



## Setting and curing of mortars obtained by alkali activation and inorganic polymerization from sodium silicate and silica aggregate



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### HIGHLIGHTS

- Water insoluble silicate mortars were produced.
- Optimum properties were obtained by controlling processing temperature and composition.
- Higher level of mechanical properties were achieved in silicates aggregates.
- Compared to cement, lighter and better sustainable silicate mortars were produced.
- Thermal conductivity of silicate mortars was less compared to Portland cement mortar.

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### ABSTRACT

This research is focused on sodium silicate bonded silica aggregates for making sustainable construction materials such as bricks and precast products. Different compositions are investigated to produce castable mortars. The mortars are cured at temperatures ranging from 150 to 300 °C and characterized, in particular microstructural and mechanical properties are investigated. Very high compressive strength of 100 MPa and elastic modulus of 5 GPa are obtained for samples with optimized compositions and heat treatments. Solubility and degradation study of the samples in water demonstrate that alkali silicates are prone to be soluble if not treated at 200 °C or above. Transformation of Si–OH to Si–O–Si not only increases the strength but also makes it insoluble in water. It is concluded that sodium silicate bonded bricks and blocks are very promising and affordable materials for construction. They represent an alternative to Portland cement concrete bricks and to sintered clay bricks, providing higher strength and representing an eco-friendly material.

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### 1. Introduction

Currently infrastructure and housing sector make use of huge amounts of cement concrete and clay bricks. Both the production of cement and ceramic construction materials require extensive energy and result in CO<sub>2</sub> emissions. Therefore environmental activists and government regulations are continuously forcing scientists and engineers in development of new alternatives to cement and sintered ceramics which could be able to fulfil the desired requirements [1,2]. The earth crust is mostly composed of aluminosilicates, and most of the researches are trying to mimic the natural stone formation processes in the labs which can be viable for

commercial production. Among the various processes available, the ones using alkali silicate binders are particularly interesting. When an aluminosilicate material and an activating agent like sodium hydroxide are combined, a partially crystalline solid is obtained. The class of these materials is designated as geopolymers. The aluminosilicate sources can be naturally occurring or industrial wastes like fly ash, clays tailing, kaolin and pozzolans [3,4]. Geopolymerization reaction also occurs without aluminum, forming Si–O–Si type network. This Si–O–Si bonding gives much higher strength but the drawback of these kinds of materials is that they are water soluble [1]. These types of bonds (Si–O–Si) can be stabilized by carbonation from atmospheric CO<sub>2</sub> which is a well-known process to harden the inorganic silicate paints [5]. If a similar process is achieved in-situ by the use of sodium carbonates and mild thermal treatments (above 200 °C), the mortar may be

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hardened and stabilized to water. This in-situ carbonation has already been successively used for the hardening process of geopolymers [6]. It is also known that the higher the amorphous silica content, the higher is the geopolymerization reaction due to higher dissolution of the silica and other contents [7,8]. To initiate the chemical reaction between silica aggregates and alkali, three components are necessary namely, a critical amount of reactive mineral phase in the aggregates, pH of the alkali solution and moisture [9]. For the chemical reaction to take place, the alkali concentration should be high; pH should be higher than 11. For that purpose usually a 14 M solution of sodium silicate is used for the dissolution of the aggregates [10,11]. Higher pH of activating solution results in higher geopolymerization and strength [7].

In this research, we have studied the binding effect of sodium silicate on naturally occurring silica aggregates rather than aluminosilicate minerals as it is done for geopolymers. The investigated binding process is similar to geopolymerization but with lower amount of aluminum hence without true geopolymerization reaction. We have used compositions as reported by Temuujin et al. and Sarkar for the fly ash geopolymers to make the silica inorganic geopolymer bricks by using silica sand aggregates instead of fly ash or any other aluminosilicate [10]. With respect to geopolymerization reaction more emphasis is given to Si–O–Si polymerization rather than Si–O–Al (geopolymerization) hence named differently as an inorganic polymerization.

We also study the effects on the silica inorganic polymerization by increasing amounts of sand aggregates and in-situ carbonation using sodium bicarbonate. The physical and mechanical properties of as prepared silica inorganic polymer samples are carefully reported.

