Dielectric Study on Fly Ash Blended Cement

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Received 19 June 2008; Revised 12 September 2008; Accepted 5 November 2008

Abstract: In this paper, the hydration behaviour of ordinary portland cement (OPC) and fly ash blended cement (10, 25 and 40%) replaced by two different fly ashes (FA) were investigated. The samples were hydrated with distilled water (DW) in water to solid ratio 0:4 and its setting time and dielectric measurement are carried out. Results of the study found that the fly ash blended cement composites have slow hydration than OPC during early stages (up to 24 h).

Keywords: Dielectric Study, Fly Ash Blended Cement, OPC, Hydration behaviour.

Introduction

Supplementary cementitious materials such as blast furnace slag, silica fume and fly ash, *etc.* are increasingly being used in construction industry due to its technical, economical and environmental reasons¹. The incorporation of various supplementary cementing materials either as ingredient in blended cement system or separately in concrete has been investigated in different countries by significant number of researchers². This gives an encouraging result regarding the mechanical property and durability of concrete.

Presently about 112 million tonnes of coal-ash is generated in India from more than 70 thermal power plants³. By the year 2012 this is predicted to be increased to 170 million tonnes per annum. Due to huge availability of fly ash at zero price producing eco-friendly and higher strength concrete is of considerable interest in the present scenario and forms the aim of the paper.

Initial hydration kinetics of either pure or blended cement is of complex in nature. Usually physical and chemical changes of the cement paste can be well observed with electrical methods. The microwave method (dielectric) is one of the best tools to monitor the dynamics of cement hydration during early hydration⁴.

Cement chemistry notation

C₃S-Tricalcium silicate, C₂S-Dicalcium silicate, C₃A-Tricalcium aluminate, C₄AF-Tetra calcium aluminoferrite.

Hence, the authors preferred the microwave (dielectric) technique to monitor the hydration behaviour of pure and fly ash blended cement paste.

Experimental

American Standard for Testing Materials (ASTM), type-I ordinary portland cement (OPC) and fly ashes (FA) collected from North Chennai Thermal Power Station (F1) and Neyveli Lignite Corporation (F2), Tamil Nadu, India were used in this study and its chemical analysis are given in Table 1.

Table 1. Results of the chemical analysis (wt %).

Composition	CaO	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	SO ₃	MgO	Na ₂ O	K ₂ O	LOI	Others
OPC	63.0	21.79	5.75	3.25	2.35	1.97	0.50	0.28	1.00	0.11
Fly ash (F1)	2.88	59.09	26.32	5.80	0.10	1.09	0.82	0.71	1.74	1.45
Fly ash (F2)	15.62	44.91	24.38	6.04	0.60	2.84	0.88	0.94	1.99	1.80

From the Table 1, the F1 fly ash is found to be a low CaO fly ash ('F' type) and F2 fly ash is found to be high CaO fly ash ('C' type). The above two fly ashes were mixed with OPC in 10, 25 and 40% by weight replacement basis. The control (OPC) and fly ash composites (F1 and F2) were hydrated with distilled water in water to solid ratio (w/s) 0:4. Setting time of the samples is carried out using Vicat's apparatus by ASTM C 191 procedure⁵ and the results are given in Figure 1.

Figure 1. Setting time of control, F1 and F2 fly ash blended cement composites

From the Figure 1, the initial and final setting of control paste is observed around 2 h and 6 h respectively. In F1 composites (10, 25 and 40%), the initial and final setting is observed at around 2-3 h and 7-8 h respectively whereas in F2 fly ash composites, initial and final setting values are around 2-2.5 h and 6.5-7 h respectively. It is clearly observed that as fly ash percentage increases the setting time also increases compared to control paste. However, the F2 composites have approximately 0.5 h shorter time (quick setting) than F1. It is supported by the observations of Dan Ravina and Mehta, (1986)⁶. According to the author, setting time was delayed for both type fly ashes (class 'C' and 'F') compared with the control paste.

For dielectric measurement, the control and fly ash blended cement composites are filled in the sample holder and butted against polystyrene to avoid leakage if any.

The measurements are made during the first 24 h of hydration at a frequency of 9.54 GHz which has been selected after a pilot study. The first measurement was carried out after 5 min of hydration and is taken as zero. Further measurements are noted at every 5 min during first 10 h and then at an interval of 0.5 h over the next 14 h. Using these observations, the real part of dielectric constant (ϵ) are computed using C^{++} program and the ϵ values are plotted.

Results and Discussion

Dielectric constant (ϵ) vs hydration time are plotted for control and fly ash (F1) blended cement composites and are shown in Figure 2.

When anhydrous cement particles are in contact with water, various simultaneous hydration processes takes place. Various alkali oxides and sulphates present in cement dissolve completely, resulting in an increase of cations and anions (Ca^{2+} , K^+ , Na^+ , SO_4^{2-} and OH^-) in the aqueous media⁷. The primary ions (Ca^{2+} and OH^-) which were rapidly dissolved from C_3S and C_3A grain's surface causes an increase in ion concentration and forms fibrous ettringite products. During this period, most ions are unbound charges in the aqueous phases. These unbound charges being polarized moves easily in the electrical field, resulting in a large dielectric constant. Hence the initial dielectric values of control are higher up to first 15 min from starting of the hydration and decrease rapidly up to 1 h hydration. This stage is called pre-induction period.

