

Open porosity of cement pastes and their gas permeability

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Abstract. This paper presents the results of extensive research work on the open porosity and gas permeability of cement pastes. Tests were conducted on cement pastes with different water/cement ratios and types of cement. The three most popular cements in Poland from the CEM I, CEM II and CEM III groups were tested after the pastes had been cured for 90 days in laboratory conditions. The scope of experiments included the assessment of open porosity determined using three different methods: comparing the bulk and specific densities, mercury intrusion porosimetry and saturating the material with water. In addition, this article contains an analysis of the porosity characteristics based on the distributions produced by porosimetry examinations. Gas permeability was determined using the modified RILEM-Cembureau laboratory method. The results of the completed test allowed a quantitative determination to be made of the impact of water-cement ratio and type of cement used on open porosity assessed by various methods, and the influence of these parameters on the gas permeability of the paste. The quantitative changes in the content of capillary pores and meso-pores in the cement pastes analysed are also presented.

Key words: cement paste, water-cement ratio, open porosity, helium porosity, MIP porosity, gas permeability.

1. Introduction

Cement concrete is a non-uniform, composite material in which distributed grains of aggregate, most frequently stone, form inclusions, while the hardened cement paste is the matrix. The characteristics of the hardened cement paste largely determine the characteristics of the concrete. For this reason, the characteristics of the paste, and particularly of its open porosity, is of interest to many researchers [1–7]. Many methods exist for assessing this porosity, but the methods customarily used are subject to many limitations and thus provide incomplete information. It is therefore justified to use several methods at the same time to assess the structure of open pores. Information thus collected allows the results to be analysed in depth and better supported conclusions to be formulated.

As the effects of environmental substances, liquid or gaseous, usually have a negative effect on the in-service behaviour of the material, knowing its permeability allows its potential durability to be assessed. Permeability, characterised by the coefficient defined below, is one of the measures of the accessibility of the porous structure of the material to external liquid and gaseous substances.

One of the phenomena occurring in cement materials is carbonation, generally caused by the penetration of CO₂ into the material [8]. As in reinforced concrete elements this phenomenon reduces or even eliminates the ability of the external reinforcement cover to protect steel bars, concrete should be sufficiently tight against CO₂, in other words, of sufficiently low permeability for this gas.

So far, the most popular technique for measurement of cement material permeability has used water. However, since the

new generation cement composites used in practice are particularly distinguished by their much reduced and qualitatively modified porosity, this measurement technique has become unsuitable. Distinguishing the extent to which their internal structure is accessible to water has become very difficult or impossible because of their tight texture. Measuring by methods based on gas flow provides a much more subtle ability to distinguish the extent to which the interior of the material is accessible. Previously, such methods were mainly used for rock materials [9–11]. Determining the permeability of the material this way gives a more reliable representation of the extent of its accessibility to gaseous substances from the environment [12–17]. As the cement paste constitutes the most permeable component of concrete with stone aggregate, its permeability can provide information allowing the permeability of the entire composite to be predicted and designed.

The literature review carried out has shown that the permeability of cement paste determined using gas flows has not previously been of particular interest. In addition, researchers did not examine the relationship between the paste porosity characteristic and permeability in much depth. This article presents an attempt to quantitatively assess the impact of material factors on the characteristics of the open porosity and related permeability of pastes. Permeability tests were carried out using an adapted RILEM-Cembureau method with a flow of gas (nitrogen) [18, 19].

2. Experimental procedures

2.1. Material and specimen preparation. The pastes analysed were produced using three types of cement, class 42.5 compliant with EN 197–1 [20] Portland cement CEM I; Portland-fly ash cement CEM II/A-V and Slag cement CEM III/A. The char-

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acteristics of these cements are shown in Table 1. Regardless of the cement type used, the cement pastes also differed in their water/cement ratio (0.3, 0.4, 0.5 and 0.6). Cement pastes were prepared in compliance with the EN 196–1 standard [21].

Table 1
Chemical and physical characteristics of cements

PARAMETERS	CEM I 42.5 R	CEM II/A–V 42.5 R	CEM III/A 42.5N
<i>Chemical Characteristics</i> (Oxide analysis, % m)			
SiO ₂	18.6	23.2	30.0
Al ₂ O ₃	5.3	8.0	6.2
Fe ₂ O ₃	2.9	3.3	1.7
CaO	62.7	55.1	50.3
MgO	1.50	1.59	4.98
SO ₃	3.22	2.96	2.41
Na ₂ O	0.19	0.27	0.37
K ₂ O	0.96	1.12	0.70
eqNa ₂ O	0.82	1.01	0.83
Cl ⁻	0.060	0.029	0.016
<i>Physical Characteristics</i>			
Specific area (Blaine method), m ² /kg	340	366	465
Setting time (minutes)			
– start	199	176	221
– end	270	221	266
Compressive strength, N/mm ²			
– after 2 days	29.3	25.4	13.7
– after 28 days	55.1	56.2	50.7

