

# Mitigation of alkali silica reactions in concrete using multi-crystalline intermixed waterproofing materials

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## ABSTRACT

Concrete deterioration by Alkali Silica Reactions (ASR) is a severe issue of concrete durability associated with porosity and permeability. Most of the industrial solutions for mitigating ASR rely on controlling the mix design by mineral admixtures or lithium compounds. An innovative approach for mitigating ASR through a secondary role of crystalline waterproofing materials is presented. An aqueous solution of Multi-Crystallization Enhancer (MCE) is intermixed with water or added to the concrete mixture, at a dosage of 2% by weight of cement, then upon curing reduces the permeability under pressure by more than 99%. This study shows that ASR mitigation can be accomplished by incorporating the MCE in the fresh concrete mixture or by prewetting the aggregates. The experiments were made according to the methods of ASTM C1260. The investigated independent experimental variables included water to cement ratio, types of aggregates, method of the MCE addition, and time. The MCE can change the performance of aggregates from reactive to be equivalent to non-reactive. The findings demonstrate that the length expansion from ASR increases with increasing the w/c ratio for all types of aggregates attributed to the increase in the permeability. The MCE addition to mixtures with reactive aggregates enhances the resistivity against ASR by a percentage in the range of 45%–77%. The functionality of the MCE in mitigating the ASR is also confirmed using concrete specimens with long term ASR testing (ASTM C1293).

## 1. Introduction

Concrete is a composite material composed mainly of the hydrated cement paste and the aggregates [1]. The paste is subjected to continuous attacks during concrete casting and curing periods and its service life. Concrete durability is its capability for resisting conditions of service such as weathering impacts, chemical attacks and abrasion [2], or the ability of concrete to resist any process of deterioration [3]. Concrete durability governs its service life under conditions reactivity and controls the sustainability of its structures when exposed to moisture. The sustainability is threatened by the decline of concrete quality from deterioration impacts. Moisture in concrete pores is the carrier and the media for various types of lethal reactions. Most problems of concrete durability are caused by the penetration of water associated with harmful chemicals which then lead to many types of physicochemical interactions. The long-time durability requires a dense and waterproofed concrete [4], with disconnected capillary networks [5].

Alkali aggregate reactions (AAR) composes a group of deleterious

chemical reactions, which occur between the soluble alkalis (from cement) and the reactive mineral compounds that are embedded within the aggregates chemical structure [6,7]. The hydroxide ions come mainly from the alkali content of the cement and additionally from the soluble portlandite generated from the cement hydration reactions [8]. AAR include alkali silica reactions (ASR) and alkali carbonate reactions (ACR) [8,9]. The ACR are associated with  $\text{CaMg}(\text{CO}_3)_2$  content of the aggregates while the ASR are associated with their silica content. In this paper, the focus is on ASR which involves slow (first order reaction [10]) reactions that lead to the formation of a swelling gel. Such an expansive gel promotes concrete cracking within 10–20 years of concrete age. The ASR creates the greatest durability problem of concrete pavements [11]. The structures of aggregates commonly include amorphous (reactive) and crystalline non-reactive silica contents and hence they are classified as reactive and non-reactive aggregates [11,12]. The severity of ASR is dependent on (1) the alkaline conditions in the pore solution [13], (2) the type of aggregates (its  $\text{SiO}_2$  content and type [14]), and (3) the moisture content in concrete [15]. Rajabipour et al. [16] provided a

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detailed review on the fundamental mechanism of deterioration due to ASR in concrete. In general, ASR requires the condition of high relative humidity (80–90%) [15] since water serves as a diffusion environment for the alkali ions and soluble silica, and as a liquid for swelling-expansion of the resulting gel [17]. The main ASR reaction occurs when the alkaline ions are mixed with the solubilized silica content of the aggregates [13]. Then, the hydroxyl ( $\text{OH}^-$ ) ions react with the alkali metal ions, while the solubilized silica ions associated with  $\text{H}^+$  react to produce hydrates of alkali silicates (Si-O-R) [13]. The literature discusses various opinions about the correlation between the chemical composition of ASR gel and its swelling characteristics [6,13,14,17,18]. The gel creeps from aggregate structure and drifts through the open capillary pores and cracks, where it then reacts with the calcium ions forming alkali calcium silicate as a gel [3,17]. In general, the sodium silica gel tend to remain liquids while the calcium-bearing gels are solids [17].

Calcium hydroxide, the by-product of cement hydration, plays a crucial role in the ASR process [13,18,19]: it contributes with the hydroxyl ions within the pore solution that facilitate the dissolution of the silica content [6,13]. The calcium ions undergo cation exchange with alkalis in aggregates and hence increase the dissolution from aggregates [19,20]. The availability of calcium ions enhances the reactivity with dissolved silica forming the lethal gel surrounding the aggregate surface [13,20]. The resulting calcium silicate gel has a high affinity for water with a good swelling characteristic, which is associated with capillary forces that decrease the internal pressure and hereafter permits water suction driven by the depression pressure. The basic mechanism of ASR expansion of concrete was investigated by Struble and Diamond [17] using synthetic sodium and sodium calcium silica gels: they found that the free swelling capacity of the silica gel ranged from very values of 0.5 to high values of 80%, and the maximum created swelling pressures had a wide range of 0.1 to 11 MPa. The reported upper pressure limit (11 MPa) exceeds the tensile strength of most concrete applications [17]. The viscosity and the yield strength of the ASR gel increase with calcium ions. Struble and Diamond [17] highlighted that the presence of calcium in their synthetic gels did not cause a significant reduction in the activity (i.e. free-swelling or its pressure-developing ability). When the ASR gel is formed in the presence of alkalis in pore solution, a reaction gel with a swelling capacity is formed, while when the ASR gel is formed in the presence of calcium hydroxide without alkalis, a structural C-S-H gel (with decreased swelling capacity and strength enhancement) is formed [6]. Similar observations of obtaining a non-swelling lime-alkali-silica complex were reported by Powers and Steinour [14]. Furthermore, Dent Glasser and Kataoka [18] confirmed that the C-S-H is formed as long as a significant concentration of calcium ions are available in the solution. Decreasing the ionic strength may lower the depression pressure and consequently reduce the swelling rate [21]. Furthermore, the water binding capacity of ASR gel depends on the calcium to silicon ratio (Ca/Si) [17]. The experimental study of Hou, Struble et al. [13] indicated that the ASR gel is produced when the pore solution contains lower Ca content and higher Si content than typical bulk pore solution of ordinary Portland cement paste. According to Chatterji [19], field observations and laboratory testing showed that the presence of free calcium hydroxide is essential ASR expansion condition and hence its complete elimination suppressed ASR. Moreover, the level of ASR expansion depends on the type cement in the concrete mixture (i.e. K/Na ratio which is reflected in the pore solution and in the gel) [8]. Upon swelling, the calcium silicate gel binds additional water from pores allowing them to be physically bound within the gel structure. Then, the expansion of concrete under ASR attack is due to the swelling of the solid alkali-silica complex and to the generated hydraulic osmotic pressure [14]. Water swelling creates expansive characteristics of the calcium silicate gel which then cause large internal stresses that surpass the tensile strength of the cement paste and eventually lead to cracking and a decline in the mechanical properties of concrete and its integrity [11]. The process proceeds as a kind of chain reaction, in which the resulting

cracks lead to more suction of water, further cracking and more deadly ASR [12,22], after which surface macrocracks are formed with depths in the range of 25–50 mm [3].

