



Geopolymerization behavior of fine iron-rich fraction of brown fly ash



Sujeet Kumar^a, Jean Noël Yankwa Djobo^{b,c}, Anil Kumar^a, Sanjay Kumar^{c,*}

^a Department of Applied Science & Humanities, NIFFT Ranchi, 834003, India

^b Laboratory of Applied Inorganic Chemistry, Department of Inorganic Chemistry, Faculty of Science, University of Yaoundé I, P.O. Box 812, Yaoundé, Cameroon

^c CSIR, National Metallurgical Laboratory, Jamshedpur 831007, India

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ABSTRACT

Iron rich brown fly ash has been segregated into (a) coarse, and (b) fine size fractions using air classification. The suitability of fine iron-rich fly ash (CFA) has been evaluated for the synthesis of geopolymer. The behavior of CFA based geopolymer in relation to reactivity, NaOH concentration and sodium silicate to sodium hydroxide (S/H) ratio has been studied. The concentrations of NaOH (6, 8, 10 and 12 M) and S/H ratios (0.33, 1.0 and 3.0) were the variable parameters. Calorimetric studies revealed that the total heat release increased with NaOH concentration, but decreased with the increase in S/H ratio. The geopolymer synthesis was done by thermal curing at 60 °C for 24 h. It was found that the compressive strength increased with an increase in the NaOH concentration. The increase in S/H ratio from 0.33 to 1.00 resulted in a significant increase in the compressive strength, but a further increase from 1.00 to 3.00 resulted in a slight decrease in compressive strength. High strength geopolymer mortar up to 70 MPa at 28 days was obtained, when the mixture was formulated with 12 M NaOH and S/H ratio of 1.00. From SEM-EDS studies, an increase in the degree of reaction and formation of geopolymer gel was observed with increase in NaOH concentration. Also it revealed that the geopolymer gel obtained was ferro-sialate based polymers with chemical formula close to $[Ca, Na]_{-}[-Fe-O]_{x}[-Si-O-Al-O]_{1-x}[-Si-O]_{y}$, wherein “x” is less than or equal to 0.5, and “y” is a value between 0 and 25. Formation of the compact microstructure has resulted in improved strength properties of geopolymer.

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1. Introduction

Geopolymers are semi-crystalline aluminosilicate polymers synthesized by the reaction of a solid aluminosilicate powder with an alkaline solution [1–4]. From a terminology point of view, if geopolymer hardens at room temperature like Portland cement it is called “geopolymer cement”, whereas it is called “geopolymer binder” if it requires heat treatment for hardening [5]. Geopolymer binders are considered as potential alternative to Portland cement because of its binding properties resulting in high strength, low permeability, and excellent durability [6,7]. Moreover, its production is less energy-intensive with 80% less CO₂ emission compared to Portland cement [8–10].

The utilization of fly ash for geopolymer synthesis have been one of the most explored research areas in the last decades. This is due to the huge availability of fly ash all over the world and the needs to extend its different uses for bulk volume utilization [11].

In the present work, a brown color fly ash was collected from a coal-based thermal power plant in Mundra, India. The brown color of this fly ash is due to the high percentage of iron content. Thus, at many places, it is not acceptable as pozzolanic material for Portland pozzolana cement as it gives brownish color to cement. We have observed that the concentrations of iron oxides are more in lower size fractions of brown fly ash. Thus, we have used the air classification to segregate coarser and finer fractions. The segregated coarser fraction was grey in color. Thus, a study on their use as pozzolanic material for cement has been carried out and communicated elsewhere [12]. The iron rich-fly ash (Fe₂O₃ or Fe₃O₄) is generally avoided because it is believed that it decreases the compressive strength of geopolymer cements/binders [13]. But for the mass production of fly-ash geopolymer binders, such limitation should overcome. Elsewhere, it was reported that by segregating finer portion fly ash, its reactivity toward geopolymerization was considerably enhanced [14,15].

This paper reports the study of the geopolymerization and strength behaviors of fine iron-rich fly ash-based geopolymers. The characterizations of fly ash were done using X-Ray Fluorescence (XRF), X-ray diffractometry (XRD) and Particle size distribution (PSD). The geopolymerization reaction in various NaOH

* Corresponding author.

