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Performance of Fresh Portland Cement Pastes – Determination of Some Specific Rheological Parameters

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1. Introduction

The hard, strong and durable cement-based product required by the user is only achieved following a period of plasticity but the attention paid to its fresh properties is small, despite the far-reaching effects of inadequate fresh performance. Pumping, spreading, moulding and compaction all depend on rheology and thanks to an increasingly scientific approach it is becoming possible to predict fresh properties, design and select materials and model processes to achieve the required performance. Rheology is now seriously considered by users, rather than being seen as an inconvenient and rather specialised branch of cement science.

A number of papers [1-3] have been published on the variations in the technological properties of Portland cement blended with active mineral additions. One of the properties that varies significantly once hydration begins is rheology, with the change of state in the material, in whose measurement and analysis a series of different methodologies are called into play [4-7].

The rheological behaviour of pastes, mortars and concretes continues to be a subject of analysis in light of the large number of factors involved in cement blending, mixing and hydration (such as type of cement, type and proportions of mineral additions and presence or otherwise of admixtures). Very generally, rheology describes the deformation of a “body” subjected to loading. The “body” in this case refers to solid and liquid materials. Ideal solids deform elastically, whereby the energy required in the deformation is recovered when the load is removed. Ideal fluids, by contrast, deform irreversibly because they flow. The energy required for deformation is dissipated in the fluid as heat and cannot be recovered by merely removing the load involved. Real bodies behave neither like ideal solids nor ideal fluids,

and may be irreversibly deformed under the effect of sufficiently large forces. The vast majority of liquids exhibit behaviour somewhere in between fluids and solids: they are viscoelastic bodies. Solids may be subjected to perpendicular and tangential stress, whereas fluids can be subjected to tangential (shear) stress only.

Fluid viscosity, represented as η , is defined as its resistance to flow when subjected to shear stress. Newton was the first to formulate a law for viscosity, known as his friction law, according to which for ideal liquids:

$$\tau = \eta \cdot \dot{\gamma} \quad (1)$$

where τ is shear stress, η is viscosity and $\dot{\gamma}$ is strain or the shear rate. The correlation between shear stress, τ , and strain, $\dot{\gamma}$, is defined as the liquid's fluid behaviour. This correlation, known as a flow curve, is plotted in Fig. 1.

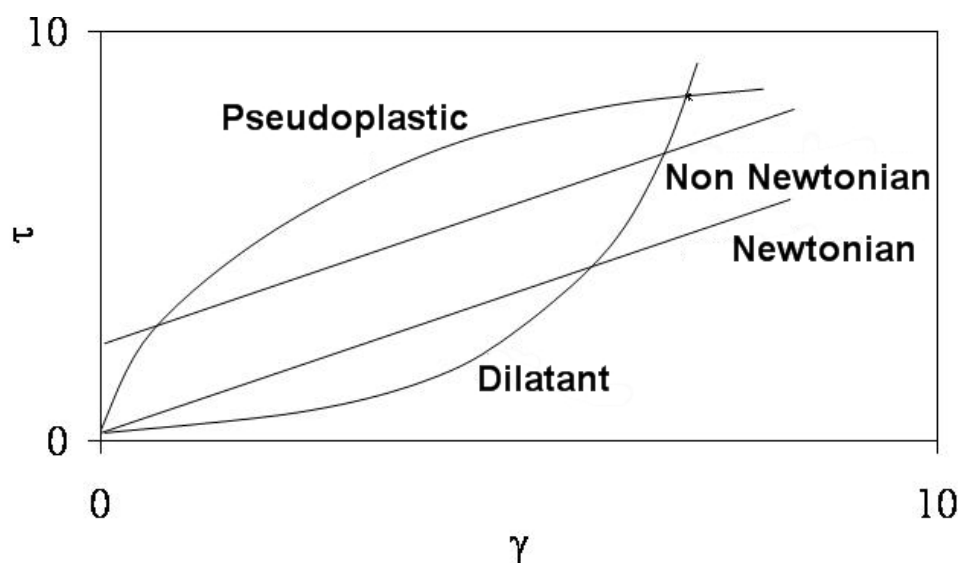


Figure 1. Fluid types.

For ideal liquids, the flow curve is a straight line: the quotient of all the τ - $\dot{\gamma}$ pairs on that line is a constant. In other words, viscosity, η , is unaffected by changes in shear rate. All liquids for which this relationship holds are called “Newtonian” and all others “non-Newtonian” fluids. Cement paste fluid behaviour cannot be described by a flow curve such as in Fig. 1. Rather, since these pastes tend to form flocs, a certain minimum shear stress needs to be applied before they begin to flow. In this case the flow equation can be expressed as shown below.

$$\tau = \tau_0 + \mu \cdot \dot{\gamma} \quad (2)$$

This equation describes the so-called Bingham model, where τ is shear stress; τ_0 , threshold shear stress; μ , plastic viscosity; and $\dot{\gamma}$, shear rate or strain. Plastic viscosity is an indication of the number and size of the flocs, while threshold shear stress is a measure of the strength and number of interactions severed when stress is applied.

In addition to the difference between Newtonian and non-Newtonian fluids, the latter may exhibit *dilatant* or *thixotropic* behaviour, as illustrated in Fig.1 [8, 9].

Actually, there are qualitative and quantitative disagreements between the results for cement paste reported by different research workers. The flow curve has been reported to fit several different mathematical forms, all of which indicate the existence of a yield stress:

Bingham [10]

$$\tau = \tau_0 + \mu\dot{\gamma} \quad (3)$$

Herschel-Bulkley [11]

$$\tau = \tau_0 + A\dot{\gamma}^B \quad (4)$$

Robertson-Stiff [12]

$$\tau = A(\dot{\gamma} + B)^C \quad (5)$$

Modified Bingham [13]

$$\tau = \tau_0 + \mu\dot{\gamma} + B\dot{\gamma}^2 \quad (6)$$

Casson [11]

$$\tau^{1/\nu} = \tau_0^{1/\nu} + (\mu\dot{\gamma})^{1/\nu} \quad (7)$$

De Kee [13]

$$\tau = \tau_0 + \mu\dot{\gamma}e^{-A\dot{\gamma}} \quad (8)$$

Yahia and Khayat [13]

$$\tau = \tau_0 + 2\left(\tau_0\mu_p\right)^{1/2}\left(\dot{\gamma}e^{A\dot{\gamma}}\right)^{1/2} \quad (9)$$

where A, B and C are constants.

Additionally the numerical values reported for the rheological parameters cover a very wide range, which cannot be wholly explained by variations in the materials used. It can only be accounted for by accepting that differences in experimental technique and apparatus of different workers have a much greater effect than has been generally realised. Differences in the shear history at the time of test, undetected plug flow and slippage at the smooth surfaces of a viscometer could all combine to give experimental variations as large as those reported. However, there is general agreement on two fundamental qualitative aspects of the behaviour of cement pastes.

First, the material breaks down during the test and hysteresis loops with the downcurve falling to lower stresses than the upcurve are obtained when the flow curve is determined over a short cycle time. The shape changes systematically with increasing cycle time through loops with a crossover point to loops showing structural build up [14], attributable to chemical reaction during the course of the test, but Hattori and Izumi [15] explained the effect in terms of the competition between coagulation and deflocculation processes. The apparent need to fit the range of models in equations 1–7 may be the result of not allowing for the possibility of structural breakdown during the test.

Second, the material has a yield stress which decreases, in line with reductions in the apparent viscosity indicated by the rest of the curve, as the total amount of shearing energy experienced by the paste increases. Thus successive hysteresis loops fall to progressively lower values of torque in a coaxial cylinders viscometer [16], yield stress and plastic viscosity fall to an equilibrium value as the time of mechanical mixing is increased [17] and the effect can be quantified in terms of the total shear energy received by the sample prior to the test [18,19]. This structural breakdown has been amply confirmed by experiments carried out under both continuous steady shear rate and continuous steady stress. In the former the relationship between shear stress and time is affected by the shear rate in the experiment and was explained theoretically by Tattersall [16] using a linkage theory, in which the links between particles are broken by the work done in shearing the paste.

A material's rheology is measured with rheometers or viscometers. A rheometer is a device that measures the viscoelastic properties of solids, semi-solids and fluids, whereas a viscometer is a more sensitive instrument that cannot accommodate large particles.

