Third International Conference on Sustainable Construction Materials and Technologies http://www.claisse.info/Proceedings.htm

Concrete Repair Materials from Clinkerless Fly Ash Based Formulations Containing Inorganic and Organic Polymers

Anjan K Chatterjee[1*]
[1]*Conmat Technologies Private Limited*
CF-318, Sector I, Salt Lake, Kolkata – 700 064, India
**E-mail : technologiesconmat@gmail.com*

ABSTRACT

The idea of formulating the concrete repair and protection material based on chemically activated fly ash does not seem to have caught up with the scientific community or the repair industry, which is still engaged in dealing with two very basic types of repair materials – cementitious and polymeric. In view of this situation, an attempt has been made to explore the effects of inorganic polymer like sodium silicate and organic polymers like styrene butadiene latex, acrylic copolymer emulsion and redispersible vinyl acetate – ethylene copolymer powder on the basic strength development characteristics of crystalline Class F Indian fly ash. The lab-scale trials indicate that prima facie there is a possibility of developing concrete repair materials from Class F fly ash, despite its crystalline nature, in combination with sodium silicate and redispersible vinyl acetate powder severally. The combination of the two binders tends to depress the binding properties.

Keywords. Fly Ash, Inorganic Polymers, Organic Polymers, Concrete Repair Materials, Alkali Activation.

INTRODUCTION

It is wellknown that the worldwide inventory of concrete structures provides many opportunities for repair to prolong their service life. Consequently, in recent years repair of concrete including protection and retrofitting has become an economically important and scientifically important field. Globally investments for maintenance, repair and restoration of superstructure and infrastructure are continuously on the increase. This, in turn, has led to the developments of different strategies and solutions including material development. The first generation repair materials were developed on the basis of hydraulic cement alone. Although these materials have been or are still being used, they suffer from shortcomings of delayed setting and hardening, low tensile strength, low elongation, etc. These shortcomings led to the extensive introduction of polymeric binders in partial or full replacement of hydraulic binders. Needless to emphasize that the currently used products in the above groups mostly suffer from the shortcoming of not fulfilling the attributes of green chemistry.

In this backdrop, an attempt has been made to explore the possibility of using abundantly available crystalline Class F Indian fly ash in combination with small proportions of selected inorganic and organic polymers to yield concrete repair materials. The objective of the study is focused on developing a concrete repair material with more sustainable characteristics.

CURRENT RESEARCH EMPHASIS ON POLYMER AND FLY ASH COMPOSITES

The present research trend in the polymer fly ash composites has been on studying the effectiveness of fly ash as a polymer filler. The performance of filled polymers is generally determined on the basis of the interface attraction of fillers and polymers. Fillers of widely varying particle size and surface characteristics are responsive to the interfacial interactions with polymers. As illustrations one may mention about some of the published studies, which include viscoelastic, mechanical and thermal characterization of variously surface-treated fly ash filled ABS composites (Bonda et al, 2012); investigation pertaining to the influence of the Class C fly ashes on the hardening process of the unsaturated polyester resin (Czarnecki et al, 2010); effect of fly ashes of differing particle size and surface characteristics on filling Nylon 6 (Bose et at, 2004); fundamental understanding of high-strength polymer fly ash composites based on polypropylene and polyvinyl alcohol (Nath & Bandyopadhyay, 2011); adhesion property determination of epoxy resin with 10% by volume of acetone+silane treated fly ash (Kishore et al, 2002); etc.

Most of these investigations dealt with fly ash filling ratio from 10 to 50 per cent by volume. In other words these studies were essentially on the modification of polymer properties caused by filling with treated and untreated fly ash. The development of composites with higher proportions of fly ash component and small additions of polymer as binders was not attempted in these studies. The present paper, however, is aimed at examining such compositions from the perspective of their effectiveness of repairing concrete.

EXPERIMENTAL INGREDIENTS

Fly Ash Characteristics

The Indian Class F fly ash is essentially crystalline in nature with impoverished chemical reactivity (Chatterjee, 2010; Chatterjee, 2011; Ganguly and Chatterjee, 2010). One such typical fly ash was selected for this study, the chemical composition of which is given below in weight per cent.

