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Pore Size Distribution and Surface Multifractal Dimension by Multicycle Mercury Intrusion Porosimetry of GGBFS and Limestone Powder Blended Concrete

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Abstract: Eco-friendly concrete mixtures make efficient use of constituents with reduced environmental impact to secure durable structures. Ternary mixes containing Portland cement, ground granulated blast-furnace slag (GGBFS) and limestone powder (LP) have demonstrated a good balance between environmental impact, economic cost and technical performance. The pore structure of cement-based materials determines the transport of species; hence its description is a valuable tool for predicting their durability performance. In this paper, textural analysis of the pore structure of Portland cement concrete and GGBFS and limestone powder blended concrete is assessed by multicycle mercury intrusion porosimetry (MIP). Results from three intrusion-extrusion cycles were used for determining pore volume, size distribution and surface multifractal dimension. The hysteresis during the experiments is mainly explained by the combined effects of ink-bottle pores and different contact angles for the intrusion and retraction. The analysis of the surface multifractal dimension of the pore structure showed no significant effects of GGBFS and limestone powder on the pore wall texture of concrete samples. The outcome depicts the advantages of using multiple intrusion-extrusion cycles during MIP experiments, as well as the effect of 35 wt.% GGBFS, 25 wt.% GGBFS + 10 wt.% LP, and 25 wt.% of LP, on concrete pore structure.

Keywords: mercury intrusion porosimetry; fractal geometry; GGBFS; pore texture



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1. Introduction

The detailed description of the pore structure of cementitious materials has a significant practical interest. The analysis of the pore structure of concrete feeds the numerical modelling of macroscopic transport properties such as permeability, diffusivity, conductivity and electrical resistivity. All these estimations need microstructural data as input.

The complexity of the pore system of cementitious materials complicates the characterisation of the pore structure. Thus, the challenging description of geometry is normally limited to the assessment of the so-called pore entry size distribution, pore volume and specific surface area. However, additional information can contribute to a better understanding of the connection between the pore structure and transport processes. Pore wall roughness, pore connectivity and coordination with neighbouring throats are some of the parameters that are usually required for modelling. A wide-spread technique to describe the pore structure of cementitious systems is mercury intrusion porosimetry (MIP) [1–4].

Traditionally, data from MIP is interpreted by assuming a cylindrical-shaped pore network with variable sizes. This simplification allows the determination of the pore entry size distribution but limits the efficiency of the method for describing the pore structure and for providing sensible information for modelling. The conventional three-dimensional description of the pore structure can be expanded with an additional dimension that describes the self-similarity of the pore surface. Fractal geometry analysis is a statistical method

that describes irregular geometrical shapes with non-integral dimensions [5]. The fractal dimension characterises the self-similarity by the box-counting method (Equation (1)).

$$D = \lim_{\delta \rightarrow \infty} - \frac{\log N(\delta)}{\log \delta}, \quad (1)$$

where D is the fractal dimension, δ is the magnification factor or scale, and $N(\delta)$ is the number of self-similar parts under the fixed magnification factor.

The pore texture or irregularity can be described by considering the surface fractal dimension. Fractal analysis can contribute to more accurate models for interpreting MIP results by considering all features of the pore system.

When described by electrical resistivity measurements, cementitious materials with ground granulated blast-furnace slag (GGBFS) demonstrate an increase in the tortuosity of hardened cementitious systems [2,6]. To a lesser extent, limestone powder (LP) can increase tortuosity if its particle size distribution adequately complements the particle size distribution of cement and the packing of the system is improved. Supplementary cementitious materials (SCMs) are increasingly used in replacement of Portland cement thanks to their dual effect: (1) they have a much lower environmental impact than Portland clinker, and (2) they improve the microstructure by causing pore refinement and increased tortuosity. The impact of these SCMs on the pore structure is comprehensively depicted by MIP. A fair description is obtained by single-cycle MIP [2,7]. However, multicycle MIP may offer additional information of the action of SCMs. This paper describes the pore structure of blended concrete mixes by the analysis of multicycle MIP. Concrete mixes containing GGBFS and LP were tested and compared to Portland cement concrete samples. The interpretation of results focuses on the additional value of multicycle MIP to describe the effect of GGBFS and LP on the pore structure of concrete, also applying fractal analysis to describe the texture of pore walls.

An interesting aspect for analysis regarding the complexity of pore surfaces is the presence of GGBFS. Changes in the pore structure are confirmed with the substitution of Portland cement by GGBFS, but these are generally indicated as changes in the pore size distribution or pore volume. The texture of pore walls is also worth analysing. Some researchers have determined that GGBFS has a significant effect, but mainly on the micro-fractal dimension [8]. This seems a good indication of the contribution to the tortuosity of the pore structure. A more complex pore surface can increase tortuosity for some transport properties, whereas other mass transfer processes remain relatively the same. The most significant effect of GGBFS on cement-based materials is the huge increase in electrical resistivity. In general, this effect is attributed to the pore refinement [6,9,10] and binding of ions leading to a lower pore liquid conductivity [11,12].

The present paper describes the results of multicycle MIP of GGBFS and LP blended concretes. The analysis focuses on confirming the origin of the usually reported hysteresis in single MIP, as well as the effect of GGBFS and LP on the reversibility of the process. Moreover, the effect of GGBFS and LP on the pore wall texture is quantified by means of the surface multifractal approach described in Section 3. Results of multicycle MIP and surface multifractal analysis are rarely covered by the literature, even less combined in a single experimental program. Another uncommon approach is the analysis of the retraction hemicycle. Almost all analyses in the literature only use the intrusion hemicycle by considering a single value of the contact angle. The analysis of the retraction is also possible if a different contact angle is considered for that hemicycle, as discussed in Section 2. To our knowledge, this is the first time that data is presented on the study of GGBFS+LP+PC concrete mixes by combining multicycle MIP with analysis of surface multifractal dimension.

