

# THE EFFECT OF SUPERABSORBENT POLYMERS ON PERFORMANCE OF FLY ASH CEMENTITIOUS MORTARS EXPOSED TO ACCELERATED FREEZING/THAWING CONDITIONS

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## ABSTRACT

The paper is focused on identification of micro-structural and mechanical alterations in porous matrices of Portland fly ash cement mortar, during frost deterioration. An attempt is made to assess the efficiency of superabsorbent polymer (SAP) 'protection' based on analysis of three SAP types with different water absorption/desorption capacities. Two different exposure regimes have been adopted in the study; the exposure to freeze/thaw cycles and the exposure to freeze/thaw with de-icing solution. In order to evaluate the effect of SAPs on the micro-structural features of deteriorating mortars comprehensive MIP and SEM analyses were performed. It has been found that SAPs with high water absorption capacities may prevent flexural strength reduction caused by frost action. The limitation in micro-cracks propagation by SAP additions can be attributed to the higher tensile strength of 'SAP pores' walls, resulting from densification of CSH gel. This is consistent with the finding of higher 'breaking pressure' for 'SAP pores'. Nevertheless, it was shown that the additional exposure to salt ions reduces the initial resistance to less than one month. Desorption characteristics of SAPs may play a particularly important role in the case of very early exposure to F/T cycles. Too slow release of water does not sufficiently facilitate densification of structure prior frost action. Neither can it create a suitable network of air pockets for the expansion of ice and freezing water as in air-entrainers. This is particularly relevant to fly ash cementitious composites due to delayed pozzolanic reaction.

**Keywords:** Freezing/thawing cycles, micro-structural characterisation, Portland fly ash cement, salt crystallisation, superabsorbent polymers.

## 1 INTRODUCTION

Crystallisation and ice growth in cementitious materials is one of the major causes of deterioration [1, 2]. The volume, radius and size distribution of pores affect the freezing point of pore solution and the amount of ice formed in pores. Within a certain temperature interval, more frozen pore solution induces greater internal hydraulic pressure and, consequently, more severe frost damages [3]. Thus the volume of ice created in pores reflects the frost durability of porous composites.

Salt solutions may further deteriorate cement matrix by chemical and physical reactions. Salt ions in combination with water can reduce integrity and strength of cement matrix and further the propagation of moisture [4]. In principle, free water progresses to zones with high salt content through the process of osmosis increasing hydraulic pressure. In contrast, de-icer with appropriate concentration may be beneficial for freeze/thaw resistance by lowering the temperature when water turns into ice and limits number of the cycles [5].

One of the common approaches mitigating negative influence of F/T on composites performance is application of supplementary cementitious materials, in particular fly ash. The effect of fly ash on concrete has been widely researched over last couple of decades [6–9].

More recently the attempts have been made to incorporate superabsorbent polymers (SAPs) to reduce the degradation of cementitious composites by frost action [10]. This

concept is based on the assumption that SAPs form a system of fine, evenly distributed pores, which are filled with swollen polymers in fresh or young concrete. At the later ages these empty pores, created as the result of water consumption during the hydration process of cement, can act similarly to air-entrained pores. Unlike unstable air bubbles formed by the air-entraining agents (AEAs), ‘SAP pores’ can reach higher robustness and thus improve the F/T resistance of concrete in contact with de-icing solution [11]. Furthermore, part of irregular capillary pores could be replaced by larger spherical voids formed by saturated polymers. Mönnig and Lura [12] have indicated that the effect of SAP on concrete resistance depends on polymers water absorption capacity, their particle size distribution, SAP percentage in a composite and distance between particles. However, according to Laustsen *et al.* [13] the spacing factor only insignificantly influences the frost resistance, while the amount of air in hcp is a decisive factor.

Studies presented by Mönnig and Lura [12], Laustsen *et al.* [13], Brüdern and Mechthcherine [11], Sikora and Klemm [14] and Reinhardt *et al.* [15–17] confirmed the positive effect of SAP on freeze/thaw performance of concrete. It should be noted that there is lack of published reports indicating the negative effect of SAP on F/T performance. Nevertheless, the type of SAP and its absorption/desorption characteristics may have stronger effect than originally anticipated [18]. Different polymers may, therefore, offer different degree of protection.

It has to be stressed that the previously published studies were focused on Portland cement (CEM I) without supplementary cementitious materials. This paper endeavours to identify micro-structural and mechanical alterations in porous matrices of CEM II cement mortars modified by three types of SAPs during deterioration under severe service conditions.

