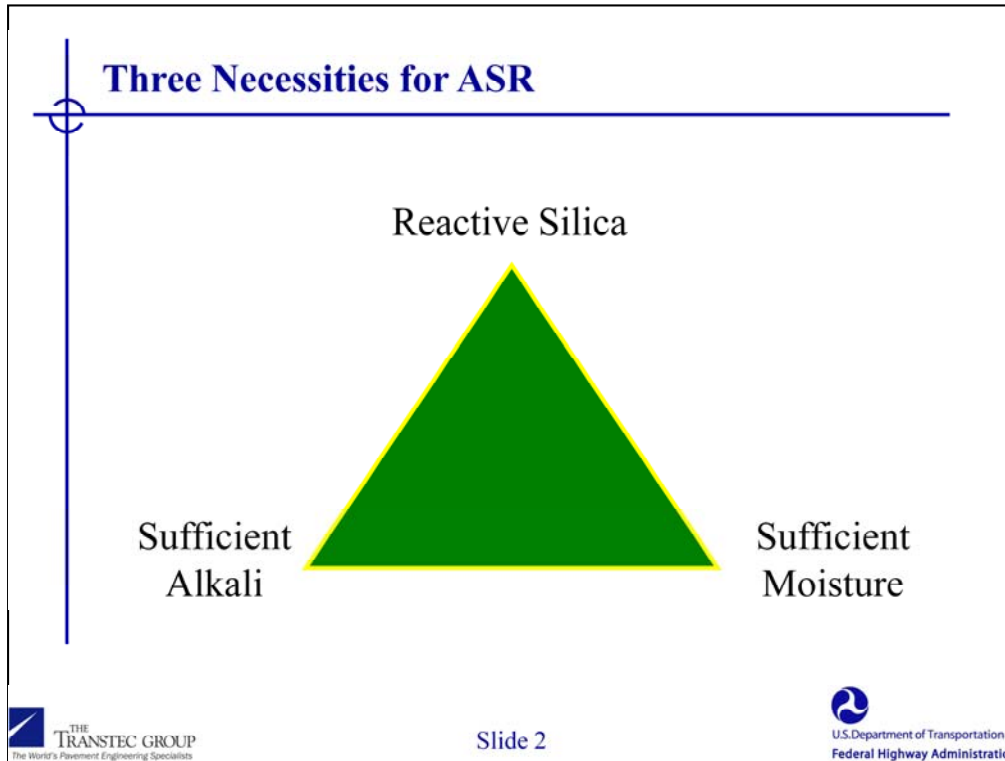


FHWA Workshop

Alkali-Aggregate Reaction

Session 05: Prevention of ASR





Remember from the presentation on “Fundamentals of ASR” we learned that there are three requirements for ASR expansion to occur; these are:

A sufficient quantity of reactive silica ... which is provided by the aggregate

A sufficient quantity of alkali ... which is supplied ... predominantly ... by the portland cement

And a supply of moisture during service

If we can limit one of these requirements ... we should be able to prevent damaging ASR from happening

Preventive Measures for ASR

- | Use of non-reactive aggregate
- | Use of low-alkali cement
- | Limit alkali content of concrete
- | Use of supplementary cementing materials
- | Use of suitable chemical admixtures

For a consideration of these three requirements we can produce a list of measures that might work

Use of a non-reactive aggregate ensures that there is insufficient reactive silica available in the concrete

We should really consider the second and third bullet together ... Limiting the alkali content of the concrete – perhaps through the use of low alkali cement – ensures that there is insufficient alkali for damaging ASR

The use of supplementary cementing materials can also be seen as a means for limiting the alkali content ... in a way ... although the use SCMs may not reduce the alkali content of the concrete it can reduce the availability of the alkalis for reaction ... this will be discussed later

The fifth bullet concerns the use of chemical admixtures – namely lithium-based compounds. This doesn't seem to be helpful in reducing any of our three requirements for ASR ... in fact lithium is an alkali. However, lithium works by changing the path of the reaction as we will see later.

Note that limiting water is not on this list. Generally it is not practical to control the exposure condition of a civil-engineering structure such as a pavement or bridge. It might be our only option when dealing with an existing structure that already has ASR and therefore already contains a sufficient amount of alkali and reactive silica which can't be removed – but with new construction it is easier to adopt one of the measures listed here than to eliminate water.

Preventing ASR – Use of Non-Reactive Aggregate



Mactaquac Dam, New Brunswick, Canada

Aggregate passed ASTM C 227 – “non-reactive”

The use of a non-reactive aggregate is, perhaps, the most obvious strategy. However ... how sure are we that aggregate is really non-reactive. We have to put a great deal of faith in our test methods to tell us the correct answer. We looked at some of the symptoms of ASR in this structure in a previous presentation. Well the aggregate used for this structure was tested by appropriate test methods of the day – and was deemed to be non-reactive. Sixty years later the dam is 7 inches taller than when it started!!!!

