

Degree of Hydration of OPC and OPC/Fly ash Paste Samples Conditioned at Different Relative Humidity

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Abstract

Degree of hydration of cement paste controls many properties of hardened concrete and/or mortar such as compressive strength. During the drying process, the degree and the rate of hydration of cement paste in concrete/mortar samples are significantly affected by the ambient relative humidity of the exposure conditions. There are various parameters such as the amount of calcium hydroxide, Ca(OH)_2 in the paste, quantity of the chemically bound water, specific gravity of the paste, fraction of un-hydrated cement, liberated heat of hydration and strength of the hydrated cement may be used to determine the degree of hydration of the cement paste. This paper presents the results of the experimental investigation for the determination of the degree of hydration of 100% cement paste and fly ash blended cement pastes. After 28 days moist curing, the samples were conditioned in 100%, 75%, 65%, 40% and 12% relative humidity. Conditioning of samples in different relative humidity had significant effects on the compressive strength of the mortar samples and the degree of hydration of the paste samples. Conditioning of samples in 100% RH resulted in higher compressive strength and the degree of hydration. Because of the 28 days moist curing and 12 weeks moisture conditioning in different RH, fly ash based samples showed better compressive strength than the OPC samples.

Keyword: Hydration, OPC, OPC/Fly ash paste, Humidity.

1.0 INTRODUCTION

When cement mixes with water, the different cement compounds start to react with some part of mixing water so the cement starts to hydrate and that part of water becomes chemically bound. The degree of hydration (α) is defined as the ratio of the hydrated cement and the original cement content. According to Power and Brown yard [1], the maximum amount of chemically bound water requires to the system is about one quarter of the weight of cement. Continuous hydration process results in the growth of reaction products in the form of crystals, thus the cement gel produces. Microstructure of cement paste consists of the capillary pores and the gel pores.

Capillary pores are long continuous pores that exist within the un-hydrated cement paste and the gel pores are of very small dimension that occur in the reaction products. With the progress in hydration reaction the volume of capillary pore is decreases because the growing cement gel diminishes the size of the capillary pores. The size of capillary pores in the system gradually shortens until the connection among them is ceased.

The degree and the rate of hydration of concrete during its drying process are significantly affected by the ambient relative humidity, RH of the exposure conditions. Nilsson [2] in his experimental investigation has observed a substantial decrease in the rate of hydration when the ambient humidity fell below 80%. However, progress in hydration process was noticed until the RH was lowered down to 40%. In the available literature, there is very little reported on the study of the effects of the moisture conditions on the rate of hydration. Progress of hydration of cement paste samples those were dried and conditioned for two months in different relative humidity [2].

Generally, the degree of hydration of cement paste is determined by estimating one of the factors such as; the amount of calcium hydroxide, Ca(OH)_2 in the paste, quantity of the chemically bound water, specific gravity of the paste, fraction of un-hydrated cement, liberated heat of hydration and strength of the hydrated cement. Estimation of the amount of calcium hydroxide is mostly used to determine the degree of hydration of cement. There are various methods available for measuring the amount of Ca(OH)_2 ; such as the extraction of Ca(OH)_2 using solvents, quantitative X-ray diffraction technique and the thermal analysis. Because of the application of different principles and approaches in each of the measurement methods, therefore many variations may arise in the results. For example, chemical extraction method may over-estimate because it measures the total concentration of calcium ions in the solution and some of them may belong to the other phases. Quantitative X-ray diffraction technique measures the crystalline material present in the hydrated cement, however it does not detect the disordered mineral. Differential-thermal analysis (DTA) monitor the thermal changes and the thermo-gravimetry (TG) determines the weight changes involved in driving-off the water when calcium hydroxide decomposes at around 500°C [3]. Midgley [4] made a comparison of all these methods and concluded that the results obtained from thermal analysis were most reliable. All the available methods have been proved well to determine the degree of hydration of 100% cement paste, however, none of them is capable to estimate the degree of hydration of binary or tertiary cementations system such as fly ash blended cement system.

The main objective of this research study was to determine the degree hydration of 100% cement pastes and fly ash blended cement paste conditioned at different

moisture conditions. Here the term moisture condition is defined as the drying of the paste samples in different relative humidity regimes until the constant weight was achieved that is referred as equilibrium condition.

