Effect of supplementary cementitious materials on capillary sorption: relation with drying rate and testing time

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Abstract. The water sorption phenomenon in a cementitious matrix is responsible for the ingress of several deleterious agents, and it is directly related to pore connectivity and pore volume. One of the most common tests used to describe this mechanism is the capillary sorption test. Furthermore, the drying rate (DR) is a process that strongly depends on the transport properties and also provides valuable information related to porosity and durability.

Supplementary cementitious materials (SCMs) are known to enhance durability-related properties, especially pore refinement with time due to the pozzolanic action. Therefore, changes in the pore structure could be assessed by means of the capillary sorption and drying rate.

For this study, mortars with ground granulated blast-furnace slag, natural pozzolan and limestone powder at three different levels of replacement were made and the capillary sorption test was performed at 28 and 90 days. Weight loss was also assessed at 28 days and the DR was calculated.

Calculation of the weight gain, weight loss, DR and capillary sorption rate (CSR) is made considering the stoppage of the test at different stages. A comparison between different approaches in the calculations is made. Also, the relation of DR and CSR is assessed. Results show the effect of SCMs with time, and also the influence of the calculations on the CSR and DR values.

Introduction

Nowadays, supplementary cementitious materials (SCMs) are normally used as a partial replacement of cement. This has the advantage of reducing clinker consumption and hence increase sustainability, however, at the same time it increases the effect of time on pore structure and transport properties [1-4]. In this sense, SCMs are commonly acknowledged for enhancing durability-related properties due to the pore refinement at advanced ages as a consequence of the pozzolanic action. On the other hand, some non-hydraulic SCMs, as limestone powder (LP) may enhance the pore structure of cementitious materials at early age due to the promotion of hydration of cement [5].

Capillary sorption is among the commonly involved processes in the ingress of aggressive agents into cementitious materials, since it is related to pore structure and connectivity. This mechanism is usually described by the capillary sorption test. Furthermore, inferences about concrete durability are often based on this property [6-9] and its relation with other processes, such as carbonation or freeze-thaw attack. Therefore, in this study, the capillary sorption test is used to describe the SCMs effect with time, and evaluate their influence on the pore structure.

Similarly, the Drying Rate (DR) can be used as a durability-related index since it also describes water transport. In this sense, DR as a transport index has two main advantages: it requires a short test time in comparison with other tests, such as the sorptivity test; and it is consistently linked to other transport indexes or transport-related properties, such as sorptivity and electrical resistivity

[10]. Although several techniques for drying may be applied, their effect on the pore structure has to be considered to avoid damage due to over drying. Several authors have studied the impact of different drying techniques on microstructure and pore size distribution [11-15]. Additionally, and as described by [14], the drying procedure should come down to one of logics and ease of use. Considering this, drying at 50°C was chosen as a convenient balance between proper conditioning and practicality.

Ground granulated blast-furnace slag (S), natural pozzolan (NP) and limestone powder (LP) were used at three different levels of replacement of cement in mortars. The effects of the amount of replacement of the different SCMs on capillary sorption and drying rate were evaluated. The results from samples cured for 28 and 90 days were used to calculate the capillary sorption rate (CSR) and the DR. Moreover, the relation between DR and CSR was assessed and a good correlation was found. Results show the effect of SCMs with time, and also their influence on the CSR and DR values as a preliminary evaluation of the potential effect of the different SCMs on the pore structure.

Materials and mixes

Three different SCMs were used for this study: ground granulated blast-furnace slag (S for simplicity), natural pozzolan (NP), which is a volcanic tuff, and limestone powder (LP). The chemical composition of the materials is shown in Table 1. The chemical analysis was performed by X-ray fluorescence and the density was determined according to ASTM C188-15 [16]. Table 2 shows the values of surface area, dv10, dv50 and dv90 of each SCMs, using laser diffraction with the procedure and the optical parameters indicated in [16]. The calculations of the surface area were made under the assumption of spherical particles. Furthermore, detailed physical characterization of the SCMs used in this study can be found in [17].