Oxides	%	Oxides	%
SiO_2	60.17	SO_3	0.13
Al_2O_3	26.73	LOI	0.72
Fe_2O_3	4.04	Na_2O	0.39
CaO	2.49	K_2O	1.08
MgO	0.89	**Total**	**96.64**

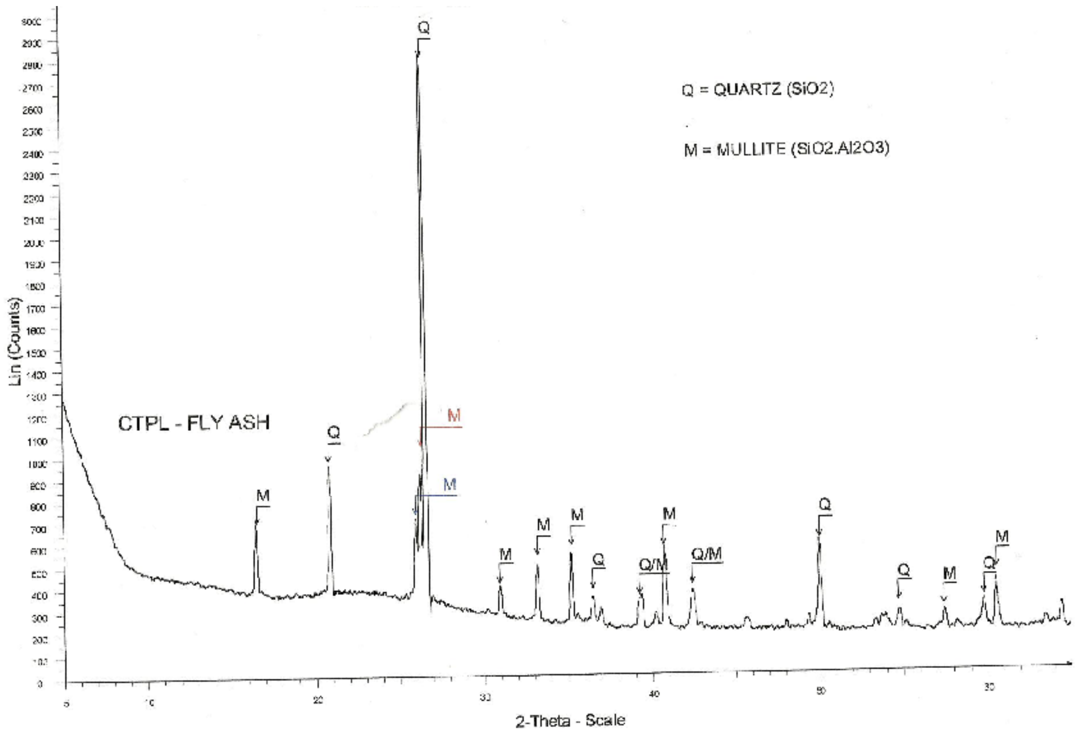
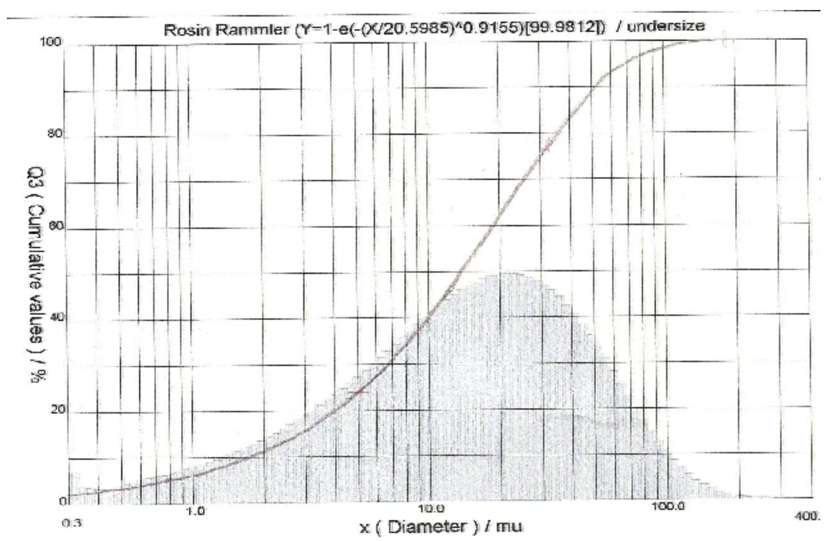


Figure 1. X-ray diffractogram of the fly ash



Customer defined classes					Rosin Rammler / undersize					
x	1.00	3.00	5.00	8.00	12.00	15.00	20.00	32.00	38.00	45.00
Q3	6.08	15.75	23.94	34.34	45.65	52.67	62.22	77.61	82.65	87.06
x	55.00	70.00	90.00	110.0	135.0	165.0	212.0	260.0	320.0	400.0
Q3	91.43	95.33	97.89	99.03	99.63	99.88	99.98	100.00	100.00	100.00

x : diameter / mu Q3 : cumulative value / % q3 : population density / %

Figure 2. Particle size distribution of the fly ash determined by a Laser Granulometer

The X-ray diffractogram of the fly ash sample is given in Figure 1 which shows its crystalline nature with quartz and mullite as the primary mineral phases with little glass content. The particle size distribution of the fly ash as determined by a laser granulometer is shown in Figure 2. With about 14 per cent residue on 45 μm the fly ash can be considered to be reasonably fine in particle size distribution. The fly ash was pozzolanic in nature with lime reactivity of 5.2 MPa as tested in accordance with the Indian standard testing procedure.

