Calorimetric and Thermal Analysis Studies on the Influence of Coal on Cement Paste Hydration

Noureddine, Bentaieb*+; EL Abidine, Benarima Zine; Salah, Belaadi
Reaction Engineering Laboratory, Faculty of Mechanic and Engineering Process (USTHB), B.P. 32, El-Alia, Bab-Ezzouar, Algiers, ALGERIA

ABSTRACT: *Composite Portland Cement, CEMII (cement with additives of limestone, slag from blast furnaces, tuff, and pozzolan) represent a significant share of the cement manufacturing in the world. These additives can increase cement production and reduce the energy consumption in this sector, their incorporation in the milling process of the clinker allow also to obtain hydraulic blinders better homogenized and more responsive. Blended types of cement are grounded more finely than the pure cement between 3500 to 5000 cm^2/g. The use of industrial waste, as well as natural products such as pozzolan and limestone as partial replacement of clinker in cement and concrete, saves energy[1.2.3], and it reduces emissions of greenhouse gas. This results in the production of concrete non-polluting and sustainable environmentally. Our work was based on the incorporation of coal as additives (CEMI)and study the effect of this addition during the hydration reaction of the cement paste of the studied samples, with a heating rate of 5°C/mn, the percentages of coal used were (10% ,20% ,30%). Previous studies showed that coal has the ability to increase the mechanical resistance of cement, this is due to the chemical composition of the coal (SiO_2, Ca, Fe_2O_3, Mg, Na), which affects the grind ability of the cement and its reaction with water(hydration reaction). Thermal analysis allows us to evaluate the heat released by the studied cement during its hydration and to exploit the results by using various models. The degree of hydration, the rate constant, and activation energy are determined, this energy is global, as it relates to all phases of hydration reactions of cement namely (C_3S, C_2S, C_3A, and C_4AF).*

KEYWORDS: *Cement paste; Hydration; Calorimetry; Coal.*

INTRODUCTION

The hydration reactions depend on many factors such as the fineness of cement, the mass ratio water/cement (w /c), temperature, mixing technique and the presence of additives in blended cement, as well as pozzolan,tuff and Slag from blast furnaces. Studies on blended cement hydration have been intensively conducted in the past by many research works, some of them were done in systems containing blast furnace, slag [1-5], silicafume, and fly ash [6], which are among the mineral additives. The aim of this work is to replace a part of the clinker by coal in order to reduce gas emissions such as CO_2 ,SO_2, NOx, and CO, as well as the negative environmental impacts associated with the production of the fuels used in cement manufacture. We also studied the hydration reaction of Portland cement

** To whom correspondence should be addressed.*
+ E-mail: djamel_nour@hotmail.com
1021-9986/2020/6/237-244 8/$/5.08

Table 1: Simplified mineralogical composition of the clinker.

C_3S %	C_2S%	C_3A%	C_4AF%
57.44	17.36	9.52	9.75

Table 2: Chemical composition of analyzed clinker.

Oxides	Mass rate (%)
Co	66.16
SiO_2	21.50
Al_2O_3	5.69
Fe_2O_3	3.28
MgO	1.96
(NaO_2, K_2O)	1.12
Insoluble residue (RI)	1.36
Fire loss	0.08
Lime (CaOL)	0.47

to determine the kinetic parameters under adiabatic conditions. Ordinary Portland Cement contains four major compounds namely tricalcium silicate (C3S), dicalcium silicate (C2S), tricalcium alumina te (C3A), and tetracalcium aluminoferrite (C4AF). Both C3S and C2S react with water (H) to form hydrate (CSH) and calcium hydroxide (CH) as their principal hydration products[7.8.9]. We have incorporated the coal at different percentages and by thermal analysis

following the effect of these additives on the generated heat. We have also studied the thermograms from the cement samples to determine their kinetic parameters.

EXPERIMENTAL SECTION

Materials and sample preparation

Clinker

Clinker used in this work was collected from Mitidja Cement, (Algiers,area), the particle size was reduced by grinding and lies in the range [1.6mm - 1.12mm] in an adequate way ,as shown in Tables 1 and Table 2 which represent the mineralogical composition of the clinker.

Composite cement with coal additives

Four different samples were mixed and the coal to the cement Portland was added at different rates of 10%, 20% and 30% and Table 3 shows the components of each sample.

