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REDUCING CONCRETE PERMEABILITY BY USING NATURAL POZZOLANS AND REDUCED AGGREGATE-TO-PASTERATIO

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Abstract. Improved durability of concrete is mainly achieved with low-permeability. Permeability depends on permeability of the bulk cement paste (CP) and that of its interfacial transition zone (ITZ). Even though permeability of CP is well understood and can be adequately controlled, permeability of ITZ is not well understood yet. This paper shows that minimizing permeability of concrete requires minimizing permeability of CP by using a supplementary cementing material (SCM) such as natural pozzolans (NP) and minimizing ITZ by reducing aggregate content until maximum cement content. This was done by comparing performance of concrete made with ordinary Portland cement (OPC) and blended cement (OPC+NP) at the same w/b, and by comparing performance of concrete with different amount of ITZ at the same w/b. All of this was performed through testing of mechanical properties, air permeability, sorptivity, chloride ion diffusion, and aggregate specific surface. Results show that NP reduced air permeability by 84% and chloride ion diffusion by 66%, but increased sorptivity up to 140%. ITZ has an important effect in all properties; especially in air permeability where sensitive reduction of more than a 90% was achieved. ITZ effect seems to be as important as using SCMs in improving durability of concrete.

Keywords: durability, natural pozzolans, transport mechanisms, air-permeability, sorptivity, chlorides.

Introduction

Relevance of durability

Sustainability one of the most important challenges that construction industry faces nowadays, and it is still not clear how to specify structures for sustainability. Over-specification is both wasteful and unfair to the client while under-specification leads to premature and costly repair work (Richardson 2004), and neither of these practices are sustainable. Further, deterioration of materials makes structures unsafe which also poses a sustainability concern. Durability of materials, specifically that of reinforced concrete, has gained a main role in advancing sustainable construction by increasing safety and reducing maintenance and rehabilitation of structures (Shen *et al.* 2007). Nevertheless, specifications for durable concrete are still a challenge.

Compressive strength is the main, and most of the time the only, property used to specify hardened concrete. Therefore, traditionally mixture designs focus on achieving the specified strength without considering other concrete properties affecting durability (Mindness 2005) and these can be as important as compressive strength.

Although compressive strength and durability depend on similar factors, achieving one of them does not guarantee achieving the other, so special care needs to be taken to achieve both (Hooton 2006). Since there is no a recipe to ensure durability (Neville 2001), there is the need to investigate different ways to improve concrete durability without affecting compressive strength.

Even when some designers are more aware of the importance of evaluating durability of structures to ensure the mechanical properties during service life and to estimate the actual cost of the structure (Mehta, Monteiro 2006), contractors usually do not have a thorough knowledge about how to ensure durability. The problem becomes more complex because the information from durability tests is fragmented and cannot be easily synthesized to understand durability from a broad point of view (Mehta 1991).

Four deleterious agents have been identified as critical to concrete durability because their potential to produce corrosion in reinforced concrete. They are: water, chlorides, carbon dioxide, and oxygen. Thus, the ease with which these agents enter into and move through concrete, referred to as permeability (Neville 2004), needs to be measured to assess concrete durability.

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It is well accepted that permeability is a good indicator of durability potential (Bentz 2002).

Permeability of concrete is adequately explained by the transport processes in concrete which are mainly four: (1) transport of water under a hydrostatic pressure head; (2) transport of water by capillary suction; (3) diffusion of ions under a concentration gradient; and (4) transport of ions by moving fluid (Alexander 2005; Garboczi 1995).

Concrete permeability testing cannot be replaced by using the many probabilistic models developed to explain concrete deterioration, as proposed by Ferreira (2010) and by Kliukas and Kudzys (2004), despite their recent considerable improvements.

Supplementary cementing materials (SCMs) in durability of concrete

The addition of SCMs is an effective way to decrease permeability of concrete (CEB 1997; Mehta, Monteiro 2006; Neville 2004). Silica fume and fly ash are among the most widely used SCMs, but natural pozzolans have proven to greatly impact concrete performance (CEB 1997).

Pozzolans are natural or artificial materials containing silica in a reactive form (Neville 2004). Pozzolans react with the calcium hydroxide, derived from cement hydration, and water forming new calcium silicate hydrates (C-S-H) that increase compressive strength and reduce permeability.

The use of SCMs have proven to improve durability of concrete and provide additional benefits such as improvement in workability, reduction of the heat of hydration, reduction in permeability, increase in ultimate strength, increase in resistance to sulphate attack, and reduction in alkali-silica reaction (Rodríguez-Camacho, Uribe-Afif 2002; Uzal, Turanli 2003; Papadakis, Tsimas 2002).

Among many types of SCMs, natural pozzolans have gained more attention lately because they might be widely available, such as some clays and volcanic ashes. These materials do not depend on other industries, unlike SCMs such as silica fume, fly ash and ground granulated blast furnace slag.

As with other SCMs, the use of natural pozzolans modifies concrete microstructure, improving concrete properties such as strength and permeability (Colak 2002; Sabir *et al.* 2001). Even more, the improvement in permeability appears to be very significant when compared to that in strength (Lopez, Castro 2010).

Factors affecting permeability

Permeability of concrete depends on the permeability of the cement paste, aggregate, and interfacial transition zone (ITZ). However, according to many (for example, (Richardson 2004), permeability of concrete is predominantly controlled by the permeability of cement paste and that of ITZ. For porous and permeable aggregates, hydration products can penetrate superficial pores "sealing" the aggregate and restricting the overall permeability to that of the cement paste or ITZ. For non-porous aggregates the tortuosity of the pore structure increases drastically, decreasing intrinsic permeability to values lower than that of cement paste or ITZ (Carcasses, Ollivier 1999).

Water-to-binder ratio by weight (w/b) appears to be the main factor controlling permeability of cement paste (CEB 1997; Neville 2004), since it determines the initial space between unhydrated cement and the porosity and ultimately depercolation of pore structure (Powers *et al.* 1959; Powers 1960).

