

Freeze/thaw performance of polymer modified cementitious mortars exposed to NaCl solution

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KEY-WORDS

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ABSTRACT

The paper presents part of a larger research project on the effect of alternating long term freezing and thawing cycles on the micro and macro scale properties of cementitious mortars containing superabsorbent polymers (SAP).

This study analyses a relationship between the alterations of cement paste morphology caused by the omnidirectional exposure to freeze/thaw cycles in presence of NaCl ions. The effect of a number of alternating freezing and thawing cycles on the performance of mature mortars is assessed. Research work focuses on characterization of mortars modified by two different polymers – copolymer of acrylamide and acrylic acid and a polymer based on acrylic acid. Experimental results confirmed a noticeable impact on the mechanical properties and f/t performance of mortar mixes. It was noted that the effect of SAP changes over time.

1. INTRODUCTION

Increasing expectations and requirements for building materials are nowadays widespread and constantly evolve. Durability and long life cycle, even under severe environmental conditions, is essential evaluation criteria for new high-performance materials. Therefore even more crucial challenge is to fulfil sustainability trends, having in mind ecological, safety and energy consumption considerations.

It is believed that in order to meet above expectations cementitious composites can be modified by superabsorbent polymers (SAP). SAP are crosslinked networks of hydrophilic polymers, mostly based on polyacrylate and polyacrylamide, with a high capacity for water uptake and have a variety of valuable applications. A large amount of water from surroundings (under 5000 times to SAP weight) can be absorbed by them and retained even under pressure [1]. The use of SAP as an admixture for concrete has been extensively described in the work of O. Jensen and P. Hansen [2]. Main advantage of SAP

introduction to cement matrix is prevention of self-desiccation by retention of water in mixes with low water to cement ratios. Further studies were carried on the SAP applications in concrete technology as internal curing agent in subsequent years and have been well documented in the literature [2-5]. Nevertheless, there is still lack of investigations regarding their ability to enhance concrete performance in adverse service conditions, in particular in freeze/thaw environment. From the practical point of view to obtain overall assessment of these additives, the effect of de-icers on cementitious materials should be investigated. One of the most popular de-icer in a common use is chloride based de-icer NaCl.

Sodium chloride solution may deteriorate cement matrix by chemical and physical reactions. NaCl in combination with water can reduce integrity and strength of cement matrix and further the propagation of moisture [6]. In principle, free water progresses to zones with high salt content through the process of osmosis increasing hydraulic pressure. On the other hand 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.

Continuous release of water during the process of hydration achieved by addition of SAP may prevent the self-desiccation and in consequence mitigates destructive effects of freezing and thawing [2]. The empty pores are the result of water consumption during the hydration process of cement. The porosity is mainly determined by the amount and particle size distribution of SAP and the water absorption characteristics. Additionally, it is expected that part of irregular capillary pores can be replaced by larger spherical voids formed by saturated polymers [7]. The importance of polymers particles is based on assumption that SAP forms systems of fine, evenly distributed pores, which are filled with swollen polymers in fresh or young cement paste, but then leave empty cavities at later ages. Therefore, after drying out, in the collapsed stage SAP creates air filled pores, which act similarly to air-entrained pores. However, SAP-pore system, unlike the air bubbles obtained by air-entrained agent application, is very robust and results in a high predictability of its properties and durability to the processing and transport [8]. It is also expected that SAP affects the air content of fresh concrete mixes and consequently porosity of hardened concrete matrix. During mixing small air bubbles may adhere to polymers surface and increase air content [9].

In the light of the above considerations a comprehensive research program is essential to verify available data and enable the formulation of deterioration models. This paper aims to address the problem by presenting some preliminary investigation.

