

Effect of molar ratios on strength, microstructure & embodied energy of metakaolin geopolymer

Aref A. Abadel, Abdulrahman S. Albidah, Ali H. Altheeb, Fahed A. Alrshoudi,
Husain Abbas and Yousef A. Al-Salloum*

Chair of Research and Studies in Strengthening and Rehabilitation of Structures, Dept. of Civil Engineering, College of Engineering,
King Saud University, P.O. Box 800, Riyadh 11421, Saudi Arabia

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Abstract. In this study, twenty-five geopolymer (GP) mixes were prepared by varying the alkaline solids to Metakaolin (MK) and sodium silicate to NaOH ratios from 0.1 to 0.5 and 0.2 to 1.0, respectively, thus giving a wide range of molar ratios of silica to alumina, sodium oxide to alumina and water to sodium oxide. The compressive strength of these GP mixes was determined for four curing schemes involving oven curing at 100°C for 24 h and three ambient curing with the curing ages of 3, 14, and 28 days. The test results revealed that for the manufacture of GP binder for structural applications of strength up to 90 MPa, the molar ratio of silica to alumina should be greater than 2.3, sodium oxide to alumina should be between 0.6 to 1.2, and water to sodium oxide should not exceed 12. The compressive strength of ambient cured GP mortar gets stabilized at 28 days of ambient curing. Experimental findings were also corroborated by GP microstructure analysis. The embodied energy of MK-based GP mortars, especially of high strength, is significantly less than the cement mortar of equivalent strength.

Keywords: metakaolin; geopolymer; compressive strength; microstructure; molar ratios; embodied energy

1. Introduction

The geopolymer (GP) based on alkali activation of aluminosilicate materials has shown worldwide interest during the past four decades, which is mainly due to its thermal stability being better than the polymer binders and its mechanical properties being at par with cements. This makes it an excellent green alternative to ordinary Portland cement (OPC) as it is one of the largest source of man-made CO₂ emissions (e.g., Davidovits 2013, Duxon *et al.* 2007a, b, Mehta and Siddique 2018, Morsy *et al.* 2018, Panda *et al.* 2017). In recent years, the rapid research and development of GP has shifted from the interests of thermal resistant applications (Feng *et al.* 2015, Zhang *et al.* 2015) towards construction and building materials (Pacheco-Torgal *et al.* 2008a, b). Recently, there is also a trend of employing geopolymer in 3D printing for speeding up the construction of buildings (Xia and Sanjayan 2016). Although significant research has been conducted on alkali-activated fly ash and alkali-activated slag (e.g., Rao and Rao 2017, Jindal *et al.* 2017, Shaikh 2014), research conducted on metakaolin-based geopolymer is relatively limited to address both the process of geopolymerization and influence of curing on various properties.

Sagee-Crentsil and Weng (2007) and Weng and Sagee-Crentsil (2007) studied the metakaolin (MK) activation using sodium silicate (Na₂SiO₃) and sodium hydroxide (NaOH) solutions. The study showed that there is

significant effect of the concentration of Na₂O and the dissolved silica on the exothermal peak shape. Zhang and Sun (2007) and Zhang *et al.* (2009) investigated the dissolution of MK and polymerization of alumina and silicate oligomers and reported that MK was more reactive in NaOH solution than in KOH. Yao *et al.* (2009) varied the types and concentration of alkaline activators (KOH, NaOH, Na₂SiO₃ and K₂SiO₃) to study their effect on the geopolymerization process. Wang *et al.* (2005) investigated the effect of sodium hydroxide molarity (4 to 12 M) on the mechanical properties of MK-based geopolymer paste and concluded that improved properties are obtained when higher molarity solution is used.

Rovnanik (2010) investigated the influence of curing time and temperature on the compressive and flexural strength of MK-based geopolymer mortar. It was concluded that higher curing temperature improves the early age strength gain, however, better strength was achieved for ambient cured specimens at 28 days compared to heat cured samples. Mo *et al.* (2014) also investigated the effect of curing temperature (20 to 100°C) and reported 60°C as the optimal curing temperature for achieving excellent mechanical properties of GP. Similarly, Muniz-Villarreal *et al.* (2011) studied the effect of curing temperature (30 to 90°C) on the geopolymerization process of MK-based geopolymer and observed that the best geopolymerization process was achieved at curing temperature of 60°C. Investigations on feasibility of geopolymer at ambient curing temperature have also been reported by Jindal (2018).

Jian *et al.* (2014) proposed a scheme that was to seal the cast specimens in molds and cured at 50°C for 9 days and subsequent room temperature curing to achieve high

*Corresponding author, Professor
E-mail: ysalloum@ksu.edu.sa

strength. Zhang *et al.* (2012, 2013) reported that the increase in curing temperature accelerates the geopolymerization rate. The authors also proposed a thermochemical model to quantify the general reaction extent by using the isothermal conduction calorimetric data. Perera *et al.* (2007) investigated the effect of curing at ambient and controlled relative humidity with mild heating (40–60°C) for metakolin-based geopolymer and confirmed that sealing samples in a container could be used to avoid rapid drying and hence cracking of specimens.

The embodied energy of GPs has been studied by several researchers (e.g., Menzies *et al.* 2007, Sakulich 2011, Turner and Collins 2013). Narayanan and Shanmugasundaram (2017) tried to achieve low energy consumption by reduced curing period. As the processes of milling and curing conditions (temperature and duration) are energy intensive, appropriate selection of fineness and curing conditions for optimizing the embodied energy is required for making it more practical.

Considering the aforementioned review, it is evident that most research was devoted on samples of MK-based geopolymer paste (without fine aggregate), however, studies on mortar and concrete are considerably less. This research was taken up with a comprehensive test matrix of MK-based geopolymer mortar mixes to: (i) understand the influence of various mix design parameters on the geopolymerization process and their interaction with the strength development rate, (ii) propose a high strength mortar for future use in concrete repair applications, and (iii) optimize embodied energy for MK-based geopolymer production.

The experimental program involved a wide range of parameters such as alkaline solids to MK ratios of 0.1, 0.2, 0.3, 0.4, and 0.5, sodium silicate to NaOH ratios of 0.2, 0.4, 0.6, 0.8, and 1.0, and four curing schemes comprising oven curing and ambient curing at the ages of 3, 14, and 28 days. These mixes cover the compressive strengths varying from low to high strength binders. The microstructure of the GP so produced was studied using X-Ray Diffraction (XRD), scanning electron microscopy (SEM), and Fourier transform infrared (FTIR) spectroscopy. The embodied energy of the GP mixes was also calculated based on the energy consumed in different processes. The calculated embodied energy of GP mixes is compared with the equivalent cement mortar mixes.

2. Significance of the study

This paper investigates the influence of a wide range of molar ratios of $\text{SiO}_2/\text{Al}_2\text{O}_3$, $\text{H}_2\text{O}/\text{Na}_2\text{O}$, and $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$ on the strength and microstructure of GP mortar binders. Although recently some researchers have investigated the effect of some of these molar ratios (e.g., Alanazi *et al.* 2017, Soutsos *et al.* 2016) on the mechanical properties of MK-based GP, the research is needed to investigate the effect of the three crucial molar ratios (i.e., $\text{SiO}_2/\text{Al}_2\text{O}_3$, $\text{H}_2\text{O}/\text{Na}_2\text{O}$, and $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$). It is expected that the data obtained in the study would provide a basis for selecting the molar ratios for obtaining the desired strengths. The embodied energy calculated for different GP mixes and its

comparison with equivalent cement mortar binders will be helpful in reducing the carbon footprint through proper selection of binders for specific applications.

