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The Effect of Si/Al Ratio and Sodium Silicate on the Mechanical Properties of Fly ash based Geopolymer for Coating

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Abstract. The present study has been performed to see the effect of varying Si/Al ratio (1.85 to 3) by using same concentration of NaOH and same solid/water ratio for the development of mechanical properties at 28 days of room temperature and also select the Si/Al ratio for coating application. The performance of the geopolymer was investigated on the basis of compressive strengthSEM along with EDS. Pure sodium hydroxide specimens displayed decreased strength. However the combination of sodium hydroxide and sodium silicate specimen with aSi/Al ratio of 2 showed maximum strength, whereas the specimen after Si/Al ratio 2 showed decrease in strength.

Introduction

A geopolymer is a chemical process in which alkali reacts with fly ash and transforms into well compact skeleton. Structurally they are cross-linked aluminosilicate networks with alkali as a charge balance and also water is present in the internal pores [1].

There are many sources to produce geopolymers such as fly ash, slag and metakaolin. Fly ash is generated from coal fired power stations .The interesting part of fly ash is Silicon and Aluminum that's why it is suitable to use. Sometimes it is difficult to control its chemical composition. Thus, the only way to produce suitable composition of geopolymers is to blend fly ash with high silica source [2]. There is so many types of silica sources used in research. There are two advantages of adding silica: first, it increases Si/Al ratio and secondly, it produces higher strength [3]. Researchers have shown an increased interest in the geopolymer field. There is so much work done on different factors of geopolymers.

Geopolymerization depends on many factors including chemical composition of raw material, Si/Al ratio, Solid/Water ratio, Sodium hydroxide concentration, water content, curing time and temperature etc [1].The author [4, 5] showed that geopolymers give optimum properties by using raw material as fly ash with sodium hydroxide and sodium silicate solution. Fernandez [6] reported that for geopolymerization the quantity of Silica must be greater than Aluminum, meaning that Silica plays a main role in geopolymerization for making strong bonds. Aluminum participates in forming intermediate phases. As we can see in [3], in the structure of geopolymer [poly (sialate), poly (sialate-siloxo), poly (sialate-disiloxo)] one Al is there and to strengthen the chain of geopolymer more no of silicon atoms is required. Many researchers agree that the strength of material enhanced by increasing Si ratio [7, 8], but after getting optimum compressive strength additional silica in the matrix causes reduction in strength. However, there is no agreement on a single Si/Al ratio which shows higher compressive strength. This might be due to the difference in raw material composition which varies from place to place. Moreover all reported researchers showed different optimum Si/Al ratio for their work of interest.

In this paper our interest is to examine the properties of different Si/Al ratios which will be suitable for coating application. 1.85:1 Si/Al is without sodium silicate, whereas to achieve the higher Si/Al ratio sodium silicate will be added .Specimens were investigated after 28 days of curing at room temperature. After getting geopolymeric product, the samples were examined by SEM micrographs and also to see which formulation is beneficial for coating.

Experimental

Materials and Methods

Fly ash was obtained from a nearby coal power station , sodium hydroxide (Laboratory grade 99 % pure) and sodium silicate(SiO_2=50.60%,Na_2O=16.5%,H_2O=32.90%) was supplied by R and M chemicals. The chemical composition of fly ash is given in Table 1.

Table 1: XRF Data Analysis of Fly Ash.

Elements	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	K_2O	SO_3	Na_2O	TiO_2	$P2O_5$	BaO	SrO	MnO
%	43.34	20.77	12.41	11.13	3.75	1.98	1.45	0.95	0.88	0.32	0.17	0.12	0.11

Method of mixing/geopolymer synthesis

There are four different Si/Al ratios used in this study. The solid/water ratio (4:1) and sodium hydroxide concentration (12M) were fixed for all experiments. For the first Si/Al ratio (1.85:1), no secondary silicate source used. However, the rest of the three Si/Al ratios (2:1, 2.5:1, 3:1) were made by the addition of sodium silicate. Fly ash sodium silicate and sodium hydroxide were mixed in the mixer for 3 minutes. Then geopolymer paste was poured in 50 x 50 x 50 mm cube mold compressive strength (ASTM C109) and cured the mold at room temperature for 28 days.