## 2. Experimental

### 2.1. Materials and preparation

Silica sand aggregates by Norman sand (Beckum/Germany CEN Standard Sand EN 196-1, ISO-679) were used as silica source for which the chemical composition (measured by X-ray fluorescence spectrometer (Bruker M4 Tornado)), is given in the Table 1. Sodium bicarbonate (CRUCIANI DAB E500/Italy) was used as in-situ CO<sub>2</sub> source. Water glass with 9% Na<sub>2</sub>O, 30% SiO<sub>2</sub> and 61% H<sub>2</sub>O (Prochin, Italy) and specific gravity of 1.35 g/cm<sup>3</sup>, was used in the formulation. 14 M sodium hydroxide solution was used as an activator solution.

A dense homogenized slurry was prepared by milling the sand aggregates together with sodium hydroxide solution, water glass and sodium bicarbonate (for in-situ carbonation formulation), for 10 min using a planetary ball mill and alumina balls as grinding media. Table 2 indicates sample codes and compositions utilized for sampling and testing. Water may also be added later to enhance plasticity of the mortar but with much care as it may be detrimental to uniform properties. After mixing, grinding and adjusting water contents, the mortars were cast in to polyethylene plastic molds with a height to diameter ratio more than 2 (0.9 cm diameter and 2.5 cm height). After forming, the samples were demoulded from the cylindrical vessels and cured at different temperatures (150, 200 and 300 °C) for 2 h in muffle furnace and characterized further.

### 2.2. Analysis of samples

Calorimetric properties (Differential thermal analysis) of the prepared mortar samples were measured from 25 to 700 °C by Mettler Toledo instrument. X-ray diffraction patterns were obtained by Rigaku diffractometer with Cu K $\alpha$  radiation

**Table 1**  
Composition of the inert sand aggregates by XRF analysis (mass %).

Composition (%)	Inert sand
Al <sub>2</sub> O <sub>3</sub>	3.76
SiO <sub>2</sub>	94.02
K <sub>2</sub> O	1.07
CaO	0.16
TiO <sub>2</sub>	0.13
Fe <sub>2</sub> O <sub>3</sub>	0.68
MnO	0.04
ZrO <sub>2</sub>	0.04

**Table 2**  
Compositions of silicates used.

Sample ID	Sand (%)	Sodium silicate (%)	Sodium hydroxide 14 M	Sodium bicarbonate (%)	Water
IG	85	10	4	–	1
IGBC	73	17	7	2	1
IGC	73	18	7	–	2

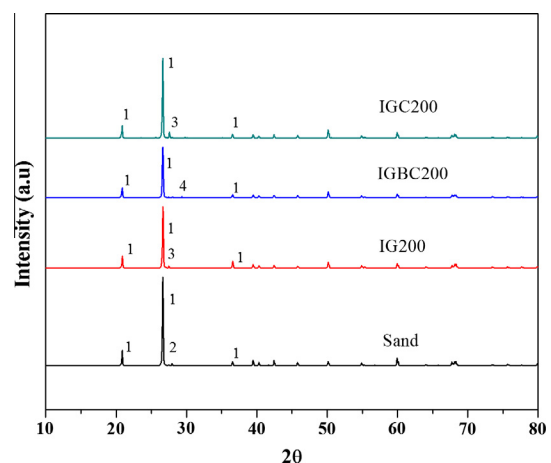
generated at 40 kV and 20 mA. FTIR analysis was performed on ATR (Attenuated Total Reflectance; Perkin Elmer) with diamond crystal as a probe. Thermal conductivities were measured by C-Therm thermal conductivity analyser.

Micrographic analysis was performed using electron microscope (Model: Zeiss, Jena, Germany). Bulk density was calculated by measuring the dimensions and weight of each samples. Mechanical properties of the samples after curing were measured using Lloyd LR5 K instrument in compression mode by applying ASTM C109 standard protocol.