Laboratory testing of the reactivity of aggregates is commonly done under accelerating conditions in short term tests using mortar specimens according to ASTM C1260 (when only cement is used with aggregates) [23] or ASTM C1567 (when a combination of cementitious materials are used such as a blend of cement and slag) [24]. ASTM C1260 and ASTM C1567 are aggressive tests using a high concentration of hydroxide (1 N) and a high temperature (80 °C) [23]. ASTM C1260 [23] and ASTM C1567 [24] specify a permissible limit of 0.1% for 16-days length expansion for innocuous behavior in most cases or a low deleterious risk of ASR in the field conditions. In previous testing references [12,25], 14-days expansion was considered while the ASTM now specifies 16-days expansion, and calls for waiting for 28 days, particularly for cases when the expansions are between 0.10 and 0.20% at 16 days [23] (see also the demand for the 28-days expansion in Federal Highway Administration in USA [25]). When the length expansion is beyond 0.2%, the test indicates that there is a potential harmful ASR attack in the field conditions. On the other hand, when the length expansion is within the range of 0.1–0.2%, the aggregates are classified as suspicious, thus a long-term testing is required using concrete specimens according to ASTM C1293 [26]. When the one-year expansion is above 0.04% (according to ASTM C1293), the aggregates are classified as potentially reactive.

The ASR rate decreases with decreasing the porosity of concrete and its transport characteristics including water permeability and diffusivity of participating ions [27]. There are variations in porosity between the bulk of the paste and the interfacial transition zone (ITZ), the latter being more porous and thus facilitates the leaching of reactive silica from the aggregates [27]. The reduction in these transport parameters can be achieved by internal waterproofing [28–32]. Mitigating ASR is strongly dependent on designing a dense and watertight concrete [33]. Practical solutions of ASR durability problems consist of preventive measures such as eliminating the use of reactive aggregate, minimizing the alkaline content of the used cement, and using supplementary cementing materials for densifying the concrete structure and consuming part of the alkalinity [34]. In fact, ACI 201.2 R-08 [35] highlights conflicting opinions about the use of SCMs for reducing ASR. The efficacy of fly ash in mitigation of ASR is governed by its mineral composition and pozzolanic activity. The addition of silica fumes by 10% (cement replacement) can lead to 50% reduction in the 28-days expansions [11]. ASR can be also mitigated by the addition of admixtures of lithium compounds (as powders or aqueous solutions [25,36]), through the lithium-bearing mechanism that stabilizes the reactive silica and forms non-swelling non-expansive precipitates [25].

Overall, traditional industrial solutions of ASR problems are based on minimizing the availability of ASR reactive components (e.g. from aggregates or cement content) or changing the characteristics of the ASR reaction products (using lithium compounds). Moisture is a crucial parameter in promoting and accelerating ASR. The use of typical internal waterproofing materials in mitigation of ASR has not been discussed in various review articles surveying the durability of concrete [37–41] or in related book chapters [42–46]. Recently published articles on crystalline powder admixtures did not focus on reducing ASR damages [42–46]. On the other hand, the literature includes studies on the use of pore lining (hydrophobic) materials for mitigating AAR in concrete through surface or topical treatment [47–50]. Additionally, ASR mitigation by a crystalline waterproofing penetrating material (dual-crystallization waterproofing engineered treatment (DCE)) applied topically to concrete surface has been demonstrated in a previous paper [51]. There is a need to investigate the performance of newly innovated water-based Multi-Crystallization Enhancer (MCE) intermixed with concrete for mitigating ASR and to quantify its efficiency in that role. MCE has a similar waterproofing technology as DCE. The mechanism and functionality of MCE in densifying and waterproofing the concrete

has been demonstrated in a previous publication [52]. The active ingredients of the MCE react with the portlandite to form hygroscopic and hydrophilic crystals that partially fill the pores and expand when exposed to moisture in both vapor and liquid phases [52]. The types of water interaction with cementations surfaces (hygroscopicity, hydrophilicity and hydrophobicity) are demonstrated elsewhere [53]. The role of MCE in managing thermal effects in concrete has been investigated in a recent paper [54]. The reduction in the porosity is believed to minimize the exposure of the reactive silica in aggregates to water; and hence enhances their stability. Other ingredients of the MCE react with active sites at the hydration products and form a hydrophilic layer that adds an additional protection mechanism [52]. This paper aims at investigating the secondary role of MCE for ASR mitigation. It answers the following research question: how efficient is MCE in reducing the ASR expansion when added at a dosage of 2% of cement. It is hypothesized that MCE reduces the ASR expansion in concrete by a percentage that depends on the mixture design, the types of aggregates and the method of addition. This study is limited to the investigated aggregates using the accelerated ASTM standard procedures and to one tested aggregate using the long-term ASTM standard procedure.

## 2. Experimental work

This experimental study included measurements of length change of cementitious structures subjected to ASR using mortar specimens for short term testing and concrete specimens for long term testing. Additionally, it included permeability testing using concrete cylinder specimens. The permeability was measured at a pressure of 1.4 MPa (200 psi) according to the standard test defined by the United States Corps of Engineering method (CRD-C 48–92) [55]. Concrete cylinders with dimensions of  $15.2 \times 30.4$  cm ( $6 \times 12$  inch) were made according to Texas DOT mix designed to achieve 28 MPa (4000 psia) with 4% air content. It was composed of 55% limestone coarse aggregates and 45% concrete sand (fine aggregates) with a w/c ratio of 0.43. The characteristics of the coarse and fine aggregates conformed to the requirements of “TxDOT Special Provisions 421, Hydraulic Cement Concrete”, Texas Department of Transportation, USA. The mixture of control sample utilized  $334 \text{ kg/m}^3$  of Type I/II cement,  $1090 \text{ kg/m}^3$  of limestone coarse aggregates and  $844 \text{ kg/m}^3$  concrete sand as fine aggregates. The MCE was added to the concrete mixture at a dosage of 2% by weight of cement. The permeabilities of the two types of specimens were measured at 435 days from casting.