3. Experimental program

3.1 Materials

The materials employed in the study were MK (used as aluminosilicate source material), fine aggregate, and alkaline activator. The locally available and commonly used red sand was employed as a fine aggregate. The fineness modulus of the red sand was 1.32. The MK used in the production of GP was obtained through the calcination of local kaolin for 3 h at 750°C. The Blaine surface area of kaolin was about 3600 cm^2/g (Morsy *et al.* 2017). The calcination procedure was found enough to produce active amorphous MK because of the elimination of most of the peaks in the XRD plots of kaolin. The chemical composition of MK is shown in Table 1. The MK was primarily glassy except a few crystal insertions of quartz, illite and hematite. The alkaline activator employed in the present investigation was obtained by mixing sodium silicate and NaOH solutions. The use of sodium silicate helped in boosting the geopolymerization process (Xu and Van Deventer 2003, Xu and Van Deventer 2000). The NaOH was in the pellet form and the purity level was 97% and sodium silicate consisted of $\text{Na}_2\text{O}=14.7\%$, $\text{SiO}_2=29.4\%$ and $\text{H}_2\text{O}=55.9\%$, with weight ratio of $\text{SiO}_2/\text{Na}_2\text{O}=2$. The unit weight of sodium silicate solution at 20°C was 1.3.

The NaOH solution of high molarity (20M) was prepared by dissolving NaOH pellets in distilled water. This was the highest molarity achieved in the preparation of NaOH solution. The use of single molar solution of NaOH (i.e., 20 M) helped in avoiding the wastage of chemical in the preparation of NaOH solutions of different molarities. The dissolving of the NaOH in water is an exothermic reaction. Thus, the NaOH solution was prepared one day before its use and the loss of water due to evaporation because of the high temperature of NaOH solution was compensated by adding extra water. The use of high molarity solution of NaOH helped in maintaining uniform desired workability by providing allowance to add extra water during the production of mortar mixes. For maintaining uniform workability, the water to geopolymeric solids ratio was kept fixed at 0.36. This was achieved by adding extra water and thus lowering the actual molarity of NaOH solution.

The fine aggregate and MK were mixed dry for approximately 5 minutes. The alkaline activator was then added and mixed for about 5 minutes so as to obtain homogeneous paste of mortar.

3.2 GP mixes

The quantity of NaOH solid being more important than the molarity (or concentration) of the solution used, the GP mixes were designed based on the quantity of NaOH solid. The percentage of fine aggregate was kept fixed at 40% of total solid including solids available in the alkaline

Table 1 Chemical composition of MK in percent by weight

Oxide Composition	Value
Calcium oxide (CaO)	1.287%
Silicon oxide (SiO ₂)	50.995%
Aluminum oxide (Al ₂ O ₃)	42.631%
Ferrous oxide (Fe ₂ O ₃)	2.114%
Sulfur trioxide (SO ₃)	0.439%
Potassium oxide (K ₂ O)	0.337%
Titanium oxide (TiO ₂)	1.713%
Phosphorus pentoxide (P ₂ O ₅)	0.051%
Magnesium oxide (MgO)	0.127%
Sodium oxide (Na ₂ O)	0.284%
Manganese oxide (MnO)	0.006%
Zinc oxide (ZnO)	0.004%
Strontium oxide (SrO)	0.012%
Total	100%

activators. Two parameters, namely alkaline solids to MK ratio, and ratio of sodium silicate (solid) to NaOH (solid) were selected for deciding the test matrix.

The alkaline solids to MK ratio was varied from 0.1 to 0.5 in a step of 0.1, thus, giving five values of 0.1, 0.2, 0.3, 0.4, and 0.5. The ratio of sodium silicate to NaOH was taken as 0.2, 0.4, 0.6, 0.8, and 1.0. Thus, for a full factorial experimental design, a total of twenty-five mixes were prepared. Although some mixes of the full factorial may not be of interest but this was considered to give an overall clear picture for the performing as well as the non-performing combinations of the two ratios (i.e., alkaline solids to MK ratio and sodium silicate to NaOH ratio). The mix proportion of each mix is presented in Table 2.

As mentioned above, besides the quantity of water available in sodium silicate and NaOH solutions, additional water was added for keeping the water to geopolymeric solids ratio fixed (=0.36). The flow table test (ASTM C230) was used for the assessment of mortar workability. The flow diameter of all the mixes varied from 100 to 120 mm (110±10 mm). The revised molarity of NaOH solution on account of the mixing of extra quantity of water is reported in Table 2.

Three molar ratios, namely SiO₂/Al₂O₃, H₂O/Na₂O, and Na₂O/Al₂O₃ calculated for different mixes are also reported in Table 2. These values indicate that a wide range of molar ratios were covered in the study. The sample calculations of the molar ratios for one of the GP mortar mix GP14 is shown in Appendix I.

3.3 Casting and curing

The GP mortar paste was cast in 50 mm cube molds for assessing the compressive strength of GP mortar. Two categories of curing schemes were adopted. First scheme involved curing of cubes at 100°C in oven for 24 h and the second scheme involved ambient curing (which is equivalent to an average temperature of 40°C and 30% relative humidity). For ambient curing, the influence of age of curing was studied by taking the curing ages as 3, 14, and 28 days. Thus, a total of 300 cubes were tested. For oven

curing, the temperature was raised at 5°C /min and the specimens were cured for one-day (24 h). The oven was then switched off and allowed to cool before taking out the specimens. Although earlier studies (Mo *et al.* 2014, Muniz-Villarreal 2011) on MK- geopolymer pastes indicated an optimum curing temperature of about 60°C, only minor strength reduction was reported at higher temperature. Moreover, this temperature not being very much different from the ambient of this study and the curing procedures also being different, it was decided to cure the mortar specimens at 100°C for the oven curing scheme. The cubes were tested in compression at the end of curing period. The pieces of crushed cubes obtained from the compression testing were powdered for studying XRD, FTIR spectroscopy, and SEM. The crystalline phases in the GP paste were recognized using the technique of XRD. A scanning speed of 2°/min was used. The FTIR spectra were acquired in the transmittance mode of up to 4000 cm⁻¹ using Jasco-6100 FTIR spectrometer. The SEM was employed to explore the alterations in the microstructure of the chemically decomposed and formed phases.

4. Results and discussion

4.1 Compressive strength

The compressive strength of MK-based GP binder is employed to measure the effectiveness of geopolymerization.

4.1.1 Effect of alkaline solids to MK and sodium silicate to NaOH ratios

Fig. 1 shows the compressive strength variation with the variation in the sodium silicate to NaOH ratio for different values of alkaline solids to MK ratio and different curing schemes. The bar charts presented in Fig. 2 show the strength variation for different values of Alkaline solids to MK ratio and different curing schemes. Each sub-figure of Fig. 2 is plotted for different values of sodium silicate to NaOH ratio varying from 0.2 to 1.0. The error bars of standard deviation are also plotted in Figs. 1 and 2. The low magnitude of error bars indicates the reliability of the average values used in making observations and deriving conclusions. The observations made from these figures are:

- The compressive strength of GP binder for the lowest value of alkaline solids to MK ratio of 0.1 is almost negligible with the highest value of 4 MPa. The strength of GP for the next higher value of alkaline solids to MK ratio of 0.2 is also low with the strength of oven-cured specimens varying from 10.5 to 17 MPa, whereas the strength of GP binder cured at ambient temperature varies from 4.7 to 14 MPa. The low strength of GP binder for low alkaline solids to MK ratio is due to low Na⁺ concentration in the activator solution due to which a weak structure is formed, thus leading to slow development of strength of GPs. In view of the low strength of GP binder for the alkaline solids to MK ratio of 0.1 and 0.2, these test results have been ignored in the subsequent discussion.
- The highest strength of the oven cured and the ambient

