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A Comparative Study Between the Early Stages Hydration of a High Strength and Sulphate Resistant Portland Cement and the Type II F Portland Cement Through Non Conventional Differential Thermal Analysis and Thermogravimetry

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This work presents a study, which compares the early stages of hydration of a High Initial Strength and Sulphate Resistant Portland Cement (HIS SR PC) with those of Type II F Portland Cement (PC II), by Non-Conventional Differential Thermal Analysis (NCDTA) within the first 24 hours of hydration. Water/cement (w/c) ratios equal to 0.5, 0.6 and 0.66 were used to prepare the pastes. The hydration of these two types of cement was monitored on real time by NCDTA curves, through the thermal effects of the hydration reactions, from which cumulative evolved energy curves were obtained. These techniques allow one to analyse the influence of each type of cement on the main stages that occur during the hydration process. Thermogravimetric analysis were also performed at 4 and 24h of hydration for both cements, to analyse the influence of each kind of cement on the amount of the main formed hydrated products. The results showed that with 4h of hydration, the total combined water amount released from the hydrated products was higher for the PC II pastes than for the HIS SR PC pastes. Otherwise, with 24h of hydration, the amount of the total combined water released from the hydrated products was higher for the HIS SR PC pastes than for the PC II pastes.

Keywords: *HIS SR Portland cement, type II Portland cement, early stage hydration, NCDTA, thermogravimetry*

1. Introduction

Thermogravimetric (TG) and derivative thermogravimetric (DTG) analyses have been used as a tool to study the hydration reactions in cementitious pastes[1-3]. These techniques allows to determine the quantitative of the main formed hydration products, to study the effects of different mineral additives, as fly ash, silica fume, for example, by pozzolanic activity[4-6], to determine the carbonation degree of cementitious materials, by the consumption of $Ca(OH)_2$ and consequently formation of $CaCO_3$, as an indicative of durability or quantifying the CO_2 captured in the own matrix[7,8].

The non-conventional differential thermal analysis (NCDTA), different from the differential thermal analysis (DTA), where the thermal effects are measured, by the control of an external heating or cooling device[2,9], is a system which operates semi-adiabatically allowing to measure, the temperature difference between a sample and an inert reference, as DTA operates, but due to the thermal effects promoted by the spontaneous cement hydration exothermal reactions. The NCDTA has been used in several studies to monitoring, on real time, the hydration reaction, by the water to cement (w/c) ratio variation[2], the mineral additives in the pozzolanic activity[4] and the use of residues within the cement in a solidification process[9].

In this work, the hydration behavior of two types of cement pastes during their first 24h of hydration was evaluated from NCDTA and TG/DTG analysis. W/c ratios equal to 0.5, 0.6 and 0.66 were used to evaluate and compare the influence of these two types of cement on the cumulative energy evolved, as well as to investigate, the amount of the mainly hydrated products formed with 4 and 24h for each type of cement, at the same time.

2. Materials

In this study, two types of cement were used, a Type II F Portland cement (PC II) and a High Initial Strength Sulphate Resistance Portland Cement (HIS SR PC), according to the Cement Portland Brazilian Association (ABCP). The PC II it's a type of cement largely used and commercialized in the most of the applications in civil engineering, characterized by the presence of 6 to 10% of carbonate material, as filler, and pozzolanic material[10]. The HIS SR PC is mainly characterized to reach high strengths at early hydration stages, due to a higher milling degree of the cement, to

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accelerate its reactions with water, by the higher specific external area of the particles, reaching a higher strength in a shorter time. This kind of cement may have a maximum of 5% of carbonates addition and aggregation of blast furnace slag or pozzolanic materials[11,12].

The chemical composition of the both cements is presented on the Table 1. The granulometric distribution curve of the PC II and HIS SR PC, is presented in Figure 1.

3. Methods

For the TG/DTG analysis, the pastes with w/c of 0.5, 0.6, and 0.66 were prepared. The use of w/c=0.66, is based in a previous work of the authors, which corresponds to the miscibility limit, between the cement and the water, achieved for the HIS SR PC cement paste[2]. The same miscibility limit was adopted to the PC II paste. The cement was inserted in plastic bags previously containing the proper amount of deionized water with which homogenization was manually done for 1 min and after, the bag was tightly closed and maintained in a controlled temperature chamber at 30 °C. After that, a sample of about 10 mg, was collected for each analysis from respective stored bag at the established times of the experiments, which were of 4 and 24h. To minimize the external environment influence, the time between collection and insertion of the sample in the thermal analysis pan was minimized. When the sample was gelly it was directly put into the pan. When it was solidified, a little amount was first collected and transferred into plastic bag, which was sealed, and then was manually milled. After that, it was fastly transferred into the pan.