The two main types of viscometers are:

- a. native stress-controlled viscometers, in which the shear stress is user-defined to find the respective shear rate (or strain)
- b. native strain- (or shear rate)-controlled viscometers, in which the strain is user-defined to find the respective shear stress. [20].

With the ultimate aim of researching the effect of active and non active (*fillers*) mineral additions on pure Portland cement rheology, the impact of the variables involved on the findings was analysed in this first stage. After establishing a measuring scheme, the variations in paste rheological behaviour were determined from initial hydration up to the first nadir on

the calorimetric curve. Its trials were conducted on two pure Portland cements with very different potential mineralogical compositions, whose behaviour in conduction calorimetry and response to sulphate attack had been studied in prior research [21-32]. Finally, this rheological study of PCs is much involved with segregation phenomena and workability of their respective concretes and mortars and, as a consequence, with their durability.

On the other hand and with regard to the filler, the particle surfaces are positively or negatively charged during grinding with Portland clinker and gypsum and/or when mixing process with water and aggregates, consequently and respectively attracting OH⁻ and Ca²⁺ ions [33] very at the start of the hydration. This first layer of anions or cations in turn attracts a second cluster of Ca²⁺ or OH⁻ ions, respectively. As the ionic layer thickens, the electrostatic force of the particles declines [34]. Besides this, the following much more important consideration has to be also taken into account when the hydration moves forward: all inorganic particles assume a charge when dispersed in water.

The charged particle surface then attracts a layer of counter-ions (ions of the opposite charge) from the aqueous phase. Due to ionic radio considerations, the strongly adsorbed counter-ions will not fully offset the surface charge. A second layer of more loosely held counter-ions then forms. At a certain distance from the particle surface, the surface charge will be fully balanced by counter-ions. Beyond this point, a bulk suspension with a balance of negative and positive electrolyte exists. The size of the double layer will depend firstly on the amount of charge on the particle surface. A large charge, whether positive or negative, will result in a large double layer that stops particles getting close to each other because of the electrostatic repulsion between those particles carrying the same electrical charge. This situation is typical of stable (deflocculated) suspensions having a low viscosity. Conversely, a low surface charge requires fewer counter-ions and smaller double layers. Accordingly, particles then tend to flocculate which leads to high viscosity suspension. The zeta potential (mV) can be related to the energy needed to shear the particle and its inner layer of counter-ions away from the outer layer / bulk medium. This phenomenon has been illustrated in Fig. 2. In short, as it was mentioned earlier that particle charge influences the double layer size and so the zeta potential. Thus, the potential in this region decays with distance from the surface, some distance until it becomes zero (Fig. 2).

When a voltage is supplied to a solution with dispersed particles, the particles are attracted by the electrode of opposite polarity, together with the fixed layer and part of the diffuse double layer. The potential in the limit of the unit, said cutting plane, between the particle and its ionic atmosphere surrounding medium, is called zeta potential.

The zeta potential is a function of the charged surface of a particle, any adsorbed layer at the interface and the nature and composition of the medium in which the particle is suspended.

The zeta potential can be calculated with the following expression Smoluchowski's:

$$\zeta = \frac{4\pi\eta}{\varepsilon} \times U \times 300 \times 300 \times 1000 \quad (10)$$

ζ =Zeta Potential (mV)

η =Viscosity of Solution

ε +Dielectric Constant

$U = \frac{v}{V/L}$: Electrophoretic Movility

v =Speed of Particle (cm/sec)

V = Voltage (V)

L = The distance of Electorode

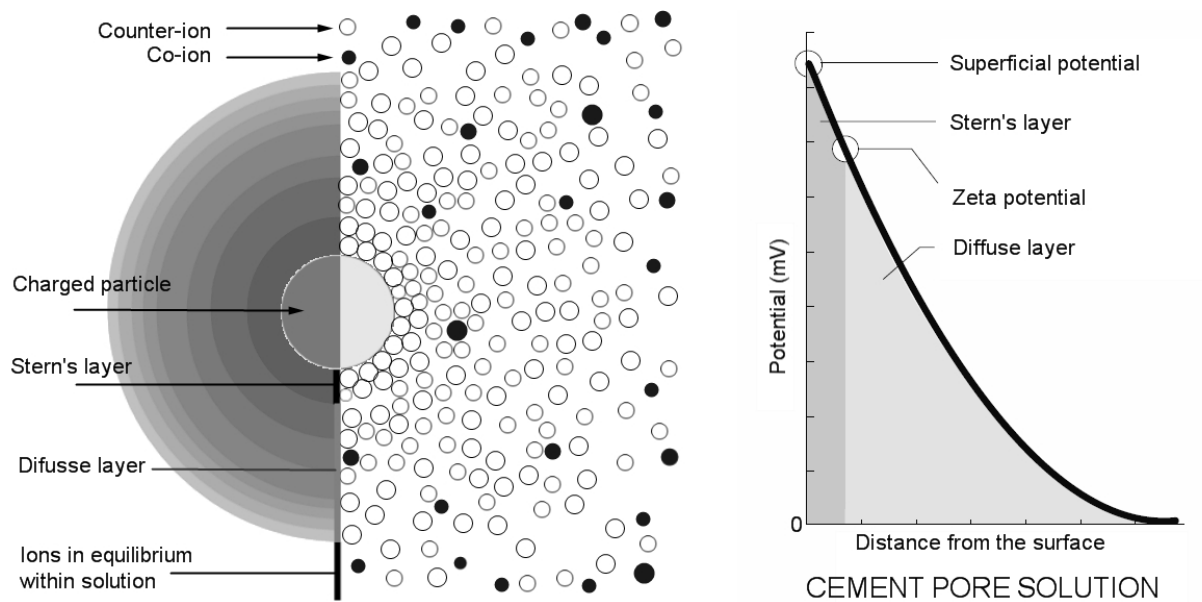


Figure 2. Electrostatic phenomenon in a solution for a charged particle. Graphical description of the Zeta potential.

Determination of the zeta potential is very simple. Applying a controlled electric field by means of electrodes immersed in a sample suspension, this causes the charged particles to move through the electrode of opposite polarity. Viscous forces acting on the particle in motion tend to oppose this movement, establishing a balance between the two forces of electrostatic attraction and viscous drag. the zeta potential has a considerable influence on the rheology of cement, so that increasing the magnitude of the zeta potential (both negative and positive) increases the low shear viscosity. The zeta potential depends on conditions of temperature, pH and others.

2. Materials and methodology

To ascertain the differences in the response depending on the variations in the rheological trial parameters, pastes were prepared with ordinary type CEM I Portland cement [35]

(whose mineralogical composition and other physical parameters, midway between PC1 and PC2, were as follows: 58.5 % C_3S ; 7.5 % C_2S ; 7.5 % C_3A ; and 11.5 % C_4AF ; density 3.06 and BSS 325), distilled water and a water-cement ratio of 0.5. The paste was mixed manually for 2 minutes in a porcelain crucible and poured into the viscometer annulus.

The rheological measurements were taken with a Haake Roto Visco 1 rotational viscometer fitted with a Z38 DIN 53018 rotor spindle, a Z43 DIN 53018 graduated flask, a temperature control unit for coaxial cylindrical systems and a DC 30-B3 circulation thermostat [20].

The measurement schemes analysed, designed by combining angular velocity, stage duration and velocity step size (in rad/sec), are shown in Fig. 3.

