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Thermal Analysis of Composite Cements

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The hydration of cement compounds gives hydrated compounds, which allow to link together the different particles and aggregate of cement and give the concrete the required qualities .The dynamics of hydration reactions will depend on many factors, such as the fineness of cement, the ratio e /c during hydration, temperature, mixing technique, and the presence of additives in blended cement, as pozzolan, tuff and slag from blast furnaces.
We studied the thermal and kinetic reactions of Portland cement hydration and its variants with different additions using a differential scanning calorimetric analysis. The parameters from these models of curves allow us to evaluate the enthalpies and the degree of progression of this blended cement and finally determine their activation energies. We can say that the hydration of Portland cement is due to a series of reactions, each with its own kinetic, the experimental measurement of heat of hydration allows us to represent the overall kinetics of these reactions values of activation energy, they are therefore apparent and global.
In our experiments, it was observed significant differences in these physicochemical parameters, depending on the additive used.

1. Introduction

WE studied the hydration of Portland cement compound and we determined the kinetic parameters in adiabatic conditions, we introduced additions as pozzolan, and tuff and we tried to compare the thermal behavior of Portland cement alone and with the additions already mentioned, their particle size are [1.6 to 1.12] mm and isolated by sieving and dried at a temperature of 55 ° C.
The composition of different cements is as follows:
Portland Cement: 95% clinker + 5% gypsum, Portland Cement (compound I): 70% clinker + 5% gypsum + 25% pozzolan, Portland cement (compound II): 70% clinker + 5% gypsum + 25% tuff.
The cement hydration process is accompanied by heat because the chemical reactions of Cement components with the mixing water are exothermic ,Calorimetry allow us to

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measure the heat release function of time with an ratio W / C selected and exploiting the thermograms of enthalpy and numerical integration it can be deduced kinetic parameters

2. Principle of Measurement

The two crucibles containing the sample and reference are in a heated oven with a programmed rate, the principle is to measure a difference in heat flow between the sensor and the reference, in the temperature range studied, and obviously the reference cell must not undergo changes
Thus, when an alteration occurs in the measuring cell (transition or melting), the electrical signal is disrupted and there is a peak representative this transformation.
The recording of the electrical signal with time and temperature displayed on the screen of the microcomputer

2.1 Preparation of samples

Our samples of different fineness are analyzed using a differential scanning calorimeter (DSC) Pyris Diamond ,type Perkin-Elmer by the adiabatic method ,we take 0.035 ml of water using a micropipette and the other weighed 100 mg of Cement and mixing for one minute ,to make a paste ,then we put a quantity of this cement paste, so that its mass does not exceed 10mg, when the sample is prepared, so with a W / C = 0.35 and placed in the DSC and we choose our temperature program with a heating rate of 5 ° C / min with a temperature range from 20 °C to 250 °C. At the end of the experiment, we obtain heat flow thermograms for each sample.

3. Calculations

3 .1 degree of hydration α

The calculation of degree of hydration is based on the method of heat, obtained by DSC curve of heat flow versus time, by integrating this curve by the original 7.5 ,we obtain the values of heat liberated.

$$Q(t) = \int_0^t \frac{dQ}{dt} \cdot dt \tag{1}$$

$$\alpha(t) = \frac{Q(t)}{Q_{\max}} \tag{2}$$

$$Q_{\max}(J) = 517M_{C3S} + 262M_{C2S} + 1144M_{C3A} + 418M_{C4AF} + 1166M_{CaO} + 850M_{MgO} \tag{3}$$

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Values: 517, 262, 1144, 418, 1166 and 850 are the theoretical values of each phase calculated by Taylor

M: mass in mg of each hydrated cement phase

3.2 Constant K

To calculate the rate constant K we applied to the Avrami-Erofeev equation

$$[-\ln(1-\alpha)]^{1/3} = kt \quad (4)$$

And the Tenoutase equation:

$$[-\ln(1-\alpha)]^{1/2} = kt \quad (5)$$

3.3 Activation energy

$$\ln k = a - \frac{Ea}{RT} \quad (6)$$

4. Results and Discussion

4.1 Influence of Blaine fineness on the enthalpy of reaction

The influence of specific surface area of Blaine (SSB) on the three types of cement are given in Tables 1, 2 and 3

Table 1: Evolution of the enthalpy ΔH_R as a function of SSB for the Portland Cement alone

Type of cement	*Grinding time (mn)*	*SSB (Cm^2/g)*	ΔH_R *(J/g)*
P. Cement 1	30	1646	172.404
P.Cement 2	60	2428	255.878
P.Cement 3	90	3495	313.671
P. Cement 4	120	3662	324.232
P. Cement 5	150	3726	328.235
P. Cement 6	180	3742	351.326

Table 2: Evolution of the enthalpy ΔH_R as a function of SSB for Portland Cement(tuff compound)

Type of cement	*Grinding time (mn)*	*SSB (Cm^2/g)*	ΔH_R *(J/g)*
CC Tuff 1	30	2460	235.025
CC Tuff 2	60	3482	273.378
CC Tuff 3	90	3526	320.601
CC Tuff 4	120	4517	358.395
CC Tuff 5	150	5128	362.290
CC Tuff 6	180	4940	364.972

Table 3: Evolution of the enthalpy ΔH_R as a function of SSB for the Portland Cement with pozzolan

Type of cement	*Grinding time (mn)*	*SSB (Cm^2/g)*	ΔH_R *(J/g)*
CC POZZ 1	30	1913	214.277
CC POZZ 2	60	2767	259.215
CC POZZ 3	90	3726	280.627
CC POZZ 4	120	3917	288.412
CC POZZ 5	150	3850	376.044
CC POZZ 6	180	5100	398.976

For the three types of cement can be seen that the evolution of the enthalpy follows the evolution of SSB and more particles of Cement are fine ,more its reaction with water increases and gives a greater heat.

