Effectiveness of Lithium Nitrate in Mitigating Alkali-Silica Reaction in the Presence of Fly Ashes of Varying Chemical Compositions

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Abstract: In this study, quantitative analysis of the combined effects of fly ash and lithium admixture in mitigating alkali-silica reaction (ASR) in portland cement mortars prepared with Spratt limestone was investigated. The results from this investigation suggested that mortar bar expansions could be correlated with specific oxide(s) content in the fly ash through exponential relationships. The dosage of lithium nitrate required for ASR mitigation in mortars containing fly ashes having CaO content less than 23.50% was found to be less than that in the control mortars. Since lithium nitrate was found to be effective in reducing the expansions of control (no fly ash) mortars and mortars containing fly ashes, economic solutions can be obtained in both. However, the use of lithium nitrate was not needed for mortars containing fly ashes having CaO content less than 14.40%. A linear relationship between the oxide content of fly ash and the lithium dosage was found to exist, that can be used to optimize the lithium dosage as a function of fly ash composition to provide an economic solution for ASR mitigation.
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Introduction

The deterioration of concrete due to alkali-silica reaction (ASR) is well known and has gained more prominence during the last two decades due to the increased need to use marginal aggregate sources and the rise in the alkali contents of modern-day portland concrete (Folliard et al. 2006). In new constructions where the previous two parameters are unavoidable, the use of supplementary cementing materials (SCMs) or lithium admixtures in concrete have been suggested as effective strategies by many investigators to counteract ASR (McCoy and Caldwell 1951; Sakagushi et al. 1989; Folliard et al. 2006; Thomas 1996). Specifically, the use of fly ash or lithium nitrate in concrete containing reactive aggregates has become popular in the recent years, as numerous studies conducted with each of these mitigation measures have shown to reduce expansions due to ASR substantially (Dunstan 1981; Shehata and Thomas 2000; Durand 2000; Collins et al. 2004; Schneider et al. 2008).

Fly ashes are usually classified based on CaO or $SiO_2 + Al_2O_3 + Fe_2O_3 (S + A + F)$ content as per the standard specifications (ASTM C 618; CSA A3001) and have been extensively used in concrete during the last four decades to solve several durability problems including ASR. The widely accepted mechanisms by which fly ashes mitigate ASR are the pozzolanic reactivity of the fly ash particles (Diamond and Lopez-Flores 1981; Ravina 1981; Mehta 1985), the alkali binding ability of calcium-silicate-hydrate (C-S-H) gel produced as a result of pozzolanic reaction (Shehata and Thomas 2000) and the reduced permeability of this C-S-H gel having low CaO/SiO_2 ratio (Mehta 1985). Most of the studies conducted using different fly ashes in concrete to address ASR problems indicated the following: (1) the replacement level of fly ash needed to achieve ASR mitigation is dependent on its CaO content, the alkali content of cement and the degree of reactivity of aggregate (Shehata and Thomas 2000; McKeen et al. 2000; Touma et al. 2001); (2) a high-replacement level between 45 and 60% and a low-replacement level between 20 and 30% may be required to mitigate ASR when using high-lime and low-lime fly ashes, respectively (Shehata and Thomas 2000); and (3) the low-lime fly ashes are more effective in reducing the pore solution alkalinity than the high-lime fly ashes (Shehata et al. 1999). Almost all fly ash can be used to mitigate ASR provided adequate dosage is used. However, high-replacement levels of high-lime fly ashes and certain intermediate-lime fly ashes pose restrictions for their use in concrete due to potentially lower strengths achieved at early ages, resulting in constructability problems (Papadakis 2002a, b). Therefore, effective strategies are required to utilize these fly ashes beneficially. In addition, the availability of fly ash is often limited by geographical region and hence in locations where only high-lime or intermediate-lime fly ash is available, effective strategies are required to utilize these materials in order to reduce material transportation cost.

The strategy of using lithium admixtures in concrete containing reactive aggregates to control expansions due to ASR was first established in 1950s (McCoy and Caldwell 1951). However, it was only in the 1990s that the use of lithium as a strategy has been more widely adopted by the industry. Several investigations conducted using different lithium admixtures for ASR mitigation suggested that lithium nitrate was the most effective (Durand 2000; Collins et al. 2004; Schneider et al. 2008; Thomas et al. 2000). The dosage of lithium nitrate (in terms of lithium to sodium ion molar ratio) required to reduce ASR expansions within permissible limits in concretes containing portland cement as binder, was found to be between 0.72 and 0.80 (Durand 2000; Thomas et al. 2000), depending up on the reactivity of aggregate used and alkali content in

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concrete. Though the mechanism with which lithium nitrate reduces expansion in concrete is not thoroughly established, the probable mechanisms as proposed by other researchers are summarized: (1) formation of a crystalline and nonswelling lithium silicate at the paste/aggregate interface because of the pessimum effect of lithium admixtures (Stark 1992; Mo et al. 2003); (2) decrease in the silica dissolution on the surface of aggregate by the lithium ions (Lawrence and Vivian 1961); (3) decrease in the repolymerization of the ASR gel into an expansive compound by the lithium ions (Kurtis et al. 2000); and (4) reduction in the ionic surface charge density of the alkali-silica gel occurring in the presence of lithium salts (Kurtis and Monteiro 2003; Bian et al. 1996). Despite the positive effects of using lithium nitrate in ASR mitigation, its use in concrete by itself as a sole mitigation agent can be cost-prohibitive. Further, the use of lithium admixture alone, unlike SCMs, does not contribute to pozzolanic reactions or refinement of microstructure in concrete that can significantly improve mechanical properties and reduce permeability in concrete. Only when no alternate strategies are available to mitigate ASR, the use of lithium nitrate or other lithium-based salts in concrete can be justified.

Research Significance

The availability of large quantity of fly ash and the possibility of using it as a partial substitute for cement in concrete, primarily to reduce its carbon footprint and to promote sustainability, is well known. Compared to high-lime fly ashes, the use of low-lime fly ashes (CaO less than 8%) to produce durable concrete has gained more importance due to their ability to improve certain durability characteristics such as resistance to sulfate attack, ASR, and others at nominal replacement levels (Thomas et al. 1999). In this study, the combined use of fly ash and lithium admixture in portland cement mortars containing a moderately reactive aggregate was investigated to study the synergy between lithium admixture and fly ash in mitigating ASR. Though some studies on using both fly ash and lithium admixture are already available (Thomas et al. 2001), the information on how the chemical composition of fly ash influences this effect with the lithium admixture is not well understood. Therefore, the objective of this study was to investigate the interactive effects of fly ashes and lithium admixture in mitigating ASR. Specifically the influence of fly ash chemistry on the dosage of lithium admixture needed to mitigate ASR was investigated.

In this study, the authors have conducted investigations using fly ashes at normal replacement level in combination with lithium nitrate to understand whether or not the use of both can provide a comprehensive solution to tackle potential ASR issues. Understanding the synergistic behavior and employing this knowledge to effectively design ASR mitigation strategies (i.e., to identify dosage of lithium needed when used in combination with a fly ash of certain composition for a given set of materials) can provide both an economical and long-lasting solution to address ASR distress in concrete.

Experimental Materials

Cement

A high-alkali ASTM Type I cement with a Na_2O_{equi} of 0.82% was used in this study, the chemical composition of which is provided in Table 1.

Table 1. Oxide Composition of Cement and Fly Ashes

Material (or) mixture ID	SiO_2 (%)	Al_2O_3 (%)	Fe_2O_3 (%)	CaO (%)	MgO (%)	SO_3 (%)	Total alkali (as Na_2O equivalent)	Specific gravity
Cement (control)	19.78	4.98	3.13	61.84	2.54	4.15	0.82	3.15
Fly ashes								
HL1	34.55	18.10	5.68	27.50	5.04	2.80	1.83	2.63
HL2	34.90	19.50	5.70	26.60	5.00	2.00	2.09	2.61
HL3	37.60	18.80	6.00	24.20	4.50	2.30	1.99	2.50
IL1	49.69	15.03	6.60	15.63	4.92	0.90	3.93	2.55
IL2	52.97	22.25	5.39	10.45	2.33	0.52	1.66	2.40
LL1	57.49	29.29	2.95	6.06	1.36	0.41	2.44	1.97
LL2	58.67	20.86	11.51	3.35	1.15	0.40	1.20	2.44
LL3	61.62	24.86	4.56	1.40	0.23	0.21	1.60	2.09
LL4	60.30	28.60	3.20	1.00	—	—	1.60	2.61

Note: The potential quantities of compounds in portland cement based on Bogue's equations yields: $C_3S = 51.65$; $C_2S = 17.74$; $C_3A = 7.9$, $C_4AF = 9.52$.

Fly Ash

Nine fly ashes differing significantly in their CaO content from 1 to 27.5% were used. Of these fly ashes, three were high-lime fly ashes (HL1, HL2, and HL3), two others were intermediate-lime fly ashes (IL1 and IL2), and four others were low-lime fly ashes (LL1, LL2, LL3, and LL4), classified based on the Canadian standards. Based on the ASTM C 618 specification, the low- and intermediate-lime fly ashes can be classified as Class F fly ash while the high-lime fly ashes were classified as Class C fly ash, depending on the $SiO_2 + Al_2O_3 + Fe_2O_3$. The effectiveness of these fly ashes in mitigating ASR was investigated at cement replacement levels of 15, 25, and 35% by mass. The chemical composition of these fly ashes is provided in Table 1.

Reactive Aggregate

Only one reactive aggregate, namely, Spratt aggregate was used in this entire study. This aggregate was obtained from Spratt Quarry in Ontario, Canada. This aggregate primarily consists of calcite with minor amounts of dolomite. The reactive component of this rock consists of 3–4% of microscopic chalcedony and black chert (Rogers 1999). This aggregate has an established history of being alkali-silica reactive when used in various concrete structures. The bulk specific gravity and the dry rodded unit weight of this aggregate were found to be 2.52 and 1,557 kg/m^3, respectively.

