

Evaluation of the Hydration of Portland Cement Modified with Polyvinyl Alcohol and Nano Clay

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Abstract. Polyvinylalcohol (PVA) is a polymer soluble in hot water, it has the property of film formation and it can improve the concrete performance. The effects of PVA modified with nano clay on the cement hydration reaction have been investigated by means of semiadiabatic calorimeter, FTIR spectroscopy and SEM. FTIR spectroscopy was employed to monitor chemical transformation of cement. The morphology of the different samples was compared by means of SEM micrographs. With the semiadiabatic calorimeter the hydration kinetic was measured to compare the heat rate of the admixtures materials. Fixing the water–cement ratio, w/c, in 0,45, the ratio of polymer to cement (p/c) was 2 wt% and the ratio of clay to polymer was 4 wt% (0.8wt.% related to cement). The polymer and modified polymer admixtures produced a retardation effect on the kinetic of cement hydration, but the clay acts as nucleating agent. The increase of the temperature with time was measured and a new model with four parameters was employed and the kinetic parameters were determined for each sample.

Introduction

The mechanism of cement hydration was studied in the literature [1]. It consists of three main periods: the early, middle and late periods. The very early period is called the pre-induction period during which a rapid chemical dissolution takes place. The early period is a dormant stage, which takes place for several hours. The third period is the middle period which occurs during 24 to 48 h, in which ions transport to and from the surfaces of anhydrous cement particles through gradually growing layers of hydration products, and it is the main period of hydration. During the late period, which is the longest and dominant one, the reaction is diffusion-controlled. The free water in macropores permeates through the hydration products formed around the anhydrous cement core, making further reactions possible.

The kinetic hydration of cement is widely studied in the literature and some of these papers reported the chemical, physical and mechanical behaviour [2-5]. Simplified models were used by Knudsen[6], Basma et al [7], Schindler and Folliard [8], Bentz [9]. The majority of these models are empirical, based on experimental observations of macroscopic phenomena, and they take into account the effects of curing temperature, water–cement ratio, fineness, particle size distribution and chemical composition of cement [5].

Polymers such as EVA, are used as admixture because they modify the elastic modulus, toughness, permeability and bond strength to various substrates in cement and mortars [10]. The polymer forms a film that creates a network inside the cement matrix, partially covering hydrated and anhydrous cement particles, sealing pores and bridging microcracks. Besides, this addition also changes the hydration rate. Silva et al [11] compare the effects of two polymers: a water soluble polymer (HPMC — hydroxypropylmethylcellulose) and a latex [EVA-poly(ethylene-co-vinyl acetate)] on

the early hydration of cement paste. Soft X-ray transmission microscopy was used for studying the hydration of two cement phases. The microscope technique allowed the observation of nucleation and growth of hydrates, as well as the effect of the polymers on the hydration. Cellulose ether delays the hydration of the cement particles as well as EVA polymer. Wang et al [12] studied the influence of styrene-butadiene rubber (SBR) latex on cement hydrates $\text{Ca}(\text{OH})_2$, ettringite, C_4AH_3 and C-S-H gel on the degree of cement hydration. With wet cure, appropriate addition of SBR promotes the hydration of cement, while the effect of SBR on the content of $\text{Ca}(\text{OH})_2$ and the degree of cement hydration is not remarkable in mixed-cured SBR-modified cement pastes. XRD results showed that SBR accelerates the reaction of calcium aluminate with gypsum, and thus promotes the formation and stability of the ettringite and inhibits the formation of C_4AH_3 .

