Measurement of Apparent Activation Energy of Portland Cement Based Materials

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ABSTRACT

The apparent activation energy of Portland cement based materials is a critical parameter for the calculation of maturity and equivalent age characteristics of concrete. The traditional, standardized method (ASTM C1074) utilizes the monitoring of temperature-time history and the compressive strength testing of specimens. In this research, the use of isothermal conduction calorimetry for the determination of apparent activation energy is investigated and compared with the traditional, standardized method. Several computational methods are used for the calculation and comparison of the apparent activation energy of cementitious materials using the isothermal conduction calorimetry testing. Accordingly, several techniques are used for the comparison of the apparent activation energy using compressive strength methods.

INTRODUCTION

❖The calculation of maturity and equivalent age of cementitious materials requires the time-temperature history in order to calculate rate of reaction (k) and apparent activation energy (E_a)[1].

❖ The calculation of equivalent age by the Arrhenius equation has been the equation most often used to describe the equivalent time per standardized test methods[2] and a large portion of available research.

❖The Arrhenius equation as proposed by Freiselben-Hansen and Pederson[3] is used to calculate equivalent time per equation 1.

$$t_e=\int_0^t e^{Q\left(\frac{1}{273+T_a}-\frac{1}{273+T_r}\right)}dt \qquad (1)$$

Where:
t_e = equivalent age at a specified temperature
Q = activation energy divided by the universal gas constant
T_a = average temperature (°C) of the concrete during the time interval dt
T_r = Specified temperature, (typically 23°C US, 20°C Europe)

❖Per the standardized test method[4], the calculation of maturity and equivalent age the testing of mortar cubes and concrete cylinders is conducted at early ages under isothermal conditions.

❖A hyperbolic equation is used to model the compressive strength evolution per equation 2.

(2)
$$S=S_u\frac{k(t-t_0)}{1+k(t-t_0)}$$

Where:
S = compres
t = test age (hours)
S_u = limiting strength / ultimate strength
t_0 = age when strength development is assumed to begin (hours)
k = rate constant

❖S_u, k and t_0 can be calculated using a best fit, curve fitting software.

❖The apparent activation energy is calculated by plotting the natural logarithm of the "k" values by the reciprocal of the absolute temperature.

BACKGROUND

❖Newer models have been proposed for the calculation Ea based on compressive strength testing which use an exponential equation to model compressive strength evolution over time as per equation 3[4].

(3)
$$S=S_u\cdot\exp\left(-\left(\frac{\tau_s}{t_e}\right)^{\beta}\right)$$

Where:
S_u = ultimate strength
t_e = test age (hours)
β = shape constant
τ = time constant for strength prediction

❖Newer models have been proposed for the calculation of Ea based on isothermal calorimetry testing[5,6].

❖ The development of a commercially available isothermal conduction calorimeter for small cementitious specimens (4-20g) has resulted in the development of models which calculate degree of hydration based isothermal conduction calorimetry testing results[6] as shown by equation 4[4,7].

(4)
$$\alpha=\alpha_u\cdot\exp\left(-\left(\frac{\tau_s}{t}\right)^{\beta}\right)$$

Where:
α = degree of hydration
t = test age (hours)
α_u = degree of ultimate hydration
β = shape constant
τ = time constant for strength prediction

❖Via the use of the isothermal calorimetry, and equation 3, the E_a is determined by equation 5, which is essentially the slope of the –ln(t) vs. 1/Temperature[7].

