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Influence of packing and dispersion of particles on the cement content of concretes

Influência do empacotamento e dispersão de partículas no consumo de cimento de concretos

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Abstract

Due to environmental issues, the concrete chain seeks to reduce CO_2 emissions. However, growing demand from developing countries causes the increase of CO_2 emissions in production to exceed decreases generated by industrial actions, such as improving kilns and clinker replacement. New strategies are important. Changes in the concrete formulation, making it more efficient, can help if these changes produce concrete with the same performance and lower cement consumption. In this regard, the improvement of packing and dispersion of particles increases this efficiency. The better the packing, the lower the volume of voids between particles, thereby requiring lower fluid content (water) to permit flow. The dispersion of the particles also decreases the water content for the same fluidity. The less the water content, the smaller the water/cement (w/c) ratio, and the greater the resistance. Thus, both strategies increase the efficiency by uncoupling obtaining fluidity from the water content.
This study investigated the influence of packing and dispersion on the efficiency of cement use in concrete. The increase of packing and the complete dispersion of fine particles has been shown to improve efficiency, as measured by the ratio between binder consumption and compressive strength (the performance parameter used in most practical applications).

Keywords: concrete, design efficiency, binder, CO_2, sustainability.

Resumo

Devido a questões ambientais, a cadeia do concreto busca reduzir emissões de CO_2. Porém, a demanda crescente de países em desenvolvimento faz com que o aumento da produção supere as diminuições geradas por ações industriais como melhoria de fornos e substituição de clínquer. Novas estratégias são fundamentais. Mudanças na formulação de concretos, tornando-a mais eficiente, podem ajudar caso produzam concretos de mesmo desempenho e menor consumo de cimento. Neste sentido, a melhoria do empacotamento e dispersão das partículas aumentam esta eficiência. Quanto melhor o empacotamento, menor o volume de vazios entre as partículas, demandando menor teor de fluido (água) para permitir fluidez. A dispersão das partículas também diminui o teor de água para a mesma fluidez. Quanto menos água, menor a relação a/c e maior a resistência. Assim, ambas as estratégias aumentam a eficiência ao desatrelar a obtenção de fluidez ao teor de água.
Este trabalho estudou a influência do empacotamento e dispersão na eficiência do uso do cimento de concretos. Demonstrou-se que o aumento do empacotamento e a completa dispersão das partículas finas permitem atingir melhor eficiência – medida pela relação entre consumo de ligantes e resistência à compressão (parâmetro de desempenho utilizado na maior parte das aplicações práticas).

Palavras-chave: concreto, eficiência de dosagem, ligantes, CO_2, sustentabilidade.

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1. Introduction

Due to the high magnitude of the CO_2 released by the production of clinker, making a sustainable concrete is currently focussed primarily on replacing clinker using mineral admixtures, assuming that the mineral admixture has lower or even zero emissions. There is also a second strategy of replacing natural aggregates by recycled aggregates, which is closely linked to the use of natural resources and reduction of waste disposal in landfills. However, the increase in recycled aggregate content in concretes, if not properly made, frequently increases the cement content and therefore also increases CO_2 emissions [1], which is, most of the time, neglected in an overall sustainability assessment. This strategy will not be discussed in this paper.

In the first strategy, the impact is typically measured in kg CO_2 emitted per cubic metre of concrete or, in a more practical evaluation, by the clinker replacement rate by such admixtures as blast furnace slag (BFS) or fly ash (FA). The lower the CO_2/m^3 or the higher the admixtures, the higher the efficiency in sustainability terms.

However, the CO_2 emissions from cement production have increased since the 1940s. This growth occurred despite some success in specific reduction (kg/kg) of emissions, mainly due to increasing energy efficiency in kilns and replacing clinker. The current mitigation strategies have not been able to accommodate the growing global demand for cement [2]. To aggravate the situation, the production growth is inevitable and important due to social issues in developing countries. In addition, there is not enough mineral admixture to increase clinker replacement rates [3], which may explain much of the increase in CO_2 emissions.

Currently, cement is responsible for 5-8% of the total global CO_2 emissions [4]. The global cement production forecast for 2050 varies between $3.69x10^9$ t/yr [2] and $5x10^9$ t/yr in a high growth scenario [5], representing a factor of 2.5 increase over the production of 2010. If the mitigation strategies remain the same up to 2050, cement production can become responsible for 20-30% of the CO_2 emissions [2,5]. This situation may be further aggravated if the allocation of CO_2 to BFS and FA becomes a rule, as is a worldwide trend [6-8], or if a future shortage of these waste materials occurs [9-10].

Another option to reduce the environmental burden on clinker production is carbon capture and storage. However, carbon capture and storage is a very expensive strategy that can further increase the cement production costs, even doubling those costs [11-12], which is not sustainable as the most affected consumers would be the developing countries that need cement to ensure the construction of infrastructure and low cost housing.

This article aims to provide a comparison between the efficiency of cement use in conventional and packing and dispersed designed concretes. This route for increasing concrete sustainability is new, since it could allow processing of concretes with the same performance and lower cement consumption – lower CO_2 emissions.

2. Theory of packing and dispersion of particles applied to concrete technology for decreasing cement content

According to the theory of packing of particles, the use of particle fractions of different sizes – where the smaller particles fill the voids between the larger particles, successively to smaller and smaller sizes – can generate a system with a significant decrease in void volume. In the concrete, a fluid is inserted to fill these voids and make particles move (ensuring the flow, which is essential to enable moulding). Therefore, the control of the voids between particles is crucial, since the lower this void volume, the lower the fluid requirement for the same flow.

In the specific case of concrete, the lower the void volume between aggregates, the lower the volume of paste (cement plus water) necessary for the flow. Considering that the concrete strength is given by the water/cement ratio (w/c), the decrease in paste volume maintaining the same w/c can mean a reduction in the final cement content maintaining resistance, which configures an increase in use efficiency of the cement. Fluidity is no longer linked exclusively to water content as in the usual dosage technology. The problem is that, currently, fluidity is seldom used in conventional concrete technology due to lack of parameters for measuring voids between aggregates.

There are several particle packing theories, many of them based on mathematical equations that try to calculate the volume of voids for a given set of particles of known size. Among these theories, this work will use the theory of Westmann and Hugill (1930) as modified by Funk and Dinger [13]. Initially, the apparent volume of each size class in the granulometric distribution is calculated per Equations 1 to 4:

$$V_{\alpha 1} = \alpha_1 . x_1 \tag{1}$$

$$V_{\alpha 2} = x_1 + \alpha_2 . x_2 \tag{2}$$

$$V_{\alpha 3} = x_1 + x_2 + \alpha_3 . x_3 \tag{3}$$

$$V_{\alpha n} = \sum_{j=1}^{n-1} x_j + \alpha_n . x_n \tag{4}$$

Where

αi = apparent volume of monodispersion *i* size class, defined by equation x; xi = volumetric fraction of size class *i*; Vαi = apparent volume calculated referenced in particle size class i; n = number of particle size classes in the complete distribution.

