

# INTERACTION OF COMMERCIAL SUPERPLASTIFICANT ADDITIVES WITH POZOLANIC CEMENTS CONTAINING CALCINED CLAY

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## ABSTRACT

*The utilization of polycarboxylate-based superplasticizer additives (PCE) in the concrete industry is widespread, and therefore, the dispersion mechanisms of these additives in cements containing supplementary cementitious materials (SCMs) present significant opportunities for investigation. This article aims to characterize the interaction between three commercial PCEs and three types of cement (pure Portland cement CPV-ARI and cement formulations containing 20 wt% and 28 wt% calcined clay content). The cement and calcined clay underwent physical-chemical characterization, whereas the PCEs were characterized through solid content determination and FTIR analysis. The interaction between cement, SCMs and additive was assessed by determining the optimal additive dosage using the mini-slump test, which was employed to evaluate its influence on kinetic mechanisms and hydration using a semi-adiabatic calorimeter, as well as mechanical strength. The PCEs exhibited high sensitivity to calcined clay, requiring higher dosages of PCEs to achieve the same fluidity compared to the system without clay.*

**KEYWORDS:** *superplasticizer additives; polycarboxylate; composite cements; calcined clay.*

## I. INTRODUCTION

The Portland cement manufacturing process directly contributes to the emission of CO<sub>2</sub>, one of the most abundant and concerning gases in terms of global warming. The International Energy Agency [1] concluded that growth production of cement increased direct CO<sub>2</sub> intensity by 0.5% from 2014 to 2018. To keep up with international agreements, an annual decline of 0.8% is required until 2030. Several studies [2-6] have sought alternatives to reduce the total CO<sub>2</sub> emissions from the manufacturing process of Portland cement. The most feasible alternative identified thus far entails blending Portland cement clinker with progressively higher proportions of supplementary cementitious materials and refining cementitious systems.

The use of calcined clay (CC) in the development of cement has shown to be an important step in the last decade. The incorporation of CC in cements, in addition to reducing the emission of carbon dioxide, also directly contributes to changes in the mechanical properties and durability of the material [6]. There

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is a tendency that the use of pozzolans leads to greater results in terms of compressive strength and durability of concrete due to their chemical and physical actions up to certain levels and mixtures depending on the pozzolan. Such benefits are mainly linked to the pore refinement process and the densification of the transition zone [7].

Despite the environmental and economic gains with the development of CC cements, the commercial application of this cement in concrete suffers from several obstacles. Cement with the addition of CC consumes more water because of its fineness and larger specific surface [8, 9]. To produce concrete with lower cement consumption, it is necessary to use superplasticizers. The application of polycarboxylate-based superplasticizers (PCE) in the world continues to play an important role in the construction industry. The greatest innovations in recent times in concrete production have been due to the development and improvement of additive production technology. The PCEs confer a considerable increase in fluidity, being widely used in the production of self-compacting concrete, as it results in high strength, workability, and durability [10]. These polymeric additives typically exhibit complex architectures and distinct molar mass distributions, necessitating appropriate physical-chemical characterization and production processes.

Additives based on synthetic polymers, such as polycarboxylates, can lead up to 40% water reduction, but generally have low tolerance to clayey minerals [11]. Several research have sought to solve the problem of interaction between PCEs and clay [12-14], mainly with the possibility that clay minerals occurring in the aggregates or limestone could have detrimental effects on the concrete, including increased water demand of fresh concrete due to the water absorption and expansion property of most clays. Typically, their interaction takes place through (1) adsorption onto their positively charged surfaces and (2) chemical sorption (intercalation) within the primary layers, which consist of aluminosilicate sheets. [10]. Thus, clays can absorb much more additive than cement, resulting in a much higher consumption of PCEs. The interaction of PCEs and CC is a point of attention for the application of these additives since clay can impair the efficiency of PCEs to the point of mitigating their dispersant properties [10]. In their study, Ferreira et al. [11] discovered that a calcined kaolin clay necessitates considerably more water in comparison to a thermally activated 2:1 clay when employing standard doses of commercially available PCE superplasticizers. Additionally, they observed a noteworthy enhancement in the rheological characteristics of such binders with the substantial improvement brought about by the inclusion of fly ash. Moreover, Akbulut et al. reported that the required dosages of superplasticizer additives for cements incorporating calcined kaolin clay were significantly elevated—up to 0.7% more—compared to the conventional levels practiced in the common cement industry. [15]. Plank et al [16] observed that the increase in the percentage of replacement of clinker by CC results in an increase in PCE dosages. This negative impact of CC on dosage is comparable for all PCE polymers, with an approximately six-fold increase for the 60:40 mix compared to pure cement. [17][18] determined that an increase in CC content in cement resulted in a decrease in fluidity relative to pure cement paste. CC affected the rheological properties of the cement by absorbing a large amount of water, with 60% of replacement of cement by CC it was no longer obtaining fluidity without the addition of superplasticizers.