E-mail addresses: sunju@nmlindia.org, sanjay_kumar_nml@yahoo.com (S. Kumar).

concentration and sodium silicate to sodium hydroxide (S/H) ratio was monitored using Isothermal calorimetry. The hardened geopolymer pastes resulting were characterized using Field emission gun-scanning electron microscopy coupled to Energy dispersive X-ray spectroscopy (FEG-SEM/EDS). This is done to address the role of iron in microstructural characteristics. The compressive strength of geopolymer mortars was also assessed to show its suitability as construction materials.

2. Materials and experimental methods

2.1. Materials

Raw brown color fly ash was collected from Tata Power Limited, Mundra, Gujrat, India. The raw fly ash (RFA) was first classified, using a laboratory air classifier (Hosokawa Alpine, 50 ATP Germany) at 7000 rpm classifier speed, into two fractions: fine brown fly ash fraction and coarse grey fly ash fraction. The fine brown fly ash fraction, labelled as CFA, was selected in present work to investigate its possible use in making geopolymer binders. Analytical grade sodium hydroxide (NaOH) pellet with 99% purity was supplied by Merck Ltd. Analytical grade sodium silicate (Na_2SiO_3) solution with composition 8.5% Na_2O , 28% SiO_2 and 63.5% H_2O by mass was provided by Loba Chemie Ltd. The standard sand conforming to BIS: 650-1991 was used for making geopolymer mortar.

2.2. Mix compositions and procedures

The alkaline activator was a mixture of NaOH solution and Na_2SiO_3 solution (by volume) and was prepared prior to all tests. The NaOH concentrations (6, 8, 10, and 12 M) and S/H ratios (0.33, 1.00, and 3.00) were the variable parameters. The liquid to CFA ratio was maintained at 0.30 in all the tests. The detailed mix compositions are presented in Table 1.

For setting time test, the geopolymer pastes were prepared by mixing CFA with alkaline solution. For each composition, 300 g of CFA was mixed with $(0.85 \times 0.30 \times 300)$ ml of alkaline solution (as per BIS: 4031 Part 5). The gauging time was 3–5 min. The test was performed at 27 ± 2 °C and under relative humidity of 65%.

For calorimetry test, 7 g CFA and 3.5 ml of activator solution were used throughout the study. The samples were mixed and then loaded into the calorimeter.

For compressive strength test, CFA and alkaline solution in the liquid/CFA ratio of 0.30 were mixed in a mechanical mixer for 3 min. Then, the standard sand was added to the mixture in the sand/CFA ratio of 1.25 and stirred for additional 5 min in a mechanical mixer to obtain geopolymer mortars. The fresh geopolymer mortar was casted in $50 \times 50 \times 50$ mm cubic moulds and

vibrated for 2 min. The temperature of mixing and casting room was maintained at 27 ± 2 °C. After completion of casting and vibration, the specimens were cured in an electric oven at 60 °C for 24 h. Thereafter, samples were demoulded and kept in a plastic bag at 27 ± 2 °C until tests performed.

2.3. Characterization of CFA, geopolymer pastes and mortars

The chemical composition of CFA was obtained by using X-ray fluorescence spectroscopy (Bruker SRS/3400). The particle size analysis of CFA was carried out using a laser particle size analyzer (MATERSIZER S, Malvern, UK). The mineralogical phases were studied using XRD patterns obtained by a Bruker X-ray diffractometer (D8 Discovery, US) using $\text{CuK}\alpha$ radiation. The degree of crystallinity, by considering integral points between 25° and 40° (2 θ), was determined as per the method reported elsewhere [3].

A Vicat apparatus (AIMIL, India) was used for measurement of setting time. The geopolymerization reaction was monitored on isothermal conduction calorimeter (TAM AIR, Thermometric AB, Jarafalla, Sweden) at 60 °C for a period of 24 h. The compressive strength of samples was tested using Automatic Compression Testing Machine (AIMIL COMPTTEST 2000, India). An average of three samples was tested for each result. The morphology of hardened geopolymer paste after 28 days was studied using Field emission gun-scanning electron microscope (Model FEI 430) fitted with energy dispersive X-ray spectrometer (FEG-SEM/EDS) and operated at 15.0 KV.

