Effect Of Na_2o/Al_2o_3, Sio_2/Al_2o_3 And W/B Ratio On Setting Time And Workability Of Flyash Based Geopolymer

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ABSTRACT

The objectives of the present research is to appreciate the effect of synthesizing parameters on setting time and workability of Fly ash based geopolymer paste . Locally available low calcium fly ash from a thermal power plant located near Kolkata, India, was used . Fly ash used are lignite coal based and falls under class F category. The broad areas of present research include: Manufacturing of Geopolymer and a comprehensive study on the effect of synthesizing parameters , Alkali content (Na_2O/Al_2O_3), Silica content (SiO_2/Al_2O_3) and Water to Geopolymer binder ratio on setting time of geopolymer paste and workability of geopolymer mortar and arrived at certain level of understanding which will be useful to the researchers and manufacturers.

1. INTRODUCTION

Geopolymers is an inorganic polymeric materials formed by activating silica-aluminum rich minerals with alkaline or alkaline-silicate solution at ambient or higher temperature level. Potential applications includes: fire resistant materials, thermal insulating material, low energy tiles , waste containment, paver blocks etc.

Geopolymerisation is a very complex multiphase exothermic process, involving a series of dissolution-reorientation-solidification reaction analogous to zeolite synthesis. High alkaline solutions are used to induce the silicon and aluminium atoms in the source material to dissolve, forming three dimensional polymeric structure consisting of -Si-O-Al-O- bonds, represented as follows

$M_n [-(SiO_2)_z–AlO_2]_n . wH_2O$

Where: M = the alkaline element or cation such as potassium, sodium or calcium; the symbol – indicates the presence of a bond, n is the degree of polycondensation or polymerisation; z is 1, 2, 3, or higher. The exact reaction mechanism which explains the setting and hardening of geopolymers is not yet quite understood, although it is thought to be dependent on the aluminosilicate base material as well as on the composition of alkaline activator.

Optimization of such a complex system requires systematic study of a number of synthesizing parameters as well as of their interactions. Secondly, fly ash from different sources show different level of reactivity under specific geopolymer synthesis conditions and consequently affects the final properties. Hence , for manufacturing high performance geopolymer binder from fly ash, it is necessary to understand the effects of a various synthesis parameters and their relationship . The Geopolymer mix composition is normally controlled by adjusting alkali and silicate content of activating solution. The SiO_2/Al_2O_3 molar ratio is an extremely important parameter which has major influence on setting time and workability which in turn affects physical and mechanical properties as well as on its microstructure.

The properties of fly ash based geopolymer state depends on chemical composition and quantity of fly ash as well as activator solution. It may be noted here that, percentage of Na_2O (by weight of fly ash) and SiO_2/Na_2O ratio of the mix significantly affect workability and setting time of geopolymer. The workability of the mix depends on its viscosity. The viscosity of gel increases with time due to geopolymerisation process. A study on loss of flow with time is necessary to determine handling time of geopolymer mix. Moreover, these studies are important for locally available fly ash for wide applications in the industry.

2. EXPERIMENTAL INVESTIGATION

The experimental investigation has been conducted at Jadavpur University, Kolkata, India. The humidity and ambient temperature in the laboratory are ranging from 75% to 90% and 25°C to 40°C respectively. The experimental methodology was divided in two main parts: (1) Preparation of geopolymer mix (2) Testing to obtain setting time of paste and workability of geopolymer mortar. Flow table test has been conducted for workability. The laboratory tests were conducted as per relevant Indian standard /ASTM codes.

2.1 Raw Materials

Typical locally available low calcium Class F fly ash from a thermal power station near Kolkata was used throughout the research. The alkaline activator solutions were prepared by mixing sodium hydroxide in pellets form in sodium silicate solution and distilled water.

2.1.1 FLYASH

The chemical compositions of the fly ash, as determined by X-Ray Fluorescence (XRF) analysis, are given in Table 2.1.