2. Mercury Intrusion Porosimetry (MIP)

The principle for MIP is simple, and it allows rapid detection speed across a wide range of pore throat sizes. MIP consists of intruding the cementitious sample with mer-

cury by applying external pressure. Thanks to the non-wetting nature of mercury, the required pressure can be converted into pore sizes according to the Washburn equation (Equation (2)).

$$r = -\frac{2\gamma \cdot \cos\theta}{p}, \quad (2)$$

where r is the pore entry radius, p is the pressure, $\gamma = 0.48$ N/m is the surface tension of mercury, and θ is the wetting contact angle of mercury. The technique has been connected with some shortcomings (e.g., possible damage to the samples, pore shape assumption, toxicity) [13,14], but it still allows a valuable indication of the pore structure of cementitious materials.

MIP studies generally report the determination of the intrudable volume, pore entry size distribution, critical pore entry size and threshold pressure. The threshold pressure denotes the largest accessible pore size that mercury can ingress into. The accessible pore entry size distribution, $PESD(r)$, is derived from the cumulative intruded volume [15], and it can be calculated as in Equation (3):

$$PESD(r) = \frac{p}{r} \frac{dV_t}{dp}, \quad (3)$$

where V_T is the intruded volume of mercury.

A single mercury intrusion-extrusion cycle of MIP is generally applied and interpreted following the cylindrical-shaped model. The cumulative volume of mercury is not fully accountable to a singular pore size. Whereas the required pressure is determined by the pore entry size, the intruded volume corresponds to the entire cavity [15]. After the first cycle, a volume of mercury remains permanently trapped, identifying the corresponding cavity volume of the so-called ink-bottle pores. These pores require higher pressure than the one corresponding to their cavity size, which depends on the narrower pore entry size. The application of multiple cycles of MIP could help in the differentiation between pore entry volume and pore cavity volume.

Moreover, hysteresis is noted between the entering volume during intrusion and the exiting volume during retraction [16]. Normally, only one intrusion is used for describing the pore entry size distribution. Several hypotheses have been suggested to explain this hysteresis. The most accepted ones relate to the presence of ink-bottle pores, different contact angles for intrusion and retraction, and pore connectivity [14,15]. Convenient simultaneous analysis of intrusion and retraction hemicycles can provide additional information.

The complex nature of the microstructure of cementitious materials requires complex geometrical models for interpreting MIP data. The fractal theory [5] provides an approach to describe the geometry of the pore structure by the fractal dimension of its surface, with values varying between 2.0 and 3.0. The higher value for the fractal dimension indicates the higher complexity of the surface. In practical terms, for a similar pore size range, a higher surface fractal dimension can be interpreted as a higher roughness. When applied to the analysis of MIP results, a linear relationship between pressure and mercury saturation can be constructed [17], and the fractal dimension is calculated as the slope of this relationship.

3. Thermodynamic Approach for Obtaining the Surface Fractal Dimension from MIP

The surface fractal dimension D describes the geometric complexity of the surface. Normally, the dimension is an integer number (1 for curves, 2 for surfaces, 3 for volumes). The usual topological dimension of a surface is increased over 2 as the surface gains complexity or roughness, up to a maximum value of 3. As a result of MIP, the value of D can be determined. As $D = 3$ correspond to the full volume filling, any value $D > 3$ has no physical justification. The usual interpretation of MIP results with a cylindrical-shaped pore network assumes the dimension of 2 and reads any increase in the intruded volume with the pressure as the intrusion of adjacent smaller pores. A significant part of this volume actually corresponds to the improved adjustment to the rough pore surface (Figure 1). In other words, the volume of the pore is a function of the scale at which this is measured.

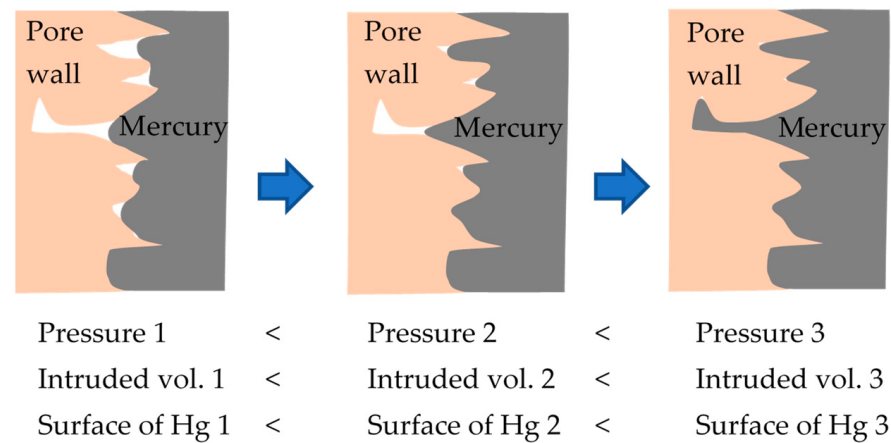


Figure 1. Correlation between pressure and the adapted surface of mercury against the rough pore wall.

