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Influence of Cellulose Superplasticiser on the Strength Property of Cementitious Materials

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Abstract

Functions of newly synthesized cellulose based superplasticiser(SP) on cementitious materials during development of strength have been studied and the results are compared with polycarboxylic ester (PCE) SP added mortar. Marsh cone test is conducted for finalizing the required amount of SP for the mortar mix. Preliminary characterization studies such as X-ray fluorescence (XRF), X-ray Diffraction (XRD) and Scanning Electron Microscopy (SEM) have been conducted on precursor materials such as Cement, Fly ash (FA), Silicafume (SF) for evaluating the elemental or oxide composition, presence of phases and surface morphology respectively. Quantification of cement and SF have been carried out through the Reitvield quantification software or Total Pattern analysis Software (TOPAS). Compressive strength studies on mortar samples have been conducted for cellulose and PCE SPs added mortar mixes and the results are compared with each other. It is found that, the mix having cement + FA (25%) + SF (10%) + cellulose SP (1.5%), shows compressive strength higher after 28th days to 60 days, when compared to the mortar mix having cement + FA (25%) + SF (10%) + PCE (2.5%). Hence, it is concluded that, activation of mineral admixtures such as SF and FA has occurred in the presence of cellulose SP, which resulted in strength gain. It is observed that there is no strength reduction by using the cellulose SP and thus it gained the confidence and added advantage to use as SP towards the promotion of mineral admixtures usage for high strength or high performance concrete.

Keywords: Cellulose, Superplasticiser, XRD, SEM, Marsh cone, compressive strength.

Introduction

In recent years, the incorporation of pozzolanic materials such as Fly ash , Lime sludge, Silica fume, Bottom ash and slag into cement or concrete have been increased[1-3]. Hence, incorporation or replacement of these materials provides or impart many proven advantages such as reduction in the heat, low permeability and resistance to sulphate attack[4,5] over existing alternatives. Among them, some materials are used as aggregates for the production of concrete[6]. Cement production is an environmentally relevant process accounting for 10% of all anthropogenic carbon dioxide emissions[7-8]. Using secondary mineral admixtures namely fly ash as a replacement for cement in mortar formulations can help to minimize global CO_2 emission[1]. Organic admixtures played a prominent role in promoting the usage of cementitious materials in construction applications, and they are considered as a more substantial than cement in such developments[9]. Super plasticisers, are one of them, from the organic admixture family, which is used while concreting to enhance the flow properties and make them as (i) more workable and easier to place; (ii) have better mechanical behaviour due to the lower water/cement ratios required; and (iii) cheaper because the cement content can be optimised[10-11]. Mainly, there are three super plasticisers, two from naphthalene and malamine formaldehyde family and one from PCE family, which are widely used. The major problem occurred in using these SPs are environmental issues for former case and scarcity of availability, because this is manufactured from petroleum by-products for later case and also expensive. Even then, PCE SP is gaining more attention, when compared to the other two SPs.

Cement paste reactions with SP: The composition of cement and their fineness will be the major phenomenon, which effects the fluidity of a cement paste during hydration of the cement. According to cement chemistry notations, the major phases or Bogue's compounds present in the cement such as tricalcium silicate (C3A), Dicalcium silicate (C2S), Tricalcium aluminate (C3A) and tetra calcium aluminate (C4AF) are called as alite, belite, aluminate and ferrite, since all the phases are impure in nature. All these phases have their own reactivity with other entities and properties, which will change with respect to their functional group arrangements. It is not possible or very difficult or we can say very rare, to find the same composition for different batches of cement produced in the factory level itself. All these properties will affect the setting time or hydration of the cement and strength as well. In one way the other, these phases have major responsibility in long term strength production and durability also. Based on their chemical entity, each groups have their own surface charge characteristics. The surface potential (Zeta) between the each phases will have crucial role, when it contacts with superplasticisers. Besides that, presence of minor compounds such as lime, sulphate containing phases (gypsum, hemi

hydrate) etc are also participate in reaction vigorously in presence of super plasticisers. The immediate response or signal from aluminates bearing group (C3A) will occur first, as soon as the SP is mixed with cement or cementations material, which results in workability loss.