3. Results and discussion

3.1. Characterization of CFA

Table 2 shows the chemical analysis and physical properties of brown fly ash fraction (CFA). The main components of CFA are SiO_2 , Fe_2O_3 and Al_2O_3 , which constitute about 82.77% of the total composition. The CaO content is 9.28%, which is slightly less than 10%. Although CFA can be classified as ASTM Class F fly ash. We have reported elsewhere [12] that the brown color of CFA is due to the high Fe_2O_3 content (31.10%). Fig. 1 shows the XRD patterns of RFA and CFA. The main mineralogical phases identified were Mullite, Quartz, Hematite, and Magnetite. There is also the decrease of peaks intensity of quartz in CFA, which corroborates the decrease of SiO_2 content in CFA compared to RFA. The degree of crystallinity (X_c) of RFA and CFA was 50% and 52% respectively. The particle size distribution (PSD) of RFA and CFA is given in Fig. 2. The characteristic particle diameter d_{10} , d_{50} and d_{90} of CFA were 0.33, 2.68, and 8.02 μm respectively against 0.33, 4.14 and 28.67 respectively for RFA.

Table 1
Geopolymer compositions.

Compositions	Activator liquid/ CFA	NaOH concentration	Silicate to hydroxide ratio
1	0.30	6 M	0.33
2	0.30	6 M	1.00
3	0.30	6 M	3.00
4	0.30	8 M	0.33
5	0.30	8 M	1.00
6	0.30	8 M	3.00
7	0.30	10 M	0.33
8	0.30	10 M	1.00
9	0.30	10 M	3.00
10	0.30	12 M	0.33
11	0.30	12 M	1.00
12	0.30	12 M	3.00

Table 2
Chemical composition and physical properties of RFA and CFA.

Constituents	RFA	CFA
Chemical analysis		
SiO_2	52.30	39.25
Al_2O_3	10.20	12.42
Fe_2O_3	23.42	31.10
CaO	8.20	9.28
MgO	2.15	2.89
Na_2O	0.48	0.68
K_2O	1.10	1.13
SO_3	0.60	0.78
$\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio	5.13	3.16
Physical properties		
Specific gravity	2.68	2.90
Blaine's fineness (cm^2/g)	3887	4174

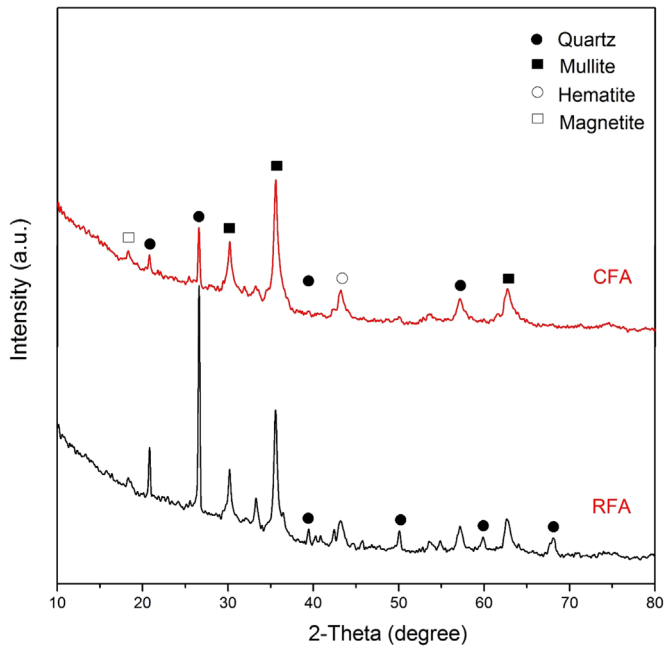


Fig. 1. X-ray diffraction pattern of RFA and CFA.

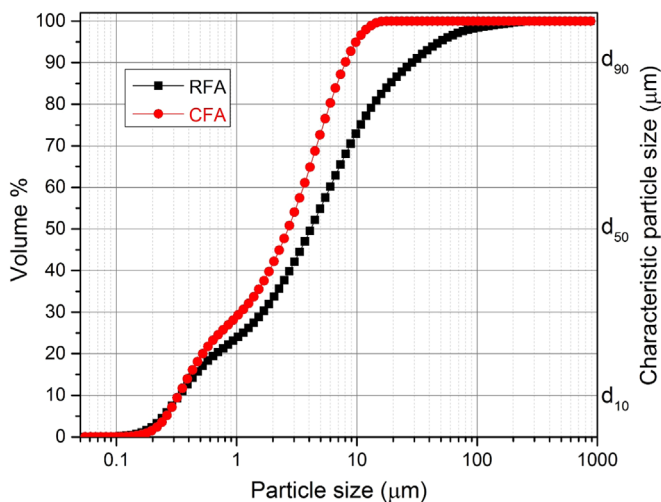


Fig. 2. Particle size distribution of RFA and CFA.

