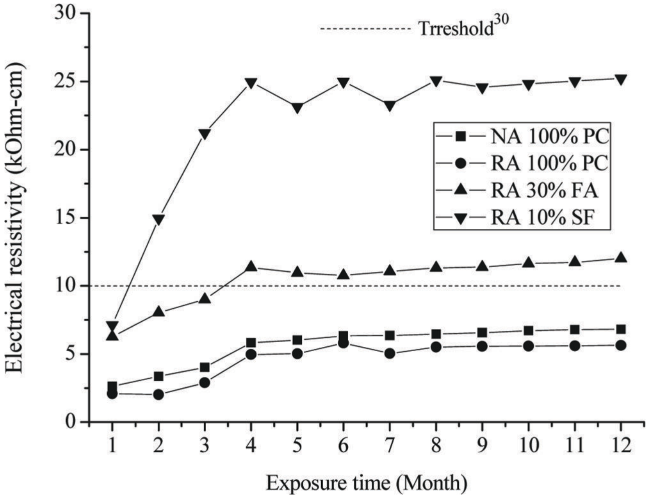

Fig. 5–Evolution of electrical resistivity as a function of exposure time

the porosity in the cementitious matrix,[11-15] which results in an increase in the electrical resistivity.

The i_{corr}, results determined from the values of Rct are presented in Fig. 6. On-going hydration leads to a decrease in measured i_{corr} up to about 4 months of chloride exposure, except for FA mix, the latter might have combined chlorides at an early age itself. Between fourth and approximately eighth month there is no change in i_{corr}, suggesting an equilibrium state on chloride binding and microstructural changes. Beyond 8 month, the two 100% PC concretes exhibited and increase in rate of corrosion, however this did not happen for concretes containing SCM.

The previous results indicate that although a significant difference of ρ in mixtures with the two SCMs exists, their corrosion resistance is of same magnitude; this is attributable to the high content of Al_2O_3 (≈17%) in the FA, contributing to the formation Friedel salt or tricalcium chloroaluminate ($3CaO.Al_2O_3.CaCl_2.10H_2O$) when chlorides penetrate. Therefore, the FA addition generates, in the cementitious matrix, a higher content of Friedel salt and, consequently, lower levels of free chlorides. The above was verified by means of XRD (Fig. 7), in which the peak at $2\theta = 11.18°$ represents Fiedel salt. It can be seen in Fig. 7 that a higher intensity is observed for the mix with FA than for the mix with 100% PC.

Resistance to chloride ion penetration

In Fig. 8, the results of charge passed according to the ASTM C1202 procedure of test are presented. The results indicate, first, that the use of 100% of RCA decreases its capacity to resist the penetration of the chloride ion in approximately 30% compared to the conventional concrete. On the other hand, it can be observed that the use of FA and SF provides to the concrete a greater capacity to inhibit the chloride ions penetration, because the charge passed in the mix RA 30% FA and RA 10% SF is three and five times smaller, respectively, than the mix RA 100% PC. According to the criterion proposed by ASTM C1202 (Table

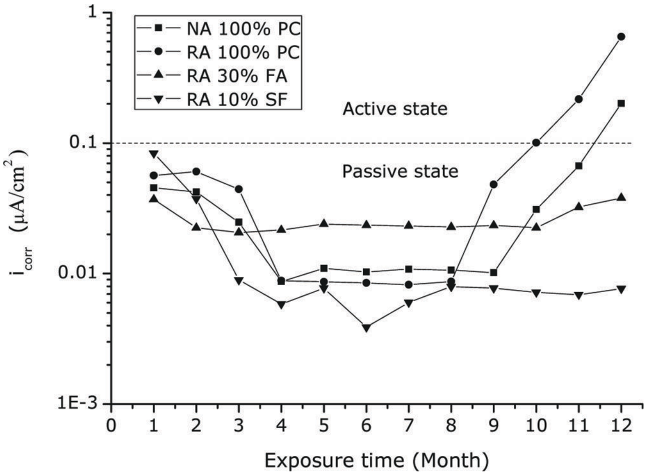

Fig. 6–Variation of corrosion current density as a function of exposure time

4), the mixes without SCMs present a high penetrability of the chloride ion because it surpasses the 4000 Coulombs, meanwhile the penetrability in mix with SCMs is classified as low because the values are between 1000 and 2000 Coulombs. These results are comparable with those reported by Ann, et al.[11]

The high resistance to chloride ion penetration in mix with SF is due to the greater densification of the cementitious matrix, as observed in Fig. 9 (micrograph obtained by SEM). This could be considering to have reduced significantly the capillary porosity and restricted the chlorides permeability. For the mix with FA, in spite of the fact that its cementitious matrix has similar compactness to 100% PC (Fig. 9a and 9b), the formation of Friedel salt in greater quantity and the obstruction of pores with particles of FA without reacting might have contributed to a smaller permeability of chloride ions.

