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Resistance of Concrete with Crystalline Hydrophilic Additives to Freeze–Thaw Cycles

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Abstract: The study explores the hypothesis that crystalline hydrophilic additives (CA) can enhance concrete's resistance to freeze/thaw cycles, crucial for assessing building durability. Employing EU standards, the research evaluates concrete resistance through standardized European freeze/thaw procedures. Monitoring concrete slabs exposed to freezing in the presence of deionized water and in the presence of 3% sodium chloride solution, the study measures surface damage and relative dynamic modulus of elasticity. Additionally, it assesses internal damage through monitoring of relative dynamic modulus of elasticity on cubes and prisms submerged in water and exposed to freezing/thawing. The pore spacing factor measured here aids in predicting concrete behavior in freeze/thaw conditions. Results suggest that the standard air-entraining agent offers effective protection against surface and internal damage due to freeze/thaw cycles. However, the CA displays potential in enhancing resistance to freeze/thaw cycles, primarily in reducing internal damage at a 1% cement weight dosage. Notably, a 3% replacement of cement with CA adversely affects concrete resistance, leading to increased surface and internal damage. The findings contribute to understanding materials that can bolster concrete durability against freeze–thaw cycles, crucial for ensuring the longevity of buildings and infrastructure.

Keywords: concrete; durability; crystalline hydrophilic additives; freeze–thaw cycles; surface damage; internal damage; pore spacing factor

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1. Introduction

The durability of buildings is mostly influenced by the durability of the materials used in their construction. A primary factor that undermines this durability is the freeze–thaw cycle [1]. When temperatures dip below zero, water within the material freezes and expands, exerting stress on the material's walls [2]. Through repeated freeze–thaw cycles, this stress leads to material damage, consequently diminishing its durability. In cement composites, such damage manifests as surface scaling or internal cracking [3].

A common approach to enhancing concrete's durability against freeze/thaw cycles involves incorporating air-entraining agents into the concrete mixture [4]. These agents introduce air bubbles during mixing, which disrupt the capillaries through which water could penetrate the concrete. By minimizing water content in the concrete, issues related to freeze–thaw cycles are mitigated. However, it is important to exercise caution with these agents, as they may adversely affect the compressive strength of the concrete [5]. The literature also suggests that concrete durability can be improved by incorporating mineral additives like slag [6], fly ash [7], and silica fume [8]. Furthermore, concrete durability can be enhanced by partially replacing aggregate with rubber [9–12], employing polymer binders [13,14], modifying [15–17] or impregnating concrete with polymers [18,19], using polycarbonate superplasticizers [20,21], employing biomimetic polymer additives [22], and utilizing polymer fibers and biofibers [23,24].

Crystalline admixtures (CA) are primarily commercially available products offered by various manufacturers (such as Xypex, Richmond, BC, Canada; Kryton, Vancouver, BC, Canada; Penetron, East Setauket, NY, USA; Harbin, China). They serve a dual function: reducing concrete permeability and repairing cracks [25]. The recommended dosage of CA in concrete typically ranges from 0.3% to 5% by the weight of the cement [26,27]. Several authors have studied the impact of CA on the durability properties of concrete by monitoring crack healing, with most concluding its effectiveness in this regard [28–32]. It was noted that the highest rate of healing was observed when samples containing CA were consistently immersed in water [28–30]. According to [29,33], calcium carbonate in the form of aragonite is formed in concrete cracks treated with CA, effectively sealing them.

Considering the confirmed effectiveness of CA in the concrete crack healing process and the fact that cracks occur in concrete during freeze–thaw cycles, it would be intriguing to precisely determine the effectiveness of CA in enhancing concrete resistance to freeze–thaw cycles. European legislation mandates testing the resistance of concrete to freeze–thaw cycles through procedures outlined in standards CEN/TS 12390-9 [34] and CEN/TR 15177 [35]. In the method outlined in CEN/TS 12390-9 [34], concrete samples saturated with deionized water or a 3% sodium chloride solution undergo freeze/thaw cycles (56 cycles), during which surface scaling and mass loss of concrete are measured. The procedure described in CEN/TR 15177 [35] can be employed to monitor damage to the internal structure. Additionally, EN 480-11 [36] is used to predict concrete behavior under freeze–thaw conditions, involving microscopic observation of hardened concrete samples, measurement of pore spacing, and calculation of the pore spacing factor which is defined as distance of any point in cement paste to the edge of the nearest air void. Cement-based materials are considered resistant to freeze–thaw cycles if the spacing factor is less than 0.2 mm.

Since the authors in [37] have already confirmed reduced water absorption by using CA in concrete as an indicator of concrete resistance to freeze–thaw cycles, and the authors in [32] have confirmed reduced water penetration in concrete with CA, the hypothesis arises that the application of CA could potentially improve concrete resistance to freeze–thaw cycles. Therefore, this study aims to examine the resistance of concrete to freeze–thaw cycles according to standardized procedures prescribed by EU standards.