## 3. Results and discussion

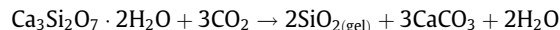
### 3.1. XRD analysis

The XRD spectra of sand aggregates and prepared samples after curing is shown in Fig. 1. In general, all the spectra indicate the absence of amorphous phases, as there is no hump or broaden peaks visible and the most abundant phase is quartz in aggregates as well as in hardened samples. In pure sand aggregates, the peaks are more intense compared to their silicate mortars, because the percentage of silica was reduced by the addition of sodium hydroxide from alkali activator and water glass. All the compositions made for this work show similar trends. There are no peaks appearing after polymerization as the samples and aggregates were mostly quartz silica. But a very small peak present in aggregates at 27.94 (Anorthite; CaAl<sub>2</sub>Si<sub>2</sub>O<sub>8</sub>, JCPDS 89-1462) is diminished after hardening where as another similar small peak reappeared in mortars without NaHCO<sub>3</sub> treated, at 27.50 corresponding to CAH10 (CaO·Al<sub>2</sub>O<sub>4</sub>·10H<sub>2</sub>O). Anorthite is a zeolitic compound where Al<sup>+</sup> is present in the four fold symmetry and its presence gives the insight of the aggregates where this was formed due to weathering and erosion and remained in contact with water for longer times. [12]. Due to dissolution of anorthite, calcium and aluminum react to form CAH10 which is cementing compound formed by calcium. In IGBC, calcium and aluminum didn't form CAH10 due to higher affinity of calcium oxide toward CO<sub>2</sub> to form CaCO<sub>3</sub>, hence CAH10 peak is absent in the samples treated with sodium bicarbonate. A very small peak for CaCO<sub>3</sub> was appeared



**Fig. 1.** XRD pattern of sand aggregates and different silicate mortar compositions cured at 200 °C. (1 = Quartz, 2 = Anorthite CaAl<sub>2</sub>Si<sub>2</sub>O<sub>8</sub>, 3 = CaO·Al<sub>2</sub>O<sub>4</sub>·10H<sub>2</sub>O, 4 = CaCO<sub>3</sub>).

at 29.33 (JCPDS card number 72-1652) as shown in Fig. 1. The amounts of these minerals were very less hence very tiny peaks were able to be visible in the XRD graphs while other smaller peaks were able to be seen in the data of XRD [13,14].



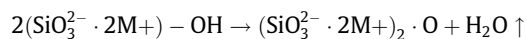
Newly born silica will form an inorganic binder which enhance the strength by fixation of other compounds making network more stable.

### 3.2. Water solubility

The samples treated at different temperatures underwent a solubility test by immersing in water for 24 h (only representative samples treated above and below 200 °C as the behavior of all the compositions was same). Fig. 2(b) shows a sample cured at 150 °C which after the solubility test looks deteriorated. On the contrary samples treated at 200 °C are insoluble in water as shown in Fig. 2. This property of stability against water is acquired due to removal of the larger fraction of –OH groups from silicates making the mass insoluble as will be explained with different tests [1,15].

### 3.3. Thermal calorimetry

Fig. 3 depicts the differential thermal calorimetry of the three compositions. The samples treated at 150 °C were chosen to record the changes occurring at 220 °C while thermal scanning up to 700 °C which actually make these samples insoluble. Up to 100 °C the physically absorbed water was evaporated and an endothermic small peak is observed. The small size of the curve indicates that there was very minute amount of water; absorbed from atmosphere or remained during heat treatment at 150 °C. This peak is little more intense in case of IG where water remained as such because of its hardest structure. All the samples treated below 200 °C were water soluble and this curve justified the reason. For all the samples there is a kink in the pattern at around 220 °C. This kink is attributed to the loss of hydroxyl groups attached to Ca, Si and other radicals [16,17]. Dehydration occurred as follows.



IG150 and IGBC150 both have similar curves as compared to IGC150 where it shows a continuous sign of heat evolution after 450 °C. IGC150 samples were having more relative amounts of

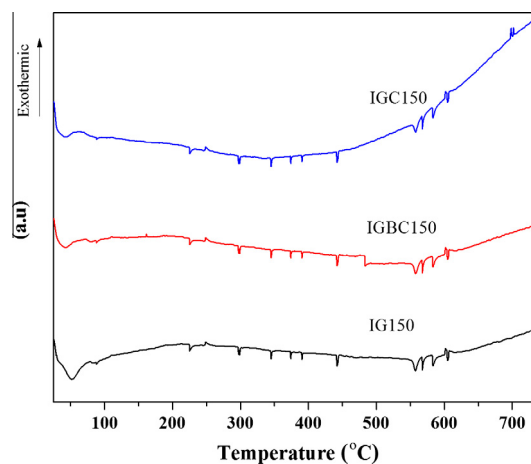


Fig. 3. DTA of silicate mortar compositions cured at 150 °C to check out the changes occurring at 200 and 300 °C.

sodium silicates and sodium hydroxides as well and that's how these were with lower degree of inorganic polymerization hence network continued to grow by heating compared to other compositions [6]. In IGBC the broader peak from 300 to 600 °C is due to decomposition of sodium bicarbonate used in its processing. Another peak at around 300 °C is due to small amount of hydrated aluminosilicates present formed due to small amount of aluminum [18]. At 220 °C, the dehydroxylation of Si–OH bonds was occurred. After dehydroxylation of Si–OH it converts to Si–O–Si type network which is stable and not soluble in water. When the mortar in the rigid dry form was treated at 200 °C for two hours, thermal agitations were sufficiently high to remove or dehydrate it although DTA of IG150 shows that at 220 °C the temperature corresponds at maximum dehydration rate.