Mixing water is indirectly responsible for the permeability of hydrated cement paste (Mehta, Monteiro 2006), since it determines total and unfilled space in the cement paste microstructure after water has been consumed either by cement hydration or by evaporation. Thus, lower mixing water contents will decrease permeability of cement paste. On the other hand, very high cement contents do not necessarily decrease permeability; there seems to be an optimum cement content for decreasing permeability (Zhang, Gjorv 1991), since increasing cement content makes concrete more prone to heating and thermal cracking.

Microcracks, normally present in the ITZ, increase permeability of concrete above that of the corresponding cement paste. From this perspective, ITZ effects on permeability become more important as aggregate volume increases (Carcasses, Ollivier 1999).

The relevance of the ITZ on permeability of concrete is not only explained by microcracks, but also by differences in microstructure with the bulk cement paste. For instance, it has been established that the thin water film formed around large aggregate particles increases w/b locally producing a weaker and more permeable zone with respect to bulk cement paste (Mehta, Monteiro 2006). For instance, Bourdette *et al.* (1995) measured very high porosity at the ITZ concluding that it plays an important role in the ion diffusion process. Additionally, another study focused on cement paste and mortars (Tumidajski 1996), observed that the conductivity of the system decreases more or less linearly with an increase in the volume fraction of the aggregates. Accounting the dilution effect of aggregates, Tumidajski concluded that the ITZ had very little effect on the electrical conductivity of the overall system for an aggregate-to-mortar ratio over 0.1. Oppositely, Ping *et al.* (1991a) used the same technique to obtain results suggesting that the ITZ had an important effect on both the electrical conductivity and permeability.

Another study (Mills 1987) concluded that for a given strength and workability (i.e. constant w/b), permeability decreases as cement content decreases because the initial amount of mixing water determines the total porosity of the system. Such results may be explained based on the low w/b and superplasticizer that make ITZ microstructure very similar to that of the bulk paste (Carcasses, Ollivier 1999).

One possible explanation to the opposing conclusions above is that the effect of the aggregate on concrete transport properties cannot be solely evaluated by simply accounting for the dilution effect; according to Carcasses and Ollivier (1999), from the model developed by Garboczi (1995), dilution, tortuosity and the intrinsic influence of porous ITZ appears to be all important in determining permeability of concrete. This is consistent with the conclusions obtained previously (Bourdette *et al.* 1995); that is, tortuosity of ITZ tends to have greater influence on the transport properties than the connectivity of the ITZ.

Igusa (Carcasses, Ollivier 1999), using a three-phase model demonstrated that permeability of ITZ is higher than that of bulk cement paste by estimating the following properties for ITZ: thickness of 20 microns, conductivity being 6 times greater than that of cement paste, and porosity being 1.7 times greater than that of cement paste.

Ping *et al.* (1991b), using quartz and limestone aggregate, determined that the thickness of ITZ decreases when reducing the maximum size of the aggregate. The ITZ using both types of aggregate was less dense than that of the bulk paste, but when using limestone, there was a critical particle size value below which ITZ becomes denser than the bulk paste. This was significant for aggregate sizes below 0.19 mm.

Overall, it can be stated that the use of natural pozzolans can be beneficial in decreasing permeability of cement paste and concrete, but controlling the permeability and amount of ITZ could be even more beneficial. Thus, assessing the amount of ITZ is necessary to estimate or understand its effect on permeability of concrete and to obtain a mixture design for low permeability.

1. Research significance

SCM are widely used as a cement replacement nowadays and their influence on durability has been extensively studied. However, there are few studies using natural pozzolans, despite their widespread use as an SCM in many countries. This paper assesses the effect of natural pozzolans on durability of concrete by measuring air permeability, sorptivity and chloride ion diffusion; In addition, it assesses the effects of ITZ on the transport properties of concrete by using different aggregate-to-paste ratios, at the same w/b. Stereology was used to determine the specific surface of aggregate, and estimate the potential amount of ITZ, to ultimately describe the effect of ITZ in permeability of concrete. It was of interest to determine the relative importance of the effect of natural pozzolans and ITZ.

2. Experimental method

The experimental program considered the fabrication of four mixtures for assessing the influence of natural pozzolans and ITZ on the permeability of concrete. Permeability was evaluated by measuring transport properties with specific methods: sorptivity controlled by water capillary suction, air permeability, and chloride penetration test controlled by chloride ion diffusion. This approach aimed to assess transport properties of concrete in both: 1) in an unsaturated pore system where sorptivity and gas diffusion may dominate; and 2) in a saturated pore system, at normal pressure, where chloride ion diffusion is the predominant transport mechanism (Zhang, Gjorv 1991). ITZ, on the other hand, was assessed based on the surface density of the aggregate by using stereology and microscopy.

2.1. Materials and mixtures

OPC and blended cement (OPC with natural pozzolans) were used in the trial mixtures. The coarse aggregate had a saturated surface dry (SSD) density of 2585 kg/m^3 and absorption of 1.4%, and the fine aggregate has a SSD density of 2810 kg/m^3 and absorption of 1.1%.

The effect of natural pozzolans in transport properties was assessed by comparing the performance of two concrete mixtures; C1 and C2. Both had the same mixture proportions, w/b of 0.5, with the only difference being the cement type: C1 used OPC and C2 used blended cement consisting of 62% OPC and 38% natural pozzolans. The effect of ITZ in transport properties was assessed by comparing the performance of three mixtures: C2, C3, and C4. All of them with the same blended cement, w/b of 0.5, with the only difference being the aggregate-to-paste ratios by volume (a/cp): C2 had a a/cp of 2.57 (335 kg/m^3 of cement), C3 had a a/cp of 3.35 (270 kg/m^3 of cement), and C4 had a a/cp of 1.94 (400 kg/m^3 of cement). Mixture designs are summarized in Table 1.