This calculation requires that the size classes of the particle size distribution follow a series of sieves with a ratio of $\sqrt[4]{2}$, such as the complete series of ASTM E11. If the distribution to be analysed does not have the complete series of sieves, it must be recalculated using interpolation. The apparent volume of monodispersions of each size class can be calculated by Equation 5:

$$\alpha_i = \frac{1}{1 - \left(\frac{1}{RTC}\right)^q} \tag{5}$$

Where

RTC = class size ratio, preferably $\sqrt[4]{2}$; q = modulus of the ideal particle size distribution according to the Westmann and Hugill model (0.37, which provides the highest packing density for perfect spheres). The Westmann and Hugill modified model is shown below.

The Westmann and Hugill modified model [13] is described in Equation 6. In this model, there is the introduction of the minimum particle size in relation to the original model. The model was designed for the calculation of the distribution module q, which indicates the slope of the accumulated granulometric curve.

$$\frac{CPFT}{100} = \frac{D^q - D_S^q}{D_L^q - D_S^q} \qquad (6)$$

Where

CPFT = accumulated percentage below D; D = particle size; Ds = smaller particle size of the distribution; Dl = largest particle size of the distribution; q = distribution modulus.

Through this model, Funk and Dinger [13] did computational simulations where they determined the distribution modulus (q) that results in the highest packaging density. For perfect spheres, this value is q = 0.37, according to Figure 1 and the value used in Equation 5.

From Equation 5, the apparent volume Vai can be calculated for all size classes of the distribution. The largest apparent volume Vαi defines the size class with the lowest degree of packing and therefore the minimum porosity (voids between particles) expected for the complete granulometric distribution. From the largest apparent volume Vαi, the minimum expected porosity can be calculated from Equation 7:

$$MPE = 40\,.\left(1 - \frac{1}{V_\alpha}\right)\% \qquad (7)$$

Where

MPE = minimum expected porosity; Va = highest apparent volume calculated in Equation 5.

For the application of the model, some premises were adopted to simplify the calculations and interpretations: 1) all the particles found in a range of two sequential sieves are of the same diameter (monomodal system); 2) all particles are spherical; and 3) the particles settle randomly in the distribution - according to [13-15], in this condition the porosity of a system of particles of equal and spherical diameters reaches 36 to 40%. In similar systems with ordered packaging (which would resemble compact hexagonal and cube-centred crystalline atomic structures), this porosity may drop to as much as 26%. This value, therefore, can be changed, but it was in this work set on the worst condition.

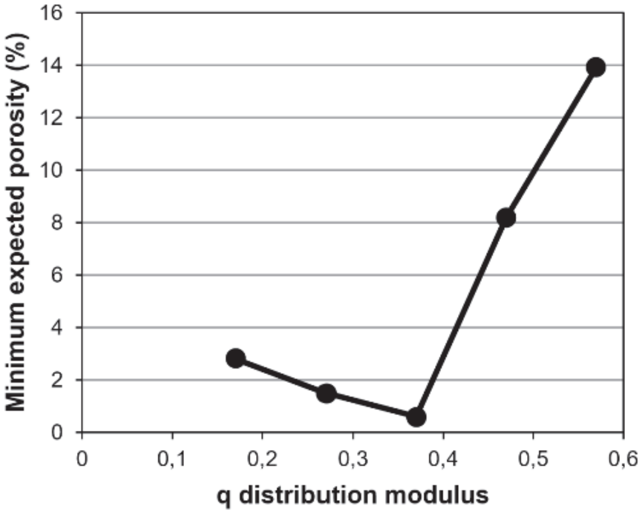


Figure 1
Minimum porosity calculated by the Westmann and Hugill modified model according to the distribution module, minimum grain of 0.17 μm and maximum of 16 mm (FUNK and DINGER, 1994)

It is true that the estimation of porosity through theoretical calculations presents errors of difficult measurement – up to 4%, according to Funk and Dinger [13] and Oliveira et al. [16] – due to the non-spherical morphology of the particles, which: 1) renders inaccurate measurement of their exact size in both sieving and imaging methods and therefore does not guarantee an accurate porosity calculation; and 2) generates variability of the actual porosity of the mixtures according to the method of densification adopted, since non-spherical particles present different forms of deposition. Even so, this estimation allows us to introduce into the dosage technology a greater precision in the knowledge of particle packing compared to conventional techniques.

Fine particles (such as cement suspensions) tend to agglomerate due to their low mass and high surface area, factors that make surface forces predominate over gravitational forces. As the balance of the electric charges of the surfaces of the different particles is not always in equilibrium, higher attraction forces are generated than the forces of repulsion. For the suspension, these agglomerates act as larger particles, which: 1) modifies the granulometric distribution; 2) hinders the mobility of flow lines, since the agglomerates move more slowly and act as blocks to the smaller particles, increasing the viscosity [16]; 3) generates voids within the agglomerates, increasing water consumption; and 4) decreases the efficiency of the binders because the surface area available for pozzolanic and hydration reactions is decreased (Figure 2). Thus, the total dispersion of the particles, especially fines, is a condition to make the packing project work. The condition of total dispersion of the paste must always be met, since without it the designed packing does not have any physical sense since it does not occur in practice. To obtain this dispersion with economic criteria, it is necessary to determine the minimum dispersant content required to generate the highest possible fluidity of the system, which can be measured with the aid of a paste rheometer (see item 3.2.1 - Determination of optimum dispersant content). If, however, complete dispersion is not guaranteed, the error associated with the condition of total non-dispersion of the pulp cannot be determined objectively because it causes very different rheological variations on a case-by-case basis.

3. Experimental planning, materials and methods

3.1 Materials

A common CP V cement from the Brazilian market was used, with three different limestone fillers, three different sands and three different gravels. The diversity of materials was due to the need for different particle sizes to achieve high levels of particle packing in concrete.

A polycarboxylate dispersant was used.

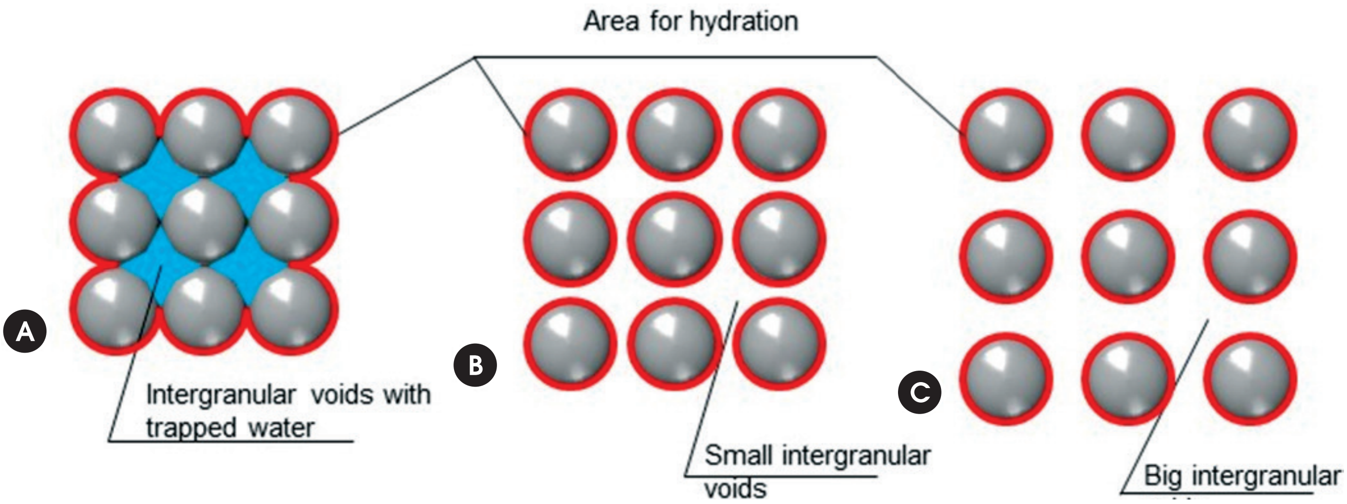


Figure 2
a) Non-dispersed particles, causing water entrapping and flow obstruction; (b) dispersed particles; (c) dispersed particles with higher distance