## 2 MATERIALS AND METHODS

### 2.1 Mix compositions

Portland cement containing minimum 30% of fly ash by weight CEM II/B-V 32.5R (BS EN 197-1) and fine sand (99% of particles below 600 µm) were used in the study. Figure 1 shows the SEM micrograph of cement with clearly identifiable particles of fly ash.

Mixes compositions are presented in Table 1.

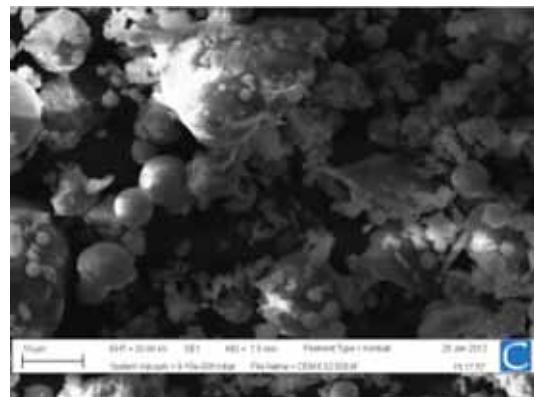


Figure 1: The SEM micrograph of CEM II/B-V 32.5; cement used in the study.

Table 1: Mixes and SAPs data.

Mix code	R	A	B	C
SAP content [%]	0	0.25	0.25	0.25
(Water/cement) <sub>tot</sub>	0.45	0.45	0.45	0.45
(Water/cement) <sub>eff</sub>	0.45	0.425	0.438	0.375–0.388
Sand/cement	1	1	1	1
SAP particles size	–		63–125 µm	
SAP composition	–	Acrylamide & acrylic acid	Acrylic acid	Polyacrylamide

Three types of SAPs (SAP A, SAP B and SAP C) used in the study are cross-linked polymers. All polymers have absorption capacity of 200–250 ml/g in de-mineralised water measured by the ‘tea bag’ technique. However, this method is not appropriate for SAP absorbency determination in cementitious environments [19]. Therefore, their absorption characteristics were measured by defining slump for the mortar mix without SAP and adjusting the slump to the identical value when SAP was added as for reference mix by increasing amount of water. This assumption is based on the idea that the swollen polymer gel does not affect the mortar rheology. Water Absorption Capacities, measured by the presented technique, differ significantly; approximately 10 g/g for SAP A, 5 g/g for SAP B and 25–30 g/g for SAP C.

Mortar specimens were cast into prismatic moulds (160 × 40 × 40 mm) and after 24 hours of curing under polyethylene cover, samples were de-moulded. In order to preserve internal structure small samples (approx 1.5 g) to be used for the MIP and SEM tests were chipped off by a hammer from the mortar prisms.

## 2.2 Curing conditions

In order to comprehensively assess the effect of SAPs on mortar performance, three different curing procedures were applied:

- The laboratory curing: Mortar prisms were packed in double polythene bags and stored in laboratory conditions: of approximately  $40 \pm 5$  RH% and temperature of  $24 \pm 2^\circ\text{C}$ .
- The effect of freeze/thaw cycles on mature mortars: Mortar specimens after 1 month of curing in laboratory conditions (as above) were exposed to F/T cycles with ambient temperature decreasing from 20 to  $-20^\circ\text{C}$ , followed by immersion in water for 24 hours to reach full saturation. Samples were subjected to four cycles per day (3 hours of freezing and 3 hours of thawing, see Fig. 2). The programmed relative humidity in the Climate Control Chamber (CCCH) was maintained at the level of 80% at the range of positive temperatures throughout the whole experimental procedure. The maximum exposure to freezing and thawing reached 600 cycles.
- The effect of freeze/thaw with de-icing solution: Samples were cured similarly to those described above, only instead of water, specimens were immersed in 3% (by weight) NaCl solution before placement in the CCCH. Every 7 days, during a thawing part of the cycle, samples were immersed for 3 hours into the NaCl solution.

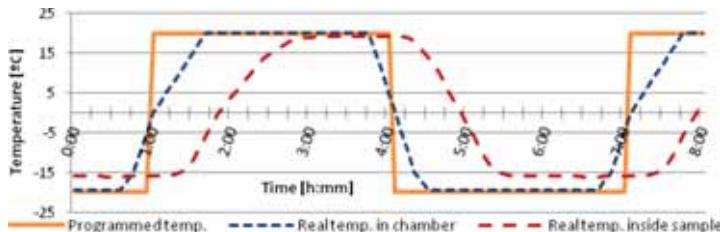


Figure 2: CCCH programme setup, recorded temperature in CCCH and inside sample.

### 3 RESULTS AND DISCUSSION

In order to evaluate the effects of different SAPs on the micro-structure alterations, induced by exposure to F/T cycles, monthly MIP analyses of mortars were performed on all samples. The established characteristics were subsequently verified by the extensive examination under SEM and analysis of alterations in mechanical properties.

