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ORIGINAL ARTICLE

Mechanical performance and chloride penetration resistance of concretes with low cement contents

Desempenho mecânico e resistência à penetração de cloretos de concretos com baixo teor de cimento

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Abstract: The concern about the environment has been leading the construction industry to adopt more sustainable practices. The main environmental impact of concrete is related to CO$_2$ emissions coming from cement, particularly from the cement content in concrete. For this reason, this research evaluates the performance of concretes with partial replacement of Portland cement by limestone filler and silica fume. These concretes were proportioned to improve particles' packing and paste volume optimization. The compressive strength was determined to assess their mechanical performance. Their durability was investigated by capillary absorption and chloride penetration resistance. Results indicate that concretes showed a better efficiency in terms of binder intensity, with values close to the minimum found in literature (5 kg.m^{-3}.MPa^{-1}). It was also observed that even concretes with cement content lower than the minimum recommended by standards showed better performance than regular concretes regarding the chloride's penetration.

Keywords: ecoefficient concrete, low binder concrete, limestone filler, durability, chloride resistance.

Resumo: A preocupação com o meio ambiente vem impulsionando a indústria da construção civil a adotar práticas mais sustentáveis. Seu maior impacto ambiental está relacionado com a emissão de CO$_2$ do cimento, particularmente do teor de cimento no concreto. Por isto, essa pesquisa avalia o desempenho de concretos com substituição parcial do cimento Portland por fíler calcário e sílica ativa. A dosagem desses concretos foi realizada utilizando conceitos de empacotamento e otimização da pasta. Foi realizado ensaio de resistência à compressão para verificar o desempenho mecânico desses materiais. A durabilidade foi analisada por ensaios de absorção por capilaridade e pela resistência à penetração dos cloretos. Os resultados indicam que os concretos otimizados, apresentaram melhor eficiência segundo o indicador Intensidade Ligante (IL), com valores próximos aos mínimos encontrado na literatura (5 kg.m^{-3}.MPa^{-1}). Foi verificado também que mesmo concretos com consumo de cimento inferior ao recomendado por normas, apresentaram desempenho superior aos concretos convencionais, quanto à penetração de cloretos.

Palavras-chave: concreto sustentável, concretos com baixo teor de cimento, fíler calcário, durabilidade, resistência à cloretos.

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1 INTRODUCTION

The population growth has led to an increase of the demand for dwellings and infrastructures and, as a consequence, for construction materials, especially concrete [1]. Over the past 10 years, the global Portland cement manufacturing grew by approximately 25% [2]. Cement production is expected to increase even more, between 12% and 24% [3]. Undoubtedly, this increase will impact in terms of energy consumption and CO_2 emissions [4].

Due to the increasing of CO_2 emissions from large-scale cement production, the Cement Industry focused on different CO_2 mitigation strategies, including the use of alternative materials in the cement composition [1]. The most common strategy for reducing the environmental impacts of cement is the replacement of clinker by mineral additions, reactive or non, such as fly ash, blast furnace slag, and limestone filler [5], [6]. However, the limited availability of fly ash and blast furnace slag, which will represent less than 20% of global cement demand by 2050, is a significant factor to consider [1], [7]. Therefore, due to the lower availability of these reactive materials, there should be a preference for inert materials such as limestone filler, with greater availability [8]. This strategy together with the reduction of cement content in concretes would facilitate the production of more sustainable construction materials [5], [8], [9]. Nevertheless, improving the durability of low binder concretes is essential to reduce the maintenance cost and increase the service-life of the concrete structures [9].

Improving the durability of low binder concretes requires an adequate mix design to allow balancing the reduction of binder and its effect against environmental aggressive agents which can induce corrosion of reinforcement.

1.1 Mix proportioning of low binder concretes

Supplementary cementitious materials (SCMs) used as clinker replacement influence the particle packing and the water demand of the mixture. The water demand is influenced by the specific surface area of these SCMs, usually higher than that of cement [10], [11]. They also contribute to the formation of nucleation points that lead to a faster hydration rate [12].

Superplasticizers are used to reduce water demand and promote the dispersion of solid particles [13]. The use of mineral additions and dispersants compensates for the cement reduction maintaining the desired workability of the mixture.

Optimizing the aggregates packing, by theoretical models [14] and/or experimental tests [15], is also needed. This process allows working with a lower volume of interparticle voids to be filled by a volume of cement paste necessary to guarantee the workability. Therefore, reducing the interparticle porosity enables reducing the paste volume [16]–[19] and also, reduce the porosity, increase the mechanical performances [20] and improve the durability.

1.2 Durability of low binder concretes and reinforcement corrosion

Corrosion of steel in concrete initially involves the transport of aggressive agents into its interior. When these agents reach the reinforcement, they can change the equilibrium conditions of the steel, and the corrosion process starts, followed by the corrosion propagation phase [21].

The corrosion initiation period is considered the period from the time when the aggressive agents penetrate the concrete until the reinforcement depassivation occurs. The duration of this initiation period defines the service-life of structures in the marine environment, as corrosion rates are usually very high [22]. Reducing the material porosity can hinder the entry of aggressive agents and increase the initiation period.

Standards establish minimum or maximum parameters for concrete according to the exposure environment of the structure, aiming to improve the durability of concrete structures. Table 1 presents some of these specifications considering national and international standards for reinforced concrete structures located in the marine atmosphere, where chlorides ions are mainly responsible for the reinforcement corrosion.