The thermal analyses were performed in a TA Instruments, SDT Q600 model TGA/DTA/DSC simultaneous apparatus with a heating rate of 10 °C min^{-1}, from 35–1000 °C, and using 100 mL min-1 of nitrogen flow. Before this, the samples were dried inside the equipment initially at 1 °C min-1 from 30 to 35 °C, followed by a drying isothermal step at 35 °C for 1h, to eliminate the residual non-combined free water[1,2]. The material of reference and sample pans was platinum.

The contents of the products were calculated using the procedure described in previous works of the authors[1,4]. It uses the TG and DTG data on the initial cement mass basis for the determination of the hydration products and the correct comparison between the curves. On this basis, all the TG and DTG curves, from which the contents of the following products were determined, were plotted:

- The water released from the tobermorite and ettringite phases decomposition, between 50 and 200 °C;
- The total combined water released during analysis, including the water lost from dehydroxylation of the $Ca(OH)_2$ between 35 and 450 °C;
- The water lost during the dehydroxylation of $Ca(OH)_2$, between 380 and 450 °C;

A simplified schematics of the NCDTA used, is presented in Figure 2. It is a system that consists in two main cups, one containing an inert reference material, where in the present case were used two different cups: one containing a hydrated HIS SR PC cement paste and another one a hydrated PC-II cement paste, both aged more than 3 months and the others, containing the paste sample analyzed. Each cup is isolated by an external polystyrene cup and has a cover through which a thermistor with 0.03 °C resolution is introduced to measure the reference or sample temperature (Tr or Ts). The temperature data acquisition is done by a controller and an interface, linked to a computer to measure the temperature difference between sample and reference on real time.

In the NCDTA procedures, the pastes were prepared as follows: the cement was inserted in each cup, previously containing the proper amount of deionized water where homogenization was manually done for 30s. Then, the cup was covered and the thermistor was introduced in vertical

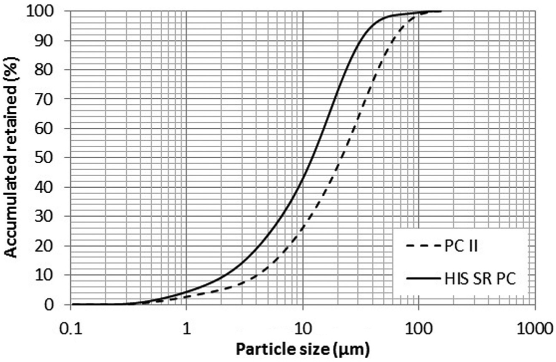

Figure 1. Granulometric curves of the HIS SR PC and PC II cements.

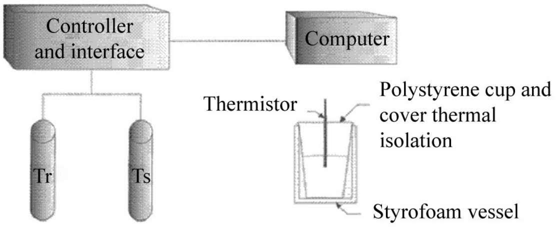

Figure 2. Simplified schematics of the NCDTA system.

Table 1. Chemical composition of the HIS SR PC and PC II.

Compound	Content / %	
	PC II	HIS SR PC
CaO	67.77	63.78
SiO2	12.62	18.12
SO3	4.16	6.75
Al2O3	3.93	4.29
Fe2O3	3.34	3.29
K2O	0.42	0.35
SrO	0.29	0.23
TiO2	0.24	0.35
ZnO	0.05	0.04
MnO	0.04	0.23
Cr2O3	0.04	-
CuO	0.02	0.02
*LOI	7.08	2.55

*LOI – Loss of ignition.

position through a hole at the center of the cover of each cup. Before inserting the thermistor its external surface was protected by a very thin polyethylene film. Temperature data were collected during the first 24h of hydration, every minute.

