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Effect of GGBS on water absorption capacity and stability of superabsorbent polymers partially crosslinked with alkalis

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Abstract

In an attempt to improve sustainability of construction and reduce Portland cement (PC) consumption, supplementary cementitious materials (SCM), such as ground granulated blast furnace slag (GGBS), has become a common practice. On the other hand, in order to increase durability of cementitious composites, various internal curing agents, including superabsorbent polymers (SAP), are often implemented. Due to their high capacity to absorb, retain and release water SAPs can provide additional water for continuous hydration and lead to more homogenous microstructures. They are usually neutralized by alkali metals (sodium and potassium) to increase their absorption capacities and keep them stable in PC cementitious matrices. This paper discusses the applicability of SAPs in blended systems. It aims to evaluate the effect of GGBS on water absorption capacity and stability of three partially neutralized SAPs. SAPs swelling capacity and kinetics of the absorption, pH of binder solutions over time, as well as mechanical properties of PC-GGBS matrices have been analysed. The results showed that alkalis content up to 4 wt% lead to a GGBS system comparable to a stable PC system. Above this limit, degradation of SAP starts to take place due to ion-exchange with GGBS solution components, resulting in lower compressive strength when compared to PC matrices. Thus, the excess of alkalis in SAPs network plays an important role in GGBS aqueous solution.

Keywords: Superabsorbent polymers (SAP), ground granulated blast-furnace slag (GGBS), absorption capacity, alkalinity, cementitious materials

Introduction

Construction industry is constantly searching for innovations and sustainable solutions to enhance environmental, structural and cost requirements. The massive production of ordinary Portland cement (PC), the main cementitious material, requires consumption of high energy levels and large amounts of non-renewable raw-materials. It is estimated that 5-6% of all CO_2 emissions generated by human activities is derived from cement manufacture (Damineli et al. 2010; Fairbairn et al. 2010; Flower and Sanjayan 2007; Huang et al. 2018; John and Zordan 2001; Pacheco-Torgal et al. 2013; Rodrigues and Joekes 2011; Scrivener et al. 2016). In an attempt to mitigate this environmental issue, the use of supplementary cementitious materials, such as ground granulated blast-furnace slag (GGBS), has become a common construction practice (Almeida and Klemm 2018; Hooton 2008; Li 2016; Lothenbach et al. 2011; Sales and Lima 2010; Siddique 2014). This by-product from pig iron manufacture is a latent hydraulic material that can replace PC in contents up to 85% by weight (Siddique 2014; Siddique and Bennacer 2012). However, higher GGBS contents may have serious implications on concrete durability. On one hand, it can reduce permeability and increase resistance to deleterious processes (e.g. chloride penetration, alkali-silica reaction and sulphate attack) (Almeida et al. 2015; Divsholi et al. 2014; Klemczak and Batog 2016; Krivenko et al. 2014; Loser et al. 2010; Moretti et al. 2018; Thomas 2011). On the other hand, GGBS may lead to increased carbonation rate, decreased resistance to freezing/thawing and volumetric instability (Bouasker et al. 2014; Divsholi et al. 2014; Ghourchian et al. 2018; Lee et al. 2006; Lothenbach et al. 2011; Lura et al. 2001; Valcuende et al. 2015). Overall, cementitious properties of GGBS depend on its chemical composition, fineness, glass content and alkali concentration of the reacting system (Lothenbach et al. 2011; Siddique 2014). GGBS generally contains less alkali compounds than PC clinker, which leads to lower potassium and sodium concentrations in blended systems over time. Hydroxide concentrations are also lower in the presence of high GGBS contents. In addition to lower alkali content, pH can be decreased in GGBS pore solution due to formation of reduced sulphur species, such as sulphide (HS^-), sulphite (SO_3^{2-}) and thiosulfate ($S_2O_3^{2-}$). Calcium, silicon and aluminium concentrations do not change significantly over time when compared to pure PC pore solution (Vollpracht et al. 2016). Thus, especially in high levels

of replacement (>75 wt% of the binder), GGBS can have a strong influence on the alkalinity of cementitious system.

The physical presence of GGBS leads to filler effect, resulting in higher reaction degree of the clinker phase during early ages (dilution effect) (Lothenbach et al. 2011; Scrivener et al. 2015b). Moreover, refinement of pores by GGBS increases tensile stress generated by water menisci in the capillaries (Lura et al. 2001; Tazawa and Miyazawa 1995; Valcuende et al. 2015). Consequently, GGBS may increase autogenous shrinkage and thus may lead to a high cracking susceptibility, trigged by self-desiccation processes of cementitious materials (Bouasker et al. 2014; Jiang et al. 2014; Lee et al. 2006; Lothenbach et al. 2011; Lura et al. 2001; Scrivener et al. 2015a; Shen et al. 2016; Valcuende et al. 2015). This cracking formation may have a severe impact on concrete durability; it establishes interconnections and increases permeability, facilitating entrance of aggressive agents.

In order to mitigate this negative effect of autogenous shrinkage, superabsorbent polymers (SAP) can be introduced as a novel admixture for internal curing (Hasholt et al. 2012; Jensen and Hansen 2002; Mechtcherine et al. 2013; Mignon et al. 2017; Snoeck et al. 2015; Wehbe and Ghahremaninezhad 2017). SAPs are polyelectrolyte hydrogels with high ability to bind water molecules to their polymer chains due to their hydrophilicity (Jensen and Hansen 2001; Mechtcherine and Reinhardt 2012). This water absorption leads to formation of a swollen product that store and release water over time.

Hydroxides of alkali metals, usually sodium or potassium, can be considered among the primary trunk chains to partially neutralize and prevent these chains from dissolving by forming a three-dimensional network (Mechtcherine et al. 2015; Mechtcherine and Reinhardt 2012). Moreover, SAPs modifications by alkalis as functional filler can reduce costs of their production as well as increase their water absorption capacities (Li et al. 2005). For instance, in a non-modified polyacrylamide network, $–CONH_2$ groups (bonded onto the polymer chains) can interact with each other by hydrogen bonding. This causes an increase in crosslinking density and results in a tighter network, leading to a lower polymeric expansion in water. However, when potassium or sodium salts are added into the chains, these ions can weaken the formation of hydrogen bonds between $–CONH_2$ groups. Consequently, it decreases the effective crosslinking density and helps to increase water absorption capacity (Flory and Rehner 1943). However, there is an optimal content of alkalis to acquire the

maximum SAP water absorption. Values above 6.6 wt% for potassium (Chu et al. 2008) and 10 wt% for sodium (Li et al. 2005) may lead to a significant reduction of water absorbency due to the increased ionic concentration of external aqueous solution.

Moreover, as polyelectrolytes networks, SAPs can potentially exchange ions with ionic components in solution (Horie et al. 2004; Jensen and Hansen 2001). The absorbable amount of liquid and the storage stability, therefore, depend on SAP grading and molecular composition, as well as ions dissolved in the surrounding solution (Mechtcherine et al. 2015; Siriwatwechakul et al. 2012).

