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Fresh properties, rheology and microstructure of fly ash geopolymer with acetylenic glycol, a de-aerator.

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Abstract- Geopolymer, also known as alkali activated materials, are used as alternative to Ordinary Portland cementbased materials for construction and other applications. Though these are deployed on a commercial scale production, still number of areas requires scientific study, particularly in the control of setting time, flow ability and rheology. Addition ofSP toincrease the workability , has the tendency to entrain the air that will reduce the performance of GP mixes. The present study fresh properties, strength and microstructure evaluation of geopolymer prepared using fly ash as a starting materials mixed with acetylenic glycol, a non-ionic surfactant is activated with hybrid alkaline solution of SiO_2/Na_2O of 0.95 without addition of extra water. The experimental results showed that decrease in viscosity with shear thinning on the addition of AG at 0.5% in the flyash that enhanced the wet-ability without affecting compressive strength. A small negative zeta potential (-18.3mev) of the paste confirming the adsorption process which assisting more gel formation and microstructural surface morphology, confirmed by SEM.

Key words- Geopolymer, Fly ash, Compressive strength, Zeta potential, rheology.

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INTRODUCTION:

1.1 Background and literature review:

Inorganic polymer, geopolymer is a recent emerging cementious material synthesized from siliceous material of geological origin (MK) or industrial by products (metallurgical slag, fly ash) [1,2] and activated commonlyby alkali hydroxides and/or hybrid mixture of NaOH and alkaline silicate[3-7] . The geopolymerisation reaction initiated by the dissolution of SiO_2 and Al_2O_3 followed by the rapid reaction of condensation between the oligomer chains resulting in three-dimensional polymeric network structure of $[SiO_4]^{4-}$and $[AlO_4]^{5-}$. The negative charge of $[AlO_4]^{5-}$tetrahedron on skeleton is stabilized by the cations of Na^+, K^+ and Ca^{2+} ions.Generally the FA based geopolymer unlike Portland cement matrix cured and hardenedunder hot curing temperature(25-900C) forming binding gel which depending on activator concentration and reactivity of raw material [8]. These geopolymers can be utilized as partial or total replacement of OPC and offers an excellent property such as high resistant to temperature, acid attack, sulphate attack, rapid strength gain, low shrinkage [9-11].

The association between the rheological properties(flow) and the formulation is the significant issue for the success of the mix design. Generally, lower liquid to binder ratio, improve the compressive strength and forming denser microstructure. To handle the mixes at site conditions, high range water reducingadmixtures of mineral/ organic compounds which modify the flowability[12-15]. Several studies on usage of admixtures on OPC were reported and the interactions between have established [16] and models have also proposed viz Bingham, Herschel–Bukley, Casson, [17-19].

In the case of geopolymer technology, the different types of precursors and activators are in use, and hence the control of flowability, setting time , fresh properties by general purpose admixtures those who work in the Portland cement does not found to be suitable [19-23]. Superplasticizers basically naphthalene,melamine (Second generation product) types and 3rd generation Polycarboxylate SP's have been found to be good to improve the workability. Contradictory reports are due to the variation in the alkali activator modulus used by the different researchers. However the addition of SP increase the tendency to entrain air bubbles during the mixing process and the uncontrolled entrainment may adversely affect the compressive strength.[24-26]

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1.2 Objectives:

1. Workability of the geopolymer paste was evaluated to determine the fresh properties of paste with addition of AG ranging from 0.15 to 2.0% weight of fly ash used. Workability measurements through slump cone and flow test.
2. Rheology of fly ash slurry to understand flowability of blended mixture.
3. Evaluaton of themicrostructural changes with SEM and the mechanical compressive strength.
4. Adsorption on the solid surface through zeta potential measurement using electro kinetic technique.

1.3 Scope of the study:

The adaptability of the fly ash and /or flyash blended geopolymer mortar mixes for the large scale commercial applications in the construction and other applications.