Lithium Admixture

The lithium admixture used was a commercial grade 30% weight solution of lithium nitrate. It is odorless and white to yellow in color having a pH of 8.20 at 25°C. In this study, the effectiveness of lithium nitrate solution in mitigating ASR was investigated using three lithium dosage levels: (1) 0%, (2) 50%, and (3) 100%. The lithium dosage levels of 0, 50, and 100% correspond to a Li/Na ion molar ratio of 0, 0.37, and 0.74, respectively.

Experimental Program

The experimental program consisted of three parts. The first part dealt with determining the effect of replacement level of fly ash on ASR expansion. Here, three fly ashes, namely, HL1, IL1, and LL2 were chosen in such a way that their CaO content varied

significantly from 27.5 to 3.35% and a series of ASTM C 1567 tests was conducted by replacing cement with each of the fly ash at 15, 25, and 35% dosage levels. The expansion of mortar bars containing these fly ashes was measured and their 14-day expansion was correlated to their respective replacement levels, based on the recommendation provided in the ASTM C 33 specifications. This correlation was helpful in determining the fly ash replacement level required to achieve ASR mitigation below 0.10%.

The second part involves investigation to determine the influence of oxide composition of fly ash on ASR mitigation. For this study, the ASTM C 1567 tests were conducted using different fly ashes having varying chemical compositions at a constant replacement level of 25% by mass of cement. The only variable in this study being the chemical composition of fly ash, the 14-day mortar bar expansion can be correlated with different chemical composition parameters of fly ash such as (1) CaO, (2) SiO_2, (3) CaO_{equi}, (4) SiO_{2equi}, (5) $SiO_2 + Al_2O_3 + Fe_2O_3$, and (6) $CaO + MgO + SO_3$. The CaO_{equi} and SiO_{2equi} content of the fly ashes were determined using the following formula suggested by Malvar and Lenke (2006):

$$CaO_{equi} = CaO + 0.905Na_2O_{equi} + 1.391MgO + 0.7SO_3 \quad (1)$$

$$SiO_{2equi} = SiO_2 + 0.589Al_2O_3 + 0.376Fe_2O_3 \quad (2)$$

In the third part, the effectiveness of lithium nitrate to mitigate ASR in control and fly ash mortars was assessed by dosing the lithium nitrate in the bar and soak solution at specified concentrations. A total of six fly ashes (HL1, HL3, IL1, IL2, LL1, and LL4) having varying chemical composition were used at a constant cement replacement level of 25% by mass to prepare fly ash mortars. Since the chemical composition of fly ash is the only variable within the different fly ash mortars, the various oxides of fly ashes, namely, CaO, SiO_2, CaO_{equi}, SiO_{2equi}, and $SiO_2 + Al_2O_3 + Fe_2O_3$ contents correlated to the 14-day mortar bar expansions as mentioned previously.

Experimental Methods

Standard ASTM C 1260 Test Procedure

In this test, mortar bars of size 25 × 25 × 285 mm were prepared by mixing the ingredients as per the standard ASTM C 192 specifications and curing it in a moist air chamber for about 24 h. Then, these bars were immersed in hot water maintained at 80°C for a period of 24 h before immersing them in a 1N sodium hydroxide solution maintained at a temperature of 80°C for a period of 28 days. The length change of the specimens was measured at regular intervals during this period to determine the expansion of the bars in the sodium hydroxide solution due to ASR. According to the ASTM C 33 specification, an aggregate is considered innocuous if the mortar bar prepared from it based on the ASTM C 1260 gradation shows an expansion of 0.10% or less, when the bars are soaked in a 1N sodium hydroxide solution for a period of 14 days. If the 14-day ASR expansion is greater than 0.20%, the aggregate shall be considered to be potentially reactive. In this study, ASTM C 33 guidelines were followed to characterize the aggregate reactivity and the effectiveness of ASR mitigation measures.

Standard ASTM C 1567

This test procedure is similar to the standard ASTM C 1260 test method in all aspects with the exception that a portion of the portland cement in the mortar bars is replaced with a supplementary cementing material, by mass. In this study, the standard ASTM C 1567 test was used to assess the effectiveness of fly ash in mitigating ASR.

CRD-C 662-10

The CRD-C 662 test was conducted to evaluate the ability of fly ash, lithium nitrate, and the synergetic effects of the two to control deleterious expansion due to ASR, when a reactive aggregate is used in concrete. This method is an accelerated mortar bar method in which the bars with or without fly ash were prepared similar to that indicated in the standard ASTM C 1260 test method with two significant modifications. Firstly, the lithium nitrate was dosed during the preparation of mortar bars at a specific Li/Na ion molar ratio in which the sodium ion concentration is governed by the alkali content of the cement used in the mixture. The alkali content of fly ash was not considered in the calculation of lithium dosage in the mixtures. It is assumed in these studies that the alkalis present in fly ashes are not readily available to cause ASR when fly ashes are used at sufficient replacement levels.

Secondly, the lithium nitrate was also added to the 1N sodium hydroxide soak solution at a level that resulted in a Li/Na ion molar ratio equivalent to half of that present in the mortar bars. This modification was required to minimize the effects of leaching of lithium from the mortar bars into the soak solution on mortar bar expansion. In the present study, two different Li/Na ion molar ratios were used in the mortar bars −0.37 and 0.74, representing lithium dosages of 50 and 100%, respectively. These lithium dosages were selected to potentially mitigate the ASR expansion caused by the reactive aggregate used in this study. The sample calculations for the amount of lithium nitrate to be added in the mortar bar and soak solution are subsequently shown. The water content of the 30% lithium nitrate solution was accounted for in the mixture proportions of the mortar. It should be noted that in the CRD-C-662 method, the lithium dosage to arrive at a particular Li/Na molar ratio is solely based on the mass of the cement (assuming the alkali content of the cement is 0.9% $Na_2O_{eq.}$). In the present study, the alkali content of the cement used was 0.82% $Na_2O_{eq.}$, and the lithium dosage in the mortar bar was calculated based on both the mass of the cement and its alkali content.

Sample Calculations

1. Sample calculation to determine the dosage of 30% lithium nitrate solution required to arrive at a desired Li/Na molar ratio in soak solution
   Desired Li/Na ion molar ratio in soak solution = 0.74
   Molecular weight of $LiNO_3$ = 69 g
   Amount of $LiNO_3$ salt required = Li/Na ratio x molecular weight of $LiNO_3 = 0.74 \times 69 = 51.06$ g
   Amount of 30% $LiNO_3$ solution required for 1 L of soak solution = 51.06/0.3 = 170.2 g
   Volume of 30% $LiNO_3$ solution needed for 1 L of soak solution = 170.2/1.20 = 141.8 ml
2. Sample calculation to determine the dosage of 30% lithium nitrate solution in mortar bar to arrive at a desired Li/Na molar ratio
   Desired Li/Na ion molar ratio = 0.74
   Cement content per batch of four mortar bars = 500 g
   Cement alkali content(%) = 0.82%Na_2O eq.
   Alkali content per batch (g) = 0.0082 × 500 g = 4.1 g
   Molecular weight of $Na_2O = (2 \times 23 + 16) = 62$ g/mol
   Mol of Na_2O = alkali content/62 = 4.1/62 = 0.0661 mol
   Mol of Na = 2 × 0.0661 = 0.1322 mol
   Mol of lithium/mol of Na = 0.74
   Mol of lithium = 0.74 × 0.1322

Mol of lithium = 0.0978 mol
1 mol of $LiNO_3$ contains 1 mol of lithium ion
Molecular weight of $LiNO_3$ = 69 g/mol
Grams of $LiNO_3$ that contain 0.0978 moles of Li ion = $69 \times 0.0978 = 6.753$ g
30% solution of $LiNO_3$ that contains 6.753 g of lithium = $6.753/0.30 = 22.510$ g (add to mix water).

3. To prepare 1 L of soak solution with a Li/Na molar ratio of 0.74, the following procedure is applied:

   Step 1: A stock solution of 2N NaOH by adding 80 g of NaOH pellets to 900 ml of deionized water and further diluting to prepare 1 L of 2N NaOH solution was prepared;

   Step 2: A 500 ml of 2N NaOH solution to a 1-L flask was then added;

   Step 3: A 141.8 ml of 30% solution of $LiNO_3$ to flask in Step 2 was then added; and

   Step 4: The contents of flask to 1-L solution was diluted by adding deionized water.

Results and Discussions

The Effect of Replacement Level of Fly Ash on ASR Expansion

The effect of replacement level of fly ash on the ASR expansion behavior of its mortars is shown in Figs. 1(a–d). Fig. 1(a) shows the ASR expansion behavior of control (containing no fly ash) mortars and mortars containing high-lime fly ashes in the standard ASTM C 1260 and 1567 tests, respectively. At a 15% replacement level of high-lime fly ash, the expansion at any specified immersion period was found to be slightly lower or similar than that of the control mortar and hence, a distinct ASR mitigation behavior cannot be seen. At a 25% replacement level, a definite decrease in the expansion below the control mortar was observed. At even higher replacement levels of 35%, a substantial decrease in the mortar bar expansion was observed, indicating the effectiveness of high-lime fly ash at higher dosages.

Figs. 1(b and c) show the ASR expansion behavior of control mortars and mortars containing intermediate- and low-lime fly ash in the standard ASTM C 1260 and 1567 tests, respectively. Similar to Fig. 1(a), both these figures indicate that the expansion decreases with an increase in the replacement level of the fly ash. Unlike high-lime fly ash mortars, a significant decrease in the expansion was observed even at a low-fly ash replacement level of 15%, with low-lime fly ash being more effective than the intermediate-lime fly ash. The variation in the ability of these fly ashes to mitigate ASR may be due to the variation in their chemical and physical characteristics (Shehata and Thomas 2000; Diamond and Lopez-Flores 1981; Ravina 1981). At high replacement levels of 25 and 35%, a substantial decrease in the mortar bar expansion was observed in both the intermediate- and low-lime mortars.