Principle of Measurement

The samples of different fineness were analysed using a differential scanning calorimeter (DSC) Pyris Diamond, This thermal analysis equipment with an accuracy of ± 0.1 °C, works in the range of 123-998 K by the adiabatic process. 100mg of cement were immersed in 35 ml of water for 1min to produice a paste. Then put an amount of this cement paste, so that its weight does not exceed 5 mg, when the sample was prepared with a mass ratio w / c = 0.35 and placed in to the differential scaning calorimetry equipment (DSC), the temperature program was chosen with a heating rate of 5°C / min and a temperature range from 25°C to 300°C. The heat flow thermograms were obtained for each sample , the different curves were exploited and the different kinetic parameters were deduced [10].

RESULTS AND DISCUSSION

Analysis of kinetics grinding

Blaine fineness

The different Blaine fineness of the Portland cement with and without additives are gathered in Table 4.

Particle size distribution of analyzed cements

Particle size distributions of Portland cement and composite cements, measured by laser diffraction, are illustrated in Fig. 1 and Table 5.

The analysis and comparison of particle size distributions of samples is performed on a small number of quantities, such as:

- D (v; 0.1): particle size for which 10% by volume of the paticle sample is below this value.
- D (v; 0.5): particle size for which 50% by volume of the paticle sample is below this value. This is the median diameter.
- D (v; 0.9): particle size for which 90% by volume of the paticle sample is below this value.
- D(4; 3) : mean diameter by volume.
- D(3; 2) : mean diameter in volume weighted by the surface (Sauter diameter).
- span = (D(v; 0.9)-D(v; 0.1))/D(v; 0.5) : measuring the spread of the particles size distribution by volume.

Cement hydration reaction

The thermal analysis of the hydration of a Portland cement, is summarized with a rough description of

Table 3: Cements used in the experiment.

Cement	Artificial Portland Cement	Cement N1	Cement N2	Cement N3
Adding Proportion	95% clinker 5% gypsum 0 % coal	85% clinker 5% gypsum 10% coal	80% clinker 5% gypsum 20% coal	65% clinker 5% gypsum 30% coal

Table 4: Specific surface Blaine of cement with coal additives.

Type of Cement	SSB (cm^2/g)
OPC	3717
Cement I.1	3812
Cement I.2	4167
Cement I. 3	5128

Table 5: Granulometry of coal cements.

Cements	d(0,1), µm	d(0,5), µm	d(0,9), µm	*D*(4;3)	*D*(2;3)	span
O.P.C	3.179	41.135	193.03	75.431	6.6	4.632
Cement I 1	1.862	16.367	77.46	47.75	4.173	4.535
Cement I 2	1.135	7.241	26.631	11.017	2.789	3.521
Cement I 3	3.722	36.235	190.061	73.886	8.743	5.143

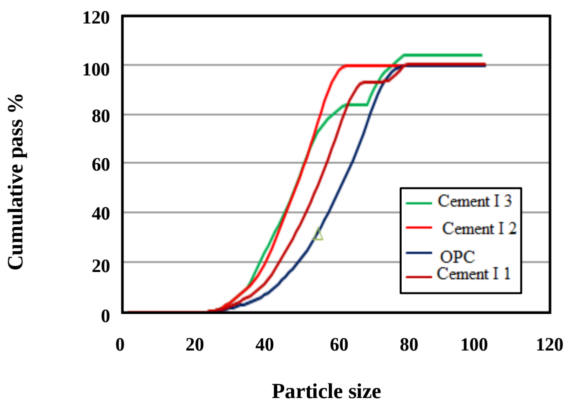

Fig. 1: Particle Size Distribution of Coal Composite Cements.

a ternary mixture of C_3S, C_3A and CSH, the hydration at the young age is considered as a system of five reactions taking place simultaneously.

Released heat from hydration reaction of studied cement

The integration of the thermograms of the thermal flux as a function of time for calorimetric experiments, carried out in heating mode 5 ° C / min represent the evolutions of released heat. The thermal flux as a function of time of O.P.C and the cement based on coal is an exothermic process reflecting all reactions of the cement setting until the exhaustion of the surface water. Figs. 2 and 3 represent the evolution of the thermal flux and the hydration heats corresponding to Portland cement without additives and cements based on coal at different percentages (10% .20% .30%) from the same supplier, but with a different Blaine fineness ,the water / cement ratio is 0.35. The slurries were prepared in the temperature range (25 - 300 ° C).The integration of the of the thermal flux as a function of time for calorimetric experiments represents the evolutions of released heats.

