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RESEARCH ARTICLE

Effect of polycarboxylate type of super plasticizer on the hydration properties of composite cements

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The work aims to study the effect of polycarboxylate type of super plasticizer on the hydration of composite cements. In this paper we have studied the hydration of 20 wt% fly ash (FA) blended Portland cement in the presence of 0.1 wt% super plasticizer (SP). Water consistency, setting times, non-evaporable water contents, compressive strength, water percolation, and air content measurements were carried out. In addition, X-ray diffraction studies were carried out to understand the hydration process. The results indicated the increase in compressive strength of the FA blended Portland cement in the presence of SP and with the increase of the hydration time.

Keywords Portland cement, fly ash, super plasticizer, hydration

1 Introduction

Cement is considered as one of the most important building materials around the world [1]. Their consumption and production is closely related to construction activity, and therefore to the general economic activity. The economical and ecological problems associated with cement production during the past 50 years have prompted the use of clinker replacement, materials that has given birth to a generic group of cements, known as 'blended cements' or 'composite cements'. Their general behavior is quite similar to that of Portland cement since they harden when mixed with water and form the similar calcium silicate hydrates (CSH) and calcium aluminates hydrates (CAH). However, additions (normally inorganic materials known as mineral admixtures) give the blend some additional properties which are used for preparing some special cement. The most common ingredients for blending Portland cement clinkers are latent hydraulic component (e. g. granulated blast furnace slag), or pozzolanic components such as natural pozzolana [2,3], fly ash [4–7], condensed silica fume [6–8], burnt clay, sugarcane baggase ash [9], rice husk ash [10] or filler component like lime stone [11–13]. Fly ash abundantly produced in India (~100 millions tones annually) is creating the waste disposal problem and it also reduces the use of land which becomes potentially available for other uses such as housing, agriculture and industries. The Portland cement could be replaced in the concrete by the supplementary cementing materials (SCM) like fly ash, which in turn will save energy, reduce CO_2 gas emissions and may improve the quality of cement [4–7].

Formulations of blended cements are associated with conservation of energy, capital, time and environment. With increasing demand on specific performance characteristics in concrete such as improved strength, low heat, sulfate resistance, improved impermeability and certain other applications, agricultural wastes and residues have imparted superior qualities to Portland cement. Recent developments in the field of mineral admixtures have shown that high performance or even ultra high performance concretes, with good workability in the fresh state and high durability in service, can be made by judicious choice of mineral admixtures and concrete mix proportions [8,10,14,15].

Another development is the use of the chemical admixture, especially super plasticizer (SP) which has become an essential part of modern concrete technology [16]. Super plasticizers can improve workability, speed finishing, increase strength, conserve cement and help reduce shrinkage and thermal cracking. Super plasticizers of the "new generation" are essentially polycarboxylate (PC) polymers. PC based SPs are not only chemically different from the older sulfonated melamine and naphthalene-based products, but also different in the action mechanism, which gives cement dispersion by steric stabilization, instead of electrostatic repulsion. Furthermore, the chemical structure of PC based SPs allows for a greater degree of chemical modification than the older-generation products, offering a range of performance that can be tailored to meet specific requirements. To understand the role of fly ash and PC based admixtures in concretes, we studied the hydration behavior of fly ash and blended cements in the presence of chemical admixtures with a brand name Glenium 51 (obtained from BASF, India). The setting time, non evaporable, water contents and free lime were determined. X-ray diffraction studies, water percolation, expansion in the corrosive atmosphere and compressive strengths were

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Table 1 Mineralogical and oxide composition of Portland cement

Oxide	Composition/wt%	Phase	Composition/wt%
SiO_2	19.5	C_3S	76.8
Al_2O_3	4.84		
Fe_2O_3	3.26		
CaO	62.66	C_2S	5.51
MgO	4.19		
K_2O	0.54		
Na_2O	0.06	C_3 A	7.31
TiO_2	0.44		
PbO	0.77		
ZnO	0.09	C_4 AF	9.92
MnO	0.15		
P_2O_5	0.03		
SO_3	2.13		

also measured. The overall mechanism of action of PC as SP during the hydration of blended cement in cement is also discussed.