Oxide	SiO_2	Al_2O_3	Fe_2O_3	TiO_2	CaO	MgO	K_2O	Na_2O
Mass (%)	55.1	30.85	3.15	1.85	2.45	0.35	0.8	0.65

Table 2.1: Chemical composition of the fly ash (mass %)

The total percentage of (SiO_2+ Al_2O_3+ Fe_2O_3) is greater than 70%. The calcium oxide content is less than 10%. Hence, as per ASTM C 6128-03, it can be classified as class F fly ash (or siliceous pulverised fuel ash conforming to IS 3812(Part-I)-2003 specifications). The colour of the fly ash was dark gray. About 90% of the particles were smaller than 45 μm, and the Blain specific surface area of fly ash was $395 m^2/kg$. The Scanning Electron Microscopy (SEM) image of fly ash show that the fly ash particle are generally spherical in shape of varying size. The mineral composition of fly ash was obtained by XRD analysis and it was found that the major crystalline constituents of fly ash included quartz (SiO_2), mullite (Al_2O_3), and magnetite (Fe_3O_4). The fly ash is also constituted of an X-ray amorphous phases indicated by the broad hump registered between 2θ =20° and 30°

2.1.2 ACTIVATOR SOLUTION

The alkaline activator was a combination of sodium silicate and sodium hydroxide solutions. The sodium hydroxide solids were laboratory grade in pellets form, with a specific gravity of 2.15, 97% purity. To avoid effects of unknown contaminants, distilled water was used for preparing the activator solutions.

The sodium hydroxide (NaOH) solution was prepared by dissolving NaOH pellets in water. The mass of NaOH solids in a solution was varied depending on the required concentration of the solution. The chemical composition of the sodium silicate solution was Na_2O=14.7%, SiO_2=29.4%, and water 55.9% by mass. The other characteristics of the sodium silicate solution were specific gravity=1.48 g/cc. The activator solution was prepared at least one day prior to its use .

2.2 MANUFACTURING PROCESS

Following steps were followed during manufacturing of Geopolymer

- Mixing of sodium silicate solution, sodium hydroxide pellets and water according to predefined proportion to make alkaline activator, at least one day prior to its use .
- Hobart mixer with rotating blades, was used for preparing geopolymer mix
- Mixing of fly ash and alkaline activator in the Hobart mixer for about five to six minutes to get a homogeneous paste.
- Setting time of paste was obtained using Vicat apparatus
- Workability test was conducted using Flow Table test

2.3 SYTHESIZING PARAMETERS

The proportion of geopolymer mix was varied by changing quantity and proportion of sodium silicate and sodium hydroxide in activating solution. The effect of alkali content (Na_2O/Al_2O_3), silicate content (SiO_2/Al_2O_3) and water to geopolymer binder ratio on setting time and workability of geopolymer paste was studied. Loss of workability with time was also studied.

2.4 MIX COMPOSITION

The effect of water content expressed as water to geopolymer binder (geopolymer binder is sum total of mass of fly ash + mass of solids in activating solution). Water to Geopolymer binder ratio was varied from 0.325 to 0.365 by changing quantity of water. The initial and final setting time of Geopolymer paste was determined at room temperature using Vicat apparatus. The Geopolymer paste were prepared by varying % Na_2O from 4.25% to 10.25% and % SiO_2 from 4.5% to 17% . The water to fly ash ratio of 0.325 was kept constant. Again, water to fly ash ratio was varied from 0.325 to 0.365, keeping % Na_2O and % SiO_2 constant. Sand to fly ash ratio was strictly maintained at 1.5.

3. DISCUSSION ON TEST RESULTS

3.1 Effect of alkali content on setting time

Geopolymers pastes prepared by varying % Na_2O from 4.25% to 10.25%. The %SiO_2 and water to fly ash ratio was 8 % and 0.325 respectively. It is observed that both initial and final setting time of Geopolymer paste decreases with increase in alkali content i.e. % Na_2O. (Ref. to Table 3.1)

Table:- 3.1 - Effect of % Na_2O on initial and final setting time

MIX ID	%Na_2O	%SiO_2	Water/ Fly ash	Initial Setting Time (min.)	Final setting time (min.)
SW1	4.25	8	0.325	250	300
SW2	6.25	8	0.325	200	245
SW3	8.25	8	0.325	182	208
SW4	10.25	8	0.325	128	145

However, the difference in initial and final setting time reduces with the increase in alkali content. Geopolymerisation get accelerated at high alkali content and as a result setting time is reduced. The faster rate of reaction also resulted in reducing difference in initial and final setting time at higher alkali content .

3.2 Effect of %SiO_2 on setting time

Geopolymers paste has been prepared by varying %SiO2. The %Na_2O and water to fly ash ratio of the mix was kept constant to 8% and 0.325 respectively.