Table 1. Requirements for concrete in marine atmosphere zones - data from national and international standards

Standard	Exposure condition	Minimum cement content (kg/m^3)	Maximum w/c	Minimum compressive strength (MPa)
NBR 12655 [23]	Marine atmosphere zone (III)	320	0.55	30
ACI 318 [24]	Exposed to moisture and an external source of chlorides (C2)	-	0.4	34.5
IS 456 [25]	Marine aerosol (IV)	340	0.45	-
NP EN 206 [26]	Exposed to airborne salt but not in direct contact with sea water (XS1)	300	0.5	30
BS 8500 -1 [27]	Exposed to airborne salt but not in direct contact with sea water (XS1)	340	0.5	35
AS 3600 [28]	Within 1 km from coastline (B2)	-	-	40

Although the normative recommendations indicate a cement consumptions above 300 kg/m^3 (Table 1), some studies suggest that concretes with cement content lower than this amount meet the durability requirements recommending a revision of these criteria [5], [15], [29], [30].

Table 2 presents results of a few studies related to concretes with low binder content that evaluated properties linked to the corrosion of reinforcement. It is easier to see the positive impact on the performance of concrete when a reactive addition is used. However, it is also possible to improve the concrete performance replacing binders by inert fillers. In this regard, there is still no agreement in the literature on the levels of binder replacement. In addition, analysed studies show that there is also no standardization on the best way to assess the transport of chlorides into these materials.

For these reasons, more studies about the assessment of performances of low binder concrete in protecting steel from corrosion are needed. Therefore, the objective of this work is to assess the transport of chlorides in low binder concrete, in which binder was replaced by limestone filler.

Table 2. Literature data on concrete with low cement consumption - mechanical strength and chloride transport

Reference	Year	Cement type	Uses particle size optimization concepts	water/fines	Water/binder	Cement content (kg/m^3)	Fly Ash content (kg/m^3)	Slag content (kg/m^3)	Limestone powder content (kg/m^3)	Quartz powder content (kg/m^3)	Compressive strength (MPa)		Rapid chloride migration (C)	Non-steady-state migration coefficient (x10^{12} m^2/s)		
											28 days	91 days	91 days	28 days	35 days	98 days
Naik et al. [31]	1996	Type I - ASTM C 150 (correspond to CP I NBR 5732)	N/A	0.31- 0.36	0.31- 0.36	375- 398					53.2- 60.7		1729- 2488			
				0.33- 0.37	0.33- 0.37	220- 328	71- 182				41.7 -56.7		1576- 1907			
				0.33- 0.37	0.33- 0.37	107- 179	216- 316				29.2 - 39.8		1620- 2750			
Isaia and Gastaldini [29]	2009	CP V- ARI NBR 5733	N/A	0.35- 0.55	0.35- 0.55	309- 540						46.1- 72.4	2380- 3134			
				0.35- 0.55	0.35- 0.55	155- 270	155- 270					25.4- 59.1	754- 1190			
				0.35- 0.55	0.35- 0.55	93- 162		216- 378				32.6- 49.1	840- 1140			
				0.35- 0.55	0.35- 0.55	31- 54	61- 108	216- 378				20 - 46.1	448- 651			
Lollini et a l. [32]	2014	CEM I 52.5R EN 197 (correspond to CP V – ARI)	Yes	0.42- 0.61	0.42- 0.61	300- 350					60 - 85	65 - 105		5- 12		
				0.42- 0.61	0.49- 0.72	212.5 - 340			37.5 - 60		45 - 85	55 - 95		11-19		
				0.42- 0.61	0.6- 0.87	210- 245			90 - 105		40 - 70	45 - 75		13- 38		
Müller et al. [9]	2014	CEM I 52.5R EN 197 (correspond to CP V – ARI)	Yes	0.26- 0.39	0.43- 0.69	112.8- 268.2				114.3- 216.4	48.5- 88			11- 20		
Palm et al. [33]	2016	CEM I 42.5 EN 197 (correspond to CP V – ARI)	Yes	0.5	0.5	320						54			17	13
		CEM II/A-LL 32,5R (Correspond to CP II-F NBR 11578)		0.5	0.5	320						52			25	15
		CEM I 52.5R EN 197 (correspond to CP V – ARI)		0.35	0.54- 1.0	133- 247			133- 247			40-80			19- 30	15- 18.5
				0.45	0.9	167.5			167.5			28-40			35- 50	21- 39
				0.5	1	160			160			30-38			48- 60	30- 50

2 MATERIALS AND METHODS

2.1 Production and characterization of concrete

Two groups of concretes, proportioned and tested in two laboratories, were analyzed. The first group (C1, C2, and C3) was characterized by a powder content of about 350 kg/m^3 in which limestone filler represented between 5 and 13% of the total powder mass; for the second one (C4, C5, and C6) the limestone content was between 40% and 70% by mass of powder (Table 3). The cement was a CP V – ARI (Portland cement with about 5%wt. of limestone), supplied by two manufacturers. A small amount of silica fume was used as cement replacement in concretes C2 and C3. Density and BET N_2 specific surface area of cements, fillers and silica fume are presented in Table 4.

