Characterization of the pore structure of hardened self-compacting cement paste

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1. Introduction

Self-compacting concrete (SCC) can be placed without any compaction, avoiding some health risks as well as environmental problems. The two essential properties of SCC are a high flowability and a high segregation resistance, obtained by the use of either a large amount of fine particles (P) or a viscosity modifying admixture and a superplasticizer. Self-compacting concrete and traditional concrete (TC) are based on different mix designs. As such, a different pore structure of the cement matrix might occur causing a different durability. The degradation mechanisms of cementitious materials are greatly influenced by the penetration ability of aggressive fluids, and there is an important relation between the 'pore structure' of solids, fluid transport properties and degradation. This means that if the pore structure of SCC turns out to be different from traditional concrete, some changes in durability behaviour might be expected as well. In this paper the pore structure of SCC and TC has been evaluated by means of mercury intrusion porosimetry on hardened cement pastes. This investigation leads to interesting information on the porosity of SCC and TC as well, since the properties of concrete and mortar are very much depending on the properties of the hardened cement paste [1]. When the aggregate grains are not porous and the compaction is optimal, according to [2], the tightness and strength of concrete is depending on the properties of the cement paste only.

2. Mixture design

The mixture proportions, parameters and compressive strength of 22 cement pastes are presented in Table 1a and Table 1b. The compressive strength has been determined on samples of 28 days old, stored in a climate room at 20°C and more than 90 % RH. The mixture proportions of the cement pastes are based on the mixture design of SCC and TC mixtures on which already many tests on durability and transport properties have been performed [3, 4, 5]. The proportion of materials used for making the cement paste correspond to the amounts of constituents in 1 m³ of concrete. Pastes PT1 and PS1 are the reference materials for traditional concrete and for self-compacting concrete respectively, with a cement content of 360 kg/m³ and a W/C of 0,46. For both cement pastes portland cement type CEM I 52.5 N is used. Limestone filler (240 kg/m³)

and a polycarboxylic ether superplasticizer were used for the cement paste PS1. The cement type is varied by the replacement of CEM I 52.5 N with CEM III/A 42.5 LA (PS2, PT2) or CEM I 52.5 HSR (PS3, PT3). The replacement of limestone filler (97.3 % $CaCO_3$) by quartzite filler (mainly SiO_2) leads to mixture PS4. For mixtures PS5, PS6 and PS7 (CEM I 52.5 N) and PS8, PS9 and PS10 (CEM III/A 42.5 LA) the C/P is varied between 0.5 and 0.75. The C/P is varied by changing the amount of cement and filler and keeping the powder content constant. The amount of water is varied for the mixtures PS11, PS12 and PS13 (CEM I 52.5 N) and PS14, PS15 and PS16 (CEM III/A 42.5 LA). This leads to a variation of the W/C from 0.40 to 0.55. Also for the traditional pastes the W/C is varied: TP4, TP5 and TP6 (CEM I 52.5 N). The average particle size of limestone filler was slightly smaller than that of the cement used. The minimum, maximum and average size is for instance respectively 0.2 µm, 80 µm and 15 µm for CEM I 52.5 N and 0.2 µm, 100 µm and 10 µm for limestone filler.

Tabel 1a- Mixture proportions of cement paste (kg/m³ concrete)

	PS1	PS2	PS3	PS4	PS5	PS6	PS7	PS8	PS9	PS10	PS11
CEM I 52.5 N [kg/m³]	360	0	0	360	300	400	450	0	0	0	360
CEM III/A 42.5 LA	0	360	0	0	0	0	0	300	400	450	0
CEM I 52.5 HSR	0	0	360	0	0	0	0	0	0	0	0
limestone filler P2	240	240	240	0	300	200	150	300	200	150	240
quartzite filler	0	0	0	240	0	0	0	0	0	0	0
water	165	165	165	165	165	165	165	165	165	165	144
superplasticizer [l/m³]	2.8	2.3	2.5	4.1	2.3	3.1	3.4	1.8	2.5	2.7	3.2
water/cement [-]	0.46	0.46	0.46	0.46	0.55	0.41	0.37	0.55	0.41	0.37	0.40
cement/powder [-]	0.60	0.60	0.60	0.60	0.50	0.67	0.75	0.50	0.67	0.75	0.60
$f_{ccub150,28}$ [N/mm²]	77.6	69.2	74.5	101.1	62.8	79.3	80.0	62.3	78.1	74.4	87.3

Tabel 1b- Mixture proportions of cement paste (kg/m³ concrete)