4.2 Determination of kinetic parameters of hydration

The rate of hydration is determined from the heat observed by scanning calorimetry of Avrami and Tenoutase

K(A) : Avrami rate constant

K(T) : Tenoutase rate constant

Table 4: variation of hydration rate and the constant rate for Portland cement with pozzolan

Type of Cement	$Q_{(max)}$ *(mJ)*	m_e *(mg)*	$\alpha_{(max)}$	$k(A)\,(s^{-1})$	$k(T)\,(s^{-1})$
CC POZZ 1	2333.126	6.0	0.308	$4.60*10^{-4}$	$4.10*10^{-4}$
CC POZZ 2	6773.804	8.8	0.340	$4.87*10^{-4}$	$4.31*10^{-4}$
CC POZZ 3	5646.53	8.7	0.394	$5.09*10^{-4}$	$4.45*10^{-4}$
CC POZZ 4	6405.501	7.0	0.440	$5.28*10^{-4}$	$4.56*10^{-4}$
CC POZZ 5	6611.698	7.6	0.449	$5.32*10^{-4}$	$4.88*10^{-4}$
CC POZZ 6	7800.53	7.8	0.64	$6.84*10^{-4}$	$6.85*10^{-4}$

We have only given the K(A) and K(T) of Portland Cement with pozzolan for the two others compounds there was no space to insert them.

4.3 Determination of apparent activation energy

The determination is based sue the Arrhenius equation to calculate the influence of temperature on reaction rate.

A graph of values of ln k versus 1 / T according to equation (VI) gives a straight line whose slope is -Ea / R.

The values of the three types of cement are given in Tables 5, 6 and 7

Table 5: Values of Ea calculated by both models Avrami and Tenoutasse for Portland Cement

Type of cement	$E_a(A)$ (KJ/mol)	$E_a(T)$ (KJ/mol)
P.Cement 1	53.570816	86.71104
P.Cement 2	73.88576	118.94272
P.Cement 3	102.59392	159.80224
P.Cement 4	127.59552	213.3664
P.Cement 5	148.49536	236.36288
P.Cement 6	230.57216	353.23392

Table 6: Values of E_a calculated by both models Avrami and Tenoutase for Portland Cement with Tuff

Type of cement	$E_a(A)$	$E_a(T)$
CC Tuff 1	1230.68608	1710.10112
CC Tuff 2	331.39392	502.51968
CC Tuff 3	215.13024	326.21888
CC Tuff 4	151.60704	236.13824
CC Tuff 5	131.06496	205.80352
CC Tuff 6	117.40352	188.91392

Table 7: Values of Ea calculated by both models Avrami and Tenoutasse for Portland cement with pozzolan

Type of cement	$E_a(A)$	$E_a(T)$
CC POZZ 1	73.13696	106.52928
CC POZZ 2	108.50944	171.42528
CC POZZ 3	128.01984	242.60288
CC POZZ 4	135.81568	207.792
CC POZZ 5	174.47872	266.48128
CC POZZ 6	247.8112	375.97248

Conclusion

According to the results ,we notice for Portland cement and Portland cement-pozzolan compound, that more SSB increases and more E_a increase, but in the presence of tuff, Ea decreases when SSB increases using the two models.

So the presence of pozzolan in Cement is more efficient and more resistant as the presence of tuff.

For the three types of Cement, it can be seen, that over the SSB is great and more ΔH_R is high, more particles of cement are fine, more its reaction with water increases, which makes the cement more responsive and then release a larger heat.

References

Cordes S., Odler I., 2002,Initial,hydratation of tricalcium silicate as studied by secondary mass spectrometry,sample preparation and calibration.Cement and concrete Research, 32, 7

Schwarz W., Sujata K. , Jenning H.M, Gerdes A.,Wittmann F.H.,1997,Chemically modified hydration of Portland Cement and its application for the kinetics of the hydration of ordinary of Portland Cement , Workshop on hydration and setting, Dijon (France)

Sha W., Pereira G.B., 2001, Differential scanning calorimetry study of ordinary Portland cement paste containing metakaolin and theoretical approach of metakaolin activity , Cement and Concrete Composites, 23

Sha W., O'Neill E.A., Guo Z. , 1999, Differential scanning calorimetry study of ordinary Portland cement. Cement and Concrete Research Elsevier, 29

Snelson David G. a, Stan Wild a, Martin O'Farr, 2008, Heat of hydration of Portland Cement–Metakaolin–fly-ash (PC–MK–PFA) blends. 38, Cement and Concrete Research Elsevier.