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Hydration Model for Backward Predictive Analysis of Its Time Lag Based on Post-Experimental Values of Super Plasticizer Input and Compressive Strength of Concrete

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Abstract: This paper presents a hydration model for backward predictive analysis of its time lag based on post-experimental values of input concentrations of super plasticizer and compressive strength of concrete. The process parameters considered were of range 15.40 - 22.0(N/mm^2), 0-3.5(%) and 7-28 (days) for compressive strength of concrete, input concentration of super plasticizer and hydration period respectively. The water-cement ratio was 0.47. The derived hydration model; $H_p = 27.8 \ln V + 3.45e^{0.41\vartheta} + 72.35$evaluates the hydration period of the cement mix as a sum of two parts; logarithm of the compressive strength of concrete and exponential of the input concentration of super plasticizer. Results generated from the hydration model indicate that at constant water-cement ratio, compressive strength of the concrete increases with increase in hydration period and input concentration of super plasticizer, in accordance with previous work. The validity of the model was rooted on the core model expression $H_p + S =$ ƀ $\ln V + K e^{N\vartheta}$ where both sides of the expression are correspondingly almost equal. The standard error incurred in predicting the model-based hydration period relative to the actual results was 0.24%. Hydration period per unit input concentration of super plasticizer were 6.0 and 5.99(days/%) as obtained from actual and model-predicted results respectively. The maximum deviation of model-predicted hydration period with respect to actual results was < 2.5%. This translated into over 97% operational confidence levels for the derived model as well as 0.97 dependency coefficient of hydration period on concrete compressive strength & input concentration of super plasticizer. The correlation coefficients between hydration period and concrete compressive strength & input concentration of super plasticizer were all > 0.99.

Keywords: Hydration model -Backward predictive analysis -Hydration period -Compressive strength -Super plasticizer addition

INTRODUCTION

There has been a growing need for effective research and development to enhance the properties of produced concrete which includes durability and compressive strength.

Addition of super plasticizer enables production of concrete with a very high workability or strength. Research [1] has shown that the mechanism of super plasticizer involves ascribing to the cement particles highly negative charge so that they repel each other due to the same electrostatic charge. Super plasticizers have positive effects on properties of concrete, both in the fresh and hardened states. In the fresh state, super plasticizer normally reduce tendency to bleeding due to the reduction in water/ cement ratio or water content of concrete. However, if water/ cement ratio is maintained, there is tendency that super plasticizer prolong the time of set of concrete as more water is available to lubricate the mix. In the case of hardened concrete, the use of super plasticizer increases compressive strength by enhancing the effectiveness of compaction to produce denser concrete.

Several researchers [2-6] have carried out experiments to establish the properties of PLC concrete. Others have derived numerical models basically aimed at predicting the properties of PLC concrete. Some researchers [7, 8] proposed a model to evaluate the heat evolution rate of PLC. In this work, the effects of limestone on the diffusion-controlling stage and the reaction-controlling stage in cement hydration were considered. Attempt was made to simulate [9, 10] the

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hydration process and microstructure development of PLC concrete. In this work, the associated heat evolution rate and porosity were calculated using the degree of hydration.

An efficiency function was proposed [11] to consider the effect of limestone on the strength development of concrete. Another researcher [12] adopted the efficiency function evaluated in [11] for simulation of the heterogeneous nucleation effect of fly ash on cement hydration. Scientists [13, 14] simulated the hydration of PLC. The research involved modeling the dilution effect, physical effect and chemical effect. The physical and chemical effects are principally nucleation effect and formation of monocarboaluminate phase respectively. On the other hand, thermodynamic modeling of PLC was carried out [15]. The results of the model derivation ensured that the evolution of phase volume fractions of hydration products was calculated.

Based on the fore going, a lot of scientists [7-10, 15] have submitted that current hydration models majorly focused on cement-limestone hydration whereas some others [11-14] believed that the focus is on strength development.

There has been an assumption [16] that all of the binders in concrete would hydrate regardless of water-to-binder ratio. Similar research [8] reported that concrete with a lower W/B has a lower ultimate degree of hydration and a slower hydration rate. It was also observed [17, 18] that the carbonation resistance of concrete was significantly enhanced on extending the curing period.

