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ORIGINAL ARTICLE

Effect of prehydration of Portland cement on the superplasticizer consumption and the impact on the rheological properties and chemical reaction

Efeito da pré-hidratação do cimento Portland no consumo de superplastificante e o impacto nas propriedades reológicas e na reação química

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Abstract: The use of pre-hydrated cement in formulation of mortar and concrete is common because there is not always effective control on the cement production, grinding, transportation and subsequent storage. This paper presents a case study on the optimization of admixture for use with prehydrated cement by assessing changes in the rheological properties of Portland cement artificially pre-hydrated. The cement was artificially pre-hydrated by exposure to relative humidity (RHs) of 90%, in an environment of NH_4Cl saturated solution. Additionally, the cement pastes were evaluated with and without superplasticizer. Stepped flow test using a parallel-plate geometry was the method choose to evaluate the rheological behavior, apparent viscosity, yield stress and hysteresis area of each paste at the early age. Oscillatory rheometry was conducted to evaluate the storage modulus (G'), comparing the consolidation with the hydration kinetics obtained by calorimetric evaluation of the same suspensions. Initial rheometer results indicate that the pre-hydrated sample presents lower level of shear stress than the reference sample, because of the higher reactivity of the non-pre-hydrated sample.

Keywords: Portland cement, prehydration, chemical reaction, rheology, superplasticizer.

Resumo: A utilização de cimento pré-hidratado na formulação de argamassas e concretos é comum, pois nem sempre há um controle efetivo na produção do cimento, moagem, transporte e posterior armazenamento. Este trabalho apresenta um estudo de caso sobre a otimização de aditivo para uso com cimento pré-hidratado, avaliando as mudanças nas propriedades reológicas do cimento Portland pré-hidratado artificialmente. O cimento foi pré-hidratado artificialmente por exposição à umidade relativa (URs) de 90%, em ambiente de solução saturada de NH4Cl. Adicionalmente, as pastas de cimento foram avaliadas com e sem superplastificante. O teste de fluxo escalonado usando uma geometria de placas paralelas foi o método escolhido para avaliar o comportamento reológico, viscosidade aparente, tensão de escoamento e área de histerese de cada pasta em idade precoce. A reometria oscilatória foi realizada para avaliar o módulo de armazenamento (G'), comparando a consolidação com a cinética de hidratação obtida pela avaliação calorimétrica das mesmas suspensões. Os resultados iniciais do reômetro indicam que a amostra pré-hidratada apresenta menor nível de tensão de cisalhamento do que a amostra de referência, devido à maior reatividade da amostra não pré-hidratada.

Palavras-chave: cimento Portland, pré-hidratação, reação química, reologia, superplastificante.

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1 INTRODUCTION

Cement prehydration is the inadvertent reaction of anhydrous cement with water, causing the partial hydration of the particle cement surface [1]. The prehydration of the cement includes the physical adsorption of water on the cement particle and the chemical reaction to form hydration products such as calcium silicate hydrate, portlandite, gypsum, ettringite and syngenite [2]. Among these ettringite and syngenite are preferably formed [3].

Many factors affect the degree of cement pre-hydration, for example temperature, relative humidity (RH), time of exposure and particle fineness [4] and prehydration can occur during the cement manufacture, transportation or storage of cement [5], [6].

The cement surface hydration can also occur during the manufacture as a consequence of the dehydration of gypsum during the grinding process in the cement mill. In addition, some producers add water into the ball mill in order to keep the temperature of the mill feed below 115ºC or add into the vertical mill to stabilize it [4]. Prehydration of cement due to gypsum dehydration may also occur during the transportation and storage.

Cements tend to sorb different quantities of water vapor depending on their phase compositions, according to [4], cements containing high levels of free lime, orthorhombic C_3A and $ß\text{-}CaSO_4.1/2H_2O$ are more sensitive to moisture.

In practice, pre-hydrated cements tend to show adverse effects on the engineering properties of cement and concrete, affecting at different levels the reactivity of each phase of hydration [4], [5] These effects include compressive strength reduction, decreased workability, open-time and setting time. According to [2], cement prehydration, measured as "corrected loss-on-ignition, (Wk)" values above 0.3% can significantly reduce compressive strength.

The changes at the cement particle due to prehydration can also affect the admixtures performance [4]. Depending of the composition of the admixtures the effects are different, for example, in one study using superplasticizer the rheological measurements of cement suspensions revealed better performance with the pre-hydrated cement than with the fresh cement [3], [7]. However, the best efficiency of each admixture depends on the synergy with the cement used in the concrete formulation since each binder is produced with distinct physical, chemical, mineralogical and surface characteristics.

The desired performance for each admixture depends on the mixing demand, transport application, workability and the stability of workability with time. In some cases, there is a need for greater workability without the need for stability over time and in other cases the opposite result is adequate [7]. Therefore, for each scenario, the appropriate evaluation of the parameters and the rheological profile of each cement composition in association with the specific admixtures is extremely important. This work seeks to add to the limited body of work discussing such interactions.

1.1 Dispersing agents (Superplasticizers)

Water-reducing admixtures for concrete are chemicals that are intentionally added to the concrete to modify concrete to suit specific applications [7]. Typical admixtures are superplasticizers, that is, they have dispersion properties, either by electrostatic effect or by electro-steric effect, and this dispersion releases trapped water allowing the mixture to flow.

Generally, the use of such chemical admixtures promotes the increase of final strength in the concrete by reducing water, improves slump retention, and in some cases, when the composition is carefully balanced, increases the initial strength. Currently, the most efficient admixtures for this purpose are the third-generation superplasticizers, generally formulated based on polycarboxylate or polyacrylate [8].

In this work, two types of polycarboxylate base dispersants were used to obtain the desired rheological properties as shown in Figure 1. The variation of the polycarboxylate content influences directly the rheological properties of the mix [3]. The increase of the admixture content in the viscosity, the shear stress and the hysteresis area (area inscribed between the stress curves vs. rate) are reduced, showing the dispersion capacity of the admixture.