4. Results and Discussion

The Figure 3 shows the TG and DTG curves of the HIS SR PC and PC II cements used.

In Figure 3, the first mass loss step, for the both cements, up to 150 °C, refers to the gypsum dehydration. The second mass loss step from 350 to 450 °C is due to calcium hydroxide dehydration. During the milling process of the clinker with the gypsum, added to manufacture the cement, partial dehydration of the gypsum occurs due to some increase of the milling chamber temperature, which contributes to some hydration of the free calcium oxide present in the clinker, forming the Ca(OH)$_2$ present in the unhydrated cement, which decomposes during analysis.

From 450 to 700 °C occurs calcium carbonate decomposition, where we can notice the higher amount of CaCO$_3$, added as filler, presented in the PC II cement in relation to the HIS SR PC cement.

Figure 4, shows the NCDTA curves of the HIS SR PC and PC II pastes.

We can see from the NCDTA curves in Figure 4 that until 4h, all the PC II pastes studied presented higher temperature differences than the HIS SR PC pastes. This behavior changes after 4h until 12h, where we can notice that all HIS SR PC pastes present higher temperature differences. Until 0.5h, the temperature of the HIS SR PC paste is higher than the PC II pastes, which can be explained by the more reactivity of the former one due to it fineness. When the HIS SR PC pastes reaches the induction period and does not occur increase of temperature, the PC II pastes reaches the induction period at a higher temperature difference, starting the acceleration period before the HIS SR PC paste. When the acceleration period of the HIS SR PC pastes starts, the higher increase of temperature, leads to a higher maximum temperature difference between 8.5 and 9.5h. Due to its faster setting, the HIS SR PC paste reaches a strength and lower porosity earlier than the PC II pastes, which explains the faster increase and decrease of the temperature difference and the higher temperature difference. In the PC II pastes, after 14h, the higher temperature difference, can be explained by the later reach of strength, where influences the decrease of the temperature later and gradually.

For the HIS SR PC and PC II pastes from 0.55 to 0.66 w/c ratio, which pastes were homogeneous, it was possible to normalize the respective NCDTA curves, on respective cement initial mass basis as detailed in a previous paper of the authors[13]. Afterwards by integration, the respective cumulative energy curves were obtained in arbitrary units as presented in Figure 5.

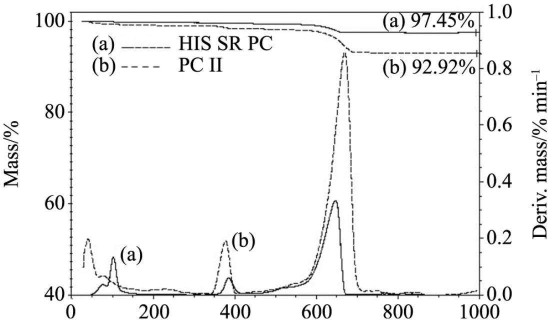

Figure 3. TG and DTG curves of the HIS SR PC and PC II.

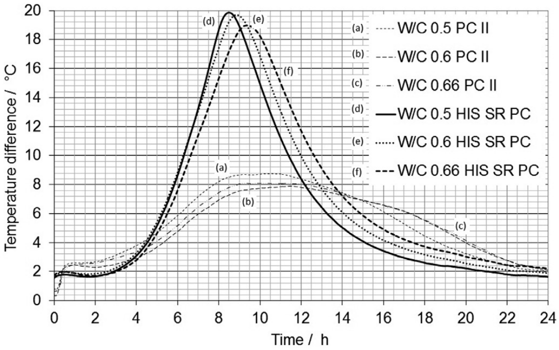

Figure 4. NCDTA curves from 0.5 to 0.66 w/c ratio in the first 24h of hydration for the HIS SR PC and PC II pastes.

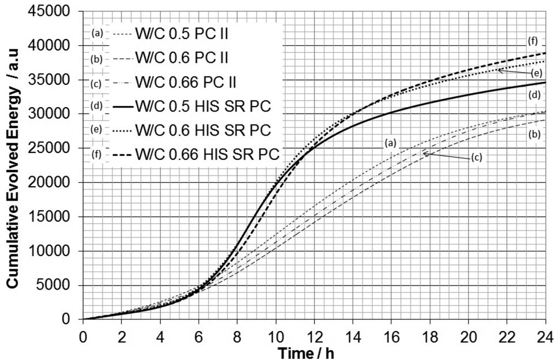

Figure 5. Cumulative evolved energy from 0.5 to 0.66 w/c ratio in the first 24h of hydration for the HIS SR PC and PC II pastes.