	PS12	PS13	PS14	PS15	PS16	PT1	PT2	PT3	PT4	PT5	PT6
CEM I 52.5 N [kg/m³]	360	360	0	0	0	360	0	0	360	360	360
CEM III/A 42.5 LA	0	0	360	360	360	0	360	0	0	0	0
CEM I 52.5 HSR	0	0	0	0	0	0	0	360	0	0	0
limestone filler P2	240	240	240	240	240	0	0	0	0	0	0
quartzite filler	0	0	0	0	0	0	0	0	0	0	0
water	180	198	144	180	198	165	165	165	144	180	198
superplasticizer [l/m³]	2.6	2.3	2.7	2.1	1.8	0	0	0	0	0	0
water/cement [-]	0.50	0.55	0.40	0.50	0.55	0.46	0.46	0.46	0.40	0.50	0.55
cement/powder [-]	0.6	0.6	0.6	0.6	0.6	1	1	1	1	1	1
$f_{ccub150,28}$ [N/mm²]	70.2	73.3	79.3	68.4	60.1	57.3	54.6	54.8	67.0	49.3	48.3

The PT cement pastes were made by mixing cement and water at a low speed for 2 minutes and at a moderate speed for another 2 minutes. For the PS cement pastes, first cement and limestone filler were blended together and then mixed at the low speed for 1 minute, and for one more minute after the addition of water. After adding the superplasticizer, the paste was mixed at the moderate speed for 3 minutes. The cement pastes were then cast into 500 ml plastic bottles and the bottles were rotated at a

speed of 5 rpm for 24 hours and a constant temperature of 20°C. After rotating the bottles, they are further stored until the time of testing in a control-climate room at 20°C. By rotating the bottles with cement paste, the influence of bleeding on the pore structure of the cement paste was avoided. At 14, 28 and 90 days, prisms of 12x12x20 mm³ were sawn from the hardened cement pastes and dried in an oven of 105°C until constant mass. During the experiments, one of the samples has been split and it was observed that the mercury was well distributed over the whole sample.

3. Mercury intrusion porosimetry

Mercury intrusion porosimetry is used to measure in a range of 0.005 µm to 10 µm, which contains the capillary pores. [6] Pressurized mercury, being a non-wetting fluid, enters the sample of cement paste. The intrusion pressure gets increased and the corresponding volume of mercury injected into the pores of a previously dessicated and degassified sample is recorded. This volume is obtained by measuring the variation of the mercury level in a calibrated capillary tube called the dilatometer. During depressurizing, the change of volume is still being recorded and gives data about the extrusion of mercury out of the sample. [2, 7] The classical method of analyzing intrusion and extrusion is based on the model of parallel cylindrical non-intersecting pores of differing radii. The relation between the radius (r) of pores being intruded and the intrusion pressure (P) is given by the Washburn equation

$$P = \frac{-2\gamma\cos\theta}{r} \qquad\qquad [N/m^2] \qquad\qquad (1)$$

where θ is the contact angle between mercury and the solid phase and γ the air-mercury surface tension, respectively. [7] In this study, the surface tension of mercury is 480.10^{-3} N/m and the contact angle is 140°. The mercury porosimeter (PMI 60-K-A-1 manufactured by Porous Materials Inc.) used could provide a maximum intrusion pressure of 420 MPa. However, the highest pressure used in these experiments was 212 MPa, according to a minimum pore diameter of 0,0069 µm. The higher the pressure, the smaller the pores which can be intruded. However, one has to keep in mind that the increase in volume obtained at high pressure can be partly caused by bigger capillary pores which can only be reached by small pores. Despite this fact the information obtained from MIP makes it possible to get an idea of the percolation of the structure and to compare different structures [6]. The **intrusion and extrusion curves** are obtained by plotting the cumulative volume of mercury versus the pore diameter. When the mass and the apparent density of the sample are known, the porosity of the sample can be calculated. The **volume pore size distribution** D_v, defined as the pore volume per unit interval of pore radius, can be deduced from the volume of mercury that intrudes within the pressure range (P; P + δP) corresponding to a pore radius range (r; r +

δr). [8] The equivalent pore size corresponding to the biggest peak in the volume pore size distribution is referred to as the **critical pore size** d_c, which is the maximum pore diameter at which the continuous mercury intrusion begins. This parameter might give an indication about the permeability of the cement paste [9]. Due to the influence on the permeability it should indicate the durability of the material too. [10, 6] Lower values of the critical pore size indicate a more dense pore structure. [11] The **mean pore diameter** d_m is the point that equals 50% of the pore size distribution. Low values indicate a dense structure of the cement matrix. [11] The values are comparable with those of the critical pore size. [1] The **specific surface** S_v of the pore structure can be calculated by integration of (2) over the whole pore volume.

$$dS_v = \frac{4dV}{d} \qquad\qquad [m^2] \qquad\qquad\qquad (2)$$

with dV the change in pore volume [m³] and d the mean pore diameter over the considered interval [m]. From the intrusion curve the total porosity can be deduced as the total volume of intruded mercury at the maximum applied pressure per gram of the sample. The ink-bottle porosity (ml/g) can be calculated as the cumulative extrusion volume minus the cumulative intrusion volume at the lowest pressure. The effective porosity can be calculated as the total porosity minus the ink-bottle porosity. [12] The **retention ratio** is calculated as the ink-bottle porosity divided by the total porosity. This ratio gives an indication about the accessible ink-bottle pores. [11]

4. Experimental results on MIP

The parameters of all mixtures measured at 14 days, 28 days and 3 months are plotted in graphs. The discussion reflects the results on all three ages. In case of a different conclusion for the different ages, this will be mentioned.

