Case study

Concrete protection by combined hygroscopic and hydrophilic crystallization waterproofing applied to fresh concrete

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ABSTRACT

Crystallization-based waterproofing is a multi-functional technology which combines hygroscopic and hydrophilic crystallization pore blocking with hydrophobic pore lining. This paper presents experimental findings of investigating dual-crystallization waterproofing engineered treatment (DCE) onto fresh concrete. The DCE has the potential to provide an effective solution to various concrete durability problems associated with all water phases of vapor, liquid and solid. The characteristics of treated and untreated concrete specimens have been investigated experimentally according to ASTM procedures. The DCE system is able to reduce moisture penetration through concrete thus enhances concrete durability. The DCE is able to increase concrete resistance against chloride ion penetration and to reduce damages from freezing and thawing cycles, scaling and ASR. Additionally, the application of DCE technology improves water retention for better cement hydration leading to an enhancement of surface characteristics (adhesion strength and surface smoothness).

1. Introduction

Concrete is a composite material that hardens by the hydration of the Portland cement through a series of exothermic chemical reactions with water yielding a hydrated amorphous porous structure [1–3]. At the initial stages of cement hydration, the loss of water vapor through the capillary network retards the cement hydration reaction [4]. Minimizing water loss from the fresh concrete through the early formation of a pore-blocking waterproofing can assist the hydration process. Water penetration through the concrete network of permeable pores and capillaries [3] is the main cause of chemical deterioration of concrete. The deterioration mechanisms involve chemical reactions and physical interactions between water and concrete components. The formation of calcium hydroxide, $Ca(OH)_2$ as a by-product of cement hydration, increases the pH of the pore solution [5]. This leads to negative impacts on the compressive strength of concrete and on its durability, since the calcium hydroxide does not provide a cementing function and its partially soluble forming the alkaline pore solution [6]. A high porosity of concrete, in particular that of the near surface layer, promotes the transport of soluble harmful chemicals, through the mechanisms of water capillary flow and molecular diffusion [7–9]. This creates several water-associated problems including (1) concrete damage as a result of internal stresses from repeated cycles of freezing and thawing [10], (2) paste deterioration and steel corrosion as a result of chloride ion penetration from sea water or de-icing salts [10–13], (3) concrete deterioration through alkali aggregate reactions such as Alkali Silica Reactions (ASR) [14–16]. Concrete wet conditions cause other problems such as concrete spalling, dusting, and efflorescence.

Traditional waterproofing solution of durability problems in concrete include cementitious coatings [17–23], pore blocking admixtures [24–28], and pore ling treatments [29–33]. Dampproofing is accomplished through pore lining by the formation of water repelling layers that reduce water capillary suction into concrete [34–39]. Water-repellent treatments cannot resist hydrostatic pressures. In a more advanced waterproofing approach, the durability and service life of concrete is enhanced by reducing concrete porosity and water penetration using permeability reducing admixtures [26,27,40] and liquid penetrating surface treatments [41]. This can be accomplished by crystallization waterproofing [25,26,40,42]. The formed crystals within concrete pores create numerous flow obstacles and restrict the flow water under pressure [43], the medium that is required for most of the harmful reactions [44]. They have a distinguished self-healing capacity through the formed crystals in the cracks with a similar composition to that of C-S-H gel [24, 43]. These enhancements may greatly reduce life cycle costs.

However, many of the integral waterproofing materials are based on the formation of hydrophilic pore blocking materials through silicate-based mineral compounds which interact with water in the liquid phase only [22,42,45–51]. A crystallization waterproofing system that interacts with water vapor as well as liquid leads to much better performance. In recent publications, it is demonstrated that multi-functional crystallization waterproofing systems have the ability to actively manage water in all phases by combining hygroscopic and hydrophilic crystallization with hydrophilic pore lining. The dual-crystallization waterproofing engineered topical treatment (DCE) has been demonstrated to have the potential to provide an effective approach for treating fully cured new as well as existing old concrete [52]. This waterproofing technology is based on the formation of two types of crystals (hydrophilic and hygroscopic) and a hydrophobic layer within a surface section of the treated cementitious materials. The surface applied solution penetrates within the concrete by capillary suction and diffusion. Then, the crystals are produced through multiple and simultaneous chemical reactions which occur within the concrete pores. The hygroscopic and hydrophilic active ingredients of DCE react with cement hydration by-products and consume a fraction of the undesired $Ca(OH)_2$, in producing a protective material. When the DCE material is applied to fresh concrete, these reactions are accelerated by the increase in concentration of the active chemicals, as a result of water consumption by cement hydration reactions and evaporation. The resulting crystals fill and block the concrete pores and capillary network. An image of scanning electron microscope for the crystalline system has been reported elsewhere [53]. Hence the pore blocking effect of DCE minimizes water transport through the concrete matrix. Their hygroscopic and hydrophilic characteristics provide them with the capability to interact with water in liquid and vapor phases and hence create larger obstacles for water permeation flow. The hygroscopic crystals interact with water vapor and grow with moisture adsorption. This mechanism contributes to concrete protection by two mechanisms: (1) it enhances pore blocking and (2) it consumes water vapor leading to a relatively dry concrete substrate that prevents moisture associated problems. The hydrophilic crystals swell when in contact with water and create larger flow obstacles. These two mechanisms are reversible: Upon drying, these crystals release back its moisture content, allowing the concrete to breath. In addition to the formed crystals, an insoluble hydrophobic molecular layer is adsorbed on the surfaces of the pores and become an integral part of the concrete [54]. This layer increases the surface tension of water and thus reduces water penetration by capillary suction in hardened concrete. Such a hydrophobicity ensures dry sub-surfaces and preventing moisture build up within the concrete. The detailed DCE mechanism is presented in a previous paper [52].