2 Experimental

2.1 Materials

Portland cement (OPC) obtained from Vikram Cement, India was used for hydration studies. The oxide and mineralogical composition are given in Table 1. Particle size distribution of OPC is given in Fig. 1. Fly ash was procured from Dadri Thermal Power Plant, India. The chemical composition of fly ash is given in Table 2. Its Blain surface area is about 3200 cm^2/g. Formulation of OPC blended 20 wt% fly ash mixtures is designated as OPC-FA. Gelenium 51 was obtained from BASF chemicals construction company, India. It is a light brown colored liquid with a specific gravity of 1.08 at 25°C, chloride content $< 0.2\%$ and pH > 6 and was used as a polycarboxylate type super plasticizer. The mixtures obtained by incorporating 0.1% super plasticizer in OPC-FA is designated as OPC-FA-SP.

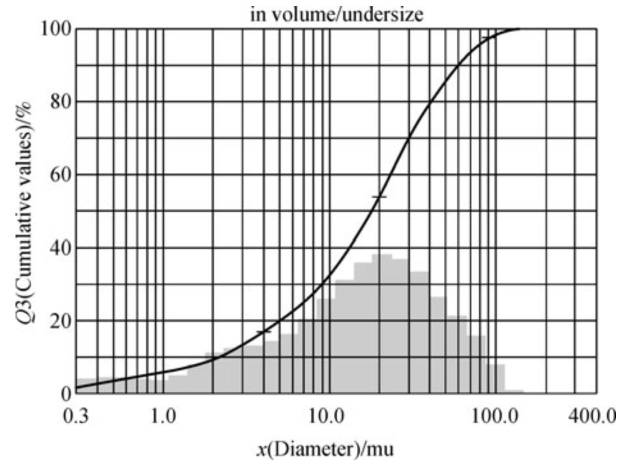

Figure 1 Particle size distribution of Portland cement

Table 2 Chemical composition of fly ash

Constituents	Composition/wt%
Silicon dioxide	59.02
Aluminum oxide	38.02
Magnesium oxide	0.28
Sodium oxide	0.47
Potassium oxide	0.22
Calcium oxide	0.94
Loss on ignition	1.05

2.2 Methods

Determination of standard water consistency and setting times The water consistencies and initial and final setting times of OPC, OPC-FA, OPC-FA-SP were determined with the help of Vicat apparatus (IS: 4031 part 4, 1988).

Preparation of hydrated samples 10 g of OPC, OPC-FA and OPC-FA-SP were thoroughly mixed in polythene bags with 3 mL water so that w/c ratio became 0.3. The air inside the bags was removed in order to avoid carbonations. The hydration reactions were allowed to continue at room temperature (~28°C) and stopped at different interval of time (1, 3, 7, 14 and 28 days) with isopropyl alcohol and diethyl ether. The hydrated samples were heated at 105°C for 1 h. The dried samples were stored in polythene bags and kept in desiccators.

Determination of different parameters for hydrated samples

(a) *Non-evaporable water contents* Approximately 1 g of the samples hydrated at different time intervals were weighed in ceramic crucibles and heated at 105°C for 1 h in order to remove adsorbed water. When removed from the oven, the mass of the crucibles and samples were determined again before being placed in a furnace at 1000°C for a minimum of 1 h. From the mass losses at 1000°C the non-evaporable water contents were calculated.

(b) *Free lime determination* About 1 g of the hydrated cement was refluxed with 40 mL of isopropyl alcohol and acetoacetic ester mixture (20∶3) for 1 h. The solution was filtered and titrated against 0.1 mol/L HCl using bromophenol blue as an indicator. The percentage of the free lime was determined by using the following equation;

$$\%\ \text{free lime} = 0.2804 \times V/W,$$

where V is the volume of 0.1 mol/L HCl used in the titration and W is the weight of the hydrated cement.

