MODELLING OF ISOTHERMAL HYDRATION HEAT OF CEMENT PASTES WITH FLY ASH

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Abstract

When fly ash is used as partial replacement material for cement, the cement hydration and the pozzolanic reaction of fly ash interact with each other. Free lime, formed during the hydration of cement, creates a condition for the pozzolanic reaction, where the calcium hydroxide is consumed. In concrete structures, thermal stresses, mainly caused by the release of heat during the hydration of the binder, can lead to serious durability issues. In the past, isothermal calorimetry has been performed to quantify the hydration of cement, but up to now no model is available for predicting the heat of hydration released by a cement-fly ash binder. In our laboratory four cement-fly ash pastes were made with different fly ash-to-cementitious material ratios and with a constant water-to-cementitious material ratio of 0.4. The hydration heat of the mixtures was measured isothermally at three different environment temperatures. The activation energy was calculated using the Arrhenius equation. A model for Portland cement and blast furnace slag cement could be adapted for cement- fly ash mixtures to quantify the measured heat of hydration.

1. Introduction

International climate agreements, such as the Kyoto Protocol or the Burden Sharing Agreement, result in an increased pressure to use more environment-conscious materials. To lower the CO_2-emissions, emitted during the production of Portland cement, more fly ash can be used in a cement composition. Besides from its use as a countermeasure to reduce the amount of CO_2-generation, fly ash also reduces the cost of the concrete production by conserving energy and resources. Small quantities of fly ash also have a positive influence on the durability of concrete [1]

At normal temperatures the pozzolanic reaction is a slower process than the cement hydration. Hanehara et al (2001) report that the starting time of the pozzolanic reaction at a curing temperature of 20°C is at the age of 28 days, but this time highly depends upon the curing temperature [2]. This results in a significantly lower compressive strength of concrete at young age, when the cement content is partially substituted by fly ash [3,4]. Special curing regimes such as prolonged moist curing may have to be used to ensure the desired concrete properties and an adequate early strength development [5]. Based on hydration kinetics, previous research reports an increase of the hydration degree of cement and a decrease of the pozzolanic degree of fly ash with increasing fly ash content [6,7]. Sakai et al (2004) confirm that the hydration of alite in the cement hydration is accelerated and that of belite is retarded at a later age. They also mention that by increasing the glass content in fly ash in cured specimens, the hydration ratio of fly ash could be increased. When the glass content of fly ash is low, the basicity of glass phase tends to decrease [8].

Thermogravimetric tests performed previously on portland cement pastes as well as on cement-fly ash binders showed that the calcium hydroxide content of the binder with only portland cement increases with time, while of the binders with fly ash and portland cement it increases till it reaches an ultimate value around 3 days, from when it starts to decrease or remains constant [9]. This is an indication that the pozzolanic reaction has started.

2. Materials and experimental program

2.1. Materials

An ordinary portland cement (CEM I 52.5 N), complying with the European Standard EN 197-1 (2000) was used in all mixtures. In this study the detailed effect of a fly ash, Class F according to ASTM Standards and with a low calcium oxide content according to EN 450, was studied on the hydration process of a portland cement–fly ash binder. Table 1 lists the chemical compositions of the portland cement and fly ash according to the EN 196-2, together with the free CaO of the fly ash, determined in accordance with NBN EN 450-1.

Tabel 1: Chemical composition of the ordinary Portland cement and fly ash

	CEM I 52.5 N	Fly ash
SiO_2 (%)	19.6	51.3
Al_2O_3 (%)	4.9	4.0
CaO (%)	63.6	3.5
Fe_2O_3 (%)	3.1	1.3
MgO (%)	0.9	1.9
SO_3 (%)	3.3	0.9
LOI (%)	2.1	4.0
Free CaO (%)	-	0.02

2.2. Experimental set-up

Table 2 summarizes the mixture proportions of the four investigated binder pastes. The water to cementitious materials ratio was kept constant at 0.40.

Table 2: Mixture proportions

Mix	Cement (g)	Fly ash (g)	W/CM (-)	W/C (-)	FA/CM (-)
Reference	7.50	0.00	0.40	0.40	0.00
FA35W40	4.50	3.00	0.40	0.67	0.40
FA50W40	3.75	3.75	0.40	0.80	0.50
FA67W40	2.48	5.02	0.40	1.21	0.67

Immediately after mixing, 14 grams of each binder paste were placed in a calorimeter to measure isothermally the exothermal hydration process. This test was performed for each binder mixture three times for three different isothermal conditions: 10°C, 20°C and 35°C. At 10°C, the calorimeter was flushed with dry air to prevent condensation. The heat evolved per time unit was monitored and recorded at 20-seconds intervals.

