PREDICTION OF THE DEGREE OF HYDRATION OF ORDINARY PORTLAND CEMENT PASTE

BAKRI ABDELRAHIM GAAFAR[1] AND CABRERA J. G.[2]

ABSTRACT

Tests were carried out on Ordinary Portland cement (OPC) paste specimens cured at 5, 20 and 35 °C in order to investigate effect of w/c ratio, age of curing and curing temperature on degree of hydration of cements. The method used is based on measurement of $Ca(OH)_2$ generated by the hydration reactions and also by measuring increase of non evaporable water of hydrated products, using thermogravimetric (TG) analysis.

The experimental data was used to propose numerical models which allow reasonably accurate predictions of hydration rate of OPC cements.

ملخص

أجريت الاختبارات على عينات من عجينة الأسمنت البورتلاندي العادي المعالجة في درجات حرارة ٥ و ٢٠ و ٤٥ درجة مئوية وذلك بغرض استقصاء تأثير نسبة الماء للاسمنت و فترة المعالجة ودرجة حرارة المعالجة على درجة الاماهة للاسمنت

تعتمد الطريقة المستخدمة على قياس هايدروكسيد الكالسيوم المنتج بوساطة تفاعلات الاماهة وايضا قياس الزيادة في الماء غير المتبخر لنواتج الاماهة وذلك باستخدام تحليل نتائج جهاز الثيرموقراف. استخدمت النتائج المعملية لايجاد عدة صيغ تسمح بتحديد دقيق لمعدل الاماهة للاسمنت البورتلاندي العادي

INTRODUCTION

The understanding of mechanisms of hydration and knowledge of the nature and morphology of hydration products of hydraulic cements and pozzolans has helped engineers in interpretation of conditions under which concretes can perform adequately(1). However, prediction of rates of hydration under different environmental conditions for different cement types is still not possible due to lack of accurate numerical models.

1 Department of Civil Engineering . College of Engineering. SUST

2 Department of Civil Engineering. University of Leeds, UK

Nevertheless, the hydration of cement has been investigated by many researchers and methods to measure hydration are established [2-10]. For example thermal analysis methods such as Differential Thermal Analysis (DTA) and Thermogravimetry (TG) have been widely used for determining the amount of $Ca(OH)_2$ in different cement paste systems [10-15].

Midgley[11] made a comparative study using DTA, TG, Quantitative X-ray, glycol extraction and alcohol-glycerol and concluded that thermal analysis techniques give the most reliable results if the total $Ca(OH)_2$ content of a set OPC is required.

This paper is limited to a laboratory study for the effect of w/c ratio, age of curing and curing temperature on the rate and extent of hydration of ordinary Portland cement and to the development of numerical models for prediction of hydration rates of OPC pastes.

EXPERIMENTAL DETAILS

ORDINARY PORTLAND CEMENT (OPC)

The OPC used was supplied by Castle Cement UK Limited in air-tight containers. It complies with the requirements of BS12 (1989) [16]. The chemical and physical properties of the OPC are shown in Table (1)

Table 1. Chemical composition and some physical properties of OPC

Oxide Composition	%
SiO_2	20.97
Al_2O_3	5.90
Fe_2O_3	3.40
CaO	63.69
MgO	2.83
Na_2O	0.27
K_2O	0.86
SO_3	2.87
Relative density (g/cm^3)	3.15
Specific surface (m^2/g)	0.341

Calculated Bogue Compound Composition (OPC)

Mineral	Percentage
C_3S	47.16
C_2S	24.63
C_3A	9.89
C_4AF	10.34

PREPARATIONS OF SPECIMENS

OPC pastes were prepared with w/c ratios of 0.45, 0.55 and 0.65. The pastes were then cured at 5, 20 and 35°C. Mixing of the cement and water was carried out by a high speed mixer for 5 minutes to obtain a uniform paste which will not settle and segregate. The mixed paste was then cast into plastic cups and covered by wet hessian and plastic sheets (to minimise evaporation of water) for 24 hours.