Result and Discussions

Compressive strength

The average compressive strength of four different Si/Al ratios of geopolymer studied in the present work is summarized in Fig. 1. Compressive strength of all samples was measured after 28 days of curing at room temperature. The compressive strength is increased from Si/Al 1.85 to 2.0 after that decreasing at Si/Al 2.5 and 3.

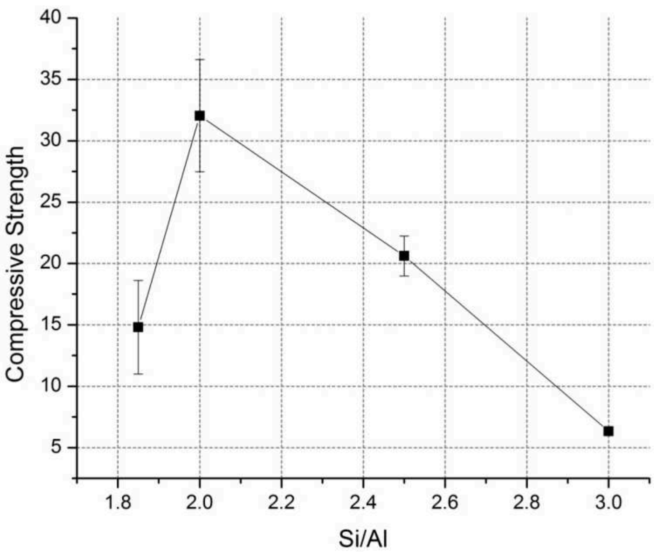

Fig. 1: Compressive Strength vs. Si/Al ratio .S/w ratio (4:1) and NaOH conc. (12M)

In [9], author reported that a high quantity of silica produces hindrance in dissolution and once the dissolution slowed down ultimately the material got less strength. According to Duxson when the Si/Al ratio is high (Si/Al > 3) compressive strength decreased, because it is depended on the mix proportions [10]. In [11], author reported that initially the appearance of soluble silicate solution increases the compressive strength of the material because limited amount of silicate species are available to react with soluble aluminate species to form a strong aluminosilicate network. After getting highest strength the extra addition of soluble silicate decrease the mechanical strength of the material because extra soluble silicate species produces hindrance in the reaction between silicate and aluminate species. Ultimately the dissolution did not occur or occur in a reduced manner then, finally the material got less strength and also most of the silica is unreacted.

Microstructural Analysis

Pure Fly Ash (FA)

In Fig. 4, the micrograph shows the general features of original fly ash. It can be seen in the figure that the fly ash is mainly composed of different sizes of spheres. Some small particles stay on the surface of big particle and also some unshaped fragments can be seen. (Fig. 4 point A).

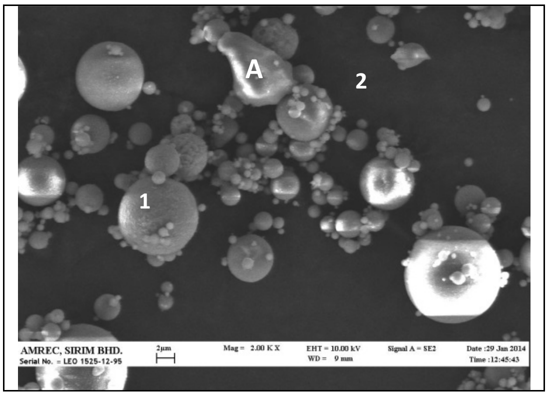

Fig. 4: SEM micrograph of original fly ash (FA).

FANaOH:

In Fig. 5, the microstructure of FANaOH (fly ash activated with NaOH, Si/Al 1.85:1), is presented. The figure shows that high concentration of NaOH solution covers all the particles and produces a dense structure but it is also deduced from the picture after reaction it produces big and small pores.