Hydration Model for Cement: An enhanced shrinking-core model has been proposed [19] to simulate Portland cement hydration. The shrinking core model looked at the influences of the cement compound composition, capillary water contents and W/C ratio on cement hydration. Results of the derived model show that the hydration model analyzes the kinetic processes during cement hydration. These processes include initial dormant period, the diffusion controlled process and the activated chemical reaction controlled process. The equation for the hydration model is shown thus:

$$\frac{d\alpha}{dt} = \frac{3(S_w/S_0)\,\rho_w C_{w}\text{-free}\ 1}{(v + wg)(1/k_d - r_0/De) + r_0/De(1-\alpha) + 1/k_r\,(1-\alpha)^{-2/3}} \tag{1}$$

where α represents the reaction degree of cement, D_e is the reaction coefficient in the diffusion-controlled stage, k_d is the reaction coefficient in the initial dormant period, k_r is the reaction coefficient of the boundary reaction process, ν denotes the stoichiometric ratio by mass of water to mass of cement (= 0.25), w_g denotes the physically bound water in hydration products (= 0.15; the values of ν and w_g depend on the compound compositions of cement [8]. In this study, for simplicity, fixed values for ν and w_g are used), ρ_c denotes the density of the cement, ρ_w denotes the density of water, C_w-freede notes the amount of capillary water at the exterior of hydration products, $r_0$denotes the radius of un hydrated cement particles (r_0=3),where,

$$\frac{S_c}{\rho_c S_c} \tag{1a}$$

is the Blaine surface area of cement), S_w denotes the effective contacting surface area between the cement particles and capillary water, and S_0 denotes the total surface area if hydration products develop unconstrained.

The initial dormant period consists of the formation of an initial impermeable layer and the destruction of this impermeable layer. Therefore, the rate of hydration decreases because of the formation of this impermeable layer. Conversely, the rate of hydration increases when this impermeable layer is destroyed. The reaction coefficient, k_d, can be determined as follows:

$$k_d = \frac{B + C\alpha^3}{\alpha^{1.5}} \tag{2}$$

where B is the rate of the initial impermeable layer formation, and C is the rate of the initial impermeable layer decay. The parameter, D_e, represents the rate of cement hydration in the diffusion-controlled stage. D_e can be calculated as a function of the degree of hydration, as follows:

$$D_e = D_{e0} \ln\left(\frac{1}{\alpha}\right) \tag{3}$$

where D_{e0} is the initial diffusion coefficient.

The amount of water in the capillary pores, $C_{w\text{-}free}$, is determined as a function of hydration degree as shown in Equation (4).

$$C_{w\text{-free}} = \left(\frac{W_0 - 0.4 * \alpha * C_0^{r}}{W_0}\right) \tag{4}$$

Here * is a multiplication sign, r is an empirical parameter that considers the accessibility of water into an inner anhydrous part through an outer hard shell of cement particles, W_0 is the water content in the mix proportion, C_0 is the cement content in mixing proportion, When the W/C ratio is higher than 0.4, r = 1.0 ; and when W/C is less than 0.4, because of the increasing constrictively and tortuosity in capillary pores and decreasing of pore connectivity, r is higher than 1, and r can be determined as:

$$\gamma = 2.6 - 4\left(\frac{W_0}{C_0}\right)[19] \quad (5)$$

For high-strength concrete with low W/C ratio at late ages, $C_{w\text{-}free}$ has significant influence on the rate of hydration.

A successful study [20] has been carried out to clearly evaluate the dependence of the reaction coefficients of the hydration model in cement compound compositions. In this research, five types of Portland cement were used: ordinary Portland cement, early hardening cement, moderate-heat cement, low-heat cement, and be lite-rich cement. The results of the study enabled establishment of the relationship between the hydration reaction coefficients and the cement compound compositions based on the analysis of the degree of hydration and the adiabatic temperature rise during hardening of the concrete. These relationships are shown as follows:

$$B_{20} = 6 \text{ x}10^{-12} \text{ x}(C_3S\% + C_3A\%) + 4\text{x}10^{-10} \quad (6)$$