Most of the investigations with SAPs for construction purposes has been based on hardened properties of cementitious matrices, predominantly using ordinary Portland cements (Jensen and Hansen 2001; Mechtcherine and Reinhardt 2012; Schröfl et al. 2017). However, their chemical interactions with blended composites (for example with GGBS) are still unclear and deficient (Beushausen et al. 2014; Klemm and Almeida 2018; Snoeck et al. 2015). Understanding of SAP's performance is essential in decision-making process and selection of suitable type of SAP for different cementitious systems (Sikora and Klemm 2015; Siriwatwechakul et al. 2012). In case of GGBS matrices, polymers with higher water storage capacity and higher retention ability may display better effectiveness in providing additional water for longer reactions (Almeida and Klemm 2018). This is because GGBS has a lower rate of hydration compared to the clinker phases (Lothenbach et al. 2011, 2012; Scrivener et al. 2015b).

This paper, therefore, aims to stress the importance of considering different types of cement in SAP performance by assessing the effect of GGBS on water absorption capacity and stability of SAPs (partially neutralized by sodium and potassium). The analyses were based on experimental data for SAPs swelling capacity and kinetics of the absorption, pH of binder solutions over time, as well as mechanical properties of PC-GGBS mortars.

Experimental Programme

Materials and mixes

Three types of superabsorbent polyelectrolytes (SAP X, Y and Z) of modified polyacrylamide with different water absorption capacities have been studied. They are crosslinked with different concentrations of alkalis salts (sodium and potassium).

The polymer behaviour has been evaluated in different systems: deionized water (DI), PC and GGBS filtrates, and PC-GGBS mortars. While Portland cement (PC) systems were prepared with 100% of CEM I 52.5N (BS EN 197-1 2011), GGBS systems comprised 75% of ground granulated blast-furnace slag (GGBS) (BS EN 15167-1 2006) and 25% of CEM I. Low reactivity of GGBS requires an alkaline activator to raise pH in the vicinity of the slag, This can be provided by CH and alkali hydroxides from CEM I hydration (Provis 2014; Thomas 2011). Table 1 shows the physical and chemical analysis of PC and GGBS used in the experimental programme.

Table 1. *Chemical and physical characterization of PC and GGBS*

Filtrate solutions have been prepared in the proportion of water/binder (w/b) ratio 5 (Mechtcherine et al. 2018). Binders (PC and GGBS) have been immersed in deionised water for 24 h with a mechanical stirrer, followed by filtration to separate binder slurry and the used filtrate solution (Mechtcherine et al. 2018; Mignon et al. 2015; Schroefl et al. 2015; Snoeck et al. 2014b). Although the ionic concentrations of diluted filtrates and pore solutions differ, all relevant ions for SAP sorptivity analysis (i.e., Na^+, K^+, Ca^{2+}, OH^- and SO_4^{2-}) are well represented in filtrate solutions (Kang et al. 2017; Schroefl et al. 2015; Schröfl et al. 2012, 2017; Zhu et al. 2015).

Mortars have been produced in the proportion of w/b = 0.5, binder : fine sand = 1:2, and SAP = 0.25% by binder mass. Mixing procedure was the same used in previous studies (Almeida and Klemm 2016a, 2018; Mechtcherine et al. 2013; Schröfl et al. 2012). Dry SAP particles were pre-blended with other dry materials before adding water to the mix. Overall procedure of mortar preparation took approximately 10 minutes, considering two mixing speeds (140 and 285 rotations/min). Table 2 shows mortars compositions used in the experimental programme.

Table 2. *Mix compositions of mortars*

143 ***Characterization of SAPs***

144 Particle sizes of SAPs were evaluated by Laser Diffraction (Malvern Mastersizer X).

145 Shape and size were also analysed by the Scanning Electron Microscopy - SEM (Carl Zeiss EVO 50).
146 Samples were not coated and observations were carried out in high vacuum mode, accelerating
147 voltage (EHT) of 15 kV and working distance (WD) of 9 mm.

148 SAPs chemical characteristics were obtained from X-ray map data by the SEM-linked to the Energy
149 Disperse X-ray spectrometer - EDX (AZtecEnergy acquisition software with the X-MaxNand X-act
150 Silicon Drift Detector).

151 pH has been analysed (Fisher Scientific accumet AP110 pH Meter) in SAP solutions with deionised
152 water, PC filtrate and GGBS filtrate for 7 days. 0.3g of SAP has been kept in a tea-bag and immersed
153 in 100ml of solution (Schröfl et al. 2017). pH of PC and GGBS filtrates only were also evaluated.

154 For all analysis, SAP samples were tested in triplicate and stored in sealed containers under laboratory
155 conditions (T = 21 ± 2 ºC and RH = 40 ± 5%).

156 Sorption characteristics were evaluated by the tea-bag method (Mechtcherine et al. 2018; Schroefl et
157 al. 2015; Schröfl et al. 2012, 2017) in deionised water (DI), PC and GGBS filtrates. Masses of SAP
158 gel were recorded at 1, 5, 10, 30, 60, 180 min, and 1, 2 and 3 days after tea-bag immersion. After that
159 period, carbonation of cement slurry solution can significantly change pH and hence affect the SAP
160 absorption behaviour, as verified by pH analysis. Before each mass record, tea-bag containing water-
161 swollen SAP was placed on a dry tissue and gently wiped for a short time (max 30 s). This was to
162 remove excess and weakly bound liquid. After weighting, the tea-bag with hydrogel was returned to
163 test solution until the next weighing step.

164 Water absorption capacities (WAC), were calculated by $WAC = (m_3 - m_2 - m_1)/m_1$, where m_1 is the
165 weight of dry SAP, m_2 is the mass of tea-bag, and m_3 is the weight of water-swollen sample. WAC
166 was expressed in grams of water per gram of dry SAP. The average WAC for three specimens per
167 solution has been used for further analysis (Mechtcherine et al. 2018; Schröfl et al. 2017).

168 A potential drawback of this method is commonly attributed to residual interparticle (capillary) liquid
169 that may remain within the samples during wiping and weighting process (Kang et al. 2017; Schröfl et
170 al. 2012, 2017). Also, the constraint from SAP particles located on the exterior could decrease the

absorption of SAP particles in the interior. However, recent studies showed that no decisive conclusion on these issues can be drawn at this stage (Mechtcherine et al. 2018). Despite these concerns, the tea-bag gravimetric method is one of the most common and widely accepted quantification techniques for SAPs sorptivity assessment, and has been proved to be more practical in terms of time dependent study (Mechtcherine et al. 2018; Schroefl et al. 2015; Schröfl et al. 2012, 2017).