Testing of cured specimens was carried out at 1, 3, 7, 28, 90, 180 and 365 days. The same testing dates were kept for all curing conditions. Samples were taken from the middle part of the specimens to minimise carbonation effects and were ground by using an electrical high speed grinder. The powder samples were dried in a Microwave oven for 5 minutes. The dried samples were passed through a 75 µm sieve (in order to improve the uniformity of the sample) and kept in a sealed bottle under nitrogen atmosphere. Great care was taken between these operations, and samples were kept in sealed polythene bags and kept in a desiccator containing Silica gel in order to minimise partial carbonation.

APPARATUS

The apparatus used in this investigation was a Stanton Redcroft model TG-760 so as to give a computerised output typical to the one shown in Figure (1) the apparatus consists mainly of an electro-microbalance, a furnace, operation programmer unit and data acquisition unit.

The platinum crucible was filled with dried powdered sample (between 6 to 9 mg), the furnace was then closed. The contents of the furnace were kept in an atmosphere of nitrogen gas, and the whole system was cooled with water at a rate between 350-400 cc/min. The samples were heated from 20°C to 1000 °C at a rate of 20 °C per minute and the weight losses were monitored continuously. The TG curves are obtained by plotting the cumulative weight loss against temperature while the DTG curves are obtained from the TG curves by plotting the percentage weight loss per degree of temperature

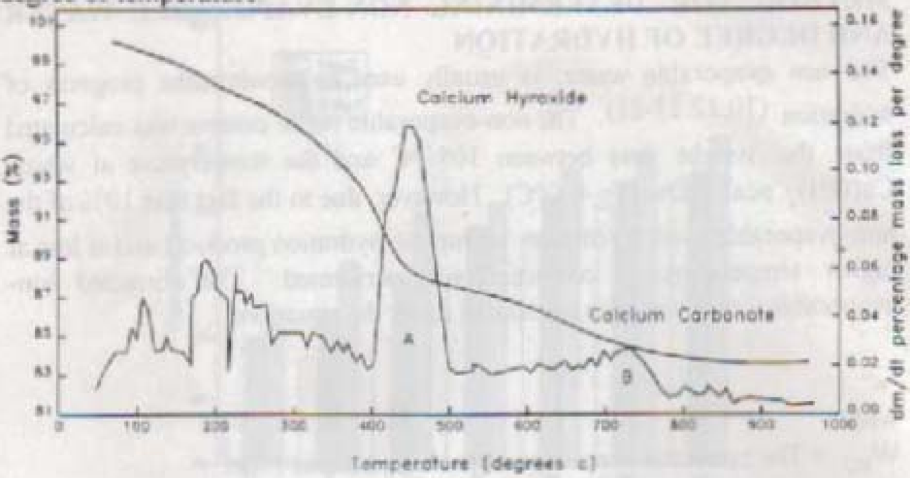

Figure (1) : Typical Thermogravimetry (TG) and the Dervative Thermogravimetry(DTG) Curves

METHOD FOR DETERMINATION OF $Ca(OH)_2$ CONTENT AND DEGREE OF HYDRATION

The total amount of $Ca(OH)_2$ can be determined from the TG results using the following equation (10)

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

Where:

$W_{Ca(OH)_2}$ = Percentage of total amount of $Ca(OH)_2$ in the sample

A = Area under the DTG curve corresponding to the dehydroxylation of calcium hydroxide (Percentage of mass lost between 420°C to 534 °C)

B = Area under the DTG curve corresponding to the decarbonation reaction (Percentage of mass lost between 600 °C to 780 °C)

The degree of hydration (DH %) is then calculated as follows

$$DH\ \%\ (\text{at age } n) = \left(\frac{Ca(OH)_2\ (\text{at age } n)}{Ca(OH)_2\ (\text{for fully hydrated paste})}\right)\times 100$$

Full hydration was considered to occur when hydration has continued for two years at 100% relative humidity (RH) and 20 °C.