A similar waterproofing system is demonstrated to have the potential to provide an effective durability solution when added as an enhancer to concrete mixture at the time of batching [55]. For some concrete structure, project specifiers demand a topical surface treatment that can be applied on freshly poured concrete, so that the waterproofing ingredients do not interfere with the concrete mix design process. A knowledge gap has been identified in the published literature on the durability performance of DCE waterproofing when applied onto fresh concrete. Additionally, the effect DCE waterproofing application onto fresh concrete on water retention is also identified. This research targets to fill these knowledge gaps. The main goal of this contribution is to investigate the durability parameters of DCE for its use as a one-step solution to several water-associated problems in concrete pavements, highways, bridges and airport runways. The research aims of this experimental study include (1) demonstrating the applicability of DCE onto fresh concrete without negative impacts on concrete curing and hydration process, (2) performing a parametric study of the effectivity of DCE in increasing the concrete resistance against chloride ion penetration and reducing damages from freezing and thawing cycles, scaling and ASR, and (3) studying the effect of DCE on the surface characteristics of concrete (adhesion strength and surface smoothness).

2. Experimental

The experimental program included measurements of various mechanical and durability characteristics of concrete treated with DCE aqueous solution applied onto freshly poured concrete at a coverage rate of 3.91–4.93 m^2/L (160–200 ft^2/gallon), according to the product specifications [54]. The dependent parameters included water retention in fresh concrete, compressive strength, adhesion strength, resistance to chloride ion penetration, resistances to freezing-and-thawing cycles, scaling, and ASR, measured for DCE treated specimens and control specimens. All tests were performed according to the applicable standard procedures specified by ASTM for each experimental parameter. Three replicates were made then average values of measurements were reported and standard errors were determined and indicated in the plots as error bars and in the tables as STD. The experiments were made in the independent laboratories of Construction Technology Laboratories, Inc. (CTL Group, 5400 Old Orchard Road, Skokie, IL, USA), and Construction Material Testing (CMT, Des Moines, Iowa, USA), with available data testing certificates.

2.1. Concrete constituent materials and mix proportions

Materials used included Portland cement (type I/II) which conformed to ASTM C150 specifications, crushed limestone as coarse aggregates, natural graded sand as fine aggregates (with about 0.85 % smaller than 2.36 mm). In the ASR experiments, two types of

Table 1

The used mix designs.

Component	Ordinary concrete OPC				Mortar				Fly ash modified concrete	
	C1		C2		C3		C4		C4-WRC20	
Cement	256 kg	563 lb	233 kg	514 lb	0.113 kg	0.248 lb	279 kg	614 lb	223 kg	491 lb
Coarse aggregates	872 kg	1921 lb	782 kg	1722 lb	none	none	677 kg	1490 lb	677 kg	1490 lb
Fine aggregates	584 kg	1287 lb	648 kg	1428 lb	0.290 kg	0.639 lb	672 kg	1479 lb	672 kg	1479 lb
Class C fly ash	none	none	none	none	none	none	none	none	55.8 kg	123 lb
Air entrainment	none	none	0.6/cwt	0.6/cwt	none	none	6%	6%	6%	6%
Water reducer	none	none	none	none	none	none	118 m L	4.0 lq oz	118 m L	4.0 lq oz
w/c	0.48	0.48	0.43–0.48	0.43–0.48	0.415	0.415	0.39–0.47	0.39–0.47	0.39–0.47	0.39–0.47

Table 2

The testing ASTM procedures and conditions for each of the investigated experimental variable.

Tested parameter	Scaling resistance	freezing and thawing	adhesion strength	coefficient of friction	Water retention	chloride ion penetration	ASR
mixture	C1	C2	C2	C2	C3	C4-WRC20	C4
w/c	0.48	0.48	0.43	0.43	0.415	0.4	Variable 0.39–0.47
DCE coverage ft^2/gallon	200	175	175	175	200	160	160
DCE coverage m^2/L	4.91	4.3	4.3	4.3	4.91	3.93	3.93
Curing agent	Yes	Yes	Yes	Yes	Yes	None	None
Test Standard	ASTM C672	ASTM C666	ASTM D7234	ASTM F609	ASTM C156	ASTM C1202	ASTM C1567