(5)
$$E_a=-\frac{\ln\left(\frac{\tau_{ref}}{\tau_c}\right)}{\left(\frac{1}{T_{ref}}-\frac{1}{T_c}\right)}\cdot R$$

Where:
τ_{ref}= hydration time parameter at reference temperature
τ_c= is reference temperature

OBJECTIVES

❖The objectives of this research include modeling the Ea and prediction of physical behavior of cementitious materials using the following methods:
–ASTM 1074 (hyperbolic method) using compressive strength of cubes
–Exponential method using compressive strength of cubes
–Exponential method using isothermal conduction calorimetry

MATERIALS

Table 1. Mixture Design Properties for Specimens *

Material	Mix 1 100% Portland Cement (lb/yd³)	Mix 2 50% Portland -50% Slag (lb/yd³)	Mix 3 65% Portland - 35% Fly ash (lb/yd³)	Mix 4 50-30-20 blend (lb/yd³)
Cement	681	341	443	341
Fly ash	0	0	238	136
GGBF Slag	0	341	0	204
Water	341	341	341	341
Fine Agg.	1095	1088	1036	1050
Coarse Agg.	1650	1668	1660	1650

*Coarse aggregate was not used for testing for Ea, fine aggregate was not used in for isothermal conduction calorimetry testing.

RESULTS

❖The models for the prediction of mortar strength using the hyperbolic vs. exponential:

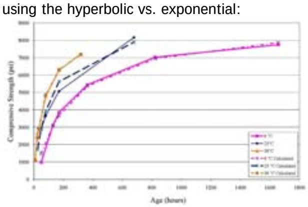

Figure 1. ASTM 1074 / hyperbolic calculated vs. measured compressive strength

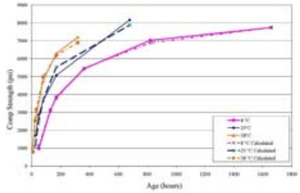

Figure 2. Exponential calculated vs. measured compressive strength

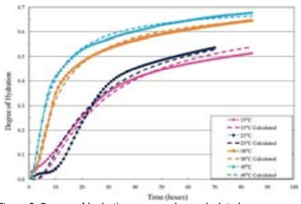

Figure 3. Degree of hydration measured vs. calculated per isothermal conduction calorimetry

Table 1.Comparision of E_a Calculation Methods

Mix Name	Compressive strength of mortar cubes: Hyperbolic (ASTM 1074)	Compressive strength of mortar cubes: Exponential	Isothermal Testing: Exponential
Mix 1	35642	37401	34235
Mix 2	33688	39932	50400
Mix 3	25757	20643	32982
Mix 4	30013	21158	37330

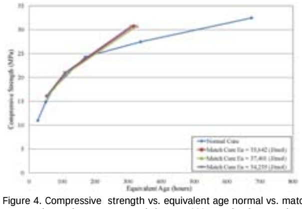

Figure 4. Compressive strength vs. equivalent age normal vs. match cure at elevated temperatures (Mix 1 - 100% portland cement)

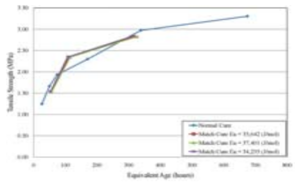

Figure 5. Tensile strength vs. equivalent age normal vs. match cure at elevated temperatures (Mix 1- 100% portland cement)

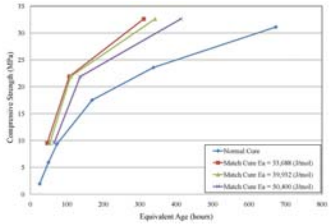

Figure 6. Compresisve strength vs. equivalent age normal vs. match cure at elevated temperatures (Mix 2- 50% portland - 50%Slag)

❖The variation of Ea is not large regardless of calculation / testing method for concrete composed of Portland cement only

❖The variation of Ea is significant based on test calculation / testing method in concrete with large replacements of portland cement

❖The prediction of physical properties based on equivalent age are relatively consistant regardless of Ea calculation method for concrete with portland cement alone.

❖The prediction of physical properties of concrete containing large replacements of GGBF slag based on laboratory cured concrete underestimates strength properties.

CONCLUSIONS

❖The hyperbolic model is just as adequate as the exponential model for the prediction of early age physical properties of concrete[1] composed of Portland cement

❖ More research is needed to verify the accuracy of prediction of concrete with large replacements of portland cement

❖Research should be conducted to establish links between Ea and phase morphology of cementitous materials

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