# DETERIORATION OF CONCRETES EXPOSED TO POTASSIUM ACETATE DUE TO ALKALI-SILICA REACTION

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## Abstract

This paper presents data on the influence of potassium acetate solution on the expansion of concrete due to alkali-silica reaction (ASR). Initial observations from deteriorated concrete airfield pavements exposed to potassium acetate (KAc) used as anti-icing and de-icing chemicals appeared to indicate that exposure to the chemical may accelerate damage due to alkali-silica reaction in concrete containing potentially reactive aggregates. However, further investigations on concrete cores extracted from damaged pavements revealed that ASR symptoms were distributed evenly throughout the full depth of the concrete with little evidence of ASR being concentrated close to the surface that was in direct contact with the KAc during service. Chemical profiles established on cores showed that the penetration of potassium was limited to the outer few millimeters even after approximately 10 years. Laboratory studies conducted at normal laboratory temperatures and at elevated temperatures have shown that exposure to KAc solution significantly increases both the rate and extent of reaction in mortars and concretes containing reactive aggregates. The use of traditional measures to prevent expansion due to ASR, such as the incorporation of supplementary cementing materials (SCM) or lithium-based admixtures, only delays the onset of expansion and cannot prevent expansion indefinitely when concrete is continuously exposed to KAc in the laboratory. Concrete slabs manufactured with reactive aggregate have been placed on an outdoor exposure site in Canada and are treated with KAc only before and after snow events. These slabs do not show any signs of damage after three winters.

**Keywords:** potassium acetate, deicers, preventive measures, supplementary cementing materials

## 1 INTRODUCTION

The potential for potassium acetate to cause concrete deterioration first hit the news in the USA when an article in The Colorado Springs Gazette [1] alleged that the use of potassium acetate as a runway deicer accelerated alkali-silica reaction necessitating repairs costing $32 million at Colorado Springs Airport. The article also suggested that similar problems may be occurring at the nearby Denver International Airport (DIA) which became the subject of another news article in the Rocky Mountain News [2]. Subsequent to the media attention a comprehensive investigation was conducted on concrete pavements at DIA to determine the extent of deterioration, possible causes and the role, if any, played by potassium acetate.

Petrographic examination revealed that three different aggregates had been used in the concrete pavements and the extent of ASR varied with aggregate type as shown in Table 1. Expansion tests were performed by monitoring the length change of large diameter (225-mm) cores stored over water at 38°C; the

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large diameter was selected to minimize the effects of alkali leaching during the test. Expansion tests were also performed on concrete prisms produced using aggregate samples retrieved from the sources used for the project. The concrete prism test was conducted in accordance with ASTM C 1293 except that the storage temperature was increased from 38 to 60°C to accelerate the test. Results of the expansion tests on cores and prisms are presented in Table 1. The results presented in Table 1 confirm that Type A aggregate is reactive and has clearly been implicated as a cause of ASR distress in the concrete pavement. Type B aggregate is marginally reactive and its use has led to some low levels of distress in the concrete. Type C aggregate is non-reactive and no ASR damage was observed in concrete containing this aggregate.

Small diameter (50-mm) cores stored in commercial grade potassium acetate solution at 38°C were observed to expand rapidly. Cores containing Type A aggregate tended to produce the most expansion although, surprisingly, cores with Type C aggregate also showed excessive expansion. The mechanism of expansion of cores containing Type C aggregate was not resolved as forensic examination of cores after testing showed no evidence of reaction or expansion of the aggregate. Examination of cores containing Type A aggregate after immersion in potassium acetate revealed multiple sites of reacting aggregate and an abundance alkali-silica reaction product (i.e. gel).

Where ASR was detected in cores extracted from concrete pavements at DIA, the symptoms were observed to occur throughout the depth of the core (approximately 425 mm) and there was no evidence of a concentration of symptoms near the surface, which may have been expected if potassium acetate was exacerbating ASR where it came in contact with the concrete. A number of cores were ground into powder samples to determine the variation in the potassium and sodium concentrations with depth. Figure 1 shows the profile of the potassium to sodium ratio. These data reveal very little augmentation of the potassium content at depth despite the regular application of potassium acetate throughout the ten-year service life of the pavement. The depth of penetration is highest for the concrete with Type A aggregate which was exhibiting some cracking due to ASR. For concrete with Type C aggregate, the depth of penetration appears to be limited to 3 mm or less. It is expected that the penetration of potassium has been aided by the cracks at the surface of the concrete with Type A aggregate.