2. Experimental Part

In the experimental part of the paper, four concrete mixtures were prepared; a reference mixture (M1), a mixture with an air entraining agent (M2), and mixtures with a crystalline hydrophilic admixture in two different amounts per cement weight (M3, M4).

2.1. Properties of Aggregates, Binders, and Additives to Concrete

In this research, dolomite was used as an aggregate in fractions 0–4 mm, 4–8 mm, 8–16 mm, and 16–31.5 mm, as well as a dolomite-type filler. The density of dolomite aggregate and filler determined according to EN 1097-6 standard [38] was 2780 kg/m^3. The specific surface area for filler determined using the BET method according to the standard ISO 9277 [39] was 2.32 m^2/g. Sieve curves for dolomite fractions are shown together with target and actual cumulative aggregate curve in Figure 1, where it should be noted that 5% of the 0–4 mm fraction was replaced with filler.

The cement used for making concrete mixtures was CEM I 52.5 N. In all mixtures, the superplasticiser ViscoCrete 5380, Sika Croatia, Zagreb, Croatia was used in the amount of 1% of the mass of binder. In mixture M2, the air-entraining agent LPS A 94 from Sika was used in the amount of 0.2% of the mass of cement. The crystalline hydrophilic admixture Penetron Admix from Penetra, Sesvete, Croatia was used in the amount of 1% of binder in mixtures M3 and 3% of the mass of binder in mixtures M4. The density of binders (cement and crystalline hydrophilic admixture) was determined according to the standard EN

1096-6 [40], and the specific surface area was determined using the BET method according to ISO 9277 [39]. The densities of the superplasticizer and air entraining agent are adopted from the additive producer. The densities of binders, superplasticizer, and air-entraining agent, as well as the specific surface areas of binders, are shown in Table 1.

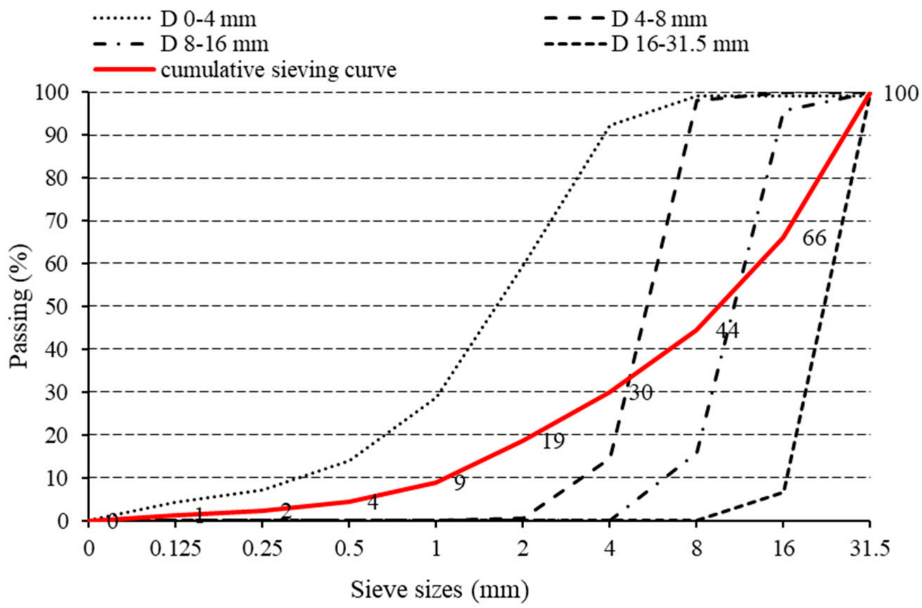


Figure 1. Fraction sieve curves, target, and cumulative sieving curves of aggregate.

Table 1. Densities of binders, superplasticizer, and air-entraining agent, and specific surface area of binders.

Components	Density, kg/m^3	Specific Surface Area, m^2/g
Cement, CEM I 52.5 N	2960	3.76
Superplasticiser, ViscoCrete 5380	1080	-
Air entraining agent, LPS A 94	1000	-
Crystalline hydrophilic admixture (CA), Penetron	2910	2.70

2.2. *Composition of Concrete Mixtures*

The composition of concrete mixtures is shown in Table 2. All mixtures have the same water/cement ratio of 0.35, the same amount of aggregate, and the same amount of binder (400 kg). In mixtures M1 and M2 it is cement, while in mixtures M3 and M4 it is the total amount of cement and crystalline hydrophilic additive.

Table 2. Composition of concrete mixtures for 1 m^3 of concrete.

