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Evaluation of Portland pozzolan blended cements containing diatomaceous earth

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Abstract

Clinker replacement by supplementary cementitious materials (SCMs) is one strategy to reduce CO_2 emissions of cement industry. Diatomaceous earth, a natural pozzolan, has been used as SCM. So, this study aimed to evaluate two Portland pozzolan blended cements with distinct content of diatomaceous earth (16DE and 49DE) and compare then with a high clinker content cement (REF). Cements were physically and chemically characterized; pastes and mortars were analyzed in terms of reactivity, water demand, and mechanical strength; finally, environmental indicators were estimated. Cements with diatomaceous earth demanded a similar volume of mix water for mortars without superplasticizer and less water than REF for mortars with superplasticizer. The chemical bound water at 91 days reduced 21% and 27% for 16DE and 49DE, respectively, in relation with REF. For binder intensity indicator, both cements had worst results compared to REF, but for carbon intensity indicator 49DE obtained better results comparing to REF.

Keywords: reactivity, water demand, environmental indicators, Portland pozzolan blended cements.

INTRODUCTION

The increasing production of cement will extend at least until 2050; studies show a demand forecast for the Brazilian market between 120 and 140 million of tons of cement and worldwide between 3.7 and 4.4 billion tons [1]. This growing production will be responsible for a large volume of CO_2 emissions, worldwide this value is approximately 10% of total anthropogenic CO_2 emissions and can reach 30% by 2050 [2]. Therefore, academy and industry have been developing strategies to reduce this environmental impact generated by the cement industry. One of these strategies is the substitution of clinker by supplementary cementitious materials (SCMs). Supplementary cementitious materials (SCMs) are finely divided materials that contribute to the properties of the final product due to: hydraulic or pozzolanic activity or those that are nominally chemically inert but contribute with 'filler effect', as for instance limestone filler (SCMs can be natural, processed natural or artificial) [3, 4]. Apart from chemical contribution, supplementary cementitious materials can also affect the mixing water when blended with Portland cement, and these two aspects impact on cement efficiency in terms of mechanical strength and durability. Nowadays the most used supplementary materials are blast furnace slag and fly ash, by-products of the steel industry and thermoelectric plants, respectively, but the increase in cement production was not accompanied by the supply of these materials. This is observed with the stabilization of world average clinker ratio since 2000 [2]. Therefore, other supplementary materials are being studied and some are already applied by the industry as is the case of diatomaceous earth.

Diatomite is a material of sedimentary and biogenic origin, that is formed from the accumulation of algae shells that were fossilized due to the silica deposit on its structure [5]. Its origin is usually associated with clay, quartz and iron oxide, composing than the name diatomaceous earth. It is classified as a pozzolan: materials that are formed by an amorphous and a crystalline phase and that in presence of water and at ordinary temperature react with calcium hydroxide precipitating hydrated phases with cementitious properties (C-S-H, C-A-S-H, AFm) [6]. The natural pozzolans need no treatment but grinding is needed to present pozzolanic activity, as is the case of pyroclastic rocks, for instance, Santorini earth, zeolites, volcanic ashes and sedimentary rocks such as diatomaceous earth [3]. Results on Portland blended cements with diatomaceous earth showed a low reactivity on the first days of hydration and better results up to 28 days [7]. The addition of diatomaceous earth normally leads to an increase in the mixing water mainly because of agglomeration of diatomaceous earth particles, high internal porosity and specific surface area [8].

The replacement of clinker by pozzolans or any other supplementary cementitious material is always attributed to having a linear correlation with CO_2 emission reduction, and this approach is valid when only the cement production

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is evaluated. Nowadays, most studies that assess CO_2 emissions of cement industry are within this frontier of study [9-11]. However, cement is produced to be used for some purpose, either for concrete, mortar, precast and others, and in these cases the clinker replacement by SCMs can affect the eco-efficiency of the final product [8]. Few researches assess the eco-efficiency of cement in its use; some of these works quantify the CO_2 emissions per m^3 of concrete [12-15], but it is important to relate these impacts to the performance of the material [13, 16]. The performance of the final product (concrete, mortar, precast, etc.) is tied with cement efficiency. This efficiency is related to two parameters: first is the binder ability to chemically combine water, and second is the water required to promote a specific rheological behavior suitable for each type of technological application. Both parameters affect the performance of the cementitious product in terms of rheological behavior, mechanical strength, and durability. Therefore, the aim of this study is to evaluate two Portland pozzolan blended cements with distinct content of diatomaceous earth (16DE and 49DE) and compare them with a high clinker content cement (REF). Cement pastes and mortars, prepared with and without superplasticizer (dispersant), were analyzed in terms of reactivity, water demand, and mechanical strength, then environmental indicators were calculated based on experimental results and literature data.

MATERIALS AND METHODS

A cement with a high content of clinker (REF) and two Portland pozzolan blended cements from the Brazilian market were analyzed as to their chemical and mineralogical compositions, physical characteristics, water and superplasticizer demand, reactivity and mechanical properties. *Types of cements*: two commercial Portland pozzolan blended cements from different plants were analyzed with distinct percentages of diatomaceous earth (16DE and 49DE) and as a reference a cement with 94% of clinker+$CaSO_4$ and 6% of limestone filler. Table I shows detailed information about the cements, the codes indicate: i) percentage of pozzolan on cement, determined by Rietveld refinement; and ii) the type of pozzolan, diatomaceous earth (DE). Cement type is according to Brazilian standards [17, 18], CP means Portland cement, CPV is a high early age strength cement with high clinker content. CPIIZ and CPIV are cement classes defined as Portland pozzolan blended cements, the difference between them is the amount of pozzolan allowed.

Characterization of anhydrous materials. Chemical and mineralogical characterization: Table II presents the results of chemical analysis obtained by X-ray fluorescence spectroscopy (Axios Advanced, PANalytical). Cement 49DE showed higher content of silica and lower content of calcia comparing to REF; on the other hand, 16DE and REF presented similar amount of calcium oxide, but 16DE had a slightly higher content of silica from the diatomaceous earth and also a higher content of magnesium oxide probably from the limestone filler. Table III presents the mineralogical composition of the materials, evaluated via X-ray diffraction (XRD, X'Pert MPD, PANalytical). For phases quantification a refinement was performed by the Rietveld method, using a software (HighScore Plus v.4.6a) and Panalytical Inorganic Structure Database. Materials with diatomaceous earth addition showed lower content of clinker phases than REF, as expected for blended cements. 16DE and 49DE presented quartz, kaolinite and vitreous phase from the amorphous silica of diatomite. Only 16DE and REF had limestone filler on their compositions. Results of limestone filler obtained from XRD and TG/DTG were quite similar, showing that both techniques agreed, also the statistical indicators Rwp (weighted-profile R-factor) and GOF (goodness of fit) were in the range defined as a good refinement [19].