METHOD FOR DETERMINING NON-EVAPORABLE WATER AND DEGREE OF HYDRATION

The non evaporable water, is usually used to monitor the progress of hydration [10,12,17-21]. The non-evaporable water content was calculated from the weight loss between 105 °C and the temperature at which $Ca(OH)_2$ peak started (≈ 400°C). However, due to the fact that 10% of the non-evaporable water remains within the hydration products and is lost at higher temperature, a correction was performed. The corrected non-evaporable water was then calculated using the equation:

$$W_{nc} = 1.1\,W_n$$

where

W_{nc} = The corrected non-evaporable water content (%)

W_n = The weight loss between (105-400°C) (% of the ignited weight)

The degree of hydration (DH), based on the non-evaporable water, was then calculated according to the following form:

$$DH\,(\%) = \frac{W_{nc}}{W_{ne}} \times 100$$

where:

W_{ne} = The non-evaporable water for sample cured at 20 °C and 99% RH for two years

Although the non-evaporable water is a good indication of the degree of hydration, it is not an absolute measure of hydration, because neither the composition of the major hydrates nor the stoichiometry of the reactions is well defined[10]. The results may also be affected by the method of drying the sample to remove the evaporable water, since some chemically bound water may be released at the same time.

RESULTS AND DISCUSSIONS

The degree of hydration for the various OPC mixes investigated at different ages, w/c ratios and curing temperatures, were calculated from calcium hydroxide content and the non-evaporable water and are presented in histograms Figures 2 to 7. The results indicate that the degree of hydration is governed by parameters such as the w/c ratio, curing temperature and age of curing.

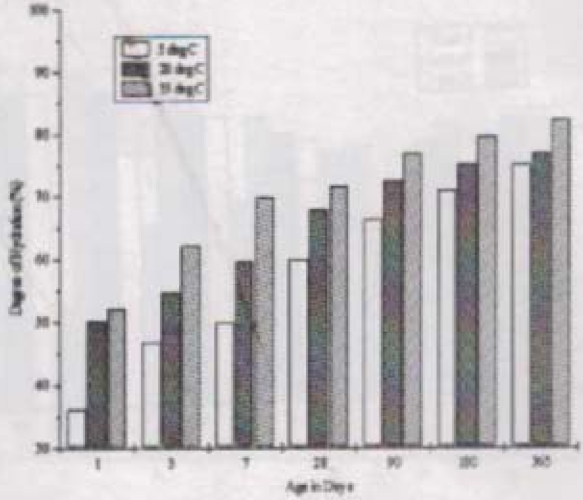

Figure (2) : Bar Chart Representation of the Degree of Hydration ($Ca(OH)_2$) Vs Age (Mix OPC w/c=0.45)

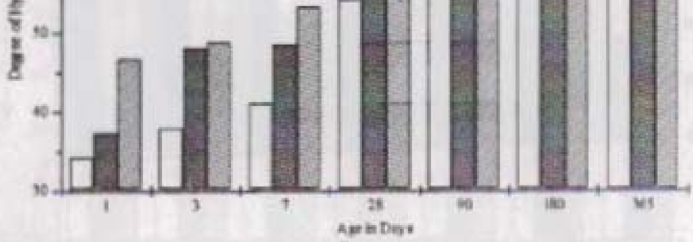

Figure (3): Bar Chart Representation of the Degree of Hydration (Non-evaporable Water) Vs Age (Mix OPC w/c=0.45)

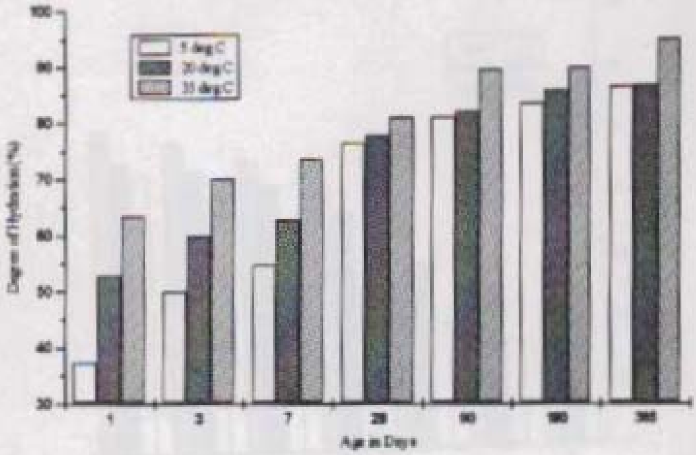

Figure (4): Bar Chart Representation of the Degree of Hydration ($Ca(OH)_2$) Vs Age (Mix OPC w/c=0.55)