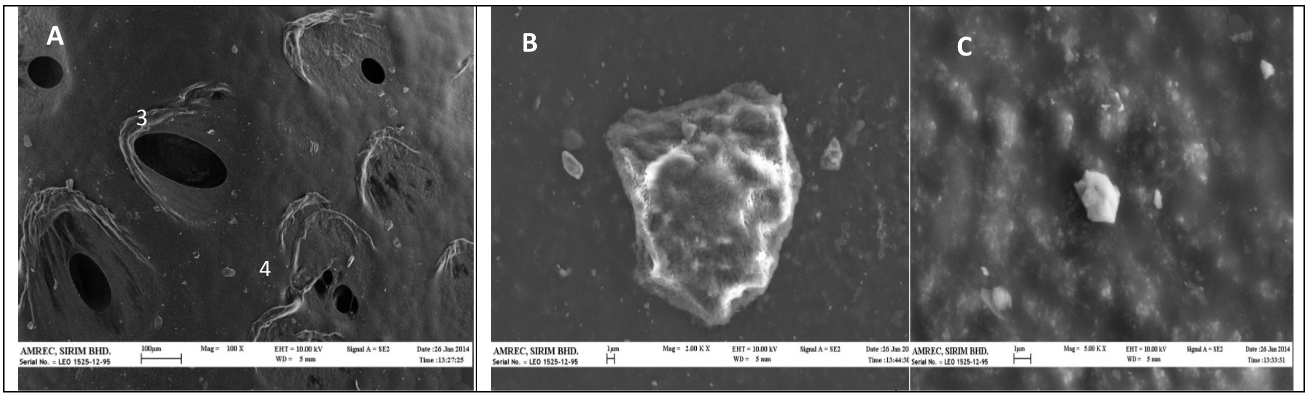

Fig. 5: SEM micrographs of FANaOH

However, the embossed area (near the pores) shows the outer surface of big particles of fly ash, whereas the rest of small particles are present in the matrix. The EDS analysis (see Table 2, Points 3 and 4), shows the composition of Si/Al = 1.6 to 1.8.
On the surface of alumino-silicate there is a big and unshaped fragment shown in Fig. 5B and that unshaped fragment is fully covered with the network of bright crystals (probably zeolite crystals)[11]. These crystals are rich in sodium and silicon as compare to the alumino-silicate matrix.
Fig. 5c indicated that the maximum particles of fly ash is present in the matrix and fully covered with the NaOH solution, only some different size of particles are present on the top of matrix.

FANW2:

In Fig. 6, the microstructure of FANW2 (fly ash activated with NaOH + Na_2SiO_3, Si/Al = 2) is described that the morphology of FANW2 is different from FANaOH sample. From Fig. 6A, all the spheres of fly ash is covered with layer of reaction product meaning that sample FANW2 contain homogeneous binder has less unreacted particles with less pores, which correlates with the maximum in compressive strength. Therefore the improvement in compressive strength strongly favors the production of Si – O – Si bond. According to geopolymeric theory the production of Si – O – Si bond makes the material stronger. Hence material showed high compressive strength, whereas the Si – O – Al and Al – O – Al bonds are weaker.If the bonds produced in the system so the material does not approach to the high strength [12]. The crystals showed in Fig. 6C (Point 5) is because of the high concentration of NaOH (12M) which appear in the form of crystals.