Overall, the mortar bar expansion was found to decrease with an increase in the replacement level of all fly ash. This decrease in the

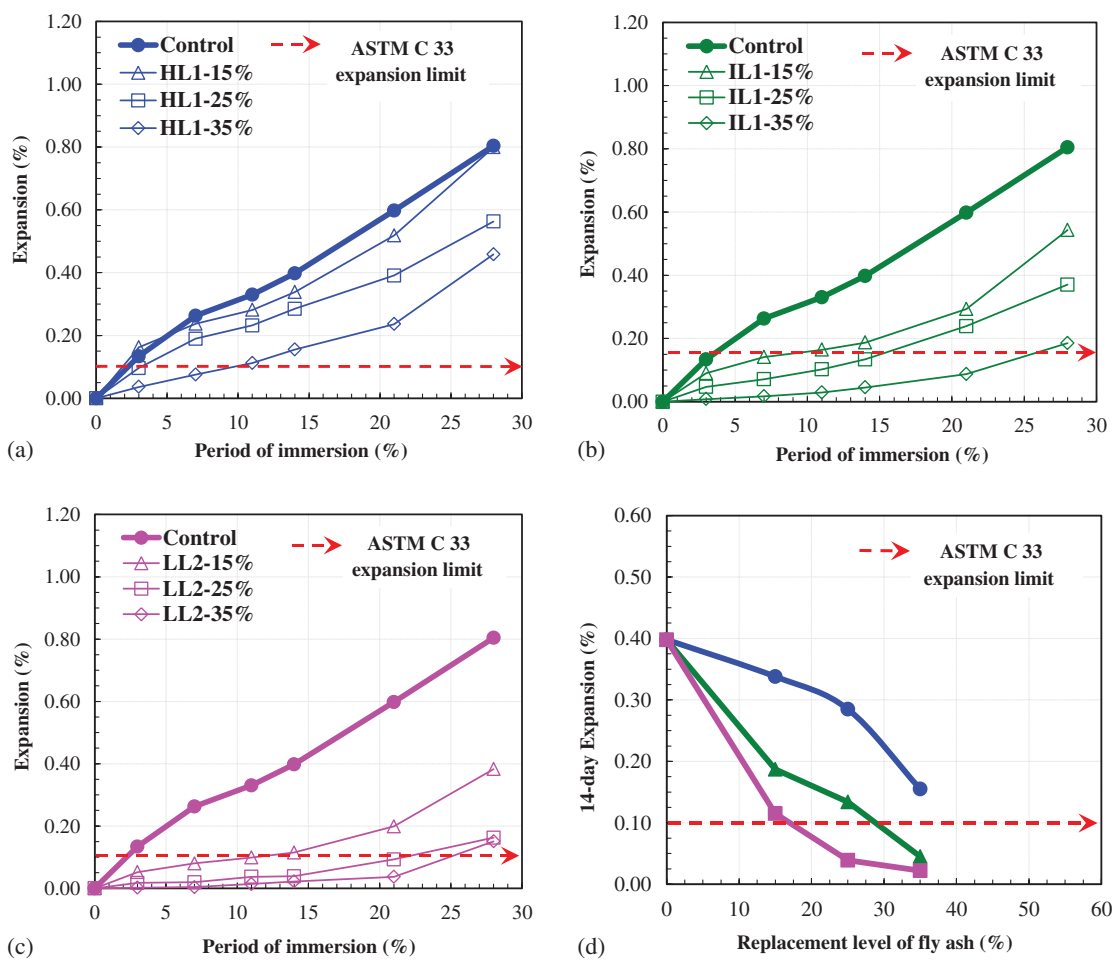


Fig. 1. Effect of replacement level of fly ash on the ASR expansion behavior of mortars containing: (a) HL1 fly ash; (b) IL1 fly ash; (c) LL2 fly ash; (d) comparison of 14-day expansion

expansion may be attributed to two reasons: (a) the reduction in the cement content of the mortar due to fly ash replacement which proportionally reduces the quantity of calcium hydroxide produced as a result of cement hydration [ACI 232 (ACI 2004)], (b) the pozzolanic reaction between the fly ash particles and the calcium hydroxide resulting from cement hydration to form the calcium silicate hydrate (C-S-H) gel (Ravina 1981; Mehta 1985). This gel has a low CaO/SiO_2 (C/S) ratio and thereby has a high tendency to bind the alkalis within it, making them unavailable to participate in the ASR.

In order to study the effect of replacement level of different fly ashes on ASR mitigation, the 14-day ASR expansion of the mortars containing all three fly ashes was correlated to their corresponding replacement level as shown in Fig. 1(d). As this figure shows, the 14-day ASR expansion decreases with an increase in the replacement level of fly ash. ASR mitigation below 0.10% was not achievable using a high-lime fly ash even at a high replacement level of 35% while the same was achievable using both intermediate- and low-lime fly ashes. For example, a minimum of 16 and 29% replacement level of low-lime and intermediate-lime fly ash, respectively, could reduce the expansions below 0.10%. The inference obtained in this study supports the findings of other investigators (Shehata and Thomas 2000; McKeen et al. 1998, 2000).

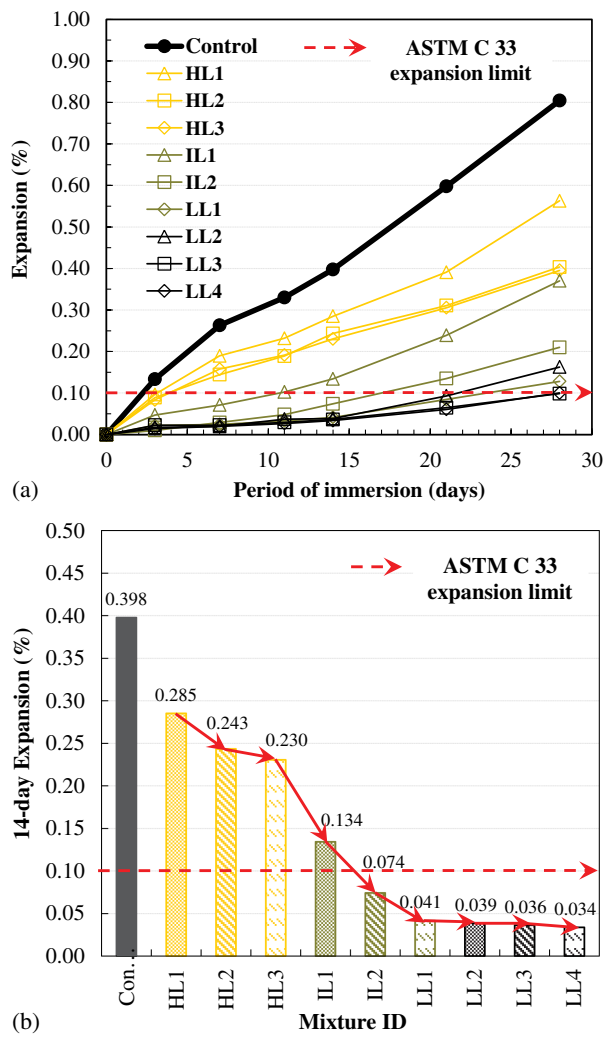


Fig. 2. ASR expansion behaviors of mortars containing virgin fly ashes at 25% replacement level for cement: (a) expansion versus period of immersion; (b) comparison of 14-day expansion

The Effect of Oxide Composition of Virgin Fly Ash on ASR Expansion

Based on the findings from Fig. 1, it is apparent that the CaO content of fly ash has a definite influence on expansion of mortar

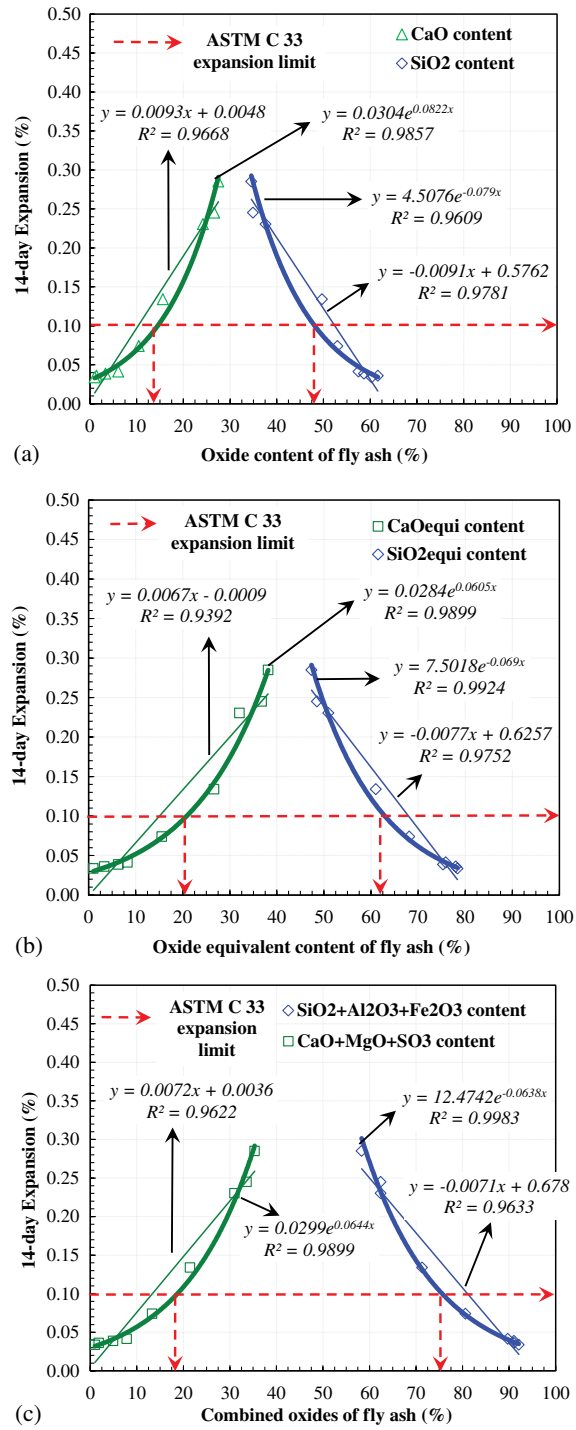


Fig. 3. Effect of oxide composition of fly ashes on 14-day ASR expansion of mortars based on 25% fly ash replacement level: (a) CaO and SiO_2 content; (b) CaO_{equi} and SiO_{2equi} content; (c) $SiO_2 + Al_2O_3 + Fe_2O_3$ content

bars in the standard ASTM C 1567 test. However, these results represent only three different fly ashes and the CaO content of ash may not be the only significant parameter that influences the expansion behavior. In order to establish a more definite correlation between fly ash chemistry and mortar bar expansion due to ASR, a detailed study involving nine different fly ashes were undertaken.

