



# Assessment of reactivity of energy efficient high volume fly ash based geopolymers through various approaches

D SABITHA<sup>1,\*</sup>, J K DATTATREYA<sup>2</sup>, N SAKTHIVEL<sup>2</sup> and M BHUVANESHWARI<sup>2</sup>

<sup>1</sup> CSIR-National Geophysical Research Institute, Hyderabad 500007, India

<sup>2</sup> CSIR-Structural Engineering Research Institute, Chennai 600113, India  
e-mail: sinnve@gmail.com; sabisinnama@ngri.res.in

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**Abstract.** Geopolymer belongs to the family of aluminosilicate polymers. The production of geopolymer generally involves the combination of silicon and aluminium atoms in a hydroxide-promoted activation, followed by a condensation reaction to form an aluminosilicate gel which gives the final hardened binder. Reactivity of geopolymer system is influenced by nature of alkaline activator, ratio of silicon to aluminium, curing time, pH and degree of polycondensation. Fly ash and ground granulated blast furnace slag have been utilized for the synthesis of geopolymers at ambient condition which does not require energy. The investigation aims at assessing the reactivity of geopolymer through various approaches such as degree of reactivity (by means of insoluble residue), infra-red spectroscopy and free alkali content involving various activators and admixtures. The results show that potassium based geopolymer with higher level of alkalinity shows more reactivity. Energy required for the production of geopolymer pastes with sodium silicate as activator ranges from 3.65 to 4.37 MJ/kg, with potassium silicate as activator ranges from 2.24 to 4.45 MJ/kg as against 4.79 MJ/kg for ordinary Portland cement paste. For geopolymer pastes using high volume fly ash 4% less carbon foot print is possible compared to ordinary Portland cement paste.

**Keywords.** Reactivity; geopolymer; energy efficiency; carbon dioxide emission; infrared spectrum.

## 1. Introduction

Building and Construction industry uses approximately 1.6% of the energy requirements globally and contributes to 5% of the total CO<sub>2</sub> output [1]. Non-Portland cement precursors were first synthesized by Purdon [2]. Although ordinary Portland cement is the widely used binder for production of concrete, there are drawbacks of high energy fuel consumption, global warming carbon dioxide emission [3] and there is a need for an alternative binder system with energy efficiency, low carbon production method and geopolymer serves the purpose [4]. Geopolymers are of the general formula  $M_n\{-(SiO_2)_z-AlO_2\}_n \cdot W H_2O$  where,  $M_n$  is an alkali metal cation (potassium, sodium or cesium),  $Z$  is 1, 2, 3, ...,  $n$  is the degree of poly condensation and  $W$  is the no. of molecules of water. Geopolymers are obtained from thermally activated natural material (e.g., kaolinite clay or weathered rocks) or industrial by-products (e.g., fly ash (FA) or ground granulated blast furnace slag (GGBS) or

metakaolin) by dissolution of amorphous aluminosilicate [5] in an alkaline solution forming the gel phase. World-wide demand for power has resulted in the increase of thermal power stations and consequent increase in the production of fly ash needs to be made into value added product. In this study high volume (80%) of fly ash is a raw material source for a successful and practically usable binder. The binder may be used for pavement applications [6, 7]. The mechanism of geopolymerisation consists of mixing, dissolution, polymerization/colloidal formation, gelation, setting [8] and hardening followed by solid-state gel transformation leading to geopolymeric gel along with undissolved particles. Reactivity is a measure of the synthetic geopolymeric gel formation. Choice of raw materials, processing conditions, pH [9], nature of alkali metal cation, silica ratio, its concentration, curing condition, insoluble residue and mechanical strength are the various factors that affect reactivity. Geopolymers are a result of high degree of polycondensation with excellent mechanical strength [10] as well as outstanding physical and chemical property like thermal stability, strength and long term durability [11]. These are easily recyclable, with a wide range of coefficient of thermal expansion depending on the raw material and also a "Green Material" as low energy is required for the synthesis and almost no waste gas emission. Plays an

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\*For correspondence  
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important role of fixation of hazardous material [12] and also fire resistant [13].

Jamieson *et al* indicated that utilising combination of industrial by-products lowers the embodied energy of Bayer-derived geopolymer and estimated that Bayer derived geopolymer concrete is only 33% of the embodied energy of ordinary Portland cement concrete [14].