CONCLUSIONS

- The use of 100% of RCA decreases the corrosion resistance of reinforcement in concrete. Nevertheless, the use of SCMs in concretes with 100% of RCA increases the corrosion resistance in an accelerated chloride exposure environment.
- The 100% replacement of natural aggregate with RCA decreases the electric resistivity of concretes and the initiation time for the reinforcement corrosion as well as increases the rate of corrosion.
- The fly ash and the silica fume doubled and quadrupled, respectively, the electric resistivity of concretes. As a consequences they delayed the onset of reinforcement corrosion and decreased its rate.
- Although the magnitude of the electric resistivity in concretes with silica fume is double that of the concrete with fly ash, both have similar corrosion resistance, due to high Al_2O_3 content in fly ash and its contribution to the formation of Friedel salt. This leads to a reduction in the permeability of chloride ion of this concrete.

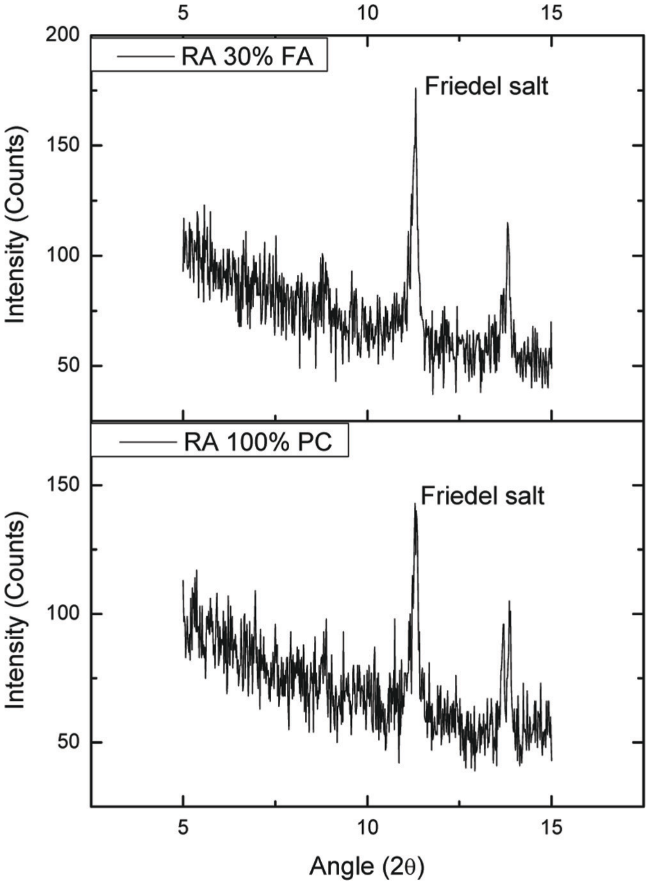

Fig. 7–X rays patterns – Friedel salt

- The RCPT results indicate that concretes manufactured with RCA have a higher chloride ions permeability than conventional concrete. The use of 30% FA and 10% SF leads to a decrease in the total charge passed through the concrete by three and five times, respectively. This signifies a considerable increase in the resistance of these concretes to chloride ion penetration.
- Overall, it has been found that any detrimental effect of the use of RCA in reinforced concrete exposed to chloride induced corrosion can be eliminated by using 30% FA and 10% SF.
- It is possible to make concrete using RCA and SCMs that is durable under the conditions tested.