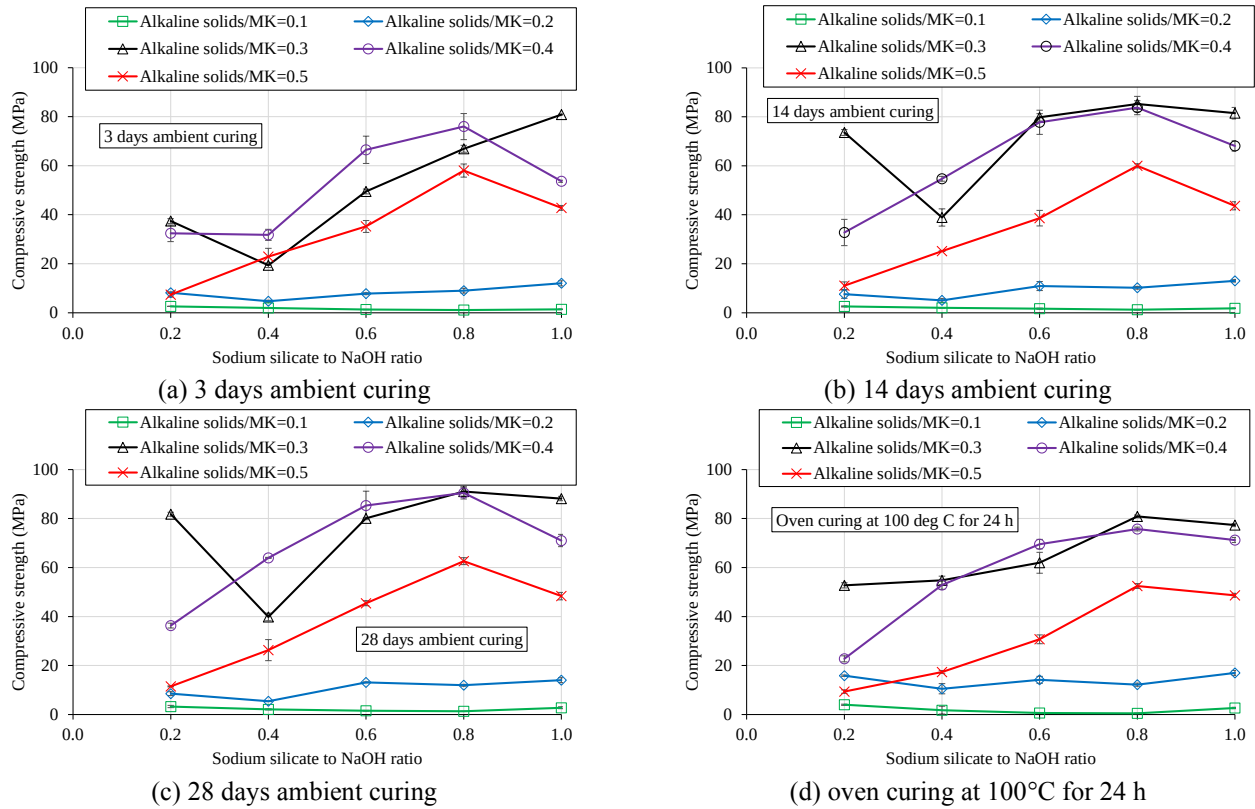


Fig. 1 Effect of sodium silicate to NaOH ratio and alkaline solids to MK ratio on the compressive strength of GP mortar

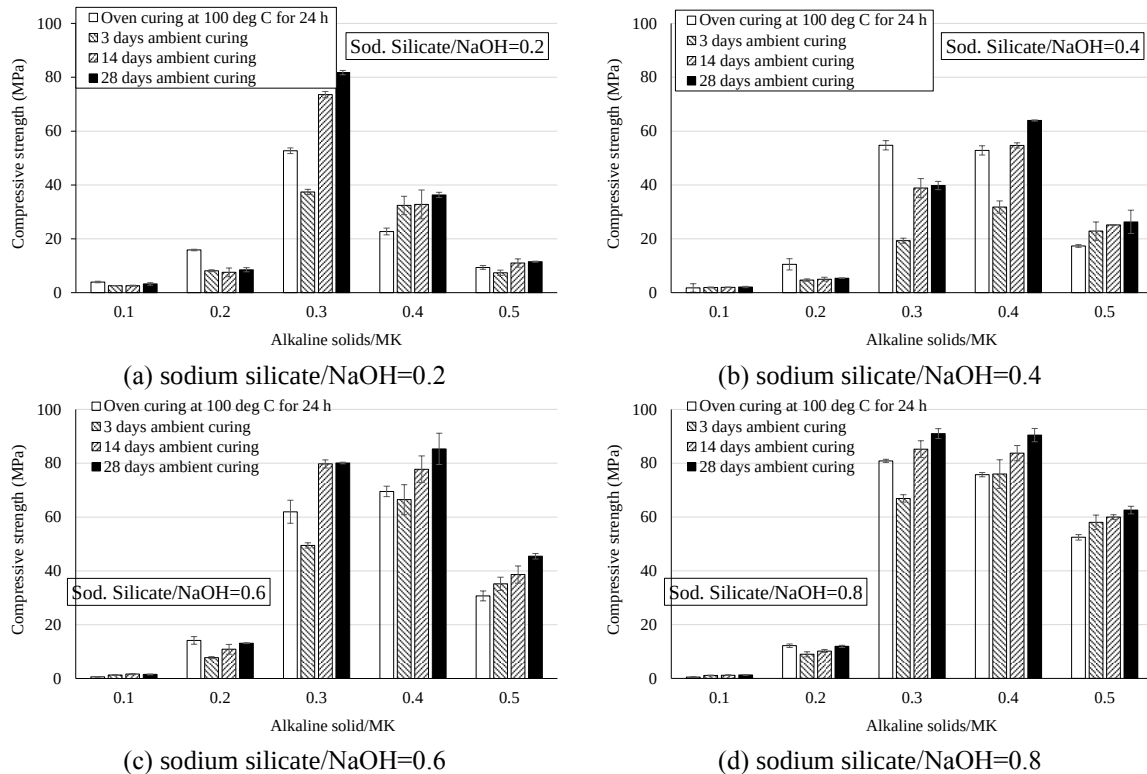
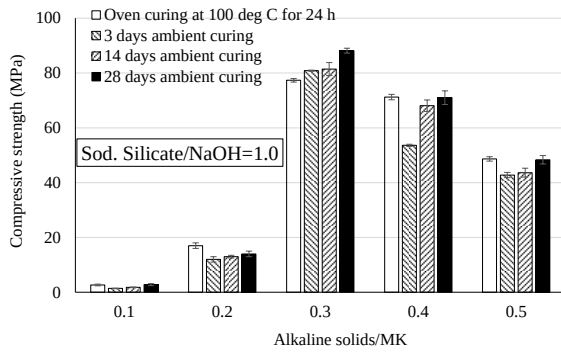


Fig. 2 Effect of Alkaline solids to MK ratio and curing schemes on the compressive strength of GP mortar for different sodium silicate sodium silicate to NaOH ratios

cured GP mortar (80-90 MPa) is obtained for GP14 and GP19. The sodium silicate to NaOH ratio for the two mixes is 0.8, whereas the alkaline solids to MK ratio for

the two mixes is 0.3 and 0.4, respectively.

- The strength of GP binder cured at ambient temperature is increasing with the curing age. Thus, the



(e) sodium silicate/NaOH=1.0

Fig. 2 Continued

highest strength is achieved after curing for 28 days. The curing time plays an important role in the acceleration and the extent of chemical reactions (e.g., Khale and Chaudhary 2007). The experimental results of Granizo *et al.* (2007) and Patil *et al.* (2014) have shown that the curing age improves the behavior of GPs. The prolonging of curing age improves the geopolymerization process leading to the strength gain. Although there is considerable enhancement in strength (1%-101%) when curing age is increased from 3 to 14 days but the gain in strength from 14 to 28 days of curing is low (0.4%-17.6%). This shows that the strength of ambient cured GP mortar gets almost stabilized at 28 days.

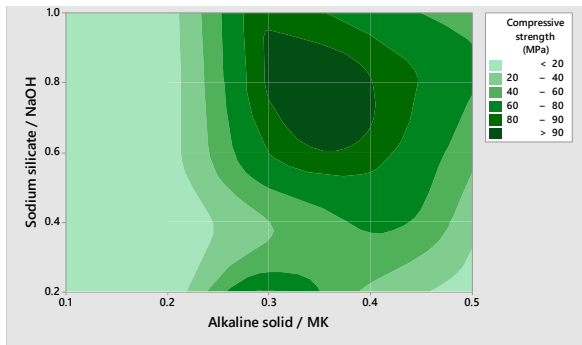
- The strength of 28 days ambient-cured GP mortar is generally more than the oven-cured GP mortar with the exception of mixes for which the alkaline solid to MK ratio is low (≤ 0.2). The exceptions may be ignored due to the low compressive strength for these GP mortars. The reason for compressive strength of oven-cured GP mortar being lower is the evaporation of water before the dissolution of MK in the alkaline solution due to fast drying.