3.2. Characteristics of fresh and hardened geopolymer

3.2.1. Setting time

The setting time of geopolymer samples is presented in Fig. 3. It is observed that the initial and final setting times increase with the increase in NaOH concentration. The increase in S/H ratio decreases the initial and final setting times. The initial and final setting time are in the range of 10–27 min and 22–48 min respectively. The short setting time of geopolymer developed may be attributed to the more reactivity due to high finesses of CFA ($4174 \text{ cm}^2/\text{g}$). This favors an easy and rapid dissolution of the aluminosilicate particles as the contact angle between surface particles and the alkaline solution is higher. On the other hand, the change in crystallinity (diminution of the peak intensity of mineral observed in CFA) and the less $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio (3.16) of CFA would have also contributed to the shortening of setting time [16,17]. In addition, CFA contains a considerable amount of CaO (9.28%) that can react during geopolymerization. It is well known that materials with higher calcium contents tend to set quicker because the dissolution rate of Ca^{2+} is greater than Si^{4+} or Al^{3+} [18]. Likewise,

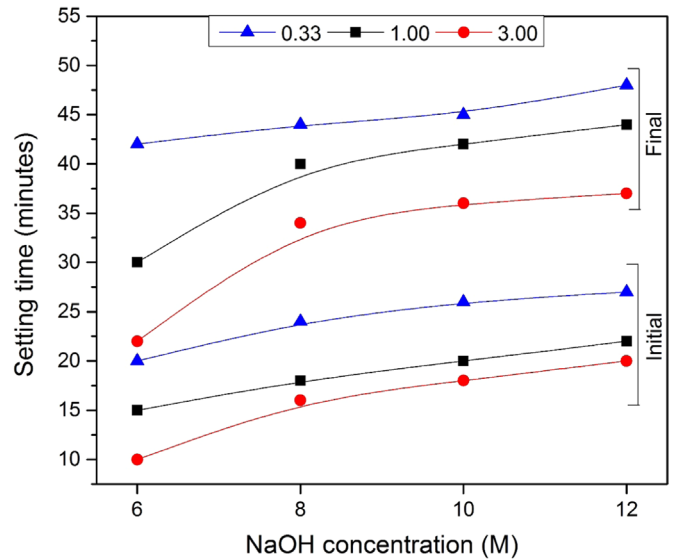


Fig. 3. Setting time of geopolymer.

the possible precipitation of some Ca-rich phases (N,C-A-S-H, C-A-S-H and C-S-H) in the system might form a basic skeleton of percolating solids, which also reduce the time for the onset of hardening [19].

The increase in setting time with an increase in NaOH concentration is because of low leaching of Ca into the solution. At low NaOH concentration, the leaching out of silica and alumina is generally low. Hence, the leaching out of Ca^{2+} ions is not hindered and the solution becomes rich in calcium, which makes the setting time short by the formation of Ca rich phases. While at high NaOH concentration, the leaching out of silica and alumina is high, and leaching of Ca^{2+} is limited because of its precipitation. The setting of geopolymer paste is then controlled by geopolymerization process and thus setting time increases [20,21]. The decrease in setting time with an increase in S/H ratio may be due to the delayed geopolymerization [16].

3.2.2. Calorimetry studies

Figs. 4–6 show the heat evolution curve of geopolymer samples at 60°C for initial 24 h. The key processes which occur during