2. MATERIALS AND TEST METHODS:

2.1 CHEMICAL ANALYSIS OF FLY ASH:

Class F Fly Ash sample were collected from Ennore Thermal Power Plant (Tamilnadu, India) directly from the hoppers of Electrostatic Precipitators (ESPs) in gunny bags. The chemical composition of fly ash(Indian) as determined by XRF are according to ASTM C 618 and it is summarized in Table.1

2.2 Microstructural analysis:

The mineralogical compositions of fly ash determined by XRD as shown in Figure 1.0, contains major mineral phases like quartz (PDF#46-1045), magnetite, mullite (PDF#85-1456), anorthite, hematite (PDF#88-2359),.

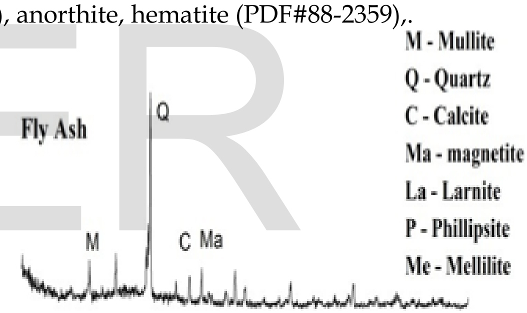

Figure 1: XRD pattern of fly ash

The FESEM micrograph pictures were shown in Figure 2.0, in which they are thin walled hollow spheres.

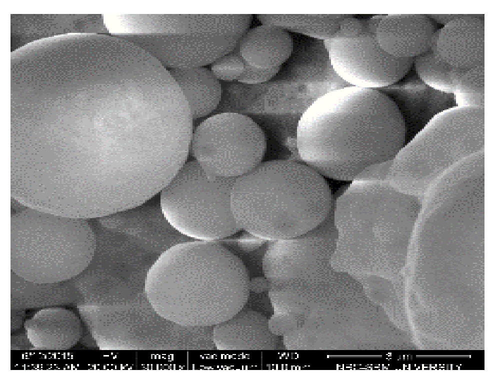

Figure 2.0 : FESEM photomicrograph of fly ash

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Table.1: Chemical composition of low lime fly ash (Indian)

Chemical component	SiO2	Al2O3	CaO	Fe2O3	K2O	MgO	Na2O
Component(wt %)	47.55	33.45	2.099	10.17	1.65	0.005	0.015

2.3 Acetylenic glycol.

Powdered Acetylenic glycol(AG) purchased from local supplier. It is a nonionic surfactant with a bilateral-symmetrical structure and an acetylene bond at the center. The molecular structure of the same is shown in Figure 3.0. Its use in drymix of cementitious mixes was documented as a patent [27], wherein the addition helps significantly reduce the mortar air content thereby increasing the wetting property. The optimum dosage was claimed as low as 0.1% that outperformed over the conventional surfactants. The performance benefits claimed are: improved outflow, a reduced dependence of the outflow rate from the hardening time and a highersurface quality (limited segregation,roughness, cracks, bubbles), long term storage (28 days) at high temperature of a fast-setting aluminosilicate.Therefore the present study aims to study its effect on fly ash slurry. The structure of Acetylenic glycol(AG) was shown in Figure 3.0.

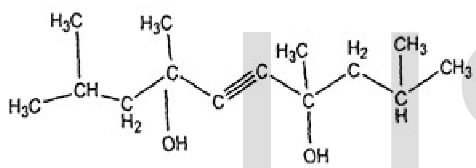

Figure 3: Molecular structure of AG

2.3 Alkaline solution:

An industrial grade sodium silicate solution (15% Na2O, 33% SiO2 and 52% H2O: molar ratio (SiO2/ Na2O -2.0), and Analytical grade NaOH in the pellets form were employed in this study. The Sodium Silicate Solution having Molar Ratio, defined by the term, SiO2/Na2O of 2.0 was used; computation of the ratio of SiO2/Na2O was done by considering the weights of SiO2 and Na2O in a solution expressed in terms of moles. The final SiO2/Na2O is 0.95.