(c) *Water percolation by permeability apparatus* The following mixtures

i. 140 g OPC + 28 g FA + 700 g sand

ii. 140 g OPC + 28 g FA + 700 g sand + 0.14 g SP

were mixed separately with 42 mL water in order to have water/solid (w/s) ratio of 0.3. The mortars were thoroughly mixed in Hobart mixer. Each mortar was placed in a mold as per IS 2645. After 24 h, the mortars were demolded and immersed in water tanks separately for 20 days. The molds were then fixed in a permeability apparatus where a pressure of 2.0 kg/cm^2 was applied (the pressure was slowly increased from 0.5 kg/cm^2 to 2.0 kg/cm^2). Water percolation was measured at every 1 h in terms of weight of percolated water for 8 h.

(d) *Air contents* Air contents of the concrete made from the above mixtures were determined with the help of Air Entrainment Testing apparatus as described elsewhere [12].

(e) *Compressive strength* Compressive strength of cement mortars (OPC:sand—1∶3) in the absence and presence of FA and SP at different intervals of time were determined with the help of compressive strength testing machine.

(f) *Corrosive atmosphere* Cylindrical molds of OPC and OPC-FA in the presence and absence of SP (diameter 3.0 cm and length 3.0 cm) were prepared at a w/c ratio of 0.3. After 24 h the cement cylinders were removed from the molds and kept under water for 28 days for curing. These molds were then kept in N/60 H_2SO_4 and expansions were measured as a function of time with the help of Le Chatelier's apparatus.

(g) *X-ray diffraction studies* Powder X-ray diffraction patterns were recorded with X-ray diffractograph using CuK_a radiations.

3 Results and discussion

The chemical reaction taking place during hydration of cement is generally more complex than the simple conversion of anhydrous compounds into the corresponding hydrates. The hydration reaction is exothermic in nature, and as soon as cement comes in contact with water, setting and hardening processes starts. To make a paste of standard consistency, certain optimum w/c ratio is required. The changes in water consistency for OPC, OPC-FA and OPC-FA-SP are given in Fig. 2. The water consistency of OPC-FA is higher than that of OPC alone. This may be due to the higher surface area of the fly ash. In the presence of SP, the water consistency is decreased as normally expected from the addition of SP. It has also been reported that different cements and cement phases adsorb different quantities of SP.

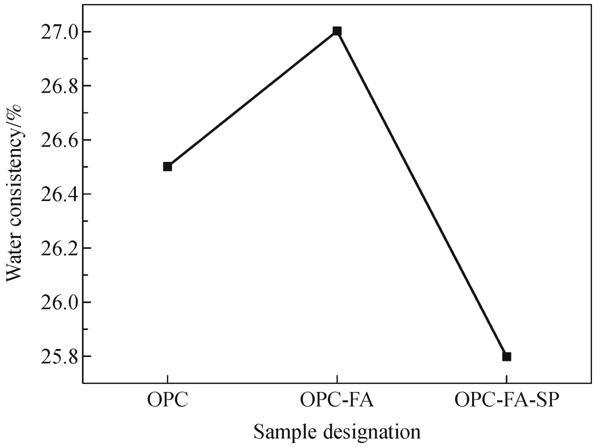

Figure 2 Variation of water consistency of blended and unblended Portland cement

The variation of initial and final setting times is shown in Fig. 3. The setting times for OPC-FA are lower than that of OPC. It has already been reported [9] that in the presence of FA, heat evolution is higher than that of OPC alone. Due to the larger amount of heat evolved, the hydration is accelerated, and hence setting times are reduced. Since SP is a water reducer and during the early hours it behaves as retarder, and hence setting times of OPC-FA-SP are increased.