The relation between the pressure and the surface of the intruded mercury can be considered to quantify the complexity of the pore wall surface. During the MIP process, the increase in pressure causes a progressive increase in the volume of intruded mercury and, with it, an increase in the surface energy of the system. The increase in the energy in the system equals the work done for the mercury to intrude the sample. On the fractally rough pore surface of the cementitious material, the correlation between the area for a fractal surface (S) and the circumscribed volume (V) is given by Mandelbrot [5] as in Equation (4). Considering the energy conservation during the MIP experiment, Zhang and Li [18] proposed a logarithm proportionality between the accumulated intrusion work W_n and the represented accumulated intrusion surface (Q_n) in Equation (5). Then, the surface fractal dimension D can be computed from Equation (6).

$$S^{1/D} \sim V^{1/3} \quad (4)$$

$$\ln(W_n) = \ln(Q_n) + C \quad (5)$$

$$\ln\left(\frac{W_n}{r_n^2}\right) = D \ln\left(\frac{V_n^{1/3}}{r_n}\right) + C \quad (6)$$

where V_n and r_n are the accumulated intruded volume and smallest pore radius for the intrusion phase n , and C is a constant. This approach has been applied in [8,19] to characterise the microstructure of cement-based materials, where a scale-dependence of the surface fractal dimension was confirmed. This means that the pore structure changes in complexity depending on the scale at which it is analysed. A microfractal region was associated with the microstructure of C-S-H, whereas the macrofractal region was associated with the capillary porosity. In other words, the self-similarity maintains for certain pore size, and then it transitions to another self-similarity, with a different value of the surface fractal dimension. An important corollary of the previous finding would be that modelling cannot be established to consider only one type of physical pore structure, but it would need to change depending on the value for the surface fractal dimension.

4. Materials and Methods

Table 1 presents the compositions and designations of the studied concrete mixes. Two concrete mixes with $w/b = 0.40$ and containing GGBFS and LP as partial replacement of Portland cement were prepared: G40 with 35 wt.% GGBFS, GL40 with 25 wt.% GGBFS + 10 wt.% LP, and L40 with 25 wt.% LP. Further, control mixes with 100% Portland cement (PC) were prepared as a reference with $w/c = 0.35$ (P35), 0.40 (P40), and 0.45 (P45). Thus, in the designation of the concrete mixes, G and L indicate the incorporation of GGBFS and LP, respectively, whereas P indicates Portland cement as the only cementitious component.

The figures in the designation of mixes indicate the water-to-binder ratio multiplied by 100. The properties of PC, GGBFS and LP are presented in Table 2. The strength activity index of GGBFS was 0.95. Additional specimens were cast for the determination of compressive strength (3 cylinders of 100 mm in diameter and 200 mm in height per age and mix) and porosity by vacuum water absorption (3 cylinders of 100 mm in diameter and 100 mm in height per mix). The entrained air was measured in the fresh state by means of the pressure method.

Table 1. Mix proportions and properties of concretes.

Materials (kg/m ³)	P35	P40	P45	G40	L40	GL40
Water	133	140	144	140	140	140
PC	380	350	320	227	262	227
GGBFS	-	-	-	123	-	88
LP	-	-	-	-	88	35
Siliceous sand	938	944	959	945	945	945
Crushed granite 6–20 mm	980	980	980	980	980	980
Superplasticizer (l)	6.2	5.9	6.0	4.9	4.2	4.1
Entrained air in fresh state (%)	3.0	3.1	3.0	3.2	3.5	3.4
Properties						
Slump (mm)	80	100	60	100	90	70
Unit weight in fresh state (kg/m ³)	2404	2417	2392	2390	2385	2354
Accessible porosity by water absorption 28 d (%)	8.02	8.68	8.90	9.10	8.78	9.49
Compressive strength (MPa)	7 d	54.2	47.6	37.8	47.6	37.4
	28 d	60.2	47.6	44.3	52.6	42.2
	90 d	63.2	52.8	45.9	58.1	47.3

Table 2. Properties of Portland cement and supplementary cementitious materials.

ID	PC	GGBFS	LP
Blaine specific surface area (m ² /kg)	380	373	476
Mass retained on sieve 75 µm (%)	1.3	<0.01	1.6
Density	3.11	2.87	2.75
Chemical composition (%)	Loss on ignition	2.14	0.87
	Insoluble residue	2.50	3.40
	SO ₃	2.41	3.58
	MgO	2.76	9.36
	SiO ₂	19.93	30.49
	Fe ₂ O ₃	4.00	0.29
	Al ₂ O ₃	4.30	10.68
	CaO	60.38	38.17
	Na ₂ O	0.14	1.42
	K ₂ O	0.85	0.44
	Cl ⁻	0.012	<0.001

For MIP measurements, prismatic concrete specimens (75 × 100 × 250 mm³) were cast and cured for 28 days in a wet room, RH > 95%, temperature (23 ± 2) °C. These specimens were aged in the laboratory, average RH ~ 75% and temperature (15–30) °C for 2 years. Uncarbonated samples of about 4 g of crushed pieces of material were taken from the core of the specimens and used for the MIP experiments.

Applying MIP to concrete samples has some advantages and disadvantages in comparison with determination on cement paste. Concrete samples include an interfacial transition zone around the aggregates with a differentiated pore structure from the one

of the matrices. The measurements on concrete samples can depict the combined effect of the binder system and the fractality of the interfacial transition zone more realistically. As a limited amount of sample is used for MIP, it is important to secure a representative sampling. This is more difficult for concrete than for cement paste due to the presence of aggregate particles. In the present study, concrete samples were carefully crushed to particles of about 5 mm. Large aggregate particles were discarded and the mortar particles were increasingly sub-sampled in a riffle splitter until obtaining the required amount of sample.

MIP was performed on a Pascal 140/440 (Thermo Fisher Scientific Inc., Milan, Italy) instrument. Samples were pre-conditioned by solvent exchange with isopropanol, as described in [20]. The samples were pre-intruded in the low-pressure device to 200 kPa to fill the interparticle space and then moved to the high-pressure device where intrusion was progressively increased to a maximum of 200 MPa. Then, the pressure was slowly released, and the retraction curve was recorded. Two additional full intruding-retracting cycles were performed on each sample. The assumed surface tension of mercury was 0.48 N/m.