$$C_{20} = 0.0003 \text{ x } C_3S\% + 0.0186 \quad (7)$$

$$kr_{20} = 8 \text{ x}10^{-8}\text{x } C_3S\% + 1 \text{ x}10^{-6} \quad (8)$$

$$D_{e20} = -8 \text{ x}10^{-12}\text{x } C_2S\% + 7 \text{ x}10^{-10} \quad (9)$$

$$\beta_1 = 1000 \quad (10)$$

$$\beta_2 = 1000 \quad (11)$$

$$E/R = 5400 \quad (12)$$

$$\beta_2 = 7500 \quad (13)$$

Observation has indicated that the cement hydration model is valid for concrete with various mixing proportions (ordinary strength concrete and high-strength concrete), various curing temperature histories, and different cement types.

The input parameters of the hydration model are cement compound compositions, Blaine surface area, concrete mixing proportions and concrete curing temperatures.

By using input parameters, the values of coefficients of the hydration model can be determined using equations (6)-(13). Furthermore, the time-dependent degree of hydration can be calculated using equation (1).

Different teams of scientists [8, 14] have reported that limestone particles can provide additional sites for the nucleation and growth of cement hydration products, which invariably enhances the cement hydration. It has been revealed [8] that cement-limestone blend scan only occur if hydrates are similarly formed on the overall surfaces of both particles of cement and limestone powder. The results of this work showed that outer layer of hydrates could be precipitated from the eluted ion phase at any location, even away from cement particles, and all surface areas of particles can contribute as a precipitation site. In this study, the ratio of surface area between limestone powder and cement is used as an indicator to express the acceleration effect of limestone powder on cement hydration. This indicator is expressed as follows:

$$L_r = \frac{LS_0 \text{ x } S_{LS}}{C_0 \text{x } S_C} \quad (14)$$

where L_r is the limestone nucleation effect indicator, $LS_0$is the mass of limestone in concrete mixing proportions, and S_{LS} is the Blaine surface area of limestone powder.

Research [21] has shown that at constant water-cement ratio, the compressive strength of concrete is significantly affected by the hydration period and addition of super plasticizer. The aim of this study is to derive empirically a hydration model which will give a backward predictive analysis of the elapsed hydration period, based on the post-experimental values of input concentrations of super plasticizer and the compressive strength of concrete produced. This model can evaluate the expected hydration period, if the post-experimental values of the quantity of super plasticizer added to the cement mix and the concrete compressive strength is also known. With achievement of reproducibility in the research, hydration periods could be predicted by just assigning desired values to the concrete compressive strength and input concentration of super plasticzer, and then substituting them into the hydration model that will be derived.

MATERIALS AND METHODS

The concrete cube size measuring 150x150x150mm in dimension was used. The batching of the concrete cubes was by weight. The concrete was produced using a range of process parameters: super plasticizer input concentration; 0-3.5% and hydration period; 7-28 days. The water-cement ratio is 0.47. The cement used is Ordinary Portland Cement (Eagle) and the super plasticizer (Poly carboxylic ether) produced and marketed by Chinese company in Lagos was also used as an admixture.

The coarse aggregate used is granite and clean river sand was used as fine aggregate. The aggregates, fine sand and cement all conform to the standards. The concrete cubes were lubricated with oil before the mixed concrete was placed inside it in order to reduce friction between the concrete and the cubes. When the concrete was properly mixed, the concrete cubes were filled one-third of their height and compacted 150 times. The cubes were later filled to two-third of their height and finally filled completely. In each of the layer, the concrete cubes were compacted 150 times respectively. The concrete cubes were cast and cured for 7, 10, 14, 17, 21, 25 and 28 days respectively. At the end of each hydration period, the concrete cubes were crushed to determine, their compressive strength [21].