Properties of GGBS-PC mortars

Fresh and hardened properties of GGBS-PC mortars modified by SAPs have been evaluated. Flow table method (BS EN 1015-3 2006) was performed in triplicate. Compressive and flexural strengths tests (BS EN 1015-11 2006) were carried out after 7, 14 and 28 days. Specimens were cast into prismatic moulds (160 x 40 x 40 mm^3) and cured in climate chamber (T = 21 ± 2 ºC and RH = 40 ± 5%) until the date of testing. For flexural strength test, three prims were broken providing six halves which, in turn, were used for compressive strength determination (BS EN 1015-11 2006). SEM micrographs were also obtained in order to evaluate porosity of GGBS mortars at 28 days (this analysis followed the same procedure described in 2.2).

Results and Analysis

Physical and chemical characteristics of SAP

Fig. 1 shows results of particle size distribution of the studied SAPs.

Fig. 1. *Particle size distribution of the studied SAPs*

Although slight differences in their distribution have been noticed (mode values for SAP Z > SAP X > SAP Y), all samples had the same particle size range, predominantly between 20 and 150 μm. This similar size range and irregular shape can be observed in the SEM micrographs (Fig. 2).

Fig. 2. *The SEM micrographs of the studied SAPs*

Table 3 show results of SAPs chemical composition (by EDX) obtained from the map sum spectrum of all X-ray data collected.

Table 3*. Chemical composition of the studied SAPs by EDX analysis (by wt%)*

199 Different alkalis content (Na + K) has been found in the composition of SAPs: 4.0%, 8.8% and 12.3%
200 for SAP X, SAP Y and SAP Z, respectively. Hydroxides of alkali metals are often used for partial
201 neutralization of polyelectrolytes (SAPs) (Jensen and Hansen 2001; Kang et al. 2017; Krafcik and Erk
202 2016; Mechtcherine and Reinhardt 2012; Schröfl et al. 2017; Zhu et al. 2015). These polymers
203 dissociate in aqueous solutions and the charged molecular chains play a fundamental role in
204 determining structure, stability and interactions of various molecular assemblies (Visakh et al. 2014).
205 Fig. 3 shows pH analysis of SAP solutions over period of 7 days. Standard deviations were below 0.1
206 for all measurements. pH values for all SAP samples in DI water did not change significantly over
207 time. SAP X presented pH around 6.8, while SAP Y and Z, about 7.4 and 7.2, respectively. This
208 lower pH for SAP X is related to the lower alkali concentration compared to the other polymers.
209 Above the content shown by SAP Y in DI water (8.8%, Table 3), no significant difference was
210 observed in pH. However, in cementitious solutions, pH had a considerable drop after the third day
211 due to carbonation effect for all SAPs systems.

212 ***Fig. 3.*** *pH analysis of SAP solutions in deionised water (DI), PC and GGBS filtrates*

213 Regarding reference solution (without SAP), lower pH of GGBS filtrate compared to PC solution is
214 related to decreased alkalis and hydroxide concentrations, as well as to formation of reduced sulphur
215 species (Vollpracht et al. 2016). However, when SAPs were added to the solutions, the changes in
216 alkalinity were very dependent on the type of cementitious system. All SAP samples had a stable
217 interaction with PC filtrate; scatter of pH results was less than 0.1. In contrast, a significant change
218 could be observed when different SAPs were used in GGBS solution, especially when carbonation
219 took place. All SAP solutions showed higher pH when compared to the pure GGBS filtrate after the
220 second day (see Arrow in Fig. 3). Most likely this was due to potential formation of chemical
221 complexes between alkalis from polymers network and species from GGBS solution (as further
222 discussed in Fig. 6). In particular, SAP X showed the same behaviour as in PC system after
223 carbonation, indicating that this polymer is the most stable SAP in both cementitious systems. In turn,
224 SAP Y and Z had the highest pH values after the second day compared to both PC and GGBS
225 solutions. It suggests their higher pH-sensitivity to the changes in cementitious concentrations
226 (Mignon et al. 2014).

227 Therefore, alkalis in concentration up to 4 wt% (defined by SAP X, Table 3) were able to interact
228 with reduced sulphur species formed in GGBS aqueous solution, keeping the same pH level of a PC
229 system (after carbonation). Above this limit (for SAP Y and Z), increased pH was recorded due to the
230 excess of alkalis in SAPs composition. There may be a chemical interaction trigged by polymers ions
231 exchange (Na^+ and K^+) with ionic components of GGBS solution (as further discussed) (Horie et al.
232 2004; Jensen and Hansen 2001). This interaction was observed until the seventh day, when alkalinity
233 level of all systems seems to converge at a pH value around 10.
234
235 ***SAP absorption capacity and kinetics***
236 Fig. 4 shows sorption behaviour of SAPs in DI water by tea-bag method.
237 ***Fig. 4.*** *Sorption behaviour of SAPs in DI water (left: up to 180 min; right: up to 3 days)*
238 Two stages of absorption could be observed in DI water. During the first stage, an initial intensified
239 swelling took place throughout the first 30 min. Absorption capacity values were around 240, 265 and
240 355 g/g, respectively for Z, X and Y samples, with standard deviation lower than 10 g/g. During the
241 second stage, a progressive water absorption up to SAP full capacity could be observed (around the
242 second day). This additional absorption was more pronounced for samples Y and Z; the increment
243 was in the order of 10%, 25% and 40% respectively for SAPs X, Y and Z.
244 Although SAPs Y and Z showed similar behaviour, there was a difference in their maximum
245 absorption capacities due to different alkalis contents. In this case, K^+ concentration seemed to be the
246 main responsible factor for reducing absorbency with values above 6.6 wt% (Chu et al. 2008). This
247 value is aligned with potassium contents of the studied SAPs and their respective water absorption
248 capacities: SAP Y (3.2 wt% K^+ and 440 g/g) and SAP Z (12.0 wt% K^+ and 340 g/g).
249 Moreover, SAPs sorption behaviour significantly changes when PC-GGBS systems were considered
250 (Fig. 5); not only in a substantial drop of water absorption capacity (around 10x less), but also in
251 storage and release of water.
252 ***Fig. 5.*** *Sorption behaviour of SAPs in cementitious solutions (left: up to 180 min; right: up to 3 days). Arrows in*
253 *the right graph indicate the difference between absorbency in PC and GGBS systems for all SAPs*

Considerable reduction in overall swelling capacity (compared to DI water) was due the presence of dissolved cations in binder filtrates, especially K^+, Na^+, Mg^{2+} and Ca^{2+} (Mignon et al. 2015). While SAP Y had the highest capacity (46 g/g), SAP X and Z had similar maximum absorption values: 39 and 38 g/g, respectively, with standard deviation lower than 1 g/g. All of them were reached during the first 30 min in both PC-GGBS systems. After that, a considerable release took place especially for SAP Y and Z; this was even more pronounced in GGBS solution.