We can see from the Figure 5 that for the HIS SR PC pastes, from 0.5 to 0.66 w/c, presents the higher total cumulative evolved energy from hydration reactions at 24h, than the respective w/c ratios of the PC II pastes. With 4h, in spite of the PC II pastes presented a little higher cumulative evolved energy than the HIS SR PC pastes, all the curves were very close. It was explained previously by the authors due to the more fluid pastes in this stage where the cement content is the regulating factor[2]. As a general rule, a higher water content promotes a higher cement hydration in a same time[1,2]. Thus, the more fluid pastes of each cement, which had the higher water contents, formed more hydrated products and presented higher cumulative evolved energies. However, for the PC II pastes, the curves of the 0.6 and 0.66 W/C ratio cases were very close and difficult to distinguish. The higher temperature difference of the HIS SR PC pastes during the acceleration period showed in the Figure 5, contributed to the higher cumulative evolved energy results in the end of 24h in relation to the PC II pastes. As proven previously by the authors[2] the more fluid pastes also presented the higher cumulative evolved energy at the end of 24h.

Figure 6 shows the TG and DTG curves of the HIS SR PC and PC II pastes from 0.55 to 0.66 w/c ratio.

From these TG/DTG curves, the main phases were quantified as detailed in materials and methods. Results are shown in the next figures, with respective discussions. In the respective DTG curves for all the studied 24h pastes, appear two decarbonation steps. The first one, which occurs from the end of calcium hydroxide dehydration to the beginning of the second more visible DTG decarbonation step peak at about 600 °C, refers to the less crystalized $CaCO_3$ decarbonation. The second much more visible step, with a more expressive mass loss and DTG peak, to the more crystallized one. The higher is the crystallinity, the higher is the structural strength, which needs a higher temperature range to be decomposed[7].

A possible carbonation of the samples during the experiments, which could have changed the final amount of $Ca(OH)_2$ formed, were determined and compensated stoichiometrically.

Figure 7 shows the content of the hydrated products of the HIS SR PC and PC II pastes from 0.55 to 0.66 w/c ratios.

From the Figure 7, according to a previous work of the authors[1,2], we can see an increase of the amount of hydrated products with the increase of the hydration time. As noticed