RESULTS AND DISCUSSION

Table 1: Variation of hydration period H_p, with compressive strength of concrete Ѵ and concentration of super plasticizer ϑ respectively [21]

(ϑ)	(Ѵ)	H_p
0	15.40	7
0.9	16.08	10
2.0	16.98	14
2.2	18.27	17
2.5	20.00	21
3.1	21.14	25
3.5	22.00	28

Computational analysis of the actual results shown in Table 1, gave rise to Table 2 which indicate that;

$$H_p + S = \text{ђ} \ln Ѵ + K e^{N\vartheta} \quad (15)$$

Introducing the value of S, ђ, K and N into equation (15) reduces it to;

$$H_p + 72.35 = 27.8 \ln Ѵ + 3.45e^{0.41\vartheta} \quad (16)$$

Re-arranging equation(16);

$$H_p = 27.8 \ln Ѵ + 3.45e^{0.41\vartheta} + 72.35 \quad (17)$$

The derived model is equation (17).

where
S = 72.35, ђ = 27.8, K = 3.45, N = 0.41; equalizing constants (determined using C-NIKBRAN [22])

(H_p) = Hydration period (days)
(ϑ) = concentration of super plasticizer (%)
(Ѵ) = Compressive strength of concrete (N/mm^2)

Boundary and Initial Conditions: A cube sized concrete block 150 x 150 x 150mm produced from a mixture of sand, aggregates and cement was considered and subjected to compressive test using appropriate crushing loads. The concreter is assumed to be unaffected by dissolved gases in the atmosphere.

The considered ranges of the compressive strength of concrete, input concentration of super plasticizer and hydration period are15.40 - 22.0N/mm^2, 0- 3.5% and 7-28 days respectively. The water-cement ratio is 0.47.

Table 2: Variation of H_p+ S with ђ lnѴ + Ke$^{0.41\vartheta}$

H_p + S	ђ lnѴ + K e$^{0.41\vartheta}$
79.35	79.47
82.35	82.21
86.35	86.56
89.35	89.27
93.35	92.90
97.35	97.46
100.35	100.42

Model Validity: Validation of the proposed model Equation (17) is the derived hydration model. The validity of the model is rooted on the core model equation (15) where both sides of the equation are correspondingly almost equal. Table 2 also agrees with equation (15) considering values of H_p + S = ђ lnѴ + Ke$^{N\vartheta}$ evaluated from the actual results in Table 1. Furthermore, the derived model was validated by comparing the hydration period predicted by the model and that obtained from the experiment. This was done using various analytical techniques which includes computational, statistical, graphical and deviational analyses.

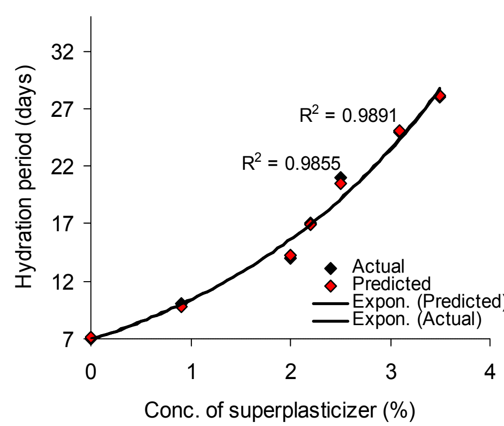

Fig. 1: Coefficient of determination between hydration period and concentration of super plasticizer input as obtained from actual and model-predicted results

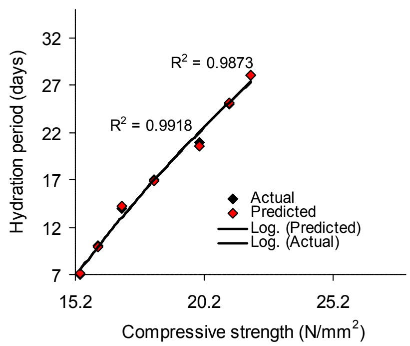

Fig. 2: Coefficient of determination between hydration period and compressive strength of concrete as obtained from actual and model-predicted results

Computational Analysis: Hydration period per unit input concentration of super plasticizer.

The hydration period per unit input concentration of super plasticizer $H_{P\text{-}\vartheta}$ (N/mm^2)/ %was calculated from the equation;

$$H_{P\text{-}\vartheta}=H_P / \vartheta \quad (18)$$

Re-written as

$$H_{P\text{-}\vartheta}=\Delta H_P/ \Delta\vartheta \quad (19)$$

Equation (19) is detailed as

$$H_{P\text{-}\vartheta}=H_{P2} - H_{P1}/\vartheta_2 - \vartheta_1 \quad (20)$$

where

$H_{P\text{-}\vartheta}$ = Change in the hydration periods H_{P2}, H_{P1} at Input concentrations of super plasticizer ϑ_2, ϑ_1.

