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USING GGBS FOR PARTIAL CEMENT REPLACEMENT IN CONCRETE: EFFECTS OF WATER-BINDER RATIO AND GGBS LEVEL ON ACTIVATION ENERGY

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ABSTRACT

Ground granulated blast furnace slag (ggbs) is a waste material generated from iron production, and is one of the cementitious materials that can be used to replace part of the cement in concrete. The aim of this research was to determine the effects of the water-binder ratios and levels of ggbs in concrete, with regard to the activation energy, which is needed for predicting the concrete's strength. A number of mixtures with different water-binder ratios (ranging from 0.30 to 0.51), ggbs levels, and curing temperatures were cast and tested at 0.5, 1, 2, 4, 8, 16, and 32 days. The activation energies were determined using the American society for testing and materials (ASTM) standard C1074, and the Freiesleben Hansen and Pedersen (FHP) method. The results of the experiment showed that the apparent activation energy was relatively independent of the water-binder ratio, and mainly affected by the ggbs level in the concrete. Higher ggbs levels in the concrete resulted in the higher apparent activation energies.

Keywords: Activation energy; Cementitious materials; Curing temperature; ggbs level; Ground granulated blast furnace slag; Water binder ratio

1. INTRODUCTION

Currently, the use of supplementary cementitious materials, whether natural, waste, or by-product, has been an increasing trend in the manufacturing of composite cements, for ecological, economical, and diversified product quality reasons. Primarily, the contents of cement appear to be similar to those of the major oxides, SiO_2, CaO, Al_2O_3, and MgO, which are found in ground granulated blast furnace slag (ggbs). Recently, the UK has been using 2.5 million tons of ggbs as a cement replacement every year, preventing over 2 million tons of carbon dioxide emissions (Euroslag, 2013). Furthermore, Euroslag has reported that approximately 230 to 300 kg of slag can be produced from one ton of iron.

The accurate prediction of on-site concrete strength is very important, since it enables engineers to make decisions about accelerating construction schedules. The activation energy, E_a, is the minimum energy needed for a chemical reaction to occur (Wikipedia, 2015), and this term was introduced by the Swedish scientist Svante Arrhenius in 1889. Moreover, the value of the activation energy is one of the parameters needed for predicting the strength of concrete. This research will discuss the effects of the water-binder ratio and ggbs level on the value of the activation energy.

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1.1. Predicted Strength Development of Concrete

In 1951, Saul published the results of his work carried out at the Cement and Concrete Association Research Station, with regard to the principles of underlying steam curing at atmospheric pressure (Saul, 1951). For the first time, he introduced the term maturity, which is a product of the concrete time and curing temperature, and reported it as an indicator of strength gain. Furthermore, he recommended that the maturity should be determined with respect to temperature (-10.5^{o}C), indicating that at lower temperatures the hydration process will cease, with no strength obtained. The Nurse-Saul maturity function was calculated as follows (Kehl et al., 1998; Hansen & Pedersen, 1977):

$$M = \sum_{0}^{t} (T - T_0)\,\Delta t \quad (1)$$

where;
M : maturity or temperature-time factor at age t (^{o}C × days or ^{o}C × hours)
t : elapsed time or concrete age, days or hours
Δt : time interval, days or hours
T : average temperature of the concrete during the time interval Δt, ^{o}C
T_0 : datum temperature

Figure 1 below illustrates the maturity concept for concrete, which has been cured at different temperatures (lower and higher). Concrete cured at a lower temperature will take a longer time than that cured at a higher temperature to reach the same level of maturity.

