



OKLAHOMA TRANSPORTATION CENTER

*ECONOMIC ENHANCEMENT THROUGH INFRASTRUCTURE STEWARDSHIP*

## **SUPPRESSION OF ASR THROUGH AGGREGATE COATING**

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<b>16. ABSTRACT</b>  Many highways, runways, parking lots and bridges are suffering from premature deterioration due to alkali silica reaction (ASR) that takes place between the alkalis contributed primarily by the cement and a reactive form of silica from specific silicon-containing rocks or minerals in the aggregates utilized in concrete production. This produces an alkali/silica gel that, in the presence of sufficient moisture, will expand and produce stresses that damage the concrete. With time, the expansion of the gel generates internal pressure that can lead to cracking of the concrete that provides pathways for ingress of deleterious materials such as water, sulfates and chlorides to the interior of the concrete matrix. This can then lead to serious durability issues such as freeze/thaw damage, sulfate attack, or corrosion of steel or rebar. Several mitigation options for ASR exist, including the use of low-alkali cements, mineral additives, or chemical additives. All of these increase the cost of concrete: for example, the addition of lithium nitrate causes an expense of over \$ 20 per cubic yard of concrete. All of these methods have another commonality – they apply the treatment globally at great expense, while the root of the ASR problem is localized surface phenomenon at the aggregate-cement interface. Therefore, the proposed solutions to the problem of ASR that were developed in this investigation targeted this interface with the aim of developing cost-effective pretreatment processes for problematic aggregates that will eliminate the alkali silicate reaction. A mineral additive was also discovered that can be added to the concrete mixture that prevents ASR expansion at as little as 1% by weight			
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## SI (METRIC) CONVERSION FACTORS

Approximate Conversions to SI Units				
Symbol	When you know	Multiply by	To Find	Symbol
<b>LENGTH</b>				
in	inches	25.40	millimeters	mm
ft	feet	0.3048	meters	m
yd	yards	0.9144	meters	m
mi	miles	1.609	kilometers	km
<b>AREA</b>				
in <sup>2</sup>	square inches	645.2	square millimeters	mm <sup>2</sup>
ft <sup>2</sup>	square feet	0.0929	square meters	m <sup>2</sup>
yd <sup>2</sup>	square yards	0.8361	square meters	m <sup>2</sup>
ac	acres	0.4047	hectares	ha
mi <sup>2</sup>	square miles	2.590	square kilometers	km <sup>2</sup>
<b>VOLUME</b>				
fl oz	fluid ounces	29.57	milliliters	mL
gal	gallons	3.785	liters	L
ft <sup>3</sup>	cubic feet	0.0283	cubic meters	m <sup>3</sup>
yd <sup>3</sup>	cubic yards	0.7645	cubic meters	m <sup>3</sup>
<b>MASS</b>				
oz	ounces	28.35	grams	g
lb	pounds	0.4536	kilograms	kg
T	short tons (2000 lb)	0.907	megagrams	Mg
<b>TEMPERATURE (exact)</b>				
°F	degrees Fahrenheit	(°F-32)/1.8	degrees Celsius	°C
<b>FORCE and PRESSURE or STRESS</b>				
lbf	poundforce	4.448	Newtons	N
lbf/in <sup>2</sup>	poundforce per square inch	6.895	kilopascals	kPa

Approximate Conversions from SI Units				
Symbol	When you know	Multiply by	To Find	Symbol
<b>LENGTH</b>				
mm	millimeters	0.0394	inches	in
m	meters	3.281	feet	ft
m	meters	1.094	yards	yd
km	kilometers	0.6214	miles	mi
<b>AREA</b>				
mm <sup>2</sup>	square millimeters	0.00155	square inches	in <sup>2</sup>
m <sup>2</sup>	square meters	10.764	square feet	ft <sup>2</sup>
m <sup>2</sup>	square meters	1.196	square yards	yd <sup>2</sup>
ha	hectares	2.471	acres	ac
km <sup>2</sup>	square kilometers	0.3861	square miles	mi <sup>2</sup>
<b>VOLUME</b>				
mL	milliliters	0.0338	fluid ounces	fl oz
L	liters	0.2642	gallons	gal
m <sup>3</sup>	cubic meters	35.315	cubic feet	ft <sup>3</sup>
m <sup>3</sup>	cubic meters	1.308	cubic yards	yd <sup>3</sup>
<b>MASS</b>				
g	grams	0.0353	ounces	oz
kg	kilograms	2.205	pounds	lb
Mg	megagrams	1.1023	short tons (2000 lb)	T
<b>TEMPERATURE (exact)</b>				
°C	degrees Celsius	9/5+32	degrees Fahrenheit	°F
<b>FORCE and PRESSURE or STRESS</b>				
N	Newtons	0.2248	poundforce	lbf
kPa	kilopascals	0.1450	poundforce per square inch	lbf/in <sup>2</sup>

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# **Suppression of ASR Through Aggregate Coatings**

**Final Report**

**August 13, 2013**

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# Executive Summary

Many highways, runways, parking lots and bridges are suffering from premature deterioration due to alkali silica reaction (ASR) that takes place between the alkalis contributed primarily by the cement and a reactive form of silica from specific silicon-containing rocks or minerals in the aggregates utilized in concrete production. This produces an alkali/silica gel that, in the presence of sufficient moisture, will expand and produce stresses that damage the concrete. With time, the expansion of the gel generates internal pressure that can lead to cracking of the concrete that provides pathways for ingress of deleterious materials such as water, sulfates and chlorides to the interior of the concrete matrix. This can then lead to serious durability issues such as freeze/thaw damage, sulfate attack, or corrosion of steel or rebar. Several mitigation options for ASR exist, including the use of low-alkali cements, mineral additives, or chemical additives. All of these increases the cost of concrete: for example, the addition of lithium nitrate causes an expense of over \$ 20 per cubic yard of concrete. All of these methods have another commonality – they apply the treatment globally at great expense, while the root of the ASR problem is localized surface phenomenon at the aggregate-cement interface. Therefore, the proposed solutions to the problem of ASR developed in this investigation targeted this interface with the aim of developing cost-effective pretreatment processes for problematic aggregates that will eliminate the alkali silicate reaction. The lessons learned from the coating-based ASR mitigation processes led to a solid mineral additive that, when added to concrete in as little as 1% by weight prevented ASR expansion.