The additives developed in the market are still focused on traditional cements, generating in most cases incompatibility between the cement composed with CC and the superplasticizer additive. As indicated by [19], existing mixtures available in the market fail to comprehensively address the adverse impacts of calcined kaolin clay (CC) in concrete, especially at costs and doses deemed acceptable by the industry. This underscores the imperative for the innovation and development of a new generation of superplasticizers. There are few studies that deal with the interaction of commercial superplasticizer additives with cements with CC. Thus, in order to give insight into the impact of polycarboxylate-based superplasticizer on the kinetic and hydration mechanisms as well as the cements mechanical strength, this article explores the techniques of determination of the solids content and analysis by infrared spectroscopy with Fourier transform (FTIR) to characterize the additives. For the characterization of cement and clay, laser granulometry, x-ray fluorescence (FRX), x-ray diffraction (XRD) and specific surface area through porosimetry analysis by gas adsorption using BET method. With the objective of analyzing the behavior that the increase of the CC content in the cement has on the superplasticizer additives based on polycarboxylate, the optimal additive dosage was evaluated with the assistance of

mini-slump tests. Based on the optimal content obtained in the mini-slump, the interaction between cement-addition-additive was investigated using a semi-adiabatic calorimeter and compressive strength.

This paper is structured as follows. Section II introduces the experimental program, comprising subsections on the materials utilized and the methods employed in this study. Section III presents the results and discussions related to the material characterization, interaction outcomes between superplasticizers and various cements, as well as the findings from calorimetry and strength tests. Finally, Section IV summarizes the conclusions of the study.

## II. EXPERIMENTAL PROGRAM

### 2.1 MATERIALS

#### 2.1.1 Cement characterization

The cements chosen to carry out the studies were collected directly from the cement factory in accordance with the Brazilian standard ABNT NBR 16697 [20]: CP1 (CPV-ARI or Ordinary Portland Cement); CP2 (CPV with 20% of CC); and CP3 (CPV with 28% of CC)

CPV-ARI is the Brazilian cement with the lowest content additions and is like the CEM I cement defined in the European standard EN 197-1, also known as OPC (ordinary Portland cement) in the technical-scientific literature. CP2 and CP3 is like CEM IV/A cement defined in the European standard EN 197-1, also known as PC (Pozzolanic cement), defined by clinker content between 65-89% with silica fume, pozzolana or fly ash replacement content between 11-35%.

The particle size distribution of the cements (as shown in Table 1) was assessed using laser diffraction in air dispersion, employing a Particle Size Analyzer CILAS 1064L with a size range of 0.04-500  $\mu\text{m}$  in liquid mode. The analysis, conducted with high precision (Accuracy:  $\pm 0.5\%$ ), utilized a Fiber and collimated Laser diodes source with wavelengths of 635 and 830 nm. Chemical composition details, as outlined in Table 1, were determined through X-ray fluorescence (XRF) using an EDX-7000 equipment manufactured by Shimadzu, Tokyo, Japan, along with an exploration of their physical properties. The specific surface area (SSA) of the Portland cement (PC) was determined through nitrogen gas adsorption measurements utilizing the Brunauer-Emmett-Teller (BET) method. This analysis was performed using an Autosorb Quantachrome Instruments in Florida, USA (Table 1). For a comprehensive understanding of the mineralogical composition, X-ray diffraction (XRD) analyses were carried out on both cements and calcined kaolin clay (CC) as illustrated in Figure 1. The XRD analysis was conducted using an X'Pert MDP diffractometer from PANalytical, Almelo, The Netherlands, operating at 45 kV and 40 mA, with CuK  $\alpha_{1,2}$  radiation ( $\lambda = 1.5418 \text{ \AA}$ ). The angular range covered  $7^\circ \leq 2\theta \leq 70^\circ$ , with a step size of  $0.0167^\circ$ .

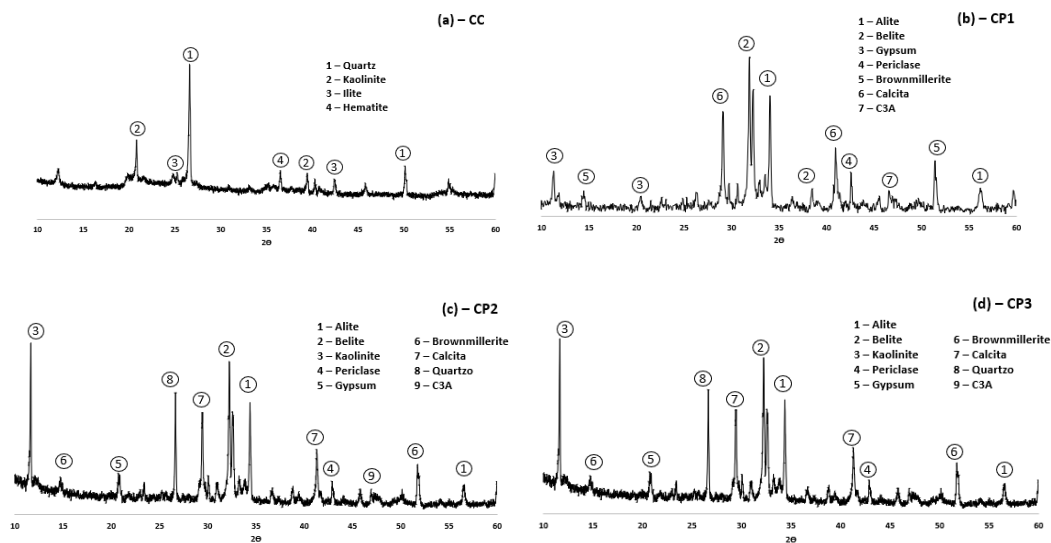
In Table 1, it is possible to observe that, regarding the incorporation of CC to the cement, the CP2 and CP3 cements present similar granulometric distribution characteristics, mainly considering the accumulated values up to D50. However, when analyzing 90% of the total volume, and the average diameter, CP3 presents a coarser characteristic, based on the higher substitution content of CC, which has a larger particle diameter. It is possible to verify that CP1 cement has a smaller average diameter when compared to CP2 and CP3 cements that have CC. This corroborates the statement made earlier that CC has an average diameter greater than that of cement.