4.1 Intruded volume of mercury - porosity

In Figure 1 the intruded volume of mercury is shown. Comparing traditional to self-compacting cement pastes (PT1-PS1: CEM I 52.5 N, PT2-PS2: CEM III/A 42.5 LA, PT3-PS3: CEM I 52.5 HSR) the intruded volume is much higher for the traditional cement pastes. The intruded volume is higher when CEM III/A 42.5 LA is used instead of CEM I 52.5 N. At the age of 3 months however for the self-compacting cement pastes the difference becomes smaller. At 3 months the traditional cement pastes show a lower intruded volume when CEM III/A 42.5 LA is used instead of CEM I 52.5 N. When CEM I 52.5 HSR is used instead of CEM I 52.5 N, a lower intruded volume is observed for both traditional and self-compacting cement paste. The intruded volume decreases with an increasing C/P, and decreasing W/C (PS5-PS1-PS6-PS7: CEM I 52.5 N, PS8-PS2-PS9-PS10: CEM III/A 42.5 LA). At the age of 14 days, the intrusion is higher

when blastfurnace slag cement is used. The difference however decreases with a higher C/P. At 28 days the intrusion is higher for a low C/P and lower for a high C/P when CEM III/A 42.5 LA is used instead of CEM I 52.5 N. At 3 months generally the intrusion is smaller for mixtures with blastfurnace slag cement. Increasing the C/P at a constant W/C increases the intruded volume (PS5-PS13: CEM I 52.5 N, PS8-PS16: CEM III/A 42.5 LA). When blastfurnace slag cement instead of portland cement is used, at 14 days the intrusion is higher and at 3 months the intrusion is lower. At 28 days the intrusion is higher for a high C/P and lower for a low C/P. When quartzite filler is used instead of limestone filler, the intrusion is somewhat increased (PS1-PS4). Increasing the W/C at a constant C/P, increases the intruded volume (PS11-PS1-PS12-PS13: CEM I 52.5 N, PS14-PS2-PS15-PS16: CEM III/A 42.5 LA). Also the traditional cement pastes have an increased intruded volume when the W/C is higher (PT4-PT1-PT5-PT6). The more, the intruded volume is much higher for the traditional cement pastes than for the according self-compacting cement pastes. Comparing mixtures with the same W/C, but a different type of cement, the following can be concluded (PS11-PS14, PS1-PS2, PS12-PS15, PS13-PS16; CEM I 52.5 N or CEM III/A 42.5 LA). At 14 days the intrusion is higher in the case of the use of CEM III/A 42.5 LA. At 28 days the intrusion is higher for a higher W/C and lower for a lower W/C. At 3 months the intrusion is equal or lower in comparison with portland cement.

The porosity can be calculated knowing the density of the hardened cement paste, the mass of the sample and the intruded volume of mercury. The discussion on the parameter study is as such according to the one of the intruded volume of mercury. Because of the determination of the density of the cement paste on the small samples, there is an additional uncertainty on the results. But, as will be shown in the following of this article, the calculated porosities are suitable to validate the theoretical determination of the capillary porosity.
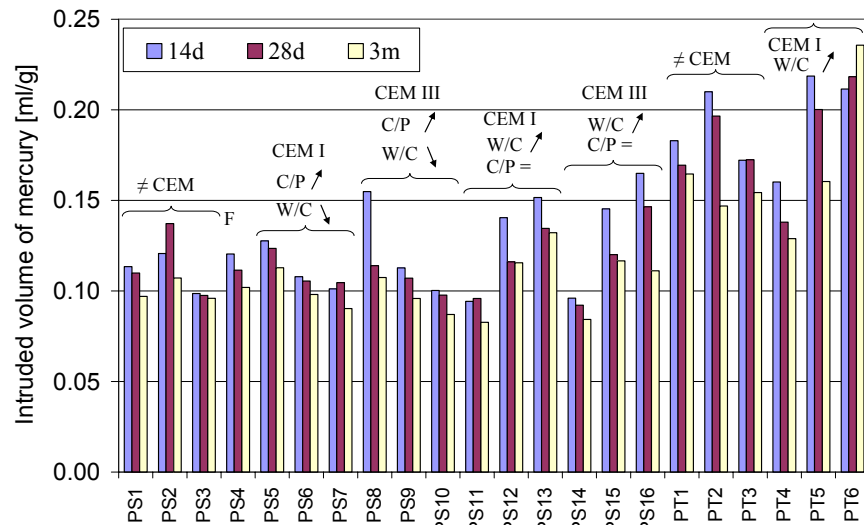