	Mixture/Components	M1	M2	M3	M4
	Cement (kg)	400	400	396	388
	Water (kg)	140	140	140	140
	Superplasticizer (kg)	4	4	4	4
	Air entraining agent (kg)	-	0.8	-	-
	Crystalline hydrophilic admixture (kg)	-	-	4	12
Aggregate	Dolomite 0–4 mm (kg)	576.6	576.6	576.6	576.6
Aggregate	Dolomite 4–8 mm (kg)	195.6	195.6	195.6	195.6
Aggregate	Dolomite 8–16 mm (kg)	469.8	469.8	469.8	469.8
Aggregate	Dolomite 16–31.5 mm (kg)	685	685	685	685
Aggregate	Filler (kg)	30.2	30.2	30.2	30.2

The aggregates used for preparing concrete were first saturated and then surface-dried. This was achieved in an artificial way by dipping the aggregates into a water tank for 24 h, taking them out, and then wiping excess water from their surface. First, coarse and fine aggregate was mixed for 1 min, then binder was added and the mixing was continued for an additional 2 min. In the end, water was added and the mixing was continued for an additional 2 min. Mixing the concrete in a pan mixer (DZ 100VS, Diemwerke, Hörbranz, Austria) took a total of 5 min.

2.3. Properties of Fresh and Hardened Concrete

The consistency of the concrete was determined according to EN 12350-2 [41], the density of fresh concrete according to EN 12350-6 [42], and the air content according to the standard EN 12350-7, with the pressure gauge method [43]. The obtained results are shown in Table 3.

Table 3. Properties of concrete mixtures in their fresh state.

Mixture	M1	M2	M3	M4
Consistency–slump (cm)	12	14	11	11
Density (kg/m^3)	2504	2439	2520	2489
Air content (%)	1.5	5	1.5	1.6

According to Table 3, all mixtures belong to consistency class S3 (10–15 cm) according to EN 206 [44]. The addition of crystalline hydrophilic admixture had no impact on workability, which is in accordance with [45]. In terms of density, all mixtures can be considered normal weight concrete. As expected, mixture M2 has the highest air content in fresh concrete, for which the air-entraining agent in the mixture is directly responsible. Crystalline hydrophilic admixture did not affect the air content in fresh concrete for both tested doses, but Shetiya et al. [46] tested mixtures with different concentrations of Penetron crystalline admixture (1% and 2.5% of the cement mass) and found that the mixture with 1% crystalline admixture had the highest air content of all tested concretes.

From each mixture, 14 cubes of dimensions 15 cm × 15 cm × 15 cm and 3 prisms of dimensions 10 cm × 10 cm × 40 cm were prepared. After casting, the concrete specimens were stored under cover for 24 h under laboratory conditions until demolding to prevent water evaporation. After demolding, the specimens were in the mist room at 20 ± 2 °C and RH ≥ 95% until the age of testing. On 3 out of 14 cubes, the compressive strength of 28-day-old specimens is determined according to EN 12390-3 [47], and the results and their corresponding standard deviations are shown in Figure 2.

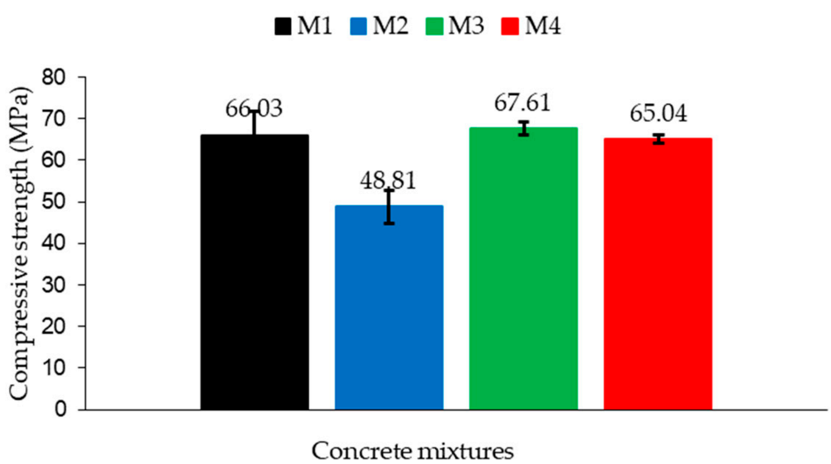
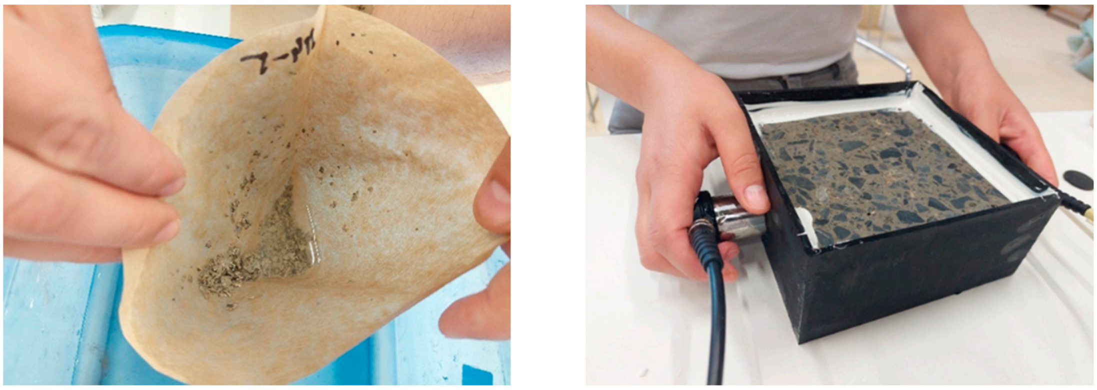