coarse aggregates were used for comparison. These include non-reactive crushed limestone aggregates with an average size of 1 inch (2.54 cm), obtained from Martin Marietta Ames Mine and reactive gravels obtained from Platte River. Each of them is mixed with an equal proportion of natural sand from Hallett Materials North Des Moines. The air entrainment and the water reducing agents were obtained from Euclid Admixture (Cleveland, Ohio, USA), GRT SA-50 and GRT 400-NC, respectively. Pavix liquid solution (patented product [54]), obtained from International Chem-Crete Corporation, Richardson, Texas, U.S.A, was used as the DCE material. The DCE is composed of a system of hygroscopic, hydrophilic and hydrophobic active ingredients with a total solid content of about 15 % [54]. It has a specific gravity of 1.1, a viscosity of 2.4 cP, and a freezing temperature of −4 °C. Class C fly ash was used as a partial replacement of cement in the modified concrete specimens. The fly ash had a specific gravity of about 2.6 and it conformed to ASTM standards (ASTM C618–12 2012; ASTM C989/C989M–12 2012). A water based white pigmented wax-based curing compound (nonvolatile content of 32 % by weight) was used after treatment with DCE, for some tests as indicated below. The used chemicals included standard solutions of NaCl, NaOH and CaCl$_2$ (4% by weight) conforming to ASTM requirements.

Experiments were performed using both mortar and concrete specimens utilizing three replicates for control and treated samples. Table 1 lists the used mix designs for the tested concrete and mortar specimens. These include a concrete mix referred to as Iowa DOT C4-WRC20 prescribed by the Iowa Department of Transportation [56], in which Class C fly ash was added at 20 % dosage as a replacement of cement, the air entrainment was added at 6% and the amount of added water reducer was 118 mL (4.0 lq oz)/100 cement weights. This is typically recommended for pavements and bridges applications. Other concrete mixes were used in some tests as mentioned below.

2.2. Procedures

Table 2 lists the ASTM procedures and the types of mixtures used for investigating each experimental parameter. Experiments for investigating the scaling resistance were made by exposing treated and control concrete surfaces to freezing-and-thawing cycles in the presence of deicing chemicals (4% by weight CaCl$_2$), according to ASTM C672 using C1 mixture (as listed in Table 1). They were fabricated and cured in accordance with ASTM C672. The water to cement ratio (w/c) was 0.48 and the slump for fresh concrete was 14 cm (5.5 in.). Experiments for investigating the effect of freezing and thawing cycles in water were executed according to the standard procedures of ASTM C666 using C2 mixture (as listed in Table 1) with w/c ratio of 0.48. The measurements included length change, mass loss and change in relative dynamic modulus. The relative dynamic modulus was measured according to the standard procedures of ASTM C215. Similar specimens (C2) with w/c of 0.43 and a slump for fresh concrete of 7.6 cm (3 in.) were used for measuring the adhesion strength according to the standard procedures of ASTM D7234. Similar concrete specimens (C2) were used to determine the surface smoothness by measuring the coefficient of friction according to the standard procedures of ASTM F609. Experiments for investigating the effect of DCE on water retention in fresh concrete were performed according to the procedures of ASTM C156 using mortar specimens (C3) (composed of 25 % cement, 65 % Ottawa graded sand and 10 % water, as listed in Table 1). Moisture readings were taken after 24 and 72 h of casting, for control and treated specimens. The same mortar specimens were used for
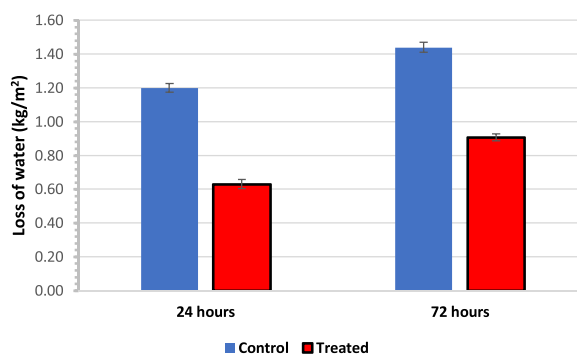
Fig. 1. Water loss from mortar specimen treated with application of DCE and the curing compound compared to control specimen, from tests according to ASTM C156 showing the error bars for measurements at 24 and 72 h.

Table 3

Compressive strength and adhesion strength for control and DCE treated mortar specimen (also shown are the values of the standard deviations (STD)).

Specimen	compressive strength (MPa)			adhesion strength (MPa)	
	average	STD		average	STD
Control specimen	47.4	1.47		1.43	0.117
Treated specimen	47.1	1.92		1.61	0.0827
Percentage Difference	−0.6%			13 %	

investigating the effect of DCE on the compressive strength after 195 days. In all these experiments, a curing agent (ASTM C309 Type I, Class B) was applied on the control specimen and on the treated specimen after DCE treatment. After casting the specimen according to relevant ASTM procedures, the DCE was applied by brushing after demolding.

