



Review

Use of simple non-destructive techniques to evaluate the hydration reactions of PVA-modified cement pastes

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HIGHLIGHTS

- Hydration reaction of PVA-modified cement paste is measured.
- Simple non-destructive techniques are used to measure the hydration reaction of cement pastes.
- Adiabatic temperature rise, ultrasound transit time and permittivity decrease are compared.

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ABSTRACT

The rapidity of the hydration reaction defines the final properties of cement-based materials. Global techniques show the overall hydration reaction and make it easier for users to evaluate it in a simple non-destructive way, to assess the product and to foresee its final properties. In this paper, three global, simple non-destructive techniques (adiabatic temperature rise, ultrasonic pulse transit time and permittivity increase) showed the same fifth stages in the hydration of two different cement pastes, being able to tell apart their singular hydration reactions. Polymers, such as PVA, are widely used in the construction industry. These affect significantly the hydration reaction of the cement based materials. This paper demonstrates the validity to measure it for PVA-modified cement pastes by means of these techniques giving the building construction industry the chance to use the most available one to evaluate its material hydration reaction as a quality control tool.

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1. Introduction

The hydration reaction of the cement paste and the events associated to it, such as heat generation, strength development and mass contractions, are the result of chemical, physical and mechanical processes. Deeply understanding it is a very important tool to predict the behaviour of the material in the long term [1–2].

Polymer modified mortars are widely used in the ready-mix industry. Polymers combined with cement-based materials generate a synergetic action that improves the cement properties and broaden its applications [3–15]. Polyvinyl alcohol (PVA) is a water-soluble polymer that forms a film in the cement matrix. This film forms during the hydration of the cement based materials behaving as an adhesive to aggregates [4,6] and improving the material performance given its low elasticity modulus and high tensile strength (68.5 MPa and 22.5 MPa, respectively [14]). This is a polymer among many others used in the constructing industry.

It is known that the addition of small amounts of water-soluble polymers to the cement paste can significantly influence in the hydration reaction of the modified cement paste [8,11–13]. This can be a setback when using these materials, then controlling the hydration reaction rate is advisable.

In previous works, the hydrating reaction of cement paste and paste modified with polymers was evaluated by measuring techniques such as temperature rise in semiadiabatic conditions, thermal analysis, infrared spectroscopy and scanning electron microscopy [16–19]. These are only some of many existing techniques to evaluate cement hydration, every time more accurate and analysed with very sophisticated instruments.

In this work, three global, non-destructive and simple techniques are studied: the temperature rise in adiabatic conditions, the transit time of ultrasonic pulses that travels through the cement paste while it hardens and the decrease of the conductivity of the cement paste during the hydration reaction. These techniques are characterized by their robustness and simplicity to perform and to analyse. They have what the building construction industry needs to evaluate the hydration.

Regarding the adiabatic temperature rise, the kinetics and mechanisms of hydration of cement pastes can be investigated satisfactorily by measuring it in adiabatic conditions and with other thermal techniques widely studied in the literature such as isothermal calorimetry, thermogravimetry and differential scanning calorimetry [7,17,20–22]. The adiabatic temperature has the particularity of reflecting the amount of temperature that the cement pastes can reach in a condition where there is no heat loss. This method is very useful to prevent, for example thermal cracking and to design mass concrete [23]. It can also reflect the chemical reactions that occur in the hydrating cement paste illustrating, as well, whether the addition of polymers to the cement paste accelerates or retards the hydration rate [7,16–17,20–22].

The hydration process of cement pastes can also be assessed by measuring the transit time of ultrasonic pulses passing through the matrix under study in a non-destructive way [24–29]. Initially the transit time of the ultrasonic pulse is very close to that of water, since water is the predominant phase. Then the pulse rate begins to diverge. This moment is known as the solid percolation threshold and corresponds to the initial setting time of the cement paste [25–27,30]. Hydration products form a network that prevents the free flow of the water solution in the cement matrix [31]. When this network is formed the hardening of the cement paste begins. The liquid phase ceases to be the predominant phase of the system, which is at this moment, the hydration products structure. The transit time will continue to increase until reaching a maximum value, and then it remains almost constant over time. The final

transit time value is related to the final elasticity modulus of the sample.

