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Multi-crystallization enhancer for concrete waterproofing by pore blocking

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HIGHLIGHTS

- MCE combines the mechanism of hygroscopicity, hydrophilicity and hydrophobicity.
- MCE reduces porosity and water penetration by a dynamic crystal growth mechanism.
- MCE enhances workability, compressive strength and abrasion resistance.
- MCE enhances concrete durability.

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ABSTRACT

Concrete porosity and moisture penetration create several durability problems. The recent industrial solutions are based on the use of integral waterproofing materials. This paper responds to the need for developing an efficient pore blocking waterproofing aqueous solution that is added with mixing water at the time of batching, without requiring further work after curing. The paper presents an innovative multi-crystallization enhancer (MCE) which combines hygroscopic and hydrophilic crystals with a hydrophobic characteristic, all integrate in the concrete structure. The performance of the MCE system was investigated experimentally using two types of prescribed mix designs of Illinois Department of Transportation (IDOT), including plain concrete and modified concrete using fly ash. The investigated parameters included permeable pores, relative humidity in pores, water absorption, moisture emission, density, compressive strength, abrasion resistance and workability. Experiments were performed according to ASTM procedures. Test results showed that MCE reduced the porosity and the permeability of concrete. MCE also reduced the humidity within pores and actively managed free moisture through its dynamic crystal growth mechanism. Furthermore, MCE increased the workability, the compressive strength and the abrasion resistance. MCE is an effective solution to concrete durability problems.

1. Introduction

The characteristics of concrete, as a porous material, are governed by its constituents, compositions, and chemical additives [1]. Thermal, chemical and biological attacks create various distresses to concrete durability and to the sustainability of structures subjected to water. These concrete structures include road pavements [2], which are in a continuous growth worldwide [3]. Concrete pavements are associated with major economic losses related to their construction, maintenance and rehabilitation [4]. Problems of concrete pavements include thermal attack from freezing and thawing cycles [5], chemical attack from alkali-silica reactions [6] and corrosion of steel due to chloride ion diffusion [7], and biological attack due to mold growth [8]. Internal moisture provides a carrier and a diffusion medium for all types of attacks. Water-associated problems result from water penetration, which is dependent on many factors including concrete mix design, content of supplementary cementing materials (SCMs) and other admixtures, pore size and distribution, air voids, and transport characteristics. Water penetrates concrete structure by the capillary absorption and/or by the water flow through permeable capillary pores under a hydrostatic pressure. Concrete permeability can be reduced by blocking the capillary network in the cement paste, while capillary absorption can be reduced by making the cementi-

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tious surfaces water-repellents. Concrete durability and service life are then governed by the type and the efficiency of waterproofing technology in reducing water penetration.

Most of the traditional cementitious coatings and some barrier waterproofing systems [9–17] are not suitable for pavements, due to erosion effects resulting from traffic loads. Many surface treatments of existing concrete structures are based on the use of solutions of water glass to partially neutralize concrete content of alkali materials (calcium hydroxide) through a chemical reaction to produce a water-absorbing silica gel inside the pores (as per a U.S. Patent No. 5,747,171) [18], which is referred to as a hydrophilic waterproofing. Also, oil based and water-repellent patented materials are used for the surface treatment of concrete [19–22], and are referred to as hydrophobic waterproofing materials. On the other hand, integral waterproofing materials [23,24] are added to the concrete mixture at the time of batching, at a prescribed percentage by weight of cement or cementitious content [25]. ACI 515.2R-13 report [26] refers to these additions as permeability reducing admixtures (PRA). The report classifies materials that reduce concrete permeability and materials that hinder wetting under this category. In fact, water-repellent integral waterproofing materials reduce capillary action only [27], while the hydrostatic pressure is resisted by pore-blocking mechanism, which is usually achieved using crystalline waterproofing materials [28].

Several industrial traditional and innovative solutions are available for integral waterproofing and for reducing the durability problems of concrete. Traditional solutions are usually based on modifying the mix design of concrete by adding supplementary cementing materials (e.g. fly ash and slags) [29–32], or by using typical chemical admixtures. Chemical admixtures that reduce water-cement (w/c) ratio such as lignosulphonate reduce the permeability of hardened concrete and thus may be considered as integral waterproofing materials. In a recent study, modified lignosulphonate [33] was used as an integral waterproofing material. Similarly, shrinkage-reducing admixtures (SRA) reduce water absorption of concrete as reported in a recent review paper [34]. On the other hand, ACI 212.3R-10 report [25] defines internal waterproofing admixture as a chemical which is added to the cement matrix that promotes the development of additional gel or other precipitate within concrete voids, after its diffusion to the pore water. The formed materials within concrete pores are generally based on crystallization mechanisms [9,35–41].

Most of the available integral waterproofing materials utilize a single waterproofing treatment of silicate-based materials and other mineral compounds [24,40–47]. These single functional (hydrophilic or hydrophobic) treatments are not sufficient for solving concrete durability problems. Concrete with hydrophilic waterproofing products can resist a hydrostatic pressure, while hydrophobic waterproofing products can secure sufficient concrete dryness. Some of the available aqueous solutions do not have sufficiently low viscosity, in order to guarantee enough penetration depth for effective waterproofing, when used as a surface treatment. Consequently, they have a limited effectiveness in reducing water penetration and they are not practical for pavement applications. In addition, the mechanisms of various integral waterproofing treatments are limited to the control of water in liquid phase [9,39,40], and thus they fail to deal with water problems associated with vapor phase.

Hygroscopic crystals can be formed within concrete pores and then remain interactive with water vapor through vapor adsorption. Chem-Crete integral waterproofing materials based on such a technology have been investigated in previous papers [37,48]. At the level of laboratory testing, a single-hygroscopic crystallization system based on sodium acetate has been tried [49], however, it was inadequately described as a single hydrophobic crystallization. Recent publications studied the dual crystallization engineered (DCE) treatment, using Chem-Crete patented aqueous material [50] that is applied as a surface treatment onto fresh concrete [38] or onto fully cured or old concrete [37].

This paper aims at responding to the industrial need for a multi crystallization enhancer (MCE) to be added to mixing water which can build the concrete waterproofing functions and become an integral part of concrete structure during concrete curing process, without the need for a further treatment. No previous publication on MCE technology is available in the literature. The main goal of this novel contribution is to investigate the efficiency of MCE as a multi-solution to water-associated problems for pavements, highways, bridges and airport runways. The research objectives include (1) demonstrating the formation of pore blocking crystals and their interactions with moisture through measuring the internal humidity and moisture emissions and (2) performing a parametric experimental study of the effects of MCE on permeable pores, water absorption, density, compressive strength, abrasion resistance and workability.

