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Improving Freeze–Thaw Resistance of Concrete Road Infrastructure by Means of Superabsorbent Polymers

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Abstract: The scope of the paper is to report an investigation on durability of infrastructure concrete for roads and bridges by creating a size and shape-designed pore systems in concrete in order to improve it, especially in terms of freeze–thaw resistance. By means of this experimental laboratory study, an alternative for usage of air entrainment agents (AEA) in concrete infrastructures was found in the way of using superabsorbent polymer materials (SAPs). The effect of the addition of SAPs of different amounts and different types into fresh concrete mix was investigated, including: compressive strength tests, weight loss measurements, visual and microscopic inspections and scanning electron microscopy (SEM) analysis. The detrimental strength reduction effect was not observed. The freeze–thaw procedure was varied, using different types of de-icing salts and heating/cooling regimes. It can be concluded that an improvement of the freeze–thaw resistance of concrete infrastructure depends on the particle size and optimal amount of SAPs added into concrete mix. The addition of 0.26 wt % of dry SAPs into the fresh concrete reference mix led to the significant decrease of scaling up to 43% after 28 freeze–thaw cycles. Both dosage and particle size of the SAPs had a significant impact on the obtained results and the freeze–thaw resistance in this experimental laboratory study.

Keywords: concrete road infrastructure; superabsorbent polymers (SAPs); freeze–thaw resistance; scaling

1. Introduction

Belgium has a very extensive motorway system, which is one of the densest in the world, and is one of the busiest transit countries in Europe. Approximately 40% of the Belgian roads are made of non-reinforced and reinforced concrete [1]. The quality and condition of road infrastructure differs from region to region. Most road construction and maintenance is observed in the north of Belgium in the Flemish Region (Flanders). Flanders invests 350 million euros in the maintenance of roads and bridges every year. The road infrastructure in the south of Belgium (Wallonia) and Brussels-Capital Region is in a quite poor condition where no maintenance is being carried out. Over the past five years there has been an increase of potholes [2,3] as a result of severe winter weather, primarily through the physical process of freeze–thaw and the ingress of water.

Concrete infrastructure elements should have adequate strength and durability in order to guarantee the proposed design life. The performance of both flexible and rigid pavements is significantly influenced by environmental conditions [4]. The impact of freeze–thaw cycles plays a key role in defining the bounds of the environmental impact on the performance of the pavement. In Belgium, road engineering applications are regulated by the Standaard Bestek 250 (SB250) [5].

In this code, the concrete composition restrictions are listed (water-to-cement ratio, choice of cement type and amount, minimal compressive strength, water absorption ratio and scaling/exfoliation), in order to come to a durable concrete application. In practice [3], a lot of damage of the Belgian concrete roads is visible. According to Jones et al. [2] freeze–thawing is the second main deterioration process affecting the concrete's durability, besides steel corrosion in reinforced concrete elements. The main factors contributing to concrete failure are the impact of the environment, poor concrete quality, and insufficient handling and curing of the freshly cast concrete. During harsh Belgian winters under condition of negative temperatures, cycles of freezing and thawing, and in combination with the use of de-icing salts, concrete infrastructure (roads and bridges) suffers from scaling, which increases the roughness of the surface with following decrease of the thickness of the concrete pavement and internal mechanical degradation due to freeze–thaw attack [6]. This exfoliation of the outer concrete layers results in a reduction of durability, comfort and safety of its practical application [6]. Dooms et al. [3] also mentioned that in the case where supplementary cementitious materials (SCMs) such as blast furnace slags and fly ashes are used, the effect of the curing duration and handling is of major importance in order to come to a durable and frost resistant concrete. In cases where de-icing salts are used, the impact of the freeze–thaw effect is worsened, mainly due to the scaling effect (chlorides lower the freezing point and the temperature gradient due to the de-icing effects leading to exfoliation of the outer concrete layer) and the osmotic pressure (due to salt concentration gradient).

In order to overcome internal mechanical degradation, concrete has to contain small cavities/pores in the concrete matrix which form a connecting network of pressure vessels. This network of pores can react to increasing pressure of the freezing water reducing the tension pressure in the upper and inner concrete layers. In SB250 [5], the standard measure to overcome frost damage (with or without the use of de-icing salts), is the use of air entrainment agents (AEA) for a durable concrete. It is well known that inducing additional air into a concrete matrix leads to reduction of the tensile and compressive strength of the material (one percent induced air leads to a roughly five percent strength reduction) [7]. In Belgium, in the case of traditional concrete, air entrainment agents (AEA) are added into concrete mix in order to increase resistance against freeze–thaw actions. In the case of heavy load bearing structures, addition of AEA into concrete mix is not desirable since it gives significant strength losses [7]. An improvement in degradation resistance of concrete pavements can be obtained by modifying the composition of the considered pavement or its components. The use of fibers and/or polymer modified binders in asphalt has proven to be very efficient for concrete layers [8]. A study conducted by [9] mentioned the improvement of frost scaling resistance by replacing Ordinary Portland Cement (OPC) of the reference concrete mix with fly ash (FA) and/or silica fume (SF) (up to 15% by weight of cement). However, it was noted that scaling values of the FA specimens without SF were less than control specimens' scaling, but they did not satisfy the capillary suction, se-icing agent and freeze–thaw-test (CDF) criterion. The obtained ternary concrete mix with 15% OPC replacement with 10% of fly ash and 5% of silica fume showed a significant reduction up to 50% of the scaling. This was also confirmed by Dooms et al. [3] evaluating the scaling of concrete (W/C-ratio of 0.45, 340 kg of added cement) with various cement types. In the case where sufficient curing (56 days under water) of the specimens was applied, specimens containing blast furnace slag clearly performed better compared to the ones containing OPC. The difference between specimens that were cured in open air (relative humidity of 60%) was much smaller. In practice [3], concrete infrastructure elements using blast furnace slag cements or other supplementary cementitious materials suffer severely from freeze–thaw actions, especially in cases where the curing time was insufficient.