Silicate-Based Inorganic Binders

Soluble silicate binders have been used effectively for decades in various end uses. As inorganic binders, soluble silicates do not face the handling, safety and environmental issues associated with NO_x and VOC's. Amongst the soluble silicates, sodium silicate turns out to be a cost-effective binder for agglomeration of waste or low value materials. In our experimental studies an extra-pure sodium silicate solution containing 35 per cent solid was used. Some experiments were carried out with a mix of sodium silicate and sodium sulfate in order to ascertain the latter's influence on the binding property. For mixes containing both polymer and sodium silicate, the latter used was in powder form with SiO_2/Na_2O ratio of 1.62.

Organic Polymeric Binders

Three different organic binders were selected : Styrene butadiene latex, acrylic co-polymer emulsion and a redispersible co-polymer powder of vinyl acetate and ethylene. Their broad characteristics are given in Table 1.

Table 1. Broad characteristics of the organic polymeric binders

Serial No.	Parameters	SB latex	Acrylic co-polymer emulsion	Redispersible Vinyl Acetate & Ethylene co-polymer
1.	Appearance	Free flowing milky white liquid	Free flowing milky white liquid	White powder
2.	Density g/cm^2	1.02 – 1.04	1.10 – 1.24	1.12 – 1.21
3.	Solids content %	42 – 44	52 – 55	98 – 100
4.	pH value	7 - 9	7.0 – 8.5	--

ACTIVATION OF FLY ASH – SAND MORTARS

Although a large volume of published literature is available on the design and activation of fly ash based geopolymer concretes, not much is known about the activation behavior of fly ash – sand mortars and their resultant properties. Since the hydraulic cement based repair materials include normal Portland cement – sand mortars generally, of 1:2 to 1:4 ratio and dry pack mortars commonly of 1:2.5 ratio, an attempt was made to study the effect of varying ratios of fly ash to sand on the development of compressive strength of mortar cubes. The results of some trials carried out with mortars prepared with the fly ash sample activated with 5 per cent sodium silicate and a sand of 2 mm top size are shown in Table 2. The strength levels in the table were achieved after curing the cubes for 48 h at 50^0C. From these results it seems that prima facie there is a possibility of formulating repair mortars with activated fly ash in which some proportion of fine aggregate is necessary for compaction. Based on further experiments it was observed that for the given fly ash sample an addition of two per cent sodium sulfate on 95 per cent fly ash mixed with 5 per cent sodium silicate the compressive strength could increase by 40 per cent at 3 days and 20 per cent at 7 days, over what has been reported in Table 2.

Table 2. Effect of fly ash-sand ratios on the mortar cube strength with 5% sodium silicate binder

SiO_2:Na_2O molar ratio	FA/sand ratio	Fluid/solid ratio	Compressive strength, MPa	
			3-day	7-day
1.52	1 : 3	0.33	16.0	19.2
1.62	1 : 1	0.32	5.0	6.5
1.55	1 : 0	0.30	3.8	5.6

In another set of experiment (Radhakrishna et al, 2006) sodium hydroxide flakes (96 per cent pure) and the sodium silicate solution were used to prepare the alkaline activators of different molarities. With the same fly ash but with fluid of different molarities an attempt was made to determine the impact of fluid-fly ash ratio on the mortar strength and the results are shown in Figure 3. It can be seen that for the same fluid/fly ash ratio the strength development markedly increased with the molarity of the fluid as expected. Further, the pattern of strength variation is comparable to that of normal Portland cement mortars with varying water-to-cement ratio.