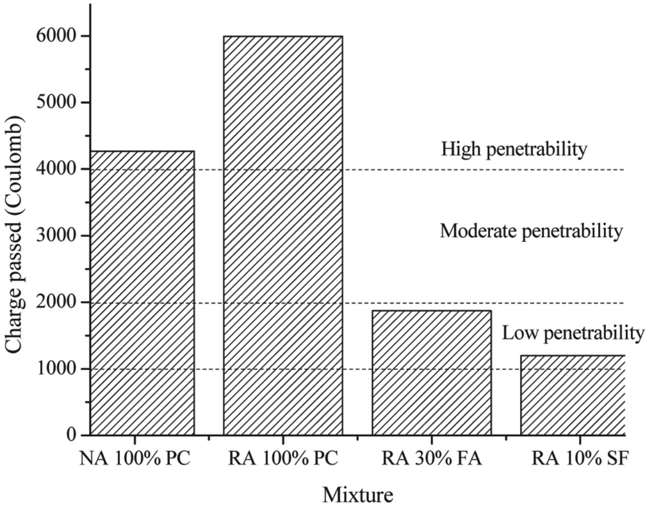

Fig. 8–Resistance to chloride ion penetration

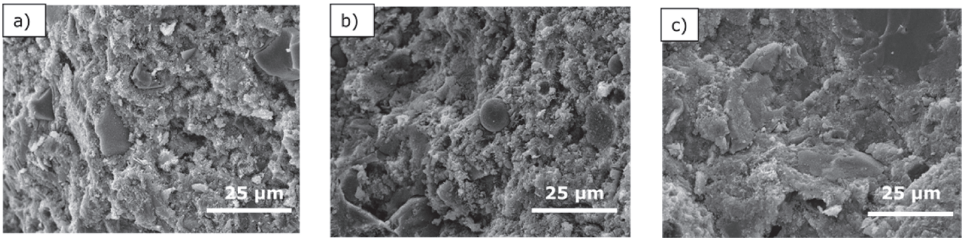

Fig. 9 a)–Microstructure of cementing matrix after 90 days of hydration: 100% PC; b)–Microstructure of cementing matrix after 90 days of hydration: 70% PC – 30% FA; and c)–Microstructure of cementing matrix after 90 days of hydration: 90% PC – 10% SF

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The Long-Term Monitoring of Large-Scale Concrete Specimens Containing Lithium Salts to Mitigate Alkali-Silica Reaction

by Thano Drimalas, Jason H. Ideker,
Anthony F. Bentivegna, Kevin J. Folliard,
Benoit Fournier, and Michael D. A. Thomas

Synopsis: The effectiveness of lithium salts to prevent alkali-silica reaction (ASR) in laboratory samples has been known since the early 1950s; however, the long-term effectiveness of lithium on concrete in the field has not yet been established. This paper details the long-term exposure of large-scale concrete specimens and one monitored concrete pavement section subjected to outdoor field conditions containing either lithium hydroxide (LiOH) or lithium nitrate ($LiNO_3$) as an admixture to control ASR. Four different locations were chosen to investigate the impact of varying climatic conditions on the progression of ASR in concrete, including three land-based sites: Austin, Texas (USA), Ottawa, Ontario (Canada), and one marine site at Treat Island off the coast of Eastport, Maine (USA). A concrete pavement containing lithium (LiOH) in New Mexico, USA, was also monitored for 18 years since placement. The results of these studies confirm that different dosages are needed depending on the aggregate mineralogy, based on realistic exposure conditions, and it may take up to 16 years (or even more) for some concretes to begin deteriorating based on exposure conditions and the reactivity of the aggregate. Combinations of lithium and fly ash have shown that both synergistically beneficial and detrimental effects (e.g. increased expansion) may occur.

Keywords: lithium admixture; alkali-silica reaction; exposure site, lithium, concrete durability

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INTRODUCTION

This paper focuses on the use of lithium salts to control alkali-silica reactivity under realistic exposure conditions (e.g. not accelerated laboratory conditions). To determine the long-term efficacy of lithium as a chemical admixture to control ASR, concrete blocks containing lithium (mainly $LiNO_3$), and with combinations of fly ash plus lithium, were cast and placed in outdoor exposure sites across North America. The use of different outdoor exposure conditions provided information on the impact of environmental conditions on the progression of ASR and the efficacy of mitigation measures. A concrete pavement containing lithium hydroxide monohydrate in New Mexico, USA, was also monitored for 18 years since placement. Fournier and co-workers demonstrated that concrete exposure blocks cast with alkali-silica reactive aggregates in warmer climates tend to show a more rapid onset of expansion than concrete exposure blocks incorporating the same reactive aggregate types exposed to cooler climates.[1] This work focused on aggregate reactivity and not mitigation measures.

While the use of lithium salts to mitigate ASR in relatively small laboratory samples is well known[2-4] ; the long-term efficacy of lithium salts to control ASR in real exposure conditions has not been established. Many of the early laboratory research was performed using the ASTM C 227 mortar bar test, which has numerous drawbacks including small bar size, increased leaching and mass loss during the test. McCoy and Caldwell determined, based on testing a large number of different lithium salts, that a lithium-to-alkali molar ratio of 0.74 or above was sufficient enough to suppress expansion for alkali-silica reactive aggregate (Pyrex glass). Later work by Sakaguchi and co-workers showed that a molar ratio of lithium (based on LiOH) to alkali of 0.90 or above was sufficient to control detrimental alkali-silica reactivity.[4] Work by Thomas conducted at the Building Research Establishment (BRE) in the UK in 1994 included investigations into laboratory samples containing lithium salts and outdoor exposure of concrete blocks at the BRE exposure site.[5] Thomas found similar results to that of McCoy and Caldwell showing that a 0.70 molar ratio or above was able to suppress expansion for $LiNO_3$ for certain aggregate types, but a molar ratio of 0.85 was needed for LiOH (owing mainly to the contribution of increased $[OH]^-$ from LiOH).