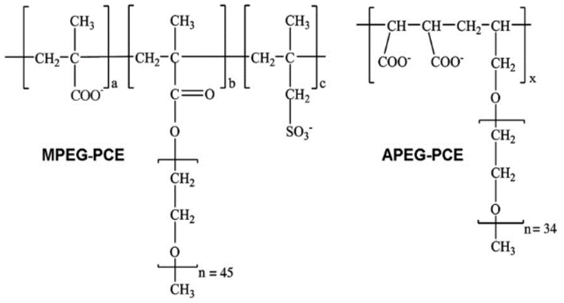


Figure 1. Structure of the chemical composition in the comb polymer of a sodium polycarboxylate molecule: PCE-methacrylic to the left and PCE of allylic ether to the right [8].

The mode of action of the polycarboxylates is based on the dispersion of the cement particles by electro-steric effect. The main chain of the admixture has anionic charges that are attracted by the positive charges present on the surface of the cement at the beginning of the hydration. The chain is deposited/adsorbed on the cement surface, while the side chains are extended from the surface, pushing the particles apart. Different dispersion efficiencies are obtained from the use of the different types of polymers and are dependent on the type of cement. After the cement particles are dispersed, hydration products begin to grow, and the polycarboxylate polymers are covered up and entrapped.

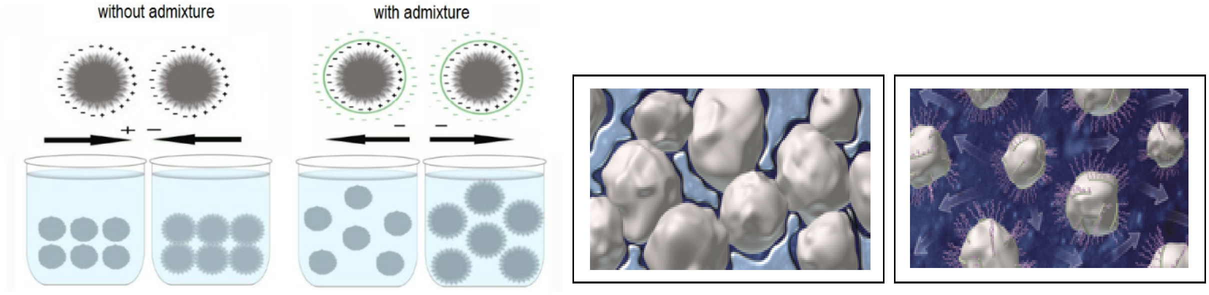


Figure 2. Simulation of cement particles dispersion electrostatic effect (left) and polycarboxylate adsorption (right). GCP Applied Technologies rights.

Cement particles have a natural tendency to agglomerate when mixed with water due to their polarity and Van Der Waals attraction force between these cement particles. Water is entrapped between them reducing the flowability of the concrete [9]. With the use of dispersing agents, the cement particles are deflocculated and dispersed, releasing the water and increasing the fluidity of the concrete (Figure 2). Since the cement particles cannot approach one another, the energy required to induce the flow in the system is reduced. The dispersed cement also lubricates the aggregates of the concrete mix, further improving the pumpability. Dispersed particles disturb the flow less than the agglomerated particles, so the water is free to hydrate the surface of the cement and fluidize the mixture [7].

The variation of the admixture content also results in alteration of the properties of the concrete under flow which affects the transport and the application of the concrete [8]. In addition, the amount of water in the system is reduced considerably which generates a dense, less permeable matrix, enhancing the durability of the concrete. In the experiments below, superplasticizer content is systematically increased, the time of the concrete flow is reduced until the saturation point is reached, this point being considered as the *optimum content* [10]. In the conditions of this study, this optimum content varies according to the physical, chemical and mineralogical composition of each cement using the same admixture; in addition, polymer type, water-to-solids ratio, and other variables can alter the flow of concrete, many studies are necessary to conclusively define the optimum type and content of each admixture for a particular cement [10].

1.2 Portland cement and admixtures interactions

The rheological properties of the concrete are modified by the interaction of cement and admixtures [10]. Other factors such as mode and time of addition of the admixture or water/cement ratio may also affect the performance of the concrete in the fresh state [10].

Among properties of the cement, surface area, particle size and porosity, prehydration and chemical/mineralogical composition are factors that affect rheological properties and hydration kinetics of the paste [11]. The chemical nature of each cement influences the interaction with superplasticizer mainly in the fresh state [12]. Other factors such as alkali-soluble sulfate content, admixture addition time (normal or delayed addition) [12], and temperature of the concrete, influence the hydration process of cement mixtures and many of them have a synergistic effect [12]. The structure of each polycarboxylate polymer also influences the hydration of cement, with the length of the main and lateral chain of each molecule of polycarboxylate, and molecular weight, being important parameters. To understand the system, it is important to study the cement-admixture "pairs" [10].

The superplasticizers react with the cement particle and interfere with the hydration in the early stages, either in the nucleation process, hydration reaction rate or both [10], [13]. Because of the strong interaction with the various mineral phases of the cement, the admixture interferes in several phenomena. The SO_4^{-2} ions added intentionally in the cement manufacture act as hydration controllers reacting with the aluminate phases preferentially, and the polynaphthalene sulfonate base admixture or polycarboxylate also have higher affinity for the aluminate phases, competing with the sulfates for surface area on the aluminate phases [14]. Moreover, the PCE can intercalate on hydration compounds formation by different mechanisms, it can explain the distinct content of the same admixture on pre-hydrated and non-pre-hydrated mixes. The undersulfated systems allows the PCE intercalation, where the quick soluble sulphate to stoichiometrically transform all the C_3A into AFm and Aft [13], [11].

Studies have shown that the prehydration directly affects the fluidity of the concrete in the presence of polycarboxylate, since the cement particle size is reduced by the formation of hydration products, increasing the specific area of the cement [13], [11]. Some problems such as rapid loss of workability or increased rigidity, excessive delay or pumping difficulties are common when there is incompatibility between cement and admixture[11]. Studies have shown that polycarboxylate are better compatible with different types of cement, and cement / admixture compatibility is more affected by the amounts of alkali sulphates in the cement [13]. However, these studies have not included the detailed rheological studies described here.

