



Properties of geopolymerised low-calcium bottom ash aggregate cured at ambient temperature



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ABSTRACT

This paper discusses the factors influencing the pelletization and properties of lightweight aggregate using bottom ash through alkali activation and curing at ambient temperature. The experiments were designed using central composite design of Response surface methodology. The alkaline activators used for the synthesis of geopolymer aggregate are NaOH and Na_2SiO_3 . $\text{Ca}(\text{OH})_2$ has been used along with the alkaline activators to facilitate hardening of the geopolymer aggregate at ambient temperature. The influence of various factors and their interaction effects on the pelletization efficiency, bulk density, ten percent fines value, open porosity and water absorption on geopolymer aggregate cured at ambient temperature were identified. Addition of $\text{Ca}(\text{OH})_2$ resulted in the increase in pelletization efficiency. The molarity of NaOH and dosage of $\text{Ca}(\text{OH})_2$ enhanced the TPFV. The open porosity and water absorption of the aggregate reduced considerably with an increase in NaOH molarity and $\text{Na}_2\text{SiO}_3/\text{NaOH}$ ratio.

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1. Introduction

Geopolymer aggregate was manufactured using conventional geopolymerisation method with low-calcium bottom ash by activation in an alkaline medium and curing at moderate temperatures between 50 and 80 °C for 24 to 48 h [1]. As a next step, studies on enhancing polymerization at ambient temperature have been taken up in this paper. In this connection the relevant literature has been reviewed.

Conventional geopolymers are prepared by activating the low-calcium fly ash in an alkaline medium and curing at moderate temperatures between 50 and 90 °C. The properties of geopolymer cement and concrete using low calcium fly ash has been reported by several researchers [2–4]. Initially, for the geopolymers low-calcium fly ash was preferred as a source material rather than high-calcium fly ash as the presence of high amounts of calcium may interfere with the polymerisation process and alter the microstructure [2]. Later on it was established that addition of 4% of high-calcium containing slag greatly improved the compressive strength of fly ash based geopolymers [4]. Adding 3–5% quicklime to a fly ash/cement system has been reported to accelerate the hardening process and increase the strength [5]. Metakaolin and ground granulated blast furnace slag subjected to alkaline activation has both geopolymeric and C-S-H gels forming simultaneously [6]. Addition of calcium to fly ash based geopolymer will affect the amount of alkaline liquid required and the final chemical and mineralogical

composition. The most important aspects of adding calcium to a geopolymer system is to improve its ability to harden at ambient temperature, as $\text{Ca}(\text{OH})_2$ gets incorporated into the geopolymeric network [7]. Calcium compounds (CaO and $\text{Ca}(\text{OH})_2$) have significant influence on the mechanical properties of fly ash based geopolymers [8,9]. Geopolymer was synthesized using metakaolin at room temperature [10]. Geopolymers produced using class-F fly ash were subjected to different curing modes like room temperature and oven curing [11–13]. Geopolymers were prepared using class-F fly ash and kaolinite subjected to ambient and temperature curing. Oven curing of geopolymer at 50 to 80 °C for 12 to 48 h involved significant energy consumption. Studies show that the geopolymer products cured at ambient temperature exhibited similar properties to that cured in oven except the strength, which was higher in the oven cured geopolymer concrete. Hence it was felt desirable to investigate the application of activation techniques to geopolymerise bottom ash aggregate at ambient curing conditions for producing pelletised aggregate. This paper focuses on the properties of geopolymerised low-calcium bottom ash aggregate supplemented with $\text{Ca}(\text{OH})_2$ at ambient curing conditions.

2. Materials and methodology

The bottom ash that was used for the study was procured from a local thermal power plant, the properties of which are presented in Table 1. A combination of Sodium Silicate solution (Na_2SiO_3) and Sodium Hydroxide (NaOH) solution was used as the alkaline liquid. The alkaline liquid was prepared by mixing both the solutions

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Table 1

Properties of pulverised bottom ash.

Specific gravity	Fineness (m^2/kg)	SiO_2	CaO	Al_2O_3	Fe_2O_3	MgO	Na_2O	SO_3	Carbon	LOI%
1.6	212	53.68	1.24	18.91	7.7	0.48	0.7	0.19	5.51	8.35

Table 2

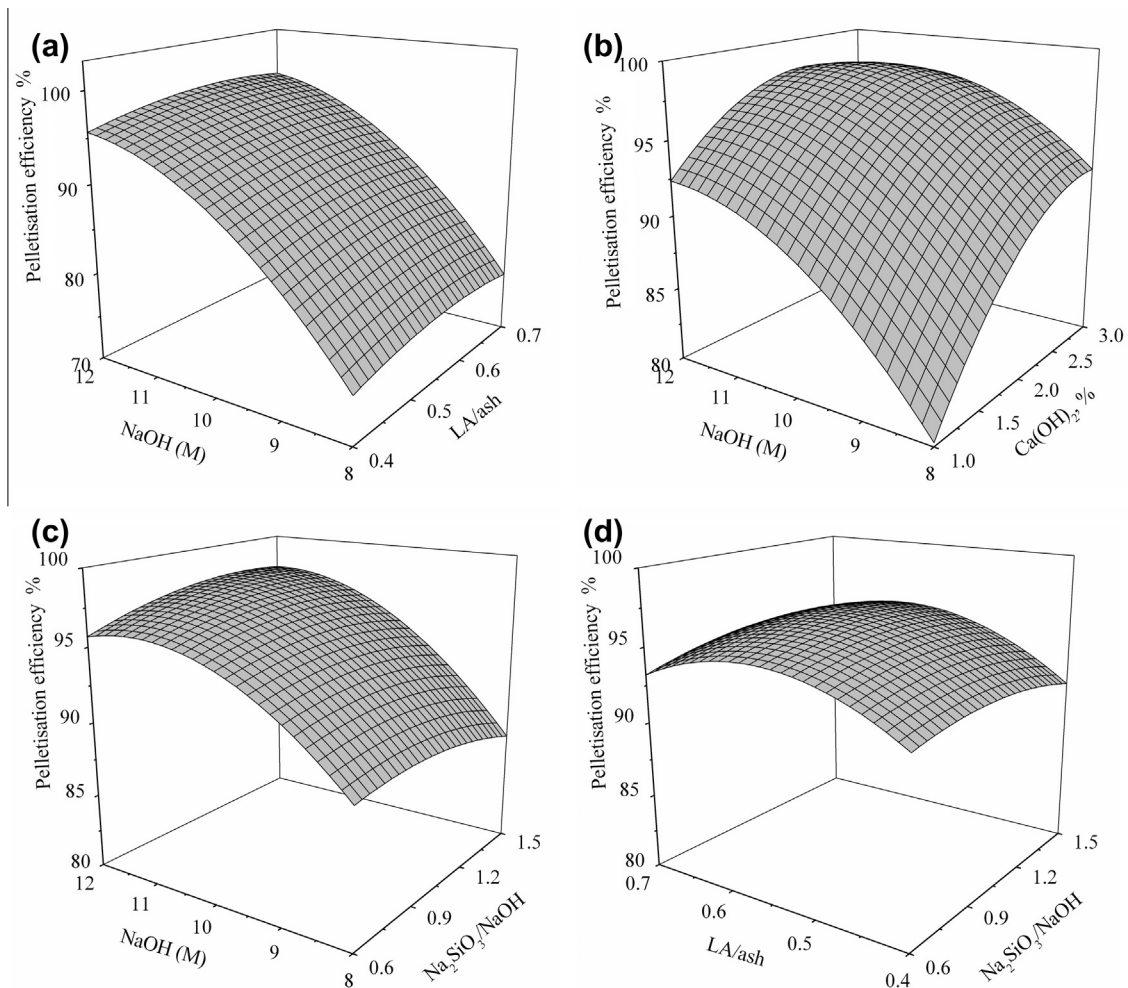
Factors in terms of uncoded values for the coded values.