2. MATERIALS AND METHODS

Portland cement CEM II, in accordance with EN 197-1 [10], was mixed at 1:1 ratio with fine sand (99% of particles distributed below 0.6 mm). Throughout the investigation a total water to cement ratio of 0.45 was maintained. In order to modify internal microstructure of the cement mortar, two types of the SAP were used in concentration of 0.25 % by weight of cement content. Detailed information about mix composition is presented in Table 1.

Table 1: Cement mortar composition & fresh mortar properties

		Mix code		
		R - reference	A - SAP	B - SAP
$(\text{Water/Cement})_{\text{tot}}$		0.45	0.45	0.45
$(\text{Water/Cement})_{\text{eff}}$		0.45	0.425	0.438
SAP content [%]		0	0.25	0.25
Air content [%]		0.45	0.75	0.30
Flow [mm]	Before jolts	217.5	100	192.5
	After 15 jolts	>250	197.5	>250

Abbreviations used in this text means:

R, A, B – reference samples (without SAP), mixtures with SAP A, mixtures with SAP B
 (R, A, B) -S – mixtures subjected to freeze/thaw cycles and NaCl solution (after 1 month of initial laboratory curing)

(R, A, B)-L – mixtures cured in laboratory conditions.

The SAP used in the study, were cross-linked polymers provided by BASF. SAP A is a copolymer of acrylamide and acrylic acid and SAP B is a polymer based on acrylic acid. Products had absorption capacity of 200-250 ml/g in demineralised water. The absorption in mortar depended on the product and was approximately 10 g/g for SAP A and 5 g/g for SAP B. Both materials were prepared by grinding and screening to a size of 63-125 μm , but there was also minor (less than 10%) finer particles' content. The particles' shape was irregular.

The part of mortar prisms of 160x40x40 mm after 1 month (30 days) curing in laboratory conditions (40 ± 5 RH% and 24 ± 2 °C; under polythene cover) were exposed to freezing and thawing cycles with ambient temperature ranging from +20 to -20 °C proceeded by the 24 hours immersion in 3% NaCl solution. Samples were subjected to 4 cycles per 24 hours. Figure 1 presents designed and real temperature variations in the climatic cabinet.

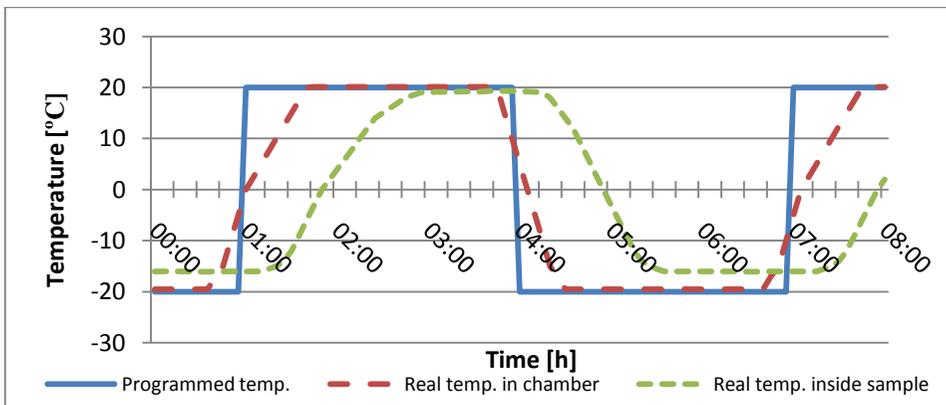


Figure 1: Temperatures in climatic chamber

Every seven days, during a thawing part of cycle, samples were placed for 3 hours into the NaCl solution. The programmed relative humidity in the Climate Control Chamber was maintained at the level of 80% at the positive range of temperature. In monthly intervals, F/T samples were tested concurrently with those stored in laboratory conditions. The samples have been exposed to the maximum of 360 cycles of F/T.

The analyses of mechanical properties (compressive strength) were performed using standardized procedures for compression and flexural tests in accordance to BS 1881-119:1983 [11]. Microstructural examination has been carried out with the use of Porosimeter Autopore IV 9500 by Micromeritics with a pressure range up to 60000 psi.

