

EFFECT OF VINSUPERPLAST ON THE HYDRATION STUDY OF RICE HUSK ASH BLENDED CEMENT

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Abstract

For civil engineering the basic need is to produce high quality and high strength concrete. superplasticizers are used as high range water reducer and they improve the workability of concrete and mortar. In the present work several experimental programmes have been carried out in order to study the effect of Vinsuperplast on RHA blended cement. 2% Vinsuperplast with RHA blended cement and ordinary Portland cement increases the hydration and strength of cement which was measured by consistency measurement, setting time, non-evaporable water content, and free lime determination. 20% RHA blended cement gives better results in comparison to 10% RHA blended cement. The hydration mechanism of RHA blended cement with Vinsuperplast were tried to understand by using XRD, DSC and SEM techniques.

Keywords: OPC (Ordinary Portland cement); Vinsuperplast (superplasticizer); RHA (Rice husk ash) Blended cement; XRD; SEM; DSC.

1. INTRODUCTION

In order to save resource and energy, it is now a common practice to use blended cement, made from Portland cement and agricultural / Industrial wastes [1-5]. The aim of blending is to utilize the agricultural and industrial wastes to produce high quality and high strength cement, which reduces the environmental pollution. [6-8]

Rice husk is the outer cover of paddy and accounts for 20-25 % of its weight. It is removed during rice milling and is used mainly as fuel for heating in Indian homes and industries. Its calorific value is 13-15 MJ/kg and is lower than most woody biomass fuels. However, it is extensively used in rural India because of its widespread availability and relatively low cost. The annual generation of rice husk in India is 18-22 million tons and this corresponds to a power generation potential of 1200 MW. Few rice husk-based power plants with capacities of 10 MW are already in operation and based either on direct combustion or through fluidized bed combustion. [9-10]

Research on producing rice husk ash as a blend for cement is not new [11-12]. Pitt developed a fluidized bed furnace for the controlled combustion of rice husk at a fixed temperature and heating time give highly pozzolanic rice husk ash [13].

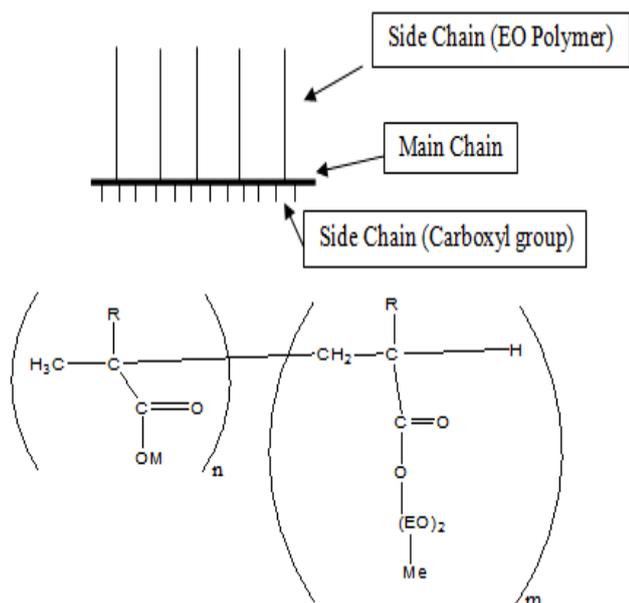
Rice husk is characterized by low bulk density and high ash content (18-22% by weight). The large amount of ash generated during combustion has to be continuously removed for a smooth operation of the system. Silicon oxide is the main component (90-97%) of the ash with trace amounts of CaO, MgO, K₂O and Na₂O [14-15].

The use of RHA in concrete has been associated with the following essential assets. Increased compressive and flexural strengths [Zhang et al, 1996; Ismalia 1996; Rodriguez 2005], reduced permeability [Zhang et al; 1996; Ganesan et al; 2007], reduced effects of alkali silica reactivity [Nicole et al 2000], enhanced workability of concrete [Counthio 2002; Habeeb et al 2009; Mahmud et al 2004], reduced amount of superplasticizer [Sata et al 2007]. Various studies have been published that deal with the effect of superplasticizer on the physiochemical properties of Ordinary Portland Cement [16-20]

Superplasticizers are linear polymers containing sulphonic acid groups attached to the polymer backbone at regular intervals. Superplasticizers are broadly classified into four groups, sulfonated melamine-formaldehyde condensates (SMF), sulfonated naphthalene-formaldehyde condensates (SNF), modified lignosulfonates (MLS), and polycarboxylate derivatives. Many group of scientists investigated hydration of ordinary Portland cement and mechanism of interaction with superplasticizer. [21-24]

The molecular structure of polycarboxylate (PC) superplasticiser admixtures is shown in Fig.1 [25-27] their 'comb-type' molecule consists of one main linear chain with lateral carboxylate and ether groups. According to the literature the carboxylate groups are instrumental in the adsorption of these admixtures to cement particles. Dispersion is due to electrostatic repulsion (as in melamine and naphthalene admixtures) owing to the carboxylate groups, but primarily to the steric repulsion associated with the long lateral ether chains. The high degree and duration of the fluidity that this admixture affords concrete are related to structural factors. The long lasting fluidity is

induced when the main chain is shorter with longer and numerous lateral chains^[28]. The use of PC admixtures makes it possible to reduce the water content by up to 40% producing workable high performance and increases the resistant of concrete.^[29-30]



M = Metal, Me = Methyl, EO = Oxyethylene

Fig 1. Chemical structure of Polycarboxylate admixture

Table 1 Oxide Composition of Ordinary Portland Cement 43 grade

Oxide	CaO	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MgO	SO ₃	LOI (loss on ignition)
Composition(%)	63	22.7	5.8	3.26	3.80	3.10	5.0

2.2 Rice Husk Ash:

Rice husk ash was obtained from biomass gasification plant Family Bread Tarna Varanasi. It was further heated at 600°C

in muffle furnace for an hour and sieved by mesh size 250-300µm. Chemical compositions of rice husk ash are shown in table 2.