In order to eliminate microscopic defects from forming in the specimens because of shrinkage and thermal effects, a decision was made to minimise the volume of specimens. Numerous trials showed that these phenomena can be avoided in the case of cylindrical samples 10 mm in diameter and about 60 mm in height. It should be emphasised that, in the case of material as uniform as cement paste, specimen dimensions ensure that the requirements of representativeness is fulfilled. These specimens were formed in rigid plastic tubes. After the tube was filled with paste, which was compacted by shaking, both ends of the tube were stopped with plugs to prevent water from evaporating. It should be emphasised that the fluidity of all pastes was high and made it possible to compact them precisely. After 28 days, the specimens were demoulded and the ends were dry grinded and polished to produce a height of 50 mm. Then, for the next 72 days, the specimens were stored in laboratory conditions at a temperature of 20°C and relative humidity of 60±5%, after which the samples were dried at a temperature of 40°C to constant weight. Drying at the relatively low temperature of 40°C made it possible to reduce the impact of temperature on the change in characteristics of the pastes being analysed to the greatest possible extent [3]. All the tests presented were carried out after 90 days of curing and drying in the above conditions.

Every property of paste analysed in this article was evaluated on a series of three specimens.

Irrespective of the type of cement used, the paste compositions were the same (Table 2). The only variable was the water-cement ratio. This wide range of the water cement ratios represents most concrete compositions applied in practice.

Table 2
Composition of cement pastes

w/c ratio	Cement, kg/m ³	Water, dm ³ /m ³
0.30	1605	483
0.40	1383	554
0.50	1217	608
0.60	1083	650

Cement pastes characterized by water/cement ratio 0.3 and 0.4 were supplemented with superplasticizer in order to obtain similar fluidity of all suspensions. This ensured comparable compaction index of all samples. Slight sedimentation effect was observed only in the case of cement pastes with water/cement ratio 0.6. As it was mentioned above top and bottom all the cylindrical specimens were grinded so that to remove the layers which were not representative. This procedure was especially important in the case of pastes with high water content.

2.2. Methods

2.2.1. Gas permeability. The permeability of pastes was determined using the RILEM-Cembureau [18, 19], method dedicated to concretes, and expressed by the so-called permeability coefficient.

The coefficient of permeability (k) was determined using following equation:

$$k = \frac{2QP_a\eta L}{A(P^2 - P_a^2)} \quad [\text{m}^2] \quad (1)$$

where:

- Q = V/t – the measured gas flow intensity [m³/s],
- P_a – atmospheric pressure [1 bar = 10⁵ Pa],
- P – pressure (absolute) [Pa]
- A – cross-section area of the sample [m²],
- η – viscosity of the gas; η = 17,15 [Pa s]
- L – thickness of the sample [m].

This is because the standard samples used to measure concrete permeability in this method are 150 mm in diameter. The measurements were taken using an appropriately modified device (Fig. 1) allowing measurements of small specimens 10 mm in diameter. The greatest difficulties were encountered in adapting suitably tight chambers in which specimens of such a small diameter are fixed. These chambers must be absolutely gas-tight where the chamber wall meets the side wall of the cylindrical specimen that is tested. When the cross-sectional surface of the specimen and hence the amount of flowing gas, are so small, sealing the sample in the chamber is of key importance for obtaining reliable test results.

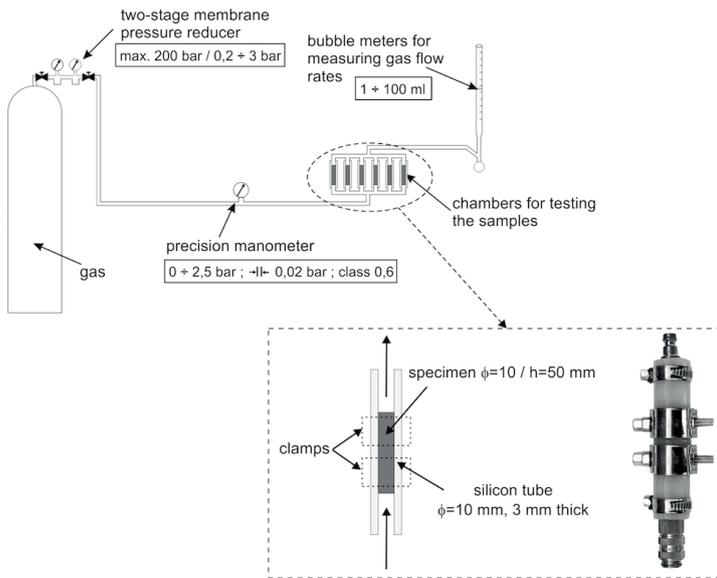


Fig. 1. RILEM-Cembureau gas permeability measurement apparatus and details of specimen fixing in a silicon tube chamber

The test procedure was similar to that recommended in [18, 19]. In essence, the test boils down to measuring the volume of gas (nitrogen) flowing through the specimen within a specified time using calibrated tubes (burettes) of different volumes, equipped with a pump that allows an indicator in the form of a soap bubble to be created in it. Equipping the device with a set of burettes with measurement volumes from 1 to 100 ml ensured real range of measurement of the k coefficient for the permeability for paste specimens described in section 2.1 ranging from 1×10^{-16} to $1 \times 10^{-13} \text{ m}^2$. Burettes were selected so that single volume measurements of the flowing gas would take between approximately 20 and 60 s. The flow time was measured with an accuracy of ± 0.1 s. A diagram of the device for permeability measurement and a detailed view of specimen fixing are shown in Fig. 1.