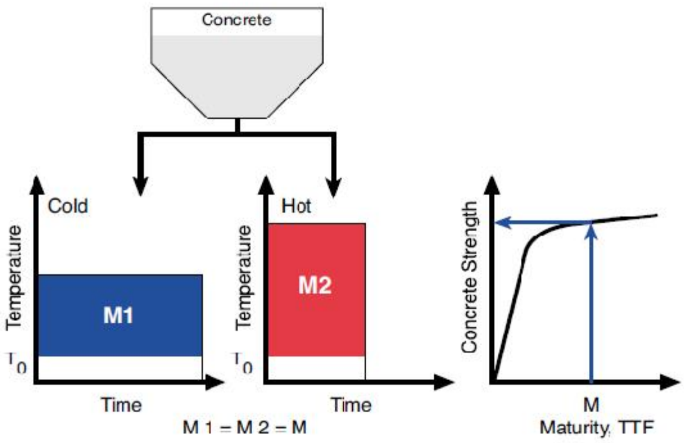

Figure 1 Saul's maturity rule using a temperature-time factor (Kehl et al., 1998)

Kehl et al. (1998) found that when the same concrete mixture was cured in both cold and hot conditions, it reached the same maturity when the temperature-time areas were equal, as seen in Figure 1: M1 = M2 = M. It is obvious that concrete will reach a certain maturity much quicker in hot curing conditions than in cold curing conditions; therefore, the time needed to reach the maturity of the two curing conditions will be different as well, as shown in the equation below (Tank & Carino, 1991):

$$t_e = \frac{\Sigma (T\ T_0)}{(T_r - T_0)}\ \Delta t \quad (2)$$

where;
t_e : equivalent age at the reference temperature T_r (which is usually 20^{o}C)

Furthermore, Equation 2 above can be written as the following:

$$t_e = \Sigma \beta \Delta t \tag{3}$$

where;

$$\beta \frac{(T\ T_0)}{(T_r - T_0)} = \frac{k}{k_r} \tag{4}$$

where;
β : age conversion factor
k : rate constant at temperature T
k_r : rate constant at reference temperature T_r

Freiesleben Hansen and Pedersen (FHP) proposed a method that was developed based on the Arrhenius equation to calculate the equivalent age, which can be mathematically expressed in the equation below (Hansen & Pedersen, 1977):

$$t_e = \sum_0^t e^{-\frac{E_a}{R}\left[\frac{1}{272+T} - \frac{1}{273+T_r}\right]} \Delta t \tag{5}$$

where;
E_a : apparent activation energy, J/mol
R : universal gas constant, 8.314 J/mol K

The age conversion factor can be calculated as follows:

$$\beta = e^{-\frac{E_a}{R}\left[\frac{1}{273+T} - \frac{1}{273+T_r}\right]} \tag{6}$$

The effect of the temperature on the age conversion factors of different maturity methods is illustrated in Figure 2 below.

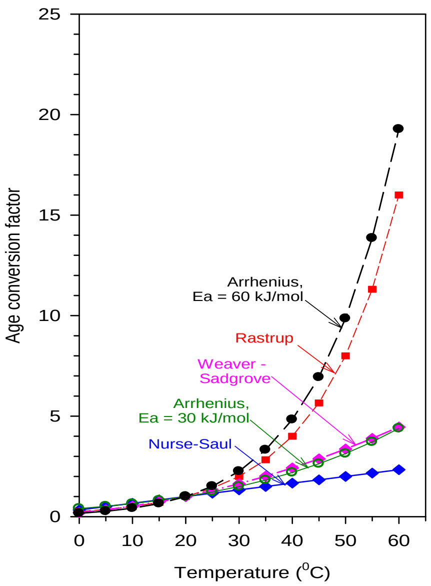

Figure 2 Age conversion factor vs. temperature (Turu'allo, 2013)

Figure 2 shows that at curing temperatures between 5 and 25^oC, all of the maturity methods present good agreement. However, the values of the age conversion factor were significantly different for all of the maturity methods, when the concrete was cured at higher temperatures (i.e. above 25^oC). The use of a higher value for the activation energy to determine the age conversion factor results in a huge difference in the value of the age conversion factor. Furthermore, the relationship between the age conversion factor and curing temperature becomes more nonlinear.