3. Results

Immediately after mixing a first peak appears. Because the mixing takes place outside the calorimeter, this peak has not been measured entirely. In practice, concrete is not cast immediately after water addition : the heat corresponding to the first peak remains in the concrete mixer and only contributes to a slightly higher initial temperature [10,11,12,13]. The heat generation during the first peak only amounts to a few percent of the total heat liberated. The first peak can be left out from the further analysis [10,11]. The second correction performed on the measured data is due to the bias of the calorimeter. From previous investigations it was found that the magnitude of the bias can be modelled by a uniform distribution with an average of 0.07 J/gh for measurements at 20°C and 35°C and with an average of 0.15 J/gh for measurements at 10°C. This bias has also been acknowledged by other researchers [14].

The rate of heat development q and the cumulative heat generation Q are both normalized by the weight of the cement of each binder. Their average development in time is given for the three temperatures in figure 1. By normalizing the rate of heat development by the total weight of cement of each binder, all measured heat is considered to be derived from the hydration of cement and all water is considered to be available for the latter reaction. The active effect of fly ash in this case is limited to its promoting role in the hydration of cement clinker. From figure 1, it can be seen that at 10°C the acceleration period is mainly retarded with increasing fly ash content, while at 35°C the second peak decreases with decreasing cement content. At 20°C both phenomena can be detected. At all the three temperatures, a third hydration peak appears for cement-fly ash pastes. Comparison with thermogravimetric tests on pastes at the same age suggests that this peak is not caused by the pozzolanic reaction of the fly ash, but by the influence of the fly ash on the hydration of cement [9]. The total heat production of the reference binder at 35°C has reached an asymptotic, final value. The total heat release of the other binders is still slightly increasing after 7 days.