As an alternative solution for the improvement of scaling resistance, the use of superabsorbent polymer materials (SAPs) can be recommended. SAPs are cross-linked hydrogel networks consisting of water-soluble polymers which generally are composed of ionic monomers and need a low cross-linking density in order to create a large fluid uptake capacity. SAPs can take up and hold aqueous solutions up to several hundred times their own weight while retaining it even under pressure [10]. As the SAPs will release their water during hardening, they will leave behind air-filled pores. During freeze–thaw cycles, these voids can protect concrete in a similar way as by using air entrainment [11]. With SAPs, the dimensions of the voids are fixed to the swollen state of the SAP during mixing, in contrast to regular air entrainment. Addition of SAPs does not necessarily need to affect the compressive strength [12] and seems to be promising independent from local raw materials and production processes [13].

The scope of this paper was to report an investigation under laboratory conditions on concrete durability by creating a size and shape-designed pore systems using SAP in concrete mixes, as an in alternative to AEA, in order to improve its durability, especially in terms of freeze–thaw resistance.

2. Materials and Methods

2.1. Materials

2.1.1. Raw Materials

In the research, the concrete mix composition was selected as the reference concrete composition (REF) which was an application-based concrete mix (water-to-cement ratio of 0.45) frequently used for infrastructure concrete and complies with the BENOR regulations for traditional concrete (NBN EN 206-1:2001) and with the Belgian guidelines and requirements for road concrete (SB250) [5]. In REF concrete mix, the following were used: blast furnace slag cement CEM III/B 42.5 N LA; natural round river sand 0/1 and crushed limestone sand 0/4, crushed limestone aggregates 2/6 and 6/14; a polycarboxylic ether-based plasticizer (3rd generation) which was added for the improvement of the flowability of the fresh concrete mix.

2.1.2. Superabsorbent Polymers (SAPs)

In the research, two types of SAPs (SAP_{CT} and SAP_{PT}), which are bulk polymerized, covalently cross-linked acrylamide/acrylic acid copolymers obtained from one individual industrial producer, were used (see Figure 1). SAP_{CT} is a commercially available polymer and SAP_{PT} is a prototype (under development) (see Figure 2).

Figure 1. Visualization of superabsorbent polymers (SAPs): SAP_{CT} (left) and SAP_{PT} (right) containing absorbed water.

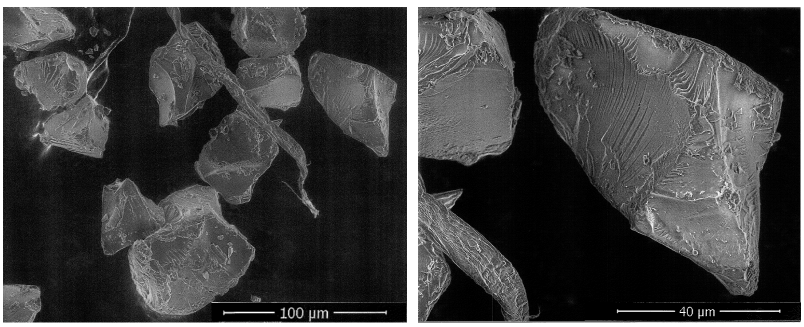


Figure 2. SEM images of SAP_{PT} particles.

Both polymers have an irregular particle shape as they were produced by the bulk polymerization technique, followed by crushing into single particles. The density is 700 kg/m^3, their particle size distributions in the dry state are presented in Figure 3. The mean particle size is 95 µm and 560 µm for the prototype and the commercial type, respectively.

The absorption capacity was determined by means of the so called 'tea bag method'. As the absorption capacity of SAPs is very dependent on the pH of the fluid to be absorbed, this parameter was determined for different liquid types: demineralized water (pH = 6.64), tap water (pH = 7.75) and a cementitious pore solution containing blast furnace slag cement (pH = 12.6). The results are presented in Figure 4 and Table 1. The finer prototype has a higher sorptivity compared to the coarse commercial type: 39.4 g pore fluid/g SAP vs. 13.5.

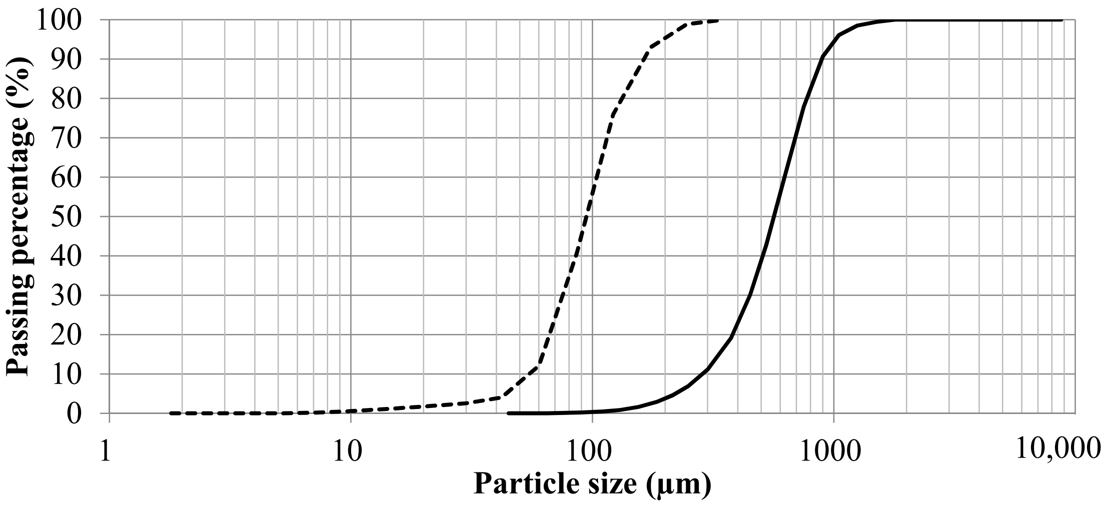


Figure 3. Particle size distribution of SAP_{CT} (bold line) and SAP_{PT} (dashed line).

