

# RECLAMATION

*Managing Water in the West*

## Leaching Lithium

**Research and Development Office  
Science and Technology Program  
(Final Report) ST-2016-1938-01**



U.S. Department of the Interior  
Bureau of Reclamation  
Research and Development Office

September 2016

## **Mission Statements**

The U.S. Department of the Interior protects America's natural resources and heritage, honors our cultures and tribal communities, and supplies the energy to power our future.

The mission of the Bureau of Reclamation is to manage, develop, and protect water and related resources in an environmentally and economically sound manner in the interest of the American public.

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# Executive Summary

Short term testing (8 months of exposure) was completed this fiscal year. Two lithium treatments were investigated:

- Admixture applied as a surface treatment after 28-days of curing (Series A) and
- Admixture intermixed in the fresh mortar (Series B).

Analysis from Laser Ablasion Inductively Coupled Plasma Mass Spectroscopy (LA-ICP-MS) showed that mortar from Series A had a fairly uniform distribution of lithium throughout the paste before exposure to water. Similarly, Series B achieved full penetration of the lithium admixture and had a relatively consistent presence of lithium throughout the paste. After 8 months of exposure to running water, there was no evidence that the admixture leached out of the mortar in both series. This implies that the lithium is effective in the short term for hydraulic structures exposed to flowing water. While LA-ICP-MS is an appropriate method for detecting lithium, the results were scattered since mortar is non-homogeneous and would require many more scans to get more statistically significant results.

# Contents

Executive Summary.....	vi
Abbreviations.....	2
Abstract .....	2
Background .....	3
Previous Work.....	3
Methodology.....	4
Experimental Set Up.....	4
Laser Ablation Inductively Coupled Plasma Mass Spectroscopy (LA-ICP-MS) .....	5
Results .....	8
Conclusions and Recommendations.....	10
References .....	11

## Figures

Figure 1. (a) Sample preparation for two lithium admixture treatments (b) Samples exposed to constantly flowing water .....	5
Figure 2. (a) Laser ablation system and (b) mass spectroscopy system.....	6
Figure 3. Sample configuration used for LA-ICP-MS. Green line indicates direction of measurements from top to bottom.....	6
Figure 4. Samples loaded in chamber for laser ablation .....	7
Figure 5. Sample A-1: Control mix with ponded lithium .....	8
Figure 6. Sample A-2: Ponded sample with 239 days of exposure to water .....	8
Figure 7. Sample B-1: Control mix with integral lithium.....	9
Figure 8. Sample B-2: Integral lithium with 239 days of exposure to water .....	9

## Tables

Table 1. Mixture proportions for mortar samples with and without LiNO <sub>3</sub> admixtures. ....	5
Table 2. Analyzed specimen description.....	7

# Abbreviations

ASR	alkali-silica reaction
ASTM	American Society for Testing and Materials
CGSL	Concrete, Geotechnical and Structural Laboratory
cps	counts per second
LA-ICP-MS	Laser Ablation Inductively Coupled Plasma Mass Spectroscopy
Li/Ca	lithium to calcium ratio
RH	relative humidity
SSD	saturated surface dry
USGS	US Geological Survey
WRA	water reducing admixture

## Abstract

There are at least 22 Reclamation dams that have been effected by alkali-silica reaction (ASR). Once ASR has begun, there are limited methods available to stop the reaction. Lithium based admixtures can be used in new construction or, in some cases, applied to existing structures to mitigate ASR. Lithium salts in concrete have been studied in the laboratory since the 1950s. There are a limited amount of long-term studies on structures containing lithium-based admixtures. Most of the field implementations has been in transportation infrastructure (pavements, bridges, etc.) and not in hydraulic structures. Many of Reclamation's structures are in contact with constantly flowing water. This research investigates the short term (8 months) effect of running water on concrete containing lithium-nitrate admixtures (a) introduced as a surface treatment on cured concrete (Series A) and (b) intermixed in the fresh concrete (Series B).