The multiphase characteristics of the cement and its hydration products are essential factors for the affinity of the organic admixtures however, undesirable side effects can be seen during the preparation of the concrete in the fresh state [13], [11]. If not studied and compensated for, the interaction between cement–admixture these side effects can adversely affect the final performance [11]. The particle size also influences admixture interaction; the smaller the particle size of cement or larger the specific area higher the amount of admixture to obtain the same dispersion of a bigger particle [13]. Modifications in the admixture addition time also affect the rheological properties of the concrete. Delayed addition leads to a reduction in the heterogeneous adsorption of the system, so the admixture is more adsorbed by the alite [12].

For all the reasons cited above, it is important that new admixtures are constantly developed, improving the interaction with the cement, anticipating the interaction problems and correcting them with the adjustment of specific admixtures for each type of cement. This will allow optimization of the content, avoiding waste which brings both economic and environmental benefits.

2 MATERIALS

The cement chosen to carry out this work is a CPV-ARI according to the Brazilian standard, collected directly at the cement plant, and was named in this work as a *non-pre-hydrated*. This is the Brazilian cement with lower content of additions and is like to the CEM I cement defined in the European standard EN 197–1, which is also called OPC (ordinary Portland cement) in the technical-scientific literature.

A polycarboxylate-base admixture containing 2 types of polymers blended, as shown in Figure 1 was the superplasticizer adopted to evaluate the changes when the system is dispersed.

3 METHODS

3.1 Cement characterization

Particle size distribution: equipment used: Malvern Instruments model Mastersizer 2000/2000E. The test was performed wet, in absolute ethyl alcohol.

X-ray fluorescence: according to ISO/FDIS 29581-2:2009 (E) - equipment used: Panalytical model Minipal Cement, from melt pellets on a Claisse model M4 melting machine using melt-based lithium tetraborate / lithium metaborate mixtures MAXXIFLUX (66.67% Li_2B4O_7, 32.83% $LiBO_2$ and 0.50% LiBr), with a ratio of 1g of sample), 6.75g of flux.

X-ray diffraction: according to [15] - equipment used: Rigaku model Windmax 1000, operating on copper Kα radiation with 40kV - 20mA and scanning of 2°/min. Identification of the compounds was performed using Panalytical X-pert High Score Plus software (version 3.0) and diffraction patterns provided by the International Center for Diffraction Data (ICDD).

The Figure 3 presents the particle size distribution of each sample, Table 1 shows the chemical species of the binders, obtained by X-ray fluorescence, and Table 2 illustrates the mineralogical composition.

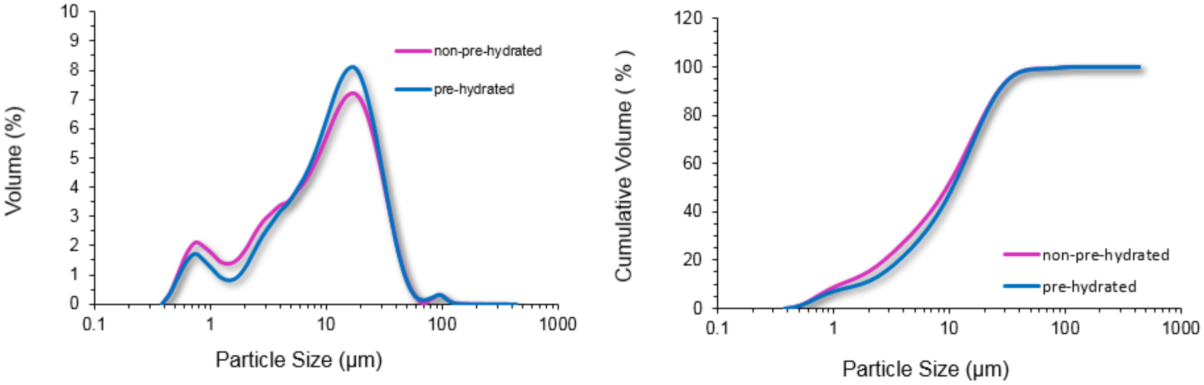


Figure 3. Left: Particle size distribution of the cement samples Right: Cumulative particle size distribution.

Table 1. Chemical composition by X-ray fluorescence.

Analyte, %	Non-pre-hydrated	Pre-hydrated	Standard 16697-2018 Requirements
Loss on ignition – LOI	2.19	3.50	≤ 6.5
Silicic Anhydride (SiO_2)	18.5	18.3	-
Aluminum oxide (Al_2O_3)	3.99	3.93	-
Ferric oxide (Fe_2O_3)	2.71	0.68	-
Calcium oxide (CaO)	61.1	61.5	-
Magnesium oxide (MgO)	5.82	5.83	≤ 6.5
Sulfuric anhydride (SO_3)	3.31	3.28	≤ 4.5
Potassium oxide (K_2O)	1.17	1.15	-
Titanium oxide (TiO_2)	0.22	0.21	-
Manganese oxide (Mn_2O_3)	0.10	0.10	-
Strontium oxide (SrO)	0.07	0.07	-
Phosphorus oxide (P_2O_5)	0.17	0.18	-
Others	2.84	3.77	-

Table 2. Mineralogical composition calculated by Rietveld refinement using the data of X-ray diffractometry.