Table 3.2 Effect of %SiO_2 on initial and final setting time

MIX ID	% Na_2O	%SiO_2	Water/ Fly ash ratio	Initial Setting Time (Minutes)	Final Setting Time (Minutes)
SW5	8	0.00	0.325	160	183
SW6	8	4.5	0.325	115	130
SW7	8	8.75	0.325	177	206
SW8	8	13	0.325	212	248
SW9	8	17.00	0.325	232	289

It can be seen that, the setting time of paste suddenly reduced after addition of silicate. At lower silicate modulus and higher alkali content , rate of polycondensation was very high due to large quantity of Si and Al dissolved in the initial process of dissolution. The dissolves species coagulate very fast with limited quantity of soluble silicate available in the mix which resulted in faster rate of setting. Addition of higher soluble silicate, inhibits the process of polycondensation resulted in higher setting time.

3.3 Workability

The workability of fresh Geopolymer mortar was studied according to ASTM C-124, using mini slump cone. The flow diameter was measured immediately after completion of mixing of Geopolymer mortar in Hobart mixer. The workability of mix was determined by measuring diameter of mortar flow on flow table in two perpendicular directions. The following test were designed to study the effect of various synthesizing parameters on workability of Geopolymer mix.

a) The effect of alkali content (% Na_2O)
b) The effect of silicate ratio (SiO_2/Na_2O)
c) The effect of water content
d) Effect of dosage of plasticizer

The minimum flow diameter of 150± 10 mm was considered as desirable as the mortar could be easily placed in the mould for casting the Geopolymer specimens. However, based on the flow diameter the workability of mix may be classified as shown in the Table 3.3.

Table 3.3 Workability criteria of Geopolymer mortar

Sl. No.	Flow Diameter	Workability
1.	Above 250	Very High
2.	180 to 250 mm	High
3.	150 to 180 mm	Moderate
4.	150 to 120 mm	Stiff
5.	Below 120 mm	Very Stiff

The loss of flow with time was also studied .

3.3.1 Effect of % Na_2O on Workability

Geopolymers mortar prepared by varying % Na_2O from 4.25% to 10.25%. The silica content and water to binder ratio of the mix wad kept constant to 8% and 0.325 respectively.

Table 3.3.1 Effect of % Na_2O on Workability

MIX ID	% Na_2O	%SiO_2	Water/ Fly ash	FLOW DIAMETER
SWM1	4.25	8	0.325	270± 12mm
SWM2	6.25	8	0.325	194± 10mm
SWM3	8.25	8	0.325	159± 8mm
SWM4	10.25	8	0.325	131± 7mm

It has been observed that, the flow diameter decreases almost linearly with the increase in % of Na_2O. Since the water content of the all mixes was 0.325, increase in % Na2O increases viscosity of the mix and resulted in reduction of flow diameter. It is observed that flow diameter decreases with the increase in alkali content. Increase in alkali concentration increases viscosity of Geopolymer mix resulted in reduction in flow diameter.

3.3.2 Effect of %SiO_2 on Workability

Table 3.3.2 presents mix proportion and the flow diameter of the fly ash based Geopolymers mortar prepared by varying silicate ratio SiO_2/Na_2O. The % Na_2O t and water to binder ratio of the mix wad kept constant to 8% and 0.325 respectively.

Table 3.3.2 Effect of %SiO_2 on flow diameter of Geopolymer mortar

MIX ID	% Na_2O	%SiO_2	Water/ Fly ash	Flow Diameter
SWM5	8	0.00	0.325	218± 11mm
SWM6	8	4.5	0.325	178± 9mm
SWM7	8	8.75	0.325	156± 8mm
SWM8	8	13	0.325	137± 7mm
SWM9	8	17.00	0.325	127± 5mm

It is observed that flow diameter decreased almost linearly with increasing %SiO2. The viscosity of the Geopolymer mix increases with increase in soluble silicate dosage. Higher %SiO_2 yielded lowest flow diameter of 127±5 mm as the mix was highly viscous.

3.3.3 Effect of water content on Workability

The change in water to fly ash ratio was achived by increasing water content of the mix from 325% to 365% keeping quantity of fly ash constant. % Na_2O and %SiO_2 was kept constant to 8% .

Table 3.3.3 Effect of water content on flow diameter of Geopolymer mortar

MIX ID	% Na_2O	%SiO_2	Water/ Fly ash	Flow Diameter
SWM1	8	8	0.325	167± 6mm
SWM2	8	8	0.335	176± 8mm
SWM3	8	8	0.345	178± 9mm
SWM4	8	8	0.355	210± 9mm
SWM5	8	8	0.365	258± 11mm

It has been observed that the flow diameter increased with increasing water to fly ash ratio from 0.325 to 0.365. The rate of increase flow is less below water to fly ash ratio of 0.345. However, increasing water to fly ash ratio above 0.345, very rapid increase in flow was observed.