2. Chemical and theoretical aspects of Multi-Crystallization enhancer for concrete protection

The MCE technology is based on an advanced multi-crystallization system that is characterized by internal triple functions of hygroscopicity, hydrophilicity and hydrophobicity, and formed within the concrete capillary system after the initial cement hydration process. The MCE material is simply mixed with the fresh concrete at a recommended percentage of 1–4% by weight of the binder of concrete mix, at the time of batching by dissolution in the mixing water. No further specific requirements are needed for the MCE performance. The crystallization system is physically and chemically interactive with moisture and with the by-products of cement hydration, mainly the calcium hydroxide (CH). Some reactions of MCE active ingredients take place on the surfaces of $Ca(OH)_2$ particles, reducing its harmful effects, and producing a protective hygroscopic and hydrophilic crystals. Consequently, MCE reactive ingredients enhance hydration through such a partial consumption of CH. MCE also assists in temperature control and moisture management, as detailed below.

During concrete curing, water content decreases through its consumption in cement hydration, its physical bonding within concrete pores and through its evaporation due to the exothermic heat of hydration reactions and surrounding effects. The concentrations of active ingredients of MCE are then increased within the produced concrete pores and they start to react with water and with CH through simultaneous chemical reactions. The reactions are accelerated by the increase in the concentration of the chemicals as a result of water loss, forming hygroscopic and hydrophilic crystals, in a similar fashion as described in our previous publication of dual crystallization waterproofing [37]. Then, the crystals that are formed within the paste capillaries interact with residual water (in liquid and vapor phases) and grow into larger sizes. Consequently, they generate a multi-crystallization network that fills and blocks the concrete capillary network. In addition, another reaction occurs between the active ingredients of MCE and the available carbon dioxide from air, the product of which bonds to silicone sites of the calcium silicate hydrates. It produces an insoluble water-repelling stable layer, as an integral part of the concrete structure, which is resistant to alkalinity conditions of the pore solution and to other chemical attacks. The net products include hygroscopic, hydrophilic and hydrophobic surfaces which become an integral part of the concrete structure. They are uniformly distributed throughout the paste fraction of the concrete. Then, they minimize water transport through the concrete capillary network by these tripled functions.

During concrete service, when partial water penetration occurs, the hygroscopic crystals maintain their characteristics of being interactive with water vapor. The adsorption of water vapor at the surface of the hygroscopic crystals maintains the MCE system in a dynamic process, in order for the crystals to attain an equilibrium with the humidity in air. Thus, the crystals consume excess water vapor and enhance pore blocking efficiency, resulting in a low moisture content with the concrete. They are also attracted to moisture source and thus effectively sealing it off. When excessive liquid water exists, the hydrophilic crystals swell and expand, thus preventing further water from penetrating through large pores. The crystals maintain in a reversible equilibrium process, and thus when the moisture content in concrete decreases, they release the moisture and shrink. In this way, the system provides an excellent opportunity for concrete breathing process. Both of the hygroscopic and the hydrophilic crystals reduce water permeation in water damped condition under a hydrostatic pressure. On the other hand, the adsorbed hydrophobic invisible materials make the concrete surface hydrophobic and increase the surface tension of water, and consequently minimize water penetration by capillary absorption. In addition to the above described efficient process of decreasing the pore size of concrete structure, the dynamic process of MCE crystal growth provides a self-healing mechanism for hairline and thermal cracks in concrete. The resulting integral waterproofing mechanism provides a long-term sustainable solution to many water-related problems faced by concrete structures. The technology provides a protection to concrete pavements, bridges, highways, airport runways and taxiways against various thermal, chemical and biological attacks that are associated with water penetration and its phase change. This is achieved by reducing the amount of water which is the carrier and the diffusion medium of the harmful materials in concrete pores. This paper focuses on MCE performance as a concrete enhancer, while its resistance to other thermal, chemical and biological attacks will be demonstrated in future works.

3. Experimental study

The experimental program included measurements of characteristics of fresh and fully cured concrete. The investigated parameters included the workability of fresh concrete, the rate of development of compressive strength, abrasion resistance, internal humidity of concrete, moisture emission, water absorption, permeable pore space, and density of fully cured concrete. Two types of concrete samples were prepared for investigated parameters, including control and 2% MCE dosed specimens, or dosed specimens at various MCE percentages. All experiments were made in the independent laboratories of Construction Material Testing (CMT, Des Moines, Iowa, USA), with data testing certificates.

3.1. Concrete constituent materials and mix proportions

The binder consisted of Type I Portland cement which conforms to ASTM C150 specifications. For modified concrete with SCM, Class C fly ash was used as a partial replacement of cement. It conforms to ASTM standards (ASTM C618–12 2012; ASTM C989/C989M–12 2012) and has specific gravity value of about 2.6. The used enhancer was Pavix® MCE® aqueous material from International Chem-Crete Corporation (Richardson, Texas, U.S.A.). It is a patent-pending chemical solution composed of a system of active ingredients of hygroscopic, hydrophilic and hydrophilic materials, integrated into a total solid content of about 15%. It has a specific gravity of 1.1, a viscosity of 2.4 centipoise, and a freezing temperature of 28 °F (−2.2 °C). Crushed limestone aggregates with an average size of 1 in. (2.54 cm), obtained from Martin Marietta Ames Mine, were used as coarse aggregates. Natural sand from Hallett Materials North Des Moines were used as fine aggregates. The air entrainment and the water reducing agents were obtained from Euclid Admixture (Cleveland, Ohio, USA), GRT SA-50 and GRT 400-NC, respectively. Other testing chemicals such as anhydrous calcium chloride conformed to ASTM tests requirements.

Two mix designs (IDOT C4 and IDOT C4-WRC20) prescribed by Illinois Department of Transportation were used, as listed in Table 1 [51]. In IDOT C4-WRC2, Class C fly ash was added at 20% dosage as a replacement of cement, the aggregates were the same as in the case of IDOT C4. In both cases, the air entrainment was 6% and the amount of added water reducer was 4.0 lq oz. For one field testing, a ready-mix concrete from Standard Ready-Mix Concrete Co (Sioux City, IA, USA), was used for comparing strength performance. Its mix design was for a high-performance concrete of grade D (HPCD), according to IDOT prescribed mix designs [51]. Various values of water to cement (w/c) ratio were investigated, they were within a range of 0.37 to 0.54. For HPCD ready mix concrete, the w/c was 0.42.