Analyte, %	Non-pre-hydrated	Pre-hydrated
C_3S	63.8	61.0
C_2S	8.00	9.00
C_3A cubic	5.90	4.70
C_3A orthorhombic	0.40	0.50
Gypsum	1.90	0.80
Bassanite	3.30	2.50
Periclase	6.10	6.10
Brownmillerite	7.60	7.40
Calcite	1.70	1.70
Portlandite	1.30	1.50
Syngenite	-	2.60
Ettringite	-	2.10

Syngenite and ettringite were detected by X-ray diffraction, characteristic phases of pre-hydrated cements. According to Silva et al. [1], normally commercial cements presents prehydration (Wk) ≈ 0.15 to 0.3% when leaving the cement mill; values above 0.3% can significantly impact the cement performance properties. The pre-hydrated cement presented fewer fines particles than the reference cement, which indicates the agglomeration of the particles of the pre-hydrated sample. These characteristics affect the packing and the distance between the particles.

The pre-hydration was carried out at 23±2 °C and ≥ 90% relative humidity in a plastic hermetic container for 7 days and indicated as a *pre-hydrated* sample using ammonium chloride, this level of pre-hydration was adopted considering as an worse condition that the cement is submitted in field.

3.2 Mixing Procedure

The dry powder was weighed in a beaker and the water plus admixture in another, keeping the water-to-cement ratio at 0.35. The mixture was run on a Eurostar P1, IKA mechanical stirrer for 2 min keeping the rotational speed at 1200 rpm. Then, the rotation was increased to 2000 rpm for a further 1 min, totaling 3 minutes of homogenization / dispersion [16].

The suspensions were used in the spreading (Kantro cone), rotational and oscillatory rheometry and isothermal conduction calorimetry tests [16], [17].

The same samples were subjected to the test at the same time to reduce variability on the results.

3.3 Paste characterization

Rotational rheometry

The rheological behavior of cement pastes or concrete is influenced by several factors, some of them mentioned above, other factors are the volumetric concentration of the particles, physical-chemical and mineralogical characteristics of the cement, interparticle separation distance (IPS), and surface interactions [10]. Rheology is a science in which the flow and deformation of materials are studied. In this case the interaction between materials in suspension, cement particles with water and in some cases admixture, which are homogeneously distributed, is being studied [13], [11]. The cement reacts over time with the water forming crystals of hydration, modifying the stiffness of the cement-water- admixture set [16]. In this paper, rheometry helps to understand the interaction between the different types of cements with the admixture.

The rheological and strength properties of concrete are essential parameters required for concrete performance, so it is necessary to study the interaction between cement and admixture, since not all admixture/cement pairs function optimally together, even if both meet the published standards. For example, especially at low water/cement ratios incompatibility between cement and admixture can be detected with rheology before concrete is made, avoiding concrete that exhibit problems such as false set, fast flowability loss, handle retardation, excessive air entrainment [10], [11].

The rheological methods chosen for this study were rotational and oscillatory rheometry. Rotational test indicates the rheological behavior of pastes, viscosity, hysteresis profile, and others, always in function of changes on the shear rate. For oscillatory methods, the information is obtained over time, or in function of changes in strain, or even frequency applied, depending on the kind of application desired for the products or monitoring the hardening stage after application.

Rotational rheometers are high precision equipment, and accurate results can be obtained regarding the behavior of the material [16].

The cementitious pastes were mixed as described above and added to an Anton-Paar rheometer, model MCR302, shown in Figure 4. The tests were performed using cross-hatched stainless-steel parallel plate geometry with Diameter of 25mm (PP25/P2), to guarantee shear without slipping during the tests. A stepped flow test was used for the determination of rheological parameters and the type of behavior under flow request. The shear rate was increased from $0.1s^{-1}$ to $50s^{-1}$ (acceleration period) and then returned to $0.1s^{-1}$ (deceleration period). It was applied 10 steps by each period, each one with 10s. These results were used to obtain the optimal content of admixture [16], [18].

Oscillatory Rheometry: The mixed oscillatory test was applied using strain/time sweep tests. During the first stage, the amplitude was changed from 10^{-5} to 10^{-1}, keeping the frequency constant at 1Hz, while in the time sweep test the frequency was maintained at 1Hz and strain at 10^{-4}. In this second case the test was performed for 30 minutes. The strain/time cycle was repeated 8 times, totaling almost 3 hours of testing. An illustration of the schedule is shown in Figure 5 . However, the results presented are equivalent to the time sweep test. This strategy was adopted to try to maintain a correlation with the flow test as a function of time, after breaking down the microstructure under formation [16], [18].

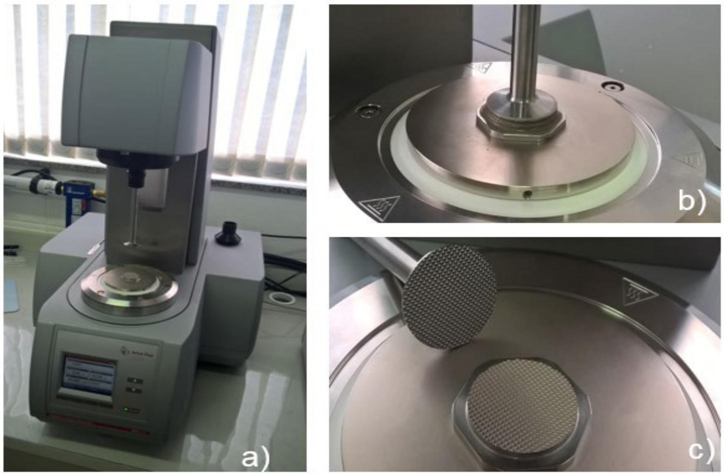


Figure 4. a) rheometer; b) addition of the paste c) geometry - cross hatched.

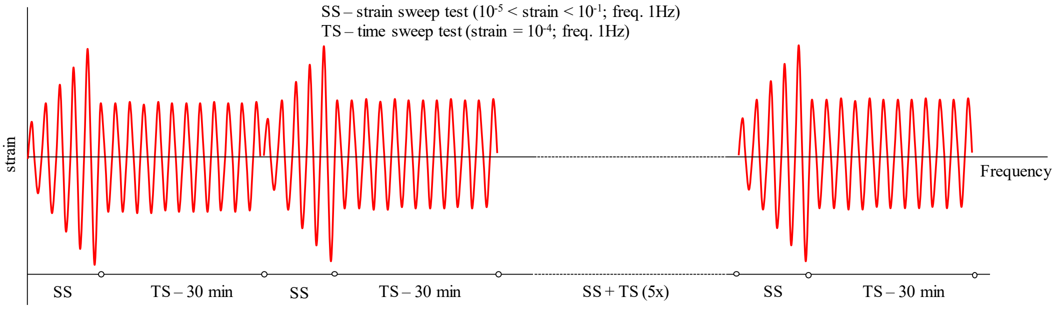


Figure 5. Illustration of oscillatory rheometer programming with mixed tests of strain sweep and time sweep. (For the discussion were used only the results of time sweep test) [11], [16].