Preventing ASR – Use of Non-Reactive Aggregate

- Aggregate may be incorrectly identified as “non-reactive” (e.g. “false passes” in ASTM C 1260 – AMBT)
- Aggregate reactivity may vary from a given source
- Some specifications require other preventive measures in addition to using “non-reactive” aggregate
- In some geographic locations – sources of “non-reactive” aggregates may be scarce
- Use of “non-reactive” aggregate may not be economically prudent

Of course – some of our more rapid tests fail a great many aggregates that are non-reactive and there may not be a suitable aggregate that passes this test in a given geographic area – so – in the absence of data from more reliable but longer-term tests – we have to assume the aggregates are reactive and adopt preventive measures if we want to use them.

In some locations most of the aggregates may really be reactive and there may be no choice but to use them with appropriate preventive measures

Preventing ASR – Use of Non-Reactive Aggregate



Mactaquac Dam, New Brunswick, Canada

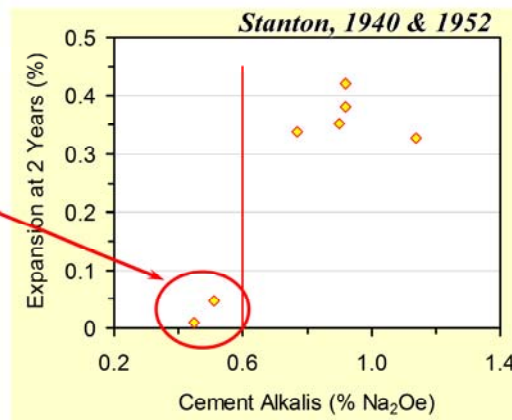
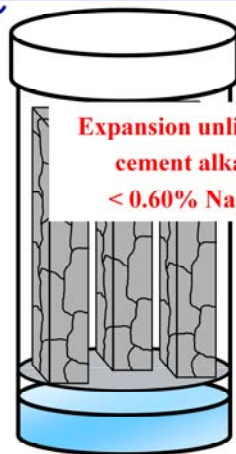
Concrete structures likely to be replaced ~ 2030

Owner wants to use the same reactive aggregate in the reconstruction!!

Returning to the ubiquitous Mactaquac Dam ... here is a structure that will be rebuilt in less than 20 years and the owners are considering using the same reactive aggregate once again.

The reason for this is one of economy ... rebuilding the concrete structures will require approximately half a million cubic yards of concrete or about three quarters of a million tons of aggregate. Sufficient aggregate will be produced by the excavation of bedrock required for the new structure and – although this same rock is responsible for the existing problems – we have to find a way to use it again.

Preventing ASR – Use of Low-Alkali Cement



This early work of Stanton defined the concept of “low-alkali cement” and it is still generally believed today (wrongly so) that the use of such cement is a sufficient measure to avoid damaging ASR

Stanton developed the first expansion test for ASR. He produced mortar bars using different cements and various reactive aggregates and measured the expansion of these bars when exposed to moisture.

He found that the expansion with a particular aggregate was strongly influenced by the alkali content of the cement. Typical expansion results after 2 years are shown for mortar bars made with a highly reactive sand from Ventura County, California.

Excessive expansion and cracking of the mortar bars only occurred with cements with alkali contents in excess of 0.7 percent N-A-2-O-E.

It was from this work that in 1940 – Stanton made the recommendation that damaging ASR was unlikely provided that the cement alkalis were below 0.6% sodium equivalent.

This defined the classification of low-alkali cements in the United States – low-alkali cements being cements with less than or equal to 0.6% equivalent alkalis.

Many jurisdictions in the U.S. still specify the use of low-alkali cement as means of preventing damaging ASR. As we will see later in the course, such a measure is NOT sufficient to guarantee that damage does not occur.

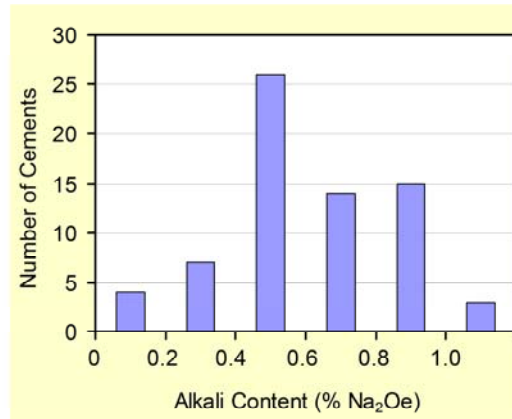
Preventing ASR – Use of Low-Alkali Cement

Alkali Contents of North American Cements

Alkali contents of 69 sources of Type I cement in North America
(from Gebhardt, 1995)