3.1.1 Chemical and mineralogical characterization

Table 1 shows the chemical characterization of the fines used (cement and fillers) obtained by X-ray fluorescence using a semi-quantitative method, analysis of fluorine and uranium chemical elements, in an Axial Advanced PANalytical sequential spectrometer. Table 2 presents the mineralogical characterization obtained by X-ray diffraction performed in PANalytical X'Pert PRO equipment with X'Celerator detector, with quantification by the Rietveld method with the aid of the PANalytical Inorganic Structure Database.

3.1.2 Physical characterization

All materials exhibited the following physical properties:

A) Real density in He pycnometer, Quantachrome MVP 5DC equipment;

B) Particle size distribution (materials with particles>500 μm) by the vibrating sieving test using the complete series of sieves described in ASTM E11. Each sieving was performed for a minimum of 20 minutes. The series of sieves used was up to a minimum diameter of 106 μm, and the material passing through this sieve was characterized by laser granulometry (test b), and the final granulometric particle size distribution was obtained through the interaction between the sieving results and laser granulometry weighted by the mass of material of each diameter;

C) Particle size distribution (materials <500 μm such as cement, fillers and fines of gravel and sand passed in the 106 μm sieve), by laser granulometry in a Malvern Mastersizer granulometer. The particles were mixed in a liquid environment (water for non-reactive materials, alcohol for cement) at approximately 15% concentration, and ultrasonically dispersed at 2000 RPM for 2 minutes prior to the test to disperse and individualize the particles and, thus, to determine the granulometric distribution with higher precision. The possible variations of density of the particles by size range were neglected, with adoption of the average real density measured by the test of He pycnometry;

D) Specific surface area by BET [18], Micromeritics Gemini 2375 equipment, with the use of nitrogen gas. The samples were previously treated by a degassing procedure coupled to the equipment, necessary to remove the possible impurities (gases) present on the surface of the sample, which significantly changes the results obtained. The degassing was carried out by application of vacuum pressure to the samples for 24 hours at a temperature of 100°C for the fillers and 40°C for the cement.

In the sieving test, the use of the complete sieve series of the ASTM E11 (19000 μm, 16000 μm, 12000 μm, 11200 μm, 9500 μm, 8000

Table 1
Chemical characterization of materials by X-ray fluorescence

Oxides (%)	CP V	Limestone 1	Limestone 2	Limestone 3
CaO	64.5	51.4	54.6	60.7
SiO_2	15.5	2.21	2.26	3.68
Al_2O_3	2.81	0.05	0.07	0.1
Fe_2O_3	3.17	0.04	0.03	0.04
MgO	1.5	6.17	3.49	5.76
SO_3	7.98	0.01	0.02	0.02
K_2O	1.12	0.01	0.23	0.02
Na_2O	0.3	–	–	–
P_2O_5	0.18	0.03	0.02	0.05
TiO2	0.26	–	–	–
Outros	0.34	0.03	0.04	0.04
PF	2.34	40.05	39.24	29.59

µm, 6300 µm, 5600 µm, 4750 µm, 4000 µm, 3350 µm, 2800 µm, 2360 µm, 2000 µm, 1700 µm, 1400 µm, 1180 µm, 1000 µm, 850 µm, 710 µm, 600 µm, 500 µm, 425 µm, 355 µm, 300 µm, 250 µm, 212 µm, 180 µm, 150 µm, 125 µm, 106 µm) is critical when packing of the particles needs to be determined, since the theoretical packing calculation models use all the particle size classes to improve the accuracy of void measurements between particles, as seen in item 2.

In the combination between sieve and laser granulometry, the difference in size reported in the literature between results of sieving and laser granulometry (approximately 20%) was neglected [17]. The difference is higher the more the particles move away from the spherical shape since in sieving, the particle size is determined by its smaller size, whereas in the laser test, the particle size is the result of the average of several measurements taken at random angles (http://www.malvern.com/en/products/technology/laser-diffraction/default.aspx).

For the measurement of the surface area, Blaine's diffused method was not performed because this technique does not yield precise results for the characterization of very fine particles with dimensions smaller than 10 µm [19]. NBR NM 76:1998 states that this technique is used mainly to verify the uniformity of the milling process of a cement factory and allows only a limited determination of the properties of the cement and may not provide significant results for cements containing ultrafine materials. This error occurs because the Carman-Kozeny equation, used in this method, is not valid for particles smaller than 10 µm [20]. We also observed that the results of Blaine present a low correlation with the fluidity of pastes containing fillers, whereas results obtained by the BET technique present more correlation with rheological responses [21].

However, the BET test also presents possible sources of error in the measurements. Experimentally, it has been determined that the time and degassing temperature have an influence on the results. Generally, the higher the sample surface area, the higher the temperature and time need to be. However, some samples (such as cement) cannot be exposed to high temperatures in the degassing, under risk of chemical deterioration and alteration in the results. For the tested materials, a variability stabilization and an increase in the reproducibility of the measurements were observed for a 24-hour degassing time (performed in 2 laboratories by 2 different technicians). The equipment user's manual suggested 3-hour degassing, a value that did not yield good repeatability and reproducibility for the samples studied – higher variation and lower surface area values were found if compared to the values obtained after 24-hour degassing.

The sample amount also changes the BET results. For the correct measurement of the surface area, there must be a sample mass with a minimum of 1-5 m^2 (50 m^2 for measurement of the complete isothermal adsorption curve). Thus, the lower the specific surface area, the higher the required sample mass. If the specific area is too small (too much mass required), there is the possibility that there is no container available for the test.

The BET result cannot be interpreted as an absolute value because the BET result is dependent on the surface interaction between the gas and the surface of the particle (there are variations of the positive and negative surface charges of both, as well as the orientation of the adsorbed molecules and the possibility of a double adsorption layer, depending on the charges). The adsorption of the gas may be weaker or stronger depending on the ratios between the charges. If they are weaker, the gas does not penetrate the surfaces between the layers and the smaller voids or pores, because the actual measurement is only in the outer layers [22]. Different gases can deliver different results.