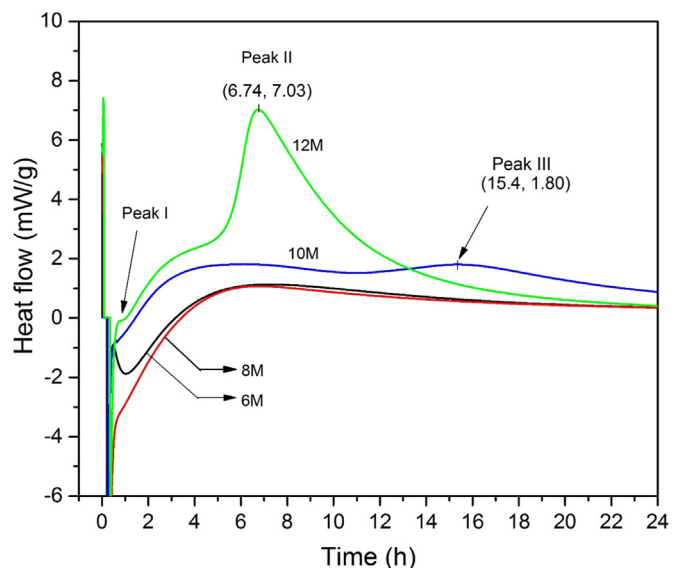


Fig. 4. Heat evolution in the samples with 0.33 S/H ratio and varying NaOH concentration.

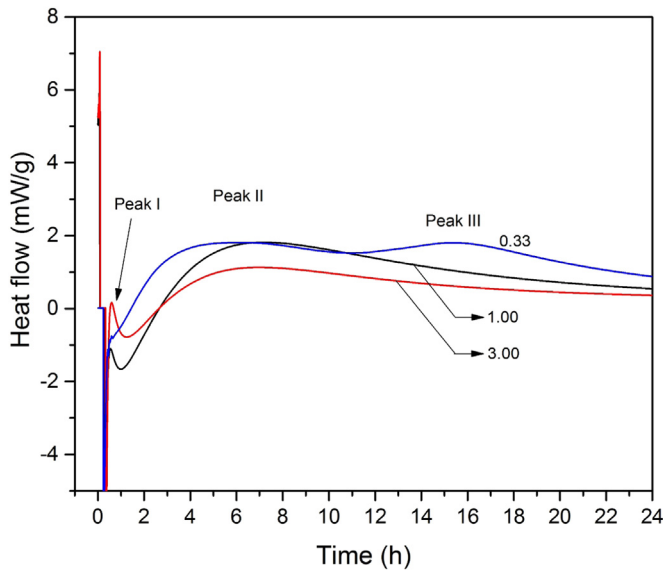


Fig. 5. Heat evolution in samples having 10 M NaOH concentration and varying S/H ratio.

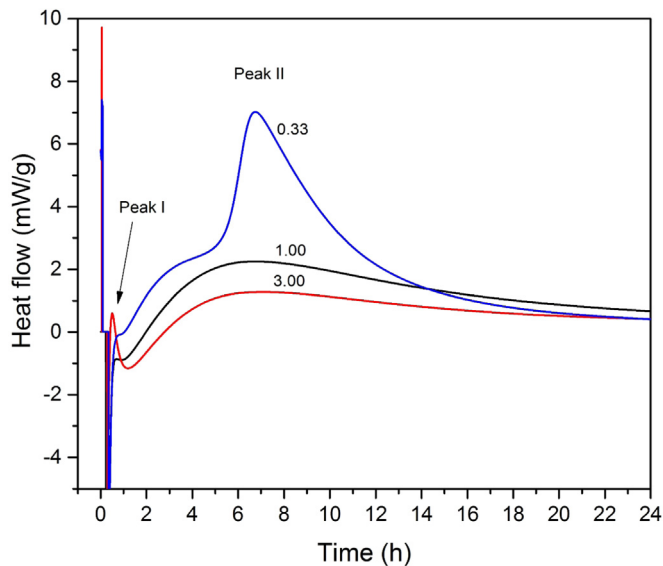


Fig. 6. Heat evolution in samples having 12 M NaOH concentration with varying S/H ratio.

geopolymerization are dissolution, precipitation, gelation, re-organization, polymerization and hardening [22,23]. The heat generation in samples directly subjected to geopolymerization is associated with the combined effect of dissolution, gel formation, and polycondensation. Since the reaction steps overlap each other, calorimetry cannot detect these steps separately [14]. The calorimetry response of geopolymerization reaction using different NaOH concentration at constant S/H of 0.33 is depicted in Fig. 4. The straight line (a very sharp peak) appears in all the samples immediately, when the activator liquid is mixed with CFA, which can be convincingly attributed to the instant physical absorption of the solution on the surface of CFA [10,24,25]. Apart from this, there are two distinct peaks (I and II) appearing as reaction progress in all samples.

For all the samples studied, the first peak is observed approximately between 27 and 42 min depending on the NaOH concentration. This peak is associated to the wetting of fly ash and start of dissolution of Si^{4+} and Al^{3+} into the alkaline solution [26].