Table 1: Chemical compositions of the SCMs.

wt [%]	S	NP	LP
CaO	36.16	1.34	48.85
SiO_2	28.89	62.53	8.15
MgO	12.14	1.13	1.41
Al_2O_3	8.62	10.76	1.28
Na_2O	1.91	5.66	1.25
SO_3	1.85	0.34	0.05
Fe_2O_3	0.95	1.81	0.88
TiO_2	0.46	0.09	-
K_2O	0.43	3.67	0.28
MnO	0.43	0.06	0.04
LOI	0.54	nd	37.29
Density [g/cm^3]	2.92	2.41	2.71

nd = not determined

Table 2: SSA, dv10, dv50, and dv90 of the SCMs.

	S	NP	LP
dv10 [µm]	1.14± 0.03	1.36±0.001	1.27 ± 0.12
dv50 [µm]	12.73 ± 0.67	7.05± 0.02	7.67 ± 0.63
dv90 [µm]	66.27 ± 7.18	28.14± 0.16	72.88 ± 10.4
Specific surface area [m^2/kg]	566 ± 13	701±2	606 ± 13

Nine mortar mixes were designed with a water/binder (w/b) ratio of 0.45 and a sand/binder (s/b) ratio of 3. Ordinary Portland cement (OPC), normalized siliceous sand (0/2) and tap water were used in all mixes. Part of the OPC was replaced in weight (w/w) with the different SCMs as follows: S (20, 40, and 60%), NP (20, 40, and 60%) and LP (10, 20, and 30%). The designation of the mixes corresponds to the level of replacement. Then, the mix S20, is a mix with 20% w/w of S with respect to the total binder content. The procedure for the mixing of mortars was in accordance with EN 196-1 [18]. Mortar samples were cured in a humid chamber at 20 ± 2°C and 95 ± 5% RH for 28 and 90 days, and then conditioned for testing.

Methods

Compressive strength. For each age, six tests on 3 mortar prisms of 4x4x16 cm prisms were performed according to EN 196-1 [18].

Water absorption, apparent density and open porosity. For the determination of the water absorption, apparent density and open porosity, samples were tested at 90 days. First, they were submitted to vacuum for two hours and then water was drawn into the vacuum chamber until the sample became fully immersed. After 24 h the sample was removed and weighed, which was denoted as saturated mass in air (msa). The samples were also weighed in water, and denoted as saturated mass in water (msw). Then, samples were subjected to oven drying at 50°C until the change in mass was lower than 0.1% in a 24h period, and this weight denoted as dry mass (md). The apparent density was calculated as md·dw/(msw-md), with dw=density of water. The open porosity was calculated as (msa-md)/(msa-msw).

Drying rate. The DR test was performed on 5x5cm mortar cylinders, sawed from cylindrical specimens of 5x7.5cm, discarding the lowest part of samples. The lateral cylindrical surfaces of the samples were waterproofed in order to ensure one-dimensional transport. The samples were first water saturated, and then taken into an oven at 50 ± 2 ºC for drying. The weight loss was registered at intervals of 24 h. The drying procedure was finished when the weight loss was lower than 0.1% w/w in a 24 h period. This final weight was designated as the initial dry mass for capillary sorption tests (md). The drying rate was determined for samples cured for 28 days, and it was calculated as the slope of the least square fitting line on the weight loss-square root of time relationship.

Capillary sorption. The same samples used for DR were subsequently used for determining CSR. Here, only one face of these dried samples (the one corresponding to the plane at 2.5 cm from the base of the original cylindrical specimens) was put in contact with water, 3mm depth, and weight gain was determined at intervals 0.5, 1, 2, 3, 4, 5, 6, 24 h, and from then on, every 24 h up to a weight gain lower than 0.1% w/w in a 24 h period.

Experimental results

Compressive strength. Figure 1 shows the results of compressive strength at 28 and 90 days for all mixes.

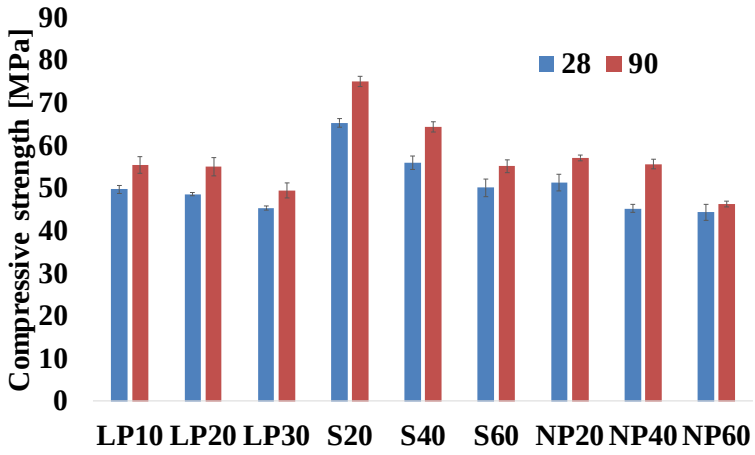

Figure 1. Results of compressive strength for all mixes at 28 and 90 days.