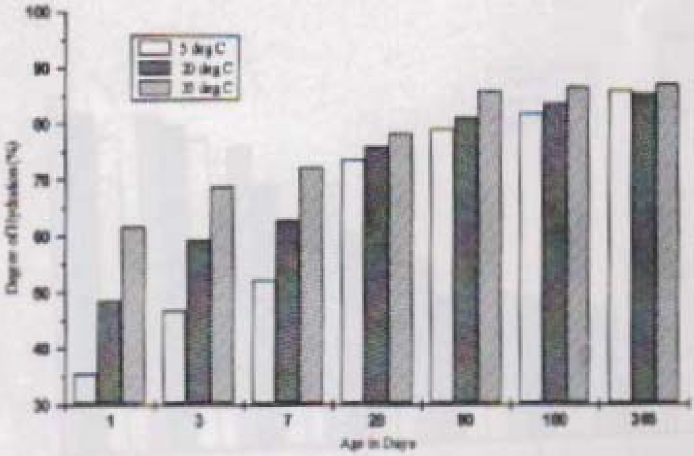

Figure (5) Bar Chart Representation of the Degree of Hydration (Non-evaporable Water) Vs Age (Mix OPC w/c=0.55)

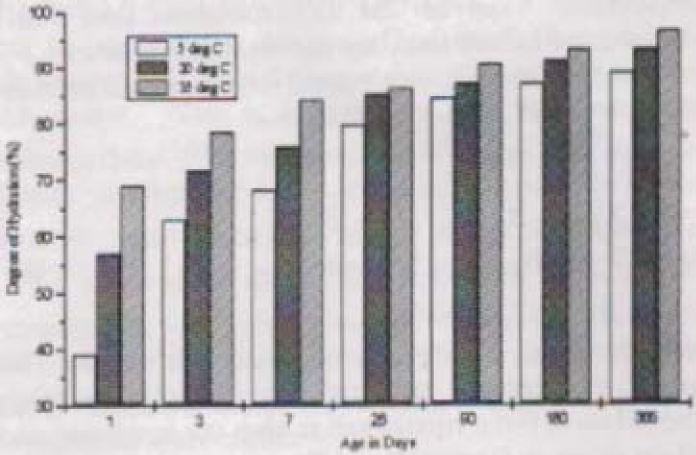

Figure (6): Bar Chart Representation of the Degree of Hydration ($Ca(OH)_2$) Vs Age (Mix OPC w/c=0.65)

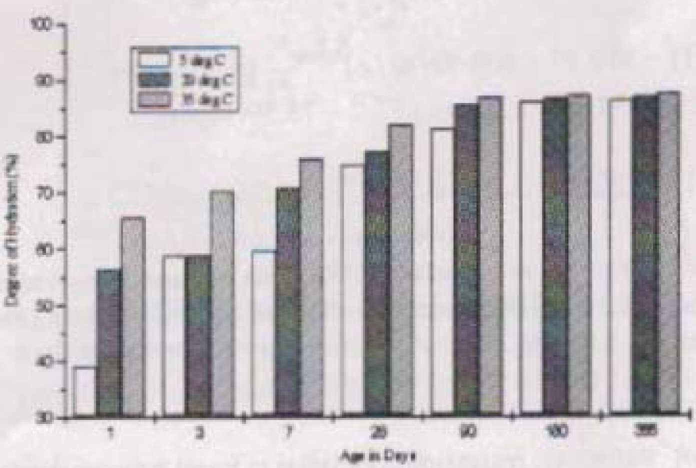

Figure (7) Bar Chart Representation of the Degree of Hydration (Non-evaporable Water) Vs Age (Mix OPC w/c=0.65)

A statistical analysis was carried out on data obtained from different OPC mixes using Statistical Analysis System Package (SAS) in order to develop statistical models to predict degree of hydration calculated from $Ca(OH)_2$ and non-evaporable water at the 95% confidence limit from related variables investigated i.e. w/c ratio, age and curing temperature.