2.2. Test methods

Compressive strength, splitting tensile strength, modulus of elasticity, sorptivity, air permeability and chloride ion diffusion were measured at different ages. The surface

Table 1. Concretes mixture design (amounts in kg per cubic meter of concrete)

Concrete	C1	C2	C3	C4
Material	Weight (kg)	Weight (kg)	Weight (kg)	Weight (kg)
Cement	335	335	270	400
Water	167.5	167.5	135	200
Coarse Aggregate	1130	1109	1202	1024
Fine Aggregate	753	739	801	682
Superplasticizer	2.3	3.0	0.4	0.5
w/b	0.5	0.5	0.5	0.5
Aggregate content by volume (%)	71	69	75	64
Paste content by volume (%)	29	31	25	36

density of the aggregate for all mixtures was measured from an unbiased stereology technique.

Compressive strength was measured on 100×200-mm cylinders according to ASTM C39 / C39M – 10 at the age of 4, 7, 28, 90 and 150 days. Splitting tensile strength was also measured on 100×200-mm cylinder according to ASTM C496 / C496M – 04e1 at the age of 28, 90 and 150 days. Modulus of elasticity was measured on 150×300 mm cylinders according to ASTM C469 / C469M – 10 at the age of 28, 90 and 150 days.

Sorpitivity was measured on 100×50-mm cylinders according to ASTM C1585-04 at age of 28 and 90 days. The test consists of measuring the change in mass with time of a concrete specimen, previously dried at 50±2 °C and 80% relative humidity. One flat side of the specimen is exposed to water which produces a change of mass by capillary suction. Water loss is prevented by sealing the other sides and of the specimens by a plastic bag to avoid water evaporation. Figure 1 shows a schematic of the test.

Data collected during the first 6 hours of the test correspond to the "initial absorption" while that collected between 1 to 7 days correspond to the "secondary absorption". Results are plotted as the cumulative change in mass divided by exposed area and density of water (Y axis), versus the square root of time (X axis). The slopes of the initial and secondary absorption are calculated. Because each stage represents different mechanisms (i.e. capillary suction for the initial and diffusion for the secondary), a single coefficient is calculated from the intersection of the two slopes. According Castro *et al*. (2011), sorptivity results were normalized by paste content and by aggregate absorption because the important effect they have in the test.

It is important to note that sorptivity can be considered as an index for estimating potential durability of concrete (Hazaree *et al.* 2010; Pereira de Oliveira *et al.* 2006).

Air permeability was measured on 200-mm cubes according to SN EN 206-1, 2003 (Swiss-Standard 2003) at age of 28, 90, and 150 days. Six measurements (one on each face) were taken on each specimen.

The test method consists of estimating air permeability by applying vacuum and measuring the air influx from within concrete. The perpendicular flow of air through concrete at the level of the surface is ensured by a guard ring that prevents air from the exterior affecting the measurement. Saturated or partially saturated pores will affect the air permeability, so the results need to be corrected by moisture (Torrent, Ebensperger 2010). In order to measure air permeability in a unsaturated pore system, specimens were removed from the fog room and kept at 50% RH and 23 °C to air dry the superficial pores two days before testing. Figure 2 shows a schematic of the test. Since specimens were preconditioned, it is expected that internal relative humidity is similar for all mixtures; and therefore, results are comparable. However, this does not necessarily assure that water within the pore network is the same.

It is important to note that air permeability has become the preferred method for specifying and measuring durability of concrete in Switzerland (Swiss-Standard 2003).

Chloride ion diffusion was measured on 100×50-mm cylinders according to ASTM C1202-05 at the age of 35 and 97 days. In this method, an electrical potential of 60 V is maintained across the flat ends of saw-cut cylinders (previously conditioned), for 6 hours. One end is immersed in a NaCl solution and the other in a NaOH solution. Chloride ions travel across the specimens and the current is measured periodically. At the end of the 6 hours, the total charge passed, in coulombs, is calculated, and the concrete's ability to resist chloride ion penetration is obtained. Figure 3 shows a schematic of the test.

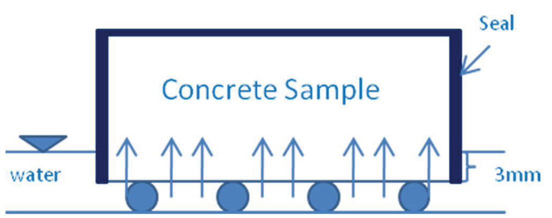

Fig. 1. Schematic of sorptivity test

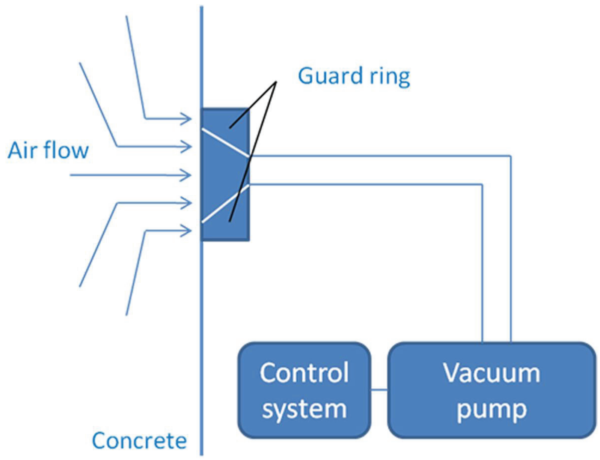

Fig. 2. Schematic of air permeability test

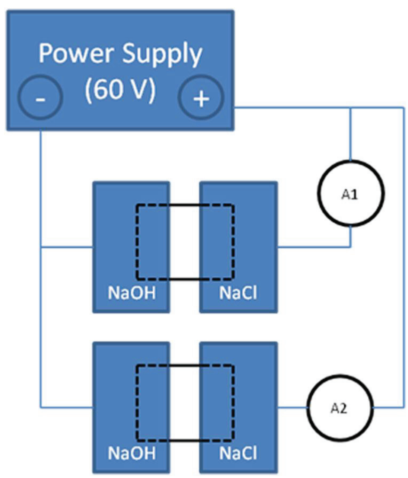

Fig. 3. Schematic of chloride ion diffusion test

ITZ was assessed through measuring aggregate surface by means of stereology parameters, specifically "surface density". The estimation of surface density was made from vertical uniform random (VUR) sections using an unbiased stereology technique based on cycloids. Cycloids were used because they are considered isotropic lines on vertical uniform random sections in 3D space (Howard, Reed 2005).