Figure 3 presents total porosities measured by the MIP for all analysed samples. A characteristic feature for laboratory cured samples was a small decrease in porosity with time confirming the progress of hydration. In case of CEM II the hydration of hydraulic compounds as well as pozzolanic reaction of fly ash may be strongly affected by water stored and subsequently released by polymers. The presence of SAP manifests itself in an increase of total porosities for samples A and C, and in a decrease for B samples in comparison with corresponding reference samples. The increase of pore volumes can be associated with intensified formation of 'SAP pores' in the collapsed state of polymers. Since both polymers (A and C) have a high capacity of water absorption from the very early stages by the time of the first measurement (after 2 months) they created the network of pores subsequently filled with CSH gel. Total porosities recorded by the mercury porosimetry for samples subjected to F/T cycles with or without de-icers show only small variations. The results suggest rather insignificant influence of 3% solution of sodium chloride on the freeze/thaw performance in all studied mortars.

However, the variations in total porosities cannot be considered on its own in the micro-structural analysis and the pore size distributions (PSDs) need to be assessed in parallel. Figure 4 presents the results of PDS for laboratory cured samples. In general, two distinctive pore size ranges can be identified: 30–70 and 200–700 nm. A strong effect of SAP A after 2 months of laboratory curing can be identified. Polymer A has a strong affinity for water but it also releases it faster than polymer C resulting in formation of high peak for 200–700 nm. These empty spaces created by the collapsed polymer A cannot be filled with new hydration products due to a possible water deficiency. The lack of clearly defined peak on the PSD curve for sample A at 4 months is likely to carry some errors, when compared with observations from the previous and following months and should be disregarded. In contrast, the effect of SAP B is very limited. Similarities in micro-structural characteristics of samples B and the reference samples could be attributed to the relatively low absorption capacity of SAP B.

SEM micrographs of the internal structure of selected 6 months old samples are shown in Fig. 5. Big shapeless pores ranging several dozen micrometers could be identified for samples containing SAP A and SAP C regardless of their age. It is likely that the high water absorption capacity of these polymers allows creation of pores with such big diameters.

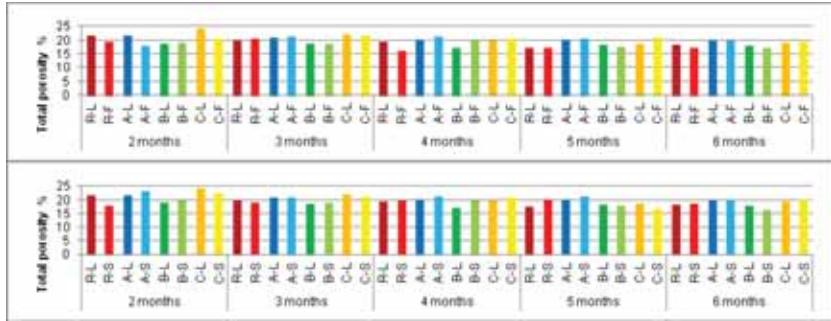


Figure 3: Comparison of total porosities development for samples cured in laboratory conditions, subjected to F/T cycles, and samples subjected to F/T cycles and NaCl solution.