Finally, measuring the conductivity of cement pastes provides a non-destructive technique for monitoring the development of its hydration. This method has the advantage that it can be performed in situ [31–32]. The conductivity monitoring is based on the assumption that a system that goes under physical and chemical changes shows variations in its electrical parameters [31,33–34]. The amount of water of the cement paste and its interaction with the anhydrous cement has a significant influence on the dielectric response [32–33,35]. Similar to the strength, the dielectric properties of cement mixtures still vary over several months after mixing, although the most significant variations will occur within the first few days [32]. By monitoring the conductivity, it is possible, with the help of experimental and theoretical correlations, to assess the degree of hydration of cement-based materials [29,32,34–35].

Levita et al. [31] studied the relationship of the loss of connectivity of the macroscopic porosity, which they called “depercolation”, with this technique and found a coincidence between it and the Vicat Test. They established that this method was able to lead to a more general comprehension of the evolution of the microstructure of the system that could be incorporated in process and quality control protocols which is an essential requirement nowadays.

The aim of this work is to evaluate the hydration of two cement pastes, pristine cement paste and PVA-modified cement paste, with very different hydration behaviours, by means of three simple non-destructive techniques. To analyse whether these techniques are sensible enough to evaluate and differentiate their hydration and to assess them as quality control tools.

2. Materials and methods

2.1. Materials

Pure portland cement class 50, (CPN 50 according to the Argentinian regulation: IRAM 50000), equivalent to CEM I 52.5, from Loma Negra S.A. was used. Its chemical composition was provided by the company and is detailed in Table 1. It has an ignition loss of 1.67% and a Blaine surface of 442 m²/kg.

Poly(vinyl alcohol) (PVA) was used to modified the cement paste. Its commercial name is *Celvol 823* from the company Celanese Chemicals. *Celvol 823* is a poly(vinyl acetate) hydrolysed an 87–89%. In Fig. 1 its chemical structure can be appreciate.

PVA was received as pellets. It was dissolved in water at 80 °C by means of stirring. For homogenization, the solution was

Table 1
Chemical composition of CPN50.

Main phases	%
C ₃ S	61.2
C ₂ S	13.3
C ₃ A	2.7
C ₄ AF	13.4
Oxides	%
CaO	63.53
SiO ₂	20.71
Fe ₂ O ₃	4.40
Al ₂ O ₃	3.81
SO ₃	2.87
MgO	0.79
K ₂ O	0.92
Na ₂ O	0.06
Loss on ignition	1.67
Insoluble residue	0.26

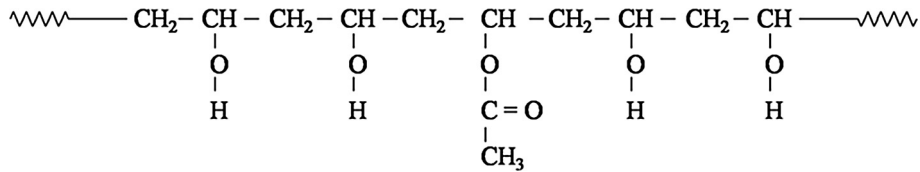


Fig. 1. Chemical structure of the partially hydrolyzed poly(vinyl alcohol).

Table 2

Composition of the cement sample (CP) and the PVA modified cement sample (CP + PVA).

	CP [kg/m ³]	CP + PVA [kg/m ³]
Cement	1290	1257
Water	580	569
PVA	0	22
Defoamer	0	2
Total	1870	1850

sonicated. The solution replaced the mixing water for PVA-modified cement paste.

2.1.1. Composition and sample preparation

To study the hydration reaction of the cement paste and PVA modified cement paste, water to cement ratio (w/c) was fixed at 0.45. PVA modified pastes were prepared with a polymer to cement ratio (p/c) ratio of 1.80%, taking into account the results of Kim and Robertson [4]. To prevent the incorporation of air introduced by PVA an antifoaming agent was used in a 0.16% by weight of cement.

The mixing of the cement and the water or the PVA solution was performed as recommended by the PROCELAB Cementing Manual [36]. All materials were weighed in a precision balance. The dry fraction was manually homogenized before being mixed with the liquid fraction. A Chandler Engineering mixer, model 30–60 with a 1 litre capacity and a Chandler Engineering, Model 30–70 with a 4 litre capacity were used. Both mixers have a tachometer and a timer for precise control of time and rotation speed. The PROCELAB Cementing Manual recommends a mixing speed of 4000 rpm for 15 s, for a volume of 600 ml of paste. During this time, the

dry phase is added to the liquid phase contained in the mixer. The speed is then increased to 12,000 rpm and held on for 35 s. When mixing 1800 ml the speed was maintained at 2970 rpm for 110 s.