2.0 EXPERIMENTAL PROGRAM

2.1 Material Specification, Sample preparation and Moisture Conditioning

In this study 3 different paste systems identified as OPC, FA40 and FA50 were prepared; the details are given in Table-1. Ordinary Portland cement conforming to BS 12-1991, low calcium class-F fly ash conforming to ASTM C-618-1991 and fine quarry sand in accordance with BS 812, Part-2 1991 were used throughout this experimental study. The paste was mixed in a high-speed mixer for about five minutes, and then poured into plastic cups, which were covered with wet sacks and polythene sheets for overnight. 5 samples were cast from each of the paste systems. After 24 hours the samples were removed from the cup and then placed in the fog room for 28 days initial curing. After the initial curing; one of the samples from each of the paste system was transferred into the 12%, 40%, 65%, 75% and 100% RH regime for moisture conditioning. The weight of the samples was monitored at weekly interval until it reached to a constant value at that stage they were referred as equilibrium samples. It took 12 weeks to reach at equilibrium condition. The equilibrium samples were ground in a mechanical grinder for about five to six minutes, after that the ground powder was dried in a microwave oven for five minutes, which is simulated to oven drying at 105°C for 24 hours [5]. Finally, the dried samples were passed through 75- μ m sieve; the sieved samples were stored in sealed glass bottles.

The mortar cubes (50 x 50 x 50 mm) were cast to determine the compressive strength in order to determine the relationship between the degree of hydration and the compressive strength. After 28 days initial curing in the fog room, the cubes were dried until the moisture equilibrium was achieved in 12%, 40%, 65%, 75% and 100% RH, it took about 12 weeks.

3.0 THERMAL ANALYSIS

Thermo-gravimetric is defined as the technique whereby the weight of a substance, in a heated or cooled environment is recorded at a controlled rate as a function of time or temperature [6]. In this study, Stanton Red croft model TG-760 was used. The instrument mainly consists of; a furnace capable of igniting the sample up to 1000°C, an electro-microbalance for measuring the weight loss due to temperature rise and an operation programmer unit composed of a computer and plotter.

4.0 EXPERIMENTAL PROCEDURE FOR THERMOGRAVIMETRY TEST

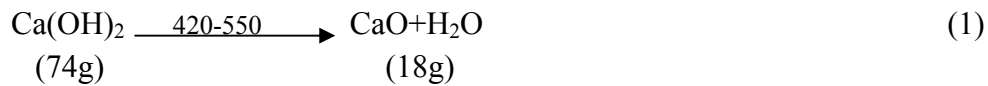
The platinum crucible was first filled with 6 to 9 mg of dried sample then it was placed in the furnace. The contents of the furnace were kept in an atmosphere of nitrogen gas and the whole system was cooled by water flowing at the rate of 350 to 400 ml/minute. The samples were heated from 20°C to 1000°C at the rate of 20°C per minute. The weight loss was continuously monitored through TG balance which was linked to a computer that captured the output data. The data was decomposed using Poisson distribution fitting procedure for the calculation of degree of hydration [7].

5.0 ANALYSIS OF TG RESULTS

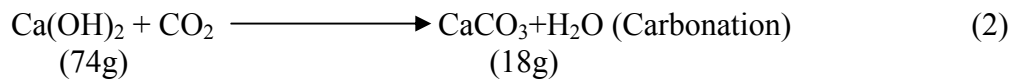
The derivative thermo-gravimetry (DTG) is the rate of weight change of a sample in a heated or cooled environment at a controlled rate that is recorded as a function of time or temperature. In the TG curve, the cumulative weight loss was plotted against temperature whereas in the DTG curve, the weight loss per degree of temperature was plotted against temperature. The area under the DTG curve is directly related to the change of weight of the sample. There are several peaks detected in the DTG curves. These peaks represent certain types of hydration activities occurring in that particular range of temperature [7, 8, 9].

5.1 Quantative Analysis of Calcium Hydroxide Content From Tg Results

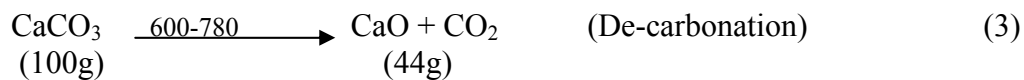
The dehydration of Ca(OH)_2 occurs at a temperature in the range of 420-550°C. Following chemical reaction usually takes place in this region:



Equation (1) indicates that the weight loss corresponding to one gram molecule of water (18g/mol) is originated from the de-hydroxylation of one gram-molecule of calcium hydroxide (74g/mol). However, there is always possibility of some carbonation of the calcium hydroxide, even though if much care is taken during the preparation of specimens for testing, the reaction is shown in equation (2) [7].



