CONCRETE RESEARCH LETTERS

www.crl.issres.net Vol. 1 (3) – September 2010

Degree of Hydration of OPC and OPC/FA Pastes Dried in Different Relative Humidity

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Abstract

In this research; the degree of hydration of the pastes and the compressive strength of the 50 mm cubes prepared with the 100% cement and fly ash blended cement was determined. 24 hours after casting mortar cubes and the paste samples were cured for 28 days in the fog room. After 28 days curing; a set of 3 cubes and a paste sample was dried in the 100%, 75%, 65%, 40% and 12% ambient relative humidity at the constant temperature of 27°C. Drying conditions showed significant effects on the compressive strength and the degree of hydration. Highest compressive strength of 70 MPa was measured for mortar cubes dried in 100% RH; similarly 97% degree of hydration was determined for 100% cement samples dried in the 100% RH. For mortar cubes dried in 12% RH, the compressive strength was measured between 47 and 53 MPa. The similar paste samples showed the maximum degree of hydration as 81%. In conclusion, drying conditions have significant effects on the degree of hydration of cement pastes, therefore other properties are also affected such as compressive strength.

Keywords: Cement hydration; Calcium hydroxide; fly ash; drying conditions.

1. Introduction

Upon addition of water in the cement; different cement compounds start to react with water that is called the cement hydration and that part of water becomes chemically bound. The degree of hydration (□) is defined as the ratio of the amount of the hydrated cement and the original cement content. According to Power and Brownyard [1], the maximum amount of chemically bound water requires to the system is about one quarter of the weight of the cement. Cement hydration is a continuous process that causes the growth of reaction products in the form of crystals.

Microstructure of the cement paste consists of the capillary pores and the gel pores. Capillary pores are long continuous that exist within the un-hydrated cement paste. Whereas, the gel pores are of very small size that occur in the reaction products. When the hydration reaction progresses, the volume of the capillary pores decreases; because of the growth of the cement gel reduces the size of the capillary pores. Reduction in the size of the capillary pores is continued until the connection between them is ceased.

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Ambient relative humidity during drying of concrete has significant effects on the rate and the degree of hydration of the cement paste. Nilsson [2] found a substantial decrease in the rate of hydration of cement when it was subjected to the RH conditions below 80%. However, some progress in hydration process was noticed until the RH was lowered down to 40%. Nilson [2] has reported the results of the progress of hydration of cement paste dried and conditioned for two months in different relative humidity. Effects of the ambient moisture conditions on the rate of hydration are not very widely investigated.

The degree of hydration of cement paste is generally estimated by measuring 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, heat of hydration and the strength of the hydrated cement. The amount of calcium hydroxide is widely used to estimate the degree of hydration of cement. Various methods are available for measuring the amount of Ca(OH)2; some of them are the extraction of Ca(OH)2 using solvents, quantitative X-ray diffraction technique and the thermal analysis.

Different principles and approaches are used in each of the measurement methods; therefore the results obtained from each of the methods may be varied. Chemical extraction method usually over-estimates the degree of hydration. In this method; total concentration of the calcium ions in the solution is measured, a part of them might be belonged to the other phases. Crystalline material present in the hydrated cement is determined using the quantitative X-ray diffraction technique; however this technique does not detect the disordered mineral. Differential-thermal analysis (DTA) determine the thermal changes whereas the thermo-gravimetric method (TG) determines the weight changes occurs during driving-off the water when calcium hydroxide decomposes at around 500^{o}C [3]. Midgley [4] made a comparison of all these methods and concluded that the results obtained from the 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 cementitious system such as fly ash blended cement system.

The main objective of this research study was to investigate the effects of the drying conditions on the degree of hydration of the cement pastes and the compressive strength of the mortar cubes. Paste samples and 50mm mortar cubes were made of 100% cement and fly ash blended cement. The samples were initially cured for 28 days in 100% RH. After the curing was done, the samples were dried in different relative humidity at constant temperature of 27^{o}C. The samples were dried until they achieve the constant weight in their drying regime, which is called the equilibrium condition.