The lack of potassium penetration and evidence of accelerated ASR at the surface of the 10-year-old concrete at first seems to be in conflict with the rapid reaction and expansion of small-diameter cores stored in potassium acetate solution in laboratory. However, this probably reflects the difference in the exposure conditions in the laboratory and the field. When potassium acetate is applied as a deicer or an anti-icer in the field the concrete is presumably close to saturation and frozen which would tend to impede the penetration of the solution. On the other hand, elevated temperature in the laboratory tests would tend to increase the rate of diffusion and penetration. This highlights the need to conduct tests under conditions representative of field conditions.

Since problems were reported at these airports, laboratory investigations have confirmed that potassium acetate, and other alkali acetates and formates used as de-icing or anti-icing chemicals, can exacerbate alkali-silica reaction in concrete [3]. However, much of the laboratory testing has been conducted at elevated temperatures using accelerated tests such as concrete expansion tests at 38°C or mortar-bar expansion tests at 80°C. In the current study reported here, efforts have been made to determine the impact of potassium acetate on alkali-silica reaction in concrete samples exposed to lower temperatures in the laboratory or to field conditions on outdoor exposure sites.

It should be noted that some workers have demonstrated that some form of interaction may occur between potassium acetate and concrete that is independent of alkali-silica reaction [4,5] which may result in concrete deterioration. Such phenomena are the subject of ongoing research but are not discussed further in this paper.

## 2 INITIAL STUDIES AT UNB

Initial studies at the University of New Brunswick (UNB) were aimed at determining whether preventive measures usually found to be effective in controlling expansion due to alkali-silica reactive in concrete containing reactive aggregate would provide protection indefinitely if the concrete was exposed directly to potassium acetate. Although a wide range of materials, specimens and exposure conditions were used in these early studies the expansion results presented here are restricted to selected data shown in Figure 2. The results are for mortar bars (25 x 25 x 250-mm gauge length) containing a highly-reactive (Jobe) sand which, after curing in limewater at 23°C for 28 days, were exposed to a commercially-available anti-icing chemical containing approximately 50% potassium acetate (KAc)[1] at 23°C. Data are shown for five mixes; these are: (i) control mix with portland cement (PC), (ii) mix with PC + 40% Class F (low-lime) fly ash, (iii) mix with PC + 50% ground granulated blastfurnace slag, (iv) mix with PC + lithium nitrate at a dose sufficient to produce a lithium-to-alkali ratio of [Li]/[Na+K] = 1.48, and (v) mix produced with a calcium aluminate cement (CAC) binder. Previous testing of concrete prisms (ASTM C 1293) and outdoor exposure blocks have shown that the levels of fly ash, slag, and lithium nitrate used should be sufficient to eliminate damaging expansion with this reactive aggregate. However, the data in Figure 2 clearly show that this is not the case in the presence of KAc. These measures were not able to eliminate damaging expansion indefinitely, although they were able to decrease the maximum amount of expansion observed. It is interesting that the mortar manufactured with CAC showed significantly less expansion.

An experiment was conducted to determine whether there is any interaction between cement paste and potassium acetate solution. Samples of pre-hydrated PC and CAC paste were crushed and placed in bottles containing a commercial-grade potassium acetate solution (KAc solution with approximately 50% $CH_3COOK$) such that the solution-to-solids ratio was 10:1. Changes in pH were then measured with a pH meter. In the presence of PC paste the solution pH increased with time from the initial value of approximately 9 to somewhere in excess of 14. In comparison, the increase in the pH of the solution containing CAC was very small. It is thought that the pH increase is the result of interaction between the potassium acetate and calcium hydroxide in the hydrated PC resulting in an increase in the hydroxyl concentration of the solution which will increase the rate of dissolution of silica in the reactive sand thereby increasing the rate and extent of ASR. This phenomenon does not occur with CAC as there is no source of calcium hydroxide.