- For the GP mortar with alkaline solids to MK ratio of 0.3 or more, the strength is increasing with the increase in sodium silicate to NaOH ratio until 0.8 and its subsequent increase to 1.0 generally causes reduction in the compressive strength. The reduction in strength is probably because of the excess of Na^+ ions (Khale and Chaudhary 2007). This shows that the optimal ratio of sodium silicate to NaOH found in this study is 0.8, which is primarily because of the activation of MK becoming quicker and stronger. Considering the grid spacing of the full factorial experiment, the actual optimal ratio of sodium silicate to NaOH may lie within the range of 0.75 to 0.85.

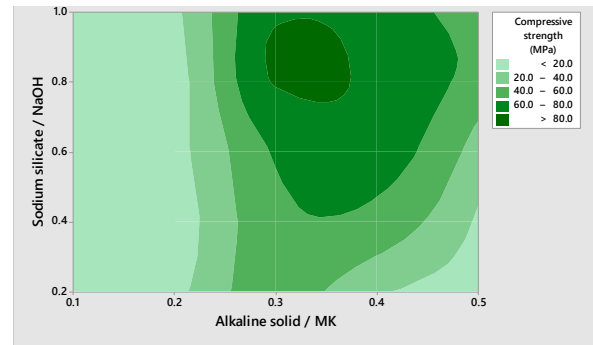
- The strength of GP binder generally increases with the increase in the ratio of alkaline solids to MK initially up to 0.3 or 0.4 and further increase in its value causes reduction in the strength of mortar. The increase in alkaline solids to MK ratio from 0.3 to 0.4 increases the amount of NaOH which helps in increasing the solubility of aluminosilicate (Xu and Van Deventer 2000, Khale and Chaudhary 2007). However, further

Table 2 Mix proportion and molar ratios (dry unit weight=2200 kg/m³)

Mix	Mixture Proportion (kg/m ³)					Revised molarity of NaOH solution	Molar ratios		
	Sand	MK	Sodium silicate	NaOH	Added water		$\text{SiO}_2/\text{Al}_2\text{O}_3$	$\text{H}_2\text{O}/\text{Na}_2\text{O}$	$\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$
GP1	880	1200.0	45.4	100.0	365	5.1	2.07	19.09	0.29
GP2	880	1200.0	77.7	85.7	359	4.6	2.11	20.31	0.27
GP3	880	1200.0	102.0	75.0	354	4.2	2.13	21.36	0.26
GP4	880	1200.0	120.9	66.7	351	3.8	2.15	22.26	0.25
GP5	880	1200.0	136.1	60.0	348	3.5	2.16	23.04	0.24
GP6	880	1100.0	83.1	183.3	273	9.1	2.12	11.43	0.57
GP7	880	1100.0	142.5	157.1	262	8.6	2.18	12.12	0.52
GP8	880	1100.0	187.1	137.5	254	8.1	2.23	12.71	0.49
GP9	880	1100.0	221.7	122.2	247	7.6	2.27	13.22	0.47
GP10	880	1100.0	249.4	110.0	242	7.2	2.30	13.67	0.45
GP11	880	1015.4	115.1	253.8	195	12.4	2.16	8.74	0.84
GP12	880	1015.4	197.4	217.6	180	12.0	2.26	9.22	0.77
GP13	880	1015.4	259.0	190.4	169	11.7	2.33	9.64	0.73
GP14	880	1015.4	307.0	169.2	160	11.4	2.38	10.00	0.69
GP15	880	1015.4	345.4	152.3	153	11.1	2.43	10.32	0.67
GP16	880	942.9	142.5	314.3	128	15.1	2.21	7.36	1.11
GP17	880	942.9	244.3	269.4	110	15.1	2.33	7.74	1.03
GP18	880	942.9	320.7	235.7	96	15.1	2.43	8.07	0.96
GP19	880	942.9	380.1	209.5	85	15.1	2.50	8.35	0.92
GP20	880	942.9	427.6	188.6	76	15.1	2.56	8.60	0.88
GP21	880	880.0	166.3	366.7	71	17.3	2.25	6.52	1.38
GP22	880	880.0	285.1	314.3	49	17.8	2.41	6.84	1.28
GP23	880	880.0	374.1	275.0	32	18.3	2.53	7.11	1.20
GP24	880	880.0	443.4	244.4	20	18.8	2.62	7.35	1.14
GP25	880	880.0	498.9	220.0	9	19.3	2.69	7.55	1.09



(a) 28 days ambient curing



(b) oven curing at 100 °C for 24 h

Fig. 3 Contour plot of the compressive strength of GP mortar on the grid of Alkaline solids to MK ratio and sodium silicate to NaOH ratio

enhancement in alkaline solids to MK ratio to 0.5 results in excess number of the Na^+ ions, which caused reduction in strength. Thus, the optimal ratio of alkaline solids to MK lies between 0.3 and 0.4.

Fig. 3 shows the contour plots of the compressive strength of GP binder against the two variables, namely the alkaline solids to MK ratio and sodium silicate to NaOH ratio. The contour plots are shown for oven-cured and 28-days ambient-cured mortars. The contour pattern for the two schemes of curing is almost same. The contours clearly indicate that the topmost plateau, corresponding to the peak strength of 80 MPa or more, lies within the range of alkaline solids to MK ratio of 0.3-0.4 and the range of sodium silicate to NaOH ratio of 0.75-1.0. The steepest slope, indicating highest rate of change in the strength of GP binder, is observed for the alkaline solids to MK ratio of 0.25-0.35 and the sodium silicate to NaOH ratio of 0.75-0.9.

The above observations corroborate the earlier findings that the higher concentration of NaOH dissolves MK particles in a much effective way and yields monomer with more reactive bonds which results in GP having increased inter-molecular bonding strength. In addition, the alkali solution partially or completely dissolves MK particles to yield soluble and reactive ingredients containing Al and Si as the tetrahedral aluminosilicate. The soluble silicate catalyzes the process of polymerization by giving self-polymerizing species and by starting a polymerization between silicate oligomers, or/and between AlO_4^- and silicate oligomers (tetrahedral aluminosilicate). The output of this reactive process is basically amorphous.

4.1.2 Effect of molar ratios

For studying the effect of molar ratios of silica to alumina (i.e., $\text{SiO}_2/\text{Al}_2\text{O}_3$), water to sodium oxide (i.e., $\text{H}_2\text{O}/\text{Na}_2\text{O}$), and sodium oxide to alumina (i.e. $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$) on the compressive strength GP mortar after 28 days ambient curing, contour maps were plotted on two grids of molar ratios, as shown in Figs. 4-5. The experimental data points are also plotted in these figures. It is worth mentioning here that the contours plotted in these figures do not cover full grid due to the limited zone of experimental data points for the calculated molar ratios, which was not the case for the contour maps plotted in Fig. 3. Moreover, the extrapolation of contours outside the zone covered by

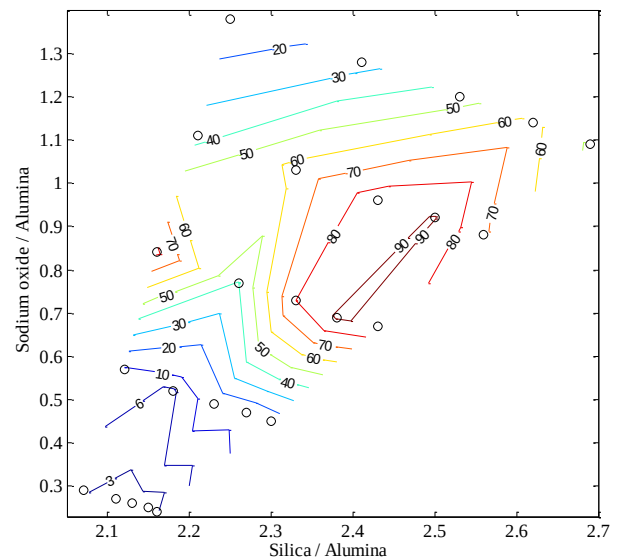


Fig. 4 Contour plot of compressive strength (MPa) of geopolymer mortar after 28 days ambient curing showing the effect of the molar ratios of silica /alumina and sodium oxide/alumina (Note: Experimental data points are shown with black circle legend symbol)

the experimental data points was also avoided to eliminate the experimentally unverified zone of this study.