2. Experimental program

2.1. Material properties, Sample preparation, curing and drying

Three different paste systems designated as the OPC, FA40 and FA50 were prepared; the details are given in the Table-1. Ordinary Portland cement, OPC 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 the experimental study. The paste was mixed in a high-speed mixer for about five minutes, and then poured into the plastic cups, which were covered with wet sacks and polythene sheets for overnight. 5 samples for each of the paste systems were made. After 24 hours; the samples were removed from the cup and then placed in the fog room for 28 days initial curing. Upon completion of the initial curing; one out of five samples of each of the three systems was placed in the humidity control chambers that was set at 12%, 40%, 65%, 75% and 100% RH.

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

The weight of the samples was measured every week until the constant weight was attained; such samples were called the equilibrium samples. It took 12 weeks to attain the equilibrium condition. The equilibrium samples were ground in a mechanical grinder for about 5 to 6 minutes then the ground powder was dried in a microwave oven for about 5 minutes, which is simulated to oven drying at 105 ^{o}C for 24 hours [5]. Finally, the dried samples were passed through 75-µm sieve; the sieved samples were stored in sealed glass bottles.

50 mm cubes were cast to determine the compressive strength of mortar in order to determine the relationship between the degree of hydration and the compressive strength. Mortar cubes were cured and dried in the same manner as the pastes samples i.e. initially cured for 28 days in the fog room then drying in the12%, 40%, 65%, 75% and 100% RH for 12 weeks.

2.2. 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 Redcroft model TG-760 was used. The instrument mainly consists of; a furnace capable of igniting the sample up to 1000 ^{o}C; an electro-microbalance for measuring the weight loss due to temperature rise and an operation programmer unit composed of a computer and plotter.

2.3. 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 ^{o}C to 1000 ^{o}C at the rate of 20 ^{o}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].

3. 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].

3.1. Quantitative Analysis of Calcium Hydroxide Content from TG Results

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

$$Ca(OH)_2 \xrightarrow{420-550} CaO + H_2O$$
$$(74g) \qquad\qquad (18g)$$

(1)

Equation (1) indicates that the weight loss corresponding to one gram molecule of water (18g/mol) is originated from the dehydroxylation 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].

$$Ca(OH)_2 + CO_2 \rightarrow CaCO_3 + H_2O\,(carbonation)$$
$$(74g) \qquad\qquad (100g)$$

(2)

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:

$$CaCO_3 \xrightarrow{600-780} CaO + CO_2\,(decarbonation)$$
$$(100g) \qquad\qquad (44g)$$

(3)

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 thermogram [7]:

$$Ca(OH)_2 = \left(\frac{74}{18}\right)(A) + \left(\frac{74}{44}\right)(B)$$

(4)

Where:

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

B = Area under the DTG curve total mass lost due to the decarbonation reaction

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

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

(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%.

3.2. 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 1. 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 shown in the Figure 1.

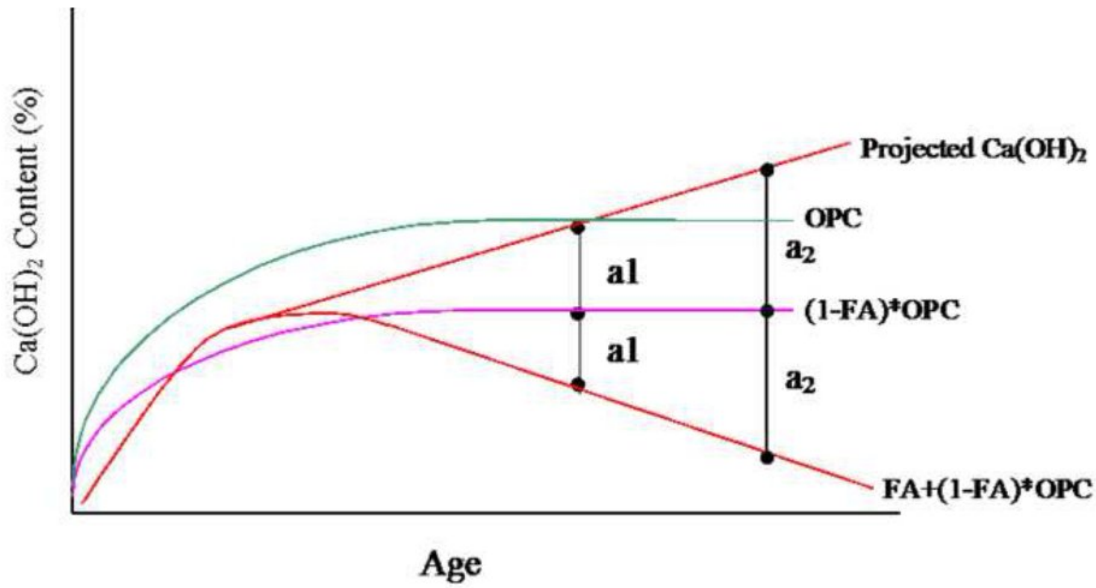

Figure 1: Correction of degree of hydration for fly ash based pastes

3.3. Compressive strength of mortar cubes

50 mm 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.