Therefore the amount of Ca(OH)_2 is corrected using the amount of CaCO_3 detected in the TG output. Calcium carbonate decomposes as follows:



Above equations show that one gram molecule of CO_2 is generated from the decomposition of one gram molecule of CaCO_3 . However, the weight of calcium carbonate is generated, in first place, from the carbonation of one-gram molecule of calcium hydroxide. Therefore, the weight loss of one gram molecule of CO_2 corresponds to one gram molecule of Ca(OH)_2 originally present in the cement paste. The total amount of Ca(OH)_2 in the test specimen is calculated using the DTG thermo-gram as shown in Figure-2 [7]:

$$\text{Ca(OH)}_2 = \frac{74}{18} A + \frac{74}{44} B \quad (4)$$

Where:

A = Area under the DTG curve corresponding to the total mass lost due to the de-hydroxylation of calcium hydroxide.

B = Area under the DTG curve total mass lost due to the de-carbonation reaction.

The degree of hydration (α_{CH}) is then calculated as follows:

$$\alpha_{CH} = \left[\frac{Ca(OH)_{2i}}{Ca(OH)_{2FH}} \right] 100 \quad (5)$$

Where:

i = Hydration at age (i)
FH = Full hydration

A sample of 100% OPC was cured in 100% relative humidity condition for two years is considered as fully hydrated, the amount of $Ca(OH)_2$ was obtained as 26.69%.

5.2 Correction for Calcium Hydroxide Content in OPC – Fly Ash System

It was noted that due to the pozzolanic reaction of fly ash, the calcium hydroxide that is produced during cement hydration reacts with the silicate and aluminate phases thus produces calcium silicate and aluminate hydrates [10]. However, the cement hydration and the pozzolanic reactions do not proceed independently, therefore due the addition of fly ash as partial replacement of the OPC reduces the $Ca(OH)_2$ content of the mix.

Cabrera proposed a correction method for the calculation of degree of hydration from $Ca(OH)_2$ contents for fly ash blended cement pastes [11]. The correction is based on the assumption that the calcium hydroxide of OPC/FA paste must be expressed in terms of OPC rather than OPC/FA. Based on ratio of the OPC/FA blend the calcium hydroxide content is corrected assuming that the ignited sample to be $[(1-FA)*OPC]$ of the cement as shown in Figure-4. For example, if in the OPC/FA blend, the FA content is 40% then the corrections are carried on the basis that the 60% ignited sample produces 60% of the $Ca(OH)_2$ content of the 100% OPC mixes. For the calculation of degree of hydration based on calcium hydroxide content, projected value is estimated according to that given in Figure-4.

5.3 Compressive strength of mortar cubes

50mm size mortar cubes were conditioned in 12%, 40%, 65%, 75% and 100% RH after 28 days curing in the fog room. The cubes were tested for measuring the compressive strength, which was determined to develop the statistical correlation between the degrees of hydration of cement paste with the compressive strength of the mortar cubes.

6.0 RESULTS AND DISCUSSION

6.1 Effects of moisture conditioning on compressive strength

Compressive strength of mortar cubes equilibrated in the 12%, 40%, 65%, 75% and 100% RH is drawn in Figure-2. All the samples conditioned in 100% RH showed the highest compressive strength as compared to the corresponding samples conditioned in lower RH. Compressive strength of FA40 samples conditioned in 100% RH was obtained as highest and considered as reference value of 100%. Table-2 contained the relative value of

compressive strength of all the samples that was calculated with respect to the reference value of 100%. The maximum reduction of 21-25% in compressive strength was observed for all the samples conditioned in 12% RH. This trend of may lead to a conclusion that the moisture condition of the concrete/mortar significantly affects the rate and the development of compressive strength. It was noted that FA40 and FA50 mortar mixes have shown the higher compressive strength as compared to that of OPC mortar samples. One of the possible reasons may be pozzolanic reactivity of the fly ash, because at the time testing (nearly 16 weeks from the date of casting), first the samples were undergone 28 days moist curing followed by moisture conditioning in different RH. During this period fly ash has become fully active to promote pozzolanic reaction. In general, mortar mix FA40 showed 11 to 14% higher compressive strength as compared to that of the OPC mix.