The expansion behavior of the mortar bars containing nine different fly ashes at a constant cement replacement level of 25% in the ASTM C 1567 test is shown in Fig. 2(a). As this figure shows, mortars containing all the nine fly ashes registered lower expansion than that of the control mixture throughout the period of the test. To understand the relative performance of different fly ashes, the 14-day expansions of all the mortar bars were compared as shown in Fig. 2(b). As this figure shows, all the mortars containing high-lime fly ash registered a 14-day expansion higher than 0.10% while all those containing low-lime fly ash registered a 14-day ASR expansion lower than this value. Of the two intermediate-lime fly ash mortars, one of them registered a 14-day expansion higher than 0.10% while the other registered expansion lower than this value. Figs. 3(a–c) show the CaO, SiO_2, CaO_{equi}, SiO_{2equi}, $CaO + MgO + SO_3$, and $SiO_2 + Al_2O_3 + Fe_2O_3$ content in them was plotted against their 14-day mortar bar expansion since the fly ashes are widely classified based on their chemical composition. These figures clearly indicate that the 14-day expansion increases with an increase in the CaO, CaO_{equi}, and $CaO + MgO + SO_3$ contents of fly ash, and the same decreases with an increase in its SiO_2, SiO_{2equi}, and $SiO_2 + Al_2O_3 + Fe_2O_3$ contents.

Both a linear and an exponential trend was found to closely fit all the expansion data points, with high R^2 values between 0.95 and

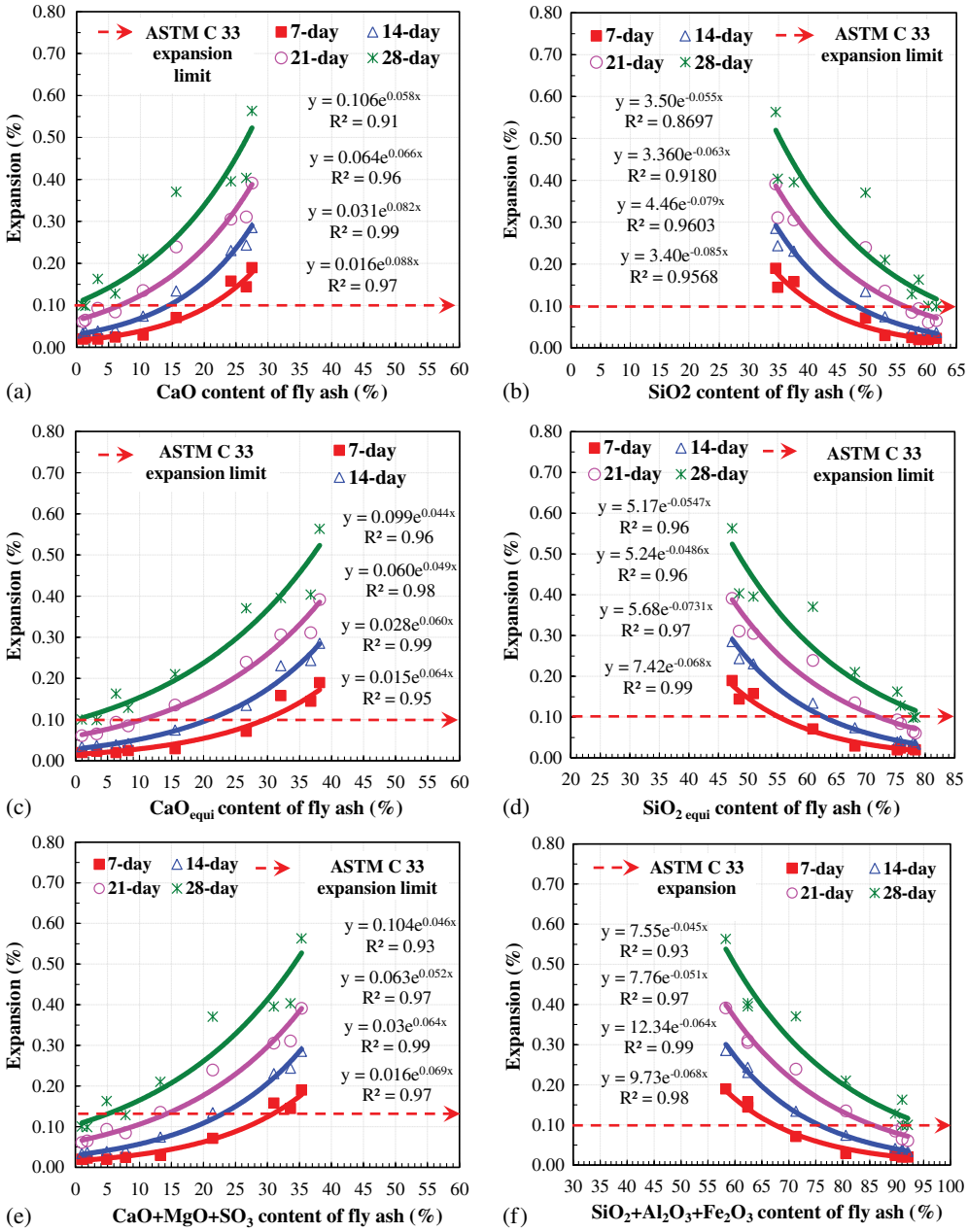


Fig. 4. Effect of oxide content of fly ash on mortar bar expansion for different periods of immersion at 25% fly ash replacement level: (a) CaO content; (b) SiO_2 content; (c) CaO_{equi} content; (d) SiO_{2equi} content; (e) $CaO + MgO + SO_3$ content; (f) $SiO_2 + Al_2O_3 + Fe_2O_3$ content

0.99. Even though the exponential fit can be observed to be an ideal fit in this situation, the underlying mechanism associated with this trend can be explained by considering the composition of fly ash and the properties of accompanied pozzolanic reaction product. The composition of fly ash is dominated by a siliceous-rich glass and the different alumino-silicate phases present in the case of low- and intermediate-lime fly ashes (i.e., CaO ranging from 0 to 18%). There is very little, if any, of free calcium available in such fly ashes that promote the creation of expansion inducing ASR gel (Bleszynski and Thomas 1997). However when using high-lime fly ashes, the composition of fly ash is dominated by calcium-rich glass as well as other compounds such as C_3A, CaO, and $C_4A_3\hat{S}$ (Klein phase). In addition, low-lime fly ashes tend to produce a lower C/S ratio C-S-H gel in the pozzolanic reaction compared to high-lime fly ashes, thereby providing a better alkali-binding matrix, which inhibits ASR-related distress. The distinct behavior of low- and high-lime fly ashes in mitigating ASR is therefore better represented by an exponential function rather than a linear function. Malvar and Lenke (2009) used exponential functions successfully to correlate the oxide contents of fly ash and its chemical index (C_{fa}).

To establish a generalized exponential function which represents the individual and combined oxides of fly ash as a function of the mortar bar expansion at any period of immersion, four immersion periods, namely, 7-, 14-, 21-, and 28-day were considered and the expansions at these specified periods were plotted versus the individual and combined oxides as shown in Figs. 4(a–f). As these figures show, the exponential trend appeared to closely fit the expansion data points for all the immersion periods. However, the degree of correlation between the oxide parameters and the percentage expansion appears to be higher at earlier immersion periods than at 28 days. This tendency may be better explained in the case of highly reactive Spratt limestone aggregate by the fact that at later ages, the matrix is cracked and this can result in significant variability in the expansion observed. For moderately or slowly reactive aggregates, the trend may be more consistent.

In addition, the equation for correlation between the expansions of mortar bars at any given immersion period and the CaO or CaO_{equi} or $CaO + MgO + SO_3$ contents of the fly ash can be generalized as follows:

$$y = ae^{bx} \quad \text{(or)} \quad x = \frac{1}{b}\log_e\left(\frac{y}{a}\right) \tag{3}$$

where a and b = functions of the immersion period.

Similarly, the equations for correlation between the expansions of mortar bars at any given immersion period and the SiO_2, SiO_{2equi}, and $SiO_2 + Al_2O_3 + Fe_2O_3$ contents of the fly ash can be generalized as follows:

$$y = ae^{-bx} \quad \text{(or)} \quad x = -\frac{1}{b}\log_e\left(\frac{y}{a}\right) \tag{4}$$

where a and b = functions of the immersion period.

