ray diffraction pattern of clay.

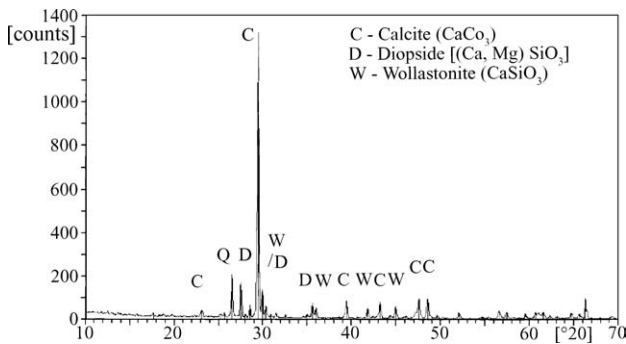


Fig. 3. X-ray diffraction pattern of marble dust.

(CaSiO_3) and diopside $[(\text{Ca}, \text{Mg})\text{SiO}_3]$. Little amount of free quartz is also found. This phase analysis confirms the presence of silica in the marble dust and also justifies, the presence of silica in the marble dust and also justifies, the presence of MgO . Thermogravimetric analysis (TGA) and differential thermal analysis (DTA) of marble dust up to 1000°C (Fig. 4) marks only a sharp endothermic peak at 868°C and loss in weight also corresponds to this temperature, an amount of about 21.4%. This TGA–DTA plot confirms the decomposition and loss of calcium carbonate and the amount of loss is in good agreement with the loss obtained in chemical analysis.

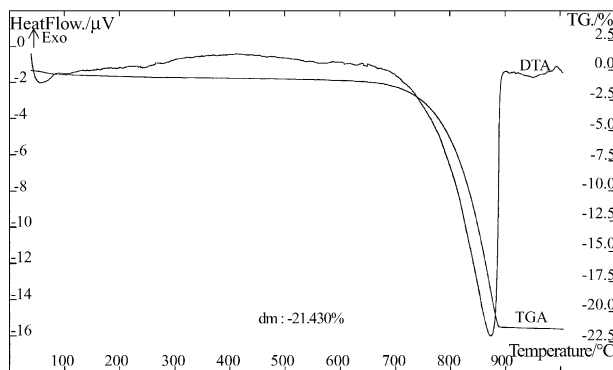


Fig. 4. Differential thermal analysis (DTA) and thermogravimetric analysis (TGA) plot of marble dust.

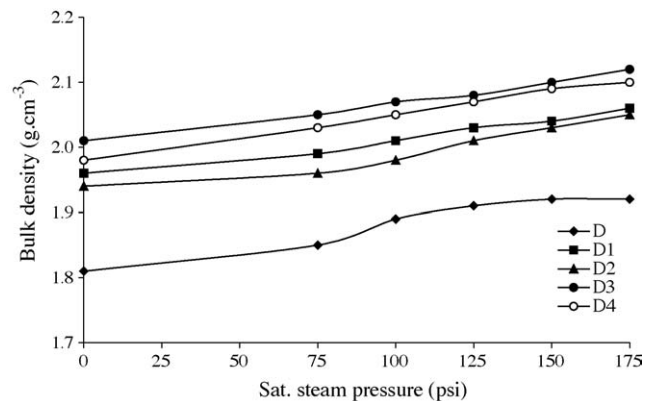


Fig. 5. Variation in bulk density of different batches with saturated steam pressure.

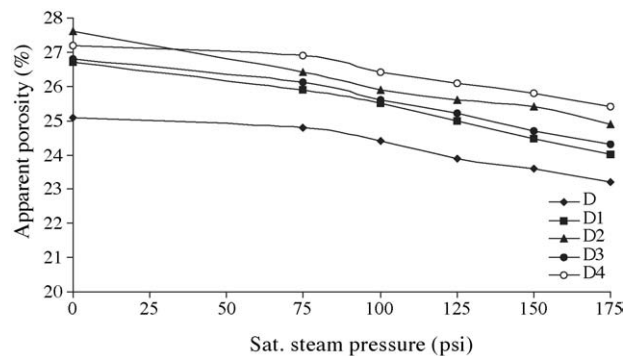


Fig. 6. Variation in apparent porosity of different batches with saturated steam pressure.