The reference concrete (C1) was proportioned according to recommendations of NBR 12655 [23] for aggressiveness class III - marine atmosphere environment (Table 1). This concrete was proportioned to have a 28-days compressive strength $\geq$ 30MPa, a water-to-cement ratio of 0.55 and a cement content of 350 kg/m^3. In the other concretes, mineral additions were used partially replacing the Portland cement. The packing of the mixture was improved by blending fine and coarse aggregates with different grain size distributions. The concrete workability was adjusted by using water-reducer admixtures. It is noteworthy that for the C4, C5, and C6 concrete, the grain size distribution of aggregates, the volume of paste (cement + filler + water) were kept constant (Figure 1).

Table 3. Mix design of the cement reduced concretes.

Materials	C1	C2	C3	C4	C5	C6
Water (kg/m^3)	192.6	148.3	139.1	160	160	160
Filler 1 (kg/m^3)		12.1	24.5			
Filler 2 (kg/m^3)		12.1	24.5			
Filler 3 (kg/m^3)				139.84	139.84	139.84
Filler 4 (kg/m^3)				54.5	100.22	189.22
Silica fume (kg/m^3)		10	17.7			
Portland cement (kg/m^3)	350.1	319.5	284.7	300	250	150
Binder (clincker + gipsite + pozolana) (kg/m^3)	332.6	313.5	288.2	286	237.5	143
Polycarboxylate-based superplasticizer content (mass % of cement)	0.5	2.55	2.8	3.63	2.21	1.85
Lignosulfonate-based plasticizer content (mass % of cement)		1	1			
Fine sand (kg/m^3)		544.6	544.6	684.36	684.36	684.36
Coarse sand (kg/m^3)	903.6	445.6	445.6	634.78	634.78	634.78
Gravel 12.5 - 4.75 mm (kg/m^3)		449.2	449.2	535.13	535.13	535.13
Gravel 19 - 4.75 mm (kg/m^3)	983.8	548.2	548.2			
Total fines (kg/m^3)	350.1	353.7	351.4	480.38	477.56	472.07
Water/binder (kg/kg)	0.55	0.46	0.49	0.53	0.64	1.07
Water/fine (kg/kg)	0.55	0.42	0.4	0.33	0.34	0.34
Slump (cm)	12	15.5	7	SCC*	SCC*	SCC*

*Self-consolidating concrete.

Table 4. Physical characterization of fines.

Material	F1	F2	F3	F4	SF	Cem 1	Cem 2
Density (g/cm^3)	2.77	2.7	2.76	2.74	2.12	3.13	3.06
BET N2 SSA (m^2/g)	2.23	4.07	3.73	1.16	1.5	1.16	0.97

The optimization of the paste was achieved by reducing the cement and water content, increasing the proportion of filler and silica fume in some cases. The mixture C3 presents a reduction in cement content of 19% compared to C1. This reduction is 57% in C6, i.e., 30% Portland cement and 70% limestone filler (Figure 2).

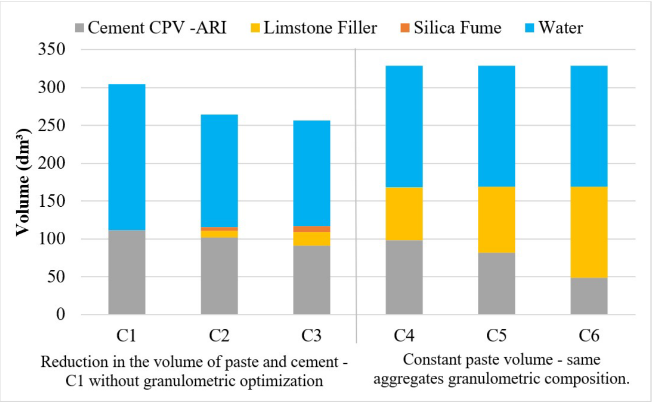

Figure 1. Volume of phases in cement paste.

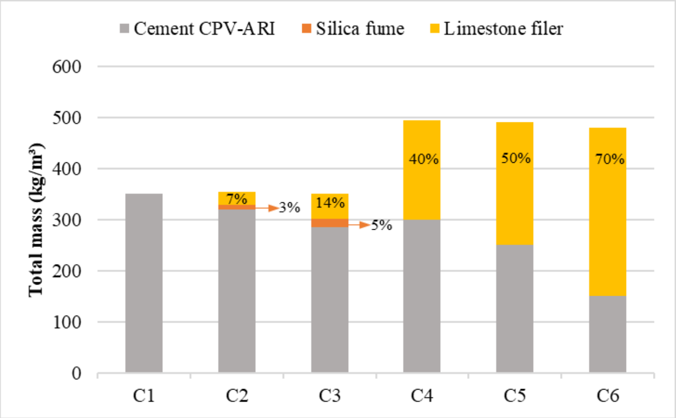

Figure 2. Amount of powder by mass per cubic meter in studied concretes. Percentages represent the filler and silica fume content by mass of powder.

After mixing, cylindrical specimens (ø 10 x 20 cm) were casted according to the recommendations of NBR 5738 [34]. Specimens were demolded after 24 hours and wet-cured for seven days. This period represents conditions closer to construction site reality. Then, specimens were stored in the laboratory environment until the age of the tests. Compressive strength at 28 days was carried out according to NBR 5739 [35] and sorptivity according to NBR 9779 [36].