During hydration, water reacts with cement constituents forming hydrated compounds. Two types of water: evaporable and non-evaporable water are present in the hydrated cement. The evaporable water can be determined by heating at 105°C, or by freezing out or removing the solvent. The non-evaporable water contents (W_n) or chemically combined water has a rough estimate of the degree of hydration and can be determined from the weight loss at 1000°C. The variation of W_n with hydration time is given in Fig. 4. The value

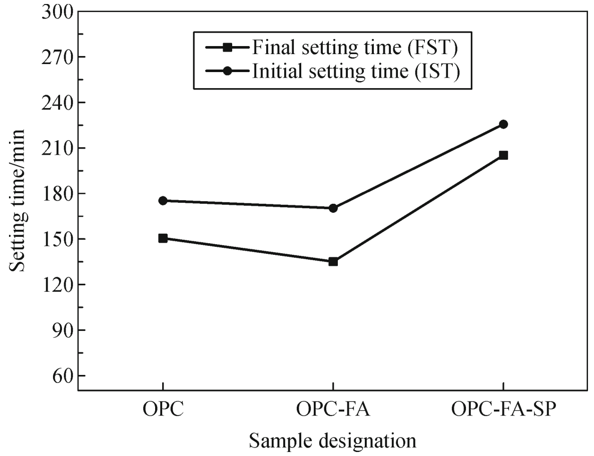

Figure 3 Variation of setting times of blended and unblended Portland cement

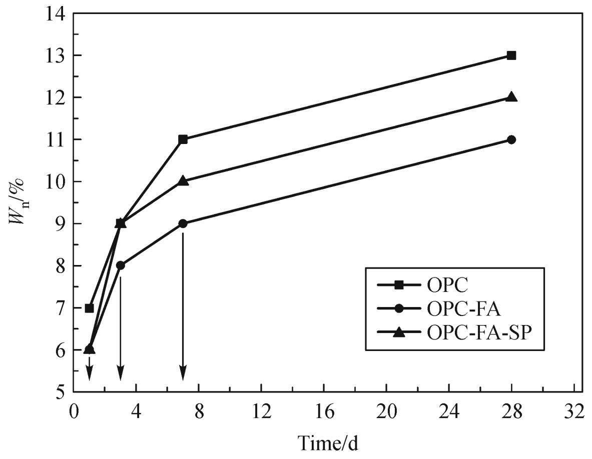

Figure 4 Variation of non-evaporable water content of blended and unblended Portland cement with hydration time

continuously increases with time, similar to that has been reported in presence of PVA and rice husk [10]. In the case of OPC-FA, the values are lower up to 3, 7 and 28 days. W_n values are higher for OPC-FA-SP as compared to that of OPC-FA.

The different mineral phases within the cement hydrate at different rates forming various reaction products. Some products deposit on the unreacted cement particle surfaces (surface products), while others form as crystals in the water-filled pore space between cement particles (pore products). For simplicity, cement paste can be thought of as consisting of four phases:

(i) unreacted cement,

(ii) surface products (like C-S-H),

(iii) pore products (like calcium hydroxide), and

(iv) capillary pore space.

FA reduces CH and increases C-S-H. The surface products grow outward from the unreacted cement particles and contain connected (percolated) gel pores, while the pore products are generally polycrystalline and fully dense, with no connected pores. The capillary pores are the water-filled space between solid phases and generally range from about 0.01 to 0.1 μm in size, in a reasonably well-hydrated cement paste, although during early hydration, they can range up to a few micrometers in size. These pores are responsible for water percolation in the concretes. The percentage of water percolation for mortars in the presence of SP is shown in Fig. 5. The presence of FA and SP during hydration reduces the pore size, giving a dense structure. This is because of the formation of additional amount of C-S-H. Due to the decrease in the pore size and the pore size distribution the water percolation decreases too. From Fig. 5, it is apparent that in the presence of FA and SP, the structure of hydration products is denser as a result the decrease of the water percolation.