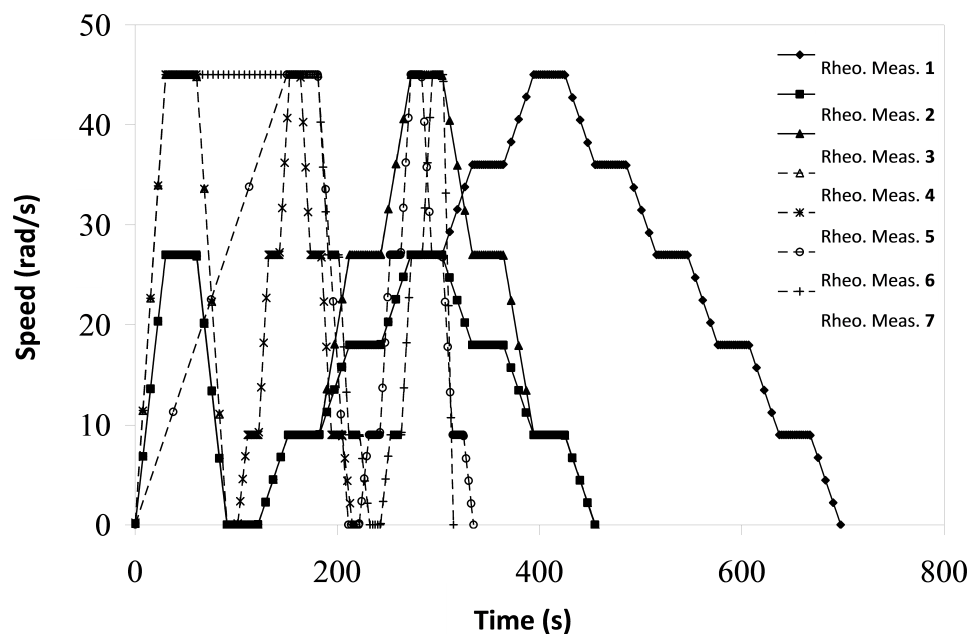


Figure 3. Rheological Measurement Schemes

Based on the results obtained in the preceding stage, a measurement scheme was designed and trials were conducted every 20 minutes (up to the time of the respective first nadir on the calorimetric curve [21-26] (Fig.3)) on two pure Portland cement pastes whose mineralogical composition was diametrically opposed. This compositional difference explained the difference in test time [21-26]: 120 minutes in paste PC1 and only 100 minutes in paste PC2, because 100 minutes is very near to 97 minutes 12 seconds \approx 97 minutes, which was really the age of the 1st nadir for PC2. The physical-chemical characteristics of the two Portland cements are given in Table 1, along with their potential mineralogical composition, density and Blaine specific surface (BSS).

The two Portland cements exhibited similar fineness (Table 1 and Fig. 5), and the difference in their density could be partially attributed to their mineralogical composition. The water demand to prepare a standard consistency paste [36] was higher in PC1 than in PC2, a finding related to the capacity to form new hydrated compounds that required more chemically

combined water. Setting times [36], in turn, were shorter in PC1 (Initial Setting Time: 200 minutes) than PC 2 pastes (IST: 270 minutes) [21-32]. This was also related to the formation of the new hydrated compounds that contribute to early age mechanical strength, primarily C_3A in this case [21-32][37]. The two Portland cements were also mixed with water at a w/c ratio of 0.5 and placed in warm (25°C) water until tested.

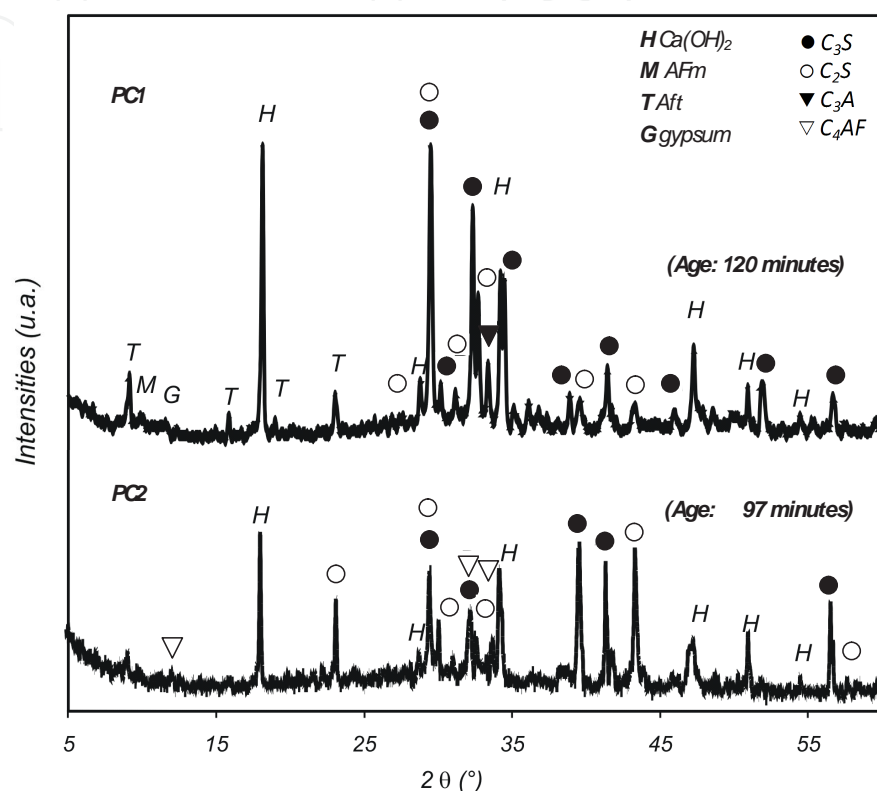


Figure 4. XRD analysis at the calorimetric curves nadir stages [16] for early hydration of PC1 (1st nadir at 120 min. age) and PC2 (1st nadir at 122 min. age)

In addition, the two PCs were analysed with the Frattini test [38] at very early ages: PC1 at 20, 40, 60, 80-100 and 120 minutes and PC2 at 20, 40, 60, 80 and 100 minutes (Figs. 6(a) and (b)). This test [38] is valid for pozzolanic or type CEM IV cements only [35]. Nonetheless, even though neither PC had to pass it, both were tested to compare their $[\text{CaO}]$, $[\text{OH}^-]$ and liquid phase pH at such early ages to better explain and understand their behaviour in the subsequent rheology tests. In the Frattini test for POZC, the calcium hydroxide content in the aqueous solution in contact with the hydrated sample kept at 40°C for 2, 7 and 28 days was compared to the solubility isotherm for calcium hydroxide in an alkaline solution kept at the same temperature. The mineral addition is regarded to produce pozzolanic activity (= positive result) when the calcium hydroxide concentration in the sample solution was below the solubility isotherm curve, but as both PC are plain, i.e., both of them had not any pozzolan amount and, for this reason, the $[\text{Ca}]$ and $[\text{OH}^-]$ contents of their respective liquid phase have to be, in contrast, necessarily over the solubility isotherm curve for calcium hydroxide in alkali solution (= negative result). The findings are given in Figs. 6(a) and (b).

Materials Parameters	Portland cements	
	PC1	PC2
C ₃ S, %	51	79
C ₂ S, %	16	2
C ₃ A, %	14	0
C ₄ AF, %	5	10
Álcalis eq., %	1.5	0.4
Density (Kg/l)	3.08	3.21
SSB, m ² /kg	319	301
Water demand, w/c	0.31	0.28
Initial setting point, min	3:20	4:30
Final setting point, min	5:10	6:15