Table 2 shows the composition of both the cement sample (CP) and the PVA-modified cement paste (CP + PVA).

2.2. Experimental

2.2.1. Study of the cement hydration by measuring the temperature rise in adiabatic conditions

The adiabatic temperature rise was measured on a special device designed for this purpose in the LABEST of the Universidade Federal do Rio de Janeiro. Fig. 2 shows a sketch of the equipment. It has water baths where the samples are introduced. Each bath has two thermometers, one associated to the bath and the other to the sample. Thermometers measure the respective temperatures constantly and are associated to a controller, which is also associated to a heating and cooling controller. This system keeps the difference between sample's temperature and the bath's temperature with a maximum difference of 0.1 °C. Every tenth of a Celsius degree that the sample increases due to the hydration reactions of cement paste, the temperature of the water in the bath where the sample is immersed increases, as recommended by RILEM [37]. In the baths, connected to the heating and cooling system, shakers constantly remove the water in order to maintain constant the temperature throughout the whole volume.

The thermometer associated with the sample is placed in the centre of a metal mould of 150 mm diameter (1800 cm³). The sample is completely isolated from the water by the mould. It is also thermal insulated and sealed to prevent water ingress.

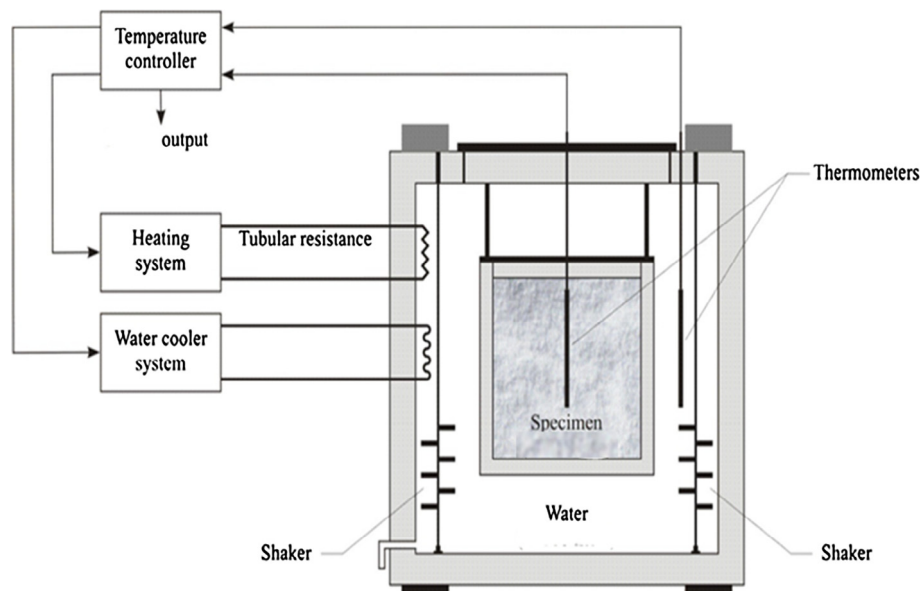


Fig. 2. Schematic description of the adiabatic calorimeter [38].

Since the baths have water, the maximum temperature measurable is 100 °C. To get as much data as possible the initial temperature was set between 8 and 10 °C. Thus, it was possible to study an adiabatic gap of 92 °C.

Time zero is considered when the water or the polymer solution gets in contact with anhydrous cement. For each result, the test is repeated twice. The reported results show the average temperature. Each measurement was performed until the sample reached 100 °C.

2.2.2. Study of the cement hydration by measuring the transit time of an ultrasonic pulse

The cement paste hydration was also studied by measuring the transit time of an ultrasonic pulse through the cement paste during the hydration reaction. This was done using the “Ultrasonic Cement Analyzer” (UCA), Chandler Engineering, model 4262. This device has sensors that continually determine the speed at which ultrasonic pulses pass through the cement pastes. Its design is based on the transmission characteristics of ultrasonic compression pulse through cement slurries. The analyser measures a transit time (reciprocal of velocity) of an ultrasonic pulse through a sample continuously, recording the results in a non-destructive way.

In this case, the test was conducted at atmospheric pressure and isothermally at 24 °C. Samples of 200 cm³ were placed in the equipment immediately after mixing. Time zero is considered when the water or the polymer solution gets in contact with anhydrous cement. The measurement was performed for a week.