# Background

Alkali silica reaction (ASR) still has the potential to severely damage the Bureau of Reclamation's concrete structures. ASR is a form of concrete deterioration caused by a reaction between alkalis in the cement and certain siliceous aggregates. The reaction was discovered in the 1930s, and methods were developed to prevent the reaction from damaging concrete structures. ASR requires three elements in order to occur: free alkalis in the pore solution, silica from aggregates, and moisture [1]. When those conditions are met, a gel is formed from the reaction of the aggregate and the alkalis. In the presence of sufficient water, the gel can be very expansive and lead to cracking of the concrete. In order to prevent the reaction, one of those elements must be eliminated. Typical measures to avoid ASR include limiting the amount of alkalis in the cement to 0.6%, adding Class F fly ash or slag, using non-reactive aggregates, or ensuring the concrete stays dry (less than 80% internal relative humidity, RH) during service.

However, these methods are no longer as effective as they were once considered. This is due to various factors, including the lack of economically available high quality aggregate sources and changes in coal-fired power plant regulations effecting the supply supplementary cementitious materials. In addition, limiting alkalis in the cement requires more energy during production, so because of energy costs, alkali contents are increasing. It seems ASR will always be prevalent in areas of the country, and will likely begin to be more of a problem in the foreseeable future. Fortunately, a mitigation method has been found that has the potential to reduce or eliminate ASR in new concrete structures. Lithium nitrate or lithium hydroxide-based admixtures can be used in ASR mitigation for new and (in limited cases) existing structures.

In areas where ASR is deemed probable, lithium admixtures are typically added to fresh concrete for new construction [2]. For existing concrete, lithium nitrate solution can be applied as a topical surface treatment or impregnated from the surface using a vacuum [3]. When added to concrete, lithium chemically mitigates the formation of ASR by suppressing expansion of the alkali-silica gel, thus maintaining durability and increasing service life [4]. One concern with using lithium to mitigate ASR is leaching of the lithium by water out of the concrete. If the lithium were to leach out of the concrete, over time the concrete would be at risk of suffering from ASR, then expanding and developing cracks. Knowing the long term leaching characteristics would help us determine if lithium is a viable solution for ASR mitigation for concrete exposed to water. This is particular interest to Reclamation's many concrete water conveyance projects.

This study evaluated short term leaching lithium in concrete utilizing two methods of introducing lithium to concrete. Multiple methods were analyzed to better understand the potential outcome for Reclamation. Some of the methods focused on lithium being added to hardened concrete while others focused on freshly made concrete. This could be key to protecting Reclamation's existing and future structures from potential ASR.

## Previous Work

There has been extensive research on the use of lithium nitrate to mitigate ASR, however, there is little research on how effective it is in hydraulic structures constantly exposed to running water. There is a concern that the lithium compounds can leach out of the concrete over time and become less effective at mitigating ASR. Since the admixture is expensive, a long service life would be required to make the use cost effective.

There are a handful of journal articles and reports by Drimalas et al. that investigated the long-term performance of large-scale test blocks exposed to a marine environment [3]. The standard dose of  $\text{LiNO}_3$  ( $[\text{Li}]/[\text{Na}+\text{K}] = 0.74$ ) was mixed in with the concrete when the blocks were cast. At the time of publication, the blocks had been exposed to sea water and wetting and drying cycles for approximately 5 years. During the course of the 5 years, only one mixture (not containing lithium nitrate) has shown signs of ASR. The authors hypothesized that alkalis have possibly leached out into the sea water, decreasing the amount of available alkalis for ASR to occur. No definitive chemical testing was performed at the time.

The research presented in this report has been funded by Reclamation's Science and Technology Program and was managed by Mr. Bret Robertson of the Concrete, Geotechnical, and Structural Laboratory (CGSL) until his departure from Reclamation in July of 2016. Reporting was completed by Katie Bartojay of the CGSL.

## Methodology

One-inch thick mortar tiles were cast, cured and then exposed to continuously running water for 8 months. The mortar was treated with lithium in two ways:

1. Applied as a surface treatment to plain mortar to simulate lithium nitrate used on an existing structure. These tests were labeled "Series A"
2. Integrated as an admixture into the fresh mortar to simulate lithium nitrate used in new construction. These tests were labeled "Series B"

Control specimens were cast for both lithium treatments and stored without exposure. For the test samples, after exposure to water, the relative lithium concentration in counts per second (cps) was measured throughout the cross section of the mortar using Laser Ablation Inductively Coupled Plasma Mass Spectroscopy (LA-ICP-MS). The  $\text{Li}^+$  concentration profile of samples exposed to water was compared to a sample that was not exposed to water.