In general, particles sizes have a great influence on kinetics of SAPs (Esteves 2010; Mechtcherine et al. 2015), and it could potentially be observed in the test with deionised water. SAP Y, the finest polymer, had the fastest water intake, while SAPs X and Z had similar absorption in the first 10 min. However, considering the small range between the particle sizes (Fig. 1), the effect of SAP diameters was not noted in cementitious solutions (Fig. 5). When both PC and GGBS filtrates are considered, SAP Z (with the largest particles) showed the fastest water absorption, contradicting the concept of the finer particle the faster absorption. Its faster absorptivity may be related to its high alkali content that increases charge concentration of the system. The high amount of K^+ in SAP Z increases osmotic pressure difference between the polymer and the cementitious aqueous solutions, which results in a faster water absorbency (Li et al. 2005). Thus, particularly for this study, it seems that the type of polymer in terms of chemical composition was the main factor influencing sorption characteristics of the studied SAPs in cementitious systems.

In PC solution, after the max WAC is reached, SAPs Y and Z started to release water: up to the first day for SAP Y, and up to the second day for SAP Z. Thereafter, both SAPs had the ability to re-absorb water up to its max WAC (reached during the first 30 min).

However, in GGBS system, this initial release of water was higher (for both SAPs) and no further absorption was noted. This may indicate degradation of SAP Y and Z, due to the loss of their stability of water retention.

In turn, SAP X, although had a slight increment of absorbency in PC solution, it kept nearly unaltered over time in GGBS system. It indicates higher stability of this polymer in both cementitious solutions. Thus, its alkali content of 4 wt% may rule the stability of the polymer in GGBS systems, which seems

281 enough to bind with reduced sulphur species. Above this concentration, exchange of ions between
282 polymers and aqueous solutions may lead to low ability to store water.
283 This effect of SAP instability was described as polymer degradation (Mignon et al. 2014, 2015;
284 Tachibana et al. 2017). It means a decrease of network integrity; chain junction knots can hydrolyse
285 resulting in a drastic swelling reduction. It has been reported that solutions with higher cation
286 concentrations (especially divalent cations) are concomitant with reduced hydrolysis (Dho and Choi
287 1995; Mignon et al. 2015). Indeed, desorption capacity was even higher in GGBS system (with
288 reduced Ca^{2+} content, see Table 1), indicating greater sensitivity of SAPs Y and Z. The difference
289 between absorption/storage capacities in PC and GGBS systems was clearly higher for these SAPs
290 (when compared to SAP X) during the first three days (see arrows in Fig. 5); almost no difference was
291 noted for SAP X during the first 180 min of test.
292 These results are aligned with pH analysis (Fig. 3) where SAP Y and Z have also showed instability in
293 GGBS system, most likely due to their high alkalinity (Table 3). Addition of K^+ and Na^+ in SAPs
294 chains have the ability to weaken hydrogen bonds formation and, in consequence, facilitate (or
295 induce) complex bonds between the polymeric network and metal ions from cementitious solutions.
296 Moreover, the presence of S^{2-} in SAP X could indicate that this ion contributes to greater polymer
297 stabilization by forming disulphide bonds. These are very strong bonds able to hold polymers in their
298 respective conformations, and therefore, play an important role in their folding and stability (Brandt et
299 al. 2017). Disulphide bonds can only be cleaved by external stimulus, such as oxidation-reduction
300 potential (Tachibana et al. 2017). However, as SAP Y also contains sulphide, it is suggested that high
301 alkali content seems to be the main responsible factor for SAP Y and Z degradations in GGBS
302 systems.
303 Surrounding cementitious solutions with univalent cations (e.g. K^+ and Na^+) have the easiest
304 interaction with a crosslinked potassium/sodium hydrophilic network, followed by mediums with
305 divalent (Mg^{2+} and Ca^{2+}) and then trivalent (Al^{3+} and Fe^{3+}) cations. Thus, water absorption capacity of
306 SAP and its storage stability decrease with the increase of ionic strength of external saline solution;
307 the stronger salt ions bonds (from solution), the lower is the effect on the charge of SAP chain. Thus,

the ease of interaction is in the following order: $K^+ = Na^+ > Mg^{2+} > Ca^{2+} > Al^{3+} > Fe^{3+}$ (Chu et al. 2008).

It is worth noting that potassium/sodium modified SAPs are more likely to interact with Mg^{2+} than with Ca^{2+} from cementitious solutions. This ionic preference can explain how SAPs Y and Z had more unstable performances in GGBS systems compared to PC solutions; MgO content is 4.4 times higher in GGBS than PC (Table 1). The presence of divalent cations form strong complexes with the polymer chain and act as additional cross-linker, resulting in low swelling degree (Mignon et al. 2015). Al_2O_3 can also contribute to form complex bonds with those SAPs in GGBS environments, since Ca^{+2} concentration is lower than PC and this ion is also "disputed" with carbonation reactions (observed in both PC-GGBS filtrates). Univalent cations content seems to be very low compared to other elements, especially in GGBS systems (lower than PC's), resulting in negligible interactions with SAPs. Such interaction is schematically represented in Fig. 6, particularly with Mg^{2+} and Al^{3+} ions.

Fig. 6. *Polyacrylamide structures and their modifications (adapted from Chu et al. 2008)*

Therefore, SAP X is more stable and less sensitive to the type of cement, in particular in PC-GGBS matrices. It seems that there is a certain limit of alkali content in SAPs of around 4 wt% that can retain stability of GGBS system similar to PC solution. These alkalis can interact with reduced sulphur species (HS^-, SO_3^{2-} and $S_2O_3^{2-}$) formed in GGBS aqueous solution that generally are not found in PC systems (due to its higher alkali concentration compared to GGBS). Consequently, SAP's alkalis (up to 4 wt%) combined with GGBS reduced sulphur ions keep SAP-GGBS system stable similarly to the SAP-PC system.

Above this limit, additionally to this chemical interaction, ion-exchange can take place between "extra" SAP alkalis (Na^+ and K^+) and additional ions of Mg^{2+} and Al^{3+} from aqueous solution (compared to the amount of these ions in PC system). This ion-exchange can lead, however, to SAPs degradation and hence, reducing their stability in water retention.

336 ***Effect of SAPs on GGBS-PC mortars***

337 Fig. 7 compares results of consistency of fresh mortars modified by SAPs with their respective
338 reference samples. Overall, all SAPs decreased flowability for both PC-GGBS systems (Filho et al.
339 2012).

340 ***Fig. 7.*** *Flow-table results of PC-GGBS mortars modified by SAPs*

341 Duration of flow-table test had a significant impact on the results. SAP X had a slightly lower
342 absorption rate compared to SAP Y and Z in the first 30 min (Fig. 5). In consequence, this polymer X
343 resulted in the highest flow values among SAP mortars, even though its final WAC was between Y
344 and Z samples in cementitious filtrate solutions. Moreover, addition of sand can imply a "dilution
345 effect" of PC-GGBS ions. Sorption behaviour of SAPs obtained in mortars (by flow-table test) was
346 similar to that in DI water (by tea-bag method after the first day). The use of mechanical mixer for
347 mortars preparation could have stimulated SAPs to reach their maximum WAC during mixing/casting
348 procedures. Thus, SAP X had the lowest absorption capacity in mortars, as in DI water.