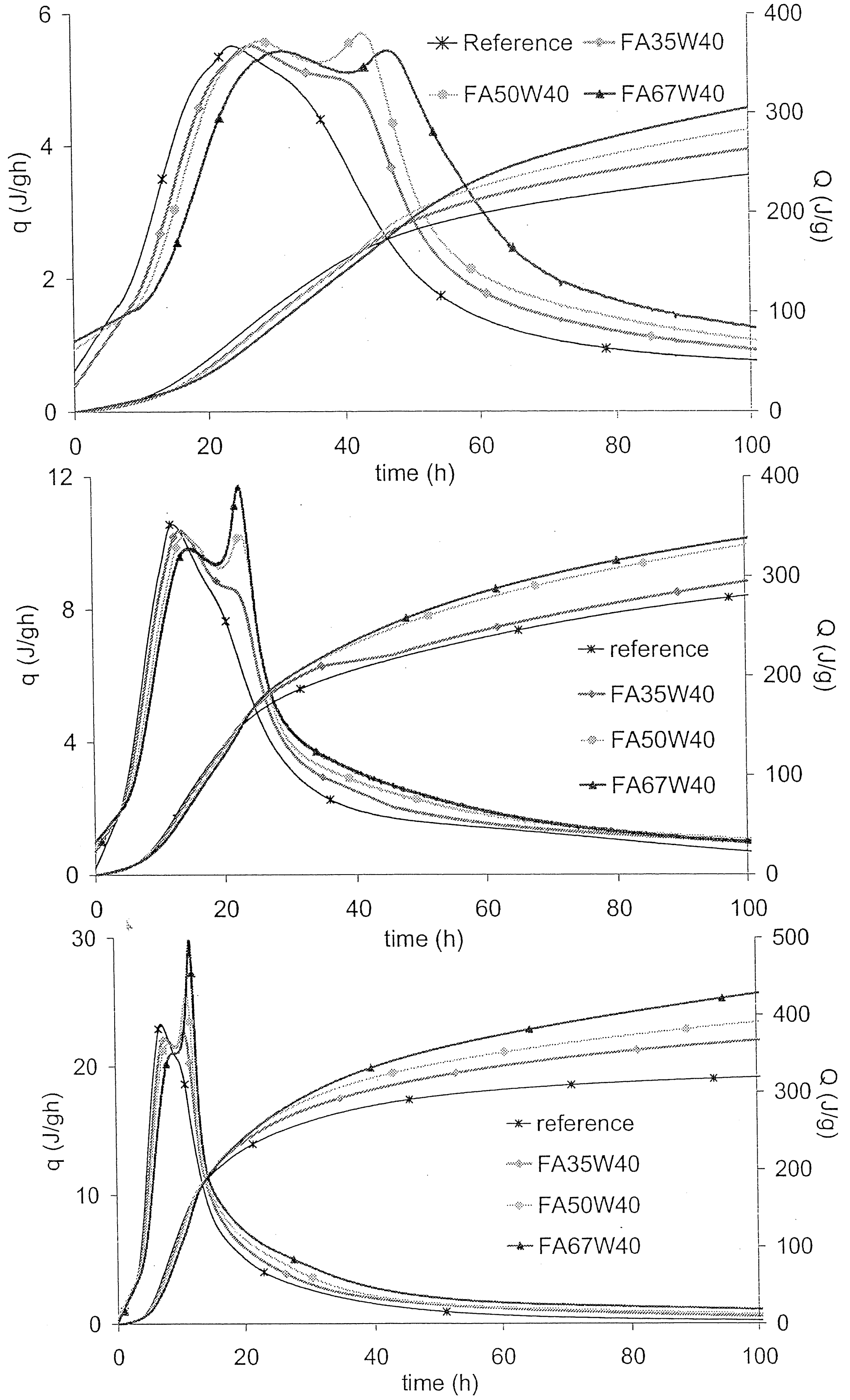

Figure 1: Average rate of heat development q and average cumulative heat Q at 10°C (above), 20°C (middle) and at 35°C (below)

This increase is higher for the binder with higher fly ash content, which could indicate that the pozzolanic reaction is active at this moment (7 days). The measured signal of the heat released during this latter reaction, will however be too small to be representative for a quantitative estimation of the pozzolanic reaction.

4. Hydration model

Based on the hydration model developed by De Schutter et al a similar model was made to predict the rate of heat production of fly ash – cement mixtures. In this model, the time axis t of figure 1 is transformed into an axis of reaction degree r with r defined as the fraction of the heat of hydration that has been released [10, 11];

$$r = \frac{Q(t)}{Q_{\max}} = \frac{1}{Q_{\max}} \int_0^t q(t)dt \tag{1}$$

By dividing the values of each hydration rate curve by their maximum value q_{max} of the second peak, the obtained curves corresponding to the different temperatures, are quite similar in shape. The obtained curves for portland cement can be described as follows

$$\frac{q}{q_{\max}} = f(r) = NF \cdot [\sin(r\pi)]^a \cdot \exp(-br) \tag{2}$$

With NF, a and b constants.

The effect of the temperature can be described separately by an Arrhenius temperature function g(θ) [3] :

$$g(\theta) = \exp\left[\frac{E}{R}\left(\frac{1}{293} - \frac{1}{273+\theta}\right)\right] = \frac{q_{\max}}{q_{\max,20}} \tag{3}$$

with R = 0.00831 kJ/molK (the universal gas constant), E activation energy (kJ/mol), θ = temperature in °C.

The rate of heat hydration of a cement-fly ash paste can be divided into two reactions : a reaction very similar to the reaction of portland cement (which is called in our study the P-reaction) and a second reaction which corresponds with the third hydration peak (the F-reaction). For each reaction, a reaction degree can be defined as the fraction of the cumulative heat liberated by that reaction. In figure 2, the ratio of the rate of both functions (the P- and F-reaction) with their maximum value can be plotted in function of their reaction degree. The total rate of heat development of a cement-fly ash mixture can be modelled by applying the superposition principle (eq.4 till eq.7).