Several possible approaches were used to target the surface chemistry of ASR-prone aggregates to combat the subsequent detrimental harmful reactions. The simple solution is to coat their surface with an alkali-resistant coating. Such a coating process would need to be simple and inexpensive and would need to produce reasonably defect-free coatings to prevent ingress of alkali. A second approach attempted to steer the reaction of alkali with reactive silica towards the formation of a crystalline non-swellable product (aluminosilicate) via the deposition of aluminum hydroxide on the aggregate surface utilizing either a spray on approach with an

aluminum sol or polymer. The third approach to negating the ASR reaction was to pre-react the alkali-sensitive aggregate with an alkaline solution of certain select salts. In this manner, the potential for reaction with caustic can be quenched before incorporation into concrete. The key here is to form a reaction product that does not swell in the presence of moisture. The addition of lithium nitrate to concrete mixtures was previously developed for this goal but this procedure necessitates the use of excess lithium since it must be distributed throughout the cement at concentrations high enough to prevent ASR at the aggregate surface. In this investigation, we deliberately promoted the formation of either lithium or calcium silicates on the surface of aggregates.

# Introduction

## Problem

Alkali-silica reaction (ASR) is the source of serious durability problems in concrete because of its ability to crack the concrete and compromise the impermeability of the concrete.<sup>1,2</sup> Once concrete loses its impermeability other durability problems can occur such as freeze thaw damage or corrosion that leads to permanent damage and even structural failure. Typically it can take ten to fifteen years before ASR damage shows surface damage for a concrete structure. However, in Texas damage has been seen in less than 6 months. The formation of ASR gel can take some time since the high alkali pore solution must attack and break down the silica rich surface of the aggregates. The resultant gel that forms between the transition between the aggregates and the cement paste is not damaging unless it absorbs water. However, once it begins to absorb water and cause cracking additional water can then enter the system and cause more ASR expansion. As a result of this, very little warning is given before damage can become extensive.

According to a recent report by Williams *et al.* concrete bridge structures in the USA have been experiencing an unusually high level of premature concrete deterioration caused by ASR.<sup>3</sup> The characteristic damage was longitudinal cracking along the bottom flange of the beam ends of prestressed girders, cracking in unreinforced areas of cast-in-place concrete, and general map cracking with discoloration on concrete surfaces. For example, in the last two years, four concrete bridges along Harris County, Texas' toll road system have developed telltale cracks that are costing millions to repair.<sup>4</sup>

Thus, the presence of ASR places a heavy toll on highway safety, the lifetime of highway infrastructure, and the cost of construction and maintenance of transportation infrastructure. This is a worldwide problem that requires a facile, highly effective, and inexpensive solution that does not impact other properties of the concrete. Targeting the problematic aggregate with surface treatments to produce ASR-resistant construction

materials is an extremely viable method for preventing ASR and saving millions in transportation infrastructure costs.

### **Background and Proposed Technology**

All of the mechanisms of ASR are still not completely understood. However, the following description provides the current understanding. ASR occurs when high alkali cements and siliceous aggregates are used in conjunction. The high inherent pH of pore solution in concrete (around 13.5) causes the non-ordered silica at the surface to be dissolved. The available alkali in the system then starts to react with the silica released from the aggregates. This reaction causes the formation of a gel around the aggregate, often referred to as an ASR gel. When external or internal moisture reaches the gel, there is typically expansion, followed by cracking if the pressure exceeds the tensile capacity of the concrete (Figure 1). As the concrete cracks, the ASR gel progresses into these cracks and can cause further cracking as it expands. Eventually, this cracking will reach the surface of the concrete leading to telltale map cracking pattern (Figure 2) and surface staining.

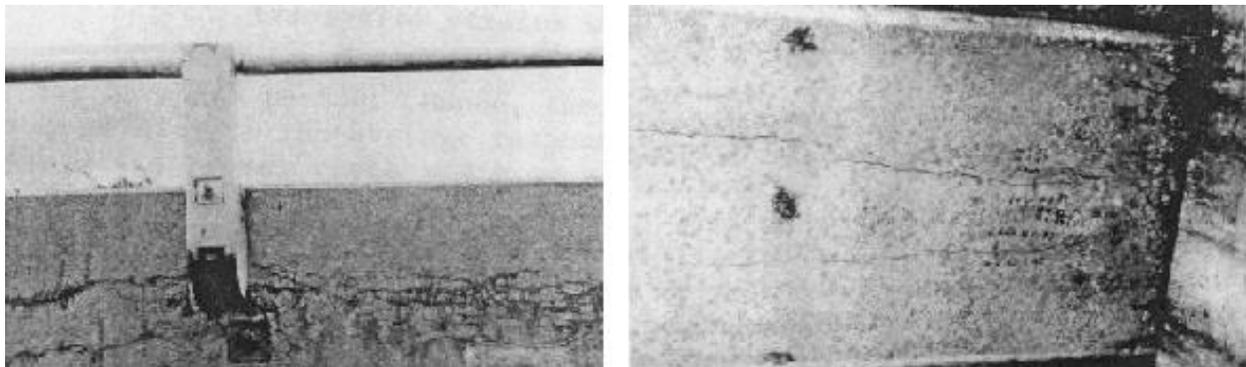


Figure 1: Severe Cracking Caused by ASR on the Susan River Bridge<sup>5</sup>



**Figure 2:** Severe ASR Damage<sup>6</sup>

The following schemes have been historically used to control ASR:

- Limit the amount of alkali in the concrete
- Limit the reactive silica in the aggregates
- Limit the moisture available to the system
- Control the ability to bind alkali
- Control the behavior of the ASR gel

To limit the amount of alkali in the concrete, producers try to use a low alkali cement of less than 0.6% of  $\text{Na}_2\text{O}$  equivalents ( $\text{Na}_2\text{O} + 0.658 \text{K}_2\text{O}$ ). Sometimes aggregates or other admixtures also provide alkali to the system. While the alkali limit is different for different aggregate types, most specifications suggest that the total alkali content is limited to four pounds per cubic yard if ASR is expected to be a problem.

The most typical solution to prevent ASR is for a producer to select an aggregate source that has been shown to not have ASR problems. However, this aggregate may not be available from a convenient source and may have to be shipped a far distance contributing a large expense to the project. Many kinds of aggregates had been found to be alkali-reactive since the alkali-silica reaction was first identified as a cause of

concrete deterioration.<sup>7</sup> The most reactive types of silica are disordered forms, such as opaline silica and volcanic glass.<sup>2</sup>

Another option is to limit the moisture available to the system. There are two approaches to this problem. Coatings can be applied to protect the concrete from moisture after the concrete has hardened and is in service. Another solution is to produce concrete with low permeability. This low permeability will provide a barrier to keep the moisture out. One way to achieve a low permeable concrete is through a good curing process or the use of mineral admixtures.