Table 1. Chemical composition and physical parameters of two Portland cements

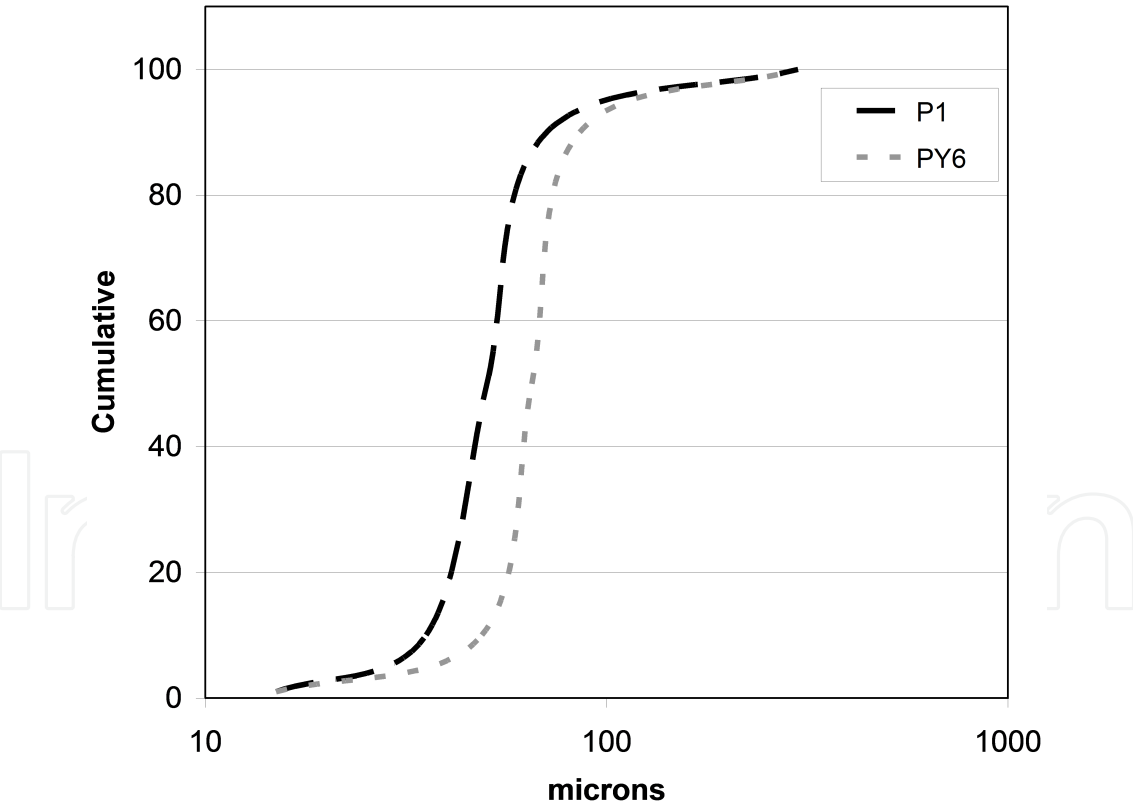


Figure 5. Particle size distribution of two Portland cements (Laser granulometry)

The effect of different mineralogical composition on the zeta potential of cement P1 and P2 was determined on a Malvern Instruments ZETASIZER 2000 particle sizer. The measuring

principle consisted of forcing the particles to be studied across an electric field using laser light scattering techniques. After the bombardments of the particles, the refracted laser will be collected by a correlator in order to transform the data of measurement of the electric potential of double-layer of particle. An aqueous solution in contact with the hydrated sample were injected into the analyser. After stirring, the solutions introduced in the injection equipment to various ages: 20, 60, 120 minutes, initial and final setting time, first minimum and second maximum of the calorimetric curve. Then conducted a total of nine measurements for each solution.

3. Results and discussion

3.1. Frattini test: [CaO], [OH⁻] and liquid phase pH values (Figs. 6(a) and (b))

The Frattini test findings, (Fig. 6(b)), confirmed that both PCs were pure Portland type materials, for neither passed the test at any age (nor would they pass it at any age, naturally), as all the pastes were above the solubility isotherm for Ca(OH)₂ in an alkaline solution. The test nonetheless afforded the following information.

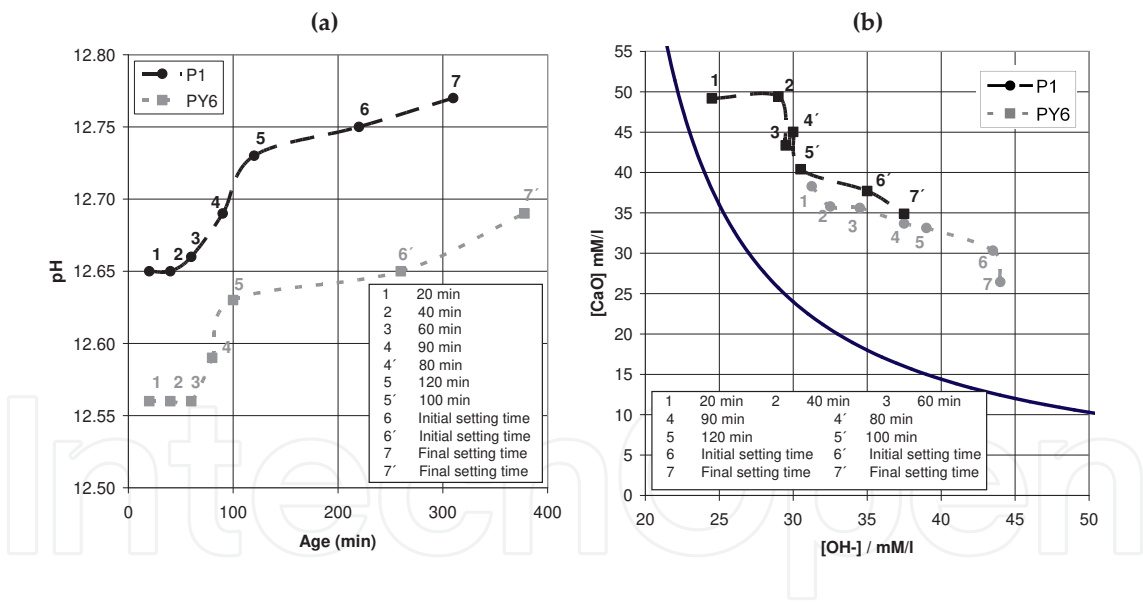


Figure 6. pH values and Frattini test results of the liquid phase for the two PC: PC1 and PC2

1. Regardless of the test age considered and all else being equal, the [CaO] values were consistently higher and the [OH⁻] values were consistently lower in PC2 than in PC1. The reason was the enormously different mineralogical composition of the two cements (Table 1), with PC2 having 79 % C₃S, 2 % C₂S, 0 % C₃A and 0.56 % Na₂Oeq., and PC1 51 % C₃S, 16 % C₂S, 14 % C₃A and 1.24 % Na₂Oeq. Consequently, more hexagonal crystal portlandite precipitated in the PC2 than the PC1 paste during hydration. By contrast, more KOH and NaOH were generated in PC1. Being much more soluble and exhibiting

greater exchange capacity [39], they remained in the liquid phase at increasing concentrations, especially NaOH, raising the alkalinity and the pH values of that phase (Figs. 5(a) and (b)) as hydration moved forward. These findings should have been reflected as well in paste behaviour in the rheology test: all else being equal, the shear stress values would necessarily be consistently higher in paste PC2 than in paste PC1. This expected behaviour was in fact observed in the present study (see Table 2 and the final paragraphs of item 3.2).

2. The decline in [CaO] in the liquid phase during the test, along with the rise in the [OH⁻] values, was more or less sinusoidal in both cements (Figs. 6(a) and (b)). These findings might well be mirroring PC hydration and portlandite formation. Initial mixing with water until each liquid phase reached supersaturation would be reflected as the segments more or less parallel to the X axis. The concomitant precipitation of portlandite crystals in each paste would appear as the segments sloping more or less downward on the two curves. This would be followed by further hydration until the liquids again became supersaturated, and subsequent precipitation of more portlandite. This process would continue in both PCs until their entire stock of C₃S and C₂S was depleted.

Since neither NaOH nor KOH crystals would ever precipitate during hydration in this test [38], the respective pH values in the liquid phase of each paste would logically rise throughout hydration (Fig. 6(a)). And the higher the Na₂O (%) and K₂O (%) values in the PC, the steeper would that rise be. By contrast, the shear stress values in the respective paste or solid phase (Table 2) should have declined with rising alkali concentration. Both relationships, direct and indirect, were in fact found in this study (see Table 2 and the final paragraphs of item 3.2).

Shear Stress (Pa) of PC1						Shear Stress (Pa) of PC2					
Time (min.)	A	B	C	D	E	Time (min.)	A	B	C	D	E
20	62.35	32.61	6.41	31.86	7.54	20	163.1	76.10	14.55	50.06	12.86
40	71.09	36.98	6.03	34.78	8.16	40	168.0	81.95	14.61	47.94	13.41
60	79.33	48.03	11.01	44.52	9.97	60	176.2	77.65	13.78	47.76	12.93
80-100	93.12	56.12	14.09	46.57	13.18	80	172.5	79.11	12.39	42.55	11.38
120	91.91	54.07	12.30	46.15	11.35	100	162.5	75.78	12.04	42.87	12.83

Table 2. Most important Shear Stress values of two Portland cements

All the above findings were observed, moreover, despite the higher C₃A content in PC1 (14 %) than in PC2 (0 %). As a result,

- together with the formation and precipitation of portlandite crystals, prismatic, likewise hexagonal ettringite or *AFt* phase needles should also form in paste PC1; these would later evolve into hexagonal *AFm* phase needles (Fig. 4), in addition to CSH gels generated by C₃S and C₂S; and

- the initial setting time of PC1 should be shorter [36].

