TECHNICAL ARTICLE

Comparison Between D_{crit} Considering the Abrupt Variation and Inflexion in the Concrete Mercury Intrusion Porosimetry Curve

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Abstract

Mercury intrusion porosimetry (MIP) has been widely used to evaluate the quality of concrete through the pore size distribution parameters. Two of these parameters are the critical pore diameter (D_{crit}) and the percentage of the most interconnected net of pores compared to the total volume of pores. Some researchers consider D_{crit} as the diameter obtained from the inflexion point of the cumulative mercury intrusion curve while others consider D_{crit} as the diameter obtained from the point of abrupt variation in the same curve. This study aims to analyze two groups of concretes of varying w/c ratios, one cast with pozzolanic cement and another with high initial strength cement, in order to determine which of these diameters feature a better correlation with the quality parameters of the concretes. The concrete quality parameters used for the evaluations were (1) the w/c ratios and (2) chloride diffusion coefficients measured at approximately 90 days. MIP cumulative distributions of the same concretes were also measured at about 90 days, and D_{crit} values were determined (1) from the point of abrupt variation and alternatively, (2) from the inflexion point of each of these plots. It was found that D_{crit} values measured from the point of abrupt variation were useful indicators of the quality of the concrete, but the D_{crit} values based on the inflexion points were not. Hence, it is recommended that D_{crit} and the percentage of the most interconnected volume of pores should be obtained considering the point of abrupt variation of the cumulative curve of pore size distribution.

Introduction

Mercury intrusion test for the purpose of concrete pore size distribution has been widely used to correlate the quality of the concrete. Amid the information obtained from this test, a key resulting parameter is the critical pore diameter (D_{crit}), which can be defined as the smallest diameter of pores that form an interconnected net of voids,[1] that is, the network of pores at which the aggressive agents may penetrate easily.

Such interconnected network of pores (capillary system) is responsible for making easier the exchanges with the external environment, by promoting the transport of water and vapor between the internal pore structure and the external environment. Therefore, the pores of this network can dry or soak much easier than the pores with smaller diameter, which are less connected, and consequently making the moisture more difficult to be extracted, as inferred from the works of Mehta and Monteiro[2] and Quénard and Sallée.[3]

Another important information is the ratio between the volume of pores with diameter equal or greater than the critical diameter and the total volume of pores, that is, the percentage of the most interconnected pores. Hence, the percentage of the most interconnected volume of pores is a function of D_{crit}. The smaller the percentage is, the more refined is the net of pores and, therefore, the more difficult is for the aggressive agents to penetrate into the concrete. This factor is more important than the total volume of pores in terms of concrete quality, because it depends on both the quality and the content of hardened cement paste.

Questions have been raised regarding the mercury intrusion test, especially considering the analysis of the results.

Mehta and Manmohan[4] consider D_{crit} as the point of abrupt variation of the cumulative pore size distribution curve. According to Garboczi,[1] the D_{crit} is at the inflexion point of the cumulative curve of mercury intrusion into concrete. Katz and Thompson[5] affirm the same for tests performed in rock when permeability and porosity are correlated. Nonetheless, Garboczi and Bentz[6] point out that cement-based materials are also porous but with a different nature than rocks. Apart from this, it needs to be considered that the penetration of aggressive agents does not have the permeability as the only mechanism and, in many cases, such mechanism is not the predominant one.

This study focuses on the analysis of two groups of concretes each group prepared at several different w/c ratios. One set was cast with pozzolanic cement and the other with high initial strength Portland cement. It aims to determine which diameter (if either related to the abrupt variation or to the inflexion in the porosity curve by mercury intrusion) presents better correlation with the quality parameters of concrete such as w/c ratio and chloride diffusion coefficient.

Methodology

Specimens were cast for the two groups of concrete. Their properties are shown in Tables 1–4.

Table 1 Pozzolanic cement—mix proportion, slump test, specific mass of fresh concrete and cement content (C)

Concrete	Dosage (cement:sand: gravel:w/c)	Slump (mm)	Specific mass of fresh concrete (kg/m^3)	C (kg/m^3)
P1	1:2.12:2.88:0.54	110	2350	359
P2	1:1.60:2.40:0.45	110	2285	419
P3	1:2.64:3.36:0.63	110	2325	304
P4	1:1.60:2.40:0.54	220	2275	411
P5	1:2.64:3.36:0.54	12	2325	308

Table 2 Portland cement of high initial strength—mix proportions, slump test, specific mass of fresh concrete and cement content (C)