Prepared concrete specimens included MCE enhanced and control specimens. For the enhanced concrete specimens, MCE was added to the mixing water at 2% of cementitious materials, as recommended by the material technical data sheet. For the purpose of comparisons, other dosages of 1% and 4% MCE were used in some experiments, as indicated where applicable.

3.2. Test procedures

3.2.1. Measuring the workability of fresh concrete

The workability of fresh concrete was determined using the standard slump test method (ASTM C143/ C143M). The retention of workability was determined by measuring the slump as a function of time, as shown in Fig. 1, for two w/c ratios using standard IDOT C4 mix design. Then, the measured slump was plotted as a function of time.

3.2.2. Measurements of mechanical properties

The compressive strength of control and MCE enhanced concrete specimens was determined according to the standard procedures of ASTM C39, for standard IDOT C4 mix design with w/c ratio of 0.37, and for IDOT C4-WRC20 utilizing 20% Class C fly ash at w/c ratio of 0.4. In addition, concrete strength gain was measured using the maturity method according to ASTM C1074, by measuring the temperature–time factor (TTF) and the compressive strength development, for control and 2%-MCE enhanced IDOT C4 concrete specimens with a w/c ratio of 0.42. For field applications, the compressive strength of control and enhanced concrete specimens was determined for HPCD ready mix concrete. All dosed specimens for compressive strength measurements were with 2% MCE.

The abrasion resistance of fully cured concrete was determined according to the standard procedures of ASTM C779, Procedure B, using IDOT C4WRC20 design mix, for two types of concrete mixtures (containing 1% or 2%MCE), with varying w/c ratios of 0.44, 0.49 and 0.54. The results were plotted as curves of depth of wear as functions of elapsed time.

3.2.3. Measurements of concrete transport properties

Measurements of concrete density, water absorption, and voids in hardened concrete were performed according to the standard procedures of ASTM C642. The tests were conducted using fully cured IDOT C4-WRC20 concrete specimens after 28 days curing, for various w/c ratios of 0.37, 0.44, 0.49 and 0.54.

Measurements of the relative humidity inside the concrete pores were performed according to the standard procedures of ASTM F2170 using 12x12x12 inch block, with probe holes placed at 2, 3 and 4-inch-deep to allow for varying depth readings. The

Table 1
The two used mix designs as prescribed by Illinois Department of Transportation [51].

Component	IDOT C4		IDOT C4-WRC20	
Unit	British Units	SI units	British Units	SI units
Cement	614 lb	278.8 kg	491 lb	222.9 kg
Coarse aggregates	1490 lb	676.5 kg	1490 lb	676.5 kg
Fine aggregates	1479 lb	671.5 kg	1479 lb	671.5 kg
Fly ash	None	None	123 lb	55.8 kg
Air entrainment	6%	6%	6%	6%
Water reducer	4.0 lq oz	118 ml	4.0 lq oz	118 ml
w/c range	0.37–0.54	0.37–0.54	0.37–0.54	0.37–0.54

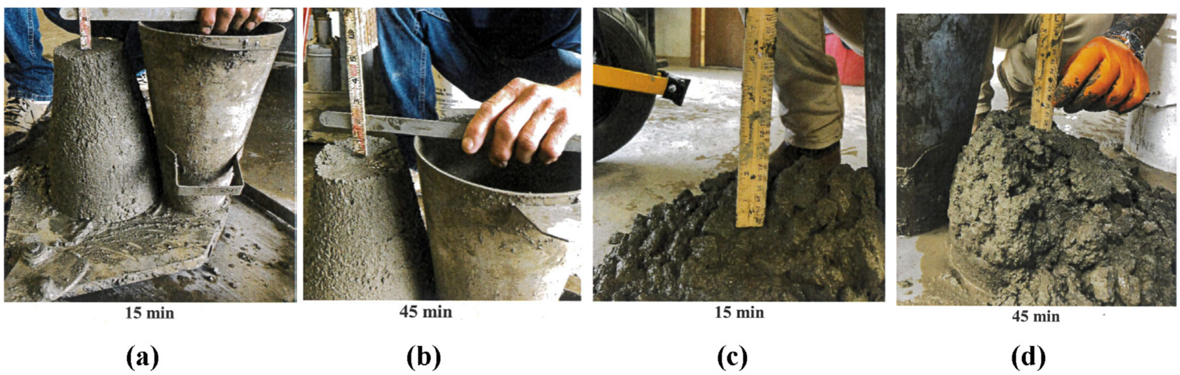

Fig. 1. Measurement of slump as a function of time for fresh concrete, using IDOT C4 mix design with slump target of 1 in. (a, b) and 7 in. (c, d).

temperature of control and enhanced concrete samples, for all depths were kept constant at 77 °F.

The rate of moisture vapor emission of concrete was determined according to the standard procedures of ASTM F1869 using anhydrous calcium chloride. Fig. 2 shows the used experimental set up. The test was conducted on slabs (11.5x9.5 in. and 2 in. thick) placed over a wood form. A 1.75-inch diameter hole was cut in the bottom of the form to allow water vapor to be introduced by boiling a flask containing 300 ml of water. Over a period of 40 days, the samples were boiled 6 times for 1-hour durations each time. Normal emissions were captured when not boiling. In addition, the rate of moisture emission was measured at various concrete ages according to ASTM F2659 (Floor Moisture Emissions), for control and MCE enhanced IDOT C4 concrete slab specimens. Two dosages were investigated in these experiments (2% and 4% MCE).

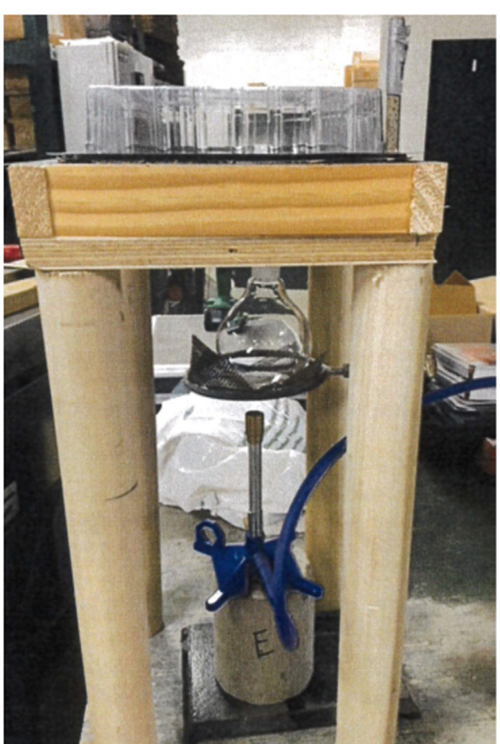

Fig. 2. Moisture emission testing apparatus.