Notation	Factor	Coded values				
		+1.414	+1	0	−1	−1.414
Uncoded values for factors						
X_1	NaOH (M)	8	8.9	10	11.10	12
X_2	Liquid alkaline/ash	0.4	0.47	0.55	0.63	0.7
X_3	Na ₂ SiO ₃ /NaOH	0.6	0.8	1.05	1.3	1.5
X_4	Ca(OH) ₂	1	1.41	2	2.59	3

together 24 h prior to use. The Sodium Silicate solution with SiO_2 -to- Na_2O ratio by mass of approximately 2, i.e., $\text{SiO}_2 = 29.4\%$, $\text{Na}_2\text{O} = 14.7\%$, and water = 55.9% by mass, was used. Commercially available NaOH pellets with 97–98% purity were used. The solids were dissolved in water to vary the concentration of NaOH solution in the range of 8–12 Molar. In order to facilitate hardening of the aggregate at room temperature, 1 to 3% of $\text{Ca}(\text{OH})_2$ was added along with the alkaline liquid. The aggregates so produced using

a disc pelletizer were allowed to harden in ambient temperature ranging from 30 to 32 °C for 28 days. For each trial, the hardened aggregates of size greater than 4.75 mm was used to calculate the pelletization efficiency, which is ratio of mass of aggregate and bottom ash used. Strength of the aggregate was determined through 10% fines value (TPFV) by IS 2386: part IV (2002) [14]. Since the crushing value exceeds 25%, the strength of cold-bonded aggregate has been evaluated through ten percent fines value (IS 2386: part IV, 2002). For the determination of 10% fines value, aggregates with grain size 10–12.5 mm were used and its 24-h water absorption were determined on aggregate size fraction 12.5–10 mm. The quantitative estimation of open porosity was determined using vacuum saturation method. This paper discusses the influence of factors and its optimum level on properties of geopolymer aggregate.

Considering the factors in Table 2, the Response Surface Methodology (RSM) of Central Composite Design, with 21 sets of designed experiments was used for the study. The phases that were formed as a result of geopolymerisation in the aggregate were studied using X-ray diffraction. SEM micrographs were taken on

**Fig. 1.** (a–d) Variation of pelletization efficiency with alkaline.

a fractured surface of 12.5–10 mm bottom ash aggregate. In order to know the bonding that resulted in the geopolymer aggregate Fourier Transform infrared (FTIR) spectra were recorded on a FTIR PERKIN ELMER FT-IR spectrometer. Pellets were prepared from a mix of 1 mg of sample and 300 mg of potassium bromide (KBr). The spectral range adopted was 400–4000 cm^{-1} .

Table 3
ANOVA for pelletisation efficiency.

Factors	DF	E^2	F-S	Prob > F
X_1	1	36.125	15.6477	<0.0001
X_2	1	2.42	1.04823	0.3454
X_3	1	0.05122	0.02219	0.8865
X_4	1	31.205	13.5165	<0.0001
X_1^2	1	14.2328	6.165	0.0476
X_2^2	1	11.7715	5.09884	0.0647
X_3^2	1	1.54792	0.67048	0.4442
X_4^2	1	17.4947	7.57789	0.0332
$X_1 X_2$	1	15.8375	6.86008	0.0396
$X_1 X_3$	1	0.78125	0.3384	0.5819
$X_1 X_4$	1	1.3296	0.57592	0.4767
$X_2 X_3$	1	0.21125	0.0915	0.7725
$X_2 X_4$	1	5.69043	2.46483	0.1675
$X_3 X_4$	1	1.36125	0.58963	0.4717
Residual	13.8519	6	2.30865	

3. Properties of ambient temperature cured geopolymer aggregate

3.1. Pelletization efficiency

As shown in Fig. 1 (a), the pelletization efficiency increased with an increase in NaOH molarity. At 8 M NaOH and with an increase in LA/ash ratio, there was no enhancement in the pelletization efficiency. At constant LA/ash ratio, an increase in NaOH molarity resulted in higher pelletization efficiency. The addition of $\text{Ca}(\text{OH})_2$

Table 4
ANOVA for bulk density.

Factors	DF	E^2	F-S	Prob > F
X_1	1	22155.1	14887.8	<0.0001
X_2	1	126.405	84.9415	0.0058
X_3	1	623.435	418.935	0.032
X_4	1	1280.18	860.254	0.0028
X_1^2	1	83.6725	56.2261	0.0003
X_2^2	1	466.761	313.653	0.0081
X_3^2	1	348.424	234.134	0.051
$X_1 X_2$	1	3786.94	2544.74	<0.0001
$X_1 X_3$	1	45.6012	30.6431	0.0015
$X_2 X_4$	1	26.94	2544.74	0.005
$X_3 X_4$	1	58.8613	39.5535	0.0008
Residual	8	1.48814		

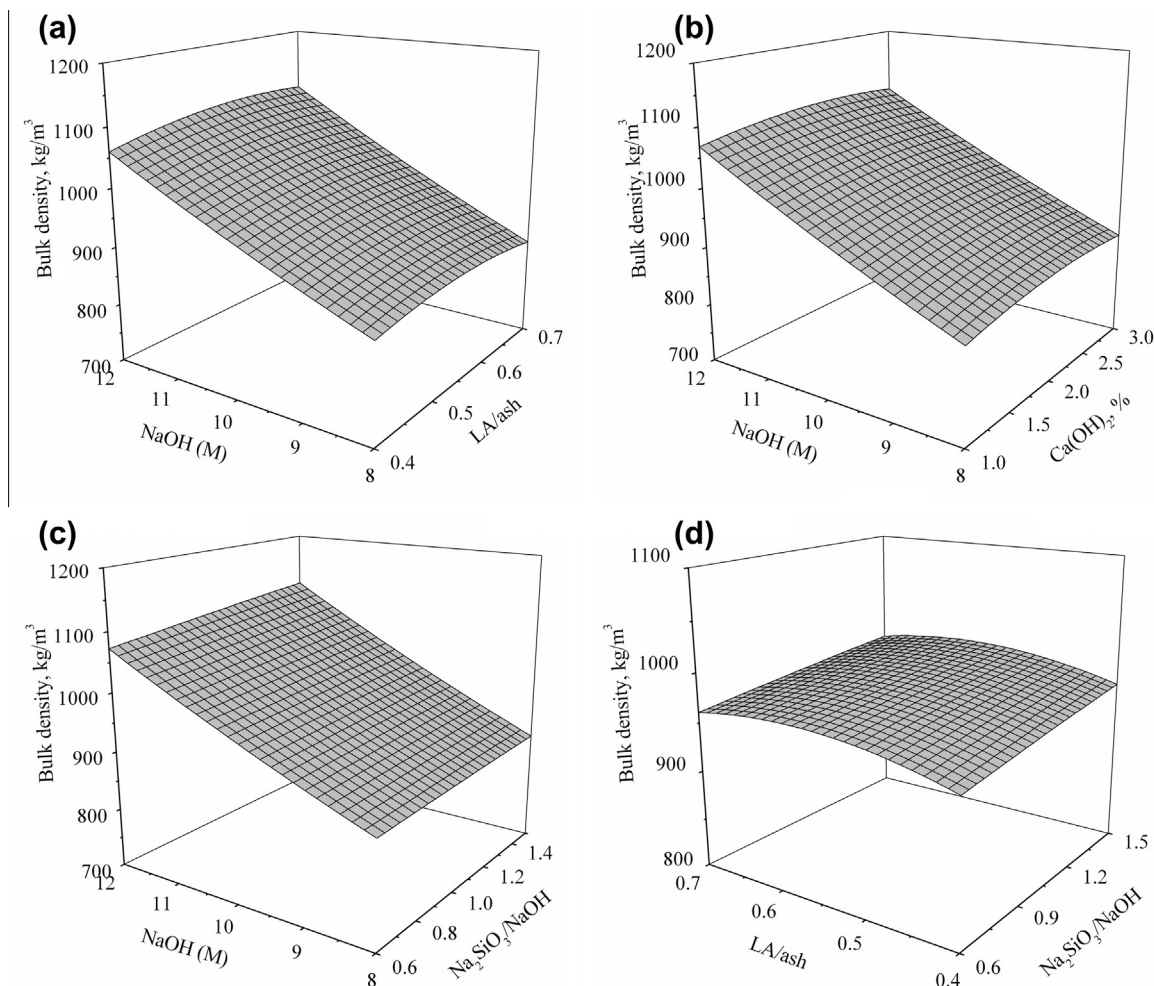


Fig. 2. (a–d) Dependence of bulk density on alkali activation parameters.