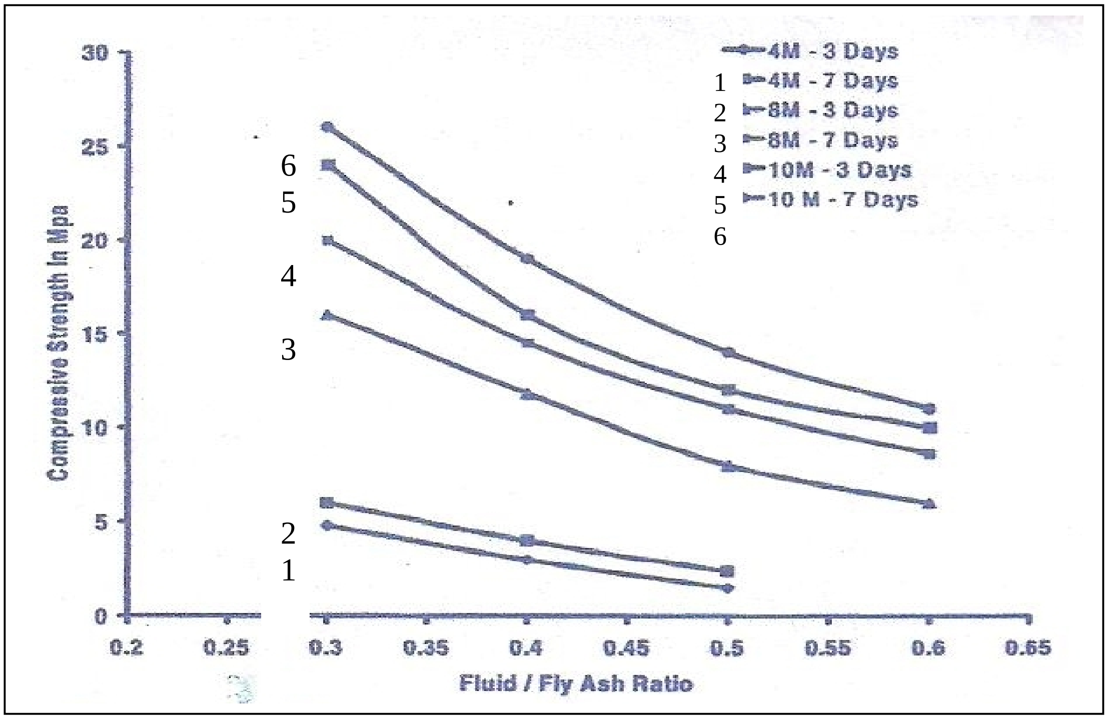


Figure 3. Variation of strength with age for different molarities of the binder

During the course of the study it was also observed that the flexural strength of the activated fly ash-sand mortars was generally about 12 per cent of the compressive strength, which is also similar or close to the behavior of normal Portland cement as the binder. Hence, it was thought pertinent to try out polymers with or without sodium silicate so as to find out whether the flexural behavior of the fly ash-polymer composites was influenced by the silicate binder.

Effect of Polymers

As already mentioned, three types of polymers were tried with the fly ash powder, the level of addition being 10 per cent. A set of data is given in Table 3. Sodium silicate addition was attempted only with the redispersible polymer as the other two polymer mixes gave lower flexural strength than with redispersible polymer. All the specimens were cured at 50^0C till the age of crushing.

Table 3. Effect of polymers on fly ash powder

Serial No.	Properties	Polymers			
		SB latex	Acrylic copolymer emulsion	Redispersible Vinyl Acetate Ethylene copolymer	Redispersible Vinyl Acetate-Ethylene powder plus 5% sodium silicate
1.	Fluid/FA ratio	0.15	0.19	0.25	0.33
2.	Flow, mm	170	165	150	Stiff mix
3.	Compressive strength,MPa				
	3-day	0.5	0.3	0.3	0.2
	7-day	3.5	1.7	5.6	3.8
4.	Flexural strength, MPa				
	7-day	1.05	0.7	2.32	0.73
5.	Pull-out strength, MPa	--	--	2.45	0.93

From Table 3 it is evident that the redispersible vinyl acetate-ethylene copolymer powder was apparently more effective than the SB latex and acrylic copolymer emulsion. Further, it was also noticed that simultaneous use of sodium silicate and redispersible powder tended to depress the strength properties in all respects.

DISCUSSION OF THE FINDINGS

The hydrolysis of silicates and aluminates defines the initial reactivity of the substrate and leads to reactive aluminosilicate surfaces. The rate of aluminosilicate hydrolysis can be linked to the mainly glassy structure of the substrates used (Moesgaard et al, 2010, Duxson and Provis, 2008). Unlike what is, thus, required for reactivity, the Indian Class F fly ash in the present instance and, also in general is highly crystalline with low glass content.

So far as this kind of crystalline fly ash is concerned, it appears that sodium silicate is likely to act as a fairly effective binder as it has a unique characteristic of forming films by the evaporation of water or other solvent. Loss of a small portion of water, even under ambient conditions, will result in a strong, rigid, glassy film. Rate of drying will depend on ratio, concentration, viscosity, film thickness as well as temperature and relative humidity. Moisture resistance can also be obtained by simply drying the silicate more completely through the addition of heat. Because of these attributes, fly ash-sand based repair mortars seem feasible to be tailor-made by optimizing the binder proportion as well as binder mixing, application and curing processes. Another advantage is the opportunity available to enhance the penetration and adhesive quality of soluble silicates with surfactant/wetting aid.