Table I - General description of the investigated cements.

Code	Type of cement[a]	Description[a]	Clinker+$CaSO_4$ content[a] (%)	Pozzolan content[a] (%)	Filler content[a] (%)	Type of pozzolan[b]
REF	CPV-ARI	High early strength cement	95-100	-	< 5	-
16DE	CP II Z	Portland pozzolan blended cement with low pozzolan addition	76-94	6-14	< 10	Diatomaceous earth
49DE	CPIV	Portland pozzolan blended cement with high pozzolan addition	45-85	15-50	< 5	Diatomaceous earth

[a] - according to Brazilian standards [17, 18]; [b] - according to the manufacturer.

Table II - Chemical composition of the used raw materials determined by X-ray fluorescence spectroscopy.

Oxide (%)		CaO	SiO_2	Al_2O_3	Fe_2O_3	SO_3	MgO	Na_2O	K_2O	TiO_2	Loss on ignition
OPC	REF	59.7	19.1	4.5	2.6	3.0	1.3	0.3	0.9	0.2	4.7
Diatomaceous earth	16DE	57.1	21.9	4.9	4.4	2.2	4.0	0.2	0.2	0.3	4.2
	49DE	44.1	35.2	4.2	3.4	2.6	1.8	0.4	0.7	0.5	4.6

Table III - Mineralogical composition of the used raw materials determined by XRD with Rietveld refinement.

Compound (%)	OPC	Diatomaceous earth	
	REF	16DE	49DE
Clinker and sulfate phases			
Alite	60.8	43.6	30.9
Belite	13.3	14.7	5.3
C_3A	8.2	4.4	5.3
Ferrite	8.0	5.2	3.1
Periclase	0.0	4.8	1.9
Calcium sulfate phases	3.5	3.8	4.3
Clinker and sulfate content	93.8	76.5	50.9
Pozzolan phases			
Quartz	0.0	1.6	7.9
Kaolinite	0.0	3.0	9.0
Vitreous phase	0.0	11.5	32.3
Pozzolan content	0.0	16.1	49.2
Limestone filler			
Limestone filler[a]	4.9	7.4	0.0
Limestone filler[b]	6.0	8.0	0.0
Statistical indicators of refinement			
Rwp	9.2	13.1	11.6
GOF	2.1	3.3	3.1

[a] - determined via TG/DTG; [b] - determined via XRD.

Scanning electronic microscopy: materials were assessed by scanning electronic microscopy (SEM, FEI, Quanta 600FEG) with energy dispersive spectroscopy (EDS, Bruker, SSD Xflash Quantax 400). The operating conditions for obtaining SEM images were: high vacuum; high voltage - 10 kV; and secondary electron detector. Software Esprit was used to analyze EDS results. Fig. 1 presents the images of 49DE cement, which had the addition of diatomaceous earth. Fig. 1a shows a diatomite stick covered with kaolin plates identified by EDS with silicon and aluminum: the aluminum came from the kaolinite as diatomite had only silicon in its composition (Fig. 1b); also, the stick morphology is characteristic of a diatomite [20]; in both sides clinker grains can be seen with some hydration spots. Fig. 1c presents a particle with multiple layers and pronounced texture that appears to be a cluster of kaolin plates, identified by EDS with silicon and aluminum (Fig. 1d). In both cases, EDS showed platinum element, because the samples were coated with a fine layer of platinum to provide electrical conduction as well as to obtain high magnification images. Fig. 1e presents a clinker particle covered by kaolin plates and with some hydration spots, while Fig. 1f displays the corrugated texture of the clinker and the kaolin plates lying on its surface.

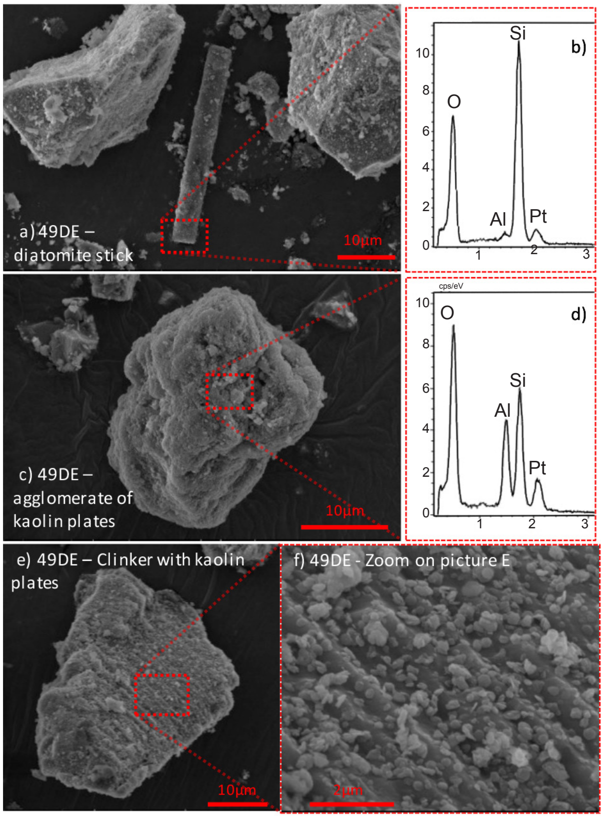

Figure 1: SEM micrographs of 49DE cement: a) diatomite stick with corresponding EDS spectrum (b); c) kaolinite plates with corresponding EDS spectrum (d); e) clinker grain with kaolin plates and zoom of the delimited area (f).

Physical characterization: the physical parameters were obtained by the following methods: i) particle size distribution was determined by laser diffraction (Helos/KR, Sympatec) with the particles dispersed in deionized water (Sucell, Sympatec); the powder was mixed with water for 60 s at 1500 rpm with a rotational mixer, then part of the suspension was inserted on the basin that already had deionized water; the stirrer and pumping parameters were set at 40% and 50%, respectively; immediately before the test, ultrasound dispersion was employed for 90 s and, then, the measurements were performed during 10 s three times in a row; the same protocol was followed for the suspensions with and without superplasticizer; admixture content used was the one obtained as described ahead; ii) specific surface area was determined by BET method (Belsorpmax, Bel Japan) using nitrogen adsorption; and iii) true density was measured by a helium pycnometer (Multipycnometer Quantachrome MVP 5DC).