Experiments for studying the effect of DCE on resistance to chloride ion penetration were made using concrete modified with Class C fly ash with prescribed mix design commonly used for pavements (IDOT C4-WRC20 as listed in Table 1). The application rate of DCE was 3.93 m^2/L (160 ft^2 per gallon). The current passage was measured after 7 days of curing according to ASTM C1202. The electrical current passage through treated and control concrete specimens was measured as functions of time, according to ASTM C1202. One side of the concrete specimen (IDOT C4-WRC20 with a w/c of 0.4) was subjected to NaOH, while the side was subjected to NaCl. The performed experiments included cases with the application of DCE to NaOH side, to NaCl side, and to both sides. The total charge passed was determined by estimating the area under the current time curve for 360 min according to ASTM C1202 method. The effect of DCE on ASR was investigated using mortar specimens mixed with equal proportions of fine and coarse aggregates, according the prorations in the prescribed mix design commonly used for pavements (Iowa DOT C4 mix design [28] as listed in Table 1), at three w/c ratios of 0.39, 0.43 and 0.47. The size of the coarse aggerates was sized down to be less than 4.75 mm (No. 4), as required by ASTM C1567. The length change due to ASR was measured as a function of time under ASR conditions according to the standard procedures of ASTM C1567 for control and treated specimens for the two cases of reactive aggregates (Platte River Gravel) and non-reactive aggregates (Ames Mine).

3. Results and discussion

3.1. Crystallization mechanism and mechanical characteristics

The crystal formation during the normal curing process of concrete has a positive water retention effect during the early stage of cement hydration. Fig. 1 shows experimental results of water loss from control and DCE treated mortar specimens after 24 and 72 h from tests according to ASTM C156. These results (obtained from moisture readings for control and treated specimens) reflect the effect of DCE on water retention in fresh concrete, as per ASTM C156, which is commonly used in qualifying curing agents. The test evaluates the ability of DCE to hinder the escape of water from the surface of treated mortar during the early curing period. These results confirm ability of the investigated DCE system to control moisture within the mortar during the early stages of cement hydration. Obviously, the moisture retaining ability of fresh concrete is improved by the application of DCE and the curing compound by a percentage in the range of 40–50 %. The moisture retaining ability of DCE reflects its contributing to an appropriate concrete curing condition. This is accomplished by retaining water in fresh concrete to enhance the hydration reactions, since the rapid escape of water may lead to strength loss and cracking. Retaining water in the fresh concrete is essential for enhancing the cement hydration process, and for attaining the required strength. Enhanced curing conditions would prevent shrinkage, cracking, and the loss of abrasion resistance of the cured concrete. In addition, the retained water remains available for further crystallization growth. The two-pronged system also helps in temperature control, which reduces curling and other detrimental reactions.

Table 4

Slip index and coefficient of friction at various test angles for DCE treated and untreated surfaces.

Parameter	Specimen	Test angle				average
		0	90	180	270	
Slip Index	Control specimen	>8	>8	>7.9	>8	>8
	Treated specimen	>8	>8	>8	>8	>8
Coefficient of friction	Control specimen	>0.8	>0.8	0.79	>0.8	>0.8
	Treated specimen	>0.8	>0.8	>0.8	>0.8	>0.8
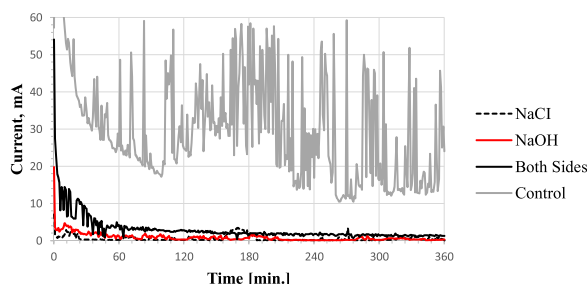
Fig. 2. Curves of current passage through treated and control concrete specimens as functions of time. Curves for treated specimens include treatment from the side exposed to NaOH, treatment from the side exposed to NaCl and treatment from both sides.

Table 5

Total charge passed and percentage reductions.

Parameter	Control	DCE at NaCl side	DCE at NaOH side	DCE at both sides (NaOH and NaCl)
Charge passed (Coulombs)	646	13	18	60
Percentage reduction		98 %	97 %	90 %

Table 3 lists the obtained results of compressive strength for control and treated mortar specimen after 195 days. No major difference in compressive strength of the tested mortars was observed when concrete surface is treated with DCE. In fact, an enhancement of the compressive strength of concrete specimen with DCE technology was reported in a previous study [57]. Also, an enhancement of concrete compressive strength was reported when similar triple effect waterproofing crystallization material was added as an enhancer to concrete mixtures at the time of batching [58]. The current and the previous findings confirm that the partial utilization of water for crystallization does not compete with the hydration process and the application of DCE on fresh concrete has no negative impacts on concrete mechanical properties. The results of adhesion strength are listed in Table 3. DCE improves the adhesion strengths by 13 %. This is due to dryness of the surface as a result of the consumption of any available moisture content in crystal growth. The effect of applying DCE technology on other mechanical properties of concrete has been demonstrated in another publication (by applying DCE to cured concrete) [59]: No major differences were observed in the pull off strength of untreated and treated concrete. A slight improvement in the abrasion resistance for treated concrete was obtained [59]. Table 4 lists the obtained slip index at various test angles. It indicates that no significant differences in the skid resistance could be detected for treated and untreated surfaces.