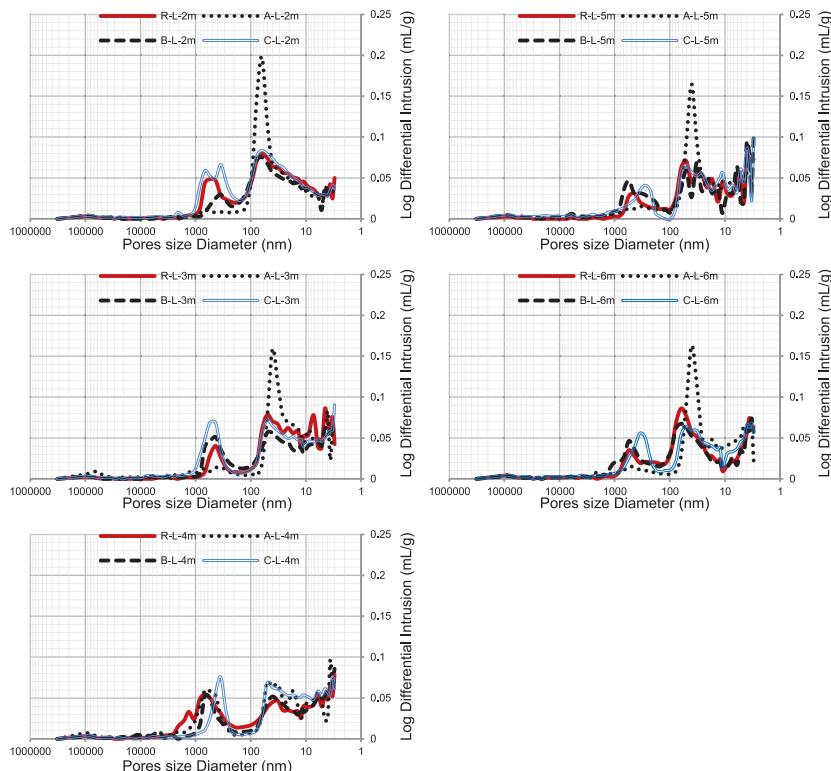


Figure 4: Pores Size Distribution curves for laboratory cured samples in age between 2 and 6 months.

Figure 6 presents the results of PSD for samples subjected to alternating F/T cycles. The reference samples analyses suggest that the main damage take place between the first and second month of alternating F/T conditions. These observations indicate that both SAP A and C can reduce these damaging processes during the first 3 months. However, a prolonged exposure (exceeding 4 months) leads to inevitable structural alterations. In contrast, the effect



Figure 5: SEM images of samples R, A, B, and C after 6 months of laboratory curing.

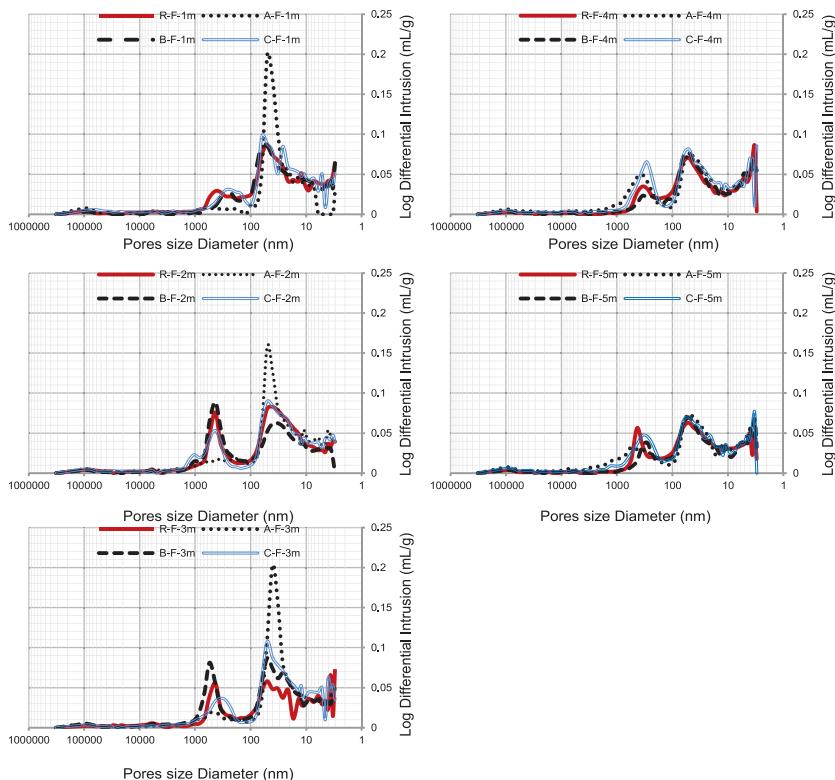


Figure 6: Pores Size Distribution curves for samples exposed to F/T cycles for 1 month to 5 months.

of SAP B is very limited. Similarities in PSDs of B and the reference samples could be attributed to the relatively low absorption capacity of SAP B.

SEM analyses of the internal structures confirm a degree of frost damage (Fig. 7) well evidenced in micro-crack formations. These micro-cracks are particularly well developed in samples R, B and C, all at least 1 month old. Identification of micro-cracks appearance in A samples is possible only after 5 months of alternating F/T cycles. This may suggest a positive effect of SAP A on the limitation of frost damage. Another characteristic feature observed in samples containing SAP A and to a lesser extent C, regardless curing regime and age, are big shapeless pores of several dozen micrometers (Fig. 7). High water absorption capacity and a relatively fast desorption facilitate formation of larger air pockets, similarly to air-entrainment. The most pronounced effect is therefore visible in samples A.



Figure 7: SEM images of samples R, A, B, and C exposed to F/T cycles.