There is no clear trend in this peak intensity with different NaOH concentration. This first peak is followed by a short dormant period in all the samples. The occurrence of the second peaks is attributed to the heat released due to the continuous dissolution of remaining unreacted particles along with the beginning of precipitation and polycondensation process [10,25,26]. The maximum heat evolutions (Peak II) are observed approximately between 6–7 h, is almost same for 6 and 8 M, but increase sharply from 10 to 12 M. This demonstrates the higher reactivity of alkaline solution when the NaOH concentration increases. Elsewhere, the sample with 10 M NaOH concentration develops a third peak at around 15 h with intensity more or less equal to the previous one (peak II), which may be due to the pseudo-acceleration of geopolymerization [27].

The change occurred on samples with 10 and 12 M NaOH concentration and different S/H ratios are depicted in Figs. 5 and 6. The peak intensity of peak II decreases with increasing S/H ratio (Fig. 6) but is almost same for S/H ratios 0.33 and 1.00 in Fig. 5. In the later, it appears a little bit later with increasing S/H ratio. In addition, the third peak observed in the sample with 10 M NaOH concentration has disappeared with increasing S/H ratio. These results indicate that increasing S/H ratio delayed the geopolymerization reaction, and this is more pronounced when S/H ratio is higher than 1.00. This is due to the increase in viscosity of the solution because of the high silicate content. This hinders the dissolution reaction with the consequence of delaying the polycondensation process as fewer aluminate species are available. Accordingly, there is rather a condensation between silicate species, whose rate of reaction is slower than the condensation between aluminates and silicates [16].

3.2.3. Compressive strength

The compressive strength (Fig. 7) increases with an increase in the NaOH concentration. Since at high NaOH concentration, the dissolution of Si^{4+} and Al^{3+} ions from fly ash increases and the formation of sodium aluminosilicate is enhanced [21]. This result is consistent with the calorimetric study, which showed an increase in the extent of reaction with NaOH concentration (Fig. 4). The compressive strength increases with S/H ratio up to 1.00 and then decreases regardless the NaOH concentration. The highest compressive strength of sample with S/H ratio 1.00 can be due to the high reactivity of that solution. As it was reported that the

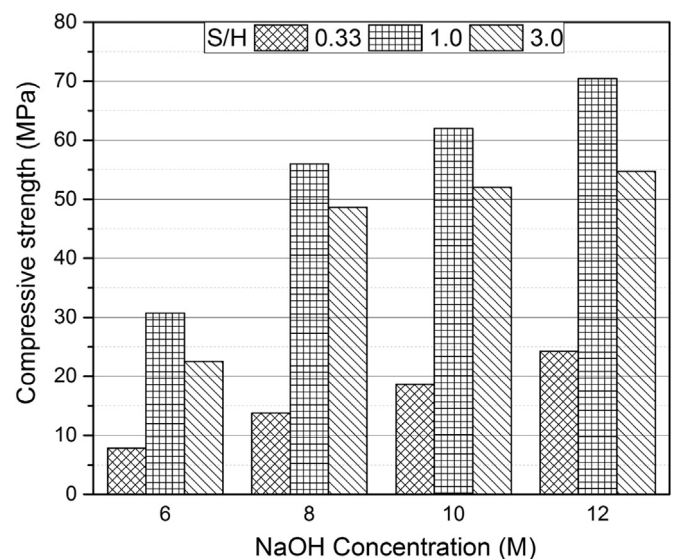


Fig. 7. Effect of NaOH concentration and S/H ratio on 28 days compressive strength of geopolymer mortar.