The observations made from the contour maps of Figs. 4-5 are as follows:

- The lower range of molar ratio of silica to alumina of up to 2.25 together with the molar ratio of sodium oxide to alumina less than 0.6 gives very low strength GP which may not be stable and are non-structural (< 15 MPa).
- There is an overall trend of increase in the compressive strength of GP mortar with the increase in the molar ratio of silica to alumina of up to about 2.45 at which the strength achieved is 90 MPa and further increase in this molar ratio causes decrease in strength but the strength is still high.
- The increase in the molar ratio of sodium oxide to alumina causes initial increase in strength and the peak (about 90 MPa) is reached in the range of 0.65 to 0.90. The subsequent increase in this molar ratio causes decrease in the strength of GP mortar.

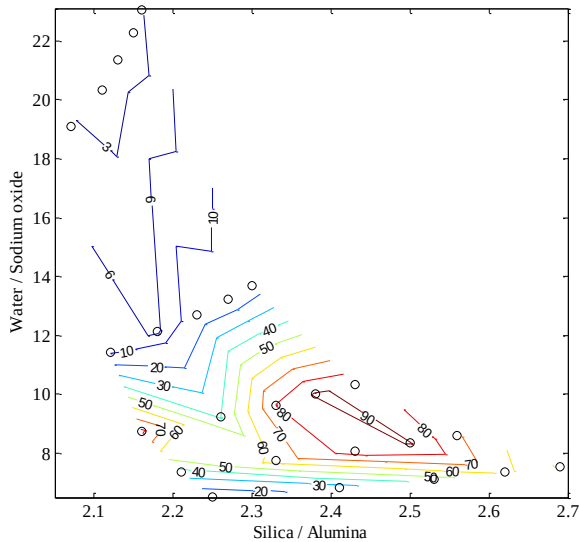


Fig. 5 Contour plot of compressive strength (MPa) of geopolymer mortar after 28 days ambient curing showing the effect of the molar ratios of silica /alumina and water/sodium oxide (Note: Experimental data points are shown with black circle legend symbol)

- The increase in the molar ratio of water to sodium oxide causes sharp decrease in the strength of GP mortar. The increase in this molar ratio beyond 12 makes it a non-structural mortar binder. Similar results are also reported in earlier researches on MK-based GP binders (Kamalloo *et al.* 2010).
- The desirable range of molar ratios for obtaining GP mortar for structural applications are: (a) molar ratio of silica to alumina should be greater than 2.3, (b) molar ratio of sodium oxide to alumina ratio should be lie between 0.6 to 1.2, and (c) molar ratio of water to sodium oxide should not exceed 12 (preferably less than 11).

The above observations indicate that although the molar ratios for obtaining high strength GP binder are more or less in the range of the values reported in literature for MK-based GP concrete (e.g. Pouhet and Cyr 2016, Mohseni 2018), the quantities of binder constituents (i.e. MK, sodium silicate and NaOH) differ due to the relatively low silica content present in the MK used in the study as compared to some of the earlier researches (e.g. Pouhet and Cyr 2016).

4.2 XRD test results

XRD patterns of MK and some of the selected GP mixes are depicted in Fig. 6. Four GP mixes namely GP7, GP9, GP17, and GP19 were identified for the study of their XRD pattern. Three mixes are selected for oven curing (24 h at 100 °C) and two mixes for 28 days ambient curing. Mix 9 is used for comparing the two curing schemes. The quantities of alkaline activator, i.e., sodium silicate and NaOH, in these mixes were responsible for the activation.

The XRD diffraction patterns indicate that a few insoluble constituents (e.g., mullite and quartz) in the MK remain in all the reaction outputs. Crystalline quartz

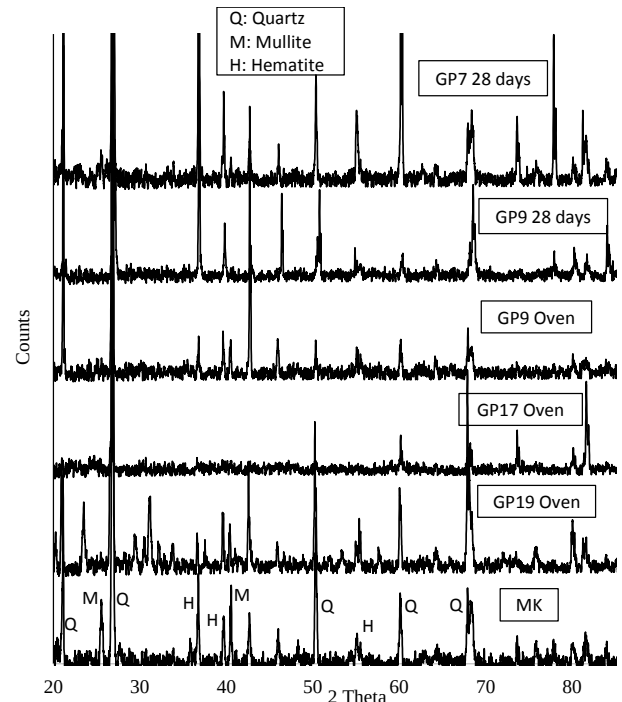


Fig. 6 Comparison of XRD patterns of MK and geopolymer mortars oven-cured at 100°C and cured at ambient for 28 days

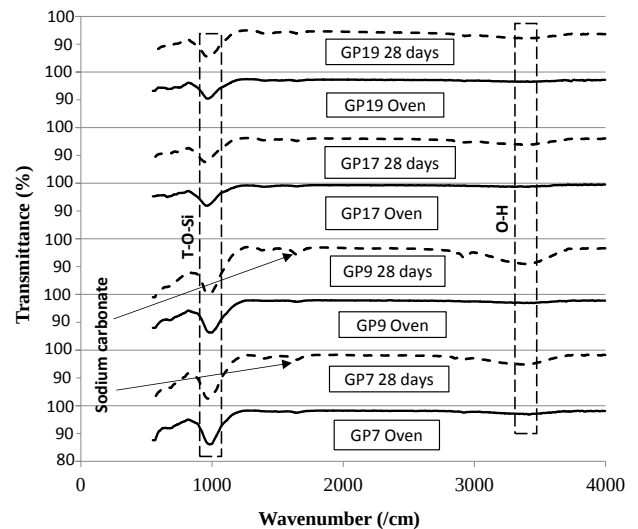


Fig. 7 Comparison of FTIR patterns of geopolymer mortars cured at 100°C in oven and cured at ambient for 28 days (T: Al or Si)

compounds possess strong bond between silicon and oxygen atoms, which react with a relatively higher alkaline solution. This is evident in the XRD diffraction patterns of GP7 and GP9 mixes due to the low alkalinity of the activator, which resulted in a low compressive strength of these mixes. The mixed amorphous and semi-crystalline structure of GP is indicated specimens of GP17 and GP19, thus, resulting in high compressive strengths. A comparison of the two curing schemes for GP9 shows that the higher curing temperature of oven resulted in a relatively better geopolymerization. Furthermore, the XRD patterns clearly