Table 2 Chemical Composition of RHA:

Oxide	SiO ₂	Fe ₂ O ₃	CaO	MgO	Na ₂ O	K ₂ O	LOI (loss on ignition)
Composition(%)	85.4	0.2	0.2	0.9	0.8	1.0	11.5

2.3 Superplasticizer:

VIN-SUPERPLAST PC-99 is an advanced superplasticizer has been taken from Kryton Build tech.

water/cement ratio was 0.5. The concentrations of superplasticizer solution were 1% and 2% by wt. with respect to cement. The polythene bags were kept in an incubator maintained at 30°C. The hydrations were stopped at different interval of time by using isopropyl alcohol and ether. The hydrated samples were dried at 105°C for an hr. and then stored in sealed polythene bags in an incubator.

3. METHODS

3.1 Preparation of Hydrated Sample:

20 g of cement with 20% and 10% rice husk ash was weighed in polythene bags and 10cc of water or superplasticizer solutions were added to the cement so that

Hydration mechanism of cement is very complicated and becomes more complicated in presence of different blends with admixture^[31-35]. This study had been carried in order to understand the hydration mechanism of OPC and rice husk ash blended cement in the presence of superplasticizer. Since in structural concrete the acceptable level of replacement is from 15-30%^[36-40] and in present study cement is mixed with 10% and 20% R.H.A in presence of 1% and 2% Vinsuperplast.

2. EXPERIMENTAL MATERIALS

2.1 OPC:

Ordinary Portland cement 43 grade was used for the hydration studies. The oxide and mineralogical composition are given in table 1.

The fineness / blain surface area was 285m²kg⁻¹.

3.2 Consistency Measurement:

The consistency of the control and blended cement in the presence and absence of superplasticizer were determined by Vicat apparatus.

3.3 Determination of Setting Time:

Initial and final setting times of OPC and rice husk ash blended cement in presence and absence of superplasticizer were determined by Vicat apparatus.

3.4 Determination of Free Lime:

The percentage of free lime in the hydrated samples (water/solid = 0.5) was determined by the Franke extraction method. The percent free lime was calculated using the Franke equation:-

$$\% \text{ free lime} = 0.2804(V/W)$$

Where V is the volume of 0.1N HCl and W is the weight of sample.

3.5 Non-Evaporable Water Content W_n :

Approximately 1 g of the hydrated sample (w/s = 0.5) was heated in a platinum crucible at 105°C for 1 hour, and then heated at 1000°C for another one hour, then cooled and weighed. From the weight loss, the non-evaporable water content was calculated.

3.6 Soundness Test:

Le-Chatlier moulds were used to conduct the soundness experiment. The cylindrical moulds were filled with OPC and R.H.A blended cement in presence and absence of superplasticizer. The paste were prepared by gauging cement of different composition with 0.78 times water required to give a paste of standard consistency, the gauging time should be in between 3-5 minutes. After filling the mould it should be covered by a piece of glass sheet and small weight then submerged the whole assembly in water and kept it for 24 hr at the temperature of 27°C. After that cylinder were removed from water and measured the distance between the indicator points gives the value D_1 . Again put the whole assembly in boiling water for about 3 hr and after cooling measured the distance which is denoted as D_2 . The difference in expansion indicates whether the cement is sound or unsound.

3.7 Compressive Strength:

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

3.8 X-Ray Diffraction:

The X-ray Diffraction pattern of the hydrated sample (W/S = 0.5) were recorded by using Cu $K\alpha$ radiations.

3.9 Scanning Electron Microscope:

SEM pictures were taken by using model FEI- Quanta 200S, to study microstructural changes in the OPC and RHA blended cements in the presence and absence of superplasticizer during hydration.

3.10 Thermal Analysis:

Thermal analyses were carried out with a NETZSCH DSC 404F3A analyser. Samples were heated in crucible upto 1300°C in an inert atmosphere (N_2).

4. RESULT AND DISCUSSION

Hydration of cement is generally a more complex reaction. It is the chemical combination of cement and water to form hydration products. Hydration of cement can be understood by two mechanisms:

- (I) *Through Solution*: Which involves dissolution of anhydrous compounds to their ionic constituents formation of hydrates in solution and eventual precipitation due to their low solubility.
- (II) *Topochemical or solid- state hydration*: which involves that reaction takes place directly at the surface of anhydrous compound without going into the solution, formation of hydration products over time leads to stiffening (loss of workability) Setting (solidification) and Hardening (strength gain).

The required water for standard consistency as a function of RHA content and the percentage of superplasticizer mixed are shown in Fig. 2. The result shows that water demand for RHA blended cement is higher than OPC alone. As the percentage of ash replacement increases, the value of standard consistency also increases. The water demand for RHA blended cement increases due to the relatively higher surface area of RHA, but the value of standard consistency decreases when the different percentage of superplasticizer were introduced in RHA blended cement. Addition of polycarboxylate superplasticizer reduces the mixing of water; this may be due to the formation of thin film around cement grains. Polycarboxylate superplasticizer is an anionic surfactant when adsorbed on cement particles they become negatively charged causing repulsive effect with each other, consequently the fluidity of cement particle increases and hence the water demand decreases.