The interpretation of the cumulative mercury intrusion is very dependent on the contact angle assumed for the mercury. This contact angle has a direct influence on the calculated pore entry size as indicated in Equation (1), but its exact determination is not straightforward. Even though the physical-chemical characteristics of the pore walls can affect this contact angle, it is generally assumed at a fixed value for comparative purposes. The surface roughness generally increases the effective contact angle [21]. In this sense, the fractal dimension of the pore structure can contribute to explaining differences in the intrudability of samples by changes other than pore throat size. With a fixed contact angle, a higher pressure required to intrude a certain pore volume is directly translated into a finer pore structure. However, this could also be due to an increase in the contact angle due to increased roughness. SCMs can demonstrate pozzolanic activity that affects the pore structure. Such effects are normally defined as caused by pore refinement, but even less noticeable changes in pore wall texture can affect some transport processes. The effect of GGBFS on the surface fractal dimension would suggest the need for a different value for contact angle.

An important derivation of the contact angle concerns the hysteresis occurring between the intrusion and retraction hemicycles. By considering a different value for the advancing and the receding contact angles, a significant part of this hysteresis could be explained. However, only if re-intrusion and retraction curves have a similar shape, the hysteresis can be fully attributed to different contact angles. To a lower extent, other elements can also contribute to this hysteresis, such as ink bottle pores and pore connectivity. The literature explains an effect of the pore wall texture that causes a significant increase in the advancing contact angle while the receding contact angle is not significantly affected [22]. Such difference has been evaluated in controlled pore glass and generalised for other porous systems [23]. In fact, a part of the irreversible intrusion of mercury can be attributed to the different values in the contact angle. The pressure required to move the mercury with convex menisci into the pore system is higher than the receding pressure, as the component of the surface tension is proportional to $\cos(\theta)$. In the present study, intrusion and retraction contact angles were estimated in ranges of 140–142° and 102–104° [24], respectively. Both ranges of values are not exact, but they are defined as the most probable. It is believed that the contact angle will vary with age, binder type and pre-conditioning of the sample, probably causing a larger difference between the advancing and receding contact angles for a resulting rougher pore wall surface.

5. Results

Figure 2 shows the cumulative MIP curves with pressures converted into pore entry sizes. The assumption of different contact angles results in very similar curves for all hemicycles except for the first intrusion. Some hysteresis for the first cycle maintains even with the consideration of the different contact angles. A supplementary explanation is thus

needed for this first intrusion. For the second and third cycles, the change in the contact angle seems sufficient to fully explain the hysteresis. As the retraction curve is parallel to the second and third cycles, the second contributor to the hysteresis during the first cycle is most likely the filling of ink-bottle pores.