Concrete	Dosage (cement:sand: gravel:w/c)	Slump (mm)	Specific mass of fresh concrete (kg/m^3)	C (kg/m^3)
H1	1:2.12:2.88:0.55	95	2320	355
H2	1:1.60:2.40:0.48	100	2326	419
H3	1:2.64:3.36:0.66	95	2285	297
H4	1:1.60:2.40:0.55	225	2308	416
H5	1:2.64:3.36:0.57	18	2340	304

Table 3 Pozzolanic cement—compressive strength (MPa), total porosity (%), and chloride diffusion coefficient of saturated concrete (D_{sat})

Concrete	Average strength at 28 days (MPa)	Average strength at 60 days (MPa)	Total porosity (%)	D_{sat} (mm^2/s)
P1	29.63	35.88	18.63	$4.62 \cdot 10^{-6}$
P2	32.85	38.48	18.72	$5.88 \cdot 10^{-6}$
P3	27.80	30.33	15.66	$6.25 \cdot 10^{-6}$
P4	30.05	36.56	23.14	$4.62 \cdot 10^{-6}$
P5	33.70	39.16	13.81	$5.88 \cdot 10^{-6}$

Table 4 Portland cement of high initial strength—compressive strength (MPa), total porosity (%), and chloride diffusion coefficient of saturated concrete (D_{sat})

Concrete	Average strength at 28 days (MPa)	Average strength at 60 days (MPa)	Total porosity (%)	D_{sat} (mm^2/s)
H1	39.19	46.33	12.35	$1.34 \cdot 10^{-5}$
H2	42.54	50.08	12.20	$9.13 \cdot 10^{-6}$
H3	29.40	37.16	17.36	$1.45 \cdot 10^{-5}$
H4	35.71	47.91	13.22	$1.23 \cdot 10^{-5}$
H5	36.28	45.55	14.81	$1.38 \cdot 10^{-5}$

Table 1 refer to concretes made with pozzolanic cement Type IV CP 32,[7] with an approximately fly ash content of 50%, named in text as concretes P. Table 2 refer to concretes with high initial strength cement and sulphate resistant, CP V RS type, according to Brazilian standards,[8,9] named in text as concretes H. The high initial strength cement had a 12% fly ash content in mass. The w/c ratios used ranged from 0.45 to 0.66.

The compressive strength tests were performed on cylindrical specimens of concrete with 100 mm diameter and 200 mm length and tested after 28 and 60 days of curing in a wet chamber with a relative humidity of 98% and 20°C, to confirm that the strength development in the concretes was as expected.

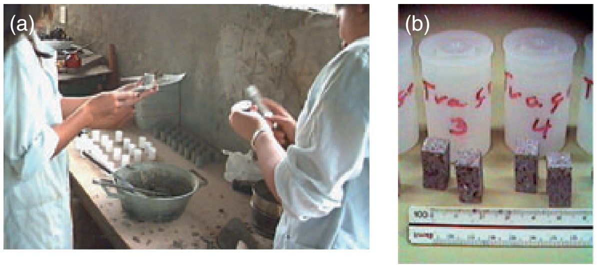

Figure 1 (a) Specimens of 30 mm diameter and 40 mm in height made with sieved concrete. (b) Tests samples of 10 × 10× 20 mm used in mercury intrusion porosimetry tests.

Owing to restrictions on the size of the diffusion test specimen proposed by Guimarães and Helene,[10,11] after casting the specimens for compressive strength, a portion of each one of the fresh concretes was sieved through a 9.5-mm sieve, in order to prepare the representative small concrete specimens required for diffusion tests and mercury intrusion porosimetry (MIP). All specimens for the same mix proportion were cast from the same batch. At the same time, one team was responsible for the casting of the concrete specimens, while another one was engaged in sieving the concrete to cast the smaller specimens (30 mm diameter and 40 mm in height), with the resulting sieved mortar, for MIP and chloride diffusion tests (Fig. 1(a)). These specimens were cured for 28 days in a wet chamber with a relative humidity of 98% and 20°C, and kept under laboratory environment for approximately 6 months (199 days) from casting until they were tested. The diffusion tests were performed directly on the abovementioned small cylindrical specimens. The specimens for MIP tests were cut in samples of 10 × 10 × 20 mm which were extracted from the center of the specimen and sent to laboratories for the MIP tests (Fig. 1(b)). At least two samples were tested for each material.

For the diffusion tests the sieved mortar samples were contaminated with a limited amount of solid sodium chloride. This salt was previously ground to pass through a number 100 sieve. A pool of plastic tube was attached to the test surface of the cylindrical specimens (always the bottom mould surface) and the sodium chloride was deposited within the pool. The purpose of the plastic pool was to avoid the falling of a chloride solution over the lateral surface of the sample, due to water condensation at the top during the diffusion test. Then, specimens were stored in a desiccator partially immersed in a saturated $Ca(OH)_2$ solution. The part of the specimens penetrated by chlorides during the diffusion tests remained above the liquid level (Fig. 2).

