Microstructure alterations of PC-GGBS mortars by superabsorbent polymers (SAP)

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Microstructure alteration of PC-GGBS mortars by superabsorbent polymers (SAP)

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Abstract. Despite its worldwide popularity, the use of blended cements, such as, ground granulated blast-furnace slag (GGBS), requires a special attention predominantly due to their capacity to slow down cement reactions. Superabsorbent polymers (SAP), in turn, can be used as an internal curing agent to enhance durability of cement-based composites by mitigating autogenous shrinkage triggered by self-desiccation process. The paper aims to evaluate the effect of SAPs addition on microstructure of GGBS-PC mortars. Development of microstructural characteristics and selected mechanical properties were analysed during the first 90 days. Four levels of Portland cement (PC) replacement by GGBS (0%, 25%, 50% and 75%) and two types of SAP with different water absorption capacities were considered. The results showed that SAP with higher water absorption capacity is able to develop larger pores after 28 days for any GGBS content. SAP can also facilitate GGBS hydration and its later products can be deposited into the smaller nano pores. Despite increased total porosity, mechanical strength of SAP modified mortars is comparable to the reference samples for low GGBS contents in advanced ages. Therefore, the type of SAP and concentration of GGBS play a considerable role in microstructure alteration of mortars.

Introduction

The hydration process of cementitious materials is commonly related to a gain of strength over time by chemical reactions of Portland cement (PC), which essentially consists of reactive calcium silicates (C_3S and βC_2S). Calcium silicate hydrates (CSH) produced during cement hydration are primarily responsible for its adhesive characteristic, creating a rigid, dense and stable skeleton. Additionally, other compounds are produced, such as, calcium hydroxide ($Ca(OH)_2$) that can increase alkalinity of concrete and also improve densification of the interfacial transition zone. Overall, the hydration process of cementitious materials leads to formation of a heterogeneous distribution of different types and amounts of solid phases, pores and microcracks. In turn, all these elements are subject to change with time, environmental conditions and composition of raw materials. Thus, as a result of the chemical changes when PC comes in contact with water, development of microstructure determines concrete properties [1-4].

Due to its high proportion, CSH is the most important phase that determines the properties of paste and microstructure formation. CSH is a colloidal amorphous gel, which contains gel pores of approximately few nanometres in size; their solid-to-solid distance is about 0.5 to 2.5nm. Gel porosity has a major effect on hydration rates, because its pores exist inside the hydration products that accumulate between liquid phase and anhydrous cement grains. When a cement grain is fully hydrated, the bulk volume of CSH gel requires about 60% more volume than the original volume of unhydrated cement grain and water. This expansion, in turn, moves into capillary pores, which have highly irregular shape and diameter size in the range between 2nm and 10μm. As hydration proceeds, the amount and distribution of capillary and gel pores changes considerably; the capillary

pore volume is reduced because they become filled with hydration products, and the CSH gel pore volume increases. As a result, there is an overall net reduction in total porosity [1-2]. Fig. 1 illustrates final dimensional range of solids and pores in a hydrated cement paste.
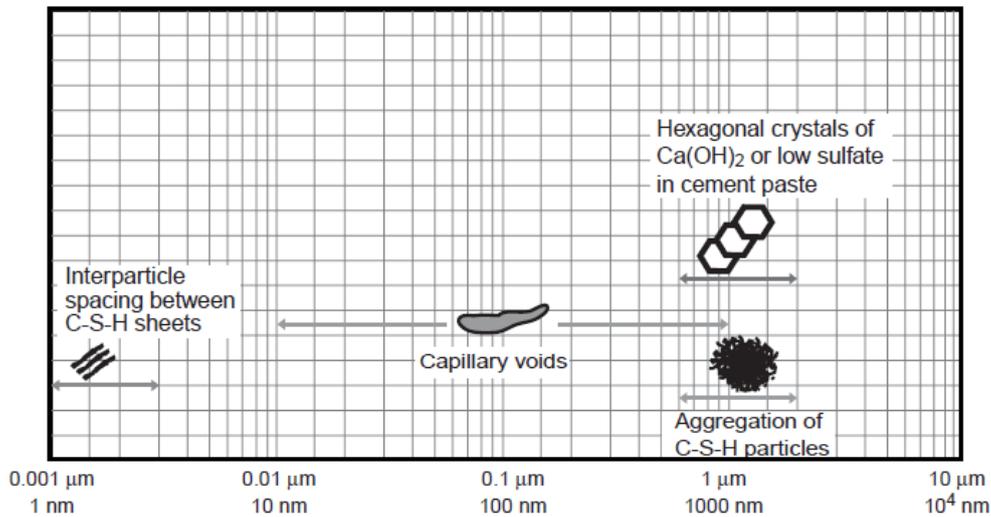

Fig. 1. Dimensional range of pores and main hydration products of fully hydrated cement paste (adapted from [1]).

However, when any admixture is added to concrete, hydration rate and its microstructure formation can be substantially modified. For instance, supplementary cementitious materials, such as ground granulated blast-furnace slag (GGBS), can slow down cementitious reactions and densify the weak CH-laden interfacial transition zone, improving long-term properties [5-6]. Supplementary cementitious materials can usually result in formation of large amounts of capillary pores in the range between 2 and 50nm [2]. However, their ability to create finer capillaries (filler effect) and their potential high degree of hydration can intensify the self-desiccation process and hence increase autogenous shrinkage [7-11].