1.2. Activation Energy

FHP have been recognized as the first researchers to propose a method to calculate the activation energy. They proposed formulas to calculate the activation energy for curing temperatures of over (or equal to) 20^oC, and lower than 20^oC, as follows (Hansen & Pedersen, 1977; Malhotra & Carino, 2004):

$$\text{For } T \geq 20\text{ C},\ E_a = 33{,}500 \text{ J/mol} \tag{7}$$

$$\text{For } T < 20\text{ C},\ E_a = 33{,}500 + 1470\,(20 - T)\text{ J/mol, T is the curing temperature } (^oC) \tag{8}$$

Malhotra and Carino summarized the values of the activation energies for various types of cement, which were obtained by conducting experiments. The values of the activation energy varied from 41 to 67 kJ/mol, which were quite a bit higher than the values that were obtained using the FHP formulation. In general, Malhotra and Carino found that concrete mixes with a lower water-binder ratio have higher activation energy values. The effect of the water-binder ratio on the value of the activation energy has been a topic of discussion, up until now.

Additionally, Tank and Carino (1991) conducted research into the development of isothermal strength in concrete and mortar cubes. In their research, they applied different cementitious materials with two different water-binder ratios. Moreover, they verified that the value of the activation energy for a concrete mixture could be obtained from the strength data of a mortar specimen with the same water-binder ratio as the concrete. This experiment led to the use of equivalent mortar in determining the value of the activation energy of concrete, as recommended in ASTM standard C1074. Tank and Carino (1991) concluded the activation energy results from their work in Table 1, as follows:

Table 1 Activation energy values based on compressive strength tests of concrete cylinders and mortar cubes (Malhotra & Carino, 2004; Carino & Tank, 1992; Tank & Carino, 1991)

Cementitious Material	Activation Energy [kJ/mol]			
	w/c = 0.45		w/c = 0.60	
	Concrete	Mortar	Concrete	Mortar
Cement Type I	63.6	61.1	48.0	43.6
Cement Type II	51.1	55.4	42.7	41.1
Cement Type III	43.6	40.1	44.0	42.6
Cement Type I + 20% FA	30.0	33.1	31.2	36.6
Cement Type I + 50% Slag	44.7	42.7	56.0	51.3
Cement Type I + Accelerator	44.6	54.1	50.2	52.1
Cement Type I + Retarders	38.7	41.9	38.7	34.1

The values of the activation energy, which are given in Table 1 above, were remarkably higher than those gained by the FHP formulations. For the mix incorporating the ggbs, the lower water-binder ratio resulted in the lower value of the activation energy when compared to the mix with only Portland cement (Malhotra & Carino, 2004). However, it was conversely related to the value of the activation energy for the ggbs concrete with a higher water-binder ratio. Therefore, Malhotra and Carino recommended calculating the value of the activation energy using the data from the experiment, rather than using the typical values of the activation energy available in Table 1 above.

1.2.1. Determination of activation energy based on ASTM C1704

ASTM standard C1074 proposes one method to determine the value of the activation energy according to Arrhenius' law. This method was based on the experimental results from mortar cubes, which were cured isothermally at three or more different temperatures. An equivalent mortar mix of concrete was used to prepare the mortar cubes, and the mortar mix should have had a similar strength to that of the concrete being investigated. The mortar cubes were then tested at different ages to identify the strength development of the mortars cured at the different temperatures. Moreover, the strength-age relationship can be expressed as follows (Tank & Carino, 1991):

$$S = S_\infty \frac{k_t (t - t_0)}{1 + k_t (t - t_0)} \tag{9}$$

where;

S : compressive strength, N/mm^2

S_∞ : limiting strength, N/mm^2

t : actual curing at temperature T, hours or days

t_0 : age when strength development is assumed to begin, hours or days

k_t : rate constant determined by Arrhenius' equation, $hour^{-1}$ or $days^{-1}$

They also expressed the relationship between the activation energy, constant rate, and curing temperature, which can be written mathematically as follows:

$$E_a = R (T + 273) \ln \left(\frac{k_T}{A}\right) \tag{10}$$

where A is a constant ($days^{-1}$ or $hours^{-1}$).

