An *IPRF* Research Report

Innovative Pavement Research Foundation

Airport Concrete Pavement Technology Program

Report IPRF-01-G-002-04-6

Lithium Admixtures ($LiNO_3$) And Properties of Early Age Concrete

Programs Management Office
5420 Old Orchard Road
Skokie, IL 60077

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Lithium Admixtures ($LiNO_3$) And Early Age Concrete Properties

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TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

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EXECUTIVE SUMMARY

The effects of lithium nitrate ($LiNO_3$) admixture addition on early age concrete properties were evaluated. This was accomplished through a review of the literature, published through May 2005, and through a statistical analysis of field and laboratory measured properties determined during airfield concrete pavement construction, which included a lithium nitrate admixture, at Hartsfield-Jackson Atlanta International Airport (H-JAIA).

There was limited data available in literature regarding the effects of lithium admixture on early age properties such as setting time, unit weight, air content, slump, temperature, and compressive strength. Publications with information on finish, flexural strength, or maturity were not found during the search. Various researchers report that $LiNO_3$ has no effect on setting time; others report that setting times may be shorted by as much as 90 minutes. Lithium admixture addition appears to have no effect on unit weight, and adequate air entrainment systems were achieved in concrete containing $LiOH{\cdot}H_2O$ and $LiNO_3$, although increased air-entraining admixture dosages may be required. Research findings regarding the effect of $LiNO_3$ on slump show that the admixture may not have a significant effect alone but in combination with other admixtures there was an effect. When used in combination with other chemical admixtures these effects were exacerbated in the presence of high alkali cements. Likewise, lithium admixtures have been observed to have impact compressive strength with variable results. As with slump, some link with cement alkali content may be made, as higher alkali cement concretes containing lithium generally exhibited lower 28-day strengths as compared to controls, while lower alkali cement concretes with lithium displayed higher strengths than control mixtures. Only one study examined shrinkage in concrete that included a lithium admixture. That study did not report on the effect on shrinkage occurring after 28 days. Effects of lithium admixtures on early age shrinkage have not been reported.

An experimental program was designed to accomplish the objective of the research, that is, does lithium have any effect on the early age properties of production airfield concrete? The program included sampling and testing concrete for plastic and hardened properties, as well change of phase properties (shrinkage and early-age hydration characteristics). The effects of varying the lithium dosage on these properties were included in the program.

Mixes were sampled during the reconstruction of the Ramp1 taxi lane pavement at Hartsfield-Jackson Atlanta International Airport (H-JAIA) in the late summer and early fall of 2005. Production mixes of concrete were produced with lithium nitrate ($LiNO_3$) dosages of 0, 50, 100, 200, and 400 percent of the manufacturer's recommended dosage (i.e., $[Li]/[Na+K]= 0.74$). The control mix included a Type I cement with a Class F fly ash at 20 percent by mass cement replacement. There was no observed effect of lithium dosage on measured air content, slump, unit weight, or maturity. The analysis of variance (ANOVA) performed on strength data suggests that lithium has no significant effect on flexural strength. However, there was an observed impact on compressive strength. Compressive strength decreased as dosage of lithium nitrate increased. These effects become statistically significant with dosages in excess of 50%.

A secondary study, performed in the laboratory, looked at concretes that included lithium nitrate ($LiNO_3$) dosages of 0, 100, and 400% using the a Type I cement. Thee was no significant effect of lithium dosage apparent for air content, slump, unit weight, or temperature/maturity when the lithium dosage varied. ANOVA performed on the results of strength testing suggests that lithium

nitrate in the mixes has a significant effect on both flexural and compressive strength, particularly in for first three days of age. The analysis suggests that a higher lithium dosage results in significantly stronger concrete, which is contrary to the results obtained from the field-produced mixtures. However, the production concrete included fly ash.

As a part of the laboratory study, the effects of lithium nitrate dosages in combination with a matrix of six different cements were examined. The purpose of the study was to examine the influence lithium nitrate and the total cement alkali (Na_2O_{eq}) and tricalcium aluminate (C_3A) contents. The Lafarge Roberta cement from the H-JAIA construction project was tested alone and with fly ash at 20 percent by mass cement replacement.

Isothermal calorimetry clearly reveals that the presence of lithium nitrate admixture has an impact on the early heat of hydration for the cements tested. A general conclusion is that the higher lithium dosages result in accelerated hydration. The accelerated hydration due to lithium dosing may explain the higher flexural and compressive strengths during the first three days of curing. Accelerated hydration was observed in cements with lower alkali and C_3A contents. This suggests a more sensitive response in the cement hydration when lithium is present. However, early age calorimetry profiles varied more for different cements than those recorded for a varied lithium nitrate dosage. Fly ash replacement in the Roberta cement appeared to reduce – or dilute - the effects of lithium nitrate on the observed early age heat of hydration profiles.

Chemical shrinkage, determined by ASTM C 1608-05, suggests some parallels to the heat of hydration curves. Additionally, lithium appears to affect the hydration of cements at the ages of one and ten days differently depending on the C_3A content of the cement. Autogenous shrinkage results indicate that higher lithium dosages lead to less linear shrinkage up to ten days of hydration and then there is greater shrinkage.

Vicat time of setting, determined by ASTM C 191-04, suggests a clear impact of lithium nitrate dosage on the low alkali cement used in the study. There were no trends evident in the other five cements included in the study. For the low alkali cement, an increasing lithium nitrate dosage decreased the initial and the final set time. Dosage at 100% of the recommended amount decreased initial setting time by 15% and final setting time by 22% or reduction of 15 to 20 minutes.

Limitations: The research conducted is limited to a particular lithium compound, namely lithium nitrate ($LiNO_3$), supplied by a single producer. Therefore, conclusions regarding the analyses of data collected are restricted to the materials used. Effects using different aggregate, different cements, fly ash, or other supplementary cementing materials, different mix proportions and different lithium compounds have not been explored.

1. INTRODUCTION.

There are successful demonstrations on using lithium admixtures to mitigate expansion in existing concrete that is the result of alkali-silica reaction (ASR). The results of the demonstrations have encouraged the industry to incorporate lithium admixtures into fresh concrete mixes. In doing so, it is necessary to understand the impact of lithium admixtures on the early age behavior of concrete because in modern construction, where effects on setting time, workability, rate of strength gain, and shrinkage could have significant negative economic consequences, the impacts could also be detrimental to long-term performance. There are limited laboratory studies that provide information on the impact that lithium admixtures have on concrete properties. There are no reports on the influence of lithium admixtures on the properties of field production concrete.

This study was undertaken with the intent to accomplish a statistical analysis of test results obtained as a result of side-by-side testing accomplished during the construction of an apron at Hartsfield-Jackson Atlanta International Airport (H-JAIA). The primary objective was to determine if lithium admixtures have an adverse effect on the plastic or early age hardened properties of production concrete used for airfield paving and where adverse impacts are observed, the upper limit of the dosage of lithium nitrate was defined.

The three goals of this study are: assemble and synthesize the data available in existing literature that describes the effect of lithium compounds[1] on early age behavior of concrete;[2] collect and analyze test results collected from the H-JAIA construction to determine the effect, if any, of different lithium dosage on slump, air content, concrete temperature (maturity), flexural strength (and rate of flexural strength gain), compressive strength (and rate of compressive strength gain); and complete a laboratory study to determine if there are differences in dosage rates that influence change of phase properties. All of the goals were realized.

2. LITERATURE REVIEW.

The beneficial effects of lithium in mitigating expansion by ASR have been examined extensively; however, little research has been done to specifically examine the effects of lithium admixture use on other concrete properties. Rather, information noting the effects of lithium admixtures, if any, on concrete properties has been included as peripheral information, rather than as the focus of a research effort. This section presents a review of the literature - published through May 2005 - which addresses, the effects of lithium admixtures on the chemistry of the pore solution and hydration products and concrete setting time, workability, strength, and shrinkage.

While the effects of lithium addition and dosage on other early age properties, such as finish characteristics and maturity, are clearly important to consider, no data was found in the available literature. These properties are explored as part of the experimental plan, as identified in Section 3.

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[1] Because of the limited amount of data presented in the literature regarding the effects of lithium addition on concrete properties (other than ASR durability), the most common lithium compounds will be considered in this review, rather than restricting the review to the effects of lithium nitrate only.

[2] For the purpose of this review, "early age" will be defined as the first 28 days of age, with a particular emphasis on plastic properties, shrinkage, and strength development.

In addition, much of the research in the literature examines lithium dosage of 100% or lower.[3] One objective of the research is to examine whether an upper dosage limit exists beyond which early age concrete properties begin to become negatively effected. However, data is lacking in the literature in this regard, particularly the influence of dosage rates in excess of 100%.

2.1 EFFECTS OF LITHIUM ON PORE SOLUTION AND HYDRATION PRODUCT CHEMISTRY.

A variety of lithium compounds, including LiF, LiCl, LiBr, LiOH, $LiOH \cdot H_2O$, $LiNO_3$, $LiNO_2$, Li_2CO_3, Li_2SO_4, Li_2HPO_4, and Li_2SiO_3, have been considered over years of laboratory studies on alkali-silica reaction. Of these, $LiNO_3$ has shown the most promise for practical use for a number of reasons. While LiOH, and other lithium compounds, can increase the hydroxyl ion (OH^-) concentration in the pore solution, and thus increase the risk for ASR, the $LiNO_3$ does not seem to increase the pore solution alkalinity [Diamond and Ong, 1992; Diamond, 1999]. Other lithium salts, such as LiF and Li_2CO_3, are poorly soluble and generate LiOH in solution, making them less suitable for use in concrete mixtures, while $LiNO_3$ is fully soluble and is neutral [Diamond, 1999]. Poorly soluble lithium compounds such as Li_2CO_3 have also been shown to have adverse effects on setting time [Mo, in review]. In addition, when LiOH, Li_2CO_3, and LiF are used in insufficient dosages, their use may actually increase expansion by ASR, rather than reduce it – a "pessimum effect" [Stark et al., 1993; Thomas et al., 2000; Diamond and Ong, 1992; Diamond, 1999]. $LiNO_3$ is safe to handle, does not increase the pore solution pH, does not exhibit a pessimum effect, and has been shown to be more effective than other lithium compounds in controlling expansion in very reactive aggregate. Due to these advantages, $LiNO_3$ is the most common active component in commercially available, lithium-containing liquid chemical admixtures for control of expansion associated with ASR.

However, it is known that much of the lithium added to ordinary concrete during mixing will become bound in the hydration products. For example, Diamond and Ong [1992] found that 40% of the lithium added to non-reactive mortars was taken up by the hydration products by 1 day of age. Berubé and co-workers [2004] found that only 35% of the lithium, added as $LiNO_3$, remained in the pore solution at 90 days.

Often, lithium is used in combination with pozzolanic materials, such as fly ash, to minimize the potential for damage by ASR in new construction. With fly ash concrete, this lithium binding effect could be exacerbated because the use of fly ash in Portland cement-based materials is known to decrease the Ca/Si ratio in the calcium silicate hydrate (or C-S-H), which is the primary strength-giving phase. Class F fly ash, with its lower CaO content, has a greater effect than Class C fly ash on lowering the Ca/Si ratio. A lower Ca/Si ratio in the C-S-H has been shown to increase alkali (Na^+ and K^+) binding within the cement hydration product. Lithium is also an alkali earth metal, and its binding within the C-S-H structure will also likely be increased in fly ash mixtures where the Ca/Si ratio is decreased [Bhatty and Greening, 1978; Stade, 1989]. In addition, there is evidence that the binding of lithium in the cement hydrates may be preferable to binding of Na or K [Collins et al., 2004; Berubé et al., 2004]. The net effect of increased Li binding in hydration products would be a reduction in the amount of "free" lithium (that which remains in the pore solution or loosely bound)

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[3] In this report a 100% dosage is equivalent to [Li]/[Na+K]=0.74

which is able to participate in reactions to mitigate expansion by ASR *and* which may affect other plastic and hardened properties of the concrete.

2.2 SETTING TIME.

Some research found that lithium admixtures may shorten the time of set in Portland and calcium aluminate cements. Another report suggests that lithium nitrate may have negligible effects on setting. Wang et al. [1996] reported setting times shortened by 20-40 minutes when LiOH was used in combination with an ASTM Type A (water-reducing) admixture and by 40 to 90 minutes when used with a Type F (superplasticizing) admixture in mixtures with a water to cement ratio (w/c) of 0.33. The effect was exacerbated for those cements with higher alkali contents. The authors suggest that the shortened setting time may be offset by other means, if necessary. However, methods and proportions for achieving equivalent setting times were not provided and data for setting time when lithium was used in combination with retarding admixtures was also not reported.

Shortened setting times have also been reported for $LiCO_3$ [Mo, in review; Gajda, 1996] and LiOH [Mo, 2005] when used in Portland cement pastes. In the most severe case described in the literature, Gajda [1996] reported $LiCO_3$ shortened setting times by a factor of 2 or 3. However, this effect may be due to the poor solubility of $LiCO_3$, which could contribute to early precipitation, and the earlier stiffening and setting observed by Mo and Gajda. In addition, it should be noted that the paste setting times in Mo's studies were already substantially shorted by raising the equivalent alkali content to 3.0%, and the addition of lithium compounds produced only small additional decreases in setting time, when comparing the alkali-loaded samples (both with and without lithium) to the control pastes. However, lithium salts have been shown to act as set accelerators for high-alumina or medium-alumina cements [Novinson and Crahan, 1988], suggesting that some accelerating effect may be possible in Portland cements, although for lithium admixtures used in practice (e.g., $LiNO_3$) the effect is expected to moderate acceleration, if any effect is observed at all.

In Portland cement concrete, Thomas et al. [2003] reported setting times to vary by ±20 minutes, with the addition of $LiNO_3$. This data suggests that the lithium addition may not always lead to acceleration and may have no discernible effect in practice on setting time. This conclusion is counter to the conclusion of Wang et al. [1996], although both groups investigated $LiNO_3$ in concrete mixtures with similar water-to-binder ratios. One important difference may be that the concretes examined by Thomas et al. contained fly ash, which may delay set, and which may also bind lithium, thus decreasing the set accelerating effect of the $LiNO_3$. No fly ash was included in the mixtures examined by Wang and co-workers.

There is also some evidence that the lithium admixture dosage rate may influence setting characteristics. Certain chemical admixtures, such as $CaCl_2$, for example, can act as set accelerators at low dosages and set retarders at higher dosages. Novinson and Crahan [1988] proposed that the concentration of the lithium salt and its effect of pore solution pH (which is related to the anion associated with the lithium) are important factors in determining the effect of lithium addition on setting time.

Because of the varied findings on set time, the influence of lithium admixtures and their dosage on setting time should be the subject of further study. Additionally, research is needed to evaluate the influences of cement composition and temperature in the presence of lithium to best anticipate the effects of lithium use in practice.

2.3 AIR CONTENT AND UNIT WEIGHT.

Air content (most commonly determined by the pressure method, ASTM C 231) and unit weight (ASTM C 138) are generally measured in the field as a part of the quality control process. However, there was little data in the literature to describe the effect, if any, of lithium on air content and unit weight. The effect on unit weight, in particular, received only scant attention in the literature. Britain's Building Research Establishment (BRE) reports no change in wet density in concrete mixtures containing $LiOH \cdot H_2O$, as compared to ordinary concrete [Hooper et al., 2001].

The effects of lithium admixture addition on air content, in air-entrained concrete, may be examined through work presented by Wang et al. [1996], Lane [2002], and Thomas et al. [2003]. Wang et al. [1996] report no significant effect of LiOH use on air-entrainment, with the air content of lithium-containing fresh concrete *generally* deviating little from the control samples, in some cases containing slightly more air and in others less. In a study by Lane [2002], concretes were prepared with w/cm ratio of 0.45, with a constant cement content and air entrainment dosage, in combination with $LiOH \cdot H_2O$ or $LiNO_3$ at 75 and 100% dosage. An adequate air entrainment system developed in all samples, providing excellent freeze-thaw resistance, as measured by ASTM C 666 Procedure A (i.e., 98-101). Air contents of 4.2 to 6.1% were achieved in lithium-containing mixtures, compared to 4.0% in the control. Thomas et al. [2003] recorded air contents of 5-7% were for air-entrained concretes produced with $LiNO_3$ dosages of 0, 75, and 100% of the standard dosage. It is worth noting, however, that the dosages of air entraining admixture (AEA) in these lithium-containing concrete mixtures were, in some cases, *up to 50% higher* than in the control mixtures; Thomas et al. did not comment on the reasoning or need for higher AEA dosage in these mixtures, and air contents are not provided for many of the mixtures examined. When tested according to ASTM C 666 Procedure A, all of the concretes exhibited high durability factors of 96-99%, regardless of the lithium admixture dosage, indicating that a stable and sufficient system of air entrainment was achieved. It is not clear if a higher dosage of AEA was required to achieve the necessary amount of entrained air in the presence of lithium nitrate.

2.4 WORKABILITY.

There are limited research publications that examine the influence of lithium admixtures on slump. Thomas et al. [2003] measured slump in concrete mixtures with w/cm of 0.35, Type II cement, 13-21% fly ash by weight of cement, and water reducing and air entraining admixtures. A lithium admixture (as 30% solution of $LiNO_3$) was used at dosage rates of 100 and 75%, based on the alkali contributed by the cement, and also at 100%, when the dosage was based on the alkalis contributed by the cement and fly ash. The authors concluded that the effect of lithium admixtures on slump, at these dosage rates, was insignificant.

Likewise, Sakaguchi [1990] and co-workers also reported no change in mortar flow with the addition of $LiOH \cdot H_2O$ and $LiCO_3$, and no changes in slump of concrete mixtures has been noted during extensive examination of $LiOH \cdot H_2O$ by BRE [Hooper et al., 2004].

However, Lumley [1997] remarked that both $LiOH \cdot H_2O$ and $LiCO_3$ produced "noticeable" early stiffening in concrete mixtures prepared at water-to-cement ratios of 0.50 and 0.525, respectively. The stiffening in one case was severe enough to prohibit proper compaction. Subsequent mixtures in Lumley's experimental program were prepared at higher water to cement ratios. The choice of lithium compound appears to be significant as Lumley reported only minor stiffening in mixtures containing LiF; the use of $LiNO_3$ was not addressed in that research effort.

The effect of LiOH on slump has also been addressed by Wang et al. [1996] who found that its use could both increase slump, particularly when used in combination with ASTM Type A (water-reducing) and Type D (water-reducing and retarding) admixtures, and could lead to decreased slump, particularly when used with cements with high alkali contents. Reduced slump was particularly apparent in cements with alkali equivalents of 0.80 and 1.02% when Type F superplasticizing and Type G superplasticizing and retarding agents were used.

2.5 STRENGTH.

The rate of strength development is an important consideration when planning construction operations. However, the effect of lithium admixtures on strength development has not been well addressed by the published literature. When strength data is presented, the effect of lithium on *compressive* strength is reported. While compressive strength is the most common measure of concrete quality in practice, it is less typically used for pavement or airfield construction where flexural strength development is most relevant. No information could be found regarding the effect of lithium on the flexural strength of concrete.

Lithium has been shown by various researchers to have different effects on strength. In an investigation of two different concrete mixes where the cement content varied, Thomas et al. [2003] found the compressive strengths of lithium-containing concrete (at 75 and 100% $LiNO_3$ dosages) to be nearly identical to those concretes without lithium at the ages of 3, 7, 28, 56, and 90 days. Likewise, no detrimental or beneficial effect on compressive strength was reported by Ohama et al. [1990] for mortars containing LiF or Li_2CO_3 and independently by Johnson [1997], Stokes [2001], and Lane [2002] for $LiNO_3$-containing concretes.

The results of Thomas et al. [2003] suggest no accelerating effect with $LiNO_3$ use. At $LiNO_3$ dosages of 75, 100, and 125%, McKeen et al. [2000] concluded that the admixture-containing concretes generally exhibited higher 7, 14, 28, 56, and 90-day strengths, but that the increases in strength (shown in figure 2-1) were not statistically significant. Also, it should be noted that the air contents of the lithium-containing concrete were slightly lower than the ordinary concrete for both the air-entrained (4.0% vs. 6.2%) and non air-entrained (0.9% vs. 1.1%) mixtures, which could be the reason that higher strength was observed.