Water absorption, apparent density and open porosity. Figure 2 shows the results of the , apparent density (AP) and open porosity (OP) determined from the water absorption.

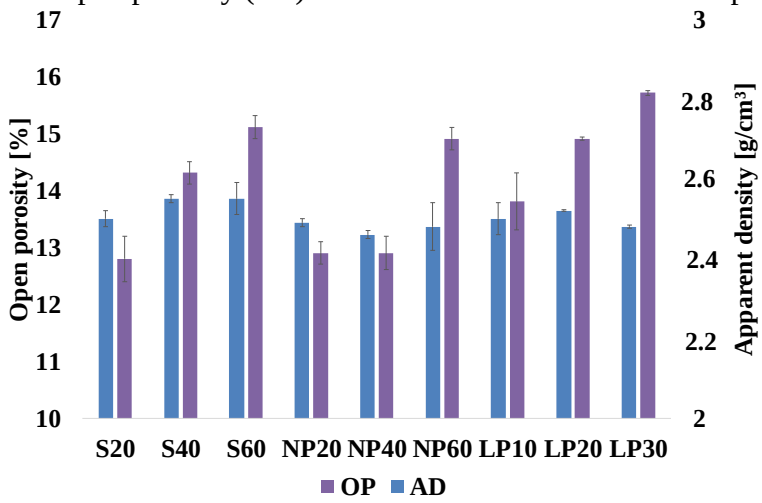

Figure 2. Results of AD and OP for all mixes.

Drying rate. Table 3 shows the results of the DR and the coefficient of determination (R^2) for all mixes. The weight loss variation per m^2 (weight loss capacity or WLC) with the square root of time is shown in Figures 3–5 for LP, NP, and S, respectively.

Table 3: Results of DR at 28 days for all mixes.

Mix	LP			NP			S		
replacement [%]	10	20	30	20	40	60	20	40	60
DR [g/m²]	1.95	2.28	2.64	1.08	0.97	1.19	1.18	1.13	1.23
R^2	0.989	0.974	0.989	0.979	0.986	0.977	0.950	0.989	0.959

Capillary sorption. The weight gain (wg) at the time x was calculated as the difference between the weight at the time x, and the md. The capillary sorption capacity (CSC) was calculated as the wg divided by the area in contact with water. Figures 3-5 show the results at 28 days of the evolution of the CSC in function of the square root of time, for LP, NP, and S series, respectively. The respective results for 90 days are presented in Figures 6-8.

The CSR was calculated as the slope of the least square fitting line of the variation of CSC in function of the square root of time. Different values were obtained from the fitting over different testing periods: 0-24 h (CSR_{t24}), 0-96 h (CSR_{t96}), and from the beginning until the weight gain was lower than 0.1% in a 24 h period ($CSR_{w0.1}$). Results of the different CSR at 28 and 90 days for all the mixes are shown in Figure 9.

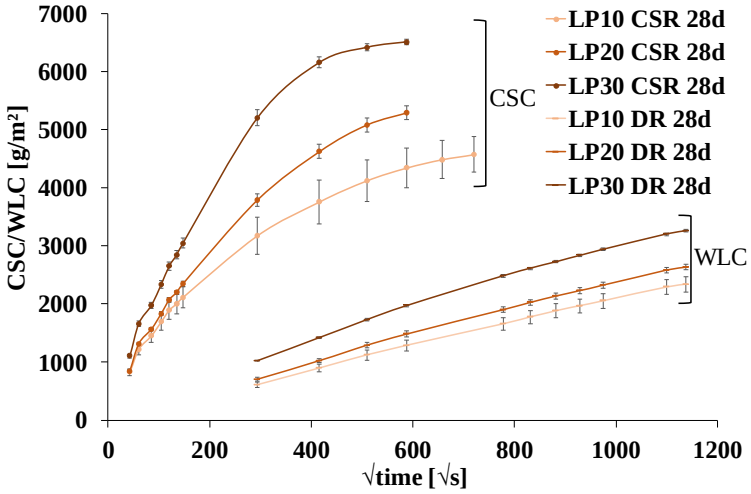

Figure 3. Variation of CSC and WLC with the square root of time for LP mixes at 28 days.