Rearranging Equation 10 above gives the following equation:

$$\ln k_T = -\frac{E_a}{R (T + 273)} + \ln A \tag{11}$$

Furthermore, the value of the activation energy can be determined by plotting ln k_T against the reciprocal of the absolute value of the curing temperature (T+273), which is shown in Equation 11 above. A regression analysis was conducted to obtain a best-fit line, where the slope of the best-fit line was equal to $-Ea/R$.

1.2.2. Determination of activation energy based on the FHP method

The strength-age relationship was expressed in a different way by Freiesleben Hansen and Pedersen, as follows (Hansen & Pedersen, 1977):

$$S = S_\infty e^{\left(\frac{\tau}{t}\right)^a} \tag{12}$$

where τ and a are the characteristic time constant in hours^{-1} or days^{-1} and the shape parameter, respectively. With relation to the equivalent age t_e, Equation 12 can, therefore, be written as:

$$S\,(t_e) = S_{r,}\ e^{(\frac{\tau_r}{t_e})^a} \tag{13}$$

where;
$S\,(t_e)$: strength of mortar at equivalent age t_e, N/mm^2
τ_r : characteristic time constant at reference temperature, hour^{-1} or day^{-1}
$S_{r,\infty}$: limiting strength at reference temperature, N/mm^2

Poole et al. (2007) developed a correlation between the rate constant at temperature T and reference temperature T_r, with the hydration time parameters as shown in the following equation:

$$\frac{k\,(T)}{k\,(T_r)} = \frac{\tau_r}{\tau} \tag{14}$$

The apparent activation energy can then be determined according to the estimated hydration time parameters as follows:

$$-\frac{E_a}{R} = \frac{\ln\frac{\tau_T}{\tau_r}}{(\frac{1}{T_r} - \frac{1}{T})} \tag{15}$$

The equation above can be simplified as:

$$\ln\,(\tau) = -\frac{E_a}{R\,T_r} + \frac{E_a}{R\,T} + \ln\,(\tau_r) \tag{16}$$

Furthermore, the determination of the value of the activation energy can be accomplished by plotting the value ln (τ), which was obtained from the regression analysis using Equation 12 above, against the reciprocal of the absolute value of the curing temperature T, as shown in Equation 16. A regression analysis was then carried out in order to obtain a best-fit line, where the slope of the best-fit line was equal to E_a/R.

2. EXPERIMENTAL WORK

Two grades of concrete were used (C45 and C75), with ggbs levels of 0, 20, 35, 50, and 70% used to replace some of the cement in the concrete. The mortar equivalents to the concrete mixtures under investigation were prepared in accordance with ASTM standard C1074. A quantity of 0.30 m^3 of each mortar mixture was then prepared using a horizontal pan mixer. The materials were added in the following order over three minutes: cement/ggbs, sand, and water mixed with superplasticizers. Next, the mortar was cast into 50 mm 3-gang cube molds. The concrete was cast in a similar way, while the molds were filled in two phases and compacted. Then, the specimens were wrapped in cling film immediately after casting, transferred to a water tank set (if it was used), and mixed at 30, 40, and 50^{o}C. The cubes were demolded after curing for 24 hours, and transferred back into their curing tanks. The mortar cubes cured at 20^{o}C were covered with damp hessian and polythene sheeting and left on the vibrating table. After 24 hours, they were demolded and transferred to a water tank set at 20^{o}C, while the mortar cured at 10^{o}C was cured in a Temperature Match Curing (TMC) tank, which could be set to 10^{o}C. Subsequently, the mortar cubes were tested for compressive strength at the defined ages mentioned above (Turu'allo, 2013).

3. RESULTS

Based on Equation 9 above, a regression analysis was carried out by using a SigmaPlot to determine the curve of best-fit on a plot of the strength data of the cubes cured under the different isothermal curing temperatures of 10, 20, 30, 40, and 50^{o}C, against the age of each mortar cube. Linear regressions were conducted to obtain results for the S_∞, k, and t_0 for all of the mortars. The rate constants (k) obtained from the first regression analysis of each mixture were then plotted against the reciprocal of the absolute temperature in Kelvin degrees (K^{-1}) for both the mortar grades (C45 and C75; recommended in ASTM C1074), as shown in Figure 3 below. Then the second regression analyses were carried out based on Equation 11 above to determine the best-fit straight line of each mixture. Therefore, the slope of the best-fit straight line is equal to the $-E_a/R$, as shown in Equation 11, and the value of activation energy of all of the mortars can be calculated as presented in Table 3.