The BET equation also assumes that 1) the heat of adsorption of all the molecular layers after the first is equal to the heat of liquefaction, and 2) in equilibrium, the surface condensation rate is equal to the evaporation rate of the first or subsequent layers, which may intro-

Table 2
Mineralogical characterization of materials by X-ray diffraction – Rietveld quantitative method

% estimated		Material			
Name	**Chemical formula**	**CP V**	**Lim1**	**Lim2**	**Lim3**
Alite (C_3S)	Ca_3SiO_5	54	–	–	–
Belite (C_2S)	Ca_2SiO_4	19	–	–	–
Calcite	$CaCO_3$	7	70	85	75
Brownmillerite	$Ca_2(Al, Fe^{+3})_2O_5$	6	–	–	–
Dolomite	$CaMg(CO_3)_2$	–	28	12	18
Calcium sulphate dihydrate	$Ca(SO_4)\ (H_2O)_2$	5	–	–	–
Calcium sulphate hemydrate	$Ca(SO_4)\ (H_2O)_{0,5}$	4	–	–	–
Aluminium calcium oxide	$Ca_3Al_2O_6$	3	–	–	–
Portlandite	$Ca(OH)_2$	2	–	–	–
Quartz	SiO_2	–	1	2	1
Tremolite	$Ca_2Mg_5Si_8O_{22}(OH)_2$	–	–	1	3
Diopside	$CaMgSi_2O_6$	–	–	–	3
Chalk	$Mg_3(Si_2O_5)_2(OH)_2$	–	1	–	–

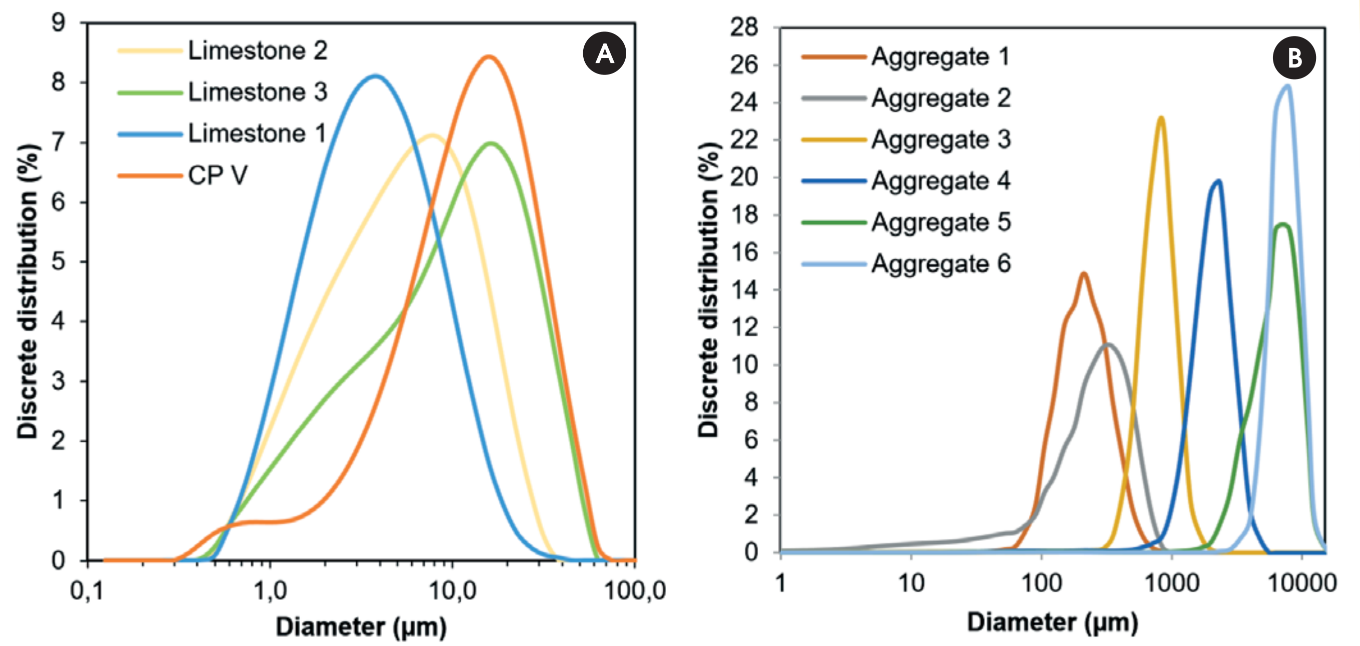


Figure 3
Particle size distribution of materials: a) fines (cement and limestone filler, d < 125 µm); b) thick (aggregates – sand and gravel, d > 125 µm)

duce intrinsic errors to the measurements. Finally, the BET equation is most useful under relative pressures of 0.05 to 0.45 – that is, it is not valid for any pressure [22]. For all these reasons, surface area measurements should be used with caution. However, because as in this study they are comparative measures with standardized procedures, they are valid for the assessments performed.

Figure 3 shows the particle size distribution of the materials. Table 3 presents the surface area (BET), m^2/g, and the real density (He picnometry), kg/dm^3.

The CPV cement used had 33% water of normal consistency (NBR NM 43), 3:25 of start setting time and 4:45 of end setting time (NBR NM 65) and surface area of 5410 cm^2/g by the Blaine method.

The dispersant used was a polycarboxylate powder (100% solids) based on polycarboxylic ether, with a yellow colour appearance, density 0.30-0.60 (kg/dm^3), pH 6.5-8.5 (measured in 20% solids solution, temperature 20°C), and dosage recommendation of 0.05 to 1.00% in relation to the total mass of fines (data supplied by the manufacturer).

Table 4 presents the characterization of the selected aggregates for the experimental planning according to the related technical norms.

3.2 Methods

As the present study evaluated the influence of particle packing and dispersion on the rheological behaviour and the efficiency of cement use in concretes, concrete dosages were determined by varying the particle packing levels. The flow characteristics in fresh state and compressive strength in the hardened state were measured. All compositions were made with complete dispersion of fines by using the lowest dispersant content possible (optimum content), obtained by experimental test described in the following section.

3.2.1 Optimum dispersant content determination

As explained in item 2, the condition of total dispersion of the paste must always be met for guaranteeing the occurrence of the designed packing. An optimum dispersant content determination test was performed, which, experimentally, proved to be the lowest content necessary to achieve the minimum possible viscosity and can be experimentally determined using a paste rheometer. The dispersant content was obtained individually for each of the fine materials by the steps:

1) Definition of a fixed water/solids (w/s) ratio – in this case, 0.35. This ratio was a suitable experimental value for the materials, as determined by adding water to a constant solid powder mass to the point where the suspension could mix, even with difficulty, without dispersant use according to the method by Fennis (2011). For each material, the chosen w/s was the one that provided the highest possible solid concentration without a visible suspension desegregation, caused when the solid content is higher than the water can make wet (very low water, high

Table 3
Real density and surface area (BET) of materials

Category	Material	Real density (kg/dm^3)	Área superficial (m^2/g)
Cimento	CP V	2.89	1.78
Fillers	Limestone1	2.62	2.97
	Limestone2	2.63	2.15
	Limestone3	2.65	1.46
Aggregates	Aggregate 1	2.63	0.21
	Aggregate 2	2.82	0.34
	Aggregate 3	2.81	0.20
	Aggregate 4	2.75	<0.10
	Aggregate 5	2.71	<0.10
	Aggregate 6	2.71	<0.10