### 3.4. SEM analysis

The microstructural details were evaluated using SEM micrographs as shown in Fig. 4. Fig. 4(a) and (b) shows the micrographs of IG200 and IG300 respectively. Fig. 4(a) shows a quite uniform structure compared to Fig. 4(b). The uniform microstructure of IG200 indicates that the sand particles were uniformly ground by the activating solution creating a uniform mass. The uniformity depicts the hard nature of the mortar which is also confirmed later

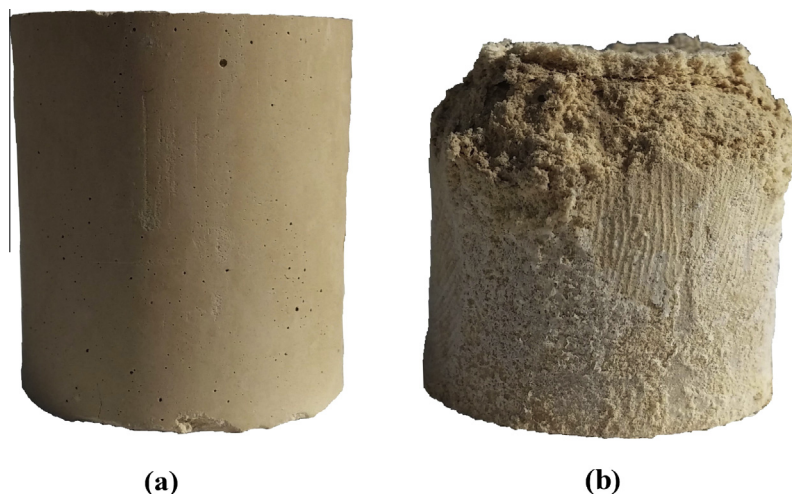


Fig. 2. Digital photograph after water solubility tests of silicates mortars (a) IG200 and (b) IG150 (representative to all categories treated at 200 and 150 °C respectively).