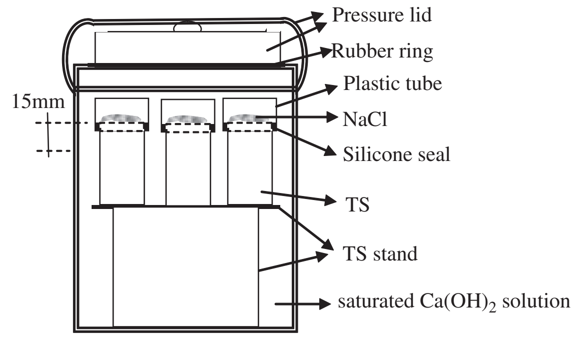

Figure 2 Test specimens during diffusion experiments in saturated conditions.

The duration of the diffusion tests was 7 days. Then, the salt was removed and the surface was cleaned with compressed air. Then, samples were ground using a lathe. Samples were ground up to a depth of 12 mm in layers of 2 mm each. Powder samples were analyzed by potentiometric titration.[12,13] The experimental chloride profiles were fitted to the error-function solution of Fick's Second Law (Eq. 1) of diffusion.[14]

$$C(x,t) = C_S \operatorname{erfc}\left(\frac{x}{2\sqrt{Dt}}\right) \qquad (1)$$

where C is the chloride concentration (% Cl^- relative to total mass), x is the depth, t is time, and the fitted parameters are D (diffusion coefficient) and C_s (surface concentration).

The chloride diffusion coefficient results in saturated condition of sieved mortar with pozzolanic cement were obtained by Guimarães and Helene[10] while the results of the concrete with high initial strength cement were obtained by Guimarães et al.[11]

Mercury intrusion porosimetry is a common technique for characterizing the porous microstructure of hardened cement paste and mortar,[15–19] although it has also been used for research on concrete.[20–23] In this work, oven drying at 105°C for 24 h, ensuring mass constancy, was the selected method for preconditioning the samples to be tested by MIP. It is known that the method used for concrete drying affects the pore volume analysis by MIP.[18,19,24] Nevertheless, some authors recommended or have used the oven drying at 105°C for the pretreatment practice.[16,22,23] Care was taken in order to select samples of approximately the same size from each one of the sieved concretes for MIP tests.[17,18] The porosimeter used in this research was an Autopore IV from Micromeritics. It works with several pressure steps. After each step the pressure is hold for 60 s until pores are assumed to be filled, then, it goes to another step and the

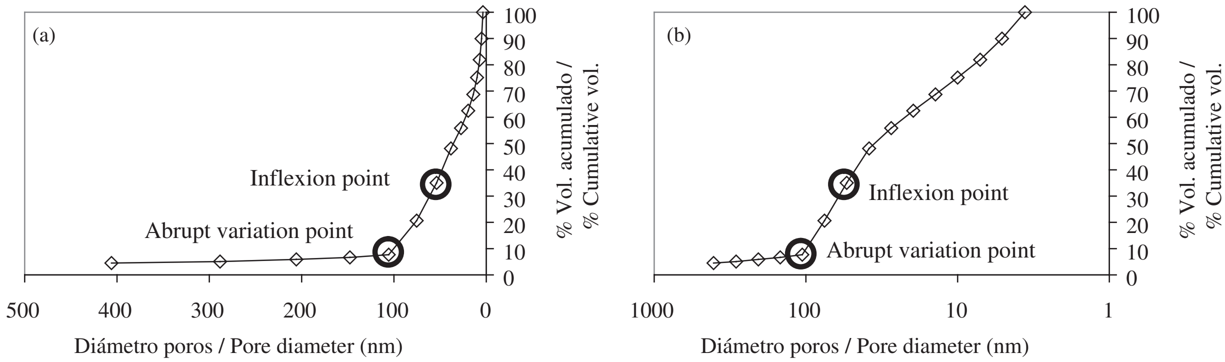

Figure 3 Mix proportion P1—part of the cumulative curve of pore size distribution which contains the point of abrupt variation and the inflexion point: (a) conventional scale and (b) logarithmic scale.

process starts again. The selected mercury contact angle was 130° and the surface tension was taken as 0.485 N/cm.

Results and Analysis

Tables 3 and 4 refer to the results of compressive strength tests, total porosity, and diffusion coefficients. Strength tests were performed at 28 and 60 days in order to follow the development of strength.