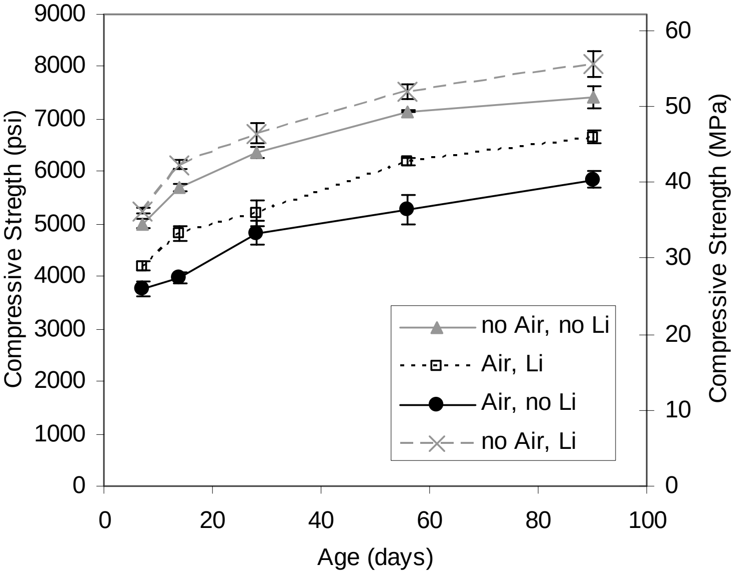
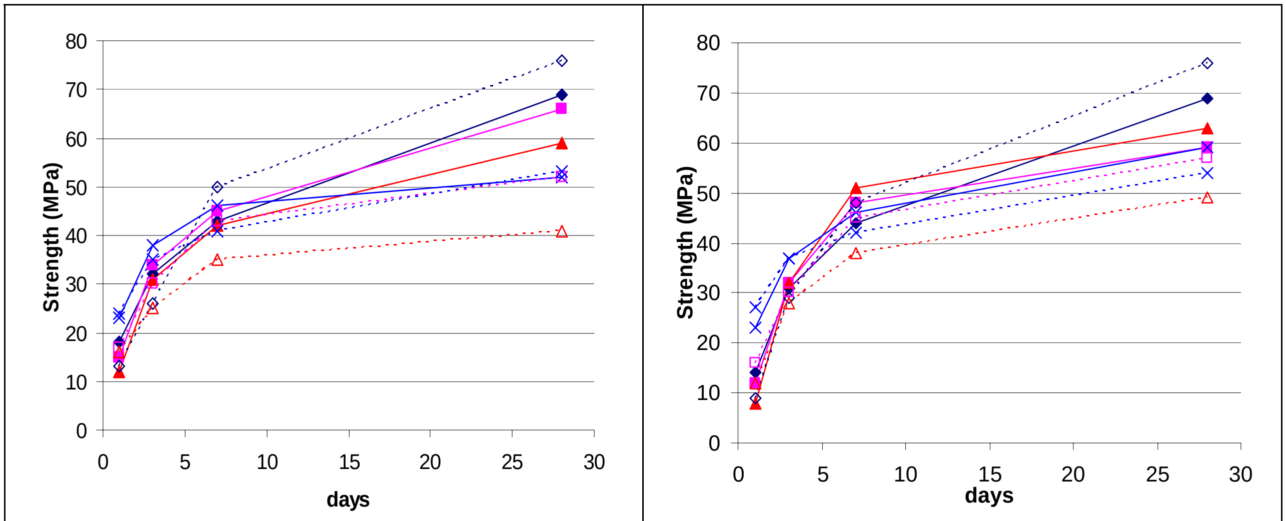


Figure 2-1. Data from McKeen et al. [2000] shows lithium-containing concrete (with and without air entrainment) to exhibit higher compressive strength, although the difference was concluded to not be statistically significant.

The use of LiOH in concrete examined by Wang et al. [1996] suggested that, in general, strength was not affected except for somecases where compressive strength was negatively affected (figure 2-2). In particular, in high alkali cements (e.g., Na_2O_e of 0.80% or more in Wang et al.'s study), 28-day compressive strength was reduced by as much as 25% in the presence of lithium, although often 1-day strengths were greater than the control concretes. Also, concretes prepared with lower alkali cements showed equivalent or even higher compressive strength in the presence of lithium, suggesting that the detrimental effect on strength may be linked to the cement alkali content for $LiNO_3$.

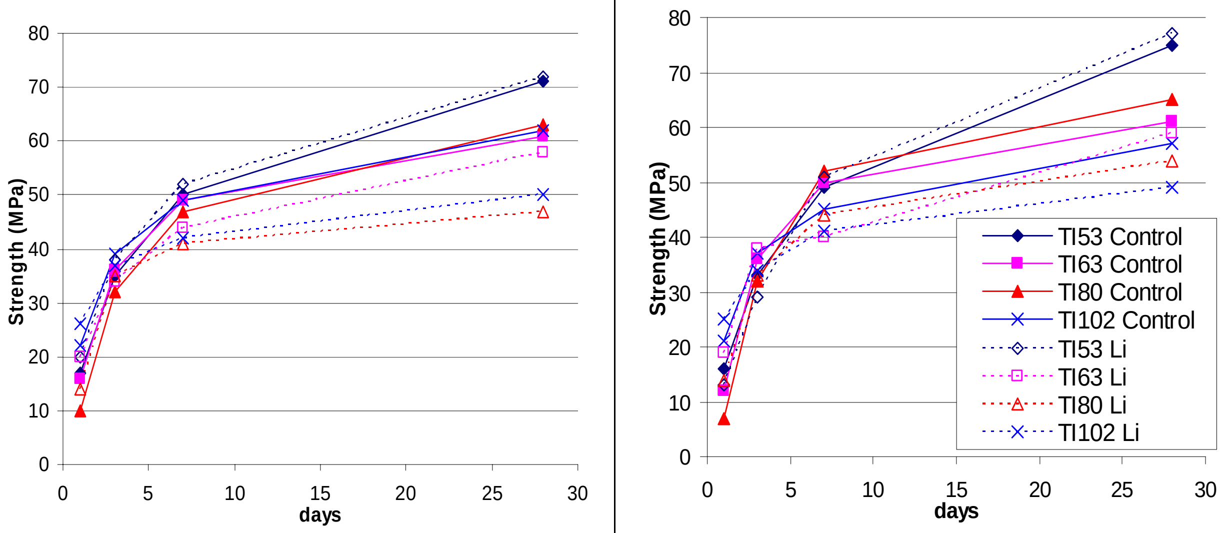
Tests performed by BRE (figure 2-3) also indicate that reductions in 28-day compressive strength are possible in concrete containing $LiOH{\cdot}H_2O$ [Hooper et al., 2004]. Lane [2002] also concluded that compressive strength was decreased when $LiOH{\cdot}H_2O$ was used at a 100% dosage rate. Also, as stated previously, Mo [2005] has reported that compressive strength of mortars decreased with increasing LiOH content, and the rate of strength developed seemed to lag behind control mixtures. However, mortar flexural strength was relatively unaffected by lithium hydroxide addition. This data supports Wang et al. [1996] observation that $LiOH{\cdot}H_2O$ can act as a hydration retarder.

Clearly the effects of $LiNO_3$ – as this is the most commonly used lithium admixture in practice – on strength and strength development should be the subjects of a comprehensive study. Further, the effects (if any) of $LiNO_3$ on concrete flexural strength should be clearly identified.



(a) Type A admixture

(b) Type D admixture



(c) Type F admixture

(d) Type G admixture

Figure 2-2. In research investigating potential interactions between LiOH admixture and ASTM Type A, D, F, and G admixtures, compressive strength was found to generally be reduced when lithium was used in mixtures with higher alkali cements. The cement alkali content is noted in the legend as the last two digits in the sample type designation (e.g., TI53 cement has a total equivalent alkali content of 0.53% and TI102 has 1.02%). Data is from Wang et al. [1996].

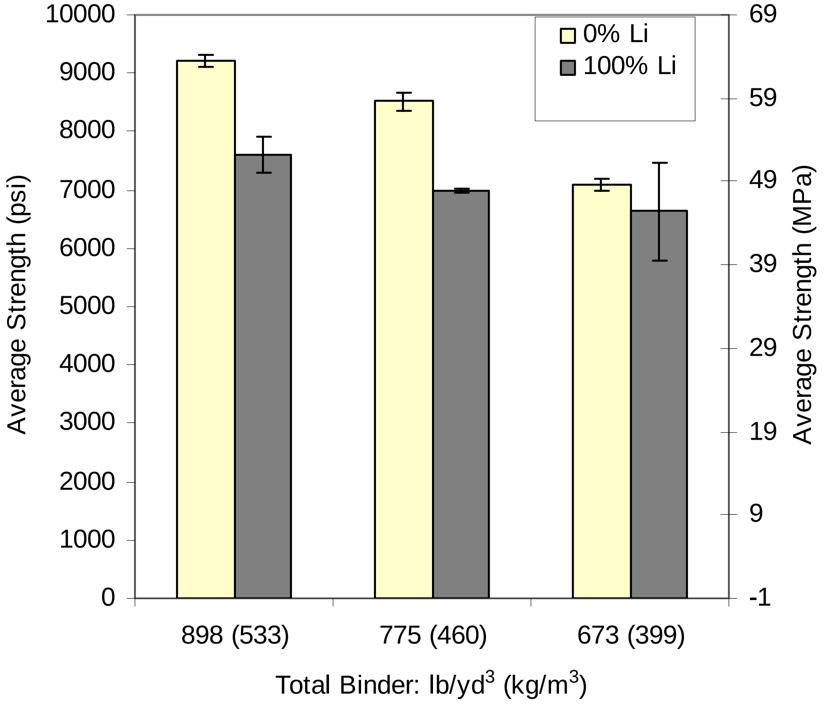


Figure 2-3. Hooper et al. [2004] report lower 28-day concrete compressive strength at 100% LiOH·H_2O dosage in samples prepared and monitored by BRE.

2.6 SHRINKAGE.

Because shrinkage is related to the finer capillary porosity in the cement paste, shrinkage is particularly problematic in concrete with a higher cement content, a lower water content, a higher proportion of very fine reactive particles (cement or SCM), a more refined pore structure, and where set has been accelerated. Some lithium admixtures are suspected to accelerate setting [Mo, 2004, in review] and perhaps the rate of strength gain [McKeen et al., 2000]. Also, concretes with increased alkali contents – and lithium is an alkali – have been shown to be more susceptible to shrinkage cracking [He and Li, 2005].

To date, Lane [2002] is the only author to address shrinkage in lithium-containing concrete. Lane used a method described in ASTM C 157 to examine shrinkage in 28-day moist-cured air-entrained concrete prisms prepared with w/cm ratio of 0.45 and cement content of 378 kg/m^3 at LiOH·H_2O and $LiNO_3$ dosages of 75 and 100%. One-year shrinkage data, after exposure in a 50% relative humidity environment, showed no difference between the lithium-containing concrete and the ordinary concrete. However, the cement content in Lane's mixtures is relatively low for an experiment which examines shrinkage and shrinkage occurring prior to 28 days is not captured by the ASTM C157 procedure. Because shrinkage cracking is problematic in sections of high surface area-to-volume ratios, specifically flat work, the influence of increasing lithium dosage on early shrinkage must be examined thoroughly.

3. EXPERIMENT DESIGN.

An experiment matrix was developed that was used as a roadmap to asses the effect of lithium compound on the early age properties of airfield concrete. The experiment was designed around the reconstruction of airfield pavement located within Ramp 1 at Hartsfield-Jackson Atlanta International Airport (H-JAIA).

A construction contract awarded to APAC-Swing JV in the summer of 2005 included the demolition of an existing concrete pavement and construction of a new concrete pavement 22-inchs thick. The construction specification required low-slump concrete for slipform paving operations. The Contractor mobilized a batching facility on-site, stockpiled aggregates and tank-stored cement, fly ash and liquid admixtures. Included in the mobilization was a state-of-the-art laboratory facility (casting, curing and testing) that was to be used for quality control.

The concrete mix provided by the contractor satisfied the primary objectives of the owner (650psi flexural strength at 28 days). The owner also specified maximum natural sand content, a Type I cement with less than 0.4% alkali content, and a 20% Class F fly ash replacement. In a cooperative arrangement between the City of Atlanta, the Contractor and the research team, the specified concrete mix was modified to allow lithium compound dosages ranging from 0 percent to 400 percent of the recommended dose. Each mix was verified in the lab prior to construction. A minimum of 100 cubic yards of each was produced and placed on the field placement as paving production (Phase I). The matrix in table 3-1 outlines the experiment. The matrix provides a measure of flexural (three replicates) and compressive (ten replicates) strength at 36 hours, and then 2, 3, 7 and 28 days. In addition maturity of each mix was monitored.

The production concrete on Ramp 1 had limitations (i.e., single sources of lithium compound, coarse aggregate, natural sand, cement and fly ash, in an 80-20 proportion, in only one proportion). Therefore the experiment included small-batch mixing using the same materials except fly ash (Phase II). Fly ash was not used in the small batch study portion of the experiment. The matrix at table 3-1 outlines this part of the experiment.

The total experiment was organized to evaluate what, if any, influence lithium dosage has on mixes that contain 100% Type I cement (small batch study) and similar mixes that contain 80% Type I cement and 20% Class F fly ash (production mixes). The lithium dose was selected to represent a broad range which, on the upper end, represents a dosage that is most likely economically unfeasible for use in production concrete.

To determine if there was change of phase properties with varying lithium dosage, a third part of the experiment was developed. The third part makes use of precise measurements of mortar pastes in a tightly controlled laboratory environment (Phase III). The effects of lithium dosage on the control cement, with and without fly ash, could be examined. In addition, the effects of lithium dosage and variations of alkali content and tricalcium aluminate (C_3A) content could be determined. Variations of cement content were selected as shown in the Phase III (table 3-1). The selected cements and respective chemical properties are summarized in tables 3-2 through 3-4.

Table 3.1. Experimental Design Matrix

PHASE1 - FIELD PRODUCTION **PHASE2 - LAB PRODUCTION**

		Treatments (values in each cell indicate number of replications from a single batch)									
		control	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**
SCM Replacement Level (fly ash) by Wt. of Cement		***20%***	***20%***	***20%***	***20%***	***20%***	***0%***	***0%***	***0%***	***0%***	***0%***
Lithium dose (% of recommended by manufacturer)		***0%***	***50%***	***100%***	***200%***	***400%***	***0%***	***50%***	***100%***	***200%***	***400%***
water:binder ratio (w/b)		***constant***	***constant***	***constant***	***constant***	***constant***	***constant***	***constant***	***constant***	***constant***	***constant***
Property	**Test Method**										
Plastic Concrete											
Slump	ASTM C143	1	1	1	1	1	1		1		1
Air Content	ASTM C231	1	1	1	1	1	1		1		1
Unit Weight	ASTM C138	1	1	1	1	1	1		1		1
Maturity	ASTM C1074	5	5	5	5	5	2		2		2
Workability/Finishability	Interviews[1]	1	1	1	1	1					
Hardened Concrete											
Flexural Strength (36 hrs)	ASTM C78	3	3	3	3	3	3		3		3
Flexural Strength (48 hrs)	ASTM C78	3	3	3	3	3	3		3		3
Flexural Strength (72 hrs)	ASTM C78	3	3	3	3	3	3		3		3
Flexural Strength (7 days)	ASTM C78	3	3	3	3	3	3		3		3
Flexural Strength (28 days)	ASTM C78	3	3	3	3	3	3		3		3
Compressive Strength (36 hrs)	ASTM C39	10	10	10	10	10	10		10		10
Compressive Strength (48 hrs)	ASTM C39	10	10	10	10	10	10		10		10
Compressive Strength (72 hrs)	ASTM C39	10	10	10	10	10	10		10		10
Compressive Strength (7 days)	ASTM C39	10	10	10	10	10	10		10		10
Compressive Strength (28 days)	ASTM C39	10	10	10	10	10	10		10		10
Core for Air Void Analysis (6-in.)	ASTM C42	2	2	2	2	2					
Air Void Analysis[2]	ASTM C457	2	2	2	2	2	2		2		2
Compressive Strength (28 days)[3]	ASTM C39	4	4	4	4	4					

PHASE3 - ANCILLARY LABORATORY STUDY

		Treatments (values in each cell indicate number of replications from a single batch)									
		control	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**
SCM Replacement Level (fly ash) by Wt. of Cement		***20%***	***20%***	***20%***	***20%***	***20%***	***0%***	***0%***	***0%***	***0%***	***0%***
Lithium dose (% of recommended by manufacturer)		***0%***	***50%***	***100%***	***200%***	***400%***	***0%***	***50%***	***100%***	***200%***	***400%***
water:binder ratio (w/b)		***constant***	***constant***	***constant***	***constant***	***constant***	***constant***	***constant***	***constant***	***constant***	***constant***
Property	**Test Method**										
Change of Phase											
Heat of Hydration[4]	Isothermal Calorimetry	1	1	1	1	1	6	6	6	6	6
Vicat Time of Setting[4]	ASTM C 191-04	3	3	3	3	3	18	18	18	18	18
Chemical Shrinkage[4]	ASTM C 1608-05	3	3	3	3	3	18	18	18	18	18
Autogenous Shrinkage[4]	Jensen-Hansen method	3	3	3	3	3	18	18	18	18	18
Bleed Water	ASTM C 232-04	3	3	3	3	3	3	3	3	3	3
Slump	ASTM C 143-05	1	1	1	1	1	1	1	1	1	1
Free Shrinkage	ASTM C 157-04	3	3	3	3	3	3	3	3	3	3
Restrained Shrinkage	ASTM C 1581-04	3	3	3	3	3	3	3	3	3	3
Accelerated ASR Test	ASTM C1260						3				

1. Interviews with select field Paving Crew personnel performed to assess finishability of production concretes.
2. Air void counts performed on disks cut from cores at approximate 28-day curing time, and from lab-cast cylinders for Treatments 5, 7 and 9.
3. Compressive strength tests performed on core sections located above and below 1-inch disk cut from midpoint of core length.
4. Six variations in cement composition (varying in alkali content and C_3A content) without fly ash replacement.

Table 3-2. Oxide analysis and bogue potential composition for cements and fly ash tested

	Roberta cement	Low alkali cement	High alkali cement	Low C_3A cement	Moderate Alkali & C_3A	High C_3A cement	Class F fly ash
SiO_2 (%)	20.06	20.44	20.13	21.00	20.98	19.29	50.77
Al_2O_3 (%)	4.89	5.24	5.48	3.62	4.72	5.62	19
Fe_2O_3 (%)	3.00	3.99	3.26	3.47	2.99	2.82	17.72
CaO (%)	64.22	63.22	60.93	62.52	63.56	64.21	5.1
MgO (%)	2.68	1.05	2.45	4.29	2.24	0.86	0.91
SO_3 (%)	2.74	3.74	4.00	2.43	2.61	3.54	1.56
Na_2O (%)	0.115	0.069	0.344	0.231	0.165	0.257	0.65
K_2O (%)	0.444	0.343	0.866	0.404	0.523	0.464	2.31
NaO_2 Equiv. (%)	0.407	0.295	0.91	0.50	0.509	0.562	2.17
P_2O_5 (%)	0.076	0.092	0.157	0.054	0.335	0.256	0.12
TiO_2 (%)	0.274	0.318	0.214	0.172	0.241	0.614	1.08
SrO (%)	0.038	0.065	0.194	0.050	0.035	0.231	0.04
Mn_2O_3 (%)	0.088	0.079	0.173	0.064	0.150	0.040	0.05
Cr_2O_3 (%)	0.012	0.012	0.025	0.005	0.008	0.014	
LOI (%)	1.37	1.33	1.78	1.69	1.44	1.79	0.62
C_3S (%)	64.1	50.4	42	59	55.9	62.9	
C_2S (%)	9.2	20.6	26	16	18.0	7.9	
C_3A (%)	7.9	7.1	9	4	7.5	10.1	
C_4AF (%)	9.1	12.2	10	11	9.1	8.6	
Blaine Fineness (m2/kg)	345	380	384	377	369	368	161

Table 3-3. Cements used for alkali range comparison

	Low alkali	**Moderate alkali**	**High alkali**
Na_2O (%)	0.069	0.165	0.344
K_2O (%)	0.343	0.523	0.866
NaO_2 Equiv. (%)	0.295	0.509	0.91
C_3S (%)	50.4	55.9	42
C_2S (%)	20.6	18.0	26
C_3A (%)	7.1	7.5	9
C_4AF (%)	12.2	9.1	10

Table 3-4. Cements used for C_3A range comparison

	Low C_3A	**Moderate C_3A**	**High C_3A**
Na_2O (%)	0.231	0.165	0.257
K_2O (%)	0.404	0.523	0.464
NaO_2 Equiv. (%)	0.50	0.509	0.562
C_3S (%)	59	55.9	62.9
C_2S (%)	16	18.0	7.9
C_3A (%)	4	7.5	10.1
C_4AF (%)	11	9.1	8.6

3.1 MATERIALS.

The airfield concrete mix included the following materials:

Coarse aggregate, *granitic gneiss* (No.4) – Florida Rock (Mountain View, GA)
Coarse aggregate, *granitic gneiss* (No.67) – Florida Rock (Mountain View, GA)
Fine aggregate (river sand) – Martin Marietta (Shorter, AL)
Cement (Type I) – LaFarge (Roberta Plant)
Fly ash (Class F) – SEFA (Cumberland)
Lithium Nitrate compound ($LiNO_3$) – Euclid Chemical Co., by Chemicals (Integral Arc)
Mid-range water reducer – Euclid Chemical Co., by Chemicals (Plastol 341)
Retarder – Euclid Chemical Co., by Chemicals (Eucon NR)
Air Entrainment – Euclid Chemical Co., by Chemicals (AEA 92)

The mix proportions are proprietary. The combination of cementitious materials in a cubic yard was 764 pounds. The water to cement ratio (w/cm) for the mix was held constant for all mix variations at 0.307.

The lithium nitrate ($LiNO_3$) admixture dosage was varied from 0, 50, 100, 200, and 400% of the manufacturer recommended dosage and corresponding to 0.55 gal./lb. of cement alkali equivalent (Na_2O_e). The dosage is based on an optimal [Li]/[Na+K] molar ratio of 0.74 for ASR expansion suppression [Berubé, 2004].

3.2 MIX PRODUCTION AND SAMPLING.

Each part of the experiment required using different techniques to mix the concrete. Large batches were produced by the Contractor during production (Phase I). Small batches were produced using a portable small batch mixer (Phase II) and mortars were produced in bowls using mechanical Hobart mixers (Phase III).