Another technique to combat ASR is to combine the alkalis in different hydration products. This is typically done by using pozzolanic supplementary cementitious materials (SCMs). These products form a secondary hydration product with calcium hydroxide, the alkalis in the pore solution, and reactive silica from the SCM. The most common pozzolanic SCMs used in concrete are slag and Class F fly ash. Both of these materials are waste products from the production of steel and the combustion of coal respectively. With this solution the performance of the concrete can be greatly increased for a small modification of the mixture. These modifications typically lead to improvements in sustainability, economy and a reduction in the long term permeability in addition to the binding of the alkalis that cause ASR problems. The reduction in permeability will also help to keep moisture out and increases the overall durability of the concrete. Class C fly ash has also been shown to have the ability to bind alkalis; however, higher amounts of Class C fly ash are necessary because of the higher CaO content. It is hypothesized that the higher calcium to silicon ratio of the amorphous phases in the Class C fly ash make it less effective in binding alkalis.<sup>8</sup>

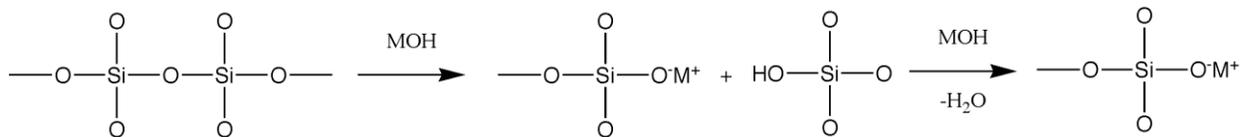
The ASR gel can also be controlled through the use of lithium nitrate ( $\text{LiNO}_3$ ).<sup>9</sup> This chemical when used in high amounts seems to stop the expansion of the ASR gel. A lithium treatment can be used before or after the concrete has been cast. The lithium seems to react with the ASR gel and stop all expansion. As stated earlier the

fundamental mechanisms is still not understood and the cost of lithium nitrate is significant.

## Objectives and Scope

### Inert Barrier Coatings on Aggregate

The first step of the ASR is the scission of siloxane networks in aggregates by hydroxide ( $\text{OH}^-$ ) ions to generate alkali silicate and silicic acid (Scheme 1). The latter is a weak acid that immediately reacts with additional  $\text{OH}^-$  ions to convert to more alkali silicate. Therefore, a protective barrier coating for aggregates must prevent the initial attack by hydroxyl ions. There are many ceramic materials that are resistant to high pH (pore water in concrete has a pH of 13.5) and this investigation focused on two possibilities, titania and hydroxyapatite. The coating methods that were developed needed to meet the following requirements: simple, used inexpensive reagents, and produced strongly adherent coatings that are free of defects. They also must not impact the bond between the cement paste and the aggregate as this is important for the strength and long-term durability of the resulting concrete.



**Figure 3:** The Alkali-Silica Reaction (M = Na or K)

### Reactive Neutralization of ASR Reactivity of Aggregate Materials

As mentioned above, the actual composition of the gel that is generated by the alkali-silica reactions plays a major role in determining whether the product is innocuous or whether it can swell and cause concrete deterioration. For example, the presence of lithium in the gel nullifies swelling behavior and is the principle upon which the addition of lithium nitrate prevents ASR. In addition, gels that have either low or high calcium content were found to be non-expansive.<sup>2</sup> It is impossible to maintain a low calcium

content due to the high calcium content of pore water. However, conversion of the reactive silica on the surfaces of aggregates into stable calcium silicates could provide a facile method for prevention of ASR. The same is true for reacting the ASR-susceptible surfaces with lithium hydroxide – the procedure should be as effective as adding lithium nitrate to concrete but will require much less lithium since only the reactive sites will be targeted. The procedure that was used for these experiments was contacting an ASR-susceptible aggregate with solutions of saturated calcium hydroxide, aqueous lithium hydroxide, or aqueous barium hydroxide with mild agitation.

#### **Solid Additive for Prevention of ASR**

The lessons learned from the treatment of aggregates were utilized to identify a list of solid reagents that could possibly be blended into concrete to prevent ASR. These were tested and one material was identified that can prevent expansion due to ASR with loadings as low as 1% by weight.