2.2.2. Open porosity. The percentage of open pores by volume in the pastes was determined using three methods:

- helium porosity (p_H), comparing bulk density with true density;
- porosity determined on the basis of mercury intrusion porosimetry measurements (p_{MIP});
- porosity determined on the basis of mass water saturation measurements (p_{WS}).

Helium porosity (p_H) was calculated using the following relationship:

$$p_H = \left(1 - \frac{\rho_{bulk}}{\rho_{true}}\right) 100 [\% \text{ vol.}] \quad (2)$$

where: ρ_{bulk} – bulk density [g/cm^3],
 ρ_{true} – true density (helium pycnometry) [g/cm^3].

The bulk density of samples was determined by a powder pycnometry method, using the Micrometrics GeoPyc 1360. This method is based in on displacement theory which an enables

sample volume determination. Knowing the accurate mass of the sample, envelope density can be established. The procedure was described in [22] in detail.

This method has been successfully implemented for determinations of the density of many materials. In the tests, a chamber 19.1 mm in diameter was used, the consolidation force amounted to 38 N and the conversion factor was as recommended by the operating manual, i.e. $0.2907 \text{ cm}^3/\text{mm}$ [22].

True density was determined using a helium pycnometer. In essence, this instrument measures the volume of the skeleton of the material tested with an accuracy of 0.0001 cm^3 . A measurement chamber with a rated volume of 10 cm^3 was used in the tests, with the cement paste specimens filling the chamber to about 40% as recommended in the method that was followed [23]. In presented studies the Quantachrome Ultrapycnometer 1200e was used.

Mercury intrusion porosimetry (MIP) is a widely used method for assessing the microporosity characteristics of cement materials. Regardless of its many drawbacks, this method is considered to be very valuable and to provide a lot of information about the structure of the material being tested. Because of the broad range of pore identification, this method is also used to assess the microporosity structure of many other materials with a mineral skeleton, including advanced cement composites like High Performance Concrete (HPC), Ultra High Performance Concrete (UHPC) and Reactive Powder Concrete (RPC) [24–26].

This method is also successfully used to assess changes in the porosity structure of cement composites subjected to the effect of factors which cause progressive material destruction [27, 14]. Interesting relationship between pore structure determined by mercury intrusion porosimetry and mechanical properties of cementitious composites was presented in [28].

The principle of mercury intrusion porosimetry measurement is based on the fact, that volume of introduced mercury into material is directly related to applied pressure [1]. Tests were conducted using the Quantachrome Poremaster 60 mercury porosimeter with a pressure range from 0.1 to $400 \text{ N}/\text{mm}^2$. Tests were conducted using a Quantachrome Poremaster 60 mercury porosimeter with a pressure range from 0.1 to $400 \text{ N}/\text{mm}^2$. This range of pressure applied aided the identification of pores accessible to mercury and of diameters ranging from 3.75 nm to ca. 0.25 mm. This pressure is given by the Washburn equation as seen below:

$$d = \frac{-4 \gamma (\cos \phi)}{p} \quad (3)$$

where: d – pore diameter [nm];
 γ – surface tension of the mercury, 0.480 N/m;
 ϕ – angle between the mercury and the pore wall, 130° ;
 p – pressure [N/mm^2].

It was assumed that the volume of pores accessible to water (p_{WS}) can be treated as identical to bulk water saturation. It was therefore calculated on the basis of measured mass water absorption (w_a) and the bulk density of paste (ρ_{bulk}) using the following relationship.

$$p_{WS} = w_a \times \rho_{bulk} \quad (4)$$

3. Test results

The results obtained for the paste properties tested are presented in Table 3. These are averages from three measurements.

The test results obtained were characterized by high homogeneity, and the maximum noted variation coefficients did not exceed 5%. The exception was the permeability test, where this factor was about twice as big, which is natural homogeneity of this feature.

Table 3
Results of tests conducted

Cement type	w/c ratio	Properties						Coefficient of permeability k [10 ⁻¹⁶ m ²]
		Bulk density	True density	Helium porosity	MIP porosity	Water saturation porosity		
		ρ_{bulk} [g/cm ³]	ρ_{true} [g/cm ³]	P_{H} [% vol.]	P_{MIP} [% vol.]	P_{WS} [% vol.]		
CEM I 42.5 R	0.30	1.744	2.308	24.4	17.3	31.4	2.73	
	0.40	1.628	2.250	27.6	20.5	36.5	3.95	
	0.50	1.495	2.165	30.9	23.5	41.4	10.50	
	0.60	1.398	2.116	33.9	26.5	44.5	24.70	
CEM II/A-V 42.5 R	0.30	1.785	2.232	20.0	11.3	33.2	0.99	
	0.40	1.614	2.141	24.6	19.5	39.2	3.50	
	0.50	1.466	2.084	29.6	24.7	43.0	5.39	
	0.60	1.342	2.031	33.9	28.4	47.4	8.83	
CEM III/A 42.5 N	0.30	1.727	2.214	22.0	13.3	30.0	1.70	
	0.40	1.586	2.098	27.4	19.5	35.5	2.79	
	0.50	1.391	2.071	32.8	26.4	39.2	3.57	
	0.60	1.346	2.017	33.4	30.4	45.0	6.63	