3.2a. Phase I samples were collected during production from mass concrete placed as a part of the pavement reconstruction. Ten cubic yard batches were produced during production. A single batch for use as a part of the experiment (control plus treatments 1-4) was sampled in the following manner:

1. Approximately five cubic yards of mix was discharged from the drum to a transport vehicle,
2. Approximately one cubic yard of mix was discharged into the loading bucket of a front-end loader, and
3. The remaining mix was discharged into the transport vehicle and delivered to the construction site.

The single yard of mix was transported to the QC laboratory, located within 200 feet from the batching area, and discharged onto a moistened concrete apron. Several engineers and certified technicians immediately accomplished the specified field testing and documented the results of slump, air content, ambient and plastic concrete temperatures, and unit weight. Fifteen beams and 52 cylinders were cast. The beams and cylinders were cast within 35 minutes of concrete sampling. The beams were cast in one lift and consolidated with an electric vibrator by using five slow penetrations across the plan area. Cylinders were made in two lifts, each lift consolidated with an electric vibrator by three slow penetrations across the diameter of plastic cylinder molds.

Maturity meters were immediately installed and initialized at the approximate center of two cylinders. Beam and each cylinder placed directly into an initial curing trailer (controlled temperature of 60-80^oF per ASTM) for 24-hours. Following initial cure, each beam and each cylinder was stripped from the mold, labeled and placed in a limewater-curing tank until the time for strength testing. For the strength testing of cylinders, sulfur-capping compound was used on the rough end while elastomeric pads were used on the molded ends. Leather straps were used between all breaking head strip loads and the concrete beams.

The transport vehicle carrying concrete from the remaining portion of bulk concrete was followed to the construction location where its location of placement was documented. A small sample from this material was taken and documented for air content and slump. Following slipform paving, maturity meters were installed at 6-inch depth intervals and initialized. The maturity data from the meters were downloaded following the 28-day curing period.

Following the download of maturity data, two 6-inch diameter cores were extracted from the pavement from a location within one foot of the maturity meter location. A 1-inch thick disk was cut from the middle of each core and air content determined by petrographic examination of the disk. Remnants from the core above and below the middle were measured for length and diameter and the compressive strength determined.

3.2b. Phase II mixes were prepared in the same proportions at the contractor's QC laboratory from materials used in the production concrete. A portable one cubic yard batch mixer was used to prepare samples. Small quantities of chemical admix, obtained from Euclid Chemical Co. and reported to be the same as those used in production concrete were incorporated. The cementitious material used for these small batches was 100% cement, 764 pounds of cement. To obtain a workable mix the water was adjusted to a water to cement ratio of 0.34.

The one cubic yard mix was discharged following a ten-minute mixing time. The research team cast, cured and tested beams and cylinders in a manner similar to that described in *Section 3.2a.* A 1-inch thick disk was cut from the mid-length of two cylinders and examined petrographically for air content.

3.2c. Phase III mix samples were prepared at the Georgia Institute of Technology Research Laboratory using the materials sampled from the production concrete. Mixes were prepared using a small mechanical mixer. Proportional quantities of chemical admixtures were obtained from Euclid Chemical Co.. The mix constituents and proportions, including water to cement ratio, were kept the same as the *Phase I* mixes, except where a different proportion was specified by the test standard (i.e., ASTM C 1260 specifies w/c ratio of 0.485).

ASTM standard testing procedures were used to perform the tests identified in table 3.1. For the calorimetry and autogenous shrinkage testing the following procedures were followed:

In calorimetry testing, heat generation data was measured in hydrating cement paste specimens under isothermal conditions. Batches of 0.45 lb (204 g) of paste were mixed for 60 seconds using an electric hand mixer at a water-to-cementitious material ratio of 0.30. 5-gram specimens from these batches in 20 mL plastic ampoules were monitored by a 3114 TAM Air Isothermal Calorimeter. Heat generation data was recorded every 60 seconds for each paste specimen. The calorimeter maintained the specimens at a temperature of 25 degrees Celsius.

In autogenous shrinkage testing, linear deformation of sealed paste specimens were measured using a method described by Jensen and Hansen (1995). Cement paste specimens were sealed in flexible corrugated plastic tubes which allow linear deformation with minimal resistance. A dilatometer was used to measure specimen length, starting from the time of final set. Samples were stored in a 25 degrees Celsius environmental chamber.

4. RESULTS OF THE EXPERIMENT.

The following section provides a summary of the data collected for each phase of the experiment.

4.1 PHASE 1.

The research team successfully coordinated a plan wherein the Contractor would produce each of the five different mixes (different lithium dosage) during a 10-day period (Construction Phase

11). The reasoning used for spacing the mixes close together was to minimize uncontrolled variables within the experiment (effects of ambient temperatures; air and mix source water). The results of the concrete production sampling and plastic property testing are provided in table 4-1.

Table 4-1. Phase I Mix Production and Sampling Information

Field Production Mix Information					
Date	28-Sep	5-Oct	29-Sep	6-Oct	6-Oct
Time	8:56 PM	9:06 PM	8:56 PM	9:38 PM	10:54 PM
Mix ID	0%Li	50%Li	100%Li	200%Li	400%Li
Plastic Properties					
Temp$_{\text{Air}}$	71	70	65	71	69
Temp$_{\text{Mix}}$	85	82	86	84	81
%Air$_{\text{Lab}}$	6.0	5.4	5.5	5.8	5.8
%Air$_{\text{Field}}$	4.4	4.4	5.0	4.0	4.5
Slump$_{\text{Lab}}$	1 3/4	1 1/2	1 1/4	1 3/4	2
Slump$_{\text{Field}}$	1 1/2	1 1/2	1 1/4	1 1/4	2
Unit Weight	142.5	143.4	143.5	144.3	144.5

Each concrete batch was sampled in the evening hours (after sundown) when air temperatures and mix temperatures were stable and similar in value to those recorded at previous sampling times. The temperature stability was an important observation because of the effect of temperature on the results of very early breaking ages. The similarity of temperatures for all treatments (mixes) provides reasonable confidence that any strength or maturity differences detected can be attributed primarily to the treatment material variable or the lithium dosage.

The results of testing are graphically summarized in figures 4-1 through 4-5. Tabular results, including elementary statistics (average, standard deviation, coefficient of variation), are provided in Appendix A.

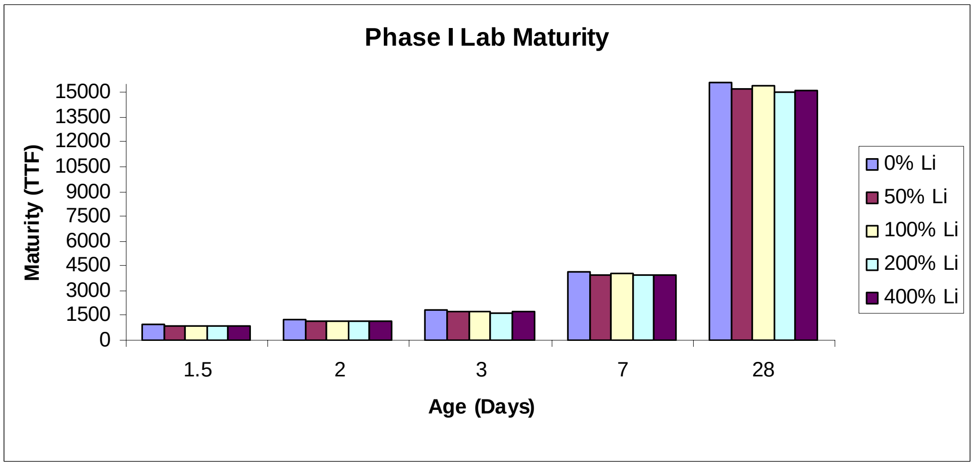


Figure 4-1. Maturity of Phase 1 Lab-Cured Cylinders

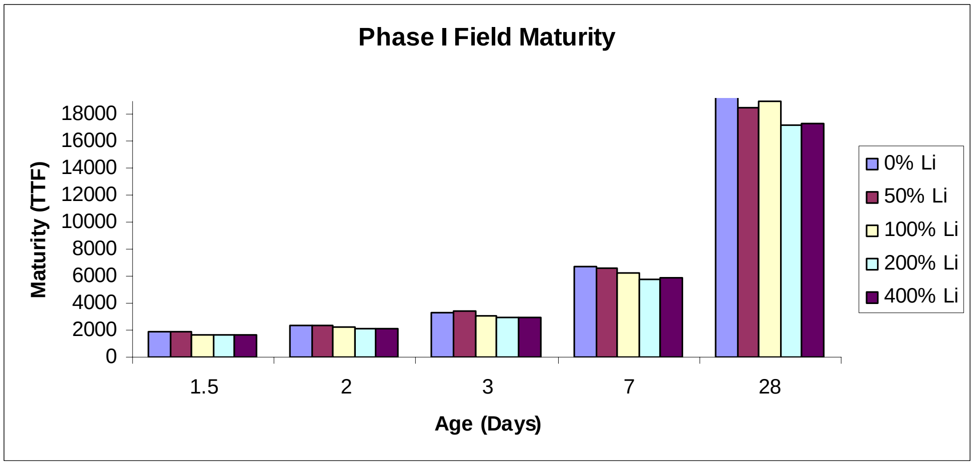


Figure 4-2. Maturity of Phase I Pavement Slabs

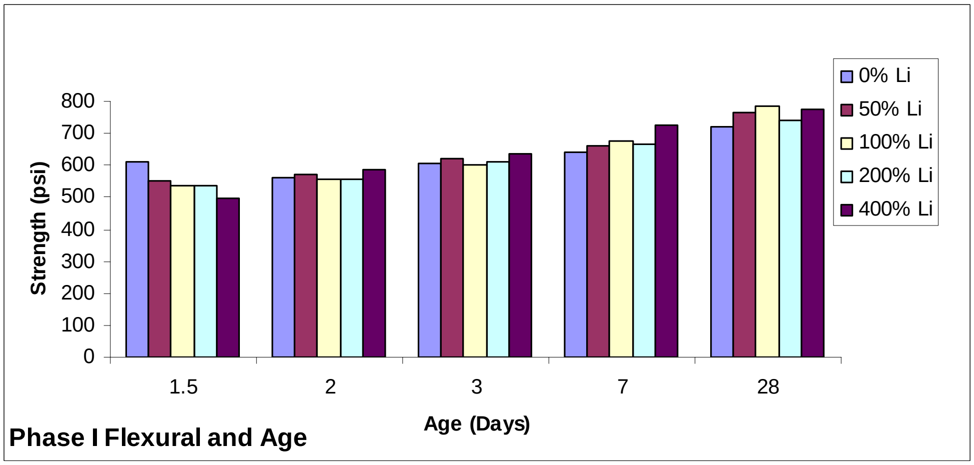


Figure 4-3. Flexural Strength of Phase I Lab-Cured Beams

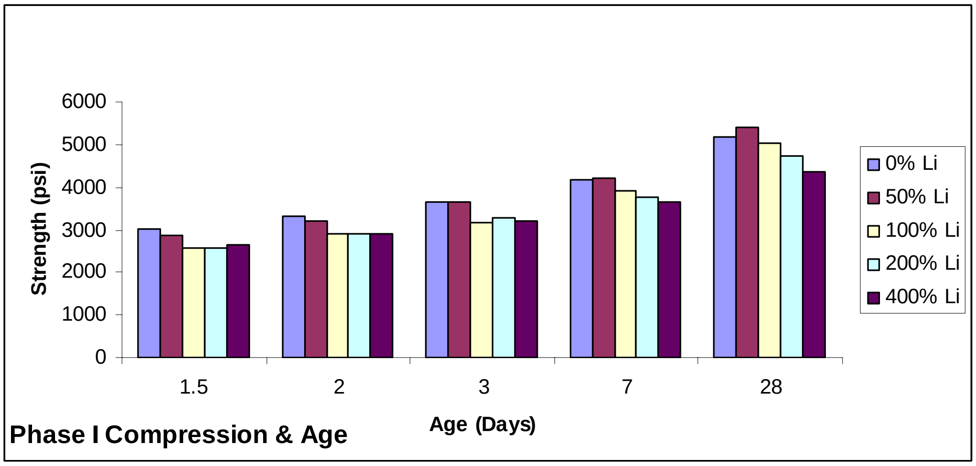


Figure 4-4. Compressive Strength of Phase I Lab-Cured Cylinders

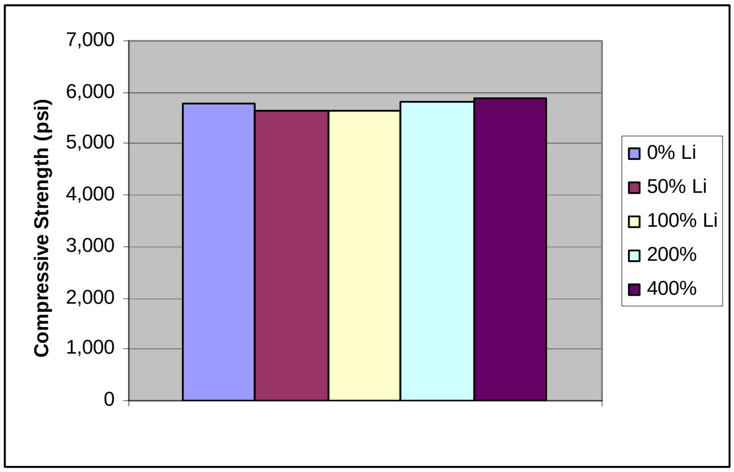


Figure 4-5. Compressive Strength of Phase I Cores

Following a 28-day curing period, 6-inch diameter cores were obtained from the pavement near locations where maturity meters were installed. A 1-inch thick disk was cut from the middle of each core and the hardened air content was determined (ASTM C457). The upper and lower parts of the cores were used to determine compressive strength. These results are summarized in figure 4-5.

Table 4-2. Hardened Air Content of Phase I Field Cores

Field Production Mix Information					
Date	28-Sep	5-Oct	29-Sep	6-Oct	6-Oct
Time	8:56 PM	9:06 PM	8:56 PM	9:38 PM	10:54 PM
Mix ID	0%Li	50%Li	100%Li	200%Li	400%Li
Properties					
Temp$_{\text{Air}}$	71	70	65	71	69
Temp$_{\text{Mix}}$	85	82	86	84	81
%Air$_{\text{Lab}}$	6.0	5.4	5.5	5.8	5.8
%Air$_{\text{Field}}$	4.4	4.4	5.0	4.0	4.5
%Air$_{\text{cores}}$	5.6	4.4	6.1	4.7	5.5
Slump$_{\text{Lab}}$	1 3/4	1 1/2	1 1/4	1 3/4	2
Slump$_{\text{Field}}$	1 1/2	1 1/2	1 1/4	1 1/4	2
Unit Weight	142.5	143.4	143.5	144.3	144.5

Observations. The following observations are offered:

- There are no significant noticeable difference between the measured properties of plastic concrete at the time of sampling (slump, air, unit weight) and what would be considered normal. The lithium dosage has a negligible impact on these properties.
- There appears to be a small negative effect on maturity as the lithium dosage increases (figures 4-1 and 4-2) and age of specimens increases.

- Concrete appears to mature at a faster rate in the field as compared to the laboratory. This could be attributed to large mass hydration versus small sample hydration.
- Lithium dosage appears to have aa effect on flexural strength (figure 4-3) but the differences are within the expected variation of the test procedure.
- There appears be a negative effect on compressive strength as lithium dosage increases (figure 4-4).
- The hardened air content (table 4-2) is somewhat greater than the air content observed from tests performed on the plastic concrete. Attempts to separate entrapped air and entrained air were not made on the petrographic air content determination on cores. Visual observation made of the disks extracted from the cores indicated entrapped air pockets. The differences between air contents measured on plastic concrete and hardened core sections is attributed to consolidation.

4.2 PHASE II.

Upon the Contractor's substantial completion of the reconstruction project, the research team coordinated with the Contractor to produce small batches of concrete absent of fly ash replacement. The following controls were implemented to reduce the variables:

- The materials used for the Phase I mixes were used for Phase II (not including flyash).
- Samples for Phase II were cured using the same procedures as the Phase I samples.
- Each of the three Phase II mixes were batched on the same day and thus reducing the impact of ambient temperatures (air and mix source water).

The water to cement ratio required adjustment to 0.34 to obtain a workable mix. The decision to stray from the design w/c is reasonable because there was no intent to compare a Phase I data point with a Phase II data point. The results of the sampling and plastic property testing are presented in table 4-3.

Table 4-3. Phase II Mix Production and Sampling Information

Lab Production Mix Information			
Date	19-Nov	19-Nov	19-Nov
Time	12:15 PM	2:00 PM	4:00 PM
Mix ID	0%Li	100%Li	400%Li
Plastic Properties			
Temp$_{Air}$ (^oF)	55	54	50
Temp$_{Mix}$ (^oF)	62	58	57
%Air$_{Lab}$	4.6	4.7	4.0
Slump$_{Lab}$ (in.)	1	1	1 ¼
Unit Weight (pcf)	150.0	150.0	151.5

The results of this phase of testing are graphically summarized in figures 4-6 through 4-8. Tabular results, including elementary statistics (average, standard deviation, coefficient of variation), are provided in Appendix A.

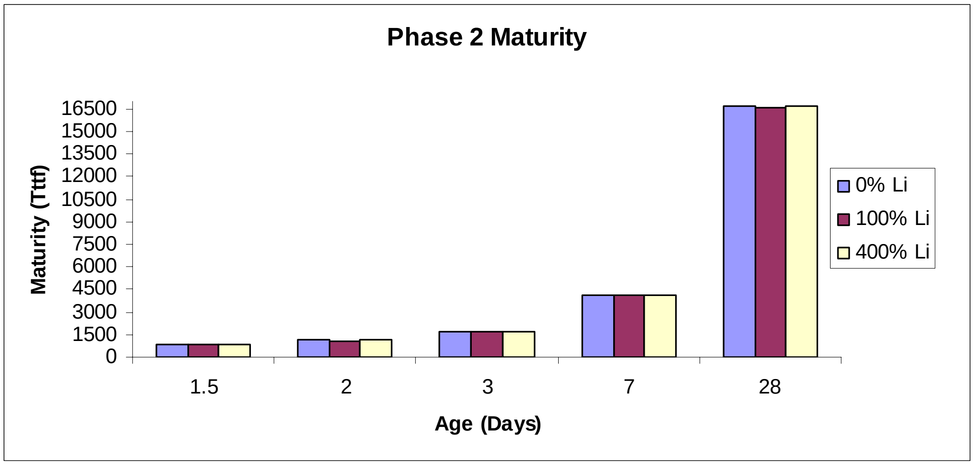


Figure 4-6. Maturity of Phase II Lab-Cured Cylinders

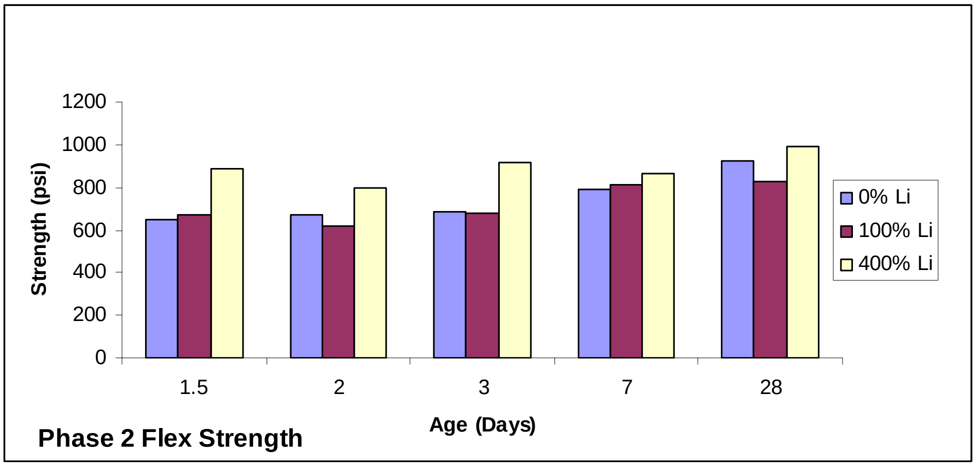


Figure 4-7. Flexural Strength of Phase II Lab-Cured Beams

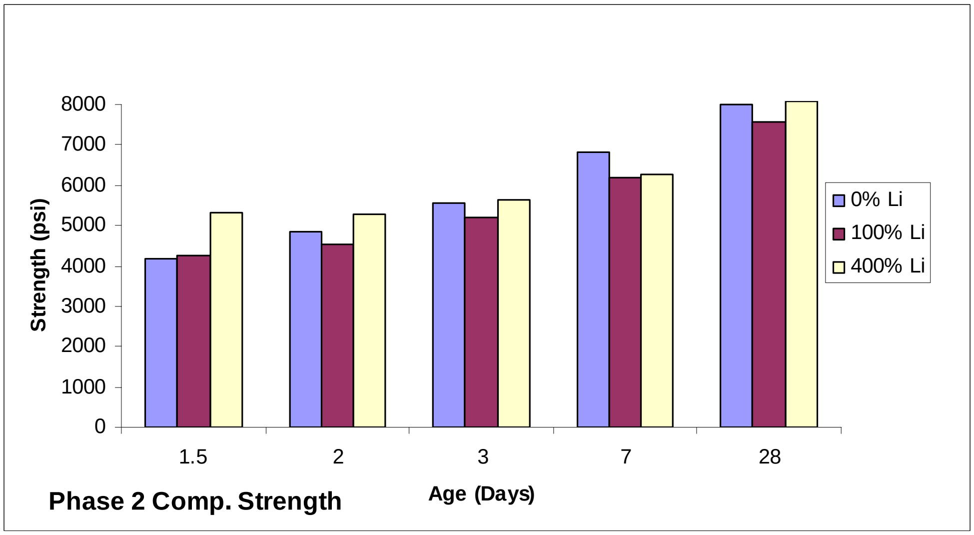


Figure 4-8. Compressive Strength of Phase II Lab-Cured Cylinders

Following a 28-day curing period, two 6-inch diameter cylinders from each of the three mixes were used to obtain a 1-inch thick disk cut from mid-length for hardened air content determination (ASTM C457). The results are presented in table 4-4.