# Accomplishments

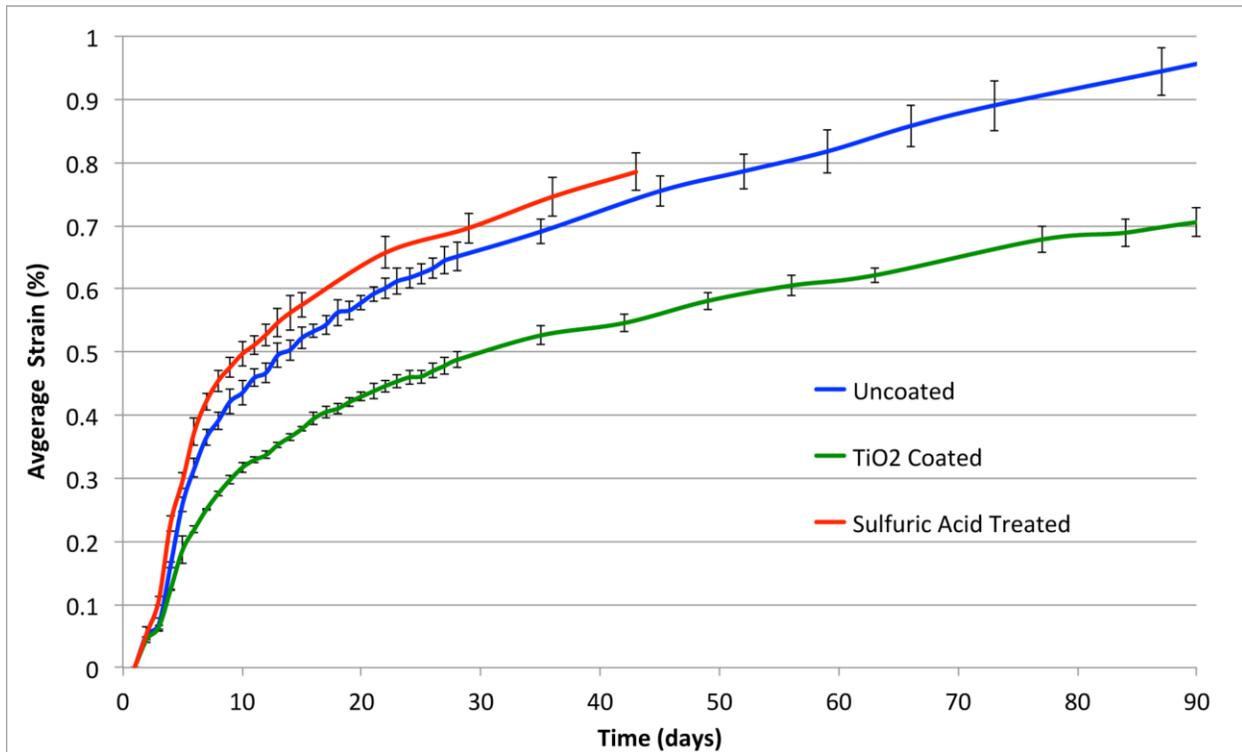
## Inert Barrier Coatings on Aggregate

There are several possible approaches that can be used to target the surface chemistry of ASR-prone aggregates to combat the subsequent detrimental harmful reactions. Perhaps the simplest approach is to coat their surface with an alkali-resistant coating. Such a coating process needs to be simple and inexpensive and must produce reasonably defect-free coatings to prevent ingress of alkali. One potential coating for this purpose that was investigated was titanium dioxide (also called titania). A procedure was developed in which titania was deposited by a solution growth process from a metastable solution of titanyl sulfate. Titanyl sulfate was dissolved in refluxing water and sulfuric acid and the resulting solution was cooled to room temperature. Heating this mixture to 80°C causes it to slowly precipitate titanium dioxide that formed a coating on the vessel walls and glass slides suspended in the solution. In order to coat an ASR-causing sand (Jobe sand) the sand and the solution growth solution were placed in hybridization tubes and these were placed on a rotisserie in a hybridization oven at 80°C for 24 hours. The coated sand was characterized by X-ray fluorescence spectroscopy that showed a significant increase in the concentration of titanium while X-ray photoelectron spectroscopy showed that the predominant surface species on the sand were titanium and oxygen. In order to test for any effect that sulfuric acid might have on the sand, the Jobe sand was treated in the same manner as was used for the titanyl sulfate process but with the substitution of sulfuric acid in approximately the same concentration as the titanyl sulfate solution.

The “Accelerated mortar bar test”, ASTM C 1260, was used to investigate the performance of the aggregates in concrete. This test serves as a baseline as it is widely accepted, and provides results within 14 days. In it, mortar bars are created and stored in 1 N NaOH at 176 °F. The bars are removed from the test containers at designated times and their length is measured. As ASR begins to progress through the bar the length increases. Although this test is typically only run for 14 days the length of the test was expanded in this research to determine how long the designated coatings

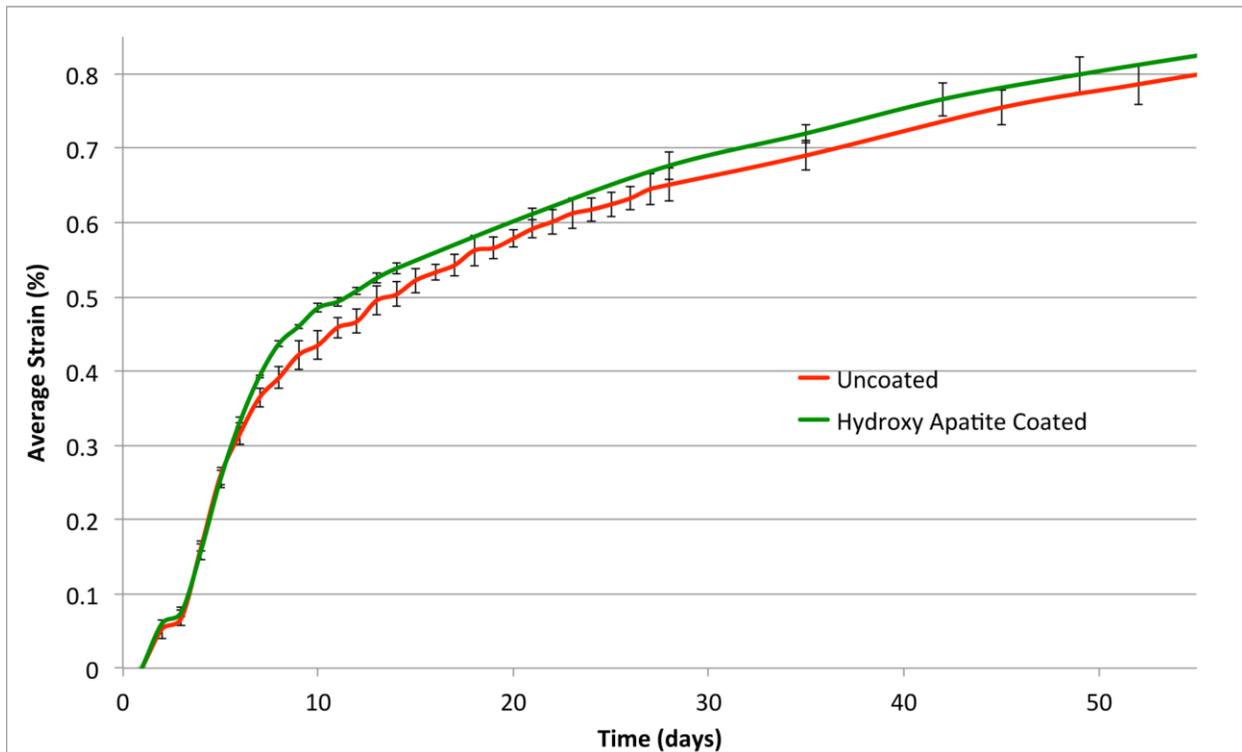
can survive in this extreme environment. The results for the titanium-treated sand, uncoated sand, and sulfuric acid treated sand are shown in Figure 1. It can be seen that the titanium dioxide coating markedly reduced the expansion due to ASR. For example at 40 days, the concrete with the titania coated aggregate had undergone an expansion of 0.52% while the control sample expanded by 0.74%. At 90 days, the expansions were 0.63% versus 0.96%, respectively. Thus, a 34% reduction in expansion was achieved. This effect was not caused by the sulfuric acid present since the treatment with sulfuric acid produced an aggregate that caused slightly higher ASR as compared to the untreated control sample (0.78% at 40 days). Since ASR was slowed down but not arrested thicker coatings were investigated but, surprisingly, these performed worse than the uncoated Jobe sand – indeed the greater the amount of titania, the worse the performance beyond the initial improvement. The possibility that this unusual result could be caused by the sulfuric acid was tested by utilizing a sol-gel procedure in which titanium dioxide was coated on the aggregate surface by coating it with a titanium isopropoxide/butanol/acetic acid mixture and then allowing the coating to hydrolyze in the air. In ASR testing, this specimen performed almost identically as the untreated sand despite the fact that a thick continuous film of titania was present on the aggregate particles. We are forced to conclude that we may have discovered a new ASR-like reaction that involves titania – that could perhaps be termed alkali titania reaction (it is too bad the acronym ATR is already taken). If so, this could be an important consideration for aggregates used to prepare concrete. To test this hypothesis, we performed ASR testing with rutile sand (rutile is the most common mineral form of titanium dioxide) replacing the Jobe aggregate. No expansion was observed so the effect must be due to amorphous titania or perhaps the anatase phase of titanium dioxide.