2.2 Rapid Chloride Migration (RCM) test

The resistance to chloride penetration was analyzed using the rapid chloride migration test according to NT BUILD 492 [37]. The test specimens (ø 10 x 5 cm) cut from cylinders (ø 10 x 20 cm) were saturated in a calcium hydroxide solution before the exposure to the test.

During the test, the specimen was interspersed between a 10% sodium chloride solution by mass (used at the cathode) and a 0.3N sodium hydroxide solution (used at the anode). A voltage of 30 V was applied, which generated an initial current. According to its value, the applied voltage was adjusted to 50 V, and the duration of the test was determined (24h). The applied voltage makes the chlorides present in the cathode solution to migrate, through the specimen, towards the anode solution.

At the end of the test, the specimen was split by diametral compression and a 0.1M silver nitrate solution sprayed on the fractured surface. When the white silver chloride precipitation on the split surface is clearly visible, the chloride penetration depth can be measured (Figure 3).

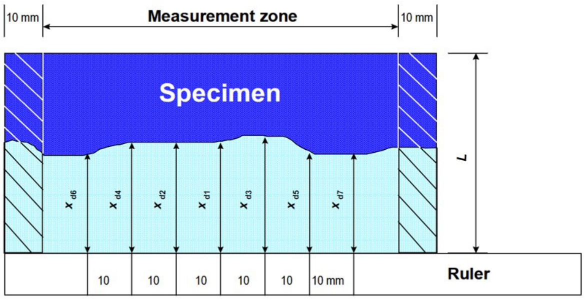

Figure 3. Illustration of the chloride penetration depth measurements [37].

The average chloride penetration depth x_d (mm) was measured and the non-steady-state migration coefficient was calculated by Equation 1.

$$D_{nssm} = \frac{0.0239\,(273+T)L}{(U-2)t}\left(x_d - 0.0238\sqrt{\frac{(273+T)Lx_d}{U-2}}\right) \qquad (1)$$

Where: D_{nssm} = non-steady-state migration coefficient, x 10^{-12} m^2/s; U = absolute value of the applied voltage, V; T = average value of the initial and final temperatures in the anolyte solution, °C; L= thickness of the specimen, mm; x_d= average value of the penetration depths, mm; t= test duration, hours.

According to the value of this coefficient, the concrete can be classified corresponding to its resistance to chloride penetration, based on the values (Table 5) proposed by Nilsson et al. [38].

Table 5. Classification according to resistance to chloride penetration

Diffusion coefficient (D_{28} x 10^{-12} m^2/s)	Resistance to chloride penetration
>15	Low
10-15	Moderate
5-10	High
2.5-5	Very high
<2.5	Extremely high

2.3 Rapid chloride permeability (RCP) test

Rapid chloride permeability (RCP) test according to ASTM 1202 [39] was performed at 28 days. For each mixture, three specimens (ø 10 x 5 cm) cut from cylinders (ø 10 x 20 cm) were tested.

Each specimen was placed between a 3% sodium chloride solution by mass and a 0.3 N sodium hydroxide solution. In each solution, a conductive plate was introduced and connected to a source of 60 ± 0.1 V. The test lasted 6 hours and electric current readings were taken every 30 min. The electric current multiplied by time, expressed in coulombs (C), represents the passing charge on the concrete, which indirectly indicates the resistance of concrete to chloride ions penetration, according to the classification presented in Table 6.

Table 6. Chloride Ion Penetrability Based on Charge Passed [39].

Charge passed (C)	Chloride ion penetrability
>4.000	High
2.000 – 4.000	Moderate
1.000 – 2.000	Low
100 – 1.000	Very Low
<100	Negligible

2.4 Unidirectional diffusion test

The unidirectional diffusion test, by the ponding method, was carried out in accordance with the EN 12390-11 [40]. Cylindrical specimens (ø 10 x 10 cm thick), extracted from prismatic ones, were tested.

Before starting the test, a slice 1mm-thick was used to determine the initial content of free and total chlorides. The following slices were used to determine these parameters over the specimen thickness.

Specimens, after being sealed by epoxy resin on the lateral surface, were saturated with deionized water and placed in a calcium hydroxide saturated solution for 18 hours. Then, a pond was placed to the cross surface of the specimen, sealed and filled with a 3% NaCl deionized water solution. Afterwards, the specimens were stored in a chamber (relative humidity ≥ 95%vol.) to avoid loss of surface moisture. After 90 days of exposure, eight successive and parallel layers were dryly ground from the specimen, starting at the exposure surface. Then, these samples were sifted and used to determine the chloride content by potentiometric titration by using an automatic titrator from Metrohm.

The chloride concentration in each layer enables the determination of the chloride profiles, from which the diffusion coefficient (D), and the surface concentration (Cs) for each analyzed concrete were determined by fitting the solution of the Fick's second law (Equation 2) to the experimental data.

$$\mathrm{C(x,t)} = C_s + (C_0 - C_s)\cdot\left[\mathrm{erf}\left(\frac{x}{2\sqrt{D_{nss}\cdot t}}\right)\right] \qquad (2)$$

Where: $C_{(x,t)}$ is the chloride content measured at average depth x and exposure time t, % by mass of concrete; C_s is the calculated chloride content at the exposed surface, % by mass of concrete; C_0 is the initial chloride content, % by mass of concrete; x is the depth below the exposed surface to the mid-point of the ground layer, m; Dnss is the non-steady-state chloride diffusion coefficient, m^2s^{-1}; t is the exposure time, seconds.