## Experimental Set Up

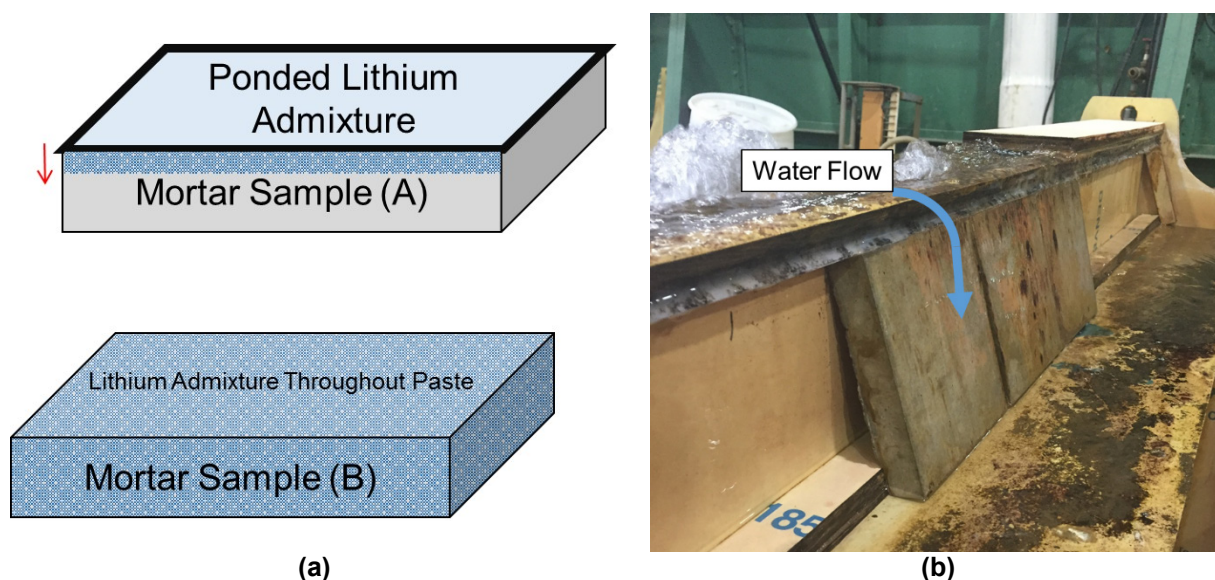
Mortar samples were prepared in accordance with ASTM C305. Mixture proportions for plain mortar (Series A) and mortar containing RASIR (Series B) are summarized in Table 1. RASIR is a 30% lithium nitrate solution manufactured by GCP Applied Technologies. RASIR is dosed based on cement content and alkali content of the cement. There are multiple suitable admixtures commercially marketed for this purpose in the concrete industry.

Type I/II cement with an alkali content of 0.60% was used, which required a dosage of 2.5 gal/y<sup>3</sup> (25 lb/yd<sup>3</sup>) of the lithium admixture. The mortar was cast in 6-in. x 6-in. x 1-in. molds. The mortar tiles were cured in 100% relative humidity at  $73 \pm 3^\circ\text{F}$  for 28 days.

**Table 1. Mixture proportions for mortar samples with and without LiNO<sub>3</sub> admixtures.**

Material	SSD Batch Weight (lb/yd <sup>3</sup> )	
	Plain Mortar (Series A)	With LiNO <sub>3</sub> (Series B)
Type I/II Cement	750	750
Sand	1500	1500
Pea Gravel	1275	1275
Water	375	326
WRA (oz)	15	15
LiNO <sub>3</sub> Admixture (gal)	--	2.5
w/c	0.50	0.50
Air (%)	3.5	5.4