349 Results of mortars compressive strength over the first month are shown in Fig. 8. Overall, GGBS has
350 reduced compressive strength for all samples due to its slower hydration rate. As reported by
351 Lothenbach et al. (2012) about 90% of GGBS hydrated during 3.5 years. Moreover, overall porosity
352 of PC-GGBS matrices is higher due to the lower total volume of C-S-H formed by GGBS when
353 compared to pure PC systems (Lothenbach et al. 2011).

354 ***Fig. 8.*** *Compressive strength results of PC-GGBS mortars modified by SAPs*

355 The type of SAP had a greater impact than the type of binder. In PC mortars, all compressive strength
356 values were comparable. In contrast, when GGBS was considered, a clear pattern was observed for all
357 ages: while SAP X was very similar to the reference sample, SAP Y and Z had the lowest strength
358 values during the first 28 days. In particular for SAP Y, whose higher WAC could have aggravated
359 mechanical properties of mortars. This is because greater swelling rate may lead to macro-pore
360 formation in the hardened state (Almeida and Klemm 2018; Farzanian et al. 2016; Farzanian and
361 Ghahremaninezhad 2017; Pourjavadi et al. 2013; Schröfl et al. 2012; Snoeck et al. 2014a).

362 Their lower compressive strength results (for SAP Y and Z) may be also related to the instability in
363 GGBS systems. Both SAPs have not showed a reliable capacity to store water for longer periods (Fig.

5). Thus, after polymer collapses, SAPs left behind larger pores, which could not be refilled with hydration products due to the lack of water. It is very likely that this collapse of SAP took place in the first week of hydration, since the pattern was the same for all studied ages.

In summary, reduction in compressive strength for SAP Y and Z mortars (during the first month) can be related to two main concomitant factors: larger pores formation and low ability to water retention. Their macropores are even larger than those formed by SAP X, due to their higher WAC (collapsed SAPs). Once these larger pores are formed, there is not enough water to induce longer GGBS reactions, and hence, to refill those macropores with later hydration products. This outcome is aligned with previous detailed studies on microstructure alteration of SAP-PC-GGBS mortars (Almeida and Klemm 2016b, 2017, 2018). Fig. 9 illustrates these larger macropores formation at 28 days, especially for SAPs Y and Z mortars.

Fig. 9. *SEM micrographs of GGBS mortars at 28 days (indication of larger pores in samples modified by SAP Y and SAP Z)*

Therefore, SAPs chemical composition, in particular its potassium/sodium salt modifications, has a significant influence on compressive strength. This is even more evident in GGBS matrices.

Regarding flexural strength, no significant difference in the overall pattern could be identified between specimens modified by SAPs (Fig. 10).

Fig. 10. *Flexural strength results of PC-GGBS mortars modified by SAPs*

However, at 28 days, SAP-GGBS mortars showed less variation in results than SAP-PC mortars when compared to their respective reference samples. This could be explained by the sensitiveness of the test to smaller pores. GGBS refines capillaries and leads to a denser structure of micropores (below 50 nm for high GGBS content) (Almeida and Klemm 2017, 2018; Li et al. 2010). Thus, results of flexural strength for GGBS mortars are more similar to each other, regardless the addition of SAP. In contrast, a slight reduction in strength can be observed in some PC mortars modified by SAP.

Thus, the type of SAP had a considerable effect on compressive strength of GGBS mortars up to 28 days. However, no significant impact was observed on flexural strength, especially for high GGBS contents.

Conclusions

Based on the experimental data, the following can be concluded:

- Behaviour of SAPs with alkali content around 4 wt% in GGBS systems is similar to a stable PC system. Up to this concentration, sodium/potassium ions may bind with reduced sulphur species formed in GGBS solutions. This combination is able to retain pH of GGBS solution at the same level as pH of the PC solution after carbonation;
- SAPs with alkalis contents above 4 wt% lead to increased polymer degradation in GGBS solution, characterized by loss of water storage capacity and increased pH. The excess of alkalis may lead to ion-exchange between potassium/sodium in SAP and di- and trivalent ions in GGBS. It is most likely due to the higher contents of MgO and Al_2O_3;
- Absorption capacity of SAPs changes according to type of cementitious environment. Aggregates can also lead to a "dilution effect" of PC-GGBS ions by its addition to the mix. In this case, SAPs sorption patterns are more similar to those obtained for DI water than for PC-GGBS filtrate solutions;
- SAP instability, due to excess of alkalis in the polymer network, may affect mechanical properties of GGBS matrices, in particular compressive strength. Its limited ability to store water for longer periods results in formation of larger pores that cannot be filled with later GGBS products (due to slower reaction of slag compared to clinker phases);
- SAP X, with 4 wt% of alkalis crosslink in its composition, showed itself to be the most stable and suitable for both cementitious systems studied. It results in formation of cementitious matrices with similar compressive strength to the reference samples.

Therefore, although the studied SAPs have been designed for a stable performance in Portland cement systems, the excess of alkalis in SAPs compositions leads to chemical interactions with GGBS aqueous solution (with reduced pH) and hence, to instability of the polymeric network.

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Table 1. Chemical and physical characterization of PC and GGBS

Parameter	Unit	PC	GGBS
CaO	wt%	62.44	38.53
SiO_2	wt%	20.07	34.53
Al_2O_3	wt%	4.85	13.4
MgO	wt%	2.20	9.74
TiO_2	wt%	-	0.82
Fe_2O_3	wt%	2.72	0.21
SO_3	wt%	3.15	0.35
Na_2O	wt%	0.31	0.17
K_2O	wt%	0.62	0.59
MnO	wt%	-	0.22
Cl^-	wt%	0.06	0.02
LOI	wt%	2.77	0.64
Bulk density	kg/L	1.28	1.11
Specific surface	m^2/kg	410	390

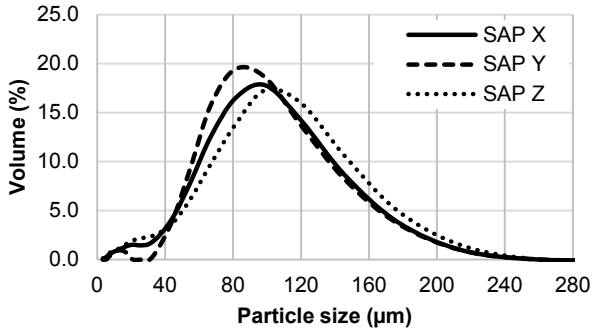
Table 2. Mix compositions of mortars

Sample name	Type of SAP	PC content (%)	GGBS content (%)	Mass of materials (g)				
				PC	GGBS	SAP	Sand	Water
R0	-	100%	0%	587.0	-	-	1174.0	293.5
X0	SAP X	100%	0%	587.0	-	1.5	1174.0	293.5
Y0	SAP Y	100%	0%	587.0	-	1.5	1174.0	293.5
Z0	SAP Z	100%	0%	587.0	-	1.5	1174.0	293.5
R75	-	25%	75%	146.8	440.3	-	1174.0	293.5
X75	SAP X	25%	75%	146.8	440.3	1.5	1174.0	293.5
Y75	SAP Y	25%	75%	146.8	440.3	1.5	1174.0	293.5
Z75	SAP Z	25%	75%	146.8	440.3	1.5	1174.0	293.5