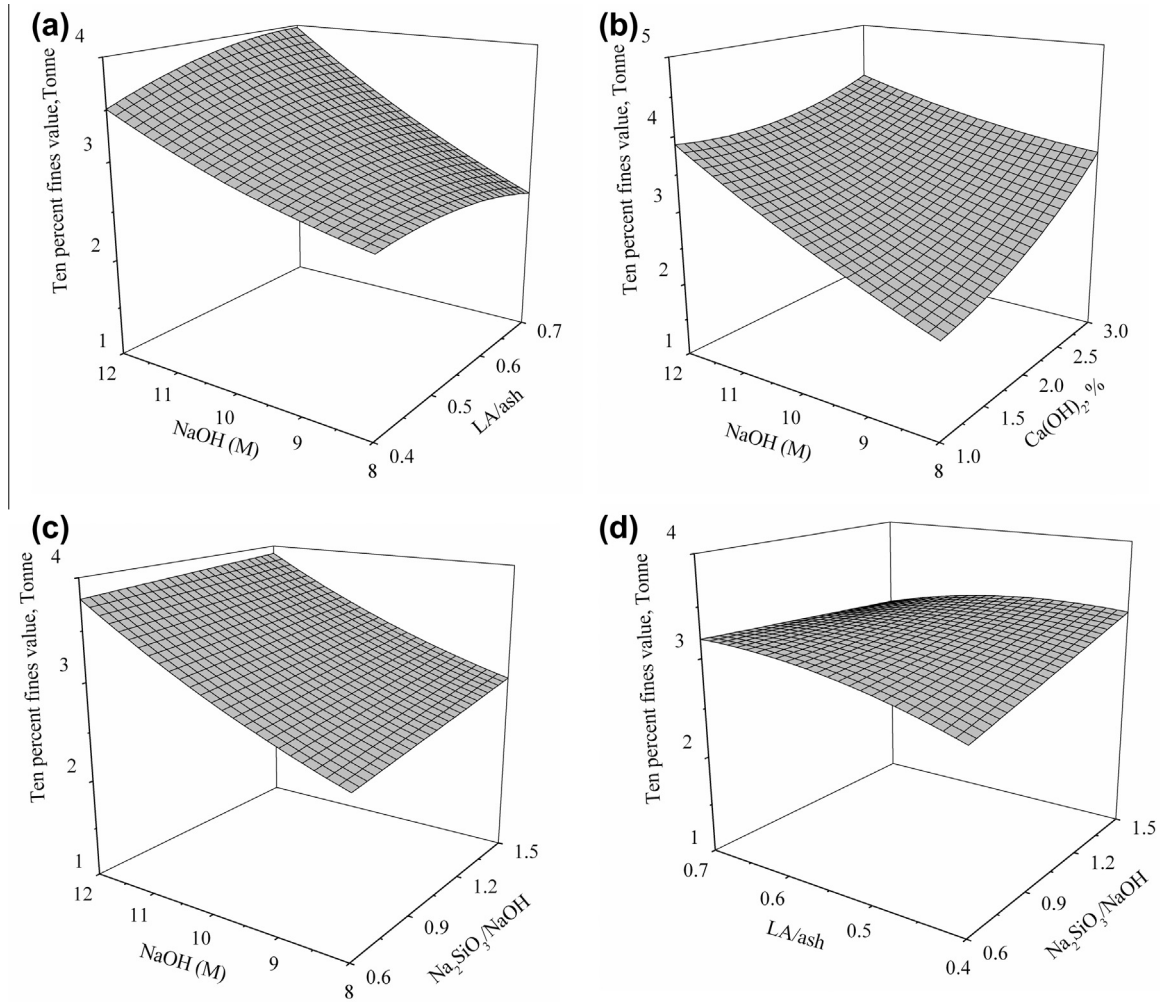


Fig. 3. (a–d) Dependence of TPFV on alkali activation parameters.

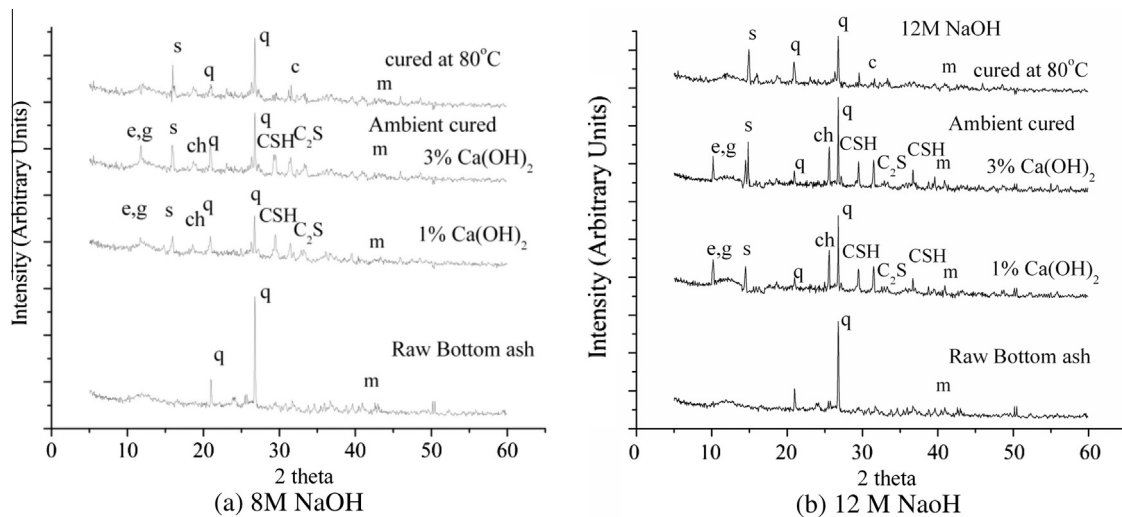


Fig. 4. (a and b) XRD of bottom ash geopolymer aggregate.

accelerated the nuclei formation and resulted in better agglomeration which enhanced the pelletization efficiency [15] (Fig. 1(b)). Though addition of $\text{Ca}(\text{OH})_2$ enhanced the pelletization efficiency,

it was not used in aggregate made using conventional geopolymerisation with oven curing at 50 to 80 °C for 12 to 48 h as it resulted in reduction of TPFV of about 20%. The addition of $\text{Ca}(\text{OH})_2$ resulted in

a reduction in duration of pelletization (7 to 10 min) as against geopolymer aggregate without Ca(OH)_2 (10 to 13 min). The average duration is 10 to 15 min. The addition of Ca(OH)_2 (i) accelerated the agglomeration process and facilitated formation of “seed” or nuclei which is the time consuming stage, and (ii) enhanced coagulation between particles and improved the specific area of the mix thereby increasing the growth of pellets. Hence addition of Ca(OH)_2 has resulted in the reduction of the pelletization duration. The pelletization efficiency increased with an increase in NaOH molarity as shown in Fig. 1 (a) and (b). At high molarity of NaOH, there was enhanced agglomeration between particles resulting in higher pelletization efficiency. Hence even at lower liquid alkaline

(LA)/ash ratio, an increase in molarity of NaOH enhanced the pelletization efficiency.