6.2 Effects of moisture conditioning on degree of hydration

Figure-3 shows the degree of hydration of various paste samples conditioned in 5 different RH for 12 weeks after 28 days moist curing. Degree of hydration was calculated using the amount of calcium hydroxide, $\text{Ca}(\text{OH})_2$ that was calculated from the DTG curves obtained during TG test. It is discussed as above that the amount of calcium hydroxide produced in the paste containing fly ash is usually consumed during pozzolanic reaction held by fly ash. Figure-4 shows the weight loss versus temperature curve of fly ash and OPC paste samples those were conditioned in the 100% RH. The fly ash graphs have confirmed the above hypothesis. Similarly compressive strength results of fly ash mixes also proved the activation of pozzolanic reaction. Therefore, the correction method as proposed by Cabrera [11] was applied for the calculation of the degree of hydration of fly ash pastes.

It was noted that all the paste samples conditioned in 100% RH showed the highest degree of hydration. A value of 94.6% was determined as the degree of hydration of OPC samples conditioned in 100% RH. Whereas the degree of hydration of FA40 and FA50 samples conditioned in 100% RH was determined nearly 70%. It is because of the reason that the partial replacement of cement by fly ash slows down hydration at early ages. The degree of hydration of OPC sample conditioned in 100% RH is considered as reference sample. The value of unity was assigned to it as the reference degree of hydration. Relative degree of hydration of all other samples was calculated with respect to the reference value, which is listed in the Table-3. For OPC samples conditioned in 12% RH, nearly 14% lower degree of hydration was achieved with respect to the reference samples. There was determined a wide reduction of 25-29% in the degree of hydration of FA40 and FA50 samples conditioned in 12% RH as compared to fly ash based samples conditioned in 100% RH. This trend may support the hypothesis that for high pozzolanic reactivity of fly ash requires the presence of large amount of moisture during process.

The trend of the effects of moisture conditioning on the degree of hydration was found similar to that was obtained for the compressive strength of mortar samples. Therefore, statistical operations were performed between the results of the degree of hydration and compressive strength of OPC samples and FA40 & FA50 samples as shown in Figure-5. Following correlations were obtained:

For 100% OPC

$$\alpha_{CH} = 53.325e^{0.009f_{cu}} \quad R^2 = 0.9034 \quad (6)$$

For OPC/Fly ash

$$\alpha_{CH} = 12.331e^{0.026f_{cu}} \quad R^2 = 0.9061 \quad (7)$$

7.0 CONCLUSIONS

Based on the results and discussions following conclusions were drawn:

- Mortar and paste samples conditioned in 100% RH showed the highest compressive strength and the degree of hydration as compared to the corresponding samples conditioned in lower RH.
- Because of the 28 days moist curing prior to conditioning in different RH, fly ash based samples showed higher compressive strength as compared to the corresponding OPC samples.
- The addition of fly ash as partial replacement to cement slows down the rate of hydration, all fly ash based samples showed lower degree of hydration in comparison to the relevant OPC samples.
- Fly ash based samples conditioned in 12% RH showed very low degree of hydration as compared to the fly ash based samples conditioned in 100% RH. Because the dry ambient conditions affected the pozzolanic reactivity of the fly ash contents.
- Best statistical correlations were obtained between the compressive strength and the degree of hydration of OPC and OPC/fly ash samples.

8.0 ACKNOWLEDGEMENTS

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9.0 REFERENCES

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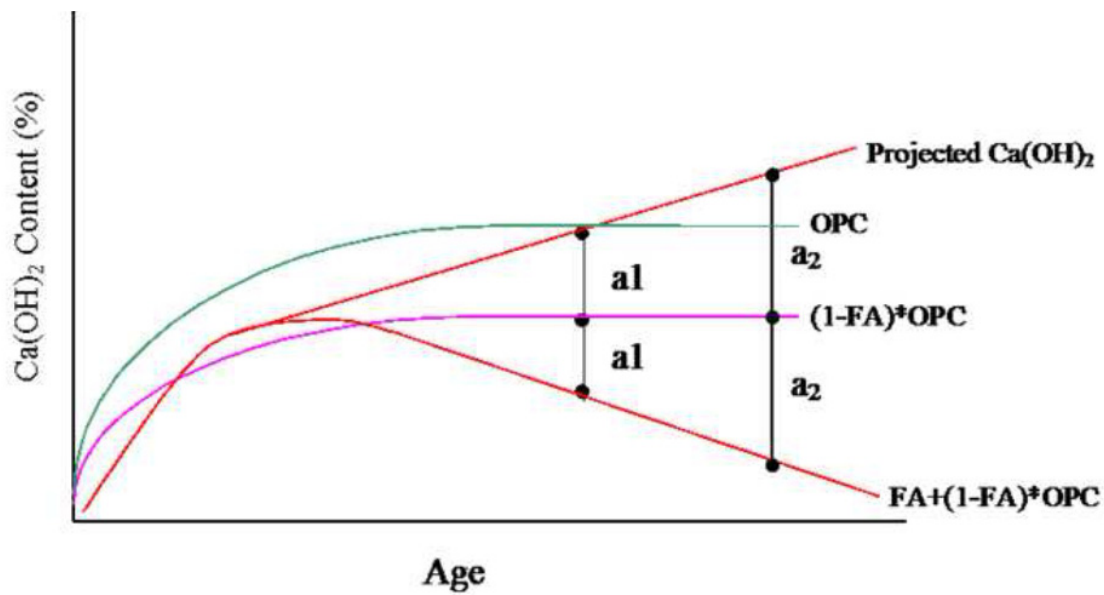