This Fig. 3 clearly identifies two peaks and a shoulder. It is possible to associate the first peak as the hydration of silicates, while the second corresponds to the hydration of the aluminates. Through the curve, we note that the amount of heat flux of the samples is between 7 and 8 mW / g, it is also found that the amount of the heat produced by the O.P.C cement and the cements based on coal are between 8000 J /g and 12 000 J /g for all the samples as shown in Fig. 3.

Table 6 summarize the data obtained from thermograms of cement.

KINETICS PARAMETERS

Degree of hydration of the cement

The degree of hydration assessment of cement paste,

Table 6: Maximum heat Q_{max} for composite cement based on coal.

Type of Cements	SSB (cm^2/g)	Q_{max} (J/g)
OPC	3717	8405.51
Cement I 1	3812	9658.09
Cement I 2	4167	10160.12
Cement I 3	5128	12459.77

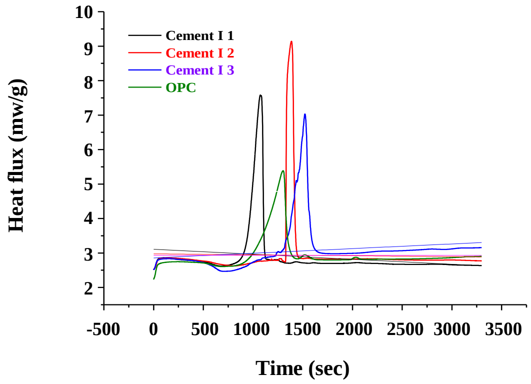

Fig. 2: Evolution of heat flux of O.P.C and composite cement based on coal as a function of time.

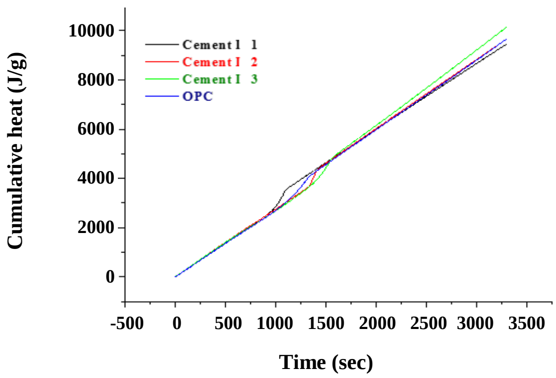

Fig. 3: Evolution of the released heat of O.P.C and composite cement based on coal as a function of time.

from differential thermal and thermogravimetric analysis data has been performed by several authors, that have offered a number of proposals for the technical application to blended cements. In this paper, two calculation methods are studied in detail with a proposal of the degree of hydration calculation for blended cements [11.12], based on the analysis of experimental results of DCS.

$$\alpha(t)=\frac{Q(t)}{Q_{max}} \quad (1)$$

Fig. 4 represents the evolution of the degree of hydration as a function of time of composite cement based on coal, we observe three phases:

1- **Phase 1:** The presence of a low humidity level was observed, which causes the types of ionic and chemical elements to start immediately after the contact between cement and water. Formation of hydrates near the surface, and the reach of humidity temperature level are important steps to cement, Silicate and aluminates.

Silicates and aluminates are metabolized during the liquid phase, although their concentration is still very low. This is the period in which we get a low degree of hydration between 0-1200 (sec).

2- **Phase 2**: A significant in the degree of hydration is observed for a short duration between 1200 sec - 1800 sec), which results in the gradual decomposition of a protective layer C-S-H, with a maximum degree of hydration α_{max} between 0.35 to 0.48 for all the samples studied. This phase is called the acceleration period.

3- **Phase** ***3:*** A decrease of Humidity temperature was observed (Humidity temperature fixed), which is explained by the cover of bubbles in the cement into a chemicals layer of more and more thick which result in a decreased humidity. This is the slow and solid period.

As seen in the tables and graphs, the maximum humidity degree increases as the percentage of added coal is increased.We conclude that the coal has the ability to raise the humidity degree and accelerate the interaction. The values of the maximum degree of hydration (α_{max}) for each type of cement are summarized in Table 7.

Determination of the kinetic parameters of the cement hydration reaction

The hydration of cement is a complex phenomenon since several minerals hydrate at the same time and interact together.

Table 7: Hydration rate of studied cements.