Before starting to analyze the results from the MIP an explanation must be done. It is known that the pore size distribution determined by MIP is affected by the so-called ink bottle effects. Because of this, the results given here must be considered as related with apparent porosity.[18,19] From the analysis of the pore size distribution curves (Figs. 3 and 4), it can be noticed that the inflexion of the curve is almost imperceptible (e.g. mix P1, Fig. 3(a), second point after the abrupt variation), what can be best observed using a logarithmic scale (Fig. 3(b)). The abrupt variation, however, is usually clearly visible both in the normal and logarithmic scale curves. The curve in Fig. 3(b) is similar to the curves presented by Mehta and Manmohan,[4] who consider the D_{crit} exactly at the abrupt variation point (approximately 100 nm for the P1 mix).

In some curves the abrupt variation is less noticeable due to the fact that the change is slower, which creates a smoother bending curve (e.g. P5 mix, Fig. 4). In these cases, D_{crit} is obtained by two straight lines adjusted to the points before and after the zone where the abrupt variation is noticed. The meeting point of the two straight lines allows to determine the D_{crit} value in the absence of a clearly visible abrupt variation feature. For the specimens with pozzolanic cement, D_{crit} was obtained by interpolation, because the pressure steps used in their tests were too large and therefore the determination of the abrupt variation point was less precise.

Results of D_{crit} and percentage of the most interconnected pores for the group of sieved mortars cast with pozzolanic cement are shown in Table 5.

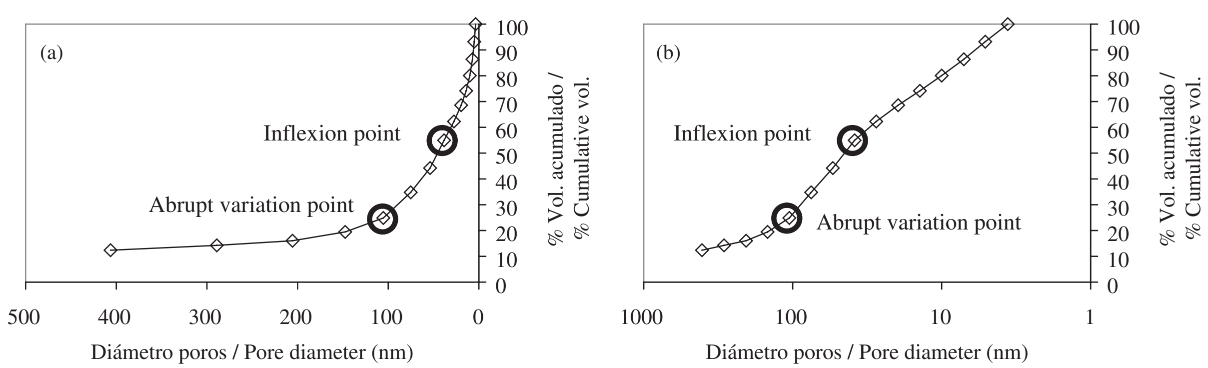

Figure 4 Mix proportion P5—part of the cumulative curve of pore size distribution which contains the point of abrupt variation and the inflexion point: (a) conventional scale and (b) logarithmic scale.

Table 5 Pozzolanic cement—D_{crit} and percentage of the most interconnected pores considering the point of abrupt variation and the inflexion of the curve

Pozzolanic		Point of abrupt variation		Inflexion of the curve	
Dosage-w/c-slump (mm)	Specimen	D_{crit}	% Cumulative volume	D_{crit}	% Cumulative volume
P1-0.54-110	Sample 1	106	7.7	54	25.3
	Sample 2	106	8.8	75	35.1
	Average	106	8.3	65	30.2
P2-0.45-110	Sample 1	111	7.9	75	25.7
	Sample 2	109	4.1	75	23.6
	Average	110	6.0	75	24.7
P3-0.63-110	Sample 1	110	16.0	75	32.9
	Sample 2	111	8.7	75	26.1
	Average	110	12.3	75	29.5
P4-0.54-220	Simple 1	107	13.6	74	28.6
	Sample 2	115	11.3	75	28.4
	Average	111	12.5	75	28.5
P5-0.54-12	Sample 1	110	13.1	38	47.4
	Sample 2	116	21.3	38	55.0
	Average	113	17.2	38	51.2

In regard to D_{crit} values determined by considering the abrupt variation, the differences are small. The smallest averages of percentages of the interconnected volume of pores correspond to the smallest averages of D_{crit}, and the highest averages of percentages of the interconnected volume of pores are associated to the highest averages of D_{crit}, as expected.

Considering the inflexion point, the highest percentages of the interconnected volume of pores (P1 and P5) correspond to the smallest values of D_{crit} while the smallest percentages of the interconnected volume of pores are related to the highest values of D_{crit}. This behavior is the opposite of that expected. The average percentage of the most interconnected pores of the P3 mix is also slightly smaller than that obtained for the P1 mix, although P1 mix has a lower w/c ratio in comparison to P3 mix.