4. Discussion

4.1. Open porosity, the w/c ratio and cement type. The relationship between open porosity assessed by the three methods described above and w/c ratio is presented in Fig. 2. It is clearly visible that open porosity, regardless of the method by which it is determined, strongly depends on the water/cement ratio of the cement pastes tested. As the w/c ratio increases, the open porosity of pastes obviously goes up. A change of the w/c ratio from 0.3 to 0.6 was accompanied by as much as a two-fold increase of open porosity (e.g. for a paste with CEM II, p_{MIP} increased from 11.3 to 28.4% vol. and for a paste of the CEM III cement, p_{MIP} rose from 13.3 to 30.4 % vol.). It is also visible that this relationship is quasi-linear in nature. The values of open porosity determined by the three methods are clearly different. In every case, the highest values are achieved by porosity determined based on water saturation (p_{WS}), and the lowest by that determined using mercury intrusion porosimetry (p_{MIP}). A similar difference in the open porosity assessed by the three methods used was found by the authors of [5].

On the one hand, such a high difference in open porosity assessed by mercury intrusion porosimetry and based on absolute water saturation can be explained by the fact that the cement paste contains pores smaller than 3.75 nm and greater than 0.25 mm, which cannot be identified by mercury intrusion porosimetry [2]. On the other hand, water saturation porosity (p_{WS}) did not

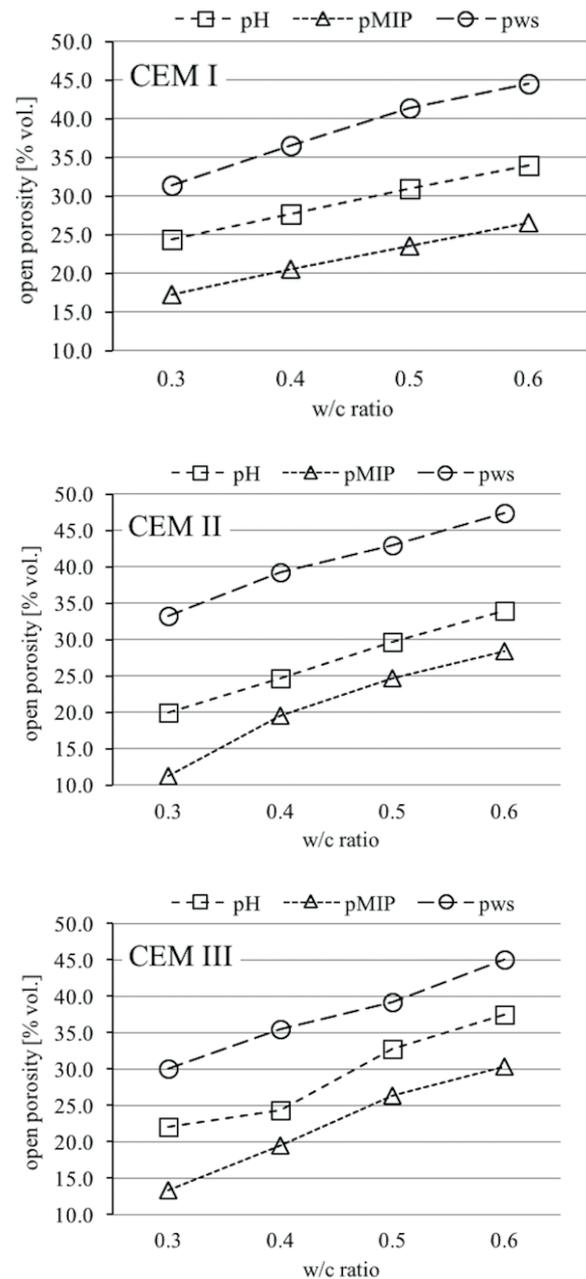


Fig. 2. The relationship between the helium porosity (p_{H}), MIP porosity (p_{MIP}), porosity determined based on water saturation (p_{WS}) and the w/c ratio [29]

reflect the real open porosity of the material because water, as a strongly polar liquid, is adsorbed by the cement gel as so-called interlayer water. Its molecules slip in between the mineral layers of the C-S-H phase, thus increasing the distances between them and forming "additional porosity". This phenomenon is also the reason why cured cement materials swell when stored in water.

The results presented indicate that the type of cement has a significant impact on the open porosity of cement pastes analysed. The relative difference in porosity was found to be caused by the type of cement used, regardless of the method by which this porosity was assessed, and was the higher the lower the