Table 4
Characterization of the aggregates according to the related standards – unitary density (UD) (NM 45), real density (RD), apparent density (AD) (NM 52 – sand or NM 53 – gravel), water absorption (NM 30 – sand or NM 53 – gravel) and powder content (NM 46)

	UD (kg/dm^3)	RD (kg/dm^3)	AD (kg/dm^3)	Absorption (%)	Fines <75 µm (%)
Fine aggregates	NBR NM 45	NBR NM 52	NBR NM 52	NBR NM 30	NBR NM 46
Aggregate 1	1.69	2.64	2.63	0.24	1.12
Aggregate 2	1.86	2.64	2.62	0.91	14.7
Aggregate 3	1.64	2.77	2.75	0.85	1.12
Aggregate 4	1.51	2.62	2.60	0.91	0.76
Coarse aggregates	NBR NM 45	NBR NM 53	NBR NM 53	NBR NM 53	NBR NM 46
Aggregate 5	1.52	2.65	2.61	1.38	0.23
Aggregate 6	1.54	2.66	2.70	1.60	0.60

viscosity) or when solids are so distant that fluidity is made by water behaviour (high water content, low viscosity). The use of a fixed w/s ratio also allowed direct comparison between the different mixtures. This condition (maximum solid concentration) makes the suspension more difficulty to disperse since particles are close and attractive forces are ageing. The ion concentration is increased, which decreases the thickness of particle dual layer. This situation is the worst for a dispersant, so the dispersant will be required in its maximum capacity.

2) Mixture of 50 g powder with water (fixed w/s) without dispersant. The mixing was done adding powder to water in an IKA R1303 “Dissolver Stirrer” blender (Figure 4a) for 2 minutes at a rotational speed of 600 RPM. Then, blender rotation was raised to 1500 RPM, and the blending was performed for an additional 3 minutes.
3) Paste was placed on the AR-550 rheometer, TA Instruments, plate-to-plate geometry (Figure 4b).
4) The rheological curve (shear rate x shear stress) was determined by a flow rheometry test. The test was standardized to increase (acceleration) the shear rate from 0 to 400 s^{-1} within the time of 1 minute, with a shear rate measurement every 4 seconds. Then, the shear rate was decreased (decelerated) from 400 to 0 s^{-1}, and shear stress was measured, resulting in a round-trip rheological curve.
5) Repeat procedures 2 to 4 for increasingly dispersant contents. Rheometry flow test for each blend (one test for each dispersant content) followed steps of Figure 5.
6) For each test, the apparent viscosity at the point of highest shear rate tested (400 s^{-1}) was determined (the rate of 400 s^{-1} was adopted because it allows a more complete analysis of the rheological behaviour of cementitious materials).
7) Graphic “Dispersant content x apparent viscosity” was made for the determination of the lowest apparent viscosity level reached with the lowest possible dispersant content.

Figure 6a shows the various curves “shear rate x shear stress” for one of the materials studied. Figure 6b shows the graph “dispersant content vs. apparent viscosity” resulting from the curves of Figure 6a.

The optimum dispersant contents of the materials CP V, Lime-

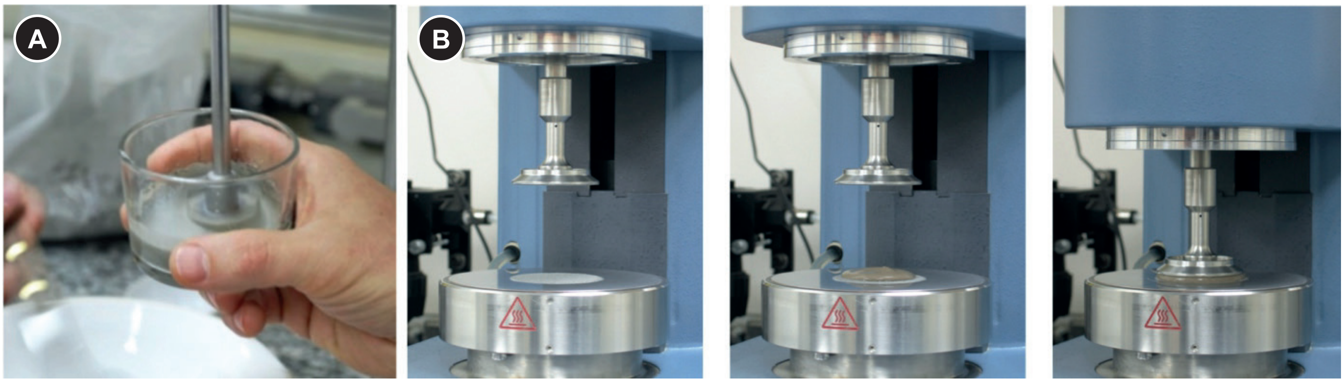


Figure 4
a) Paste mixing equipment, IKA R1303 "Dissolver Stirrer"; b) paste rheometer AR-550, TA Instruments

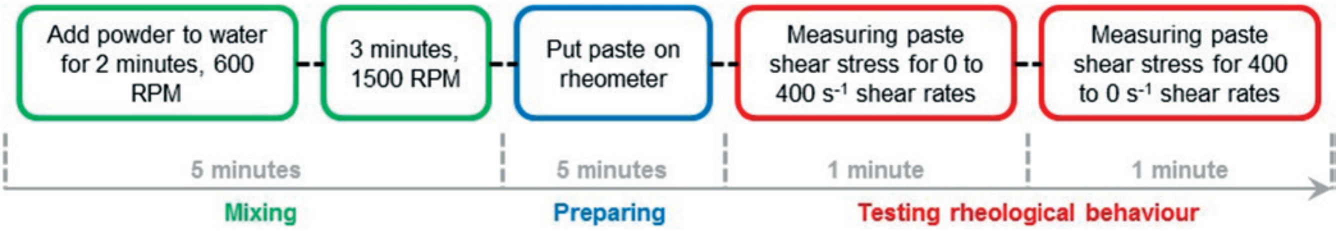


Figure 5
Flow diagram of continuous flow rheometry test

stone1, Limestone2 and Limestone3 were, respectively, 0.50%, 0.225%, 0.20% and 0.125%.

Nine experiments were randomly selected and repeated to determine the experimental variation (determined by difference between repeated test results). The average variation found was approximately 0.035 Pa·s, a small value if compared to the orders of magnitude of the apparent viscosities measured.

3.2.2 Design of high-packing concrete formulations

Several concretes were designed with various combinations of materials aiming for the increase in the packing of particles [23]. Packing was determined by the method of Westmann and Hugill (1930) modified by [13], as described in item 2.

For all combinations, the optimum dispersant content by mass weighted average of the optimum dispersant values found for each fine were used (item 3.2.1).

Table 5 shows the compositions, including two reference concretes designed by a conventional Brazilian method (one with no dispersant, and other with dispersant at optimum content).

3.2.3 Slump flow test

The concretes had the slump flow measured by the procedures of the NBR NM 67. Concretes with high slump had measured their scattering from

1) performance of the standard slump flow test procedure on a surface demarcated in diameters from 500 mm to 1000 mm, intervals of 100 mm;
2) determination of the time t necessary for the concrete to reach the 500 mm spreading;
3) determination of final scattering size achieved.