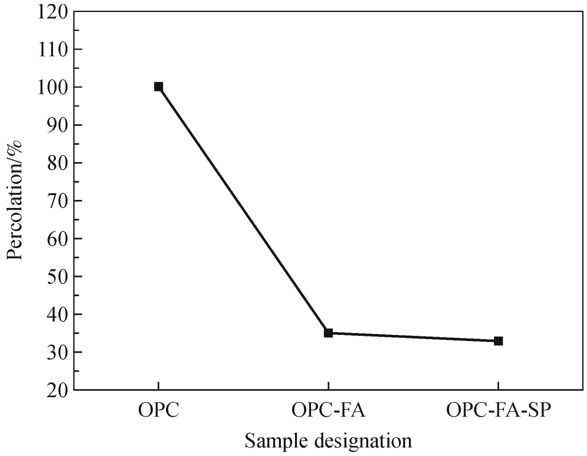

Figure 5 Water percolation of blended and unblended Portland cement

The air contents of blended and unblended Portland cements are shown in Fig. 6. The results show that in the presence of 0.1 wt% SP, the air content is the minimum. This again confirms that the structure in the presence of SP gets dense and the pore sizes are decreased.

The variation of compressive strengths with hydration time is given in Fig. 7. The results show that the values of compressive strengths are higher in the presence of 0.1 wt% SP. The strength is higher than that of the control, i.e., OPC and it increases with the hydration time [4,5]. This again shows that the pore sizes are decreased and the structure is more compact. The percentage expansion for OPC-FA-SP in the presence of N/60 H_2SO_4 is decreased considerably due to the decreased pore size and pore size distribution (Fig. 8).

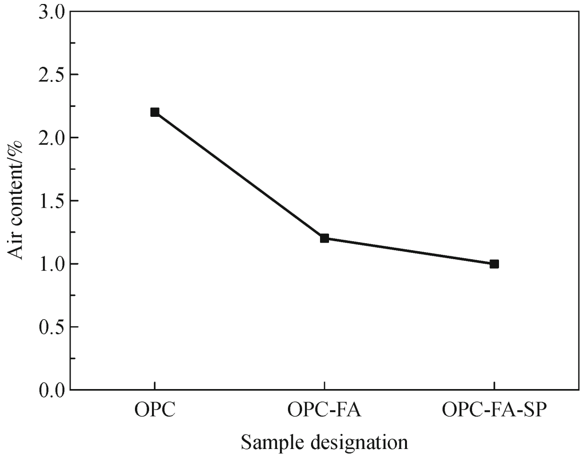

Figure 6 Air content of blended and unblended Portland cement

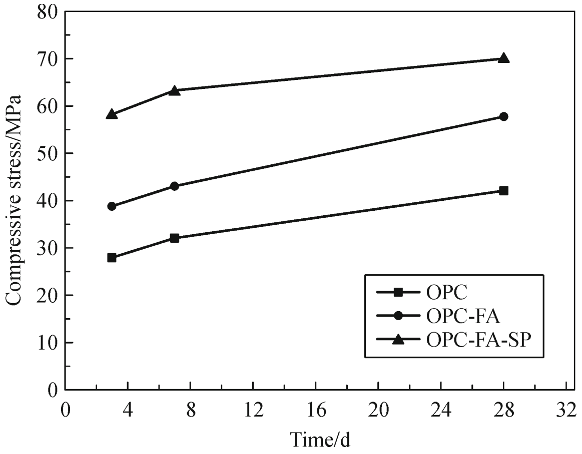

Figure 7 Variation in compressive strength of blended and unblended Portland cement with hydration time