2.2.3. Study of the cement hydration by measuring the dielectric properties

Conductivity was measured with the *Consensor2.0* [35]. This equipment is controlled by a microchip that allows a sensor to measure continuously the conductivity. Cement sample are moulded in PVC moulds of 100 × 200 mm (1600 cm³). The sensor is placed in the middle of the sample. The mould is sealed and immersed in a water bath isothermally at 23 ± 1 °C by means of a cooling system to maintain the measurement isothermal. The system frequency was of 20 MHz to minimize the effects of the interface between the electrode and the cement paste [32–35].

Time zero is considered when the water or the polymer solution gets in contact with anhydrous cement. The measurement was performed for a week.

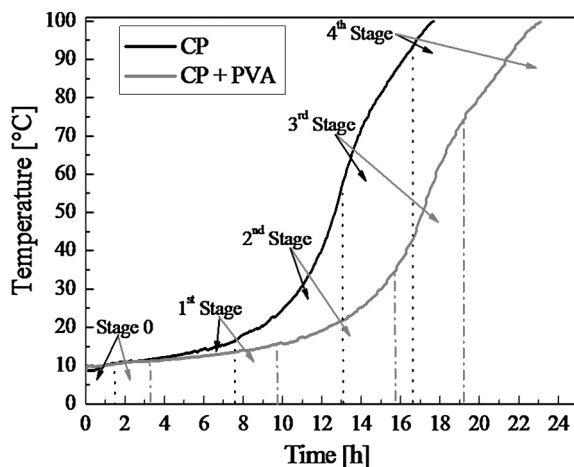


Fig. 3. Temperature raise of CP and CP + PVA in adiabatic conditions.

2.3. Results and discussion

2.3.1. Evaluation of the cement hydration by measuring the temperature rise in adiabatic conditions

In Fig. 3 it is shown the temperature rise in the adiabatic calorimeter of the cement paste (CP) and the cement paste modified with PVA (CP + PVA) during the hydration reaction. The temperature rise is measured up to 100 °C, which is the equipment limit.

The delay of the hydration of CP + PVA is visibly differentiated. Five stages can be observed for both curves. The first one, *Stage 0*, a pre-dormant period, it is longer for CP + PVA than for CP. During this stage, the temperature barely increases and lasts 1.2 h for CP and 3.2 h for CP + PVA. This hydration retardation generated by the addition of water-soluble polymers was explained before by many authors. *E. Knapen* made a review of the retarding mechanisms of the water-soluble polymers on her PhD Thesis [5]. Adsorption on the unhydrated cement particles, nucleation control, complexation of the rate-control alkalis, precipitation of insoluble complexes, incorporation of the polymer in the protective membrane around cement particles and decreased ion mobility are mentioned. She suggests that probably a combination of these mechanisms could explain every aspect of the retardation that occurs when water-soluble polymers, such as PVA, are added to the cement paste.

In previous work, by means of different techniques, the retardation was explained taking into account both adsorption of the PVA on the unhydrated cement particles and decreased ion mobility in the more viscous CP + PVA [16]. In other words, in CP + PVA, anhydrous cement is surrounded by PVA, which retains water and release it gradually provoking a delay at the beginning of the hydration reaction rate that would be reflected in the paste setting time.

After a *Stage 0* a 1st *Stage* begins and lasts 6.4 h for CP and 6.6 h for CP + PVA. Reactivity of both samples starts increasing slowly. During the 2nd *Stage* temperature raises rapidly. Both accelerating slopes are nearly parallel and this period lasts 5.3 h for CP and 5.9 h for CP + PVA.

During the 3rd *Stage* the rise temperature rate decreases. This means that the hydration reaches the so called deceleration period, where diffusion starts to dominate the hydration reaction. The length of this period and the amount of heat is almost the same for both samples, which means that PVA no longer influences the hydration rate of the cement paste, then the final strength properties of the cement paste are not affected when modified with PVA, actually, they improve [39].

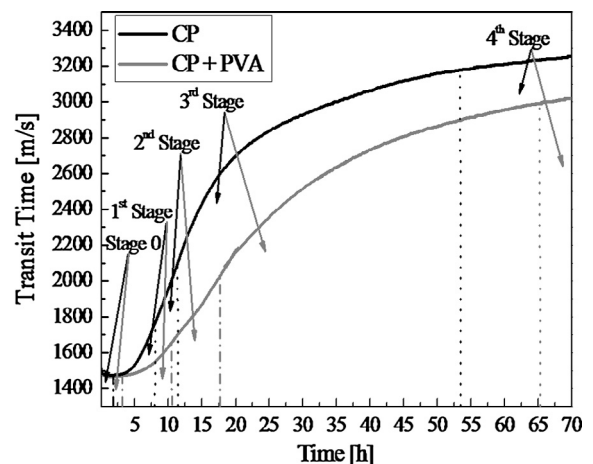


Fig. 4. Variation of transit time of the ultrasonic pulse during the hydration reaction of CP and CP + PVA.