As given in Fig. 1(c), for a given molarity of NaOH, there was no increase in the pelletization efficiency with an increase in $\text{Na}_2\text{SiO}_3/\text{NaOH}$ ratio. The pelletization efficiency increased with an increase in NaOH molarity even at lower $\text{Na}_2\text{SiO}_3/\text{NaOH}$ ratio. Fig. 1 (d) exhibits that there was not much increase in the pelletization efficiency with an increase in LA/ash and $\text{Na}_2\text{SiO}_3/\text{NaOH}$ ratio. The ANOVA results summarized in Table 3 shows that molarity of NaOH and dosage of Ca(OH)_2 are the significant factor affecting the pelletization efficiency. There was no interaction effect between these factors in influencing the pelletization efficiency.

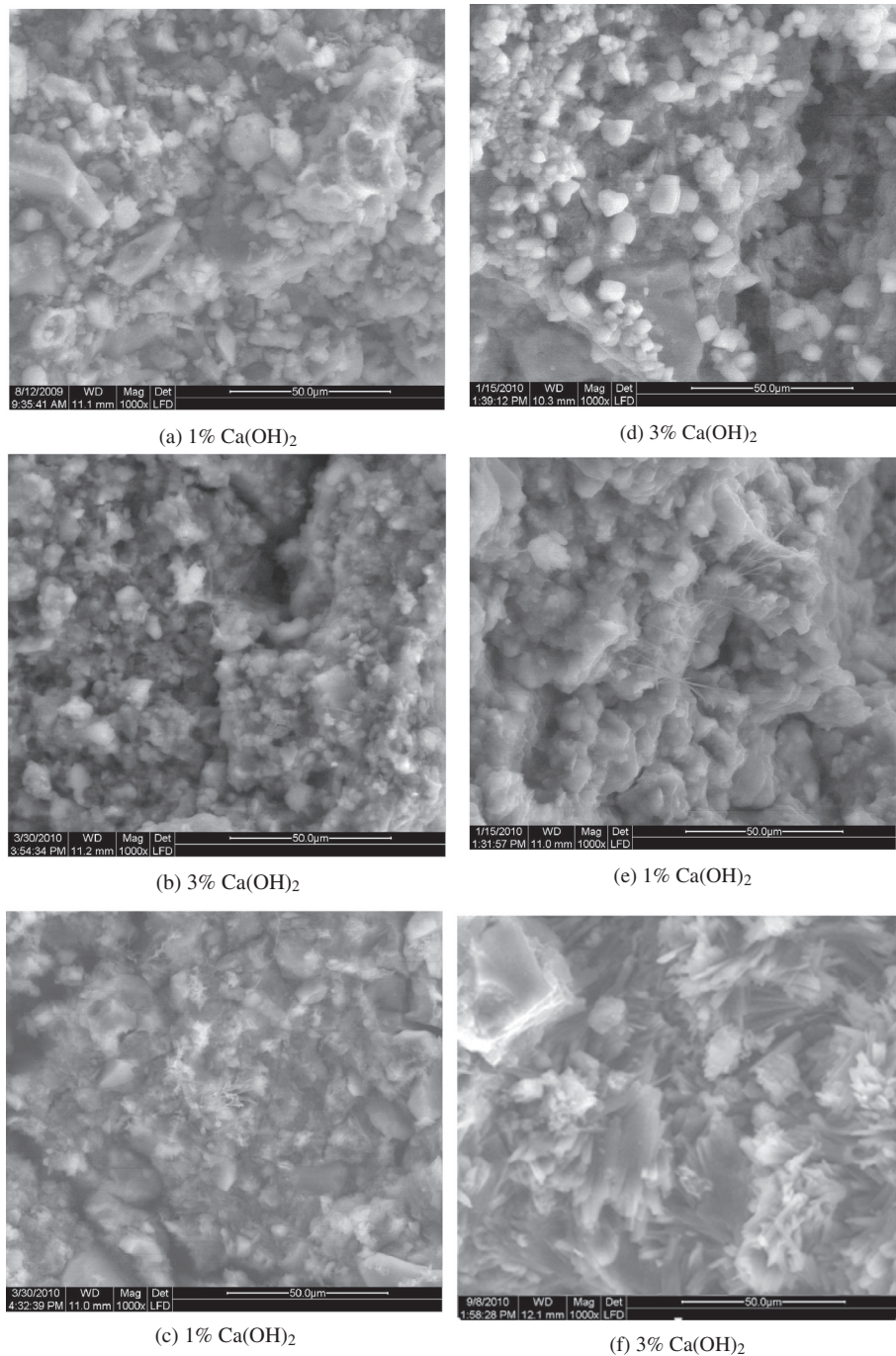


Fig. 5. SEM images of geopolymer aggregate activated with 8 M NaOH (a and b), 10 M NaOH (c and d) and 12 M NaOH (e and f).

3.2. Bulk density

Fig. 2 (a) shows that the bulk density increased linearly with molarity of NaOH. At a given molarity of NaOH (i) an increase in $\text{Ca}(\text{OH})_2$ did not increase the bulk density as given in Fig. 2 (b) and (ii) an increase in LA/ash or $\text{Na}_2\text{SiO}_3/\text{NaOH}$ did not result in increased bulk density (Fig. 2a and c). Increase in LA/ash and $\text{Na}_2\text{SiO}_3/\text{NaOH}$ did not have much influence on the bulk density as shown in Fig. 2 (d). The ANOVA results summarized in Table 4 shows that molarity of NaOH and the interaction effect between NaOH molarity and LA/ash ratio are the factors significantly influencing the bulk density of geopolymer aggregate.

3.2.1. Ten percent fines value (TPFV)

3.2.1.1. Influence of alkaline activators. At a given LA/ash ratio, an increase in NaOH molarity resulted in significant increase in TPFV (Fig. 3 (a)). At lower NaOH molarity, increase in LA/ash ratio did not contribute to increase in strength. At higher NaOH molarity, increase in LA/ash ratio resulted in marginal increase in TPFV. For a given $\text{Na}_2\text{SiO}_3/\text{NaOH}$ ratio, an increase in NaOH molarity resulted in an increase in TPFV. But for a given NaOH molarity, increase in $\text{Na}_2\text{SiO}_3/\text{NaOH}$ ratio did not increase the TPFV (Fig. 3 (c)). Fig. 3 (d) shows that, at constant molarity of NaOH, variation in LA/ash and $\text{Na}_2\text{SiO}_3/\text{NaOH}$ ratio resulted in marginal increase in TPFV. The XRD of geopolymer aggregate activated with 8 and 12 M NaOH and cured for 28 days are shown in Fig. 4 (a) and (b) along with geopolymer aggregate cured at 80 °C for 48 h and raw bottom ash. The main mineral components of geopolymer aggregate were mullite, quartz, anhydrite, and ch-calcium hydroxide. The broad and amorphous hump is the characteristic peak of amorphous gels including geopolymeric gels and calcium silicate hydrate (C-S-H) gels. It indicated that the geopolymeric reaction and the hydration reaction occurred at the same time within the single system. Additionally, peaks of a zeolite (s-hydroxysodalite) were also observed in the XRD pattern geopolymer aggregate. The intensity of the hydroxysodalite is high in ambient cured aggregate with 12 M NaOH and the oven cured aggregate which indicates that more reaction products are formed due to enhanced geopolymerization which is attributed to the increase in TPFV.

3.2.1.2. Influence of $\text{Ca}(\text{OH})_2$. For a given molarity of NaOH, an increase in $\text{Ca}(\text{OH})_2$ increased the TPFV (Fig. 3 (b)). For a constant $\text{Ca}(\text{OH})_2$ dosage, an increase in NaOH molarity enhanced the TPFV.

At higher molarity of NaOH, $\text{Ca}(\text{OH})_2$ did not contribute to enhancement in TPFV. There are several reports on the formation of the C-S-H phase within the geopolymer binder in the presence of significant amounts of calcium [16,9]. The presence of $\text{Ca}(\text{OH})_2$ favoured the formation of products that gave rigidity to the geopolymer paste [17].