2.1.3. Concrete Mix Proportioning, Specimens Preparation and Storage Conditions

During experimental program the amount of SAP varied from 0.13 wt % up to 0.39 wt % (dry SAP, relative to cement weight) in the concrete mixes ($SAP0.26_{CT}$, $SAP0.13_{PT}$, $SAP0.26_{PT}$, $SAP0.39_{PT}$). The amount of 0.2–1.0 wt % dry SAP by weight of cement had been found to be most beneficial throughout numerous test campaigns and for multiple benefits and applications [14–16]. According to Hasholt et al. [17], 0.3 wt % SAP/C is preferred as an appropriate addition of SAPs for concrete mixes with moderate W/C-ratios (0.40 < W/C-ratio < 0.50). No additional water was added to the concrete mixes containing SAPs. To cope with the effects of SAPs on the fresh concrete's consistency, superplasticizer was added to come to a target consistency class S3–S4. The total W/C-ratio was kept constant at 0.45. By means of the absorption capacity (see Table 2) it is possible to calculate the amount of pore fluid that is absorbed by the SAPs (W_{SAP}) and the effective water amount in the concrete mix ($W_{eff} = W_{total} - W_{SAP}$). Absorption capacity of SAPs can be seen in Figure 4, these are equilibrium values reached when mass increase in between two measurements is less than 0.1%. All six concrete mix compositions (REF, with air entrainment agents (AEA) and with SAPs) are given in Table 2.

The concrete mixes comply with the regulations for concrete structures (roads and bridges) in external environment in contact with de-icing salts (EE4 according to NBN EN 206-1): a maximal water-to-cement ratio of 0.45, a minimal cement content of 340 kg/m^3 of concrete and a minimal strength class of C30/37. According to SB250 the minimal cement content must exceed 375 kg/m^3, the water-to-cement ratio must be less than 0.50 and the mean compressive strength after 90 days must exceed 50 MPa. The mixing procedure of the concrete mix compositions with SAPs was following: first the dry aggregates were mixed with half of the amount of mixing water, then the cement and dry

SAPs were added. After 30 s of mixing, the remaining water together with plasticizer (HRWRA) was added. In total, 10 min of mixing time was applied.

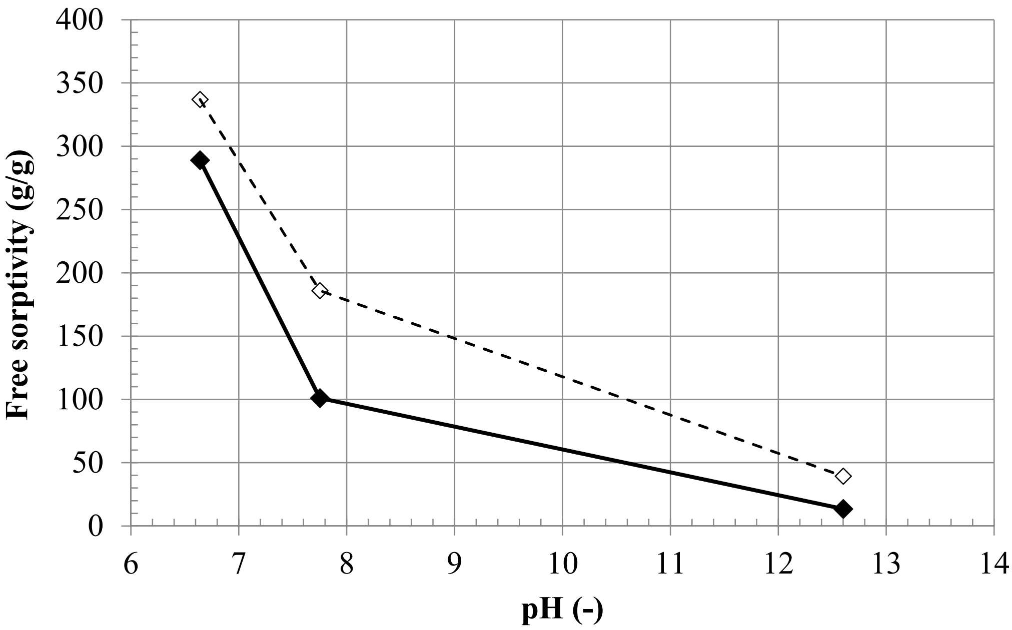


Figure 4. Absorption capacity (free sorptivity) of SAP_{CT} (bold line) and SAP_{PT} (dashed line).

Table 1. Particle size and absorption capacity (g pore fluid/g SAPs) of SAP_{CT} and $SAP_{PT.}$

	pH	SAP_{CT}	SAP_{PT}
Demineralized water	6.64	289 ± 7.5	337 ± 1.0
Tap water	7.75	101 ± 2.3	186 ± 1.1
Cement pore solution	12.6	13.5 ± 1.3	39.4 ± 1.4
d_{10}	µm	290	55
d_{50}	µm	560	95
d_{90}	µm	900	170

Table 2. The concrete mix compositions.