Surface density is then estimated from:

$$s_V\left(Y.ref\right)=\frac{2\times\sum_{i=1}^{n}I_i}{\frac{1}{p}\times\sum_{i=1}^{n}P_i}, \quad (1)$$

where: I_i is the number of intersections; P_i the points hitting the reference space; and *l/p* is the length of test line per grid point at the level of the tissue, corrected for linear magnification (Howard, Reed 2005; Zhang, Han 2005).

Surface density of the aggregate was also estimated based on their particle size distribution (sieve analysis) and assuming spherical particles.

3. Results and discussion

3.1. Cementitious materials

Oxides analysis, specific weight and Blaine fineness was made for both, OPC and blended cement. The results are summarized in Table 2.

Blended cement had a considerably higher SiO_2 content and lower specific gravity than OPC because of the inclusion of natural pozzolans. Content of CaO, Fe_2O_3, and Al_2O_3, are all lower in blended cement than in OPC. The relatively high insoluble residue in the blended cement represents the natural pozzolans. Blaine fineness is similar in both cements.

Natural pozzolans present in the cement used for C2, C3 and C4, had a volcanic origin and could be classified as a Type-N pozzolan according to ASTM C618 (2008). It corresponded to a volcanic glass known as rhyolite pumicite. The chemical compositions of NP and OPC used in this investigation are shown in Table 3.

Table 2. Cements characterization

	Ordinary Portland cement	Blended cement (62% OPC + 38% natural pozzolans)
SiO_2 (%)	19.4	33.6
CaO (%)	63.3	39.1
Fe_2O_3 (%)	2.9	1.6
Al_2O_3 (%)	6.4	4.0
SO_3 (%)	2.7	2.62
MgO (%)	0.8	1.1
Loss on Ignition (%)	1.4	3.4
Insoluble Residue (%)	0.8	33.5
Specific gravity	3.15	2.82
Specific surface (cm^2/gr)	4697	4876

Table 3. Chemical composition of natural pozzolans (Espinoza *et al.* 2010)

SiO_2 (%)	Al_2O_3 (%)	Fe_2O_3 (%)	CaO (%)	MgO (%)	K_2O (%)
69.2	13.2	1.7	2.7	0.8	3.0
SO_3 (%)	Na_2O (%)	TiO_2 (%)	P_2O_5 (%)	LOI (%)	
0.1	3.9	0.2	0.1	4.36	

The chemical composition of the natural pozzolans used in this investigation suggests an almost negligible hydraulic activity (2.7% of CaO content), and a relatively high pozzolanic activity due to its 69.2% of SiO_2.

3.2. Concrete mixtures

Average results for compressive strength, splitting tensile strength and modulus of elasticity at different ages are shown in Table 4, and average sorptivity coefficient, air permeability and chloride ion diffusion, are shown in Table 5.

3.3. Effect of natural pozzolans

The effect of the natural pozzolans in mechanical properties and permeability is analysed by comparing the performance of C1 with OPC and C2 with blended cement

Table 4. Mechanical properties of mixtures under investigation

Concrete	Age (days)	Compressive strength (MPa)	Split test (MPa)	Elastic modulus (MPa)
C1	4	25.59	–	–
	7	32.05	–	–
	28	34.17	3.82	24.83
	90	39.47	3.32	29.58
	150	45.04	3.8	28.44
C2	4	17.50	–	–
	7	20.74	–	–
	28	26.25	3.03	23.53
	90	31.15	2.94	27.78
	150	35.01	3.24	26.79
C3	4	12.24	–	–
	7	14.73	–	–
	28	21.66	1.35	23.89
	90	25.35	2.38	25.68
	150	27.23	3.88	26.36
C4	4	19.52	–	–
	7	22.68	–	–
	28	29.86	2.45	26.67
	90	37.69	3.61	29.11
	150	45.53	4.54	27.92

Table 5. Durability properties of mixtures under investigation

	Sorptivity coefficient		Air permeability			Chloride ion diffusion	
	$mm/s^{0.5}$		10^{-6} m^2			Coulombs	
days	28	90	28	90	150	28	90
C1	0.60	0.21	1.10	0.40	0.11	4315	4437
C2	0.89	0.51	0.14	0.07	0.05	1522	1705
C3	1.34	0.69	0.98	1.22	0.50	2990	1432
C4	0.52	0.17	0.09	0.04	0.03	2327	781

using the three proposed methods for characterizing transport properties.

3.3.1. Compressive strength

Figure 4 shows the compressive strength obtained for each of the mixtures under study.

When comparing C1with OPC and C2 with blended cement with natural pozzolans, it can be concluded that the use of OPC provides higher compressive strength than the blended cement under investigation for all ages considered in this investigation. The maximum difference of 11.3 MPa was obtained at 7 days of age representing 55% of the strength of C2. At 150 days of age, the difference was 10 MPa and represented 28% of the strength of C2. That is, the relative difference between C1 and C2 decreased over time suggesting that the pozzolanic reaction of the natural pozzolans contributed to increased strength of C2 over time. Mixtures C3 and C4 also presented lower compressive strength than C1 at almost all ages with the main difference being that the difference in compressive strength between C1 and C3 increased with time and between C1 and C4 decreased with time; in fact 150-day compressive strength of C1 and C4 were almost the same.