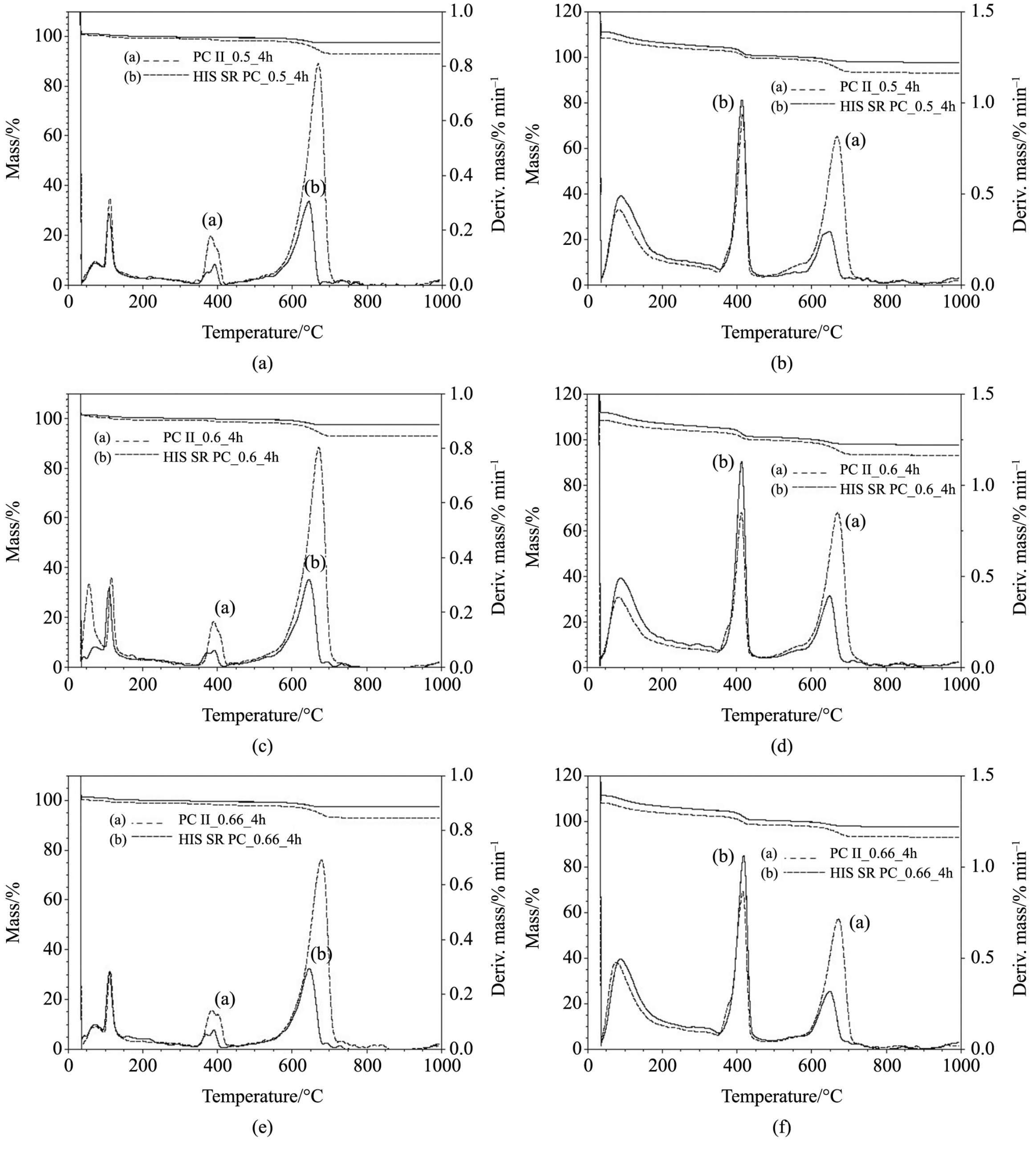

Figure 6. TG/DTG curves of the HIS SR PC and PC II pastes (a) for w/c=0.5 with 4h, (b) for w/c=0.5 with 24h, (c) for w/c=0.6 with 4h, (d) for w/c=0.6 with 24h, (e) for w/c=0.66 with 4h, (f) for w/c=0.66 with 24h.