Table 3. Chemical composition of the studied SAPs by EDX analysis (by wt%)

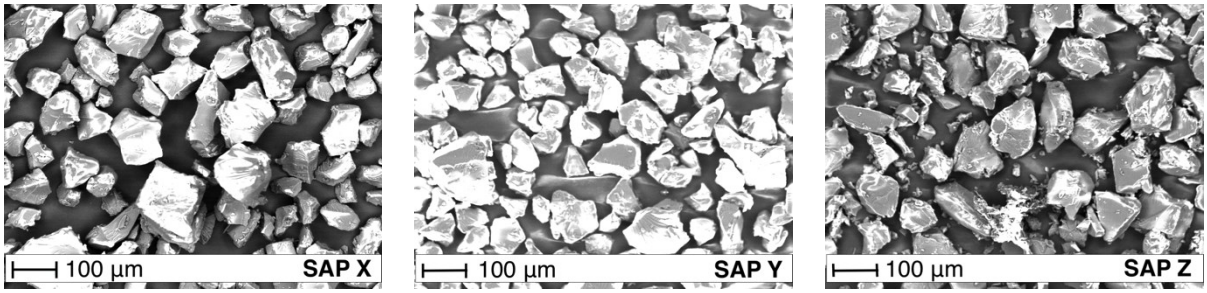
Elements	SAP X		SAP Y		SAP Z	
	Average	SD	Average	SD	Average	SD
C	49.8	1.8	47.3	1.6	46.9	0.8
O	28.2	1.0	30.8	0.5	29.3	0.5
N	12.7	0.4	11.0	0.7	11.2	0.8
K	0.0	0.0	3.2	0.3	12.0	1.3
Na	4.0	0.3	5.7	0.5	0.2	0.1
S	5.3	0.5	2.1	0.2	0.3	0.1

Note: SD = standard deviation



		SAP X	SAP Y	SAP Z
d(v,0.5)	µm	84.88	85.13	89.55
d(v,0.1)	µm	32.96	49.72	26.01
mode	µm	95.19	85.74	102.51
d(v,0.9)	µm	140.00	139.64	147.24

Fig. 1. Particle size distribution of the studied SAPs



SAP X **SAP Y** **SAP Z**

Fig. 2. The SEM micrographs of the studied SAPs

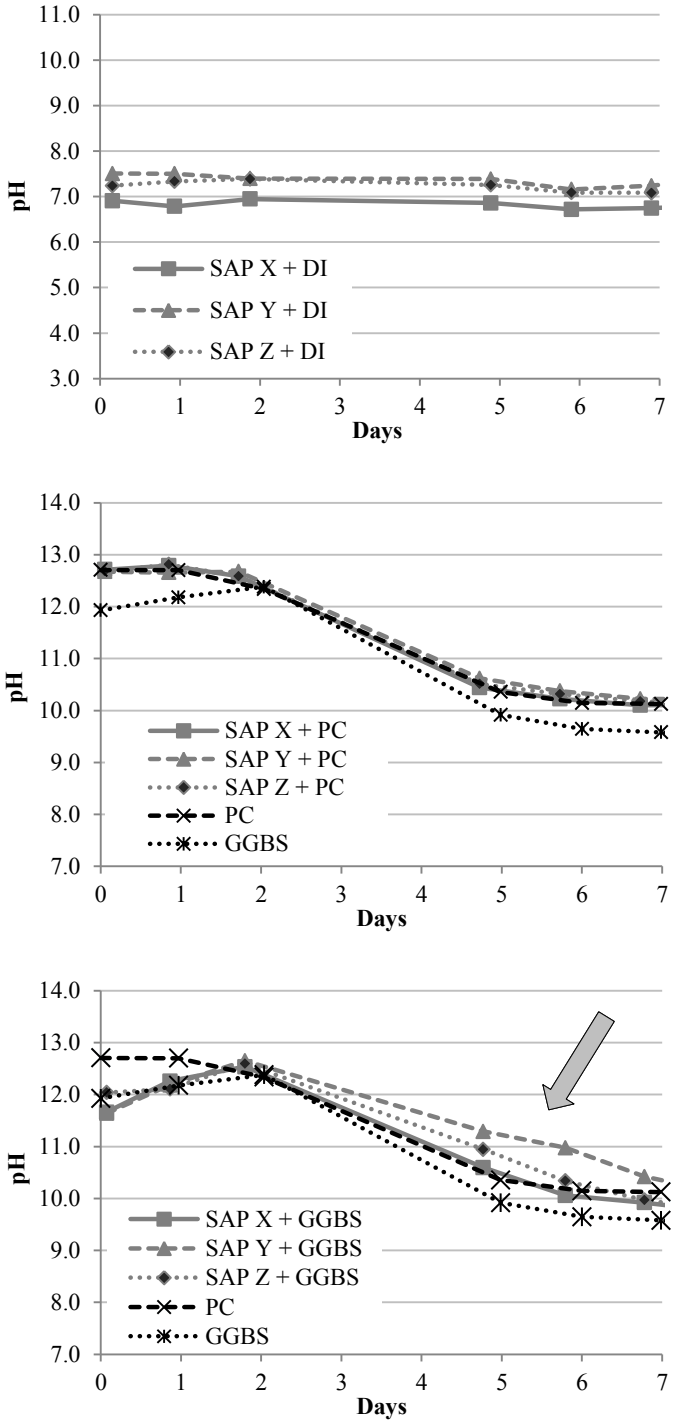


Fig. 3. pH analysis of SAP solutions in deionised water (DI), PC and GGBS filtrates

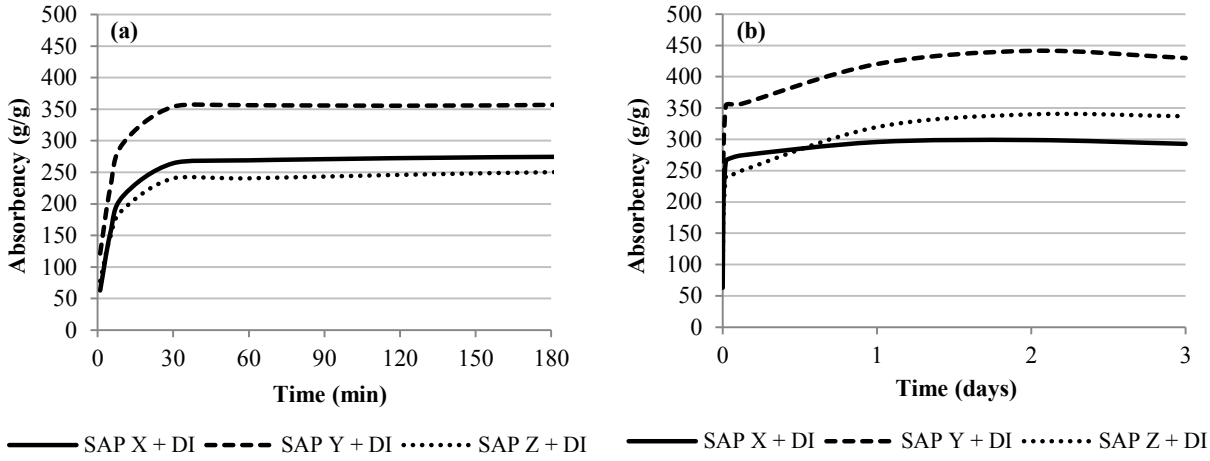


Fig. 4. Sorption behaviour of SAPs in DI water: (a) up to 180 min; (b) up to 3 days