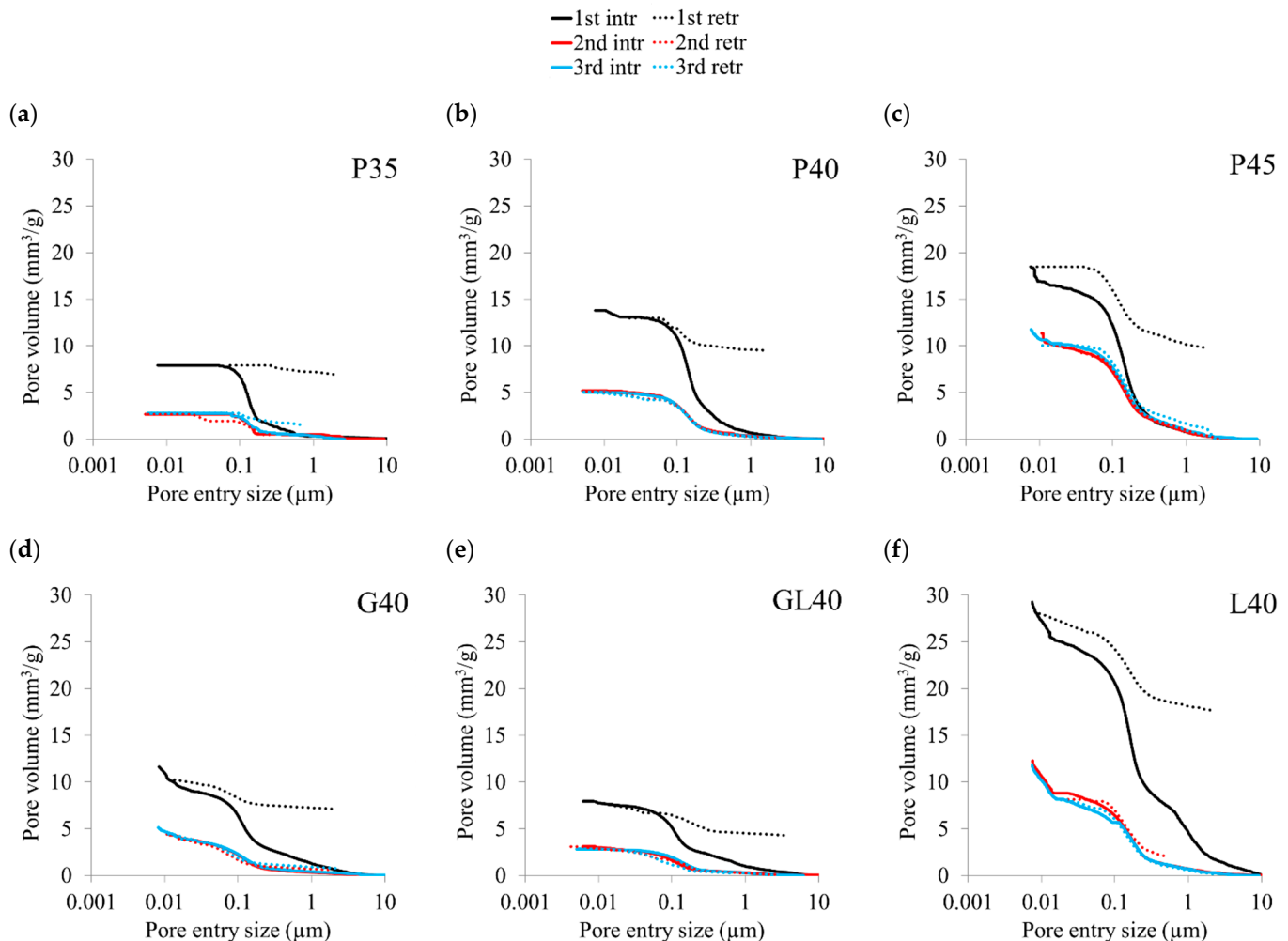


Figure 2. Cumulative curves for the multicycle MIP for mixes (a) P35, (b) P40, (c) P45, (d) G40, (e) GL40 and (f) L40.

The intrusion for the second and third cycles are almost identical for all the series. Only two MIP cycles are required to collect all the information. The third cycle is useful for confirming the data from the second cycle, but it does not provide new information.

The pore volume of each sample correlates to the corresponding w/b ratio. For mixes only containing Portland cement, the w/b ratio is the only parameter determining the porosity of the samples with a same curing treatment. The inclusion of GGBFS in G40 and GL40 series contributes to a reduction of the pore volume in comparison with P40, which has the same w/b ratio. In fact, results of G40 and GL40 are comparable to P35, meaning that in practical terms, the use of GGBFS is equivalent to a reduction from $w/b = 0.40$ to a $w/b = 0.35$.

Moreover, the differences between the first intrusion and the second intrusion are smaller for samples containing GGBFS than for samples without GGBFS. This difference is interpreted as the irreversible process of filling ink-bottle pores. The absolute value for the irreversibly intruded volume is lower for G40 and GL40. The highest irreversibly intruded volume relative to the total intruded volume is between 66% (P35), and the lowest is 39% (P45). Values for all mixes were within this range, with values near 60% as the most frequent. No consistent relationship between the relative irreversibly intrudable volume of

the samples and their composition was detected. It would be reasonable to consider this volume as an indirect assessment for pore connectivity, but more research in this regard is necessary for conclusive results.

The effect of LP was relative to the overall composition of the mix. For GL40, the low LP content and its synergy with GGBFS did not result in significant differences compared to G40. For L40, the individual effect of the LP can be mostly regarded as dilution of cement phases. In this case, the MIP showed higher porosity for L40 than for P40 and even P45. This effect could have been different if LP is incorporated by intergrinding with clinker during cement manufacture, as in that case, the particle packing of the system improves thanks to the lower hardness of limestone in comparison with clinker [25].

Figure 3 shows the derivative MIP curves with the pore entry size distributions for all samples. The pore entry size distribution from the first intrusion shows a similar shape as for the second and third cycles. After the first cycle, no noticeable modification of the pore entry size distribution is noted with the applied procedure up to a maximum pressure of 200 MPa. The critical pore entry size and threshold pore entry size are indicated for each sample. No significant differences for this parameter are observed for the three cycles.