However, it seemed from our results that the film forming effect of sodium silicate was a deterent to the combined use of soluble silicate binders along with organic polymers. Hence the organic polymers needed to be tried as independent binders, which was attempted in this study.

Under our experimental conditions vinyl acetate-ethylene copolymer showed better strength characteristics of the fly ash composites than the SB latex and acrylic copolymer emulsion. The tough-elastic film properties of VA-E copolymer might have helped in achieving better compressive and flexural strengths. Since this is an on-going project, studies are continuing in arriving at more decisive conclusions.

TENTATIVE CONCLUSIONS

The Class F fly ash in India is generally crystalline with quartz and mullite as the primary phases with low glass content. Further, the silica-to-alumina ratio is generally more than 2. Because of these characteristics, this kind of fly ash is not easily amenable to alkali activation, unless alkali-enriched soluble silicates are used. Since these silicates can also serve as binders, in the present study an attempt has been made to explore if this kind of fly ash can be converted into concrete repair mortars with sodium silicate with or without sodium sulfate as the binder. The preliminary experiments indicate that with proper particle size distribution by adding optimum proportion of fine aggregate, the Class F fly ash can be converted into mortars like Portland cement based repair materials.

However, these formulations are not expected to achieve high flexural properties and hence use of organic polymeric binders was taken recourse to. Effect of redispersible powder of vinyl acetate and ethylene copolymer on the compressive and flexural strength properties as well as the pull-out strength of the untreated fly ash powder composite was found to be encouraging. But the use of alkali activated fly ash, when composited with organic polymers showed significant reduction in strength values. On the whole, the approach towards formulating concrete repair mortars can either be with the use of soluble silicates as the binder on one hand, or the organic redispersible powder of vinyl acetate and ethylene copolymer as a binder on the other. However, in both the cases significant optimization of ingredients and the preparation process is necessary.

REFERENCES

Bonda,S., Mohanty,S., and Nayak,S.K. (2012); "Viscoelastic, mechanical and thermal characterization of fly ash filled ABS composites and comparison of fly ash surface treatments", *Polymer Composites*, 33, 1, 22-34.

Bose,S. and Mohanwar, P.A. (2004), "Effect of fly ash on the mechanical, thermal, dielectric, rheological and morphological properties of filled Nylon 6", *J. Minerals & Materials Characterization & Engineering*, 3, 2, 65 – 89.

Chatterjee, A.K. (2010), "Indian fly ashes, their characteristics and potential for mechanochemical activation for enhanced usability", *Proc. 2nd International Conference on*

Sustainable Construction Materials and Technoliogies (Eds.) Zachar, J., Claisse, P., Naik, T.R.and Ganjian, E., Ancona, Italy, Vol. I, 41 – 51.

Czarnecki, L., Garbacz, A., and Sokolowaska, J.L. (2010), "Fly ash polymer concretes". *2nd International Conference on Sustainable Construction Materials and Technologies, Proc. Honor Sessions (Eds.) Naik, T.R., Canpolat, F., Claisse, P. and Ganjian, E.*, Ancona, Italy, 127 – 137.

Duxson, P. and Provis, J.L. (2008), "Designing precursors for geopolymer cements", *J.Am. Ceram. Soc., 91, 3864 – 3869*.

Ganguly, P.P. and Chatterjee, A.K. (2011), "Alkali activation of highly crystalline Indian fly ashes towards developing clinkerless binders", *Abstracts & Proceedings, XIII ICCC, (Eds.) Palomo, A., Zaragoza, A. and Agui, J.C.L.,* Madrid, Italy, p. 169.

Kishore, Kulkarni, S.M., Sunil, D. and Sarathchandra, S. (2002), "Effect of surface treatment on the impact behavior of fly ash filled polymer composites", *Polymer International*, 51, 1378 – 1384.

Moesgaard, M., Keding, R., Skibsted, J. and Yue, Y.Z. (2010), "Evidence of intermediate-range order heterogeneity in calcium aluminosilicate glasses", *Chemistry of Materials*, 22, 4471 – 4483.

Radhakrishna, Shashishankar, A. and Nagraj, T.S. (2006), "Phenomenological model for assessment of strength development in Class F fly ash based geopolymer mortars", ICI Journal, Chennai, India, 23 – 27.