Non-linear models in the following general form were used to relate degree of hydration to w/c ratio, age and temperatures:

$$Y = B_0 + B_1 X_1^{B_2} + B_3 X_2^{B_4}$$

$$Y = B_0 + B_1 X_1^{B_2} + B_3 X_2^{B_4} + B_5 X_3^{B_6}$$

Where: $B_0, B_1, B_2, B_3, B_4, B_5\ B_6$ = Constant

X_1, X_2, X_3 = Variable

All relevant equations for these models are shown in Table (2). Comparison of predicted and measured experimental degree of hydration values showed much better representation when this non-linear model was applied and are shown in Figures (8) and (9).

Table 2 Relation between degree of hydration (DH) and w/c ratio, age and curing temperature

5 °C

$$DH\%(CH) = 126.77 - 10.95(w/c)^{-1.48} - 61.29(Age)^{-0.23}$$

$$DH\%(W_n) = 150.37 - .45(w/c)^{-4.79} - 103.62(Age)^{-0.099}$$

20°C

$$DH\%(CH) = 539.97 - 409.98(w/c)^{-0.092} - 53.14(Age)^{-0.164}$$

$$DH\%(W_n) = 134.69 - .125(w/c)^{-6.32} - 78.59(Age)^{-0.102}$$

35°C

$$DH\%(CH) = 122.56 - 3.01(w/c)^{-2.59} - 44.70(Age)^{-0.167}$$

$$DH\%(W_n) = 132.757 - 0.0068(w/c)^{-9.89} - 68.33(Age)^{-0.085}$$

2- Degree of Hydration's as a function of W/c ratio Age and Temperature

$$DH\%(CH) = 135.76 - 230.92(w/c)^{-0.96} - 52.149(Age)^{-0.191} + 0.664(Temp)^{0.89}$$

$$DH\%(W_n) = 131.54 - 0.085(w/c)^{-6.78} - 83.28(Age)^{-0.097} + 0.41(Temp)^{0.96}$$

A significant statistical regression correlation is found between degrees of hydration calculated from total calcium hydroxide content DH%(CH) for the different samples cured at different temperatures and the corresponding ones calculated from the non-evaporable water content DH%(Wn) as shown in Figure (10). The linear relationship was found in the following form:

$$DH(CH) = 9.701 + 0.93DH(Wn) \qquad (r^2=0.96) \qquad (1)$$

According to equation (1), degrees of hydration calculated from calcium hydroxide content are generally higher than those calculated from the non-evaporable water. This is in agreement with the results reported by previous researchers[10]. However, it can be seen from equation (1) that the difference in calculated degree of hydration from $Ca(OH)_2$ content and non-evaporable water decreases as the degree of hydration increases. Greene [22] observed that the $Ca(OH)_2$ peak grew in size and shifted to a higher temperature with higher maturity of the paste. This could explain this difference as the $Ca(OH)_2$ peak is formed at relatively lower temperatures at a lower degree of hydration, causing an underestimation of the non-evaporable water content.