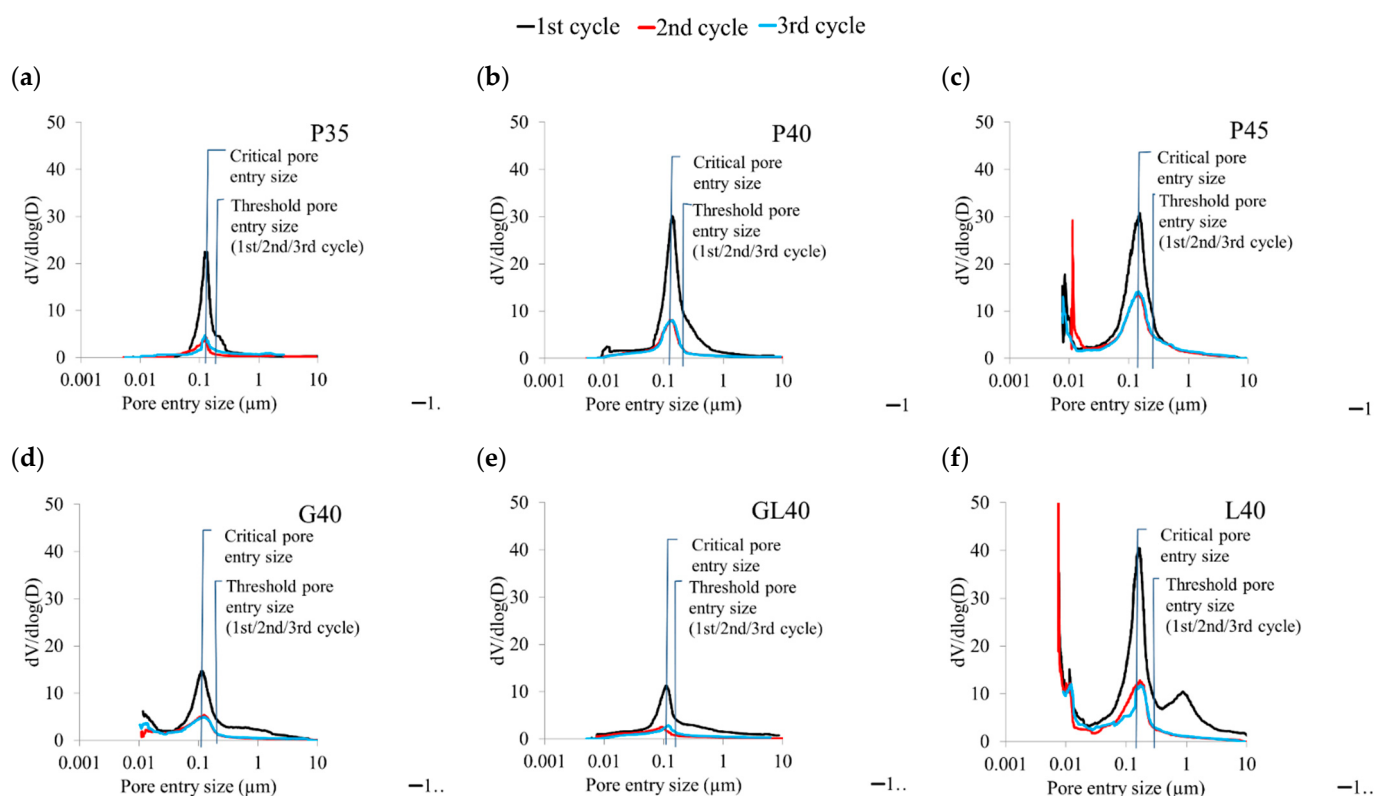


Figure 3. Derivative curves for multicyle MIP for mixes (a) P35, (b) P40, (c) P45, (d) G40, (e) GL40 and (f) L40.

The pore entry size distribution correlates with the expected pore structure for each sample. For the most porous samples, P45 and L40, a second peak for pore entry size emerges in the micropore size range. For the rest of the mixes, this peak is beyond the measured range of pore entry sizes, as a maximum pressure of 200 MPa was applied in all cases.

Figure 4 presents the values of the surface fractal dimension for the tested samples during the first and third intrusion hemicycles. The analysis is performed with a multiscale approach as suggested in [26]. Multiple linear regressions of data to Equation (5) are made in each case. The large capillary porosity and the fine C-S-H porosity can usually be regarded as pore surface fractals, whereas a transition zone in between them is identified as non-fractal. The slope of the transition zone is generally over 3, with no direct physical

meaning. The limits of the macrofractal and microfractal were decided so the determination coefficient was above 0.99. The only exception was the microfractal for the first intrusion of P35, where it was not possible to achieve such a degree of correlation due to the limited produced data. The explanation for the non-fractal transition is not totally clear. Zeng et al. [19] suggest it is due to the presence of ink-bottle pores. However, this can be only partially true, as for the third intrusion cycle the transition zone remains, with the sole difference of some additional work required per unit volume of mercury. As explained, the whole intruded volume in the third cycle was reversible, and no volume of unfilled ink-bottle pores participated in that cycle.