Recently, Scrivener and Kirkpatrick [13] have written about innovations in concrete technology. They discussed the use of nanoparticles as a route of innovation in cement technology. Nanoclays are now widely used as fillers in polymer matrices [14]. The composite obtained by mixing clay and polymer can be different types: microcomposites when the silicate layers are agglomerated into the polymer, intercalated when the polymer chains are intercalated between the clay layers, and exfoliated nanocomposites when the clay layers are completely distributed into the polymer matrix. Polyvinylalcohol is a good candidate for obtaining a good dispersion of clay in this polymer [15-16]. Due to the hydrophilic nature of the clay and the polymer, these compounds can be well dispersed by water. PVA is a thermoplastic polymer with high elongation at break and as consequence low Young modulus. Besides, water acts as plasticizer of the polymer and decreases the modulus. The addition of clay increases the modulus of the polymer matrices [15, 17]. In this way, the mixture of clay and PVA can produce a reinforced polymer.

The aim of the work is to develop new cement admixtures by using bentonite clay, PVA and their mixture. The study of the effect of PVA and clay on the hydration rate of cement paste will be done, as well as, characterization of the final modified cement by means of FTIR, TGA and SEM. From our knowledge, there is not previous publication utilizing these admixture combinations in cement.

Experimental

Materials and Methods. The Portland cement used was ternary blend cement, "Cemento 5-5", from Cemento Loma Negra, Argentina, with $300 \text{ m}^2/\text{kg}$ of blaine surface. PVA was provided by Química Oeste, Buenos Aires, Argentina, and the hydrolysis degree is 88%. The clay was provided by Minarmco, Argentina. It was a sodic bentonite and it was used as received.

An automatic/manual mortar mixer Hobart model N° 50 was utilized. The cement was mixed with water that was poured into the mixing bowl after adding the cement. The ratio of water to dry cement, as received, was 0.45 by weight. The water was carefully added and the paste was mixed on the mixing blade.

PVA was dissolved in water (4wt.%). The mixing was made at 80°C and using a 1900 rpm agitator for 2 h. The solution was cooled down until room temperature and stored for 24 h before use.

To include clay the procedure was similar. The clay in 0.8wt% to cement was one of the studied samples. Other sample was prepared with clay in a 4wt% concentration of PVA. Clay was included in hot PVA at 80°C during 30 min at 1900 rpm. Then, it was sonicated for 30 min. Again, the solution was cooled down until room temperature and stored for 24 h before use.

These solutions replaced water when the paste was made. The cement paste was mixed for 3 min at 60 rpm with a stop in between for 30 s to scrape the paste from the inside walls, and for 30 s at 120 rpm.

An adiabatic box of 200 mm x 200 mm was fabricated with 80 mm Styrofoam top, base and wall thickness. The temperature was determinate with a Concrete Madurimetry Tester model H 2680. The room temperature was measured as well as the temperature in centre of the paste. The zero

hydration time was measured from the instant when the water was added to the cement. At least, three specimens were measured for each sample, and an average value was obtained for the results. The volume of the sample was a cylinder of 80 mm of diameter and 200 mm height.

FT-IR spectra was analysed with a Nicolet 8700 spectrometer. Powdered samples are mixed with KBr and pressed into pellets. The analyses are carried out in the frequency range of 400–4000 cm^{-1} , using 4.0 resolution and 32 scans.

For thermogravimetric analysis (TGA), a Shimadzu TGA-51 is used. The samples are heated from room temperature to 1000 $^{\circ}\text{C}$ with a heating rate of 10 $^{\circ}\text{C}/\text{min}$ in a N_2 atmosphere.

For these analyses the paste was mixed as commented afore and the samples were covered for 2 days before demolding. The curing implied storage, after demolding, in a moist room for 1 day (20 $^{\circ}\text{C}$, 93% R.H.).

The microstructure of the paste was investigated with a Zeiss Supra 40 Scanning Electron Microscope (SEM) and Energy Dispersive X-Ray spectroscopy (EDS). For the analysis in the secondary electrons (SE) mode, the paste was converted in powder and some fragments where polished.

Adiabatic temperature measurement and kinetic parameters determination. The reaction rates may be followed using a thermocouple immersed in a relatively large volume of sample and adiabatically isolated [18]. The adiabatic temperature rise method was applied by taking into account corrections for heat losses. The thermal energy balance may be written as:

$$cp(dT_{\text{exp}}/dt) = (-\Delta H)(d\alpha/dt) - U(T_{\text{exp}} - T_o) \quad (1)$$

where U is a global heat transfer coefficient per unit mass, T_{exp} is the measured temperature and T_o is room temperature, cp is the specific heat, t is the time and α is the cure degree or hydration degree.