Fig. 2a shows the particle size distribution curves of cements with and without superplasticizer. For materials without superplasticizer (solid lines) cement REF presented a higher volume of particles between 10 and 30 µm when compared with Portland pozzolan blended cements; on the other hand, cement 49DE presented higher volume of particles between 0.2 and 6 µm comparing to 16DE and REF indicating that the addition of diatomaceous earth produced a cement with finer particles. With the incorporation of superplasticizer (dashed lines), the curves moved to the left (lower particle sizes); for cement REF the curve maintained a similar shape, but for 16DE and 49DE there was a visual increase on volume of particles between 0.5 and 8 μm, less pronounced for 16DE. Fig. 2b shows the difference between particle size distribution of cements without and with superplasticizer; for cement REF and 16DE the addition of superplasticizer led to a decrease in volume of particles between 20 and 100 μm and an increase in the range of 0.2 and 20 μm; this also happened for 49DE, but in this case there was a higher increase in volume of particles between 0.7 and 8 μm when compared with REF and 16DE. Combining these results with the images obtained by SEM, it was supposed that when superplasticizer is added on cements containing diatomaceous earth there was a dispersion of some clusters of kaolin plates (Fig. 1c) and therefore a system with finer particles, which explain why Portland pozzolan blended cements with superplasticizer presented a higher increase on volume of fine particles when compared to REF.

Table IV presents the results of physical properties of the materials, differentiating as to the use (SP) or not (noSP) of superplasticizer, when applicable. All cements had similar particle true density, but there were clear differences on specific surface area. The cements with diatomaceous earth had a higher specific surface area and, consequently, higher volumetric surface area and shape factor. These parameters are important since they affect water demand, especially the shape factor [21] that gives an idea of morphology; particles with high specific surface area, angular shape or with high internal porosity demand more water to achieve a specific rheological behavior. The parameters related to particle size distribution (D10, D50, and D90) were reduced by half when superplasticizer was incorporated.

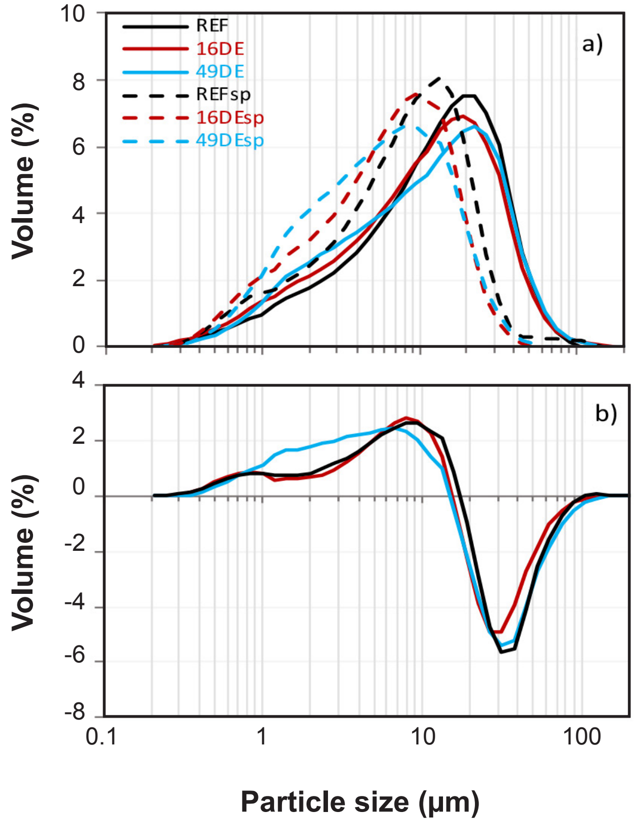

Figure 2: Particle size distribution curves obtained by laser diffraction of cements without (solid line) and with (dashed line) superplasticizer (a), and difference on particle size distribution curves of compositions without and with superplasticizer - positive values mean that total volume of particles in that specific size range is higher when comparing to compositions without dispersant and vice versa (b).

Table IV - Physical properties of the used raw materials.

Parameter	OPC		Diatomaceous earth			
	REF		16DE		49DE	
	noSp	Sp	noSp	Sp	noSp	Sp
ϱ_s [a] (g/cm³)	3.08		3.11		3.03	
D_{10} (μm)	2.3	1.6	1.8	1.2	1.9	1.4
D_{50} (μm)	14.4	9.0	12.5	5.9	12.5	6.2
D_{90} (μm)	39.0	23.4	37.2	16.0	39.4	19.1
SSA_{LD} [b] (m²/g)	0.36	0.49	0.44	0.63	0.39	0.58
SSA_{BET} [c] (m²/g)	1.64		2.41		4.30	
VSA_{BET} [d] (m²/cm³)	5.0		7.5		13.0	
Shape factor, ξ [e]	4.6	3.3	5.5	3.8	11.0	7.4

[a] - particle true density by He pycnometry; [b] - specific surface area by laser diffraction granulometry; [c] - specific surface area by BET method; [d] - volumetric surface area obtained by the SSA_{BET} *and* ρ_s*; [e] - shape factor calculated from* SSA_{BET} *and* SSA_{LD}*.*

Analysis of paste. Superplasticizer saturation content: for the determination of superplasticizer saturation ratio, pastes with 0.3 water/cement were produced. The superplasticizer used was a polycarboxylate (ADVA CAST 527), which acted with electrosteric stabilization mechanism, had a water/solid ratio of 0.6 and a specific mass of 1.075 g/cm³. The mixture of the pastes occurred in three steps: i) adding water in the powder in 5 s; ii) manual mixing with scoop for 50 s; and iii) dispersion in 10000 rpm rotation mixer for 1.5 min. Immediately after mixing, the pastes were subjected to rotational rheometry (Rheometer MARS 60, Haake), using plate-plate geometry with 35 mm in diameter and gap of 1 mm. The shear program used was the stepped flow test in two cycles of acceleration and deceleration, varying the shear rate from 0 to 50 s^{-1}. The first cycle was run only for paste normalization (structural breakdown), while the second cycle was considered for data collection. At this stage, for each superplasticizer content yield stress was obtained in shear rate of 0 s^{-1}. The saturation content was defined as the posterior point to stabilization of the yield stress.

Reactivity: of the cements was measured by quantifying the chemically combined water and portlandite content at 7, 28 and 91 days of hydration. Pastes with water/cement ratio of 0.5 were mixed in the same manner as described above, then they were placed in cylindrical molds of 2.5 cm in diameter and 8 cm in height and stored at 23 °C and 90-100% relative humidity. After 24 h, they were relocated to larger containers (3 cm in diameter and 10 cm in height) filled with deionized water, sealed and stored at 23 °C until the age of interest. Slices from the cylindrical specimens were removed with 2 mm of thickness and, then, underwent to three immersion cycles in isopropanol, the first two immersions of 1 h each and the third immersion of 24 h. Finally, the isopropanol was exchanged for diethyl ether, with the samples immersed for 16 h, and subsequently dried in chamber at 50 °C for 30 min. After the hydration stoppage, samples were ground and then subjected to thermogravimetric test (TGA, STA 409PC/PG, Netzsch). The quantification of the chemically bound water (B_w) and the portlandite content (CH) were determined with the following equations [22]:

$$B_w=\frac{W_{40}-W_{500}}{W_0} \tag{A}$$

$$CH=\frac{W_{400}-W_{500}}{W_{500}}\cdot\frac{M_{Ca(OH)_2}}{M_{H_20}} \tag{B}$$

where M is the molar mass, W_x is the percentage of mass loss at temperature x (°C) and LOI is loss on ignition.