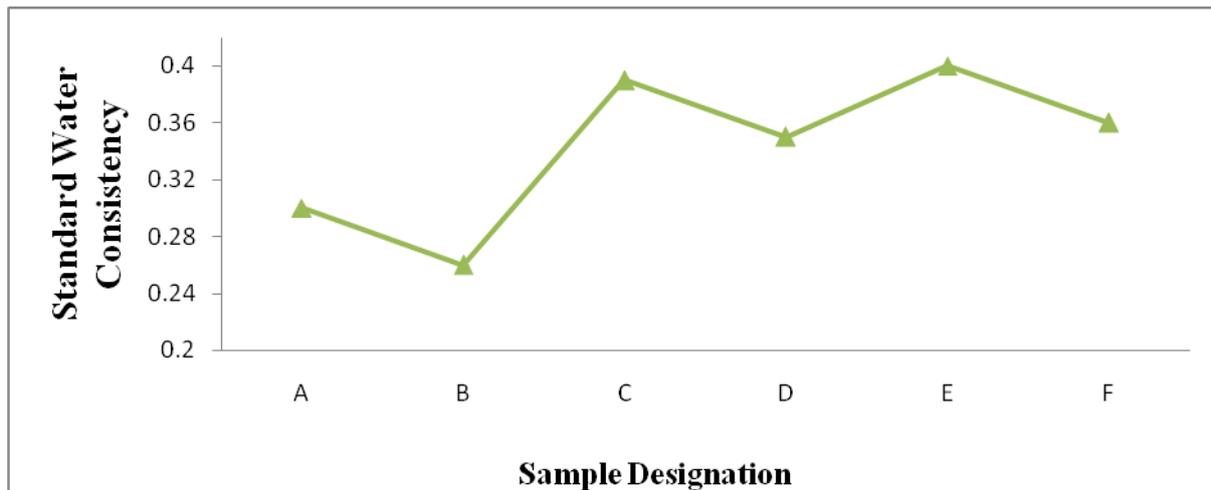


Fig. 2 Standard Water Consistency

A=OPC, B = OPC + 2% SP, C = OPC + 10% RHA, D = OPC + 10% RHA + 2% SP, E = OPC + 20% RHA, F = OPC + 20% RHA + 2% SP

The initial and final setting time of OPC and RHA blended cement in the presence and absence of superplasticizer is shown in Fig. 3. The RHA blended cement has longer setting time than those of OPC; this is due to increase in water demand. The ash and early hydrated product form a coating layer around the cement particles, which further delays the hydration and hence setting time elongated. As

the percentage of superplasticizer increases the setting time increases, this may be assigned due to the electrostatic repulsion among the negatively charged superplasticizer cement particle causing better dispersion and fluidity. In the presence of superplasticizer the retardation action takes place which strongly inhibits the growth of hydrates, this leads to the shifting of setting time to longer duration.

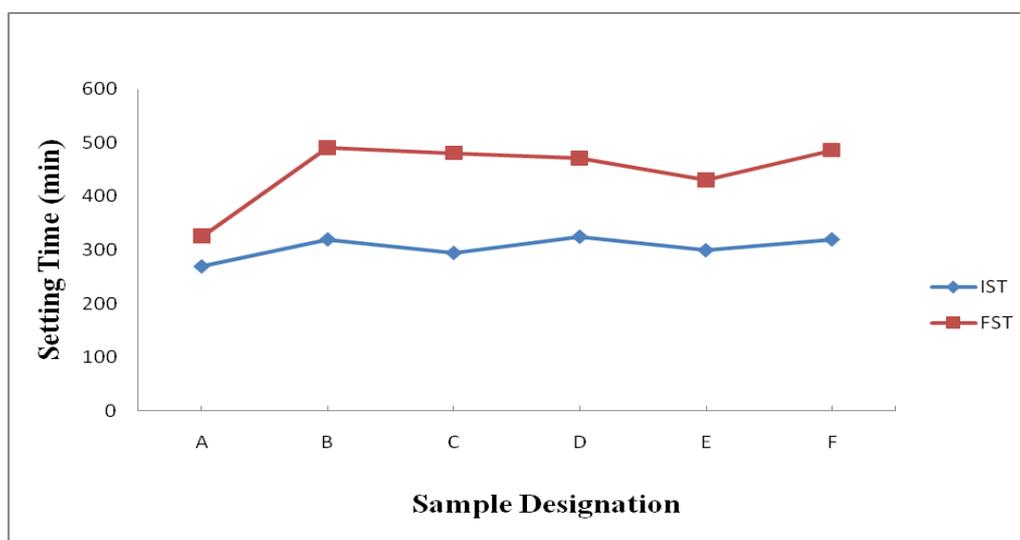


Fig. 3 Initial and Final Setting time (minutes)

A=OPC, B = OPC + 2% SP, C = OPC + 10% RHA, D = OPC + 10% RHA + 2% SP, E = OPC + 20% RHA, F = OPC + 20% RHA + 2% SP

The value of free lime content of hydrated OPC and RHA blended cement in the presence and absence of superplasticizer are plotted in Fig. 4. The result indicated that free lime value of OPC increases up to 15 days and after that there is decrease in the value till 28 days and after 28 days free lime value again increases upto 45 and 90 days. This is attributed due to the reason that in early stage mainly upto 15 days C_3S undergoes hydration. But in later period at 28 days due to lower hydration of β - C_2S free lime value

slightly decreases and after 28 days hydration of β - C_2S increases the free lime content. From Fig. 4 it is quite obvious that the value of free lime were lower in superplasticized RHA blended cement in comparison to OPC. This may be due to two factors: the first one is the decrease of clinker content due to RHA replacement, and the second is highly pozzolanic activity of RHA consuming the liberated lime.