In order to mitigate this negative effect, superabsorbent polymers (SAP) can be used as an internal curing agent for concrete and mortars [12-15]. Its high capacity to absorb water from the fresh mix and release it over the time can contribute to longer hydration processes, promoting creation of a denser network of CSH. However, when SAP collapses, it leaves behind pores that can significantly change microstructure of hardened concrete [16-17].

Although there are some studies related to application of SAP in PC-GGBS materials [18-21], its effects on their microstructure are still unclear and deficient. Knowledge of the microstructure and properties of the individual components of cementitious materials, and their relationship to each other is essential for understanding their effects on performance and behaviour of concrete.

Some techniques can be applied in order to evaluate pore structures in cement based materials, such as, Mercury Intrusion Porosimetry (MIP). Although MIP has limitations, especially in measuring the actual inner size of pores and in adopting numerous assumptions, it has still great capacity to contribute to characterization of porous materials [22-23]. MIP is valuable in making comparative assessments of pore refinements that take place within a given system, and in making comparison of different systems within the same condition [22]. It also provides a wide range of information, e.g. the pore size distribution, the total pore volume or porosity, the skeletal and apparent density, and the specific surface area of a sample [23]. Thus, from MIP parameters, property-microstructure relations can be established.

This paper, therefore, aims to evaluate microstructural alterations in mortars with different levels of GGBS content modified by two different types of SAPs, by relating results of MIP/SEM and mechanical strength development during 90 days.

Methodology

Prismatic samples of mortar (160x40x40 mm) have been produced in the proportion of 1:2 (binder/sand) and water/binder (w/b) ratio of 0.5. Fine sand used as fine aggregate contained at least 90% of particles sizes distributed below 0.425 mm (BS EN 13139:2013) [24]. Four levels of PC replacement (CEM I 52.5N) by GGBS have been considered: 0%, 25%, 50% and 75% (by mass). Table 1 shows the chemical and physical analysis of both binders used in the experimental study.

Table 1 – Characterization of CEM I and GGBS.

	Chemical composition [%]									Fineness [m^2/kg]
	SiO$_2$	Al$_2$O$_3$	Fe$_2$O$_3$	CaO	MgO	SO$_3$	Na$_2$O	K$_2$O	LOI	
CEM I	20.1	4.9	2.7	62.4	2.2	3.2	0.3	0.6	2.8	410
GGBS	34.5	13.1	0.2	38.5	9.7	0.4	0.2	0.6	0.6	390

The presence of finer particles of CEM I in comparison with GGBS can be observed in Fig. 2.
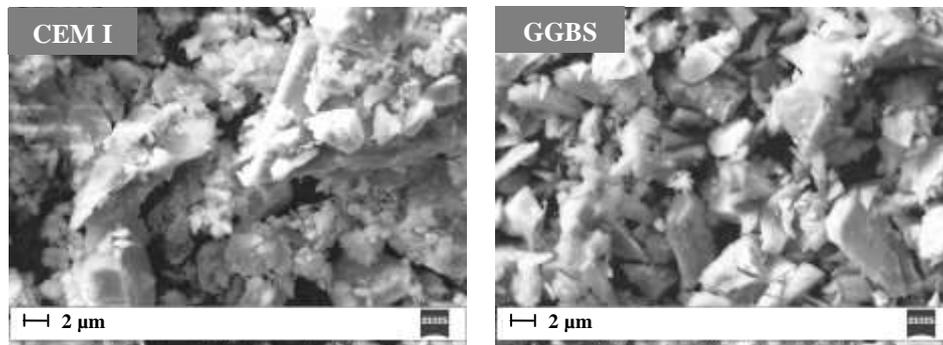

Fig. 2. SEM micrographs of CEM I (left) and GGBS (right).

Two types of modified polyacrylamide SAPs have been used in the proportion of 0.25% by mass of binder. SAP X and SAP Y with water absorption capacities (WAC) in cement paste solution of 25-30g/g and 35g/g respectively. Fig. 3 shows SEM micrographs of both SAPs used, which presented particles sizes in the range of 63-125µm.
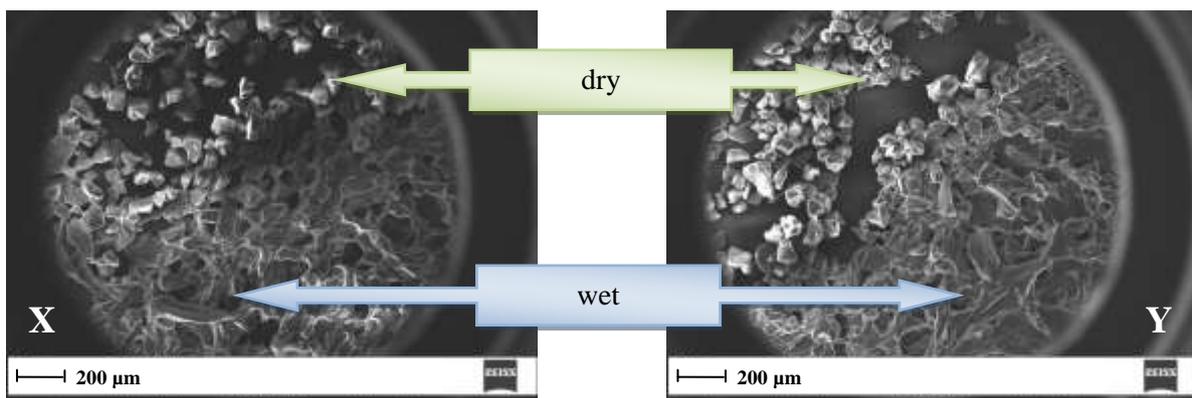