Study by Criado *et al* [15] shows increase in the soluble silicate concentration on fly ash in an alkaline solution enhances the reactivity of fly ash by increasing primary phase dissolution. At low silicate concentrations ( $\text{SiO}_2/\text{M}_2\text{O} = 0.2$ ,  $\text{M} = \text{Na}$  or  $\text{K}$ ), availability of Al favours crystallization of zeolites [16] and at higher silicate concentrations ( $\text{SiO}_2/\text{M}_2\text{O} = 0.5, 1.79$  and  $2.0$ ,  $\text{M} = \text{Na}$  or  $\text{K}$ ), there is polymerisation of geopolymer gel. Addition of impurities in the geopolymeric raw materials like fly ash or slag plays an important role in altering the product of geopolymerisation [17]. Addition of impurities like calcium, iron in fly ash and slag has the effect of change in material property, setting time, slump, strength and shrinkage.

Xu *et al's* work [18] reveals that the minerals with a greater extent of dissolution exhibit better compressive strength after polymerization. The amount of calcium oxide, potassium oxide, molar ratio of Si/Al in the solution during dissolution has a significant effect on strength.

Final compressive strength is affected by the calcium content present in the raw materials. Both geopolymeric and calcium silicate hydrate gels fill the voids and pores of the formed binders in low alkalinity systems. The geopolymeric gel becomes the predominant phase with higher alkalinity. Mechanical strength of the final product is increased due to the bridging of different hydrated phases and unreacted particles [19].

It is difficult to predict the performance of geopolymers because the type, composition and reactivity of raw materials, type of activator [20], temperature, pH and cations [21] play a major role in controlling the chemistry of resulting geopolymer and hence the properties. Variation in widespread use of geopolymer is restricted due to lack of detailed scientific understanding regarding reactivity especially in construction industry. Reactivity can be evaluated by nature and composition of raw material as well as product formed by various means such as unreacted alkalis, degree of reactivity (by means of insoluble residue), infra-red spectroscopy [22], X-ray diffraction [23] and pH. Assessing reactivity of geopolymer is challenging and hence the present study aims to investigate it through various approaches by means of pH, degree of reactivity, free alkalis, infra-red spectroscopy and compressive strength. As high temperature calcination is required for ordinary Portland cement production which is eliminated in geopolymer it saves energy. Energy in the form of thermal curing is used for the synthesis of geopolymer in general. Ambient curing in the present study eliminates the need for thermal energy.

## 2. Methodology

### 2.1 Materials used

The basic source materials in the present study required for the synthesis of geopolymer are FA (Class F) and GGBS procured from Ennore Thermal Power Station, Chennai and Andhra Cements Ltd., Visakhapatnam, respectively.

FA conforming to grade 1 (IS : 3812 : 1981) [24] and GGBS conforming to Indian standard (IS : 12089 : 1987) [25] are used.

The chemical composition of FA used is given in table 1. Table 2 gives the physical properties FA and GGBS used in the study. Table 3 gives the chemical composition of GGBS used in the study. The geopolymer pastes are prepared in the Hobart mixer by dry mixing the binder material comprising of 80% FA and 20% GGBS for 10 min followed by the addition of the alkaline activator solution (AAS) consisting of sodium hydroxide (NaOH) with sodium silicate ( $\text{Na}_2\text{SiO}_3$ ) or potassium hydroxide (KOH) with potassium silicate ( $\text{K}_2\text{SiO}_3$ ) such that the liquid/binder (l/b) is 0.6 and 0.5, respectively. The properties of sodium, potassium silicate solutions used to prepare the AAS solution are given in table 4. While handling sodium hydroxide, potassium hydroxide and alkaline activator solution gloves was used and care was taken. Naming of the mixes is based on the alkaline activator solution, additives used with the raw materials and is given below.

- PHPS - Potassium hydroxide + potassium silicate
- PHSS - potassium hydroxide + sodium silicate
- FALL - Fly ash + lime + sodium hydroxide + sodium silicate
- SHSS - sodium hydroxide + sodium silicate
- PPS - Potassium hydroxide + potassium silicate + sucrose (2%)
- SSST - sodium hydroxide + sodium silicate + sucrose (2%) + tartrate (0.5%)
- SHSST - Sodium hydroxide + sodium silicate + tartrate (0.5%)
- SHSSU - Sodium hydroxide + sodium silicate + sucrose (1%)
- SSS - Sodium hydroxide + sodium silicate + sucrose (2%).

In order to improve the workability of fresh paste, attempts are made using sugar and tartrate for a few samples. Attempt has been made using lime to increase the reactivity but it failed due to poor binding with fly ash. The fresh slurry is placed in a  $50 \times 100$  mm cylinder mould. The specimens are compacted in 3 layers, each layer vibrated for 10 s in the vibrating table. The specimens are wrapped in wet gunny bag for a day. The demoulding of the specimens is carried out depending on the setting time and kept at ambient temperature until the testing age. The compressive strength test is performed at the age of 7th and 28th days. The reported strengths are the average of three tests.