3 RESULTS

3.1 Compressive strength

Table 7 shows the average values of compressive strength at 28 days. Concretes C2, C3, and C4 had higher compressive strength than the reference concrete (C1). Despite a binder content 30% lower than C1, C5 achieved a comparable compressive strength. On the other hand, C6 concrete, with a cement content of 150 kg/m^3, had the lowest compressive strength.

The binder intensity (BI), the total amount of binder necessary to deliver one MPa of compressive strength [41], of the analyzed concretes were also calculated. Table 7 summarizes the BI of concretes.

Table 7. Compressive strength and binder intensity of the concretes.

Concrete	C1	C2	C3	C4	C5	C6
Binder content (kg/m^3)	332.6	313.5	288.2	286	237.5	143
Compressive strength at 28 days (MPa)	42.94	60.43	61.39	52.8	41.8	28.4
BI (kg.m-3.MPa^{-1})	7.75	5.18	4.69	5.42	5.68	5.04

This indicator was around 5 kg.m^{-3}.MPa^{-1} for concretes with low binder content and close to 8 kg.m^{-3}.MPa^{-1} for reference concrete. C3 obtained a reduction in BI of approximately 9.5% compared to C2 and 39.5% compared to C1. The C4, C5, and C6 concretes presented reductions in the binder intensity between 27% and 35% when compared to the reference C1.

Figure 4 presents the calculated binder intensity *versus* compressive strength of Brazilian concretes [41] and of those studied in this work. The greater the strength for the same binder content, the lower the BI, thus the efficiency, in terms of the use of binder is greater. Damineli [5] claims that the lower BI values of Brazilian concretes are linked to improved aggregate packing or the combination of a low water/cement ratio and superplasticizer. The results in this study corroborate this statement.

Concretes with low binder content were characterized by BI close to the minimum values found in literature, which are slightly lower than 5 kg.m^{-3}. MPa^{-1} for concretes strength classes higher than 40 MPa. However, C1 presents value within a typical range for usual concretes. C6 has a much lower BI than other concretes of the same strength class, demonstrating its efficiency.

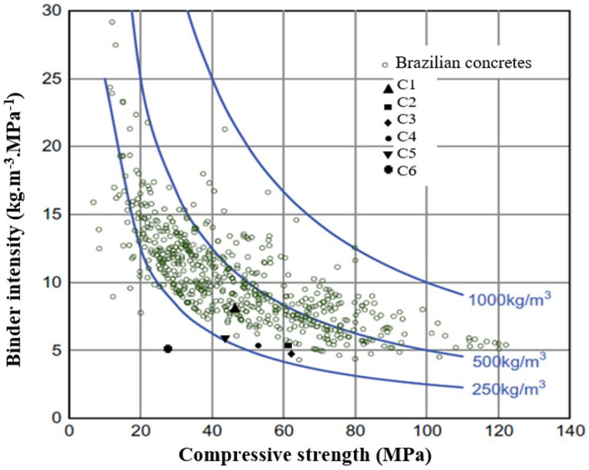

Figure 4. Binder intensity versus Compressive strength. Adapted from Damineli et al. [41].

3.2 Sorptivity

Sorptivity or capillary water absorption, expressed in g/cm^2, is a linear function of the square root of time (Figure 5). The capillary absorption coefficient (c) is represented by the slope of regression lines. Table 8 presents the values of 'c' and the maximum water penetration height.

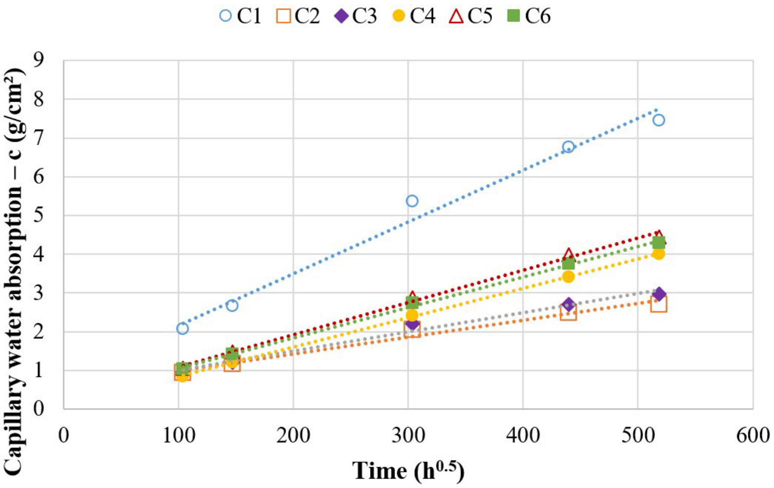

Figure 5. Capillary water absorption versus square root of time.

Table 8. Capillary absorption coefficient and maximum water penetration height.

	C1	C2	C3	C4	C5	C6
c (g/cm^{2}h^{0,5})	0.0829	0.027	0.0308	0.0474	0.0519	0.0492
I (mm)	7.46	2.70	2.97	4.01	4.46	4.29

The higher capillary absorption coefficient of C3 compared to C2 can be explained by its porous structure, which possibly has smaller pores, favoring faster capillary absorption. This same relationship may explain the higher coefficient of C5 compared to C4 and C6. The C1 absorption coefficient was much higher than that of optimized concretes, even though they probably have smaller pores. This is due to its void volume, which is much higher, and yet, it certainly has greater pores interconnectivity. It is also noteworthy that C6, even with lower mechanical strength than the reference concrete, had a lower absorption coefficient than C1 concrete.