3.2.4 Casting and cure

The 10x20 cm cylindrical specimens were cast. Procedures followed the recommendations of NBR 5738. After 1 day, specimens were taken to the humidity chamber (relative humidity ~ 100%, temperature 23 ± 2°C) and kept under moist cure for 28 days.

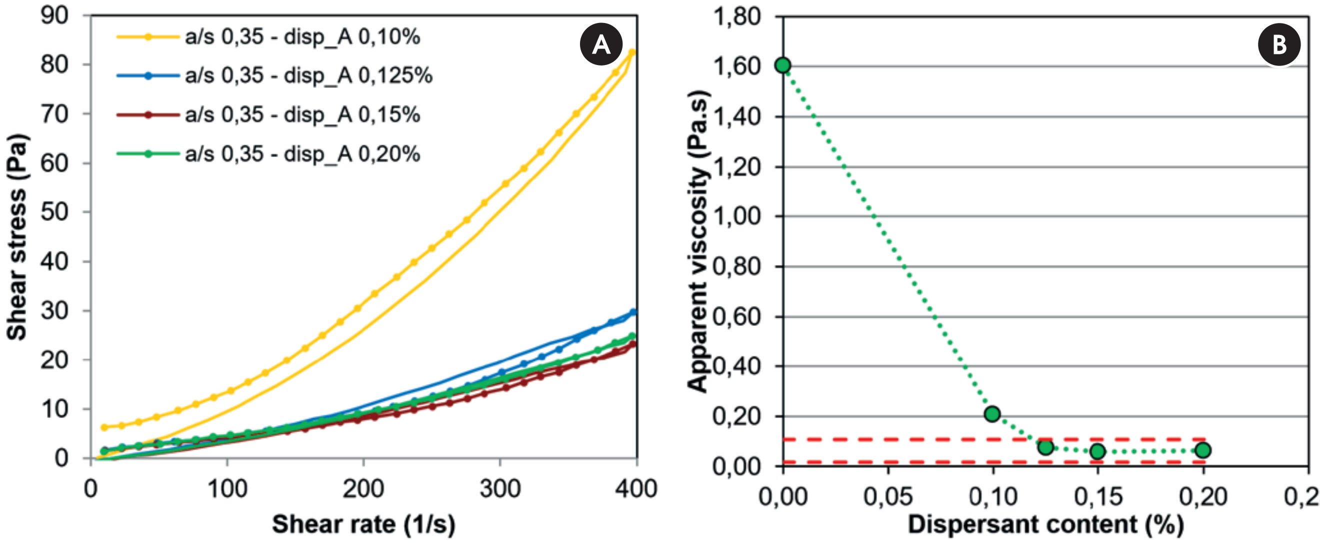


Figure 6
Determination of the optimal dispersant content of the Limestone3: a) shear rate curves x shear stress curves for 4 dispersant contents (4 different flow rheometry tests); b) "dispersant content x apparent viscosity" of the same tests.The rheological curve for the dispersant content = 0 was not shown since viscosity achieved was very high

3.2.5 Compressive strength

The determination of the compressive strength was performed at 7 and 28 days according to the procedures of NBR 5739, three specimens for each age. Tests were carried out with the specimens in the wet state. Regularization of top and bottom surfaces was done in grit. The compressive strength test was performed in a Shimazdu press with a capacity of 200 tons.

3.2.6 Cement use efficiency

If, on the one hand, the emission of low CO_2 levels can be achieved in conventional concretes by replacing clinker with mineral admixtures such as blast furnace slag and fly ash, this is controversial, since: 1) usually CO_2 emissions are simplified by these admixtures, a fact already disputed by many researchers and even by the European Community [6-8]. If everyone were to implement this strategy, there would be an insufficient supply of these admixtures to lower the content of clinker significantly on a global scale [3,24].
Therefore, the decrease of the CO_2 footprint of a concrete must also be achieved by strategies of optimization of the use of binders – summarizing, designing to achieve the same level of performance with lower total binder content, whatever the binder. As seen in item 2, packing and dispersion of particles can help significantly in this task.
Thus, to evaluate the improvement of cement use efficiency in the concretes of this work from the strategies of packing and dispersion of particles, the indicator "Binder Index" (BI) [25] will be used. This BI is calculated by the ratio between the total binder content, in kg·m^{-3}, and the performance (in this case, the compressive strength, in MPa), according to Equation 8:

$$IL = lig/rc \qquad (8)$$

Where
binder is the total binder content of the blend, in kg·m^{-3}; CS is 28-day compressive strength, in MPa.
This indicator, expressed in kg·m^{-3}·MPa^{-1}, allows the analysis of the relationship between the total amount of binders (economic and environmental impact) and a performance measurement (the most commonly used measurement for concrete is compressive strength). The higher the BI, the higher the binder content required for same performance and therefore the lower the eco-efficiency, and vice versa.

4. Results and discussion

Table 6 shows the total consumption of binders, water, rheological parameters, compressive strength at 7 and 28 days and BI calculated for each concrete mix.
Data from Table 6 show that concretes C01 to C10 were designed with a common concern of reaching a high degree of packing – low intergranular porosity, between 4-8%, was obtained for all formulations. The concrete designed by the conventional method reached almost 23% of the intergranular voids, a much higher value compared to C01-C10, possibly showing that the usual design methods do not take care with the intergranular void content.
For the packed C01-10 concretes, BI values achieved were lower than conventional reference concretes – even compared to the reference with dispersants at optimum content. Reference concretes presented higher BI even obtaining higher compressive strength – a situation in which it is often easier to reduce BI [25]. Just for comparing, conventional concrete with dispersant reached 47.4 MPa

Table 5
Concretes designed by packing technology

Mixing n°	Composition (% volume)											Dispersant (% mass fines)
	Fines <125 µm				Aggregates >125 µm						Water	
	CPV	Lim1	Lim2	Lim3	Ag1	Ag2	Ag3	Ag4	Ag5	Ag6		
C01	8.8	8.8	–	4.4	9.3	19.6	11.2	15.4	–	22.6	16.0	0.31
C02	7.2	7.2	–	3.6	9.7	20.5	11.7	16.2	–	23.8	15.5	0.31
C03	8.0	8.0	–	4.0	9.5	20.0	11.4	15.8	–	23.2	16.0	0.31
C04	8.0	8.0	–	4.0	4.1	20.5	16.4	17.6	–	21.5	16.0	0.31
C05	6.3	9.0	–	2.7	4.0	20.0	16.0	18.9	–	23.1	14.0	0.30
C06	7.7	11.0	–	3.3	9.0	19.1	10.9	15.8	–	23.2	14.2	0.30
C07	8.0	8.0	–	4.0	22.6	–	18.5	23.4	–	15.6	16.0	0.31
C08	8.0	8.0	–	4.0	22.6	–	18.5	23.4	–	15.6	13.0	0.31
C09	8.0	8.0	–	4.0	10.3	17.2	13.5	17.6	11.7	9.8	16.0	0.31
C10	5.1	8.5	–	3.4	10.4	17.4	13.7	18.7	10.4	12.5	14.0	0.28
without dispersant	16.1	–	–	–	–	38.1	–	–	–	45.7	23.4	–
Ref. with dispersant	16.1	–	–	–	–	38.1	–	–	–	45.7	16.0	0.50

at 28 days using 392 kg/m^3 of cement, while C08, for example, reached 40.2 MPa resistance using about half the amount of cement (201 kg/m^3).