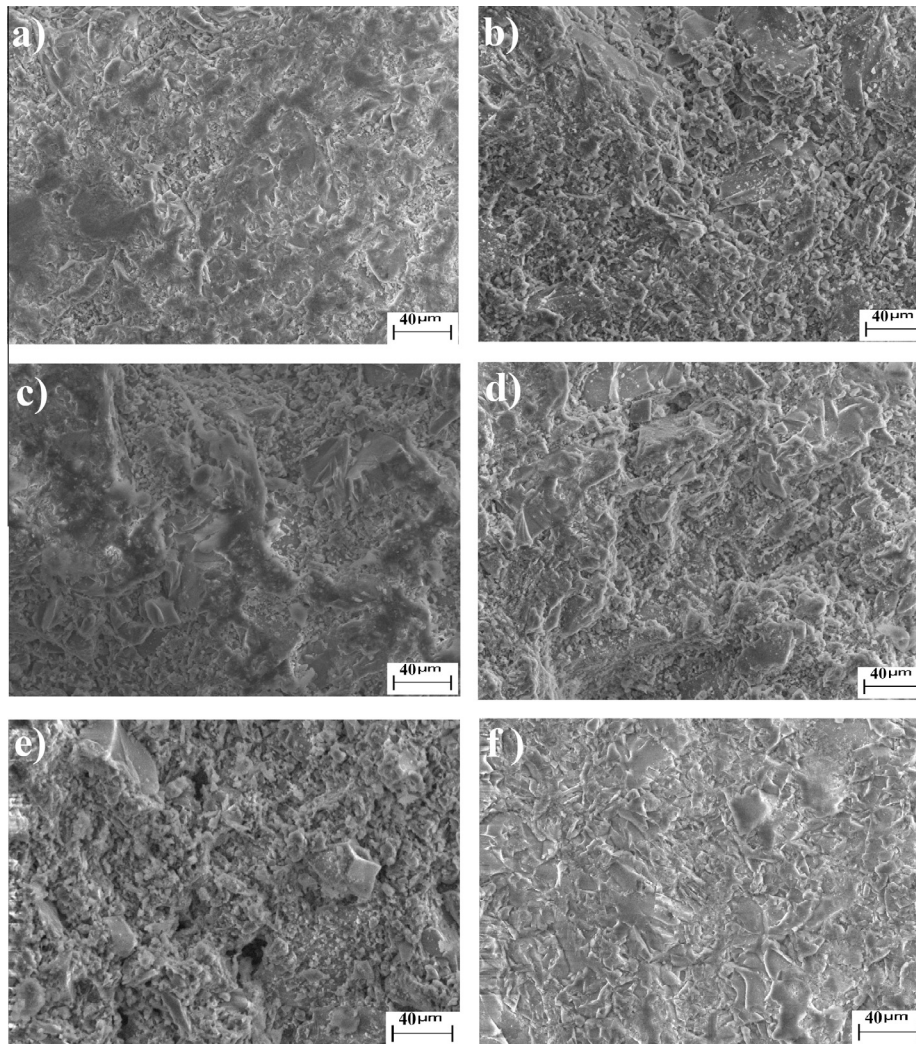


Fig. 4. SEM micrographs of silicate mortar compositions treated at 200 and 300 °C.

in mechanical testing. The samples at 300 °C reveal a porous structure due to evolution of chemically bonded water molecules through the network at 300 °C (dehydroxylation of small amount of aluminosilicates formed due to presence of aluminum). The effect of carbonation can be seen in the microstructure of IGBC200 and IGBC300 (Fig. 4(c) and (d) respectively) with more densely packed structure with very less porosity for IGBC200 while relatively more for IGBC300 as aluminosilicate formed dehydroxylated at 300 °C and also decomposition of carbonates starts at that temperature. More dense structure for IGBC200 was due to higher degree of polymerization of silica particles initiated by the  $\text{CO}_2$  derived by the decomposition of sodium bicarbonate [19]. In contrast to previous two cases, the microstructure of IGC200 and IGC300 shows porous structures as shown in Fig. 4(e) and (f). IGC200 is more porous because more water was added for processing which increases the amount of physically absorbed water. IGC300 seems dense and uniform compared to IGC200 due to contraction and reduction in volume after treated at 300 °C; evaporation and dehydroxylation created strong capillary action, which resulted in shrinkage [20].

### 3.5. Density, porosity and thermal conductivity

The porosity of samples with different composition and heat treatment is determined by measuring the bulk and the apparent

densities of the samples and is given in Table 3. It is noted as soon as the curing temperature is increased the porosity is also increasing because of the removal of volatile components out of the samples. The highest porosity is found in IGBC treated at 300 °C although there is minor difference from IGBC200 because the large amount of bicarbonate is dissociated between 150 and 200 °C. The higher porosity is attributed to the removal of water and sodium bicarbonate dissociation. The least porosity is calculated for the stable (insoluble in water) sample IG200, due to least amount of water utilized while processing. For IGC, the porosity is similar to IG although prepared with higher amount of water; due to the contraction because of capillary forces while curing [20]. Thermal conductivities range from 0.11 to 0.18 W/mK which are not only lower than ordinary Portland cement mortars but also from conventional geopolymers [6].

### 3.6. Compressive strength

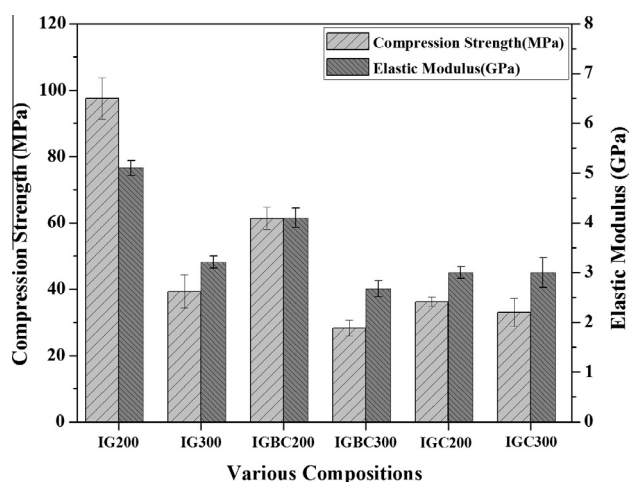
Mechanical strength of the different samples is measured through mechanical compression tests and the behavior is shown in Fig. 5, given in Table 3. The compressive strength and Young's modulus for IGC are comparatively more than the previously ever achieved for the geopolymer mortars [21,22]. The uniform structure in SEM micrographs also predicts higher strength levels as the structure is uniform and intact. But the strength is decreased