Samples for analysis for pH, degree of reactivity and free alkali are prepared by breaking the paste specimens at the

**Table 1.** Chemical composition of Ennore fly ash (% by mass).

SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	CaO	MgO	Na <sub>2</sub> O	K <sub>2</sub> O	TiO <sub>2</sub>	Mn <sub>2</sub> O <sub>3</sub>	SO <sub>3</sub>	LOI	Insoluble residue	Reactive silica
62.1	27.44	4.57	0.83	0.55	0.04	1.17	1.09	0.04	0.40	0.76	86.92	31.79

**Table 2.** Properties of fly ash and GGBS.

Sl.No	Type	Fly ash	GGBS
1.	Specific gravity (SSD <sup>a</sup> )	2.2	2.9
2.	Fineness (Sq.m/kg)	419	400
3.	Loss on Ignition (%)	0.76	2.1
4.	Bulk density (SSD <sup>a</sup> ), kg/m <sup>3</sup>	995	1720

<sup>a</sup> Saturated surface dry condition

**Table 3.** Chemical composition of GGBS (% by mass)

CaO	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Na <sub>2</sub> O	K <sub>2</sub> O	MgO	LOI	Insoluble residue	Reactive silica
40.3	43.4	12.5	0.9	0.6	1.5	2.1	62.23	30.51

**Table 4.** Properties of silicate solutions.

Parameter	Potassium Silicate	Sodium Silicate
Specific gravity	1.38	1.50
K <sub>2</sub> O	12.50	–
Na <sub>2</sub> O	–	14.20
SiO <sub>2</sub>	26.30	31.26
Total solids %	38.8	45.46
Hardness (baume)	40	50
Viscosity (cP)	440	900

age of 28 days. These samples are finely ground in a mortar with pestle and sieved through a 75 micron sieve. The sieved samples are kept in a tightly closed container to avoid carbonation.

## 2.2 Insoluble residue

It is determined by digestion with HCl and is a combination of procedures [26, 27], which is a measure of the portion that does not go into the insoluble residue. The degree of reactivity or “ $\alpha$ ” and the insoluble residue are determined with equations (1) and (2).

$$\text{insoluble residue (\%)} = M(\text{final})/M(\text{initial}) \quad (1)$$

$$\alpha(\%) = 100 - \text{insoluble residue (\%)} \quad (2)$$

where  $M_{\text{initial}}$  is the initial weight of the sample;  $M_{\text{final}}$  is the final weight of the insoluble residue after the HCl treatment and calcination at 1000 °C; insoluble residue is the unreacted percentage of fly ash and  $\alpha$  is the percentage of reaction product.

## 2.3 Flame photometer

About 1 g of finely ground sample taken in a china dish, 25 mL of distilled water and 5 mL of concentrated HCl are added and stirred well. About 50 ml of water is added and digested on a steam bath or hot plate for 15 min at 140–160 °C. It is filtered through a medium textured Whatman filter paper and the solution is made up to 100 mL in a standard flask. A series of standard sodium chloride and potassium chloride solutions having the concentration 10, 20, 30, 40 and 50 ppm are prepared in standard flasks and using these, calibration is carried out. The unknown sample is taken and its concentration is measured for sodium and potassium. From this, the concentration of the free alkali is measured.

## 2.4 pH determination

The pH of the paste sample is determined at 1: 5 dilution as adopted by ISO [28] by titration against 0.1 M HCl using

methyl red as indicator. From the titre value, the concentration of  $[\text{OH}^-]$  of the sample is determined.

$$\text{pOH} = -\log[\text{OH}^-].$$

The above equation is related to pH as  $\text{pH} + \text{pOH} = 14$ ,  $\text{pH} = -\log[\text{H}^+]$ .

### 2.5 Infrared spectroscopy

Sample preparation for Infrared spectroscopy is made by standard KBr disc technique for geopolymer pastes. FTIR (Fourier transform infrared) spectrum is scanned from 400 to  $4000\text{ cm}^{-1}$  range using Perkin Elmer FTIR Spectrophotometer.