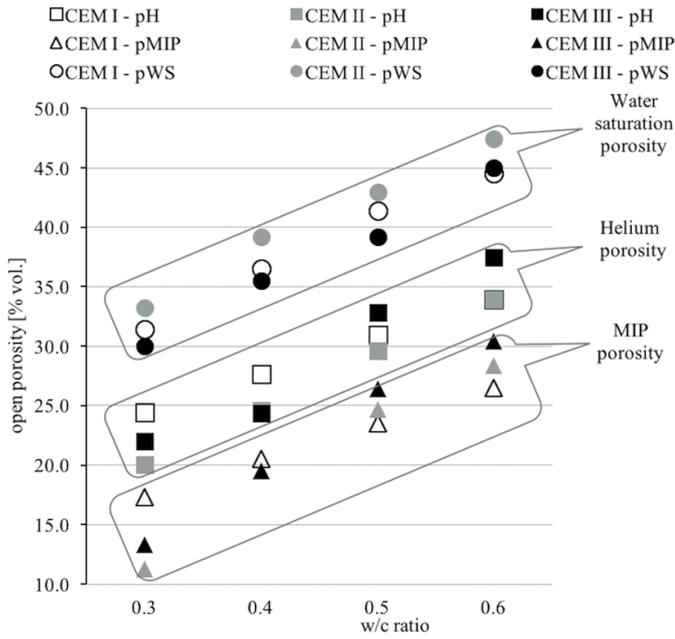


Fig. 3. A summary table of the relationship between the helium porosity (pH), MIP porosity (pMIP), porosity determined based on water saturation (pWS) and the w/c ratio for all cements

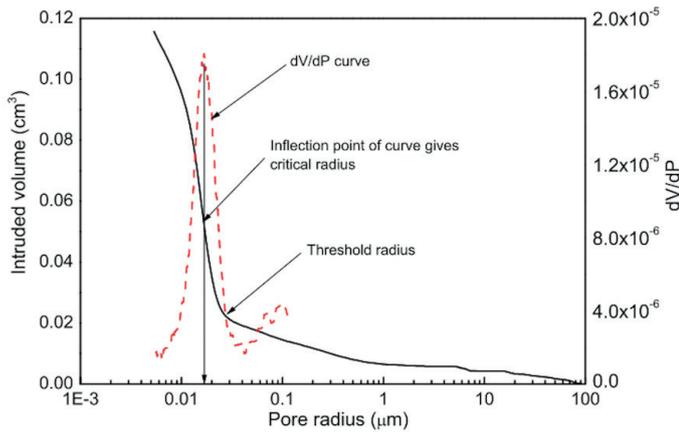


Fig. 4. Definition of critical and threshold pore radius [30]

water/cement ratio of the paste tested. In other words, along with decreasing water/cement ratio the greater impact of cement type on porosity was observed. The greatest difference was observed in pastes with a w/c of 0.3 and porosity assessed by mercury intrusion porosimetry of 11.3 and 17.3% vol. ($p_{MIP} = 6\%$ vol.) for pastes with CEM II and CEM I, respectively. In the remaining cases, the absolute difference between the porosity caused by the type of cement amounted to about 3.2% vol.

The results presented above, and their analysis, are based on assessing the total open porosity determined by various methods. Mercury intrusion porosimetry was also used to determine pore distribution curves and two parameters characterising them: critical pore size, and threshold pore size. The threshold pore size is defined as the diameter of pores at which significant filling of the system of open pores with mercury in the tested material

starts. The critical diameter is the diameter of pores at which the distribution curve reaches the maximum, so this parameter demonstrates what diameters are the most frequent, and therefore dominant, in the structure of the material tested (see Fig. 4). In their publications, many researchers [1, 30, 31] have proven that a comparison of these two values is very useful when studying and analysing cement pastes with different w/c ratios.

Fig. 5 shows the $dV/d\log D$ distribution curves for all pastes, grouped according to cement type. Fig. 6 presents cumulative distributions.

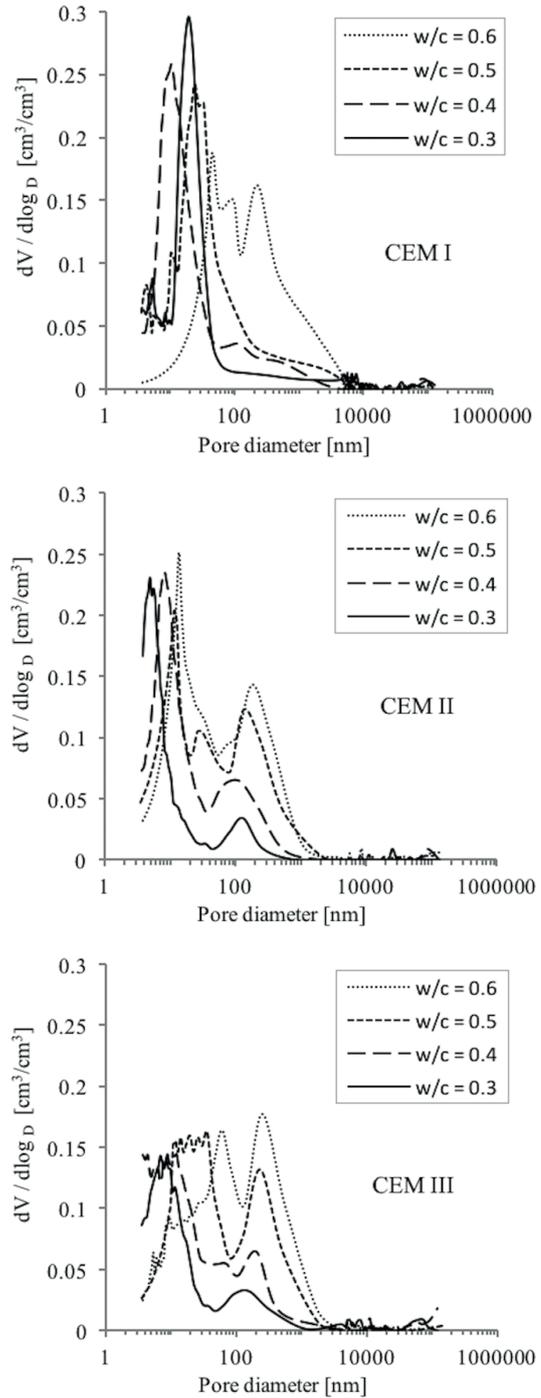


Fig. 5. Differential pore size distribution of cement paste with different types of cement