Kantro Cone Test: The Kantro test, also known as a miniature cone test, is a simple method to evaluate the comparative dispersing effect of an admixture, it is a mini stainless-steel cone, and this method allows to evaluate only the interaction of the cement - admixture + water, since only paste is used, without the influence of aggregates [17].

The process involves filling a cone set on a metal plate well leveled horizontally with cement paste, and then removing the excess paste with a spatula for the surface levelling. After this, the cone is removed, thus the paste flows by the action of gravity and weight of its own body to the equilibrium in the state of rest. The parameters of spreading of the sample are measured, such results are compared with the yield stress data obtained by the paste rheometer [16], [17].

The test was performed according to Kantro *apud* Bucher [19]. About 100g of paste was added to the Kantro mini cone and the spreading is performed on a wet metal base, quantified when spreading ceases after removal of the mold. The Kantro cone test is used to evaluate the paste spread with the use of the admixture, with small amounts of paste it is possible to evaluate the sample spread parameters, thus determining the fluidity of the mixture with the different contents and types of admixture, which can often be related to the flow voltage data obtained by the rheometer [17].

Isothermal calorimetry: equipment used: TA Instrument isothermal calorimeter model Thermometric TAM AIR. The results of this technique allow the evaluation of the kinetics of the chemical reactions that occur during the first 72 hours of hydration of the cement [1], [20].

4 RESULTS AND DISCUSSION

A portion of cement was pre-hydrated for comparison with cement without prehydration. Paste was prepared from pre-hydrated cement and the reference cement and analyzed in rotational and oscillatory rheometry. The optimal content of the admixture was determined for cement with and without prehydration using the Kantro cone test and rotational rheometry. In this case, the prehydrated cement required less admixture. In the Kantro cone test, the spread is associated with the gravity action (single point test), the results of rotational rheometry are obtained for different shear conditions (multipoint test). These data make possible the quantification of a rheological profile, viscosity, yield stress and hysteresis area. Results obtained using each method will be presented in sequence.

The isothermal conduction calorimetry test was carried out to evaluate the flow heat during Portland cement hydration reaction without and with pre-hydration, with and without superplasticizer in the optimal contents found through the rotational rheometry test. The same paste sample was used to run the tests in rheometry and Kantro cone test, another paste was prepared on the same conditions to run calorimetry tests.

4.1 Admixture Optimization

The results obtained from rotational rheometry are usually presented in the form of shear stress versus shear rate graphs, but for the determination of the optimal admixture content, the results are presented in terms of apparent viscosity, yield stress and hysteresis area depending on the percentage of admixture used [21]. The yield stress was quantified as the shear stress value at the lowest rate used in the test. As the tests are performed in two steps (acceleration and deceleration), the result obtained in the deceleration was used, since the material had already undergone the condition of greater imposed shear and there is a natural tendency of re-agglomerate. The apparent viscosity was estimated at the maximum shear rate [21]. The hysteresis area is equivalent to the area inscribed between the acceleration and deceleration curves in the stress graph vs. shear rate. A well dispersed suspension should have low flow stress and apparent viscosity, and hysteresis area close to zero. Positive hysteresis areas (thixotropic profile) indicate that the material that was deagglomerated during the acceleration step (increase in shear rate) showed slower re-agglomeration during deceleration. The variation in the apparent viscosity and in the yield stress of the pastes is indicated as a function of the type of mixing procedure, Figure 6 shows an schematic illustration on how the apparent viscosity data and yield stress data was obtained. There are different ways to get these values [22]. One of them is from the application of rheological modeling, such as from Herschel-Bulkley, Casson, Bingham, etc . In these cases the viscosity obtained is plastic, but care must be taken with the model parameters, as they often result in negative flow values, very low plastic viscosity and very high modeling errors . Another way of comparing the values is to collect raw data directly in the graph. In this scenario, the values of apparent viscosity was obtained at the maximum shear rate applied in the test, since it is the state of greater dispersion of the particles. In the graph of stress vs. shear rate, viscosity is the ratio of both. The yield stress was quantified as the shear stress value at the lowest rate used in the test: as the tests were performed in two stages (acceleration and deceleration) the results of the deceleration step were adopted, since the material had already passed through the higher imposed shear condition, and there is a natural tendency for re-bonding [21].