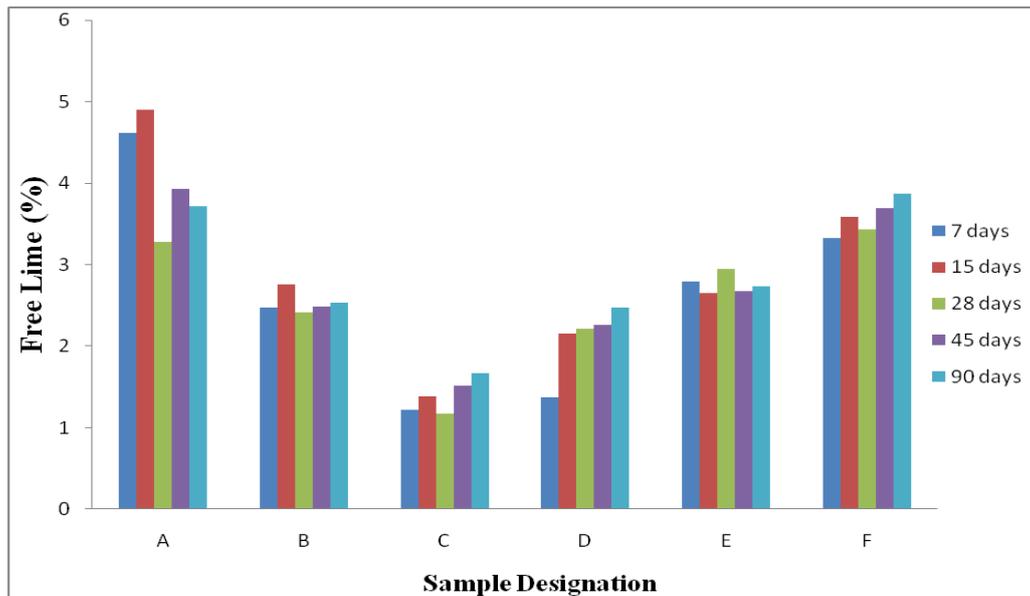


Fig. 4 Variation of free lime with hydration time

A=OPC, B = OPC + 2% SP, C = OPC + 10% RHA, D = OPC + 10% RHA + 2% SP, E = OPC + 20% RHA, F = OPC + 20% RHA + 2% SP

The degree of hydration is measured from the combined water content, the variation of degree of hydration are plotted in relation to the hydration time are represented in Fig. 5. The degree of hydration increases with hydration time. This is mainly assigned due to continuous hydration of cement. Wn (Nonevaporable water content) values for RHA

blended cement in the presence of 2% superplasticizer have comparable value with the OPC. This may be due to fact that as the amount of RHA and superplasticizer increased degree of hydration increases due to high reactivity to form additional C-S-H.

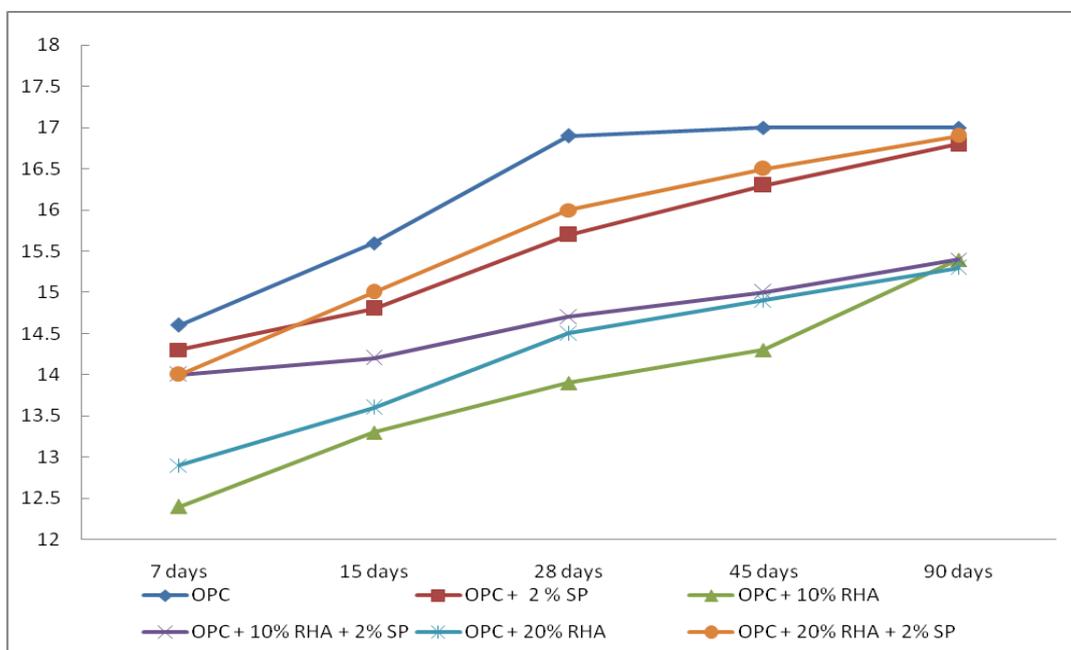


Fig. 5 Variation of Non-evaporable water content with hydration time

Soundness test indicate the rate of volume change and results were presents in Fig. 6. The expansion test result for OPC ranges in between 0.75 mm to 1.00 mm which is in accordance to IS standard. As we move from OPC to RHA blended expansion increases and is maximum for RHA with

superplasticizer, which shows the appreciable difference in chemical composition, but change in the volume of expansion in all cases shows that the presence of uncombined lime, magnesia and calcium sulphate are in limit, and hence cement is sound.