Figure 1 Intruded volume of mercury [ml/g]

4.2 Critical pore size

In Figure 2 the critical pore size is plotted for all mixtures. The critical pore sizes of the traditional cement pastes, between 0.10 µm and 0.15 µm, are remarkably higher than those of the self-compacting cement pastes, between 0.06 µm and 0.11 µm. At 14 and 28 days the mixtures with CEM I 52.5 HSR (PT3-PS3) have a smaller critical pore size compared to the mixtures with CEM I 52.5 N (PT1-PS1). At 3 months the difference is even more explicit. Replacement of CEM I 52.5 N by CEM III/A 42.5 LA (PT2-PS2) tends to a lower critical pore size in the case of self-compacting concrete at all three ages. For traditional concrete, on the contrary, at 14 and 28 days the critical pore size gets higher. At 3 months however, the critrical pore sizes of the mixtures are very close in value. Although the variation is small, the critical pore size decreases somewhat when the C/P is higher, and W/C is lower (PS5-PS1-PS6-PS7: CEM I 52.5 N, PS8-PS2-PS9-PS10: CEM III/A 42.5 LA). The mixtures made with CEM III/A 42.5 LA have lower values of the critical pore size as the mixtures made with CEM I 52,5 N. For the mixtures with CEM I 52.5 N increasing the C/P at a constant W/C (PS5-PS13) tends to a lower critical pore size at 14 and 28 days and a higher value at 3 months. For the mixtures with CEM III/A 42.5 LA (PS8-PS16) increasing the C/P decreases the critical pore size at 14 days and increases the parameter at 28 days and 3 months. Replacement of limestone filler by quartzite filler gives a lower critical pore size (PS1-PS4). An increase of the W/C at a constant C/P increases the critical pore size (PS11-PS1-PS12-PS13: CEM I 52.5 N, PS14-PS2-PS15-PS16: CEM III/A 42.5 LA, PT4-PT1-PT5-PT6: CEM I 52.5 N).
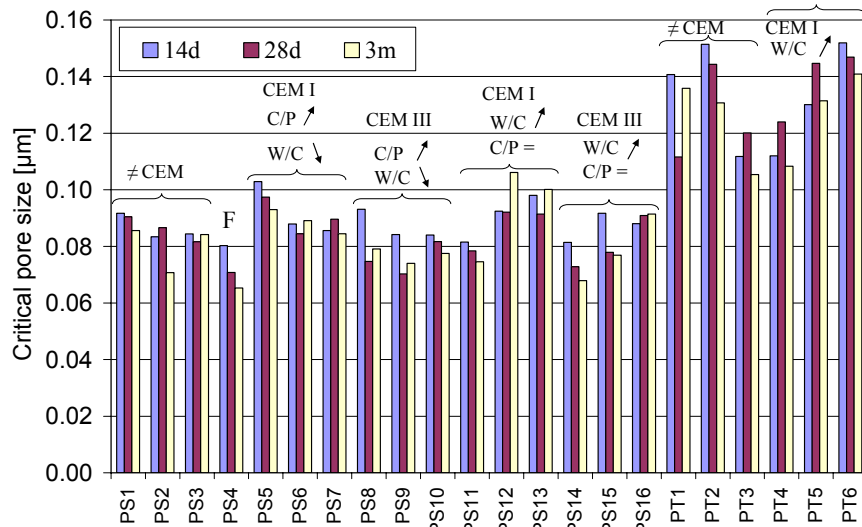

Figure 2 Critical pore size [µm]