Considering the points (0, 7) & (3.5, 28) and (0,7.12) & (3.5,28.07) as shown in Fig. 3, designating them as (ϑ_1, H_{P1}) & (ϑ_2, H_{P2}) for actual and model-predicted results, and then substituting them into equation (20), gives the slopes: 6.0 and 5.99 days/%respectively as hydration period per unit input concentration of super plasticizer. Previous research [21] shows that at constant water-cement ratio, compressive strength of the concrete increases with increase in hydration period and input concentration of super plasticizer. The hydration model has shown (as in Figs. 1-4) remarkable degree of validity by predicting same trend of results distribution as in previous work [21].

Statistical Analysis

Correlation: The correlation coefficient between hydration period and compressive strength &concentration of super plasticizer were evaluated by substituting values of the coefficients of determination R^2 (obtained using Microsoft Excel Version 2003) from results of the actual and derived model (in Figs 1 and 2) into equation (21). These results are 0.9959 and 0.9936 & 0.9927 and 0.9945, respectively.

$$R=\sqrt{R^2} \quad (21)$$

Standard Error (STEYX): The standard error incurred in predicting the model-based hydration period relative to values of the actual results is 0.24%. The standard error was evaluated using Microsoft Excel version 2003.

Graphical Analysis: The validity of the derived model was further verified by plotting values of the actual, besides the model-predicted results using Microsoft Excel (version 2003) to evaluate the trend of both results. Figs. 3 and 4 indicate very close alignment of curves which depicted significantly similar trend of data point's distribution for the actual and derived model-predicted hydration periods. This shows proximate agreement between both results.

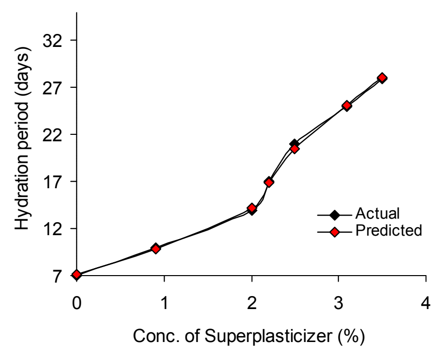

Fig.3: Variation of hydration periods with concentration of super plasticizer input as obtained from actual and model-predicted results

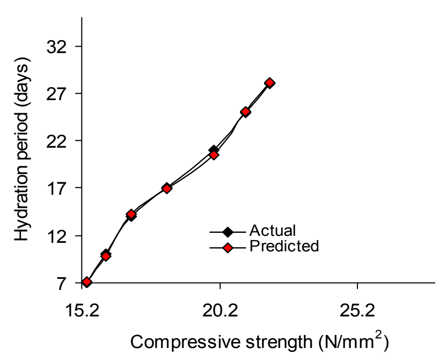

Fig. 4: Variation of hydration periods with concrete compressive strength as obtained from actual and model-predicted results

Deviational Analysis: Analysis of the hydration periods obtained from the actual and model-predicted results shows single digit deviation of model-predicted results from the actual. This was attributed to the fact that the effects of the surface properties of the cement which played vital roles during the hydration were not considered during the model formulation. This necessitated the introduction of correction factor, to bring the model-predicted hydration period to those of the corresponding experimental values.

The deviation Dv, of model-predicted hydration model from the corresponding actual result was given by;

$$Dv \left(\frac{H_{P-P} - H_{P-E}}{H_{P-E}} \right) x\ 100 \quad (22)$$

where,

H_{P-E} and H_{P-P} are hydration periods evaluated from experiment and derived model respectively.

Fig. 5 shows that maximum deviation of model-predicted hydration period from the actual results was less than 2.5%. This translates into over 97.5% model operational confidence. The figure shows that the least and highest deviations of model-predicted results (from actual results) are 0.25 and -2.14 %.