Analysis of mortar. Mortars preparation: in the study of water demand, 1:3 (cement:sand weight ratio) mortars were produced with a water/cement ratio adjusted for each sample. Standard sand [23] was employed and a mix composed of four fractions of different nominal sizes, 0.15, 0.3, 0.6, 1.2 mm, each fraction corresponding to 25 wt%, was prepared. The superplasticizer type and dosage were according to described above; cements used were the ones presented in Table I. This mortar composition was elaborated according to the Brazilian standard [24] for determination of cement strength classes which agreed with European standards [25]. The mortars were mixed according to EN 196-1 standard [25]. Right after the mixing procedure, it was measured the incorporated air according to NBR 13278 standard [26].

Water demand: flow table test was used to analyze the water demand for a specific rheological behavior of cements. After measuring the incorporated air, mortars were placed in a conic mold, the excess material and the mold were removed, and the table then underwent 30 falls in 30 s from a height of 12.5 mm, method according to NBR 13276 standard [27]. After this procedure, final mortar spread on the table was recorded by measuring three diameters, which composed an average, also pictures of mortars before and after the flow table test were taken to visual analysis. A different mortar batch was used for each water/cement ratio. The tests for each composition were initiated from the water/cement (w/c) ratio of 0.48, the value used by the Brazilian, European and American standards for the classification of cement compressive strength class [25, 28, 29]. The other mortars were prepared with the w/c ratio dosed with the objective of achieving an average spread of 240±10 mm, in which the mortars presented adequate consistency for molding. The spread value of 240 mm was adopted after several preliminary tests were performed; at first, the range of 265±10 mm was used, but it was noticed phase separation in some mortars, the range was then reduced.

Compressive strength: after the flow table test, for evaluation of compressive strength, mortars were molded in specimens of 40x40x160 mm^3, according to EN 196-1 standard [25]. For each age of interest, three specimens were molded and then placed on moist air room for the first 24 h, then they were demolded and immersed in water until testing. At the age of interest (7, 28 and 91 days), they were tested for flexural strength through the three-point loading method, followed by compressive strength test on the half parts of the prism according to EN 196-1 standard.

Porosity: was calculated according to Power's model [30]. However, in this case, the degree of hydration and bound water in the age of interest were calculated based on experimental data obtained as described in Reactivity subsection. The apparent density was calculated by measuring the dimensions and mass of the specimens for each age and the theoretical density was calculated from the density of raw materials and the mortar composition. The total mortar porosity was calculated according to:

$$Total_{porosity}=\frac{V_{capillary\ porous}}{V_{total}}+\frac{1-D_{apparent}}{D_{theoretical}} \tag{C}$$

where V_{total} is total volume, $V_{capillary\ porous}$ is the volume of capillary pores, $D_{apparent}$ is the density of the test body, and $D_{theoretical}$ is theoretical density. As 49DE had a large proportion of pozzolan it was considered that all materials were totally hydrated at 180 days. The combined water at 180 days ($Bw_{180days}$) was estimated through extrapolation of the experimental curve (7, 28 and 91 days).

Binder intensity, carbon intensity, and CO_2 emissions: two indicators were calculated in this work: binder intensity (BI) and carbon intensity (CI). Both were presented in [16]: the BI relates the amount of binder per m^3 of concrete to deliver a unit of a performance indicator; the CI relates the amount of CO_2 emitted to a unit of a performance indicator. Different from the method applied in [16], in this work, BI and CI were calculated for modeled concretes with 28 and 91 days of hydration, since Portland pozzolan blended cements tended to react more at long ages. In this study for calculations of BI and CI, a concrete with 300 dm^3 of paste was modeled; from this value, the volume of cement according to the water/cement ratio of each system was calculated. The compressive strength of concrete was estimated by multiplying the compressive strength of mortars by a factor of 0.8 [31]. It was considered a CO_2 emission factor of 857 kgCO_2/t clinker, Brazilian average value [32], for CI and CO_2 emission calculations. In both cases, emissions relating to the process of production, grinding, and transportation of supplementary cementitious materials were not incorporated into the calculations, a common procedure in the literature [33]. For calculation of CI, the emissions concerning the extraction, beneficiation, and transportation of the aggregates, as well as production and transportation of the concrete, were considered null in this study. The amount of CO_2 absorbed during the carbonation was also neglected. All of these factors when summed up did not significantly change the results since the production of clinker is the most contributing step for the CO_2 emissions of the concrete [12].

RESULTS AND DISCUSSION

Superplasticizer demand: the results of rotational rheometry test is shown in Fig. 3 where the yield stress is expressed according to the superplasticizer content in percentage of cement mass. The results showed that for the same volume of mixing water, the cements with diatomaceous earth demanded a higher volume of superplasticizer to achieve the same rheological behavior (Fig. 3), due to their larger specific surface area and shape factor. Data in Table V demonstrate that saturation content ranged from 0.6 to 1.4 wt%, showing the importance of correctly determining the volume of additive. In addition to the saturation content, analysis of the specific consumption was made, that is additive consumption divided by the specific surface area as measured by BET. The specific content of superplasticizer was in the same range for REF and 49DE and a little above for 16DE, which may be connected to the chemical composition or because of particle adsorption [34].

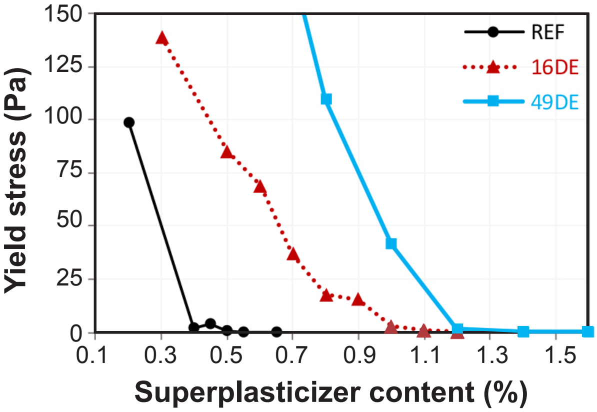

Figure 3: Yield stress at 0 s^{-1} from the downwards shear rate ramp as a function of the superplasticizer content for the analyzed systems.

Table V - Water/solid (w/s) ratio, saturation dispersant content, specific dispersant content and yield stress (τ_0) of the studied systems.