Since the maximum temperature measurable with the equipment is 100 °C, *4th Stage* is only shown until this temperature, but, as it is shown in Fig. 4, temperature would have continued to increase with the same slope. Considering that the cement paste releases adiabatically about 0.1 °C per kilogram of cement in a cubic meter both samples should have increased 43 °C for CP and 60.6 °C for CP + PVA [40]. Then, theoretically, CP will reach the maximum temperature, 138 °C after 23 h and CP + PVA 134 °C after 28 h. The small difference is due to the total cement amount is not exactly the same for both samples.

2.3.2. Evaluation of the cement hydration by measuring the transit time of an ultrasonic pulse

Fig. 4 shows how the transit time of the ultrasonic pulse passing by the cement pastes increases during 4 days. The transit time of ultrasonic pulses passing through the cement pastes under study change during the different hydration periods, therefore the hydration could be studied. Trnikt et al. [26] divided an ultrasonic measurement in five stages. Interestingly, they found that the end of the first phase and the initial setting time are the same. So did Reinhardt and Grosse [30] and Zhang et al. [28]. Trnikt et al. [26] additionally propose to establish the final setting time for a transit time of 1650 m/s given experimental results, while Reinhardt and Grosse [30] established that the final setting time is reached when the transit time was 1500 m/s. The afore mentioned worked with cement mortars, while Trnikt et al. [26] with cement pastes.

During *Stage 0* not much happens. Both pastes behave the same and the ultrasonic speed remains constant, almost the same as the one of the water. This stage is, again, shorter for CP (endure 1.7 h) than for CP + PVA (endure 3.2 h) and should be related to the initial setting time. Then, the initial setting time happens before for CP than for CP + PVA. During this stage, the paste is still in a liquid phase so that the ultrasonic pulse circulates through the water or polymer solution with anhydrous cement. Subsequently, hydration reaction reaches the solid percolation threshold as Zhang et al. also established [28]. This threshold is related to the initial setting time, when the cement paste should not be mixed [26–28,30,32]. After this threshold is reached the main phase in the sample are the hydrated reaction products, then the ultrasonic pulse cannot go through the water without being interrupted by any solid. This means an increase in the transit time. The more the hydration products present in the sample, the more the transit time. Throughout the dormant period (*1st Stage*) the transit time slowly accelerates for both samples. During this stage the final setting is

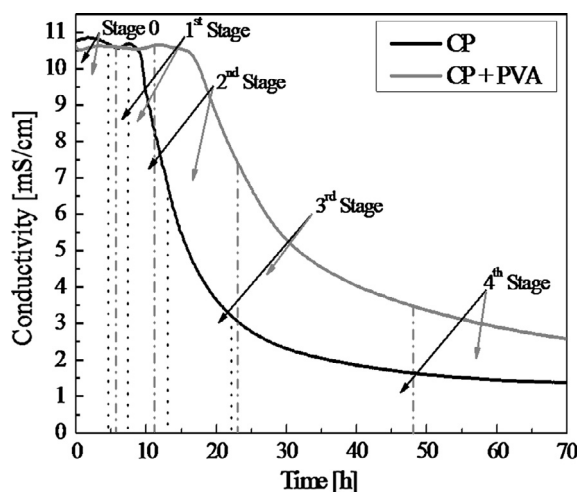


Fig. 5. Variation of the conductivity during the hydration reaction of CP and CP + PVA.

reached. This stage, again, is shorter for CP (endure 6.2 h) than for CP + PVA (endure 7.2 h).

After reaching the solid percolation threshold, the *2nd Stage* or acceleration stage begins. During this stage, the transit time increases the fastest. This period would begin after 7.9 h of hydration for CP and end after 11.3 h, and begin after 10.8 h for CP + PVA and end after 17.6 h. After this, there is a third big change of in the transit time raise slope (*3rd Stage*). The transit time increases but slowly. This is due to the diffusion phenomenon that, at that time, would begin to influence the hydration slowing the reaction rate. The slope of the increasing transit time decreases over time in the same way for the two pastes. Finally, there is the *4th Stage*. During this stage the curves reaches a transit time of 3400 m/s for CP and 3300 m/s CP + PVA, although, this last one looks that it might reach a higher level with more time. These values are in concordance with those of Reinhardt and Grosse [30] whose maximum average value of 3500 m/s and of Trnikt et al. [26] who report a maximum average value of 3000 m/s. The difference between the maximum transit time of CP and CP + PVA is an indicator that CP + PVA has a lower elasticity modulus as established in previous work [41].