3.2. Characteristics of hydrothermally treated samples

3.2.1. Density and porosity

A general trend of increasing bulk density with increasing saturated steam pressure was observed for all the batches due to better compaction at higher pressure (Fig. 5). The density values are much lower in D batch where chemical grade lime source was used. This may be due to formation of higher extent of hydrated phases (having relatively lower density) due to higher reactivity of lime, as confirmed by phase analysis (Fig. 8) and microstructure (Fig. 11). Again higher amount of marble dust resulted higher density. Calcination at 1000°C showed relatively lower density value than the batches with marble dust calcined at 900°C . Calcined marble dust has a higher density than the clay based material and at higher amount (lesser clay content) results higher density. Again decomposition of marble dust occurs at 868°C and higher temperature calcinations causes reduced reactivity of marble dust and agglomeration, which adversely affects the compaction behavior resulting lower density. Apparent porosity plot (Fig. 6) does not reveal much. However, lower density containing batches with marble dust calcined at 1000°C showed higher porosity values. But D batch, with chemical grade calcium carbonate as the source of lime, has the lowest porosity (as well as the lowest density). This may

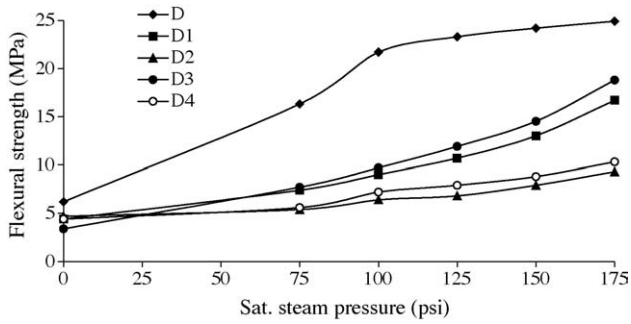


Fig. 7. Variation in flexural strength of different batches in relation to saturated steam pressure.

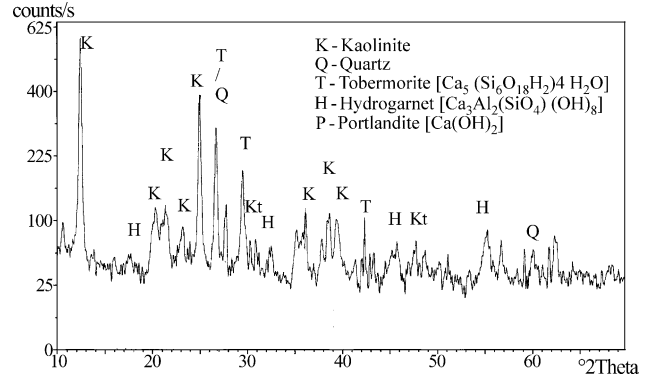


Fig. 9. X-ray diffraction pattern of the D1 batch, hydrothermally treated at 150 °C.

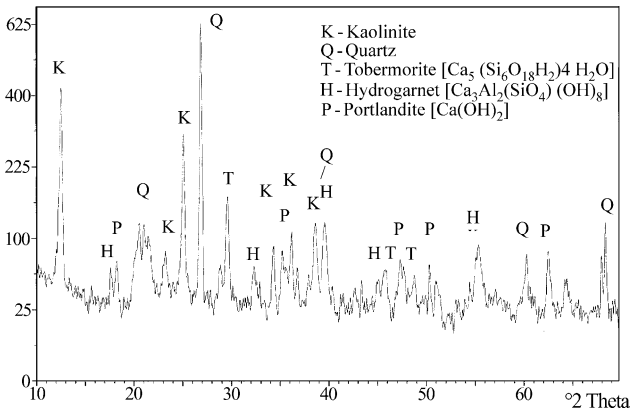


Fig. 8. X-ray diffraction pattern of the D batch, hydrothermally treated at 150 °C.

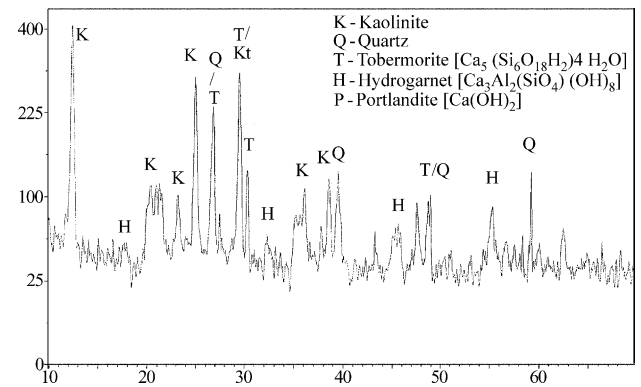


Fig. 10. X-ray diffraction pattern of the D3 batch, hydrothermally treated at 150 °C.

be related with greater formation of hydrated phases due to more reactive pure lime source and filling up of the porosities (inter-particle free space) during the hydrothermal treatment.