The fact that a small amount of titania does produce protection against ASR can only be explained by some specific reaction between the titanyl sulfate solution and the siliceous phases that lead to the alkali silica reaction. While this is interesting, it would be impractical to use this as a treatment process for prevention of ASR since getting the correct dose would be difficult.



**Figure 4:** ASR Test Results for Mortar Bars Produced Using Titania-Coated Aggregate.

Another protective coating process that was developed was the deposition of hydroxyapatite,  $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ , the mineral component of bone. The reason for selection of this material is 2-fold, one is as a protective coating, and the second is the possibility that, if silicophosphate minerals form in the concrete due to the presence of phosphate ions, alkali metals will be consumed as counterions into a non-expansive mineral phase (e.g.  $\text{MSiPO}_4$ ). Coatings were prepared by dipping glass slides in a concentrated calcium nitrate solution and then into a diammonium phosphate solution. These coatings were found to be both thick and strongly adherent to the silica surface. Therefore, Jobe sand was first saturated with a calcium nitrate solution and then immersed into a diammonium phosphate solution. The formation of a uniform calcium phosphate coating could be seen visually. The resulting material was subjected to the ASR Mortar Bar test and was found to be equally expansive to the control sample. Thus, hydroxyapatite coatings completely failed to halt the progression of ASR. It is suspected that this is due to poor coating quality and a lack of affinity of hydroxyapatite for growth on and adhesion to the ASR-prone silica phases.



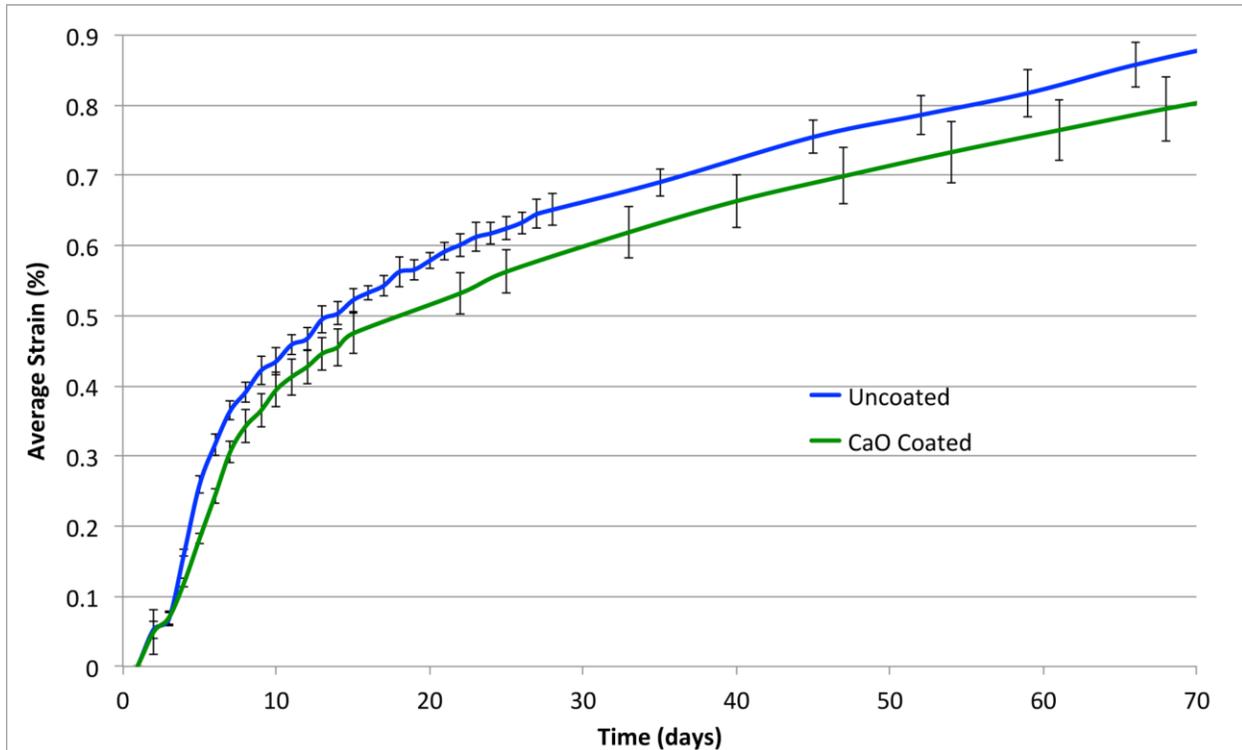
**Figure 5:** ASR Test Results for Mortar Bars Produced Using Hydroxyapatite-Coated Aggregate

### Reactive Neutralization of ASR Reactivity of Aggregate Materials

A second approach to preventing ASR is to pre-react the alkali-sensitive aggregate with an alkaline solution of certain select salts. In this manner, the potential for reaction with caustic can be quenched before incorporation into concrete. The key here is to form a reaction product that does not swell in the presence of moisture. The addition of lithium nitrate to concrete mixtures was previously developed for this goal but this procedure necessitates the use of excess lithium since it must be distributed throughout the cement at concentrations high enough to prevent ASR at the aggregate surface. In this investigation, we deliberately promoted the formation of lithium or calcium silicates on the surface of aggregates. It has previously been demonstrated that ASR gels that are high in calcium are not swellable so the reaction of aggregate with calcium hydroxide is expected to be another approach to prevent cracking of concrete caused by ASR. Therefore, we tried a reaction of 200 ml of saturated calcium hydroxide solution with 150 g of Jobe sand at 80°C using the hybridization tube procedure described above. Within 24 hours, all of the calcium had been consumed.