Increasing water content of the mix reduces molar concentration of alkali activator which resulted in reduction in viscosity of mix as well as slow rate of Geopolymerisation resulted in increasing workability. The Geopolymer mortar mix with water to binder ratio of 0.325 was found suitable for mixing and casting of Geopolymer specimens. At higher water to binder ratio of 0.365 some segregation of sand took place and specimen with uniform structure could not be casted.

3.3.4 Effect of dosage of plasticizer

Geopolymers mortar prepared by varying dosage of Naphthalene based superplasticiser from 0% to 4%. The superplasticiser was added by weight with respect to weight of fly ash in Geopolymer mix. The % Na_2O and %SiO_2 were 8% . The water to fly ash ratio was kept constant 0.325 .

Table 3.3.4: Effect of dosage of superplasticizer on flow diameter of Geopolymer mortar

MIX ID	% Na_2O	%SiO_2	Water / Fly ash ratio	Dosage of Plasticizer	Flow Dia
SWMP1	8	8	0.325	0%	155± 6mm
SWMP2	8	8	0.325	1%	164± 7mm
SWMP3	8	8	0.325	2%	193± 9mm
SWMP4	8	8	0.325	3%	224± 10mm
SWMP5	8	8	0.325	4%	270± 11mm

It has been observed that flow diameter increased with increasing dosage of plasticiser. At lower dosage of 1% there is no substantial improvement in workability. However , plasticiser dosage above 1% indicated rapid improvement in workability was observed. At 1% dosage of plasticizer, the flow was moderate whereas at 4% dosage it was very high.

3.3.5 Loss of workability with time

The loss of workability was measured with respect to relative reduction in flow diameter of mortar with time. Decrease in flow was measured with respect to initial mortar flow measured immediately after mixing of mortar. Table 3.3.5 shows the values relative flow diameter Relative flow , at different alkali content of the mix (% Na_2O) with respect to time. The flow diameter was measured at every 30 minute interval using mini slump cone.

Table 3.3.5 : Relative flow at various time for different alkali content

Time (min.)	Relative flow at different alkali content of the mix (% Na_2O)							
	4.25%		6.25%		8.25%		10.25%	
	Flow dia (mm)	Relative Flow	Flow diameter (mm)	Relative Flow	Flow diameter (mm)	Relative Flow	Flow diameter (mm)	Relative Flow
0	262	1.00	186	1.00	154	1.00	134	1.00
30	261	0.99	188	1.00	154	1.00	138	1.00
60	257	0.98	186	1.00	156	1.00	139	1.00
90	249	0.95	181	0.97	150	0.99	133	0.99
120	238	0.92	173	0.92	143	0.95	127	0.95
150	224	0.86	161	0.87	137	0.89	120	0.91
180	206	0.77	147	0.80	127	0.84	111	0.84
210	189	0.72	135	0.74	116	0.77	104	0.78
240	170	0.66	128	0.68	106	0.73	98	0.72

- Relative flow is the ratio of flow at time zero to flow at any time.

It has been observed that the flow of mortar is almost linearly decreased with elapsed time. The rate of flow loss increased with alkali content indicating higher rate of Geopolymerisation reaction at higher alkali content. It was found that during initial 30-60 minutes after mixing slight improvement in flow was observed. It may be due to the some quantity of water released during the process of Geopolymerisation. However, with increasing time higher rate of reaction generated more quantity of gel making mortar mix more viscous resulted in reduction of flow diameter. It has been observed that the rate of loss of flow was higher for higher alkali content. Maximum reduction in flow up to 90% for all mortar mix indicated that the mix could be handled up to 120minutes without any effect on other properties. In the present study, when alkali content of the mix increased beyond 10.25% very rapid setting of the Geopolymer mix took place. At higher alkali content large quantity of oligomeric precursor is made available in a very short time due to faster dissolution rate.

CONCLUSION

The study on effect of geopolymer synthesizing parameters revealed that the development of setting time and workability as well as microstructure depended basically on alkali content , silica content and water to binder ratio . Strong alkali solutions are needed to dissolve fly ash during the process of geopolymerisation. Water plays important role during dissolution, polycondensation and hardening stages of geopolymerisation. The water content should be adjusted to the minimum level considering desired workability of the geopolymer mix.

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