Effect of SP dosage in general: Dosage finalization is an important and major phenomena, while using SP as water reducer. In research filed, to find out the necessary requirement of SP for a specified mix can be done through by conducting Marsh Cone test. Even for field application also, trials should be made or conducted, according to the desired mix, to reduce the risk, which is caused by improper usage of SP. Though some SPs produce some goodness at early stage even at higher dosage, the problems due to it on durability aspect namely leaching to the environment, is not clearly reported in the literature. A proper optimization of dosage is required to get the property of SP, as it is indented too.

The basic objective of the present research is mainly focus on the evaluation of the role of bio-polymer based namely Cellulose SP, on the effect of strength improvement in cementitious mortar. Systematic comparative study have also been made on the mortar mixes having the PCE SP.

Material and Methods

The materials used for this study and their physical properties are given below.

Cement: The physical properties of ordinary portland cement (OPC) tested as per IS: 4031 are given below: Grade-53 (OPC), specific gravity- 3.15, particle size range-31µm to 75µm, normal consistency- 28%, initial setting time-110 minutes, final setting time-260 minutes.

Silica Fume (SF): The physical properties of silica fume are given below, specific gravity-2.2, particle size range-0.2µm to 25µm, percentage of passing-92%(45µm sieve in wet sieve analysis)

Fly ash (FA): The physical properties of fly ash are given below: specific gravity-2.1, particle size range-0.1µm to 20µm, percentage of passing-96% (45µm sieve in wet sieve analysis).

Superplasticizers: Two types of SPs namely PCE and cellulose based SPs are used. The properties of PCE based SP is given below: Appearance - light yellow coloured liquid, pH- 6.5, volumetric mass at 20°C -1.06kg/litre, The properties of cellulose based SP is given below, appearance - Pale yellow or colorless liquid, pH- 6.8

Marsh Cone Test: Since, SPs are used in our present study, it is necessary to know the optimum dosage of it. Thus the Marsh cone test is carried out to know the optimum dosage of SP. The dosage is obtained from the saturation point in the marsh cone test. The Marsh cone is a funnel with a long neck and an opening of 15 mm. The test is conducted by using the following procedure. A marsh cone is attached to a stand so that the small orifice is pointing down and glass graduated cylinder is placed under the cone. Closing the small orifice with a finger, cement paste is poured into the cone. The orifice is opened and stop watch is started. The time for 1 litre of cement paste to flow is recorded

Determination of Compressive Strength: From the prepared mixes, cube specimens of sizes 50 mm X 50 mm are tested for compressive strength using compressive testing machine with constant rate of loading, at the ages of 3, 7, 14, 28, 45 and 60 days under normal curing. Three specimens for each mixture are tested and the average compressive strength is used for analysis and interpretation.

XRF Studies of Cement: The oxides present in the cement samples will be detected qualitatively as well as quantitatively from XRF results. The XRF used in this study is Brucker's S8 TIGER model. The sample preparation method for XRF studies is discussed below.

Sample Preparation for XRF: This method requires the sample surface to be kept flat and pure, meaning no contaminants. To prepare the sample, 6.0 grams of lithium borate-lithium bromide and 1gram of cement are mixed in a crucible. The crucible is then placed into a fusion instrument, which is operated according to the manufacturer's recommendations. The fused sample should appear disk shaped and be clear in color. The prepared sample wafer is placed into the XRF individually and a scan is performed. The resultant spectrum is analyzed further to detect the oxides composition.

Table-1
XRF analysis of Fly ash

Formula	Al	Ca	Fe	K	Mg	Na	O	Si	Ti
Elemental concentration (%)	15.74	0.76	3.07	1.13	0.27	0.09	49.20	28.08	1.16

SEM Studies on Cement: The surface morphology and microstructure of the cement is studied by using SEM. The SEM used in this research is a JEOL JSM 840. All images are scanned at 15 kV acceleration voltage. A location of particles is chosen such that it accurately represented the powder as a whole. The presence of C3S, C2S, C3A, and C4AF are discussed based on this study. Further, the surface morphology of FA and SF are also studied. The sample preparation method for SEM studies is discussed below.