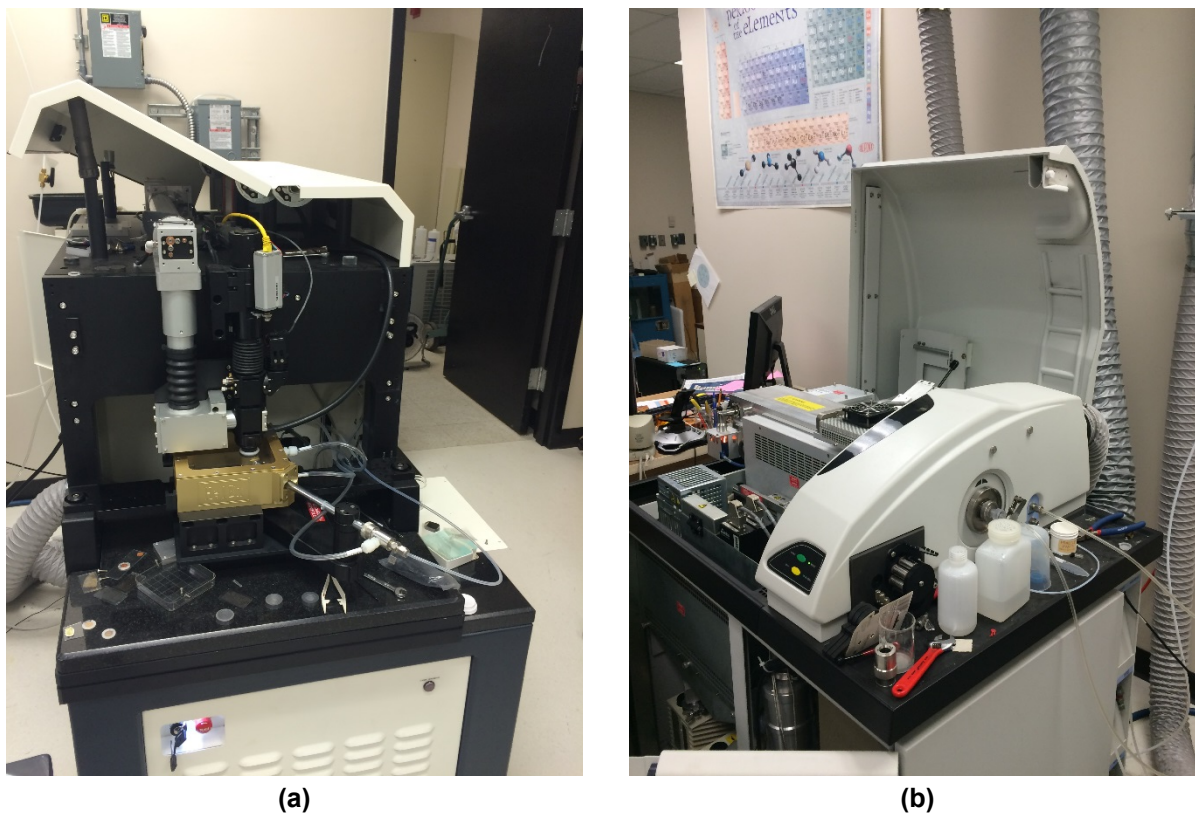
Once cured, mortar tiles from Series A were moved to a 50% relative humidity environment and lined with silicone bead along the top edge. RASIR was ponded on the top surface to penetrate into the mortar for 28 days, shown in Figure 1a. Tiles from Series B remained in the fog room during this time. Once the specimens were prepared, they were placed in a trough with continuously running water as shown in Figure 1b. The tiles remained in contact with water for 8 months before being removed for analysis. Control specimens remained in the fog room for the remainder of the study.



**Figure 1. (a) Sample preparation for two lithium admixture treatments (b) Samples exposed to constantly flowing water**

## **Laser Ablasion Inductively Coupled Plasma Mass Spectroscopy (LA-ICP-MS)**

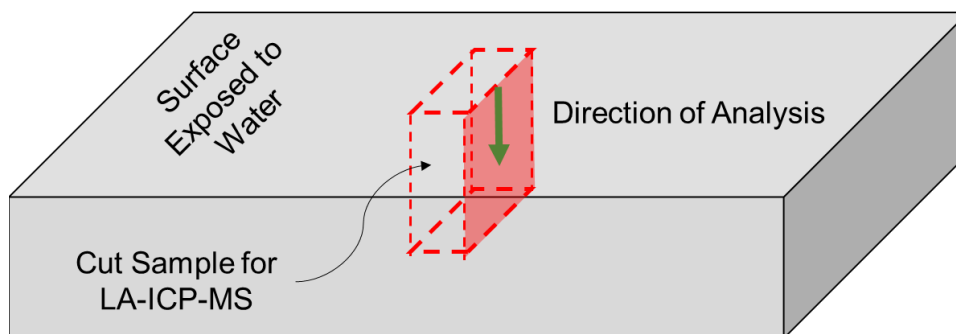
LA-ICP-MS was performed at the Crustal Geophysics and Geochemistry Science Center at the US Geological Survey in Denver, CO. Samples were analyzed using a 193 nm ANALYTE Excite Excimer Laser Ablasion system and a PerkinElmer ELAN DRC-e quadrupole ICP-MS system as seen in Figure 2. The laser used a rectangular spot size of 0.79-in. (20-mm) by 5.9-in. (150-mm) and a 2-in. (50-mm) per second scan speed.