Figure 2. Compressive strength of concrete at the age of 28 days.

From Figure 2, it is evident that CA present in concrete mixtures M3 and M4 did not significantly affect the compressive strength of the concrete, which is in line with the conclusions presented in [32,48,49]. The presence of air entraining agent in mixture M2 significantly reduced the compressive strength of the concrete which is consistent with the well-known fact that air entraining agent negatively affects concrete strength [5].

Furthermore, from each of the eight cubes, one slab of dimensions 15 cm × 15 cm × 5 cm (total of eight slabs) was sawn out to monitor scaling due to freeze/thaw cycles according to CEN/TS 12390-9 [34], and the relative dynamic modulus of elasticity due to freeze/thaw cycles according to Clause 8 of CEN/TR 15177 standard [35] using an ultrasonic pulse transmission time device, and one slab of dimensions 10 cm × 15 cm × 4 cm to measure the spacing factor according to EN 480-11 standard [36]. Half of the slabs intended for scaling and relative dynamic modulus of elasticity monitoring were subjected to freeze/thaw attack in the presence of a 3 mm deep layer of deionized water, and the other half were subjected to freeze/thaw attack in the presence of a 3% sodium chloride solution. Figure 3 shows all the slab samples in the freezing and thawing chamber (producer: Schleibinger, Buchbach, Germany), and Figure 4 shows the monitoring of the amount of scaled material and dynamic modulus of elasticity during exposure to freeze/thaw cycles.

Figure 3. Slab samples in the freezing/thawing chamber.



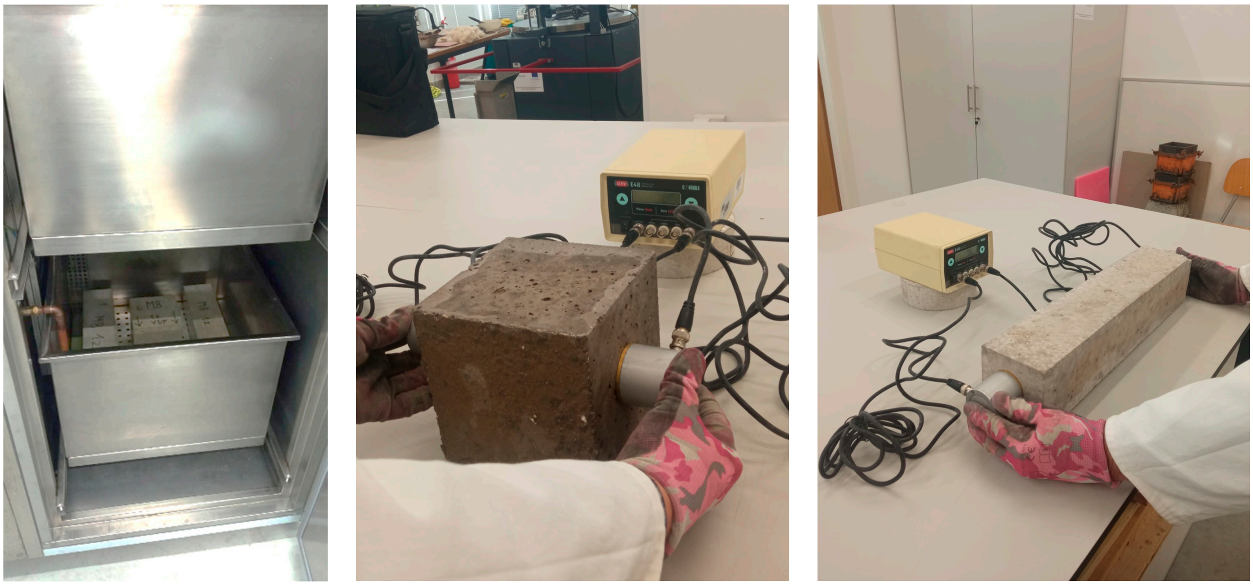
(**a**) (**b**)

Figure 4. Measurements during exposure of panels to freeze/thaw cycles: (**a**) scaling; (**b**) monitoring of dynamic modulus of elasticity.