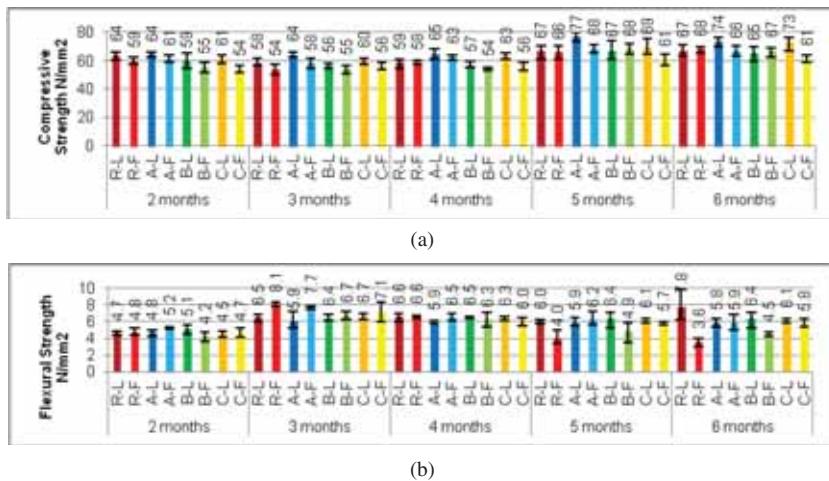


Figure 8: Compressive (a) and flexural (b) strength development of samples cured in laboratory conditions in comparison with samples subjected to F/T cycles.

Figure 8 shows compressive and flexural strength developments in samples cured in laboratory conditions in comparison with samples subjected to F/T cycles. Compressive strength values for samples cured in laboratory conditions and subjected to alternating freeze/thaw cycles increase with time. After 6 months laboratory cured samples A and C have higher values than the reference. In turn, lower values can be observed for samples A and C subjected to F/T in comparison to the reference sample cured in the same conditions. This behaviour is more pronounced for sample C, particularly after 5 months, which can be associated with the prolonged water release. The results of long-term autogenous shrinkage and X-ray absorption published elsewhere [20] confirmed that SAP A and SAP C may provide water for continuing hydration for more than a month. This delayed release of water is even more pronounced in case of SAP C. Due to initiation of F/T exposure just after 1 month of laboratory curing, water from these swollen polymers does not support full hydration and thus cannot facilitate formation of denser structure, as in the laboratory cured samples. The release of smaller amount of water by SAP B is faster, making only a very small contribution to structure modification. Hence the results of compressive strength for samples B are very similar to the reference for both curing methods. Desorption characteristics of SAPs may play an important role in case of very early exposure to F/T cycles.

There are no significant differences in flexural strengths until the fourth month (3 months of alternating F/T exposure) (Fig. 8 (b)). The damaging effect of frost action on flexural

strength can be observed from the fifth month and only for B and R samples. Composites modified by A and C type of polymers do not show any flexural strength reduction. The 'SAP pores', only partially filled with CSH gel, can provide an outlet for expansion of ice and freezing water and thus they can limit the overall damage. It should be also noted that the mortars under presented investigation have a high cement content, which may lead to the creation of less permeable microstructure affecting water transport phenomena. The PSD of samples simultaneously subjected to F/T cycles and to NaCl is shown in Fig. 9. This combined exposure results in reduction of the peak corresponding to small pores in samples A. The most pronounced changes take place during the first month. Continuing exposure to F/T cycles and de-icers leads to a small shift of the peak towards bigger pores suggesting some frost damage.

PSD curves for samples C have a similar pattern to the corresponding specimens C cured in the climatic chamber. This may suggest the presence of closed pores or pores with very narrow openings that are not accessible to salt solution (not pressurised unlike mercury in MIP method). Hence, no visible effect of additional damage resulting from the exposure to salt. The fact that the similar effect cannot be observed for samples A may be explained by a smaller contribution of inaccessible pores and thus different kinetics of water release. As anticipated, micro-structural characteristics of samples B very much resemble the reference samples, regardless of curing regime. The prolonged exposure to F/T cycles and NaCl results