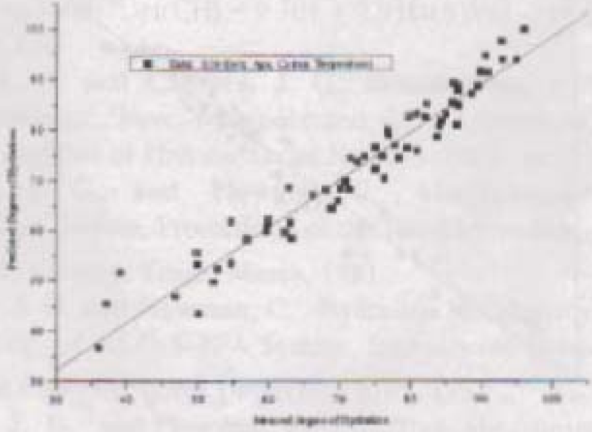

Figure (8): Comparison between measured and predicted degree of hydration based on calcium hydroxide($Ca(OH)_2$) content

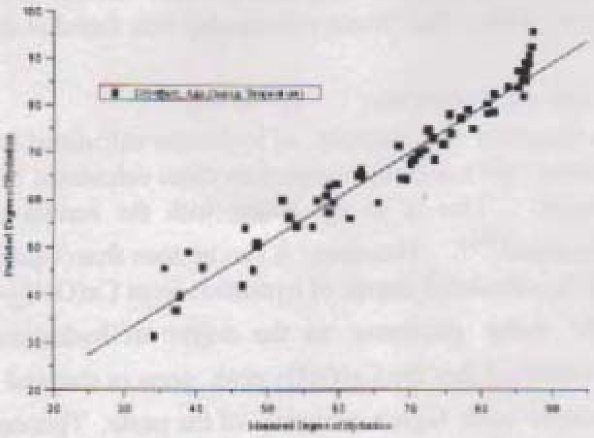

Figure (9): Comparison between measured and predicted degree of hydration based on non-evaporable water content

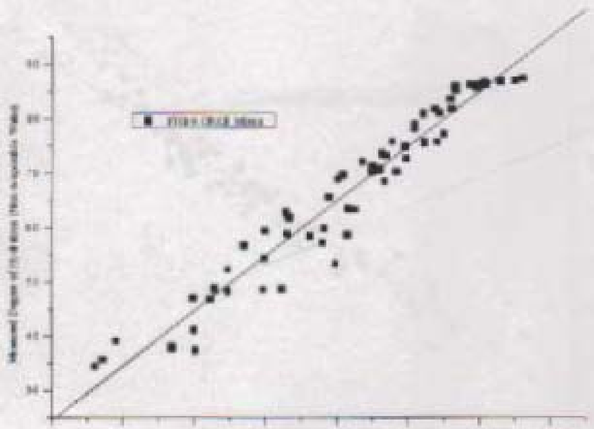

Figure (10): Comparison between the degree of hydration based on measured calcium hydroxide($Ca(OH)_2$) and non-evaporable water content

CONCLUSION

1 The rate of hydration is directly affected by w/c ratio, age of curing and curing temperature.

2 Calcium hydroxide content is more reliable than non-evaporable water content in determination of degree of hydration. The degree of hydration determined from non-evaporable water content is lower than that obtained from calcium hydroxide content at lower degrees of hydration, however, identical results could be obtained from both methods at relatively higher degrees of hydration.

3 Statistically valid numerical relations which relate the degree of hydration to w/c ratio, age and curing temperature have been found to be in the following form:

$$DH(CH) = 135.76 - 230.92(w/c)^{-0.96} - 52.149(Age)^{0.193} + 0.664(Temp)^{0.89}$$

$$DH(W_n) = 131.54 - 0.085(w/c)^{-6.78} - 83.28(Age)^{-0.087} + 0.41(Temp)^{0.96}$$

4 A valid statistical relationship was found to exist between degree of hydration calculated from $Ca(OH)_2$ and non-evaporable water the in following form: $DH(CH) = 9.701 + 0.93DH(Wn)$ $r^2 = 0.96$

REFERENCES

1 **Cusens, A. R. and Cabrera, J. G.,** Developments in Concrete and Related Materials, "New Materials and their Application", Edited by S.G Burnay, Institute of Physics, Series No. 89, , 1987, pp. 237-249

2 **Cabrera, J. G., and Plowman, C.** , Morphological Changes in Hydrating C_3A System, Proceedings of the Third International Conference on Cement Microscopy, Texas, March, 1981.