Figure 5 shows the slab prepared for measuring the spacing factor and the measuring device for the measuring. The remaining 3 out of a total of 14 cubes and 3 prisms of each mixture were subjected to freeze/thaw cycles in the presence of water in the Mis 600 chamber, LT, Slovenia at 28 days of their age and the relative dynamic modulus of elasticity was monitored during freeze/thaw cycles according to Clause 7 of CEN/TR 15177 standard [35]. Figure 6 shows specimens in the chamber immersed in water and measuring of the pulse transmission time on the cube and prism specimens.

(**a**) (**b**)

Figure 5. Spacing factor measuring: (**a**) concrete slab prepared for spacing factor measuring; (**b**) spacing factor measuring device.



(**a**) (**b**) (**c**)

Figure 6. Measuring during exposure of cubes and prisms to freeze/thaw cycles in the presence of water: (**a**) Cubes and prisms immersed in water; (**b**) measuring of the pulse transmission time on the cubes; (**c**) measuring of the pulse transmission time on the prisms.

3. Test Results

The results of scaling tests due to freeze/thaw cycles according to CEN/TS 12390-9 [34] with corresponding standard deviations are shown in Figure 7, and the results of testing the relative dynamic modulus of elasticity due to freeze/thaw cycles according to Clause 8 of CEN/TR 15177 standard [35] are shown in Figure 8. Each point on the curves presented in Figure 7 represents the mean value of four measurements. While the standard deviation of results is expressed for absolute values (Figure 7), this was not possible for relative values (Figure 8). However, it should be noted that the relative values were calculated from the mean absolute values of four absolute measured values, with the exclusion of all values that deviated from the mean absolute value by more than 10%.