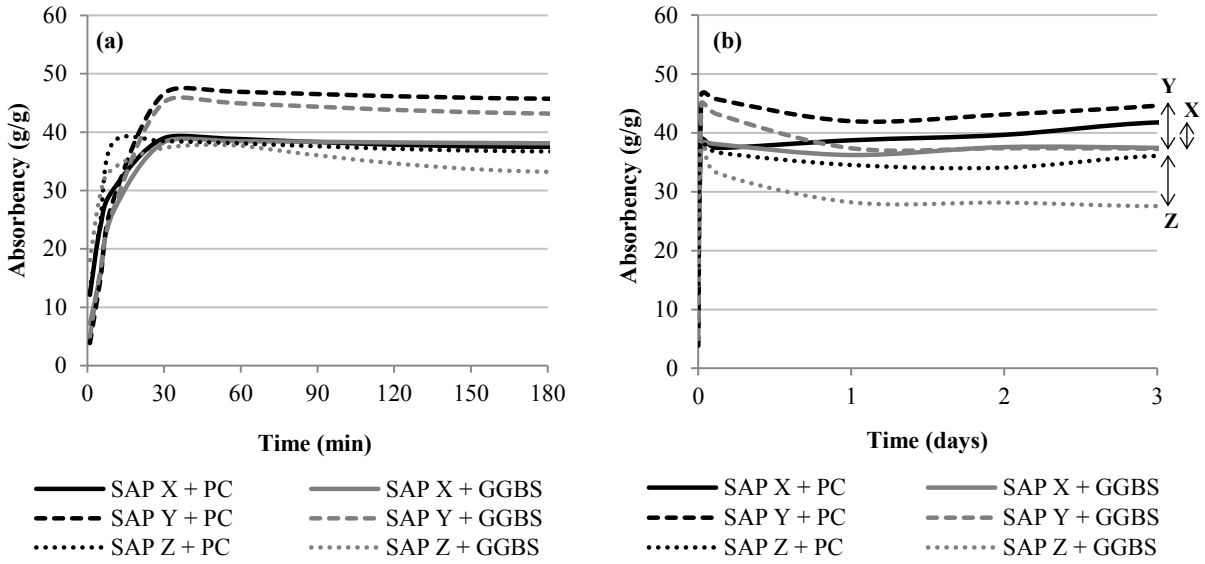


Fig. 5. Sorption behaviour of SAPs in cementitious solutions: (a) up to 180 min; (b) right: up to 3 days. Arrows in graph (b) indicate the difference between absorbency in PC and GGBS systems for all SAPs

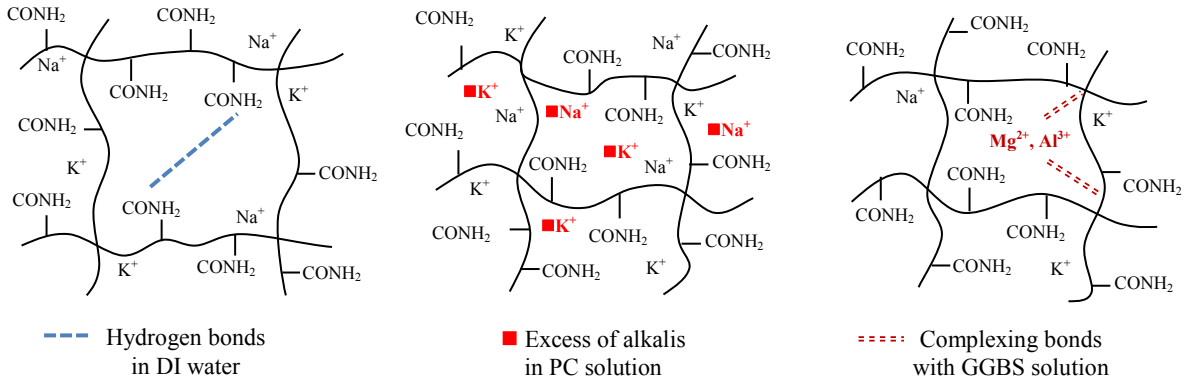


Fig. 6. Polyacrylamide structures and their modifications (adapted from Chu et al. 2008)