4. Results and Discussion

4.1. Effects of drying conditions on the compressive strength of mortar

Compressive strength of cubes dried in the 12%, 40%, 65%, 75% and 100% RH is presented in Figure 2. Samples dried in the 100% RH showed the highest compressive strength as compared to the samples dried in the other four RH conditions. Highest value of compressive strength was measured for FA40 mortar cubes dried in the 100% RH; for such compressive strength a reference value of 100% was assigned. Relative value of compressive strength of all other mortar samples were calculated with respect to the reference value and given in the Table-2.

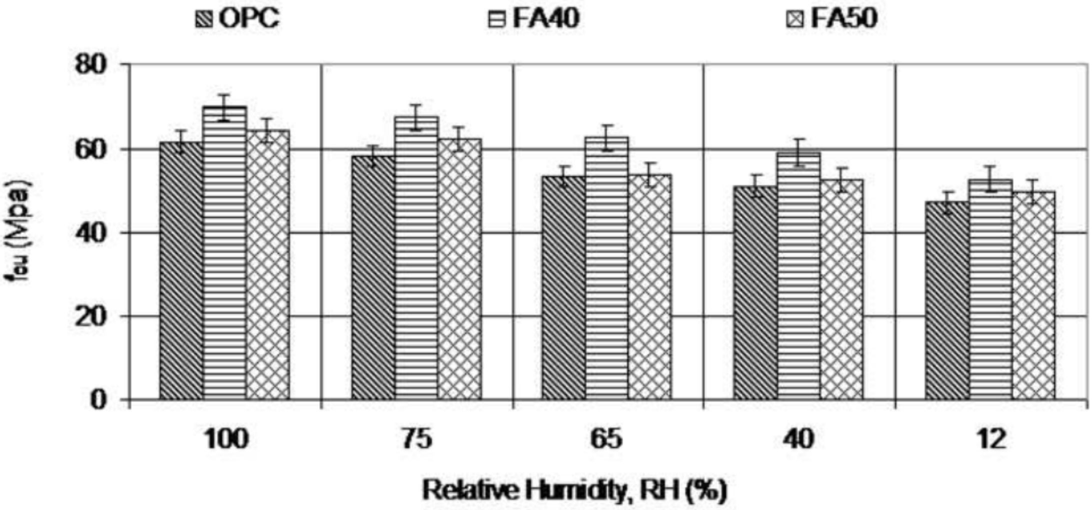

Figure 2: Effect of Relative humidity on the compressive strength of mortar

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

Mortar cubes dried in the 12% RH showed the maximum reduction of about 25% in compressive strength with respect to the reference value. Results of the compressive strength of mortar cubes dried in different RH draw a conclusion that the ambient moisture conditions significantly affect the compressive strength of the concrete. It was also noted that the partial replacement of cement with 40% and 50% fly ash content improved the compressive strength of the mortar dried in different relative humidity. On an average approximately 10% to 14% higher compressive strength was measured of all fly ash based mortars as compared to their corresponding 100% OPC based mortar cubes. It is because of the reason that after 28 days initial curing in the fog room; fly ash has undergone to pozzolanic reaction, which was accelerated when the cubes were dried in higher RH such as 100% and the 75% RH.

4.2. Effects of drying conditions on the degree of hydration of cement

Figure 3 shows the degree of hydration, α_{CH} of the paste samples dried in different RH, was estimated using the amount of the calcium hydroxide, $Ca(OH)_2$ that was determined from the TG test. It was discussed that the amount of the calcium hydroxide produced in the paste containing fly ash is usually consumed during pozzolanic reaction held by fly ash. This hypothesis is further confirmed in this research study. In Figure 4, the weight loss versus temperature curves of the fly ash samples show little loss as compare to the 100% OPC samples. Pozzolanic reactivity of fly ash was also noted in the compressive strength test results of such mixes. Therefore, the correction method as proposed by Cabrera [11] was applied for the calculation of the degree of hydration of fly ash based paste samples.