4. Results and discussion

4.1. Effect of MCE on the workability of fresh concrete

Fig. 3 presets the results of workability retention of fresh concrete, for two cases of slump targets of 1 and 7 in.. The addition of MCE results in retaining the target workability for at least 30 min. For the purpose of comparing workability of control and dosed concrete, Table 2 lists the measured slump of two types of selected fresh concrete samples, for IDOT C4-WRC20 with SCMs and for HPCD ready mix concrete. The workability of fresh concrete increases when MCE is added to HPCD ready mix concrete; the slump was increased by about 33%: for control sample the measured slump was 3 in., while for MCE dosed sample the measured slump was 4 in.. This is attributed to the plasticizing role of the hydrophobic constituent of MCE, which assists in creating a more homogeneous mix and thus improves the flowability of the fresh concrete. This is achieved because MCE disperses the cement particles and promotes their stability in water and thus, they behavior as suspended individual particles for a sufficient period of time. For modified concrete with SCMs (IDOT C4-WRC20), the slump is high due to the existence of fine particles of fly ash, as well reported in literature [32]. The addition of MCE has resulted in a minor difference in slump. These results indicate that for a mix design with a certain slump target, the required w/c ratio can be reduced when MCE is dosed to fresh concrete. This reduction of water improves

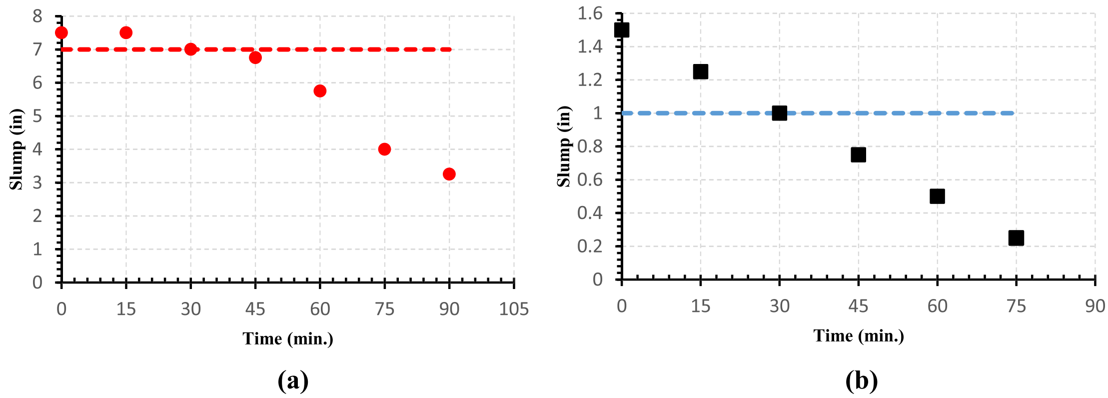

Fig. 3. Workability retention of fresh concrete plotted as curves of slump as functions of time, using IDOT C4 mix for two slump targets of 7 in. (a) and 1 in. (b).

Table 2
Measured slump for fresh concrete samples.

Mix Design	Description	Slump (in)	
		Control	Enhanced
IDOT C4-WRC20	Concrete with SCMs (Fly ash C)	6.5	6
HPCD	Ready mix concrete 5300 psi at 28 days	3	4

the final characteristics of fully cured concrete, such as reducing its permeability and increasing its compressive strength. A similar workability enhancement was reported for other integral waterproofing admixtures [33]. Such an enhancement of the performance of fresh concrete prevents segregations of water and aggregates at early stages of concrete.

4.2. Reduction of internal humidity and vapor emission through MCE crystal growth

Fig. 4 presets curves of the measured internal relative humidity of concrete as functions of concrete age for block specimens at various depths, for control and MCE dosed concrete. It is clear that there are major reductions in the values of relative humidity for MCE dosed concrete (Fig. 4a) compared to control concrete (Fig. 4b). At 28–days of curing, these reductions in humidity were 21.9%, 16.7% and 12.5% for the depths of 2, 3 and 4 in., respectively. As the temperature remained constant for control and enhanced concrete (at 77 °F at all depths), the mass balance indicates that these reductions are associated with an increase in the mass (and volume) of the interactive hygroscopic crystals, that absorb water vapor in their growth. These results confirm the reactivity of the hygroscopic crystals with humidity, as demonstrated in section 2 above. This behavior is attributed to the fact that the hygroscopic crystals suck water vapor from air by promoting its adsorption on the crystal surface. Consequently, the vapor consumption causes a reduction in the relative humidity within pores. The adsorbed water allows the crystals to grow as a result of the mass gain, and thus enhances pore blocking efficiency. This behavior of crystal interaction with vapor was not reported for other integral waterproofing systems [23,24]. This interaction with water vapor does not interfere with the cement hydration since the hydration reaction occurs with water in its liquid phase. In fact, the results in section 4.3 emphasis that such a hygroscopic crystal growth does not decrease the compressive strength at a later stage. This reduction in humidity adds other positive impacts on concrete durability, as it promotes concrete breathing process and increases concrete resistivity to mold growth, as reported in previous publications [8]. Such a reduction in relative humidity is not limited to surface layers; in fact, the hygroscopic crystals are attracted to moisture sources at all depths and then effectively attract moisture sealing the source off.

These results are also supported with the observed reduction in the measured moisture emission for 2% MCE dosed concrete com-

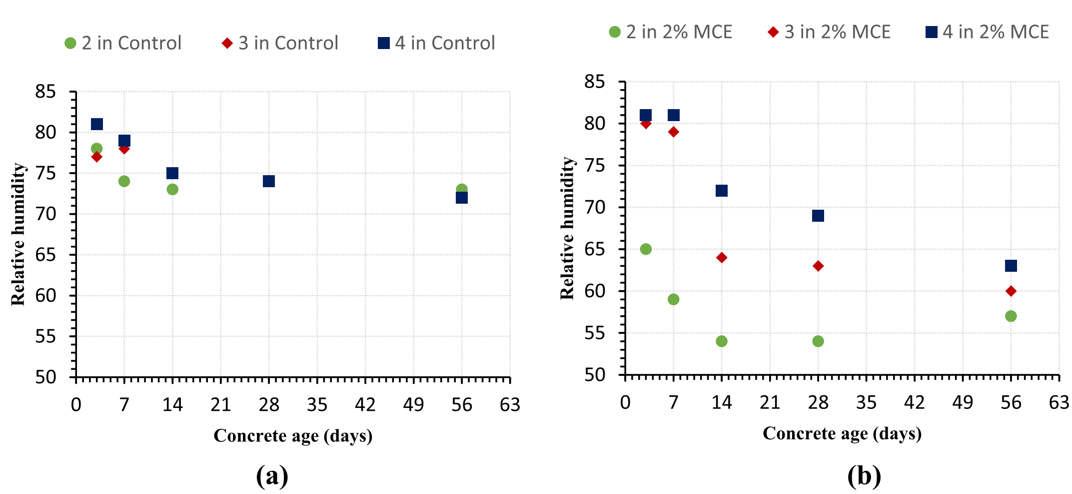

Fig. 4. Internal relative humidity of concrete as functions of concrete age for blocks (12x12x12 inch) with probe holes placed at 2, 3 and 4-inch-deep, using IDOT C4 mix design with w/c ratio of 0.42 for control concrete (a) and MCE dosed concrete (b). The reported data points were the averages of three readings.