The investigated independent parameters in the ASR study included the types of aggregates, method of the MCE addition, water to cement (w/c) ratio and time. The experimental dependent variable was the expansion due to ASR. Two groups of specimens were prepared for each of the investigated parameters, one for control mix design and the other one for 2% MCE dosed specimens. Two different proportions of limestone and sand aggregates were used in making the mortar specimens for ASR analysis. These include a blend composed of 50% limestone aggregates and 50% sand aggregates (labeled as 50/50) and 100% limestone aggregates (labeled as 100/0). The ASR experiments (with the standard 100/0 proportions) were done according to ASTM C1260 “Standard Test Method for Potential Alkali Reactivity of Aggregates (Mortar-Bar Method)” [23]. For experiments with 50/50 proportions or with w/c ratio other than 0.47, the specifications set by ASTM C1260 were modified accordingly. For these modified experiments, the allowable limit of 0.1% for ASR expansion (set by ASTM C1260) is adopted in this research for the purpose of comparing the performance of the investigated aggregates and for commenting on the performance change between control and MCE-dosed or MCE wetted aggregates. These experiments were performed in independent laboratories of CMT (Des Moines, Iowa, USA. Additional long-term ASR experiments using concrete-prism test according to ASTM C1293 ASR (CPT) “Standard Test Method for Determination of Length Change of Concrete Due to Alkali-Silica Reaction” were made in the independent laboratories of

Jensen Hughes (Chicago, USA). Independent testing certificates for all data are available.

Type I Portland cement conforming to ASTM C150 specifications was used as a binder. In the accelerated ASR tests with 50/50 proportions of sand and limestone aggregates, the sand aggregates were non-reactive from Hallett Materials from North Des Moines (NDM) with a water absorption of 0.84% and conforming to ASTM C-33 fine aggregate with grading as listed in Table 1. Five types of limestone aggregates from five locations in North America were tested. These include reactive aggregates from North Platte NE, Texas, Platte River in USA and from New Brunswick in Canada, as well as non-reactive aggregates from Ames Mine in USA. The aggregates from Platte River are gravels known to be highly reactive. As requested by the ASTM specifications, the tested limestone aggregates were sized down to match the grading as listed Table 1.

Table 2 lists the information related to the investigated limestone aggregates and the relevant testing procedures. The mortar specimens with the standard 100/0 proportions were prepared according to the standard mixing proportions specified by ASTM C1260 with aggregates to cement ratio of 2.25 [23]. The mortar specimens with 50/50 proportions were prepared with a mixing proportions of sand and limestone equivalent to those of Iowa DOT C4 mix design [56]. For the dosed specimens, the MCE was intermixed with the mixing water at 2% by weight of cement. The MCE is a patented aqueous solution including reactive ingredients of hygroscopic, hydrophilic and hydrophobic compounds. It contains combined alkali tartrate and organosilicon compounds with 15% solid content and a specific gravity of 1.1 [57]. Its viscosity is 2.4 centipoise and its freezing temperature is  $-2.2 \text{ }^\circ\text{C}$  ( $28^\circ\text{F}$ ) [52,57]. In addition to the aforementioned experiments with direct addition of MCE to the concrete mixture, experiments for a new approach of prewetting the aggregates with the MCE solution were performed. This was done using reactive Platte River gravels with two different proportions of 100/0 and 50/50 using Iowa DOT C4 mix proportions. In the case of 100/0 Platte River gravels, the mass of sand aggregates is replaced with an equivalent mass of gravels. The gravels were wetted by spraying them with the MCE and then left for drying in surrounding air to stimulate the treatment of aggregates stockpile prior to concrete batching. The saturation process of aggregates with MCE was done to achieve a net MCE absorption in Platte River gravels of 0.91% and in Hallett sand of 0.56% (measured according to ASTM C127/128 “Standard Test Method for Relative Density (Specific Gravity) and Absorption of Coarse Aggregate”).

For all types of aggregates, the w/c ratio was set at 0.47 as specified by ASTM C1260 For Research purposes, with the two types of aggregates obtained from Ames Mine and Platte River, the effect of w/c ratio was investigated by modifying ASTM C1260 using a modified mixing ratio at various w/c ratios (0.39, 0.43 and 0.47). The mixing temperature was in the range of  $21\text{--}22 \text{ }^\circ\text{C}$  ( $70\text{--}71^\circ\text{F}$ ). The casted mortar bars were cured in a proofing oven for 24 h, then they were placed into the solution of sodium hydroxide and maintained at a temperature of  $80 \text{ }^\circ\text{C}$  ( $176^\circ\text{F}$ ) for the duration of the test. The tests were performed with chemical grade sodium hydroxide, as a reagent confirming to the requirements of ASTM C1260. Then, intermittent measurements of the length change of the bars were obtained according to the predetermined intervals of 4, 7, 14 and 28 days. Three replicates were used to determine the measured

**Table 1**  
grading of limestone and sand aggregates.

Standard Sieves and openings	limestone aggregates	sand aggregates
> 4.75 mm (No. 4)	0	5%
4.75 mm (No. 4) 2.36 mm (No. 8)	10%	8%
2.36 mm (No. 8) 1.18 mm (No. 16)	25%	14%
1.18 mm (No. 16) 600 $\mu\text{m}$ (No. 30)	25%	32%
600 $\mu\text{m}$ (No. 30) 300 $\mu\text{m}$ (No. 50)	25%	31.1%
300 $\mu\text{m}$ (No. 50) 150 $\mu\text{m}$ (No. 100) 15	15%	9.9%

**Table 2**  
types of aggregates, mixing proportions and experimental details of each investigated type.

Code	Types of aggregate Source	History	Ratio of percentage limestone aggregates/sand aggregates	Testing Standard	w/c ratio	Testing
NP-NE	North Platte, NE, USA	reactive	100/0	ASTM C1260	0.47	MCE dosing
NBS	New Brunswick stone, Canada	reactive	100/0	ASTM C1260	0.47	MCE dosing
TXT	Texas, USA	highly reactive	100/0	ASTM C1260	0.47	MCE dosing two tests
AM	Ames Mine, USA	non-reactive	50/50	Modified ASTM C1260	0.39, 0.43 and 0.47	MCE dosing
PR	Platte River, west of Omaha, Nebraska, USA	highly reactive gravels	50/50	Modified ASTM C1260	0.39, 0.43 and 0.47	MCE dosing
PR-C50	Platte River, west of Omaha, Nebraska, USA	highly reactive	50/50	Modified ASTM C1260	0.47	Wetting the two aggregates with MCE
PR-C100	Platte River, west of Omaha, Nebraska, USA	highly reactive	100/0	ASTM C1260	0.47	Wetting the aggregates with MCE

parameters for each cement-aggregate combination.