The differences in splitting tensile strength between mixtures with OPC (C1) and bended cement (C2, C3, and C4) are in most cases below 1.0 MPa and all decreases between 28 and 150 days of age.

Modulus of elasticity showed small differences between mixtures with OPC (C1) and bended cement (C2, C3, and C4) being most below 2.0 GPa (7%).

3.3.2. Sorptivity coefficient

Figure 5 presents the results for sorptivity coefficient normalized by the respective volume of paste content and aggregate absorption according to Castro *et al*. (2011) at 28 and 90 days of age. Results suggest that concrete containing natural pozzolans (C2) present a higher sorptivity coefficient than concrete with OPC. Even though it has been demonstrated that the pozzolanic reaction of natural pozzolans produce more calcium silicate hydrates and create a more refined pore structure, this is not reflected in capillary suction of water at 90 days of age as shown previously (Lopez, Castro 2010).

Both concrete mixtures showed a decrease in sorptivity between 28 and 90 days of age; however, C1 with OPC decreased more importantly relatively to C2 with natural pozzolans making the difference between them more important with age. Additionally, variability in sorptivity coefficient of C1 with OPC was lower than that of C2 with natural pozzolans.

3.3.3. Air permeability

The results for air permeability in logarithmic scale versus the age at testing are shown in Figure 6, and Table 6 presents the standard deviation.

Even though C2 showed consistently lower air permeability than C1, differences could not be very significant when considering the variability of the results.

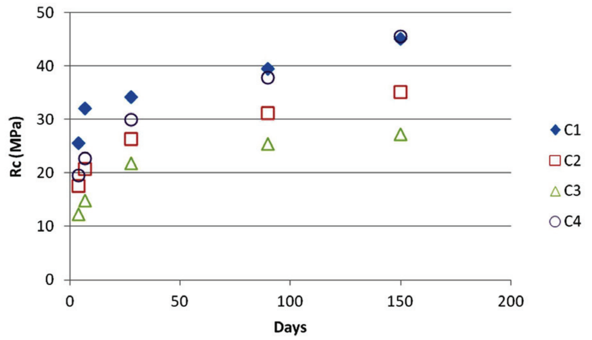

Fig. 4. Strength gain of C1, C2, C3 and C4 concrete mixtures

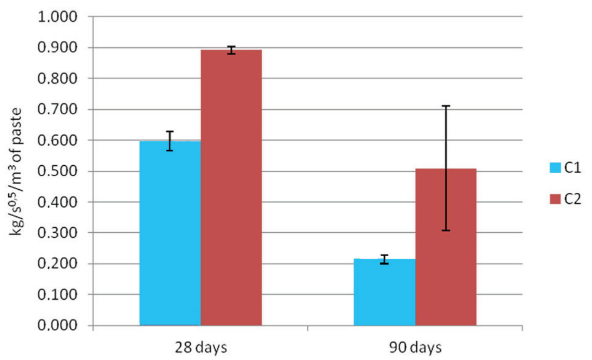

Fig. 5. Sorptivity change in time of C1 and C2 concrete mixtures normalized by paste content by volume

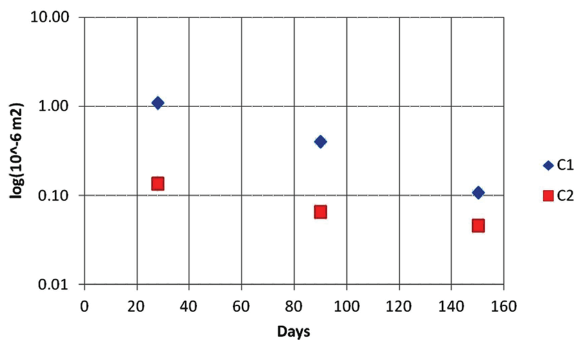

Fig. 6. Air permeability change in time of C1 and C2 concrete mixtures

Table 6. Standard deviation of air permeability

Age (days)	28	90	150
dv C1	0.39	0.62	0.13
dv C2	0.10	0.06	0.06

Both concrete mixtures, C1 and C2, showed constant decrease in air permeability with age. Since air permeability is shown in logarithmic scale, the decrease in permeability between 28 and 150 days was 88 and 84% for C1 and C2, respectively.

Initially (i.e. 28 days of age), C2 with natural pozzolans showed an air permeability of about one tenth than that of C1 with OPC. However, C1 showed an important decrease between 28 and 150 days reaching an air permeability of approximately 2 times of that of C2. It is important to consider that C2 showed significantly lower variability than C1 which suggest a more uniform pore structure.

3.3.4. Chloride ion diffusion

Since the use of SCMs, such as natural pozzolans, can have a very significant effect on the chemistry of the pore solution affecting the electrical conductivity of concrete (Shi 2004), the comparison between chloride ion diffusion of C1 and C2, might not represent solely a change in microstructure but also an effect of the testing method.

The test of the samples presented problems that could not give representative results, so they were omitted. Nevertheless, a previous study (Lopez, Castro 2010) made with the same constituents, and test equipment showed beneficial effects with the inclusion of natural pozzolans in chloride ion diffusion. In that study, which tested mixtures similar to C1 and C2, the use of NP decreased chloride ion diffusion at 90 days by 50%.

3.4. Effect of ITZ

The effect of ITZ on compressive strength and transport properties is analysed by comparing the performance of C2, C3, and C4 concretes all with the same constituents and w/b, but different aggregate-to-paste ratio; i.e. different ITZ content.

ITZ was assumed to be proportional to the surface density of the aggregate of concrete. A first approach to estimate the aggregate surface was made assuming aggregates particles as spheres. Each aggregate particle was represented by a sphere inscribed at its minimum dimension. The amount of particles of each size was calculated based on the sieve analysis and the actual mixture design.

In order to determine the goodness of this approach, an unbiased stereology technique was applied to micrographs obtained using optical microscopy. Two different magnifications were used, 18x and 54x, in order to establish the best for measuring the surface density of the aggregate (*Sv*) according to Eqn (1). Four micrographs were used from each concrete mixture to assess *Sv*at each magnification.