3.2.2. Flexural strength

Batch with chemical grade lime source (D) showed much higher strength values than the marble dust containing batches (Fig. 7). Greater extent of hydrated phase for-

mation for this batch is the reason for improved strength characteristics. A general trend of increasing strength values with increasing pressure of hydrothermal treatment is observed for all the batches. Among the marble dust containing batches, calcination temperature of 900 °C resulted much better strength values and higher lime containing compositions also showed higher strength. Calcination of 1000 °C for marble dust resulted reduced reactivity and agglomera-

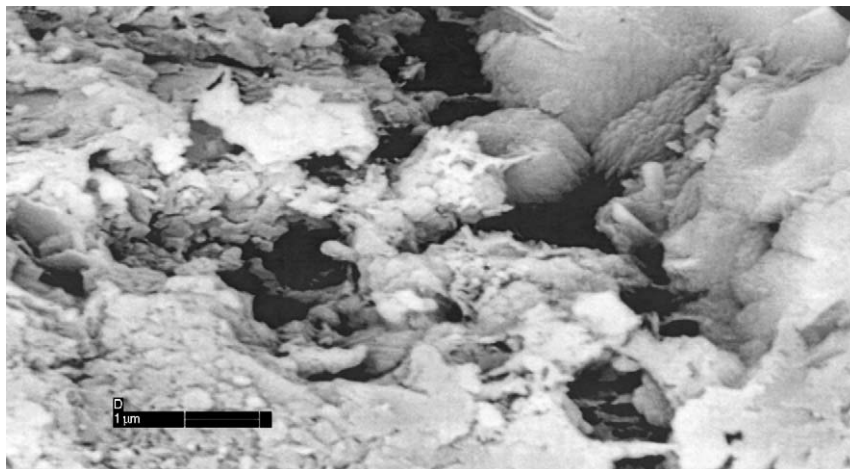


Fig. 11. Scanning electron photomicrograph of the unhydrated D batch.

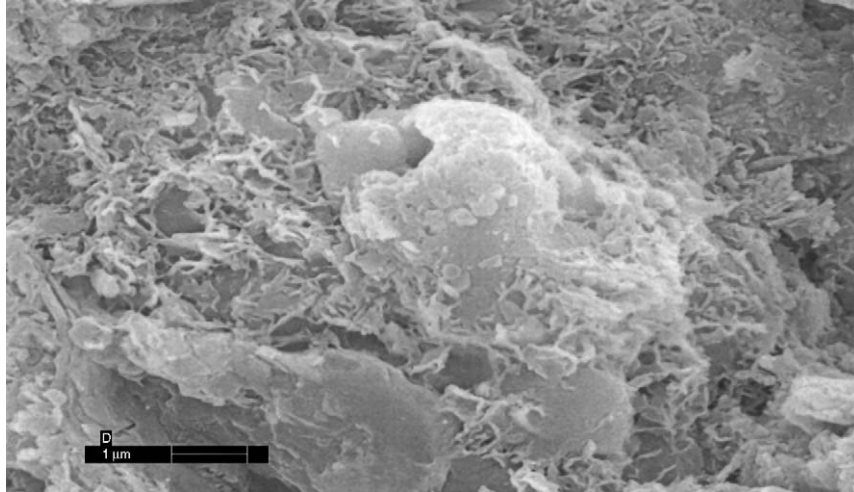


Fig. 12. Scanning electron photomicrograph of the hydrated D batch.