Types	SSB (cm^2/g)	α_{max}
O.P.C	3717	0.37
Cement I 1	3812	0.35
Cement I 2	4167	0.45
Cement I 3	5128	0.48

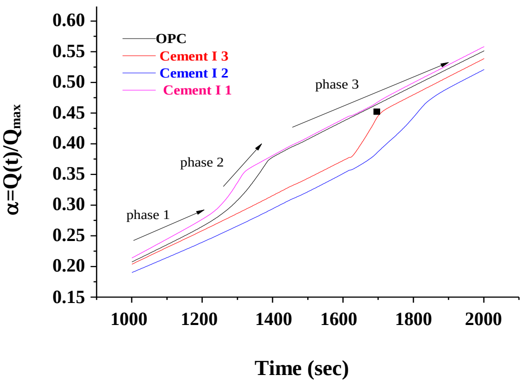

Fig. 4: Degree of hydration of composite cement based on coal as a function of time.

The hydration kinetics of cements is a reflection of the overall result of these interactions. The modification of some initial parameters in the composition of the cement slurry and the addition of certain chemical additives can modify the global kinetics of hydration reactions and their dependence with temperature. The knowledge of the kinetic parameters of cement hydration and their variations with the experimental conditions is of considerable practical importance.However it may also on a more fundamental level, reveal changes in hydration reactions, which can lead to different hydration products.

Modeling the global hydration reaction

To determine the kinetic parameters of cement hydration, and their thermal variation, and their application to experimental data of kinetic equations derived from the models. In our study, we have identified an equation developed by Avrami, to describe the cement hydration .This equation has the advantage of being simple, of generating a single rate constant and allowing easy calculation of single activation energy value. In general, this equation allows the experimental data to be well represented at low hydration levels.

The Avrami's model describes the kinetics of the phase transformation under the assumption of spatially random nucleation. In this paper, we provide a quasi-exact analyical solutions of the Avrami model when the transformation takes place under continuous heating.

Researchers used Avrami-Erofeev equation given by [13-16].

$$(\alpha) = K\,t = \left[-\ln(1-\alpha)\right]^{\frac{1}{n}} \qquad (2)$$

With a non-isothermal analysis at a heating rate by adding β to our equation

$$\frac{d\alpha}{dt} = \frac{1}{\beta} f(\alpha) A \exp\left[-\frac{E_a}{RT}\right] \qquad (3)$$

The use of this equation gives access to kinetic parameters, such as the reaction order and activation energy.

The parameters from these models of curves allow us to evaluate the enthalpies and the degree of progression of this blended cement and finally to determine their activation energies. The account of these results has been exploited by using the origin 8. 1 program.

This figure represents an example of an adjustment of the *Avrami* model for portland cement with coal addition, this linearization gives us a straight line where the slope equal to n and the ordered at the origin equal to n lnk . The set of kinetic parameter values are given in Table. 8. The exploitation of the Avrami model allowed us to deduce the order of the global hydration reaction n which is equal to 2 and the constant of speed k being between 3.5×10^{-4} and 5×10^{-4} .

Determination of apparent activation energy

Defining the activation energy implies that the hydration reaction follows the Arrhenius law which governs the acceleration of chemical reactions when the temperature rises,the activation energy is calculated from the slope of Arrhenius equation (Eq. (4) and Fig.6) .