Material	w/s	Saturation dosage (wt%)	Specific dispersant (mg/m^2)	τ_o (Pa)
REF	0.3	0.6	3.4	0.3
16DE		1.1	4.6	0.9
49DE		1.4	3.3	0.2

Reactivity: Fig. 4 presents the results obtained by hydration stoppage. Cement REF combined more water and had a higher portlandite content in all ages, compared to 16DE and 49DE, due to its higher percentage of reactive phases. Both Portland pozzolan blended cements had a similar evolution on bound water but the results were less pronounced when compared with REF. The progressive reduction of portlandite content is an indicative of pozzolanic activity, in which pozzolan phases consume $Ca(OH)_2$ to produce hydration phases with cementitious properties. 16DE was the most reactive Portland pozzolan blended cement on early ages, but over time the results of portlandite content showed that pozzolan on this cement reacted less than the diatomaceous earth on 49DE. Cement 16DE had 11% of amorphous phase on its composition and consumed only 0.24 gCH/100 g cement; on the other hand, 49DE cement had 32% of amorphous phase and consumed 1.44 gCH/100 g cement between 7 and 91 days of hydration; so 16DE had three times less amorphous phase but consumed six times less portlandite than 49DE. Concluding, diatomaceous earth and limestone filler of 16DE actually acted in a mechanism called 'filler effect' [35], providing sites for nucleation and space for the hydration products of the clinker phases, thus giving a greater reactivity to the material in the first ages, although stabilizing in the long term.

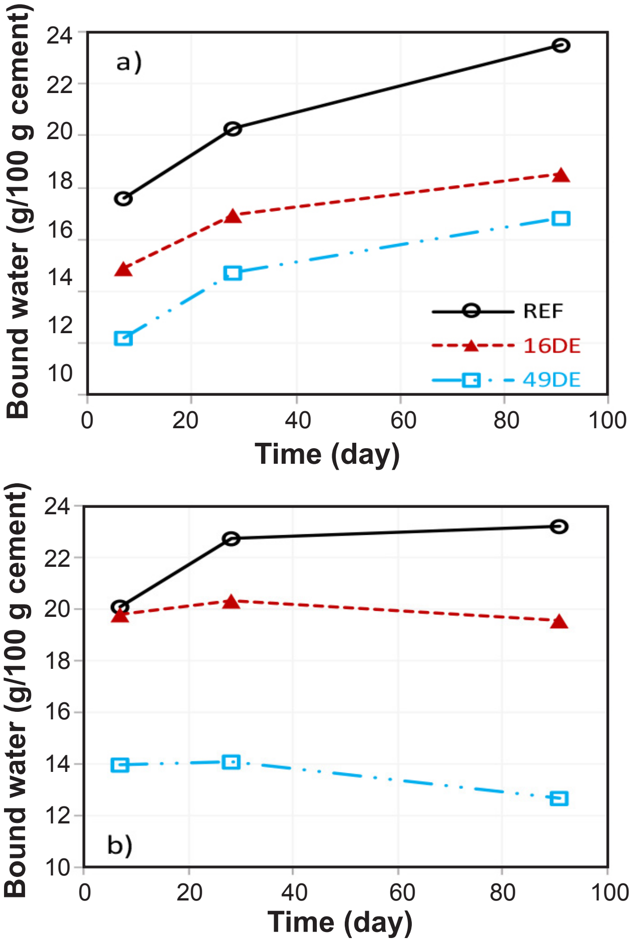

Figure 4: Content of bound water (a) and portlandite (b) obtained from TGA for all systems at 7, 28 and 91 days of hydration.

Fig. 5 shows the results of bound water relative to REF versus clinker substitution. Cement 16DE on 7 days of hydration stayed above the dilution line (dashed line), that is, the reduction in the chemically bound water was lower than the reduction in the clinker content when compared to REF, indicating an enhance on reactivity on the first days, but at 91 days of hydration the relative bound water moved to below the dilution line, ratifying that, in this case, the diatomaceous earth on 16DE did not react much on long term ages. The 49DE cement achieved better results, staying above the dilution line at all ages. At 91 days of hydration this cement had a 27% reduction in bound water, but with a clinker substitution of 43%, compared to REF. Therefore, the clinker substitution by diatomaceous earth on this case was favorable to reactivity, because part of diatomaceous earth also reacted by consuming the portlandite and producing other hydration products with cementitious properties, thus contributing with an increase in the chemical bound water.

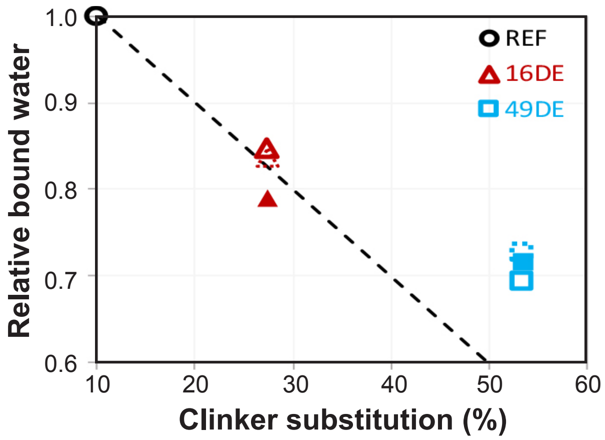

Figure 5: Relative bound water (REF) versus clinker substitution. The empty icon corresponds to 7 days of hydration, pointed icon 28 days and filled icon 91 days. The black line corresponds to a direct dilution.

Water demand: maintaining a fixed water/cement ratio of 0.48 in mass (1.45 to 1.49 in volume), as suggested by the Brazilian, European and North American standards, the mortars without superplasticizer showed dry aspect and inappropriate consistency for molding as shown in Figs. 6a and 6e. Images captured after the test indicated that mortars did not spread, but instead underwent fracturing due to the lack of cohesion between the cementitious matrix and the aggregates (Figs. 6b and 6f). Determination of cement compressive strength based on a fixed water/cement ratio is not the best option, because the result of the test is highly dependent on the energy applied during the molding process. Therefore, the minimum water demand must be based on a rheological behavior adequate for easily molding the mortar samples. In this study, a fixed rheological behavior was adopted: spreading on flow table equal to 240±10 mm; for this value, mortars presented better cohesion without segregating, which guaranteed a good molding and proper spreading as indicated on Figs. 6c, 6d, 6g, and 6h.

Figure 6: Images before (left) and after (right) the flow table test (dropping the table 30 times) of mortars made with different water/cement (w/c) ratio: a,b) REF mortar with 0.48 w/c; c,d) REF mortar with 0.53 w/c; e,f) 49DE mortar with 0.48 w/c; and g,h) 49DE mortar with 0.53 w/c.