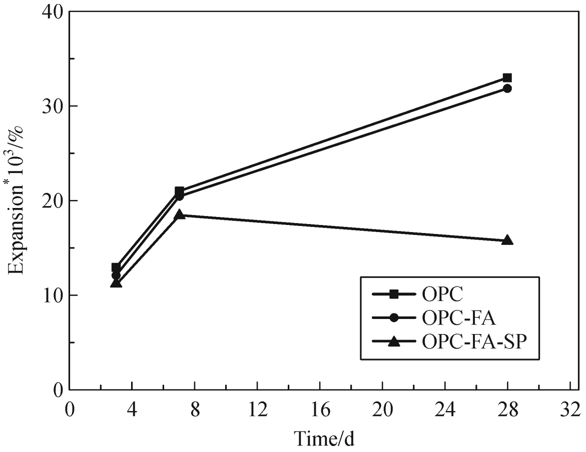

Figure 8 Variation in percentage expansion of blended and unblended Portland cement with time in N/60 H_2SO_4

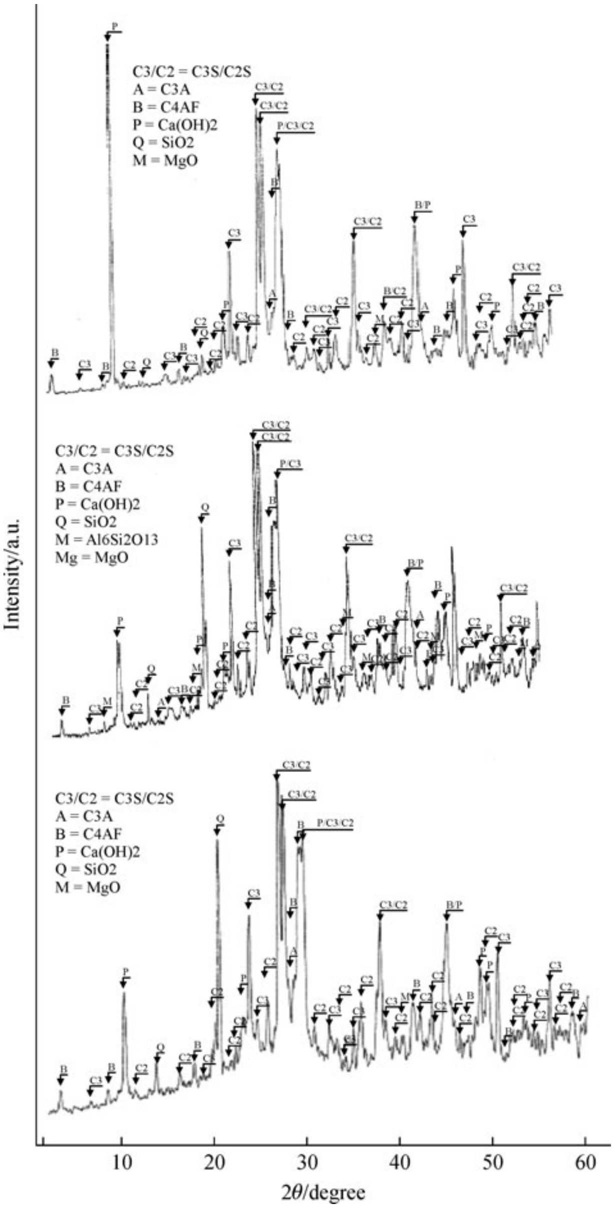

Figure 9 X-ray diffraction of (a) OPC (b) OPC-FA (c) OPC-FA-SP after 28 days of hydration

X-ray diffraction patterns (Fig. 9) clearly shows that CH is decreased in the presence of FA and SP. Owing to this more C-S-H is formed. This makes the structure more compact and the compressive strength is increased. Due to the reduction in the pore size the corrosive action of H_2SO_4 get lower too. The overall results show that the addition of fly ash increases the formation of C-S-H in the paste, and SP is adsorbed at the surface of cement grains, which make the structure of hydrated matrix more compact.

4 Conclusions

From the results it is concluded that OPC-FA-SP gives a very compact and dense structure which in turn reduces the pore size and pore size distribution. As a result, water percolation and air content are decreased. The system/formulation discussed in this paper can be used in damped area without using water proofing admixtures.

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