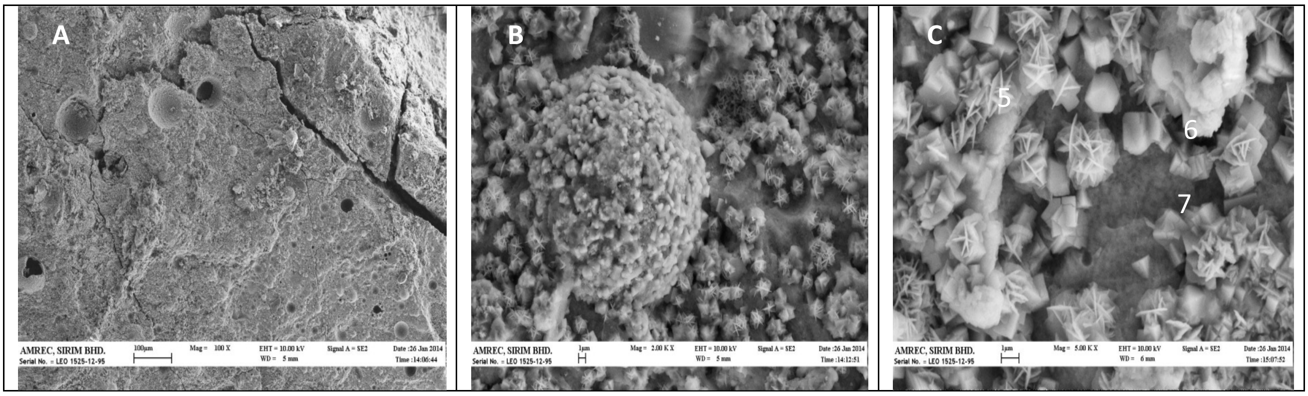

Fig. 6: SEM micrographs of FANW2.

In Fig. 6C, according to the EDS analysis (Point 6, Table 2) theplatystructure identified as quartz because they contain Silicon and Oxygen in higher concentration as compare to the other elements.
Finally through 6C, the EDS analysis (Point 7, Table 2) of main reaction product i-e aluminosilicate showed that this aluminosilicate is basically a mixture of Si, Al, Na and Ca, but Si is present in major quantity.

FANW2.5

In Fig. 7A, the microstructure of FANW2.5 (fly ash activated with NaOH + Na_2SiO_3, Si/Al = 2.5:1) showed cracks and from Fig. 7B large spheres are partially covered with the reaction product. Which produce the low mechanical strength material.According to the Author [10] at certain limits the quantity of silica produces a stronger material and after that the more addition of Si results the formation of reduced alumino-silicate. From EDS the Reaction product (see Point 8, Table 2) contained mainly Si, Al, O, Na are presents, whereas the niddle like structure (see Point 9 and 10, Table 2) made up both calcium and sodium.

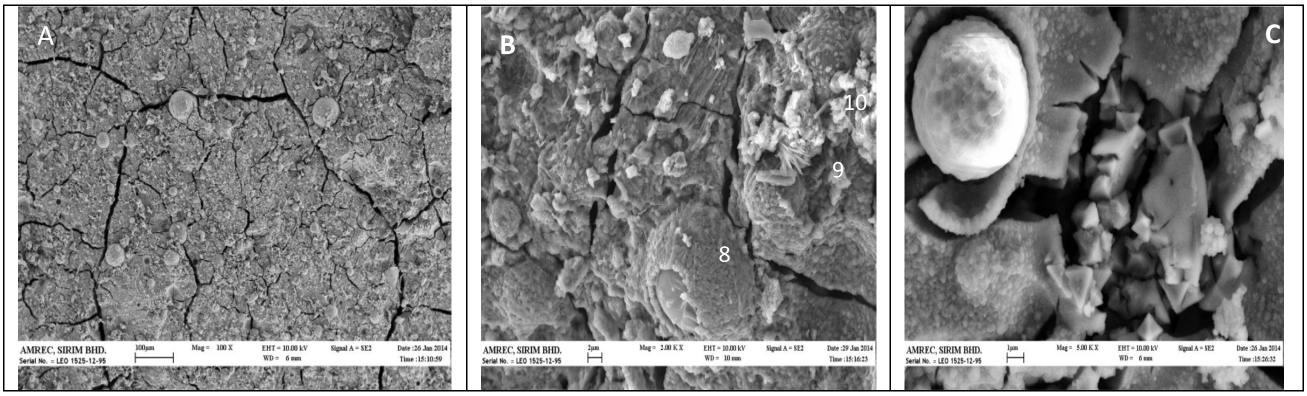

Fig. 7: SEM micrographs of FANW2.5.

It can be seen from Fig. 7c that the adherence between the fly ash particles is not good with the reaction production. Both are loose and also the matrix is not continuous. There are many gaps or pores that are present and that is why the material showed low strength as compared to FANW2.