Fig. 7a shows the results of flow table test for mortars without (empty icons) and with (filled icons) superplasticizer. Without superplasticizer, all cements demanded a similar amount of water to reach 240±10 mm spread, but with the addition of diatomaceous earth a slight reduction on mix water was achieved, 2% for 49DE and 4% for 16DE compared to REF. With the incorporation of superplasticizer, the cements with diatomaceous earth required a smaller volume of water to achieve the same spread; for 49DE it was obtained a reduction of 8% and for 16DE 10% when compared to REF. With incorporation of superplasticizer, cements containing diatomaceous earth presented a higher volume of fine particles compared to REF, results obtained from particle size distribution analysis (Fig. 2a), indicating a dispersion of kaolin clusters; these fine particles than had an effect of filling voids among the others, increasing the packing of the system, reducing the necessary water for the same fluidity, and explaining why cements with diatomaceous earth demanded less water than REF when superplasticizer was added. In all cements the addition of superplasticizer reduced the mix water: for cement REF a decrease of 23% was achieved, for 16DE 28% and 49DE 26%. This water reduction influenced the performance of the material, such as mechanical properties, durability, and environmental indicators.

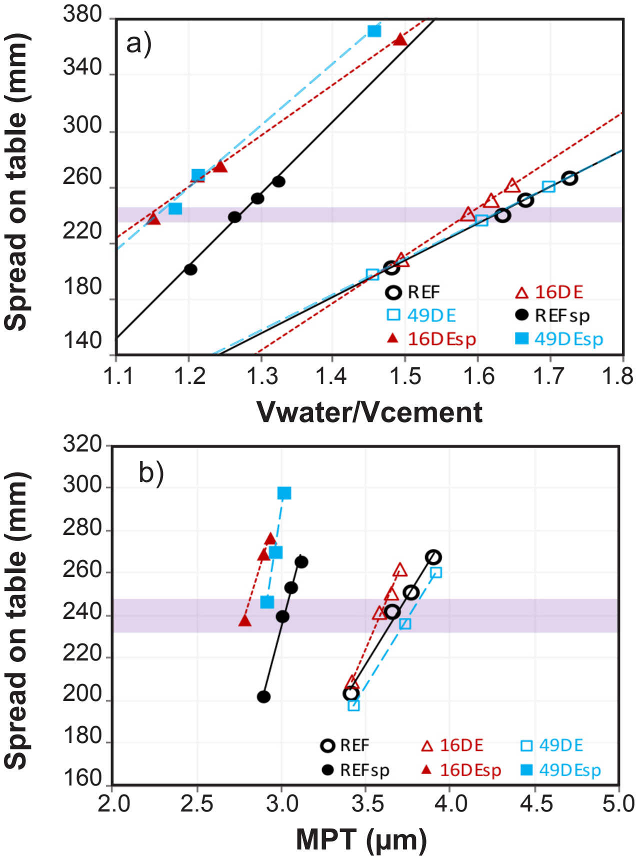

Figure 7: Spread on table versus water/cement volume ratio obtained from the flow table test (a) and maximum paste thickness – MPT (b) for mortars without (empty icons) and with (filled icons) superplasticizer. The purple band corresponds to the optimum flow (240±10 mm) defined in this study as the 'fixed rheological parameter'.

The maximum paste thickness (MPT) [36] was calculated for mortars with and without superplasticizers (Fig. 7b). MPT represents the distance between the aggregate particles and depends on the volumetric surface, packing porosity and volumetric solid concentration of the coarse particles in the mortar. A higher MPT reduces the friction between the coarse particles and consequently increases the fluidity of the mortar. From Fig. 7b it is observed that an increase on MPT led to an increase of spread on table, as expected. To achieve the stipulated spread of 240±10 mm, mortars with different cements had a similar value of MPT: for mortars without superplasticizer (empty icons) the MPT varied from 3.6 to 3.7 μm and for mortars with superplasticizer (filled icons) this variation stayed between 2.8 to 3 μm. These results demonstrated that the MPT can be a good tool to predict the water demand for each cement to achieve the specific spread on table. Since for MPT calculation is only necessary the physical characterization of the raw materials, the laboratory work can be reduced. However, a bigger data to verify this is necessary; it is also important to know that in this case it was used a standard sand and same mortar composition and mixture procedure to produce all mortars.

Compressive strength and porosity: Fig. 8 shows the results of compressive strength obtained for 7, 28 and 91 days of hydration. It was observed that the cements REF and 16DE had a greater evolution of strength in the first 7 days than 49DE. The last, a cement with high addition of diatomaceous earth, presented slower hydration kinetics due to its lower content of clinker phases and showed a higher increase on compressive strength between 28 and 91 days of hydration because of the pozzolanic activity of diatomaceous earth. These results agreed with the reactivity evaluation. It was also clear the benefit of using the superplasticizer that reduced the mixing water, reducing the porosity and consequently increasing the compressive strength. For mortars produced with REF, 16DE and 49DE, at 7 days, there was an increase of 46%, 50% and 67% on compressive strength by adding superplasticizer and reducing the mixing water, and at 91 days of hydration, this increase changed to 36%, 40%, and 53%, respectively.

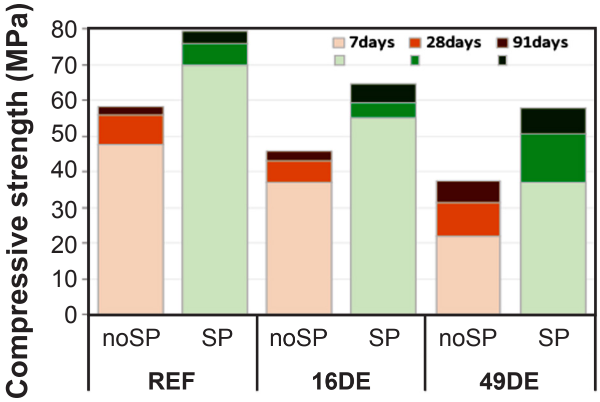

Figure 8: Compressive strength of the mortar samples without (noSP) and with (SP) incorporation of superplasticizer at 7, 28 and 91 days of hydration, for the same spread on table (240±10 mm).

The compressive strength of brittle materials, like ceramics and cementitious materials, have an exponential relation with porosity [37, 38]. Since the cements have a different reactivity and water demand, they influence on mortar total porosity and consequently on compressive strength. Fig. 9 shows three groups of results, each group corresponding to a specific cement; inside each group it can be observed: i) the effect of superplasticizer addition, difference between empty and filled icons; and ii) the influence of hydration process, difference between icons that goes from right (7 days) to left (91 days). Taking an example, for cement 49DE the addition of superplasticizer led to a decrease of 5.8% on total porosity of mortar at 7 days; this decrease on porosity was linked with reduction of mix water caused by the dispersant addition. An example on the influence of hydration process can be observed for 49DE (without superplasticizer): there was a reduction of 4.5% on total porosity between mortars at 7 and 91 days of hydration; over time materials can chemically combine more water and thus forming a larger volume of hydrated products, obtaining a lower porosity. The three groups of results, each one corresponding to a type of cement, had a different relation between total porosity and compressive strength. This fact was related to the different formed microstructure in the final product, since it depends on the chemical and mineralogical composition of cements, physical properties of raw materials and mix water.