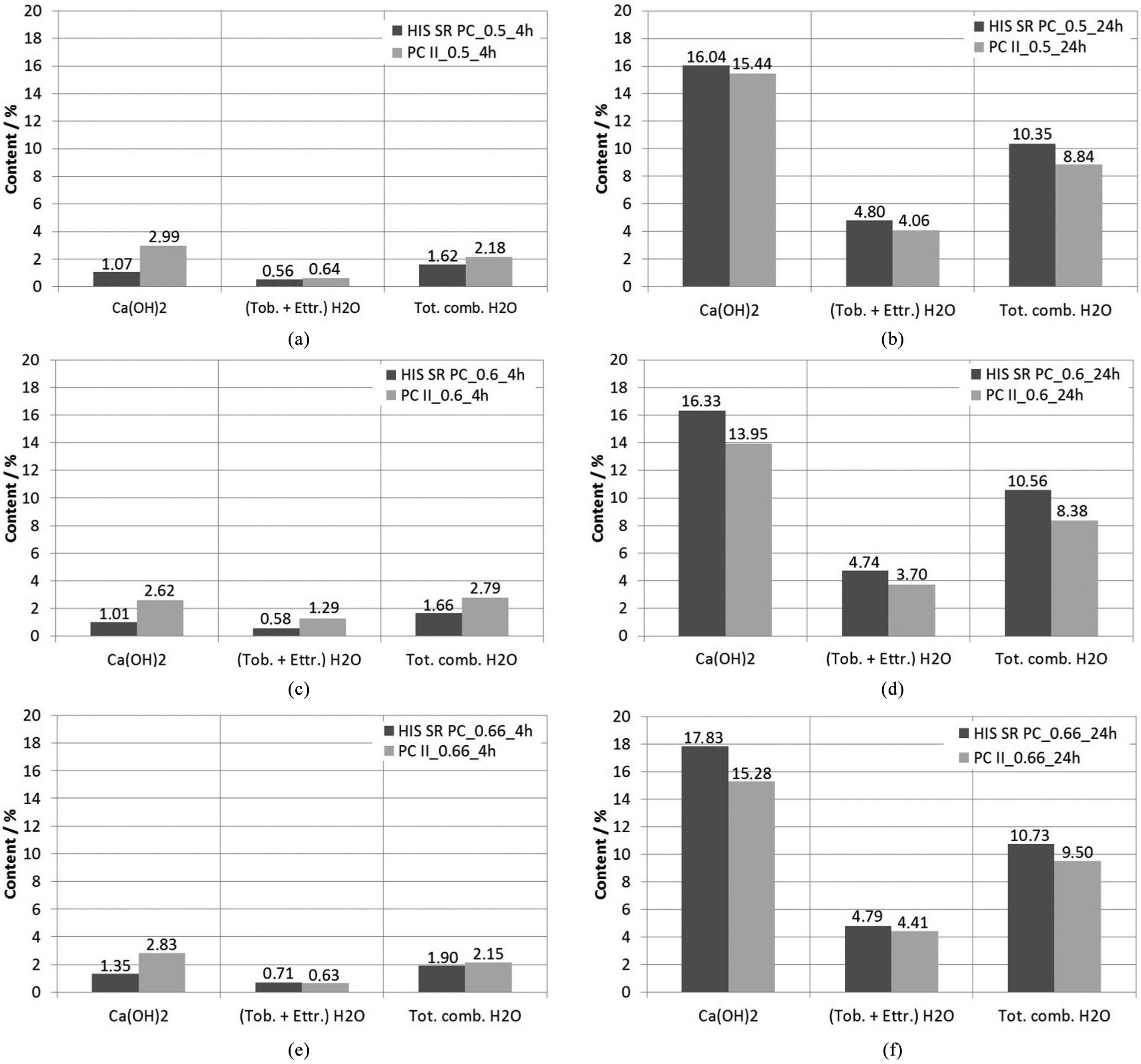

Figure 7. Content of hydrated products of the HIS SR PC and PC II pastes (a) for w/c=0.5 with 4h, (b) for w/c=0.5 with 24h, (c) for w/c=0.6 with 4h, (d) for w/c=0.6 with 24h, (e) for w/c=0.66 with 4h, (f) for w/c=0.66 with 24h.

in the Figure 4, the higher temperature difference for the PC II pastes, contributed to the higher amount of hydrated products formed than the HIS SR PC pastes until 4h of hydration time. With the hydration reaction proceeds and the water is consumed, besides the amount of hydrated products increases with the w/c ratio[2], the temperature difference of the HIS SR PC pastes is higher than the PC II pastes mainly during the acceleration step, contributing to a higher amount of hydrated products formed in the end of 24h of hydration for the HIS SR PC pastes than the PC II pastes. According to the Figure 5, the results of the cumulative evolved energy, also corroborates the explanation of the amount of the hydrated products formed, being higher for the PC II pastes than the HIS SR PC pastes until 4h, where it presents higher cumulative evolved energy values and in the end of 24h of hydration, where the HIS SR PC forms more hydrated products, presenting higher values of cumulative evolved energy.

5. Conclusions

Thermogravimetric and derivative thermogravimetric analysis allow one to quantify the hydrated products and to evaluate the influence of the HIS SR PC and PC II in the hydration reactions that occur in the first 24h.

The NCDTA analysis allow one to study on real time, the influence of the w/c ratio and the HIS SR PC and PC II in the hydration reactions, by the heat released from exothermic effect.

From the NCDTA results of the HIS SR PC and PC II pastes, was possible to correlate the exothermic effect by the temperature difference registered with the amount of hydrated products calculated by thermogravimetric and derivative thermogravimetric analysis.

Until 4h of hydration, where the PC II pastes presents higher temperature difference from the NCDTA analysis and consequently higher cumulative evolved energy, the amount of the main hydrated products were higher than the HIS SR PC pastes. With 24h of hydration, due to the higher exothermic effect of the HIS SR PC pastes during the acceleration step, shown in the NCDTA analysis and the cumulative evolved energy results at 24h of hydration, explains the higher amount of the main hydrated products than the PC II pastes at this time.

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