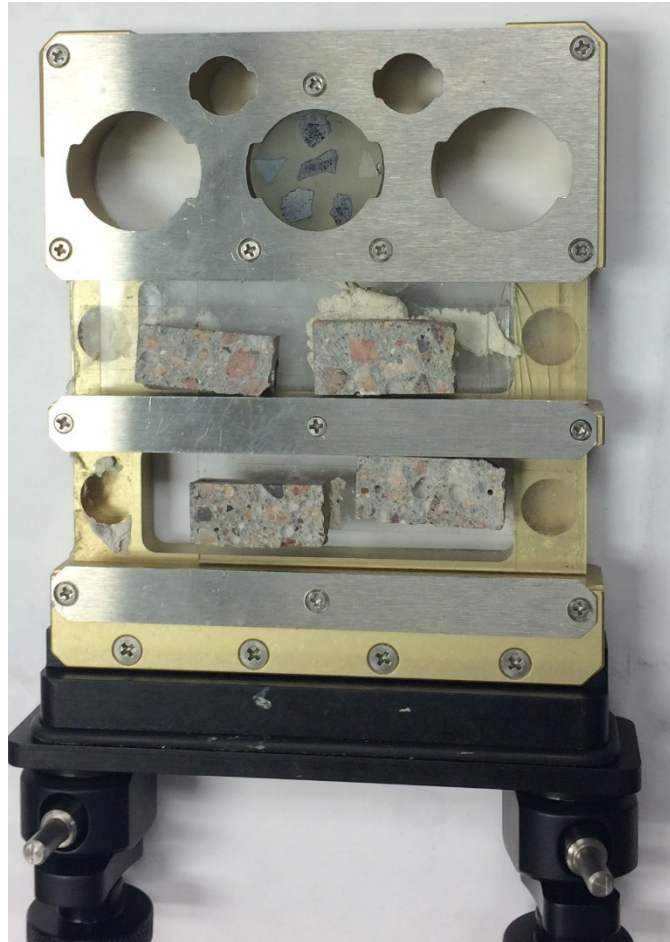
**Figure 2. (a) Laser ablation system and (b) mass spectroscopy system**

This method of analysis has been used in the past on concrete by personnel at the USGS. A 2-D map was produced along a section of the face of the concrete. In this research, a 1-D line profile was generated down the center of the mortar sample.

Control samples (Sample A-1 and Sample B-1) and samples exposed to water for 8 months (Sample A-2 and Sample B-2) were cut from the center of the mortar tiles (see Figure 3 and Figure 4) and measured from the top surface to approximately 1 in. (2.5 cm) in depth. See Table 2 for sample names and descriptions.



**Figure 3. Sample configuration used for LA-ICP-MS. Green line indicates direction of measurements from top to bottom.**



**Figure 4. Samples loaded in chamber for laser ablation**

**Table 2. Analyzed specimen description.**

<b>Description</b>	<b>Detailed Description</b>
<b>SAMPLE A-1- CONTROL MIX WITH PONDED LITHIUM</b>	Concrete top surface ponded with Lithium for 28 days and then fog cured for the duration of the testing period.
<b>SAMPLE A-2 -PONDED w/ 239 DAYS EXPOSURE</b>	Concrete top surface ponded with Lithium for 28 days and then the top surface was exposed to running water for 239 days.
<b>SAMPLE B-1 - CONTROL MIX WITH INTEGRAL LITHIUM</b>	Concrete made with integral Lithium admixture and cured for 28 days and then fog cured for the duration of the testing period.
<b>SAMPLE B-2 - INTEGRAL w/ 239 DAYS EXPOSURE</b>	Concrete made with integral Lithium admixture and cured for 28 days and then the top surface was exposed to running water for 239 days.