It should be remembered that Eqs. (3) and (4) are applicable only for the material combination used in this research. Substituting $y = 0.10\%$ in the preceding two equations and using the corresponding values of a and b for the 14-day expansion curve, it can be found that the ASR mitigation was achievable with fly ashes containing CaO, CaO_{equi}, and $CaO + MgO + SO_3$ contents lower than 14, 21, and 18.7%, respectively. Alternatively, fly ashes containing SiO_2, SiO_{2equi}, and $SiO_2 + Fe_2O_3 + Al_2O_3$ higher than 48, 63, and 75%, respectively, were also found to be effective in mitigating ASR. While the oxide contents of fly ash from bulk composition analysis provides a convenient way to correlate with the performance of fly ash in mitigating ASR, a more accurate correlation between the fly ash composition and ASR mitigation can be potentially obtained by characterizing fly ashes in terms of its glass content, glass composition, and its fineness (Ravina 1980; Obla et al. 2003). At present, new characterization techniques for fly ashes based on individual particle chemistry is being developed that may provide a better basis for ASR mitigation in future (Bumrongjaroen et al. 2007).

The Effect of Lithium Nitrate on ASR Expansion in Control Mortars

The effect of addition of lithium nitrate on the ASR expansion behavior of control mortars (containing no fly ash and lithium nitrate) in the CRD-C 662-10 tests are shown in Figs. 5(a and b). As these figures show, the control mortars containing no lithium nitrate showed higher expansion than those containing it. For example, with an increase in the dosage of lithium nitrate from 0 to 50%, the 14-day expansion decreased by 12.5%. However, with further increase in its dosage from 50 to 100%, the 14-day mortar bar expansion decreased by additional 64%. This clearly indicates the effectiveness of lithium nitrate and at this lithium dosage ASR mitigation below 0.10% at 14 days was achieved.

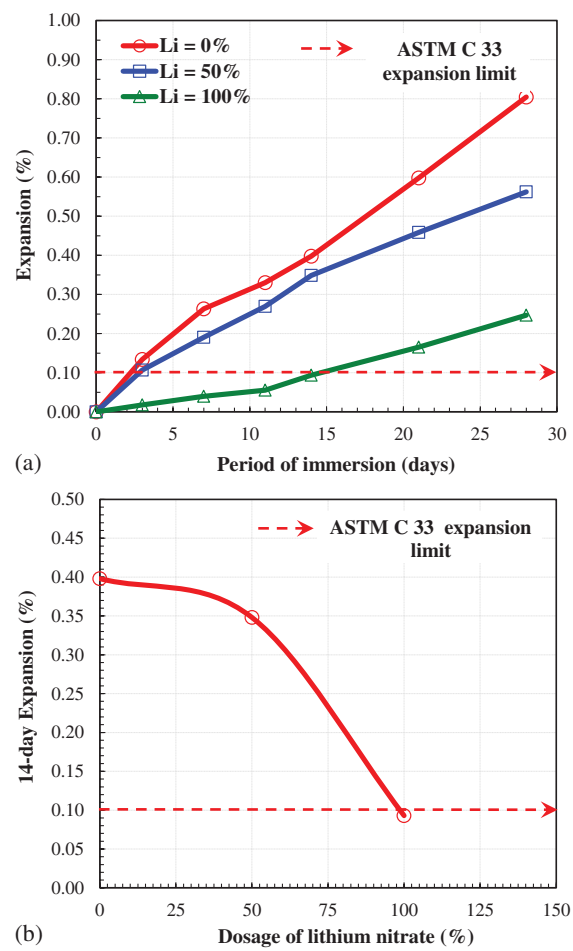


Fig. 5. Effect of lithium admixture on the ASR expansion behavior of control mortars: (a) ASR expansion of control mortar bars at different lithium dosages; (b) effect of lithium dosage on 14-day mortar bar expansion

The Effect of Lithium Nitrate on ASR Expansion in Fly Ash Mortars

The effect of lithium nitrate on the ASR expansion behavior of mortars containing high-, intermediate- and low-lime fly ashes in the CRD-C 662-10 tests is shown in Figs. 6(a–f).

The ASR expansion behavior of mortars containing HL1 fly ash as shown in the Fig. 6(a) indicates that the expansion of these mortars without lithium admixture (HL1 − Li = 0%) was found to be lower than that of their control mortars (without fly ash and without lithium admixture) at all periods of immersion, as already observed previously. With an increment in the lithium nitrate dosage from 0 to 50%, the HL1 fly ash mortars showed a slight decrease or increase in the expansion throughout the test, indicating that this increment was not effective in substantially reducing the expansion. With further increments in the dosage up to 100%, the HL1 fly ash mortars showed a significant decrease in the ASR expansion, indicating the beneficial effects of adding lithium nitrate. The expansion behavior of the HL3 fly ash mortars with increments in the lithium dosage was similar compared to that of the HL1 mortars.

Figs. 6(c and d) show the effect of lithium nitrate on the ASR expansion behavior of mortars containing the IL1 and IL2 fly ashes, respectively, while Figs. 6(e and f) show its effects on the ASR expansion behavior of mortars containing the LL1 and LL

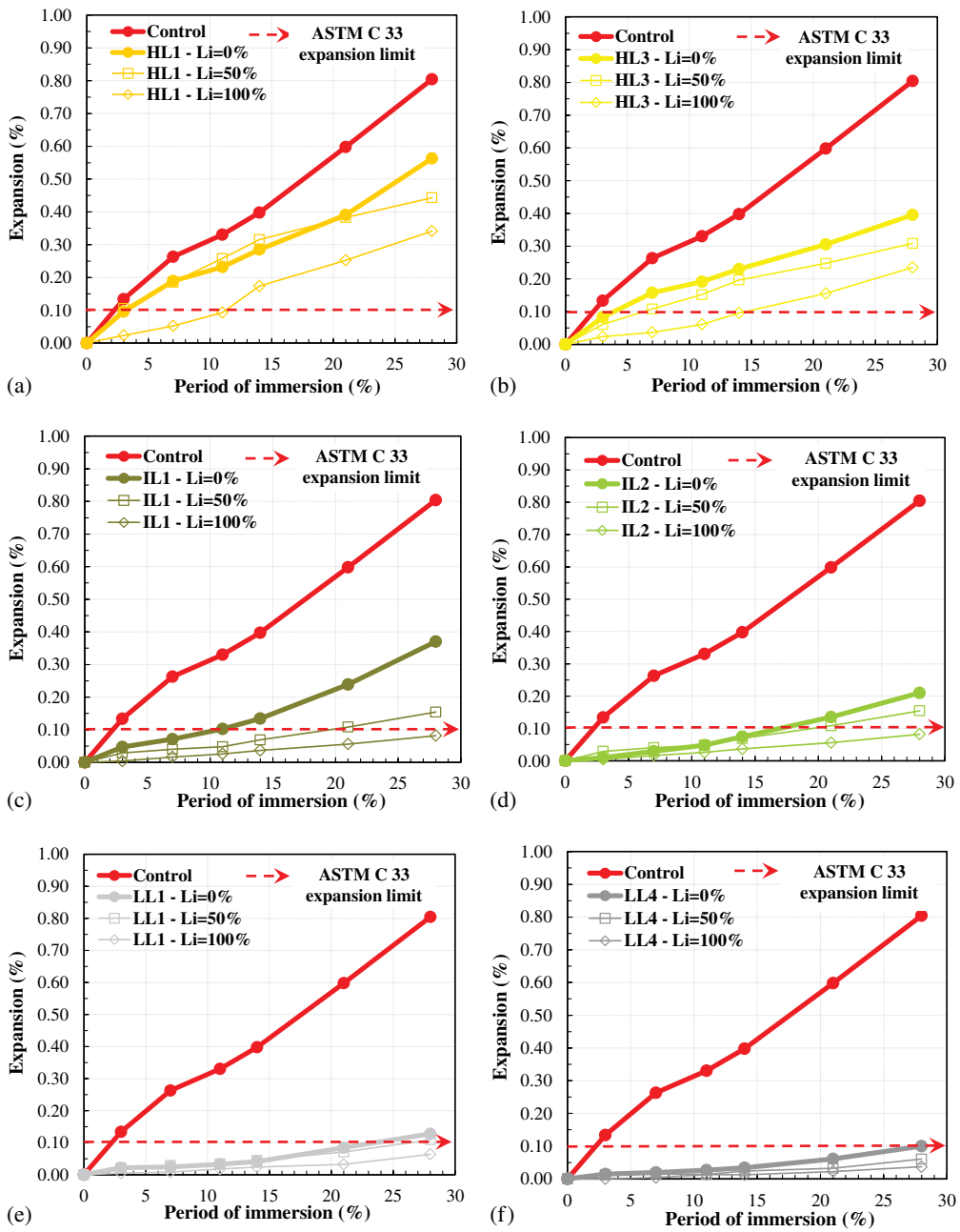


Fig. 6. Effect of lithium admixture on the ASR expansion behavior of high-lime, intermediate-lime, and low-lime fly ash mortars at 25% fly ash replacement level: (a) ASR expansion behavior of HL1 fly ash mortars; (b) ASR expansion behavior of HL3 fly ash mortars; (c) ASR expansion behavior of IL1 fly ash mortars; (d) ASR expansion behavior of IL2 fly ash mortars; (e) ASR expansion behavior of LL1 fly ash mortars; (f) ASR expansion behavior of LL4 fly ash mortars

fly ashes, respectively. The intermediate-lime fly ash mortars performed similar to each other, with the IL1 fly ash mortars showing higher expansion than that of the IL2 fly ash mortars. Likewise, the low-lime fly ash mortars performed similar to each other [Figs. 6(e and f)], with the LL1 fly ash mortars showing slightly higher expansions than the LL4 fly ash mortars. In addition, the fly ash mortars containing higher lithium dosage were found to show lower expansion than those containing lower or no lithium dosage, clearly indicating the beneficial effects of lithium nitrate in reducing the expansions. Also, most of the fly ash mortars containing lithium nitrate (HL3, IL1, IL2, LL1, and LL4) mitigated ASR within the 0.10% expansion limit at 14 days as specified by the ASTM C 33 specification except HL1.