## 3 ONGOING LABORATORY AND FIELD STUDIES AT UNB AND UTA

In 2009 laboratory and field studies were initiated at the University of New Brunswick (UNB) and the University of Texas at Austin (UTA) with the following objectives:

- To determine the rate of deterioration of concrete exposed to potassium acetate (and similar anti-icing and de-icing chemicals) under field conditions and to evaluate the extent to which preventive measures extend the service life under such conditions.

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[1] Note that the chemical formula for potassium acetate is $CH_3COOK$, but the abbreviation KAc is used here for convenience.

- To determine the mechanisms behind the non-ASR related distress that has been observed in various laboratory studies and whether such distress will occur under field conditions (i.e. in concrete with non-reactive aggregate exposed to potassium acetate).

This paper will focus on the studies related to alkali-silica reaction only.

### 3.1 Materials and Methods

The materials used are listed in Table 2. All concrete mixtures were produced with a cementitious material content of 420 kg/m$^3$ and a water-to-cementing materials ratio of w/cm = 0.40. Concrete specimens included 75 x 75 x 300 mm concrete prisms and 600 x 600 x 100 mm concrete slabs. All concretes were subjected to a 28-day, wet-cure period before being exposed to potassium acetate (or other) solution.

Concrete prisms were immersed in a commercial anti-icing chemical containing approximately 50% potassium acetate and were stored at 3 different temperatures: 23°C, 38°C, and 60°C. The slabs were placed on exposure sites at UNB in Fredericton and at UTA in Austin. The slabs at UNB are treated before and after each snow event resulting in approximately 100 applications per year. The slabs at UTA are treated approximately six times per year over the winter. The application rate at both sites is approximately 100 mL/m$^2$.

## 4 RESULTS

The expansion results for concrete prisms stored in potassium acetate are shown in Figures 4 and 5, respectively, for concrete with non-reactive aggregates and reactive (Jobe) sand. Deleterious expansion ($\geq$ 0.04%) was observed for some, but not all, mixes with non-reactive aggregate. The control mix (without fly ash) expanded rapidly at 38°C and exhibited cracking after approximately 1 year. The addition of 25% fly ash (Class F or Class C) was effective in reducing expansion at this temperature although all fly ash mixes showed expansion in the range of 0.06 to 0.08% after two years. The control concrete and concretes with 25% Class C fly ash (TK and PS) showed similar expansion (0.06 to 0.08%) when stored at 23°C, but the concrete with 25% Class F fly ash (BC) showed less expansion (~ 0.03%). Concrete with non-reactive aggregate stored at 60°C generally showed lesser amounts of expansion than companion specimens stored at the lower temperatures. Examination of the concretes with non-reactive aggregates revealed no signs of alkali-silica reaction. All of the concrete mixes containing reactive Jobe sand showed excessive amounts of expansion when stored in potassium acetate solution regardless of the presence of fly ash or storage temperature. The rate of expansion increased with increasing temperature but the ultimate expansion appears to decrease with increasing temperature; the expansion appears to reach a plateau for specimens stored at 38 and 60°C, but was still increasing after 2 years for specimens stored at 23°C. Class F fly ash did extend the time to the onset of expansion, the rate of expansion and the ultimate expansion at 38 and 60°C but was not able to prevent expansion or damage due to ASR. There was very little difference in the expansion of concretes stored at 23°C.

The expansion of slabs on the outdoor exposure site in Austin are presented in Figures 6 and 7 for, respectively mixtures containing non-reactive aggregate and reactive Jobe sand. No damage or expansion has been observed for any of the slabs produced with non-reactive aggregate. All of the concrete mixes produced with reactive (Jobe) sand have shown some level of deleterious expansion regardless of whether fly ash was used or the slabs were exposed to potassium acetate. However, in general potassium acetate increased the rate and the amount of expansion. Only the Class F fly ash was effective in significantly reducing the expansion; however, expansion did exceed 0.04% at ages beyond one year.

To date, none of the slabs exposed on the outdoor site in Fredericton, Canada, have exhibited significant expansion or show any signs of cracking or other damage, regardless of the composition of the mix and whether or not the concrete was exposed to potassium acetate. These concretes have been exposed to at least 300 potassium acetate applications over the past three winters.