Integration of Eq. (1), for sufficiently long times when $d\alpha/dt \rightarrow 0$, leads to

$$\ln(T_{\text{exp}} - T_o) = \ln(T_{\text{exp}_1} - T_o) - U'(t - t_1) \quad (2)$$

where (T_{exp_1}, t_1) is the particular set of values at the beginning of the integration and $U' = U/cp$ is assumed to be constant.

One can obtain the relationship between T_{exp} and T_{ad} , the latter being the hypothetical value of temperature under adiabatic conditions:

$$dT_{\text{ad}}/dt = dT_{\text{exp}}/dt + U'(T_{\text{exp}} - T_o) \quad (3)$$

Integrating Eq. (3), leads to:

$$T_{\text{ad}} = T_{\text{exp}} + \int_0^t U'(T_{\text{exp}} - T_o) dt \quad (4)$$

which enables the calculation of the adiabatic curve from experimental information.

The following adiabatic thermal energy may be written for an arbitrary volume surrounding the measuring point:

$$cp(dT_{\text{ad}}/dt) = (-\Delta H)(d\alpha/dt) \quad (5)$$

where $(-\Delta H)$ is de hydration heat per unit mass.

For $\alpha = 1$, $T_{\text{ad}} = T_{\text{ad max}}$, and

$$(T_{\text{ad max}} - T_o) = \Delta T_{\text{ad}} = (-\Delta H) / cp \quad (6)$$

$$\alpha = (T_{\text{ad}} - T_o) / \Delta T_{\text{ad}} \quad (7)$$

The reaction rate or kinetic expression for the cement hydration can be written as follows [19-20]:

$$d\alpha / dt = k \cdot f(\alpha) \quad (8)$$

In order to fit the experimental values to a model, an empirical expression of flow rate reaction is used:

$$f(\alpha) = \alpha^m (1 - \alpha)^n \quad (9)$$

where k is the reaction constant rate, and it can be approximated with the Arrhenius equation:

$$k = A \exp[(-E/R)(1/T)] \quad (10)$$

where A is the pre-exponential factor and E is the apparent activation energy. From the Eq. (8), (9) and (10), and using a logarithm in both sides one can obtain the following equation:

$$\ln \left[\frac{d\alpha / dt}{f(\alpha)} \right] = \ln A - \frac{E}{R} \left(\frac{1}{T} \right) \quad (11)$$

Finally the pre-exponential factor (A) and the apparent activation energy (E) can be calculated from the equation (11) drawing the left side in function of 1/T.

Results and Discussion

Adiabatic measurements and kinetic parameters. The experimental temperature measured in a semi adiabatic box and the adiabatic temperature rise, obtained from a paste with w/c=0,45, is shown in the Fig. 1. Once the adiabatic temperature is known the global heat transfer coefficient (U) can be determinate with a good correlation coefficient (Fig. 2).

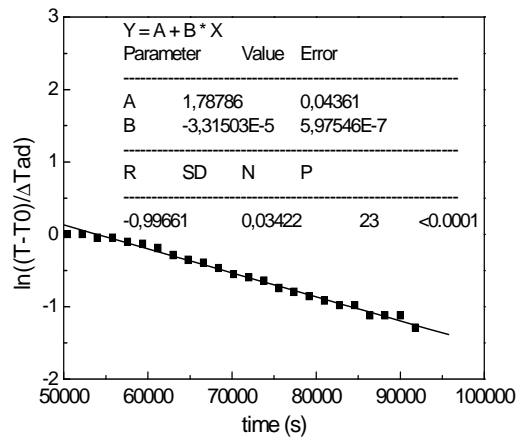
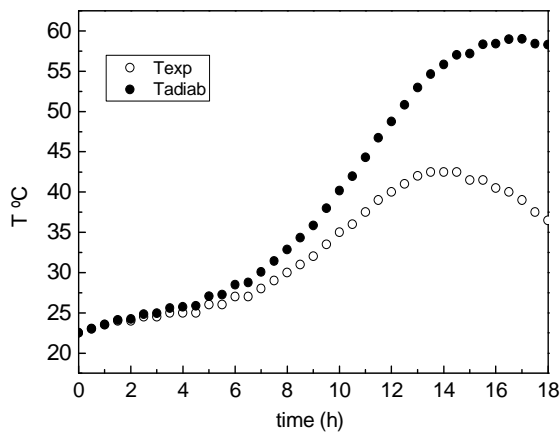