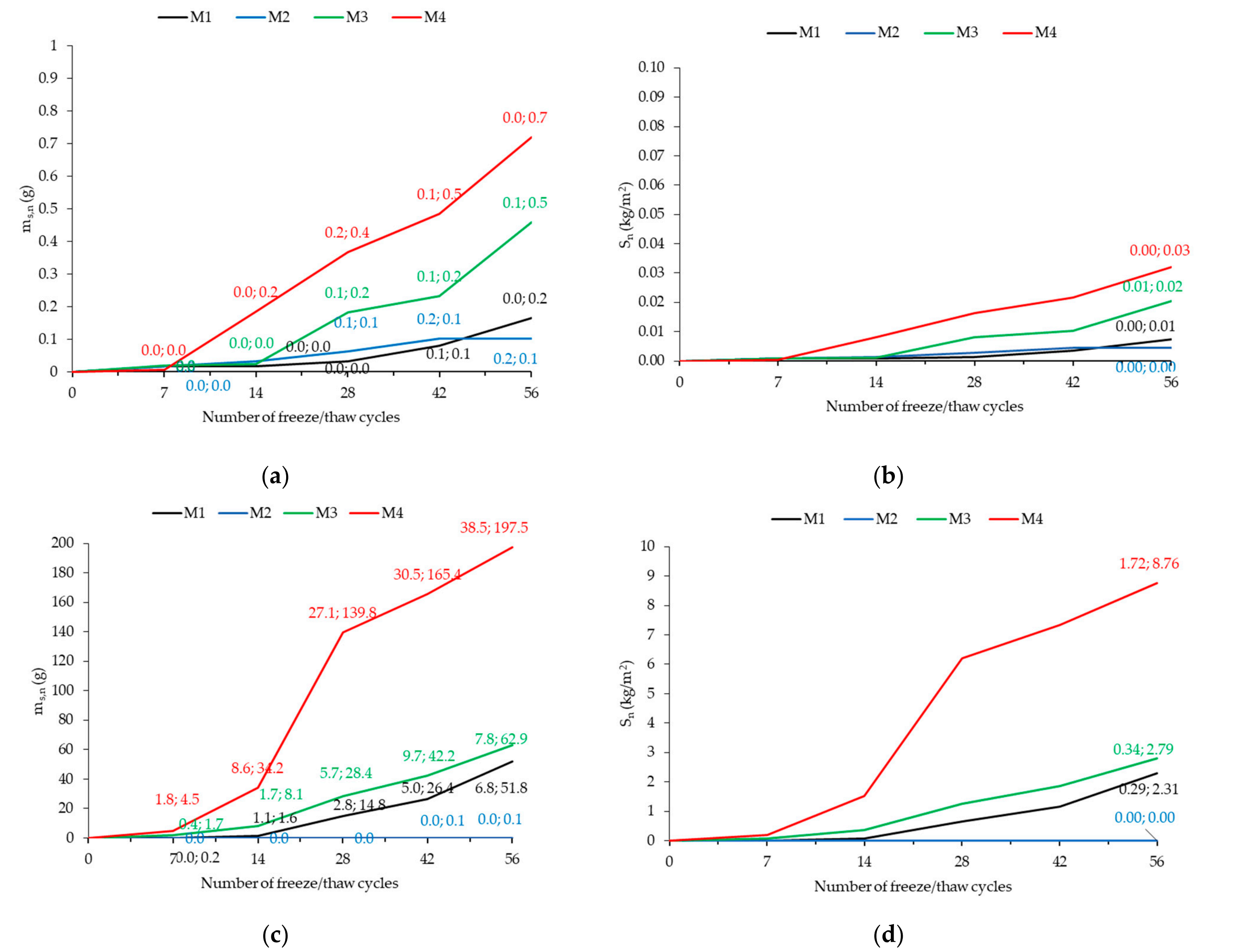


Figure 7. Scaling of concrete slabs: (**a**) scaled material mass due to freeze/thaw cycles in the presence of deionized water; (**b**) scaled material mass related to test surface due to freeze/thaw cycles in the presence of deionized water; (**c**) scaled material mass due to freeze/thaw cycles in the presence of 3% sodium chloride solution; (**d**) scaled material mass related to test surface due to freeze/thaw cycles in the presence of 3% sodium chloride solution.

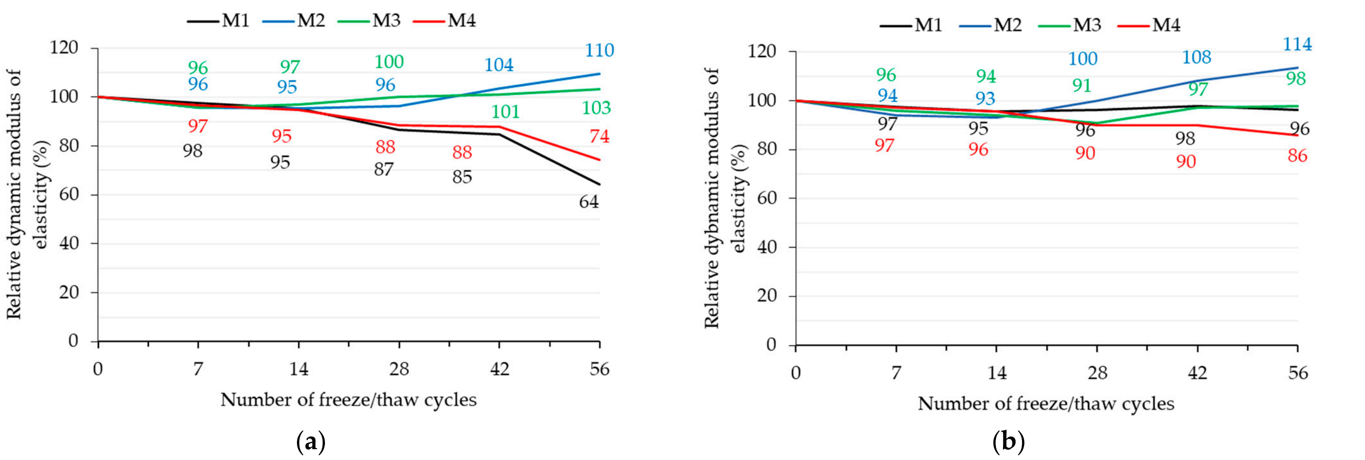


Figure 8. Relative dynamic modulus of elasticity–measured on concrete slabs: (**a**) in the presence of deionized water; (**b**) in the presence of 3% sodium chloride solution.

The results of spacing factor measurements according to EN 480-11 [36] are shown in Figure 9.

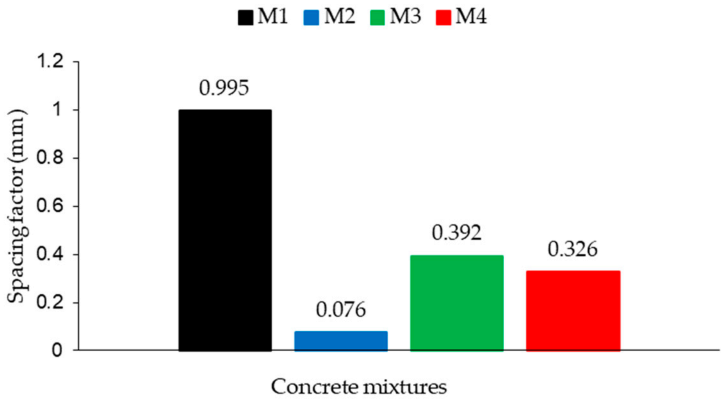


Figure 9. Spacing factor.

The results of testing the relative dynamic modulus of elasticity due to freeze–thaw cycles according to Clause7 of CEN/TR 15177 standard [35] are presented in Figure 10. The relative values were calculated from the mean absolute values of six measurements on cubes and three measurements on prisms, with the exclusion of all values that deviated from the mean absolute value by more than 10%.