From the results presented in Table 1, it appears that the Portland cement used complies with the limits of magnesium oxide ( $\leq 6.5$ ) and sulfur trioxide ( $\leq 4.0$ ), established by ABNT NBR 5732 [19]. From the results obtained with the XRF of the cements, it can be verified that the percentage of  $\text{SiO}_2$  and  $\text{AlO}_2$  increased according to the change in the CC content incorporated into the CP1 cement. This increase in the presence of these oxides demonstrates the presence of CC replacing clinker.

**Table 1** - Chemical composition by X-ray fluorescence.

Oxides (%)	CP1	CP2	CP3	CC
Silicic Anhydride (SiO <sub>2</sub> )	23.62	29.81	31.47	56.82
Aluminum oxide (Al <sub>2</sub> O <sub>3</sub> )	6.07	9.17	9.76	35.12
Calcium oxide (CaO)	55.27	43.57	40.61	-
Ferric oxide (Fe <sub>2</sub> O <sub>3</sub> )	2.94	2.88	2.83	3.42
Magnesium oxide (MgO)	4.39	4.37	4.28	0.31
Potassium oxide (K <sub>2</sub> O)	0.7	0.7	0.69	1.13
Sulfuric anhydride (SO <sub>3</sub> )	3.91	3.66	3.67	-
Sodium oxide (Na <sub>2</sub> O)	0.17	0.17	0.17	-
Others	0.89	2.01	2.26	1.87
LF	2.04	3.55	4.16	0.86
D10 (μm)	1.26	1.70	1.50	1.63
D50 (μm)	10.27	13.47	13.60	15.02
D90 (μm)	28.55	35.87	38.27	43.71
Mean particle size (μm)	12.71	16.43	17.22	18.96
Specific Surface B.E.T. (m <sup>2</sup> /g)	3.817	5.475	6.508	17.562

In view of the values obtained, it appears that the BET test presented results that corroborate what was observed by Scrivener et al. [8] and Beuntner et al. [9], since the increase in the replacement content of CC resulted in a specific surface area greater than that of cement without addition.

**Figure 1** - X-ray diffractograms of (a) CC, (b) CP1, (c) CP2, (d) CP3.

The mineralogical composition of the materials is revealed through X-ray diffractograms. In Figure 1a, which pertains to calcined kaolin clay (CC), discernible peaks corresponding to kaolinite and quartz are identified, accompanied by an amorphous halo spanning the 15° to 30° range. The presence of the kaolinite peak signifies the residual kaolinite content post-calcination, while the amorphous halo likely indicates the presence of metakaolinite formed during the calcination process. For CP1, Figure 1b, the main phases alite (Ca<sub>3</sub>SiO<sub>5</sub>), belite (Ca<sub>2</sub>SiO<sub>4</sub>), gypsum (CaSO<sub>4</sub>·2H<sub>2</sub>O), tricalcium aluminate (C3A), brownmillerite (Ca<sub>2</sub>(Al, Fe)<sub>2</sub>O<sub>5</sub>), calcite (CaCO<sub>3</sub>) and periclase (MgO) was identified. For CP2 and CP3, Figure 1c and 1d, the main phases alite (Ca<sub>3</sub>SiO<sub>5</sub>), belite (Ca<sub>2</sub>SiO<sub>4</sub>), Kaolinite (Al<sub>4</sub>(Si<sub>4</sub>O<sub>10</sub>)(OH)<sub>8</sub>,

tricalcium aluminate (C3A), gypsum ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ), brownmillerite ( $\text{Ca}_2(\text{Al}, \text{Fe})_2\text{O}_5$ ), calcite ( $\text{CaCO}_3$ ), periclase ( $\text{MgO}$ ) and quartz was identified.

Three commercial additives from different suppliers based on polycarboxylate, being chosen to evaluate the cement-addition-additive interaction. The initial characterization of the additives was obtained from the technical data sheet of each of the manufacturers:

- AD1 - polycarboxylate-based superplasticizer additive, light yellow color, with a solids content of 39 to 42%, density of 1.06 to 1.1  $\text{g/cm}^3$  and pH between 3.5 to 5.5.
- AD2 - polycarboxylate-based superplasticizer additive, brown color, solids content from 37.5 to 41%, density from 1.12  $\text{g/cm}^3$  and pH of 6.15.
- AD3 - polycarboxylate-based superplasticizer additive, orange color, solids content from 28.5 to 31.5%, density from 1.04 to 1.12  $\text{g/cm}^3$  and pH of 5.5.

Normal standardized sand according to ABNT NBR 7214/2015 [21] was used for the preparation of the mortar and local water supply was used both to produce pastes and mortar.

## 2.2 METHODS

### 2.2.1 Superplasticizer additives characterization

Determination of solids content: The determination of solids content is based on ABNT NBR 11768-3 [22].

Fourier transform infrared spectroscopy (FTIR): The samples were analyzed by Fourier transform infrared spectroscopy (FTIR) in a Varian equipment, model 640, equipped with an attenuated reflectance accessory (ATR). Measurements were obtained in the region of 4000-400  $\text{cm}^{-1}$  and spectra were obtained as the average of 32 analyses. Samples were analyzed directly in the ATR. The spectra obtained through FTIR allow identifying the different functional groups present in the additives.