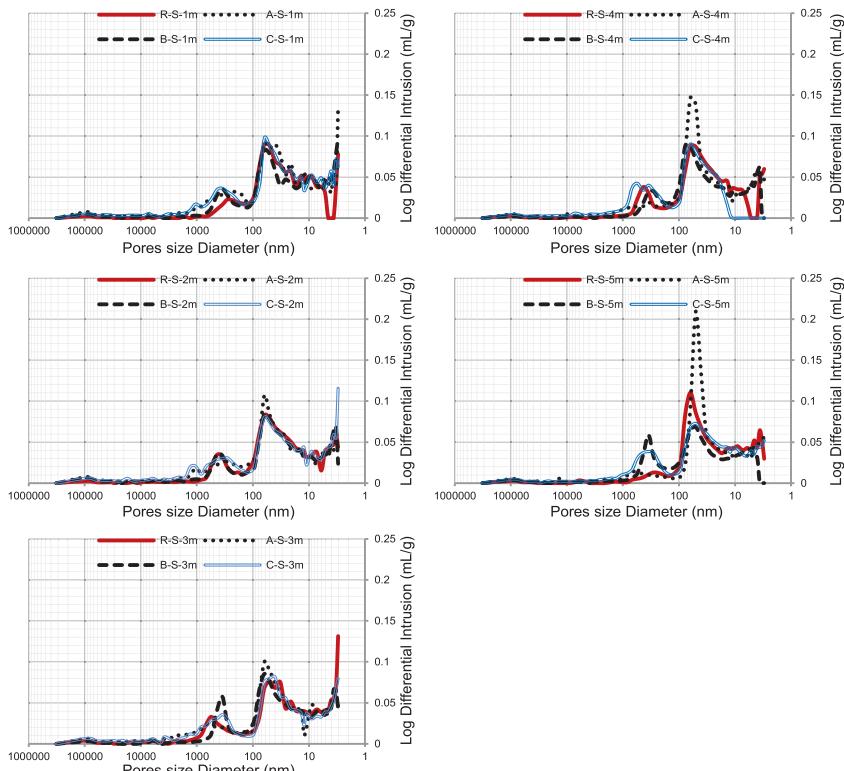


Figure 9: Pores Size Distribution curves for samples exposed to F/T cycles and NaCl solution for 1–5 months.

in a small but gradual decrease in small pores (30–70 nm) and well pronounced increase in the share of bigger pores.

Micro-structural features of samples subjected to freeze/thaw cycles and salts are presented in Fig. 10. No visible damage, in form of micro-cracking, can be observed in samples A and C and only pores of 10 µm are identifiable. However, clearly pronounced micro-cracks can be observed in samples B and R, particularly after 5 months. Both samples have comparable pore sizes. Although, SAP A and C can protect mortars from the influence of F/T cycles and de-icers for about 1 month, the prolonged exposure results in micro-cracks formation. This indicates a time limitation in SAP A and C protection.

In general, the exposure to freeze/thaw cycles and de-icers decreases the strength for all mixes, when compared with the laboratory curing, as shown in Fig. 11. Samples containing SAP A reach the highest compressive strengths in both curing methods. The exposure to freeze/thaw cycles and de-icers only marginally decreases the strengths of all mixes, when compared with the corresponding laboratory cured specimens (up to 16%, but generally approximately 5%). The only exceptions are samples R after 4 months and B after 3 months, where some reductions can be recorded. Polymer B decreases the compressive strength of mortars (by approximately 6%) but further exposure to adverse conditions does not affect the strength. In turn, it is apparent that addition of SAP A and C increases compressive strength in laboratory conditions but the effect of prolonged F/T and NaCl exposure is rather limited.

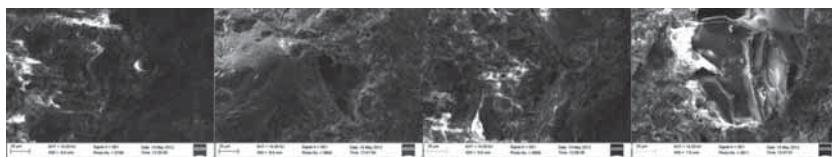


Figure 10: SEM images of samples R, A, B, and C exposed to F/T cycles and NaCl solution.

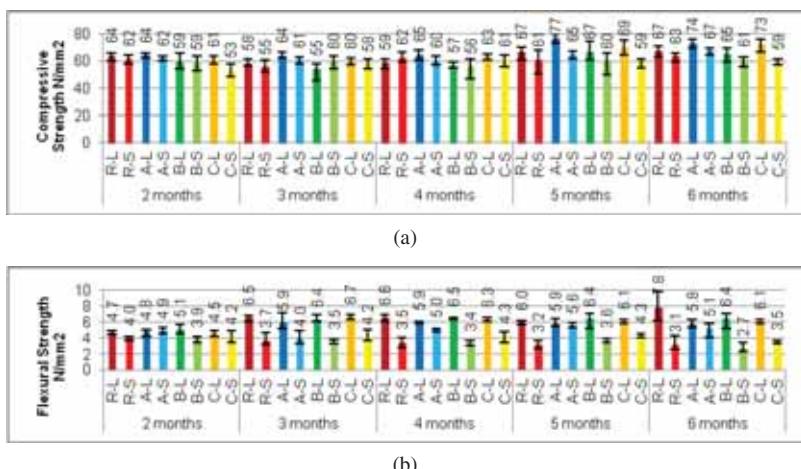


Figure 11: Compressive (a) and flexural (b) strength development of samples cured in laboratory conditions in comparison with samples subjected to F/T cycles and NaCl solution.