3.3 Rapid Chloride Migration (RCM) test

Table 9 presents the values non-steady-state migration coefficient of concretes and the classification of resistance to chloride penetration according to Nilsson et al. [38].

C1 had a penetration depth of 30.2 mm, while C2 had a penetration depth of 15.3 mm and C3 of 7.3 mm (Table 9), which indicates a significantly higher resistance to chloride penetration of optimized concretes.

Table 9. Concretes non-steady-state migration coefficient

Concrete	Average penetration depth (mm)	Dnssm ($\times 10^{-12}$ m^2/s)	Resistance to chloride penetration
C1	30.2	21.76	Low
C2	15.3	5.19	High
C3	7.3	1.81	Extremely high

C1 obtained low resistance to chloride penetration, even meeting the parameters from compressive strength, cement consumption, and water/binder established by standards. C2 and C3 showed a better performance. This is an indicator of the concrete porosity reduction probably due to the particle packing optimization, the paste volume reduction, the correct dispersion of powders, and the contribution of silica fume. Furthermore, silica fume is efficient in reducing the interfacial transition zone (ITZ) thickness [42], which contributes to reduce chloride transport into concrete [43]. The amount of cement at C3 was 11% lower than C2. For this level of reduction, the small paste volume reduction, the porosity reduction due to the action of silica fume and the filler seems to compensate the possible decrease in binding capacity due to the decrease at Al_2O_3 content in concrete. The compressive strength results corroborate the above statement.

Lollini et al. [32], Müller et al. [9], and Palm et al. [33] assessed the transport of chlorides by the same migration test analyzing Portland cement concretes where binder was partially replaced by limestone filler. Figure 6 illustrates the migration coefficient as a function of the Portland cement content for the above-mentioned studies and the results of this research. From this Figure, it is possible to observe that the migration coefficient, in general, tends to decrease with Portland cement content. However, there are some points that do not follow this relationship and present an opposite behaviour. In general, the increase of cement content leads to more aluminates available to bind chlorides. In the specific case of Müller results, the opposite behaviour is related to the decrease of the water to binder ratio as cement content decreased. In this case, there seems to be a prevalence of this last effect.

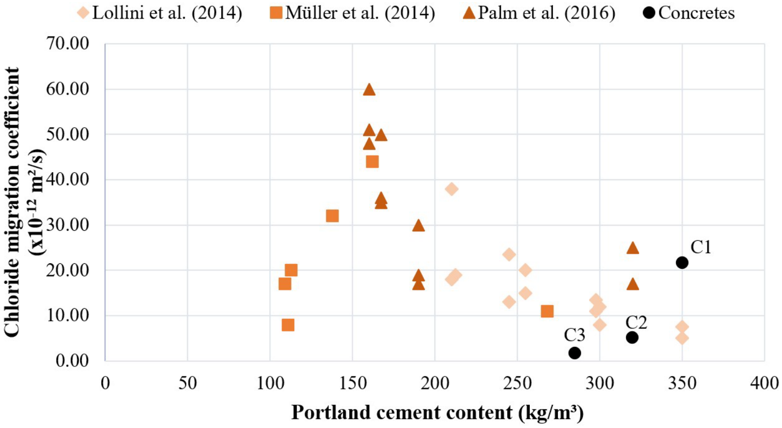

Figure 6. Chloride migration coefficient versus Portland cement content

The direct relationship between the chloride migration coefficient and the water/binder ratio (Figure 7) shows the effect of material porosity on the migration coefficient. In other words, porosity, and tortuosity of pores, obtained by particle packing optimization, seem to be more important than the amount of Portland cement. According to Ribeiro et al. [44] higher cement levels for concretes without additions and with the same characteristics (w/c, type of cement and mortar content) should favor an increase in durability (less diffusivity), as a result of the increase in the aluminate content in the mixture, originated from the Portland cement. However, this effect is less significant than the change of more representative parameters, mainly the water/binder ratio.

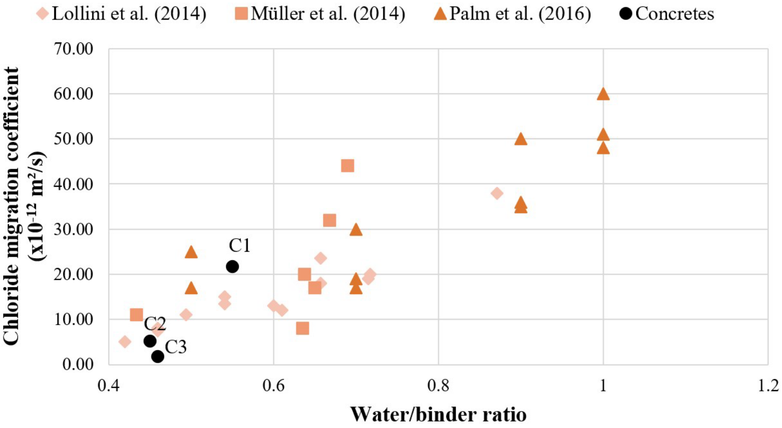

Figure 7. Chloride migration coefficient versus water/binder ratio.