2.4 Geopolymeric mix design:

The geopolymeric source material (fly ash) and aggregate(fine) were weighed using digital balance and dry mixed for 3 minutes in the laboratory concrete pan mixer. The premixed alkaline solution was gradually added into the dry mix and the mixing continued for 5 minutes to get the homogenized mixture. The non-ionic surfactant was added to the mixture (along with SP) with the dosage of 0.5 to 2.0% by weight of the mass of fly ash. The mixture is poured into pre-oiled mould and being casted in the standard 50mm diameter X 100mm height cylindrical moulds. The cylinders were compacted in three layers of equal height with standard compaction using vibrating table and rod. The moulds were sealed to minimize the moisture loss. The details of the geopolymeric mortar mix design with the liquid/solid ratio 0.5 was shown in the Table.2

2.4.1 Preparation of fly ash slurry:

The rheometric needle needs 100ml of slurry suspensions. The required concentration offly ash is weighted on a weighting scale with accuracy of 0.001gram, an alkaline solution as a solvent is measured in milliliters (ml), and its concentration is calculated by subtracting the % conc. of fly ash from 100.Required solution is mixed for 7-8 minutes for homogenous mixing. After mixing the fly ash slurry is immediately poured into geometry and geometry is thenconnected to magnetic coupling of rheometer for experiment.

Table 2: Mix proportion of geopolymer mortar

S.no	Mix ID	Mortar mixture quantity(Kg/m^3)					
		Fly ash	Sand	SP	NaOH	Na_2SiO_3	L/S
1	FA	637.67	1275.34	0	63.8	223.19	0.45
2	FA1	636.79	1273.47	3.19	63.69	222.86	0.45
3	FA2	635.8	1271.71	6.38	63.58	222.53	0.45
4	FA3	634.92	1269.84	9.57	63.47	222.2	0.45
5	FA4	634.04	1267.97	12.65	63.36	2221.87	0.45

2.5 Test methods:

Chemical compositions of FA were determined by means of Energy Dispersive X-Ray Fluorescence spectroscopy (EDXRF-Bruker), mineral composition by powder X-Ray diffraction (XRD-Phillips pW 1710" (Cu Kα = 1.54178). Microstructure characterization has been by FESEM (Qunata).

Computerized Rheometer (Model: MCR101, M/s Anton Paar Company Ltd., Germany) was used for this investigation. The rheometer (coaxial cylindrical measuring

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system) confirms to ISO 3219 [28].Rheoplus: User-friendlyapplication software with 21 CFR Part 11 compatibility and LIMS/SAP interface were used. The test was carried out by varying the shear rates from 100 s−1, 200s−1, 300s−1, 400s−1, and 500 s−1. The shear viscosity is measured by the shear rate sweap experiment. The minimum waiting time set is at 20s at each shear rate.

The workability of fresh geopolymer concrete mixtures testedbySlump cone, following
ASTM: C1437.Compressive strength test was conducted at different curing regimes 3, 7 and 28 days, with a loading rate of 0.33 MPa/s in a Controls CTM machine. Average of 3 test results was taken for calculations.

Malvern Zetasizer (Nano series) was used to measure the zeta potential with 0.5 weight % of Geopolymer paste in deionized water against the standard potassium tungsto - silicate solution and calculations were made through Zetasizer software.