Similar comments can be made to the sieved mortars group with high initial strength cement (Table 6).

Regarding the inflexion point, the average D_{crit} of H3 and H4 mix presented smaller values than the average D_{crit} of H1 mix, being expected the opposite on the basis of the compositions of the concretes. H5 mix present the smallest average percentage of interconnected pores and H2 mix presents the highest, although H2 is the one with the lowest w/c ratio and H5 presents the highest chloride diffusion coefficient (Table 4).

The results are much more meaningful for the point of abrupt variation analysis, as it can be seen in Fig. 5, on which the correlations among several parameters are presented.

In Fig. 5(a), the lower the w/c ratio, the smaller is the percentage of the most interconnected pores, what in effect means that the higher the compressive strength, the smaller is the percentage of the most interconnected pores for an equal level of consistency, understood as equal slump (P1, P2, P3 and H1, H2, H3).

Considering the point of abrupt variation, D_{crit} almost did not vary for the specimens with pozzolanic cement (P) and the correlation with the w/c ratio is very low (Fig. 5(b)). For specimens cast with high initial strength cement (H), D_{crit} increased with an increased w/c ratio when comparing concretes with same consistency, that is, the same slump, (H1, H2, and H3). The different dependence of D_{crit} on w/c ratio found for the pozzolanic (P) and the high initial strength (H) mortars can be explained by considering the development of the pozzolanic reaction for P specimens, which tends to refine the microstructure of these mortars by shifting the pore sizes to lower values, thus eventually leading to quite similar D_{crit} values irrespective of the w/c values. In this sense Atahan et al.[25] found, for hardened Portland cement pastes cured in lime saturated water during long periods, that the critical pore widths determined by MIP progressively decreased with time, and also their dependence upon the w/c ratio tended to vanish at sufficiently long curing periods (365 days), due to extensive clogging and segmenting of the capillary porosity.[25]

The relationship between the chloride diffusion coefficient of saturated concrete (D_{sat}) and the percentage of interconnected pores (Fig. 5(c)) exhibited

Table 6 Portland cement of high initial strength—D_{crit} and percentage of the most interconnected pores considering the point of abrupt variation and the inflexion of the curve

ARI-RS/high initial strength		Point of abrupt variation		Inflexion of the curve	
Dosage-w/c-slump (mm)	Specimen	D_{crit}	% Cumulative volume	D_{crit}	% Cumulative volume
H1-0.54-95	Sample 1	147	27.3	76	56.9
	Sample 2	131	19.3	98	42.1
	Sample 3	152	17.6	89	50.1
	Average	141	18.4	93	46.1
H2-0.45-100	Sample 1	116	16.3	49	59.1
	Sample 2*	180	18.6	104	43.5
	Sample 3	122	12.7	66	55.5
	Average	119	14.5	57	57.3
H3-0.63-95	Sample 1	147	19.1	76	54.4
	Sample 2*	80	25.7	49	70.7
	Sample 3	179	25.3	108	54.8
	Average	163	22.2	92	54.6
H4-0.54-225	Sample 1	147	17.1	76	51.9
	Sample 2	135	18.6	74	56.3
	Sample 3*	158	16.3	100	42.5
	Average	141	17.8	75	54.1
H5-0.54-18	Sample 1	147	24.5	76	41.6
	Sample 2*	162	8.6	73	59.6
	Sample 3	176	20.1	92	50.9
	Average	162	22.3	84	46.1

*P.s.: First results of each mix proportion were obtained from data of tests undertaken at the Eduardo Torroja Institute—Madrid, and the two remaining were undertaken at UNISINOS, São Leopoldo, Brazil.

good correlation for the high initial strength cement (H), while the correlation was poorer for pozzolanic cement (P).

The relationship between D_{crit} and D_{sat} (Fig. 5(d)), considering the point of abrupt variation, revealed a good correlation for the high initial strength cement (H). For the pozzolanic cement specimens. the correlation between both abovementioned parameters was practically inexistent.

There is a good correlation between D_{crit} and the percentage of interconnected pores (Fig. 5(e)) for the specimens cast with high initial strength cement (H) and low correlation for the ones cast with pozzolanic cement (P). This may be related again to the very different microstructures of the hardened H and P specimens. Despite this, all results show an agreement between D_{crit} and the quality parameters of concrete, between the percentage of the most interconnected pores and the same quality parameters, and finally, between D_{crit} and the percentage of the most interconnected volume of pores, that is, the better the quality of the concrete is, the smaller are the D_{crit} and the percentage of the most interconnected pores.