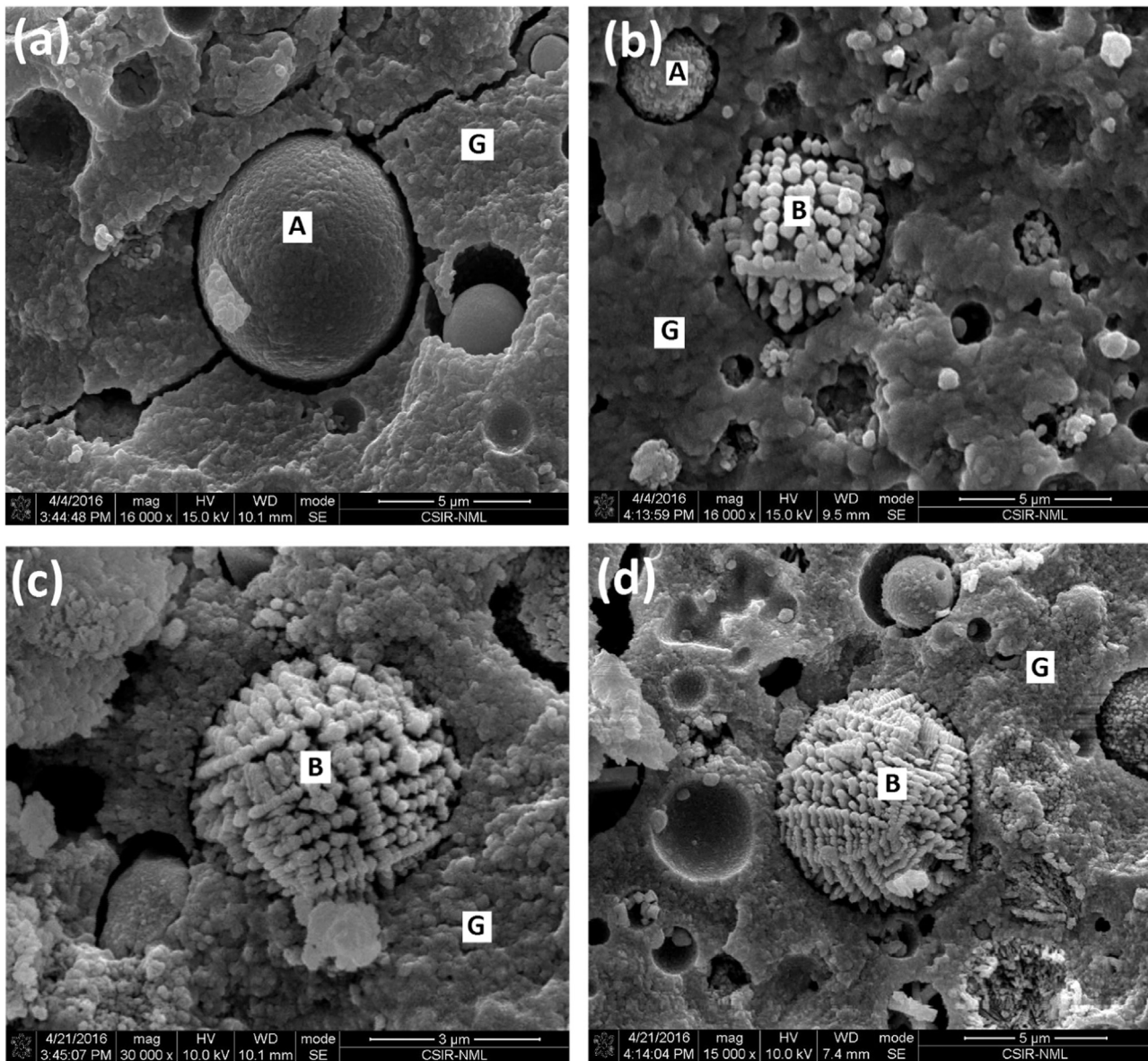


Fig. 8. Morphology of samples having S/H 1.00 and different alkali concentration a) 6 M, b) 8 M, c) 10 M, and d) 12 M.

addition of sodium hydroxide in sodium silicate is believed to depolymerize the silicate solution into small siliceous molecules ready to react [28]. The reactivity of alkaline solution depends on the amount of siliceous species and non-bridging oxygen atoms [29]. So, it may be surmised that for S/H ratio of 0.33, there is an excess of free OH^- and less amount of siliceous species and non-bridging oxygen. For S/H ratio of 3.00, there is less amount of free OH^- to allow full depolymerization of silicate, whose excess leads to the availability of more bridging oxygen. Thus, there is still more condensed silicate, which is less reactive to undergo geopolymerization [30]. While for the S/H ratio of 1.00, it might have a suitable balance between the amount of OH^- required for depolymerization of silicate and enough siliceous species and non-bridging oxygen atoms.

3.2.4. Microstructural characterization

Fig. 8a-d shows the morphology of hardened geopolymer samples cured at 60°C for 24 h after 28 days. The summary of EDS results is presented in Table 3. The morphology of geopolymer obtained is fully reacted matrix with many interesting features. The spherical shaped morphology of incorporated fly ash are

Table 3

Summary of microstructural features obtained using SEM-EDS.