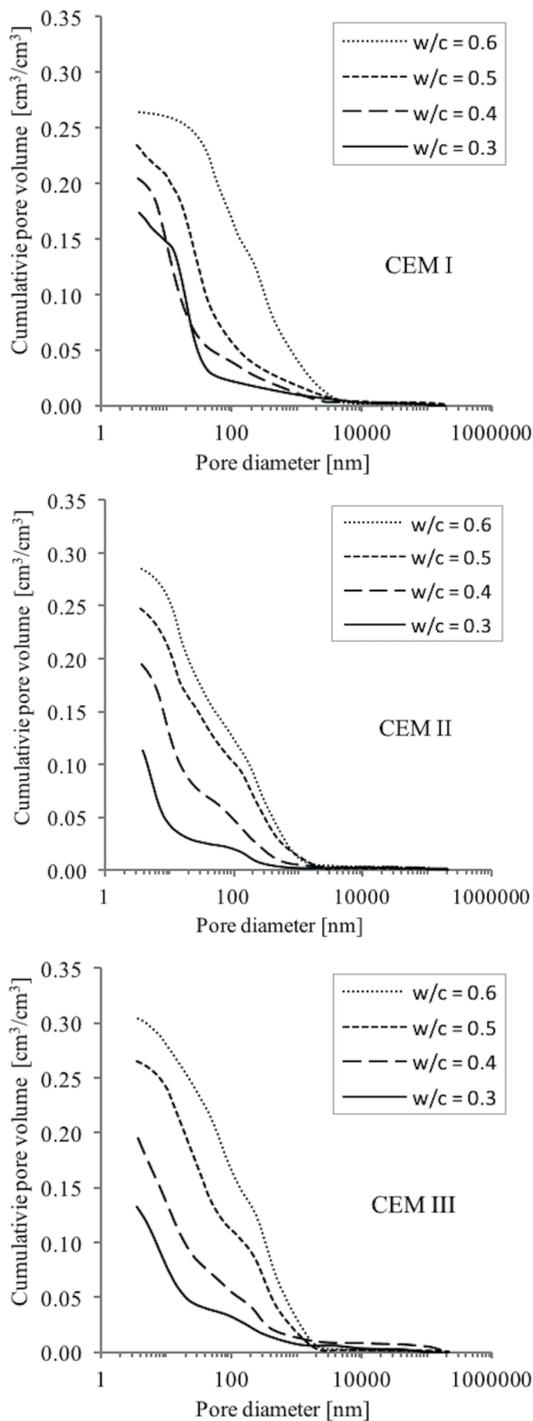


Fig. 6. Differential cumulative pore size distribution of cement paste at different type of cement

The $dV/d\log D$ distribution curves show a clear trend, particularly for cement pastes made with CEM II and CEM III cements where, as the w/c ratio decreases, the threshold pore diameter also falls within the range from 700 to 2000 nm. Thus, as the w/c falls, not only does the total porosity decrease but also the dominant pores shift towards smaller diameters. The research presented indicates that the $dV/d\log D$ distribution may be bimodal in character. If we compare the critical pore size within the range of

capillary pores ($d > 50$ nm), we see it falling along with the w/c . The intensity of occurrence of pores of this size also decreases. Similar observations concerning both cement pastes and mortars were presented by the authors of the publications [1, 31–33].

Further analysis of the resultant distribution of the structure of pores identified by mercury intrusion porosimetry consisted in dividing the entire range of pores identified by the MIP into three classes [30, 34]: meso-pores (< 50 nm), middle capillary pores ($50-100$ nm) and larger capillary pores (> 100 nm). The results of this analysis for the pastes made with the different cements tested are shown in Fig. 7.