These results show an important difference between the high initial strength (H) and the pozzolanic cement (P). Mortars cast with the latter have a constant D_{crit} which neither depend on the composition (w/c ratio) nor on the workability of the concrete. In addition, neither the chloride diffusion coefficient (D_{sat}) nor the percentage of the most interconnected pores featured any correlation with D_{crit} (Figs. 5(b, d, and e)). This may be due to the different nature of the cements H (Portland with high initial strength) and P (pozzolanic with high fly-ash content). Nevertheless, it cannot be ruled out the possibility of an effect, at least partially, of the differences of the experimental methodologies used in the porosimetry test: the pressure steps used in the MIP tests for the P specimens were higher than those used for the H specimens, thus introducing some uncertainty in the determination of the D_{crit} values. Therefore, future investigations are needed to ascertain the origin of the abovementioned differences.

Figure 6 shows that many factors present divergent behavior between the two types of mixes when the inflexion point is considered to obtain D_{crit}, as opposed to the rationale that better quality concretes present smaller D_{crit} values and smaller percentages of the most interconnected pores. In the same figure, and for other variables, the two mixes present the same tendency, yet in an unexpected behavior for concretes, on which a smaller D_{crit} would usually

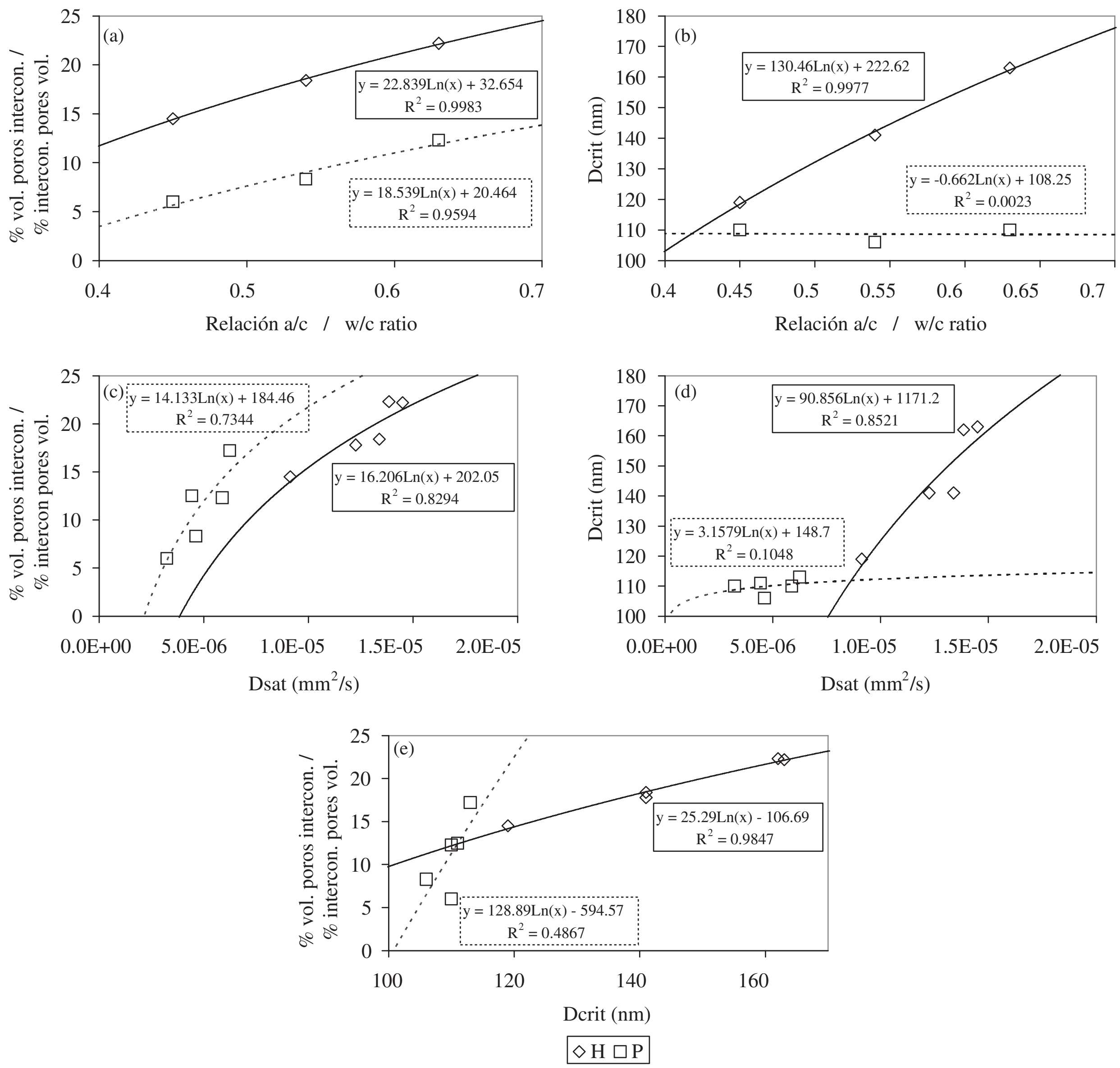

Figure 5 Point of abrupt variation—relationships between (a) percentage of interconnected pores and w/c ratio, (b) D_{crit} and w/c ratio, (c) percentage of interconnected pores and D_{sat} (diffusion coefficient of saturated concrete), (d) D_{crit} and D_{sat}, and (e) percentage of interconnected pores and D_{crit}. H, high initial strength cement; P, pozzolanic cement.

have a smaller percentage of the most interconnected pores (Fig. 6(e)). The majority of the regression curve correlations were also low due to dispersion of results.

It must be highlighted that smaller pores, with diameters between D_{crit} and 50 nm, also contributes to chloride diffusion, as discussed by Mehta and Manmohan[4] and Garboczi and Bentz,[6] but possibly in a less intense way. Nonetheless, they play an important role when the concrete has a very refined net of pores, with small and not well connected voids. Figure 7 shows that specimens cast with pozzolanic cement present smaller percentage of pore volume corresponding to diameter larger than D_{crit} and much smaller percentage of pores with diameter between 50 nm and D_{crit} than the specimens cast with Portland cement of high initial strength. These results explain the fact that H mortars presented chloride diffusion coefficients higher than P mortars (Tables 2 and 4).