Sample preparation: Required amount of sample is subjected to gold sputtering to adopt the conductive properties. After this process, samples are placed inside the sample chamber, inside the instrument.

XRD Analysis: Qualitative information on the phases present in the cement, SF, FA are analysed by using XRD. After necessary sample preparation, the samples are subjected to XRD analysis in the range of 10 to 70 (2θ). Brucker's D2-Phaser, a desktop XRD is used for analysis of sample. Copper K_α radiation is used and the power of x-ray generation is 30Kv, 10mV.

Preparation of powder specimen: The cement sample is finely ground by using mortar and pestle and then passed through 25 micron sieve, in order to avoid preferred orientation. Sample preparation is a main key step for quantitative analysis for influencing the sharp signal of related XRD of indented sample. The cement sample is prepared in such a manner to ensure that the specimen is a representative of the material and is homogeneous. This is then placed in the sampling tray, where the surface is smoothed to eliminate surface irregularities. Ball mill as shown in figure 1 (make: Retch, Germany) is used to ground the sample. Before placing the sample into ball mill, it is finely powdered by using mortar and pestle (figure 2). Loading of sample into the machine is shown in figure 3.

Figure-1
Ball Mill

Figure-2
Mortar and Pestle

Figure-3
Sample loading

After collecting the XRD data, the obtained spectrum is matched with ICDD (International Centre for Diffraction Data - PD4+) based on their PDF card number, because this is a unique finger print for particular material. Further, Rietveld refinements are carried out by using pattern analysis software namely TOPAS (Total Pattern Analysis Software) for quantitative phase identification. The Rietveld method of quantitative analysis minimizes or eliminates many of these problems, and therefore provides numerous advantages over the conventional quantitative analysis method. By using this method, the quantitative data of four main phases present in the cement such as C3S, C2S, C3A, and C4AF can be obtained. It is of interest to know the quantitative X-ray analysis of phases present in the raw materials.

Results and Discussion

XRF: The constituents present in the cement used for the present investigation is analyzed by using XRF techniques. The XRF spectrum of cement and FA are shown in figsures 4 and 5. From this study, the major oxides present in the cement such as CaO - 63.42%, SiO_2 -20.24%, Al_2O_3-5.637% and Fe_2O_3-4.074% are identified. Elemental composition of FA is shown in table 1.