## 5 DISCUSSION

The results of these tests clearly indicate that exposure of concrete containing reactive aggregate to potassium acetate solution accelerates alkali-silica reaction probably due to an increase in the concentration of potassium and hydroxyl ions. The use of supplementary cementing materials such as fly ash or slag may delay the onset of and rate of expansion. However, the main role of SCMs in controlling ASR expansion is to reduce the availability of alkalis in the pore solution and this role may be neutralized if the concrete is exposed to an inexhaustible supply of alkali ions. The extent to which potassium acetate contributes to ASR deterioration under field conditions is not clear. Periodic applications of potassium acetate to the surface of concrete slabs during the relatively warm winter months in Texas increased expansion and the amount of ASR-related damage. However, frequent applications (approximately 100 per year) of potassium acetate to the surface of slabs during the winter months in Canada has not resulted in any damage to date (after 3 winters). In this case the potassium acetate is only applied immediately before or after a snow event when the concrete surface would be expected to be at sub-zero temperatures. Examination of concrete cores taken from airport runways confirm that ASR has contributed to the observed deterioration but has produced little evidence that potassium acetate has exacerbated the deterioration. More recently, field surveys of airfields in the USA have indicated that the cases of concrete deterioration due to potassium acetate are limited and that the problem is certainly not as devastating and widespread as alleged by early media reports.

There is evidence that there may be some interaction between potassium acetate and cement hydration products that is unrelated to ASR [4,5]. However, the extent to which this occurs in concrete exposed to potassium acetate under field conditions is unknown. This is the subject of an ongoing research program.

## 6 REFERENCES

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TABLE 1: Results of Petrographic Examination of Cores and Expansion Testing of Aggregates from DIA

| Aggregate | Petrographic examination of cores | Expansion of cores stored over water at 38°C (%) | Expansion of prisms stored over water at 60°C (%) |
|---|---|---|---|
| Type A | Moderate to severe ASR | 0.031 | 0.123 |
| Type B | Low to moderate ASR | 0.015 | 0.048 |
| Type C | No ASR | 0.004 | 0.011 |

TABLE 2: Materials Used in the Study at UNB and UT Austin

| **Materials** | **UNB** | **UTA** |
|---|---|---|
| *Cements and SCMs* | | |
| Type I Portland cement (~ 0.80% $Na_2O_e$) | Type GU (CSA A 3001) | Type I (ASTM C 150) |
| Low-alkali PC (~ 0.60% $Na_2O_e$) | Type HS (CSA A 3001) | |
| Calcium Aluminate Cement | | |
| Fly Ash 1 (0-5% CaO) | BD | BC |
| Fly Ash 2 (20-25% CaO) | TK | TK |
| Fly Ash 3 (25-30% CaO) | PS | PS |
| Fly Ash 4 (25-30% CaO) | CM | |
| *Aggregates* | | |
| Fine aggregate 1 (non-reactive) | Zeeland | Evans Road |
| Fine aggregate 3 (highly-reactive) | Jobe | Jobe |
| Coarse aggregate 1 (non-reactive) | Blagdon | Martin Marrietta |
| *De-icing/Anti-Icing Products* | | |
| Potassium acetate | Commercial Grade ~ 50% | Commercial Grade ~ 50% |