In order to understand the effectiveness of lithium nitrate on ASR mitigation in the fly ash mortars, their 14-day expansions were plotted against the lithium dosage as shown in Fig. 7(a). As this figure shows, the 14-day expansion of the fly ash mortars decreases with an increase in the lithium dosage. The intermediate- and low-lime fly ash mortars (IL1, IL2, LL1, and LL4) mitigated ASR by registering a 14-day ASR expansion lower than 0.10% even at a low-lithium dosage of 50%, whereas the high-lime fly ash mortars (HL1 and HL3) did not mitigate ASR at such low-lithium dosages and required higher dosages for mitigation. Of the two high-lime fly ash mortars, only HL3 fly ash mortars mitigated ASR at a high-lithium dosage of 100% and the HL1 fly ash mortars did not. In addition, the decreasing 14-day expansion trend with

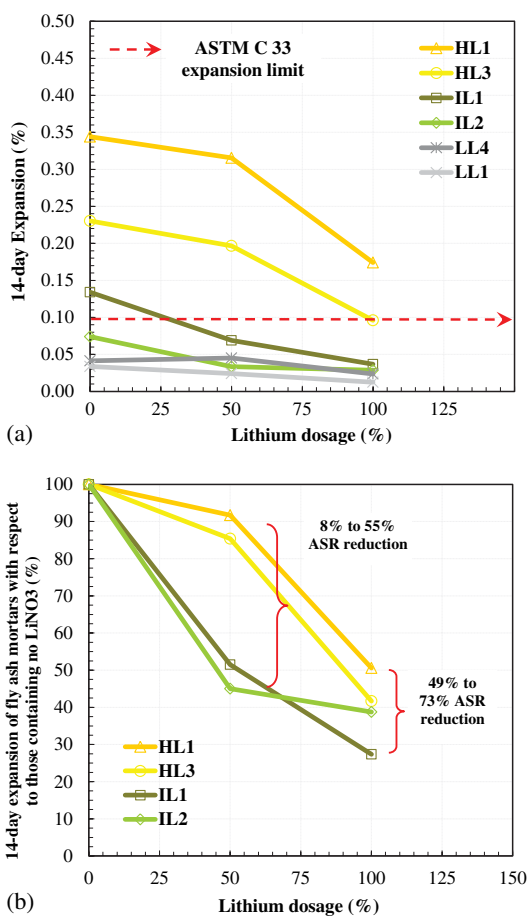


Fig. 7. Effectiveness of lithium admixture on the 14-day mortar bar expansion of fly ash mortars at 25% fly ash replacement level: (a) 14-day ASR expansion versus lithium dosage; (b) percentage decrease in the mortar bar expansion versus lithium dosage

increase in the lithium dosage was observed in all the fly ash mortars, except LL1 mortars. In the case of LL1 mortars, a slight increase in the 14-day mortar bar expansion was observed when the dosage of lithium increased from 0 to 50% beyond which the expansion decreased. However, this slight increase in expansion is not a big concern from mitigation perspective, as the 14-day expansion of LL1 mortars at all lithium dosages were already well below the 0.10% expansion limit. The use of lithium nitrate in the presence of low-lime fly ash is therefore not required.

To evaluate the effectiveness of lithium nitrate with high-lime and intermediate-lime fly ash mortars, their 14-day expansion was normalized to their respective fly ash mortars containing no lithium admixtures (HL1-Li = 0%, HL3-Li = 0%, IL1-Li = 0%, IL2-Li = 0%) as shown in Fig. 7(b). As this figure shows, compared to mixtures with 0% lithium nitrate dosage the addition of lithium nitrate up to 50% reduced the 14-day expansion by 8–55% and addition up to 100% dosage level further reduced the expansion by 49–73%, depending on the fly ash composition, In the case of HL1 and HL3 fly ash mortars, substantial reduction in expansion was observed only when lithium nitrate was used at 100%. However, in the case of intermediate-lime fly ash, significant reduction in the expansion was observed even at lithium dosage of 50%.

Combined Influence of Fly Ash Chemistry and Lithium Dosage on Mortar Bar Expansion

Fly ashes are usually classified based on their oxide composition [ASTM C 618 (ASTM 2008; CSA A3001 (CSA 2003)], hence, the effect of their oxide composition on the ASR expansion behavior of concrete has gained significant importance (Shehata and Thomas 2000; McKeen et al.1998, 2000; Touma et al. 2001). In this section, the specific oxide(s) (CaO, SiO_2, CaO_{equi}, SiO_{2equi}, $SiO_2 + Al_2O_3 + Fe_2O_3$, and $CaO + MgO + SO_3$) of the fly ashes were correlated to their 14-day mortar bar expansion at different lithium dosages.

Figs. 8(a–c) show that the 14-day expansion of the fly ash mortars increase with an increase in its CaO, CaO_{equi}, and $CaO + MgO + SO_3$ contents. Similar to Eq. (3), an exponential equation of the form: $y = ae^{bx}$ appears to closely fit all the data points. In these equations, the constants a and b are functions of lithium dosage. For instance, in the case of CaO, the values of a ranges from 0.0255 to 0.0101 and that of b remain approximately constant. In addition, the 14-day expansion also decreased with increase in the lithium dosage from 0 to 100%. The maximum allowable quantity of expansion promoting oxides (CaO, CaO_{equi}, and $CaO + MgO + SO_3$) in the fly ash to obtain a 14-day expansion below 0.10% at different lithium dosage in the mortar bars is shown in Table 2. For instance, at 0, 50, and 100% lithium dosage, the maximum allowable CaO content is 14.40, 17.60, and 23.50%, respectively.

Figs. 8(d–f) shows that the 14-day expansion of the fly ash mortars decrease with an increase in its SiO_2, SiO_{2equi}, and $SiO_2 + Al_2O_3 + Fe_2O_3$ contents. Similar to Eq. (4), an exponential equation of the following form, $y = ae^{-bx}$ appears to closely fit all the data points and the values of a and b are a function of the lithium dosage. For instance, in the case of SiO_2, the value of a ranged from 3.795 to 8.165 and that of b remains approximately constant. The 14-day expansion also decreased with increase in the lithium dosage from 0 to 100%. The minimum required quantity of ASR inhibiting oxides (SiO_2, SiO_{2equi}, and $SiO_2 + Al_2O_3 + Fe_2O_3$) in the fly ash to obtain a 14-day expansion below 0.10% at different lithium dosages in the mortar bars is provided in Table 2.

Thus within the different plots of the ASR inducing and/or promoting oxides in the fly ashes studied at a constant replacement

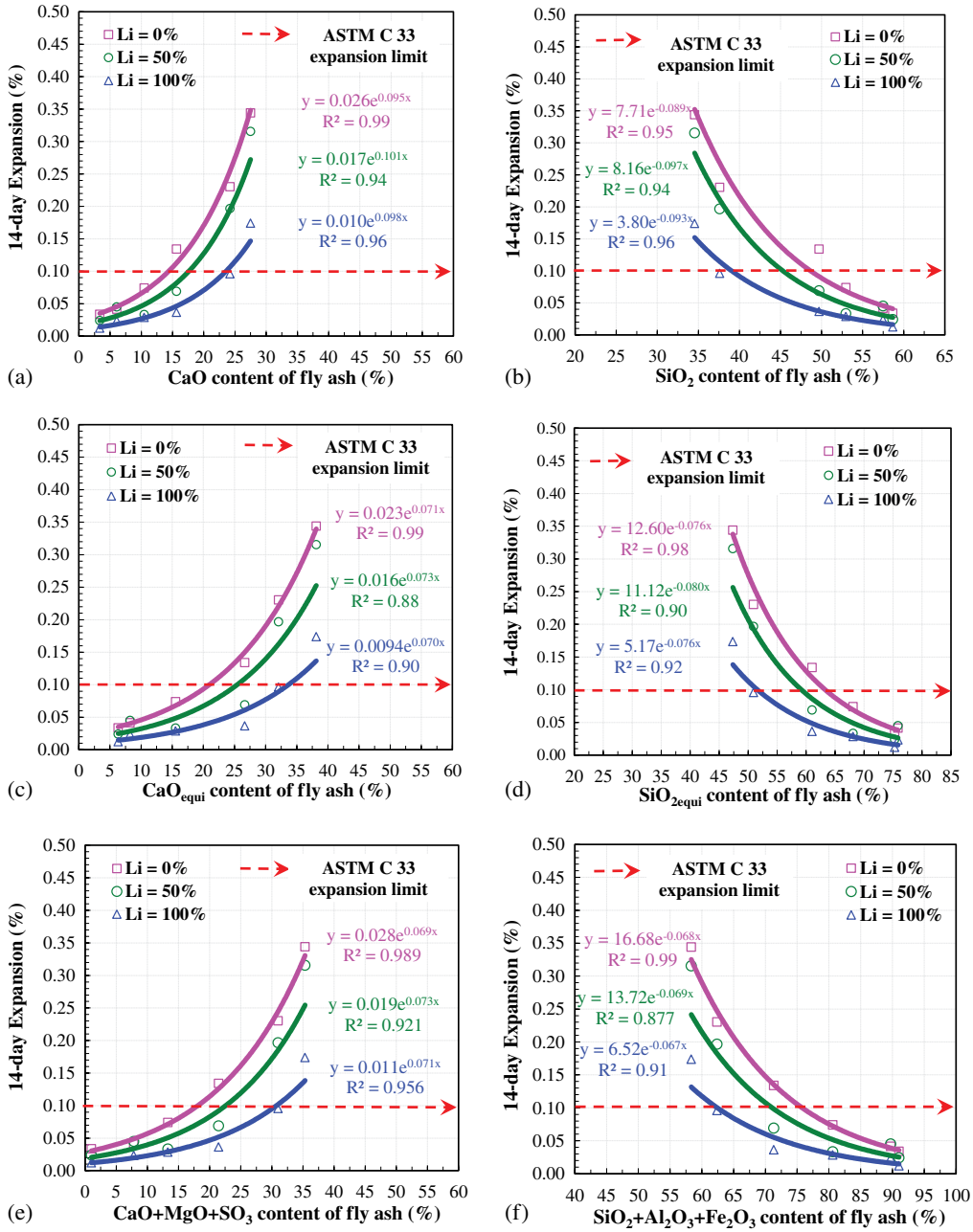


Fig. 8. Effect of chemical composition of fly ash on the 14-day expansion of mortars containing lithium admixture at 25% fly ash replacement level: (a) CaO content; (b) CaO_{equi} content; (c) $CaO + MgO + SO_3$ content; (d) SiO_2 content; (e) SiO_{2equi} content; (f) $SiO_2 + Al_2O_3 + Fe_2O_3$ content