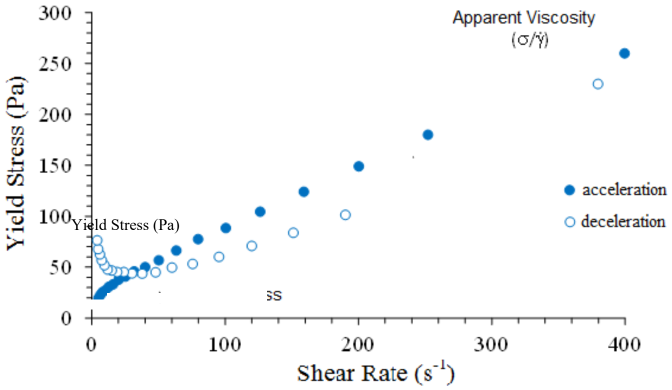
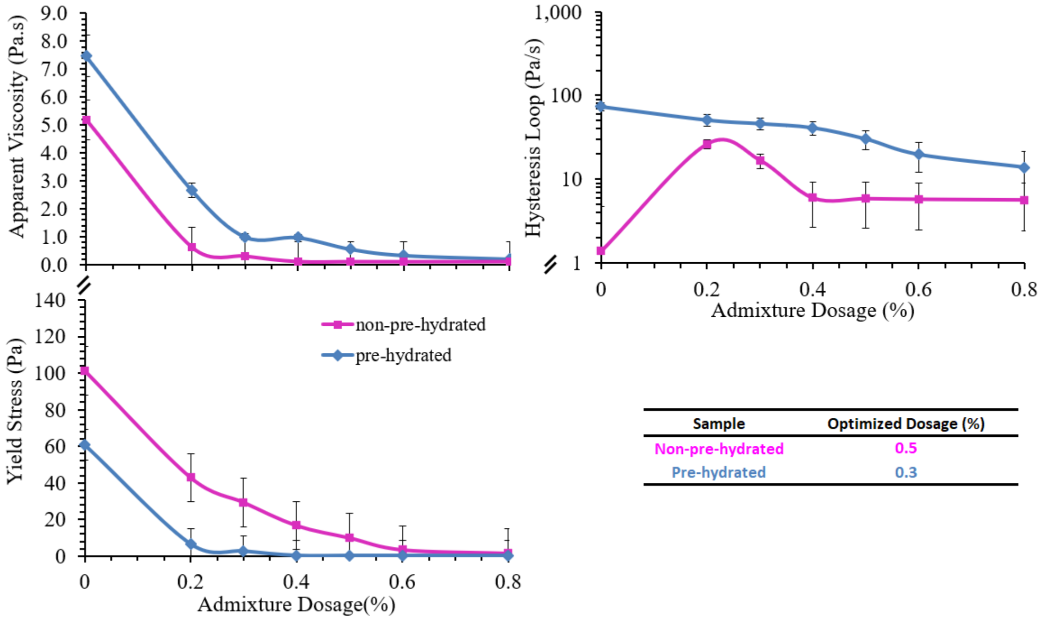


Figure 6. Schematic illustration of apparent viscosity and yield stress [21].

In the case of negative hysteresis areas, the rate of re-agglomeration is more pronounced than the deagglomeration of the particles, and the profile of rheopexy is observed. The data obtained in these experiments is shown in Figure 7. The variation in the apparent viscosity, in the yield stress and in the hysteresis area of the pastes is indicated as a function of the variation of the content of admixture. It was not used any model to represent the results obtained on this work, the data was treated using graphical method as per previous work done by Romano et al. [21].The optimal content of the admixture was quantified based on yield stress, apparent viscosity and hysteresis area, considering the lower hysteresis area, the point that the yield stress and viscosity keeps constant and lower values [21].

In the pastes with pre-hydrated cement the content of the admixture to reach the optimum was lower when compared to the cement not pre-hydrated, this happens due to the formation of crystals of hydration that has greater affinity for the polycarboxylate admixture thus requiring a lower content [22].

The optimized contents are described in the table within Figure 7 (0.5% for non-prehydrated and 0.3% for prehydrated) based on 3 tests of each dosage and were used for stability evaluation over time, presented later.



Sample	Optimized Dosage (%)
Non-pre-hydrated	0.5
Pre-hydrated	0.3

Figure 7. Apparent viscosity (Pa·s), Yield stress (Pa) and Hysteresis loop (Pa/s) of each sample in function of admixture content. Table represents the optimized content, with error bars.

In this work, the optimized contents of the admixtures were obtained from rotational rheometry tests, but it is known that companies or technical centers do not always have rheometers for the study of admixtures. Therefore, it is customary to use the Kantro cone test. Thus, the same paste was evaluated from the spreading and the results are presented in the sequence. The results presented are an average of three measurements of each sample [23].

4.2 Free flow according the Kantro's cone test

The results of a series of slurries obtained by Kantro cone test are shown in Figure 8. In the pastes with the non-pre-hydrated cement a higher the amount of polymer was required to have greater the flow. Based on the Kantro cone tests, it was difficult to define an optimal content for the admixture, and the values were from 0.4 and 0.6% for both cements [23].

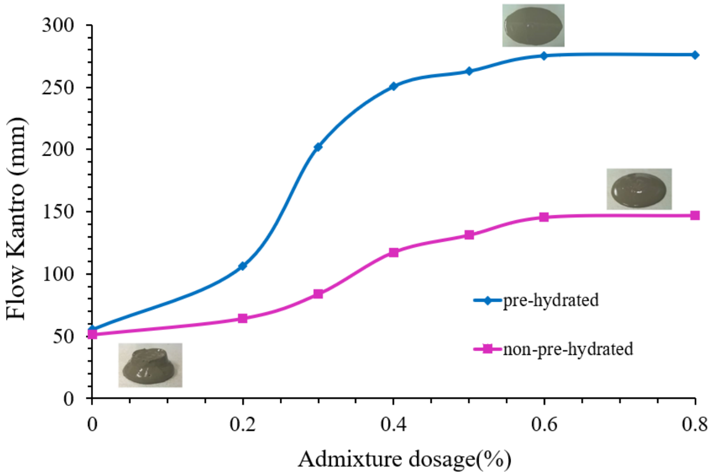


Figure 8. Flow variation at Kantro cone test.

Additionally, there is a correlation between the increase of the admixture content and the increase of the flow, but this result can be masked by the segregation in the paste and by the heterogeneous flow during the spreading. Although it is possible to measure the spread of the sample visually it is possible to verify a phase separation halo, but from the normalization it is possible to obtain an average value of the spreading diameter. With the increase of the content of the admixture and the migration of water to the surface and formation of the halo, this separation will also occur during the application, making it difficult to handle the cementitious material. This phenomena was observed on the higher content of the admixture (0.8%) [24].

In practice, such a single point test is used based on the need for each application, but it is known that the results have a good correlation with the yield stress and viscosity.