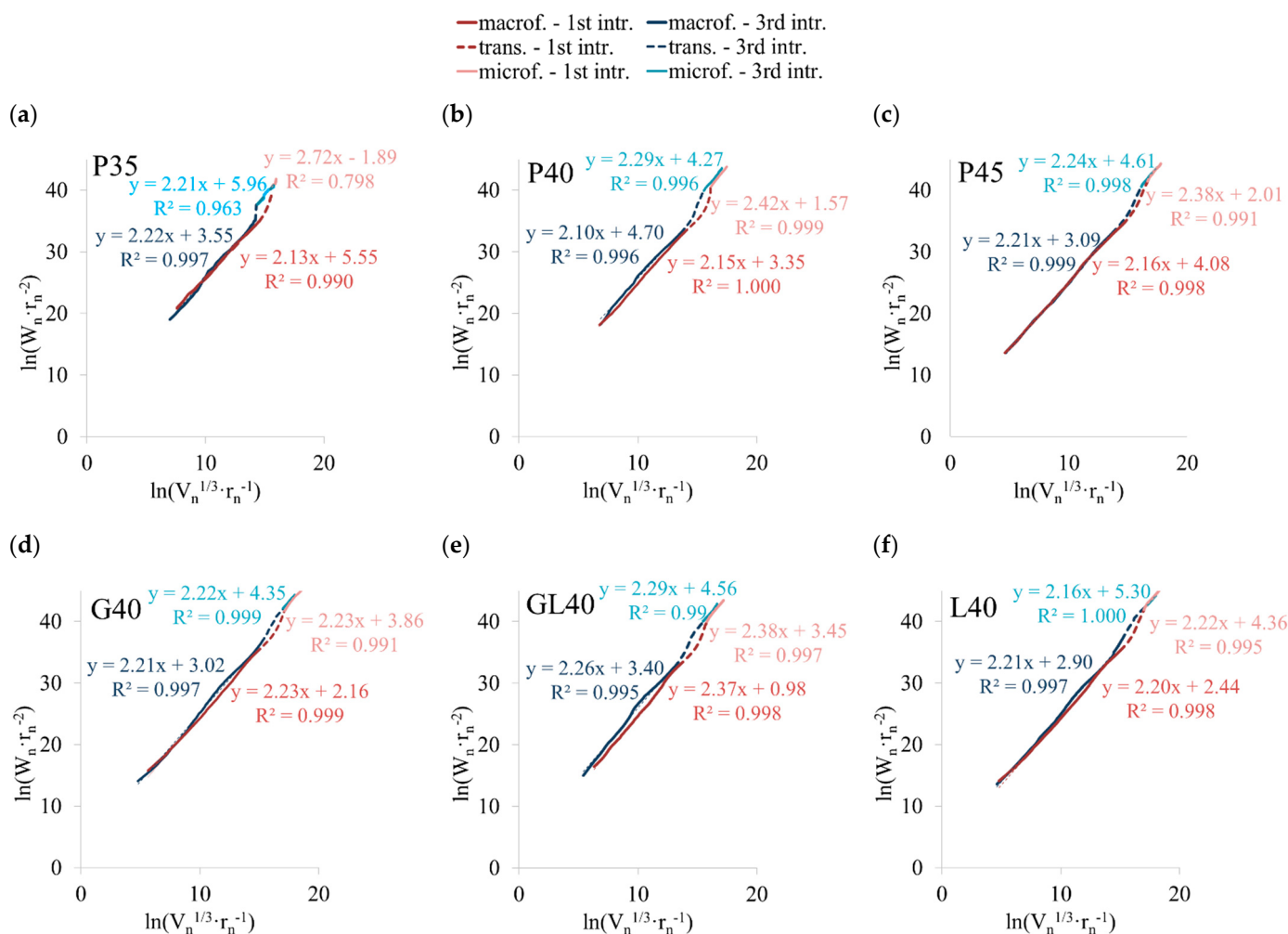


Figure 4. Surface fractal dimension values for first and third MIP cycles for mixes. (a) P35, (b) P40, (c) P45, (d) G40, (e) GL40 and (f) L40.

The value for the gel porosity is not as reliable as the value for the coarse porosity. Due to the limitation of maximum pressure to 200 MPa, there is a narrow range of gel pores over which the surface fractal dimension is computed.

The values for the surface multifractal dimension are within a certain range of values. With the only exception of the microfractal for the first intrusion of P35 (2.717), all surface multifractal dimensions are between 2.103 and 2.422. No specific correspondence with the composition of each mix is noted. Moreover, the comparison between the first MIP and third MIP cycle results in no consistent relation between the obtained values. It is possible that the range of values obtained is mostly due to the scattering of the method rather than the variable properties of mixes. The only trend is that of the value for the microfractal being in all cases higher than the corresponding for the macrofractal. More research in

this regard seems necessary to confirm these results as the maximum pressure applied in the present study allowed only a narrow micropore size range to be measure. Thus, the hydration products would demonstrate a slightly more complex arrangement than the pattern produced by particles at a larger scale.

6. Discussion

The first cycle always allows a larger volume of intruded mercury than the following cycles due to the presence of ink-bottle pores. The cavities of this type of pores are filled during the first intrusion, as the subsequent cycles showed no residual increments of the cumulated volume. All accessible ink-bottle pores are fully filled during the first intrusion and remain so later on. No effects of ink-bottle pores are produced in the subsequent cycles. Once the ink-bottle pores are filled, the process becomes fully reversible. The appreciated reversibility means that the structure remains the same during the second and third cycles.

The sole adoption of different values for the contact angle permitted to effectively explain almost all the remaining hysteresis for the second and third intrusion cycles after the effect of ink-bottle pores in the first intrusion was discounted. Since the receding contact angle is smaller, a given value of pressure corresponds to a smaller pore entry size for the retraction than for the intrusion. If the same values of 140 or 142° (instead of 102 or 104°) were also considered for the retraction of mercury, unrealistic pore sizes corresponding to between 3.2 to 3.7 times the pore sizes determined for the intrusion would have been obtained (Figure 5). The application of different values for the contact angle of advancing and receding mercury allows discarding the presence of unfilled ink-bottle pores in the entry size range already covered by the first run of mercury intrusion. As no influence of ink-bottle pores in the second and third cycles is observed, no effect of this type of pores on the critical pore entry size for the intrusion in the first cycle is derived (a shift in the value must show otherwise). The critical pore entry size applies to both the volume of the entry and the cavity. The ink-bottle pores are defined with a larger size for their cavity than for their entry, so that for 1 mm³ of pore entry the volume of the corresponding cavity should be larger than 1 mm³. Therefore, the second intrusion shows the actual distribution of the pore entries, while the volume surplus of the first intrusion in comparison with the subsequent cycles corresponds to the volume of cavities. The actual pore size distribution of cavities must be shifted towards larger sizes, but the value of this shift is uncertain. Therefore, we cannot be completely sure that the first cumulative curves efficiently represent the pore size distributions, but the second and third cycles reflect the actual volume of pore entries, i.e., the fraction for which MIP is reversible.

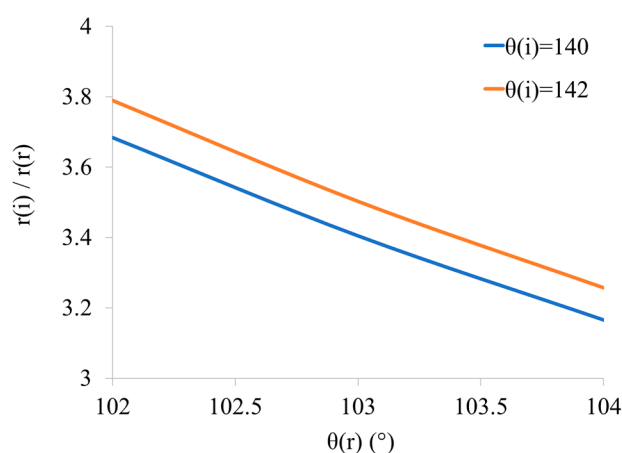


Figure 5. Ratios between the pore size $r(i)$ obtained for the retraction of mercury when considering the same contact angle $\theta(i)$ as for advancing mercury (140 or 142°) and the pore size $r(r)$ for the retraction of mercury when considering a smaller contact angle $\theta(r)$ (102 or 104°) for the receding mercury.