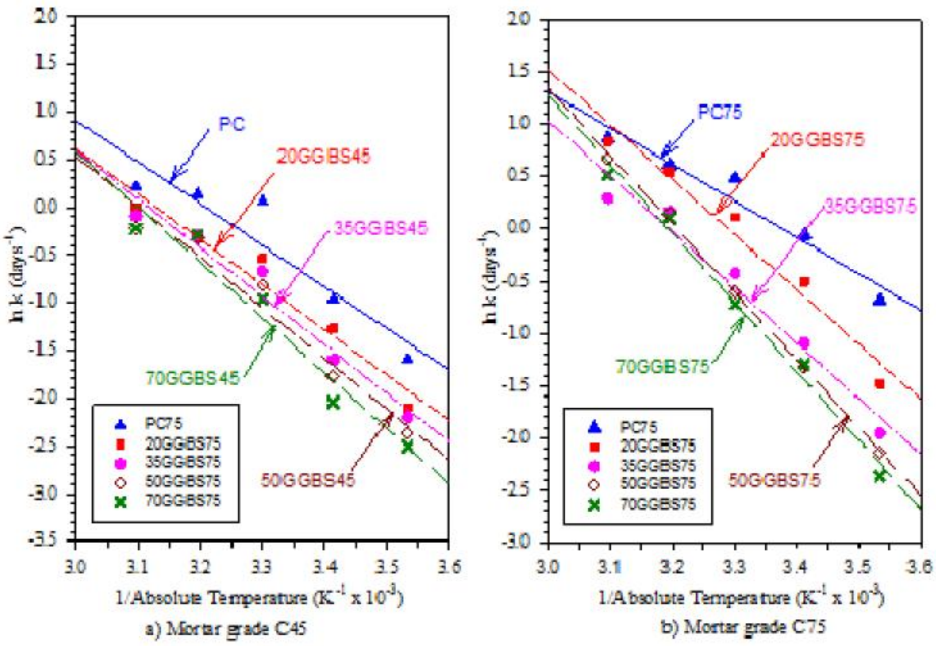

Figure 3 Natural logarithm of the rate constant (k) versus the reciprocal of the absolute temperature (K^{-1})

On the other hand, the characteristic time constant τ is needed to determine the value of the activation energy, based on the FHP method. The parameters of the characteristic time constant τ were plotted against the reciprocal of the absolute temperature (K^{-1}) for both mortar grades (C45 and C75).