2.3.3. Evaluation of the cement hydration by measuring its dielectric properties

Fig. 5 reflects the conductivity decrease of the cement pastes while the hydration reaction happens. During the first hours, any change is more visible for CP than for CP + PVA. The ionic composition of the water solution of both samples is not the same; then, a difference on the initial performance is expected.

As it was seen for the first two techniques, the initial setting time, also related to the beginning of *1st Stage*, occurs first for CP, in this case occurs after 4.7 h of hydration for CP and 5.7 h for CP + PVA. This method is also sensitive to the percolation threshold [31]. When reached the percolation threshold, water, the more conductive phase, cannot circulate freely in the cement matrix since it is trapped in the pores or adsorbed in the hydration products, then the conductivity falls significantly [34].

The way the conductivity decrease in time is different for CP and CP + PVA. The first sharp drop in conductivity occurs after 22.2 h of hydration at 3.2 mS/cm and it continues hydrating until it reaches 1 mS/cm to remain constant. This indicates that the pore structure of CP is mainly developed during this period. Then the water would be isolated in pores or adsorbed in hydration products so that the conductivity is minimal.

This value matches the one found for Princigallo et al. [34] and Levita et al. [31]. Princigallo et al. and Levita et al. also found that the final value for pristine cement paste was approximately 1 mS/cm. Levita et al. arbitrarily assumed that the percolation threshold was reached when the conductivity decreased to 10 mS/cm. CP reaches this value 2 h after the *2nd Stage*.

For CP + PVA there is a sharp drop after the first 47.8 h of hydration at 3.5 mS/cm, being the *3rd Stage* the most different from CP. Afterwards, the conductivity falls asymptotically to 1 mS/cm. This indicates that, although at lower magnitudes, CP + PVA can still conduct during more time but the ultimate pore interconnectivity of the matrix is the same as CP. The structure continues to form after 160 h.

2.3.4. Evaluation of the hydration of the cement paste and cement paste modified with poly(vinyl alcohol)

The results of the ultrasonic and conductivity measurements are shown in the same graph for CP in Fig. 6a and for CP + PVA in Fig. 6b. These techniques can be graphed together since they evolve isothermally. These figures allow observing that these global techniques for indirect measuring the hydration reaction of the cement paste, pristine or PVA-modified, are comparable. Lu