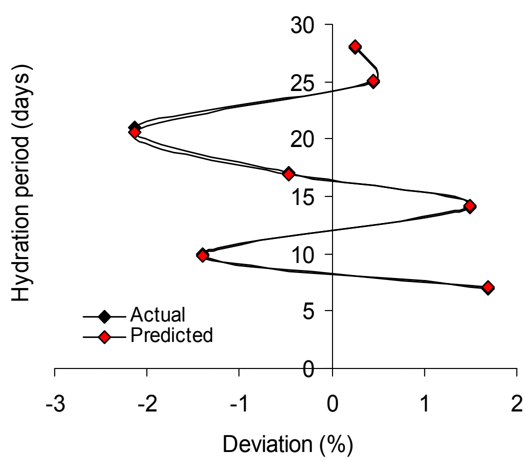

Fig. 5: Deviation of model–predicted results from actual values relative to hydration period

These deviations correspond to model-predicted hydration periods: 28.07 and 20.55 (days); compressive strengths of concrete: 22.0 and 20.0 (N/mm^2); concentrations of super plasticizer input: 3.5 and 2.5(%) respectively.

Correction factor, Cf to the model-predicted results was given by;

$$Cf = - \left(\frac{H_{P-P} - H_{P-E}}{H_{P-E}} \right) x\ 100 \quad (23)$$

Figs. 5 and 6 show that the evaluated correction factors are negative of the deviation as shown in equations (22) and (23).

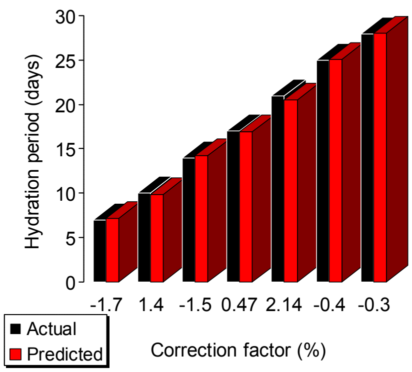

Fig. 6: Correction factor to model–predicted results relative to hydration period

The correction factor took care of the negligence of operational contributions of the effects of surface properties of the cement which actually affected the concrete hydration process. Introduction of the corresponding values of Cf from equation (23) into the model gives exactly the corresponding actual hydration period. Fig 6 indicates that the maximum correction factor to the model-predicted results was less than 2.5%. Fig 6 shows that the least and highest correction factors to the model-predicted results are - 0.25 and 2.14%. These deviations correspond to model-predicted hydration periods: 28.07 and 20.55 (days); compressive strengths of concrete: 22.0 and 20.0 (N/mm^2); concentrations of super plasticizer input: 3.5 and 2.5 (%) respectively.

It is pertinent to state that the negative and positive signs preceding numerals in reporting deviation and correction factors merely indicate deficit and surplus respectively. The actual deviation or correction factor is just the numeral.

CONCLUSION

A hydration model has been derived for backward predictive analysis of its time lag based on post-experimental values of input concentrations of super plasticizer and the compressive strength of concrete produced. The derived hydration model; H_p =27.8 lnV + 3.45e$^{0.419}$ + 72.35 evaluates the hydration period of the cement mix as a sum of two parts; logarithm of the compressive strength of concrete and exponential of the input concentration of super plasticizer. Model-predicted results indicate that at constant water-cement ratio, compressive strength of the concrete increases with increase in hydration period and input concentration of super plasticizer, in accordance with previous work. The validity of the model was rooted on the core model expression H_p + S = Ƀ lnV + K e[Nϑ] where both sides of the expression are correspondingly almost equal. The standard error incurred in predicting the model-based hydration period relative to the actual results was 0.24%. Hydration period per unit input concentration of super plasticizer were 6.0 and 5.99 (days/ %) as obtained from actual and model-predicted results respectively. The maximum deviation of model-predicted hydration period with respect to actual results was < 2.5%. This translated into over 97% operational confidence levels for the derived model as well as 0.97 dependency coefficient of hydration period on concrete compressive strength & input concentration of super plasticizer. The correlation coefficients between hydration period and concrete compressive strength & input concentration of super plasticizer were all > 0.99.

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