2. RESULTS AND DISCUSSION

Experimental program consisted of mechanical properties determination followed by the MIP analysis.

Analysis of the compressive strength results, presented in Figure 2, reveal an interesting relationship. In general, the exposure to freeze/thaw cycles and NaCl solution decreased the strength for all mixes. However it can be noticed that the ratio of strength reduction (lab curing/climatic chamber curing) is negligible for samples containing SAP B. The compressive strength results were the lowest for samples with addition of SAP B after lab curing and freeze/thaw cycles in comparison to reference samples and those containing SAP A. Moreover samples containing SAP A obtained the highest results. It is apparent that addition of SAP A increases compressive strength, but does not prevent the deterioration of cement matrix. SAP B decreases the compressive strength of mortars and further exposure to adverse conditions does not affect the strength. The effect of polymers has the predominant role in these cases.

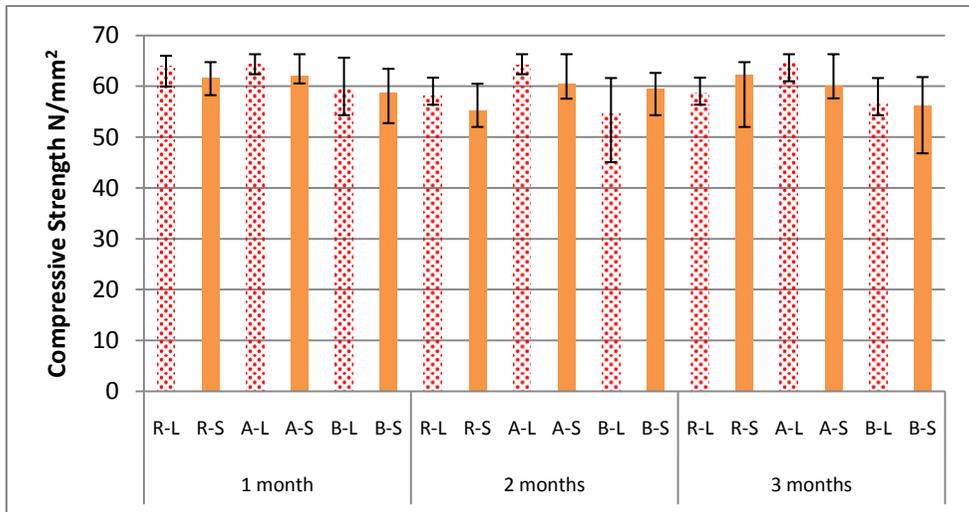


Figure 2: Compressive strength of samples cured in lab conditions in comparison with samples subjected to f/t cycles and NaCl solution (age corresponds to period of f/t curing)

The results of the total porosity (Table 2) indicate rather insignificant influence of Sodium Chloride exposure on the freeze/thaw performance of tested samples. Only the porosities of reference and mixture with SAP A were higher when subjected to freeze/thaw cycles. Once again there was no such dependency for samples containing SAP B. Increase in the total porosity has been recorded for samples containing SAP A.

Table 2: Total porosity of samples [%]

Age	Mix					
	R-L	R-S	A-L	A-S	B-L	B-S
1 month	17.96	17.84	20.22	21.44	18.81	18.16
2 months	19.83	19.03	20.98	20.79	19.51	18.84
3 months	18.20	19.59	18.06	21.00	19.65	19.56

The average pore diameters (Table 3) obtained for the tested samples confirm that superabsorbent polymers influence the microstructural characteristic of mortars. The results for samples cured in laboratory conditions were higher for mixes with superabsorbent polymers. It is noticeable to a greater extent for SAP A. Additionally to previous reflections, the results between samples exposed to sodium chloride and freeze/thaw cycles clearly differ from those obtained for samples cured in lab conditions. It is particularly clearly seen for the reference samples and mixtures with SAP A. These differences are not so pronounced for samples with SAP B addition.