Table 4-4. Phase II Mix Production and Sampling Information

Lab Production Mix Information (Phase 2)			
Date	19-Nov	19-Nov	19-Nov
Time	12:15 PM	2:00 PM	4:00 PM
Mix ID	0%Li	100%Li	400%Li
Plastic Properties			
Temp$_{Air}$ (^{o}F)	55	54	50
Temp$_{Mix}$ (^{o}F)	62	58	57
%Air$_{Lab}$	4.6	4.7	4.0
%Air$_{hardened}$	2.7	2.8	3.5
Slump$_{Lab}$ (in.)	1	1	1 1/4
Unit Weight (pcf)	150.0	150.0	151.5

Observations. The differences observed between the lab air (pressure method on plastic concrete) and the hardened air content is attributed to the method of consolidation (samples for the plastic air content were consolidated by rod whereas cylinders were vibrated in two lifts).

The following observations are made:

- Lithium dosage does not appear to impact measured slump or air content (table 4-3).
- There does not appear to be impact on maturity as lithium dosage increases (figure 4-6).
- At high lithium dosage there appears to be an acceleration on flexural and compressive strength development at the very early ages (figures 4-7 and 4-8).

4.3 PHASE III.

Isothermal calorimetry was performed at 25°C on cement pastes from all cements at 0%, 50%, 100%, 200% and 400% dosages. An additional test was performed using fly ash combined with the Lafarge Roberta cement at 20% replacement. Data was recorded for 72+ hours, however, testing of the low alkali mixes was ended prematurely due to a power outage.

In general, as the dosage of lithium nitrate increased, early heat of hydration increased, and the early hydration reactions (i.e., hydration of C_3S and C_3A) were generally accelerated. This is apparent by observing the heat of hydration curves in figures 4-9 through 4-16. The curves shift upward and the peaks shift to the left at the higher lithium admixture dosages. Also, the second “hump” of the heat profile appears to be accelerated slightly more than the overall profile. This second hump is generally attributed to reactions of the C_3A component of the cement.

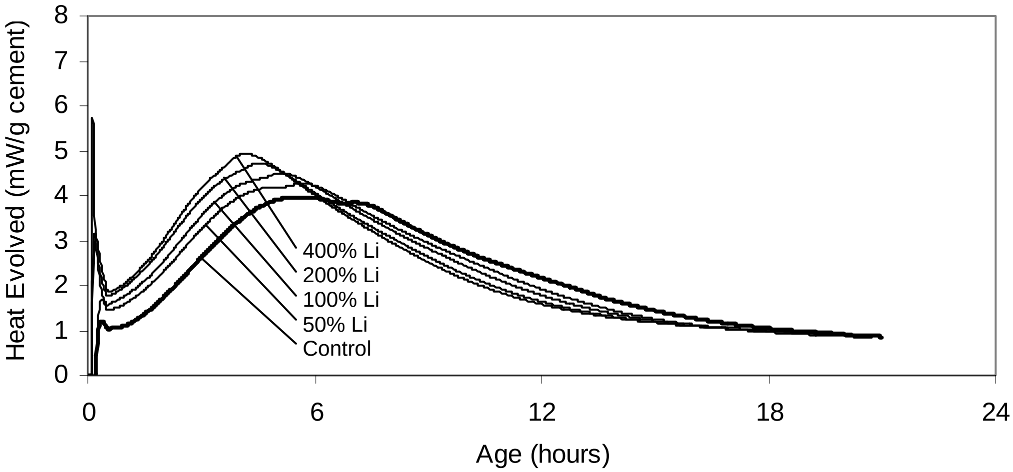


Figure 4-9. Calorimetry results for the low alkali cement

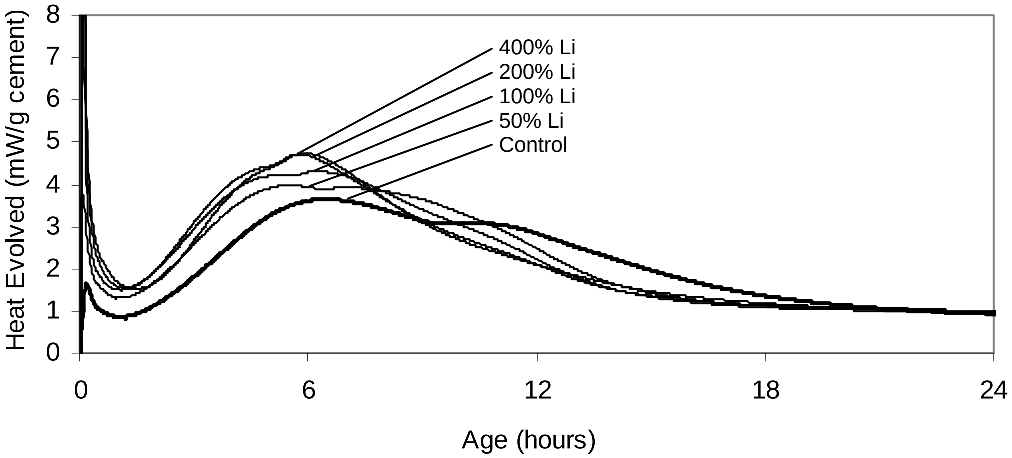


Figure 4-10. Calorimetry results for the moderate alkali cement

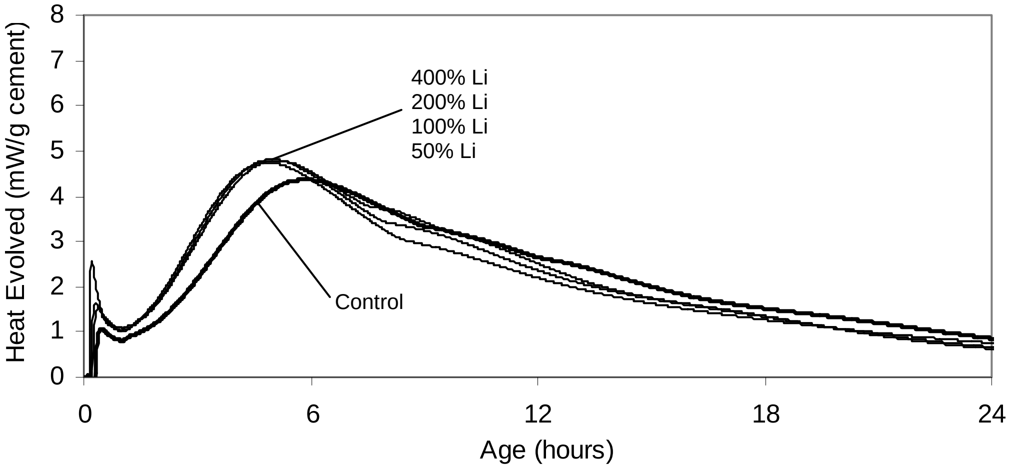


Figure 4-11. Calorimetry results for the high alkali cement

Figures 4-9 through 4-11 illustrate the heat of hydration effects of lithium nitrate on the low, moderate, and high alkali cements. The data for the moderate and high alkali cements (figures 4-10 and 4-11) suggest that above some level of lithium dosage, further increases in heat of hydration may not occur. In the data for the high alkali cement (figure 4-11), increases in heat of reaction are no longer apparent above the 50% lithium dosage (corresponding to 1.5 gallons per cubic yard for the admixture based upon the mix design used in this research.) In the data for the moderate alkali cement shown in figure 4-10, no further increases are apparent above 200% dosage (corresponding to 3.4 gallons per cubic yard). The data for the low alkali cement shows continued heat increases up to the highest level tested, 400% dosage (corresponding to 4 gallons per cubic yard). Apparently, low alkali cements continue to generate greater heats at increasing lithium dosages, while higher alkali cements reach a maximum heat of hydration profile at lower dosages. This observation suggests that lower alkali cements are more susceptible to greater heat evolution increases due to the addition of lithium.

This could be explained by the dependence of heat of hydration on the total alkali ion concentration [$Li^+ + Na^+ + K^+$] in the mix water [Bentz, 2005]. Addition of Li^+ ions to cement that is already high in Na^+ and K^+ ions has relatively little effect on total alkali concentration, while addition of Li^+ ions to a cement mix that is low in Na^+ and K^+ ions seems to have a greater effect on total alkali concentration. Further, the results in figures 4-9 through 4-11 suggest that at some level of total alkali concentration, a maximum early heat generation profile is reached. This alkali concentration is reached at lower lithium dosages for high alkali cements, because the total alkali concentration is already very high.

In figures 4-12 through 4-14 the heat of hydration effects of lithium nitrate on the low, moderate, and high C_3A cements is presented. All three cements had increased early heat generation with the addition of lithium. Also, greater effects on the heat of hydration are measured when higher lithium dosages are used. The data in figure 4-12 for the low C_3A cement show an acute shift to the left, indicating a significantly faster rate of reaction with increasing addition of lithium. The data for the high C_3A case in figure 4-14, however, show a very subtle shift to the left at increasing dosages. This suggests that the accelerating effects of lithium nitrate on the hydration reactions are more noticeable in lower C_3A cements. This may be due to the lower sulfate level present in low C_3A cements. Gypsum ($CaSO_4 \cdot 2H_2O$) is typically added to cement to reduce the rate of dissolution of C_3A and to delay its very rapid hydration. Greater amounts of gypsum are typically required for higher C_3A cements. [Hewlett 1995] It may be that the higher levels of gypsum in the high C_3A cement suppress the hydration-accelerating effects of the lithium.

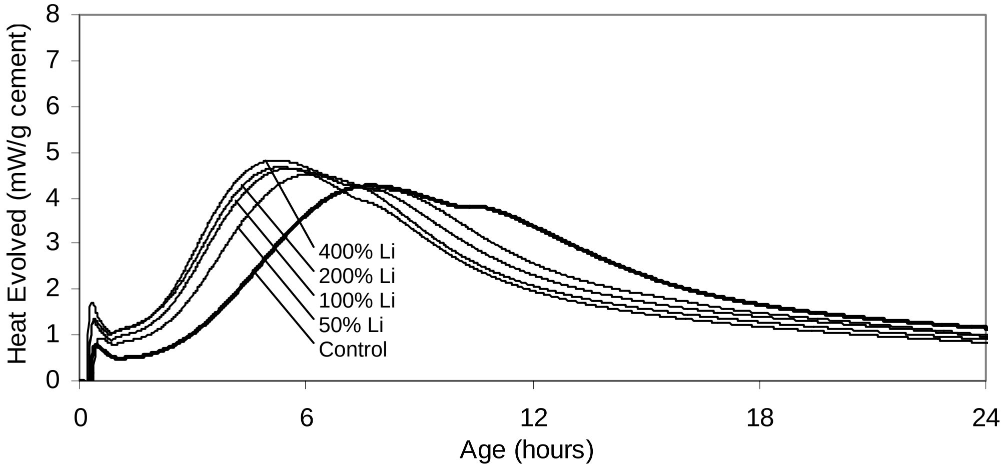


Figure 4-12. Calorimetry results for the low C_3A cement

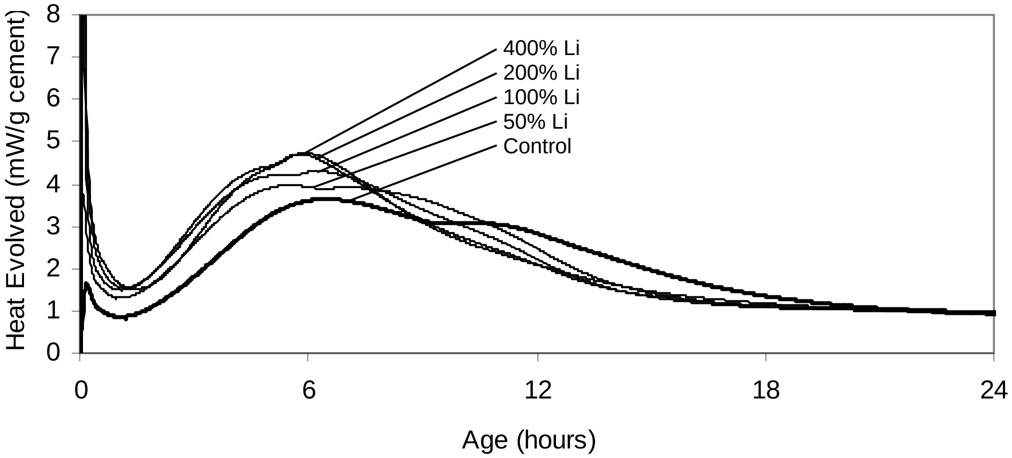


Figure 4-13. Calorimetry results for the moderate C_3A cement

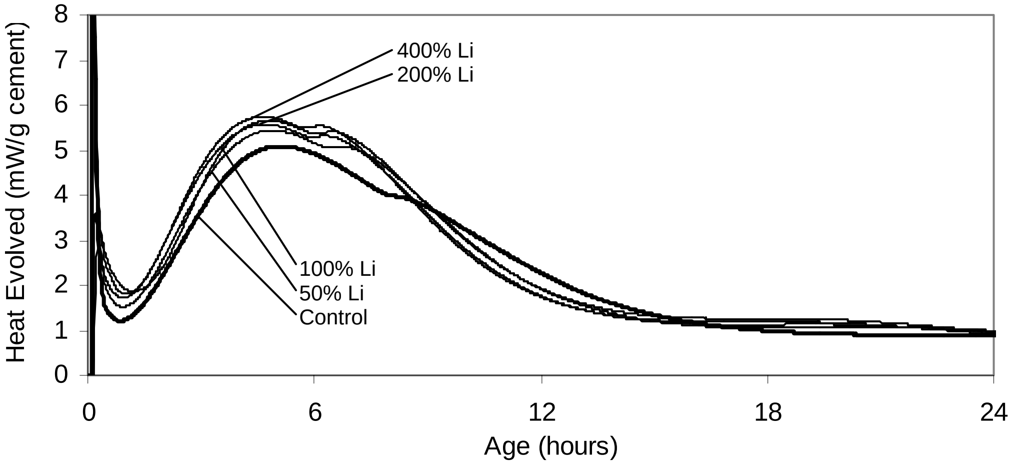


Figure 4-14: Calorimetry results for the high C_3A cement

By comparing heat of hydration data gathered on cements with varying composition and with increasing lithium addition (as in figures 4-15 and 4-16), the practical effects of lithium nitrate addition rate may be assessed.. In figure 4-15, heat of hydration curves for the low C_3A cement at 0%, 100%, and 400% dosages are compared to the hydration curve for the high C_3A cement with no lithium. Although the heat of hydration curves for the low C_3A cement show a shift to the left at increasing dosages, the curves are not shifted to the left of the high C_3A cement. Further, at all ages up to 24 hours, the cumulative heat curves for the low C_3A cement at all lithium dosages are lower than the cumulative heat curve for the high C_3A cement. Thus, this comparison indicates that variations in the rate early heat evolution and the cumulative heat evolved in low C3A cement are likely no greater than the variations to be expected with higher C_3A content.

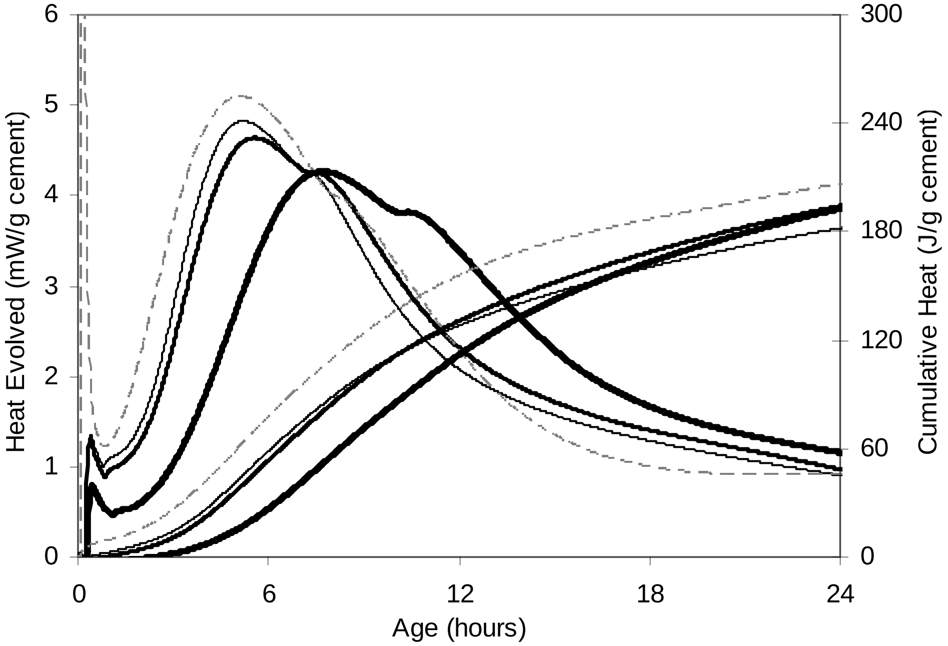


Figure 4-15. Lithium dosed low C_3A cement vs. high C_3A cement

Figure 4-16 suggests that the low alkali cement hydration is accelerated by the addition of lithium nitrate. At the 400% dosage, it appears that the low alkali cement hydration curve is shifted to the left of that for the high C_3A cement. Of the cements tested, the low alkali cement appears to be the most susceptible to acceleration effects of lithium. However, it should also be noted that cumulative heat generated in the first 24 hours by the low alkali cement at 100% lithium dosage is less than the cumulative heat generated by the high C_3A cement. The cumulative heat evolved in the low alkali cement at the 400% dosage is similar to that of the high C_3A cement in the first 6 hours, but lower than the high C_3A cement by 24 hours. This implies that although the use of lithium nitrate admixture at normal dosages may increase concrete temperatures, effects should be comparable or less than the effects expected by the selection of a higher C_3A cement.

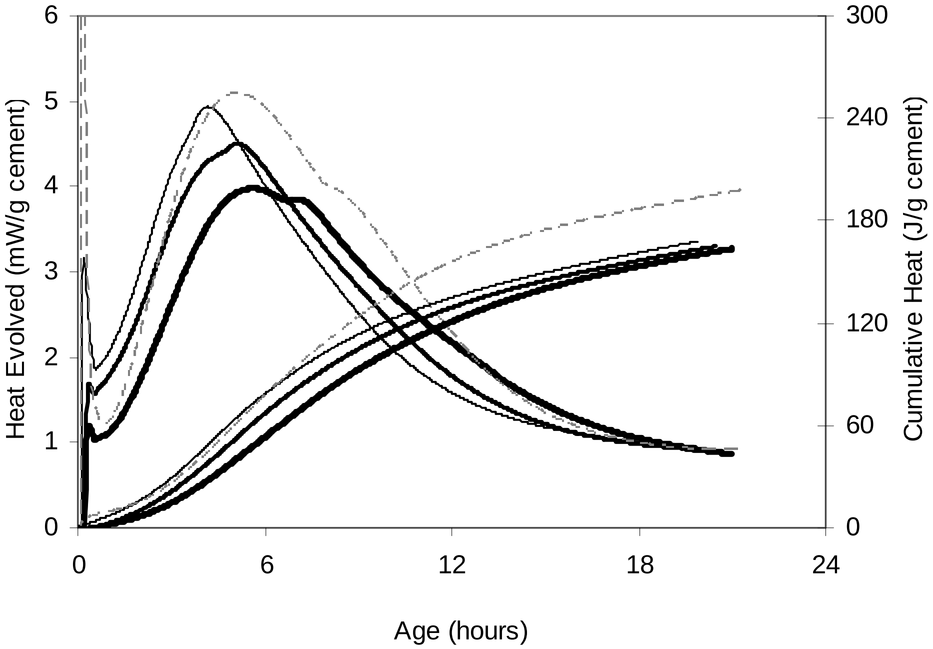


Figure 4-16. Lithium dosed low alkali cement vs. high C_3A cement

In addition to the examination of cement composition, isothermal calorimetry was performed on the sample of Lafarge Roberta cement taken from the H-JAIA runway project. Figure 4-17 shows results for this cement alone and with Class F fly ash used at 20% by weight of cement replacement. As expected, at a constant w/cm ratio of 0.30, lower heats were generated with the 20% fly ash replacement than with the cement alone. This is due to the dilution of the cement sample by the use of fly ash. In these plots, heat generated is reported as joules per gram of cementitious material.