Among the group of C01-C10 that obtained low BI, there are some (C01, C02, C03, C04, C07, C09) that achieved a lower BI than the conventional, even reaching slump values higher – 230 to 280 mm, or self-compacting. In the standard design conditions, slump increase is achieved with the increase of water – consequent increase of w/c, decreasing the compressive strength and hence increasing BI (considering the cement content unchanged). Thus, a higher packed concrete could be able to increase flowability (slump test measurement) without increasing water content (their water content, in L/m^3, are very similar). In this case, considering that the dispersion was standardized for all these concretes from the use of optimum dispersant content (and, in absolute levels, conventional concretes contained even more dispersant than the others), the relationship between water content and packing level can explain the flowability. Therefore, changes in the composition of concrete aggregates, with the use of particle packing tools, modify the concept of conventional design processes where total water content is mainly responsible for the flow. When intergranular voids are modified and controlled, these voids have a higher influence than the water content on the flowability, since, according to the packing theory presented, reduced void volume is responsible for optimizing the use of the fluid – less fluid is used to fill them, and more fluid is effectively used for the particle separation.

Regarding dispersion, comparing conventional concretes with and without dispersant, the not dispersed concrete required a much higher water content to obtain a much lower flow, resulting in loss of strength and hence significant increase in BI.

It follows, therefore, that increasing the use efficiency of binder is related to the efficient use of water in the fresh state to cause particles to depart. The water content directly influences the characteristics of the hardened state. The total paste porosity in the hardened state can be calculated by Eq. 9.

$$Paste\ porosity = \frac{V_{pores}}{V_{total}} = \frac{V_{H_2O_{total}} - V_{H_2O_{combined}} + V_{H_2O_{contraction}}}{V_{solids} + V_{H_2O_{total}}} \quad (9)$$

Where

V_{H2O} combined = volume of total combined water = 0.23 g/g cement

V_{H2O} contraction = volume contraction of water due to chemical reaction, based on [25] (Equation 10):

$$V_{H_2O_{contraction}} = V_{H_2O_{combined}} x\ 0.254 \quad (10)$$

Table 6

Data of material consumption, fresh state parameters, compressive strength at 7 and 28 days

Design conventional parameters							Rheological parameters			Compressive strength		Efficiency
Mixing	C (kg/dm^3)	Water (l/m^3)	a/c	α	m	Voids (%)	Slump (mm)	Scattering (mm)	t (s)	CS 7 (MPa)	CS 28 (MPa)	BI (kg.m^{-3}.MPa^{-1})
C01	213.8	160.0	0.75	0.62	9.8	5.72	280	670	13.9	33.7	35.3	6.1
C02	176.0	155.0	0.88	0.60	12.2	7.38	230	–	–	23.4	25.3	7.0
C03	194.4	160.0	0.82	0.61	10.9	6.57	270	600	18.5	27.6	29.2	6.7
C04	194.4	160.0	0.82	0.61	11.0	4.18	270	595	30	27.4	28.2	6.9
C05	156.7	140.0	0.89	0.58	14.2	4.62	60	–	–	27.1	28.1	5.6
C06	191.1	142.3	0.74	0.61	11.4	5.44	190	–	–	34.0	34.9	5.5
C07	194.4	160.0	0.82	0.61	10.8	7.66	270	600	19.7	26.2	29.1	6.7
C08	201.3	130.0	0.65	0.61	10.8	7.66	40	–	–	39.0	40.2	5.0
C09	194.4	160.0	0.82	0.61	10.9	6.10	270	600	20	25.0	27.2	7.1
C10	126.9	140.0	1.10	0.60	17.6	7.09	20	–	–	19.5	21.5	5.9
Ref without dispersant	357.7	234.0	0.65	0.55	5.0	22.89	140	–	–	32.1	32.0	11.2
Ref with dispersant	392.2	160.0	0.41	0.55	5.0	22.89	230	–	–	43.3	47.4	8.3

Legend: C = cement consumption; w/c = water/cement; α = mortar content; m = aggregates content; Porosity = intergranular porosity calculated from the Westmann and Hugill (1930) model modified by Funk and Dinger (1994); scattering = total final scattering; t = time to reach scattering 500 mm; CS = compressive strength for the indicated age; BI = Binder Intensity

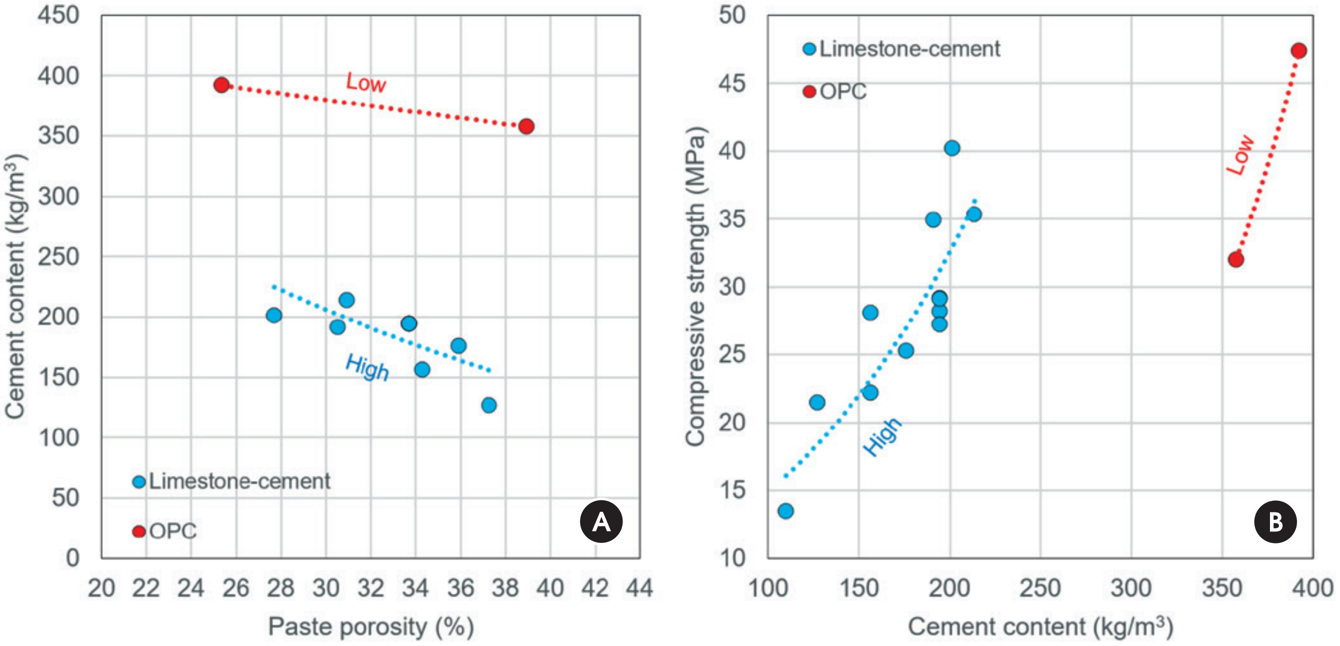
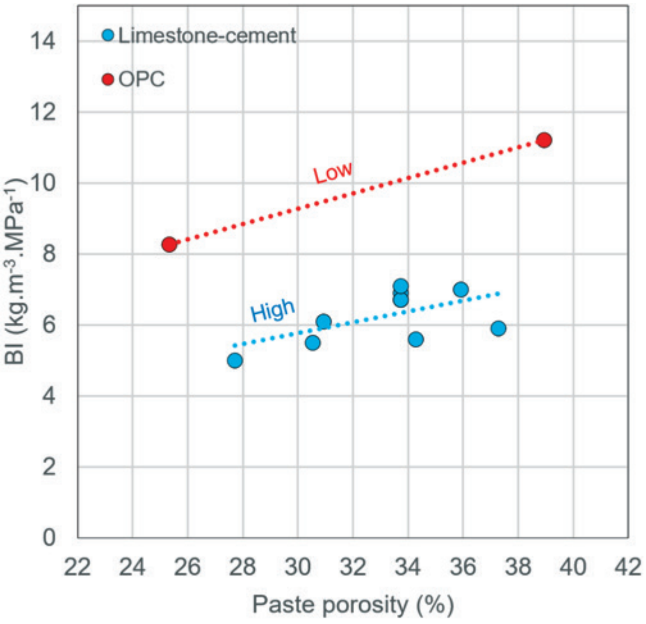