4.3 Mean pore diameter

The mean pore diameter is plotted for all mixtures in Figure 3. Generally speaking the traditional mixtures have a higher mean pore diameter than the corresponding self-compacting mixtures, although the difference is mostly small. When CEM III/A 42.5 LA is used instead of CEM I 52.5 N, merely lower values of the mean pore diameter are found. When CEM I 52.5 N is replaced by CEM I 52.5 HSR the variation of the diameter is rather small. Changing the W/C and C/P has an effect on the mean pore diameter, but it is difficult to find a clear trend in the results. A lower mean pore diameter is found when a quartzite filler is used instead of a limestone filler.
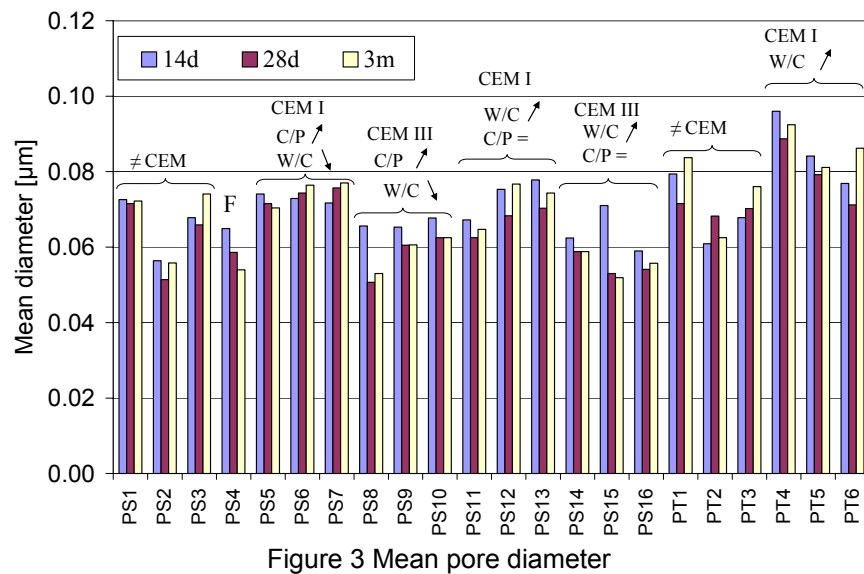
Figure 3 Mean pore diameter

4.4 Specific surface

Figure 4 represents for all mixtures the results of all mixtures on the specific surface. Replacement of CEM I 52.5 N by CEM I 52.5 HSR (PT1-PS1, PT3-PS3) doesn't change much. Replacement by CEM III/A 42.5 LA however increases in an important extent, for both traditional mixtures and self-compacting mixtures, the specific surface. The increase is higher when the W/C is higher. When the C/P increases, and W/C decreases, the specific surface decreases (PS5-PS1-PS6-PS7: CEM I 52.5 N, PS8-PS2-PS9-PS10: CEM III/A 42.5 LA). Increasing the C/P at a constant W/C increases the specific surface (PS5-PS13: CEM I 52.5 N, PS8-PS16: CEM III/A 42.5 LA). The specific surface increases a little when quartzite filler is used instead of limestone filler (PS1-PS4). Increasing the W/C at a constant C/P increases the specific surface (PS11-PS1-PS12-PS13: CEM I 52.5 N, PS14-PS2-PS15-PS16: CEM III/A 42.5 LA). Also for the traditional mixtures the specific surface increases with an increasing W/C (PT4-PT1-PT5-PT6). Generally speaking the traditional cement pastes

have higher values for the specific surface compared to the corresponding self-compacting cement pastes. The specific surface decreases with the age of the samples, due to continuing hydration. In order to interpret the specific surface well in Figure 5, at the age of 14 days as an example, the specific surface is plotted against the intruded volume of mercury. This figure makes it clear that at a higher intruded volume, or higher porosity, there is a higher specific surface. When two mixtures with the same porosity are compared to each other, the mixture with the highest specific surface has a more dense structure than the other one. Based on this fact, from the figure it can be told that the traditional cement pastes have a less dense structure compared to the self-compacting cement pastes. Also it can be seen that a more dense structure can be obtained when CEM I 52.5 N is replaced by CEM III/A 42.5 LA. The advantage of using CEM III/A 42.5 LA increases with the age of the cement paste.
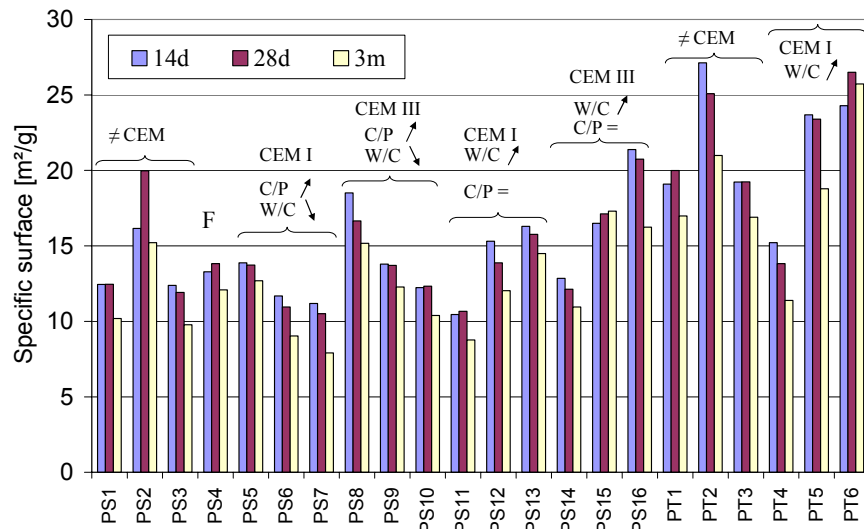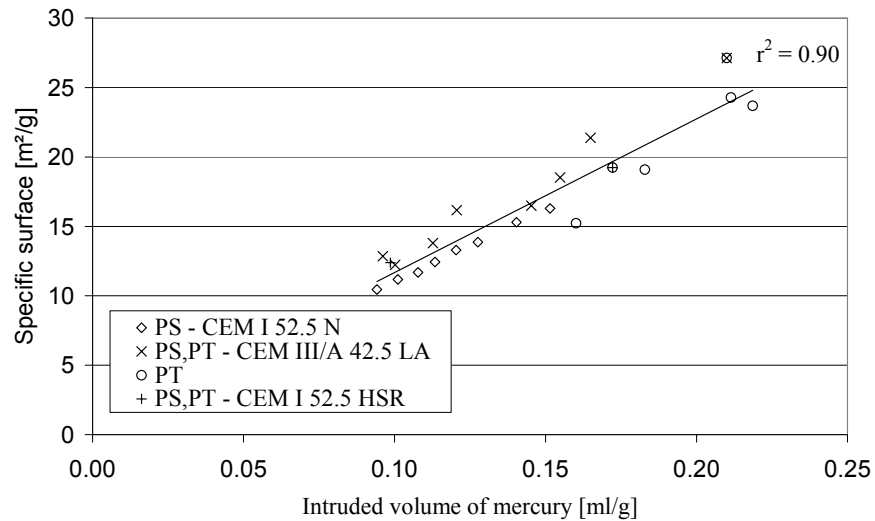
Figure 4 Specific surface