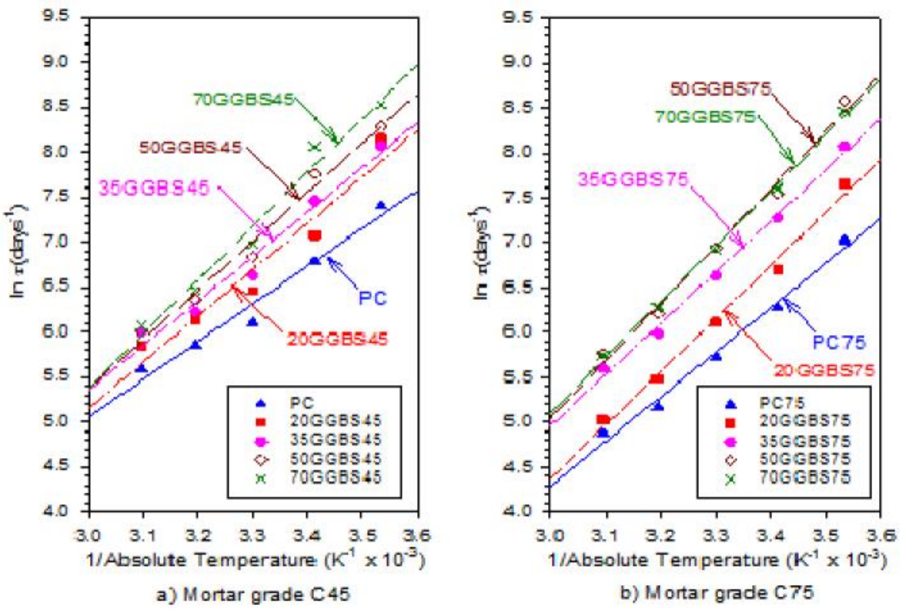

Figure 4 Natural logarithm of the characteristic time (τ) versus the reciprocal of the absolute temperature

The S_∞, τ, and a were obtained from the regression analysis based on Equation 12 above, by plotting the strength data against the age of each mortar cured at 10, 20, 30, 40, and 50^{o}C. Finally, regression analyses were carried out to find the best-fit straight line using Equation 16 above, where the slope of the line is equal to the Ea/R, as shown in Figure 4 above.

The values of the apparent activation energy obtained from each method (ASTM standard and FHP) were found to be similar, as presented in Table 2.

Table 2 Apparent activation energies for mortar grades C45 and C75, based on the ASTM C1074 and FHP methods

ggbs Level (%)	Activation Energy (kJ/mol) based on ASTM method		Activation Energy (kJ/mol) based on FHP method	
	Grade C45	Grade C75	Grade C45	Grade C75
0	36.18	28.87	34.88	37.13
20	39.42	43.54	42.71	43.83
35	42.33	44.03	43.58	44.14
50	44.05	53.89	45.34	46.65
70	48.24	54.71	49.65	49.79

Table 2 above shows that the values of the activation energies varied between 28 and 55 kJ/mol. For the mortars with the same grade, the higher the level of the ggbs, the higher the value of the activation energy. It also shows that the higher the activation energy, the higher the effect of the temperature on the strength development of the mortar mixtures.

The value of the apparent activation energies of the different concrete grades obtained from a previous study (Barnet et al., 2006), are presented in Table 3, for a comparison to the results from this work. These values were calculated based on ASTM standard C1074.

Table 3 Apparent activation energies for mortar grades C30, C60, and C90, based on ASTM standard C1074

ggbs Level (%)	Activation Energy (kJ/mol) based on ASTM method		
	Grade C30	Grade C60	Grade C90
0	34.8	35.1	32.9
20	36.6	35.2	36.8
35	47.1	47.0	46.8
50	54.6	48.0	52.6
70	58.8	62.1	57.9

4. DISCUSSION

All of the values of the activation energies obtained from the previous study (Barnett et al., 2006) for concrete grades C30, C60, and C90 and this work (grades C45 and C75) are plotted in Figure 5. Overall, the apparent activation energy shown in the figure is relatively independent from the water-binder ratio, and primarily dependent on the ggbs level in the binder.

It appears that higher replacement levels of ggbs in concrete lead to higher apparent activation energies. They increase approximately linearly with the increasing levels of ggbs in the concrete mixture; and the correlation factor obtained from the regression analysis was 96.85%. A linear regression analysis was carried out to establish a mathematical model to determine the value of the apparent activation energy of the ggbs concrete, as given in the following equation:

$$E_a = 31.98 + 0.3835\, r \tag{17}$$

where E_a is the value of the apparent activation energy (kJ/mol) and r is the ggbs level (%). This equation could be used to predict the value of the activation energy of concrete with other levels of ggbs.