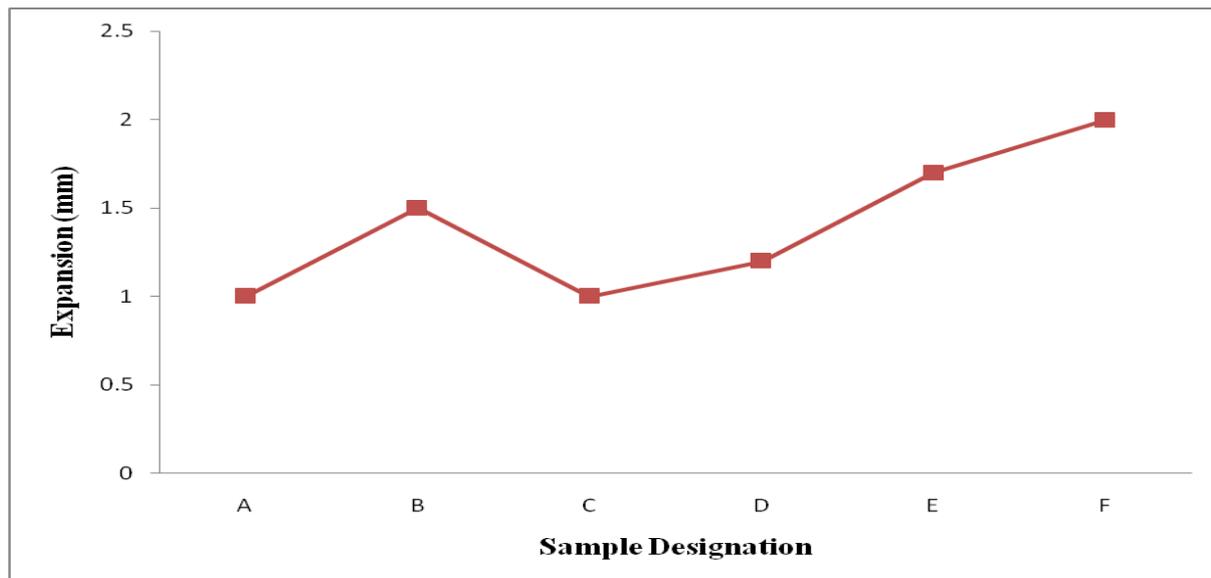


Fig. 6 Soundness test of different sample

A=OPC, B = OPC + 2% SP, C = OPC + 10% RHA, D = OPC + 10% RHA + 2% SP, E = OPC + 20% RHA, F = OPC + 20% RHA + 2% SP

The compressive strength of the cement mortars is the most important property. From result it is quite obvious that strength increases with curing time and this is due to formation of tobermorite gel, which is the main source of strength but at the same time strength of RHA blended cement decreases due to higher water demand Fig 7. The

strength development mainly depends on the formation of C-S-H, which is precipitated into water filled space to form a more compact structure. The compressive strength increases with superplasticizer dosage and this is due to decrease in mixing water as well as total pore volume.

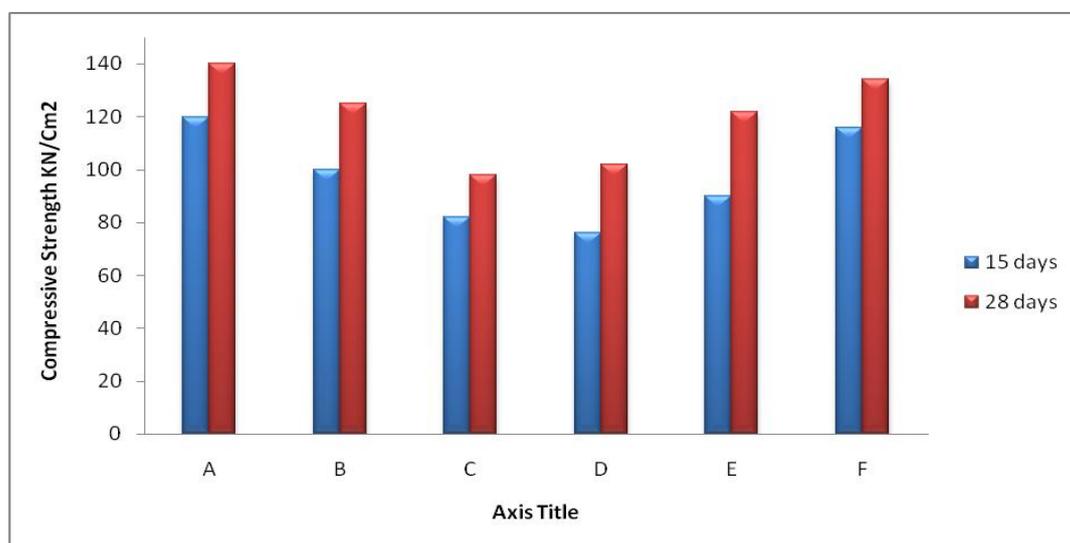


Fig.7 Variation of compressive strength at 15 & 28 days of hydration

A=OPC, B = OPC + 2% SP, C = OPC + 10% RHA, D = OPC + 10% RHA + 2% SP, E = OPC + 20% RHA, F = OPC + 20% RHA + 2% SP

An XRD analysis used to study the pozzolanic behaviour of RHA in the presence and absence of superplasticizer and to identify the hydration products formed during the hydration of OPC Fig 8. The XRD pattern of OPC, OPC + 2% SP, OPC + 20% RHA, OPC + 20% RHA + 2% SP at 28 days of hydration. From diffraction pattern it can be seen that peaks of ettringite, $\text{Ca}(\text{OH})_2$, C-S-H & $\text{C}_3\text{S}/\text{C}_2\text{S}$ appeared in all hydrated samples. The actual change takes place in the

peaks of CH [$\text{Ca}(\text{OH})_2$]. It diminishes as moving from OPC to RHA blended cement. This indicates, the pozzolanic reaction between $\text{Ca}(\text{OH})_2$ and amorphous silica present in RHA. The XRD pattern clearly shows the retarding effect of PC superplasticizer in presence of 20% RHA with respect to OPC because relative intensity peak of unhydrated $\text{C}_3\text{S}/\text{C}_2\text{S}$ increases.