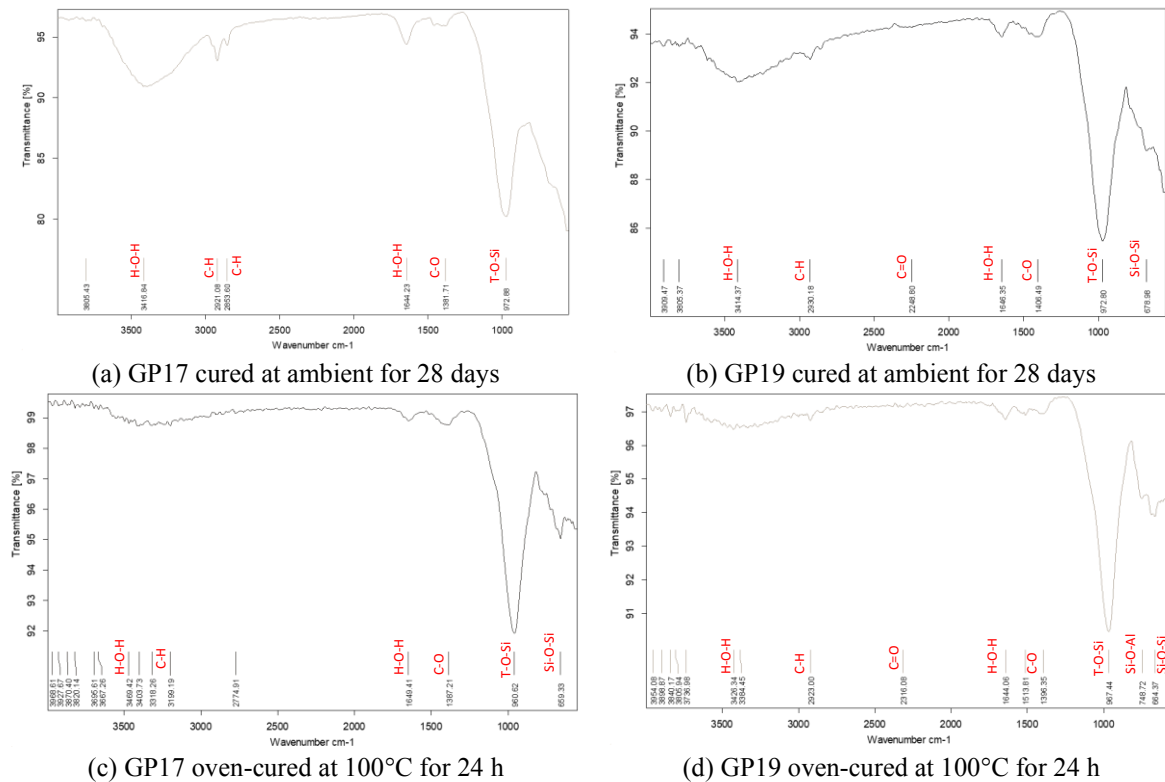


Fig. 8 Comparison of FTIR patterns of geopolymers (T: Al or Si)

illustrate that more is the NaOH concentration, more will be the amorphous content in the reaction outputs.

4.3 FTIR test results

The FTIR spectra of MK and GP products of the four GP mixes (GP7, GP9, GP17, and GP19), is compared in Fig. 7 for the two curing schemes namely oven curing (24 h at the magnified view of FTIR spectra for GP17 and GP19 (i.e., 100°C) and ambient curing for 28 days. The bonds associated with the visible peaks are marked. Fig. 8 shows mixes giving higher strength). The bonds associated with most of the peaks for the two mixes (GP17 and GP 19) are marked in Fig. 8. The FTIR helps in identifying the functional molecular groups based on the infrared (IR) transmittance (or absorption) when the incoming light frequency matches the vibrational frequency of the molecular bond. The low transmittance for a wavenumber (or frequency) implies high concentration of bonds whose vibrational energies correspond to the incident light.

The transformation that occurred during the process of geopolymerization can be judged from the varying levels of transmittance frequencies of MK and GPs. The primary band in the FTIR spectrum of GP is asymmetric stretching vibration (T-O-Si, where, T=Si or Al) in the wavenumber range of 959 to 968 cm⁻¹. Other major bands are broadbands in wavenumber range of 3000-3500 cm⁻¹ and 1650-1655 cm⁻¹ which represent the stretching and deformation vibration of H-O-H and OH groups of water molecules. The bands at about 1400 cm⁻¹ are assigned to the carbonates. Bands at around 700 and 660 cm⁻¹ show the characteristics of amorphous polymer formed, which is the Si-O-Al and Si-

O-Si symmetric stretching. The band attributed to asymmetric stretching vibrations of Si-O-T is of greater intensity and somewhat shifted to lower frequency in comparison to MK. This shows the formation of a new product, an amorphous aluminosilicate gel phase. This product reveals the great extent of geopolymerization which results from the amorphous MK that interacts with geopolymeric materials.

The shift in wavenumber at peak for the GPs as compared to the MK suggests that there are changes in chemical bonding. A comparison of the two curing schemes (ambient cured for 28 days and oven cured) indicates that generally the ambient cured GP shows greater extent of geopolymerization. The small difference between the FTIR spectrum of MK and GP for some ranges of wavenumber suggests that some part of unreacted MK is still retained in the synthesized GP.

4.4 SEM micrographs

Fig. 9 shows SEM and energy dispersive X-ray spectroscopy (EDS) analysis performed on 28 days ambient cured specimens of GP7 and GP9 mortars. The alkaline solids to MK ratio is same (i.e., 0.2) for the two mixes, whereas, the sodium silicate to NaOH ratio is 0.4 and 0.8, respectively for the two mixes. The difference in the microstructures of the two mortars can be conveniently distinguished for the two sodium silicate to NaOH ratios. It can be observed from the figure that the morphology of MK has been activated by different sodium silicate to NaOH ratios. However, at sodium silicate to NaOH ratio of 0.4 (Fig. 9(a)), the degree of reaction is the lower leading to

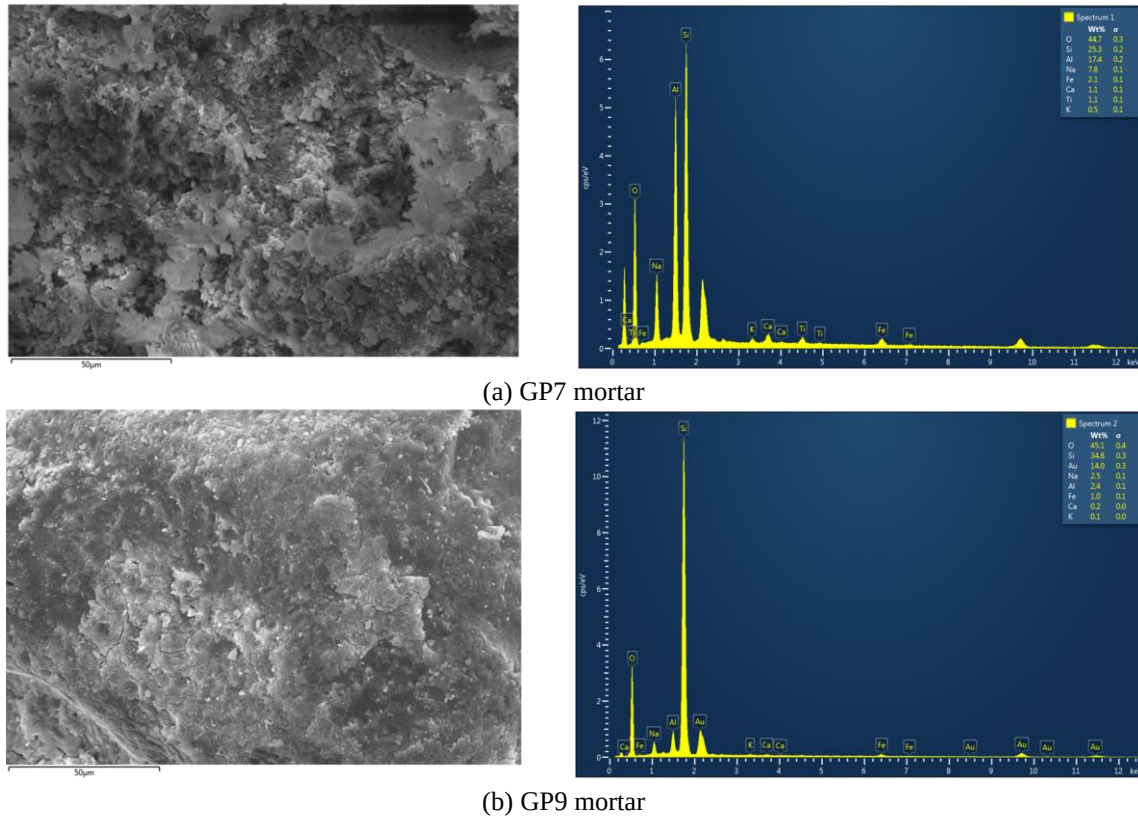


Fig. 9 SEM/EDS analysis results of 28 days ambient cured specimens

less sponge-like microstructures with voids. The sponge-like gel formed, indicates the growth of the structure, which shows that the geopolymerization reaction has taken place. As shown in SEM micrograph, sample with sodium silicate to NaOH ratio of 0.8 (Fig. 9(b)) appeared to have more sponge-like amorphous gel and fiber stripe shape, which contributes to higher compressive strength.