		REF	AEA	$SAP0.26_{CT}$	$SAP0.13_{PT}$	$SAP0.26_{PT}$	$SAP0.39_{PT}$
CEM III/B 42.5 N LA	[kg/m^3]	380	380	380	380	380	380
River sand 0/1	[kg/m^3]	144	144	144	144	144	144
Limestone 0/4	[kg/m^3]	608	608	608	608	608	608
Limestone 2/6	[kg/m^3]	422	422	422	422	422	422
Limestone 6/14	[kg/m^3]	726	726	726	726	726	726
HRWRA	[kg/m^3]	1.88	1.88	1.88	2.58	2.58	5.57
AEA	[kg/m^3]	-	1.14	-	-	-	-
SAP_{CT}	[kg/m^3]	-	-	1.0	-	-	-
SAP_{PT}	[kg/m^3]	-	-	-	0.5	1.0	1.5
W_{total}	[kg/m^3]	171	171	171	171	171	171
W_{SAP}	[kg/m^3]	-	-	13.5	19.7	39.4	59.1
W_{eff}	[kg/m^3]	-	-	157.5	151.3	131.6	111.9
$(W/C)_{total}$	[-]	0.45	0.45	0.45	0.45	0.45	0.45
$(W/C)_{SAP}$	[-]	-	-	0.04	0.05	0.10	0.16
$(W/C)_{eff}$	[-]			0.41	0.40	0.35	0.29
wt % SAP/C	[-]	-	-	0.26%	0.13%	0.26%	0.39%

2.2. Methods

2.2.1. Fresh Properties

The consistency of each concrete mix was characterized by means of the slump test with Abrams cone according to NBN EN 12350-2. The air content and the density were obtained according to NBN EN 12350-7 and 12350-6, respectively.

2.2.2. Mechanical Properties

Out of each concrete mix, 20 cube specimens with a side of 150 mm were cast and stored immediately in a climate chamber (+20 °C, 90% RH) according to NBN EN 12390-2. At the age of 1, 2, 7, 28 and 90 days the compressive strength tests were performed according to NBN EN 12390-3. According to the requirements defined in SB250 the mean compressive strength must exceed 50 MPa (after 90 days) for road applications. According to NBN EN 206-1 concrete in contact with de-icing salts must have a strength class of C30/37, meaning the characteristic strength of the cubes must exceed 37 MPa after 28 days of hardening.

2.2.3. Freeze–Thaw Resistance

The resistance of the specimens and the different concrete mixes against freeze–thaw attack can be evaluated by means of material loss weighing measurements (scaling or exfoliation) after 5 to 8 freeze–thaw cycles. Freeze–thaw resistance of the concrete mixes was determined according to two procedures was determined according to two procedures: CEN/TS 12390-9 and ISO/DIS 4846-2 (see Table 3).

Table 3. Comparison of CEN/TS 12390-9 (FT1) and ISO/DIS 4846-2 (FT2) freeze–thaw methods.

	Unit	FT1	FT2
Code	-	CEN/TS 12390-9	ISO/DIS 4846-2
Specimen	-	cube	cylindrical
Dimensions	mm	150/50	φ100 × H45
Exposed area	dm^3	2.250	0.785
Deicing salt	-	3 wt % NaCl	3 wt % $CaCl_2$
Freeze–thaw cycle	-	curve 1	curve 2

The first procedure is based on CEN/TS 12390-9, slab test described by Tang and Peterssen [18], with freeze temperature −20 °C, thaw temperature +20 °C and a continuous temperature drop (see Figure 5, FT1). Cubic specimens (150 mm^3) were cured at +20 °C in a humidity controlled environment. At the age of 21 days, a 50 mm thick slab was sawn from each cube, perpendicular to the top surface and the two most parallel side surfaces, so that one cut surface was located in the center of the cube and becomes the test surface. During the tests, the top surface of the specimens (surface area = 2.250 dm^2) were exposed to a salt solution containing 3 wt % NaCl and 97 wt % demineralized water. To ensure that the solution stays on the top surface, a rubber slab was placed around the sawn specimens and evaporation is limited by means of a plastic foil placed on top of the specimens. The specimens were subjected to 28 consecutive freeze–thaw cycles; after each 7 cycles the exfoliation on the exposed surface was measured: the solution comprising the scaled material was filtered, and afterwards the paper filter was dried to constant mass. The exfoliation can be expressed in dry mass per unit of exposed area (g/dm^3).

The second procedure is a comparison between the CEN/TS 12390-9 method and an alternative freeze–thaw test method according to ISO/DIS 4846-2 applied for a composition REF, AEA and $SAP0.26_{CT}$ with freeze temperature −18 °C, thaw temperature +20 °C, sudden temperature drop (see Figure 6, FT2). This alternative method was used to determine concrete mix resistance against scaling. Cylindrical cores with a height of 45 mm and a diameter of 100 mm were drilled out of a cast concrete plate. The concrete plates were produced and stored immediately after mixing in a climate chamber (+20 °C, 90% RH) for 90 days. During the tests, the top surface of the specimens (surface area = 0.785 dm^2) was exposed to a salt solution containing 3 wt % $CaCl_2$ and 97 wt % demineralized water. The specimens were also provided with a tight rubber slab. The specimens were subjected to 30 consecutive freeze–thaw cycles: after each 5 cycles the exfoliation on the exposed surface was measured in the same way as above described. Four specimens were tested for each concrete mix composition. The SB250 acceptance criterion is a maximum mean scaling of 10 g/dm^2 after 30 freeze–thaw cycles.

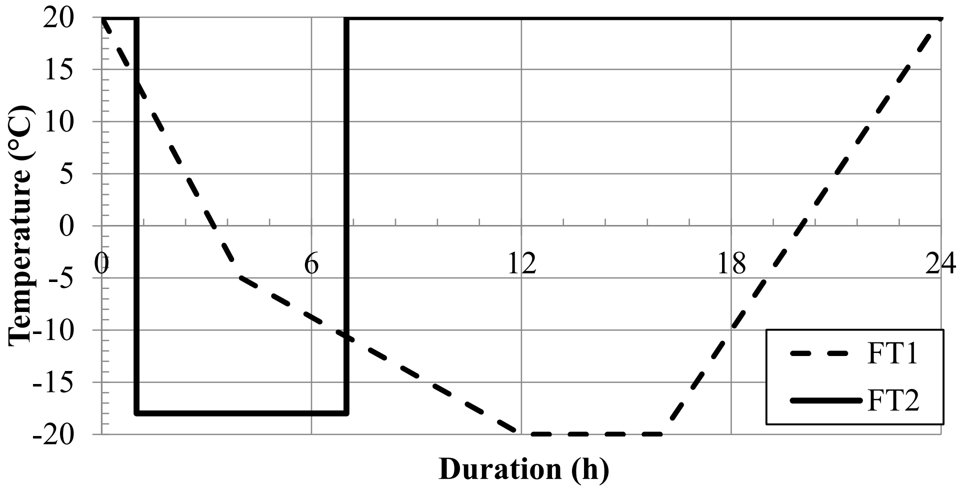


Figure 5. Freeze–thaw temperature cycles of the CEN/TS 12390-9 (FT1) and the ISO/DIS 4846-2 (FT2).