In the long-term ASR experiments using the concrete-prism (ASTM C1293), the source of reactive coarse aggregates was Knife River (WY, USA) and that of the fine non-reactive aggregates was Plum Run, Peebles (OH, USA). The aggregates gradings and the proportions of the concrete mixture were designed as defined in ASTM C1293. The concrete control mixture utilized 420 kg/m<sup>3</sup> cement, 1095 kg/m<sup>3</sup> of coarse aggregates and 682 kg/m<sup>3</sup> fine aggregates with a w/c ratio of 0.42. Sodium hydroxide was added to adjust the alkali content of the cement (Na<sub>2</sub>O equivalent) to 0.89%. The MCE was added to the concrete mixture at a dosage of 2% by weight of cement. The specimens were cured and stored in accordance with ASTM C157/C157M without placing it in lime water, as required by ASTM C1293. Thereafter, the specimens were kept at 38 °C in storage containers in accordance with ASTM C1293. Then, the expansion was measured at various time intervals as described in ASTM C1293 up to one year.

The ASR curves were plotted using the average values and the error bars obtained from standard error were indicated on the plots. Comparisons of the performance of concrete specimens for control and MCE treatment were made based on the 0.1% expansion limit. The reduction in ASR expansions after 28-days were also estimated.

### 3. Results and discussion

#### 3.1. Permeability

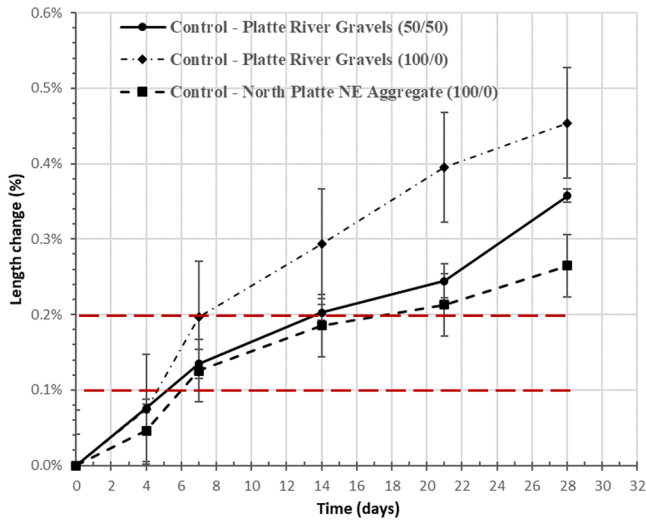
The results of permeability are listed in Table 3. The permeability coefficient of MCE dosed concrete is reduced by four orders of magnitude. It is indicated that over 99% reduction in the permeability coefficient could be obtained. This is attributed to the reduction in porosity, as well reported in the literature [27]. Such a high reduction in permeability under pressure is achieved as a result of the pore blocking mechanism of the combined hygroscopic and hydrophilic crystals. This performance is comparable with that of powder admixtures of the hydrophilic crystalline waterproofing [58,59]. The industrial literature of hydrophilic powder admixtures commonly indicates that the reduction in the permeability coefficient (measured at 1.4 MPa) is about 70%. Furthermore, the scientific literature reported a reduction in permeability of concrete with crystalline admixture by more than 60% [43] or within the range of 57–75% [59]. These previously reported reductions are lower than the obtained reduction with the MCE. This watertightness with MCE is attributed to the multiple actions of hygroscopic and hydrophilic crystals which surpasses the ability of a single-hydrophilic crystalline action.

#### 3.2. ASR analysis

Fig. 1 shows the typical ASR curves as plots of length expansion (%) versus time comparing the performance of two control specimens of known reactive aggregates: Platte River gravels and North Platte NE aggregates. The error bars, representing the standard errors of three replicates, indicate a reasonable accuracy from repeated measurements. For these two aggregates (with 100/0), the expansion at 16-days is

**Table 3**  
permeability of control and MCE enhanced concrete specimens.

Parameter	Control concrete	MCE enhanced concrete
Mix design	Texas DOT mix	Texas DOT mix with MCE at 2% by weight of cement
Curing time	435 days	435 days
permeability coefficient cm/s	$2.2 \times 10^{-6}$	$5.2 \times 10^{-10}$
Percentage error reduction in permeability	–	<5% >99%



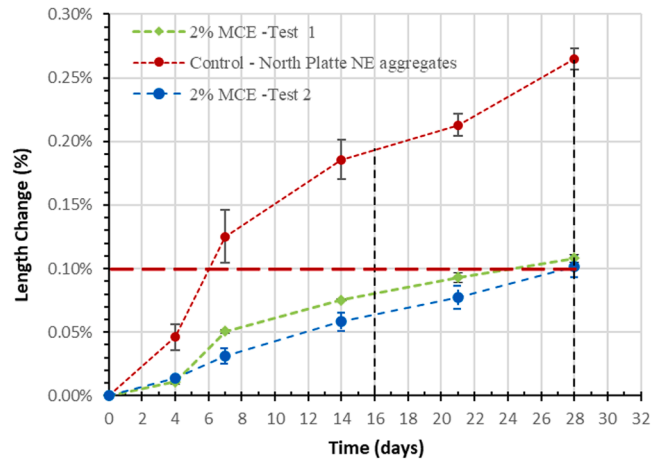
**Fig. 1.** length expansion curves of two types of control specimens made with Platte River Gravel and North Platte NE reactive aggregates for the case of 100/0, at w/c 0.47. Also shown is the curve for control specimens using Platte River reactive aggregates for the case of 50/50. The standard errors of three replicates are shown as error bars.

larger than the ASTM allowable limit of 0.1% for non-reactivity classification (set by ASTM C1260 [23]). Hence, these aggregates cannot be classified as low ASR. It is clear that the expansion for Platte River gravels at 16-days is larger than the 0.2% and hence these aggregates are confirmed to be reactive. For the case of North Platte NE aggregates, the 16-days-expansion is close to 0.2%, however, they are known to have a history of ASR reactivity.