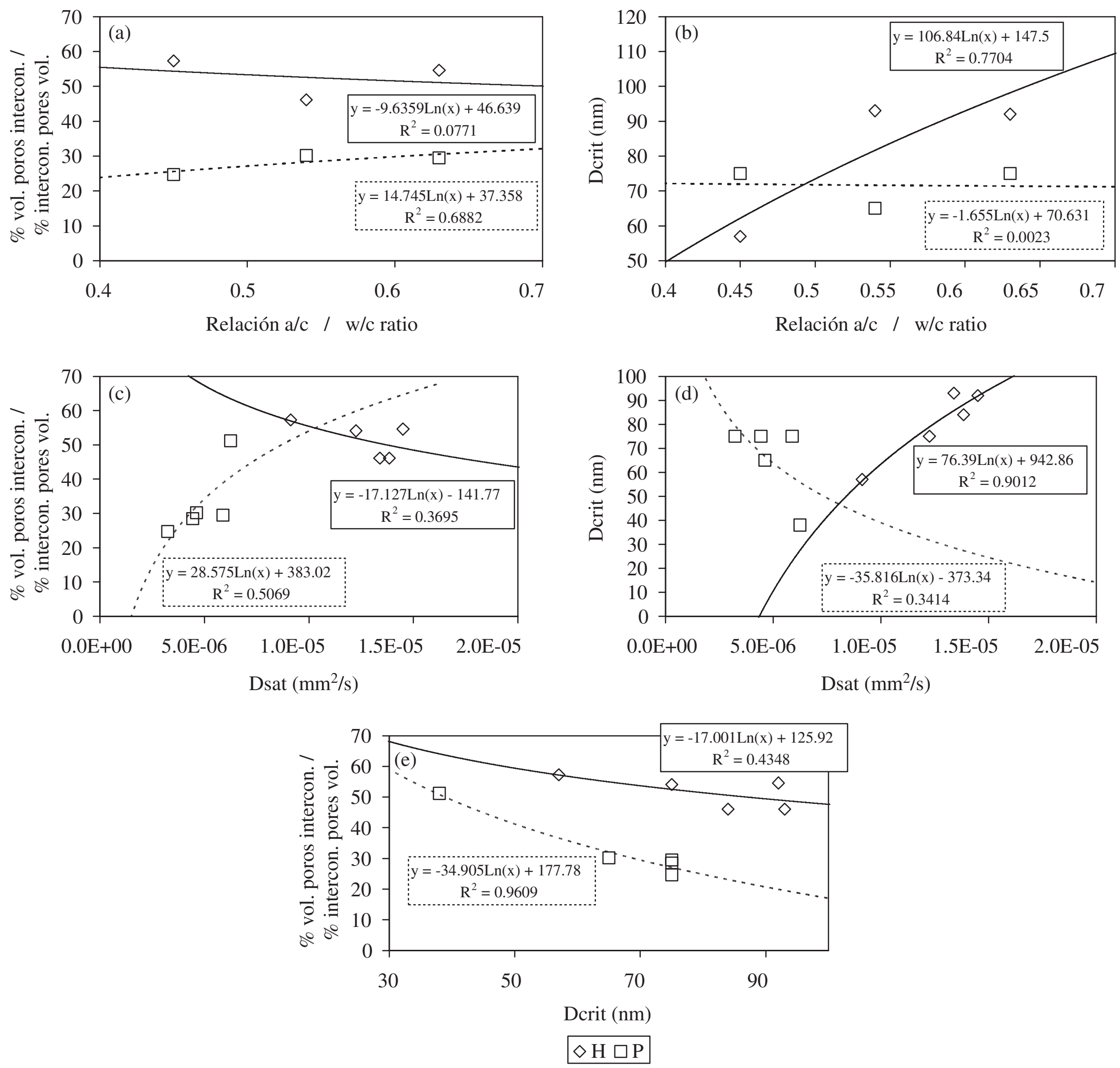

Figure 6 Inflexion point—relationships between (a) percentage of interconnected pores and w/c ratio, (b) D_{crit} and w/c ratio, (c) percentage of interconnected pores and D_{sat} (diffusion coefficient of saturate concrete), (d) D_{crit} and D_{sat}, and (e) percentage of interconnected pores and D_{crit}. H, high initial strength cement; P, pozzolanic cement).

Conclusion

In addition, the diameter of the pores in the point of abrupt variation and the volume of pores with same size or larger diameter presented both a good correlation between themselves and with the concrete quality parameters, such as w/c ratio and chloride diffusion coefficient, mainly for the concretes made with high initial strength cement. Concretes made with pozzolanic cement showed very low correlations when D_{crit} was associated with the same quality parameters, however, the volume of the most interconnected pores presented a very good correlation with the w/c ratio and a little weaker with the diffusion coefficient. This is most probably due to the different nature of the microstructure of the hardened mortars containing pozzolanic cement. Nevertheless, more research is needed on the origin of the differences found for the two cement types.

When D_{crit} values and most interconnected pore volume percentages are obtained in relation to the inflexion point, instead of the abrupt variation point, bad correlations are found with the quality parameters of concrete, that is, their values increase when w/c and the diffusion coefficient decrease, in some cases.