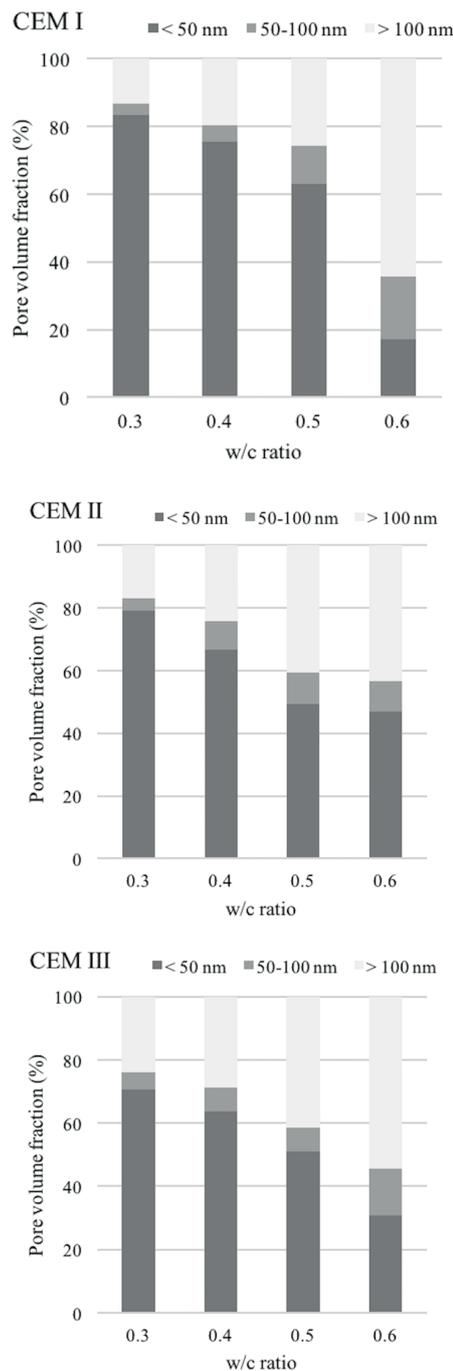


Fig. 7. Pore volume distribution of cement paste with pore classification

The analysis presented above confirms earlier observations that an increase of the w/c ratio causes a greater capillary porosity in all the cement pastes analysed. For example, in pastes made with blast furnace cement at a w/c of 0.3, capillary pores accounted for 18%, while in a paste with the w/c of 0.6, this amount increased to 64%. Obviously, as the number of capillary pores increases, the number of meso-pores, namely pores with a diameter below 50 nm, falls.

4.2. Permeability, w/c ratio and open porosity. Fig. 8 shows the relationship between the permeability coefficient of pastes made of different cements and the w/c ratio. The type of cement can be said to have a significant impact on this relationship. Just like the total open porosity and the share of capillary pores, permeability also increases along with the w/c [35]. For pastes made with particular cements, this relationship can be described sufficiently accurately by the exponential regression equations shown in the figures ($R^2 > 0,9$).

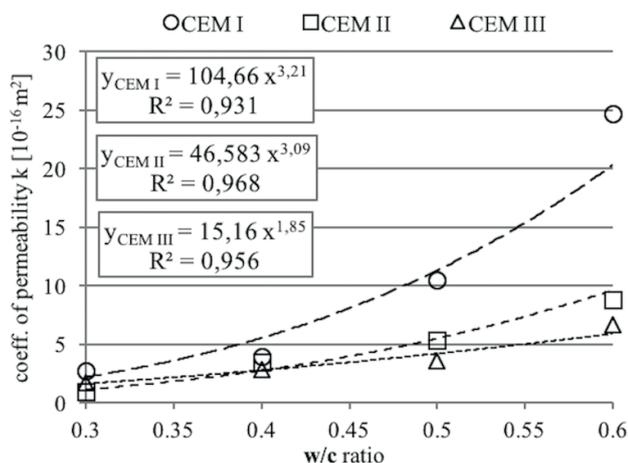


Fig. 8. Coefficient of permeability vs. w/c ratio [29]

The greatest impact of the w/c ratio on permeability is visible in the case of pastes made with CEM I cement. For pastes made with CEM II and CEM III, this impact is much weaker. In addition, these pastes feature lower gas permeability. The permeability coefficient of pastes made with CEM I and CEM II cements increases nine-fold as a result of the w/c rising from 0.30 to 0.60. In contrast, for pastes made with CEM III, the permeability increases only about four times.

Next, the dependencies of the permeability coefficient on the open porosity measured by helium pycnometry, mercury intrusion porosimetry and water saturation were analysed. These relationships are illustrated by Figs. 9–11 and the regression equations presented there.

In all cases, a good correlation between permeability and open porosity determined by various methods can be found. However, it should be noted that it is impossible to formulate a general dependency of cement paste permeability on its open porosity. It turned out that pastes made with different types of cement had to be analysed separately.

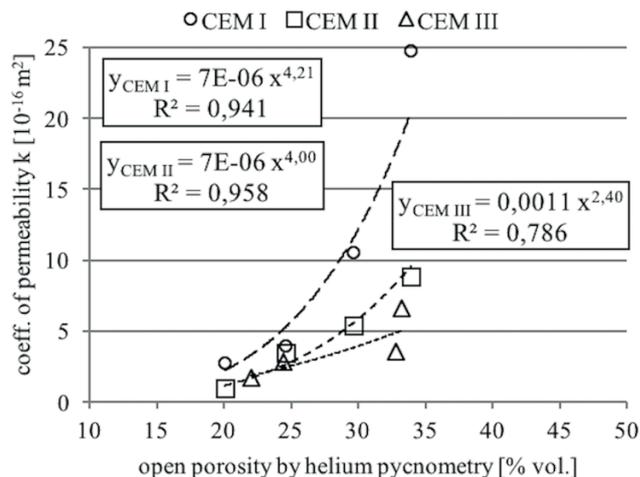


Fig. 9. Coefficient of permeability of cement paste vs. helium porosity [29]