### 2.2.2 Determination of the optimum additive content

The determination of the optimal content/saturation aims to determine the maximum amount before the additive no longer has a significant effect on the flow time and spreading of the cement paste. The methodology adopted for making the paste for the tests below consists of mixing the cement with 90% of the mixing water, mixed at low speed during the first two minutes. During the third minute, the remaining 10% of the mixing water with the additive content evaluated at low speed were added. In the fourth minute, the mixture was homogenized at low speed. In the fifth minute, the mortar was turned off to clean the shovel and the bottom of the bowl using a spatula. Finally, in the sixth minute, mixing was done at low speed to ensure final homogenization.

The determination of the saturation content by the mini-slump test was carried out in a truncated cone like that of Abrams on a reduced scale, the upper diameter measuring 20 mm, the lower one 40 mm and the height equal to 60 mm. The truncated cone is placed on a glass plate and filled with fresh paste. After filling, the cone is removed vertically at a speed of 5 mm/s to minimize inertia effects, subsequently taking 2 measurements with a caliper of the diameters perpendicularly [23].

### 2.2.3. Semi-adiabatic calorimetry

Calorimetry provides information on the influence that additives have on cement reaction processes [24]. Second Hartmann and Plank [25], the heat of hydration can be evaluated through calorimetric tests carried out in a semi-adiabatic calorimeter. Because it allows the evaluation in real conditions of the performance problems of cementitious mixtures, the main one being the incompatibility between the materials. The monitoring of the heat flux during the cement hydration reaction was carried out the semi-adiabatic calorimetry tests are performed using a four-channel semi-adiabatic calorimeter. The calorimeter used consists of a thermal insulation block, with 4 holes of 10 cm in diameter and 12 cm

deep. Sensors were positioned inside each hole to record the temperatures obtained in each container every minute. The installed system reads and saves the data that are later analyzed in the AdiaLog program. The procedure for preparing the paste for performing the test consists of weighing 100g of the cement sample to be analyzed; weigh in another container weigh 40 mL of water; Weigh the saturation content of each additive as defined by the Marsh cone and mini-slump; Perform the mixture for a time of 60 seconds and place the mixture in the calorimeter; Repeat the procedure for the other samples and start the test in the AdiaLog program. For each test, the samples were placed in the calorimeter and confined for at least 72 h in a climate-controlled room at a controlled temperature equal to  $23\pm 2^{\circ}\text{C}$  [26].

### 2.3.4 Compressive strength

The production and determination of compressive strength of mortars is based on ABNT NBR 5752 [27], which has its procedures for mixing the materials, molding the test specimens, curing conditions, and determining the compressive strength, inferred from ABNT NBR 7215 [28] at ages 1, 3, 7 and 28 days. The unit composition of the mortar was equal to 1.0:3.0:0.48 (cement: fine aggregate: water), using 25% by mass of each fraction of normal sand, according to standard NBR 7215.

For the proposed study, two water/cement ratios were used. For the reference mortar without additive, the ratio 0.48 was used according to ABNT NBR 7215, keeping the flow at  $180\pm 20\text{mm}$ . For the mortar with the optimum content of superplasticizer additive, the same 0.4 water/cement ratio established in the Mini-slump test was adopted to evaluate the resistance gain while maintaining the spread in  $180\pm 20\text{mm}$ . The mortars were prepared with the optimal levels of additive found in the Mini-slump test, being composed of 624g of cement, 1872g of normal Brazilian sand and replacing the expected mass of water of 300g by 249.6g, maintaining a ratio of 0.4 of water/cement. The mortars were initially prepared in a mechanical mixer, respecting the mixing times established by the ABNT NBR 7215.

## III. RESULTS AND DISCUSSIONS

### 3.1 SUPERPLASTICIZER ADDITIVES CHARACTERIZATION

For the characterization of the three additives, the solids content was first determined. The results obtained are shown in Table 2. Based on the observed solids content, the additives AD1, AD2 and AD3 have levels of approximately 41%, 41% and 30%, respectively.

**Table 2** - Solids content of additives.

	AD1	AD2	AD3
Solids content (%)	41.2	40.61	30.07

Infrared Spectroscopy (FTIR): FTIR measurements allowed to identify the different functional groups present in the additives. Figure 2 shows the FTIR spectrum of the superplasticizer additives.

The absorption peaks observed at  $3300\text{--}3400$  and  $1644\text{ cm}^{-1}$  are attributed to the O–H bonds present in water [29]. Additionally, peaks at  $2927$  and  $2885\text{ cm}^{-1}$  can be ascribed to the stretching vibration of C–H bonds found in aliphatic groups [30]. Further analysis reveals peaks at  $1460$ ,  $1349$ ,  $1247$ ,  $1087$ , and  $950\text{ cm}^{-1}$ , corresponding to  $\text{CH}_2$ ,  $\text{CH}_3$ , C–O, C–O–C, and C–C bonds, respectively [16, 17]. These distinctive peaks are indicative of the aliphatic, carbonyl, and ether groups present in the superplasticizer additive [18]. A similar behavior was found among all the additives analyzed here, proving the presence of functional groups characteristic of superplasticizers based on polycarboxylates. However, more tests are necessary for a broader observation of the structure and connections present in the additives.