Figure 1. Correction of degree of hydration for fly ash based pastes

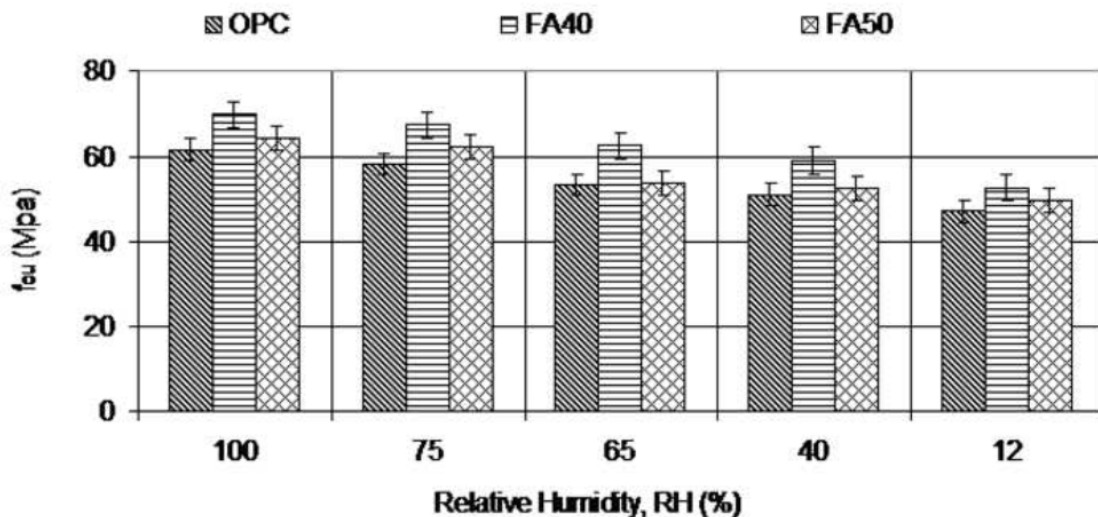


Figure 2. Effect of Relative humidity on the compressive strength of mortar

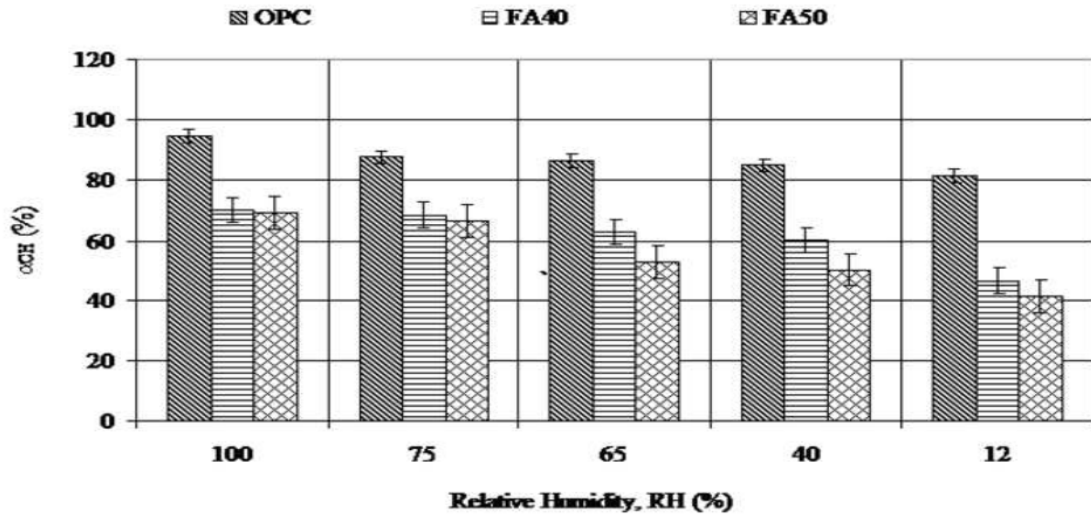


Figure3. Effect of Relative humidity on the degree of hydration of paste

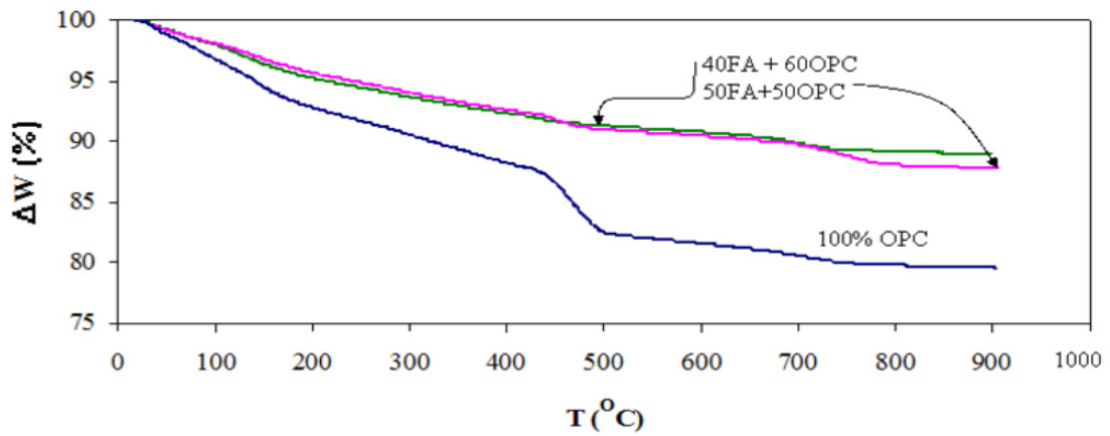


Figure 4. TG Thermo gram of a paste sample

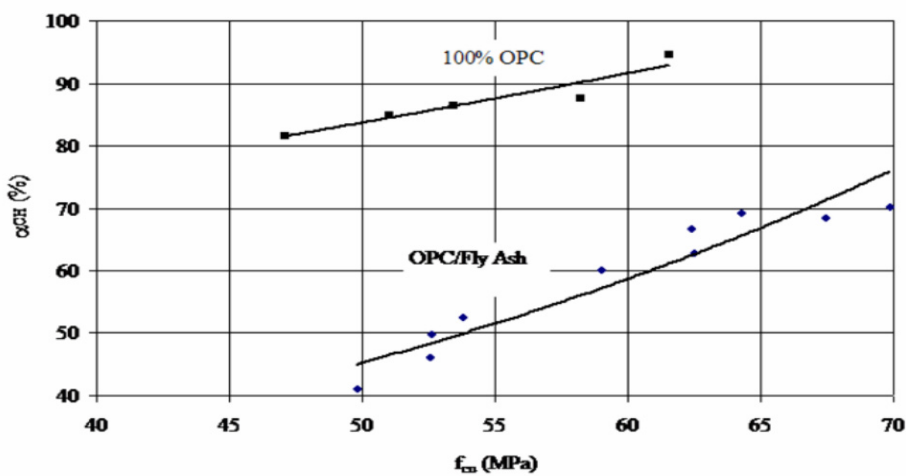


Figure 5. Relationship between degree of hydration and compressive strength

Table 1. Details of OPC and OPC – Fly Ash paste System

Mix Type	OPC	PFA	W/C	Sand (for mortar)
OPC	1	0	0.55	2.5
FA40	0.6	0.4	0.55	2.5
FA50	0.5	0.5	0.55	2.5

Table 2. Relative Compressive strength of all mortar samples conditioned in different RH

RH (%)	Relative value of compressive strength		
	OPC	FA40	FA50
100	88	100	92
75	83	97	89
65	76	90	77
40	73	84	75
12	67	75	71

Table 3. Relative degree of hydration of all pastes conditioned in different RH

RH (%)	Relative value of compressive strength		
	OPC	FA40	FA50
100	1.00	0.74	0.73
75	0.93	0.72	0.70
65	0.91	0.66	0.56
40	0.90	0.64	0.53
12	0.86	0.49	0.44