pared to control IDOT C4 concrete, as listed in Table 3. In fact, the moisture absorption of the 2% MCE dosed concrete is higher than that of control concrete by more than 100%. These results indicate that a larger amount of water vapor is transferred from the flask to the MCE dosed concrete sample (see Fig. 2), and consumed by the MCE dosed concrete in crystal growth. This is evidenced by the reported findings of higher values of moisture absorption and unit weight gain than those for control concrete. The MCE dosed concrete sample allowed a less moisture emission through the slab and it captured a larger fraction of moisture than the control concrete (Table 3). This is associated with the process of hygroscopic crystal growth by absorbing the free moisture within the crystalline structure, as described above, yielding a high concrete unit weight increase for MCE dosed concrete specimen, with more than 460% increase in concrete unit weight over that for control concrete.

Fig. 5 presents the curves of the measured rate of moisture emissions as functions of curing time, comparing 2% and 4% MCE dosed IDOT C4 concrete specimens and control specimens. At early stages of concrete curing, small differences in moisture emissions between MCE enhanced and control specimens are observed, while such a difference becomes much larger at later curing periods. This is attributed to the crystal growth with moisture adsorption that becomes more active. The small differences in moisture emissions between MCE enhanced and control specimens confirm that the crystallization mechanism does not impact the cement hydration process. When the available water starts to decrease during curing process and when the relative humidity starts to decrease within the pores (as indicated in Fig. 4), the hygroscopic crystals grow at a higher growth rate, and thus they result in a major reduction in the rate of moisture emissions as observed in Fig. 5, for 14 and 28 days. These results confirm the effectiveness of MCE in crystal formation, as an integral part of the cement hydration products.

4.3. Effect of MCE on the compressive strength and hardness

Fig. 6 shows the curves of temperature time factor (TTF) and compressive strength as functions of curing time and the curve of compressive strength versus TTF as well. All measurements are within few percentages. These results indicate minimal differences between control and MCE dosed mixes, until 56 days. The similarity in the measured curves of strength maturity for control and MCE dosed concrete confirms that the interactivity of the hygroscopic crystallization system with water, as discussed above, does not impact the process of strength development. This is in agreement with previous results of the tests using the similar crystallization system (DCE) as surface treatment on fresh concrete [38]. This is because the hygroscopic crystal interacts only with water vapor and does not compete with cement hydration reactions on liquid water. The crystallization does not affect TTF or compressive strength until the final maturity is achieved. The final compressive strength of MCE dosed concrete is higher than that of control concrete. This is attributed to the role of MCE in dispersing

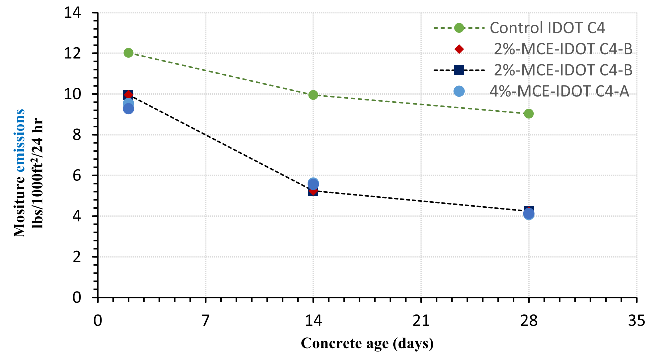

Fig. 5. Curves of the measured rate of moisture emissions as functions of concrete age, according to ASTM F2659, for 2% and 4% MCE dosed concrete specimens (two samples for each) compared to control specimens of IDOT C4 with w/c ratio of 0.42.

the cement particles and to the capacity of crystallization system for holding moisture through its hydrophilic reversible behavior and then releasing a fraction of the absorbed water at later stages for further cement hydration.

Fig. 7 shows the curves of compressive strength development of control and enhanced concrete specimens for IDOT C4 at a w/c ratio of 0.37, for IDOT C4-WRC20 at a w/c ratio of 0.4 and for HPCD ready mix concrete. Obviously, adding MCE as an enhancer to fresh concrete increases the compressive strength of fully cured concrete. This appears well at 28-days and at 56 days. This positive effect of MCE on concrete strength is accomplished for ordinary concrete (IDOT C4) and for modified concrete with fly ash (IDOT C4-WRC20), as well as for the commercial ready mix concrete (HPCD). For IDOT C4 and HPCD concrete mixtures, there is a limited slowdown in the rate of strength development for MCE enhanced concrete at the early stage (e.g. within the first 3 days period). For MCE modified concrete with fly ash (IDOT C4-WRC20), which is mostly used in concrete pavement, the addition of MCE increases the compressive strength at all stages. This strength enhancement is in agreement with previous results for other integral waterproofing materials [33]. As mentioned above, the increase in the compressive strength for MCE dosed concrete is attributed to the plasticizing role of MCE and to the reversible swelling behavior of hydrophilic crystals. As described in a previous publication [38], the absorption of liquid water within the hydrophilic crystals is a reversible process and thus these crystals release a fraction of water into the pores and make it available for further cement hydration at late stages. This mechanism of moisture management during curing is also supported with a temperature control mechanism. This is related to the capacity of MCE dosed concrete for storing a fraction of the heat of reaction of cement hydration for a longer time period than that of the control concrete. This assists in utilizing such a thermal energy in promoting further hydration at late stages. This is because the formed crystallization system reduces the thermal conductivity of concrete and thus decreases the rate of heat transfer though concrete

Table 3
Results of the rate of moisture vapor emission of concrete, for fully cured concrete (IDOT C4), over a period of 40 days, with w/c ratio of 0.42 from tests according to ASTM F1869.