3.4 Rapid chloride permeability (RCP) test

The values of passed charge and the classification for chloride penetration according to ASTM 1202 [39] are presented in Table 10. C4, C5, and C6, which were those submitted to this test, presented an increase in the charge passed as the replacement ratio increases. However, all of them met the moderate condition of resistance to chloride penetration.

Table 10. Results of charge passed and chloride ion penetrability

Concrete	Charge passed (C)	Chloride ion penetrability
C4	2235.00	Moderate
C5	2906.76	Moderate
C6	3534.27	Moderate

Figure 8 illustrates the values of the charge passed as a function of the concrete binder content. The dotted lines represent the limit for the charge passed values to classified chloride penetration resistance according to ASTM 1202 [39]. The values found in the literature refer to concretes without mineral addition subjected to the same test conditions as the concretes studied in this research. The Portland cement content in these concretes ranged from 260 kg/m^3 to 550 kg/m^3. The concretes that showed low penetration to chlorides had a water/cement ratio ranging from 0.28 to 0.38 [45]–[47]. Despite having parameters close to these, concretes with a water/cement ratio of 0.35 to 0.40 and cement content of 450 kg/m^3 [48] to 500 kg/m^3 [49] presented moderate chloride penetration resistance. Concretes studied by Das et al. [50], with cement contents from 300 kg/m^3 to 360 kg/m^3 and water/cement ratio from 0.4 to 0.55 were within this same class.

In this research, concretes with low cement contents had a similar or better performance than concretes with higher cement contents. For instance, the concrete C6, which had 70% of the fines constituted by limestone filler, presented a charge passed value comparable to that of concrete with a cement content of 300 kg/m^3. Based on this test, although the reduction of cement content leaded to an increase in the total passed charge, this increase was not enough to change the level of chloride ion penetrability according to ASTM 1202 [39] classification. From a practical point of view and considering only this test, the mixture optimization including cement replacements up to 70% by lime filler was not enough to significantly compromise the performance of concretes, remaining them at the same level of chloride ion penetrability.

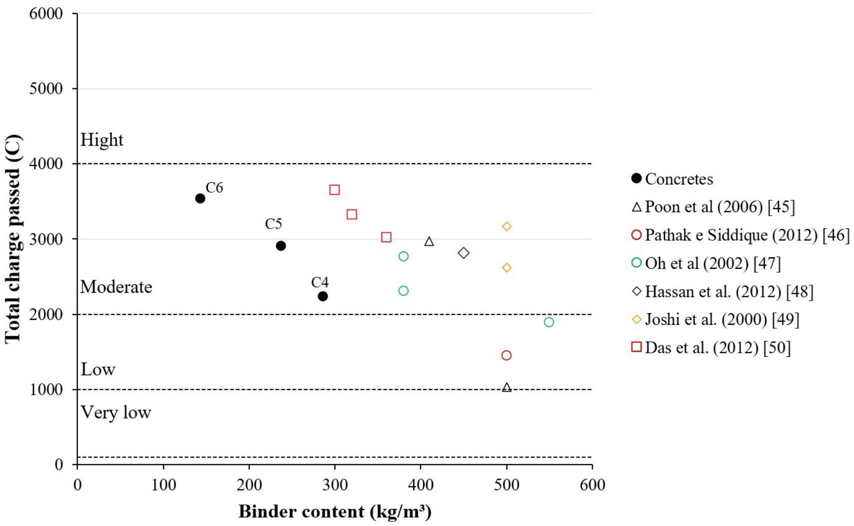

Figure 8. Charge passed versus binder content

3.5 Unidirectional chloride diffusion test

The chloride diffusion test was performed on concretes C4, C5, and C6. The chloride concentration profiles were used (Figure 9) to determine the diffusion coefficients (D) and the surface concentrations (Cs) applying the solution of the 2nd Law of Fick (Table 11). Variations in chloride concentration are expected and are related to the difference in the amount of aggregates present in each sample layer.

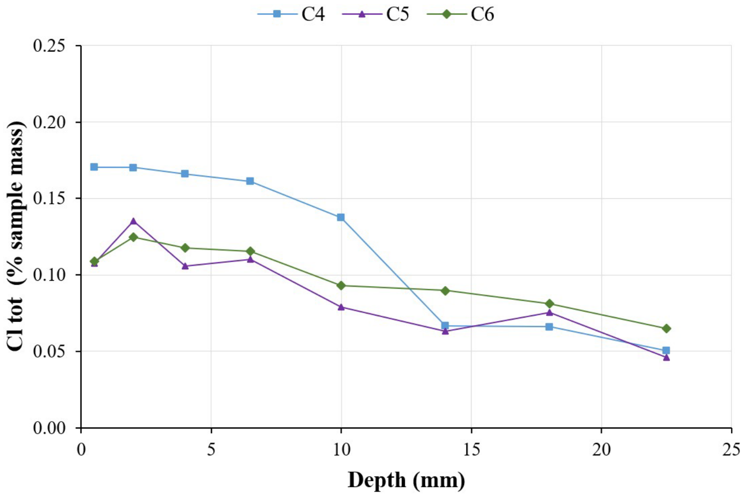

Figure 9. Chloride content as function of the depth from the exposed surface.