3.2. Effect of DCE on resistance to chloride ion penetration

Fig. 2 presents curves of electrical current passage through treated and control concrete specimens as functions of time. The decrease in the passage of electrical current through concrete provides an indirect measurement of concrete's ability to resist chloride ion penetration. In a previous investigation of DCE on cured concrete, results from ASTM C1202 testing and chloride bonding were inline [52]. For DCE application on fresh concrete, only results of electrical current passage are presented. Similar low curves were obtained for cases with DCE applied to NaOH side, to NaCl side, and to both sides. From the plots in Fig. 2, the area underneath each curve is integrated over during the six hours test period to obtain the total charged passed in ampere-seconds, or coulombs. The obtained total charge passed is listed in Table 5 for each case.

Fig. 2 shows that control specimens allowed a noticeable level of current passage. This level of charge passage through the untreated concrete is higher than the 100 coulombs limit designated by the ASTM C1202 for negligeable chloride ion penetration, but it is in the range of 100–1000 designated by the ASTM for very low chloride ion penetration. The low chloride penetration level is obtained since the control concrete mix design includes fly ash and it is made at low w/c ratio as reported in previous studies [9]. On the other hand, for all cases with DCE (regardless of the side of the application), a negligeable chloride ion penetration was observed (all values are < 100 coulombs). In fact, there are minor differences in the charge passage for various cases of DCE treated specimen surfaces, whether it is from the NaOH side, NaCl side or both sides. The control specimen is much more permeable to chloride ion flux due to
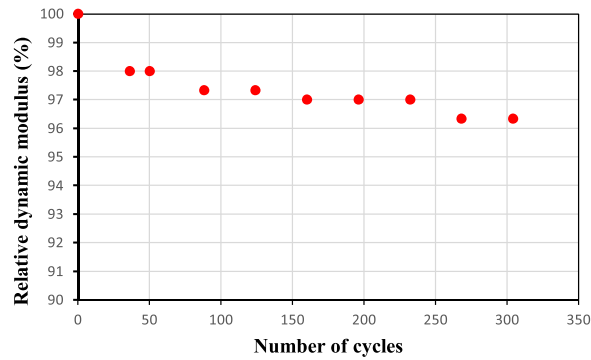
Fig. 3. Relative dynamic modulus (%) as a function of number of cycles of freezing and thawing.
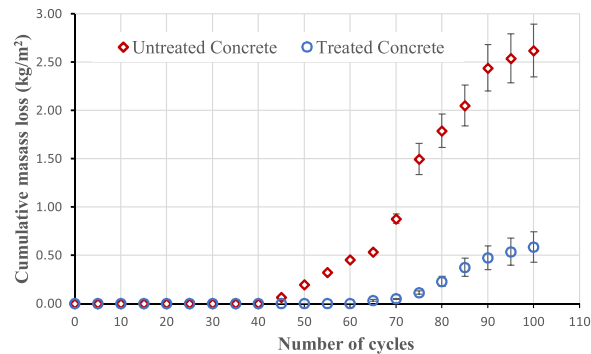

Fig. 4. Cumulative mass loss as a function of number of cycles of freezing and thawing in the presence deicing chemicals (CaCl$_2$).

concrete porosity and the high level of moisture saturation resulting from water penetration. It has been demonstrated that the diffusivity of chloride ion increases with increasing concrete porosity and saturation [9]. This is because water is the carrier of the hurtful chemicals by transport fluxes including ionic diffusion and water penetration. The negligible values of charge passage indicate a negligible permeability and a denser concrete that is less susceptible to chemical attack. For treated specimens, there is a reduction in water permeability of concrete resulting from crystallization pore blocking by the DCE. This is accomplished by the dynamic hygroscopic crystallization system, which consumes free moisture in the pores and thus eliminate the medium for the activity of chloride ions. DCE treatment involves also the role of the hydrophobic layer within pores that maintains relatively dry concrete pores and assists in preventing the continuity of water medium. Thus, it hinders the diffusional flux of soluble chemicals into concrete structure providing effective protection. This clearly reflected in the major reductions in the total charge passed as listed in Table 5. At least 90 % reduction in the percentage chloride ion penetration was obtained for treated concrete with DCE. One side treatment has slightly higher percentage reduction (97–98 %) than two sides treatment. Such a high reduction in chloride ion penetration indicates the ability of the DCE system to reduce chloride-associated problems such as corrosion of reinforcing steel and chloride binding resulting from the chemical attack of chloride ions to the concrete matrix [10–13]. Such a protection from chloride ion penetration prevents the propagation of cracks and surface dusting. A similar performance was reported for the efficacy of hydrophilic crystalline waterproofing admixtures in reducing chloride ion penetration according to rapid chloride permeability test (ASTM C1202) [27,46]. The use of hydrophilic crystalline admixture lead to a percentage reduction in chloride ion penetration is in the range of 20–25 % for ordinary Portland cement concrete [27]. Similarly, for a commercial crystalline admixtures, Azarsa et al. [46] reported a percentage reduction 20 % using the same ASTM. MCE seems to achieve much higher reductions. This might be attributed to its combined hydrophobicity and crystalline pore blocking functions.