Table 2. Maximum and Minimum Allowable Oxide Contents in the Fly Ash to Mitigate ASR in Mortars Containing Spratt Aggregate in the Presence of Fly Ash at a 25% Replacement Level for Cement

Lithium dosage (%)	Maximum allowable ASR promoting oxides in fly ash to mitigate ASR (%)			Minimum required ASR inhibiting oxides in fly ash to mitigate ASR (%)		
	CaO	CaO_{equi}	$CaO + MgO + SO_3$	SiO_2	SiO_{2equi}	$SiO_2 + Fe_2O_3 + Al_2O_3$
0	14.40	20.90	18.45	48.80	63.60	75.25
50	17.60	25.40	22.75	45.30	58.90	71.32
100	23.53	33.60	31.08	39.10	51.90	62.34

level of 25% by mass, it can be observed that any of the oxide(s) can be used to correlate with the mortar bar expansion. The acceptable level of oxide content in the fly ash to achieve complete ASR mitigation can be affected by the dosage of lithium admixture in the mortar. Fig. 9 shows the correlation between the minimum oxide contents (for ASR inhibiting oxides) or maximum oxide contents (for ASR promoting oxides) and the lithium dosage needed to achieve effective ASR mitigation. As this figure shows, a linear

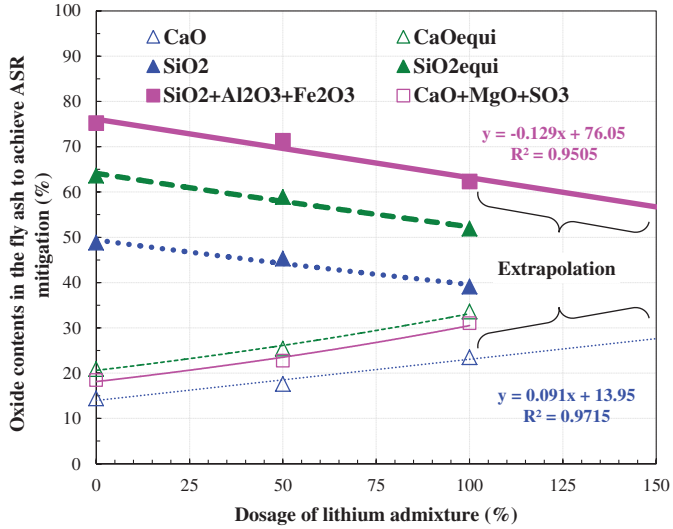


Fig. 9. Correlation of chemical contents of fly ash and lithium dosage required to achieve ASR mitigation at 25% fly ash replacement level

trend exists between the dosage of lithium nitrate and any of the oxide contents in the fly ash. The relationship between the two can be represented in a generalized form as follows:

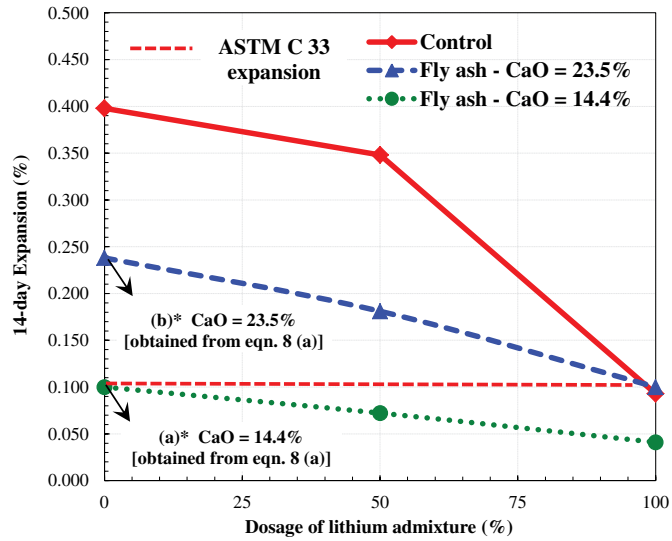
$$y = mx + c \tag{5}$$

where m = slope of the line which depends on the aggregate type; c = y-intercept which represents the maximum or minimum allowable oxide content required to mitigate ASR in the absence of lithium admixtures depending on whether the oxide considered is an ASR promoting or inhibiting oxides. While these oxide limits and the corresponding lithium dosages are specific to the materials used in this study, the trends are expected to be similar for other material combinations. Using linear extrapolation, the oxide contents in the fly ash required to mitigate ASR at a very high lithium nitrate dosage of 150% can also be established.

Comparison of Expansion of Control and Fly Ash Mortars Containing Lithium Nitrate at Different Dosage Levels

In order to understand the beneficial use of combinations of fly ash and lithium nitrate in mixtures containing reactive aggregate and to provide cost-effective solutions for ASR mitigation, the 14-day expansion of the control mixture was compared with that of two fly ash mixtures having specific CaO content (14.40 and 23.50%) as shown in Fig. 10. The CaO content values of these fly ash mixtures (14.40 and 23.5%) indicate the maximum quantity of CaO in the fly ash required to mitigate ASR at lithium nitrate dosage of 0 and 100%, respectively. These values were obtained by using the exponential equations established in the Fig. 8(a) and previously discussed.

As Fig. 10 shows, at a lithium nitrate dosage of 0%, the expansions of the fly ash (CaO = 23.5%) and fly ash (CaO = 14.4%) mixtures were found to be below that of the control mortars, indicating that the effectiveness of fly ash at 25% replacement level. Within the two fly ash mixtures, a significant difference in the expansion values was noted primarily due to the variation in the oxide contents of the fly ash, as already observed in the previous sections. In the case of control mixtures (containing no fly ash), the use of lithium nitrate was effective in achieving mitigation only at l00% dosage level.



Note:*
(a) Lithium nitrate is not required in the mixtures containing fly ash having CaO content lower than 14.4% to completely mitigate ASR.
(b) Lithium nitrate is required in the mixtures containing fly ash having a CaO content ranging from 14.4% - 23.5% to completely mitigate ASR, the dosage of lithium nitrate is dependent on the composition of specific fly ash.
(c) The use of fly ash having CaO content higher than 23.5% may require lithium dosages higher than 100% for complete ASR mitigation. In such cases, the lithium nitrate alone be used without fly ash to completely mitigate ASR.

Fig. 10. Comparison of 14-day expansion of control and fly ash mixtures having specific CaO content obtained from Fig. 8(a) at 25% fly ash replacement level

In the case of fly ash mixtures, mitigation could be achieved at a lithium dosage of 100% or below, only when fly ashes having a CaO content equal to or below 23.50% were used. Since the fly ash (CaO = 23.5%) mixture registered a 14-day expansion just below 0.10% at a lithium nitrate dosage of 100%, fly ashes containing CaO content above 23.50% are mostly likely to register expansions above 0.10% at 100% lithium nitrate dosage, indicating that still higher dosages may be required when using such fly ashes. Also, since the control mortars themselves require only 100% lithium nitrate to mitigate ASR, the use of fly ashes with CaO content more than 23.50% needs to be carefully assessed from economic considerations. For instance, a fly ash with lime content greater than 23.5% at a 25% cement replacement level may require lithium dosage greater than 100%, which potentially increases the cost of concrete. However, using the fly ash at a greater cement replacement level may reduce the need of higher lithium dosage levels and this can offset the cost increase. The balance between the fly ash dosage and lithium dosage needs to consider both constructability issues as well as economic considerations.

In addition, in the case of mixtures containing fly ash having CaO content less than 14.40%, mitigation could be achieved even without the use of any lithium nitrate. Hence in such situations, the use of lithium nitrate is not beneficial and cost-effective. However, this is true only when fly ashes are used at a 25% cement replacement level by mass. In situations where lower replacement levels of fly ash are used, the use of lithium nitrate can still be beneficial.

Conclusions

This study focused on investigating the influence of lithium and fly ash dosages and their interactions on ASR mitigation. The materials used in this study include a siliceous limestone from Spratt

quarry, 30% lithium nitrate admixture, and a range of fly ashes having CaO contents from 1.00 to 27.5%. The fly ash dosage in the study was maintained at a constant 25% cement replacement level by mass when lithium admixture was varied from 0 to 100%, based on a Li/Na molar ratio of 0.74 being 100%. In studies employing fly ash alone as the sole ASR mitigation measure, the dosage of fly ash was varied from 15 to 35%. The test methods employed in this investigation include ASTM C 1567 and CRD-C662-10. Based on the studies conducted the following conclusions can be drawn:

1. The effectiveness of a fly ash to mitigate ASR is a function of its chemical composition and replacement level. Fly ashes with high-calcium oxide content did not adequately mitigate ASR even at a cement replacement level of 35%, whereas low-lime fly ashes were able to mitigate ASR at lower replacement levels.
2. For a given fly ash replacement level of 25%, the relationship between the chemical composition (oxide content) of fly ash and 14-day mortar bar expansion can be generalized by exponential relations such as $y = ae^{bx}$ and $y = ae^{-bx}$ depending on whether the oxide being considered is either ASR promoting (CaO, CaO_{equi}, and $CaO + MgO + SO_3$) or ASR inhibiting (SiO_2, SiO_{2equi}, and $SiO_2 + Al_2O_3 + Fe_2O_3$) oxide, respectively. Both these ASR promoting and inhibiting oxide parameters showed a high degree of correlation with the 14-day mortar bar expansion, and hence any of the parameter can be used to predict the potential level of mitigation offered by a given fly ash.
3. The lithium nitrate was found to be effective in reducing the ASR expansion of mixtures both with and without fly ashes. The dosage of lithium nitrate needed to mitigate ASR in the presence of a fly ash is strongly dependent on the chemical composition of fly ash. With fly ashes having a CaO content less than 23.50%, the dosage of lithium needed to mitigate ASR is less than that required for control mixtures (i.e., where only lithium admixture is used). In cases of some high-lime fly ashes, whose CaO content is greater than 23.50%, the lithium dosage needed was found to be more comparable to that of the control mixtures.
4. A linear relationship was found to exist between the oxide composition of fly ash and lithium dosage needed to mitigate ASR.