Figure 5 Specific surface versus intruded volume of mercury

4.5 Retention ratio

The retention ratio of all mixtures is shown in Figure 6. Generally speaking the traditional mixtures have lower retention ratios than the self-compaction mixtures. This could indicate a more uniform distribution of the sections of the pores for the traditional pastes. Also the self-compacting pastes could have more ink-bottle pores. This can be caused by the presence of finer pores and therefore, a more dense structure. Only when the W/C is varied together with the W/P, there is a clear variation of the retention ratio. High values of the W/C correspond with low values of the retention ratio (f.e. PS13, PS16 and PT6). The highest retention ratios are mostly found at the age of 3 months. When CEM III/A 42.5 LA is used instead of CEM I 52.5 N the retention ratio tends to have lower values. It is less likely for mercury, during extrusion, to remain in a coarse structure than in a dense structure. When the structure becomes more dense because of the hydration process, the pores are less uniform and it is more difficult for mercury to leave the pores.
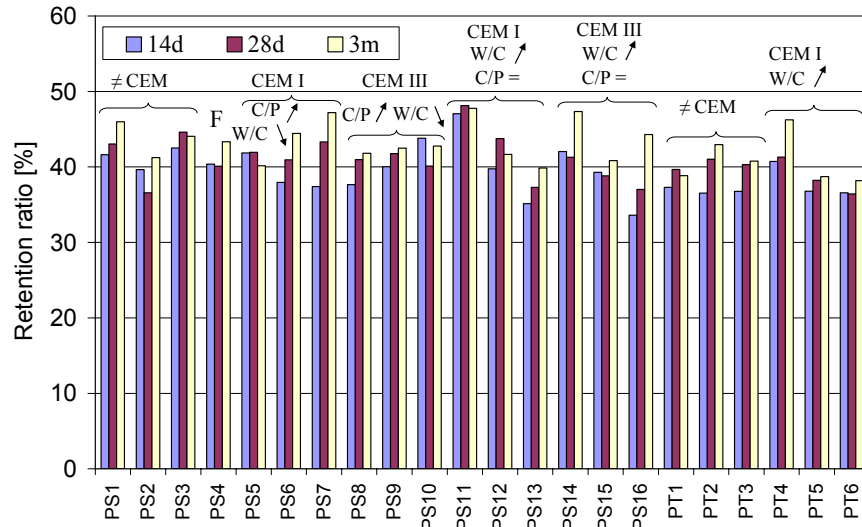

Figure 6 Retention ratio [%]

5. Experimental porosity – calculated porosity according to Powers

The theoretical capillary porosity of hardened cement paste can be calculated by means of (3) and (4). It is the proportion of the volume of capillary pores $V_{cap\,por}$ and the initial volume of cement paste V_{tot}.

$$V_{cap\,por} = \frac{W - 0{,}319\alpha C}{\rho_w} - \frac{0{,}132\alpha C}{\rho_c} \qquad [m^3] \qquad (3)$$

$$V_{tot} = \frac{W}{\rho_w} + \frac{C}{\rho_c} + \frac{F}{\rho_F} \qquad [m^3] \qquad (4)$$