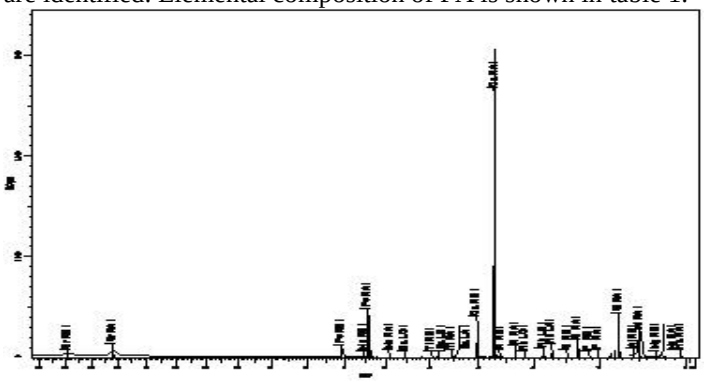

Figure-4
XRF spectrum of Cement

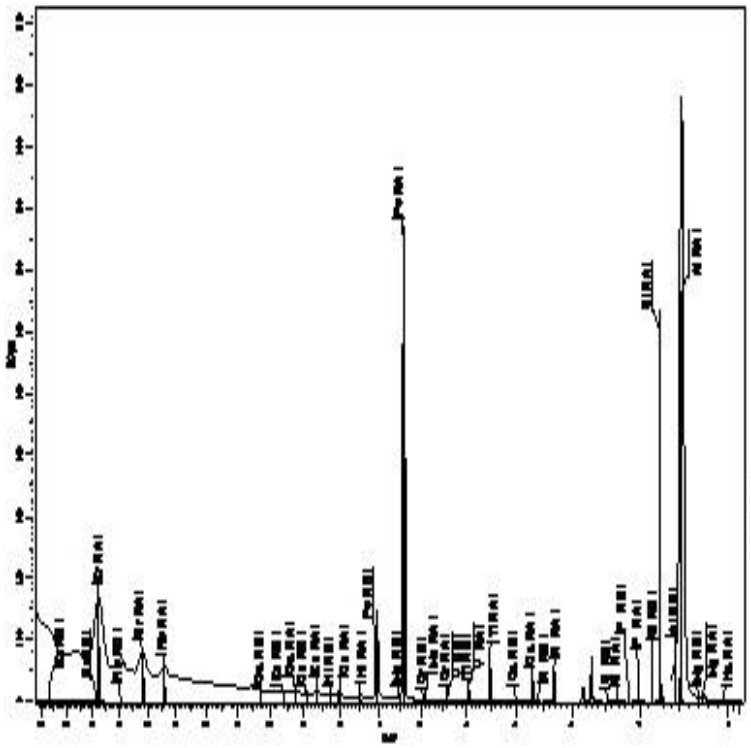

Figure-5
XRF spectrum of FA

XRD: The phase identification and crystalline nature of the raw materials such as cement, SF and FA are analyzed through XRD and the details are given below. As mentioned earlier, sample preparation is a main key step for quantitative analysis for influencing the sharp signal of related X-ray diffraction of indented sample. The diffraction patterns of Cement, SF and FA are collected as shown in figures 6 to 8. Each peak in the diffraction pattern of cement, reflects to their individual phases such as C3S, C2S, C3A and C4AF. The amorphous nature of SF is understood from the figure 7 and small hump of peaks indicate the presence of small amount of quartz and cristobalite in the bulk form in crystalline region. The XRD pattern of FA represents the some mullite, calcium, silica and iron bearing compounds in a complex manner.

From figures 6 to 8, the quantitative amount of individual phase is estimated. The quantified phase in the cement are C3S - 47.90%, C2S- 21.50%, C3A-3.13%, C4AF-14.37%, Calcite-8.04%, gypsum-1.69%, lime 0.12%, magnesite-3.01%, periclase-0.43%, quartz-1.19%, rutile-0.15% and for silica fume, even though it shows amorphous peaks, the background correction is carried out and quantified. The values are quartz – 34.29% and cristobalite- 65.71% for the presence of crystalline region alone. However, it may not be an accurate due to the signal to noise ratio. For FA, quantification is very difficult, since it consumes lot of time for extracting the individual phases. Hence FA quantification is not included in this paper. The presence of complex amorphous nature due to the carbon content in FA can be clearly observed from the XRD peaks.