## 3. Results and discussion

Alkali activator plays a crucial role in the initial formation of the gel. Si/Al ratio affects the geopolymeric network formed depending on the curing time. Davidovits [29] proposes that the ranges of the oxide molar ratios suitable for geopolymer synthesis under thermal curing may be as follows  $0.2 < \text{Na}_2\text{O}/\text{SiO}_2 < 0.48$ ,  $3.3 < \text{SiO}_2/\text{Al}_2\text{O}_3 < 4.5$  and  $10 < \text{H}_2\text{O}/\text{Na}_2\text{O} < 25$ . Based on tests performed on geopolymer pastes where calcined kaolin is the source material [30], it is found that the optimum composition occurs when the ratio of  $\text{Na}_2\text{O}/\text{SiO}_2$  is 0.25 and the ratio of  $\text{H}_2\text{O}/\text{Na}_2\text{O}$  is 10.0.

The degree of reactivity, pH and compressive strength of geopolymer pastes with different activators and chemical admixtures carried out without thermal curing in the present investigation are given in table 5. Free alkali content of the pastes is provided in table 6. Annexure I contains molar computation of geopolymer mixes. Based on previous trials choice of dosage, molarity have been chosen.

Variation in the amount of potassium silicate solution causes a drastic change in the compressive strength of

geopolymer pastes. Paste of PHPS-1 with hydroxide: silicate: water of gave a compressive strength of 10.32 MPa whereas that of PHPS-2 gave a compressive strength of 43 MPa due to molarity of hydroxide being low and high. The ratio of  $\text{H}_2\text{O}/\text{K}_2\text{O} = 1.12, 0.42$ ,  $\text{SiO}_2/\text{K}_2\text{O} = 0.9, 0.85$  respectively for the above pastes (Annexure I). As the ratio of  $\text{H}_2\text{O}/\text{K}_2\text{O}$  increases the compressive strength decreases, which is in good agreement with Hardjito *et al's* work [31] though their work is with sodium silicate system. When there is not enough potassium oxide present with respect to the amount of silica, geopolymerisation is hindered. When there is enough hydroxide solution present the glassy phase of the fly ash, slag gets corroded and dissolution starts up and polycondensation takes place giving rise to higher reactivity. As sucrose and tartrate interfere with polycondensation and dissolution process decreased the compressive strength and is supported by degree of reactivity.

It is observed that potassium hydroxide-potassium silicate (PHPS-2) combination provides compressive strength of 43 MPa compared to that of sodium hydroxide-sodium silicate where the compressive strength is 16.8 MPa due to the presence of sodium silicate causing less geopolymeric network formation and the degree of reactivity is high for PHPS-2 as the solubility of potassium silicate is high compared to sodium silicate. Chemical admixtures such as lime, sucrose, sucrose along with tartrate decreased the compressive strength marginally. Efflorescence is observed in the case of sucrose admixed geopolymer revealing that the binding of the geopolymeric matrix is not proper due to the presence of unreacted alkali and crystalline compound formation. Disodium tartrate cannot perform as a binding aid in the presence of sucrose. Chemical admixtures such as lime, sucrose, sucrose along with tartrate interfere with the aluminosilicate gel formation and hence there is decrease in the strength.

Degree of reactivity is higher for PHPS-2 and the compressive strength is also higher. Higher reactivity of potassium compounds compared to sodium favour dense polycondensation and hence increased strength. With fly

**Table 5.** Degree of reactivity, pH and compressive strength of geopolymers.

Sl.No	Sample ID	Insoluble residue (%)	Degree of reactivity (%)	pH	Compressive strength 7 days (MPa)	Compressive strength 28 days (MPa)	l/b
1	PHPS-1(P)	62.362	37.638	12.518	5.1	10.32	0.54
2	PHSS(P)	57.83	42.17	12.605	13.4	14.99	0.54
3	FALL(P)	54.5785	45.4215	12.356	5.7	15.36	0.54
4	SHSS-1(P)	60.68	39.32	12.396	14.8	16.83	0.54
5	SHSS-2(P)	44.564	55.436	13.488	11.2	12.98	0.6
6	PHPS-2(P)	35.89	64.11	13.238	23.4	43.03	0.5
7	PPS(P)	41.52	58.475	13.208	17.8	25.83	0.5
8	SHSST(P)	42.475	57.525	12.94	8.2	16.88	0.6
9	SHSSU(P)	43.115	56.885	12.64	12	13.30	0.6
10	SSST(P)	46.3255	53.6745	13.63	6.4	11.41	0.6
11	SSS(P)	35.3315	64.6647	13.65	11.5	11.98	0.6