With C, W and F respectively the mass of cement, water and filler [kg], ρ_c, ρ_w, ρ_F the according densities [kg/m³] and α the hydration degree [-]. It has been checked whether there is a relation between the porosity obtained by mercury porosimetry and the theoretical calculated capillary porosity. This

has been done on samples wich have been cured for 3 months in a sealed condition at 20°C. It can be assumed that the ultimate degree of hydration has been reached. In [13] it has been found that the formula of Mill is suitable to calculate the ultimate degree of hydration α_u (6) [14], especially in the case of CEM I 42.5 R, corresponding with CEM I 52.5 N used in this paper.

$$\alpha_u = \frac{1{,}031\dfrac{W}{C}}{0{,}194 + \dfrac{W}{C}} \qquad\qquad [-] \qquad\qquad\qquad (6)$$

Cement with a higher or lower fineness will achieve a higher or lower ultimate degree of hydration. This can be taken into account by a correction factor. Also the type of cement has its influence and should be taken into account. As suggested in [15] and proven in [16] the value of α_u should be increased with 5% if CEM III/A 42.5 LA, CEM I 52.5 HSR or CEM I 52.5 are used instead of CEM I 52.5 N. In Figure 7 the theoretical calculated capillary porosity is plotted versus the experimental porosity from MIP. Not only is there a rather good correlation, but also the values match very well in size. This could mean that the measured porosity from MIP represents the capillary porosity. This is in accordance to the assumption of [6, 17].
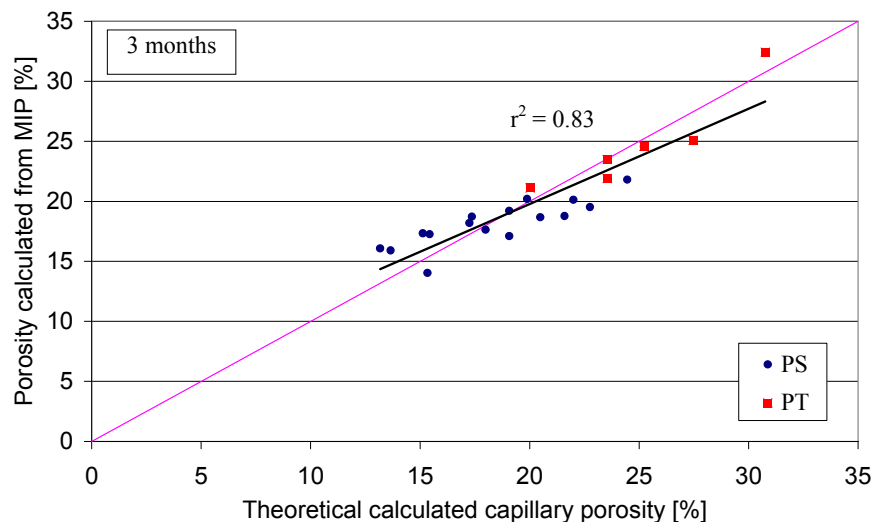

Figure 7 Porosity from MIP versus the theoretical capillary porosity at 3 months

6. Traditional cement paste versus self-compacting cement paste

The difference in porosity between traditional and self-compacting cement paste can be explained by the difference in total volume V_{tot}. The volume of the capillary pores might be the same, but the total volume of the self-compacting pastes is bigger.

When the pore size distribution curves of mixtures PT1, PT2 and PT3 are compared with PS1, PS2 and PS3 (Figure 8), the following differences can be seen. When there is almost no intrusion yet for the PS mixtures,

there is already a clearly visible intrusion for the PT mixtures. This indicates a less dense and more permeable microstructure of the PT mixtures. For the PT mixtures, the biggest peak, indicating the critical pore size, is shifted towards bigger pore diameters compared to the PS mixtures. This means that for traditional mixtures the microstructure percolates at a higher pore diameter. For PS mixtures at pore diameters smaller than the critical pore size there is only a small increase in intruded volume compared to the PT mixtures. This means that for self-compacting pastes, once the microstructure is percolated there are few pores left to be filled. As for the traditional mixtures there are still a lot of pores to be filled. This indicates probably a more dense structure of the self-compacting pastes.
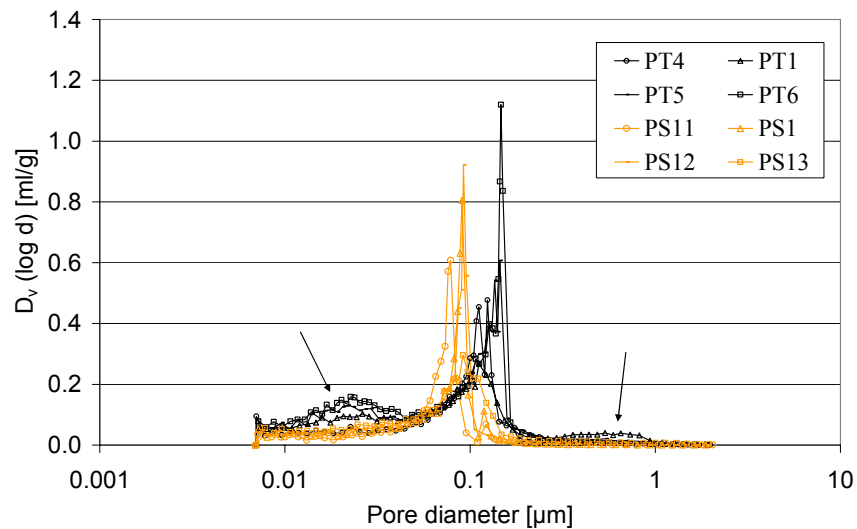