Fig. 3. SAPs in wet and dry conditions: SAP X (left) and SAP Y (right).

Table 2 shows the nomenclature of mortar samples, considering the type of SAP and binder content used in this experimental programme.

Table 2 – Nomenclature of mortars samples.

Sample nomenclature	Type of SAP	CEM I [%]	GGBS [%]
R0		100	0
R25		75	25
R50	-	50	50
R75		25	75
X0		100	0
X25	SAP X	75	25
X50		50	50
X75		25	75
Y0		100	0
Y25	SAP Y	75	25
Y50		50	50
Y75		25	75

Microstructural features and mechanical properties were evaluated after curing in a climate chamber (T = 21±2 ℃ and RH = 40±5%) at 7, 14, 28 and 90 days. Microstructural characteristics were analysed in terms of total porosity (%) and pore size distribution (nm) using Mercury Intrusion Porosimetry (MIP) and Scanning Electron Microscopy (SEM) techniques. Minimum of two repetitions were considered for each sample. Mechanical properties were verified by standard flexural (average of 3 samples) and compressive (average of 6 samples) strength determination methods according to BS EN 1015-11 [25]. Average of three and six samples was considered for flexural and compressive analysis respectively.

Results and discussions

Fig. 4 shows results of total porosity of mortars. Overall, porosity has decreased with time for all samples. Also, the higher GGBS content the higher is total porosity during the first 90 days (indicated by arrows with traced lines).
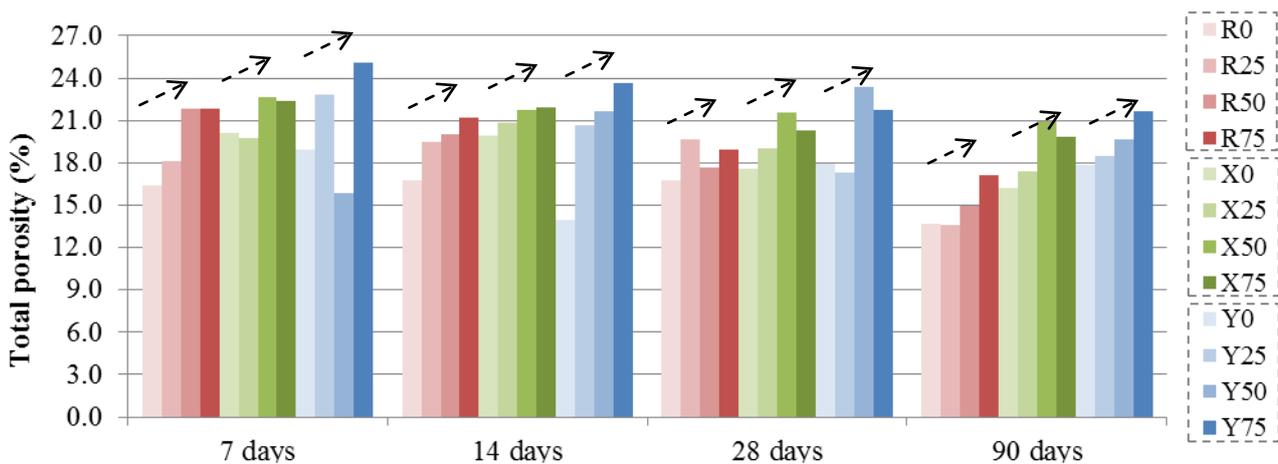
Fig. 4. Results of total porosity.

Not only GGBS has altered microstructure of hardened mortars, but also SAPs had a considerable influence on porosity, especially when it is analysed at further ages. Analysis up to 90 days indicated that SAPs increased total porosity; this increment was more pronounced for polymer with higher WAC. SAP Y was able to absorb more water from the fresh mix and to form larger pores when it collapsed. This increment in porosity caused by SAPs can be observed on SEM