Table 3: Average pore diameter [nm]

Age	Mix					
	R-L	R-S	A-L	A-S	B-L	B-S
1 month	13.2	18.7	15.6	16.5	14.2	13.3
2 months	12.9	16.4	14.4	18.8	15.1	16.6
3 months	16.2	13.5	14.3	17.5	14.0	15.7

Figure 3 below present the results of pore size distribution of all analysed samples. Log differential intrusion vs. pore size diameter of samples (R,A,B) subjected to f/t cycles and NaCl solution for 1,2,3 months in comparison to corresponding samples cured in lab conditions is shown. In general two distinctive pore size ranges can be indentify: 30-70 nm and 200-700 nm. The largest share of pores occurred for diameters of approximately 30-40 nm for samples containing SAP A and cured in laboratory conditions. It is clearly noticeable at all presented ages of curing (peaks for A-L). Samples of the same composition subjected to NaCl solution and freeze/thaw cycles had a reduced number of 30-40 nm diameter pores and peaks moved slightly towards the bigger pores with time.

A strong effect of SAP A after 2 months of lab curing has been noticed. This effect has been visibly limited with time. Furthermore the reduction of SAP A effect was significantly accelerated by the exposure to freeze/thaw cycles and salt. In fact it was already very small in samples cured 1 month in climatic chamber.

An addition of SAP A seems to improve the performance of mortars. This is evidenced by the similarity of pores size distribution of samples cured 3 month in the chamber to those cured in lab conditions.

On the other hand, the effect of SAP B is minimal. Microstructural characteristics of samples containing SAP B were very similar to the reference samples regardless of curing type.

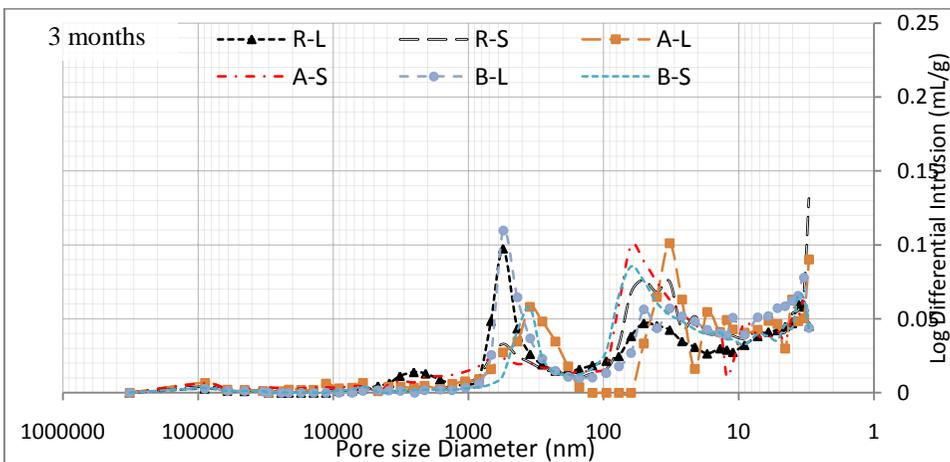
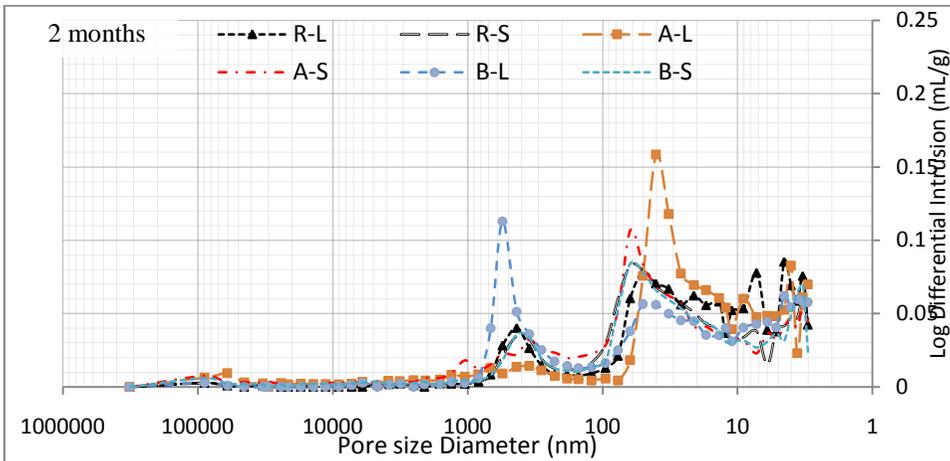
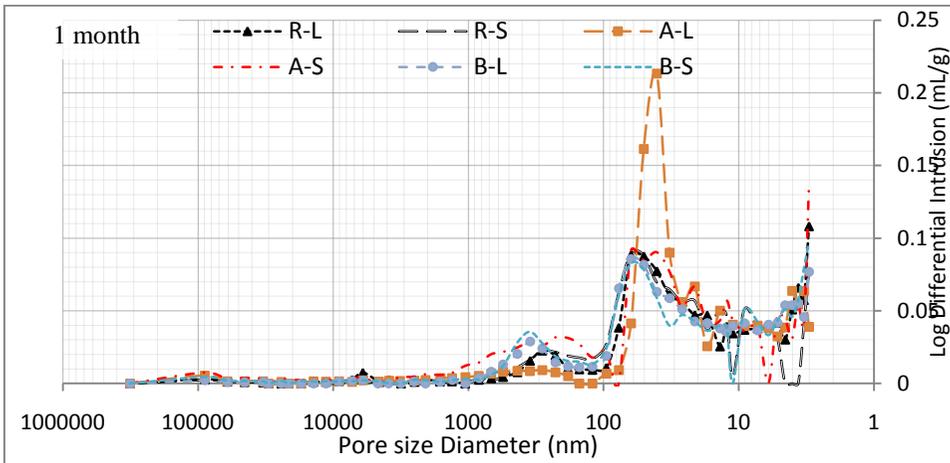