**Table 6.** Free alkali in geopolymers.

Sl.No	Sample ID	At the time of casting (%)		After 28 days (%)		Mix proportion Binder:l/b
		Na <sub>2</sub> O	K <sub>2</sub> O	Na <sub>2</sub> O	K <sub>2</sub> O	
1	PHPS-1(P)	0.94	24.778	0.080676	1.036129	1:0.54
2	PHSS(P)	12.196	10.09	0.856612	0.983424	1:0.54
3	FALL(P)	–	–	1.236414	0.168588	1:0.54
4	SHSS-1(P)	21.496	1.77	1.585836	0.12042	1:0.54
5	SHSS-2(P)	34.403	1.77	1.470674	0.4710	1:0.6
6	PHPS-2 (P)	0.94	24.48	0.401459	0.845216	1:0.5
7	PPS(P)	0.94	3.243	0.346656	4.181346	1:0.5
8	SHSST(P)	34.403	1.77	1.369688	0.368891	1:0.6
9	SHSSU(P)	34.403	1.77	1.658369	0.305783	1:0.6
10	SSST(P)	13.473	1.77	0.967072	0.308256	1:0.6
11	SSS(P)	13.473	1.77	1.201271	0.35019	1:0.6

ash and slag as raw materials the degree of reactivity lies in the range 37.6–64.6% at 28th day. Jimenez *et al* [32] reports the degree of reactivity in the range of 60–90% with the temperature range 85–200 °C by the alkaline activation of metakaolin–fly ash mixtures at the age of 1 day. In the metakaolin samples the degree of reactivity is greater than in the fly ash with metakaolin samples at any of the tested temperatures. In the present work 80% FA with 20% GGBS at ambient temperature as against 50% FA with 50% metakaolin is used and the results are convincing mainly because the metakaolinite reacts almost in its entirety, whereas in the fly ash, only the glassy phase reacts and not fully; the other phases present in the fly ash (quartz, mullite, etc.) are practically not altered at the activation conditions used. Energy required for the production of geopolymer pastes with sodium hydroxide and sodium silicate system ranges from 3.655–3.993 MJ/kg, with potassium hydroxide and potassium silicate ranges from 2.246 to 4.456 MJ/kg as against 4.798 MJ/kg for ordinary Portland cement paste.

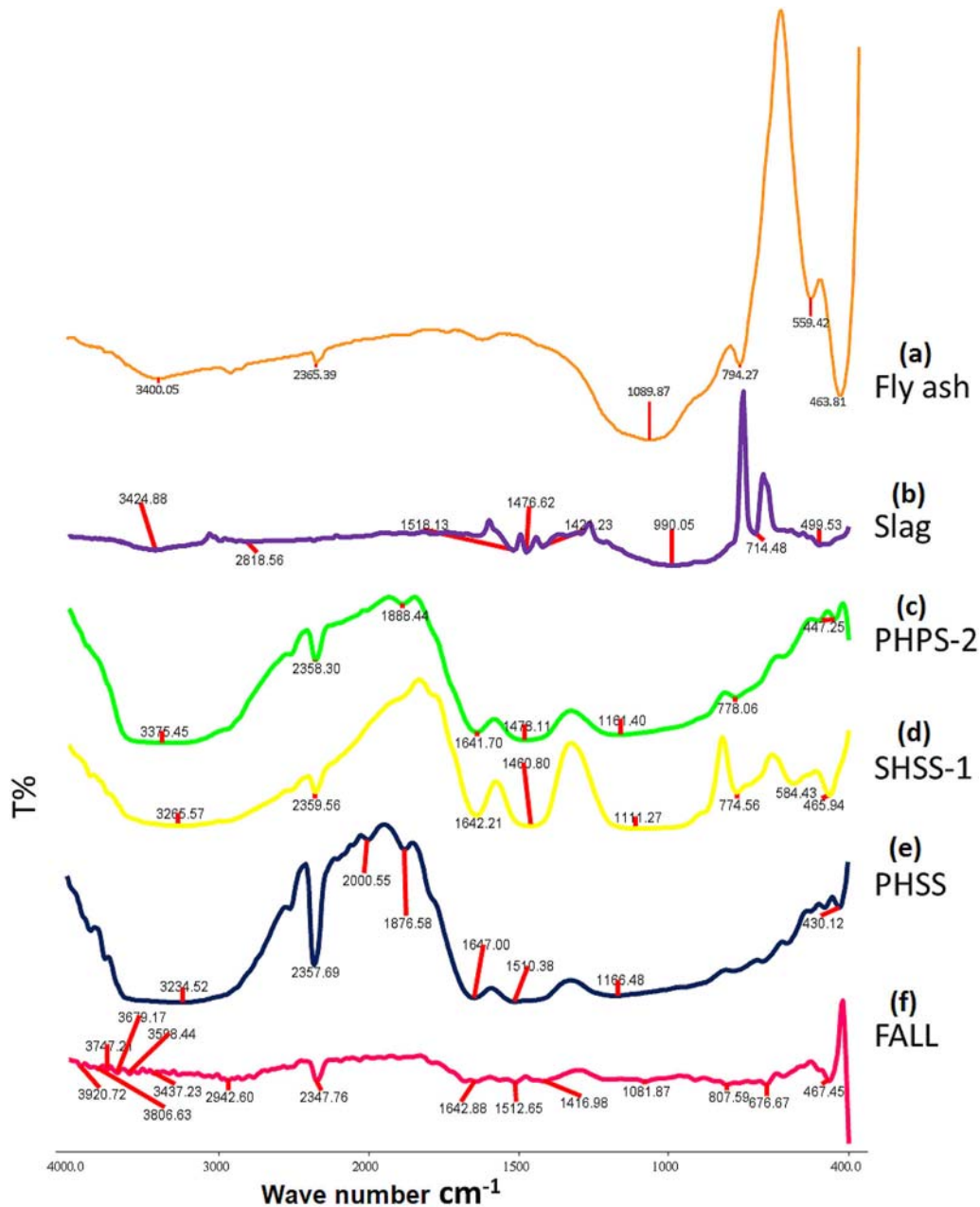
pH of the geopolymer samples has been found to affect the geopolymerisation due to the presence of alkali hydroxides and silicates. In cement powder, the pH of the hardened powder sample solution is generally greater than 12.45. In order to find the alkaline nature of samples the test is carried out. Addition of chemical admixtures does not cause a remarkable change in pH as well as degree of reactivity of the geopolymer pastes. In case of PHPS pastes it is seen that the difference of pH from 12.5 to 13.2 causes a remarkable change in the compressive strength as well as degree of reactivity. This is due to the tendency of highly alkaline solution of greater molarity that can break the glassy phase of FA and GGBS. In case of FALL the pH is 12.35 (less than 13) where in which it is not possible to speed up the activation of FA and this agrees with Fraay *et al*'s work [33].