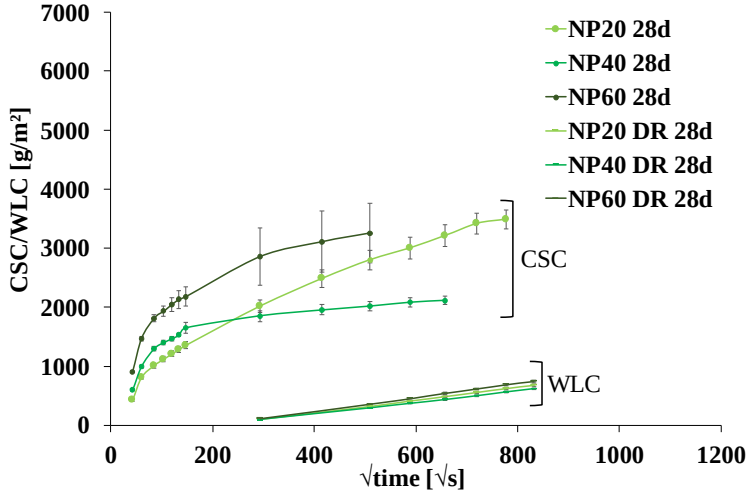

Figure 4. Variation of CSC and WLC with the square root of time for NP mixes at 28 days.

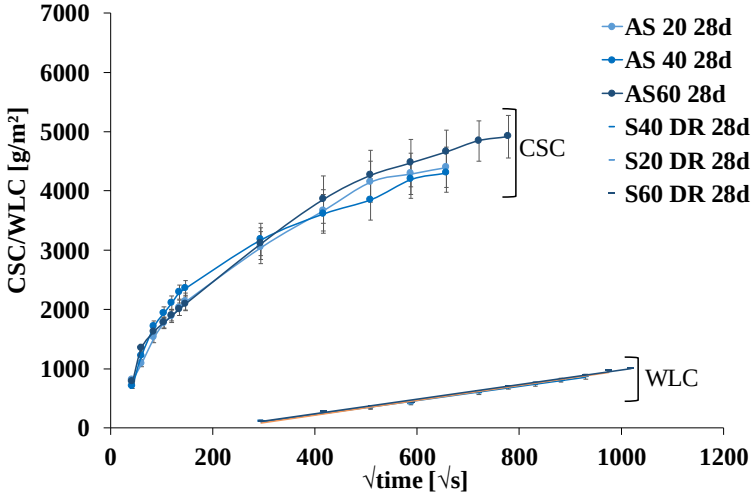

Figure 5. Variation of CSC and WLC with the square root of time for S mixes at 28 days.

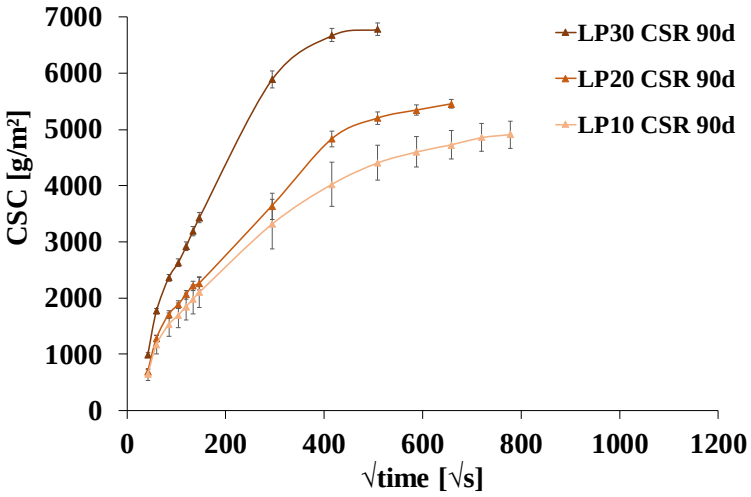

Figure 6. Variation of CSC with the square root of time for LP mixes at 90 days.