As mentioned earlier, other limits at 28 days are also considered, at which more obvious departure from the 0.2% limit occurs for the two types of these reactive aggregates. In this paper, the 16-days expansion is considered for classifying the performance of aggregates as per the ASTM C1260 specifications. For determining the reductions with the MCE addition, the 28-days expansions are used. In principle, ASTM C1260 uses mix proportions of 100/0, as it specifies the test for one type of aggregates. However, for the purpose of comparison, Fig. 1 shows the expansion obtained for the reactive Platte River gravels with 50/50 proportions of limestone to sand aggregates. For this case, lower expansions are observed at all times. This is ascribed to the decrease in amount of the reactive aggregates (replaced by an equivalent amount of the non-reactive sand). With mixed aggregates (50/50), the expansion curve still indicates that the 16-days expansion is close to 0.2% and hence these combined aggregates are labeled as reactive. This is in agreement with the historical records of these aggregates. In fact, mitigation of ASR can be achieved by replacing a fraction of reactive aggregates with non-reactive aggregates, as shown in the two cases of Platte River gravels (100/0 and 50/50).

### 3.3. Mitigation of ASR using the MCE

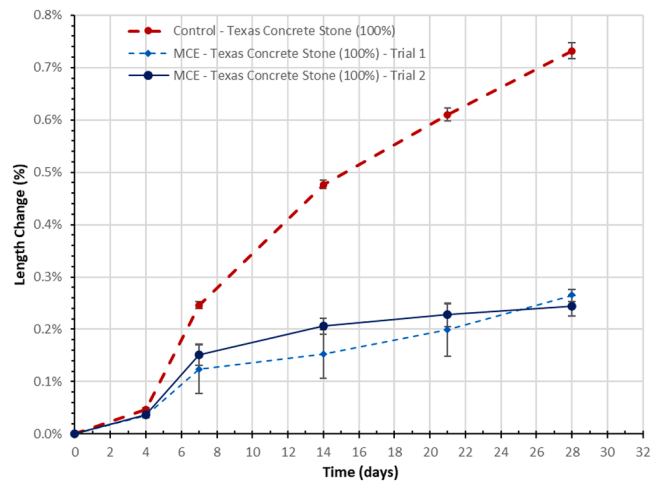
Fig. 2 shows the plots of length expansion for MCE-dosed and control specimens made with North Platte NE aggregates (for the standard case of 100/0 proportions). Again, short error bars are observed indicating a good level of experimental accuracy. It is clear that when the MCE is added to the mixture, significant reductions in expansion are obtained for the two separate trails at all days. The two separate trials of MCE dosed specimens show approximately similar performance with reductions at 28-days of 59% and 62% (the average is about 61%), which confirms the repeatability of the experiments and the validity of the results. The expansion at 16-days for the two MCE-dosed trails is below the 0.1%-allowable ASTM limit. On the other hand, the expansion for



**Fig. 2.** length expansion curves of two tests of MCE-dosed specimens compared to that for control specimens, all made with North Platte NE aggregates (for the case of 100/0 proportions) and w/c = 0.47. The standard errors of three replicates are shown as error bars.

control specimens is nearly at the edge of 0.2% limit. This indicates that upon the MCE addition, the performance of these North Platte NE aggregates is shifted from reactive to non-reactive. Such a non-reactive performance (with MCE) is nearly valid even if the 28-days expansion is considered for these aggregates; since the expansion for MCE-dosed mixture remains at the edge of the 0.1% limit. The performance of the MCE depends on the types of the aggregates, however, the role of the MCE in mitigating the ASR is maintained with different types of aggregates. Similar results were obtained when the MCE is dosed in mixtures prepared with New Brunswick Stone aggregates as appeared elsewhere [32]. For such a case, the expansion at 16-days was less than the ASTM allowable limit of 0.1% and the addition of the MCE to the mixture changed performance of New Brunswick Stone aggregates from reactive to non-reactive. The reduction in ASR expansion at 28 days was about 77% (i.e. larger than that obtained for the reactive North Platte NE aggregates (Fig. 2)).

On the other hand, when the aggregates are very highly reactive, the MCE remains functioning in reducing the ASR, but it may not lead to shifting the performance to non-reactive regime. This is the case with Texas aggregates as shown in Fig. 3 which shows curves of length expansion for MCE dosed and control specimens made with Texas



**Fig. 3.** length expansion curves of two tests of MCE-dosed specimens compared to that for control specimens made with Texas Concrete Stone aggregates (100/0 proportions) at w/c = 0.47. The standard errors of three replicates are shown as error bars.

Concrete Stone aggregates. The length expansions of control specimens using such highly reactive aggregates are much higher than those for all other tested aggregates in this work. For example, the 16-days expansion for these aggregates is over 0.5% while that for North Platte NE aggregates is at the edge of 0.2% (Fig. 2) and that for the reported expansion for New Brunswick Stone aggregates is lower than 0.3%. In this case (Texas aggregates), the expansion at 16-days for MCE-dosed specimens is higher than the ASTM acceptable limit of 0.1%. Using MCE changes the performance of these highly reactive aggregates from reactive to suspicious. However, as in the other two types of reactive aggregates, adding 2% MCE to the specimen mixture led to major reductions in the expansion at all days. Fig. 3 shows that the reduction in ASR expansion at 28 days is 63.8% and 66.6% for trials 1 and 2, respectively. The average reduction of the two trials is 65%. This value is close to the obtained value for the previous aggregates in Fig. 2 (i.e. 61%).

At the same w/c ratio of 0.47, a similar ASR mitigation performance was observed for non-reactive aggregates (Ames Mine) but with a reduction of 33% since the level of reactivity of these aggregates is already low. The performance of these non-reactive aggregates and other highly reactive aggregates of Platte River gravels as functions of w/c are presented and discussed in the following section.