Alkali ions may be bound in the geopolymeric matrix for charge balancing or held in the surface of the geopolymers.

Sodium compound geopolymers have the tendency to effloresce. Potassium compounds are superior in this respect and hence are utilized as activators in this study. The free alkali content is almost 1% or less in all the samples except PPS and the free alkali oxide content is less for potassium silicate than with sodium silicate samples indicating that binding of alkalis by potassium is more effective than with sodium (table 6). Since the maximum amount sodium oxide present in the sodium hydroxide–sodium silicate geopolymer is only 1.65% at 28 days it is negligible as it is in the geopolymer matrix. As there is no free sodium/potassium hydroxide let into the environment the effect of causticity is not of a major concern. In the presence of sucrose the free alkali content is more, confirming that there is no dense network formation which is further confirmed by lower compressive strength.

The infrared spectra of the untreated FA (figure 1a) shows two main spectral peaks at about 463 and 1089 cm<sup>-1</sup>, which could be attributed to Si–O–Si and O–Si–O bending and asymmetric stretching [34, 35], respectively. In addition, other peaks associated with Al–Si framework, which are of much lesser intensity, occur at about 794 and 559 cm<sup>-1</sup> due to symmetric stretching of Si–O–Si and Al–O–Si bond. The presence of bands in the region 800–600 cm<sup>-1</sup> arises from the presence of sillimanite and mullite. The occurrence of silicon-oxygen band at 1080 cm<sup>-1</sup> is due to high degree of polymerisation. Peaks at 465, 564, 724 cm<sup>-1</sup> indicate network tetrahedral aluminosilicate from mullite.

The spectrum of GGBS (figure 1b) indicates the amorphous nature of the material (broad band). The peaks in the range 900–650 (band at 990 cm<sup>-1</sup>) and 680–400, 850–700 cm<sup>-1</sup> (714 cm<sup>-1</sup>) are due to asymmetric stretching of Al–O–Al, Al<sub>V</sub>O<sub>4</sub> (Coordination number of Al is VI–(Si<sub>2</sub>O<sub>7</sub>)<sup>6-</sup>) octahedra, and pure aluminate. The most intense band at 990 cm<sup>-1</sup> proves the glassy phase in the structure of slag [35].