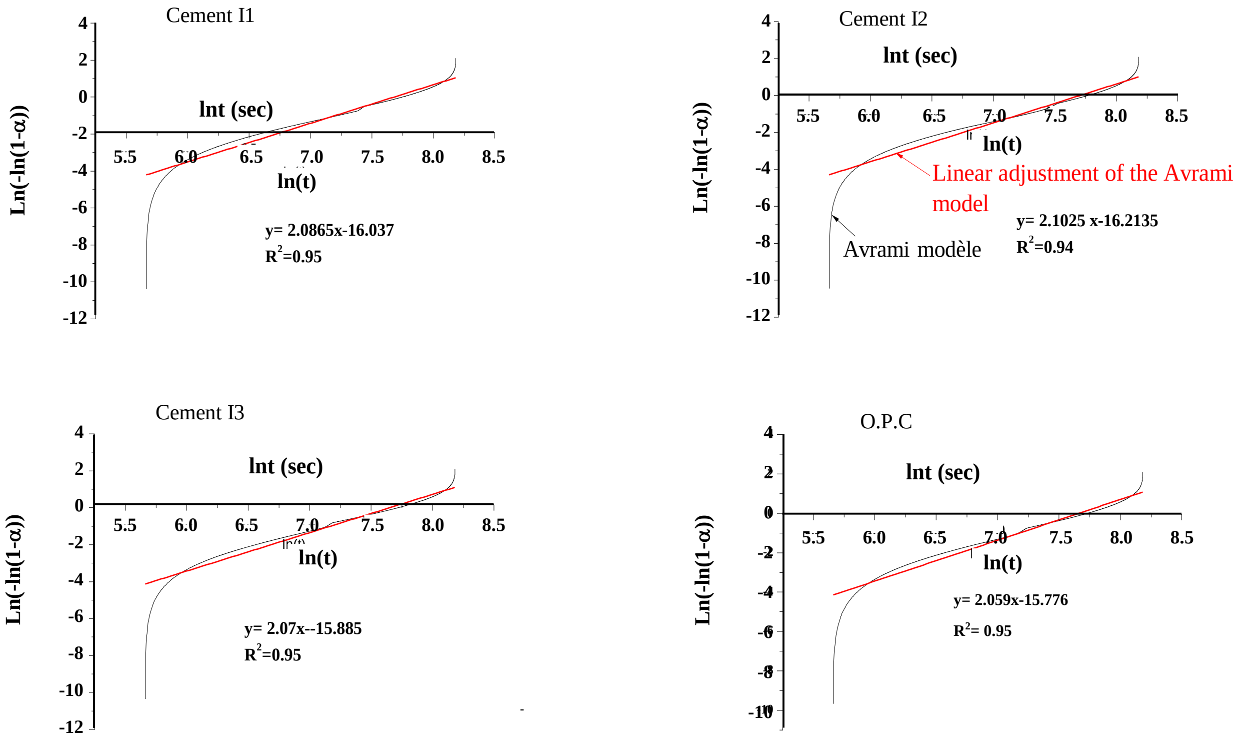

Fig. 5: Adjustment of the Avrami model of composite cement based on coal.

$$\ln K = a - \frac{E_a}{RT} \quad (4)$$

The plot (Ln k) vs .(1/T) gives a straight line whose slope is equal to ($-E_a/R$) [17-20].

The calculation of the apparent activation energy shows that :

- The energy E_a released by the Portland cement with additives is greater than that without additives.

- The increase in the percentage of additives of the coal increases the activation energy, thus causing the increase of the mechanical strength of the cement.

CONCLUSION

1. The experiments of thermal hydration analysis of Portland cement, with additives and heating speed of 5 °C /min and temperature range from 25°C to 300°C, showed that the additives used, facilitate the grinding operation and increase the Blaine fineness SSB.The evolution of the physico-chemical characteristic of cement (SSB) is related to the percentage of coal addition, the values were between 3812-5128 (cm^2/g) and 3713 cm^2/g for OPC cement.

2. The analysis of each type of cement shows that the augmentation of the Blaine fineness leads to the increase of the hydration heat, which remains important for Portland cement and to a lesser degree for composite cements. This evolution was between 9658 - 12459(J/ g) for the cement based on coal and 8405 J / g for the OPC cement.

3. The hydration rate of portland cement with coal addition is higher than without, and the values were between 0.35 - 0.48.

4. The application of the Avrami model to the experimental results, allows the determination of the rate constants, as well as the activation energies of the hydration reactions in a limited and linear domain.

We could get the order of the global hydration reaction, n=2 and the rate constants k was between

3.5.10-4 and 5. 10^{-4}.

5. The additives of coal help to accelerate the cement hydration reaction in relation to the reactivity of its chemical composition.

6. The activation energy Ea released by Portland cement with addition is greater than without and the values were in the range of 14.72 - 16.70 (J).

Table 8: Values of Kinetic Parameters of composite cement based on coal.