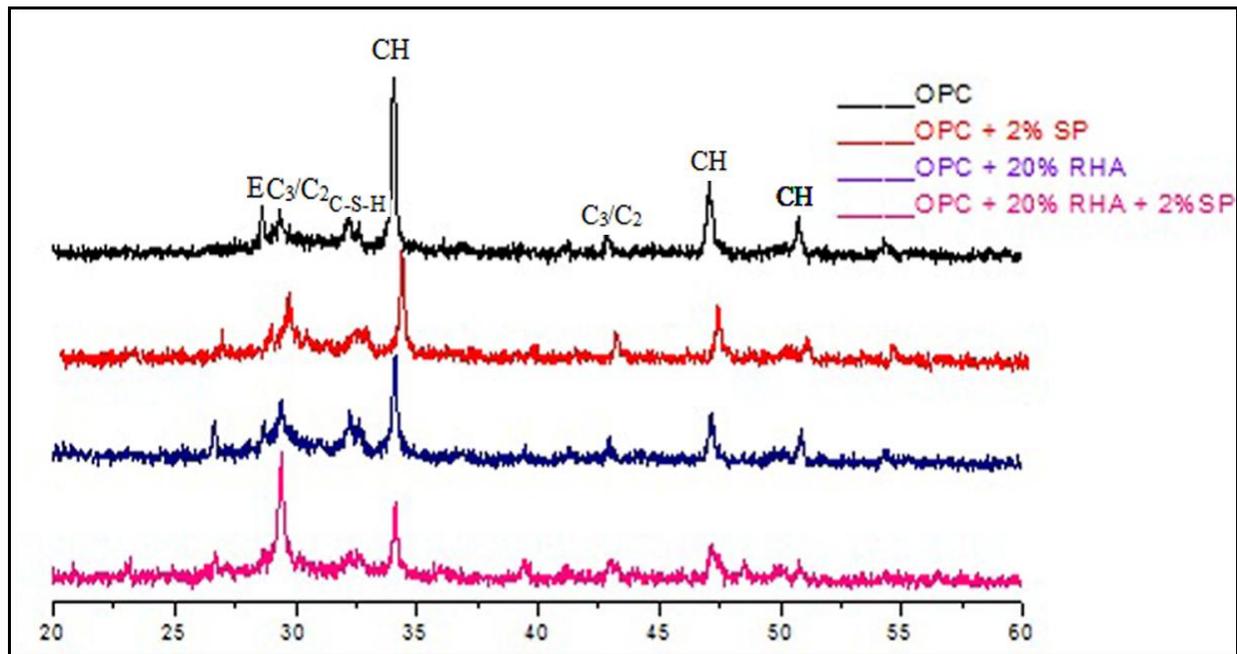


Fig. 8 XRD of 28 days hydrated Sample

E = Ettringite, C₃S = tricalcium silicate, C₂S = dicalcium silicate, C-S-H = Calcium silicate hydrate, CH = Calcium hydroxide

The DSC thermograms of 28 days hydrated OPC, RHA blended OPC and superplasticized RHA blended OPC Fig 9. The graph is attributed due to three peaks. The first endothermic peak near to 400°C, is due to the dehydration of the bound water from amorphous C-S-H and calcium sulphoaluminates, the peak assigned in between 450°C-500°C temperature range is due to decomposition of

Ca(OH)₂. Endothermic peak in between 650°C- 750°C is due to the decarbonation of CaCO₃. From the DSC graph it is quite clear that enthalpy of Ca(OH)₂ phase decreases as moving from the OPC to superplasticized RHA blended sample. This indicates that pozzolanic activity increases in RHA blended cement in the presence of Polycarboxylate superplasticizer.