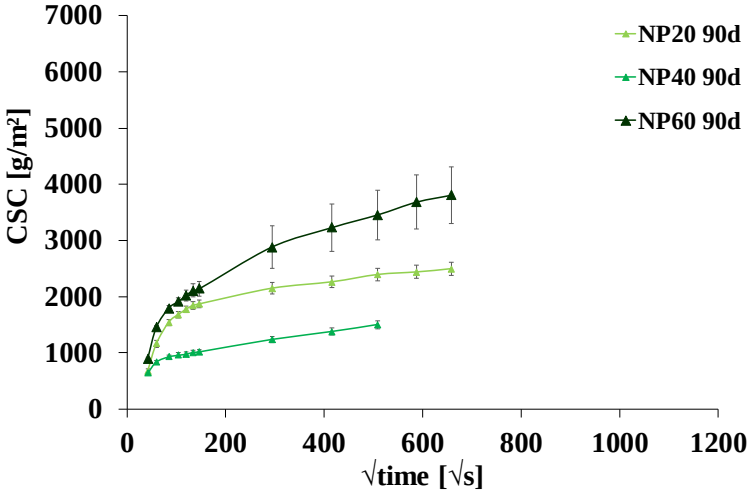

Figure 7. Variation of CSC with the square root of time for NP mixes at 90 days.

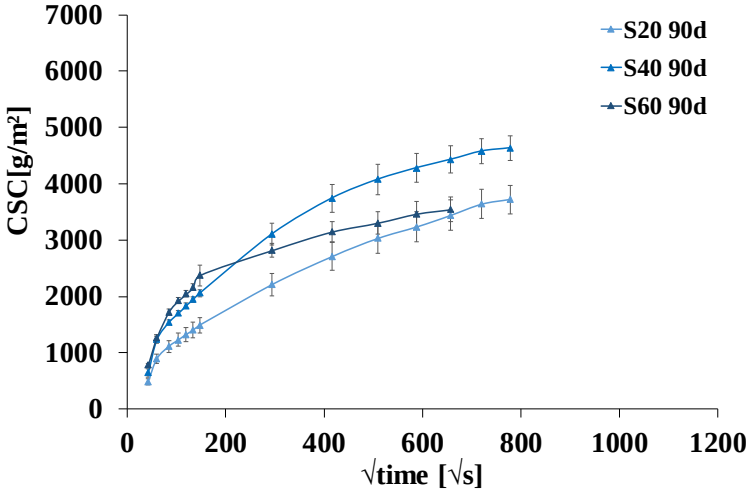

Figure 8. Variation of CSC with the square root of time for S mixes at 90 days.

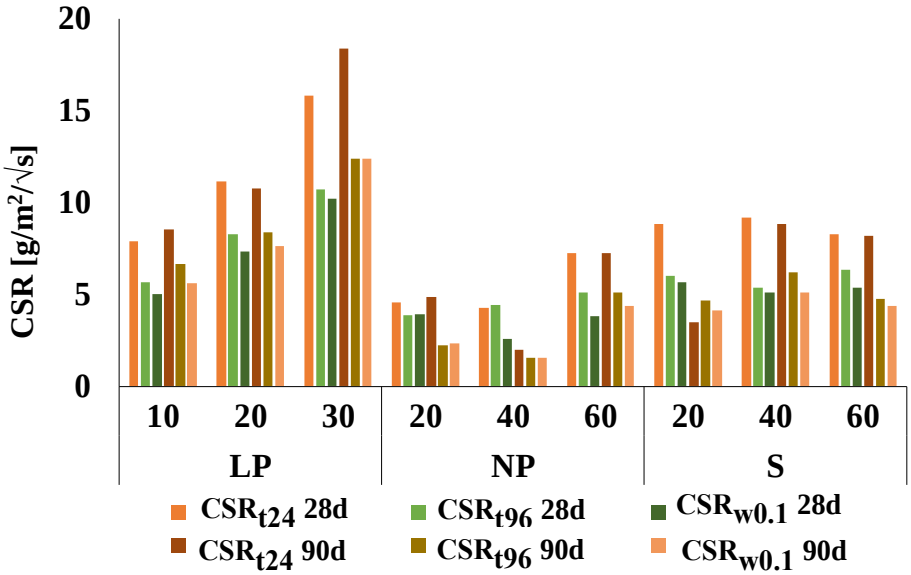

Figure 9. Values of CSR_{t24}, CSR_{t96}, and $CSR_{w0.1}$ for all the mixes at 28 and 90 days.