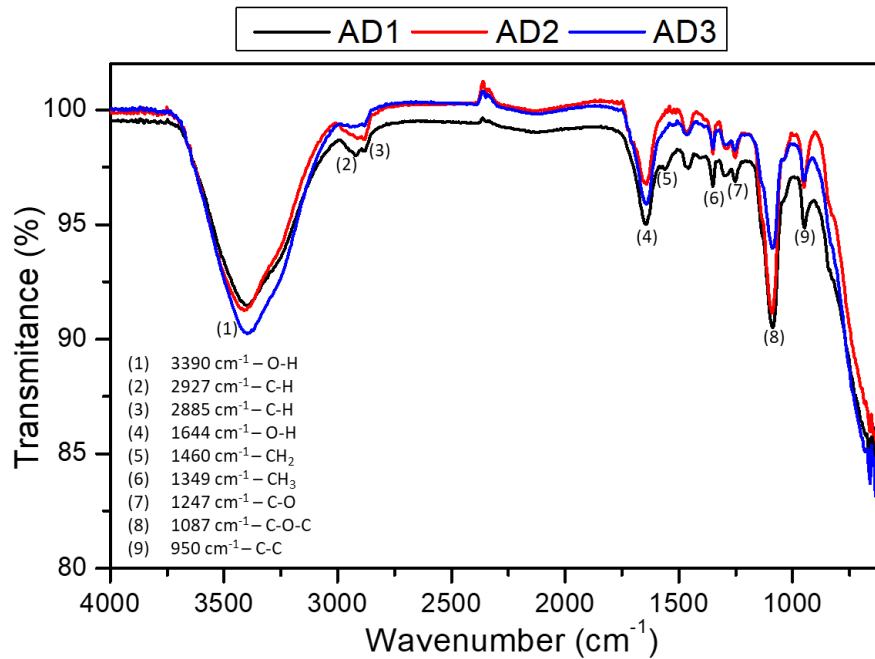


Figure 2 - FTIR spectrum of the polycarboxylate-based superplasticizers.

### 3.2 Optimal Content/Saturation – Mini-Slump

From the mini slump flow, the behavior of the three additives (AD1, AD2, AD3) was observed with cements CP1 (Figure 3a), CP2 (Figure 3b) and CP3 (Figure 3c).

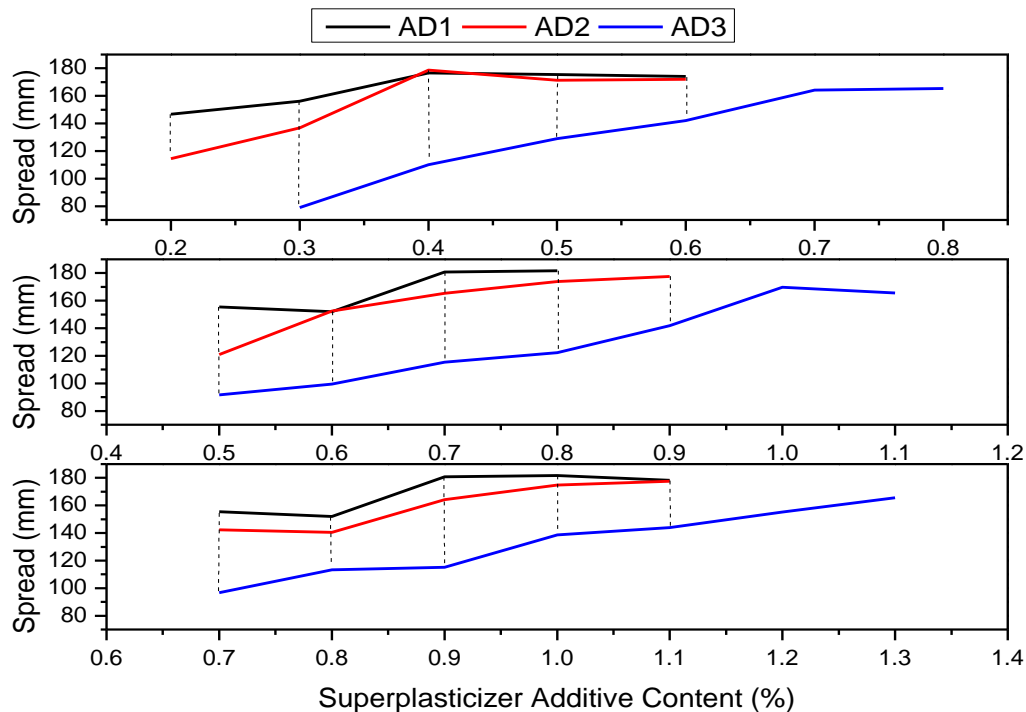


Figure 3 - a) Mini-slump for mixtures with CP1 + additives. b) CP2 + additives. c) CP3 + additives.

Evaluating the flow curves, FTIR and solids content of each additive, presented in Figures 2, 3 and Table 2, a similar performance was identified between the additives AD1 and AD2, in comparison with the additive AD3, which presented considerably lower performance for those remaining in all cements.

The behavior of additives AD1 and AD2 was considered equivalent, as the spreading curves showed similar development, with optimal content values at the maximum point of 0.4% CP1, 0.7% CP2 and 0.9% CP3, when compared to the AD3 additive in all cements of 0.7% CP1, 0.9% CP2 and 1.2% CP3. Furthermore, the spreading level of the AD1 and AD2 additives was reached from very similar solids contents (approximately 41%). Another analogous point between the two additives is the approximate maximum spreading values with the same additive content ( $170\pm 10\text{mm}$ ), which are significantly higher than those of the AD3 additive ( $150\pm 10\text{mm}$ ).