Parameter	Unit	Control IDOT C4	2%-MCE IDOT C4	Difference (%)
Moisture emission	lbs/24 hrs/1000 ft^2	15.4	9.7	37.0%
Moisture absorption	g	77.1	158.7	105.8%
Moisture absorption	%	28.3	58.3	106.0%
Flask loss moisture weight reduction	%	0.18	0.26	44.4%
Slab moisture weight gain	%	28.3	41.7	47.3%
Concrete unit weight change	%	0.34	1.91	461.8%

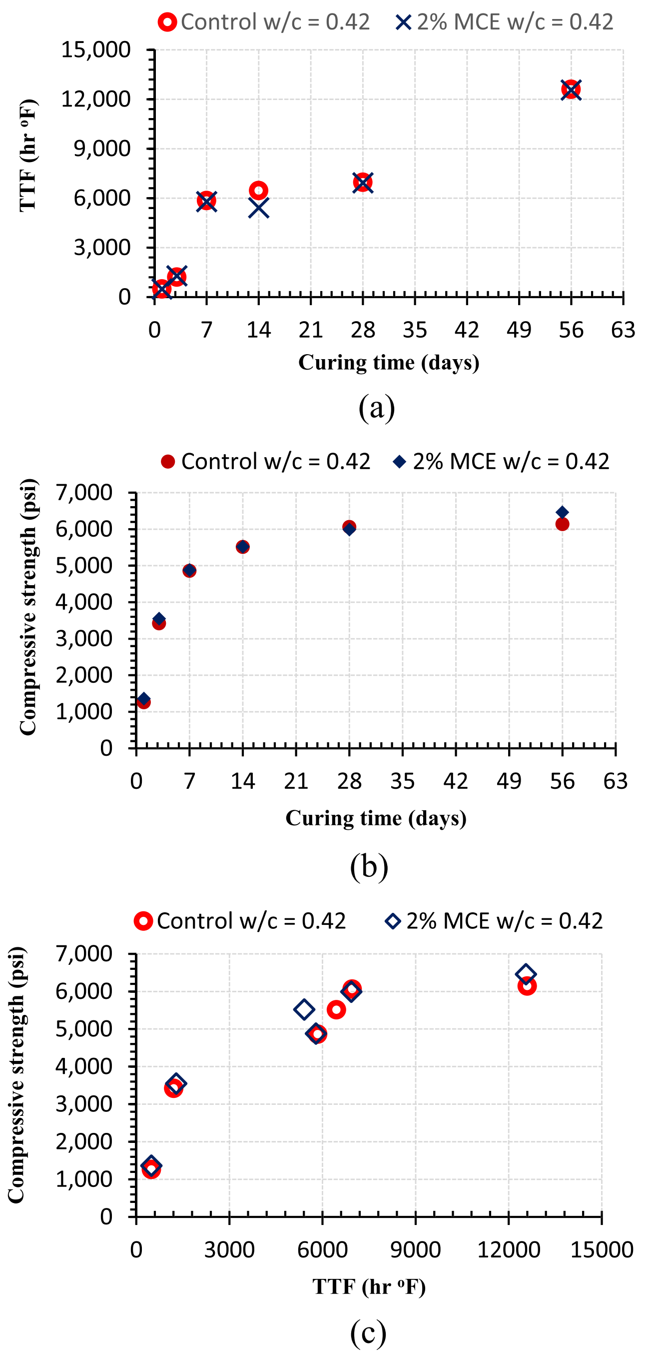

Fig. 6. a) Development of TTF with curing time; b) Development of compressive strength with curing time; (c) Curve of compressive strength versus TTF for 2%-MCE enhanced and control concretes of IDOT C4 mix with w/c ratio of 0.42.

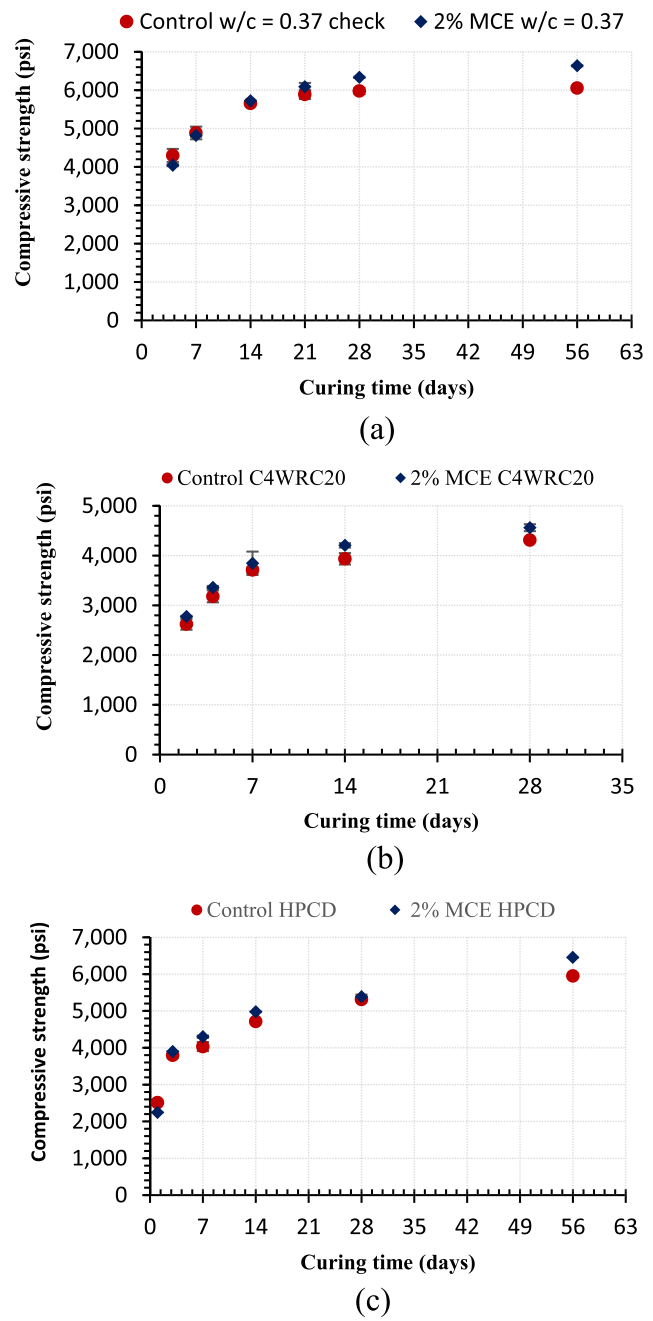

Fig. 7. Compressive strength of 2% MCE enhanced and control concrete specimens for various mix design, including: a) IDOT C4 with a w/c ratio of 0.37; b) C4WRC20 with a w/c ratio of 0.4; c) HPCD ready mix concrete.

towards the surroundings by conduction. In addition, the active ingredients of MCE are hypothesized to minimize the encapsulation of cement particles during early hydration. These kinetics and thermal aspects are recommended for future investigations.