Figure 1: Temperature vs. Time for: O: Experimental temperature, ●: Adiabatic temperature. Water/cement paste with 2 wt.% PVA, ratio w/c=0,45

Figure 2: Determination of the global transference coefficient, $U' = U/C_p$ in a water/cement paste with 2 wt.% PVA, ratio w/c=0,45. $U' = B$

Fig.3 shows the adiabatic temperature versus time for all the studied samples. The addition of clay to the cement paste produces a diminution of the induction period and an increase on the maximum of temperature. Clay accelerates the hydration ratio because it acts as nucleating agent of the CH crystallization.

By the contrary the addition of PVA (which is complete dissolve in water) produces a delay on the hydration rate and a decrease of the maximum temperature. The polymer could encapsulate

some cement particles and produces a gel around them. It has been reported that the precipitated microstructure morphologies are strongly influenced by the available interparticle spacing [21], but the compatibility of PVA for water molecules compete for water availability. Since PVA polymer is used commonly on the preparation of hydrogels, it swells and reduces the accessibility of water to the cement and acts as control release.

The addition of a mixture of PVA and clay did not make any change on the kinetic rate in comparison with the addition of pristine PVA. If the clay was intercalated or exfoliated into the PVA, it would have produced a tortuous path in the PVA and the diffusion rate of water through the polymer should have been reduced [22]. However, in this case the clay is agglomerated into the PVA (as it was confirmed by SEM) and it did not created any change on the water availability behavior.

The hydration degree, α , was calculated taking into account the adiabatic temperature, the initial temperature and the ΔT_{ad} . The maximum hydration degree varies with the formulation, i.e the addition of clay produces a higher ΔT_{ad} and as consequence higher hydration degree. However, it was considered that the sample of pristine cement paste reached the hydration degree equal to one, because it was used as reference sample. The ultimate value was obtained dividing the $\Delta T_{ad}/\Delta T_{ad}^{max}$, being ΔT_{ad}^{max} the value for the non admixture sample.

Fig. 4 shows the results for the three samples: cement paste (CTO), cement paste and PVA (CTO+PVA) and cement paste with PVA and clay (CTO+PVA+clay). In order to fitting the reaction rate, a global kinetic equation (12) was applied (Fig 5).

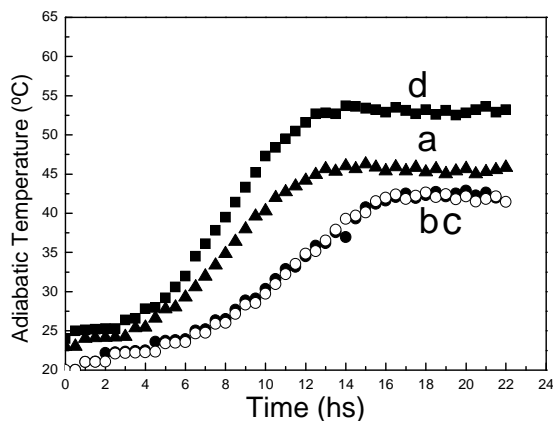


Figure 3: Adiabatic temperature vs time for different samples: a) Cement, b) Cement and PVA, c) Cement, PVA and clay, d) Cement and clay.