5. Embodied energy

This section provides calculation for the embodied energy of GP mortar mixes for which alkaline solids to MK ratio was 0.3 or more (i.e., GP11 to GP25) and the equivalent cement-sand mortar giving approximately the same strength as that obtained in GP mortar mixes cured at ambient for 28 days. The remaining GP mortar mixes (GP1 to GP10) are ignored because of their low strength. The approximate mix proportions of the equivalent cement mortars of same size specimen are based on the past experience of testing similar mortars. However, interpolations were performed for deciding the mix proportions of some of the mixes (2nd column of Table 3).

OPC is produced by grinding and blending of clay and limestone (after transportation from quarries to the cement factory), which is then calcined at high temperature to form clinker. After the grinding of the clinker, gypsum is added to form the cement product. The overall embodied energy of OPC is therefore the sum of the embodied energy of all the processes involved in its production. The major energy consumption in the production of sodium hydroxide

solution is in the extraction of salt brine, its transportation, and the electrolytic process.

The NaOH solution is then dried by evaporation of water for obtaining solid flakes that were used for making NaOH solution of desired molarity. Sodium silicate is produced by melting of silica sand and sodium carbonate thereby forming water glass. The water glass is then crushed and dissolved in water at high pressure using steam. The major consumption of energy in the production of sodium silicate is in heating at high temperature. Although many databases and inventories exist for embodied energy of different materials but so far there is no internationally accepted database. There are vast differences between the reported embodied energy for different material which result mainly from the difference in the production stages and processes considered (Turner and Collins 2013). The values of the embodied energy of different materials employed namely cement, sand, NaOH, and sodium silicate are given in Table 4. The reference for the value adopted is given in the last column of this table. The embodied energy of MK has been estimated in the subsequent section.

5.1 Embodied energy of metakaolin

As MK was obtained by the calcination of kaolin at 750°C for 3 h, therefore, the embodied energy of MK will be the sum of the energy required for heating kaolin to 750°C and that consumed in maintaining this temperature for 3 h.

The energy required for heating kaolin from ambient temperature i.e., 23°C to 750°C is calculated as the product

Table 3 Embodied energy calculation for equivalent cement mortar mixes (dry unit weight=2200 kg/m³)

GP mortar Mix	Equivalent mortar (Cement: Sand)	Quantities (kg/m ³)		Embodied energy (MJ)			Total embodied energy per unit weight** (MJ/kg)
		Cement	Sand	Cement*	Sand	Total	
GP11	1:1.25	977.8	1222.2	5378	183	5561	2.53 (3.42)
GP12	1:3.00	550.0	1650.0	3025	248	3273	1.49 (1.99)
GP13	1:1.25	977.8	1222.2	5378	183	5561	2.53 (3.42)
GP14	1:1.00	1100.0	1100.0	6050	165	6215	2.83 (3.83)
GP15	1:1.00	1100.0	1100.0	6050	165	6215	2.83 (3.83)
GP16	1:3.00	550.0	1650.0	3025	248	3273	1.49 (1.99)
GP17	1:1.70	814.8	1385.2	4481	208	4689	2.13 (2.87)
GP18	1:1.10	1047.6	1152.4	5762	173	5935	2.70 (3.65)
GP19	1:1.00	1100.0	1100.0	6050	165	6215	2.83 (3.83)
GP20	1:1.50	880.0	1320.0	4840	198	5038	2.29 (3.09)
GP21	1:8.00	244.4	1955.6	1344	293	1638	0.74 (0.97)
GP22	1:4.00	440.0	1760.0	2420	264	2684	1.22 (1.62)
GP23	1:2.50	628.6	1571.4	3457	236	3693	1.68 (2.25)
GP24	1:1.75	800.0	1400.0	4400	210	4610	2.10 (2.82)
GP25	1:2.00	733.3	1466.7	4033	220	4253	1.93 (2.60)

* Cement produced by dry process; ** Value within brackets is calculated for cement produced by wet process

Table 4 Embodied energy of different materials and processes

Material	Stages included	Embodied energy (MJ/kg)	Reference
OPC	Blending, Calcining, Milling (Wet process)	7.5	Reddy and Jagadish (2003)
	Blending, Calcining, Milling (Dry process)	5.5	
Sand	Mining, Separation	0.15	Rajamane <i>et al.</i> (2012)
NaOH	Electrolysis of brine	3.0	
Sodium silicate	Mixing, Heating, Filtration (Liquid phase)	3.0	As calculated in Section 5.1
Metakaolin	Calcination (750°C for 3 h)	0.708	

of the specific heat of kaolin (i.e., 0.000945 MJ kg⁻¹ C⁻¹) and the temperature rise which gives $0.000945 \times (750 - 23) = 0.687$ MJ/kg. If no further energy is supplied, the material will start cooling because of the energy loss due to the difference between the temperature inside and outside the oven. Tempest *et al.* (2009) reported that a heat energy loss of 0.194 MJ m⁻² h⁻¹ will occur when contents are maintained at 750°C in a well-insulated container when the outside temperature is 21°C. The energy required to compensate the heat loss for maintaining the temperature of kaolin at 750°C for 3 h has been accordingly estimated as 0.0214 MJ/kg. Thus, total energy consumption in producing MK is $0.687 + 0.0214 = 0.7084$ MJ/kg.

5.2 Embodied energy of geopolymer mortar

The quantities of materials required for the fifteen GP mixes and the equivalent cement mortar mixes are provided in Tables 5 and 3, respectively. The dry unit weight of the GP and the cement mortar is taken as 2200 kg/m³. The embodied energy of constituent materials and processes given in Table 4 are used for calculating the embodied energy of GP and cement mortar, which are given in Tables

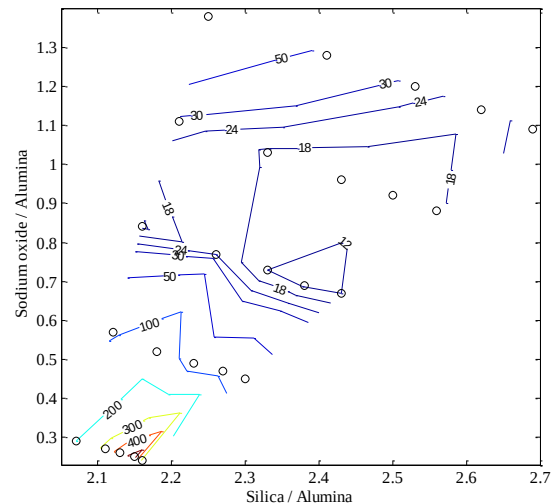


Fig. 10 Contour plot of embodied energy (MJ/g/MPa) of GP mortar after 28 days ambient curing showing the effect of the molar ratios of silica/alumina and sodium oxide/alumina

5 and 3, respectively. As the local production of OPC is based on the wet process, the embodied energy of cement mortar mixes is also calculated for these conditions.