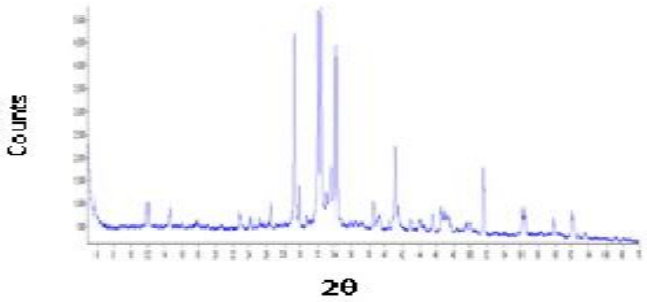

Figure-6
XRD data of cement

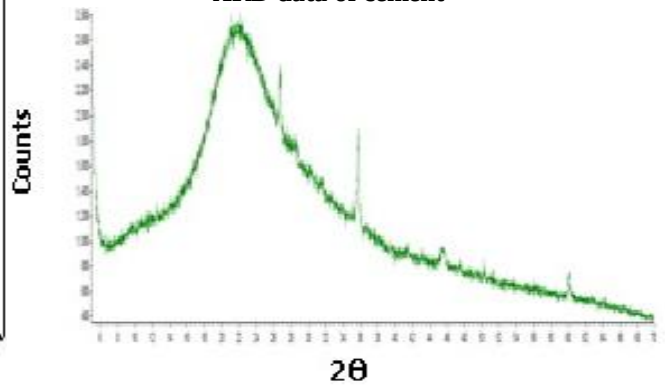

Figure-7
XRD data of Silica fume

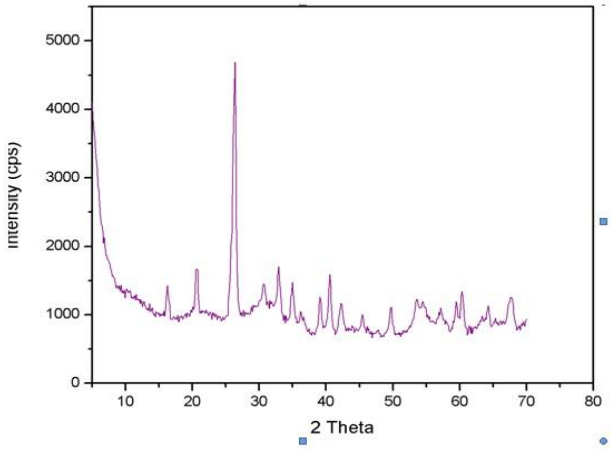

Figure-8
XRD data of Fly ash

SEM: The study towards finding out the surface morphology and microstructure of raw cement, an inorganic binder, which is going to be used in the further study, is carried out by using Scanning Electron Microscope. This surface level information will be required for further study to understand the mechanism of interaction of inorganic moieties with organic compounds and also to study their morphological effect. The SEM micrograph at magnification level of 220X is shown in Fig 9, which indicates the presence of unreacted lime, C3S, C2S and C3A. Also the micrograph of FA and SF is shown in figures 10 and 11. The spherical nature of SiO_2 present in the FA and SF are seen clearly in the corresponding figures.