3.RESULTS AND DISCUSSIONS:

3.1 Rheology behavior of fly ash slurry.

The fly ash slurry prepared with different dosages of AG. The shear rate varied from 0 to 500s-1s, and resulted shear stress was measured and graph are plotted as shown in Figures.4.1. The fly ash mixed with NaOH alkali of 8 M exhibited Newtonian pattern with a zero-yield stress, whereas shear stress decreased with the addition of hybrid solution of sodium hydroxide and silicate solution, showing a thickening effect. In the case of addition of AG, decrease in shear stress resulted thereby flowabilityof fly ash particles enhanced. It may be due to hydrophobic hydrocarbon tail and hydrophilic head with no charge adsorption on the surface of the fly ash particles that may facilitate the wetting property.
Figure 4.2 explain the effect of AG on the viscosity of the fly ash slurry prepared with alkaline solution. It was found that viscosity of fly ash control is in the range of 7-25 S-1 at shear rate applied below <200 s-1. The addition of AG in all dosage level , shows a decrease in the viscosity substantially. Above that (>200 s-1)shear rate there was not much change in the viscosity values may be related to the formation of gel by geopolymeric reaction.

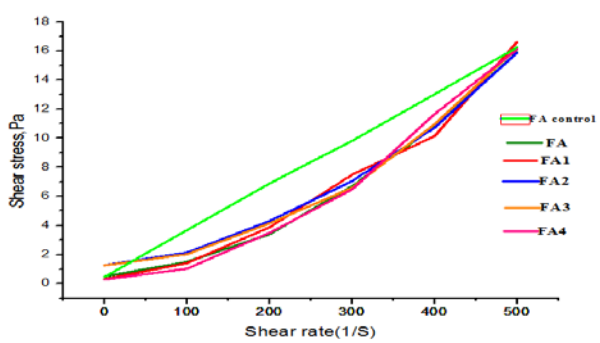

Figure 4.1:Shear stress plot of geopolymer slurrywith and without non-ionic surfactant.

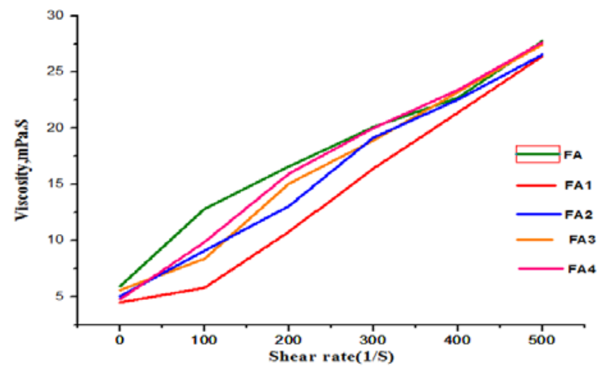

Figure 4.2: Viscosity reduction with and without addition of non-ionic surfactant in Geopolymer slurry.

3.2 Workability and compressive strength :

The workability of fly ash geopolymer mixed with AG was measured by using the flow table and Vicat apparatus to check the consistency of the fresh pastes before casting. Flow diameter measured with and without addition and the results showed that the control samples indicated that 119 mm flow diameter whereas the addition of AG improves to 190mm with enhancement of 30%. The consistency was maintained with low liquid /binder ratio of 0.35.
The fly ash mortar prepared with river sand with 1:2, using liquid to binder ratio ranging from 0.75 to 0.4and the slump values were measured both for the control and blended. The segregation or bleeding occurred under 0.75 with AG 0.5% addition. The observation of slump at 0.5 of liquid to binder ratio for the blended mixture were shown in the Fig 5.1For convenient slumps, they are divided into three groups and the mixture of non-workable condition (>230mm), workable condition (<230 mm and >80mm) and bleeding or segregation (<80mm) were considered.

The slump value increases by increasing the dosage of AG geopolymer mix and also increasing with solid content of fly ash from 300 to 600 kg/m3. It was clearly seen from the Figure 5.1, that mixes are in non-workable range below 0.5% of AG ,implies that AG tends to flow. Increasing the AG content probably reduce the air entrainment thereby increase the wet-ability and more of gel formation thereby the compressive strength is maintained.