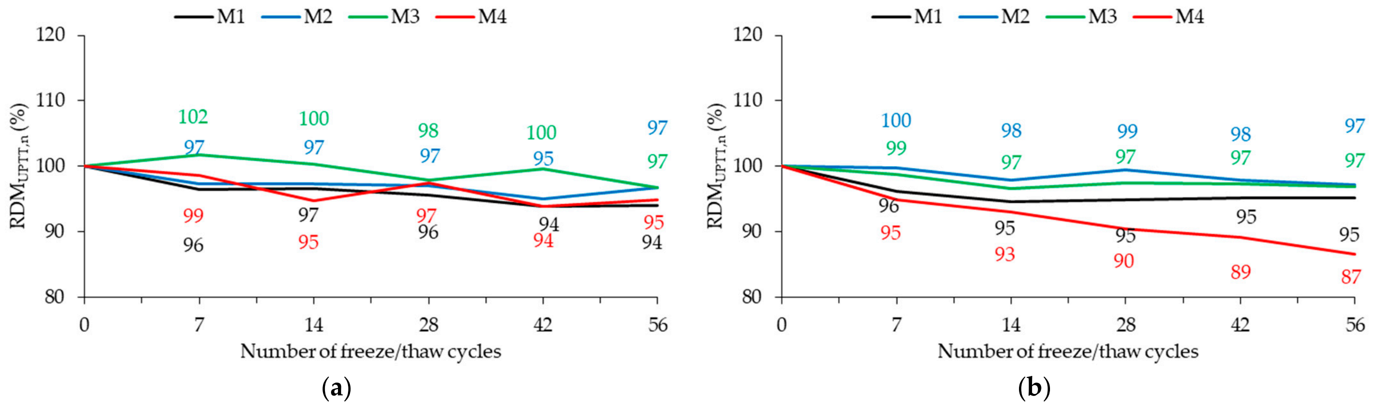


Figure 10. Relative dynamic modulus of elasticity: (**a**) measured on concrete cubes; (**b**) measured on concrete prisms.

4. Discussion

From Figure 7a,b, it is evident that in mixture M2 containing an air-entraining agent, there is a significant reduction in mass loss due to scaling after 56 freeze/thaw cycles compared to mixture M1, while the crystalline hydrophilic additive in mixtures M3 and M4 acted contrary to expectations, increasing the mass loss due to scaling, i.e., increasing the mass loss due to exposure of samples to deionized water. The mixture with a lower proportion of crystalline hydrophilic additive (M3) records a lower mass of scaled material compared to the mixture with a higher proportion of crystalline hydrophilic additive (M4). This is contrary to the observations in [50] where the mass loss ratio due to freeze/thaw cycles is significantly lower in mixtures with the addition of CA compared to the reference mixture. The mixture with the least amounts of scaled material, and therefore the best resistance to freeze/thaw cycles according to this method, and under conditions of exposure to deionized water, is mixture M2, followed by mixtures M1, M3, and M4 in sequence. From Figure 7c,d, it is noticeable that in mixture M2 containing an air-entraining agent, there is a drastic reduction in mass loss due to scaling after 56 freeze/thaw cycles compared to mixture M1, while the crystalline hydrophilic additive in mixtures M3 and M4 acted contrary to expectations, increasing the mass loss due to scaling, i.e., increasing the mass loss due to exposure of samples to a 3% sodium chloride solution. The mixture with a lower proportion of crystalline hydrophilic additive (M3) records significantly lower scaled material mass compared to the mixture with a higher proportion of crystalline hydrophilic additive (M4). The lowest scaled material mass, and thus the best resistance to freeze/thaw cycles according to this method and under conditions of exposure to a 3% sodium chloride solution, is recorded by mixture M2, followed by mixtures M1, M3, and M4 in sequence. When it comes to surface damage due to freeze/thaw cycles, the air-entraining agent is evidently the most effective additive for preventing damage, almost equally effective regardless of whether freezing/thawing occurs with or without salt presence, while the negative effect of the crystalline hydrophilic additive is significantly more pronounced during freezing/thawing in the presence of salt. Such research findings on the impact of the crystalline hydrophilic additive are even worse than the results presented in [51]. Specifically, Manhanga et al. [51] concluded in part of their study addressing the scaling of concrete exposed to a 3% sodium chloride solution that the crystalline hydrophilic additive (in amount of 0.8% per cement weight) does not affect this type of damage caused by freeze–thaw cycles.