Figure 7 shows micrographs from C2, C3 and C4 with 18x of magnification.

Sv calculated using Eqn (1) and the respective result with the "spherical approximation" are shown in Table 7. The order used to display the results starts with the mixture with more aggregate content (C3) and finished with that with less aggregate content (C4).

Since the visible aggregate particle size varies with magnification, the values obtained using stereology might also vary with magnification. It was established that the visible range at 18x magnification started at 0.11 mm while that for 54x magnification started at 0.028 mm.

The large difference between *Sv* estimated using stereology and the spherical approximation indicates that the latter is not conservative since underestimated *Sv* and so does the amount of ITZ. This underestimate is mainly due to the fact that the crushed aggregate used in this investigation do not have a round and regular shape, so their actual surface is much higher than that estimated by the spheres. Furthermore, the spheres are inscribed in the minimum size of the aggregate.

A comparison between spheres approximation and stereology with micrographs was also made, inscribing circumferences in the minimum size of aggregate particles and then applying stereology with cycloids, as show Figure 8.

The analysis showed that considering aggregate being spheres under estimate aggregate surface density by at least 44%.

When comparing the stereology results from each magnification, it can be concluded that only the results from 54x followed the expected trend of increasing *Sv* with the increase of aggregate content. Thus, *Sv* obtained at 54x was used to represent the amount of ITZ and to evaluate the ITZ effect on transport properties.

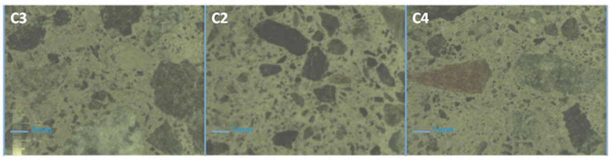

Fig. 7. Micrographs from C2, C3, and C4 concrete mixtures

Table 7. Aggregate surface density (*Sv*)

	Technique	Magnification	C3	C2	C4
Sv (m^{-1})	Microscopy	54	11770	10339	9426
dv			1.2	1.5	1.3
Sv (m^{-1})	Microscopy	18	3328	4623	3895
dv			0.2	0.6	0.7
Sv (m^{-1})	Spheres	54	716	676	637
Sv (m^{-1})	Spheres	18	745	703	663

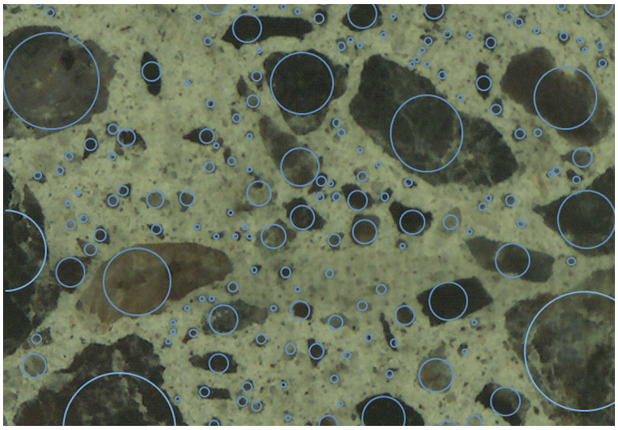

Fig. 8. Comparison between spherical approximation and stereology

3.4.1. Compressive strength

Figure 9 presents the compressive strength obtained in mixtures C2, C3, and C4 versus *Sv* as calculated using the stereology technique with magnification of 54x. Table 8 presents the standard deviation obtained in the test.

The effect of the *Sv* (and amount of ITZ) on compressive strength is very pronounced as shown in Figure 9. Compressive strength decreases as *Sv* increase; and this reduction seems to approximate to a linear relationship for all ages and more pronounced as compressive strength increases. That is, as age and compressive strength increases, the drop in strength with *Sv* shows a steeper slope.

3.4.2. Sorptivity coefficient

It is clear that high *Sv* (and amount of ITZ) leads higher capillary suction of water while low *Sv* has low capillary suction (Fig. 11). Also, reduction of sorptivity coefficient with age is not constant for all mixtures, high *Sv* has a greater reduction in sorptivity coefficient that low *Sv* between 28 and 90 days. Since all concrete mixtures have the same w/b (i.e. with similar pore structure and permeability of the bulk paste) and measurements were normalized by paste content and aggregate absorption, it is concluded that ITZ has a main role in determining sorptivity coefficient of concrete. Table 9 presents the standard deviation obtained in the test.

3.4.3. Air permeability

Sv (and amount of ITZ) has a pronounced effect on the air permeability; it is clear that high *Sv* leads to higher air permeability while low *Sv* has low air permeability (Fig. 11). However, such effect does not seem to be linear since an increase in 10% in *Sv* between C4 and C2 led to an increase in air permeability of 35%, and an increase in 12% in *Sv* between C2 and C3 led to an increase in air permeability of 91%. Table 10 presents the standard deviation obtained in the test.