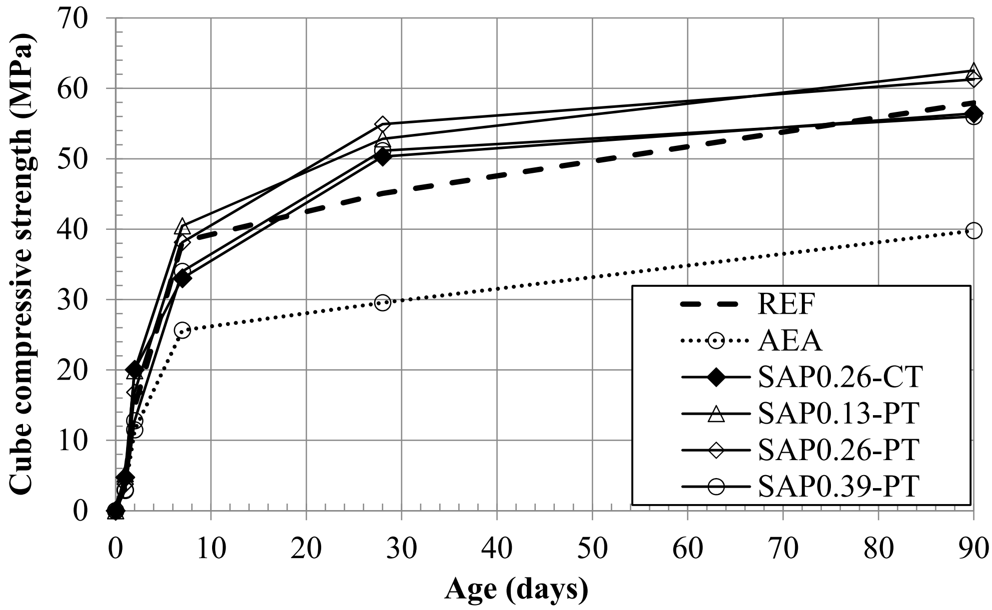


Figure 6. Cube compressive strength development of the different concrete mixes between ages of 1 day and 90 days.

2.2.4. Microstructure Analysis

Phenomena occurring in concrete subjected to frost actions can be evaluated and described by means of capillary porosity quantification and scanning electron microscopy [19]. The porosity of the specimens of the different concrete mixes can be quantified by means of the water absorption by immersion (according to NBN B15-215). According to the requirements defined in SB250 the mean water absorption has to be less than to 6.3%.

The influence of cyclic freezing and thawing of the concrete specimens and the effect of addition of SAPs upon its microstructure was investigated by means of petrographic analysis on thin sections and scanning electron microscopy (SEM) in order to identify and find the expected cavities in the concrete containing SAPs.

3. Results and Discussion

3.1. Fresh Properties

It was decided that in order to keep the total water content constant throughout the entire experimental program in order to maintain the prescribed consistency class S3–S4 of concrete mix, an additional amount of superplasticizer was needed (see Tables 3 and 4). In the case of the coarser commercially available SAP_{CT}, the amount of superplasticizer was equal to that of the reference concrete mix. As a consequence, the slump value decreased by 47%. For the finer prototype SAP, doubling the amount of superabsorbent polymer led to a decrease in a slump by 20% ($SAP0.26_{PT}$ vs. $SAP0.13_{PT}$). In order to get the same slump value, an additional amount (more than 50%) of superplasticizer was needed in case the amount of SAP was increased by 33% ($SAP0.39_{PT}$ vs. $SAP0.26_{PT}$). By adding SAPs, the air content of the fresh concrete mix increased by 20%.

Table 4. Fresh properties and porosity of the different mixes.

		REF	**AEA**	**$SAP0.26_{CT}$**	**$SAP0.13_{PT}$**	**$SAP0.26_{PT}$**	**$SAP0.39_{PT}$**
Slump	(mm)	190	220	102	193	155	150
Air%	(%)	1.9	10.0	2.7	2.4	2.4	2.3
Density	(kg/m^3)	2430	1980	2390	2440	2430	2415
Water absorption (immersion)	(%)	4.28	5.72	4.67	3.87	4.20	4.07
Water absorption (forced)	(%)	11.68	11.97	11.88	10.01	10.02	10.86
Volumetric weight	(kg/m^3)	2415	2230	2425	2450	2445	2410

3.2. Mechanical Properties

All concrete mixes, except for the one containing AEA, have met the requirement of a minimal mean compressive strength of 50 MPa according to SB250 (see Figure 6). It is evident that the amount of added SAPs influences the compressive strength.

By adding SAPs into the REF concrete mix the compressive strength evolution was noticed after 28 days in all cases (see Figure 6, increase between 10% and 20%). This increase in strength is most likely due to the decrease in effective W/C-ratio due to the addition of the polymers during mixing. It is well known that strength of concrete increases when the W/C-ratio is lowered, e.g., by adding SAPs. However, at the age of 90 days, the strength only increased in the 0.13 and 0.26 wt % prototype polymer. Addition of the coarser commercially available SAPs or a higher amount of prototype polymer had a negative effect on the compressive strength. By adding 0.13 to 0.26 wt % prototype polymer, a higher 28-day and 90-day strength was obtained compared to the concrete mix with the same amount of commercially available polymer. The higher absorption capacity of the finer prototype SAP led to a higher reduction in effective W/C-ratio. By adding air entrainment agents, the strength was lowered significantly by 33% after 28 days.