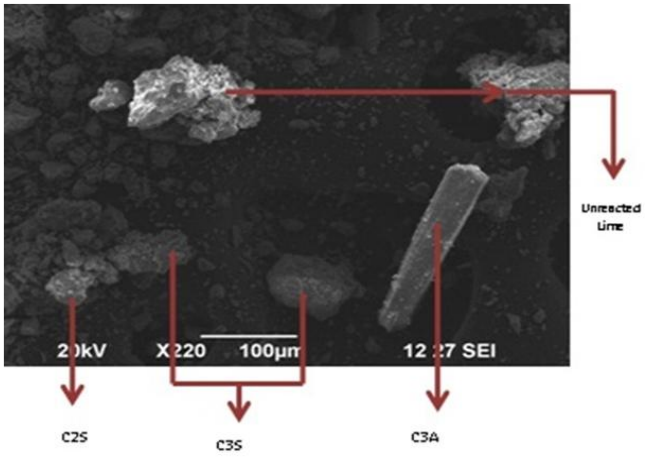

Figure-9
SEM image of Cement

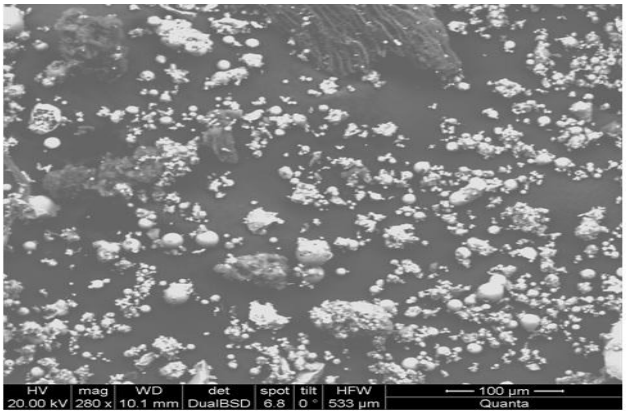

Figure-10
SEM image of Fly Ash

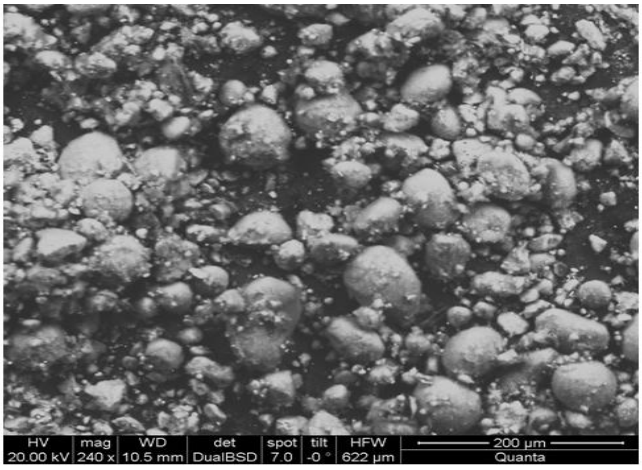

Figure-11
SEM image of Silica Fume

Strength Properties of Mortar, Evaluation of strength properties of mortar in presence of cellulose and PCE based SPs: In order to assess the strength property of mortar in the presence of cellulose based SP, work has been carried out towards finding out the setting properties of mortar in presence of cellulose SP and PCE SP. The w/c ratio was kept as 0.3. Marsh cone test as shown in figure 12 is performed to find out the optimum dosage required with respect to the w/c ratio. Casting of mortar cubes with and without mineral admixtures in presence of cellulose as well as PCE SP is carried out. The comparative evaluation of mechanical properties are discussed below.

Figure-12
Marsh cone test

Experimental studies have been conducted to compare the compressive strength of the mortar cubes having different mixes, in presence of PCE SP and cellulose SP. The Id given for the as prepared mixes are listed below. Cement to sand ratio is maintained as 1:3. mix 1: cement + PCE (1%), mix 2: Cement + FA (25%) + SF (10%) + PCE (2.5%), mix 3: cement + cellulose SP (0.6%), mix 4: cement + FA (25%) + SF (10%) + cellulose SP (1.5%).

Table-2
Compressive strength of the mortar

Designation of the mix	Compressive strength (MPa)					
	3rd day	7th day	14th day	28th day	45th day	60th day
Mix 1	44.36	54.54	55.48	56.48	60.67	63.57
Mix 2	32.13	44.10	49.85	53.78	58.14	65.50
Mix 3	45.10	53.24	55.36	57.32	61.55	64.76
Mix 4	41.12	49.75	56.35	61.50	67.58	72.53

The compressive strength values of the different mixes with respect to 3^{rd}, 7^{th}, 14^{th}, 28^{th}, 45^{th} and 60^{th} days are presented in table 2. It can be observed from table 2 that, in presence of cellulose SP, the compressive strength of Mix 4 (mineral admixtures added) has increased in all the respective days, when compared to Mix 2. It shows that, the early activation of mineral admixtures in presence of cellulose SP advances the pore refinement due to the promotion of hydration products and also it can be justified in a way that, in presence of PCE SP, due to the disturbance of pore solution pH, the strength gain could

have happened on long term basis. Further, it is also important to note that the cellulose SPs are promoting the activation of mineral admixtures and thereby increasing the compressive strength.

Many authors examined the influence of FA on the mechanical strength of mortar and concrete via the characteristic properties, form, and size of their particles and pozzolanic activity, which is one of the most common pozzolan material[12-16]. Moreover, the binding properties of fly ash can be enhanced by mechanical or chemical activation[17-18]. In the present study also, mixes having FA and SF, in presence of cellulose SP, showed higher strength due to their sphereical nature of species as well as fine particle nature, which also highlights the activation of the phases in presence of Cellulose Sp. This reported study is also in line with the studies conducted by various authors[12-16].

Conclusion

Characterisation of raw materials used in this study are carried out using various techniques. Marsh cone test has conducted for the mixes having different mineral admixtures in presence of PCE SP and Cellulose SP, for dosage optimisation. The results presented in this paper indicate that the cellulose SP used in this study induced microstructural changes or modifications in the mortar containing mineral admixtures. Whereas, the reduction in porosity and pore refinement have occurred when hydration progress. However, the presence of cellulose SP does not affect the mechanical strength of the mortar, instead, it increased the compressive strength subsequently on 28th, 45th and 60th days. Hence, it is concluded that the use of cellulose SP does not affect the strength and durability of the mixes having mineral admixtures. In general, the use of mineral admixtures in cement-based mortars provides significant environmental benefits, in addition to the help of effective superplasticiser.

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