Many times, the effect of GGBFS is said to enhance the resistance to the penetration of matter into concrete thanks to pore refinement action. The shift in tortuosity should appear as a consequence of the differentiation between the effect of GGBFS on the pore entry size rather than the pore volume. A clear difference is visible when we compare the intruded pore volume (maximum intruded volumes in Figure 2) for the first and second cycles in each of the concrete mixes. In the mixes containing GGBFS, the relative difference between both cycles is larger than for Portland cement concrete mixes (i.e., larger relative volume of ink-bottle pores). For G40 and GL40 the intruded volumes in the second cycle relative to the intruded volumes in the first cycle are 37.8 and 39.1%, respectively, similar to P35 (33.8%) which has a lower w/c ratio. The same ratios for P40 (64.3%) and P45 (63%) are higher, demonstrating less relative volume of ink-bottle pores. However, tortuosity seems to be more independent from these ink-bottle pores, as the critical pore entry size does not reduce significantly with the use of GGBFS. In this analysis, we should consider the dilution effect of the aggregates and the impact of the formed interfacial transition zone. The action of GGBFS is not the same for the bulk matrix than for the interfacial transition zone. Then the upscaling to concrete of measurements made in paste and mortar should address such dilution effect of aggregates and the corresponding interfacial transition zone.

A deeper analysis would be possible if the actual difference between advancing and receding contact angles in the different systems was determined. The collected results do not allow to perform such analysis, but this seems interesting for further research. The pore wall texture is one of the parameters affecting the contact angle, and in this sense a connection with the surface fractal dimension could be established.

The surface fractal dimension obtained from MIP can be considered as an indirect measurement of the pore wall texture, but then mainly as a statistical parameter. The intruded volume receives contributions from several sources, so the concept explained in Figure 1 cannot be used to literally reconstruct the actual pore surface. However, the value for the surface fractal dimension can be used as a statistical descriptor of the pore wall surface, and as such, being applied in the construction of a pore wall model.

For example, the pore walls can be modelled with a developable surface of variable dimension considering the outcome of the MIP. The determined values for the surface fractal dimension would allow depicting the pore wall. A parametrised, developable surface model may then be constructed by iteration.

The undistinguishable correlation between the mix composition and the surface fractal dimension is probably due to the dilution effect that aggregates produce in the concrete samples. The analysis of pastes might show more significant differences. However, the composition of the binder system poses a limited contribution to the development of the texture of the pore structure, for which aggregates seem to dominate. In concrete samples, the interfacial transition zone plays an important role in the formation of the pore structure. As such, the surface multifractal dimension is greatly determined by the interfacial transition zone. For the macrofractal it contributes to capillary porosity. For the microfractal it contributes to a different arrangement of hydration products. Zeng et al. [8] determined no significant effects of the use of GGBFS as 70 wt.% of the binder content for macrofractal surface dimension in pastes and mortar with w/b between 0.3 and 0.5. A more significant effect was obtained for the microfractal region, with values increasing from 2.3–2.4 to 2.7–2.8. This seems reasonable as, at this scale, there is no effect of aggregates and unhydrated particles. Such effects due to GGBFS contents of 70 wt.% did not replicate in the present study in which GGBFS was only 35 wt.% of the binder content. At concrete scale, it seems that the obtained differences can be attributed to statistical variations more than the effect of GGBFS and LP. The reaction of GGBFS produces C-S-H very similar to the primary C-S-H from clinker hydration. Hence, the pore refinement and densification of the pore structure does not seem to translate into major changes in the texture of pore walls. It is well known that GGBFS may consume only limited amounts of portlandite during its reaction. Some differences are possible if crystalline phases such as portlandite would be depleted. Mixes with high contents of highly pozzolanic SCMs may show a larger relative

conversion of portlandite into C-S-H with the associated gel pore volume. Then, a more significant affectation of the pore texture can be expected.

7. Conclusions

The eco-friendliness of GGBFS-blended concrete derives from a reduction of the carbon-intensive Portland clinker content in concrete with no detrimental affectation of the microstructure development. The pore refinement by GGBFS enhances concrete durability, and therefore also indirectly the eco-performance. The synergy between GGBFS and limestone powder allows further reduction of the clinker factor in the binder system. Concrete samples with Portland cement, GGBFS and limestone powder were analysed by multicycle MIP. The considerations regarding the intrudable volume, pore entry size distribution and surface multifractal dimension led to the following conclusions:

- The ink-bottle pores are filled during the first intrusion. The subsequent cycles showed no residual increments of the cumulated volume. Once the ink-bottle pores are filled, the process becomes fully reversible (i.e., second and third cycles are almost the same). Such reversibility suggests that the structure remains the same during the second and third cycles.
- The hysteresis in MIP is almost completely explained by the presence of ink-bottle pores (only applicable to the first cycle) and a different contact angle for intrusion and retraction.
- No influence of ink-bottle pores on the “critical pore entry size” was noted. The ink-bottle pores can be characterised concerning only their volume. The pore size distribution does not apply to ink-bottle pores. Thus, the first cycle is not reliable for assessing the reversibly intrudable porosity.
- GGBFS contributes to pore refinement, mostly noticed by reductions in the intrudable pore volume. Reductions in the critical pore entry size were also noted with the use of 35 wt.% GGBFS, but this second effect was less significant.
- The surface fractal dimension was successfully determined from MIP data. This can be considered as a direct statistical measurement of the pore wall texture. The actual pore surface cannot be reconstructed, but it can be modelled.
- No clear correlation between the mix compositions and the surface fractal dimension was determined. This is probably due to the dilution effect that aggregates produce in the concrete samples. The analysis of pastes might show more significant differences, but the dilution effect of aggregates and the corresponding interfacial transition zone should be addressed when upscaling interpretations.

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