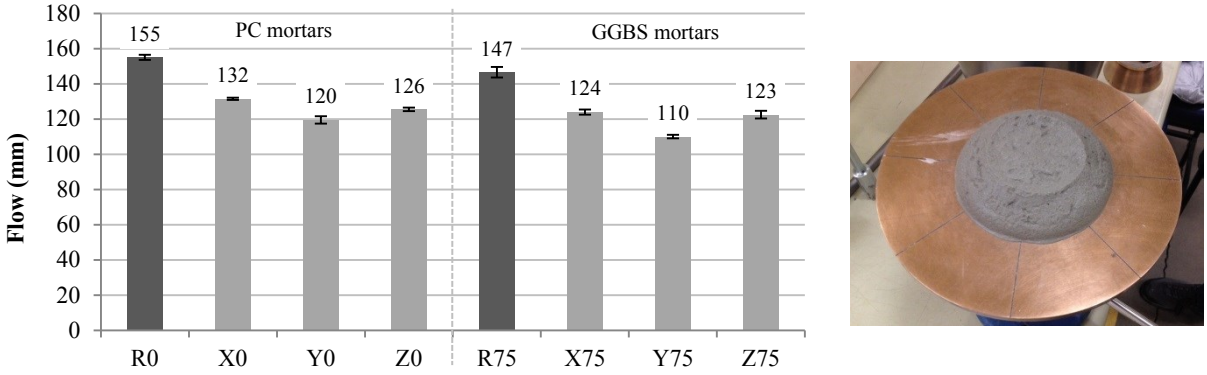


Fig. 7. Flow-table results of PC-GGBS mortars modified by SAPs

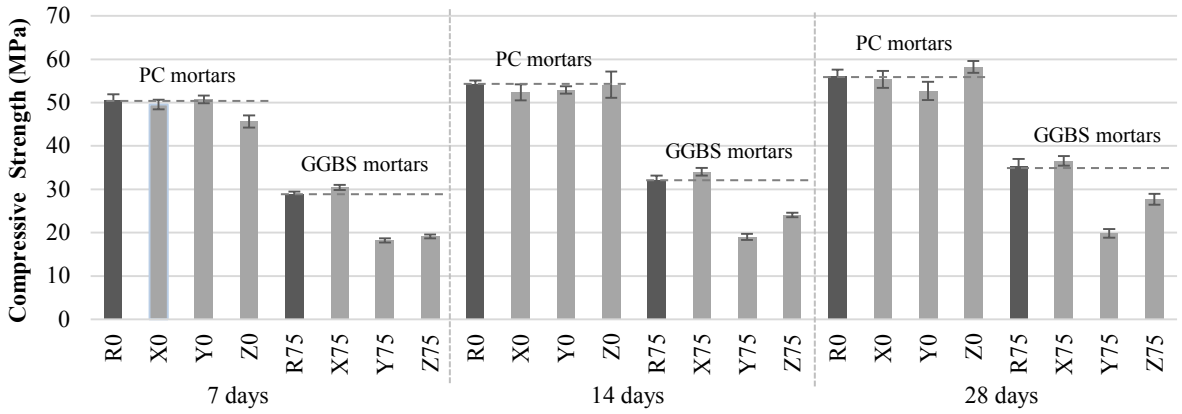


Fig. 8. Compressive strength results of PC-GGBS mortars modified by SAPs

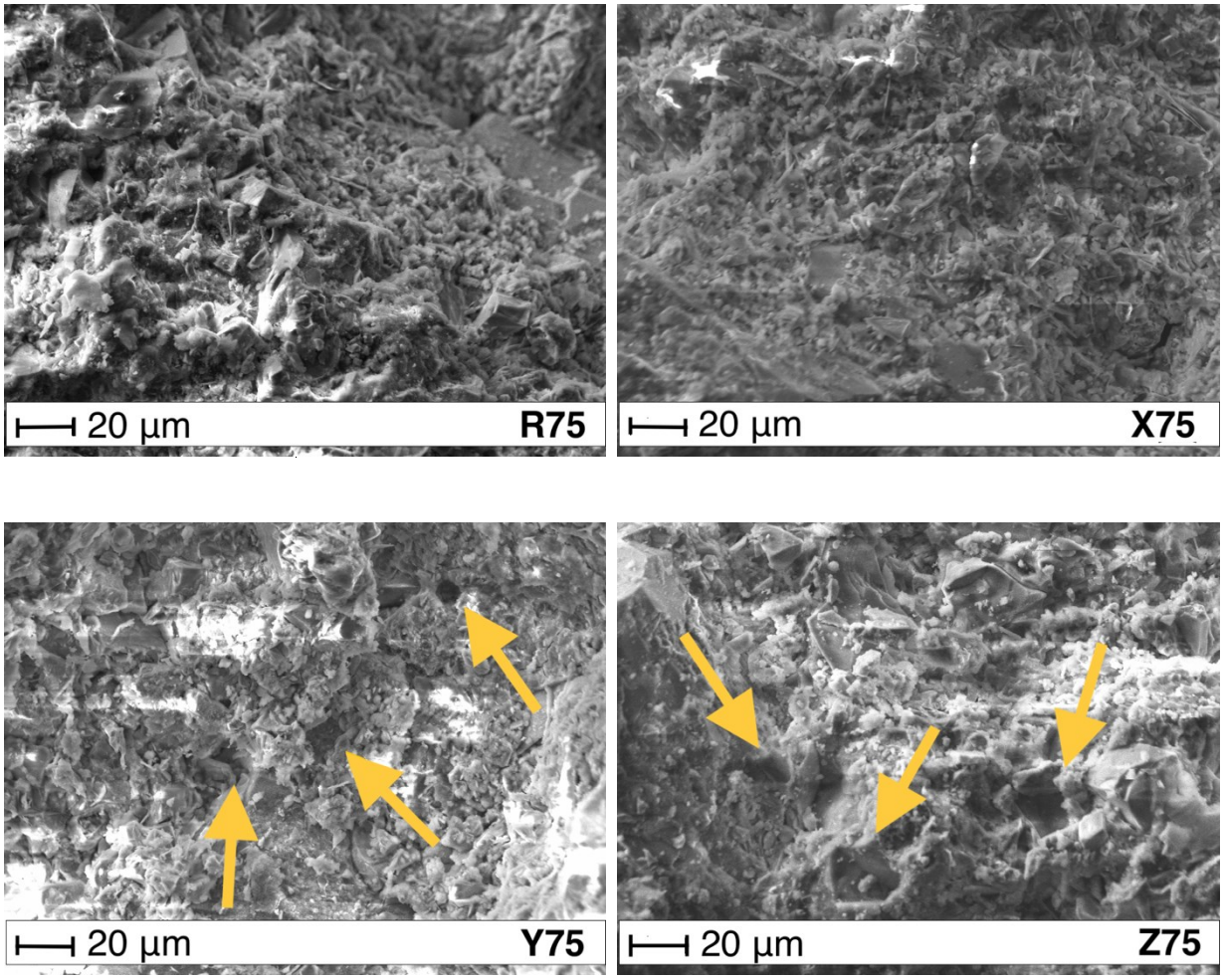


Fig. 9. SEM micrographs of GGBS mortars at 28 days (indication of larger pores in samples modified by SAP Y and SAP Z)

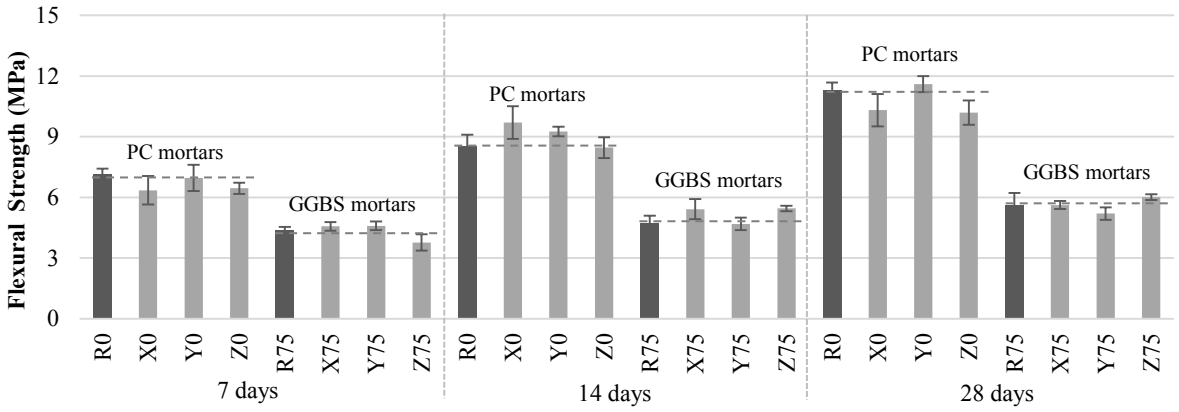


Fig. 10. Flexural strength results of PC-GGBS mortars modified by SAPs