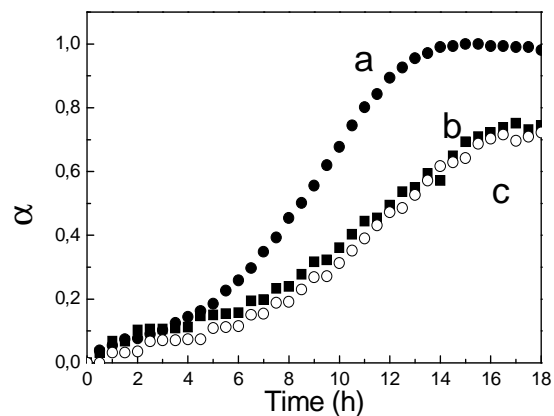


Figure 4: Degree of curing, obtained from the adiabatic temperature for a $w/c=0,45$: a) Cement, b) Cement and PVA, c) Cement, PVA and clay.

Table 1 shows the values of activation energy and pre exponential parameters. These values are within the values founded in the bibliography. For example, using different models and formulations Maekawa et al [23] and Wang and Lee [24], reports values from 37 to 110 kJ/mol. Fernández-Jiménez and Puertas [25], founded a value of 57,6 kJ/mol using activate cement.

Several different opinions are in the literature about the dependence of the activation energy value. van Breugel and Guang [26] argued that E is a function of chemical composition of cement, curing temperature and the degree of hydration. Freiesleben Hansen and Pedersen [27], on the other hand, suggested that E is only a function of curing temperature. Schindler [28] proposed an equation for E that considers the chemical composition and fineness of cement. From our applied model, the constant of the reaction rate, k , is a function of A , E and T . However, the apparent activation energy

doesn't depend on the temperature. The pre-exponential factors and E depend on the paste formulation.

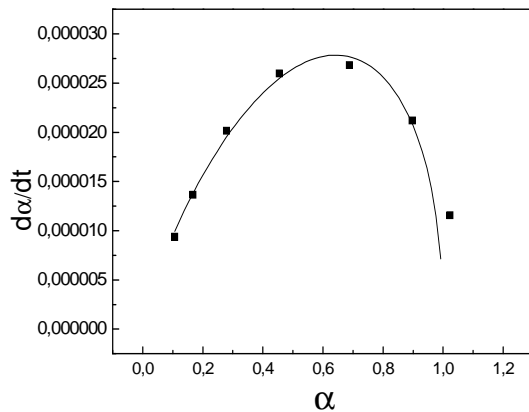


Table 1: Kinetic parameters values

Parameters Samples	A s ⁻¹	E kJ/m ol	m -	n -
W/C=0,45; 0,8wt%Clay	1,61 E03	43,5	0,701	0,667
w/c = 0,45	4,4E+04	52,4	0,739	0,353
w/c = 0,45; PVA 2wt.%	1,3E+07	67,3	0,563	0,235
w/c = 0,45; PVA 2wt.%; Nano Clay 4wt.% PVA	1,7E+07	66,7	0,803	0,447

Figure 5: Fitting of reaction rate with the model of m , n , and k parameters for cement and PVA sample: ■ experimental points, --- model.

When PVA was added to the water-cement sample, the polymer shifted the hydration process to higher times and it has lower hydration final degree and maximum adiabatic temperature, because the gel formed by the polymer hinders the hydration of cement with water, as it was stated before. As consequence, the apparent activation energy for the modified cement-water sample is higher than for pristine cement-water. The E values for PVA and PVA+clay are similar, and it is an indirect indication that the polymer has covered the clay.

FTIR characterization. The FTIR spectra (Fig. 6) of unmodified and modified cement pastes are compared after 4 days of hydration. Analysis of pristine PVA and nanoclay was also made. In the range between 3100–3700 cm^{-1} , the H_2O and OH^- stretching bands appear [29]. They are also present in the spectrum of the anhydrite paste, because of the hygroscopicity of the cement. A small increase of the OH^- band, associated with the $\text{Ca}(\text{OH})_2$ molecules, is recorded at $\sim 3643 \text{ cm}^{-1}$, when compared to the anhydrite paste. The cement samples have a higher peak than the paste with PVA and PVA/clay. A cement paste hydrated for 28 days has a higher peak than the peak hydrated for only 4 days.