Capillary sorption and drying rate. For this comparison, the CSR was calculated considering the same criteria as for the DR. Then the fitting of the points of the CSC with the square root of time were considered until the time when the weight gain was lower than 0.1% w/w in a 24 h period ($CSR_{w0.1}$). Figure 9 shows the relation between the $DR_{w0.1}$ and $CSR_{w0.1}$ for all the mixes at 28 days.

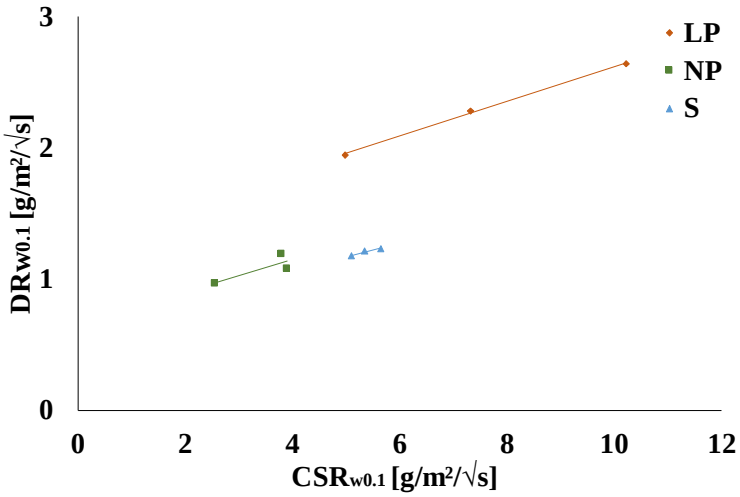

Figure 9. Relation between $DR_{w0.1}$ and $CSR_{w0.1}$ for all mixes at 28 days.

Discussions

Relation between DR and CSR. Correlation coefficients shown in Figure 9 indicate the good correlation between the CSR and DR results. This relationship is explained by the analogous phenomena and driving forces for transport involved in both mechanisms [10]. Other authors [19-21] have also found good correlations between the DR and sorptivity, and with other parameters, including gas permeability and w/b ratio. Particularly [19] analysed the DR for blends including different SCMs (ground granulated blast-furnace slag, condensed silica fume and low calcium fly ash) and found that monitoring the weight loss during the drying process can show the effectiveness of the SCMs in enhancing the pore structure. For example, it is shown in Figure 2 that increasing the level of replacement of LP contributes to increase porosity, which is also reflected in the increase of the DR.

Additionally, for the case of NP and S mixes, from the fitting it seems that both SCMs (green and blue lines) could be included in one single relationship between CSR and DR . However, for the case of LP mixes, a completely different relation is found. This could be related to the fact that both NP and S have a pore refinement effect on the microstructure, while LP does not. Then, the higher effect on tortuosity and pore connectivity of NP and S seems to also affect the correlation between DR and CSR.

Finally, an advantage of DR over CSR is that the former shows more linearity with the square root of time, which allows a standard computation of this transport coefficient. For CSR, a conventional computation method must be established due to the lack of full linearity with the square root of time, which many times makes difficult the comparison among data in the literature when authors considered different methodologies or standards. The values in Figure 9 obtained from the fittings over different test periods are example of that.

Influence of LP. All the analyzed replacement ratios for LP (10, 20, and 30%) led to an increase in both the CSR and DR. Accordingly, Figure 2 shows the highest open porosity for LP30 in comparison to LP10 and LP20. Although, from a theoretical point of view, due to possible generation of nucleation sites it may increase C-S-H content and hence reduce porosity, the results indicate that LP has a dominant dilution effect. As can be seen in Table 2, this is because LP is rather coarse, especially in comparison with NP. Then, the dilution effect prevails over the enhancement of cement hydration and a decreased performance is obtained. Similar CSR increase with LP content was previously reported in [22], where also different comparisons between CSR and capillary porosity, DR, strength loss and water accessible porosity were analysed. Furthermore, the relative increase in CSR with LP content was not influenced by the testing period considered for the computation of CSR, as the same trend for CSR_{t24}, CSR_{t96}, and $CSR_{w0.1}$ was found for these results. Although, unexpected results were found for LP30 when comparing the CSR_{t24} at 28 and 90 days, where an increase of the CSR was registered at 90 days.