Despite these two unfavourable circumstances, however, its shear stress values never exceeded the values recorded in identical conditions in paste PC2, since by that time its liquid phase was much more basic than the PC2 liquid phase.

3.2. Rheological test findings

The flow curves for rheological measurements 1 to 7 made on CEM I [35] cement paste are shown in Fig. 7. In measurement 1, which had five angular velocities rather than the three in the other measurements, higher shear was required in the downward than in the upward arm, an indication of the formation of new bonds in the interim, leading to greater strength than at the beginning of the trial. A comparison of measurements 2 and 3 reveals the effect of the step size between stages: more bonds were broken when the step was larger. The initial stage was the same in measurements 1, 2 and 3: 30 seconds at 27 rad/sec.

The difference between measurements 3 and 4 lay in the initial velocity. An increase from 27 to 45 rad/sec was found to generate a shorter hysteresis cycle.

In measurements 1 to 4, the duration of each stage was 30 seconds, whereas in measurement 5 the duration was 10 seconds. Shortening the stage duration led to an overlap between the last ramp up stage and the first ramp down stage.

In all the aforementioned cases, one velocity was ramped to the next quickly. In measurement 6, however, the angular velocity of the initial stage was raised more slowly. Under these conditions, shear strength was found to be higher and the upward and downward arms to have a steeper slope, as a comparison of measurements 5 and 6 shows

Lastly, in measurement 7 the initial stage was lengthened to 150 seconds and the ramp down was begun immediately, followed by the ramp up. In this case greater stress was observed in the ramp up, which stood as proof that fewer bonds were broken during the ramp down that preceded it.

After analysing the effect of each of the aforementioned parameters, a measurement scheme was designed with 10-second stages, three velocities and down ramping proceeding up ramping. The scheme designed, shown in Fig. 8 with five singular points, was as follows: 10'' from 0 to 45 rad/sec; 30'' at 45; 10'' from 45 to 27; 10'' at 27; 10'' from 27 to 9; 10'' at 9; 10'' from 9 to 0; 10'' at rest; 10'' from 0 to 9; 10'' at 9; 10'' from 9 to 27; 10'' at 27; 10'' from 27 to 45; 30'' at 45 and 10'' from 45 to 0. Therefore, singular points A, B, C, D and E, whose precise values for each PC tested are given in Table 2, were obtained from the measurement schemes shown in Fig. 7.

This measurement pattern was used to analyse the effect of Portland cement type (PC1 or PC2) and hydration time (at a w/c ratio of 0.5) on paste rheology. The rheological parameters were measured every 20 minutes until the first nadir appeared on the respective calorimetric curves, previously plotted with a conduction calorimeter at 25 °C [21-26] and analysed by XRD technique as well (Fig. 4). The rheological results obtained in this study are given in Figs. 9 and 10.

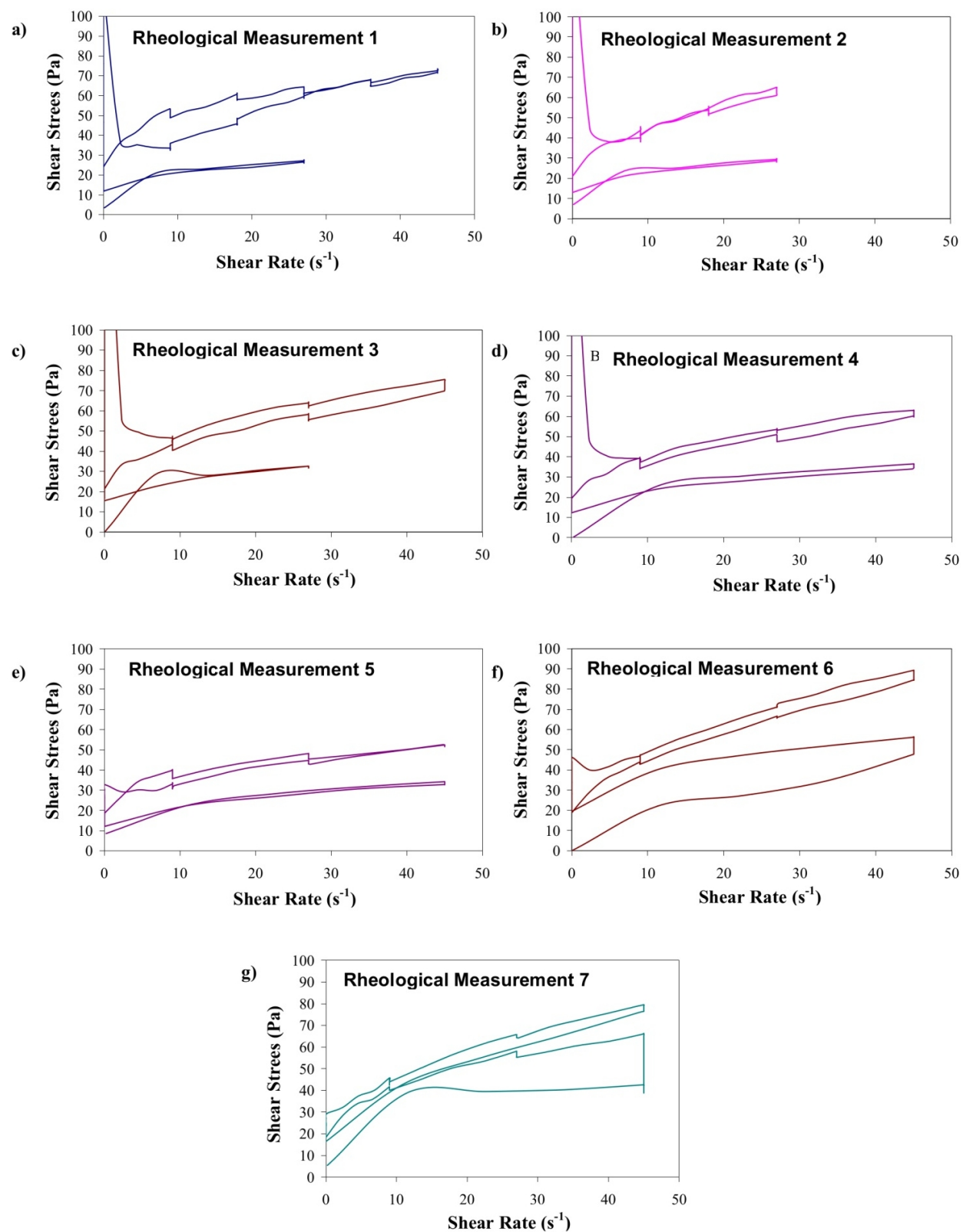


Figure 7. Flow curves of the seven rheological tests

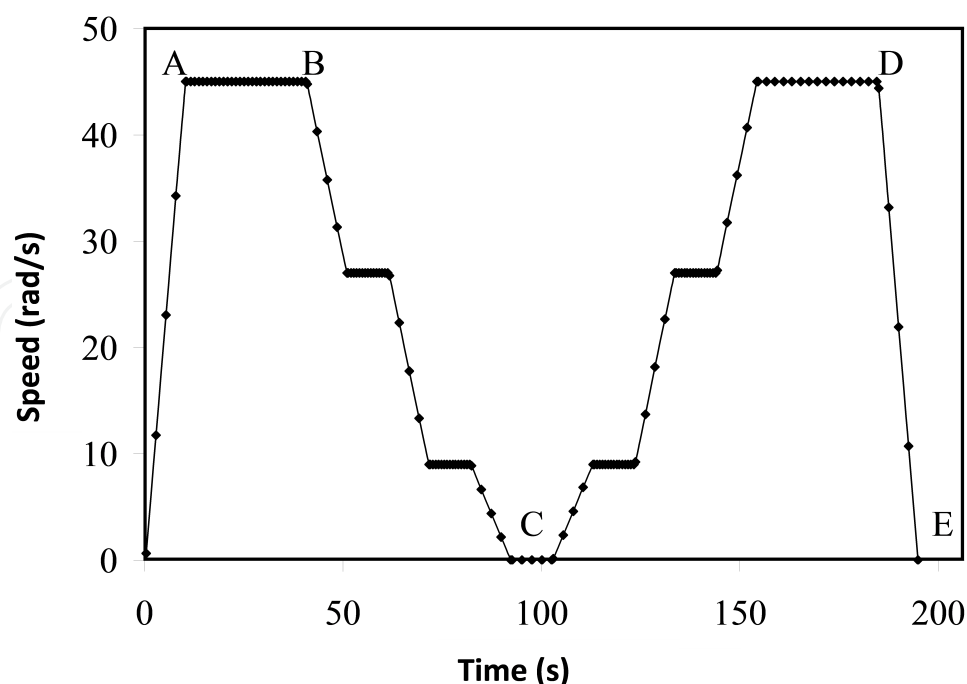


Figure 8. Rheological test finally selected for the two Portland cement: PC1 and PC2