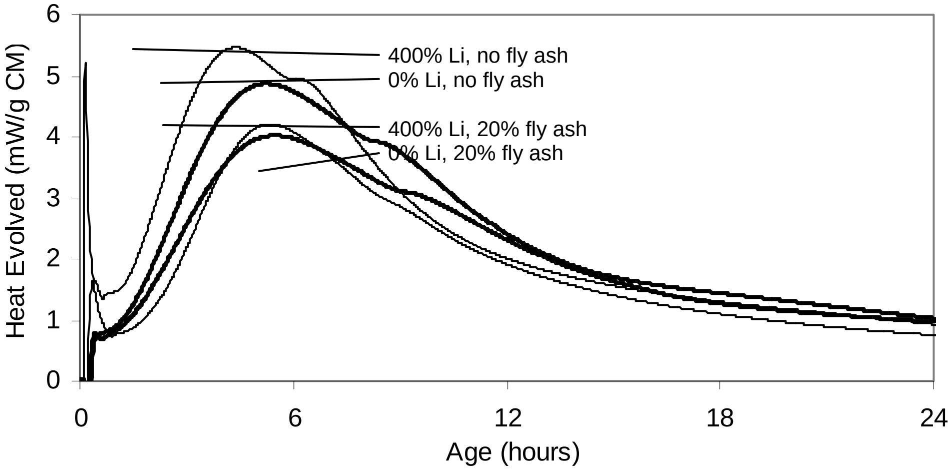


Figure 4-17. Lafarge Roberta cement alone and with 20% fly ash replacement

For the Roberta cement paste without fly ash, the addition of lithium nitrate produced both higher early heat generation and acceleration of early hydration reactions. This occurred to a lesser degree than in some of the other cements tested, such as the low C_3A cement in figure 4-

12. In the 20% fly ash case, both of these effects are much less noticeable. This suggests that fly ash replacement may decrease the effects of lithium nitrate on early heat of hydration.

Figure 4-18 shows longer-term calorimetry results for the Lafarge Roberta cement, including cumulative heat evolution data to 4 days of age. For both the cement alone, and with the 20% fly ash replacement, cumulative heat curves for the control (no lithium) case exceed that for the 400% dosage case *after* 1 day. In previous conditions, during the first 24 hours, the heat of hydration was generally increased with increasing lithium admixture dosage. Similar effects of lithium on cumulative heat beyond 24 hours were also observed for other cements, particularly in the low C_3A cement.

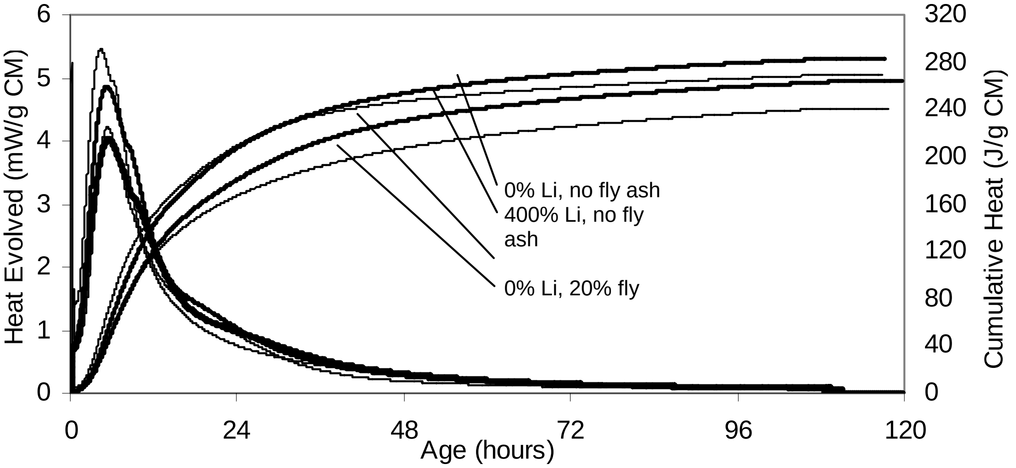


Figure 4-18. Lafarge Roberta cement cumulative heat.

Figure 4-19 shows cumulative heat data for the low C_3A cement through 4 days of age. Although the lithium-dosed pastes generate more heat initially, cumulative heat after one day is lower than that for the control (no lithium) mix. At two and three days, cumulative heat for the control mixes is 8% to 10% higher than the 400% mixes. This may indicate that the initial rapid hydration and presumed associated product formation may result in a subsequent retarded rate of hydration. Because the data here was collected only to 96 hours of age, it is not clear if the heat of hydration in the lithium-containing pastes will continue to be suppressed. However, similar hydration retardation is suggested by the maturity data collected in Phase I for the Roberta cement with fly ash.

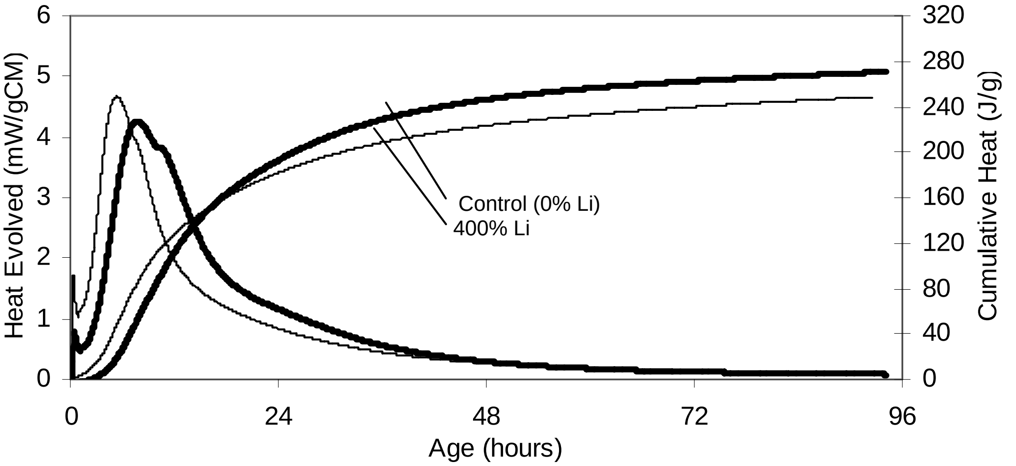


Figure 4-19. Cumulative heat curves for the low C_3A cement

Average maturity data for the lab specimens presented in figure 4-20 show lower cumulative time-temperature-factor values for the higher dosages of lithium nitrate. Figure 4-21 illustrates a more pronounced effect in the field specimens. Since field specimens come from massive slabs, where heat cannot dissipate as quickly, heat effects of the lithium admixture are expected to be more significant.

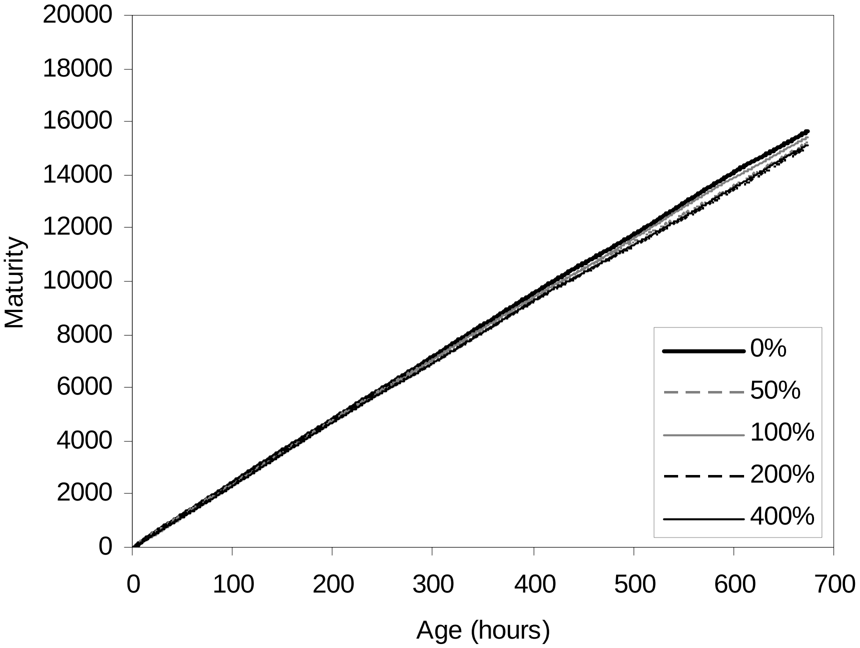


Figure 4-20. Maturity of lab specimens, Roberta cement with fly ash and Lithium

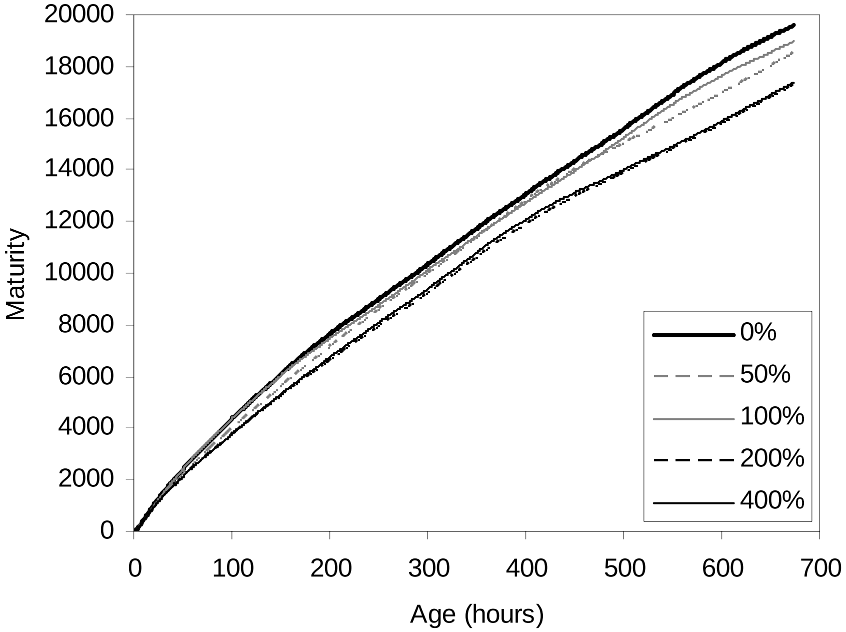


Figure 4-21. Maturity of field specimens, Roberta cement with fly ash and Lithium

Setting Time. The effect of lithium nitrate on setting time of cement pastes at w/cm of 0.30 was evaluated using the Vicat testing apparatus and the ASTM C 191-04 procedure. Cement of three alkali levels, three C_3A levels, Lafarge Roberta cement alone and with 20% fly ash replacement were tested. Figures 4-22 and 4-23 show the results of Vicat testing for the Lafarge Roberta cement with and without fly ash replacement. As expected, longer setting times were observed with the use of fly ash. However, no clear effect of lithium nitrate was observed in the Lafarge Roberta cement with or without fly ash replacement.

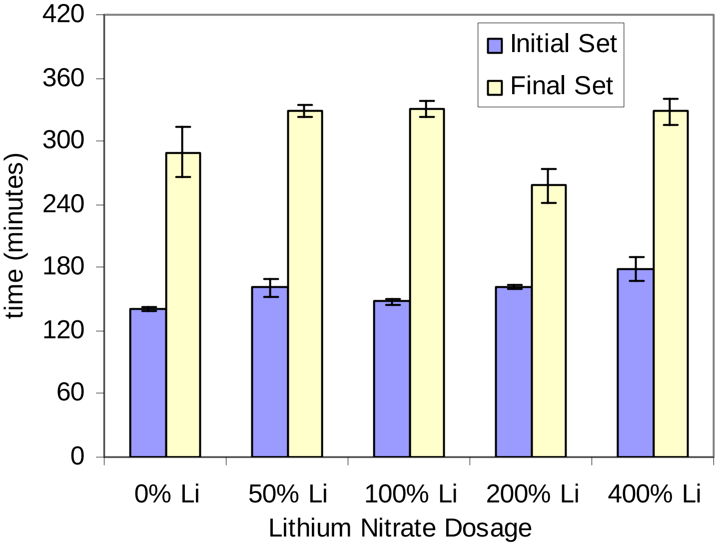


Figure 4-22. Vicat setting times for Lafarge Roberta cement with 20% fly ash replacement.

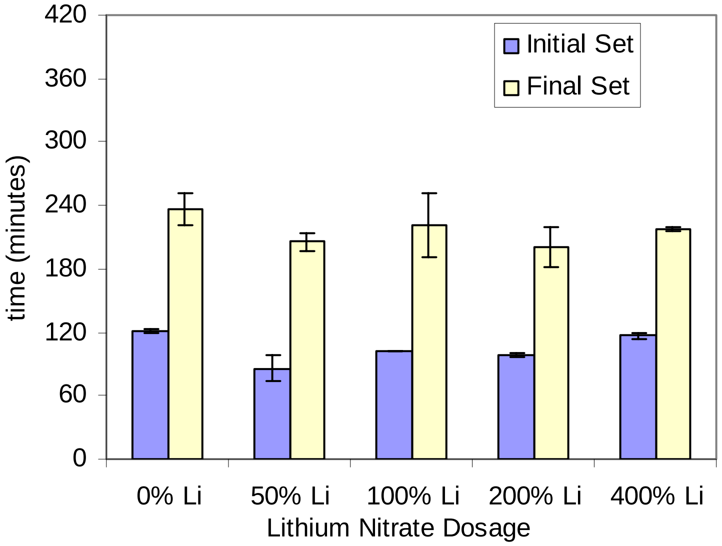


Figure 4-23. Vicat setting times for Lafarge Roberta cement, with no fly ash.

Effects of lithium nitrate on setting times were also evaluated on Vicat specimens of Roberta cement with and without fly ash replacement at an elevated temperature of 95 degrees Fahrenheit (35 C). Figures 4-24 and 4-25 show Vicat test results for these elevated temperature tests. No effect of lithium nitrate dosage was evident in these tests.

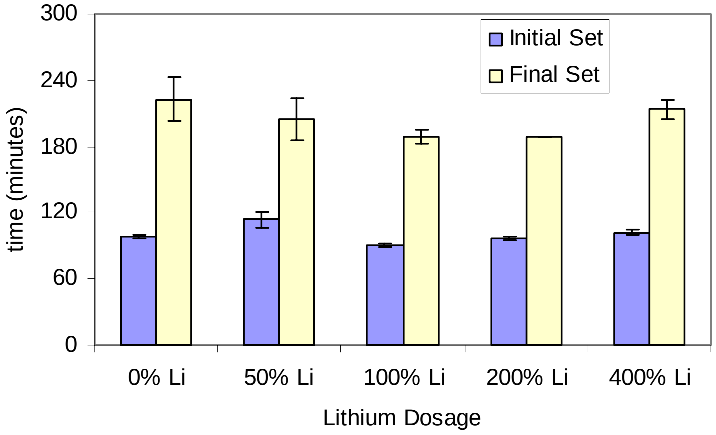


Figure 4-24. Elevated temperature set times for Lafarge Roberta cement with no fly ash.

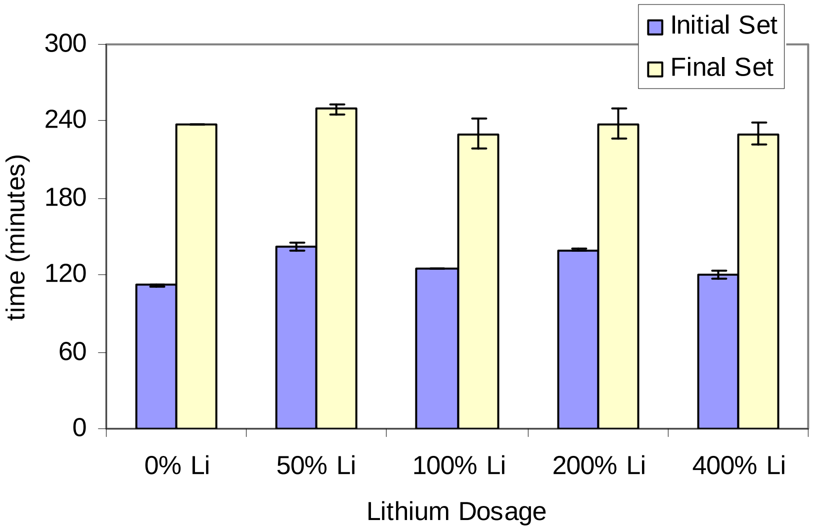


Figure 4-25. Elevated temperature set times for Lafarge Roberta cement with 20% fly ash replacement.

Figures 4-26 through 4-30 show the result of Vicat testing for the other cements included in the study. Of the seven tested, the only cement to show a setting time dependency on lithium dosage was the low alkali cement with Na_2O_e of 0.3%. Figure 4-28 shows results of testing with this cement. There are shortened setting times with increased lithium nitrate dosage. In this cement, the standard dosage of lithium nitrate decreased the initial setting time by 22 minutes, and the final setting time by 69 minutes.

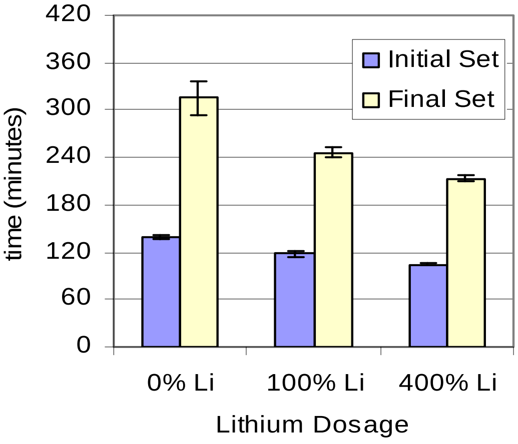


Figure 4-26. Vicat set times for low alkali cement.

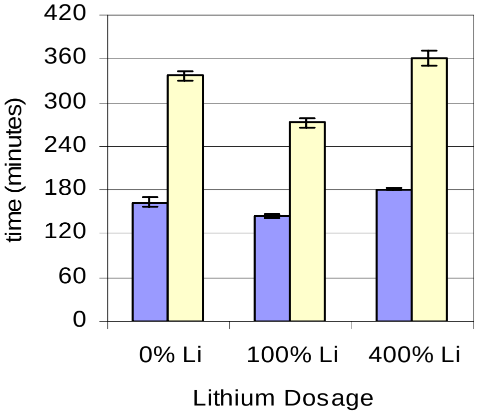


Figure 4-27. Vicat set times for high alkali cement.

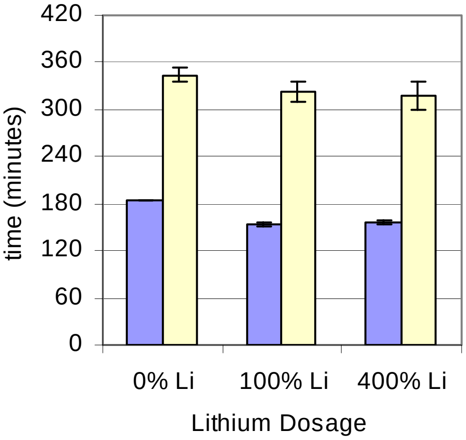


Figure 4-28. Vicat set times for Low C_3A cement.

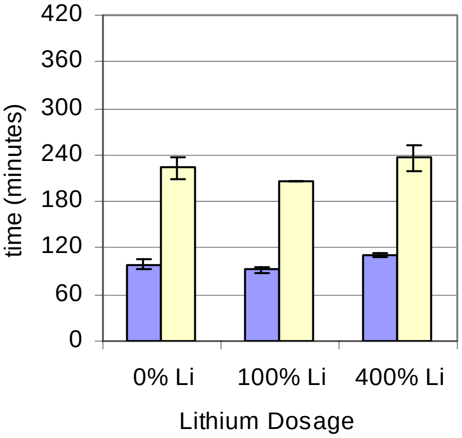


Figure 4-29. Vicat set times for High C_3A cement

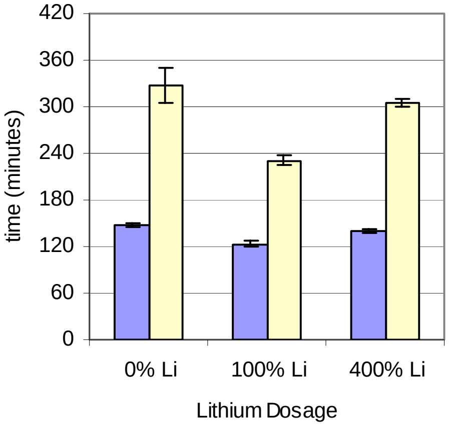


Figure 4-30. Vicat set times for moderate alkali/C_3A cement.

Chemical Shrinkage. Chemical shrinkage, the absolute volume change of hydrating cement, is approximately proportional to the extent of hydration. Six cements were examined, as well as the additional case of the Lafarge Roberta cement with fly ash replacement. Lithium was dosed at 0%, 100% and 400% for all cements, as well as 50% and 200% for the Lafarge Roberta mixes. As expected, results for chemical shrinkage performed by ASTM C 1608-05 on cement pastes, show trends similar to those obtained by calorimetry. Figures 4-31 through 4-38 indicate greater shrinkage in the first 24 hours of hydration, presumably due to greater extent of reaction as indicated by calorimetry, with increasing lithium admixture dosage. This data shows less early hydration acceleration than the calorimetry data, but does in some cases confirm an acceleratory effect.

In the chemical shrinkage data for the low C_3A cement (figure 4-34), slightly higher shrinkage is apparent in the 400% lithium mix up to 12 hours of age. However, at approximately one day of age, chemical shrinkage increases relatively in the control (no lithium) paste, and this trend continues through the observation period. This corresponds to the trends observed by calorimetry (figure 4-19) for the same C_3A. Although the lithium dosed mixes hydrate faster initially, within the first 24 hours the extent of hydration of the lithium mixes are surpassed by that of the control (no lithium) mix. This further suggests that lithium nitrate may accelerate hydration in the first 24 hours, but may retard hydration after one day, particularly in cement low in C_3A.