The compressive strength measured at 28 days of ageing under hot curing conditions was taken for evaluation and shown as contour plot in Figure 5.2. The average compressive strength of fly ash mortar was 25 Mpa. Literature on the conventional /modified SP and conventional surfactant / air entrainment control admixture reported that the addition of these chemicals

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reduce the mechanical compressive strength of mortar or concrete significantly in the order 30-35% with reference to the control. It can be noted here that the addition of AG plays an important role in fly ash mortar wherein the compressive strength values are not altered in the dosage level of 0.5 to 1% range. But there is a drastic change occurred when it is beyond 1%, may be due to the breakage of Vander Waal's forces that leads to structural deformation.

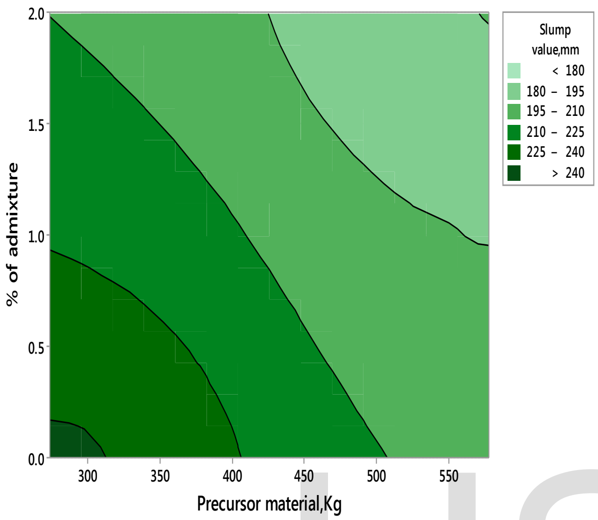


Figure 5.1

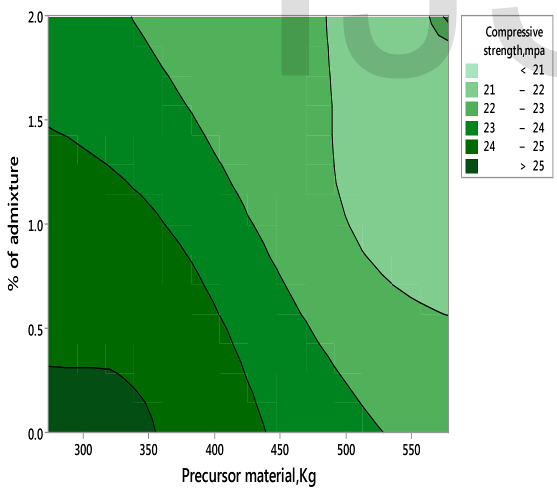
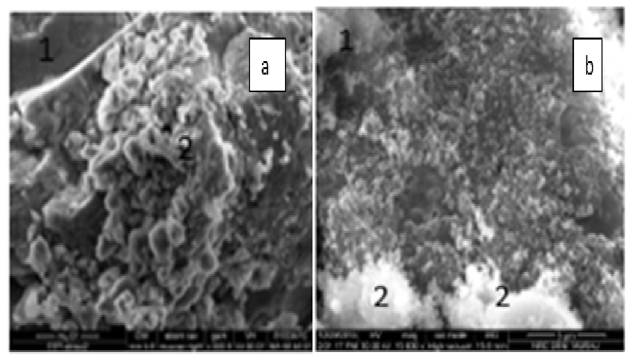


Figure 5.2

Figure 5: Effect of different parameters on slump value and compressive strength of the geopolymer mixes.

3.3 SEM image:

SEM analyses were carried out on geopolymer specimens in order to identify and verify the internal microstructure. The morphological changes of reference geopolymer and geopolymer specimens with addition AG (0.25%) were selected to assess the effect of AG. Fig 6 1 (a) presents the microstructural analysis of the fly ash pastes cured at 28 days and 6.1(b) with 0.25%AG.Products of geopolymerisation reaction represent a heterogeneous materialsi.e., comprising of aluminosilicate gel. In our case the compact structure of geopolymer found in which the fly ash spherical as well as thin walled hollow sphere had disappeared due to dissolution of silica and alumina in the aqueous environment and gel formation occurs on the surface of the fly ash particle.. The addition of AG , the surfactant does not affect the microstructure that was evident from FESEM micrograph 6(b).