micrographs. Fig. 5 shows three images of mortars without GGBS, however similar features were recorded for all samples, also for those containing GGBS.
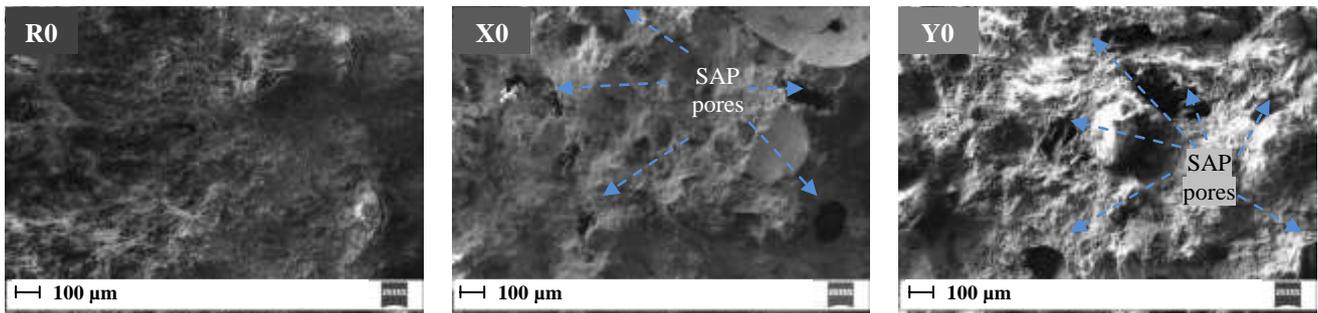

Fig. 5. SEM micrographs of mortars without GGBS at 28 days.

The development of microstructure in mortars with and without SAP is shown in Fig. 6. For comparison, pore size distribution was presented only for samples with 0% and 75% of GGBS, considering that contents of 25% and 50% represent intermediate conditions.

Overall, GGBS addition has modified mortars microstructure and changed pore size distribution models. Pore size distribution curves for mortars without or with lower amount of GGBS are of unimodal shapes, with peaks around 80-100nm. Diameter ranges have varied according to the type of mortar; mortars without polymer had predominant size of pores between 5-500nm at 90 days, while samples modified by SAP had pores between 8-3000nm for the same age.

However, as GGBS content was increased, bimodal curves started to dominate. In particular for high GGBS content, two predominant bands were formed: one with larger pores (200-2000nm) and the other one with smaller pores (below 50nm). These ranges can vary according to the analysed age and presence of SAP. In general, the change to a bimodal distribution by high contents of GGBS can be attributed to its particle size effect when compared to other dry materials.

Firstly, the presence of larger particles of GGBS when compared to CEM I (Table 1 and Fig. 2) could form the band with larger pores (peaks around 400-500nm). These larger particles could be responsible for reduction of GGBS reactivity and hence for a relatively high porosity of studied mortars. Secondly, GGBS can produce finer capillaries due to its filler effect [2-3]; its particles are smaller than fine sand. GGBS can, therefore, act as fine aggregate in early ages due to its low reaction rate. In fact, its double role as a mineral admixture and a very fine aggregate can also be noticed when analysing workability [26]. GGBS demands more water during mix preparation due to its higher capacity for absorption and adsorption compared with cement and sand respectively. Consequently, higher total porosity (as shown in Fig. 4) can be attributed to GGBS addition as a fine aggregate and reduction of cement content.