### 3.4. Effect of water-to-cement ratio

The effects of w/c ratio are shown in Figs. 4 and 5 as plots of length expansion for MCE-dosed and control mortar specimens for non-reactive aggregates of Ames Mine and reactive aggregates of Platte River gravels,

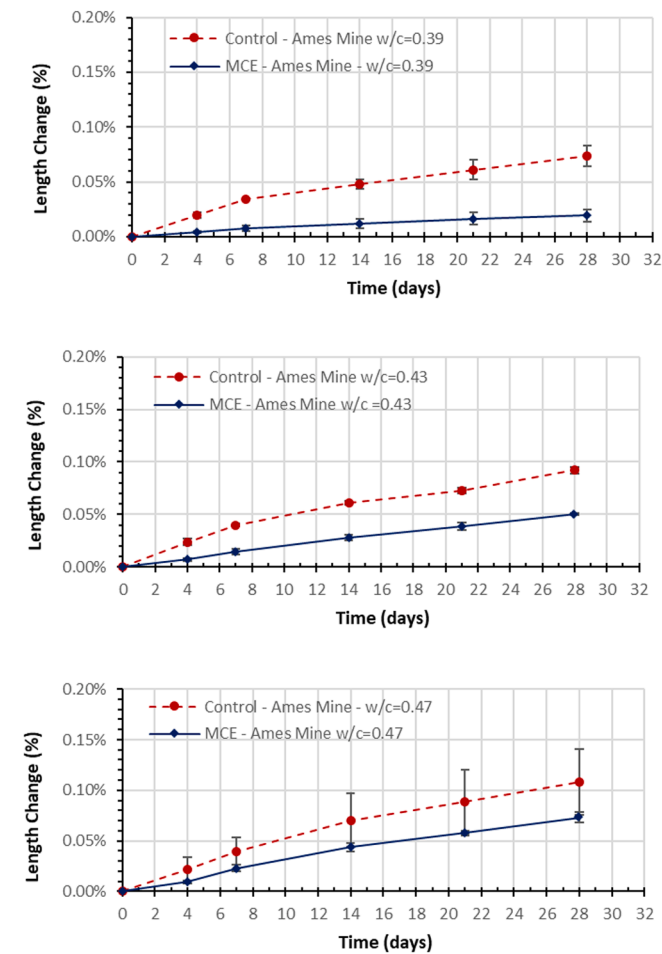


Fig. 4. length expansion curves of MCE-dosed and control mortar specimens using Ames Mine aggregates (50/50) at various ratios of w/c: 0.39 (a), 0.43 (b) and 0.47 (c).

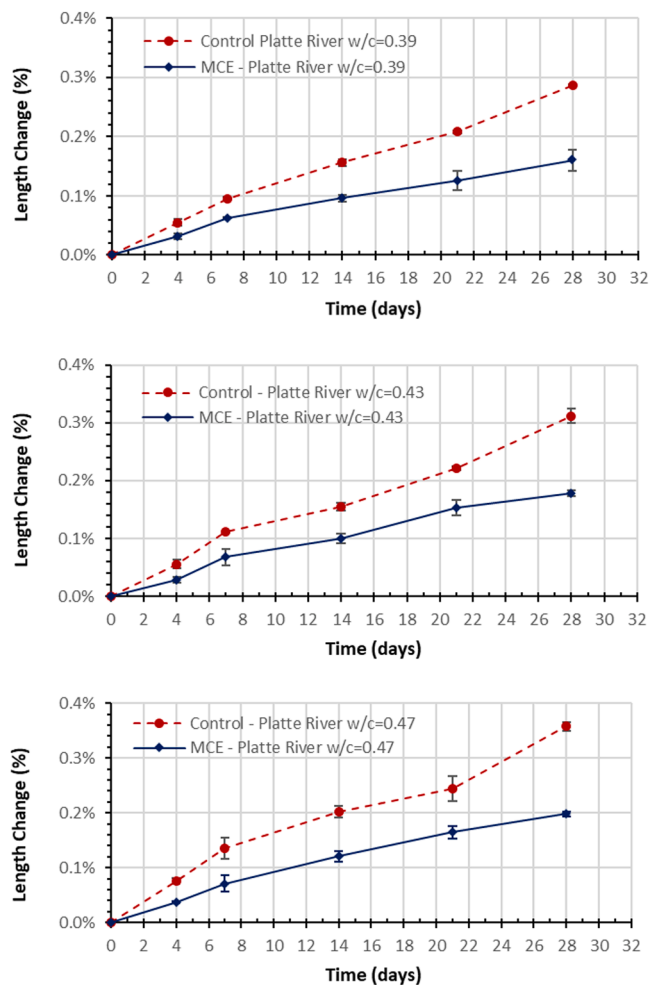


Fig. 5. length expansion curves of MCE-dosed and control mortar specimens using Platte River Gravel (50/50) at various ratios of w/c: 0.39 (a), 0.43 (b) and 0.47 (c).

respectively (for 50/50 proportions). Figs. 4 and 5 show that the ASR damages increase with increasing w/c ratio for control and MCE-dosed specimens. This is attributed to the rise in the porosity at higher w/c ratios (as well reported for concrete [60]). Regardless of w/c, the addition of the MCE decreases ASR expansion significantly.

For control specimens with Ames Mine aggregates, Fig. 4 shows that the 16-days expansion at all investigated w/c ratios are below 0.1%. Hence, these combined aggregates are already classified as non-reactive and they possess low ASR risk under field conditions without the use of the MCE. However, the use of the MCE leads to additional significant reduction in ASR expansions. In contrast, the 16-days expansions for mortars with Platte River gravels (Fig. 5) are higher than the 0.1% limit of ASTM. For the high w/c ratio (0.47), the combined aggregates are already classified as reactive since the 16-days expansion exceeds the 0.2% limit. However, for low w/c ratios (0.39 and 0.43), the expansion of control specimens at 16-days is within the range of 0.1–0.2%. Hence, ASTM C1260 demands further testing for these aggregates using ASTM C1293 [26]. In fact, the limits set by ASTM C1260 are based on the standard testing with w/c = 0.47, but reducing the w/c (to 0.43 or even 0.39) (for research purposes with modified ASTM C1260) would reduce the ASR attack due to compactness of the structure (obtaining more watertight structure). Hence, the Platte River gravels maintain the ASTM reactive classification regardless of the results at low w/c ratios, as it is well known from their historical records. When the MCE is dosed at 2% of cement weight, a substantial reduction in ASR expansion is attained at each w/c ratio, as seen in Fig. 5 for the reactive aggregates.

For all w/c ratios, the ASR expansions for MCE-dosed mortars at 16-days are either at the edge of 0.1% or slightly above it (for the standard w/c ratio of 0.47) (Fig. 5). This indicates that the use of the MCE shifts the performance of these aggregates from the region of reactivity to non-reactivity classification. The reductions in ASR expansion for the reactive aggregates are very close at 44.0%, 42.9% and 44.7% for w/c = 0.39, 0.43 and 0.47, respectively. For the non-reactive aggregates (Fig. 4), a larger reduction can be obtained at low w/c ratios (73.7%). Then, increasing the w/c ratio decreases the reduction in expansion to 45.4% and 32.7% for w/c = 0.43 and 0.47, respectively. This is attributed to the level of aggregate reactivity and how it interacts with w/c ratio towards MCE efficacy in lowering expansion.