3.3. Effect of DCE on concrete resistance against freezing and thawing cycles and scaling

Fig. 3 shows the percentage relative dynamic modulus (%) as functions of number of cycles of freezing and thawing for concrete treated with DCE. Fig. 3 shows minor changes in the relative dynamic modulus, as a durability factor, with cycles of freezing and thawing indicating a high durability of treated concrete. This performance is obtained from the role of DCE to the reduction in water penetration through concrete and from the interaction of the dynamic crystallization system with water, as explained above. The effective blocking mechanism of the DCE results in a major reduction in the available free water in the concrete subsurface, and hence it eliminates the possibility of freezing and eliminates the internal stresses resulting from freezing associated with water volume expansion. The reaction reduces the chances of scaling, as also reported in a previous paper [52]. In this experiment, the measured
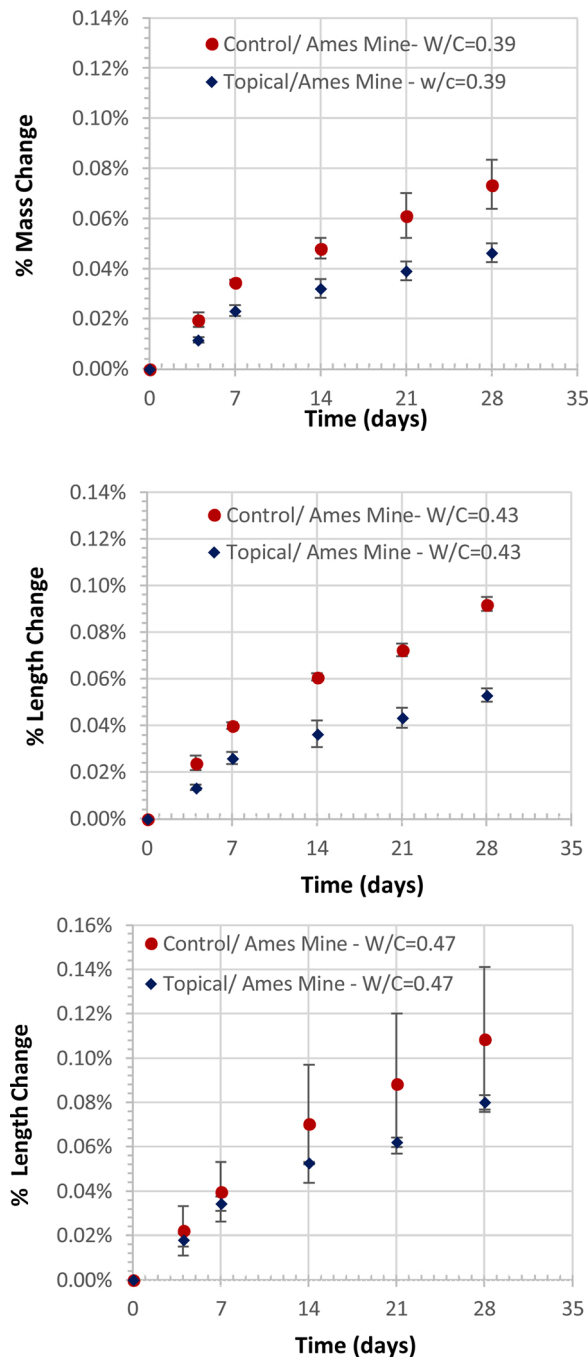
Fig. 5. Percentage length change from ASR for non-reactive aggregates (from Ames Mine) at three different w/c ratios, from tests according to ASTM C-1567, showing the averages of three replicates with error bars.

average percentage length change at 304 cycles was 0.019 %, which was smaller than the maximum allowable percentage length change set by ASTM C666 (0.10 %). This percentage length change (0.019 %) was also lower than that obtained when DCE was applied on fully cured concrete (0.039 %) as reported in a previous publication [52]. This may indicate that DCE application on fresh concrete provides a better performance for reducing damages from cycles of freezing and thawing. However, this needs further experimental investigation since comparison may not be fully valid due to variations in the mix design between the current and the previous study.