It can be concluded that by increasing the amount of SAPs the strength develops slower, but in cases where finer SAPs are used in an optimal amount, the strength is higher compared the reference concrete mix without polymers. The optimal percentage of SAP in this experimental program is the range of 0.13–0.26 wt % (weight of dry SAP relative to the cement weight).

3.3. Evaluation of the Freeze–Thaw Resistance

The mean exfoliation of the reference concrete specimens after 28 consecutive freeze–thaw cycles is presented in Figure 7. Scaling of 3.1 g/dm^2 was obtained which is less than the acceptance criterion of 10 g/dm^2 (according to SB250), mainly due to the perfect curing conditions preceding the casting.

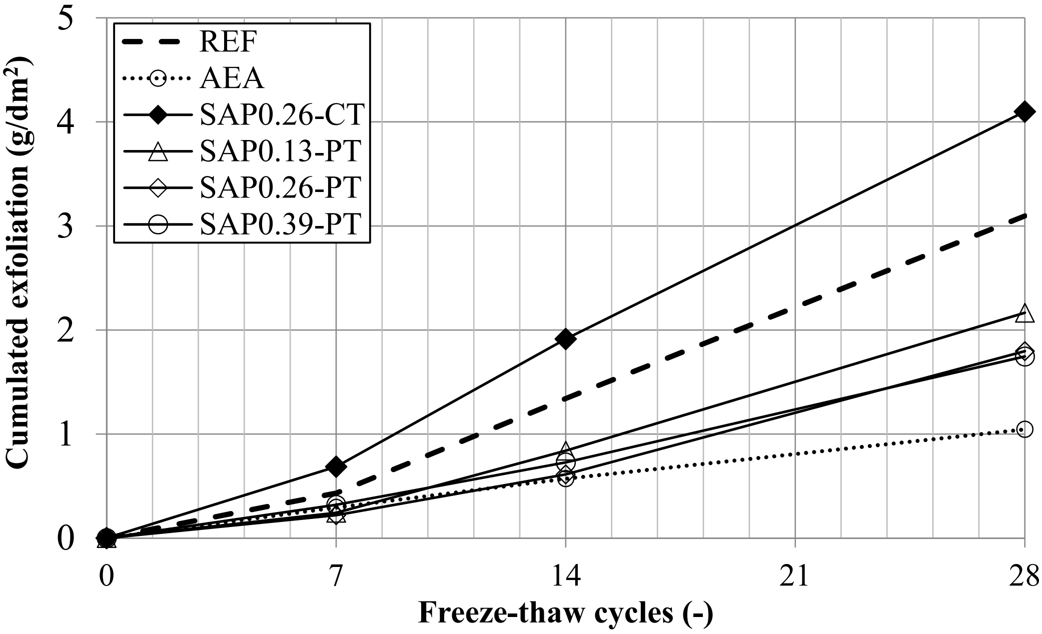


Figure 7. Cumulated exfoliation of the different mixes after 28 cycles (FT1 method).

For the commercially available polymer the resistance against scaling is lower: scaling of 4.1 g/dm^2 was obtained after 28 cycles, which is an increase of 32%. By adding the coarse and commercially available superabsorbent polymers SAP_{CT} the freeze–thaw resistance of the concrete was not ameliorated.

Addition of finer superabsorbent polymers SAP_{PT} into the concrete mix had a positive effect on the freeze–thaw resistance: in the case of 0.13 wt %, 0.26 wt % or 0.39 wt % the exfoliation after 28 cycles decreased by 30%, 42% and 43%, respectively. This proved that the amount of added SAPs and the type (more specific: the grading and retention capacity) is a decisive factor for the improvement of the freeze–thaw resistance of concretes with W/C-ratio between 0.40 and 0.50.

It can be concluded that the optimal percentage of SAPs in this research study is quite close to the percentage of 0.26–0.39 wt % (weight of dry SAP relative to the cement weight). The size of the polymers has a decisive effect on the effectiveness: SAPs with mean particle size less than 100 µm have a positive effect, while SAPs with mean particle size greater than 500 µm have a negative effect. It must be mentioned that the obtained results in this study are applicable to the concrete mixes used in it, and cannot be generalized for all concrete types.

It has to be noted that by using AEA, the cumulated exfoliation was reduced significantly compared to the reference concrete mix. The cavities created by the polymers or the air entrainment agents compensated for the expanding freezing water, where for the dense reference concrete mixes less space was available, leading towards more scaling and internal cracking. Addition of AEA significantly reduced the strength which might be undesirable for infrastructure concrete for roads and bridges.

By comparing the freeze–thaw testing procedure (FT1 vs. FT2) it became clear that this has a major impact on the obtained results (see Figure 8). The measured cumulated exfoliation is three times higher for the reference concrete mix in the case where the ISO/DIS 4846-2 method was used. The sudden temperature drop from +20 °C to −18 °C and the use of $CaCl_2$ instead of NaCl might explain the observed difference. For the concrete mixes AEA′ and SAP0.26-CT″ the exfoliation was approximately four times higher (see Figure 8). Especially after 5 to 10 freeze–thaw cycles, the concrete experience had quite high scaling.