In particular, this GGBS capacity to produce finer pores can potentially influence development of autogenous shrinkage [3,8-11]. In smaller capillaries, the force of attraction between pore walls due to water surface tension may be increased. Thus, higher tensile stress in the capillary pores (for mortars with GGBS) can result in an increased autogenous shrinkage [11]. It is expected that SAP addition may not only mitigate autogenous shrinkage in mortars with slag [7,20-21], but can also promote further hydration of GGBS. Arrows I on Fig. 6 indicate a decreased amount of small pores over time. In early ages, mortars with GGBS modified by SAP have a similar bimodal pattern compared to the reference sample. However, at 90 days, the amount of smaller pores was reduced in SAP mortars, while in the reference sample, the amount of smaller pores has not been significantly changed.
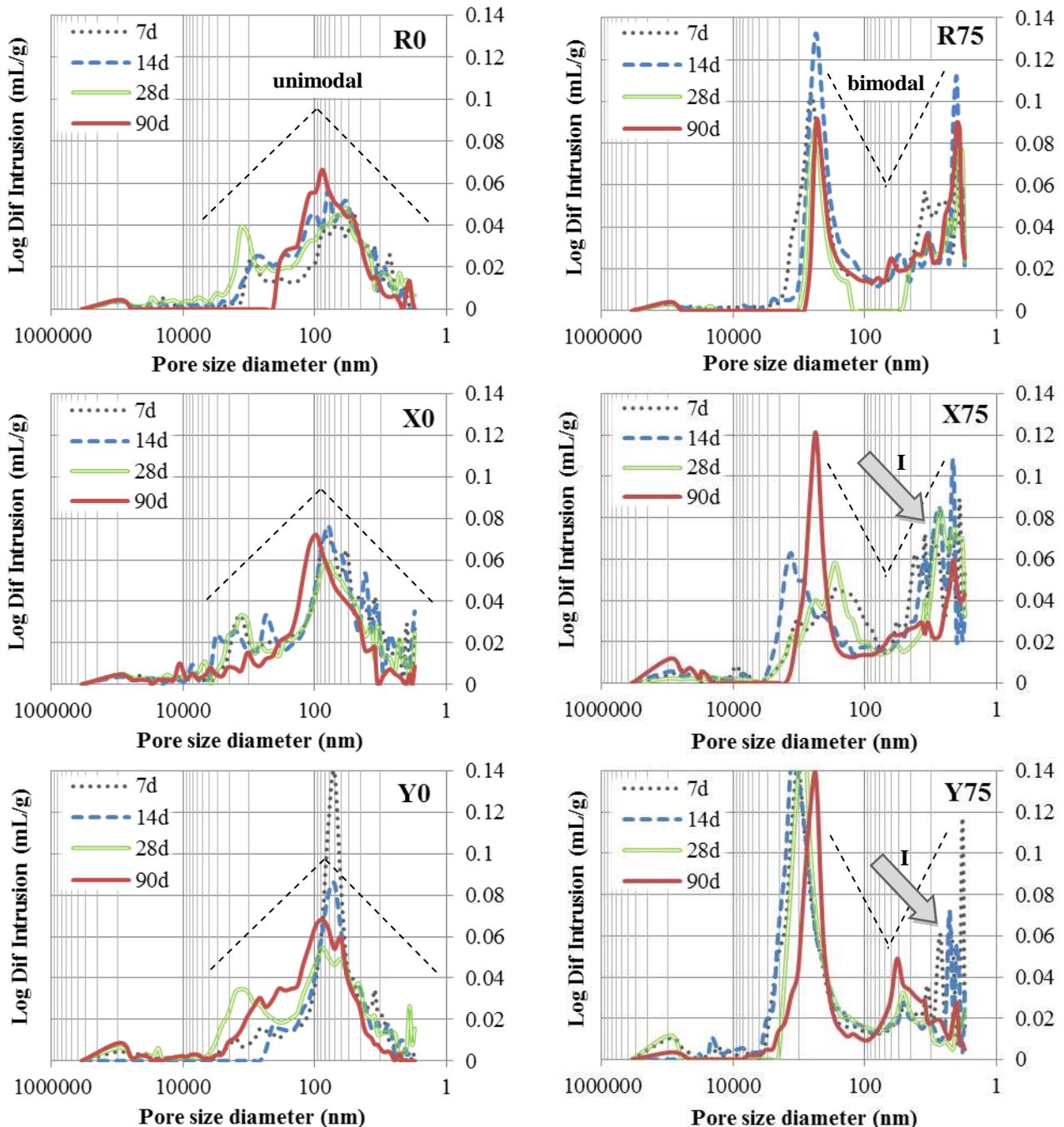
Fig. 6. Pore size distribution for samples with 0% (left) and 75% (right) of GGBS.

Pore size distribution curves for all mortars at 90 days are shown in Fig. 7. The same Arrow I indicates SAP effect on smaller pores in mortars with high GGBS content; SAP addition decreased the amount of pores with diameter under 20nm. This reduction can be attributed to the filling of nano pores with later GGBS hydration products that were facilitated by SAP's water supply. The water stored by polymer tends to move through smaller pores once they provide more surface area for water to adhere to [27]. The availability of more water can promote creation of denser network of CSH and hence reduce nano pores. In this context, SAP Y is more efficient to provide additional water for hydration and hence the observed reduction of small pores in high GGBS mortars. On the other hand, no significant reduction was recorded for the reference sample since there was not enough water for further GGBS hydration.
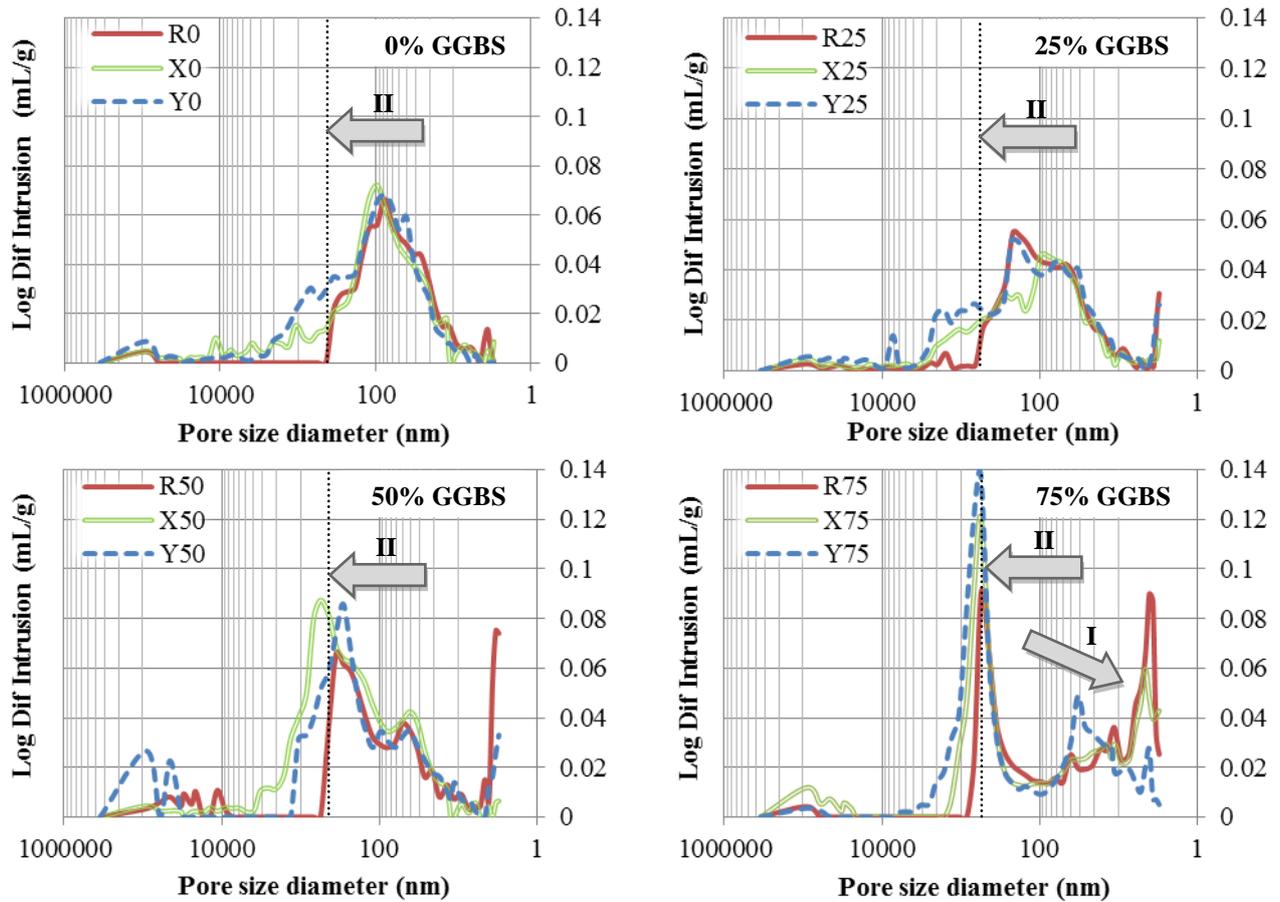
Fig. 7. Pore size distribution curves of mortars at 90 days. Arrows indicate relevant effects of SAP on PC-GGBS mortars porosity.