Fig. 4 shows curves of cumulative mass loss for treated and control concrete surfaces exposed to freezing-and-thawing cycles in the presence of deicing chemicals. Major reductions in the cumulative mass loss for treated compared to untreated concrete was obtained at all numbers of cycles after 50, indicating a significant increase in the scaling resistance. Treating a concrete surface with DCE
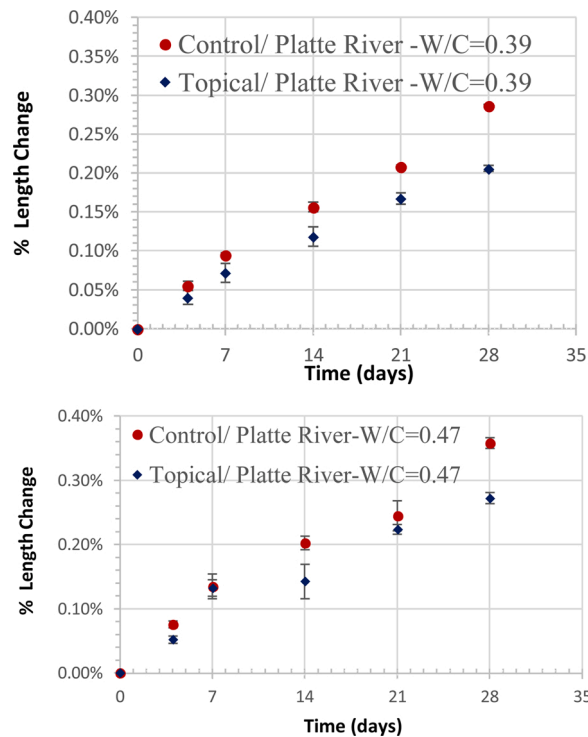
Fig. 6. Percentage length change from ASR for reactive aggregates (from Platte River) showing the curves at two different w/c ratios, from tests according to ASTM C-1567, showing the averages of three replicates with error bars.

reduces the scaling damage by about 94 % after 70 cycles testing according to ASTM C666. This has an important reflection on the durability of concrete.

As explained above, this is obtained from to the reduction in water permeability of concrete as a result of the effective crystallization mechanism of the DCE that blocks the pores, since water is the carrier of the harmful deicing chemicals. This is also resulting from the additional hydrophobic characteristics of the DCE system that ensures concrete dryness. The DCE mechanism minimizes the transport of the chloride ions from the deicing salts through concrete dryness (as shown in Fig. 2 and Table 5). In addition, reducing water penetration by pore blocking reduces the impact of internal stresses by freezing. Visual observations of the surfaces of the two specimens after 100 cycles of freezing and thawing revealed a severe scaling on the surface of the control specimen; for which the rating of the surface condition according to the standard (ASTM C672) was 4 or 5, since the coarse aggregates were visible almost over the entire surface. However, for the treated specimen, slight surface scaling after 100 cycles was observed. These results indicate that DCE has an effectiveness role in eliminating freezing internal stresses and the associated water volume expansion. In addition, it reduces the chemical attack of chloride ion to the paste of the concrete [60]. This is confirmed by observing less paste deterioration, as most of the aggregates remained covered with paste.

3.4. Effect of DCE on concrete resistance against ASR

The results of the effect of DCE on ASR are shown as plots of percentage expansion versus time in Figs. 5 and 6 for two types of aggregates (reactive and non-reactive) at different w/c ratios. Each figure compares the obtained percentage length change for treated and control mortar specimens. Overall, DCE leads to higher dimensional stability as indicated by the lowered curves of the length change below those of control specimens. For evaluating the results of accelerated mortar bar tests according to ASTM C1567, the allowable limit is set at 0.1 % for ASR expansion at 16 days (or 14-days according to some literature [6162]). When the measured percentage expansion is less than 0.1 % for certain aggregates, there is a low risk of deleterious expansion when they are used in concrete under field conditions. A mortar that expands more than 0.10 % at 16 days after casting are indicative of potentially deleterious expansion. For untreated mortar with non-reactive aggregates, the percentage length change is lower than the allowable limit set by ASTM C1567 (percentage expansion ≤0.1 % at 16 days), hence they are labeled as non-reactive. However, for untreated mortar with reactive aggregates, the percentage length change is higher than the allowable limit. The measured the percentage length change is still below the 0.2 %, and according to ASTM C1567 this confirms the aggregates reactivity without the need for additional testing using ASTM C 1293. When the results fall in the range of 0.1–0.2% expansion, the ASTM C1567 test is considered inconclusive, and hence the aggregates require further testing to finalize a conclusion whether or not they are reactive [62,63]. This is done using one year testing according to ASTM C1293 [64]. However, previous records of the use of aggregates from Platte River confirmed their ASR reactivity. Some researchers believe that the exposure period of 16 days is not sufficient for confirming low risk of aggregates reactivity
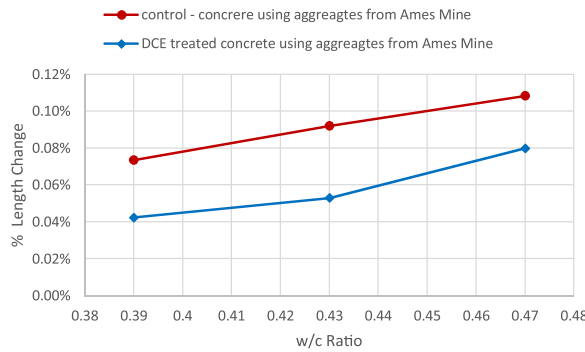
Fig. 7. Percentage length change after 28 days exposure to ASR environment for the non-reactive aggregates (from Ames Mine) as function of w/c ratios for treated and non-treated mortar.
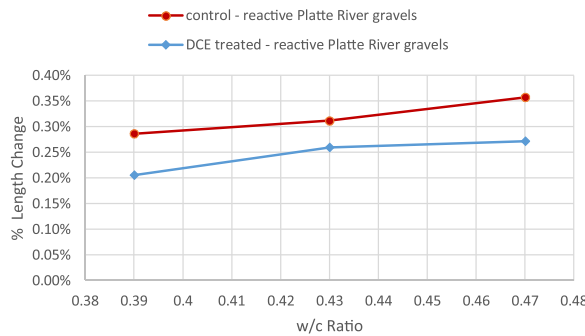