The initial hydrolysis of cement can be represented in the pre-induction and induction period on the lines of Perez Penna *et al*⁸, as follows,

In the period between 1 and 6 hour, the ϵ value continues to decrease in a slow rate. This period is called as induction period. During the induction period, the dissolved Ca^{2+} and OH^- ions leaves behind a surface layer rich in hydro silicate ions on the C_3S and C_3A phase, giving the cement grain a net negative charge. During the same period, amorphous, semi-permeable gel membrane of CSH forms outside the surface layer. This surface layer together with the grain and CSH forms an electrical double layer, resulting in a physical barrier separating the silica-rich surface layer and the diffused electrical double layer. The electrical double layer hinders the rapid dissolution of anhydrous cement grains, leading to a slow hydration rate during this period⁹. Also, Si^{4+} ion concentration decreases, whereas Ca^{2+} ion concentration increases and reaches a super saturation level. Hence, early hydration products of calcium hydroxide (CH) and Calcium silicate hydrate (CSH) nuclei begin to form (Eq.4).

The formation of these products causes a continuous increase in viscosity of the cement paste. This results in a difficult polarization and moment of the charged ions leading to a decrease in ϵ of the cement paste. End of the induction period is coincides with the setting observations.

In the period 6-15 h, the ϵ gets decreased in a faster rate indicating the formation of CH and CSH products and also the ettringite products subsequent transformation to monosulphates occur (eqn.5).

Figure 2. Dielectric constant vs hydration time plot for control and F1 fly ash blended cement composites hydrated with DW

During this period, rupturing of electrical double layer occurs and allows water to reach the cement grains leading to an accelerated dissolution of the cement grains. While Ca^{2+} ions are removed from solution, cement hydration products are rapidly increased in this period. As the hydration products build up on the cement grains, the CSH extends forming a fibrous rigid structure.

After 15 h, the ϵ values decrease in a linear fashion. This period is called deceleration period. During this period, a slow diffusion controlled formation of CSH and CH takes place. The polar molecules and ions are locked in pores and find it difficult for the contribution of polarization and hence a decrease in polarizability of cement paste occurs, increasing the hydration products with an increase in porosity resulting in a decrease of ϵ values.

Changes of the dielectric values of fly ash (F1 and F2) blended cement composites seems to be similar as that of control paste. In F1-10% composite, the initial ϵ values are lesser (first 15 min) than control paste but with the same decreasing trend within 1 h. From 1 h onwards, the change ϵ are slow in 10% up to 7 h, extending the induction period compared to control. It may be due to fly ash particles retarding the hydration of OPC. According to Zhang *et al.*, the fly ash act almost as an inert filler in the blend during the early stage of hydration¹⁰ as observed from their dielectric measurement. Similar result holds good in the present study. After the induction period, the ϵ values decrease in a faster rate up to 16.5 h.

After 16.5 h and till the end of the investigation period a linear variation of ϵ values is observed with a higher value than control paste.

In 25% and 40%, it is observed that as fly ash percentage increases a drop in initial ϵ value with a rapid decrease up to 1 h similar as that of 10% composites. The variation in the rate of decrease of ϵ in the region (induction period) 1-7.5 h and 1-8 h are very slow and extended to longer time compared to 10% composite. This indicates that, when fly ash percentage increase, the induction period is extended denoting an extension of setting time and consequently a delay in nucleation and crystallisation process. In other words, as cement content decreases, the rate of hydration also decreases. According to Zhang *et al.*, the induction period is depending on composition of cementitious materials⁹. After the induction period a rapid decrease in the ϵ values is observed up to 16.5 h. At the end of

hydration time, a slow rate of decrease (24 h) and a higher ϵ value is observed in 40% followed by 25% and 10% composite.

Figure 3 shows the dielectric constant vs hydration time plot for F2 fly ash blended cement composites. The initial ϵ value is higher and decrease rate is higher up to 1 h (10, 25 and 40%) than F1 composites. This indicates that the fly ash (F2) accelerates the hydration compared to F1 fly ash. This may be due to a higher CaO content which reacts faster and produce more Ca^{2+} ions. According to Malhotra and Ramezaniapour, the high CaO fly ashes have self cementing properties and fast reaction in early periods¹¹. This hold true in their studies.

Figure. 3. Dielectric constant vs hydration time plot for control and F2 fly ash composites hydrated with DW

The induction period was observed between 1 and 7 h for all the three percentages of FA. This is very shorter (approx. 0.5 h) than F1 fly ash composites. This indicates that, the hydration products are being formed very quickly followed by control paste. After the induction period, a fast decreases between 7 and 16.5 h is observed. After 16.5 h *i.e.*, the end of the investigation period, the ϵ values are lesser than F1 fly ash composite but slightly higher than control. The results show that the F2 fly ash acts as almost a direct cementitious material. According to Wei Fajun *et al.*, class 'C' and 'F' type fly ashes retard type I cement hydration up to 24 h¹². This is supported by the present study also.

Conclusion

- The change in dielectric values reflects the chemical reaction with setting time during early hydration (24 h).
- Compared to control, the fly ash blended cement composites extend the induction period by the delayed formation of hydration products.
- The induction period is shortened in F2 composites than F1, and coincides with the setting time observation. This is due high CaO content.
- The setting time measured with Vicat's apparatus supplement the dielectric observations. Hence dielectric reading is a suitable technique for the study of hydration behaviour of cementitious system.

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