However, recent research by Tremblay and co-workers has shown that not all aggregate types respond to lithium nitrate as an admixture in the same manner in laboratory testing (ASTM C 1260, C 1293).[6,7] Generally speaking, the faster reacting aggregates (e.g. a higher degree of disorder in the amorphous silica structure, e.g. volcanic aggregates/glass, chert) respond better to lithium than more slowly reacting aggregates (e.g. a lower degree of disorder in the amorphous silica structure and/or more finely disseminated reactive silica in the rock matrix, e.g. siliceous limestone, greywacke).[6,7] An exhaustive summary of all research done on lithium salts to control ASR is beyond the scope of this paper. Readers are directed to a recent report regarding the use of lithium salts to control ASR from Folliard and co-workers.[8]

This paper provides results of testing the efficiency of lithium salts in concrete blocks exposed to ambient environmental conditions at four different exposure sites across North America. Since the majority of these outdoor exposure blocks were cast prior to publications by Tremblay et. al,[6,7] the lithium dosage is based on a 0.74 molar ratio of Li to Na_2O_{eq}. The goal of these investigations was three-fold: 1) confirm long-term efficacy of lithium nitrate and combinations of fly ash plus lithium, 2) determine the impact of environmental exposure (not captured in laboratory testing), 3) determine long-term efficacy of lithium hydroxide monohydrate in a pavement section after 18 years of exposure.

RESEARCH SIGNIFICANCE

The use of lithium salts has been known to suppress ASR expansion in laboratory testing in fresh concrete. However, little long-term monitoring has been performed to validate in-situ efficacy of lithium-based admixtures in controlling expansion due to ASR. Only a handful of cases have been monitored over the years. It is crucial to understand the field service-life of these concretes that contain lithium admixtures to prevent ASR for improved mitigation and long-lasting concrete.

EXPERIMENTAL INVESTIGATION

The work presented herein is part of a larger experimental program. The primary focus of this paper is on the relationship between exposure blocks in different climatic conditions and the effectiveness of dosages of lithium admixtures to control ASR and combinations of lithium with fly ash. Two laboratories cast the blocks, with laboratory 1 casting blocks for the CANMET and Treat Island exposure sites, and laboratory 2 casting blocks for the Texas exposure sites. A set of five different alkali-silica reactive aggregates were chosen based on degree of reactivity. A control (reactive) block was cast for each of these aggregates along with a companion exposure block that contained a recommended 100% $LiNO_3$ dosage (standard dosage).

Materials

A wide range of aggregates and other cementitious products were selected for casting the exposure blocks. In many cases, the materials chosen are those commonly tested at each laboratory. Aggregates were chosen from all across North America. Table 1 provides the details of the aggregates studied. Aggregates were chosen to provide a wide range of mineralogical composition and reactivity. Six coarse aggregates and four fine aggregates were selected. Non-reactive aggregates are listed as well, which are incorporated with reactive aggregates in the mixtures. The reactivity level was determined through ASTM C 1260 and ASTM C 1293 testing.

Two high-alkali cements were chosen for this study. Each laboratory used a high-alkali cement; its chemical composition is shown in Table 2. A Class C fly ash (FA1) and Class F fly ash (FA2) from Texas that conformed to ASTM C 618 were used. Chemical constituents are shown in Table 3.

Admixtures

The lithium-based admixture used in this program was a commercially available lithium-nitrate solution ($LiNO_3$) with 30% solid (by mass). The manufacturer's recommended dosage (also called *standard dosage*) for this admixture is 4.63 L $LiNO_3$ solution for every kg (0.55 gal of $LiNO_3$ solution for every lb) of Na_2O_{eq} from the portland cement, which is referred in the paper to a *100% dosage*. This is also equivalent to a 0.74 lithium-to-alkali molar ratio ([Li]/[Na+K]).

Mixture Proportions and Specimens

The mixtures were cast following ASTM C 1293 mixture designs, which specifies a cement content of 420 ± 10 kg/m^3 (708 ± 17 lb/yd^3). Mixtures containing SCM's were incorporated in replacement dosages that ranged from 20-40%. The water-to-cement ratio