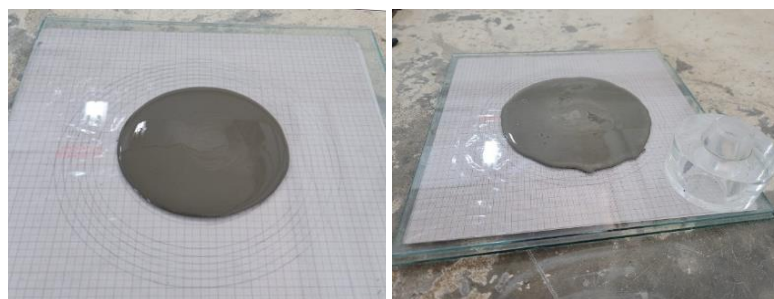
Additives AD1 and AD2 provided the cement mixtures with a more sensitive behavior in their spreading due to the higher solids content, in relation to AD3, since the difference in solids content led to a sharp increase in the consumption of additive. Additive AD3, because it has a lower solids content, needs a higher additive content to present the same spreading as the other additives [31].

After analysis of the spreading graphs and the solids content and evaluation of the quality of the mixtures produced in terms of spreading and exudation, the optimal content of additives used in the production of pastes and mortars submitted to the tests in the fresh and hardened state were defined. The determination of grades was based on values that covered the spreading achieved and the quality of that spreading. In this way, contents were defined that would guarantee, simultaneously, the maximum spreading for the three analyzed additives, avoiding the occurrence of exudation [32]. Table 3 presents the optimal additive contents defined for each type of cement according to the objective of the present work.

**Table 3** - Saturation levels for additives.

(%)	AD1	AD2	AD3
CP1	0.4	0.4	0.7
CP2	0.7	0.7	0.9
CP3	0.9	0.9	1.2

However, for the AD3 additive and CP3 cement, as seen in Figure 3, it has an increase in the amount additive used until there was exudation in the mixture (Figure 4). One of the explanations for this fact comes from the previously mentioned different solids content of the additives, as well as the difference in the surface area of the cement due to the increase in the content of CC. Akbulut et al. reported that the dosages of superplasticizer additives needed for cements with CC incorporation were significantly higher than what the industry is used to when compared to common cement (up to 0.7% higher) [15]. Plank et al. [16] observed that the increase in the percentage of replacement of clinker by CC results in an increase in PCE dosages. [33] reported that PCEs intercalate between remaining layers of CC making them ineffective as plasticizers, requiring a dosage twice as high as normal. Corroborating the statements by [10] and [34], for the mortars produced in this work, the amount of polycarboxylate additive used had its dosage increased as the replacement content of CC became higher.



**Figure 4** - Mini-slump for mixture – (a) CP3 + 0,8%AD3 and (b): CP3 + 1.3%AD3 with exudation.

### 3.3 Calorimetry

The curves do not show a pre-induction period because, as explained earlier, in the semi-adiabatic calorimeter there is heat loss to the environment due to sample preparation being done outside the equipment, thus losing the heat released in the first contact between cement and water. The temperature



risers curves determined by the semi-adiabatic calorimetry method for CP1, CP2 and CP3 cements are shown in Figures 5, 6 and 7.

In Figure 5, the calorimetry of pure CP1 cement and with additives AD1, AD2 and AD3, with contents of 0.4%; 0.4% and 0.7%. It was observed that CP1 without additive reached the peak in a shorter time (7h) and all pastes with additive showed a delay in the main peak (11h/14h), but AD1 had the shortest delay among the additives analyzed with CP1 (11h). However, there was no change in the aluminate peak and the behavior of the samples after the first 24 hours was practically the same. The behavior of additives AD2 and AD3, despite the difference in solid content, was very similar.

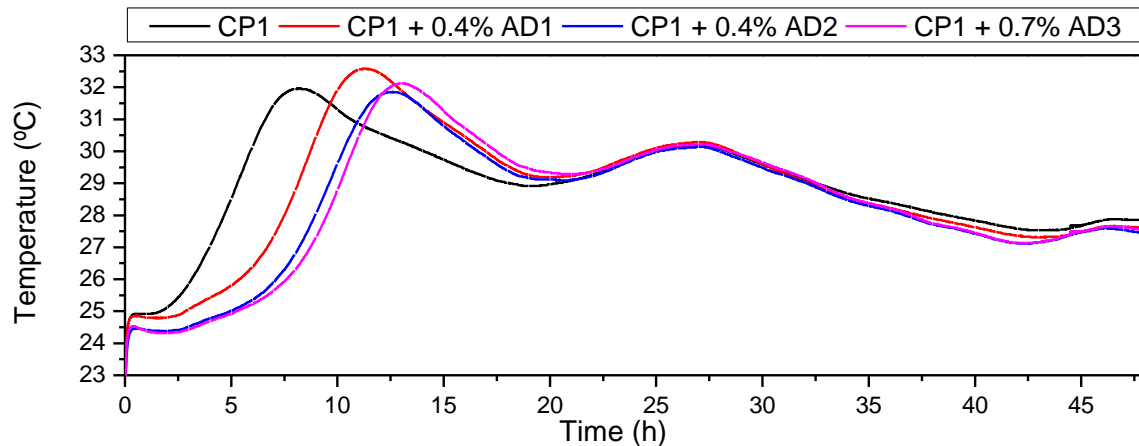


Figure 5 - Calorimetry of CP1 with additives 0.4%AD1, 0.4%AD2 and 0.7%AD3.