Given the potential mineralogical composition of PC1 (Fig. 9) and due very likely to the formation and precipitation of ettringite hexagonal prismatic needles and rosettes and hexagonal portlandite and phase *AFm* platelets [27-32] (Fig. 4), the initial shear stress at point A rose from one measurement to the next as the hydration reactions progressed. Shear resistance declined substantially (up to 30-38 Pa) (thixotropic behaviour) at point B at all measurement times, since the angular velocity was held constant up to that point, although the general pattern was the same as for point A (increase from one measurement to the next as hydration progressed). Despite the removal of the mechanical force deriving from the spin transmitted by the rotor to the paste at point C, the paste nevertheless retained a certain amount of stress, which, as in point A, rose as hydration progressed. This was very likely due to the rotational inertia that remained in the paste particles (numerous and varied), even though the rotor had been stopped completely for 10" before reaching point C. At point D, then, the stimulus was the same as at point B, although the shear resistance exhibited by the paste was 1 to 10 Pa smaller at the former for the above reasons. This infers that most of the bonds, which initially had a stiffening effect (even if only due to gravity) because of the static position of the solid particles in the paste at the outset, and which must have been broken in B, were restored. This restoration must logically have occurred more speedily at earlier ages, given the lower force needed. Lastly, at point E, at the end of the test, remnant shear stress was recorded, as at point C. But in this case the values were greater at 20 and 40 minutes and smaller at 60, 80-100 and 120 minutes, a logical result, for the pastes were closer by then to their initial setting time (3h:20m) and ettringite, portlandite, phase *AFm* and CSH gel formation and precipitation should have increased.

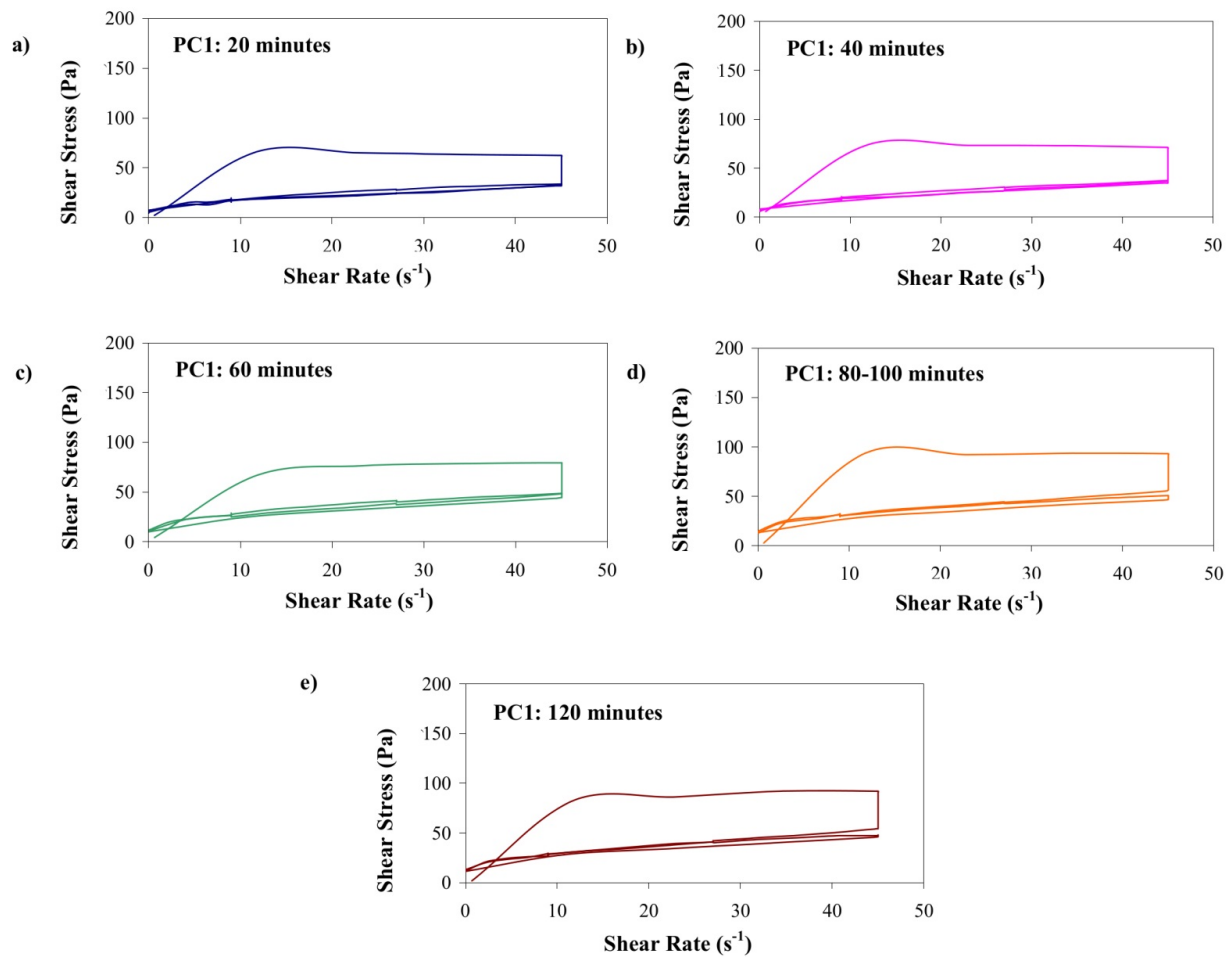


Figure 9. PC1 sequence of responses

The initial shear stress at point A likewise grew from one measurement to the next during the first hour of PC2 hydration (Fig. 10), after which it declined. Shear stress was found to be much greater than in PC1 due to the mineralogical composition, and consequently, to the nature of the many and diverse reaction products forming in the first few minutes. As in PC1, shear strength was observed to be lower (thixotropic behaviour), in this case by 87 to 100 Pa, at point B than at point A at all the test times and for the same reason, although the value climbed throughout the trial. In both PC1 and PC2, shear strength declined at point B by around one half of the value reached at point A. At point C, when the rotational force induced by the rotor and transmitted to the paste was completely removed, the PC2 paste was also observed to retain some stress, although with a clearly downward trend over time. As in cement PC1, at point D, the stimulus was the same as at point B, although the shear resistance exhibited by the paste was smaller (26 to 37 Pa). This would mean that some of the bonds which initially had a stiffening effect (even if only due to gravity) because of the static position of the solid particles in the paste at the outset, and which must have been broken in B, were restored, although this restoration was less intense than in PC1. Lastly, at point E, at the end of the trial, remnant shear stress was recorded, as at point C, but with

lower values up to 80 minutes and higher values thereafter. This would have been expected because the setting time for this cement was longer, 4h:30m. Nonetheless, the behaviour was totally different from PC1 at this point, likewise as would have been expected in light of its totally different mineralogical composition.