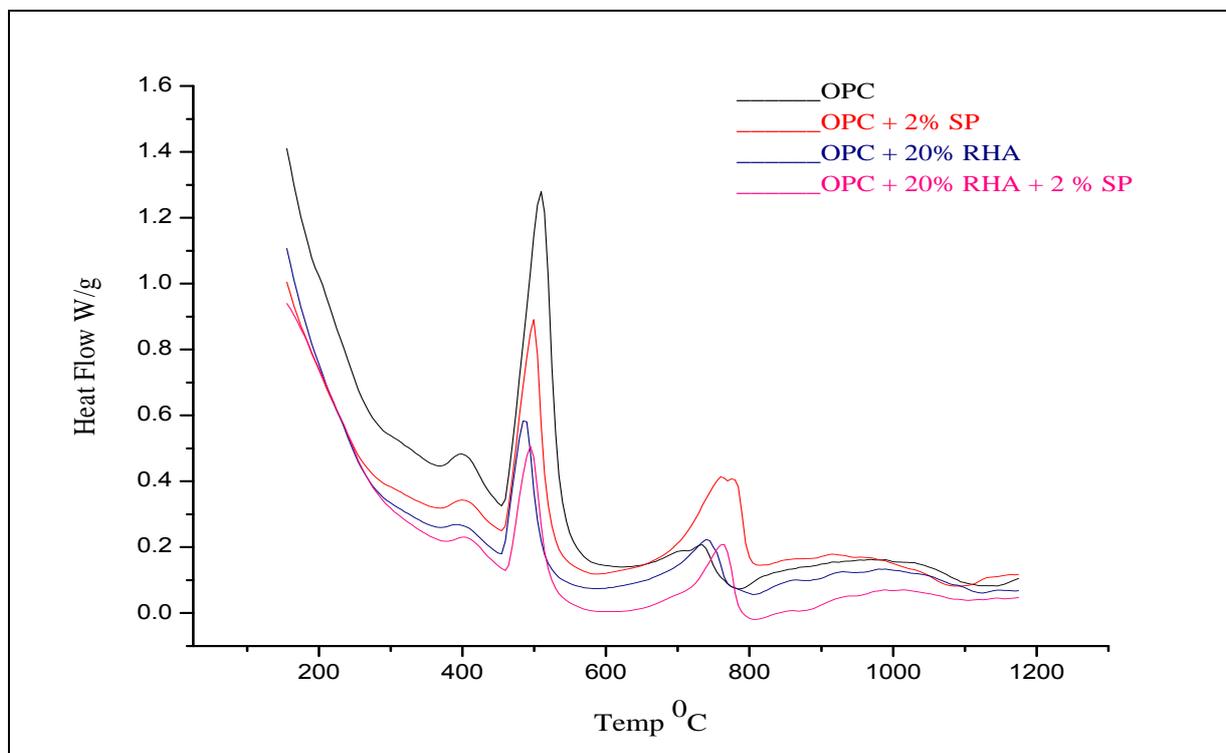
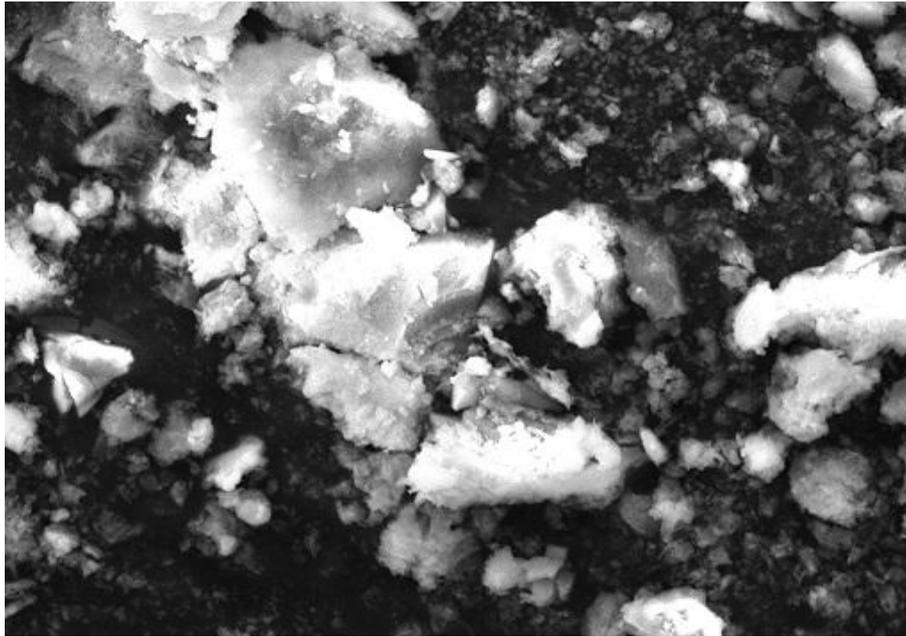


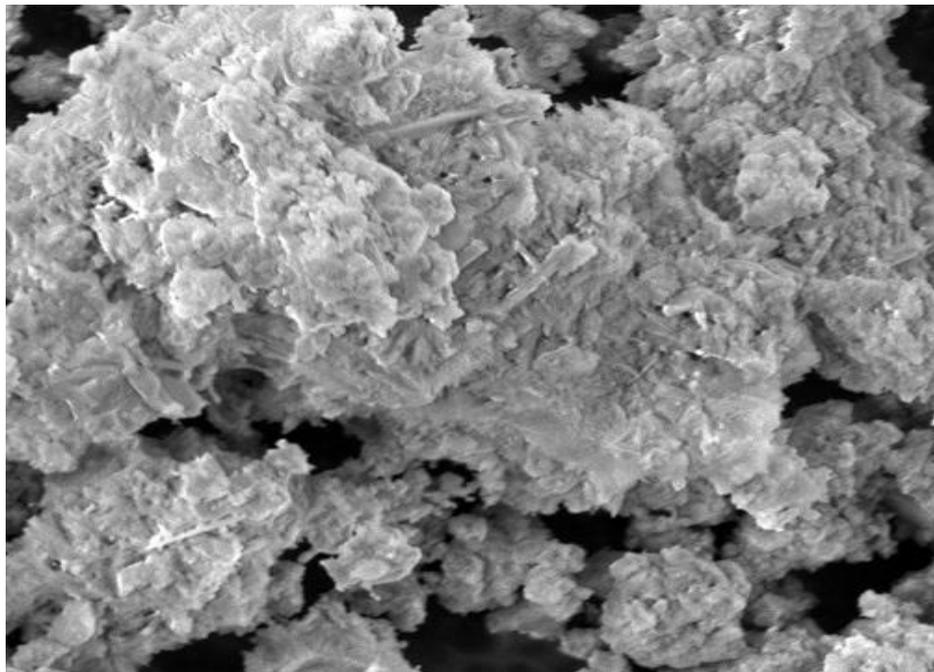
Fig. 9 DSC of 28 days hydrated Sample

The result of scanning electron microscopy [SEM] for OPC, OPC + 20% RHA & OPC + 20% RHA + 2% SP hydrated for 28 days were depicted in Fig. 10 (a) (b) (c) and (d) due to chemical reactions during hydration. Hydrated product like Calcium hydroxide [CH], tobermorite [C-S-H] and small grain structure appeared, due to chemical reactions. The hydrated grains are interconnected by outgrowth forming a continuous structure. The micrograph of 20% RHA had a flocculent and porous structure Fig. 10(c). In this paste wide pores are available for crystallization of the formed hydration than OPC, but it has lower strength due to higher