Fig. 8 shows results of the abrasion or wear resistance of fully cured concrete for MCE enhanced concrete specimens for the two cases of 1% and 2% MCE for various w/c ratios. As expected according to the material behavior, the wear damage increases with elapsed time, indicated by the increase in the depth of wear. The rate of wear damage and the level of wear increases with increasing the w/c ratio. This is because increasing w/c ratio increases concrete porosity, decreases its integrity and thus reduces its resistance to abrasion. However, increasing the dosage of MCE, from 1% to 2%, increases the abrasion resistance considerably, due to the enhancement of concrete strength. It is evident from Fig. 8 that the depth of wear decreases considerable when 2% MCE is added to concrete compared to the case with 1% MCE addition. This improvement in the abrasion resistance with MCE is in agreement with previous results of the use of the similar crystallization system (DCE) as surface treatment for hardened concrete [37]. These results provide a further evidence of the impact of MCE on enhancing mechanical strength. This indicates an improvement of abrasion resistance or hardness with MCE. This improvement is attributed to the increase in concrete strength and integrity due to better cement hydration and to the increase in the density of

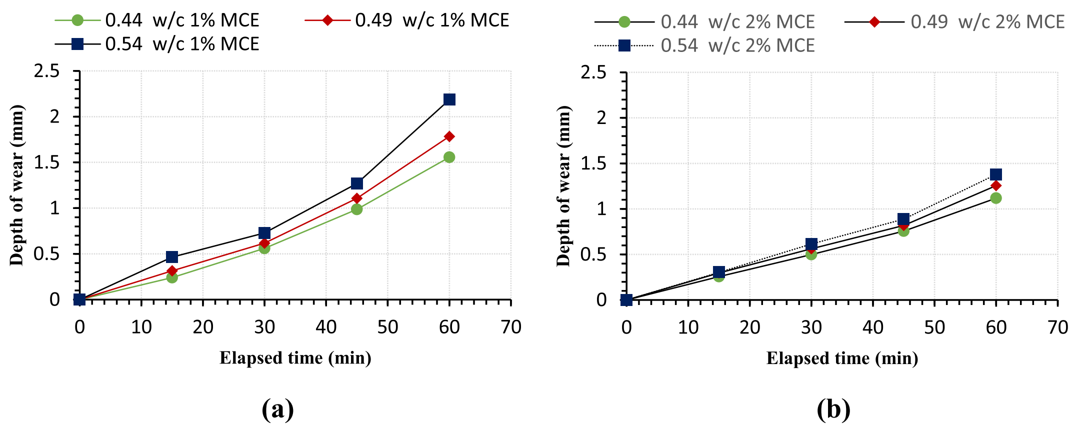

Fig. 8. Abrasion resistance of fully cured concrete for MCE enhanced specimens determined according to the standard procedures of ASTM C779, Procedure B, using IDOT C4WRC20 design mix, with: a) 1% MCE; b) 2% MCE with varying w/c ratios (0.44, 0.49 and 0.54).

MCE dosed concrete due to the pore blocking mechanism of the crystallization products, as per section 4.4 below. It is also attributed to the enhancement of concrete integrity with 2% MCE compared to 1%, resulting from more hygroscopic crystallization growth for concrete with 2% MCE than that with 1% MCE. These results support the findings of the positive effect of MCE on improving the compressive strength. In fact, both the compressive strength and the surface hardness (or the abrasion resistance) are directly related. This positive effect of MCE on the mechanical strength of enhanced concrete confirm the ability of MCE to improve the hydration of cement. Cement hydration, with MCE, is also enhanced by the conversion of calcium hydroxide through its reaction with MCE materials forming hygroscopic and hydrophilic crystals. These crystallization reactions assist in driving more cement hydration, by consuming part of the cement hydration products, according to hydration reaction stoichiometry and kinetics.

4.4. Effect of MCE on concrete porosity and permeability

Table 4 lists the experimental results of concrete density, water absorption, and voids in hardened concrete for two MCE additions (1% and 2%), with various w/c ratios. It also lists the estimated percentage differences in each parameter between the 2% MCE addition over the 1% MCE addition.

For the same concrete mix, it is obvious that increasing w/c ratio decreases concrete density, as well documented in concrete literature. This is due to the increase in concrete porosity with increasing w/c ratio. However, for each concrete mix, with a specific w/c ratio, there is a density increase for 2% MCE dosed concrete over 1% MCE dosed concrete, by percentage in the range of 3.3–4.2%. The increase in density is in agreement with previous results of the tests using the similar crystallization system (DCE) when applied as a surface treatment on hardened concrete; about 6% increase in density of DCE treated concrete over control concrete was obtained [37]. This is attributed to the fact that more reaction yield of hygroscopic and hydrophilic crystallizations is formed with 2%-MCE dosed concrete than 1%-MCE dosed concrete. The products of crystallization reactions block the capillary network by the formation of multiple crystals. These results support the above demonstrated mechanism of interactivity of the crystallization system, as evident from the observations of reductions in the internal humidity for MCE dosed concrete as presented in section 4.2. The relative increase in density is not high since the percentage dosage of MCE is low compared to concrete constituents. Also, MCE is added as just a small replacement of the cementitious binders. However, such an increase is high in terms of pore blocking, as evident in the obtained high difference (45–50%) in the percentage of volume of permeable pore space. This range is very close to the previously reported range of 45–60% for the effect of DCE surface treatment on hardened concrete [37]. These differences present additional direct evidences of the pore blocking mechanism through hygroscopic and hydrophilic crystallization. It is worth mentioning that these differences are between the two cases of dosed concrete with 1% and 2% MCE. However, larger differences (in density and in volume of permeable pore space) are obtained, when these values are compared to control concrete (especially when comparing 2% MCE with control concrete). Obviously, the effective crystallization mechanism of the MCE material decreases the pore sizes within concrete structure, through pore blocking. Decreasing the size of the capillary pores, possibly to a nanoscale, maintains a portion of water within the concrete structure as a result of increasing the flow resistance within the nanocapillaries. The entrapped water is an essential medium for cement hydration. These small size pores assist in maintaining a larger fraction of water molecules within the concrete structure, for a

Table 4
Results of concrete density (expressed as specific gravity), water absorption, and voids in hardened concrete, for fully cured concrete (IDOT C4WRC20 at 28 days) for various w/c ratios of 0.37, 0.44, 0.49 and 0.54 from tests performed according to ASTM C642.