Although the water requirement in the production of cement mortar and geopolymer mortar are not the same, the embodied energy of water has been ignored because the excess water used in the production of geopolymer gets almost compensated by the water required for curing of cement mortar. The embodied energy involved in transportation of different materials has been assumed to be the same which has thus been ignored in the above calculation. Thus, the embodied energy calculated above are not the total absolute values rather these are the relative values which are acceptable for making comparisons. In order to study the effect of molar ratios of silica to alumina (i.e., SiO₂/Al₂O₃), water to sodium oxide (i.e., H₂O/Na₂O), and sodium oxide to alumina (i.e., Na₂O/Al₂O₃) on the

Table 5 Quantities of materials required for 1 m³ of GP mortar (dry unit weight=2200 kg/m³)

GP mortar Mix	MK (kg)	Sand (kg)	Sodium silicate (kg)	NaOH (kg)	Embodied energy (MJ)					Total embodied energy (MJ/kg)	Ratio of embodied energy of GP to cement mortar*
					MK	Sand	Sodium silicate	NaOH	Total		
GP11	1015.4	880	115.1	253.8	719	132	345	762	1958	0.89	35% (26%)
GP12	1015.4	880	197.4	217.6	719	132	592	653	2096	0.95	64% (48%)
GP13	1015.4	880	259.0	190.4	719	132	777	571	2200	1.00	40% (29%)
GP14	1015.4	880	307.0	169.2	719	132	921	508	2280	1.04	37% (27%)
GP15	1015.4	880	345.4	152.3	719	132	1036	457	2344	1.07	38% (28%)
GP16	942.9	880	142.5	314.3	668	132	428	943	2170	0.99	66% (50%)
GP17	942.9	880	244.3	269.4	668	132	733	808	2341	1.06	50% (37%)
GP18	942.9	880	320.7	235.7	668	132	962	707	2469	1.12	42% (31%)
GP19	942.9	880	380.1	209.5	668	132	1140	629	2569	1.17	41% (31%)
GP20	942.9	880	427.6	188.6	668	132	1283	566	2648	1.20	53% (39%)
GP21	880.0	880	166.3	366.7	623	132	499	1100	2354	1.07	144% (111%)
GP22	880.0	880	285.1	314.3	623	132	855	943	2553	1.16	95% (72%)
GP23	880.0	880	374.1	275.0	623	132	1122	825	2703	1.23	73% (55%)
GP24	880.0	880	443.4	244.4	623	132	1330	733	2819	1.28	61% (45%)
GP25	880.0	880	498.9	220.0	623	132	1497	660	2912	1.32	68% (51%)

* Value within brackets is calculated for cement produced by wet process

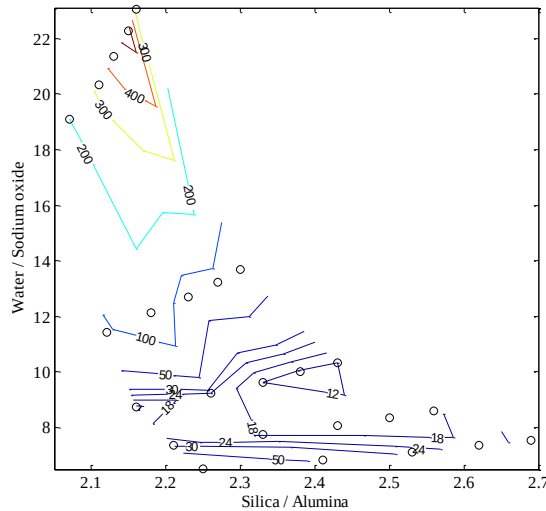


Fig. 11 Contour plot of embodied energy (MJ/g/MPa) of GP mortar after 28 days ambient curing showing the effect of molar ratios of silica/alumina and water/sodium oxide

embodied energy of GP mortar after 28 days ambient curing (MJ/g/MPa), contour maps were plotted on two grids of molar ratios, as shown in Figs. 10-11.

The experimental data points are plotted in these figures using black circle. The contour plots cover only the zone of experimental data points of calculated molar ratios. The pattern of these contour plots is similar to those of compressive strength (Figs. 4-5). The peaks of compressive strength are the valleys of embodied energy, which indicates that the observations made for increasing strength are valid for decreasing embodied energy. The plots revealed an optimal embodied energy of 12 MJ/g/MPa for achieving high strength GP binder.

A comparison of the embodied energies of GP and equivalent cement mortars indicates that the embodied energy of GP mortars, with the exception of GP21, vary from 35% to 95% to that of cement mortar (Table 5).

However, when OPC is produced through the wet process, these percentages reduce to 26% to 72%. The embodied energy of the optimal high strength GP mortars is especially quite low as compared to the cement mortars of equivalent strength varying from 35% to 42% for OPC produced by the dry process and 26% to 31% for OPC produced by the wet process.

6. Conclusions

The major conclusions drawn from the test results of the present study and the embodied energy calculation are:

- The increase in the molar ratio of water to sodium oxide causes sharp decrease in the strength of GP mortar. The increase in this molar ratio beyond 12 makes it a non-structural mortar binder. Moreover, the lowest value of alkaline solids to MK ratio of 0.1-0.2, which corresponds to the molar ratio of silica to alumina of up to 2.25 together with the molar ratio of sodium oxide to alumina less than 0.6 also gives low strength (<15 MPa) and should thus be avoided.
- The highest compressive strength (80-90 MPa) of the oven cured as well as the ambient cured (at 28 days) GP mortar is obtained for the sodium silicate to NaOH ratio of 0.8 and the alkaline solids to MK ratio lying between 0.3 and 0.4. This corresponds to the molar ratio of silica to alumina of 2.45 together with the molar ratio of sodium oxide to alumina varying from 0.65 to 0.90.
- For the manufacture of GP binder for structural applications, the molar ratio of silica to alumina should be greater than 2.3, the molar ratio of sodium oxide to alumina should be between 0.6 and 1.2, and molar ratio of water to sodium oxide should not exceed 12. These molar ratios for the MK of this study correspond to the ratios of sodium silicate to NaOH and alkaline solids to MK lying in the range of 0.75 to 0.85 and 0.3 to 0.4, respectively.

- The compressive strength of ambient cured GP mortar gets stabilized at 28 days of curing at ambient. The gain in strength from 3 to 14 days of curing is high (1%-101%) but the gain in strength from 14 to 28 days of curing is low (0.4%-17.6%).
- The compressive strength of 28 days ambient-cured GP mortar is generally greater than the oven-cured GP mortar due to the evaporation of water before the dissolution of MK in the alkaline activator.
- The embodied energy of the optimal high strength MK-based GP mortars is substantially less than the cement mortar of equivalent strength (35% to 42% for cement produced using dry process and 26% to 31% for cement produced using wet process). The embodied energy of high strength GP mortars is especially quite low as compared to the cement mortars of equivalent strength. The optimal ranges of molar ratios also result in low embodied energy (MJ/g/MPa).
- The high strength of GP mortar achieved and the observations from the present study confirm the potential for the employment of MK-based geopolymer binder as a sustainable energy efficient binder.

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Appendix I. Sample calculation of molar ratios for mix GP14

Molarity of NaOH solution=20 M (NaOH flakes=51.26% and water=48.74%)

Oxides/ Compound	Molecular weight (kg)	Chemical composition				Moles in the geopolymer mix in kg per m ³			
		MK	Na ₂ SiO ₃	NaOH	MK	Na ₂ SiO ₃	NaOH solution	Added water	Total
Mixture Proportion (kg/m ³) →					1015 (= <i>a</i> , say)	307 (= <i>b</i> , say)	330 (= <i>c</i> , say)	160	
An oxide	<i>m</i>	<i>α</i>	<i>β</i>	<i>γ</i>	<i>a α/m</i>	<i>b β/m</i>	<i>c γ/(2<i>m</i>)</i> ¹		
SiO ₂	0.06009	51.00%	29.40%		8617.00	1502.02			10119.02
Al ₂ O ₃	0.10196	42.63%			4245.47				4245.47
Na ₂ O	0.06198	0.62%	14.70%	51.26%	101.74	728.12	2115.16		2945.02
H ₂ O	0.01800		55.90%	48.74%		9533.89	8936.34	2115.16 ²	29458.74
NaOH	0.03999							8873.35 ³	

¹2 in the denominator due to the 2 moles of NaOH give one mole of Na₂O (2NaOH → Na₂O + H₂O)

²Moles of water in NaOH flakes, which is same as the Na₂O moles

³160/0.018=8873.35 kg.

Thus, molar ratios for mix GP14:

$$\begin{aligned}
 \text{SiO}_2/\text{Al}_2\text{O}_3 &= 0119.02 / 4245.47 = 2.38 \\
 \text{H}_2\text{O}/\text{Na}_2\text{O} &= 9458.74 / 2945.02 = 10.00 \\
 \text{Na}_2\text{O}/\text{Al}_2\text{O}_3 &= 2945.02 / 4245.47 = 0.6
 \end{aligned}$$