Figures 4-37 and 4-38 illustrate chemical shrinkage data for the Lafarge Roberta cement with and without fly ash. Figure 4-37 shows greater initial shrinkage (greater early hydration) in the lithium-dosed mixes, but does not clearly show a trend in shrinkage after one day as would be expected based on the calorimetry results. The effect of lithium on shrinkage in the first 24 hours is less apparent in figure 4-38. This reinforces the conclusion from calorimetry testing that the effect of lithium in the first 24 hours is less noticeable in the presence of fly ash. Chemical shrinkage data after ten days in the Roberta cement pastes did not show any clear trends with lithium dosage.

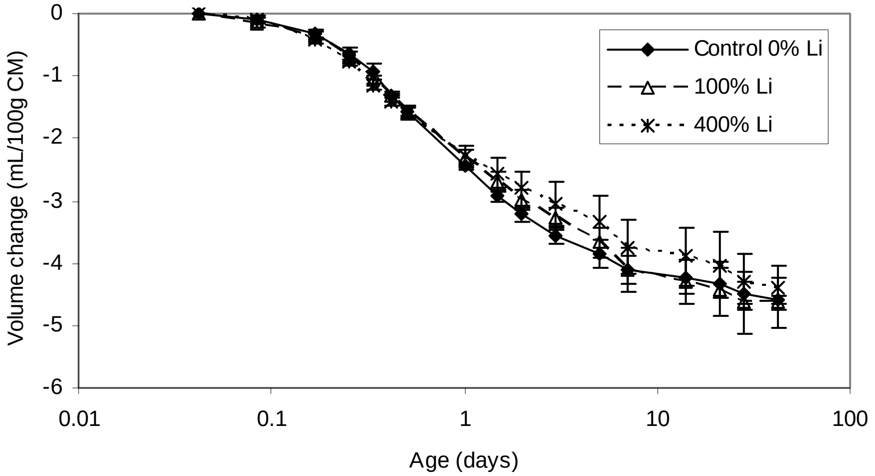


Figure 4.31. Chemical shrinkage results for low alkali cement

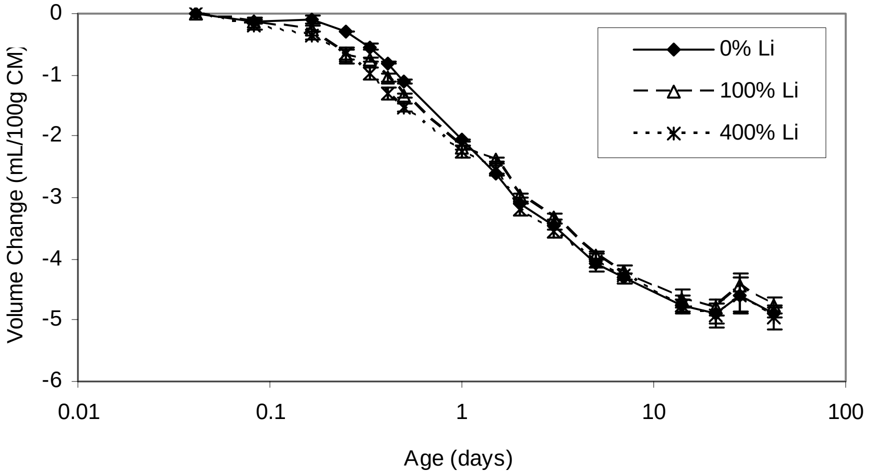


Figure 4.32. Chemical shrinkage results for moderate alkali cement

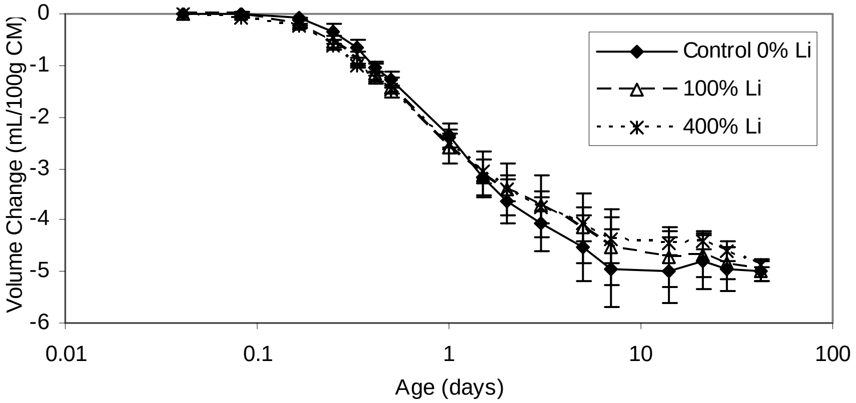


Figure 4.33. Chemical shrinkage results for high alkali cement

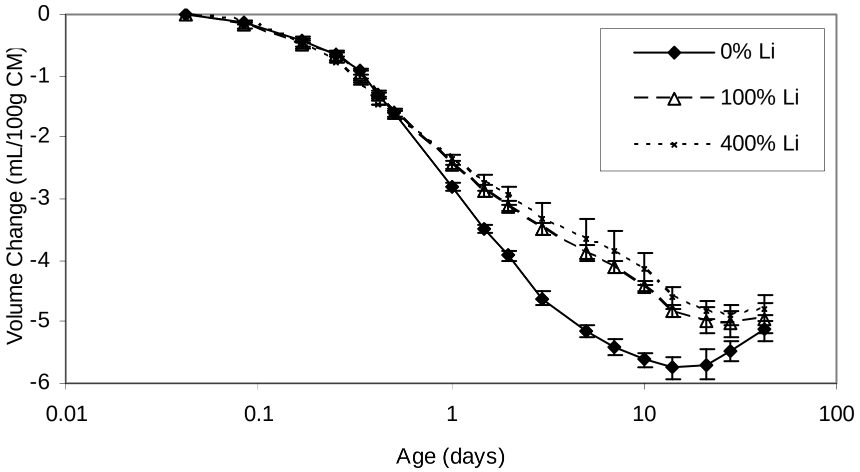


Figure 4.34. Chemical shrinkage results for low C_3A cement

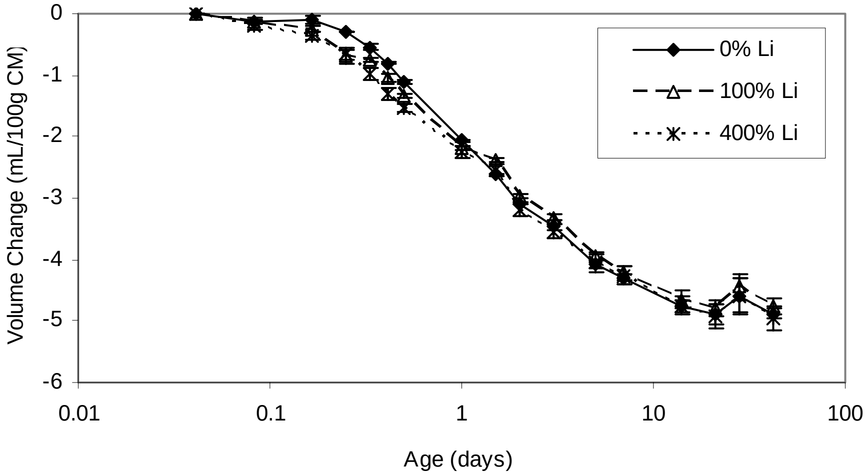


Figure 4.35. Chemical shrinkage results for moderate C_3A cement

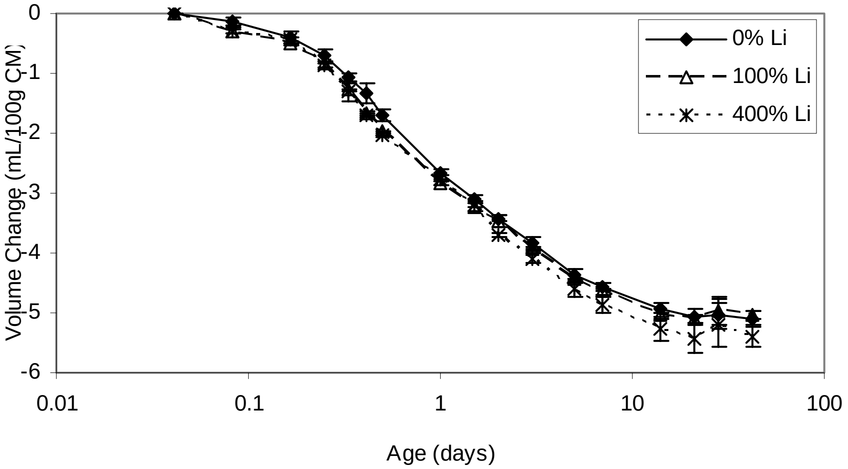


Figure 4.36. Chemical shrinkage results for high C_3A cement

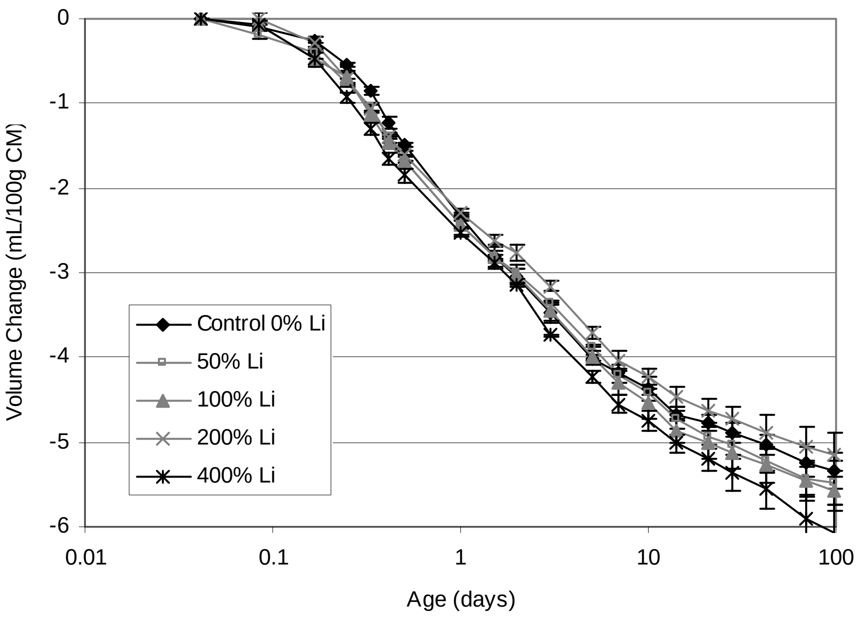


Figure 4.37. Chemical shrinkage results for Lafarge Roberta cement with no fly ash.

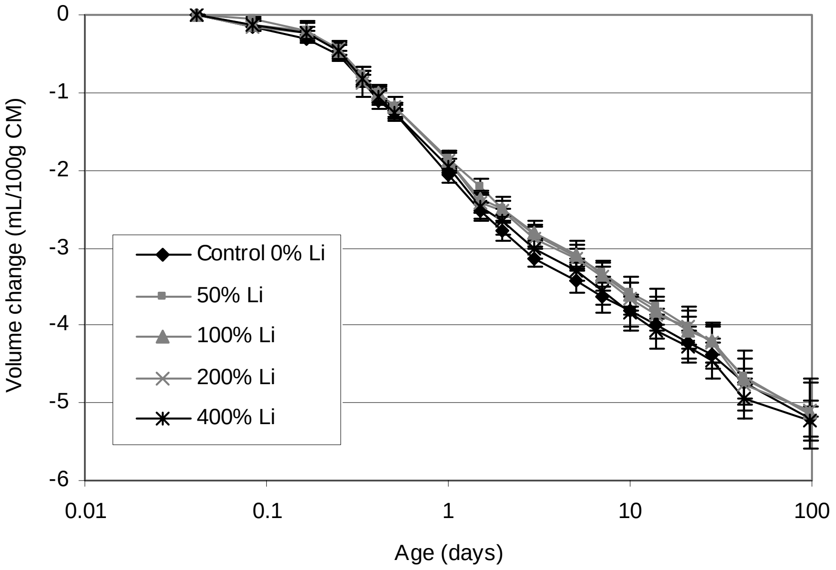


Figure 4.38. Chemical shrinkage results for Lafarge Roberta cement with 20% fly ash replacement.

Autogenous Shrinkage. Linear deformation due to autogenous shrinkage was measured in cement pastes cast in sealed, corrugated polymeric tubes by the method described by Jensen and Hansen [1995]. While chemical shrinkage is an absolute volume change from the time of mixing, autogenous shrinkage is a measured linear deformation, measured after final setting, and is largely due to self-desiccation in the capillary pores of the hydrating cement.

Effects of lithium nitrate on autogenous shrinkage were examined in six cements, as well as the additional case of the Lafarge Roberta cement with fly ash replacement. Lithium was dosed at 0%, 100% and 400% for all cements, as well as 50% and 200% for the Lafarge Roberta mixes. Results are illustrated in figures 4-39 through 4-45. Generally, as the lithium dosage increased, less autogenous shrinkage was observed in the first ten days. Often, a net expansion occurred in the first 24 hours, with greater expansions observed as the lithium dosage increased. In particular, the low C_3A cement in figure 4-42 shows expansion at the 400% lithium dosage and shrinkage at 0% and 100% dosage.

However, after 28 days, pastes with the highest (400%) dosages exhibited significantly greater shrinkage than the control sample. This suggests that higher than recommended lithium dosages may be related to greater autogenous shrinkage beyond 24 hours. However, in all conditions examined, pastes produced with the recommended dosage of lithium nitrate (100% dosage) did not exhibit significantly more autogenous shrinkage than the corresponding control (no lithium) mixes.

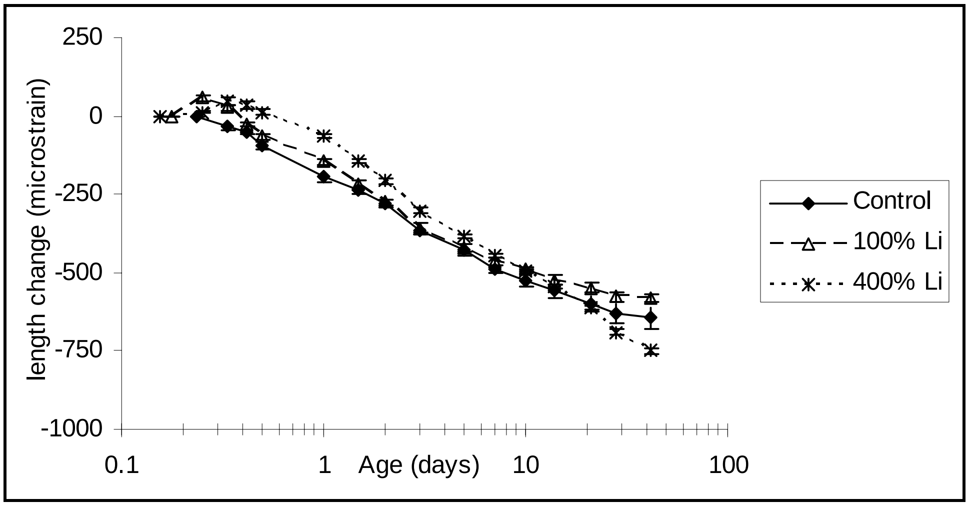


Figure 4-39. Autogenous shrinkage results for the low alkali cement

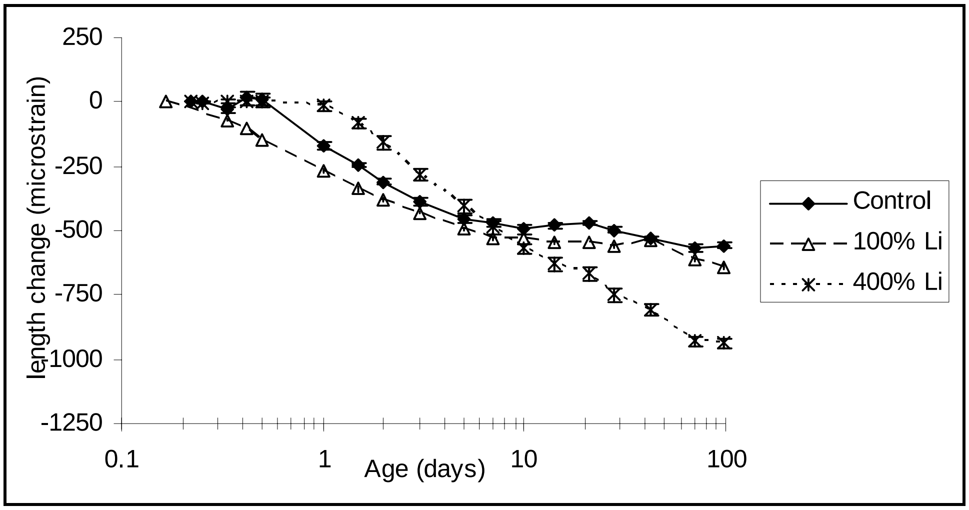


Figure 4-40. Autogenous shrinkage results for the moderate alkali/C_3A cement

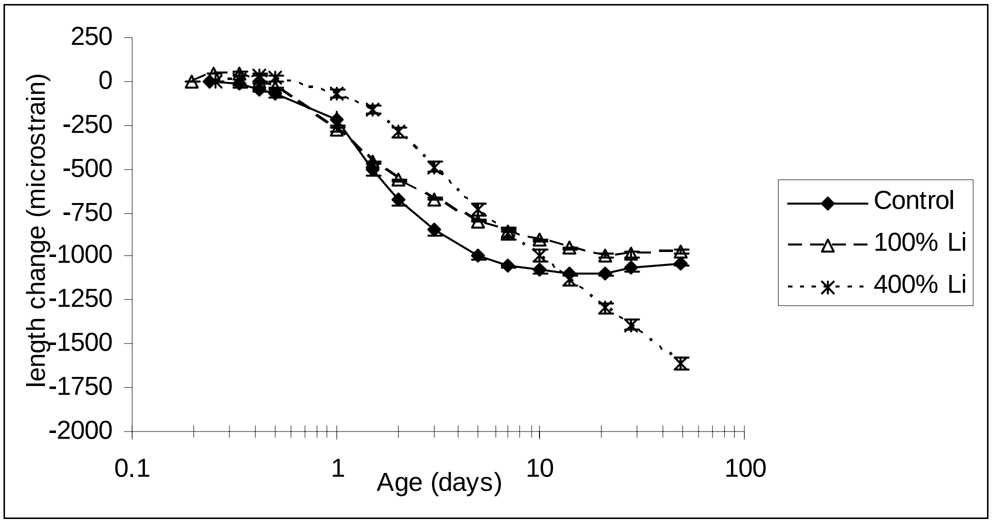


Figure 4-41. Autogenous shrinkage results for the high alkali cement

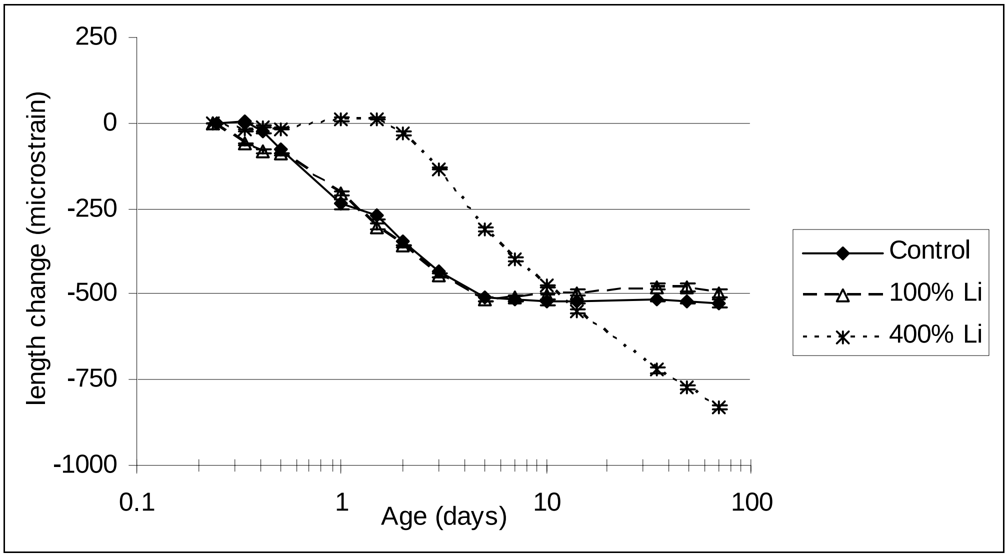


Figure 4-42. Autogenous shrinkage results for low C_3A cement

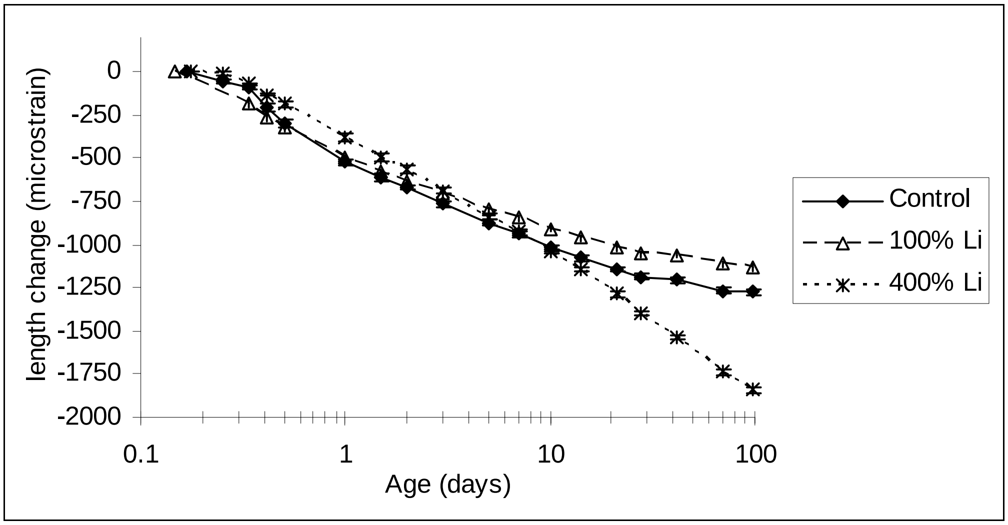


Figure 4-43. Autogenous shrinkage results for the high C_3A cement

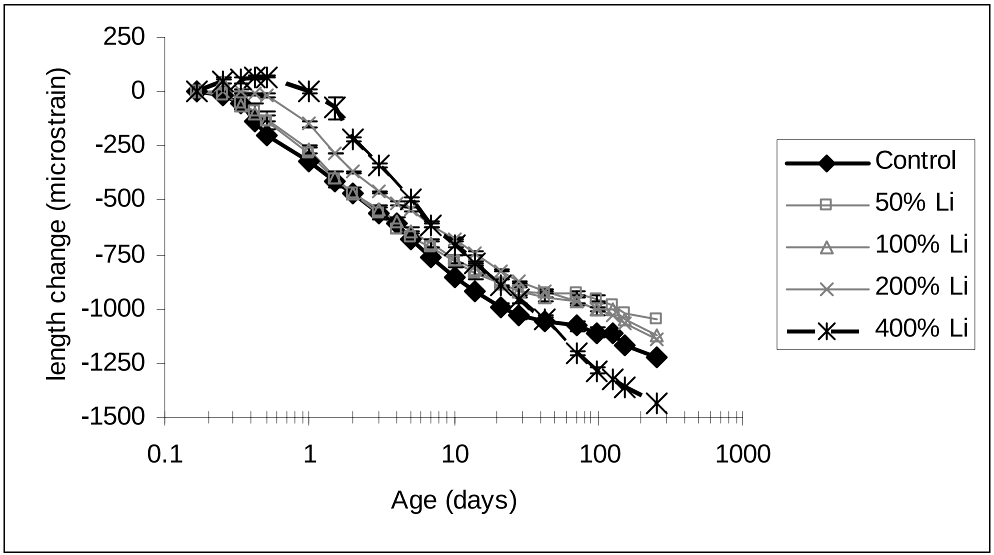


Figure 4-44. Autogenous shrinkage results for Lafarge Roberta cement with no fly ash