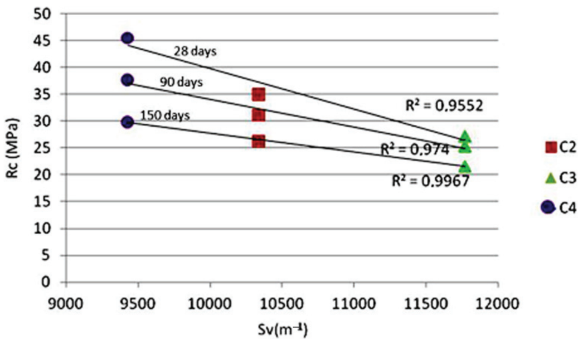

Fig. 9. Compressive strength versus surface density of the aggregate (*Sv*)

Table 8. Standard deviation of compressive strength

Age (days)	28	90	150
C3	0.97	0.89	0.61
C2	0.09	0.78	2.56
C4	0.87	0.52	0.00

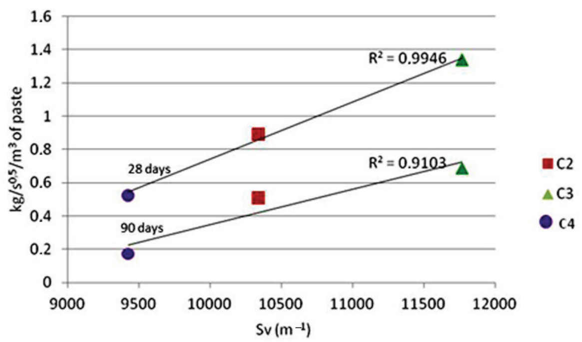

Fig. 10. Sorptivity coefficient vs. surface density of aggregate (*Sv*)

Table 9. Standard deviation of sorptivity coefficient

Age (days)	28	90
C3	0.398	0.092
C2	0.012	0.203
C4	0.006	0.176

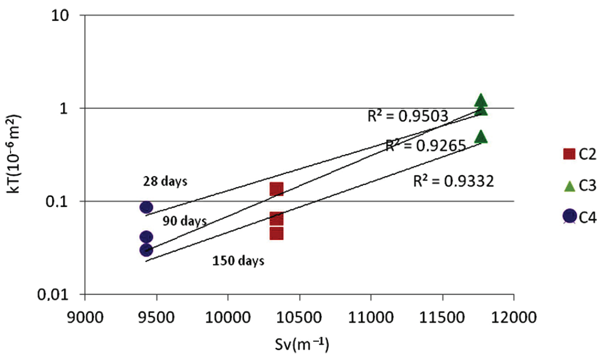

Fig. 11. Air permeability (logarithmic scale) vs. surface density of the aggregate (*Sv*)

3.4. Comparative analysis

3.4.1. Chloride ion diffusion

The effect of Sv (and amount of ITZ) is important in chloride ion diffusion; as Sv increases, chloride ion diffusion increases too (Fig. 12). This effect seems to be similar at different ages. Since the results of chloride ion diffusion of C2 were not included, it is not possible to determine whether the effect of Sv on chloride ion diffusion is linear or no not. Table 11 presents the standard deviation obtained in the test.

It is also of interest to determine which factor (natural pozzolans or amount of ITZ) has the greater effect on transport properties. C1, concrete mixture with OPC was chosen as the control mixture for analysing the effect of the natural pozzolans, and C3, concrete mixture with the highest amount of ITZ, was chosen as the control mixture for analysing the effect of ITZ. Figure 13 shows the relative effect of each factor on compressive strength.

For compressive strength, the efficiency of concrete with blended cement (68% OPC + 38% of natural pozzolans) ranged between 65 and 79% of that obtained for concrete with OPC only (C2 versus C1). It should be pointed out that there is an improvement in the efficiency of mixtures with blended cement after the first week, but it seems to stabilize after 28 days. On the other hand, the efficiency of concrete with more ITZ (Sv = 11770 m^{-1}) was approximately 65% of that obtained for concrete with less ITZ (Sv = 9426 m^{-1}) (C3 versus C4), and no clear improvement was observed at later ages. The effects of using blended cement with 38% of natural pozzolans or increasing the amount of ITZ by 44% seem to be on the same order of magnitude.

Figure 14 shows the relative effect of the use of natural pozzolans and amount of ITZ on sorptivity coefficient.

When the amount of paste is considered in the measurements, concrete with blended cement (68% OPC+ 38% natural pozzolans) had a greater sorptivity coefficient than that of concrete with OPC only (C1 versus C2). The increase in sorptivity coefficient ranged between 50 and 140% at 28 and 90 days of age, respectively when natural pozzolans were considered. On the other hand, the decrease in ITZ decreased sorptivity coefficient by 60 and 75% at 28 and 90 days of age, respectively (C3 versus C4). Since sorptivity coefficient of C1 (without natural pozzolans) was similar to that of C4 (with natural pozzolans and lower ITZ), it can be concluded that using blended cement with 38% of natural pozzolans or decreasing the amount of ITZ by 20% have a similar effect in magnitude on sorptivity coefficient of concrete.

Figure 15 shows the relative effect of the use of natural pozzolans and amount of ITZ on air permeability.

Air permeability showed a greater sensitivity to the factor under study than compressive strength and sorptivity coefficient. Contrary to what was observed

Table 10. Standard deviation of air permeability

Age (days)	28	90	150
C3	1.45	1.28	0.87
C2	0.10	0.06	0.06
C4	0.6	0.4	0.3

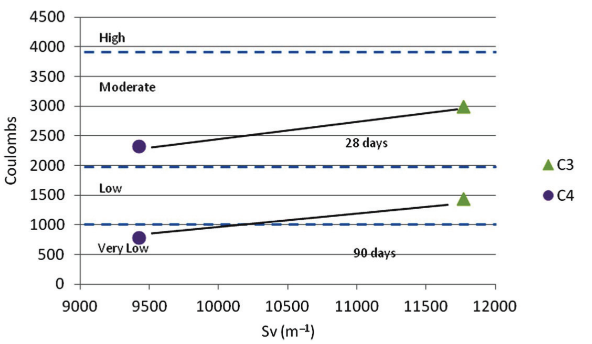

Fig. 12. Chloride ion diffusion vs. surface density of the aggregate (*Sv*)

Table 11. Standard deviation of chloride ion diffusion

Age (days)	28	90
C3	256.7	5.1
C4	391.1	0.8

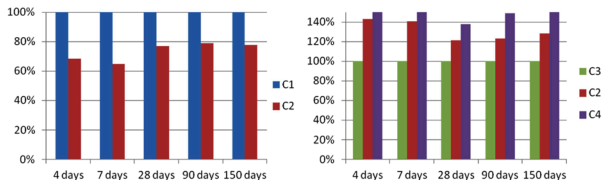

Fig. 13. Effect of the use of natural pozzolans and change in amount of ITZ in compressive strength