The progress of hydration is also characterized by a shift of the S–O asymmetric stretching vibration (ν_3) to higher wave numbers (929 to 974 cm^{-1}), due to the reaction of the SiO_4^{2-} units during C–S–H formation. The bands, associated with the polymer itself, can be detected only for PVA unmodified, recorded at $\sim 1740 \text{ cm}^{-1}$, which arises due to the carbonyl bond (C=O) of the acetate group found in partially hydrolyzed PVA polymer.

The peak at $\sim 1225 \text{ cm}^{-1}$ shows the amount of SiO_4^{2-} in the paste. It's higher when there is nanoclay due to this material is composed basically of SiO_4^{2-} .

The bentonite has peaks in the region of 3000-3700 cm^{-1} attributed to bentonite-rich smectite and also at 1000 cm^{-1} due to $\text{Al}(\text{OH})_3$ [30]. As consequence, the peaks at that position are slightly wider in comparison with the PVA/cement.

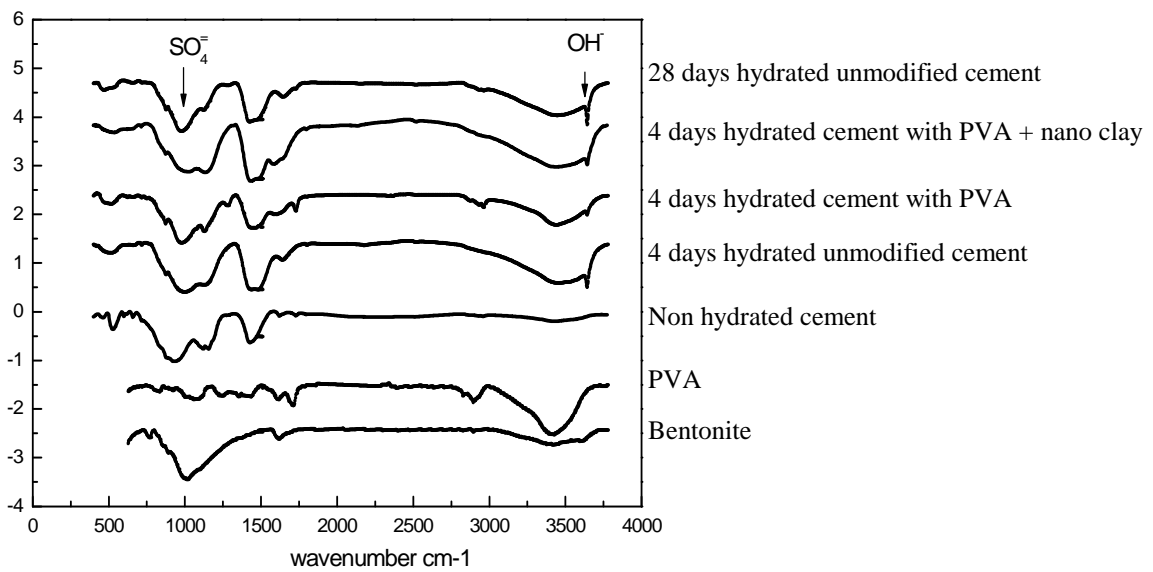


Figure 6: FTIR spectra for the different samples

SEM characterization. The results of the SEM investigation show the cement hydration. Although water-soluble polymers are added at very low polymer–cement ratios, polymer film formation is detected.

The morphology of the crystals is compared in grinded and in surface polished samples. The addition of small amounts of PVA and modified PVA retard the hydration showing less products of hydration. At high magnifications, polymer is founded between the products of hydration that grow surrounded by these layers, which act as an additional bond.