Moreover, only the reference samples have created pores within the dimensional limits for capillary voids (up to 1µm, Fig. 1). SAP, however, was able to form larger pores in collapsed state. Arrows II (Fig. 7) indicate that pores with diameter greater than 500nm may be formed by collapsing SAPs. In general, mortars with SAP Y created larger pores than other samples; it absorbed more water from a fresh mix, and consequently left behind larger voids in hardened state. Even with the reduction of the amount of smaller pores, total porosity has increased for samples with SAP (Fig. 4 and Fig. 5). This increment, therefore, can be attributed to the formation of large pores from collapsed SAPs.

Therefore, SAP addition increased total porosity in PC-GGBS mortars due to its capacity to create larger pores in collapsed state. On the other hand, SAP could aid GGBS hydration, contributing to water supply for further reactions in a prolonged time (up to 90 days). The later GGBS reaction is facilitated by SAP water that is adhered to smaller pores due to their high surface area. Thus, the later hydration products are formed in smaller capillaries filling the pores with diameter under 20nm.

Results of compressive strength are shown in Fig. 8. In general, the higher the level of replacement by GGBS, the lower the compressive strength, due to higher total porosity of mortars.
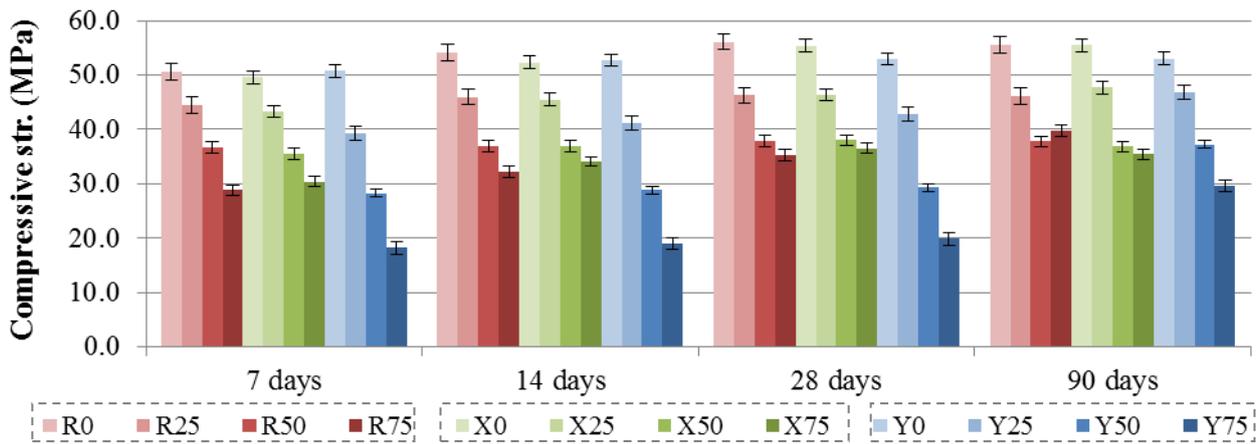
Fig. 8. Results of compressive strength.