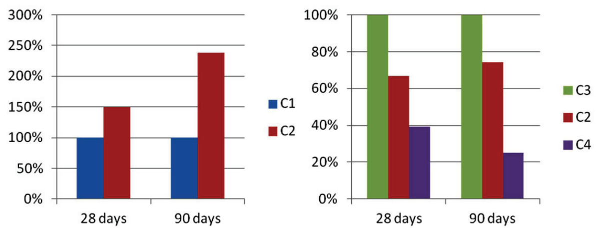

Fig. 14. Effect of the use of natural pozzolans and change in amount of ITZ in sorptivity coefficient

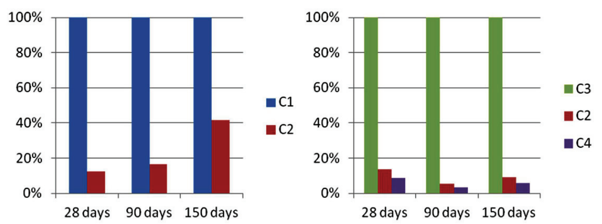

Fig. 15. Effect of the use of natural pozzolans and change in amount of ITZ in air permeability

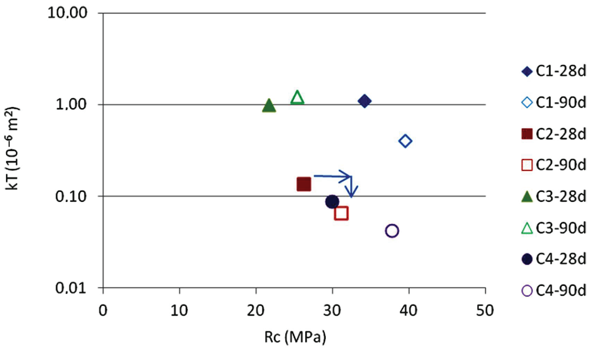

Fig. 16. Compressive strength vs. air permeability (logarithmic scale)

for sorptivity coefficient, concrete with blended cement (68% OPC+ 38% natural pozzolans) had much lower air permeability than that of concrete with OPC only (C1 versus C2). The use of blended cement decreased air permeability by 27%. On the other hand, the increase in ITZ greatly increased air permeability by 94% (C3 versus C4). In this case, using blended cement with 38% of natural pozzolans or increasing the amount of ITZ by 44% had opposite effects on concrete performance.

Overall, it can be stated that the use of blended cement with natural pozzolans has an opposite effect in compressive strength than in air permeability.

Additionally, the effect of the amount of ITZ is of much more impact on air permeability than in compressive strength. Figure 16 compares the variation in compressive strength and air permeability for all four mixtures under investigation.

Compressive strength and air permeability are greatly affected by the type of cement and amount of ITZ as shown by the wide range in both variables in Figure 16. Compressive strength varied from 20 to 40 MPa and air permeability from 0.05 to 1.1×10^{-6} m^2 for mixtures under investigation in despite of all having a w/b at 0.5. It is concluded that the type of cement and amount of ITZ are as important as w/b in determining compressive strength and air permeability.

Compressive strength and air permeability are not directly dependent on one another. For instance, C1 at 90 days had a compressive strength of 40 MPa and air permeability of 0.8×10^{-6} m^2, and C2 at 28 days a compressive strength of 25 MPa and air permeability of 0.2×10^{-6} m^2; the effect in air permeability is greater than the effect in compressive strength. Thus, specifying a high strength concrete does not mean that air permeability, and ultimately, durability are adequate.

Concluding remarks

Environmental and economic issues have increased the interest of creating more durable buildings and infrastructure. Concrete may greatly contribute to this goal by reducing its permeability.

This research aimed to determine the effect of using blended cement (OPC + natural pozzolans) and varying the amount of ITZ in reducing the permeability of concrete.

The use of blended cement with natural pozzolans decreased air permeability and chloride ion diffusion by 84 and 50% respectively, but increased sorptivity coefficient between 28 and 90 days of age by 50 and 140%. This unexpected increase in sorptivity coefficient does not necessarily mean higher permeability or a more interconnected pore structure in concrete containing NP. The increase in sorptivity coefficient might be a consequence of refinement of the pore structure and lower saturation of the pore network of concrete with NP. This needs to be further investigated.

An increase in the amount of ITZ, represented by surface density of the aggregate, decreased compressive strength and increased transport properties. Nevertheless, it is worth to notice that the effect of the amount of ITZ in air permeability is significantly higher than that on sorptivity coefficient and chloride ion diffusion. It is also of relevance to mentioned again that even reducing ITZ, by reducing surface density (aggregate content), exits a limit of cement content where heat/shrinkage related cracking may increase transport properties to and it needs to be further investigated.

Transport properties, and particularly air permeability, seem to be very sensitive to changes in the amount of ITZ even at constant w/b and cement type. It is concluded that considering ITZ, represented by surface density of the aggregate, becomes important in controlling permeability of concrete.

The surface density from the stereological approach is an accurate alternative for assessing ITZ in concrete since the amount of ITZ does not linearly depend on aggregate content and it is not well represented by assuming aggregate particles as spheres. Furthermore, an appropriate magnification for the micrographs must be chosen.

Even though compressive strength and permeability are affected by the use of natural pozzolans and changes in the amount of ITZ, those effects vary importantly. This means that an increase in strength does not necessarily imply a decrease in permeability, so minimizing permeability for a durable concrete is not equivalent to maximizing its compressive strength.

An adequate mixture design is very important in achieving a durable concrete. Mixtures with lower aggregate content will have lower permeability and better durability. Also, the use of SCMs, such as natural pozzolans, might not be enough to reduce permeability of concrete if concrete includes a large amount of aggregate (i.e. ITZ).

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