Features	EDS summary
A Partially reacted cenospheres	Si/Al \approx 2.38–5.77 Na/Al \approx 0.28–2.12 Na/Si \approx 0.12–0.38
B Spherical pattern made of prismatic needle microstructures	Si/Al \approx 0.40–1.34 Na/Al \approx 0.15–0.35 Na/Si \approx 0.18–0.47 Fe/Si \approx 2.72–5.02 Ca/Si \approx 0.24–0.97
G Gel phase	Si/Al \approx 1.55–3.16 Na/Al \approx 0.28–1.72 Na/Si \approx 0.28–0.64 Fe/Si \approx 0.20–0.31 Ca/Si \approx 0.12–1.14

observed in three states: unreacted cenospheres, partially reacted cenospheres and fully reacted cenospheres in different forms. The geopolymer gels are observed in significant amount in all the

geopolymer samples.

The following major features can be summarized on the basis of SEM-EDS analysis:

- 1) The partially reacted cenospheres (A) are more predominant in 6 M and 8 M geopolymer samples. The cenospheres are partially covered with the reaction products. The EDS confirms the formation of alumino-silicate gel rich in Na (N-A-S-H) on their surface.
- 2) The fully reacted cenospheres (B) are predominantly seen in 10 M and 12 M geopolymer samples. Lots of reaction products are observed on their surface.
- 3) The geopolymer gels (G) formed are porous to dense depending on the NaOH concentration. The increase in NaOH concentration increases the quantity of geopolymer gel as well as its compactness. The compositions of geopolymer gels formed in terms of their respective atomic ratio Si/Al, Fe/Si, Na/Al and Ca/Si are in the range of 1.55–3.16, 0.20–5.02, 0.28–1.72 and 0.12–1.14 respectively. Those compositions are typical of poly (ferro-sialate-siloxo) and poly (ferro-sialate-disiloxo) binder types with Ca^{2+} and Na^{+} as charge-balancing cations. For such binder the geopolymer formula was reported to be close to $[\text{Ca}, \text{Na}]_{-}[-\text{Fe}-\text{O}]_{\text{x}}[-\text{Si}-\text{O}-\text{Al}-\text{O}]_{1-\text{x}}[-\text{Si}-\text{O}]_{\text{y}}$, wherein "x" is less than or equal to 0.5, "y" is a value between 0 and 25 [13].
- 4) The spherical shaped patterns made of prismatic microstructures (B), formed in place of fully reacted cenospheres, are observed in the composition having higher NaOH concentration. The EDS analysis on their surface revealed that the iron content is very high with atomic percentage in the range of 8.89–17.06%. This indicates that iron has participated in geopolymerization reaction. Participation of iron oxide in geopolymerization by forming ferro-sialate has been reported elsewhere [5]. The compactness of this feature increases with an increase in NaOH concentration.

4. Conclusions

Iron rich fly ash, particularly fine fraction fly ash, has been used in making geopolymer binders. The utilization of fine iron-rich fly ash resulted in several positive effects on the properties of geopolymer binders.

The effects of factors such as NaOH concentration and S/H Ratio on the properties of fine iron-rich fly ash geopolymer were investigated. The setting time increases with the increase in NaOH concentration, while it decreases with the S/H ratio. The increase in NaOH concentration also results in more heat of geopolymerization. Whereas, the increase in S/H ratio delays the geopolymerization and produces less heat. The compressive strength also increases with the increase in NaOH concentration. The increase in S/H ratio gives no definite trend. The compressive strength first increases with S/H ratio in the range of 0.33–1.00 and then decreases with S/H ratio in the range of 1.00–3.00. The morphology of hardened geopolymer samples consists of partially reacted fly ash and geopolymer gels rich in Na, Ca and Fe. The geopolymer binders obtained are of poly (ferro-sialate-siloxo) and poly (ferro-sialate-disiloxo) polymer type binders with Ca^{2+} and Na^{+} as charge-balancing cations. The increase in NaOH concentration results in more compact microstructure of geopolymer.

The fine iron-rich fly ash can be used for manufacturing high strength geopolymer binder. There is no negative effect of high iron content on the compressive strength of geopolymer mortars. The iron rich fly ash geopolymers mainly differ in their microstructural compositions as observed in SEM-EDS.

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