1.unreacted fly ash 2. Geopolymer gel formed over the surface of fly ash

Figure 6: Photograph a & b: SEM micrograph of Geopolymer paste with and without addition of AG

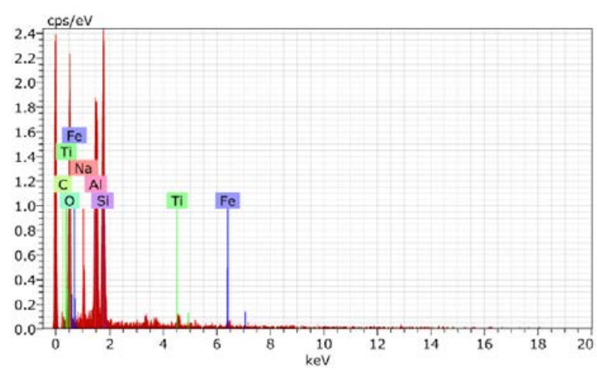


Figure 7.1

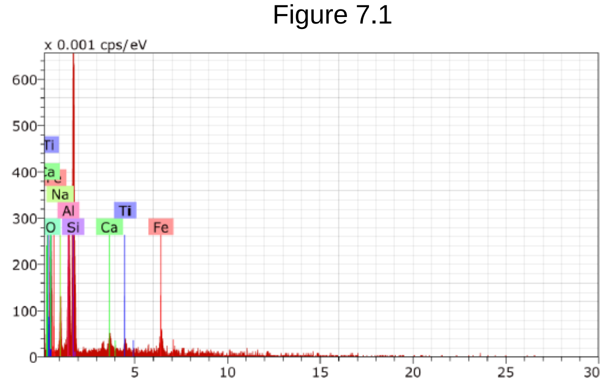


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Figure 7.2

Figure 7 EDAX of Geopolymer paste with and without addition of AG

The EDAX of geopolymer paste with and without addition of AG designate that Si/Al ratio 1.5 with small amount of Na, Fe & Ca.

3.4. Zeta potential:

The potential generated at the interface of the fly ash particle adsorbed with the non-ionic surfactant have been studied using electro kinetic technique which is capable of measuring the zeta potential. The fly ash surface contains a significant amount of readily leachable elements [30] mostly silicates(-O-SiO2-), aluminates(–O–AlO-).At alkaline medium, surface of the fly ash get deprotonated at(pH 11-12) and leaching of negatively charged soluble species in the solution forms the double layer with Na+ . The zeta potential wasfound to be-26.8mev. In thepresent study, we observed the zeta potential value for control fly ash mix in the hybrid mixture of alkaline activator was -15.8mev. The difference between these values may be attributed to more negatively charged species in the solution that favored the formation of gel, [Naz(AlO2)x(SiO2)y. nNaOH.mH2O] which is a binder in the geopolymeric matrix (N-Si-Al). The change in the value of zeta potential values to -18.3mev by the addition of 0.25% of AG evident for the adsorption without altering the species in the leachate.

4.CONCLUSION:

Rheological behavior improved significantly by the addition of non-ionic surfactant at optimum dosage of 0.5% to 1.0% along with the enhancement of workability at the low alkali activator content without any extra water added in the geopolymer mortar preparation. The compressive strength of the mortar was the range of 15-25 Mpa in the liquid to binder varied from 0.4 to 0.75. When it reduced to 0.45 the handling of mixes were found to be hard-hitting. The addition of AG improves the wet ability and workability and maintaining the compressive strength as 25 Mpa.

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