3 **Cabrera, J. G. and Plowman, C.** , Hydration Mechanisms, Mineralogy and Morphology of the C_3S-PFA System , International Symposium on the use of PFA in Concrete, Leeds University, April, 1982.

4 **Cabrera, J. G. and Plowman, C.** , Hydration Mechanism and Rate of Attack of Sodium Sulphate Solution on Cement and Cement/PFA Pastes, Advanced in Cement Research Vol. 1, No. 3 July 1988.

5 **Cabrera, J. G. and Plowman, C.** Experimental Techniques for Studying Hydration Reaction of Calcium Aluminates, Advanced in Cement Research, Vol. 1, No. 4, Oct. 1988.

6 **Castro Gomes, J. P., Cabrera, J. G. and Jalali, S.** Modelling the Degree of cement Hydration Using Electronic Backscattered Imaging, Diamond Symposium, Hawaii, USA, October 1998.

7 **Cabrera, J. G. Plowman, C. and Hobson, E.,** Morphological changes in hydrating C_3A systems, Proceedings, 3 rd international conference on cement Microscopy, Houston, 1981, pp 363-73.

8 **Cabrera, J. G. , Claisse P. A. and Lynsdale, C. J.,** Application of microcomputers in the retrieval and processing of data in the study of the durability of reinforced concrete, RILEM Journal of Materials and Structures, Vol. 26., 1993, pp 587-593.

9 **Cabrera, J. G. and Plowman, C.** , Hydration and microstructure of High PFA content concrete, Proceedings of the International CIRIA Conference on Rolled Concrete for dams, London, June 1981 .

10 **Cabrera, J. G and Lynsdale, C. J.** , The Effect of Superplastisers on the Hydration of Normal Portland Cement, Industria Italiana del Cemento, No 712, July -August 1996, pp 532-541.

11 **Midgley, H. G.**, The determination of calcium hydroxide in set Portland cements, Cement and Concrete Research, Vol. 9, 1979, pp 77-82,

12 **Keattch, C. J. and Dollimore, D.**, An introduction to thermogravimetry, Heyden and Son Ltd. 2nd edition, 1975.

13 **Longout, P.,** The use of thermogravimetric measurements in cement chemistry, Proceedigs of the 5th inter. Symp. on the chemistry of cement, Vol. 1, Part , Tokyo, 1968. pp 239-251,

14 **Ramachandran, V. S.,** Differential Thermal Method of Estimating Calcium Hydroxide in Calcium Silicate and Cement Pastes, Cement and Concrete Research, Vol. 9, 1979, pp 677-684,

15 **Berry, E. E., Hemmings, R. T., Langley, W. S. and Carette, G. G.** Beneficiated fly ash: Hydration, Microstructure, and Strength development in Portland cement systems, Proceedings, Third Intentional conference, Trondheim, Norway, 1989, pp. 241-273.

16 **British Standards Institution BS 12: 1989** - Portland Cements. BSI, London, 1989, 666-942.

17 **Lea, F. M.,** The Chemistry of Cement and Concrete, 3rd edition, Edward Arnold Publishers London, 1980.

18 **Neville, A. M.,** Properties of Concrete, 3rd edition, Reprinted by Longman Scientific & Technical, 1986.

19 **Bye, G. C.,** Portland Cement, Composition, Production and properties, Pergamon Press, Materials Engineering Practice Series, 1983, pp 149,

20 Nilsson, L., Hygroscopic Moisture in Concrete- Drying measurements and related Materials Properties, Report TVBM 1003 Lund, Sweden, 1980, pp 162

21Taplin, J. H., A Method for Following the Hydration Reaction in Portland Cement Paste, Australian Journal of Applied Science, Vol 10, 1959, pp 329-345.

22 Greene, K. T., Early Hydration Reactions of Portland Cement, Proceedings of the 4th International Congress on, The Chemistry of Cement, Vol. I, Washington, 1960, pp. 359-385