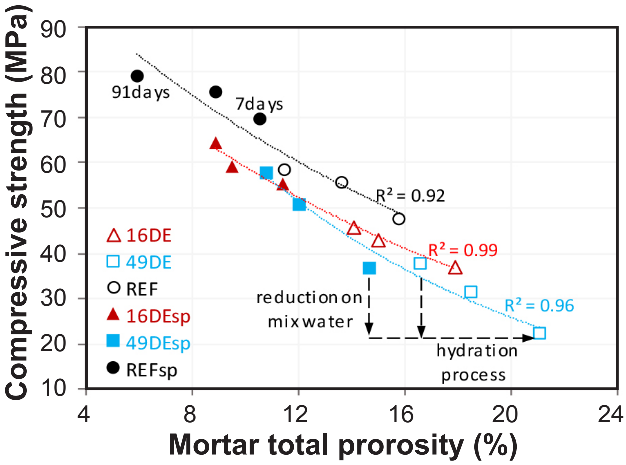

Figure 9: Compressive strength versus mortar porosity calculated from Power's model for the systems without (empty icon) and with (filled icon) superplasticizer incorporation. There are three icons for each composition: the first icon (from right to left) corresponds to 7 days of hydration, second to 28 days and third to 91 days.

Fig. 10 shows the results of relative mechanical strength of the mortars prepared with the blended cements in relation to REF. Mortars with and without dispersant produced with 16DE cement stayed below the dilution line, which represents that the reduction in mechanical strength at all ages was higher than the reduction of clinker content when compared to REF. For 49DE, the replacement of clinker by diatomaceous earth was more effective, taking into consideration the mechanical strength. Mortar without dispersant at 91 days had a reduction on compressive strength of 36% and clinker substitution of 43% compared to REF, and with the addition of superplasticizer, there was a reduction on compressive strength of 27% for mortar at 91 days compared to REF.

Binder intensity, carbon intensity, and CO_2 emissions: Fig. 11a shows the results of binder intensity (BI) for modeled concretes; this indicator relates the amount of binder in an m³ of concrete necessary to provide 1 MPa of compressive strength. The grey curves indicate constant amounts of binder in weight per m³ of concrete; in a best practice scenario concretes with 250 kg of binder per m³ are at the 'state of the art'. From Fig. 11a it can be concluded that binder intensity depended on curing age and the incorporation of superplasticizer, in other words, it depended on reactivity and quantity of mixing water. Concretes with Portland pozzolan blended cements presented higher binder intensity compared with REF, for concrete with and without superplasticizer. The cements with diatomaceous earth combined less water in their hydration process than REF, so it was necessary more binder to achieve 1 MPa of compressive strength. Concretes without superplasticizer prepared with 49DE and 16DE cements at 28 days of hydration needed 6.12 and 1.92 kg more binder to obtain 1 MPa when compared to REF; with the addition of superplasticizer these numbers reduced to 3.62 and 1.79 kg, respectively; these values are expressive when the analysis is scaled up to the volume of concrete used nowadays.

Fig. 11b presents the estimated results of carbon intensity (CI) for the studied concretes; the grey curves represent constant amounts of CO_2 emitted to produce one m³ of concrete. It was also clear that the carbon intensity indicator depended on clinker content, reactivity and mixing water; materials that chemically combine more water and require a smaller volume of mixing water produce concretes with

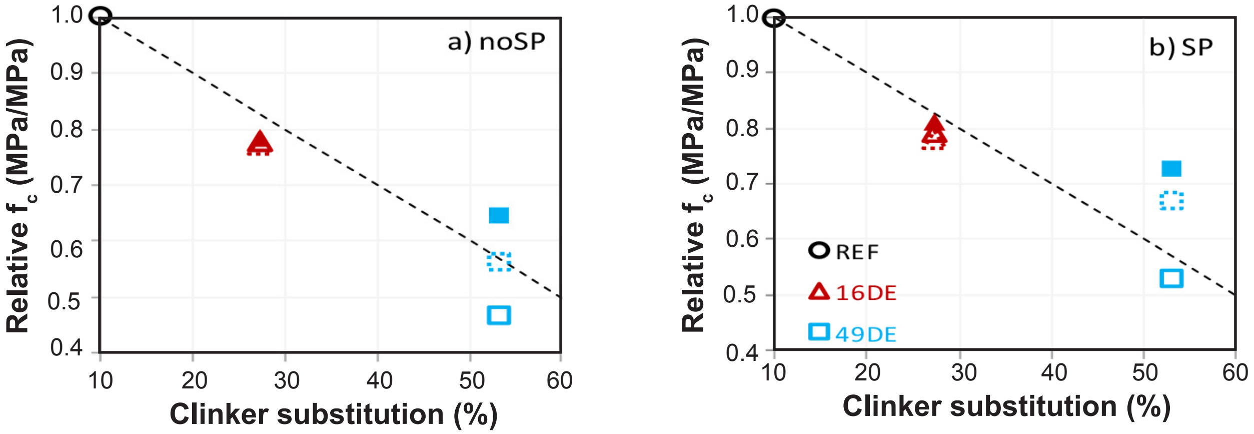

Figure 10: Relative compressive strength (f_c) - REF versus clinker substitution fraction on mortars without (a) and with (b) superplasticizer. The empty icons correspond to 7 days of hydration, pointed icons to 28 days and filled icons to 91 days. The black line corresponds to a direct dilution.