Mortars with SAP X had a very similar performance to the reference samples. Apart from mortars with high GGBS content at 90 days, all the other samples had compressive strength values of the same order as those without polymer. It can indicate that the increment in porosity by addition of SAP X may not significantly interfere with compressive strength results, especially when lower GGBS levels are considered (up to 50%).

Addition of SAP Y to the mix seemed to reduce compressive strength in the first month. However, mortars with this polymer presented comparable results to the reference samples with lower GGBS contents (up to 50%) at 90 days. As SAP X samples, mortars with 75% of GGBS modified by SAP Y also had lower values of strength in comparison to the reference sample. When results were compared over time, a considerable gain of strength can be noticed for samples with higher GGBS contents and the polymer with higher water absorption capacity (samples Y50 and Y75). Although SAP Y has reduced compressive strength because of higher porosity (compared to the reference), it improved the rate of GGBS hydration at later ages. It seemed that GGBS hydrated products may have filled pores formed by SAP Y and significantly increased compressive strength values at 90 days (compared to 28 days).

Fig. 9 shows results of flexural strength over time. Similarly to the compressive strength pattern, increase in GGBS content led to decreased flexural strength.
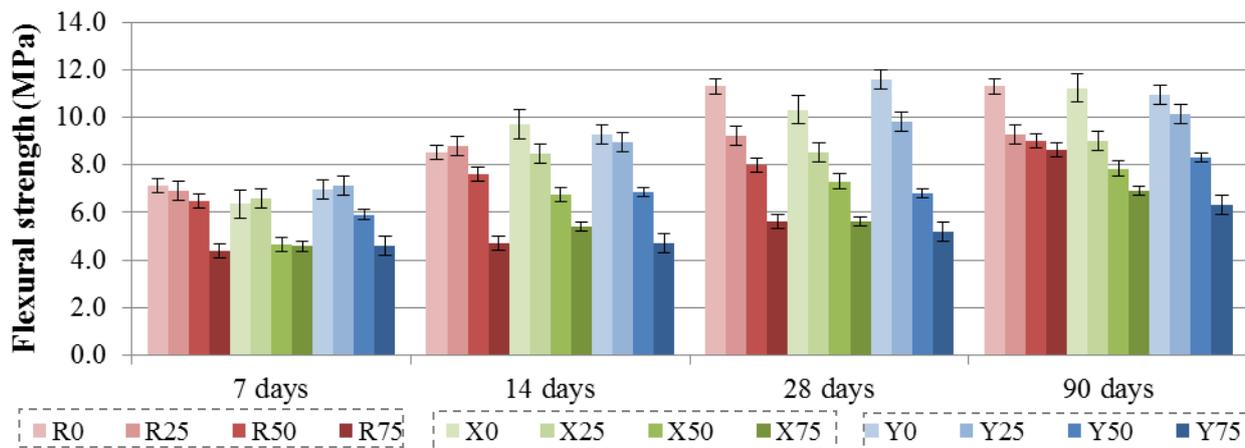

Fig. 9. Results of flexural strength.

Mortars with lower contents of GGBS (up to 25%) modified by SAPs had the same (or even slightly higher) results of flexural strength when compared to the reference samples. However, when GGBS level was increased, both SAPs modified mortars reached lower flexural strength values at the end of 90 days.

Overall, it seemed that SAP may not have significant effect on mechanical strength for lower GGBS contents, even with increased porosity in a unimodal pore size distribution. As GGBS level is increased and its pore size distribution is changed to bimodal curves, the increase in porosity by both SAP and GGBS can be evinced by reduction in strength level. In order to keep the same strength values for mortars with and without SAP, the limit level of PC replacement by GGBS should be 50% and 25% for compressive and flexural strength, respectively. Above these contents, decrease in mechanical strength can be observed.

Conclusions

From the experimental results, the following can be concluded:

- Both studied SAPs are able to supply water for later GGBS hydration. Its products can be deposited into the smaller pores (under 20nm of diameter) formed by high contents of GGBS. It is because smaller pores have greater water affinity due to their higher surface area. SAP Y is more efficient in decreasing the number of smaller pores due to its higher capacity to absorb and also to provide water for later hydration;
- Pores with diameter greater than 500nm may be formed by addition of polymer. SAP Y, with higher water absorption capacity, is able to produce larger pores than SAP X. However, this increment of porosity by SAP cannot affect mechanical strength for low GGBS contents at 90 days. Reduction in compressive and flexural strengths can be observed for substitution levels above 50% and 25% respectively when compared to the reference samples;
- Overall, although SAP increases total porosity in PC-GGBS mortars, it aids GGBS hydration and keeps the same level of mechanical strength (for low GGBS contents) when compared to the reference samples.

Acknowledgements

References

[1] P.K. Mehta, P.J.M. Monteiro, Concrete: microstructure, properties, and materials, third ed., McGraw-Hill, 2005.

[2] K.K. Aligizaki, Pore structure of cement-based materials: testing, interpretation and requirements, Taylor & Francis, London, 2006.

[3] K.L. Scrivener, P. Juilland, P.J.M. Monteiro, Advances in understanding hydration of Portland cement, Cem Concr Res 78 (2015) 38–56.

[4] B. Lothenbach, F. Winnefeld, Thermodynamic modelling of the hydration of Portland cement, Cem Concr Res 36(2) (2006) 209–226.