In this way, it can be inferred that:

- Both by rotational rheometry and from the Kantro cone spreading, it was possible to observe differences caused by the admixtures in the pastes with the cement with and without prehydration. The highest amount of admixture was required for non-pre-hydrated cement, the higher adsorption of the admixture is reached by higher fineness of cement particle, thus polymer molecules exhibits higher affinity to the available C_3A and hydration products, once the superplasticizer shows different adsorption affinity by the surface of different hydration products and mineral surfaces [2].
- The results of rotational rheometry enabled definition of optimal admixture content for each sample, which the Kantro cone test did not adequatelly;
- Correlating the flow results with the rheological parameters, it was confirmed that the change in spread is governed by both the viscosity and the yield stress, according illustrated in Figure 9, previously.
- The higher difference is that using rotational rheometry it is possible to obtain, beside of the rheological parameters, the rheological behaviour of each composition during the flow, because the fresh state properties are evaluated in different shear conditions, which can be close related to many practical applications.

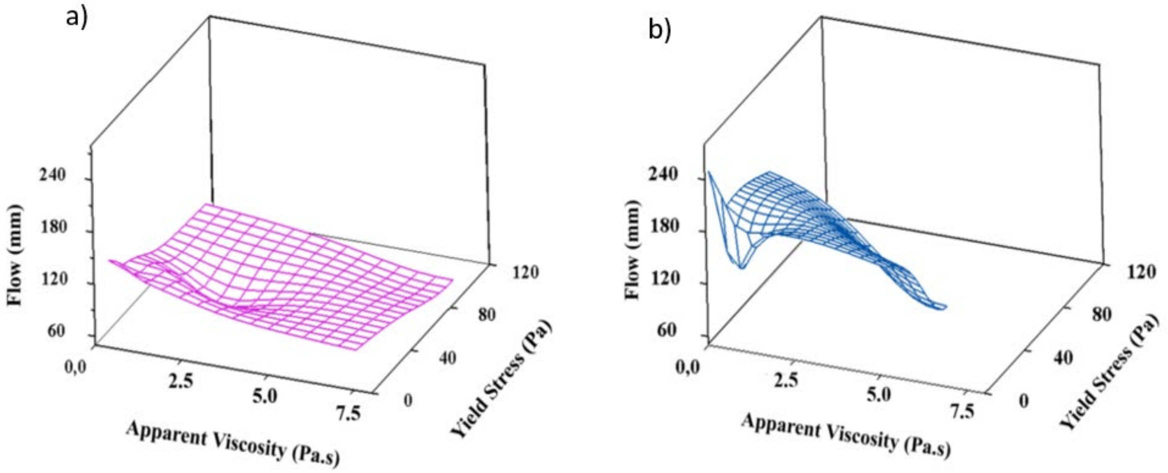


Figure 9. Flow vs Apparent Viscosity vs Yield stress for both cements changing the admixture content (a) non-prehydrated and b)pre-hydrated).

With the results presented so far, only information about the characteristics of the paste in the early age of cement hydration were obtained, since the tests were carried out 5 minutes after mixing. However, no information was obtained about the stability over time. For this, oscillatory rheometry tests were performed and the results are presented next. In this step the tests were carried out only with the admixtures in the optimal contents for each type of cement with and without the addition of superplasticizer [24].

4.3 Stability over time

During hydration, the hydrated product form a three dimensional network which makes more rigid the suspension over the time, to monitor the stiffening it's used the oscilatory rheometry [25]. Figure 10 presents the change in flow and in the storage modulus (G') from oscillatory rheometry over time. The monitoring of G' using the mixed oscillatory test illustrates the gain on consistency over time, after breaking down the agglomerates in the strain sweep test.

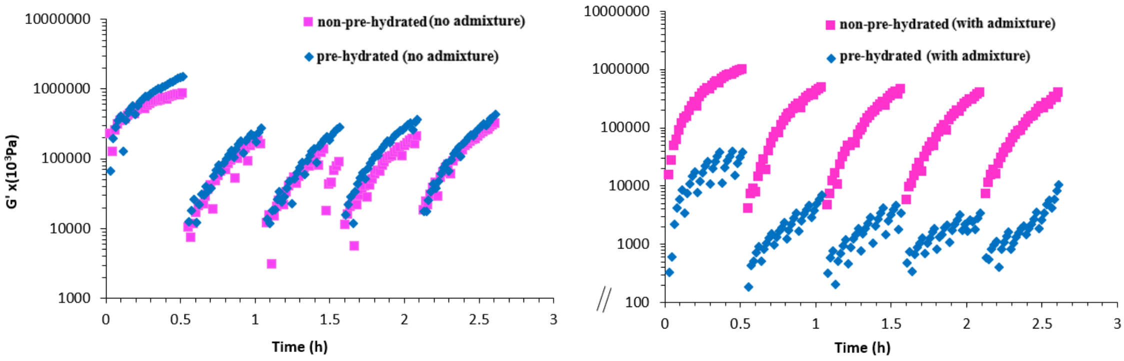


Figure 10. Storage Modulus (G') without and with admixture over time.

Without admixture, no significative differences were observed between the pastes made from prehydrated and reference cements, the pre-hidrated sample only increased the G' value at the first 2 hours slightly. In the presence of admixture, the prehyrated and reference cements show different interactions with the admixture [25]. There is a noticeable increase in final G 'in each stage of the time sweep, which indicates that the restructuring of the microstructure is occurring in an most intensive way, increasing the forces of attraction. By using admixture, the differences between non-pre-hydrated and pre-hydrated was significant, however the stability over time was 2.5 hours for both [26].

The admixture effect on pre-hydrated sample indicates that the consolidation of the paste occurs based on a physical contribution by particles reaglomeration, in addition the pre-hydrated sample shows higher amount of ettringite and smaller amount of C_3A cubic, showing that the amount of admixture for this reduced quantity of cubic C_3A is higher than the non-prehydrated cement allowing better fluidity of the paste over the time improving the cement-adimixture interaction [25], [26].

4.4 Isothermal calorimetry

The curves presented in Figure 11 and the stages of hydration reaction presented in Table 3 show how the cement reaction is affected by prehydration and use of admixture.