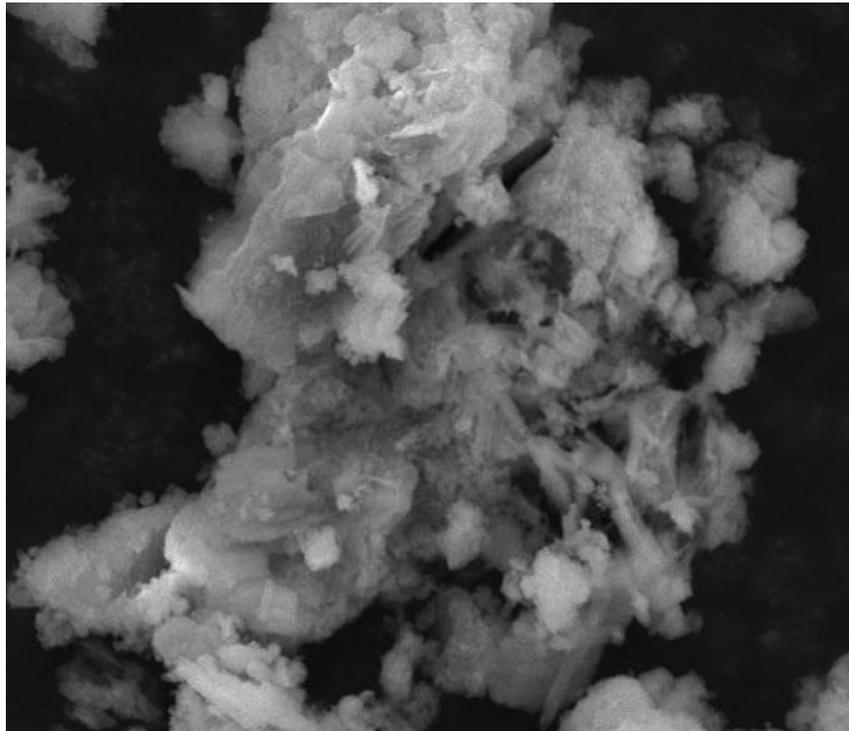
porosity. The micrograph of superplasticized RHA blended cement which indicates the formation of C-S-H gel Fig.10 (d). This has not only formed a dense surface coverage on the cement particle but is developed in the pores. The micrograph also shows longer rod like particle of C-S-H, but due to high pozzolanic activity of RHA, it will react with Ca(OH)_2 released due to hydration of C_3S & $\beta\text{-C}_2\text{S}$ to form C-S-H. The occurrence of C-S-H in large quantity is responsible for bridging cement particle and producing a rigid sym.



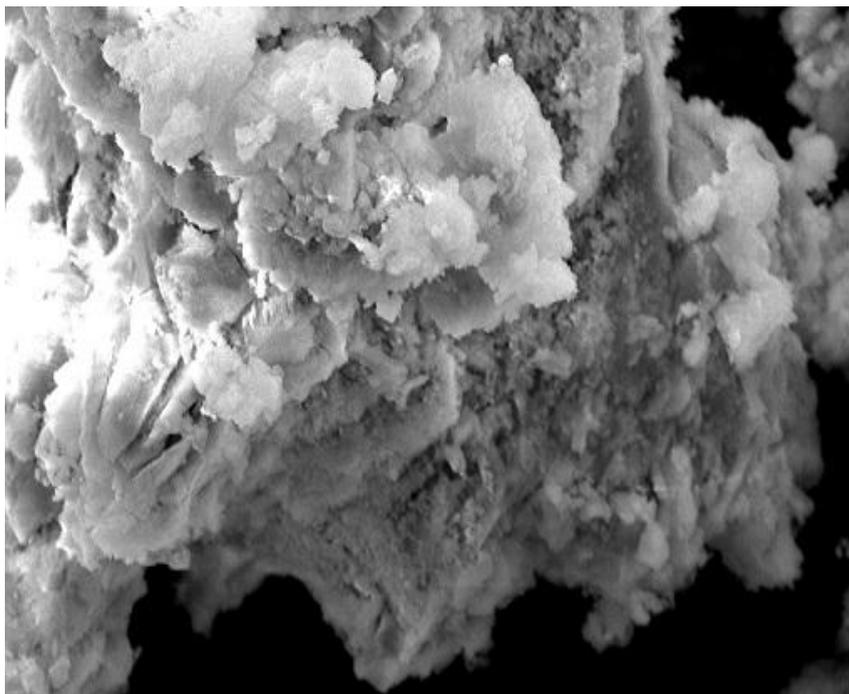
(a)



(b)



(c)



(d)

Fig.10 : (a) SEM image of 28 days of hydrated OPC, (b) SEM image of 28 days of hydrated OPC + 2% SP, (c) SEM image of 28 days of hydrated OPC + 20% RHA, (d) SEM image of 28 days of hydrated OPC + 20% RHA + 2% SP

5. CONCLUSION

The water demand for standard consistency increases with increase of RHA content but the addition of polycarboxylate superplasticizer reduces the water demand. The addition of RHA to OPC in the presence of superplasticizer increases the initial and final setting time. The result of XRD & DSC analysis indicates that addition of polycarboxylate

superplasticizer to RHA blended cement does not alter the hydration product but only affect the degree of crystallinity of the formed hydrates. Addition of polycarboxylate superplasticizer to RHA blended cement causes a slight decrease in both the values of combined water and free lime content at all ages of hydration, this is due to the decrease in the value of water/cement ratio of standard water consistency and due to pozzolanic reaction of RHA which

formed additional C-S-H. The compressive strength increases with superplasticizer dosage due to formation of dense C-S-H in large quantity and is responsible for bridging cement particle and producing a rigid system as shown in the micrographs of SEM. At last it may be concluded that addition of RHA to OPC increases the pozzolanic reactivity but shows negative effect on the mechanical properties, and to get full beneficial effect of RHA superplasticizer should be used.

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