Figure 7
Correlation between: a) paste porosity and cement content; b) cement content and compressive strength of studied concretes. Red dots are low-packing concretes made from pure cement (paste); blue dots are high-packing concretes made from limestone-cement (paste)



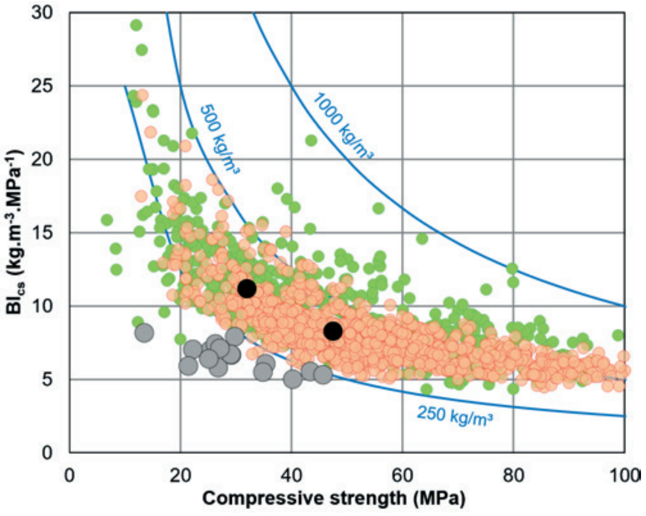


Figure 8
Correlation between paste porosity and BI of studied concretes. Red dots are low-packing concretes made from pure cement (paste); blue dots are high-packing concretes made from limestone-cement (paste)

Figure 9
Benchmark of the binder use efficiency found in the national literature (green) and international (red) [24]. The concrete measured in this study appears in grey (packing control particles) and black (conventional Brazilian design method)

Figure 7.a shows that concretes made with cement-filler pastes (high-packing), when compared to concretes with pure cement pastes (low-packing), can achieve similar paste porosity with a much lower cement content. From this observation, it is a consequence that they can achieve the same compressive strength using a lower cement content, as shown in Fig. 7.b. On both graphics, the presence of two very distinct groups is clear – the high-packed (blue) and the low-packed (red). The packing of particles was responsible for the changes in the correlations between paste porosity x cement content x compressive strength since it allows the mixing of the concretes with lower cement content using the same or lower water content. Equation 9 shows that paste porosity – which commands compressive strength – is much more influenced by a low water content (decreases total water in the denominator, by a factor of 1) than a high cement content (increases the combined water by 0.23). Figure 8 shows that BI is lower for the packed concretes compared to non-packed concretes with similar paste porosity.

Figure 9 presents data for the BI benchmark shown in [25] with inclusion of the results presented in this paper. In general, designed concretes (gray dots) showed BI lower than data found in the national literature (green dots) – with the exception of two points of the dosage by the conventional Brazilian method (black dots), which get confused with the rest of the concrete found in the benchmark, with less efficient binder use.

5. Conclusions

Even with actions by the cement industry to reduce the specific emissions of CO_2 in production, an increase in total emissions is expected due to expected increasing production. A promising strategy is to increase the use efficiency of the cement and other binders in the concrete, which means designing concrete with lower consumption and achieving the same performance.

This article demonstrated how packing and dispersion of particles may help increase the efficiency of use of binders in concrete. Concrete designed with lower intergranular voids (between particles) has been found to have water content reduced even with the same flowability in the fresh state, or, using the same water content, obtain higher flowability – less water is used to fill the voids, more water remains active for detaching particles effectively.

Reference concrete with dispersant, for example, used the same 160 litres of water (L/m^3) as the C01, C03, C04, C07 and C09, but obtained a slump of 230 mm while all others obtained slump of 270-280 mm and spreading 600-670 mm, due to the void content of 22.9% of reference concrete against values between 4-6.5% of the others. The possibility of decreasing the water content to obtain the same fluidity allows: 1) a reduction of the w/c ratio, consequently increasing the compressive strength; or 2) a replacement of part of the cement by filler (lower water content and lower cement content, maintaining w/c and compressive strength unchanged). In both cases, there is a decrease in the Binder Index (BI). In the same concretes compared above, there is an approximate reduction of the BI from 8 $kg \cdot m^{-3} \cdot MPa^{-1}$ (reference) to 5.3-6.5 (other), that is, an approximate reduction of 18-33%, which means an increase in eco-efficiency.

Moreover, the complete dispersion of particles also showed the request for lower water content to achieve the same or higher flowability with the same resulting efficiency gains.

The strategy – increasing the efficiency of use of water and binder – can be used together with other strategies that have been consolidated, such as clinker replacement by mineral admixtures to mitigate CO_2 emissions. Their combination could amplify the benefits, because in the end the final clinker content would be a multiplication of both factors (total clinker reduction in the paste plus total paste content reduction).

The particle packing tool is an application of a concept of particle physics on concrete. The interaction of this tool with established dosage methods, such as the reference method used in this work, can be useful for the design of more efficient large scale concretes, since it could introduce the control of intergranular porosity through calculations from the data of the raw materials (without the need to carry out experiments of experimental determination of the packing). This property would be highly important, since the experimental determination of the packing (also possible) requires a time that may be unviable on the scale of application of the concrete. Due to the size of the concrete production chain, a more sustainable future depends on the improvement of the dosages with emphasis on the speed and ease of application, as well as on the interaction between different clinker reduction strategies.

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