Table 11. Concrete transport parameters

Concrete	Non-steady-state chloride diffusion coefficient (x 10^{-8} cm^2/s)	Cl Surface concentration (%sample mass)	Cl Total concentration (%sample mass)
C4	10.44	0.1891	0.1125
C5	10.77	0.1272	0.0844
C6	35.51	0.1248	0.0959

The concrete C4 had the lowest apparent diffusion coefficient. In other words, the chlorides transport into its interior is slower than in the others. However, the surface concentration, which represents the availability of ions to penetrate the concrete and the average total concentration of chlorides, was higher in this concrete. This is probably a result of the better chloride binding due to its higher cement content. The apparent diffusion coefficient of C5 was slightly higher than that of C4. C5 has 17% less cement content than C4, which seems to be compensated by a performance filler that changes the pores network structure. Whereas the C6, which has 50% lower cement content than C4, had a much higher coefficient. This result indicates that, in this case, the contributions of performance filler is not enough to compensate the reduction on aluminate content in the mixture, due to the lower Portland cement volume in the mixture.

Figure 10 shows results of the diffusion coefficient as a function of the cement content; experimental data were plotted together with literature data [51]–[53] related to concretes tested under the same conditions.

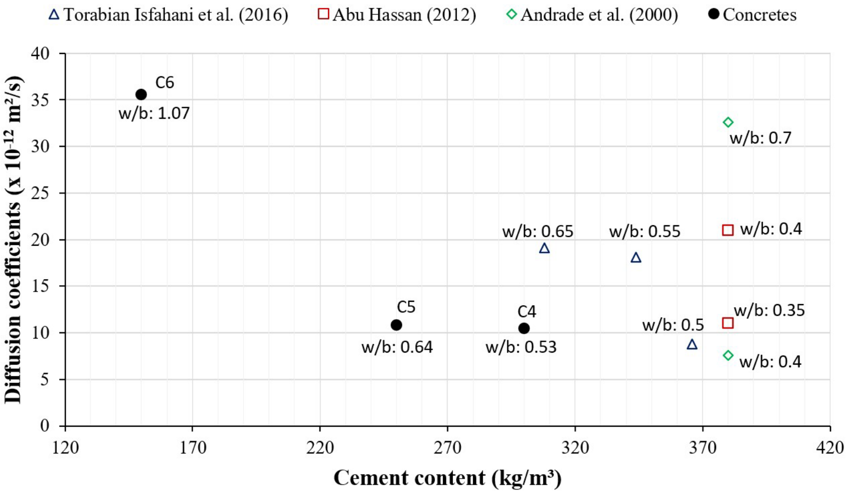

Figure 10. Diffusion coefficients – experimental and literature results; labels represent the water/cement ratio.

The results showed that the C4 and C5 presented a chloride diffusion coefficient close to the minimum obtained by Abu Hassan [52] which was 11 x 10^{-12} m^2/s, and slightly higher than the minimum obtained by Torabian Isfahani et al. [51], 8.8 x 10^{-12} m^2/s, and Andrade et al. [53], 7.6 x 10^{-12} m^2/s. The C6 had the highest coefficient value. It is noteworthy that this was close to that obtained by Andrade *et al.* [53], with was 32.6 x 10^{-12} m^2/s, for concrete with a cement content of 380 kg/m^3 and factor w/c = 0.7.

It´s known that the aluminate content in the mixture and the porosity of concrete are fundamental parameters in the control of chloride diffusion [44], [54]. Comparing the results of the optimized concretes with those from literature, the results show that the lower chloride binding capacity can be compensated using particle packing optimization to change the concrete pores network structure in concrete with low cement content until certain levels. Thus, it is possible to point out that the optimized concretes were able to meet the usually required durability properties with lower cement content.

Comparing RCP and Dns results, although it is possible to see increasing tendencies of passed charge and Dns with reducing cement content, there are differences respect to each test that impact in each data set behaviour. RCP is a fast test and conceals the Joule effect, which makes more difficult to bind more chlorides in cement paste phase. On the other hand, natural diffusion test, that is a longer test, contributes to make more evident the binding differences among C4, C5 and C6.

4 CONCLUSIONS

The Binder Intensity showed that low cement content concretes, which were proportioned to improve particles' packing and paste volume optimization, perform better than the conventionally proportioned concrete from a mechanical point of view, reaching values close to the minimum found in literature (5 $kg.m^{-3}.MPa^{-1}$).

The sorptivity test proves the modification of the microstructure, i.e., pores network, due to the particle packing optimization. The reference concrete, C1, showed higher water absorption by capillary action, indicating its higher porosity and probably less durability when exposed to aggressive agents.

The rapid chloride migration test verified that on one side the reference concrete obtained low resistance to chloride penetration, still meeting the standard requirements. On the other hand, C2 and C3 concretes showed higher resistance to chloride migration.

The rapid chloride permeability test and the unidirectional chloride diffusion test showed that C4, C5, and C6 had a performance that can be classified at a similar level of most conventional concretes found in literature.

As it can be seen from the results, the particle packing optimization and the reduction of water volume in the concrete mixture using a superplasticizer allows reducing the Portland cement content without compromising the chloride resistance. These optimized concretes may possess acceptable durability when they are subjected to aggressive exposure conditions, however research and experimental data on this field are still needed.

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