Influence of S. The different amounts of S included did not have an impact on the CSR at 28 days. This suggests that replacement of cement by slag caused little changes in the microstructure at 28 days, and the dilution effect is not noticeable. In relation with this, increase in the replacement ratio by S only led a small decrease in the compressive strength at 28 days, showing compensated effects of dilution and hydraulic activity from S. Furthermore, increased performance with further reaction of S was obtained at 90 days, as pore connectivity is affected and reflected in a clear impact on CSR results. The highest reduction was found for the lowest S content (20%), with over a 60 and 20% decreases of the CSR_{t24} and CSR_{t96}, respectively, from 28 to 90 days. Higher S contents showed reduced effectiveness at later ages, as only slight decreases was registered at 90 days. Compressive strength results at 90 days for S20 also showed the enhancement of the pore structure, although results were not as sensitive as CSR.

Influence of NP. The impact of NP does not corresponds with the replacement ratio. At both 28 and 90 days, NP40 had the lowest CSR within NP series, and also among all the mixes studied. This best performance seems to be due to a positive balance between filler effect and dilution of cement at early age, and the addition of positive pozzolanic action at later ages. However, further increase in NP content in NP60 not only increased the DR and the CSR at both 28 and 90 days, but also increased open porosity determined from water absorption. The pozzolanic action cannot fully compensate the high dilution of 60% replacement in comparison with 40%. Accordingly, compressive strength results at 90 days also showed the highest strength gain from 28 to 90 days for NP40 in comparison to NP20 and NP60. For CSR, when comparing the results obtained from different testing periods (24 or 96 h) some differences can be seen. Results at 28 days considering the CSR_{t96} showed a greater difference among NP20, NP40 and NP60 in relation to CSR_{t24} results. This is specially marked for NP20 and NP40 mixes and can also be seen in Figure 3. Although NP20 and NP40 have similar behavior during the first sorption period, as the phenomenon continues there is a clear difference in the curves of NP20 and NP40. The latter clearly has a smaller slope, which indicates a decrease in water ingress. It is possible that the first testing period is

affected by micro-cracking in the zone of contact with water due to the cutting procedure. This has a major impact on the results for 24 h of testing. Then results at later testing can be considered to be more reliable since a larger volume of the sample is involved.

Conclusions

CSR proved to be a sensitive transport index parameter regarding the SCMs effect. Results of LP showed that the main effect is dilution of clinker, since increase in LP led to increase in CSR at both 28 and 90 days. This is in agreement with its coarse PSD in comparison with the other SCMs. Regarding NP, the mix with 40% replacement had the best CSR results both at 28 and 90 days. Since this SCMs has the finest PSD and also a good pozzolanic action, it improves the pore structure at both early and late ages. The results from the S mixes showed that the effect of S is more pronounced at later ages. Nevertheless, the reaction of S allowed that mixes at 28 days did not show any distinct variation among the different replacement ratios.

According to the different computing methods for CSR, greater differences from different testing periods being considered are obtained for lower CSRs. For shorter testing periods the initial curvature has more impact on the resultant value for the parameter and these results are mainly dependent on the first layer of the sample in contact with water: This first layer is not totally representative of the pore structure of the volume of the sample but of the pore structure of the surface of the sample instead. Here, it should be mentioned that the first thin layer of the sample is likely to be altered with micro-cracks from the cutting procedure.

Furthermore, good agreement between CSR and DR for the studied blended mortars was found. The advantage of DR over CSR is that the former shows more linearity with the square root of time, which requires less considerations for the computation of a standard coefficient. For CSR, a conventional computation method must be established due to the lack of full linearity with the square root of time. This behavior makes difficult the comparison among data in the literature when authors considered different methodologies or standards.

References

[1] B. Ahmadi, & M. Shekarchi. Use of natural zeolite as a supplementary cementitious material. Cement & Concrete Composites 32 (2010), 134–141.

[2] M. Najimi , J. Sobhani, B. Ahmadi & M. Shekarchi. An experimental study on durability properties of concrete containing zeolite as a highly reactive natural pozzolans. Construction and Building Materials 35 (2012), 1023–1033.

[3] A. Bouikni, R. Swamy , A. Bali. Durability properties of concrete containing 50% and 65% slag. Construction and Building Materials 23 (2009), 2836–2845.