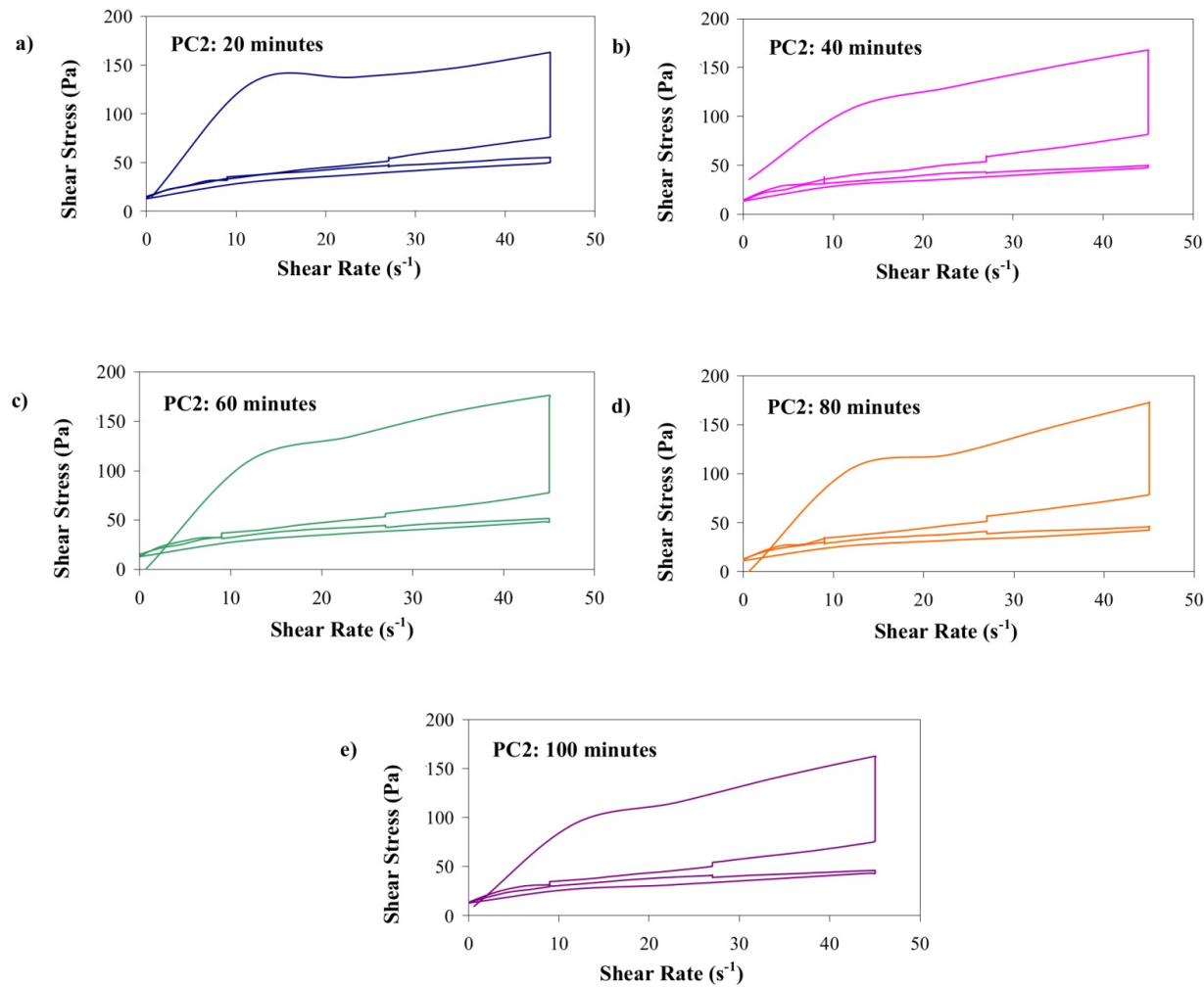


Figure 10. PC2 sequence of responses

Moreover, point by point at any given test age, the shear stress value in PC1 was consistently lower than in PC2. The reason would necessarily have been the hydroxy-induced [OH⁻] alkalinity; consequently, the pH of the liquid phase in PC1 was always higher than in PC2.

Lastly, at all five points, the shear stress on PC1 rose as hydration moved forward, but only up to the age of 80-100 minutes, after which it declines. In the PC2 paste, by contrast,

- at point A stress grew up to the age of 60 minutes, to decline thereafter through the end of the trial,
- at point B stress followed a sinusoidal pattern, i.e., rising between 20 and 40 minutes and alternately rising and falling from that time on,

- at point C (1st remnant) stress grew up to the age of 40 minutes and then declined steadily through the end of the rheological trial,
- at points D and E (2nd remnant):
- in PC1 paste, as noted, stress rose up to the age of 80-100 minutes and then declined through the end of the trial, at 120 minutes, and
- in the PC2 paste, the stress values followed a sinusoidal pattern from the beginning to the end of the trial, rising in the final, 100-minute paste.

The reason for such a broad difference in the two cements' rheological behaviour, particularly as regards points D and E, between the last but one and the last age (80-100 to 120 minutes in PC1; 80 to 100 minutes in PC2), must have been that at those ages, the alkalinity values ($[\text{OH}^-]$ and pH) of their liquid phases were more widely separated than at any other. In other words, pH was lower than at any other age in paste PC2 and higher than at any other age in paste PC1 (see Fig. 6), even though the end of the rheological trial, 120 minutes, is nearer to its initial setting time (IST: 200 minutes) in PC1, than 100 minutes in PC2 (its IST is 270 minutes). All the foregoing was the result, in turn, of the differences in the potential chemical composition of the two PCs, here specifically in terms of their $\text{Na}_2\text{O}_{\text{eq}}$ (%) content, which was $1.24\% > 0.6\%$ in PC1 (not a low alkali cement) [40] and $0.56\% < 0.6\%$ in PC2 (a low alkali cement). This, together with the higher C_3S content in the latter than in PC1 (79 compared to 51 %), would have induced more intense precipitation of microscopic hexagonal portlandite crystals and CSH gels in the solid phase of the paste, as a result of the permanent supersaturation in the liquid phase. That in turn must have raised the initial mass of the paste. Along with the hexagonal shape of the portlandite crystals, such increased mass would have led to a rise in the shear stress, reversing the decline recorded up until that time, contrary to the behaviour observed in PC1 in this regard.

Consequently, the PC1 paste behaved more uniformly at all points and ages than the PC2 paste.

3.3. Electrokinetic study

The zeta potential test findings for several pastes of Portland cements PC1 and PC2 are shown in Figure 11(a). Moreover, this figure also shows the results of conductivity (Fig. 11 (b)) and ionic mobility (Fig. 11 (c)) of all the pastes of both Portland cements.

In Figure 11 (a) shows the zeta potential at any age Portland cement PC1 was lower than for the case of Portland cement PC2. This behavior is related to the pH values obtained (Figure 6), since the more basic the pH of the sample is more negative potential corresponding value of ζ (Fig. 12). Again, the reason was that regardless of the test age considered and all else being equal, the $[\text{CaO}]$ values were consistently higher and the $[\text{OH}^-]$ values were consistently lower in PC2 than in PC1, due to the different mineralogical composition of the two cements (Table 1). Consequently, more hexagonal crystal portlandite precipitated in the PC2 than the PC1 paste during hydration. By contrast, more KOH and NaOH were generated in PC1. Being much more soluble and exhibiting greater exchange capacity [39], they remained

in the liquid phase at increasing concentrations, especially NaOH, raising the alkalinity and the pH values of that phase (Figs. 6(a) and (b)) as hydration moved forward.

The zeta potential is determined by the nature of the particle surface and the dispersion region, and as mentioned above pH is often an important parameter. Figure 12 shows an example of the variation of zeta potential and pH, The curve crosses the X axis, this point is called the isoelectric point. This means that the particles do not experience repulsion, so that the particles agglomerate. In fact there may be some attraction near this value as well, and as a rule if you want to ensure that there is repulsion between particles we must ensure that the value of zeta potential is greater than +30 mV and -30mV. Therefore, two Portland cements exhibit in the instability area of potential Z until the hydration reactions are completed and the pH is increased to stabilize. Therefore zeta potential values of the two Portland cements become increasingly approaching more negative to stable region.