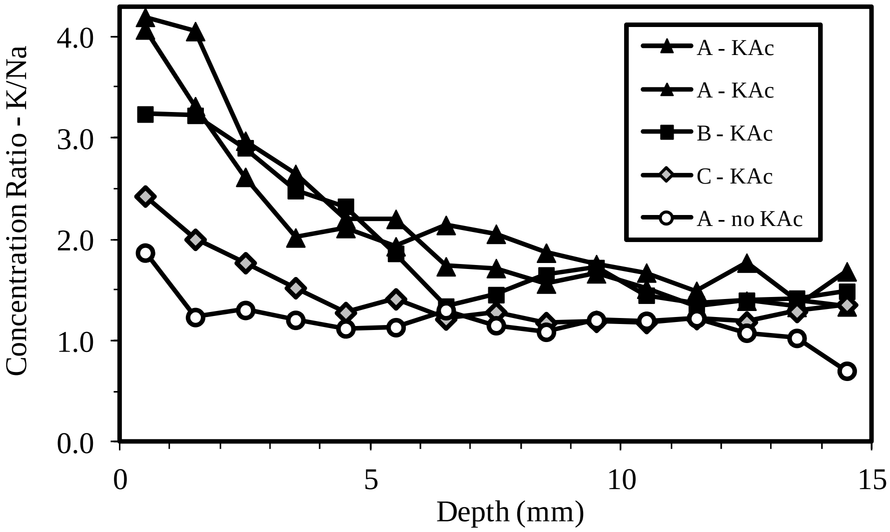

FIGURE 1: Profile of Potassium-to-Sodium Ratio (K/Na) in Cores from DIA

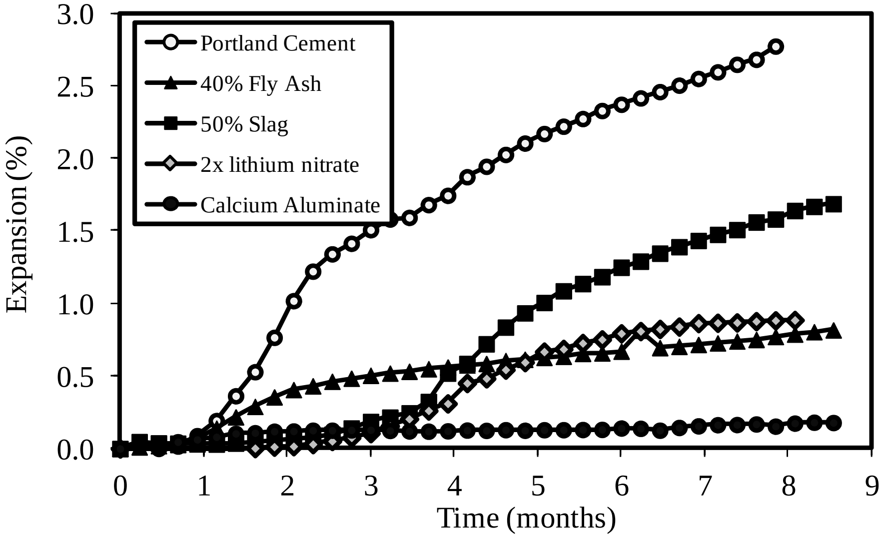

FIGURE 2: Expansion of Mortar Bars with Highly-Reactive (Jobe) Sand stored in 50% KAc Solution at 23°C