**Figure 1.** Fourier transform infrared spectra.

In case of geopolymer pastes, the peak around  $465 \text{ cm}^{-1}$  is attributed to in-plane bending of Al-O and Si-O linkage and the bands at  $1600$  and  $3450 \text{ cm}^{-1}$  are due to bending (H-O-H) and stretching of O-H groups (molecular water) [36]. The broad band due to FA (around  $1089 \text{ cm}^{-1}$ ) has decreased which shows the reactivity of FA in the highly alkaline activator medium of geopolymer leading to formation of aluminosilicate polymer (figure 1c, d, e). There is also a shift from octahedral  $\text{AlVI}\text{O}_4$  (compared to slag) to higher wave number (from  $714 \text{ cm}^{-1}$ ) which shows the

transformation of Al due to geopolymerisation. A sharp peak at  $1570\text{--}1410 \text{ cm}^{-1}$  is assigned to the vibrational stretching frequency of C-O in carbonates. Free (unreacted) alkali cations react with dissolved  $\text{CO}_2$  in order to form carbonate in the gel matrix. Through capillary pores after setting alkali-containing pore solution diffuses to the surface due to a developing concentration gradient between the core and surface of the sample causing precipitation of carbonates on the surface, known as efflorescence. Peak intensities of molecular water and carbonate are greater in

geopolymers than in raw materials. There is a shift of peak to a lower wave number upon activation suggesting a higher content of non-bridging oxygen due to hydrolysis, i.e., more Si atoms in Si-O-Si (or Si-O-Al) are replaced by M atoms.

Attempt to bring about geopolymerisation of FA with lime fails due to the low solubility of calcium oxide and its inability to get dispersed. There is no significant peak relating to geopolymerisation and the absence of peak shift from  $1089\text{ cm}^{-1}$  for fly ash indicates the absence of activation in case of FALL (figure 1f).

According to the energy calculation by Tempest *et al* [37] in ordinary Portland cement the energy required for the manufacture/production is considered whereas the energy for development is considered in geopolymer. Since fly ash and silica fume are industrial by-products, their contribution to energy is considered nil in their analysis. Energy required for production of ingredients along with carbon dioxide emission is presented in table 7a [38–41]. Fly ash and GGBS are waste products from industry. The energy of fly ash may be considered nil as collection of fly ash from flue gas is mandatory in India. GGBS involves use of grinding energy. As the geopolymers are prepared at ambient temperature curing without the need for thermal energy proved to be energy efficient. Energy of Ordinary Portland cement is  $4.798\text{ MJ/kg}$  [42]. Energy for transportation is not considered in the analysis. Energy requirement and carbon dioxide emission for the geopolymer mixes with Ordinary Portland cement paste as seen from table 7b reveals that the later has a higher energy requirement with a higher carbon dioxide emission. File containing excel sheet for the carbon dioxide emission calculation for the geopolymer pastes has been attached under supplementary section. The difference in energy required to produce PHPS-2/PPS and ordinary Portland cement paste in our study is  $0.342\text{ MJ/kg}$  under ambient curing. The difference in energy for production of  $70\text{ MPa}$  ordinary Portland cement concrete and  $67.5\text{ MPa}$  geopolymer concrete by heat curing at  $75\text{ }^\circ\text{C}$  is  $630\text{ MJ}$  or  $30\%$  higher for ordinary Portland cement concrete [37]. The embodied energy of Bayer derived geopolymer is only

**Table 7. (a).** Energy and carbon dioxide emission of ingredients.

Material	Energy (MJ/kg)	Carbon dioxide emission (per kg)
Fly ash	0	0.01 [33]
GGBS	0.31	0.083 [34]
Sodium hydroxide	20.5	1.92 [35]
Sodium silicate	5.37	1.5 [36]
Potassium hydroxide	19.2	2.2
Potassium silicate	4.3	1.3
Ordinary Portland cement	4.798	0.93 [37]
Lime	–	0.785

**Table 7. (b).** Energy and carbon dioxide emission of geopolymer mixes.

Mix	Energy (MJ/kg)	Carbon dioxide emission (per kg)
PHPS-1	2.246	0.494
PHSS	4.37	0.816
FALL	3.064	0.734
SHSS-1	3.993	0.688
SHSS-2	3.993	0.589
PHPS-2	4.456	0.719
PPS	4.456	0.719
SHSST	3.655	0.589
SHSSU	3.655	0.589
SSST	3.655	0.589
SSS	3.655	0.589
Ordinary Portland cement paste	4.798	0.944

$18\%$  of that of ordinary Portland cement [14]. Since grinding energy is considered in our work and on paste it is acceptable. Energy and carbon dioxide emission values corresponding to potassium hydroxide, potassium silicate and lime were provided by manufacturer. Geopolymer pastes made from waste by-products are energy efficient and low in carbon dioxide emission and environment friendly as the waste products are utilized effectively. It saves time when compared to ordinary Portland cement mortar that requires water curing till 28th day.