In Figure 6, the calorimetry of pure CP2 cement and with additives AD1, AD2 and AD3, with a content of 0.7%; 0.7% and 0.9%, respectively. It was observed that the CP2 paste without additive presented a delay when compared to CP1 without additive, with a peak between 8h/9h. CP2 samples with additive showed a delay in the main peak (11h/14h), but AD1 had the shortest delay among the additives analyzed with CP2, with a peak between 11h. Despite the difference between the solid contents of the AD2 and AD3 additives, a very similar behavior was observed in the curve. However, there was no change in the aluminate peak and the behavior of the samples after the first 24 hours was practically the same.

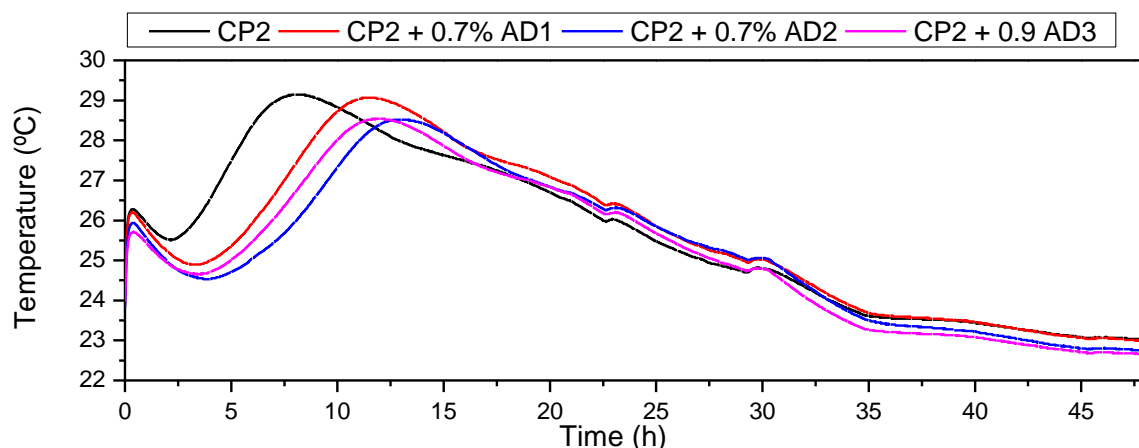


Figure 6 - Calorimetry of CP2 with additives 0.7%AD1, 0.7%AD2 and 0.9%AD3.

In Figure 7, the calorimetry of pure CP3 cement and with additives AD1, AD2 and AD3, with a content of 0.9%; 0.9% and 1.2%, respectively. It was observed that the CP3 paste without additive presented a delay when compared to CP1 and CP2 without additive, with a peak between 9h/10h. The behavior regarding the peak that was happening with CP1 and CP2 cements did not happen in CP3.

The AD1 additive that presented the lowest delay in the other cements in this cement changed its behavior, matching the other additives. In addition, there was a change in the peak of aluminates and the behavior of the samples. This effect can be attributed to the higher additive content required due to the increase in CC content. Nunes and Polesello [26] also observed this behavior in their studies. Werani and Lei [12] explains that the presence of an additive in the cementitious paste delays setting times, which varies according to the amount of additive used in the mixture.

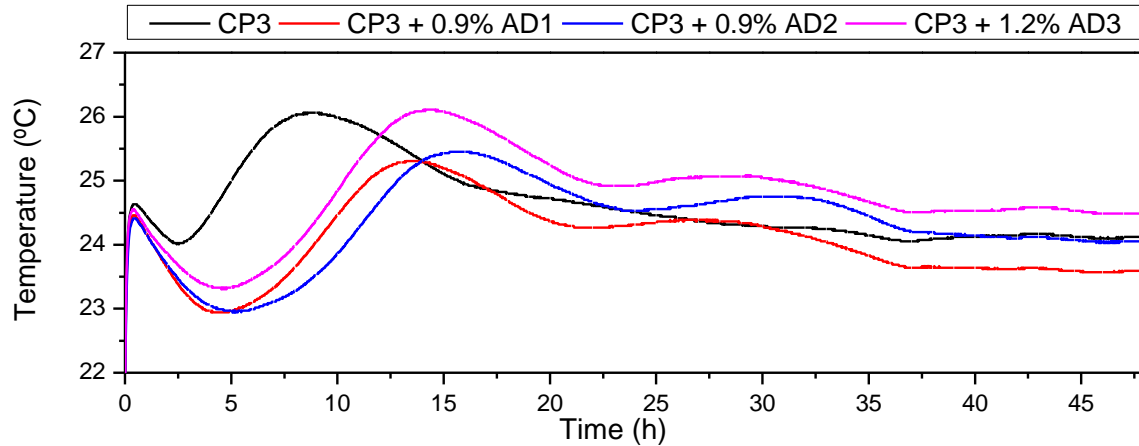


Figure 7 - Calorimetry of CP3 with additives 0.9%AD1, 0.9%AD2 and 1.2%AD3.

Based on the Figures 5-7, different behaviors of the temperature rise evolution curves can be observed for each type of cement. When carrying out the general analysis of the curves shown in Figures 5, 6 and 7, it is possible to observe that the hydration heat decreased as the amount of CC incorporated into the cement increased. For CP1 we can observe the peak turning around 32 °C. For CP2 cement with 20% of CC we already have values around 29 °C. CP3 with 28% of CC already presents the peak around 26 °C. Wang [35] observed that the addition of CC decreases the peak due to the low reactivity of CC compared to Portland cement. Because as the substitution content increases, there is a decrease in the hydration heat due to the dilution effect and a smaller extent of the reactions of the CC.