The formation of a C-S-H phase along with aluminosilicate network depended on the concentration of the alkaline liquid. The XRD of geopolymer aggregate cured at 80 °C for 48 h shows only the zeolite product along with quartz whereas apart from these products ambient cured aggregate has the other products like C-S-H, ch and C_2S which contribute to the strength of the aggregate. The addition of calcium causes a more fine and homogeneous microstructure which is attributed to the increase in bulk density. Crystals of $\text{Ca}(\text{OH})_2$ and needle shaped ettringite were seen in aggregate activated with 8 M and 12 M NaOH (Fig. 5 (b), (c) and (d)). At 12 M NaOH even with 1% $\text{Ca}(\text{OH})_2$ along with the hydration products some gel structures related to the zeolite products were seen as shown in Fig. 5 (e). In aggregates with 12 M and 3% $\text{Ca}(\text{OH})_2$ a few flaky or needle like products, attributed to the hydration of bottom ash, were observed (Fig. 5 (f)). These microstructures exhibit reticulate network of reaction products, which are likely to be Na-incorporated C-S-H gels or a combination of Na-incorporated C-S-H gel, also termed as N-C-S-H gel [18] and sodium aluminosilicate gel (N-A-S-H) which is a typical alkali activation reaction product in geopolymer systems. Moreover the calcium is distributed homogeneously within the matrix. It is a common view that the pozzolanic reaction in fly ash–cement occurs slowly at low temperatures [19]. However, fast solidification rate and increased strength of the samples with the addition of calcium suggests that the pozzolanic reaction in bottom ash–alkaline liquid occurred much faster. The presence of calcium in solid waste materials has been reported to provide extra nucleation sites for the formation of the geopolymer gel products and cause rapid hardening [20–22].

FTIR absorption spectroscopy has been useful for characterizing geopolymer concrete. The FTIR spectral bands for geopolymer aggregate cured at ambient temperature and cured at 80 °C are shown in Fig. 6 (a) and (b). The bands in the 650–720 cm^{-1} (peak 1) are attributed to the presence of Al-rich structures such as hydroxysodalite the phases that were identified in the XRD. The band at 1000 cm^{-1} identified as peak 2 and the relatively weak band at 1400 cm^{-1} (peak 3) are due to stretching vibrations of Al–O or Si–O bonds, while the band at 750 cm^{-1} is due to the

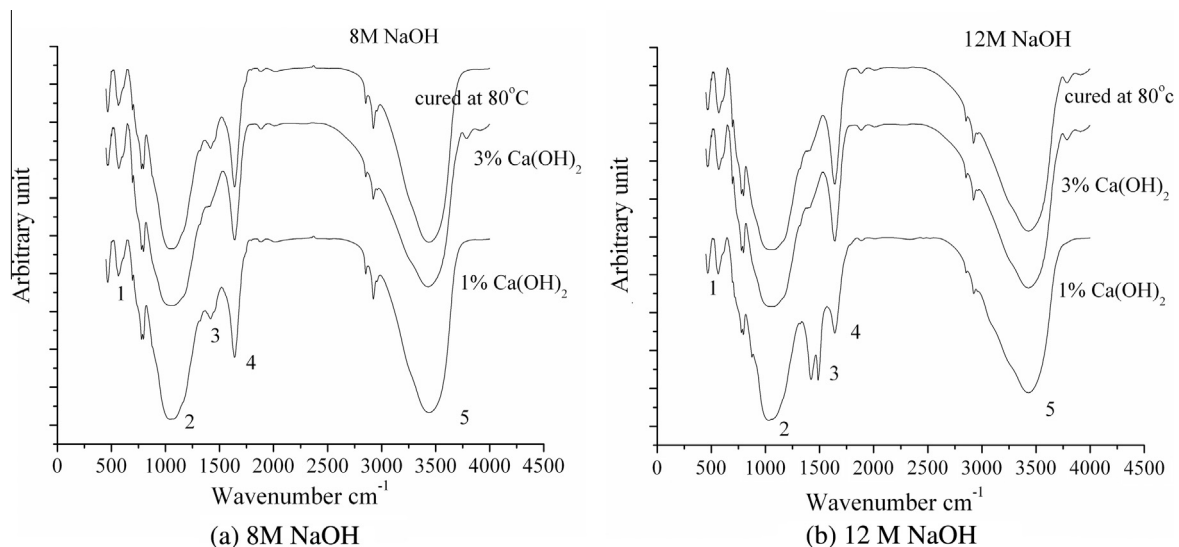


Fig. 6. (a and b) FTIR for bottom ash geopolymer aggregate.

presence of Si–O–Si or Si–O–Al [22]. The broad bands in the region of 1648–3466 cm^{-1} (peak 4 and 5) are due to the presence of OH and H–O–H groups from the weakly bound water molecules trapped in the cavities between the geopolymeric products [2]. The bands in ambient cured aggregate were similar to the bands in aggregate cured at 80 °C.

The ANOVA results summarized in Table 5 shows that molarity of NaOH and $\text{Ca}(\text{OH})_2$ dosage have significant effect in increasing

the TPFV of the aggregate. There are no interaction effects influencing the TPFV.

3.3. Open porosity and water absorption

3.3.1. Influence of alkaline activators

Fig. 7 (a) and (b) shows a reduction in the open porosity resulting in lower water absorption as the molarity of NaOH increased. But at 8 M NaOH, water absorption increased with an increase in LA/ash. The open porosity decreased with an increase in NaOH molarity for a given $\text{Ca}(\text{OH})_2$ dosage (Fig. 7(c) and (d)). For a given molarity of NaOH, variation in $\text{Ca}(\text{OH})_2$ dosage did not reduce the open porosity, but the water absorption reduced marginally. Fig. 7 (e) shows that as the molarity of NaOH increased, an increase in $\text{Na}_2\text{SiO}_3/\text{NaOH}$ ratio did not decrease the open porosity. But at lower $\text{Na}_2\text{SiO}_3/\text{NaOH}$ ratio, an increase in NaOH molarity reduced the open porosity and thereby there was reduction in the water absorption (Fig. 7 (f)). For a constant $\text{Na}_2\text{SiO}_3/\text{NaOH}$ ratio, an increase in LA/ash did not have much influence on the open porosity as shown in Fig. 7 (g) and water absorption (Fig. 7 (h)).

The SEM image in Fig. 8 (a) for aggregate with 8 M NaOH and 0.6 $\text{Na}_2\text{SiO}_3/\text{NaOH}$ ratio had some unreacted bottom ash particles which may be attributed to the higher water absorption and open porosity. With 1.5 $\text{Na}_2\text{SiO}_3/\text{NaOH}$ ratio, the aggregate had pores