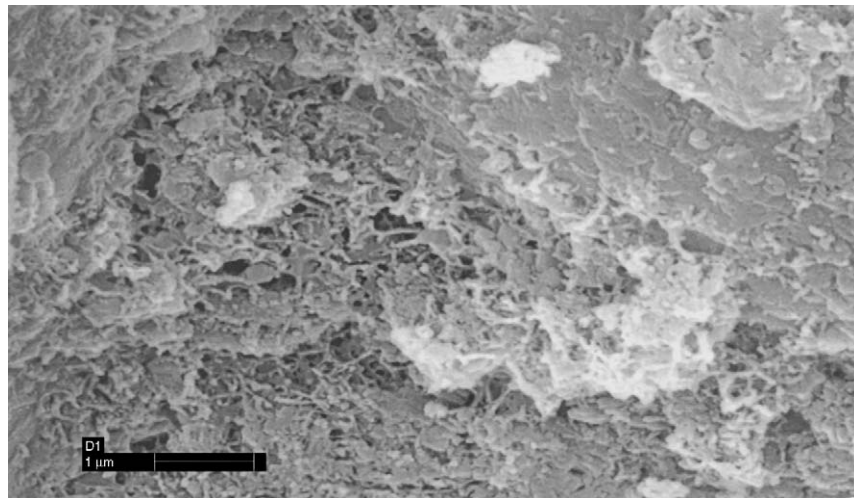


Fig. 13. Scanning electron photomicrograph of the hydrated D1 batch.

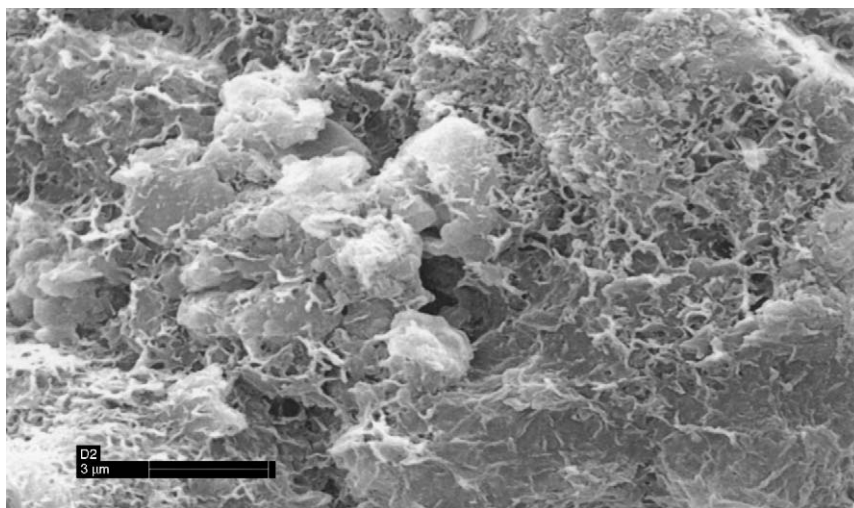


Fig. 14. Scanning electron photomicrograph of the hydrated D3 batch.

tion, which finally results in lesser extent of hydrated phase formation followed by lowering in strength.

3.2.3. Phase analysis

Phase analysis study of D, D1 and D3 batches were done using X-ray diffraction technique. All the batches showed quartz and kaolinite phases as the major one. D batch shows (Fig. 8) tobermorite $[\text{Ca}_5(\text{Si}_6\text{O}_{18}\text{H}_2)\cdot 4\text{H}_2\text{O}]$, hydrogarnet $[\text{Ca}_3\text{Al}_2(\text{SiO}_4)(\text{OH})_8]$ and portlandite $[\text{Ca}(\text{OH})_2]$ as the hydrated phases and formation of these hydrated phases is the reason for the strength development in the autoclaved products. D1 batch also reveals (Fig. 9) the presence of the similar hydrated phases but with lesser intensities, which may be the reason for the development of lower strength. Again D3 batch shows (Fig. 10) relatively higher extent of tobermorite and hydrogarnet phase formation due to the presence of higher amount of calcined marble dust in the composition, resulting relatively higher extent of hydrated phase formation and higher strength than the D1 batch. It is interesting to note that there is no portlandite phase present in the marble dust lime containing compositions, and this is also important as presence of free portlandite phase may be harmful for the prolong use of the products.

3.2.4. Microstructural analysis

Unhydrated D batch shows (Fig. 11) lumpy quartz particles and platy clay particle along with relatively bright lime bearing phases. Hydrothermal treatment of this batch produces network of hydrated phases (Fig. 12). These network of the hydrated phases contribute towards development of strength in the sample. Similar network of hydrated phases are also observed in D1 and D3 batches (Figs. 13 and 14). Relatively lesser presence of hydrated phases in the D1 batch may be the reason for the development of relatively lower strength.