Fig. 7a-c show images of the products of hydration in the cement paste. Ettringite, hydrated calcium silicates and $\text{Ca}(\text{OH})_2$ were detected due to their typical morphologies.

In order to know how it is the clay into the cement with PVA, a SEM microscopy was performed at a sample of cement paste modified with PVA (2wt.%) with 20 wt% of nanoclay on PVA. Fig. 7 d shows small round particles analyzed with EDS. The high peak of Silica (Si) confirms that it is clay and the peak of Ca shows it is over a $\text{Ca}(\text{OH})_2$ crystal. Fig 8 established that the PVA wrapped the clay due to their chemical compatibility, especially due to the non hydrolysed part of PVA (presence of acetate groups).

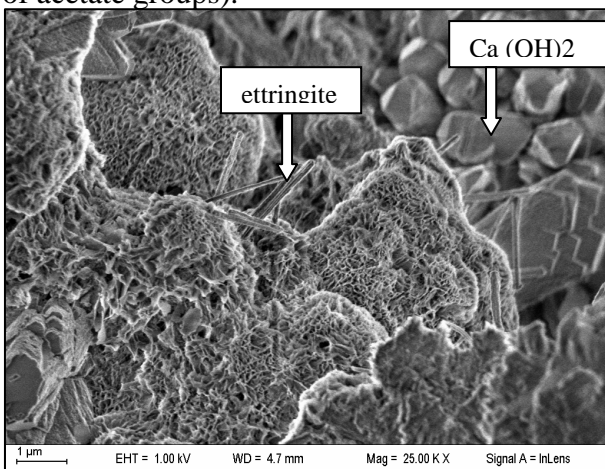


Figure 7.a: Cement hydrated ($w/c=0,45$) unmodified. Surface polished sample.

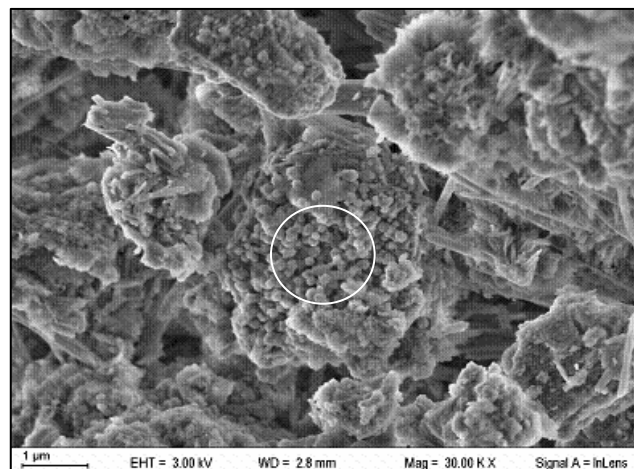


Figure 7.b: Nanoclay particles in between of polymer over a $\text{Ca}(\text{OH})_2$ crystal. Surface polished sample.

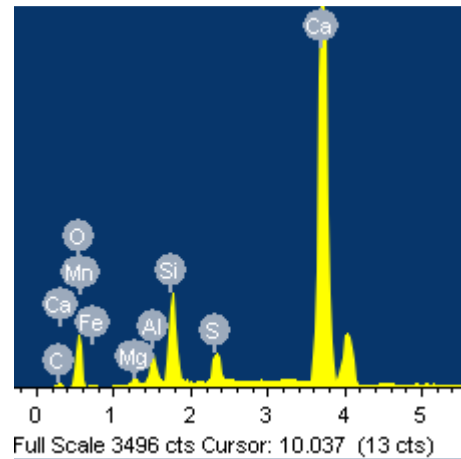
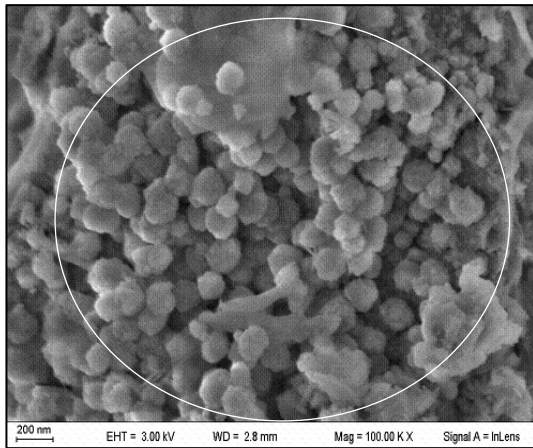