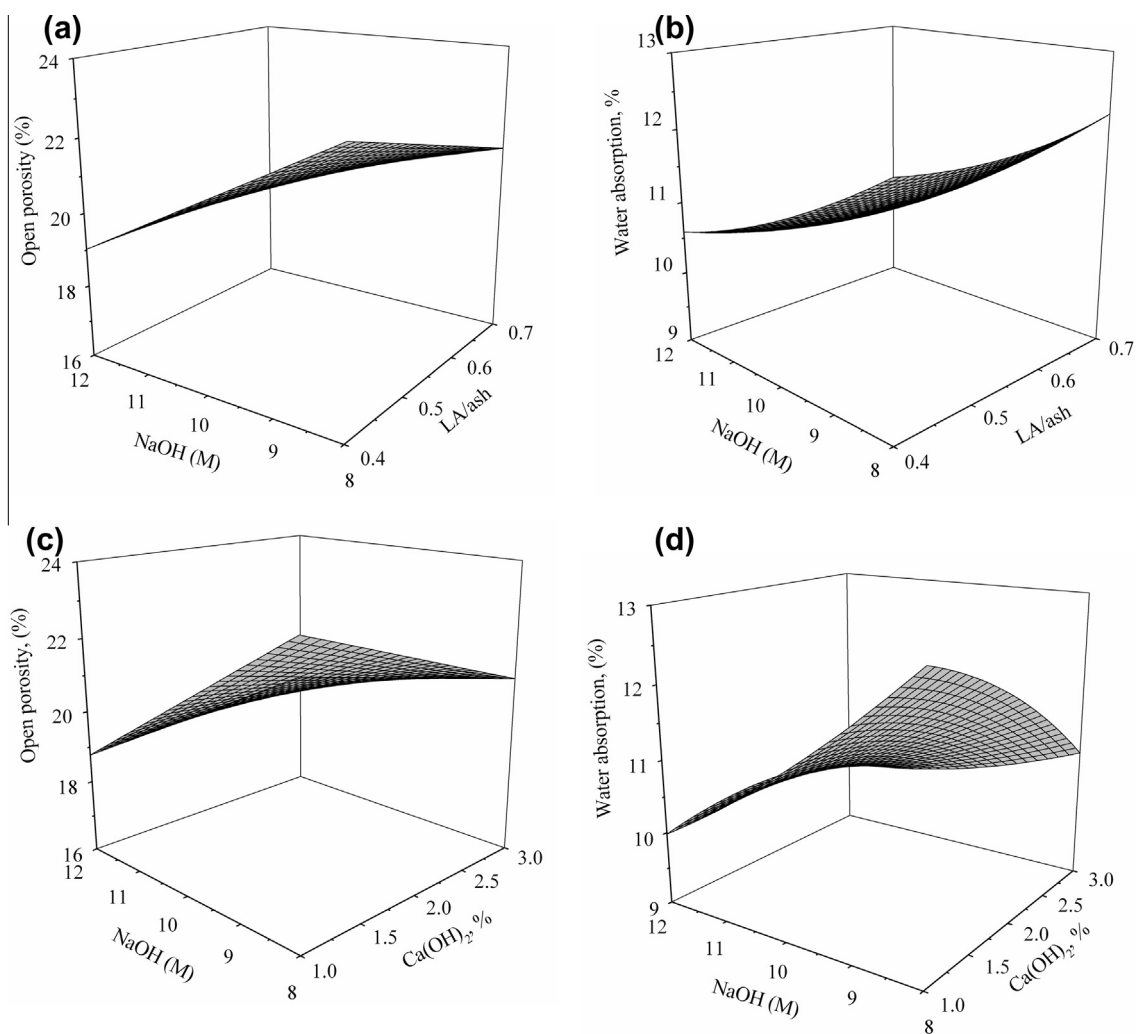


Fig. 7. Dependence of open porosity (a, c, e, g) and water absorption (b, d, f, h) of geopolymer aggregate on alkali activation parameters.

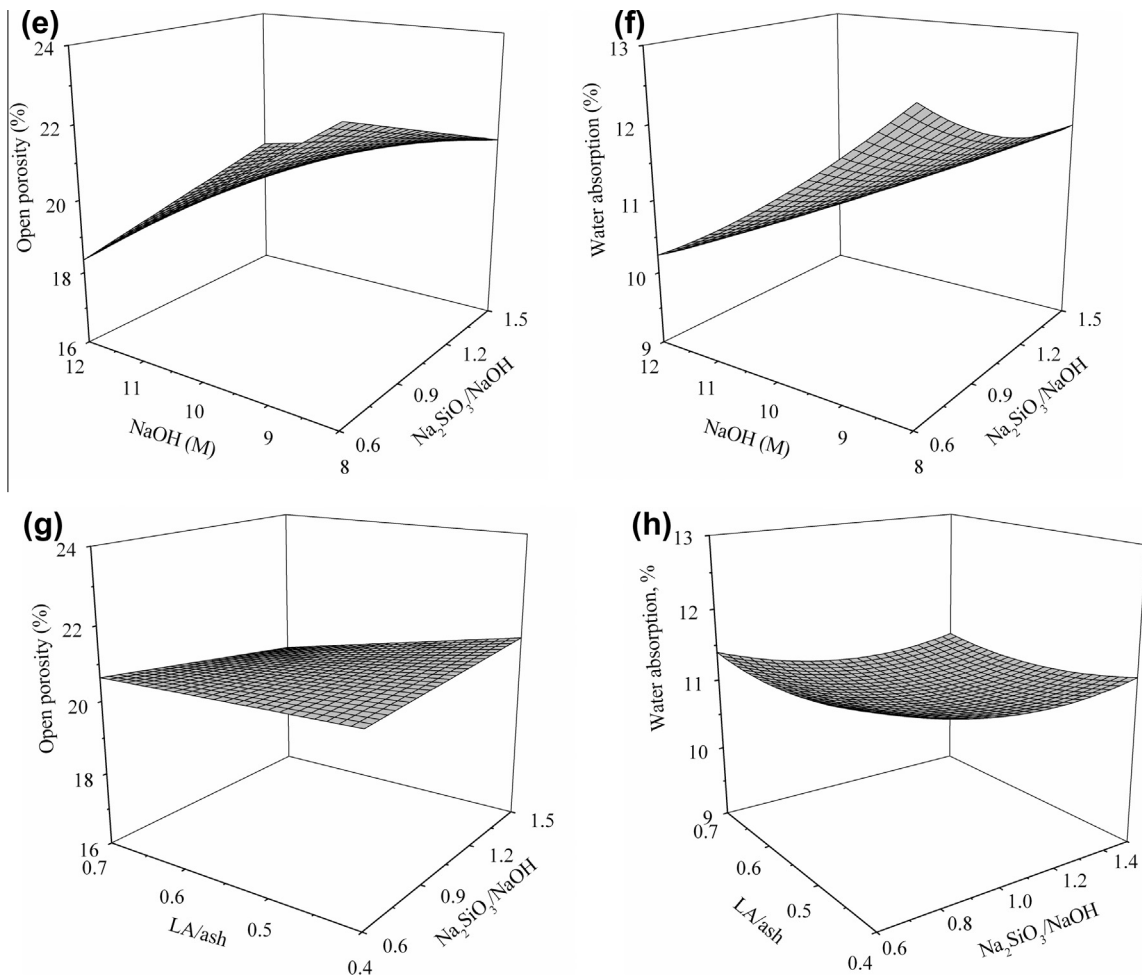


Fig. 7 (continued)

due to insufficient reaction products resulting in higher water absorption (Fig. 8 (b)). But at higher molarity of NaOH, as $\text{Na}_2\text{SiO}_3/\text{NaOH}$ ratio was increased there was reduction in open porosity and water absorption. The SEM image of aggregate with 10 M NaOH and 0.6 $\text{Na}_2\text{SiO}_3/\text{NaOH}$ ratio had pores (Fig. 8 (c)). But with 1.5 $\text{Na}_2\text{SiO}_3/\text{NaOH}$ ratio reaction products in the form of $\text{Ca}(\text{OH})_2$ crystals and some needle shaped ettringite were seen as in Fig. 8 (d) which resulted in a compact microstructure reducing the open porosity. At 12 M NaOH with 0.6 and 1.5 $\text{Na}_2\text{SiO}_3/\text{NaOH}$ ratio more gel and hydration products were formed as seen in Fig. 8 (e) and (f) thus resulting in a dense microstructure thereby reducing the open porosity and water absorption. As the molarity of NaOH increases, the concentration of NaOH in the alkaline solution also increases. This increase in the molarity of NaOH results in the formation of more reaction products resulting in densification of the aggregate thereby resulting in a compact microstructure. Hence the aggregates are strong with lower porosity. $\text{Na}_2\text{SiO}_3/\text{NaOH}$ ratio does not increase parallel with NaOH. The molarity of NaOH is varied from 8 to 12. The respective molar NaOH solution is combined with Na_2SiO_3 (water glass) gel. This is done in a ratio and the ratio is varied from 0.6 to 1.5. This combined solution is termed as alkaline solution and it is added in ratio with bottom ash in the range from 0.4 to 0.7. These upper and lower limits were taken for designing the experimental runs and various combinations were obtained, the details of which are given in the table. The experiments were carried out for the designed runs. The effects NaOH molarity and $\text{Na}_2\text{SiO}_3/\text{NaOH}$ ratio are not individual. The alkaline

solution has a combined effect in the geopolymer process. As the molarity of NaOH is increased the concentration of NaOH in the alkaline solution also increases. The ANOVA results summarized in Table 6 shows that molarity of NaOH and $\text{Na}_2\text{SiO}_3/\text{NaOH}$ ratio have significant effect in reducing the open porosity and thereby reducing the water absorption of the aggregate. There was no interaction effect between the factors influencing the open porosity and water absorption. The regression statistics results presented in Table 7 shows that the F-statics value for the models used is greater than 18.5 and Prob > F is less than 0.05 which implies that the models are significant for pelletization efficiency, bulk density, TPFV, open porosity and water absorption.