Figure 8 Pore size distribution of traditional and self-compacting mixtures

6. Conclusions

By means of mercury intrusion porosimetry the pore structure of 22 mixtures of hardened cement paste has been studied (16 self-compacting and 6 traditional pastes). Experiments are performed after three curing periods: 14, 28 and 90 days. Besides the difference between self-compacting and traditional paste, some parameters are studied: water/cement, cement/powder and water/powder ratio, type of cement and filler. The investigation is based on the total intruded volume, critical diameter, specific surface, ... , intrusion and extrusion curves and the pore size distribution. The pore structure of self-compacting paste turns out to be more dense than traditional paste and the water content is a very important parameter. A theoretical calculation of the capillary porosity is linked with the experimental results and gives good results. It can be concluded that the limestone filler used in these experiments seem to be inert and have a filling effect.

7. Referenties

[1] K. K. Aligizaki, Pore structure of cement-based materials. Testing, interpretation and requirements, Taylor & Francis, Modern Concrete Technology Series, v. 12, 2006

[2] H. Romberg, Zementsteinporen und Betoneigenschaften, Beton-Information (18-5) (1978) 50-55

[3] V. Boel, K. Audenaert, G. De Schutter, G. Heirman, L. Vandewalle, B. Desmet, J. Vantomme, Transport properties of Self-compacting Concrete with limestone filler or fly ash, Materials and Structures, available on line

[4] V. Boel, K. Audenaert, G. De Schutter, Gas permeability of SCC, Proceedings of the Second North American Conference on the Design and Use of Self-Consolidating Concrete and the fourth International RILEM Symposium on Self-Compacting Concrete, October 30 - November 2, 2005 - Chicago, Illinois, USA

[5] K.Audenaert, V. Boel, G.De Schutter, Influence of capillary porosity on the transport properties of self compacting concrete, Proceedings of the 8th CANMET/ACI International Conference on Recent Advances in Concrete Technology, June 2006, Montreal

[6] A. B. Abell, K. L. Willis, D. A. Lange, Mercury intrusion porosimetry and image analysis of cement-based materials, Journal of Colloid and Interface Science (211-1) (1999) 39-44

[7] P. Klobes, H. Riesemeier, K. Meyer, J. Goebbels, K.-H. Hellmuth, Rock porosity determination by combination of X-ray computerized tomography with mercury porosimetry, Fresenius J Anal Chem (357) (1997) 543-547

[8] F. Moro, H. Böhni, Ink-Bottle Effect in Mercury Intrusion Porosimetry of Cement-Based Materials, Journal of Colloid and Interface Science (246) (2002) 135-149

[9] D.A. Silva, V.M. John, J.L.D. Ribeiro, H.R. Roman, Pore size distribution of hydrated cement pastes modified with polymers, Cement and Concrete Research (31) (2001) 1177-1184

[10] R. A.Cook, K. C. Hover, Mercury porosimetry of hardened cement pastes, Cement and Concrete Research (29-6) (1999) 933-943

[11] E. Tolentino, F. Lameiras, G. Abdias et al., Structural evaluation and performance of portland cement concretes after exposure to high temperatures, Materials Research (5-1) (2002)

[12] G. Ye, Experimental study and numerical simulation of the development of the Microstructure and Permeability of Cementitious Materials, Doctoral thesis TU Delft, 2003

[13] A.-M. Poppe, Influence of fillers on the hydration and properties of self-compacting concrete (in Dutch), Doctoral thesis Ghent University, 2004

[14] K. van Breugel, Simulation of hydration and formation of structure in cement-based materials, Doctoral thesis TU Delft, 1991

[15] Audenaert K., Transportmechanisms in self-compacting concrete in relation with carbonation and chloridepenetration (in Dutch), Doctoral thesis Ghent University, 2006

[16] V. Boel, Microstructure of self-compacting concrete in relation with gas permeability and durability aspects (in Dutch), Doctoral thesis Ghent University, 2006

[17] M.R. Nokken, R.D. Hooton, Discontinuous capillary porosity in concrete – does it exist?, Proceedings of the International symposium: Advances in Concrete through Science and Engineering, Rilem Spring Evanston (2004)