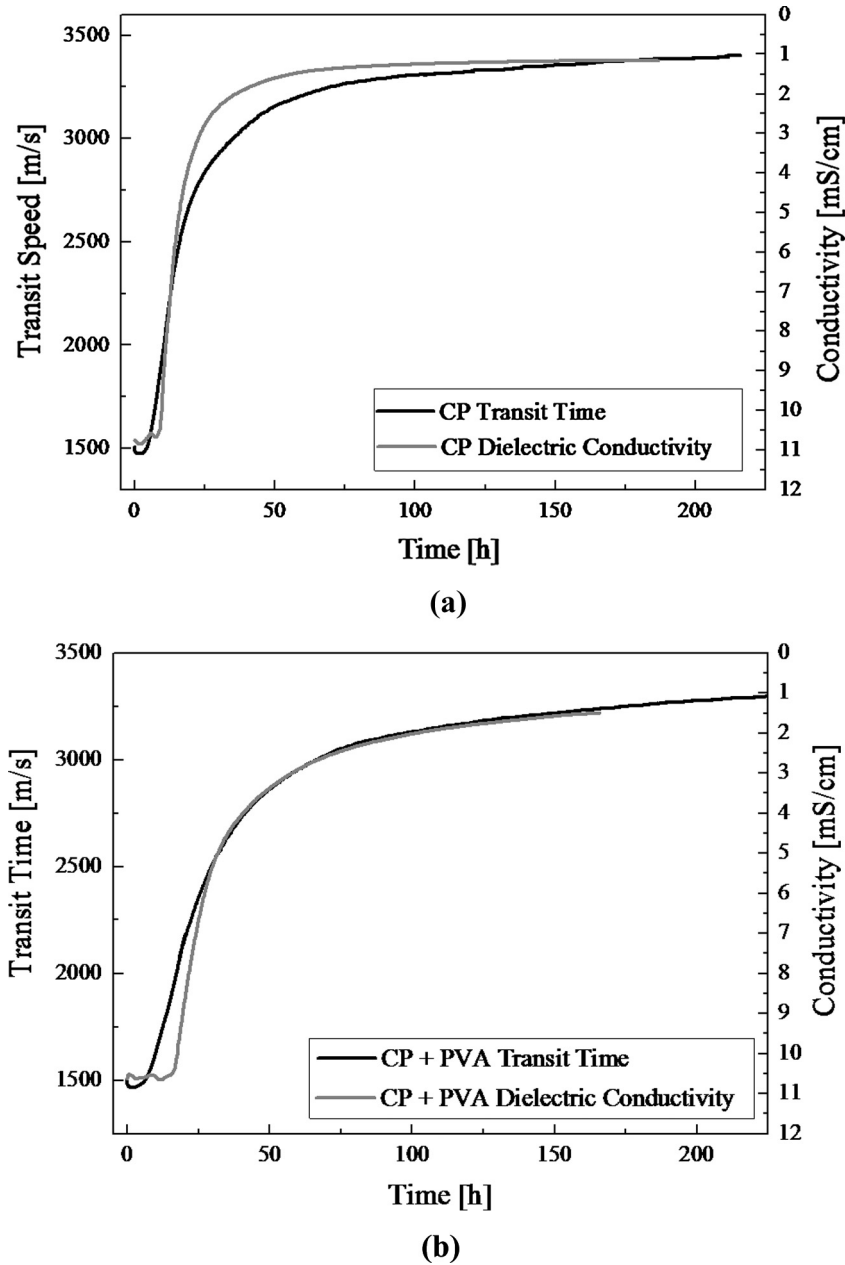


Fig. 6. Comparison of the three global indirect techniques for measuring the hydration reaction of a) of the cement paste (CP) and b) the cement paste modified with poly (vinyl alcohol)(CP + PVA).

et al. [29] also compared three different techniques and were able to divide the hydration with three characteristic time points. They obtained their results by measuring active acoustic and non-contact complex resistivity methods dividing the concrete hydration in four stages: the dissolving stage, equal to the *Stage 0* and *1st Stage*, the dynamic balance and setting stage (*2nd Stage*), the hardening stage, equal to the *3rd Stage*, and the stable stage, equal to the *4th Stage*.

Measuring the temperature rise in adiabatic conditions, the transit time of ultrasonic pulses through the hydrating cement paste and the conductivity of the pastes, a *Stage 0* with almost no activity is distinguish. During these Stages cement paste is yet a viscous slurry. Liquid phase is dominant and the main activity is the dissolution of Ca^{2+} , K^+ , Na^+ , SO_4^{2-} ions in the water solution, creating a sulphate-rich environment [29].

During the *1st Stage* with low activity during the first ~ 7 h for CP and ~ 11 h for CP + PVA the three techniques define similarly its beginning and end. These two stages conform the dormant period. Ions are consumed to form hydration product such as ettringite and calcium hydroxide. Hydration products start growing over the cement surface. When hydrates are sufficient to reach the solid percolation threshold, the setting occurs. The main characteristic of this stage is the development of a solid microstructure due to the hydration reaction. The solid phase is now predominant. As shown in Fig. 6, the inability to measure the conductivity of the samples until the solid percolation threshold is reached makes the conductivity measurement unfit to study any changes during the dormant period.

Nevertheless, when reaching the *2nd Stage*, the acceleration period, this method matches with the transit time measuring