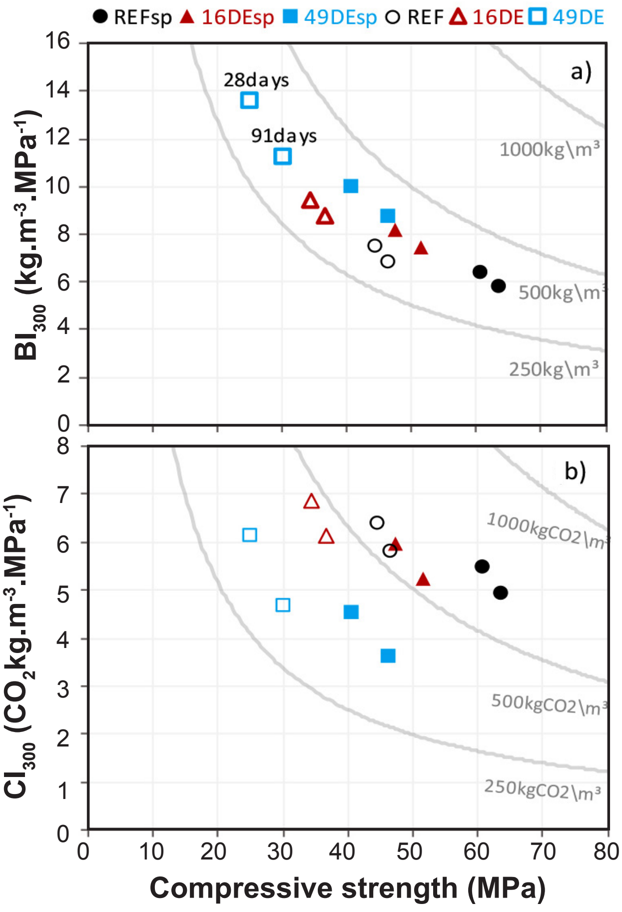

Figure 11: Estimated binder (a) and carbon (b) intensity indicator of concretes containing a fixed paste volume of 300 dm³ without (empty icons) and with (filled icons) superplasticizer. There are two icons for each composition, the first icon, from right to left, corresponds to 91 days of hydration and the second to 28 days. The grey lines represent concretes with 250, 500 and 1000 kg of binder/CO_2 per m³ of concrete.

lower carbon intensity indices. Concretes with 49DE without superplasticizer at 28 and 91 days presented reductions of 4% and 20% on carbon intensity when compared to REF; on the other hand, concretes with 16DE had an increase of 7% and 5%, respectively. By incorporating superplasticizer, concretes with 49DE at 28 and 91 days showed reductions of 18% and 27% on carbon intensity indicator when compared to REF. However, 16DE concrete had increases of 9% and 5%, respectively. Even though 49DE had a lower reactivity than REF, the best results on carbon intensity indicator was linked with the high replacement of clinker (53%), which was the material with most impact on CO_2 emissions of concrete; in this case the reduction on clinker content was accompanied by a reduction on carbon intensity, but for 16DE this did not happen. Concretes made with 16DE with or without superplasticizer led to an increase of carbon intensity when compared to REF, and the reduction on clinker content was not compensated by the pozzolan, resulting in higher carbon intensity.

Fig. 12 shows the carbon intensity of modeled concretes versus the CO_2 emitted on the production process of each cement. Each cement had an only value of CO_2 emission factor that depends on clinker content, but had many values of carbon intensity, that depend on clinker content, reactivity (curing age) and water demand (with or without superplasticizer). Concretes with 49DE, 16DE and REF at 28 days of hydration without superplasticizer had a carbon intensity indicator of 6.16, 6.88 and 6.40 kgCO$_2$.m^{-3}.MPa^{-1}, respectively, but a CO_2 emission factor of 399, 622 and 774 kgCO$_2$/t cement; in this scenario analyzing the carbon intensity, 16DE would be the cement with higher environmental impact, but analyzing the CO_2 emission factor REF would be by far the material with higher environmental impact. Thus, there was no direct relation between both indicators, showing that the reduction of CO_2 emissions in the production of cement is not always associated with a reduction of the impacts of cement in its use. It is also important to mention that the correct choice of cement based on BI and CI depends on the concrete compressive strength class required. For instance, applications that require concrete with high compressive strength (above 60 MPa), it would be advised to use cement REF with superplasticizer, that presents lower BI and CI than the Portland pozzolan blended cements. However, if a concrete with 40 MPa is needed, the best choice would be cement 49DE with superplasticizer; so, the correct user's choice is also important for reduction of environmental impact of cement and concrete industry.

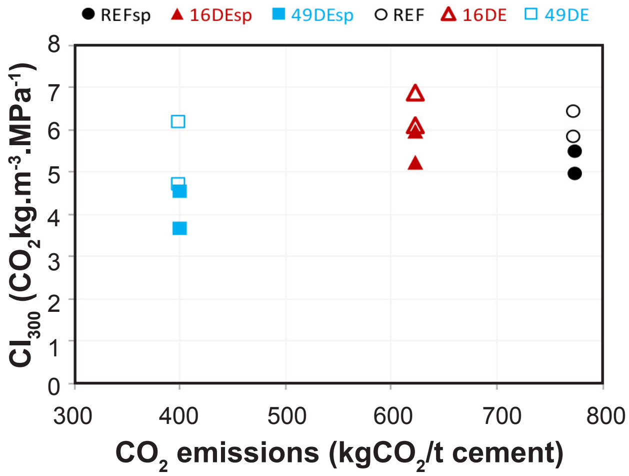

Figure 12: Carbon intensity indicator versus CO_2 emissions. Carbon intensity was calculated for concretes without (empty icons) and with (filled icons - sp) superplasticizer. There are two icons for each composition, the first icon (from bottom to top) corresponds to 91 days of hydration and the second to 28 days.

CONCLUSIONS

The SEM images showed that kaolin plates were spread on the surface of 49DE and 16DE grains, increasing their specific surface area. It was also observed a cluster of kaolin plates. Cements with diatomaceous earth required more superplasticizer than the cement with a high content of clinker (REF) to obtain the same rheological behavior, due to their higher specific surface area. 16DE cement presented a reduction on volume of chemically combined water at 91 days, higher than the reduction on its quantity of clinker, but 49DE proved to be more efficient in this regard, combining proportionately a higher volume of water compared to REF, indicating a contribution of the diatomaceous earth in the reactivity of cement. In mortars without incorporation of superplasticizer, all cements required a similar water volume to obtain a spread on table of 240±10 mm, but with the incorporation of superplasticizer, Portland pozzolan blended cements required a smaller volume of water to achieve the same rheological behavior. These two parameters, reactivity and water demand, directly influenced the compressive strength and porosity of the final product; for 16DE the reduction on compressive strength was higher than the reduction on its clinker content; on the other hand, 49DE obtained an increase in the compressive strength relative to REF for the ages of 28 and 91 days. The porosity of the mortars was influenced by the addition of superplasticizer and hydration time. The binder intensity was greater for cements with diatomaceous earth, an indicator that relates the binder efficiency and the use of materials. For carbon intensity, only 49DE cement presented a reduction of this indicator when compared with REF, showing that the reduction in CO_2 emissions of cement production (reduction of the clinker content) did not have a direct relationship with a reduction on the impacts of cement in its use. Therefore, for the strategy of substituting clinker with supplementary cementitious materials to be effective in reducing the environmental impacts of the cement industry, it is not possible to evaluate only the CO_2 emission factor (clinker factor), but the analysis should be more comprehensive involving the reactivity and water demand of these cements.

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