Figure 7.c: Nanoclay particles in between of polymer over a $\text{Ca}(\text{OH})_2$ crystal. Surface polished sample. (Figure 7 zoomed)

Figure 7.d: EDS

TGA measurements. With thermogravimetric analysis (Fig.8) the amount of $\text{Ca}(\text{OH})_2$ content for unmodified cement and modified cement pastes ($w/c=0.45$) was estimated [31]. Small mass losses appear at $\sim 450^\circ\text{C}$ ($\text{Ca}(\text{OH})_2$) and at $\sim 750^\circ\text{C}$ (CaCO_3). The amount of $\text{Ca}(\text{OH})_2$ mass loss because of ignition was calculated, results are presented in Table 2. Similar results were obtained by Knapen and Van Gemert [29].

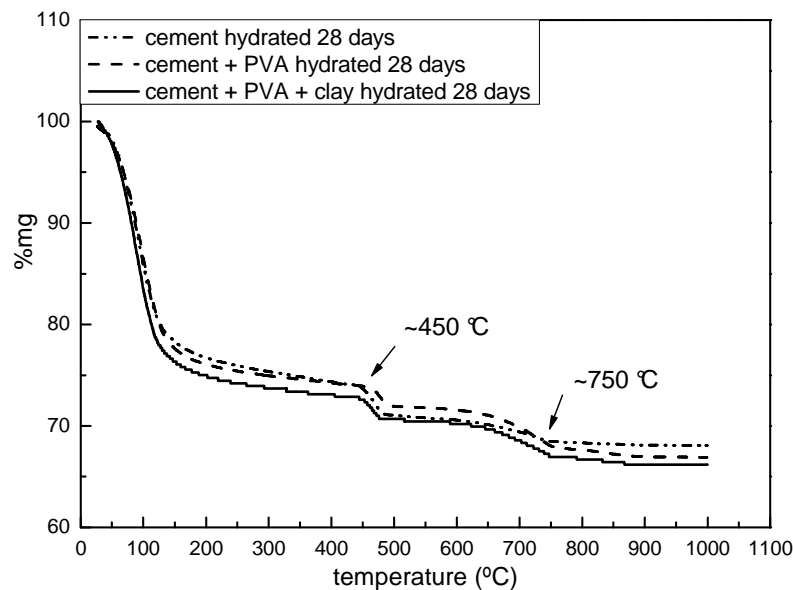


Figure 8: Thermogravimetric results for different samples

Conclusions

The study of the effect of the addition of PVA and clay to the cement-water hydration was done. A general and empirical method for determining the kinetic parameters was used. The apparent activation energy was higher for the case of the polymer and polymer-clay addition than clay and pristine cement paste. The maximum adiabatic temperature reached was for the case of cement-water and clay sample. The polymer swells and produces a film around the cement and delay the cement hydration. Instead, clay acts as nucleating agent and produces a high hydration rate. The addition of clay to PVA did not affect the hydration kinetics.

From FTIR it was possible to identify the progress of the hydration by means of the shift of the S-O asymmetric stretching vibration. PVA was identified by the acetate group. The bentonite

produces a slightly wide of the peak due to alumina-silicates. TGA have permitted to determine the $\text{Ca}(\text{OH})_2$ for each sample. SEM microscopy was a useful technique for identify each new formed compound and the morphology of the granular composite. More experimental work is being done with chemical modified clay in order to obtain different hydration rate.

Acknowledgments

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Polymers in Concrete

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