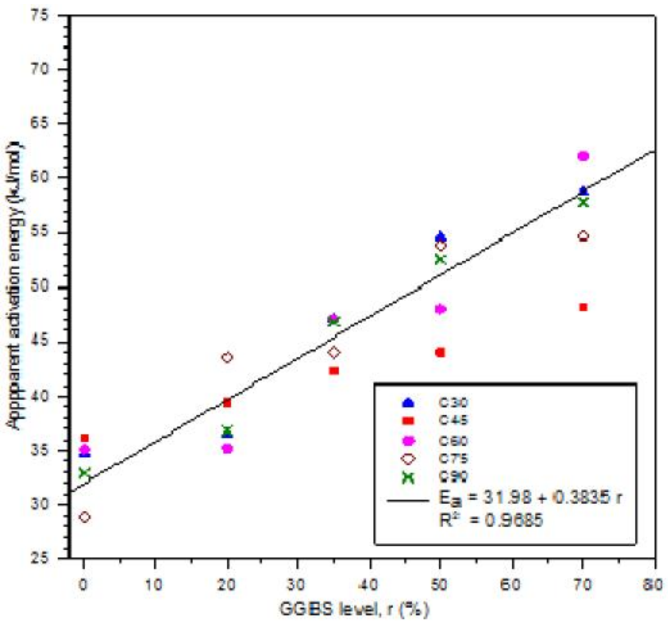

Figure 5 Apparent activation energies of varying mortar grades and ggbs levels

5. CONCLUSION

The values of the apparent activation energies (E_a) for both grades of concrete (C45 and C75) determined using the two methods (ASTM standard and FHP) were found to be similar. For concrete with the same grade, the higher the level of the ggbs, the higher the value of the activation energy. The apparent activation energy seemed to be less dependent on the water-binder ratio of the concrete, when compared to the ggbs levels of the concrete. Overall, the equation relationship between the activation energy and the level of ggbs obtained from the regression analysis can be used to reasonably predict the activation energy for other levels of ggbs in concrete.

6. REFERENCES

ASTM-C-1074, 2004. *Annual Book of ASTM Standards, Standard Practice for Estimating Concrete Strength by the Maturity Method*. West Conshoocken: ASTM International, pp. 2–8

Barnett, S.J., Soutsos, M.N., Millard, S.G., Bungey, J.H., 2006. Strength Development of Mortars Containing Ground Granulated Blast-furnace Slag: Effect of Curing Temperature and Determination of Apparent Activation Energies. *Cement and Concrete Research*, Volume 36(3), pp. 434–440

Carino, N.J., Tank, R.C., 1992. Maturity Function for Concretes Made with Various Cements and Admixtures. *ACI Materials Journal*, Volume 89, pp. 188–196

Euroslag, 2013. Granulated Blastfurnace Slag. Available online at http://www.euroslag.com/fileadmin/_media/images/Research/FACT_SHEETS/LeafletGBS.pdf, Accessed on June 2013

Hansen, P.F., Pedersen, E.J., 1977. Maturity Computer for Controlled Curing and Hardening of Concrete. *Nordisk Betong Journal*, Volume 1, pp. 21–25

Kehl, R.J., Constantino, C.A., Carrasquillo, R.L., 1998. *Match-cure and Maturity: Taking Concrete Strength Testing to a Higher Level*. The University of Texas at Austin

Malhotra, V.M., Carino, N.J., 2004. Handbook on Nondestructive Testing of Concrete. West Conshohocken, PA: *ASTM International*, Chapter 5, pp. 2–13

Poole, J.L., Riding, K.A., Folliard, K.J., Juenger, M.C.G., Schindler, A.K., 2007. Methods for Calculating Activation Energy for Portland Cement. *ACI Materials Journal*, Volume 104, pp. 303–311

Saul, A.G.A., 1951. Principles Underlying the Steam Curing of Concrete at Atmospheric Pressure. *Magazine of Concrete Research*, Volume 2, pp. 127–140

Tank, R.C., Carino, N.J., 1991. Rate Constant Functions for Strength Development of Concrete. *ACI Materials Journal*, Volume 88, pp. 74–83

Turu'allo, G., 2013. *Early Age Strength Development of Ggbs Concrete Cured under Different Temperatures*, Liverpool: Unpublished PhD Thesis

Wikipedia, 2015. *Activation Energy*. Available online at http://en.wikipedia.org/wiki/Activation_energy, Accessed on January 2015