Table 2: EDS micro analysis on specific point of the samples

S/No.	Sample	Point	Si	Al	Na	O	C	Ca	Mg
1.	FA	1	14.75	9.03	-	54.94	7.87	9.33	4.08
2.		2	21.29	13.99	1.51	60.98	-	-	2.24
3.	FANAOH	3	20.46	11.27	1.9	50.56	5.7	-	-
4.		4	22.23	10.16	-	58.03	4.65	-	15.09
5.	FANW2	5	17.93	12.44	10.22	59.41	-	-	-
6.		6	15.22	10.91	8.91	58.320	5.05	-	-
7.		7	16.09	3.22	7.78	58.63	-	14.28	-
8.	FANW2.5	8	14.16	11.18	9.38	50.56	14.71	-	-
9.		9	2.22	2.78	12.33	59.97	9.22	13.48	-
10.		10	14.49	9.43	11.36	40.09	-	24.63	-
11.	FANW3	11	2.76	3.57	16.27	59.13	5.86	12.41	-

FANW3:

Fig. 8, showed the microstructure of FANW3 (fly ash activated with NaOH + Na_2SiO_3, Si/Al = 3:1). Fig. 8(a) showed that thicker cracks appeared everywhere in the matrix as compared to FANW 2.5, FANW 2. This is because of high quantity of silica which reduced the strength as we discuss in our previous samples.

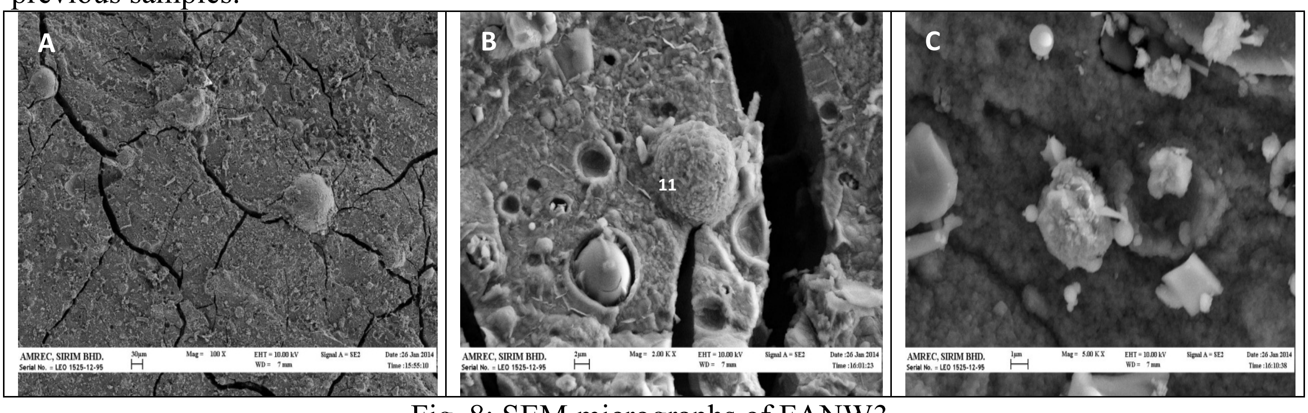

Fig. 8: SEM micrographs of FANW3.

From Fig. 8(b), we can deduce that FANW3 is more porous as compare to the other samples and crystalline like structure (see Point 11, table 2) is the combination of Ca and Na.

Figure 8c showed that fly ash particles are not adhering well to the aluminosilicate matrix because there are many gap/voids are present between them.
In Conclusion, the Si/Al ratio 1.85:1 and 2:1 both has quite different microstructures. This is due to the absence and presence of silicates in the system. Si/Al 1.85:1 showed dense but porous structure, and because of porosity the strength is decreased. However, after 1.85:1 the increment in Si boosted the mechanical property of the material. Si/Al 2:1 is the best formulation which gives dense matrix with less pores and less cracks. Whereas the decrease in mechanical strength after Si/Al 2:1 (Si/Al 2.5 and 3) suggest that the high quantity of silica affects the mechanical property.
The additional increments after Si/Al ratio 2 are not fruitful for strength because the excess Si produces hindrances in making the aluminosilicate network.
This was expected because of the low porosity and dense microstructure (Si/Al 2:1) shown by SEM in Fig. 5.

Conclusion

This study showed that variation in Si/Al ratio gives significant effect on the compressive strength. Geopolymers were examined by using SEM and Compressive strength. The SEM results of Si/Al (2:1) showed fewer pores and fewer cracks and continuous matrices. Its compressive strength was also highest among all samples. According to results Si/Al (2:1) could be suitable material for coating.

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