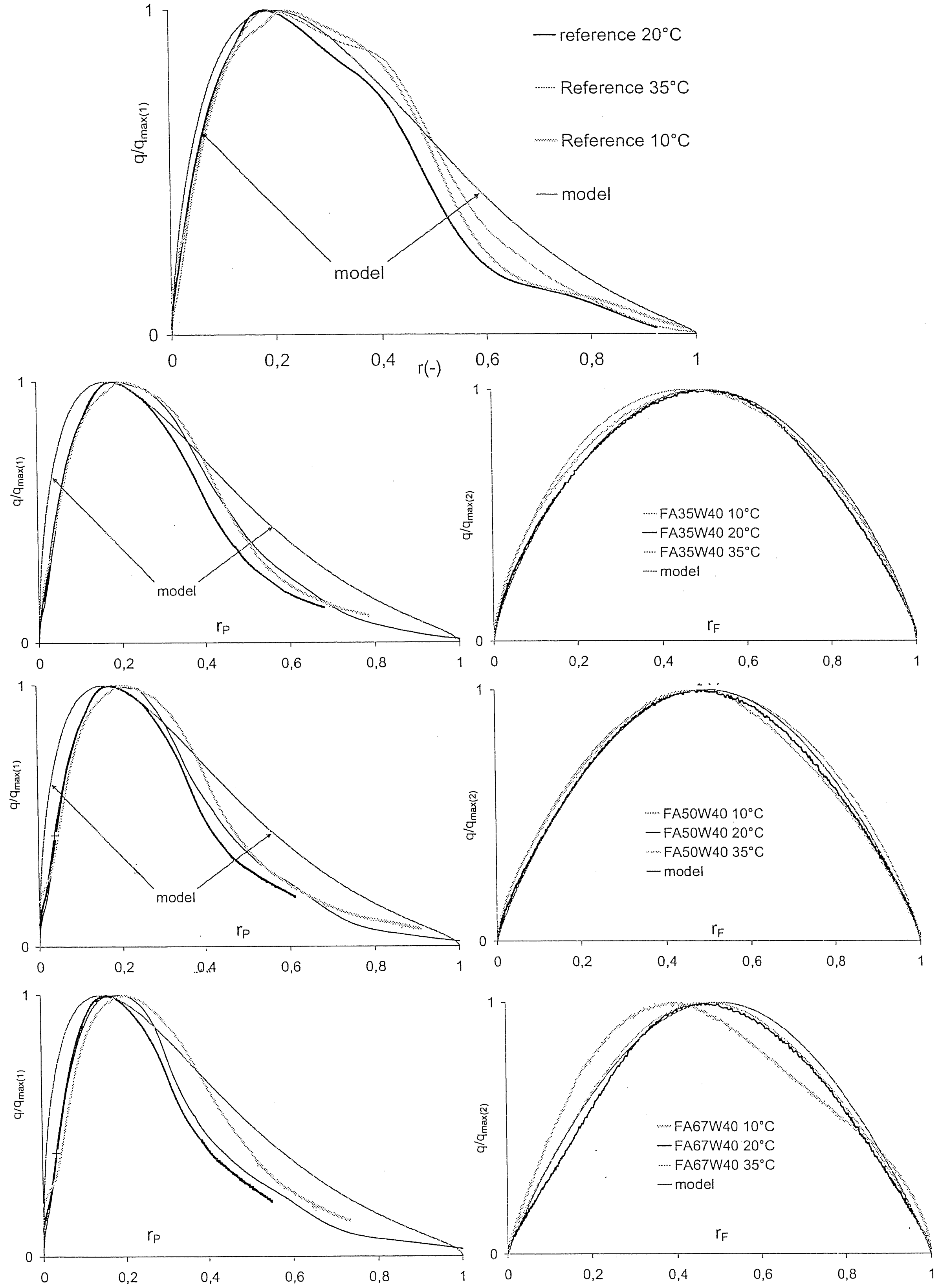

Figure 2: Rate of hydration heat, normalized by the maximum value, for Portland cement, and for the P-&F-reactions of the cement-fly ash pastes vs. respective reaction degrees

$$q = q_P + q_F = \sum_{i=P,F} q_i \tag{4}$$

$$with\ q_i = q_{i,\max 20} \cdot f_i(r_i) \cdot g_i(\theta) \tag{5}$$

$$f_i(r_i) = NF_i \cdot [\sin(r_i \pi)]^{a_i} \cdot \exp(-b_i \cdot r_i) \tag{6}$$

$$g_i(\theta) = \exp\left[\frac{E_i}{R}\left(\frac{1}{293} - \frac{1}{273+\theta}\right)\right] \tag{7}$$

$$with\ i = P\ or\ F$$

The normalized curves of the F-reaction have the shape of a pure sine function. The model constants NF_F, b_F are therefore kept zero. Table 3 summarizes the model constants for all paste mixtures. With increasing fly ash content of the binder, the model constants NF_P, a_P decrease, while the model constant of the second reaction a_F increases. The average activation energy E_P of the first reaction of all mixtures has a value of 38.4 kJ/mol. This corresponds with values from literature [12,13]. The average activation energy E_F of the second reaction of all mixtures is 46.4 kJ/mol.

Table 3: Reaction (Q_{max}, Q_P, Q_F) and model constants (NF_P a_i, b_P, E_i) for the rate of hydration heat of portland cement CEM I 52.5N (Reference) and of cement-fly ash binders (FA35W40, FA50W40, FA67W40)

	Reference	FA35W40	FA50W40	FA67W40
Q_{max} (J/g)	332	395	429	485
NF_P (-)	2.6383	2.3985	2.3722	2.2658
a_P (-)	0.6965	0.5409	0.5256	0.4659
b_P (-)	3	3	3	3
Q_P (J/g)	332	383	411	464
E_P (kJ/mol)	39.7	38.1	37.8	38.0
a_F (-)	-	0.7252	0.8305	0.8782
E_F (kJ/mol)	-	44.2	45.5	49.3
Q_F (J/g)	-	12	18	21

5. Conclusion

Isothermal hydration tests, performed on binders with variable fly ash-to-cementitious material ratio, showed a retarded acceleration period at 10°C and 20°C, while at 20°C and at 35°C a decreased second peak was noticed. At all three temperatures a third hydration peak appeared and increased with increasing fly ash content.

By separating the third reaction peak from the rest of the rate of hydration heat, the model of De Schutter could be adapted to the cement-fly ash binders. The influence of the temperature is taken into consideration by using the Arrhenius function. The activation energy of the first reaction was for all mixtures around 38.4 kJ/mol and for the second reaction 46.4 kJ/mol.

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