# Results

Lithium is expected to only be present in the paste. The laser goes through both paste and aggregate, so the lithium signal is low when the laser passes through aggregate. The data were normalized to the calcium signal since there is a much stronger presence of calcium in the paste compared to aggregate. Figures 5 through 8 show the qualitative counts per second (cps) of lithium and calcium as well as the lithium to calcium ratio (Li/Ca). In all figures, the cps are measured from the top surface toward the bottom.

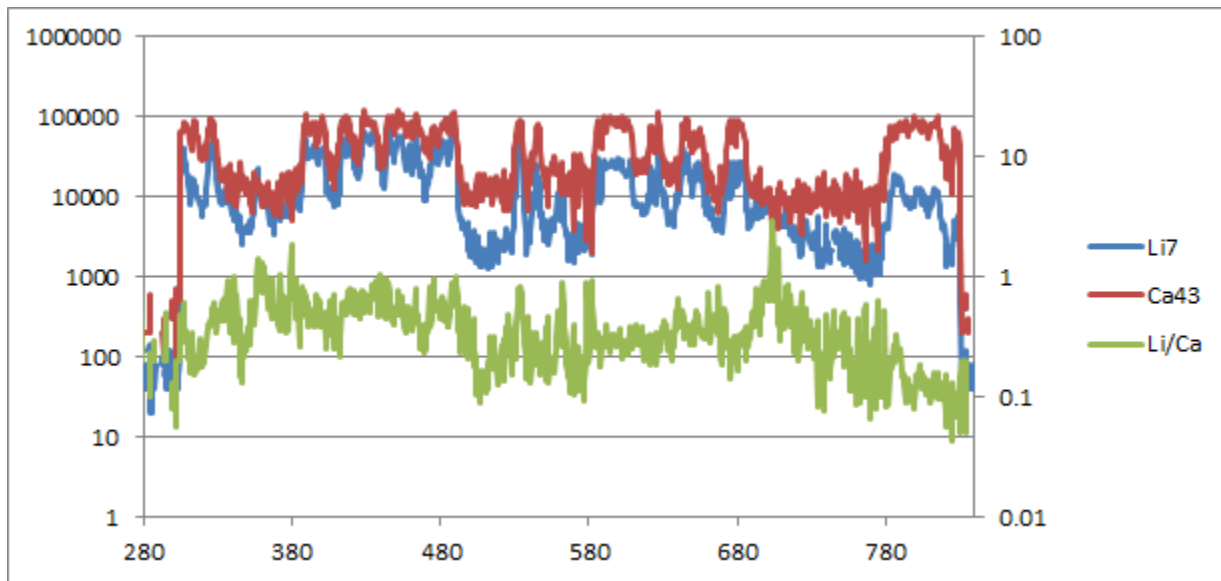


Figure 5. Sample A-1: Control mix with ponded lithium

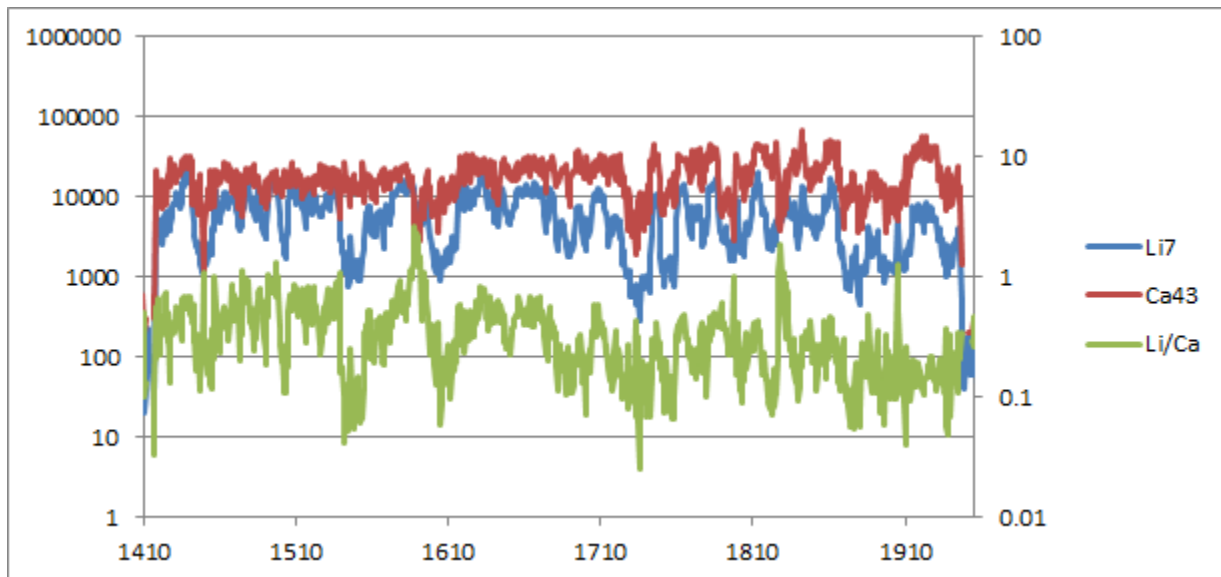
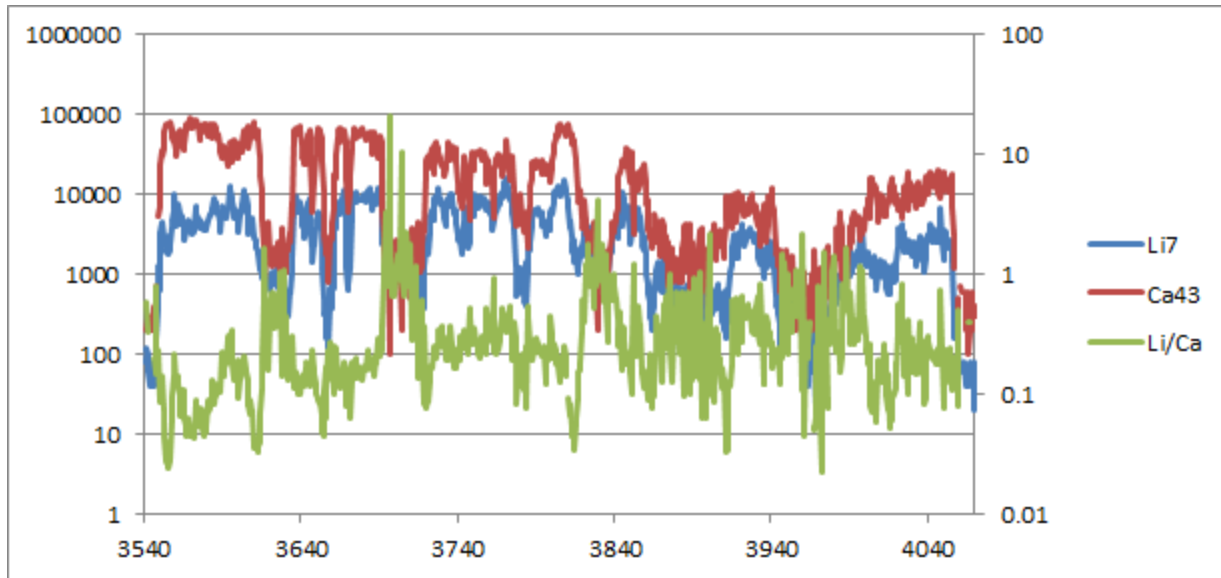
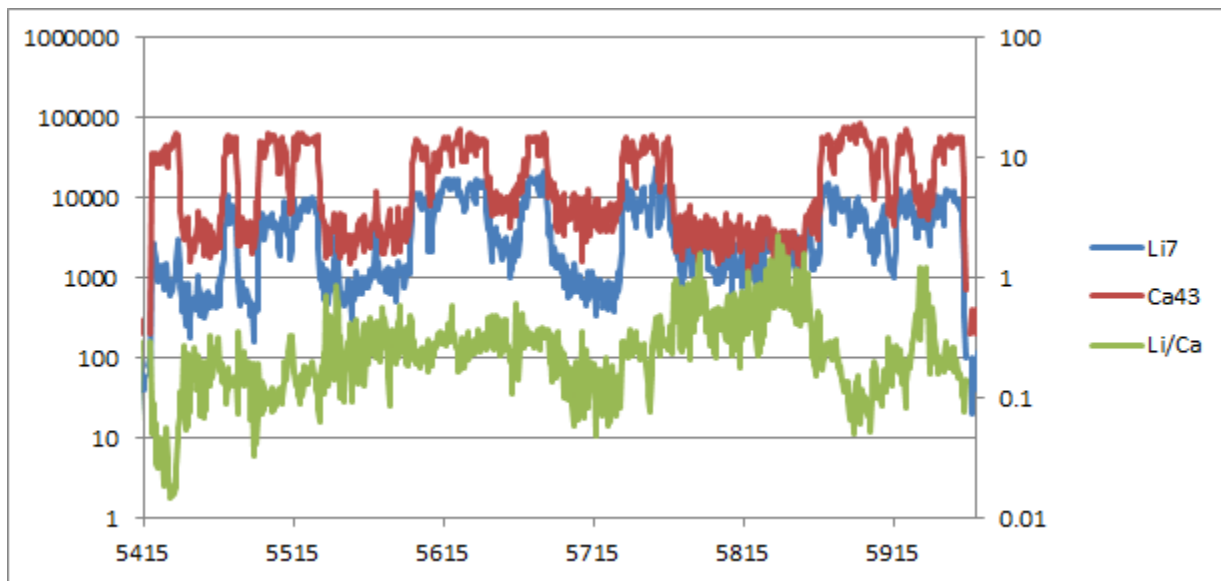