Again, flexural strengths of studied samples have shown stronger impact of freeze/thaw cycles and NaCl exposure. Flexural strength values for samples R and B show a small but steady decrease. In turn, results for sample A are similar (with one exception after 3 months) regardless the curing duration. Results for sample C are constant up to the fifth month with only a slight decrease recorded in the sixth month. Based on the analysis of mechanical properties only SAP A is capable of diminishing the severe effect of frost and de-icing salts.

According to the salt crystallization theory, the pressure that is able to cause damage can only occur in small pores (below 100 nm) [21]. Since the prolonged exposure to F/T cycles and NaCl only insignificantly influences compressive strength, it gives an indication of higher percentage of large pores than was obtained from the MIP measurements. This is most likely due to the ‘ink-bottle’ nature of pores created by SAP. However, these ‘SAP pores’ are still small enough not to reduce compressive strength in laboratory cured specimens, but rather to allow some increase. In contrast, the presence of ‘SAP pores’ does influence flexural strength, which is sensitive to the porosity changes in all ranges of pore sizes.

#### 4 ANALYSIS

Analysis of PSD graphs for samples A suggests that SAP A can resist the severe effects of F/T cycles for 3 months (Fig. 12 (a)) After 4 months, the peak representing ‘SAP pores’ decreases significantly, which could be attributed to mercury intrusion at lower pressures. This reduction in ‘breaking pressure’ is a possible consequence of micro-cracking. In turn, similar effect of ‘breaking pressure’ limitation can be recorded just after 1 month for samples exposed simultaneously to F/T cycles and de-icers. Figure 12 (b) shows pores size distribution curves for samples A exposed to F/T cycles and 3% NaCl solution for 1, 4 and 5 months.

The peak representing dominating range of pores (30–70 nm) starts to appear after 4 months most probably due to salt crystallisation inside these pores. Salt crystals occupy the pores making mercury intrusion possible only at the higher pressures. The similar observation was made for samples containing SAP C.

Figure 13 (a) shows the correlation between flexural strength and compressive strength for samples subjected to F/T cycles. While the compressive strength of the reference samples is steadily growing, its flexural strength is decreasing. Nonetheless, SAPs result in a limited decrease in flexural strength. The subsequent alternating F/T cycles lead to the propagation of micro-cracks and formation of higher number of small voids, which can reduce flexural

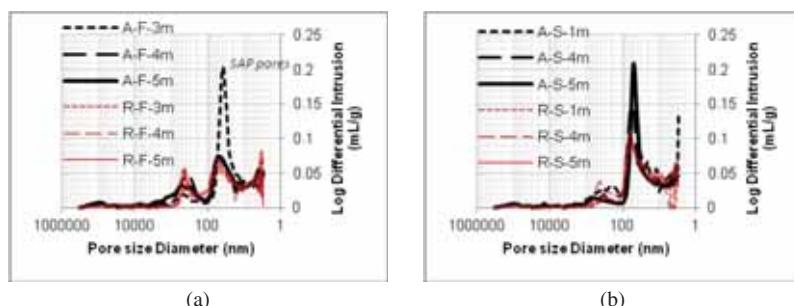


Figure 12: Pores size distribution curves for samples containing SAP A in comparison to the references exposed to F/T cycles for 3, 4 and 5 months (a) and exposed for F/T cycles and NaCl solution for 1, 4 and 5 months (b).