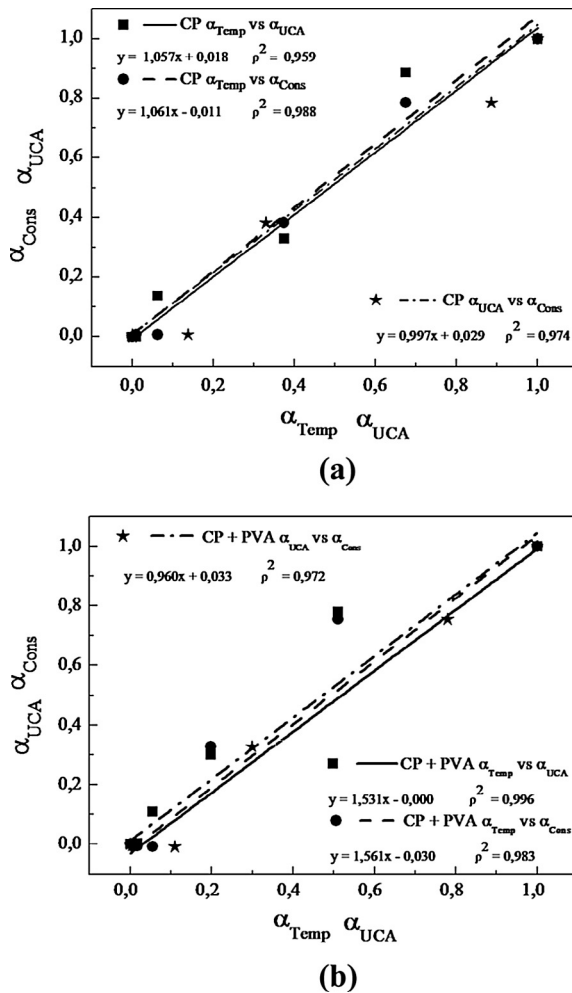


Fig. 7. Comparison of the three global indirect by comparing the degree of hydration for a) CP and b) CP + PVA.

one. The minimum conductivity and fastest transit time would be achieved when the adiabatic temperature reaches its maximum. Though this value was not measured, it would theoretically reach 43 °C more above the maximum measured for CP and 60.6 °C for CP + PVA. This would occur after 23 and 28 h of hydration for CP and CP + PVA respectively.

During the acceleration period the hydration reaction rate increases. The rate is controlled by the nucleation rate and the growth of the hydration products. Gypsum dissolves completely forming ettringite and being absorbed in the calcium silicate hydrate (CSH). More CSH is formed and $\text{Ca}(\text{OH})_2$ precipitates. Eventually, the amount of nonhydrated products diminishes, and the reaction begins to be controlled by chemical reactions and diffusion. This is when the 3rd Stage begins.

This period is called deceleration period. The hydration of Tricalcium Silicate (C_3S) and Dicalcium Silicate (C_2S) continue and the amount of CSH keeps growing but more slowly.

Lastly, there is the 4th Stage. Because of the limitations of the adiabatic method, it could only be studied by measuring conductivity and transit time of ultrasonic pulses. The curves are a little bit apart for CP, but for CP + PVA these match perfectly; then, a correlation between the methods could be made. During this time the hydration becomes completely diffusive, and then the rate is very slow. The hydration reaction will continue as long as water is available for the anhydrous cement to react.

To compare the three methods, for the beginning of each Stage, a degree of hydration (α) was estimated and compared with each other as it can be observed in Fig. 7. Every point that matched the beginning or the end of a hydration Stage was considered. Time zero corresponds with $\alpha = 0$ and the final value of the 4th Stage with $\alpha = 1$, this means, for the theoretical maximum of adiabatic temperature rise (138 °C after 22.6 h for CP and CP + PVA 134 °C after 27.2 h), of the of transit time (3403.5 m/s after 215.6 min for CP and 3308.2 m/s after 243.6 min for CP + PVA) and of conductivity (1.2 mS/cm after 150.1 min for CP and 1.2 mS/cm after 218.5 min for CP + PVA) of each sample. The values in the middle are calculated as proportional.

The relation between these values is almost 1 to 1 with a minimum ρ^2 of 0.924 demonstrating, once again, the good correlation between these three methods even for two pastes that have a different hydration reaction.

4. Conclusions

The hydration of two cement pastes, pristine cement paste and PVA-modified cement paste, with very different hydration behaviour were studied by means of three simple non-destructive techniques.

Firstly, they were studied by measuring the temperature rise due to the cement hydration in adiabatic conditions. The hydration of these samples was also studied by measuring the transit time of ultrasonic pulses constantly passing through the mixtures while it hardened. Finally, the hydration rate of the samples was studied by measuring its conductivity while the reaction occurred.

Although the three techniques measure different properties of the cement paste, the results were comparable. It was also demonstrated that the solid percolation threshold and the beginning of the acceleration period, as well as the final setting time are almost the same and that the addition of PVA to the cement paste made the dormant period longer but did not affect the other ones.

The maximum adiabatic temperature was not measurable with the equipment, but according to theoretical values and evaluating the slope of the temperature rise, it could be established that it would correspond to the inflections in the transit time rise and the conductivity decrease, which are related to the end of the acceleration period and the beginning of the diffusive one.

The three techniques proved to be valid and sensible enough to measure the hydration kinetics of PVA-modified cement pastes, providing a simple, non-destructive tool for the construction building industry.

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