For the same types of cement, the curves show different behavior depending on the solids content and on the manufacturer's design. Since these additives are of commercial origin and not pure synthesized polycarboxylates, they may contain some other polymers for maintenance gain.

### 3.4 Compressive strength

The mortars for determining hardened state strength with the ideal content of each additive for each cement were produced by altering the water-to-cement ratio specified in ABNT NBR 7215 from 0.48 for the reference mortar to a water-to-cement ratio of 0.4 for the mortars with additives, while keeping the slump at  $180 \pm 20$  mm for all mortars. The results are presented in Table 4.

Table 4 – Compressive Strength (MPa) in the hardened state.

CP1				
Time	REF	AD1	AD2	AD3
1 day	21.9	26.4	25.4	24.9
3 days	33.1	40.8	39.6	38.5
7 days	43.8	50.3	49.3	48.7
28 days	54.7	60.5	59.5	58.9
CP2				
Time	REF	AD1	AD2	AD3
1 day	13.6	18.8	17.9	18.5
3 days	30.1	37.2	35.4	36.8
7 days	38.2	46.3	44.2	45.1
28 days	50.4	57.8	55.2	56.4

Time	CP3			
	REF	AD1	AD2	AD3
1 day	13.8	16.4	17.3	18.5
3 days	28.5	35.2	36.3	37.2
7 days	36.7	44.2	46.8	47.2
28 days	48.5	56.5	57.7	59.7

<sup>a</sup>w/c = water/cement

When the results of 1 and 28 days are evaluated for cements CP1, CP2 and CP3 with and without additive, in the first ages it is possible to verify a significant difference between the results obtained by cements CP2 and CP3 in relation to CP1 in all cases, this fact caused by the reduction in resistance due to the addition and increase in the content of CC [34]. Bernal et al. [36] reported at 2 days the strength values of the mortars with a substitution content of 30% are smaller than that of the reference mortar used as a reference as the pozzolanic reaction have slower rates.

It is observed that the pastes with additive compared to pastes without additive obtained an average result 20% higher at the age of 1 day, already at 28 days an increase of 8% for CP1. For CP2 an average increase of 35% was observed at the age of 1 day and at 28 days an increase of 11%. CP3 had an average result 25% higher in 1 day and at the age of 28 days an increase of 19% on average. Zaribaf et al. [37] obtained 1-day compressive strength results (in samples with 10 and 30% metakaolin with w/w 0.4) 40 to 20% greater than those observed in the reference sample with w/c 0.5. Since for the 28 days the results were 25 and 30% higher than the sample without additive.

Based on the results analyzed, it was observed that the use of PCEs in cements with CC helped to gain strength, confirming that the dispersion of particles provided by the additive helps in the better formation of cement hydration products, as we can observe in the behavior of CP3 which presented a resistance gain at 28 days greater than that observed in the other two cements of 19% against the 8 and 11% observed in CP1 and CP2.

Strength gains at 28 days in cements with CC caused performance results between cements CP1, CP2 and CP3 much closer than those observed at other ages. This approximation of the results can be justified by the pozzolanic reactions that tend to occur at more advanced ages, providing a higher resistance growth rate in the case of cements with higher levels of replacement. According to Lei et al. [10], the benefits of incorporating CC into the internal structure are observed and are associated with several factors, such as pore refinement, caused by particles of additions that age as a nucleation point for hydration products; the filler effect, which occurs due to the filling of empty spaces by the addition particles; the increase of the resistance of the matrix in the transition zone, and also the greater consolidation of the structure. This explains the resistance even with the decrease in the clinker content in the cement. Sharma et al. [34] observed at 28 days of hydration the mortar with CC showed mechanical performances similar or even better than those of neat PC.

#### IV. CONCLUSIONS

When analyzing the results presented in the FTIR it was determined that the structural groups present in the three additives are similar, which implies that the determining factor for the behavior of the additives is in the solids content.

The results of mini-slump showed that replacing part of the clinker with CC has a direct impact on the superplasticizer additive consumption. The addition of 20% and 28% CC in CP1 results in a higher consumption of additives by up to 125% as in the case of the results obtained for AD1 and AD2/CP3.

From the heat of hydration curves presented for the cements, it was observed that with the incorporation of additives to the mixture, there was a displacement of the curves to the right, indicating a change in the beginning of the setting (delay) in each one of the pastes. Furthermore, a decrease in the peak temperature was observed as the CC content increased, changing from 32 °C for CP1 to 29 °C and 26°C for CP2 and CP3 (20 and 28% of CC, respectively). For cements CP1 and CP2, there was no change in the peaks after the first 24h, but in CP3, changes were already observed that can be attributed to the

increase in the amount of additive and consequent presence after the first 24h, a fact that needs to be verified through other test.

The mortars with additive compared to mortars without additive obtained an average result 20% higher at the age of 1 day, already at 28 days an increase of 8% for CP1. For CP2 an average increase of 35% was observed at the age of 1 day and at 28 days an increase of 11%. CP3 had an average result 25% higher in 1 day and at the age of 28 days an increase of 19% on average. At 28 days of hydration the results confirms that cement with CC (CP2 and CP3) and PCEs can achieve mechanical performances similar or even better than those of neat CP1.

Thus, it is concluded that it is necessary to carry out research seeking superplasticizing additives for use in cements with contents greater than 20% CC to obtain increasingly efficient systems.

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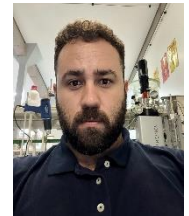
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