Parameter	1% MCE				2% MCE			% Difference		
w/c ratio	0.37	0.44	0.49	0.54	0.44	0.49	0.54	0.44	0.49	0.54
Absorption after Immersion, %	0.1785	0.2041	0.281	0.3324	0.0947	0.1247	0.175	53.6%	55.6%	47.4%
Absorption after Immersion and Boiling, %	0.255	0.4082	0.4577	0.6136	0.1994	0.224	0.325	51.2%	51.1%	47.0%
Bulk Dry Density	2.375	2.369	2.357	2.349	2.458	2.447	2.433	−3.8%	−3.8%	−3.6%
Bulk Density after Immersion	2.38	2.373	2.364	2.357	2.461	2.45	2.437	−3.7%	−3.6%	−3.4%
Bulk Density after Immersion and Boiling	2.383	2.379	2.368	2.363	2.463	2.452	2.441	−3.5%	−3.5%	−3.3%
Apparent Density	2.394	2.392	2.382	2.383	2.47	2.46	2.484	−3.3%	−3.3%	−4.2%
Volume of Permeable Pore Space, %	0.787	0.99	1.082	1.441	0.49	0.549	0.791	50.5%	49.3%	45.1%

longer period since they have a very low permeability. Thus, this mechanism minimizes the early loss of moisture. Then, the entrapped water evaporates as a result of the heat of hydration, within the nano-pores, absorbing the latent heat of evaporation. Such a heat absorption, through water phase change, minimizes the energy loss from concrete to the surroundings. The latent heat of vaporization is then given back as a sensible heat to the system upon condensation again at a later stage. Such a thermal effect can activate further cement particles for more hydration. These temperature control and water management mechanisms enhance the cement hydration process. Overall, better curing conditions are maintained for MCE dosed concrete compared to control concrete. These enhanced conditions are then reflected positively in the increase in the compressive strength at late stages (see Fig. 7) and better surface resistivity (see Fig. 8), as reported in section 4.3 above.

The observed decrease in the permeable pore space, associated with the increase in the density with MCE dosing, yields a major reduction in water penetration through concrete as indicated in Table 4. Water absorption for 2% MCE dosed concrete is lower than that for 1% MCE dosed concrete by about 50%. This reduction in water absorption with MCE is in agreement with previous results of the use of the similar crystallization system (DCE) as surface treatment for hardened [37], however, a higher reduction (60–75%) was reported with DCE. The percentage reduction is dependent on the mix design of concrete. As explained above, this is resulting from the mechanism of crystal growth with moisture, and from the dynamic interactions with vapor and liquid water phases, for the hygroscopic and hydrophilic crystals, respectively. Again, larger differences in water absorption for 2% MCE dosed concrete are expected when compared to control concrete. The reductions in water absorption after immersion and boiling, for 2% MCE compared to 1% MCE, are in the range of 47% – 51%. This range is very close to that obtained for the reduction in water absorption without boiling. This is an evidence of the stability of the crystallization system at high temperature. The hygroscopic crystals remain effective at the boiling conditions as they maintain their integrity within the pores at boiling temperature. The previously reported range of reduction in water absorption after immersion and boiling for the case of DCE treatment on hardened concrete was 47–64% [37].

The entrapped vapor and liquid water interact with the crystalline system by two mechanisms: physicochemical bonding with the hygroscopic crystals yielding crystal growth (and minimizing free water in concrete subsurface), and swelling within the hydrophilic crystals, yielding a controlled expansion. In addition to these mechanisms, the hydrophobic function of the MCE system increases the surface tension at the concrete surfaces and thus creates more resistant to water penetration through capillary absorption.

Reducing concrete porosity and water penetration (which is the carrier of the harmful chemicals) increases the resistance of MCE enhanced concrete against thermal, chemical and biological attacks, and thus provides an effective solution to these water-associated problems: MCE provides a solution for solid-state water expansion problems associated with freezing in the pores during freezing and thawing cycles. It also solves the vapor-state water problems resulting from the re-condensation of vapor, which also makes it a medium for mold growth. In addition, the major reduction in the availability of liquid water medium assists in solving other concrete durability problems of alkali-silica reactions (ASR) and chloride ion penetration. These features of the MCE technology will be demonstrated in coming publications.

5. Conclusions

The performance of MCE as an effective pore blocking waterproofing system is demonstrated. MCE is added to mixing water, and then builds the concrete waterproofing functions and becomes an integral part of concrete structure during concrete curing process. Experiments have been performed to evaluate the efficiency of MCE as a multi-solution to water-associated problems for pavements, using ordinary Portland cement concrete and modified concrete with fly ash. Based on the experimental results obtained, the following conclusions can be drawn:

1) MCE enhances concrete integrity and density, and reduces concrete porosity and permeability. This is associated with the formations of hygroscopic and hydrophilic crystals (pore blocking), and creating a hydrophobic layer at the concrete surface (reducing capillary absorption).
2) MCE reduces the internal humidity in pores and moisture emissions since it interacts with water vapor through its hygroscopicity.
3) MCE improves the compressive strength and the surface hardness, and thereby enhances concrete durability and structure sustainability. This is associated with the densifying effect from crystallization within the pore of the cement paste and from the enhancement of cement hydration process.
4) The workability of fresh concrete is increased when MCE is added to ready mix concrete by about 33%. This is associated with the capability of MCE to disperse the cement particles.

The recommendations for further research work include the followings:

1) Preparing a parametric experimental study of the impact of MCE on durability parameters and concrete resistances for various physical, chemical and biological deteriorations. These include, for example, freezing and thawing and chloride ion penetration.
2) Investigating the role of MCE in mitigating ASR using various types of aggregates.
3) Studying the thermal behavior and the hydration kinetics through calorimetric analysis, and investigating the ability of MCE for thermal management of the heat of reactions and its applications for casting concrete under very cold conditions.
4) Investigating the role of MCE in the thermal management in applications for mass concrete.

CRediT authorship contribution statement

Radi Al-Rashed: Data curation, Investigation, Methodology, Project administration, Resources, Supervision, Validation. **Maher Al-Jabari:** Conceptualization, Data curation, Formal analysis, Investigation, Methodology, Validation, Visualization, Writing - original draft, Writing - review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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