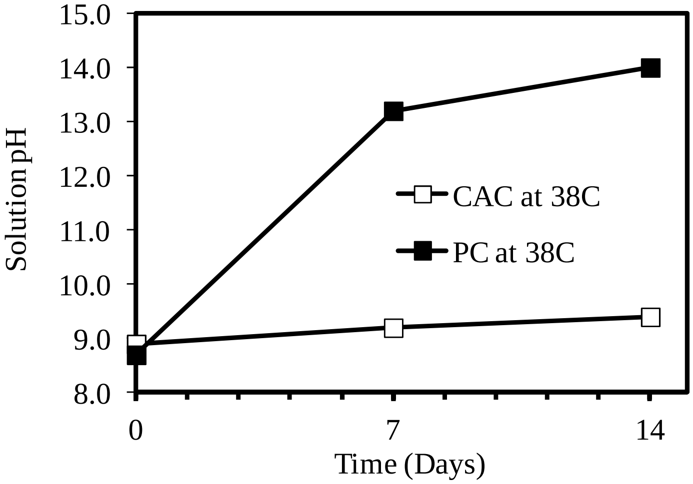

FIGURE 3: pH of 50% KAc after Immersion of Cement Paste Samples

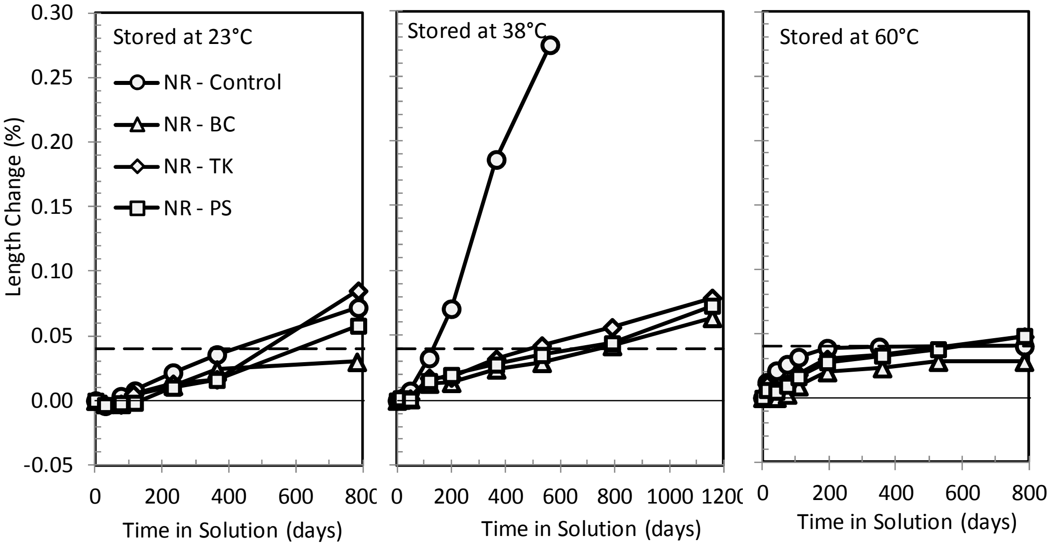

FIGURE 4: Expansion of Concrete Prisms with Non-Reactive Aggregate Stored in Commercial-Grade (50%) KAc Solution (Mixes BC, TK and PS contain 25% fly ash)

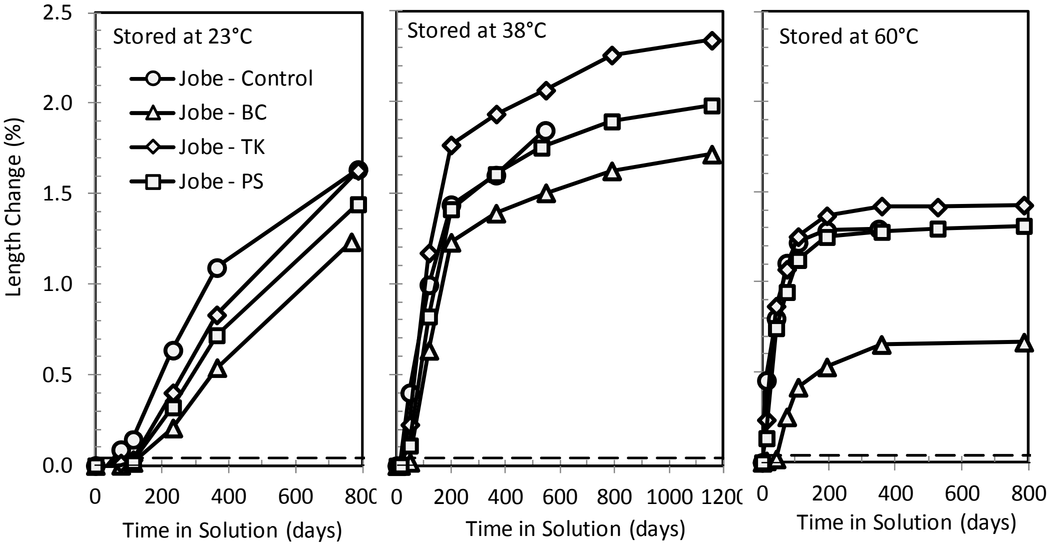

FIGURE 5: Expansion of Concrete Prisms with Reactive (Jobe) Sand Stored in Commercial-Grade (50%) KAc Solution (Mixes BC, TK and PS contain 25% fly ash)