[5] R. Siddique, M.I. Khan, Supplementary Cementing Materials, vol. 1, Springer, Berlin, 2011.

[6] M. Thomas, Supplementary cementing materials in concrete, Taylor & Francis Group, Boca Raton, 2013.

[7] F.C.R. Almeida, A.J. Klemm, Use of superabsorbent polymers (SAP) to reduce autogenous shrinkage in mortars with ground granulated blast-furnace slag (GGBS). In: YRF III, London (2016), 17, 1–4.

[8] K.M. Lee, H.K. Lee, S.H. Lee, G.Y. Kim, Autogenous shrinkage of concrete containing granulated blast-furnace slag, Cem Concr Res 36(7) (2006) 1279-1285.

[9] M. Bouasker, N.E.H. Khalifa, P. Mounanga, N.B. Kahla, Early-age deformation and autogenous cracking risk of slag–limestone filler-cement blended binders, Constr Build Mater 55 (2014) 158–167.

[10] C. Jiang, Y. Yang, Y. Wang, Y. Zhou, C. Ma, Autogenous shrinkage of high performance concrete containing mineral admixtures under different curing temperatures, Constr Build Mater 61 (2014) 260–269.

[11] M. Valcuende, F. Benito, C. Parra, I. Miñano, Shrinkage of self-compacting concrete made with blast furnace slag as fine aggregate, Constr Build Mater 76 (2015) 1–9.

[12] V. Mechtcherine, H.W. Reinhardt (eds.), Application of Superabsorbent Polymers (SAP) in Concrete Construction: State-of-the-Art Report Prepared by Technical Committee 225-SAP, RILEM: Springer, 2012.

[13] V. Mechtcherine, M. Gorges, C. Schroefl, A. Assmann, W. Brameshuber, A.B. Ribeiro, D. Cusson, J. Custódio, E.F. Silva, K. Ichimiya, S. Igarashi, A. Klemm, K. Kovler, A.N. Mendonça Lopes, P. Lura, V.T. Nguyen, H.W. Reinhardt, R.D.T. Filho, J. Weiss, M. Wyrzykowski, G. Ye, S. Zhutovsky, Effect of internal curing by using superabsorbent polymers (SAP) on autogenous shrinkage and other properties of a high-performance fine-grained concrete: results of a RILEM round-robin test. Mater Struct 47(3) (2013) 541–562.

[14] A.J. Klemm, F.C.R. Almeida, Application of Superabsorbent polymers (SAP) as novel admixture for cementitious materials, Conc Plant Int J. 3 (2016) 38-46.

[15] C. Schrofl, V. Mechtcherine, M. Gorges, Relation between the molecular structure and the efficiency of superabsorbent polymers (SAP) as concrete admixture to mitigate autogenous shrinkage, Cem Concr Res 42 (2012) 865–873.

[16] A.J. Klemm, K. Sikora, The effect of cement type on the performance of mortars modified by superabsorbent polymers. In: Alexander et al. (eds.): Concrete Repair, Rehabilitation and Retrofitting III, Taylor and Francis, London (2012) 210–216.

[17] A.J. Klemm, K. Sikora, The effect of Superabsorbent Polymers (SAP) on microstructure and mechanical properties of fly ash cementitious mortars, Constr Build Mater 49 (2013) 134–143.

[18] H. Beushausen, M. Gillmer, M. Alexander, The influence of superabsorbent polymers on strength and durability properties of blended cement mortars, Cem Concr Comp 52 (2014) 73–80.

[19] D. Snoeck, O.M. Jensen, N. De Belie, The influence of superabsorbent polymers on the autogenous shrinkage properties of cement pastes with supplementary cementitious materials, Cem Concr Res 74 (2015) 59–67.

[20] A.J. Klemm, F.C.R. Almeida, K.S. Sikora, Application of superabsorbent polymers (SAP) in cementitious materials with blended cements, Conc Plant Int J. 4 (2016) 50-58.

[21] F.C.R. Almeida, A.J. Klemm, Evaluation of hardened state properties of GGBS-PC mortars modified by superabsorbent polymers (SAP). In: International RILEM Conference on Materials, Systems and Structures in Civil Engineering, Lyngby (2016) 1–10.

[22] H. Ma, Mercury intrusion porosimetry in concrete technology: tips in measurement, pore structure parameter acquisition and application, J Porous Mater 21 (2014) 207–215.

[23] H. Giesche, Mercury Porosimetry: a general (practical) overview, Part Part Syst Charact 23 (2006) 9-19.

[24] BS EN 13139-13, Aggregates for mortar, BSI (2013).

[25] BS EN 1015-11, Methods of test for mortar for masonry – part 11: Determination of flexural and compressive strength of hardened mortar, BSI (1999).

[26] F.C.R. Almeida, A.J. Klemm, Effect of superabsorbent polymers (SAP) on fresh state mortars with ground granulated blast-furnace slag (GGBS). In: 5th International Conference on Durability of Concrete Structures, Shenzhen (2016) 1–7.

[27] D.E. Ramos, Walnut production manual, University of California, Richmond, 1998.