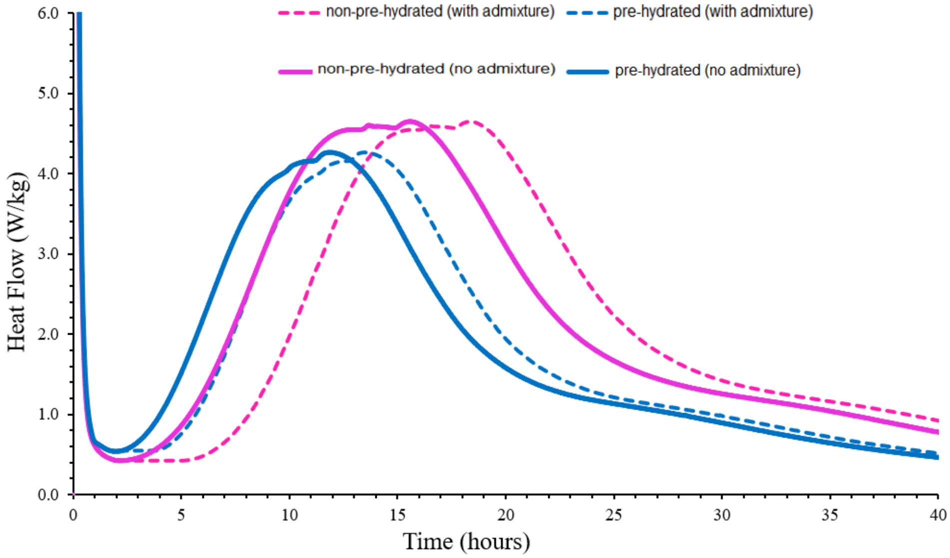


Figure 11. Heat flow over the time.

Table 3. Reaction rate, cumulative heat at initial setting, time of induction period, end of acceleration period and setting time by Vicat.

Composition	Induction period (h:min)	Reaction rate (mW/g·h)	Setting time (h:min)	Cumulative heat at initial setting (J/g)	End of acceleration period (h:min)
non-pre-hydrated	3:10	0.64	7:00	35.2	13:00
non-pre-hydrated (with admixture)	5:35	0.28	9:00	30.9	17:00
pre-hydrated	2:15	0.61	5:00	37.6	10:00
pre-hydrated (with admixture)	4:35	0.68	6:00	34.6	12:00

In general, the pre-hydrated sample affected the chemical hydration reaction, caused an acceleration in the induction period and a considerable displacement in the time of formation of the main silicate peak [25]. The pre-hydration of the cement particles results in the formation of nanoscale ettringite needles on the surface of the cement, this fenomena can affect the interaction with the superplasticizer, as observed by Winnefeld [22], the cement aging can increase the performance of polycarboxylate, it depends on the chemical and mineralogical composition of the cement used.

The differences observed between pre-hydrated and non pre-hydrated hydration kinetics, are probably associated to the degree and type of reactions at silicate surfaces once C-S-H shows enhanced growth rates in the presence of silicate hydrate seeds that provide preferred nucleation sites and thus accelerate reactions in Ca_3SiO_5 and shorten induction period [25]. The silicate surface reactions result in the generation of a type of C-S-H that generates sites for nucleation of typical C-S-H during normal hydration [25], [26].

The surface of the pre-hydrated cement particles is initially covered by an enhanced C-S-H amount, which can have the following effects:

- Reduced the exposed surface area of the anhydrous phases available for dissolution,
- Cause an earlier transition to a diffusion-controlled mechanism when a continuous C-S-H layer on the anhydrous grains has grown thick enough to limit the transport of dissolved ions to-and-from the bulk solution,
- In contrast, silicate phase surface modifications caused by the cement prehydration are gradually etched away upon normal [25], [26].

Based on the geochemical theory of dissolution, the development of chemical reaction of cement occurs even without calcium oversaturation. The C-S-H in formation acts as a point of nucleation and starts the acceleration period. So, the induced prehydration of cement presented an intense heat flow released comparing with the anhydrous cement: the balance between dissolution of anhydrous phases of cement and the precipitation of hydrated products is energetically favorable for etch pits to form [25], [26].

The use of admixture on the other hand, increases the induction period, independently of the prehydration process, but the kinetics have the same behaviour, similar that it was observed by Rojas and Cincotto [27]. This effect is expected, since the polycarboxylate admixtures improve the workability of pastes, mortars and concretes by facilitating the dispersion of cement particles by electro-repulsion, keeping the stability of the system over the time [23].

Admixtures are not homogeneously adsorbed by the cement: the C_3A and C_4AF phases are the ones with the highest affinity for the dispersants [23], so they adsorb the higher amount of admixture when compared to the C_3S and C_2S. These are also the phases most active in the initial hydration processes [25], [26].

5 CONCLUSIONS

The results showed that small percentages of prehydration can strongly impact the engineering properties of the cement, specially changing the rheological behavior of the cement.

The results obtained from the Kantro cone test do not allow us to define the optimal content of superplasticizer, while the rotational rheometry test gives us a deflocculating curve and it is possible to identify the optimum admixture content for each cement sample. Although the information obtained from the single-point test is commonly used in the market it can only serve as a comparative parameter.

For the oscillatory rheometry tests, it is possible to identify the characteristics of better stability over time for the pre-hydrated cement with the addition of superplasticizer was the best combination when compared to the cement without prehydration and with the combinations without the use of admixture.

However, the change in cement prehydration resulted in different interaction with the evaluated admixture.

In this way, the use of an admixture cannot be defined as optimal all for types of binders. The choice depends, in addition to the type of application desired, of the correct content evaluation for each type of cement and the prehydration affects the rheological and mechanical properties.

For this, it's necessary to use a better tool for the correct understanding of the causes of the variations and not only of the effects in the spreading. The calorimetry showed that only the induction period increased by using the admixture on the pre-hydrated and non-pre-hydrated cements, but the kinetics remains the same.

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