3.5. Mitigating ASR by wetting of aggregates with the MCE before batching

A new proposed approach for mitigating ASR by pretreatment of the aggregates with the waterproofing material is proposed. For the purpose of comparison, results of pretreating the reactive aggregates (Platte River Gravel) by wetting with the MCE are presented and compared with those for dosing the MCE with the mixture. Fig. 6 shows length expansion curves for control specimens of Platte River gravels and specimens prepared with MCE-wetted Platte River gravels for the standard case of 100/0 proportions at w/c = 0.47. It is clear that pretreating the reactive aggregates with the MCE leads to noticeable reductions in the expansion at all periods. However, the ASTM classification of the MCE wetted Platte River gravels remains as reactive when the 28-day expansion is considered. Fig. 7 shows length expansion curves for control specimens of Platte River gravels and specimens prepared with MCE-wetted Platte River gravels for the case of 50/50 proportions at w/c = 0.47. A similar trend of reduction in length expansion is obtained at all days as for the case with 100/0 proportions. However, the expansion at 16-days is lower than the 0.2% limit set by ASTM for reactive classification. Furthermore, the expansion at 14-days is close to the 0.1% allowable limit for nonreactive classification. On the other hand, the expansion of control specimens is larger than 0.2%. Hence prewetting these combined aggregates (50/50 proportions) changes their ASTM ASR classification from reactive to nonreactive (based on 14-days limit) and to suspicious (based on 16-days limit as obtained with the case of MCE-dosing in the specimen mixture (see Fig. 5c). This performance can be explained by the ability of the MCE absorbed within the aggregates to block their pores and hence reduces the leaching of reactive silica to the pore solutions and reduce the penetration of water to the aggregates. Additionally, it is believed that upon specimen wetting during ASR activity, the MCE crystals can extend from within the aggregates towards the ITZ at the aggregate paste interface, leading to a significant densifying effect. The reduction in ASR expansion at 28 days is 27% for mortars with

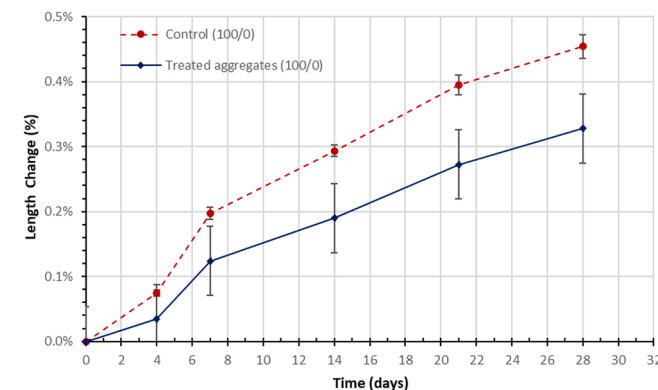


Fig. 6. length expansion curves of mortar specimen with MCE wetted aggregates and control mortar specimens using Platte River Gravel (100/0) at w/c = 0.47. The standard errors of three replicates are shown as error bars.

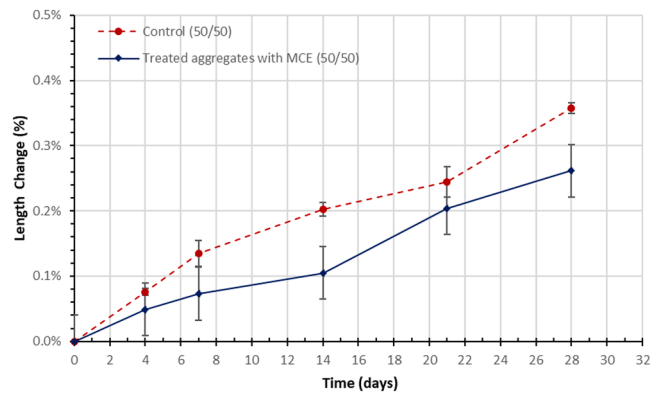


Fig. 7. length expansion curves of mortar specimen with MCE wetted aggregates and control mortar specimens using Platte River Gravel (50/50) at w/c = 0.47.

50/50 proportions and 28% for mortars with 100/0 proportions.

When comparing the ASR expansions of mortar specimens prepared with various methods of applications using this crystalline waterproofing technology (e.g. MCE-dosing to specimen mixture, MCE-prewetting of the aggregates, and DCE topical treatment of the specimen), it can be noted that all methods of applications lead to similar effects of decreasing the ASR expansion. In all cases, the performance of aggregates based on 16-days length expansion is shifted for the MCE or the DCE treatment from reactive to inconclusive. However, there are variations in the obtainable reductions in ASR: MCE-prewetting aggregates achieved 27% reduction in expansion which is lower than that obtained with the MCE dosing to the mortar mixture (45%), but it is to some extent higher than that for the DCE topical treatment (i.e. 24%) [51]. These differences are believed to be ascribed to differences in the net crystallization of the MCE within the pores in each method of application. The level of performance is governed by other factors such as the MCE soaking time, the porosity of aggregates and their moisture content. A more in-depth investigation of such an approach is recommended for future work.

3.6. Mitigating ASR using the MCE with long-term ASR testing

The results of the long-term ASR experiments using the concrete-prism (ASTM C1293) for reactive coarse aggregates of Knife River type are shown in Fig. 8 as plots of the expansion versus time for one year period for MCE-dosed and control concrete specimens. With 2%

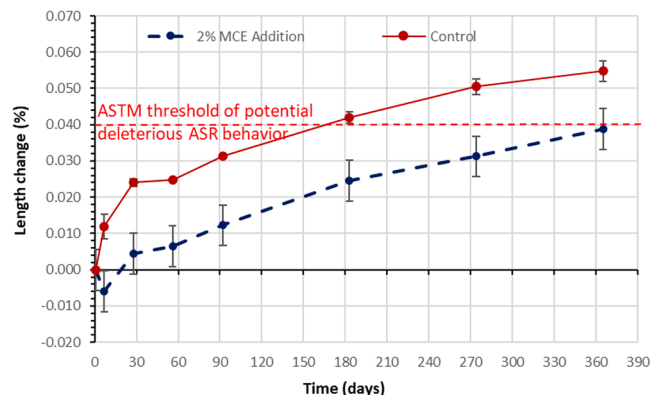


Fig. 8. curves of length expansion as functions of time for long-term ASR testing showing results for control specimens made with reactive coarse aggregates of Knife River compared to those for MCE-dosed specimens. The standard errors of the replicates are shown as error bars. Also shown is the ASTM threshold indicative of potential deleterious ASR behavior (dashed line).