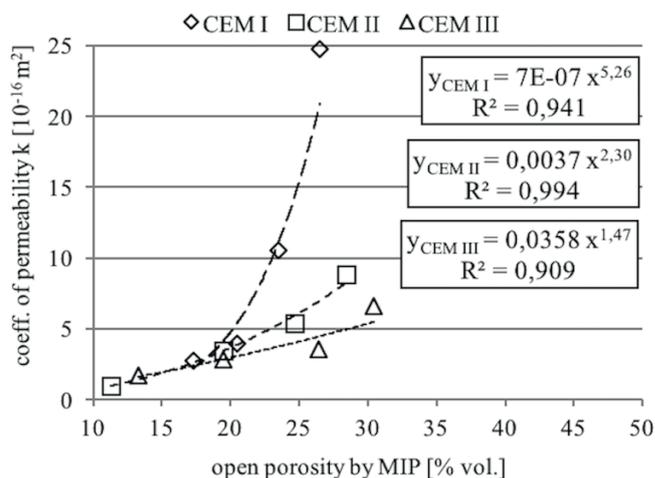


Fig. 10. Coefficient of permeability of cement paste vs. MIP porosity [29]

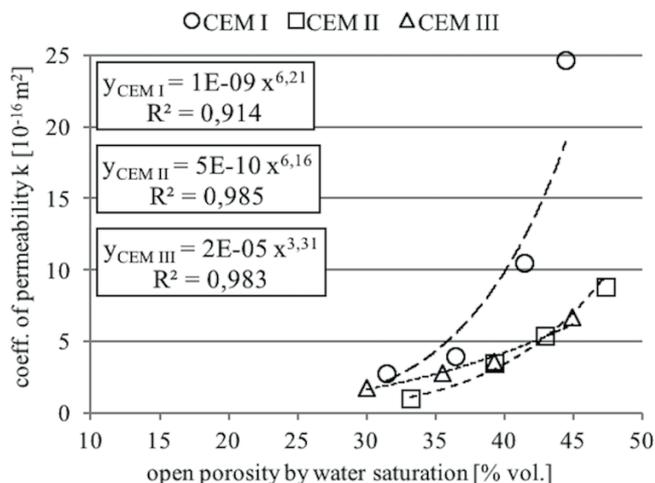


Fig. 11. Coefficient of permeability of cement paste vs. water saturation porosity [29]

Diversification of analysed binders which consists in lack or presence of additives with pozzolanic or latent hydraulic properties brings about significant changes in the microstructure of hardened cement pastes. Cement CEM II which contains high amount of reactive silica (fly ash) by pozzolanic reaction consume portlandite to produce additional amount of C-S-H phase. In the case of pastes made with CEM III the C-S-H phase is one hand more compacted and less porous, but on the other hand due to age of tested specimens one can expect lower hydration degree of cement.

The test results obtained indicate that gas permeability of cement pastes is influenced not only by total open porosity but also on pores size distribution. In other words, value of gas permeability dependance on both amount of open pores and pores diameter. This could be clearly seen when cement pastes made with CEM I and CEM III, characterized by water/cement ratio 0.6 were compared. Helium porosity is very similar and equals about 33%, but gas permeability is differentiated almost four times (see Table 3). Explanation to this phenomenon is volume fraction of capillary pores (> 50 nm), where in case of CEM I it equals 83% and CEM III it is 69%, related to total porosity.

It is difficult to clearly identify which of the presented methods for assessing the porosity is the most reliable and closest to the actual values. These methods identifies different ranges of pore size. Porosity measured by water saturation do not reflect the actual values of open porosity of the material, which is associated with phenomenon described in Chapter 4.1 i.e. with creation of “additional porosity”. Helium porosity allows to measure widest range of pores in the material structure. According to [23] very little atoms of helium can penetrate pores up to 0.25 nm in diameter. Nevertheless, as one can see from presented analysis the dependency of the permeability on open porosity can be described by exponential regression equations (almost in all cases $R^2 > 0.9$).

5. Concluding remarks

The research results presented and analyses completed support the following conclusions about the relationship between the open pore content and the composition of the paste and the impact of open porosity on permeability.

The value of the experimentally assessed content of open pores in cement paste clearly depends on the method used to measure it.

The highest values are produced when open porosity is treated as equivalent to the volumetric water saturation. However, because water additionally slips in between the layers of the C-S-H phases and leads to the swelling of the material, the above value does not represent the real proportion of open pores to volume of the material, but a higher value.

The lowest values of open porosity are produced by mercury intrusion porosimetry. The reason can be ascribed to the fact that this method does not identify pores that are smaller than 3.75 nm and greater than 0.25 mm. However, this method does provide valuable information about pore size distribution. An analysis of the results produced by it has shown that as the

w/c ratio increases, so does the share of capillary pores greater than 100 nm in diameter while the share of meso-pores, i.e. ones smaller than 50 nm, decreases. In addition, a general trend for the threshold pore diameter to decrease along with falling w/c ratio was observed. A similar nature of changes applies to critical pore size and the intensity of occurrence of pores of this size, belonging to the range of capillary pores (> 50 nm).

The dependency of the open pore content of cement pastes, determined by various methods, on the w/c ratio is quasi-linear.

The gas permeability of the paste depends on the type of cement, the w/c ratio and the associated open porosity (helium, MIP and water saturation porosity).

The gas permeability of pastes can be estimated based on the value of the w/c ratio or their open porosity using the exponential regression functions presented above.

Presented above information about the open porosity of cement pastes made with the three most popular types of common cements can be useful for designing the composition of cement concretes which are required to offer the appropriate permeability.

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