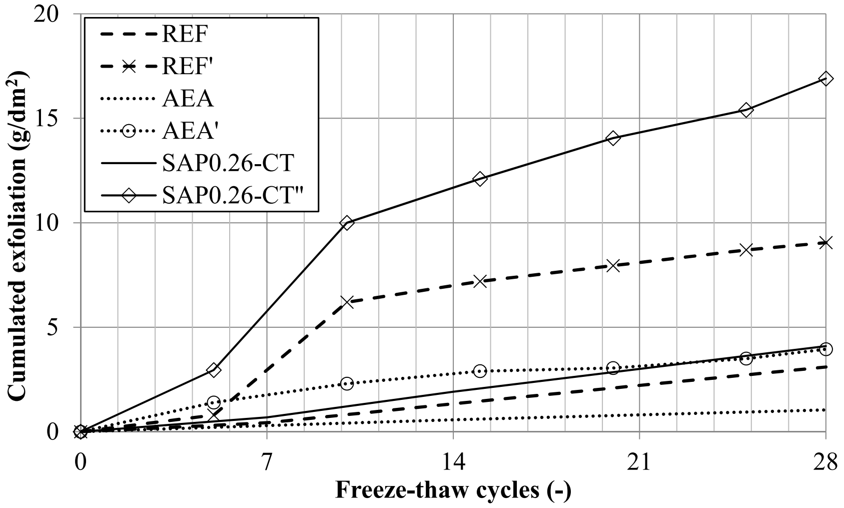


Figure 8. Cumulated exfoliation of the different concrete mixes with AEA and SAP_{CT} after 28 cycles (FT1 vs. FT2 method).

3.4. Evaluation of Porosity and the Microstructure

3.4.1. The Water Absorption by Immersion

Small differences were noticeable in the obtained results of the water absorption of the specimens of the different concrete mixes, and all concrete mixes complied with the acceptance criterion of SB250 (absorption smaller than 6.3%). In the case of SAP_{PT}, the water absorption was decreased compared to the reference concrete mix, which is not the case for the commercially available polymer (see Table 4). Addition of AEA increased the water absorption capacity of the concrete.

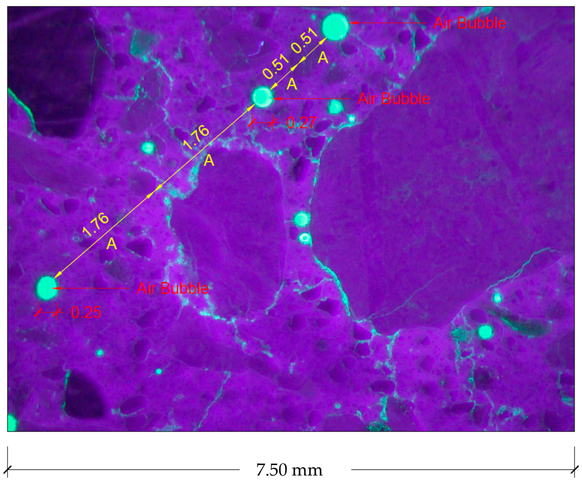
3.4.2. Scanning Electron Microscopy and Petrography on Thin Sections

By means of petrographic microscopy on thin sections the microstructure of concrete mixes REF, $SAP0.26_{CT}$ and $SAP0.26_{PT}$ were visualized (see Figure 9).

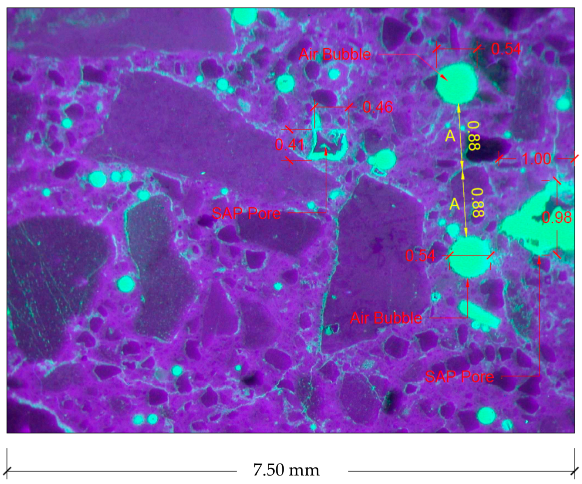
For the reference concrete mix REF (see Figure 9a) several air bubbles are noticeable with diameter in between 250 µm and 340 µm. Internal micro-cracking was observed most likely due to the self-desiccation of the matrix (e.g., autogenous shrinkage). SEM imaging (see Figure 10a) confirms the micro-cracking. A very dense matrix was also noticeable, which is typically for concrete containing blast furnace slags. The spacing factor, i.e., the distance of the shortest travel path of expanding water, varies between 510 and 1760 µm. In the literature [20], a distance factor of approximately 200–300 µm can be seen as effective. A SEM image of the AEA mix after 28 freeze–thaw cycles (see Figure 10b) proves that this distance is necessary for effective improvement of the freeze–thaw resistance. It should be noticed that the cracks move towards the air bubbles. The higher factor of the reference concrete mix can be an explanation of the experienced scaling. By using the commercially available polymer in $SAP0.26_{CT}$ (see Figure 9b) the amount of air voids and its dimensions increases significantly: voids with size up to 1000 µm were found. The voids with irregular shape are created by the superabsorbent polymer. The spacing factor also varies from 500 to 880 µm, which is too high for effective freeze–thaw resisting concrete.

In concrete mix $SAP0.26_{PT}$ with the finer prototype polymer (see Figure 9c), several air bubbles and irregular structures can be identified. The shape and size of these air bubbles are more or less the same as the air bubbles shown in the previous two images (see Figure 9a,b). However, these air voids are well scattered small irregular structures in this composition, with a spacing factor close to 200 µm. These cavities are the result of adding the prototype superabsorbent polymers: they have a smaller size than the pores created by adding commercially available type. This is the main reason why these compositions containing fine SAPs show a better freeze–thaw resistance in comparison to the reference composition.

The cavities formed by the SAPs are very recognizable due to their more irregular shape compared to air bubbles. During mixing, the superabsorbent polymer particles absorbed a part of the mixing water (pore fluid) but not at their full absorbing capacity due to the alkalinity of its environment. The absorbing capacity of pore solution was lower than the absorbing coefficient of pure water. During hardening and hydration of the cement in concrete, the minerals in the cement particles form CSH layers with the free mixing water. At a certain time, no more free water was available for the continuation of the hydration process and self-desiccation started, leading towards an under-pressure in the matrix, and autogenous shrinkage cracking in the case of the reference concrete mix. As a consequence, the water absorbed by the SAPs was gradually released and the hydration process continued in the close environment and in contact with the SAPs: small cavities between 190 µm up to 370 µm remained in the matrix. These cavities can serve as expansion vessels for expanding freezing water in the matrix.