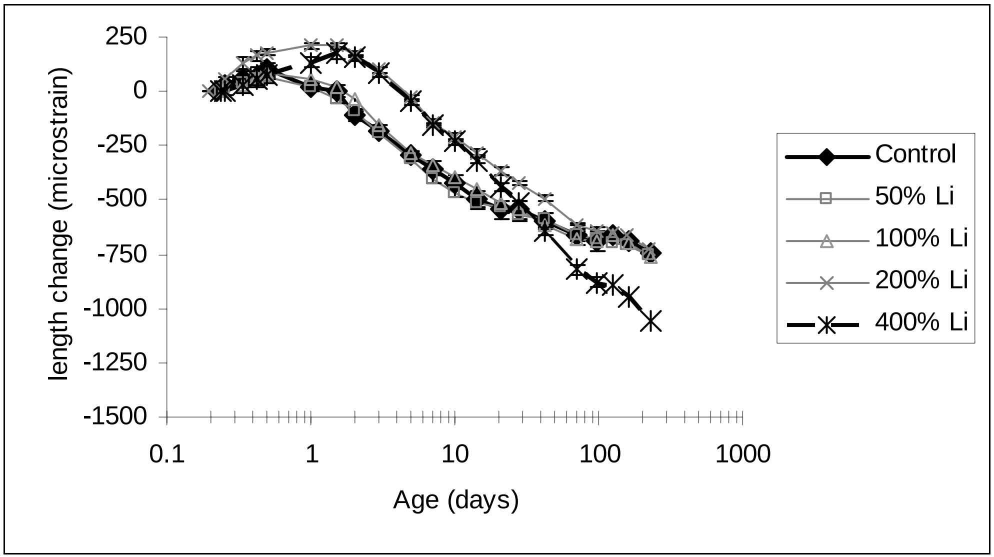


Figure 4-45. Autogenous shrinkage results for the Lafarge Roberta cement with 20% fly ash replacement

Comparison of data for autogenous shrinkage in the Roberta cement pastes prepared with and without fly ash (figures 4-44 and 4-45) shows no clear influence of fly ash replacement on the lithium effect on autogenous shrinkage. Overall shrinkage appears less in the fly ash mixes when compared to the cement alone, but the effects of lithium appear the same in both.

Free Shrinkage. Linear deformation due to unrestrained shrinkage (combined autogenous and drying shrinkage) was measured in concrete prisms by ASTM C157. Unlike the chemical and autogenous shrinkage tests, free shrinkage testing includes effects of drying and the restraining effects of aggregates. Effects of lithium nitrate on free shrinkage were examined in the Lafarge

Roberta cement, both alone and with 20% replacement by Class F fly ash. Lithium was dosed at 0%, 50%, 100%, 200%, and 400% for both cases. Results are illustrated in figures 4-46 and 4-47. In free shrinkage data up to 28 days, no trends in effects of lithium dosage on behaviour are apparent. Possibly due to additional variations introduced by the distribution and varying sizes of aggregates, the standard deviations in these results are higher than those in the tests on pastes only. The free shrinkage data for the cement with fly ash in figure 4-46 shows no significant difference in free shrinkage for any of the dosages of lithium. The free shrinkage data for the cement alone (no fly ash) in figure 4-47 indicates less shrinkage in the 50% and 200% dosage specimens. It is also possible that the comparator used in measurements was not calibrated properly before the first measurement was taken for these specimens. This would explain why the second data point for these specimens in figure 4-47 shows an expansion rather than the expected shrinkage. Regardless, in the control, 100%, and 400% specimens, which were cured simultaneously and measured at the same times, there is no significant difference in 28-day shrinkage values.

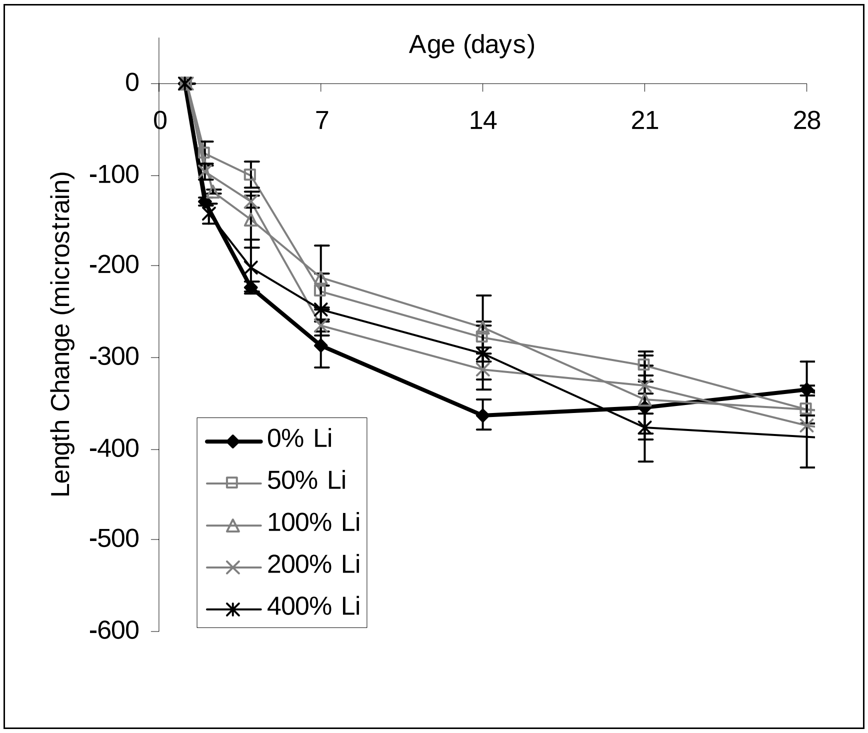


Figure 4-46. Free shrinkage results for the Lafarge Roberta cement with 20% fly ash replacement

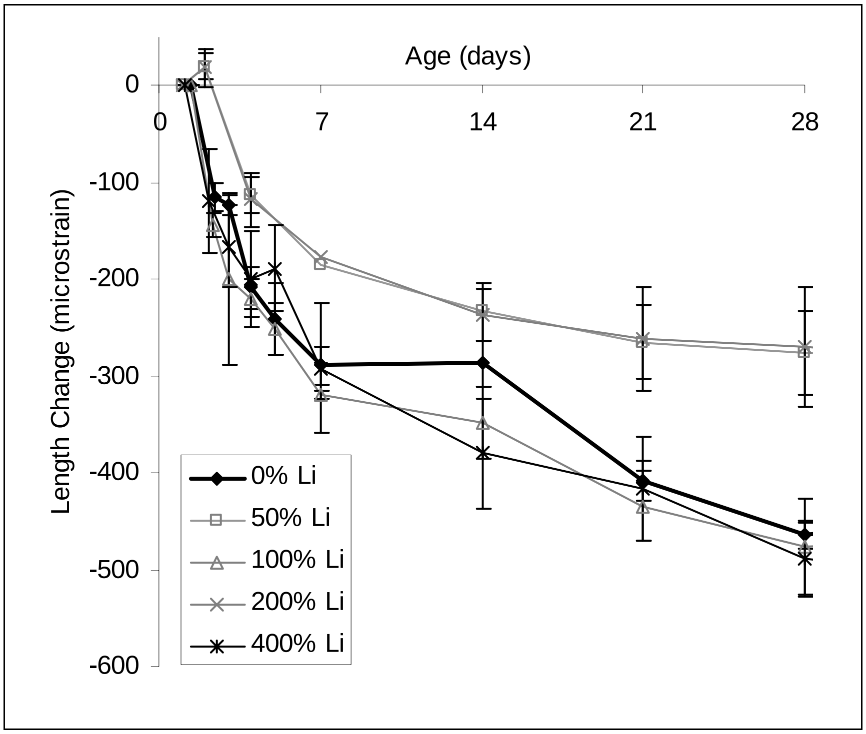


Figure 4-47. Free shrinkage results for the Lafarge Roberta cement without fly ash

Restrained Shrinkage. Effects of lithium nitrate addition on restrained concrete age at cracking were investigated using restrained rings as described in ASTM C 1581. Effects of lithium nitrate were examined in the Lafarge Roberta cement, both alone and with 20% replacement by Class F fly ash. Lithium nitrate was dosed at 0%, 50%, 100%, 200%, and 400% for both cases. Concrete rings were allowed to cure for 28 days, with shrinkage restrained by an inner steel ring. None of the rings cracked at any lithium dosage, with or without fly ash replacement, within 28 days. Since no trends were measured in the restrained shrinkage test, the potential for concrete cracking may be best evaluated using the free shrinkage results in figures 4-42 and 4-43. These results confirm that there is no evidence of a lithium nitrate effect on concrete shrinkage at early age (up to 28 days).

Workability. Tests to measure bleed water (ASTM C 232-04) and slump (ASTM C 143-05) were performed on a typical airfield pavement mix design, at lithium nitrate dosages up to 400%. No measurable bleed water was observed for any of the mixes within this range, likely due to the low w/cm ratio used (0.30). All slump measurements were less than ¼ inch, with no detectable influence of $LiNO_3$ within the range tested.

Mortar-Bar Expansion Tests. Mortar-bar expansion tests by ASTM C 1260-05 were performed using cement and aggregates from the H-JAIA runway project. Figure 4-48 shows results for expansion tests on mortar-bars containing the #4 aggregates, the #67 aggregates, and the sand. The coarse aggregates were crushed to size, and each of the aggregates was graded to meet the specifications in ASTM C 1260. For each of the aggregates, the expansion at 14 days measured less than 0.10%, classifying them as innocuous according to ASTM 1260-05.

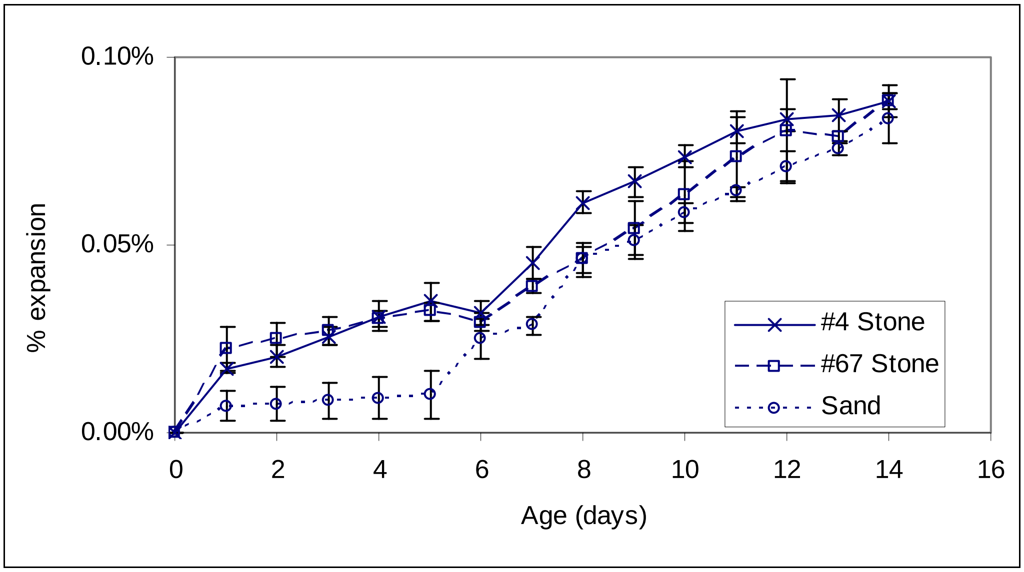


Figure 4-48. ASTM 1260 accelerated mortar-bar expansion test results

5. ANALYSIS OF RESULTS.

The experiment was designed so that an analysis of variance (ANOVA) could be conducted and thereby statistically measure differences between lithium dosages for both Phase I and Phase II strength results. ANOVA is possible given the partitioning of treatments, performing tests at various curing times, and providing reasonable test repetitions for each combination (i.e., 3 repetitions for flexural strength testing and 10 repetitions for compressive strength testing). Through ANOVA, questions such as those listed below can be answered.

Does lithium dosage have an effect on flexural strength within the first three days of cure in mixes that contain fly ash? How about those that do not contain fly ash?

The same questions for compressive strength can be analyzed with ANOVA.

5.1 ANOVA – PHASE I.

An analysis of variance was performed on the data sets for both flexural strength and compressive strength. Each ANOVA was performed with a null hypothesis, i.e., the mean values of each lithium dosage are equal. This hypothesis will be rejected (indicating that a difference does indeed exist) if the calculated F-value exceeds the F-distribution critical value [Devore and Peck, 1986]. For the ANOVA, a level of significance (α) of 0.05 was used. The results of each analysis are included in Appendix A. The ANOVA summary for flexural strength is shown in figure 5-1, compressive strength in figure 5-2. Each group of bars shows the mean value of data for each age and is identified with 'same means' or 'different means'. This annotation simply implies whether the means are statistically equal or different, it does not indicate where in the data set the differences exist.

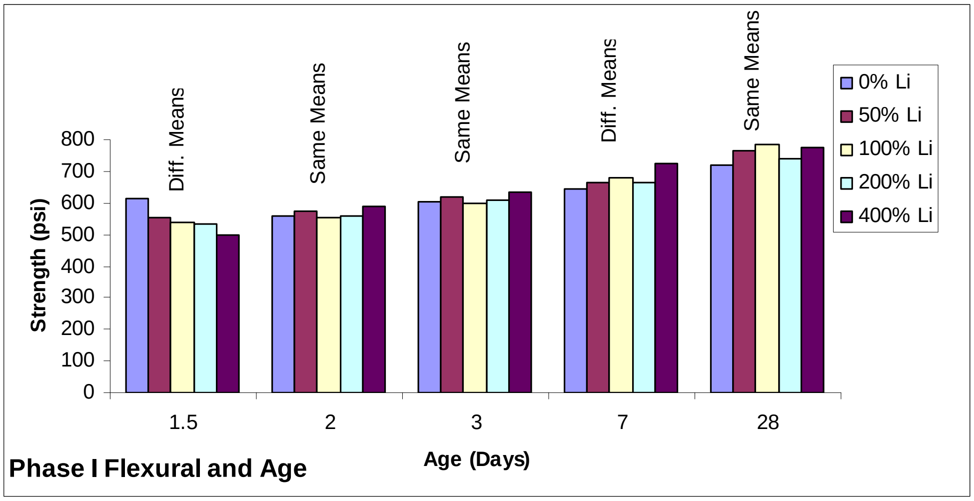


Figure 5-1. ANOVA Results for Phase I Flexural Strength

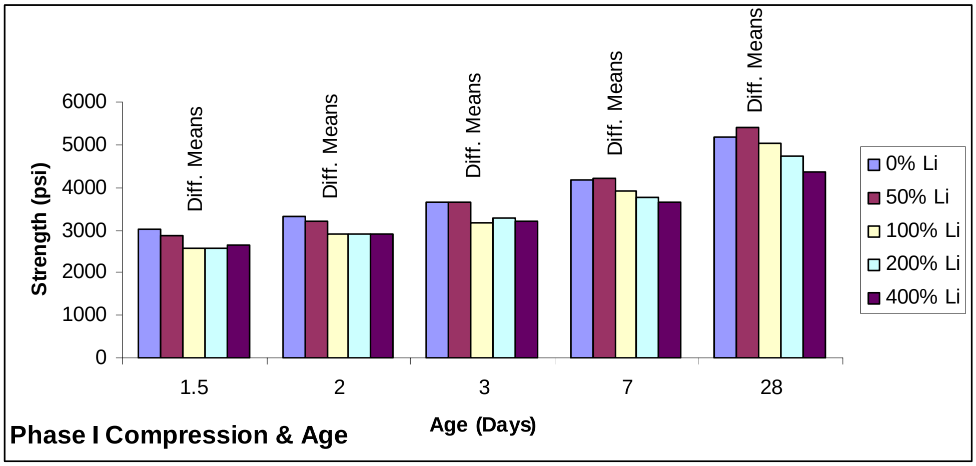


Figure 5-2. ANOVA Results for Phase I Compressive Strength

To determine differences within groups, a pooled t-test was performed [Devore and Peck, 1986] again using a level of significance (α) of 0.05. This tests the hypothesis of equal means, thus the strength at any age of each lithium dosage treatment can be compared with any other dosage at the same age. The results of these ANOVA are shown in table 5-1 (flexural strength) and table 5-2 (compressive strength). The values shown in the gray-shaded diagonal cells are the treatment mean values. The values above the diagonal indicate the computed F-statistic. Those values shaded light gray indicate that the F-statistic exceeds the critical value, thus the null hypothesis of equal means is rejected. Those not shaded indicate the means are statistically equal.

Table 5-1. Pooled t-test Results for Phase I Flexural Strength

36-hr cure					
	0%	50%	100%	200%	400%
0%	613	36.03	144.64	14.07	15.61
50%		552	1.28	0.52	3.00
100%			538	0.02	1.82
200%				535	1.05
400%					498
48-hr cure					
	0%	50%	100%	200%	400%
0%	560	0.49	0.11	0.01	13.14
50%		573	0.70	0.31	0.74
100%			555	0.02	6.25
200%				558	2.13
400%					588
3-day cure					
	0%	50%	100%	200%	400%
0%	605	0.61	0.05	0.07	2.63
50%		620	1.37	0.86	2.45
100%			600	0.34	4.59
200%				610	6.82
400%					635
7-day cure					
	0%	50%	100%	200%	400%
0%	642	1.31	4.79	2.16	18.38
50%		662	1.54	0.13	14.44
100%			678	0.83	8.62
200%				667	13.03
400%					725
28-day cure					
	0%	50%	100%	200%	400%
0%	722	2.52	7.15	0.68	4.24
50%		763	1.92	1.72	0.45
100%			785	13.00	0.26
200%				742	4.12
400%					777

Table 5-2. Pooled t-test Results for Phase I Compressive Strength

36-hr cure

	0%	50%	100%	200%	400%
0%	3028	8.95	58.47	78.23	34.73
50%		2861	33.18	52.34	14.45
100%			2586	0.06	1.47
200%				2576	2.50
400%					2654

48-hr cure

	0%	50%	100%	200%	400%
0%	3317	4.19	66.99	87.07	50.26
50%		3216	55.38	81.04	37.28
100%			2906	0.23	0.13
200%				2888	0.66
400%					2924

3-day cure

	0%	50%	100%	200%	400%
0%	3669	0.23	108.99	59.75	55.88
50%		3643	164.39	83.49	66.70
100%			3151	13.65	1.13
200%				3272	1.95
400%					3202

7-day cure

	0%	50%	100%	200%	400%
0%	4167	1.63	13.95	39.66	50.39
50%		4226	21.04	50.96	61.27
100%			3926	3.76	10.03
200%				3776	2.10
400%					3654

28-day cure

	0%	50%	100%	200%	400%
0%	5164	3.07	15.48	40.33	155.78
50%		5035	28.12	15.25	85.59
100%			5395	119.04	320.59
200%				4746	34.80
400%					4364

Discussion. By examination of figure 5-1 and table 5-1, it would appear as though lithium dosage has very little effect on the flexural strength. This is not the case with compressive strength (figure 5-2 and table 5-2), where it appears as though lithium does have an adverse effect. As lithium dosage increases, compressive strength decreases. Further, it appears as though these differences begin at a dosage level of 100% (i.e., differences do not seem to exist at 0 and 50% dosage levels). From a practical standpoint, the magnitude of strength variation is on the order of 10-15%, that is, the compressive strength determined for 0% and 50% lithium mixes was 10-15% higher than 100%, 200% and 400% lithium mixes.