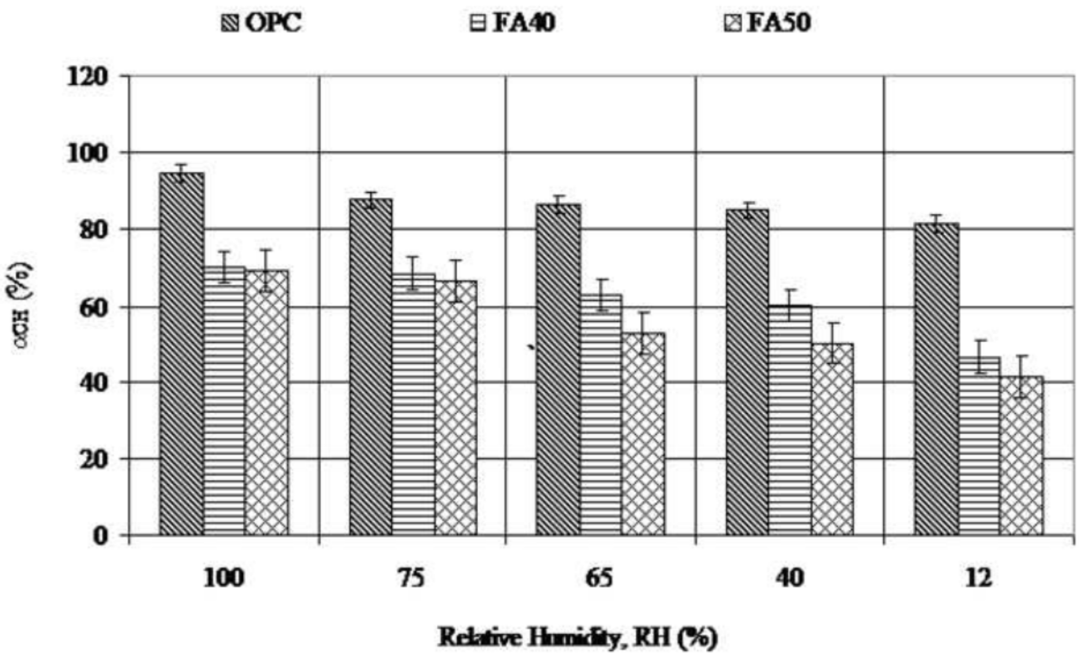

Figure 3: Effect of Relative humidity on the degree of hydration of paste

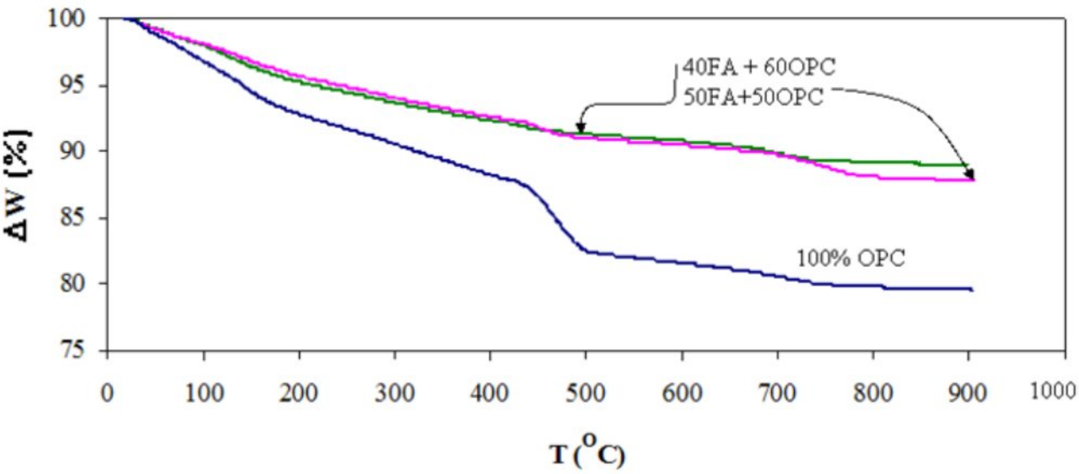

Figure 4: TG Thermogram of a paste sample

Highest value of the degree of hydration was determined of the paste samples dried in the 100% RH condition. Degree of hydration of the 100% OPC paste dried in the 100% RH was measured as 94.6%, on the other hand fly ash blended cement dried in 100% RH achieved a maximum value of about 70% degree of hydration. It may be due to the facts that the addition of fly ash in cement normally slows down hydration at early ages. If the degree of hydration of OPC dried in 100% RH is considered as the unity, the relative degree of hydration of all other samples was calculated with respect to the reference value as given in the Table 3. OPC samples dried in the 12% RH conditioned showed 14% lower degree of hydration with respect to the reference value. A huge reduction of about 28% in the degree of hydration fly ash blended cement dried in the 12% RH as compared to the fly ash blended cement dried in the 100% RH.

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

RH (%)	Relative degree of hydration		
	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

Effects of drying conditions on the degree of hydration of cement followed the similar trend that was observed during the investigation of the effects of drying on the compressive strength of mortar. A statistical analysis was performed between the results of the degree of hydration and the compressive strength of OPC that is plotted in the Figure 5. Following correlations were obtained:

For 100% OPC

$$\alpha_{CH} = 53.325e^{0.009 f_{cu}}$$

$$R^2 = 0.9034$$

(6)

For OPC/Fly ash

$$\alpha_{CH} = 12.331e^{0.026 f_{cu}}$$

$$R^2 = 0.9061 \qquad (7)$$

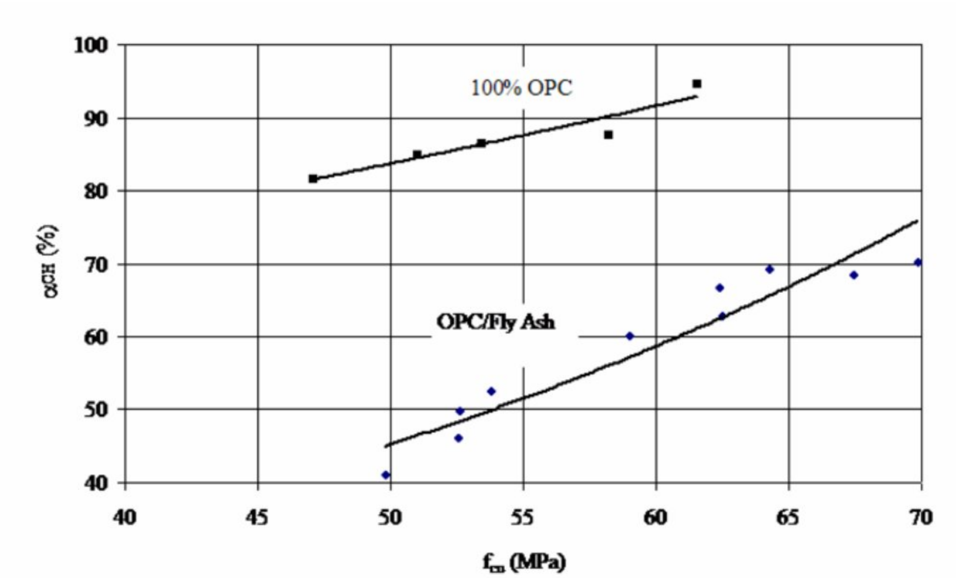

Figure5: Relationship between degree of hydration and compressive strength

5. CONCLUSIONS

Based on the results and discussions following conclusions were drawn:

1. Mortar samples dried in the 100% RH showed the highest compressive strength as compared to the similar samples when dried in the lower RH condition. Similarly, cement paste dried in the 100% RH condition achieved the maximum degree of hydration.
2. Prior to drying in different relative humidity conditions, all samples were cure in the fog room for 28 days that results in the activation of the pozzolanic reaction in the fly ash

blended cement mortar. Hence the compressive strength of mortar containing fly ash was obtained more than the compressive strength of the 100% OPC mortar.

3. 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.
4. A correction method was applied to assess the degree of hydration of the fly ash blended cement. The degree of hydration of fly ash blended cement was measured about 25% lower than the 100% OPC.
5. Statistically valid correlations were obtained between the compressive strength and the degree of hydration of 100% OPC and fly ash blended cement samples.

ACKNOWLEDGEMENTS

The authors would like to acknowledge the university technology PETRONAS for providing the facilities assistance for successfully accomplishment of this research study.

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