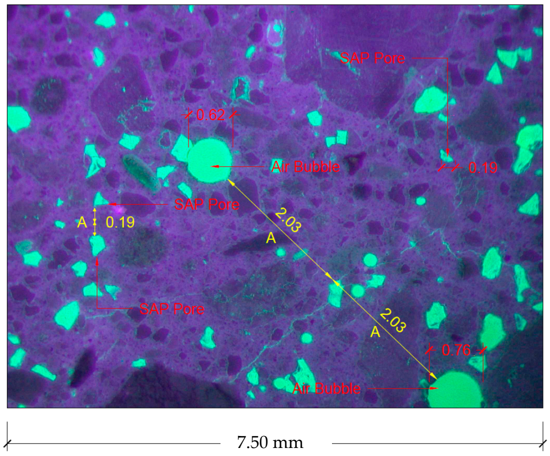


(**a**)



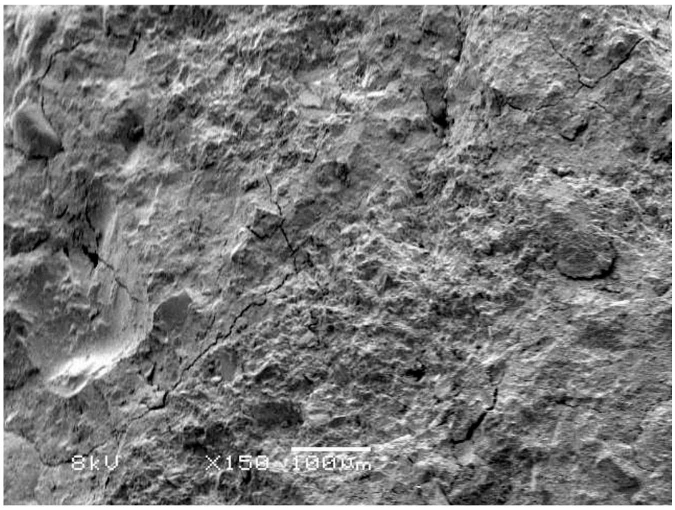
(**b**)

Figure 9. *Cont.*

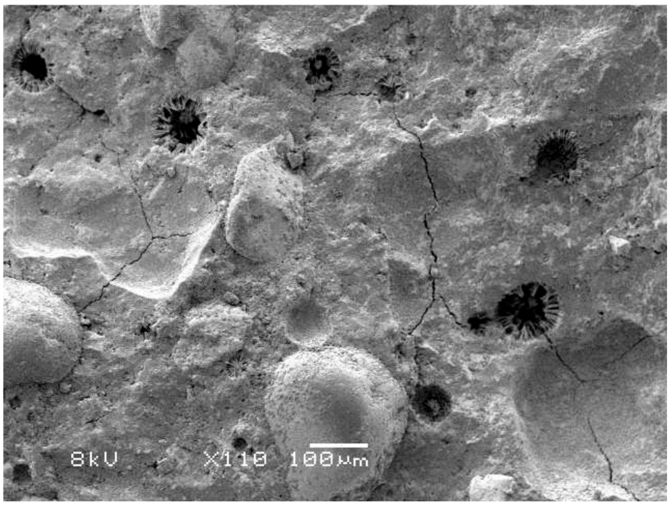


(**c**)

Figure 9. Images of microscopic analysis (petrography on thin sections) of (**a**) REF, (**b**) $SAP0.26_{CT}$ and (**c**) $SAP0.26_{PT}$.



(**a**) REF, before freeze–thaw.



(**b**) AEA, after freeze–thaw.

Figure 10. SEM image of (**a**) REF (150×) and (**b**) AEA (110×) (scale 100 µm).

4. Conclusions

Based on the reported research concerning the freeze–thaw resistance of concrete mixes used for infrastructure (road and bridges) applications, and the effect of superabsorbent polymers (SAPs) for the improvement and mitigation of its resistance as an alternative for the application of air entrainment agents (AEA), the following conclusions can be drawn:

- Addition of SAPs

Increasing the amount of SAPs in the concrete mix led to a small increase of compressive strength after 28 days of hardening, mainly as a result of the decrease of the effective W/C-ratio due to absorption of free water by the polymers during mixing. The difference decreased or even disappeared after 90 days of hardening where the amount of SAPs was too high or the size of the polymers was too large. Small cavities (between 190 μm up to 370 μm) were created in the matrix. Due to the absorbed water, self-desiccation during the hydration process was reduced, leading towards a higher ultimate degree of hydration, which clearly compensated the strength reduction due to the more porous matrix. By addition of an optimal percentage of SAPs in the range of 0.13–0.26 wt % (weight of dry SAP relative to the cement weight), there was a clear reduction of scaling. The particle size of the SAPs is a very important factor: polymers with mean size less than 100 μm had proven their effectiveness, while polymers with mean size up to 500 μm showed to be ineffective. The cumulated mass loss after 28 freeze–thaw cycles of the concrete mix can be less than 2 g/dm^2 in the case of 0.26–0.39 wt % SAPs (relative to the cement weight) were added into the concrete mix.

- Freeze–thaw testing procedure

By comparing the freeze–thaw testing procedure, it became evident that this has a major impact on the obtained results. The measured cumulated exfoliation is three to four times higher for the concrete mixes in the case where the ISO/DIS 4846-2 method is used. The sudden temperature drop from +20°C to −18°C and the use of $CaCl_2$ in the case of NaCl might explain the observed difference.

It has to be noted that the obtained conclusions regarding dosage and size of SAPs to be added are only applicable for the concrete mixes mentioned in this experimental research study.

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