Figure 3: Pore size distributions in samples cured in lab conditions and subjected to f/t cycles after 1, 2 and 3 months (age corresponds to period of f/t curing)

Samples containing both polymers exposed to NaCl solution and freeze/thaw cycles had reduced peaks associated with high share of small pores. In general, in all analysed cases the higher content of pores in range of 200-600 nm was observed in later ages (3 months).

It can be also claimed that the exposure to freeze/thaw has a limited effect in early ages. The micro characteristics of reference samples cured 1 month in chamber are very similar to these cured in the lab.

Comparing all samples after 3 months of curing in chamber with corresponding lab cured ones it can be noted that samples cured in lab condition have a smaller number of small pores (20-60 nm). This could be attributed to the restricted availability of water for hydration.

Pore size distributions for all mixes (R,A,B) cured in the chamber were similar over the whole analysed period of time. In these samples a combined effect of two processes - hydration and deterioration - need to be carefully considered.

3. CONCLUSIONS

Based on presented experimental results the following preliminary conclusions can be formulated.

Superabsorbent polymers have noticeable impact on the mechanical properties of mortars. Addition of SAP A increases compressive strength, but does not prevent the deterioration of cement matrix. SAP B decreases the compressive strength but the prolonged exposure to adverse conditions does not further affect the strength.

Additions of SAP A provide better performance of mortars. Pores size distribution of samples cured 3 month in the chamber and those cured in lab conditions were very similar. A very strong effect of SAP A noticeable in early stages of lab curing diminishes with time. The reduction of that effect is accelerated by the prolonged exposure to freeze/thaw cycles.

In contrary, the effect of SAP B is minimal. Analyses of microstructures for SAP B samples and the reference samples showed significant similarities.

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