From Figure 8a, it can be concluded that the drop in the dynamic modulus of elasticity as a measure of internal damage during exposure to freezing/thawing in the presence of deionized water is most pronounced in mixture M1. Mixture M4 has a smaller drop in the dynamic modulus of elasticity than mixture M1, while mixtures M3 and M2 recorded an increase in the dynamic modulus of elasticity. The increase in the dynamic modulus of elasticity during the freeze/thaw cycles is consistent with the increase in mass during freezing/thawing reported in [52]. The authors in [52] explain that freeze/thaw cycles promote the mobility of pore solution through osmosis. As a result, portlandite dissolved in pore water migrates, facilitating the reactions involved in the self-healing procedure. Additional ice formation in pores likely contributed to the reported mass increase, thus supporting the evolution of the self-healing process.

During exposure to freezing/thawing in the presence of a 3% sodium chloride solution (Figure 8b), the highest drop in the dynamic modulus of elasticity was recorded by mixture M4, while mixtures M1 and M3 recorded a somewhat smaller drop in the dynamic modulus of elasticity, and mixture M2 recorded an increase in the dynamic modulus of elasticity. In terms of internal damage, the air-entraining agent has shown the highest effectiveness in protecting concrete from damages caused by freeze/thaw cycles, but the crystalline hydrophilic additive at a 1% dosage (M3) has shown potential to improve concrete's resistance to freeze/thaw. This is in accordance with [53] where a positive effect on crack self-healing (monitored through the recovery of compressive strength of samples cured in water) of lower CA content has also been recorded, while a negative effect of higher CA content in the total binder quantity was noted.

Figure 9 shows that mixture M2 has the smallest pore-spacing factor, followed by mixtures M3 and M4, while mixture M1 has the largest pore-spacing factor. Considering that this testing method requires a pore spacing factor smaller than 0.2 mm for concrete to be considered resistant to freeze/thaw cycles, according to this method, only mixture M2 could be considered resistant to freeze/thaw cycles. The obtained value of the pore spacing factor of 0.076 mm for the M2 is in accordance with range from 0.07 mm to 0.16 mm for air-entrained concrete [54]. Compared with the mixture M1, the crystalline hydrophilic additive reduced the spacing factor more than 60%, but the obtained values of 0.392 mm (M3) and 0.326 mm (M4) are significantly higher than 0.2 mm requested for concrete to be considered resistant to freeze/thaw cycles. Figure 10a,b confirm the conclusions regarding Figure 8a,b, namely that regarding internal damage, the air-entraining agent has shown the highest effectiveness in protecting concrete from damages caused by freeze/thaw cycles, but the crystalline hydrophilic additive at a 1% dosage (M3) has shown potential to improve concrete's resistance to freeze/thaw cycles. Furthermore, regarding internal damages, the crystalline hydrophilic additive used in this study achieved better performance in enhancing the concrete's resistance to freeze/thaw cycles compared to the crystalline hydrophilic additive used in [51]. Specifically, Manhanga et al. [51] concluded, in part of their research focusing on the impact of the crystalline hydrophilic additive on the strength of cubic specimens exposed to freeze/thaw cycles in the presence of water, that the crystalline hydrophilic additive does not affect this type of damage caused by freeze–thaw cycles. On the other hand, Ferrara et al. [55] have indeed confirmed that the velocity of the ultrasonic wave passage is higher in concrete with a crystalline hydrophilic additive compared to reference concrete during the self-healing process of cracks in concrete, leading to the conclusion that the crystalline hydrophilic additive promotes crack healing. The results presented in this paper are in line with the results shown in Ferrara et al. [55] because cracks that occur as internal damage during freeze/thaw cycles are likely to be healed faster when concrete contains a 1% crystalline hydrophilic additive compared to reference concrete.

5. Conclusions

The paper investigates the effectiveness of the crystalline hydrophilic additive on concrete resistance to freeze/thaw cycles according to standardized EU methods. Scaling resulting from freeze/thaw cycles was observed on concrete slabs exposed to freezing/thawing under two conditions: in the presence of deionized water, and in the presence of a 3% sodium chloride solution. This served as a measure of surface damage. Additionally, the relative dynamic modulus of elasticity was assessed on concrete slabs subjected to freezing/thawing under the same conditions mentioned above. This measurement provided insight into internal damage. Furthermore, the relative dynamic modulus of elasticity was examined on concrete cubes and prisms submerged in water and exposed to freezing/thawing. This served as a measure of internal damage. Lastly, the paper explored the pore spacing factor. This factor is utilized more for predicting concrete behavior in freeze/thaw conditions rather than monitoring actual concrete behavior in such conditions. Based on the obtained results, it was concluded that the most effective protection against surface and internal damage to concrete is provided by the standardly used air-entraining agent, while the crystalline hydrophilic additive has the potential to improve concrete resistance to freeze/thaw cycles in the context of reducing internal damage only if used at a 1% cement weight dosage. A 3% replacement of cement with crystalline hydrophilic additive has shown a negative effect on concrete resistance to freeze/thaw cycles in terms of increased surface and internal damage.

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