Types of cements	n	k_{moy}	R^2	Avrami Adjustment equation
CPA	2.07	$5.25*10^{-4}$	0.9574	y =1.2664 x - 9.74
Cement I.1	2.086	$5.29*10^{-4}$	0.962	y =1.303 x - 9.83
Cement I. 2	2.102	$3.78*10^{-4}$	0.962	y =1.260 x - 9.93
Cement I .3	2.07	$5.56*10^{-4}$	0.967	y =1.277 x - 9.57

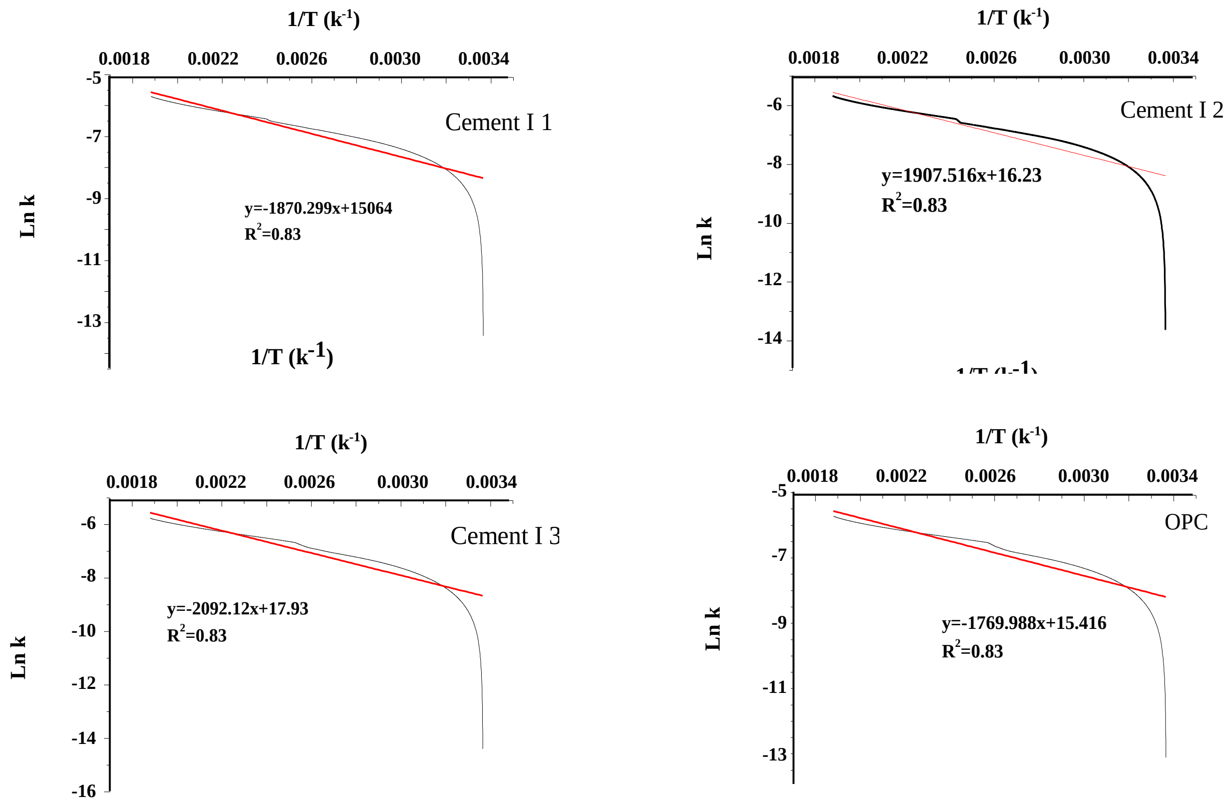

Fig. 6: Determination of apparent activation energy of composite cementbased on coal.

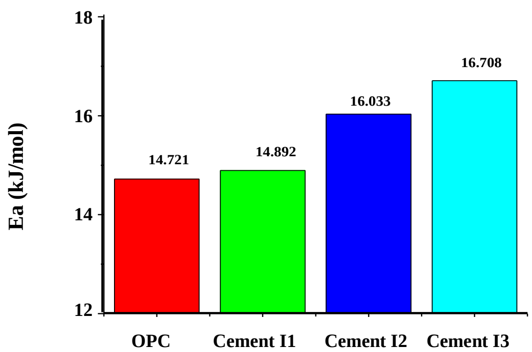

Fig. 7: Activation energy values of analysed cements.

Acknowledgments

This work was supported financialy by the Mechanic and Engineering Process Faculty (USTHB, Algiers, Algeria).

Nomenclature

w/c	Mass ratio water/cement
α(t)	Degree of hydration
Q(t)	The heat generated at the instant t, J/g
Q_{max}	The total heat evolved after complete hydration of the cement, J/g
T	Temperature, K
β	Heating rate, K/min

R Gas constant, 8.32 J/mol. K

Ea Activation energy, kJ/mol

Received : Jun. 29, 2019 ; Accepted : Sep. 16, 2019

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