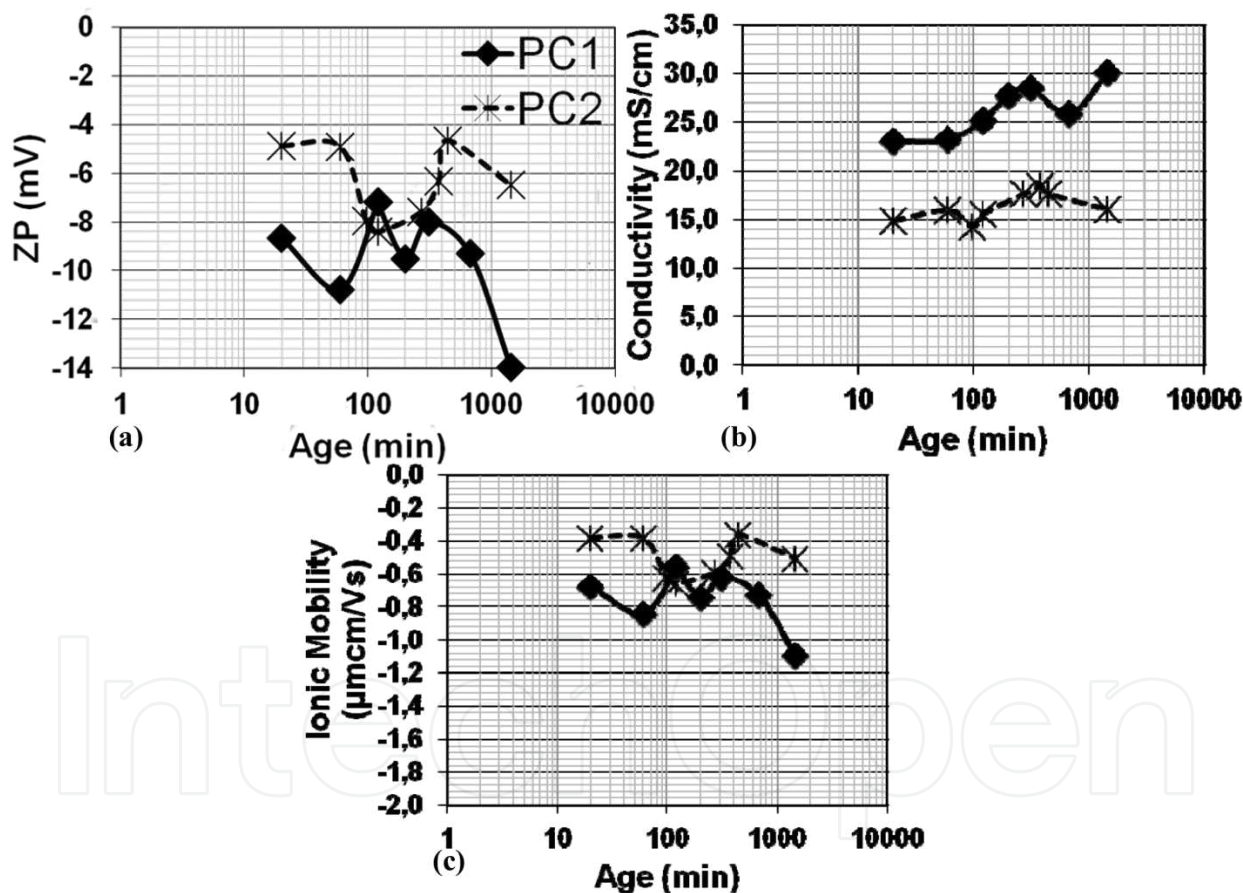


Figure 11. (a) Z Potential values of two Portland cements used PC1 and PC2. (b) Conductivity of two Portland cements used both PC1 and PC2. (c) Ionic Mobility of two Portland cements used both PC1 and PC2.

Therefore, PC1 is the Portland cement that reached the highest values of zeta potential causing further dispersion of individual particles. This means that the system approaches the stable area and consequently the corresponding viscosity of the pastes is greater PC2 cement. All the foregoing is the result, in turn, of the differences in the potential chemical com-

position of the two PCs, PC1 (not a low alkali cement) and PC2 (a low alkali cement). This statement is acuated with the water demand to prepare a standard consistency paste [36], was higher in PC1 than in PC2, a finding related to the capacity to form new hydrated compounds that required more chemically combined water. Setting times [36]. The higher C_3S content in the latter than in PC1, would have induced more intense precipitation of microscopic hexagonal portlandite crystals and CSH gels in the solid phase of the paste, as a result of the permanent supersaturation in the liquid phase. So would have led to a rise in the shear stress, reversing the decline recorded up until that time, contrary to the behaviour observed in PC1 in this regard.

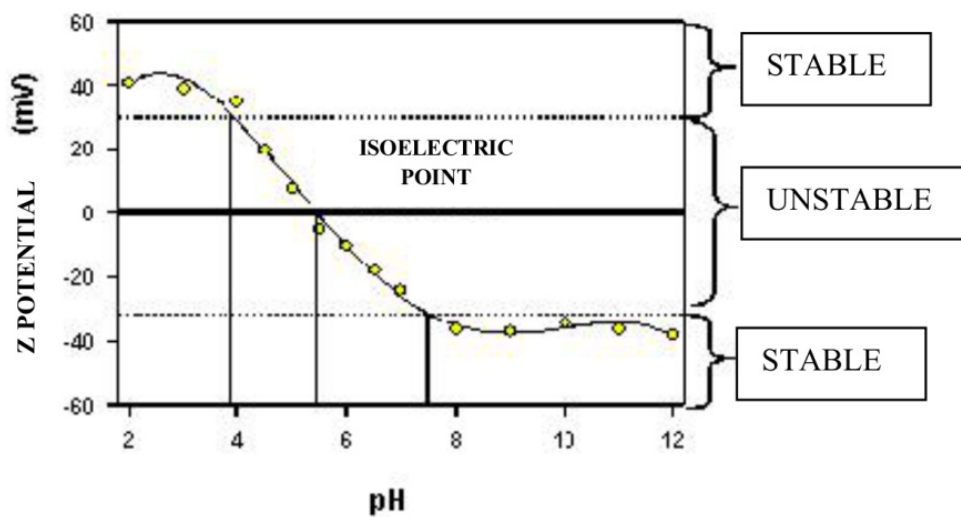


Figure 12. Dependence of Zeta Potential with pH

In Figure 11 (b) shows the evolution of the conductivity of two Portland cements with age. The differences in the two cements are mainly due to their very different mineralogical composition, specifically in terms of their Na_2O_{eq} (%) content, which was $1.24\% > 0.6\%$ in PC1 (not a low alkali cement) [40] and $0.56\% < 0.6\%$ in PC2 (a low alkali cement). Moreover, the graphs of the two Portland cements having the same pattern, however, the Portland cement PC2 lags the cement PC1, because the rate of hydration of portland cement mineral components PC1 is increased. The increased speed of hydration corresponding to C_3A , and the PC1 cement contains about 14%.

Furthermore, in connection with the ionic mobility (Figure 11 (c)) is met and the above explained through the graph shown in Figure 12. The ions present in the Portland cement samples from PC2 have higher ionic mobility. This trend is related to the zeta potential results obtained for the two Portland cements as for Portland cement PC1 values are closer to the stable zone where the ions are more dispersed. By contrast, the values for the Z potential of Portland cement PC2 are closer to the unstable zone, so that different ions tend to agglomerate, thus its ion mobility is higher.

4. Conclusions

The following conclusions may be drawn from this study.

1. Rheological measurement design has a substantial impact on the type of response. Consequently, a given stimulus may yield different shear strength values as well as both *thixotropic* and *anti-thixotropic* behaviour, depending on the measurement scheme used.
2. The following findings were observed in connection with the mineralogical composition of Portland cement and its effect on the nature and development of the many and diverse hydration products forming in the initial phases of hydration of the fresh paste.
 - a. Similar behaviour: $\approx 50\%$ decline in shear stress after 30'' of rotation and further loss when the stimulus was repeated
 - b. Clearly different behaviour: higher shear strength in paste PC2, greater bond recovery in paste PC1
 - c. Remnant shear stress (points C and E) in paste PC1 that declined throughout the trial; in paste PC2, the values at point C also declined, whereas at point E they rose, as would be expected, further to conclusion 3.
3. The explanation for the preceding conclusions, in particular conclusion 2, lies in the differences in $[\text{CaO}]$ and $[\text{OH}^-]$ in the liquid phases of the two PCs and their concomitant pH values. These, in turn, were the result of the differences in their mineralogical composition, especially with respect to their N_2O (%) and K_2O (%) contents, which determined the higher alkalinity in PC1 and the lower shear strength of the paste made from that material.
4. PC1 is the cement that reached the highest values of zeta potential causing further dispersion of individual particles. This means that the system approaches the stable area and consequently the corresponding viscosity of the pastes is greater PC2 cement. All the foregoing is the result, in turn, of the differences in the potential chemical composition of the two PCs.

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