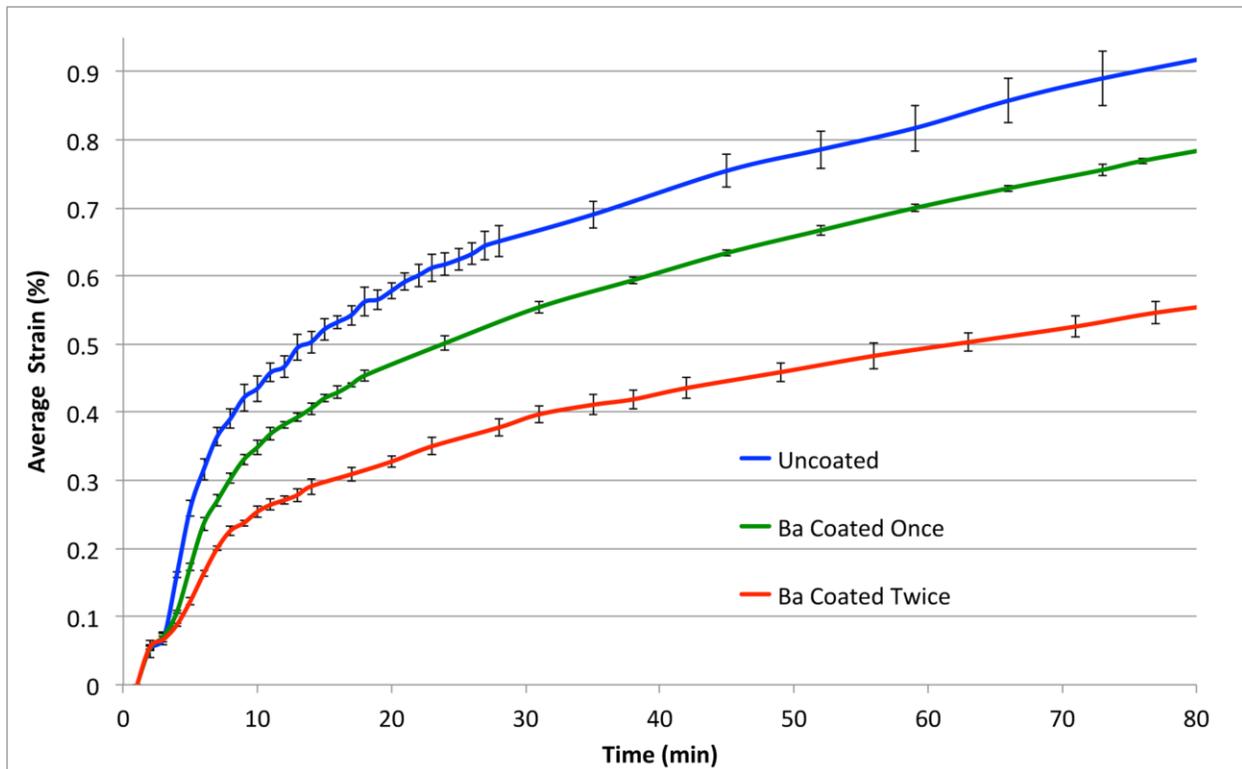
Since calcium hydroxide is not very soluble (0.173 g/100 ml @ 20°C), this reaction only deposited a small amount of calcium on the surface of the sand but even that little bit had a favorable impact on the performance of concrete prepared from the treated sand in ASR testing. Expansion of a mortar bar made with the treated aggregate lagged behind the expansion of a concrete sample produced from uncoated sand for up to 10 days. Thereafter, it performed identically with the control sample, within the experimental standard deviation. It was concluded that the calcium treatment will indeed prevent ASR but the reaction with calcium hydroxide needs to be more complete. Making this reaction go to completion can take a lot of calcium hydroxide solution – sequential reactions performed on sand samples as described above still remove all of the calcium from solution after 25 experiments. This corresponds to the uptake of 8.6 g of  $\text{Ca}(\text{OH})_2$  and the reaction of about 4.6 % of the sand (assuming it is pure  $\text{SiO}_2$ ) A sufficient amount of this material was prepared to perform ASR testing. The results, shown in Figure 6, are highly promising. The percent expansion versus time curves show a sharp increase for the first 10 days that then changes to a slower linear change with time. After 3 days, the expansion of the bar with the treated aggregate begins to lag behind the control. After 75 days its expansion is 0.75% versus 0.90% for the control. Overall, there was a 17% reduction in expansion after 75 days for concrete bars treated with calcium hydroxide versus bars containing pristine aggregate.

An attempt was made to treat aggregate with a stoichiometric amount of solid calcium hydroxide in water. It was thought that as the reaction progressed the solid calcium hydroxide would dissolve in accordance with Le Chatelier's principle. However, this led to formation of a cemented monolith rather than treated powder. This result certainly demonstrated the high reactivity of Jobe sand towards alkali but, unfortunately, negates the possibility of using this method to convert ASR-reactive aggregate to non-reactive aggregate. The result does raise the question as to whether addition of calcium hydroxide into a concrete mixture might mitigate or prevent the alkali silica reaction



**Figure 6:** ASR Test Results for Mortar Bars Produced Using Calcium Hydroxide Treated Aggregate

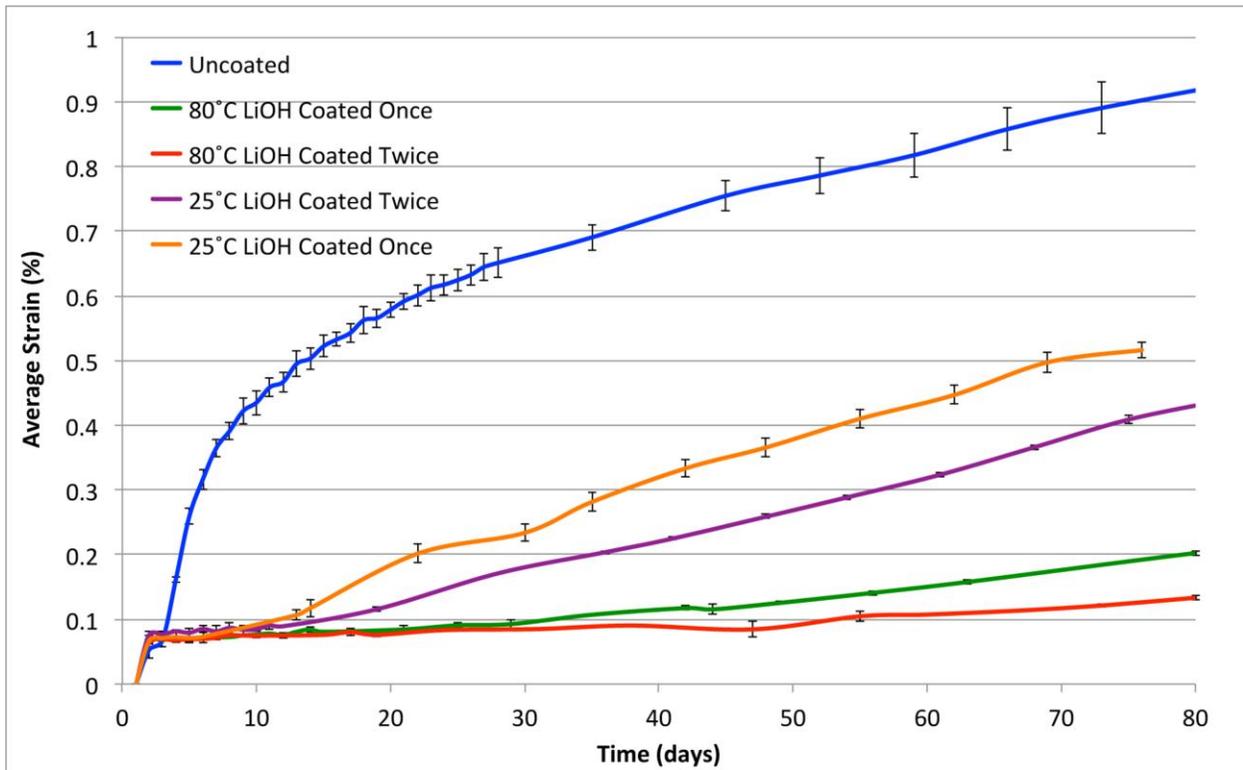
It was decided to perform reactions with barium hydroxide since barium hydroxide has the advantage that it is highly water-soluble so it is easy to react sand with an excess of it. It was found that such reactions deposit an approximate 25% by weight of barium onto the sand corresponding to reaction of approximately 10% of the sand (assuming the sand is 100% silica). It was found that good performance was realized in the ASR tests after a single treatment while a second treatment gave even better results as shown in Figure 7. After 85 days, the expansion of the mortar bar containing twice-treated was 0.46%, that of the bar with aggregate subjected to a single treatment was 0.80%, and that of the control was 0.94%. Thus, treatment of the aggregate twice with 1M barium hydroxide reduced the expansion due to ASR by 51% - more than halving it.