Fig. 8. Percentage length change after 28 days exposure to ASR environment for the reactive aggregates (from Platte River) as function of w/c ratios for treated and non-treated mortar.
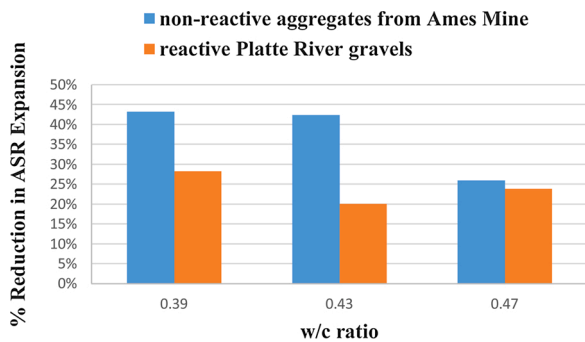

Fig. 9. Percentage reduction in ASR percentage expansion after 28 days exposure to ASR environment for two types of aggregates and using three different w/c ratios, from tests according to ASTM C-1567.

[15]. Hence, some researchers [61] prefer the use of 0.10 % at 28 days as an indication of low ASR risk in the field condition.

Figs. 7 and 8 compare the 28-days percentage expansions for treated and untreated mortar for the two types of aggregates. All the plots in Figs. 7 and 8 show that increasing the w/c ratio increases the damages from ASR. This can be explained by the increase in the porosity and mortar wetting with increasing w/c ratio: it is well documented in literature that fatal ASR attack requires the presence of sufficient moisture in concrete (80–90 % relative humidity as well as sufficient alkaline conditions, in order to facilitate the dissolution of the reactive silica (SiO_2) aggregates [16]. When DCE is used, significant reductions in percentage expansion were obtained at all w/c ratios at 28 days as shown in Figs. 7 and 8. This positive durability performance results from the role of the active ingredients of the DCE system reducing calcium hydroxide content in pores. Additionally, the product of DCE reactions with calcium hydroxide fills the pores and expands with water due to its hydrophilic behavior. This mechanism reduces the availability of free water by utilizing it in crystal growth and thus reduces the internal humidity, as reported in a previous paper for the case of adding the crystallization system to concrete mixture [58]. These combined mechanisms reduce the level of concrete wetting, the ability of solvation of calcium hydroxide, the severity of the pore solution for ASR through minimizing the availability of hydroxide ions to react with the aggregate and

silicates. Pop-outs are minimized by the reduction in aggregate moisture. Fig. 9 shows the obtained percentage reductions in ASR damage for the two types of aggregates at the three w/c ratios. At all investigated w/c ratios, the use of DCE reduces the damage from ASR significantly. The obtained percentage reductions of ASR are within the range of 20–43 %. This percentage reduction in ASR depends on the type of aggregates and the w/c ratio. Overall, the mechanism of ASR mitigation by DCE is based fundamentally on reducing the reaction activities (reactants and medium) through the role of MCE in leading to (1) a reduction and discontinuity in moisture, which is the vehicle for aggressive ions and the medium for ASR process, (2) a reduction in the alkalinity due to the reactivity of MCE active ingredients and thus reducing the severity of the pore solution and (3) Creating a hydrophobicity that minimizes the wetting of the aggregates and thus reduces the contact of the alkaline pore solution with the active silica sites at aggregate surface. All with no reduction in strength.

4. Conclusions

The application of dual crystallization waterproofing is demonstrated to have the potential to provide an effective durability solution. The DCE application on fresh concrete promotes the formation of hygroscopic and hydrophilic crystals and the hydrophobic layer within the curing process without requiring additional efforts after full curing. The DCE system assists in maintaining a suitable curing environment for concrete by improving the moisture retaining ability of fresh concrete by 40–50 %. The application of DCE on fresh concrete does not result in a noticeable adverse impact on strength and surface smoothness of treated concrete. The DCE improves concrete resistance against chloride ion penetration, cycles of freezing and thawing damage, scaling, and ASR. The DCE increases the resistance against chloride ion penetration by at least 90 %. The DCE leads to minimal changes in the percentage relative dynamic modulus (<0.019 %) that is smaller than the maximum allowable percentage length change set by ASTM C 666 even above 300 cycles of freezing and thawing. The DCE reduces scaling damage by about 94 % after 70 cycles and reduces ASR damages by percentages ranging from 20 % to 43 % depending on the type of aggregates and the w/c ratio.

Declaration of Competing Interest

The authors report no declarations of interest.

Acknowledgments

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