3.4. Multiple optimizations

The experimental investigations were based on the combinations obtained using the Central Composite Design of SAS (Statistical Analysis Software). Based on the experimental investigations multiple optimization was carried out similar to that reported by Kockal and Ozturan [23]. The criteria adopted for the multiple optimizations were maximum pelletization efficiency, bulk density and TPFV, with minimum open porosity and water absorption. The optimized values are summarised in Table 8. Aggregates were produced for the optimized values of the factors involved and the properties were determined on dried aggregate. The results of the predicted and observed values presented in Table 9 are closer which confirms the model.

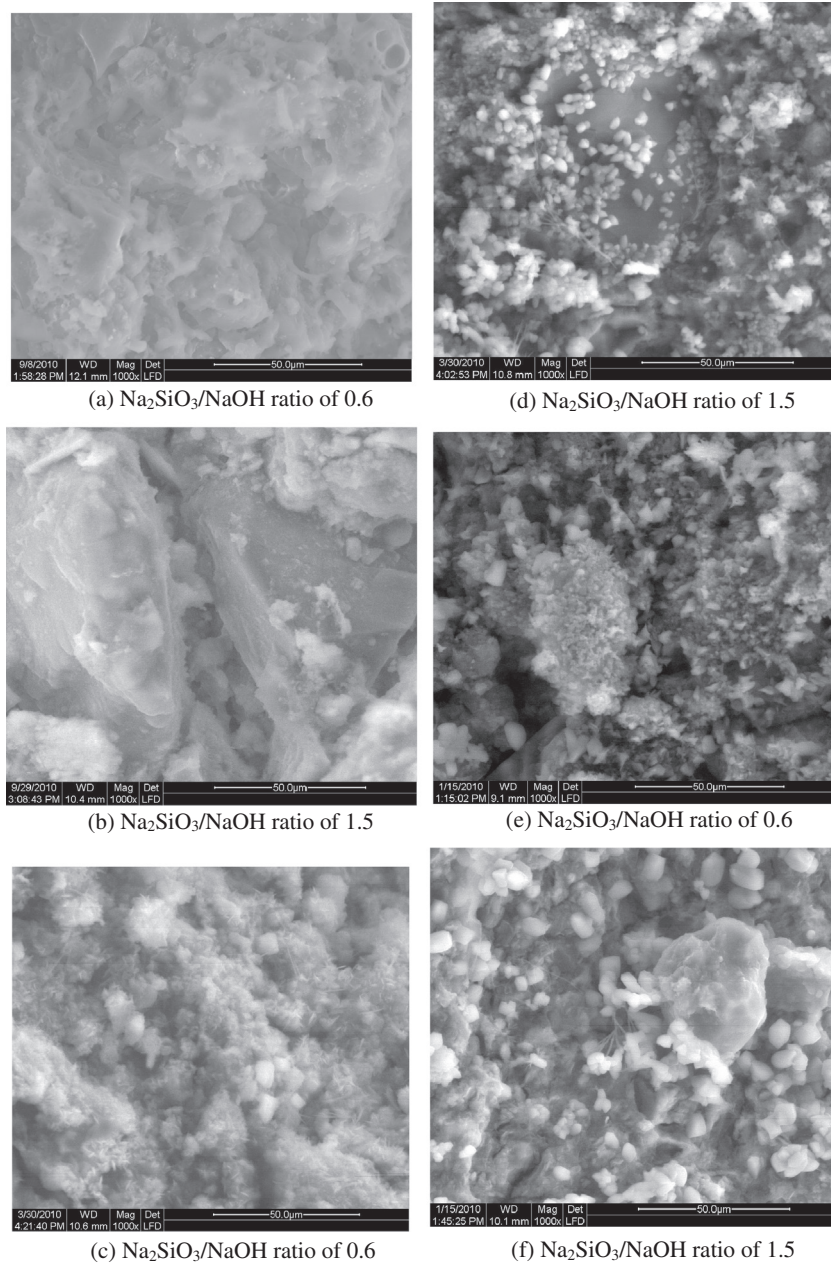


Fig. 8. SEM images of geopolymer aggregate activated with 8 M NaOH (a and b), 10 M NaOH (c and d) and 12 M NaOH (e and f).

Table 6

ANOVA for open porosity and water absorption.

Factors	DF	Open porosity			Water absorption		
		E^2	F-S	Prob > F	E^2	F-S	Prob > F
X_1	1	1.62	25.1337	<0.0001	14.9105	137.898	<0.0001
X_2	1	0.02	0.31029	0.5927	0.32	2.95949	0.1237
X_3	1	1.1054	21.63589	<0.0001	12.1603	121.48334	<0.0001
X_4	1	0.5	7.75731	0.0237	1.62	14.9824	0.0047
X_1^2	1	0.05271	0.81773	0.3923	0.06752	0.62445	0.4522
X_2^2	1	0.05271	0.81773	0.3923	0.21609	1.99853	0.1952
X_3^2	1	0.13414	2.08117	0.1871	0.21609	1.99853	0.1952
X_4^2	1	0.10057	1.56024	0.2469	0.58556	5.41548	0.0484
$X_1 X_2$	1	0.00741	0.11503	0.7432	0.0519	0.47995	0.5081
$X_1 X_3$	1	0.125	1.93933	0.2012	0.3528	3.26284	0.1085
$X_1 X_4$	1	0.09081	1.40883	0.2693	0.20243	1.87212	0.2084
$X_2 X_4$	1	0.01394	0.21626	0.6543	0.0968	0.89525	0.3718
Residual	8	0.06446			0.10813		

Table 7

Regression model statistics for aggregate characteristics.

	R-squared	Adjusted R-Squared	F-Value	Prob > F
Pelletisation efficiency	0.945	0.919	27.6	<0.0001
Bulk density	0.999	0.999	4839.02	<0.0001
TPFV	0.951	0.908	34.5	<0.0001
Water absorption	0.926	0.891	48.6	<0.0001
Open porosity	0.961	0.904	51.2	<0.0001

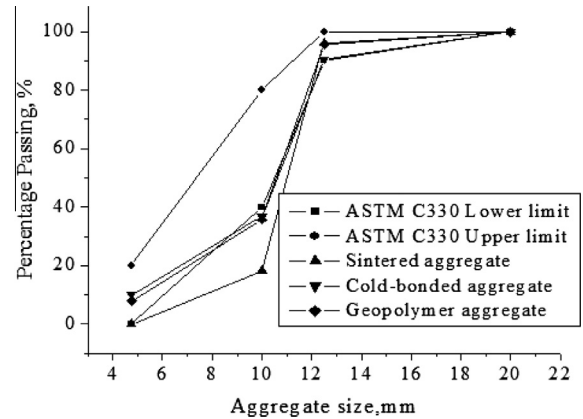
Table 8

Optimized factor values for aggregate cured at ambient temperature.