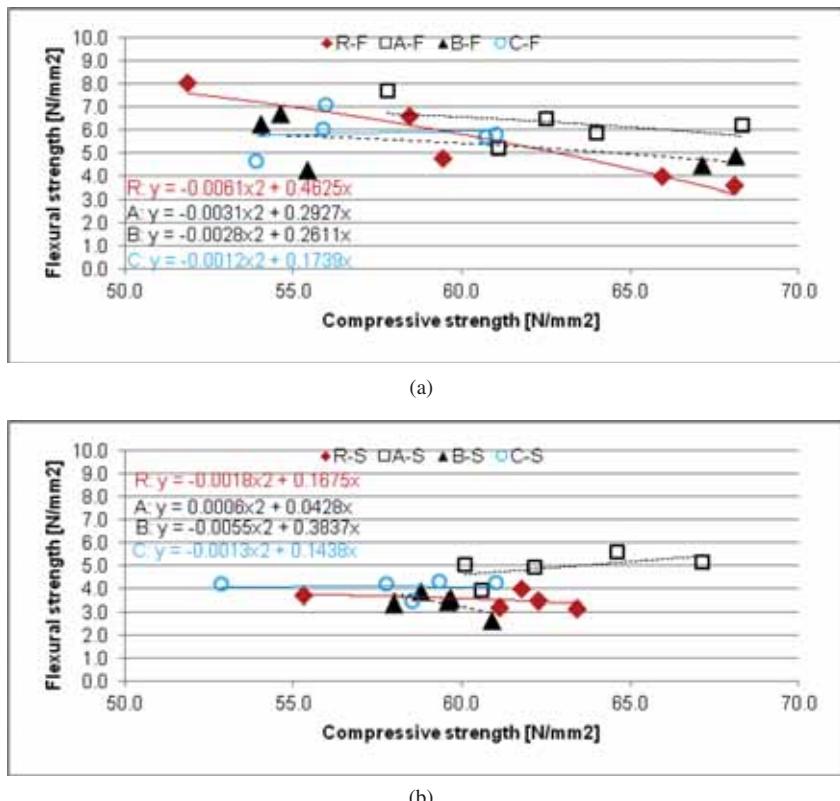


Figure 13: Correlation between flexural strength and compressive strength for samples subjected to F/T cycles (a) and subjected to F/T cycles and NaCl solution (b).

strength. However, these pores are generally too small to influence compressive strength. The limitation of this phenomenon by SAP might be attributed to a higher resistance of 'SAP pores' walls against internal pressures induced by the applied frost action. It is consistent with the finding of higher 'breaking pressure' for 'SAP pores'.

The exposure to freeze/thaw cycles and NaCl decreases the strength for all mixes, when compared with the laboratory curing. It also changes the relationships between flexural strength and compressive strength (Fig. 13 (b)).

The exposure of R samples to F/T and NaCl ions results in the small decrease of flexural strength and concurrent development of compressive strength. The presence of SAP B can even intensify this phenomenon. In contrast, SAP A counters this effect completely. The correlation for samples A subjected to F/T cycles and de-icers is similar to the correlation for the laboratory cured samples. In turn, SAP C results in a constant flexural strength and an increased compressive strength. The relatively stable results of flexural strength for all samples suggest that the total porosities are constant for different ages. However, according to MIP measurements, porosity values slightly decrease with the exposure, suggesting salt crystallisation. The explanation of this may be based on the limited accessibility of SAP pores with distinctive 'ink-bottle' shapes.

## 5 CONCLUSIONS

Based on the investigations presented in this study, the following conclusions can be formulated:

- Exposure to alternating freezing and thawing cycles after 1 month of laboratory curing does not significantly reduce compressive strength, although it may lead to the flexural strength reduction (samples R and B). The phenomena might be attributed to the changes in the range of smaller pores. It could prove that compressive strength depends on larger pores, which are not influenced by the frost action.
- SAPs with high water absorption capacity may prevent flexural strength reduction caused by frost action in cementitious composites. The limitation in micro-cracks propagation by SAP additions may be attributed to a higher tensile strength of ‘SAP pores’ walls, resulted from densification of CSH gel. It is consistent with finding of a higher ‘breaking pressure’ for ‘SAP pores’.
- Despite the initial resistance to freezing and thawing cycles in mortars modified by SAPs with high water absorption capacity, prolonged exposure (over 480 F/T cycles) may lead to some reduction in compressive strength. In addition, PSD graphs for samples with SAP A suggest that polymer A resists the severe effects of F/T cycles for 3 months. The recorded increase in the mercury intrusion accessibility of bigger pores at lower pressures by the MIP technique (reduction in the ‘breaking pressure’) may be a possible consequence of micro-cracking.
- High absorption and faster release of water (as in SAP A) in Portland fly ash cement composites may lead to the formation of larger pores suitable for ice expansion during F/T cycles. In this context, such SAPs may perform similarly to air-entrainers. This observation supports the view that the overall volume of air voids created by SAP is the key factor in the frost performance. Too slow release of water does not sufficiently facilitate densification of the structure, which would be capable of resisting internal stresses created by frost action. Neither can it create a suitable network of air pockets for the expansion of ice and freezing water as in air-entrained mortars. This is particularly relevant to fly ash cementitious composites due to delayed pozzolanic reaction.
- The additional exposure to salt ions of SAP modified mortars subjected to F/T cycles reduces the initial resistance to less than 1 month (120 cycles). The observed decrease of pore sizes in SAP modified mortars after 4 months of exposure indicated salt crystallisation in pore system.
- The exposure to freeze/thaw cycles and NaCl solution decrease the strength for all mixes, in comparison to the laboratory curing. However, despite the salt crystallisation, further prolonged exposure to de-icers and F/T does not notably alternate compressive strength giving an indication of the higher percentage of larger pores (above 100 nm) than it was obtained by the MIP measurements.

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