MCE addition, about 30% reduction in a one-year ASR expansion was achieved. It is clear that the expansion of the 2% MCE dosed specimens is lower than the one-year ASR expansion threshold set by ASTM C1293 at 0.04%. This confirms that the MCE performs well for mitigating the long-term ASR expansion and it meets the requirements of ASTM C1293 (see Fig. 8).

### 3.7. Summary of results and further discussion

Table 4 lists the reduction in ASR length expansions of mortar bars prepared with each type of the investigated aggregates at  $w/c = 0.47$  at the two periods of 14-days and 28-day. Table 4 shows that there are no major differences in the reductions between the 14-days and the 28-days expansions. For the standard 100/0 proportions, the differences are below 5%, while for the 50/50 proportions, the differences are below 9%. This means that any of the two periods can be considered for evaluating the performance based on percentage reduction in ASR expansion. The reductions in ASR of reactive limestone aggregates (with 100/0 proportions) are in the range of 61–81%. These reductions are larger than those reported previously for mixes containing SCM's, for example, the addition of silica fume 10% (as a replacement of cement) can lead to 50% reduction in the 28-days expansions [11]. In this work, lower reductions in ASR expansion (41–45%) were obtained for reactive gravels mixed with non-reactive sand (50/50 proportions), since the level of reactivity of the combined aggregates in the specimens (their availability) were already reduced upon replacing part of them with non-reactive sand. Similarly, lower reductions in ASR expansion (33–38%) were obtained for non-reactive combined aggregates (the last row in Table 4) since they were already with low reactivity due to their structural stability.

These results show that the MCE leads to significant performance enhancement in reducing ASR attacks on concrete and leads to a noticeable dimensional stability. This is hypothetically achieved because of reducing moisture content in concrete (as confirmed in a previous study under standard curing condition [52]) which is a key strategy in mitigating lethal ASR damages; since the ASR mechanism demands the availability of necessary moisture content in concrete (i.e. above 80% relative humidity) for facilitating the solubilization of the reactive silica content from aggregates [9]. Significant reductions in moisture content in MCE dosed concrete were reported in a previous publication (in terms of reducing the relative humidity) through dynamic interaction of hygroscopic crystals with moisture [52]. These reductions in moisture content are attributed to the adsorption of moisture onto the hygroscopic crystals with an associated mass increase of the crystals [52]. The formed MCE crystals reduce the accessibility of unbound moisture through its utilization in the growth of crystals and thus decrease the internal humidity within concrete as reported in a previous publication [52]. Additionally, the crystalline products of the MCE block the pores and the capillary networks and expand through their hygroscopic and hydrophilic behaviors utilizing moisture in crystal growth. Such a hypothesized mitigation mechanism is also attributed to the reactions of hygroscopic and hydrophilic active ingredients of MCE

**Table 4**  
reductions in ASR expansion of mortar bars for the investigated aggregates at  $w/c = 0.47$ .

Aggregate type/ code	ASTM Aggregates Classification	Ratio of limestone to sand aggregates	ASR Reduction in 14-days length expansion	ASR Reduction in 28-days length expansion
NP-NE	reactive	100/0	64%	61%
NBS	reactive	100/0	81%	77%
TXT	Highly reactive	100/0	62%	63%
PR	reactive	50/50	41%	45%
AM	non-reactive	50/50	38%	33%

which consume part of the alkalinity (from calcium hydroxide) that drives the aforementioned ASR mechanism (see the Introduction). These combined mechanisms reduce concrete saturation and dissolution of portlandite ( $\text{Ca(OH)}_2$ ). In brief, the hypothesized mechanisms of mitigating ASR using the MCE is based on minimizing the ASR reactions (decreasing the reactants and the availability of the medium). The validity of such hypothesizes is limited to the assumption that pore blocking and lining mechanism of MCE (described in previous work [52]) remains the same under the alkaline condition of the ASR experiments. This ability for mitigating ASR is uniquely documented for the MCE crystalline materials; as there are no ASR data for hydrophilic waterproofing materials are available in durability studies of concrete with waterproofing materials [37–41] or for crystalline powder admixtures [42–46], as mentioned in the introduction. However, a similar kind of performance was reported for some surface treatments with pore lining (hydrophobic) materials [47–50] and for a crystalline waterproofing penetrating material (DCE) [51].

## 4. Conclusions

The MCE is an effective multifunctional waterproofing system that enhances the concrete resistivity against ASR for reactive and non-reactive aggregates. This is accomplished by dosing the MCE in a concrete mixture or by pre-wetting the aggregates. When the  $w/c$  ratio is increased, the ASR expansions for all types of aggregates are increased due to the increase in the permeability. The dosing of the MCE to the concrete mixture reduces its permeability and decreases ASR expansion by a significant percentage that depends on the type of aggregates and the  $w/c$  ratio. For reactive and highly reactive aggregates, the 16-days expansion for control specimens is above the allowable limit, and the use of the MCE reduces the expansion considerably. In most cases, the addition of the MCE shifts the performance of reactive aggregates from reactive to non-reactive classification. For the non-reactive aggregates, the 16-days expansion expansions for both the control and MCE enhanced concrete are below the ASTM allowable limit, while an additional reduction in expansion with the MCE addition was observed.

Based on the reported findings for adding the MCE to the concrete mixture at 2% by weight of cement, the following conclusions are stated:

- 1) Concrete permeability is reduced by more than 99%.
- 2) The ASR expansion of reactive aggregates is reduced by a percentage in the range of 45–77%.
- 3) The ASR expansion of non-reactive aggregates is decreased by a percentage in the range of 33–74%.
- 4) The long-term ASR testing confirms the functionality of the MCE in mitigating the ASR in concrete.
- 5) Furthermore, the treatment of reactive aggregates by prewetting with the MCE can reduce ASR expansion by a percentage of about 27%.

The recommendations for further research work include

- (1) in-depth investigation of mitigating ASR by pretreatment of various types of aggregates by their wetting or soaking with the waterproofing material and further testing program using long term tests (according to ASTM C1293).
- (2) microstructure and mechanism analysis after ASR experiments (for control and MCE-dosed specimens) by measuring portlandite content (e.g. by TGA), the alkalinity of pore solution (e.g. by the extraction of pore solution), microstructure of ITZ (e.g. by the SEM-EDS).

## Declaration of Competing Interest

This research is done for International Chem-Crete Co. to which the authors belong. The testing was done in independent laboratories, with



available testing certificates. There is no conflict of interest regarding the publication of this paper.

## Data availability

All data, models, and code generated or used during the study appear in the submitted article.

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