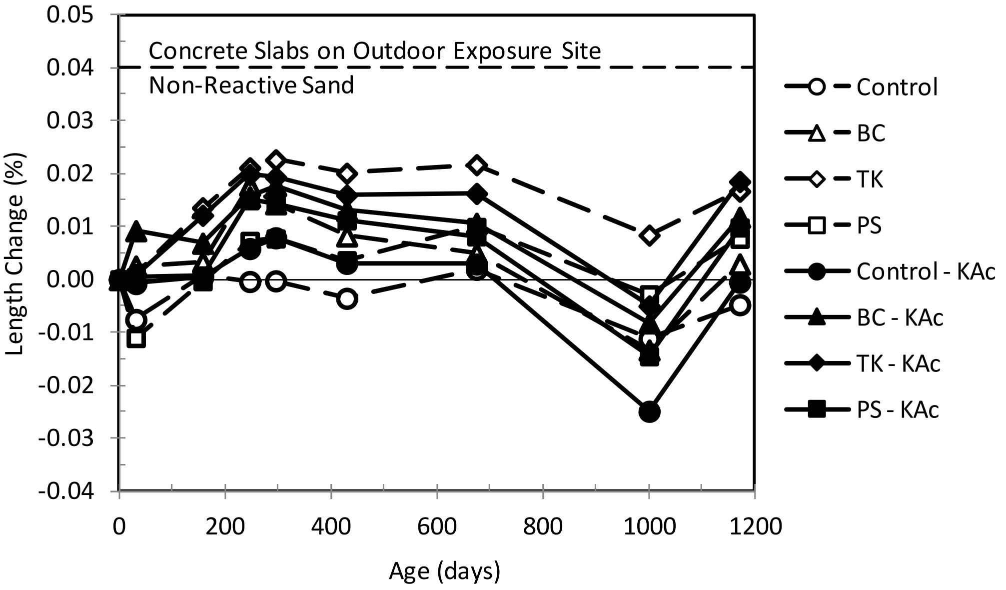

FIGURE 6: Expansion of Concrete Slabs with Non-Reactive Aggregate - Outdoor Exposure Site in Austin, Texas (Mixes BC, TK and PS contain 25% fly ash; KAc in legend indicates slabs treated with potassium acetate solution)

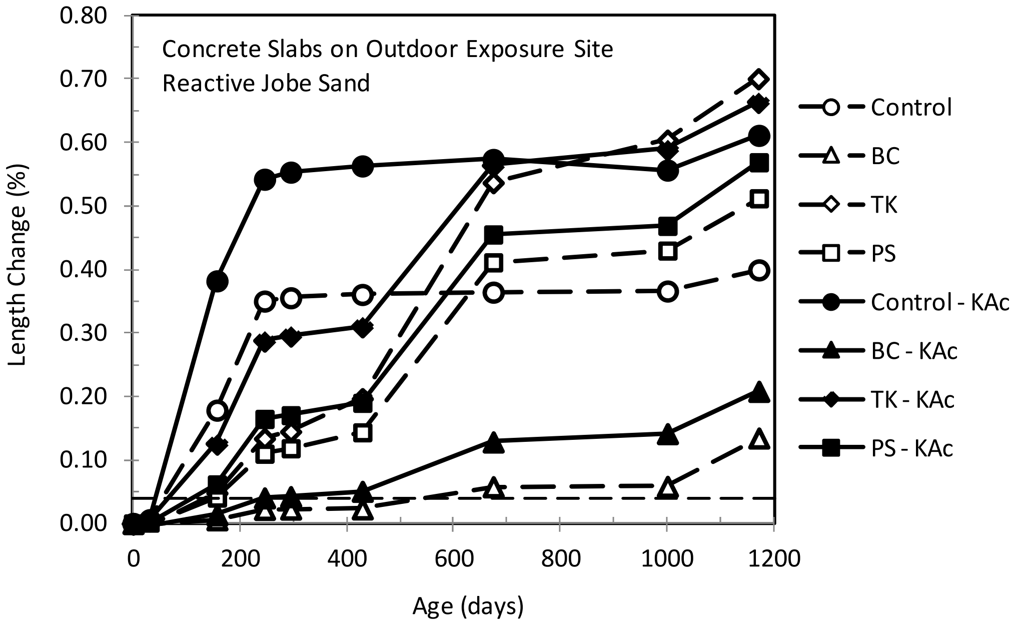

FIGURE 7: Expansion of Concrete Slabs with Reactive (Jobe) Sand - Outdoor Exposure Site in Austin, Texas (Mixes BC, TK and PS contain 25% fly ash; KAc in legend indicates slabs treated with potassium acetate solution)