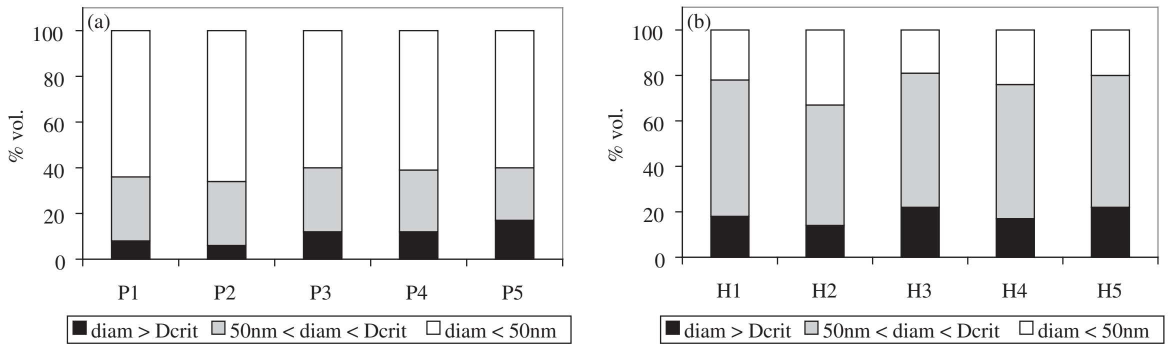

Figure 7 Percentage of volumes of pores for different ranges of diameters (a) mortars sieved from concretes with pozzolanic cement and (b) from concretes with Portland cement of high initial strength.

Therefore, if we compare the results obtained for the mercury intrusion test in relation to the abrupt variation point, with those obtained with the inflexion point, according to the aim of this work, it can be seen that the first ones are more consistent or have better correlation with the concrete quality parameters.

Hence, the properties associated to the point of abrupt variation, such as the critical diameter and the percentage of volume of the most interconnected pores, can be used as a quality parameter of concrete. Conversely, the properties associated to the inflexion point cannot be regarded as good quality parameters. It is therefore recommended that D_{crit} and the percentage of the volume of the most interconnected net of pores should be obtained considering the point of abrupt variation of the cumulative curve of pore size distribution.

Future researches should continue this work to verify the behavior of concretes made of other materials, and ascertain the influence of variations in the practice of mercury intrusion test, for example, the magnitude of the pressure steps and the time for keeping a constant pressure after each variation.

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