Figure 6. Sample A-2: Ponded sample with 239 days of exposure to water



**Figure 7. Sample B-1: Control mix with integral lithium**



**Figure 8. Sample B-2: Integral lithium with 239 days of exposure to water**

The data produced from a single laser line is clearly noisy (scattered). However, some general observations can be made. Figure 5 and Figure 6 have a similar, relatively uniform Li/Ca which implies no difference in lithium content before and after exposure to running water. The Li/Ca in Figure 7 is less uniform, possibly due to noise, but it is clear that the admixture penetrated through the complete depth of the mortar sample. Figure 8 is also noisy but the approximate Li/Ca level of 100 is maintained. There is a decrease of lithium at the surface, but there no clear conclusion can be made if that is noise or a loss of lithium in the first ~0.05 inches of the sample.

# Conclusions and Recommendations

- From preliminary results of LA-ICP-MS, the following observations have been made:
  - Lithium nitrate solution penetrated through the depth of the mortar samples over the course of 28 days
  - Concentration of lithium appears to be higher in ponded samples compared to those with lithium nitrate intermixed
    - The admixture is diluted in the mix water
  - Lithium concentrations seem to remain elevated in samples exposed to continuously running water for 8 months
- Further analysis of bulk material may yield a better understanding of the  $\text{Li}^+$  gradient with less noise than the LA-ICP-MS.
- A 28-day ponding treatment would likely not be achievable in practice to introduce  $\text{LiNO}_3$  admixtures to existing structures. The penetration of admixture into the concrete should be investigated for shorter time periods more likely to be encountered in the field.
- The high cost of lithium may restrict the use of  $\text{LiNO}_3$  admixtures in practice. Very recent reports from the concrete industry indicate that price increases and availability of  $\text{LiNO}_3$  admixtures are directly tied to the automotive industry (for Li batteries) and may limit the viability of this technology to mitigate ASR in the future.
- We strongly recommend that longer term tests be conducted to study the possibility of lithium leaching out of concrete over a longer time frame.



# References

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- [2] M. D. A. Thomas, B. Fournier, K. J. Folliard, J. H. Ideker, and Y. Resendez, “The Use of Lithium to Prevent or Mitigate Alkali-Silica Reaction in Concrete Pavements and Structures Contact,” *FHWA-HRT-06-133*, 2007.
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## **Data Sets that support the final report**

- Share Drive folder name and path where data are stored:  
\\Bor\dfs\DO\CivilEng\D8180\Science and Technology\FY16\Robertson\1938 Leaching Lithium
- Point of Contact name, email and phone: Katie Bartojay, kbartojay@usbr.gov, 303-445-2374
- Short description of the data: Literature Review, mix designs, USGS photos and results
- Keywords: concrete, Lithium, leaching
- Approximate total size of all files: 50MB