**Figure 7:** ASR Test Results for Mortar Bars Produced Using Barium Hydroxide Treated Aggregate

The addition of lithium nitrate to concrete mixtures was previously developed for this goal but this procedure necessitates the use of excess lithium since it must be distributed throughout the cement at concentrations high enough to prevent ASR at the aggregate surface. In this investigation, we are deliberately promoting the formation of lithium or calcium silicates on the surface of aggregates. 100 grams of Jobe sand (an ASR susceptible aggregate) was placed in each of 12 plastic bottles and then 115 mL of 2M LiOH solution was added to each bottle. The bottles were then placed in an 80°C rotisserie oven for 4 days. After the 4 days the sand was taken out of the bottles and washed with tap water several times. Washing was then continued with deionized water until the conductivity meter read 500 (even after 30 minutes washing the conductivity would not go under 500). The sand was then dried overnight. This approach worked extremely well – heating for 24 hours at 80°C with an excess of lithium hydroxide solution produced an aggregate that showed zero expansion to ASR expansion!. The treatment was repeated at room temperature to determine whether ASR could be successfully inhibited under more facile treatment conditions. This did leave to significant

and adequate inhibition of ASR but not as good as the elevated temperature treatment. The results from the accelerated mortar bar testing for the lithium hydroxide treated aggregates are shown in Figure 8. The curve for the untreated sample (control) shows a sharp increase for the first 10 days that then changes to a slower linear change with time. By contrast, all of the lithium-treated samples show a more rapid expansion by 0.08% in 2 days where the expansion plateaus for 12 days. Beyond this, a gradual increase in expansion begins again with the slopes of the curves in the order one room temperature treatment > two room temperature treatments >>> one 80°C treatment > two 80°C treatments. After 75 days, the expansion of the mortar bar containing singly room temperature treated aggregate was 0.51%, that of the twice treated one was 0.42%, that containing the 80°C singly treated aggregate was 0.18%, and that of the twice 80°C treated aggregate was 0.12%, while that of the control was 1.0%. The elevated temperature treatment with lithium hydroxide works better but this is probably just a kinetic effect. Expansion due to ASR can be pretty much shut down using this process.