#### 4. Conclusions

High volume fly ash based binder is synthesized without the need for energy in the form of heat making a value added product. For the same binder content and for the same alkali to silicate ratio potassium silicate shows maximum compressive strength due to greater geopolymerisation and provides better reactivity. Water added for production of potassium silicate geopolymer paste is less compared to that of sodium silicate ones. Free alkali content greater than  $1\%$  reveals less reactivity and hence lower compressive strength. The degree of reactivity is found to be maximum for the potassium silicate geopolymer paste in which the silicate concentration is more. Addition of calcium compound in the form of lime interferes with geopolymerisation as shown by the compressive strength though there is only marginal change in pH. At ambient temperature lime does not provide reactivity. Factors affecting reactivity of geopolymers at room temperature are studied (pH, degree of reactivity and alkali). During geopolymerisation,  $\text{SiO}_4$  and  $\text{AlO}_4$  are released and octahedral Al is transformed into other coordination. Higher the shift greater is the reactivity.

Infrared spectroscopy is a fast and reliable tool for assessing the reactivity of geopolymer system. Energy and carbon dioxide emissions are less for geopolymer when compared to ordinary Portland cement pastes. 4% less carbon footprint is possible with geopolymer thereby reducing global warming gas emission.

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### Nomenclature

FA	Fly ash
GGBS	Ground granulated blast furnace slag
LOI	Loss on ignition
SSD	Saturated surface dry condition
P	Paste

### Annexure I

Molar computation of geopolymer mixes.

Item	PHPS-1	PHSS	FALL	SHSS-1	SHSS-2	PHPS-2	PPS	SHSST	SHSSU	SSST	SSS
Fly ash g	844.15	844.15	896.5	844.15	844.15	844.15	844.15	844.15	844.15	844.15	844.15
GGBS g	211.03	211.03	–	211.03	211.03	211.03	211.03	211.03	211.03	211.03	211.03
Lime g	–	–	224.1	–	–	–	–	–	–	–	–
AAS g	569.80	569.80	504.3	609.37	542.99	686.11	686.11	609.37	609.37	609.37	609.37
NaOH g	–	–	109.8	132.76	132.76	–	–	132.76	132.76	132.76	132.76
KOH g	63.311	151.94	–	–	–	144.44	144.44	–	–	–	–
Na <sub>2</sub> SiO <sub>3</sub> g	–	303.89	219.7	265.52	199.14	–	–	199.14	199.14	199.14	199.14
K <sub>2</sub> SiO <sub>3</sub> g	253.24	–	–	–	–	433.33	433.333	–	–	–	–
H <sub>2</sub> O added g	253.24	113.96	174.6	211.09	211.09	108.33	108.33	211.09	211.09	211.09	211.09
Na <sub>2</sub> O Moles	–	2932	7134	7989	7837	–	–	7837	7837	7837	7837
SiO <sub>2</sub> Moles	11358	11816	12013	11616	11271	12147	12147	11271	11271	11271	11271
Al <sub>2</sub> O <sub>3</sub> Moles	2526	2606	2768	2606	2606	2526	2526	2606	2606	2606	2606
H <sub>2</sub> O Moles	14069	6331	9705	11727	11727	6018	6018	11727	11727	11727	11727
H <sub>2</sub> O/Na <sub>2</sub> O	–	2.15	1.36	1.46	1.49	–	–	1.49	1.49	1.49	1.49
SiO <sub>2</sub> /Na <sub>2</sub> O	–	4.02	1.68	1.45	1.43	–	–	1.43	1.43	1.43	1.43
SiO <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub>	4.5	4.53	4.33	4.45	4.32	4.81	4.81	4.32	4.32	4.32	4.32
Water/GPS	0.2	0.08	0.13	0.16	0.16	0.07	0.07	0.16	0.16	0.16	0.16
Na <sub>2</sub> O/(Al <sub>2</sub> O <sub>3</sub> + SiO <sub>2</sub> )	–	0.2033	0.48	0.56	0.56	–	–	0.56	0.56	0.56	0.56
K <sub>2</sub> O Moles	12607	13850	–	–	–	14292	14292	–	–	–	–
H <sub>2</sub> O/K <sub>2</sub> O	1.12	1.01	–	–	–	0.42	0.42	–	–	–	–
SiO <sub>2</sub> /K <sub>2</sub> O	0.9	0.85	–	–	–	0.85	0.85	–	–	–	–
K <sub>2</sub> O/(Al <sub>2</sub> O <sub>3</sub> + SiO <sub>2</sub> )	0.91	0.96	–	–	–	0.97	0.97	–	–	–	–



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