[4] S. Kumar, R. Kumar, A. Bandopadhyay, T. Alex, B. Kumar, S. Das, S. Mehrotra. Mechanical activation of granulated blast furnace slag and its effect on the properties and structure of Portland slag cement. Cement & Concrete Composites 30 (2008), 679–685.

[5] M. Cyr, P. Lawrence, E. Ringot. Efficiency of mineral admixtures in mortars: Quantification of the physical and chemical effects of fine admixtures in relation with compressive strength. Cement and Concrete Research 36 (2006), 264 – 277.

[6] M.Ghrici, S. Kenai, M. Said-Mansour. Mechanical properties and durability of mortar and concrete containing natural pozzolana and limestone blended cements. Cement & Concrete Composites 29 (2007), 542–549.

[7] L. Basheer, J. Kropp, D. J. Cleland. Assessment of the durability of concrete from its permeation properties: a review. Construction and Building Materials 15 (2001), 93-103.

[8] A.E. Long, G.D. Henderson, F.R. Montgom. Why assess the properties of near-surface concrete? Construction and Building Materials 15 (2001), 65-79.

[9] P. Van den Heede, E. Gruyaert, N. De Belie. Transport properties of high-volume fly ash concrete: Capillary water sorption, water sorption under vacuum and gas permeability. Cement & Concrete Composites 32 (2010), 749–756.

[10] Y.A. Villagrán Zaccardi, N. M. Alderete, A. Píttori, A.A. Di Maio. Drying rate as a transport index for concrete. Proceedings of the XIII DBMC, 2-5 September 2014, São Paulo, Brazil.

[11] L. Konecny, S. Naqvi, The effect of different drying techniques on the pore size distribution of blended cement mortars, Cement & Concrete Research 23 (1993), 1223-1228.

[12] M. Sanjuán, R. Muñoz-Martialay, Oven-drying as a preconditioning method for air permeability test on concrete, Mater. Lett. 27 (1996), 263-268.

[13] W. Dias, Influence of drying on concrete sorptivity, Concrete Research 56 (2004), 537–543.

[14] N. Collier, J. Sharp, N. Milestone, J. Hill, I. Godfrey, The influence of water removal techniques on the composition and microstructure of hardened cement pastes , Cement & Concrete Research 38 (2008), 737-744.

[15] D. Snoeck , L. Velasco , A. Mignon, S. Van Vlierberghe , P. Dubruel , P. Lodewyckx , N. De Belie, The influence of different drying techniques on the water sorption. Properties of cement-based material, Cement & Concrete Research 64 (2014), 54–62.

[16] ASTM C188, Standard test method for density of hydraulic cement, American Society for Testing and Materials, USA (2015).

[17] N. M. Alderete, Y. A. Villagrán Zaccardi, G. S. Coelho Dos Santos, N. De Belie. Particle size distribution and specific surface area of SCMs compared through experimental techniques. Proceedings of the International RILEM Conference on Materials, Systems and Structures in Civil Engineering, Conference segment on Concrete with SCMs, 22-24 August 2016, Technical University of Denmark, Lyngby, Denmark, pp. 61-72.

[18] BS EN 196-1:2005. Methods of testing cement. Determination of strength. ISBN: 0580 45670 6.

[19] S. Bahador, H.C. Jong, Study on moisture transport and pore structure of PC and blended cement concrete by monitoring the weight loss during the drying process, in Proc. 32nd Conference on Our World in Concrete & Structures, Singapore, August, 2007.

[20] M.A. Sanjuán, R. Muñoz-Martialay. Oven-drying as a preconditioning method for air permeability test on concrete. Mater. Lett. 27 (1996), 263-268.

[21] Y.A. Villagrán Zaccardi, V.L. Taus, A.A. Di Maio, A. Píttori. Relación entre la velocidad de succión capilar y la velocidad de secado de probetas de hormigón (in Spanish), in Mem. de la V Congreso Internacional y 19ª Reunión Técnica de la AATH, Bahía Blanca (Argentina), November, 2012 (AATH, La Plata, 2012) pp. 119-126.

[22] N. M. Alderete, Y.A. Villagrán Zaccardi, A. Píttori. Resistivity-sorptivity relationship in cement mortar including limestone powder. Proceedings of Int. Conference on Sustainable Structural Concrete, 15-18 Sept 2015, 99-109, La Plata, Argentina.