3.2.5. Porosimetry study

A comparative study of various porosimetric properties of the D, D1 and D3 batches are provided in Table 4. It is found that pore tortoisity and throat pore ratio of all the compositions are almost similar. Diffusion of fluids in porous solids showed effective (measured) diffusivity differs from theoretical (bulk) diffusivity due to the pore structure of solid, and the ratio of bulk and effective diffusivity is proportional to a dimensionless factor, termed as pore tortoisity.²⁷ This

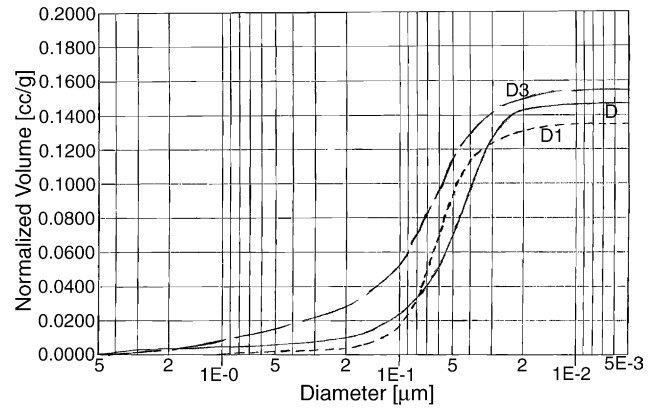


Fig. 15. Normalized volume of intruded mercury against pore size of different batches.

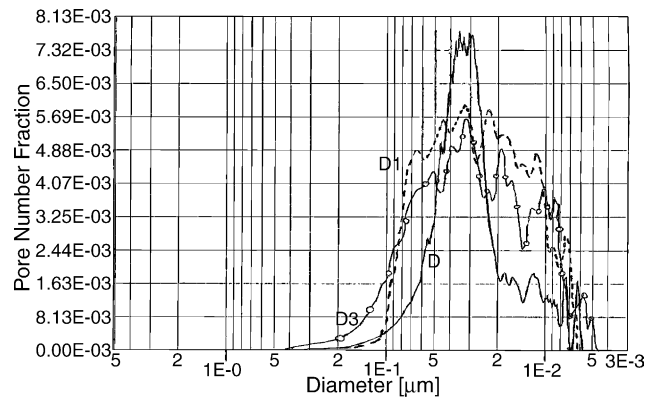


Fig. 16. Pore number fraction of different batches against pore size.

reveals that the individual pores for different compositions are similar in nature. Exposed surface area of the pores to intruded mercury is found to be higher for the D batch, which indicates that more area is available for hydrothermal reaction. Maximum pore size and mean size of the pore are higher for the marble dust lime containing compositions. But D batch, having similar CaO content as D1 batch shows ~10% higher pore volume (Fig. 15). Pore number fraction (number of pores present at a certain size) is sharp for the D batch, but is distributed for the D1 and D3 batches (Fig. 16). Again maximum pore number fraction is highest for the D batch also.

Table 4
Porosimetric study of some selected batches

Property	D	D1	D3
Pore tortoisity	2.147	2.15	2.143
Throat pore ratio	2.89	2.96	2.93
Exposed surface area (m ² /g)	12.79	9.73	10.29
Pore size range (μm)	0.003–4.86	0.003–6.67	0.003–10.98
Mean pore size (μm)	0.0458	0.0619	0.0631
Volume of intrusion (cm ³)	0.148	0.135	0.155
Max. pore number fraction	7.7×10^{-3} at 0.03 μm	5.8×10^{-3} at 0.03 μm	5.6×10^{-3} at 0.03 μm

4. Conclusions

From the present investigation, the following conclusions are drawn.

- (1) Calcined marble dust can be used as an alternative source of active CaO for hydrothermal solidification of clay–quartz mixtures.
- (2) Hydrothermal treatment of clay–quartz mixtures with calcined chemical grade CaCO₃ or calcined marble dust produces tobermorite and hydrogarnet as the major hydrated phases and a network structure of these hydrated phases contributed towards development of adequate strength in the samples.
- (3) Porosimetric data on hydrated samples reveal that chemical grade CaCO₃ containing samples had higher exposed surface area and indicate greater hydrothermal reaction. This is also supported by X-ray diffraction study where higher intensity of hydrated phases was observed than the marble dust containing compositions.
- (4) Pore size of the marble dust containing compositions was found to be in higher side.
- (5) The combined properties of low density, higher porosity and adequate strength obtained in the presently developed hydrothermally treated CaO–SiO₂–Al₂O₃–H₂O system may be suitable as new building materials where presence of mesopore with inherent micron range pore size distribution are important parameters to control humidity and temperature in buildings.

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