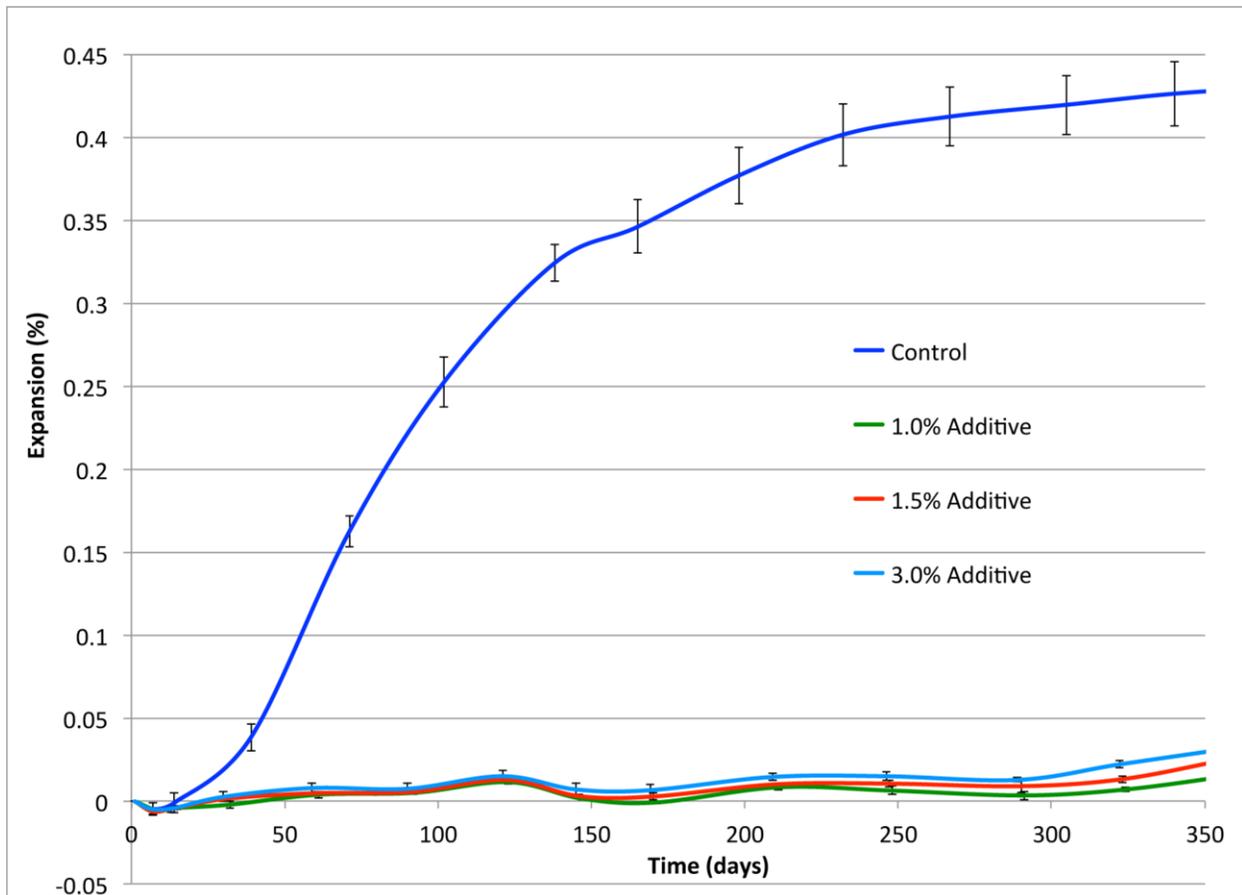


**Figure 8:** ASR Test Results for Mortar Bars Produced Using Lithium Hydroxide Treated Aggregate

## **Solid Additive for Prevention of ASR**

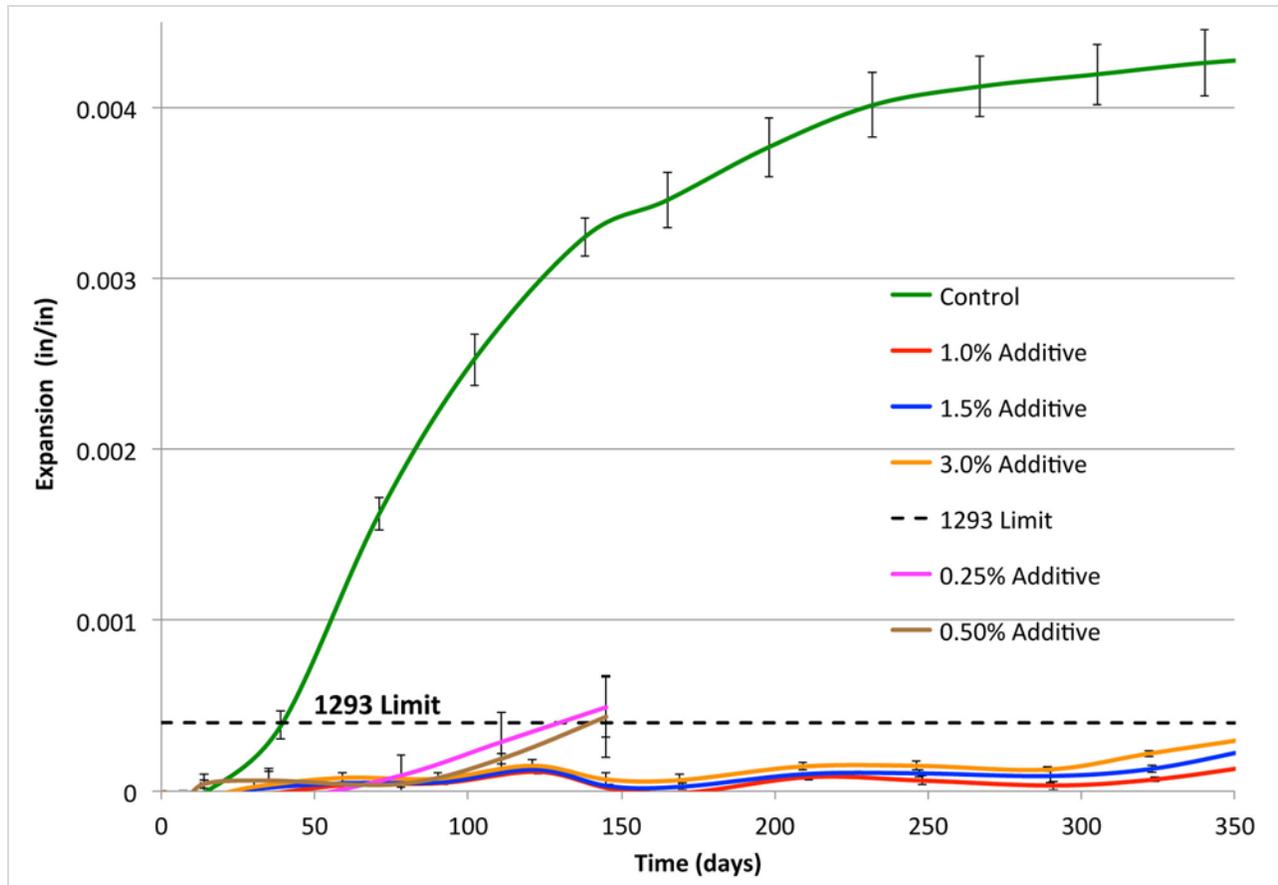
The lessons learned from the treatment of aggregates were utilized to identify a list of solid reagents that could possibly be blended into concrete to prevent ASR. These were tested and one material was identified that can prevent expansion due to ASR with loadings as low as 1% by weight. In the ASTM 1260 tests it was found that a loading with this mineral additive of 1% halted expansion for over 25 days while one of 5% completely shut down ASR. It should be noted that this test provides a very high continuous source of potassium hydroxide and is generally not run beyond 14 days so that the 1% addition of additive can be deemed to have passed this test. In the real world, the concrete will not have such an overwhelming supply of alkali. The ASTM 1293 test "Standard Test Method for Determination of Length Change of Concrete Due to Alkali-Silica Reaction provides a much better indication of the highly promising real world performance of this additive. Figure 9 shows the performance of concrete bars containing 1%, 3%, and 5% by weight of the additive by weight in the ASTM 1293 test performed over a period of a year. The results are presented as percent expansion versus time. Note that the control sample without any additive showed very high expansion compared to all of the samples that contained additive. After 1 year, it had reached 0.31% expansion while the additive-containing samples were all less than a tenth of that value.

One unusual feature of the results is the relative expansion of the additive containing samples is opposite the expected order. i.e. the 5% additive containing sample had the highest expansion while the 1% sample had the least. This could be due to the possibility that the mineral additive itself undergoes slight expansion as it reacts. If that is the case, there is likely to be an optimal amount of additive that balances the expansion of the additive with the maximum reduction of ASR expansion of the aggregate. Therefore, ASTM 1293 experiments were performed with 0.25% and 0.5% additive. The graphs of expansion versus time for all of the additive samples and controls are shown in Figure 9.



**Figure 9:** ASTM 1293 Results for Concrete Bars Containing ASR-Reducing Additive

Unfortunately, both of the concrete bars containing 0.25 and 0.5% by weight of additive were unable to pass the ASTM 1293 test (Figure 10). They exceeded the 1293 limit of an expansion of 0.0004 in per inch of bar after 145 days. On the other hand, the 1% additive-containing bar appears to be poised to pass the ASTM test when the second year of the test is completed.



**Figure 10:** Expanded ASTM 1293 Results for Concrete Bars Containing ASR-Reducing Additive

## Technology Transfer

An OSU invention disclosure has been filed on this research based on the solid additive for ASR prevention. We are in discussion with several concrete additive and cement companies concerning licensing this technology. Also, Oklahoma State University's Technology Development Center has provided funding to explore the commercialization of the additive.

## Summary and Conclusion

Several methods have been developed that prevent or mitigate alkali silica reaction. The most promising results were obtained for aggregate reacted with calcium, lithium, or barium hydroxide. However, since this technology would require large-scale chemical treatments of aggregate, the lessons learned from the direct reactions between aggregate and various metal hydroxide solutions were utilized to devise an additive that can effectively suppress alkali silica reaction in a loading of 1%.

The next step is development of a scaled up production method to produce the additive inexpensively and the exploration of similar additives that might perform well at even lower concentrations.

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