**Table 3**  
Properties of mortars (physical and mechanical).

Sample IDs	Treatment temp. (°C)	Apparent density (g/cm <sup>3</sup> )	Bulk density (g/cm <sup>3</sup> )	Porosity (%)	Thermal conductivity (W/mK)	Compressive strength (MPa)	Young's moduli
IG	150	1.99	1.88	5.5	0.143	104.2	4.5
	200	2.03	1.84	9.4	0.17	97.46	5.1
	300	2.12	1.79	15.6	0.12	39.3	3.2
	150	2.11	1.79	15.2	0.18	68.4	4.2
IGBC	200	2.21	1.73	21.7	0.14	61.31	4.1
	300	2.3	1.78	22.6	0.11	28.29	2.6
IGC	150	1.98	1.88	5	0.11	62.87	3.1
	200	2.17	1.85	14.7	0.1	36.15	3
	300	2.14	1.78	16.9	0.12	33.01	3

**Table 4**  
Comparison between silicate mortars, fly ash geopolymer, clay fired bricks and conventional cement mortar.

Properties	Treatment temperature (°C)	Compression strength (MPa)	Density (g/cm <sup>3</sup> )	Porosity (%)	Thermal conductivity (W/mK)
Silicate mortar	200	90–100	1.8	9.4	0.17
Fly-ash geopolymers [22]	40–60	40–65	1.5–1.8	33–37	0.5–0.8
Clay fired bricks [23]	910–1100	17–37	1.6–1.7	20–30	0.5–0.7
Cement mortar [24,25]	Room temperature	25–30	2.9–3.1	15–20	0.7–1.2

**Fig. 5.** Compressive strengths and Young's moduli of prepared samples.

for IG300 due to the evolution of chemically held water from the structure at 300 °C creating porosity, which weakens the structure. IG samples were having less amount of water compared to other compositions that's how the strength was higher compared to other samples cured at same temperature.

IGBC samples also showed better strength (compared to IGC but still their strength was low when we compare with IG due to higher amount of sodium silicate used in processing of IGBC.) as a result of CO<sub>2</sub> produced from sodium bicarbonate, which is helpful in mobilization of aluminum ions and fast hardening of silica network. As the aluminum amount was very less, this effect was due to reaction between silica particles by making networking between silica tetrahedra from sodium silicate and particles by carbonation. Not only the compressive strength but also a higher Young's modulus for IGBC200 is observed. The strength of IGBC300 is least amongst all compositions because not only chemically held water is evolved but also CO<sub>2</sub> from the remaining bicarbonates hence creating great structural disturbance.

For IGC200 and IGC300 the strength is similar because of the shrinkage in IGC300 due to higher evaporation on drying. But compare to other compositions, the strength is low for both 200 and

300 °C treated samples due to higher amount of water used in its preparation. The Young's moduli are still very good and fair enough to compare with literature available values [21,22]. The comparison between various properties of silicate mortar, cement blocks, fired clay bricks and geopolymer mortar, is given in Table 4. It can be seen that the greater strength with lower thermal conductivities compared to other conventional construction materials are obtained by this technique. In addition to enhanced properties, the processing time is too short comparatively.

#### 4. Conclusion

The new technique of manufacturing silica with higher mechanical properties not only can be utilized for manufacturing castable bricks but also for extruded bricks and in other processing related to silica. Silicates being most abundant minerals on the surface of the earth can be utilized through this technique as construction material effectively. Least amount of sodium hydroxide and sodium silicates are required to activate and harden the mortar. Heat treatment up to 200 °C impart insolubility properties because of the condensation reactions and the elimination of Si-OH. With respect to extruded clay bricks an enormous amount of energy is saved in the manufacturing process. Higher strength and higher young's moduli, least amount of activating and setting agents, lower thermal conductivities, cheapest raw sand and lower times of manufacturing compared to conventional Portland cement, clay bricks and geopolymer mortars, are the key advantages of this processing technique. DTA, SEM and porosity analysis justifies the higher strength and rigidity moduli of the samples in terms of polycondensation reactions of silanol groups.

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