5.2 ANOVA – PHASE II.

The same analysis of variance was performed on data sets for both flexural strength and compressive strength for the Phase II samples. The ANOVA summary for flexural strength is shown in figure 5-3, compressive strength in figure 5-4.

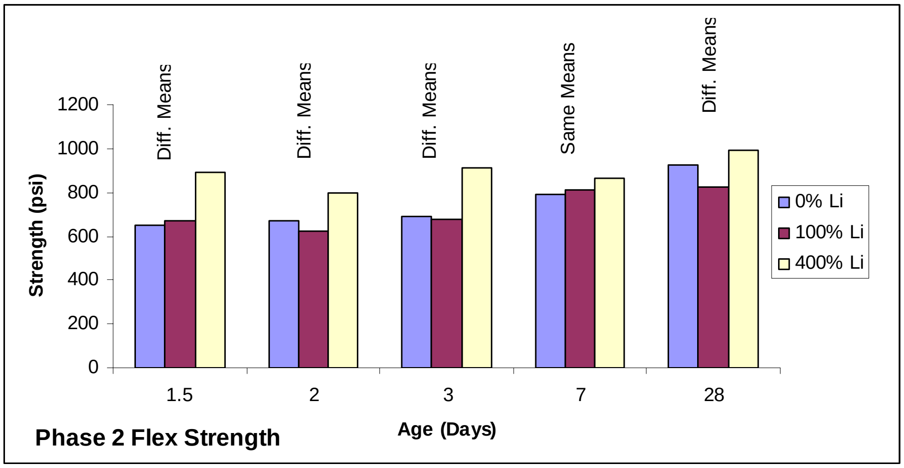


Figure 5-3. ANOVA Results for Phase II Flexural Strength

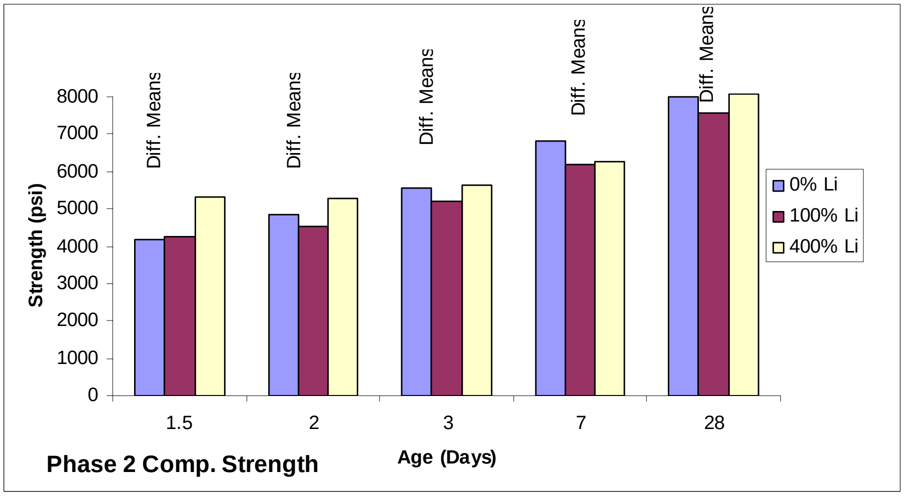


Figure 5-4. ANOVA Results for Phase II Compressive Strength

To determine differences within groups, a pooled t-test was performed [Devore and Peck, 1986] again using a level of significance (α) of 0.05. This tests the hypothesis of equal means, thus the strength at any age of each lithium dosage treatment can be compared with any other dosage at the same age. The results of these ANOVA are shown in table 5-3 (flexural strength) and table 5-4 (compressive strength). The values shown in the gray-shaded diagonal cells are the treatment mean values. The values above the diagonal indicate the computed F-statistic. Those values shaded light gray indicate that the F-statistic exceeds the critical value, thus the null hypothesis of equal means is rejected. Those not shaded indicate the means are statistically equal.

Table 5-3. Pooled t-test Results for Phase II Flexural Strength

36-hr cure

	0%	100%	400%
0%	648	1.22	91.35
100%		673	43.79
400%			888

48-hr cure

	0%	100%	400%
0%	672	5.39	7.69
100%		622	16.96
400%			797

3-day cure

	0%	100%	400%
0%	688	0.15	58.53
100%		677	173.30
400%			915

7-day cure

	0%	100%	400%
0%	793	0.13	1.55
100%		813	1.61
400%			862

28-day cure

	0%	100%	400%
0%	925	3.54	2.42
100%		827	13.62
400%			993

Table 5-4. Pooled t-test Results for Phase II Compressive Strength

36-hr cure

	0%	100%	400%
0%	4191	0.46	80.32
100%		4258	109.15
400%			5316

48-hr cure

	0%	100%	400%
0%	4863	16.43	20.98
100%		4520	152.14
400%			5264

3-day cure

	0%	100%	400%
0%	5547	7.94	0.64
100%		5211	7.94
400%			5647

7-day cure

	0%	100%	400%
0%	6811	21.11	15.52
100%		6188	0.18
400%			6248

28-day cure

	0%	100%	400%
0%	8009	7.33	0.19
100%		7555	18.49
400%			8074

Discussion. In all but one instance (flexural strength at 7 days) the hypothesis of equal means was rejected, indicating that lithium has an influence on both compressive strength and flexural strength in these mixes containing no fly ash and a very high cement content (764 pounds per cubic yard). This suggests that lithium acts as an accelerator.

6. CONCLUSIONS.

Research Objective. The objective of the research was to determine if lithium nitrate has an adverse effect on plastic or early age hardened properties of airfield paving concrete, and if so, to determine an upper limit of dosage. The research was conducted to consider materials and mixture proportions used during a construction project at Hartsfield-Jackson Atlanta International Airport. The findings and conclusions are therefore limited to the specific lithium admixture as well as the cements, fly ash and aggregates used in this study.

Based upon the findings there appear to be no significant effects on early age properties of concrete at the recommended dosage of lithium nitrate (i.e., molar ratio of [Li]/[Na+K] of 0.74, or 100%). Specifically, lithium nitrate had no observed measurable effect on unit weight, slump, air content, bleed water, and finish of fresh concrete mixes.

There were cases when the admixture, used at dosages higher than the recommended, produced statistically significant effects on concrete properties. Lithium nitrate was observed to accelerate the hydration of cement, with higher dosages leading to greater heat generation in the first six hours of hydration. However, this early heat generation appears to be minimized when a 20% replacement of cement by Class F fly ash is used. In addition, greater variations in early age heat evolution were apparent when cements of different compositions were examined than when comparing the effects of increasing lithium dosage. This apparent hydration acceleration results in decreased setting times with increasing admixture dosage in one of the seven cement types tested. In pastes made with the lowest alkali cement (total alkali = 0.3%), minor reductions (~15-20 min.) in set times were observed. These observations suggest that, in practice, the potential accelerating influence of the admixture would be similar to that observed for variations in cement composition.

After 24 hours of curing, increasing lithium nitrate dosages result in a reduced cumulative heat development, suggesting some retardation in maturity. Similarly, concrete made with fly ash and 200% and 400% dosages of lithium nitrate showed lower maturity values than control mixes. The maturity differences between control and 100% lithium nitrate dosage mixes appear insignificant. Lab specimens from mixes without fly ash showed no maturity differences at varying lithium nitrate dosages.

Statistically significant reductions in 28-day compressive strength were measured in those concrete specimens with the 200% and 400% lithium nitrate doses. These strengths were 8% and 15% lower than control specimens. Specimens made with the standard 100% dosage of lithium showed no negative effects, with 28-day compressive strengths somewhat (4%) higher than control specimens. Beams with the standard dosage of lithium nitrate showed average flexural strengths 8% higher than control specimens. Due to the inherent variability in concrete strength which occurs in field production (due to variations in ambient conditions, materials, consolidation, etc.), the effect of lithium admixtures on strength is considered negligible, even at the higher than recommended dosage rate.

In shrinkage testing, increased autogenous shrinkage was observed after 28 days for the 400% dosage for all cement pastes tested, including the Roberta cement with 20% fly ash replacement. However, no effect was apparent in pastes made with the standard (100%) dosage. Additionally, none of the dosages had any measurable effect on free shrinkage of concrete specimens, and restrained concrete specimens tested by the “ring test” did not crack at any of the dosages examined.

In summary, for the materials and mixture proportions examined in this research, the lithium admixture examined produced some negative effects on early age properties when used at higher than a recommended dosage (i.e., 200% and 400%). However, at the standard dosage, either no effects were observed or those effects were minimal and insignificant in construction practice.

7. RECOMMENDATIONS.

1. The lithium admixture used in this research had no measurable effect on the plastic properties or maturity of the production concrete when used at manufacturer dosage rates. However, the concrete had a very low water to cement ratio, 0.30, a very high cement factor, 764 pounds and Class F flyash. Trial batches should be a part of any concrete paving mix to assure that adequate plastic behavior is achieved in mixes of different materials and proportions.

2. The findings of this research should be broadened. There is a need for a comprehensive study to evaluate the potential for crossover effects related to cement composition, cement fineness, fly ash and other SCM replacement. In the absence of such research contractors are encouraged to use maturity (or calorimetry), strength testing and time of set as a measurable tool during the mix design process.

3. The heat generation and dissipation impacts of lithium nitrate will affect laboratory specimens and field placements differently. Laboratory specimens in this study showed little difference in maturity at varying lithium nitrate dosages but field measurements suggest a decrease in maturity at dosage rates higher than the recommended. A similar effect was observed calorimetry studies. Future research should consider this implied difference between effects of lithium nitrate on lab and field specimens.

4. An upper limit corresponding to 100% lithium nitrate dosage is recommended. The dosage should provide control of ASR-induced expansion while avoiding any detrimental side effects (such as long term shrinkage and effects on concrete strength) associated with dosages of 200% or more.

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APPENDIX A (Tabular Data Summaries)

IPRF Project FAA-01-G-002-04-6
Lithium Admixtures and Early Age Properties of Production Concrete
Accura Project No. IPRF2005-01
Phase 1 Field Production Mixes

Field Production Mix Information					
Date	28-Sep	29-Sep	5-Oct	6-Oct	6-Oct
Time	8:56 PM	8:56 PM	9:06 PM	9:38 PM	10:54 PM
Mix ID	PCCP+0%Li	PCCP+100%Li	PCCP+50%Li	PCCP+200%Li	PCCP+400%Li
Ticket/Load #	19	27	10	56	77
QC Set #	T-127	T-129	T-133	T-136	T-137
Location					
Phase:	10	10	11	11	11
Lane:	4	1	2	1	3
Northing:	N54+37	N53+64	N50+91	N48+48	N51+38
Easting:	E82+21	E82+86	E82+64	E82+96	E82+46
Properties					
Temp$_{Air}$	71	65	70	71	69
Temp$_{Mix}$	85	86	82	84	81
%Air$_{Lab}$	6.0	5.5	5.4	5.8	5.8
%Air$_{Field}$	4.4	5.0	4.4	4.0	4.5
Slump$_{Lab}$	1 3/4	1 1/4	1 1/2	1 3/4	2
Slump$_{Field}$	1 1/2	1 1/4	1 1/2	1 1/4	2
Unit Weight	142.5	143.5	143.4	144.3	144.5
Flexural Strength (psi)					
18hr	530	415	460	425	410
18hr	520	415	440	455	435
18hr AVG	**525**	**415**	**450**	**440**	**423**
36hr	610	550	535	565	505
36hr	615	535	570	495	445
36hr	615	530	550	545	545
36hr AVG	**613**	**538**	**552**	**535**	**498**
48hr	545	575	545	565	590
48hr	570	530	605	590	590
48hr	565	560	570	520	585
48hr AVG	**560**	**555**	**573**	**558**	**588**
72hr	570	620	625	600	625
72hr	620	570	630	605	635
72hr	625	610	605	625	645
72hr AVG	**605**	**600**	**620**	**610**	**635**
7d	625	695	660	655	700
7d	630	675	680	660	730
7d	670	665	645	685	745
7d AVG	**642**	**678**	**662**	**667**	**725**
28d	765	780	755	735	780
28d	690	800	790	730	750
28d	710	775	745	760	800
28d AVG	**722**	**785**	**763**	**742**	**777**

Data furnished by Ballenger's Quality Control Team - Trinidad Engineering and Design, Inc.

IPRF Project FAA-01-G-002-04-6
Lithium Admixtures and Early Age Properties of Production Concrete
Accura Project No. IPRF2005-01
Phase 1 Field Production Mixes

Field Production Mix Information					
Date	28-Sep	29-Sep	5-Oct	6-Oct	6-Oct
Time	8:56 PM	8:56 PM	9:06 PM	9:38 PM	10:54 PM
Mix ID	PCCP+0%Li	PCCP+100%Li	PCCP+50%Li	PCCP+200%Li	PCCP+400%Li
Ticket/Load #	19	27	10	56	77
QC Set #	0% Lithium	100% Lithium	50% Lithium	200% Lithium	400% Lithium
Location					
Phase:	10	10	11	11	11
Lane:	4	1	2	1	3
Northing:	N54+37	N53+64	N50+91	N48+48	N51+38
Easting:	E82+21	E82+86	E82+64	E82+96	E82+46
Properties					
Temp$_{Air}$	71	65	70	71	69
Temp$_{Mix}$	85	86	82	84	81
%Air$_{Lab}$	6.0	5.5	5.4	5.8	5.8
%Air$_{Field}$	4.4	5.0	4.4	4.0	4.5
Slump$_{Lab}$	1 3/4	1 1/4	1 1/2	1 3/4	2
Slump$_{Field}$	1 1/2	1 1/4	1 1/2	1 1/4	2
Unit Weight	142.5	143.5	143.4	144.3	144.5
Compressive Strength (psi)					
36hr (A)	2993	2585	2867	2600	2724
36hr (B)	2955	2729	2747	2625	2681
36hr (C)	3057	2459	2856	2513	2366
36hr (D)	2965	2598	3064	2580	2490
36hr (E)	3276	2469	2879	2563	2807
36hr (F)	3165	2577	2734	2623	2822
36hr (G)	3020	2643	2990	2619	2613
36hr (H)	3045	2409	2851	2695	2642
36hr (I)	2724	2746	2818	2470	2671
36hr (J)	3077	2643	2806	2468	2727
36hr AVG	**3028**	**2586**	**2861**	**2576**	**2654**
48hr (A)	3332	2856	3350	2886	2823
48hr (B)	3235	3012	3174	2864	2784
48hr (C)	3166	3009	3170	2881	2828
48hr (D)	3297	2952	3269	2824	2851
48hr (E)	3101	2929	3250	2801	2876
48hr (F)	3312	2985	3269	2858	3042
48hr (G)	3423	2759	3228	2915	2953
48hr (H)	3334	2837	3211	2841	2995
48hr (I)	3465	2958	3004	2988	3179
48hr (J)	3503	2768	3233	3025	2910
48hr AVG	**3317**	**2906**	**3216**	**2888**	**2924**
72hr (A)	3487	3127	3765	3233	3154
72hr (B)	3559	3137	3557	3232	3197
72hr (C)	3680	3038	3536	3194	3119
72hr (D)	3702	3194	3690	3265	3349
72hr (E)	3732	3064	3593	3270	3081

IPRF Project FAA-01-G-002-04-6
Lithium Admixtures and Early Age Properties of Production Concrete
Accura Project No. IPRF2005-01
Phase 1 Field Production Mixes

72hr (F)	3714	3244	3600	3291	3245
72hr (G)	3692	3210	3774	3326	3499
72hr (H)	3932	3218	3718	3142	3026
72hr (I)	3754	3113	3709	3414	3140
72hr (J)	3441	3160	3487	3354	3211
72hr AVG	**3669**	**3151**	**3643**	**3272**	**3202**
7d (A)	4098	3820	4087	4131	3565
7d (B)	4333	4138	4286	3629	3564
7d (C)	4064	4147	4196	3788	3699
7d (D)	4217	4103	4124	3487	3831
7d (E)	4041	3748	4109	3770	3439
7d (F)	4165	3830	4318	3769	3541
7d (G)	4208	3957	4246	3782	4070
7d (H)	4050	3958	4342	3917	3447
7d (I)	4285	3950	4395	3715	3850
7d (J)	4207	3605	4158	3768	3534
7d AVG	**4167**	**3926**	**4226**	**3776**	**3654**
28d (A)	4958	5469	4827	4719	4427
28d (B)	5027	5333	5096	4729	4278
28d (C)	5310	5361	5090	4862	4462
28d (D)	5139	5422	5413	4681	4486
28d (E)	5005	5441	5119	4473	4156
28d (F)	5165	5448	4939	4740	4428
28d (G)	5288	5535	4818	4599	4541
28d (H)	5096	5416	4890	4788	4287
28d (I)	5249	5106	5160	5009	4441
28d (J)	5399	5417	4998	4858	4137
28d AVG	**5164**	**5395**	**5035**	**4746**	**4364**

IPRF Project FAA-01-G-002-04-6

Lithium Admixtures and Early Age Properties of Production Concrete

Accura Project No. IPRF2005-01

Lab Production Mix Information (Phase II)			
Date	19-Nov	19-Nov	19-Nov
Time	12:15 PM	2:00 PM	4:00 PM
Mix ID	PCCP+0%Li	PCCP+100%Li	PCCP+400%Li
QC Set #			
Properties			
Temp$_{\text{Air}}$	55	54	50
Temp$_{\text{Mix}}$	62	58	57
%Air$_{\text{Lab}}$	4.6	4.7	4.0
Slump$_{\text{Lab}}$	1	1	1 1/4
Unit Weight	150.0	150.0	151.5
Flexural Strength (psi)			
36hr	655	710	840
36hr	655	675	915
36hr	635	635	910
36hr AVG	**648**	**673**	**888**
48hr	685	630	715
48hr	635	600	830
48hr	695	635	845
48hr AVG	**672**	**622**	**797**
72hrs	740	700	940
72hr	650	655	905
72hr	675	675	900
72hr AVG	**688**	**677**	**915**
7d	750	805	865
7d	740	865	815
7d	890	770	905
7d AVG	**793**	**813**	**862**
28d	990	820	1040
28d	920	895	955
28d	865	765	985
28d AVG	**925**	**827**	**993**

IPRF Project FAA-01-G-002-04-6
Lithium Admixtures and Early Age Properties of Production Concrete
Accura Project No. IPRF2005-01

Lab Production Mix Information (Phase II)			
Date	19-Nov	19-Nov	19-Nov
Time			
Mix ID	PCCP+0%Li	PCCP+100%Li	PCCP+400%Li
Ticket/Load #			
QC Set #	0% Lithium	100% Lithium	400% Lithium
Properties			
Temp_{Air}	55	54	50
Temp_{Mix}	62	58	57
$\%\text{Air}_{\text{Lab}}$	4.6	4.7	4.0
$\text{Slump}_{\text{Lab}}$	1	1	1 1/4
Unit Weight	150.0	150.0	151.5
Compressive Strength (psi)			
36hr (A)	3790	4220	5400
36hr (B)	4450	4180	5220
36hr (C)	4420	4430	5660
36hr (D)	4120	4140	5230
36hr (E)	4570	4240	5630
36hr (F)	3690	4450	5230
36hr (G)	4210	4270	4630
36hr (H)	4210	4150	5400
36hr (I)	4240	4040	5360
36hr (J)	4210	4460	5400
36hr AVG	**4191**	**4258**	**5316**
48hr (A)	4930	4350	5320
48hr (B)	5210	4380	4900
48hr (C)	4540	4480	5350
48hr (D)	4940	4720	5260
48hr (E)	4870	4470	5270
48hr (F)	5230	4630	5250
48hr (G)	4830	4630	5190
48hr (H)	4830	4450	5310
48hr (I)	4720	4450	5370
48hr (J)	4530	4640	5420
48hr AVG	**4863**	**4520**	**5264**
72hr (A)	5400	4790	6060
72hr (B)	5480	5460	5800
72hr (C)	5570	5360	5300
72hr (D)	5840	5520	5400
72hr (E)	5560	5160	5200

IPRF Project FAA-01-G-002-04-6

Lithium Admixtures and Early Age Properties of Production Concrete

Accura Project No. IPRF2005-01

72hr (F)	5290	4970	5890
72hr (G)	5340	5100	5830
72hr (H)	6070	5130	5490
72hr (I)	5170	5580	5700
72hr (J)	5750	5040	5800
72hr AVG	**5547**	**5211**	**5647**
7d (A)	6640	6360	5460
7d (B)	7100	6370	6250
7d (C)	6440	6100	6680
7d (D)	7020	5940	6260
7d (E)	6300	5840	5950
7d (F)	6740	5760	6360
7d (G)	7030	6560	6400
7d (H)	7060	6260	6350
7d (I)	6610	6040	6290
7d (J)	7170	6650	6480
7d AVG	**6811**	**6188**	**6248**
28d (A)	7550	7650	8240
28d (B)	8440	6980	7960
28d (C)	8300	7570	7920
28d (D)	7640	7870	8150
28d (E)	8410	7520	8280
28d (F)	7530	8020	7850
28d (G)	8380	7740	7930
28d (H)	7390	7220	8080
28d (I)	8160	7700	8490
28d (J)	8290	7280	7840
28d AVG	**8009**	**7555**	**8074**