NaOH (M)	LA/ash	Na ₂ SiO ₃ /NaOH	Ca(OH) ₂
11	0.67	1.35	2.5%

4. Comparison of aggregates using different hardening process

The production and properties of aggregate depend on the type of raw material used and the hardening process adopted. The properties of aggregates manufactured adopting hardening processes viz., sintering and cold bonding reported earlier by the authors [24,25] have been compared with those of geopolymerised aggregate cured at ambient temperature. A wide range of clay binders were used for the production of sintered aggregate and were sintered at 800 to 1100 °C [24]. The cold-bonded aggregate was produced using ordinary Portland cement and lime as binders and the aggregate were subjected to normal water curing for 28 days [25]. Alkaline activation was used for the production of geopolymer aggregate in which the aggregates were subjected to oven curing at 50 to 80 °C [1]. For the same alkali activation Ca(OH)₂ was used to facility production of geopolymer aggregate at ambient temperature. The properties of aggregate produced using above methods are summarised in Table 10. The binders facilitated the pelletization efficiency in all the types of aggregate produced. The size distribution of aggregates produced using all the hardening process presented in Fig. 9 shows that the gradation falls between the upper limit and lower limit values as recommended in ASTM C330. Only 20% of sintered aggregates have size less than 10 mm. In cold-bonded and geopolymer aggregates 30 to 33% of aggregates are less than 10 mm. The bulk density of sintered and cold-bonded aggregate ranges between 700 and 980 kg/m³ whereas for geopolymer aggregate it ranged from 800 to 1200 kg/m³. The TPFV of geopolymer aggregate cured in oven is

**Fig. 9.** LWA grading requirement and grading obtained in various hardening process.

similar to the aggregate sintered at high temperature. Open porosity and water absorption is high in cold-bonded aggregate. Geopolymer aggregate produced by both the process resulted in low open porosity.

5. Conclusions

The following conclusions are drawn for the range of parameters considered, methodology adopted and the materials used in this study:

- (1) Addition of Ca(OH)₂ resulted in the increase in pelletization efficiency because Ca(OH)₂ resulted in accelerating the nuclei formation and resulted in better agglomeration.
- (2) The properties of geopolymer aggregates are mainly influenced by the molarity of NaOH in the alkaline liquid. The bulk density increased from 800 to 1100 kg/m³ with increase in the NaOH molarity.
- (3) The TPFV of aggregate was mainly influenced by the NaOH molarity and Ca(OH)₂. The enhanced hydration and formation of zeolite products at high molarity of NaOH and Ca(OH)₂ dosage contributed to the increase in TPFV.
- (4) The open porosity and water absorption of geopolymer aggregate reduced considerably with increase in NaOH molarity and Na₂SiO₃/NaOH ratio due to finer and homogeneous microstructure that was formed as a result of the reactions.

Table 9

Confirmatory test results for optimized values.

Pelletization efficiency (%)		Bulk density (kg/m ³)		TPFV (tonne)		Open Porosity (%)		Water absorption (%)	
P	O	P	O	P	O	P	O	P	O
98.42	91.73	1054.77	1078.25	3.79	3.69	18.57	19.12	10.24	11.31

P – Predicted; O – Observed.

Table 10

Properties of coal bottom ash aggregate.

Properties	Sintered aggregate (800–1100 °C)	Cold-bonded aggregate	Oven cured geopolymer aggregate (50–80 °C)	Geopolymer cured at ambient temperature
Bulk density (kg/m ³)	700–940	750–980	800–1180	800–1200
TPFV (tonnes)	2.4–6.0	2.5–3.2	2.8–6.2	2.5–4.2
Open porosity (%)	28–33	35–45	18–25	18–23
Water absorption (%)	15–20	19–23	9.8–13.5	10–12

- (5) The properties of the geopolymer aggregate cured at ambient temperature were similar to those of oven-cured geopolymer aggregates, except for their lower strength.

References

- [1] Geetha S, Ramamurthy K. Characteristics of low calcium bottom ash pelletised aggregates using conventional geopolymerisation process. *Cem Concr Comp* (in Review).
- [2] Palomo A, Grutzeck MW, Blanco MT. Alkali-activated fly ashes, a cement for the future. *Cem Concr Res* 1999;29:1323–31.
- [3] Duxson P, Fernandez-Jimenez A, Provis JL, Lukey GC, Palomo A, van Deventer JSJ. Geopolymer technology: the current state of the art. *J Mater Sci* 2007;42:2917–33.
- [4] Li Z, Liu S. Influence of slag as additive on compressive strength of fly ash based geopolymer. *J Mater Civil Eng* 2007;19:470–4.
- [5] Antiohos S, Tsimas S. Activation of fly ash cementitious systems in the presence of quicklime. Part 1. Compressive strength and pozzolanic reaction rate. *Cem Concr Res* 2004;34:769–79.
- [6] Yip CK, van Deventer JSJ. Microanalysis of calcium silicate hydrate gel formed within a geopolymeric binder. *J Mater Sci* 2003;38:3851–60.
- [7] MacKenzie KJD, Smith ME, Wong A. A multinuclear MAS NMR study of calcium-containing aluminosilicate inorganic polymers. *J Mater Chem* 2007;17:5090–6.
- [8] Temuujin J, Van Riessen A, Williams R. Influence of calcium compounds on the mechanical properties of fly ash geopolymer pastes. *J Hazard Mater* 2009;164:82–8.
- [9] Dombrowski K, Buchwald A, Weil M. The influence of calcium content on the structure and thermal performance of fly ash based geopolymers. *J Mater Sci* 2007;42:3033–43.
- [10] Puyam S Singh, Mark Trigg, Iko Burgar, Timothy Bastow. Geopolymer formation processes at room temperature studied by Si and Al MAS-NMR. *Mater Sci Eng* 2005;396:392–402.
- [11] Hou Yunfen, Wang Dongmin, Zhou Wenjuan, Lu Hongbo, Wang Lin. Effect of activator and curing mode on fly ash-based geopolymers. *J Wuhan Univ Technol – Mater Sci Ed* 2009;711–5.
- [12] van Jaarsveld JGS, van Deventer JSJ, Lukey GC. The effect of composition and temperature on the properties of fly ash- and kaolinite-based geopolymers. *Chem Eng J* 2002;89:63–73.
- [13] Hua Xu, Van Deventer JSJ. The geopolymerisation of alumino-silicate minerals. *Int J Min Process* 2000;59:247–66.
- [14] IS 2386: Part IV. Methods of test for aggregates for concrete. New Delhi, India: Bureau of Indian Standards; 2002.
- [15] Ahmed YMZ, Mohamed FM. Variation in physico-chemical properties of iron oxide pellets using bentonite with calcium hydroxide as binder. *Metallurgia Ital* 2005;97:31–7.
- [16] Yip CK, Lukey GC, van Deventer JSJ. The coexistence of geopolymeric gel and calcium silicate hydrate at early stage of alkaline activation. *Cem Concr Res* 2005;35:1688–97.
- [17] Granizo ML, Alonso S, Blanco-Varela MT, Palomo A. Alkaline activation of metakaolin: effect of calcium hydroxide in the products of reaction. *J Am Ceram Soc* 2002;85:225–31.
- [18] Garcia Lodeiro I, Fernandez-Jimenez A, Palomo A, Macphee DE. Effect on fresh C–S–H gels of the simultaneous addition of alkali and aluminium. *Cem Concr Res* 2010;40:27–32.
- [19] Ma W, Brown PW. Hydrothermal reactions of fly ash with Ca(OH)_2 and $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$. *Cem Concr Res* 1997;27:1237–48.
- [20] van Deventer JSJ, Provis JL, Duxson P, Luckey GC. Reaction mechanisms in the geopolymeric conversion of inorganic waste to useful products. *J Hazard Mater* 2007;139:506–13.
- [21] Lee WKW, van Deventer JSJ. The effect of ionic contaminants on the early age properties of alkali-activated fly ash based cements. *Cem Concr Res* 2002;32:577–84.
- [22] Swanepoel JC, Strydom CA. Utilisation of fly ash in a geopolymeric material. *Appl Geochem* 2002;17:1143–8.
- [23] Kockal NU, Ozturan T. Optimization of properties of fly ash aggregates for high-strength lightweight concrete production. *Mater Des* 2011;32:3359–586.
- [24] Geetha S, Ramamurthy K. Properties of sintered low calcium bottom ash aggregate with clay binders. *Constr Build Mater* 2011;25:2002–13.
- [25] Geetha S, Ramamurthy K. Environmental friendly technology of cold-bonded bottom ash aggregate manufacture through chemical activation. *J Clean Prod* 2010;18:1563–9.