Overall, it can be concluded from this investigation that the use of lithium admixture in combination with majority of fly ash (i.e., CaO less than 23.5%) can yield synergistic benefits in mitigating ASR at nominal replacement levels while also addressing constructability issues, i.e., early-age strength gain and delayed setting issues.

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References

ACI. (2004). "Use of fly ash in concrete." *232.2R-03*, Farmington Hills, MI.

ASTM. (2008). "Standard specification for coal fly ash and raw or calcined natural pozzolan for use in concrete." *ASTM C 618*, West Conshohocken, PA.

Bian, Q., Nishibayashi, S., Kuroda, T., Wu, X., and Tang, M. (1996). "Various chemicals in suppressing expansion due to alkali–silica reaction." *Proc., 10th Int. Conf. on Alkali–Aggregate Reaction*, CSIRO Division of Building Construction and Engineering, Melbourne, Australia, 868.

Bleszynski, R. F., and Thomas, M. D. A. (1997). "Microstructural studies of alkali-silica reaction in fly ash concrete immersed in alkaline solutions." *Adv. Cem. Based Mater. J.*, 7(2), 66–78.

Bumrongjaroen, W., Muller, I. S., and Pegg, I. L. (2007). "Characterization of glassy phase in fly ash from Iowa State University." *Technical Rep. VSL-07R520X-1*, Turner Fairbank Research Center Federal Highway Administration, Washington, DC, 1–53.

Collins, C., Ideker, J., Willis, G., and Kurtis, K. (2004). "Examination of the effects of LiOH, LiCl, and LiNO3 on ASR." *Cem. Concr. Res.*, 34(8), 1403–1414.

CSA. (2003). "Cementitious materials for use in concrete." *A 3001*, Toronto, 30.

Diamond, S., and Lopez-Flores, F. (1981). "On the distinction in physical and chemical characteristics between lignitic and bituminous fly ashes. Effects of fly ash incorporation in cement and concrete." S. Diamond, ed., *Proc., MRS Symp.*, Materials Research Society, Boston, 34–44.

Dunstan, E. R. (1981). "The effect of fly ash on concrete alkali aggregate reaction." *Cem. Concr. Aggregates*, 3(2), 101–104.

Durand, B. (2000). "More results about the use of lithium salts and mineral admixtures to inhibit ASR in concrete." *Proc., 11th Int. Conf. on Alkali–Aggregate Reaction*, Centre de Recherche Interuniversitaire sur le Beton, QC, Canada, 623.

Folliard, K. J., Thomas, M. D. A., and Kurtis, K. E. (2006). "Guidelines for the use of lithium to mitigate or prevent alkali-silica reaction (ASR)." *Publication No. FHWA-RD-03-047, Federal Highway Administration*, U.S. Dept. of Transportation, Washington, DC.

Harish, K. V., Rangaraju, P. R., and Vempati, R. (2010). "Fundamental investigations into performance of a carbon neutral rice husk ash as a SCM." *J. Transp. Res. Board*, 2164, 26–35.

Kurtis, K., and Monteiro, P. (2003). "Chemical additives to control expansion of ASR gel: Proposed mechanisms of control." *J. Mater. Sci.*, 38 (9), 2027–2036.

Kurtis, K., Monteiro, P., and Meyer-Ilse, W. (2000). "Examination of the effect of LiCl on ASR gel expansion." *Proc., 11th Int. Conf. on Alkali–Aggregate Reaction*, Centre de Recherche Interuniversitaire sur le Beton, Quebec, 51.

Lawrence, M., and Vivian, H. F. (1961). "The reactions of various alkalis with silica." *Australian J. Appl. Sci.*, 12(1), 96–103.

Malvar, L. J., and Lenke, L. R. (2006). "Efficiency of fly ash in mitigating alkali-silica reaction based on chemical composition." *ACI Mater. J.*, 103(5), 319–326.

Malvar, L. J., and Lenke, L. R. (2009). "Alkali-silica reaction criteria for accelerated mortar bar tests based on field performance data." *World of Coal Ash (WOCA) Conf.*, Lexington, KY.

McCoy, W. J., and Caldwell, A. G. (1951). "New approach to inhibiting alkali aggregate expansion." *J. Am. Concr. Inst.*, 22(9), 693–706.

McKeen, R. G., Lenke, L. R., and Pallachulla, K. K. (1998). "Mitigation of alkali-silica reactivity in New Mexico. Report to the Research Bureau, New Mexico Dept. of Transportation." ATR Institute, Materials Research Center, Univ. of New Mexico, Albuquerque, NM.

McKeen, R. G., Lenke, L. R., Pallachulla, K. K., and Barringer, W. L. (2000). "Mitigation of alkali-silica reactivity in New Mexico." *Transportation Research Record 1698*, Washington, DC, 9–16.

Mehta, P. K. (1985). "Influence of fly ash characteristics on the strength of portland-fly ash mixtures." *Cem. Concr. Res. J.*, 15(4), 669–674.

Mo, X., Yu, C., and Xu, Z. (2003). "Long-term effectiveness and mechanism of LiOH in inhibiting alkali–silica reaction." *Cem. Concr. Res.*, 33(1), 115–119.

Obla, K. H., Hill, R. L., Thomas, M. D. A., Shashiprakash, S. G., and Perebatova, O. (2003). "Properties of concrete containing ultra-fine fly ash." *ACI Mater. J.*, 100(5), 426–433.

Papadakis, V. G. (2000a). "Effect of fly ash on portland cement systems. Part I: Low-calcium fly ash." *Cem. Concr. Res.*, 30(10), 1647–1654.

Papadakis, V. G. (2000b). "Effect of fly ash on portland cement systems. Part II: High-calcium fly ash." *Cem. Concr. Res.*, 30(10), 1647–1654.

Ravina, D. (1980). "Optimized determination of PFA (fly ash) fineness with reference to pozzolanic activity." *Cem. Concr. Res.*, 10(4), 573–580.

Ravina, D. (1981). "Production and collection of fly ash for use in concrete." *Effects of fly ash incorporation in cement and concrete*, S. Diamond, ed., *Proc., MRS Symp.*, Materials Research Society, Boston, 2–11.

Rogers, C. (1999). "Multi-Laboratory study of accelerated mortar bar test (ASTM C 1260) for alkali-silica reaction." *Cem. Concr. Aggregates*, 21(2), 191–200.

Sakagushi, Y., Takumara, M., Kitagawa, A., Hori, T., Tomosawa, F., and Abe, M. (1989). "The inhibiting effect of lithium compounds on alkali-silica reaction." *Proc., 8th Int. Conf. on Alkali-Aggregate Reaction in Concrete*, Kyoto, Japan, Elsevier Applied Science, London, U.K., 229–234.

Schneider, J. F., Hasparyk, N. P., Silva, D. A., and Monteiro, P. J. M. (2008). "Effect of lithium nitrate on the alkali-silica reaction gel." *J. Am. Ceramic Soc.*, 91(10), 3370–3374.

Shehata, M., Thomas, M. D. A., and Bleszynski, R. F. (1999). "The effect of fly composition on the chemistry of pore solution." *Cem. Concr. Res.*, 29(12), 1915–1920.

Shehata, M. H., and Thomas, M. D. A. (2000). "The effect of fly ash composition on the expansion of concrete due to alkali-silica reaction." *Cem. Concr. Res.*, 30(7), 1063–1072.

Stark, D. (1992). "Lithium salt admixtures—An alternative method to prevent expansive alkali–silica reactivity." *9th Int. Conf. on AAR in Concrete*, The Concrete Society, Wexham, U.K., 1017–1025.

Thomas, M. D. A. (1996). "Field studies of fly ash concrete structures containing reactive aggregates." *Mag. Concr. Res.*, 48(177), 265–279.

Thomas, M. D. A., Baxter, S., Stokes, D., and Hill, R. (2001). "The combined use of fly ash and lithium nitrate for controlling expansion due to alkali-silica reaction." *Int. Center for Aggregates Research 9th Annual Symp. Aggregates—Concrete, Bases and Fines*, Austin, TX, Aggregates Foundation for Technology, Research and Education, Alexandria, VA, 15.

Thomas, M. D. A., Hooper, R., and Stokes, D. B. (2000). "Use of lithium-containing compounds to control expansion in concrete due to ASR." *11th Int. Conf. on AAR in Concrete*, Centre de recherche sur les infrastructures de béton (CRIB), Laval Univ., QC, Canada, 783–792.

Thomas, M. D. A., Shehata, M. H., Shashiprakash, S. G., Hopkins, D. S., and Cail, K. (1999). "Use of ternary cementitious systems containing silica fume and fly ash in concrete." *Cem. Concr. Res.*, 29(8), 1207–1214.

Touma, W. E., Fowler, D. W., and Carrasquillo, R. L. (2001). "Alkali-silica reaction in portland cement concrete: Testing methods and mitigation alternatives." *Research Rep. ICAR 301-1F*, International Center for Aggregates Research, Univ. of Texas, Austin, TX, 520.