37 of 69 cements < 0.60% Na₂Oe

32 of 69 cements > 0.60% Na₂Oe



This slide shows the breakdown by equivalent alkali of 69 sources of Type one Portland cement from the United States – Canada – and Mexico. The equivalent alkalis can range anywhere from 0.1 percent to 1.2 percent with just under half the values being higher than 0.60% equivalent alkalis

Preventing ASR – Use of Low-Alkali Cement



Dam constructed with low-alkali cement

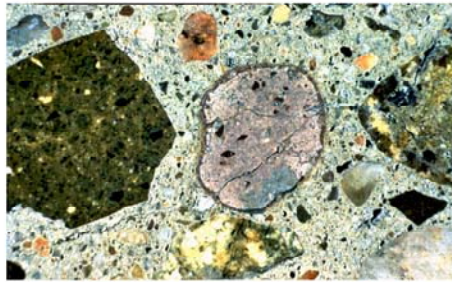
Pavement constructed with low-alkali cement



There are a number of structures that have suffered from ASR despite the use of low-alkali cement

Preventing ASR – Use of Low-Alkali Cement

- Stark, 1978
- Cracking in a 12-year-old pavement near Albuquerque
- Cement $\leq 0.48\%$ Na_2Oe



This is a well-known case of a pavement constructed with a cement with less than half a percent of alkalis

Preventing ASR – Use of Low-Alkali Cement

Bailey Tremper, 1960, State of California Department of Public Works Division of Highways

1958 distress due to AAR in 6 bridges on Route 395

Cements used were 0.55 to 0.60% Na₂Oe

Cracking in pavements & other structures in SE Wyoming

Cement ~ 0.50 to 0.60% Na₂Oe

Aggregate passes ASTM C 227 criteria with low- & high-alkali cement

Stark, 1978

A review of the literature will show that this is not an isolated case

Preventing ASR – Limiting Alkali Content of Concrete

It is now fairly well established that it is the alkali content in the concrete and not just the alkali content of the cement that influences the risk of damaging reaction for a particular aggregate. The concrete alkali content is calculated as follows:

$$\text{Concrete alkali content} = \text{Cement content} \times \text{Cement alkalis} \times \frac{1}{100}$$

$\text{lb/yd}^3 \text{ (kg/m}^3\text{) Na}_2\text{Oe}$ $\text{lb/yd}^3 \text{ (kg/m}^3\text{)}$ $\% \text{ Na}_2\text{Oe}$

Example:

If a concrete contains 600 lb/yd³ of Portland cement and the cement has an alkali content of 0.78% Na₂Oe then the alkali content of the concrete is:

$$= \frac{600 \times 0.78}{100} = 4.68 \text{ lb/yd}^3 \text{ Na}_2\text{Oe}$$

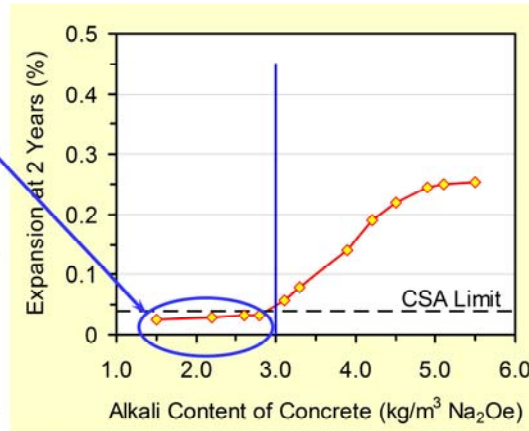
We now know that we have to control the alkali content of the concrete not JUST the alkali content of the cement ... this was discussed earlier

Preventing ASR – Limiting Alkali Content of Concrete

Effect of Alkali Content on Expansion of Concrete

Expansion unlikely
if alkali content of concrete
< 3.0 kg/m³ (5 lb/yd³)

The threshold alkali content – above which deleterious expansion occurs – varies with the type of reactive aggregate. Under field conditions expansion has been observed in concrete with less than 3 kg/m³ (5lb/yd³) Na₂Oe



There is a threshold alkali content below which expansion may not occur with a given aggregate – this threshold will vary from one aggregate to another.

Currently there is no test method for determining the threshold alkali level for a given aggregate and – as discussed previously – aggregates will generally react and cause expansion and cracking at lower alkali contents in the field than are required in laboratory tests such as the concrete prism test

Preventing ASR – Limiting Alkali Content of Concrete

Concrete Blocks with Jobe Sand – University of Texas



Cement alkalis = 6.65 pcy Na_2Oe

Companion concrete
prisms **expanded**



Cement alkalis = 3.64 pcy Na_2Oe

Companion concrete prisms
did NOT expand

Remember this example that was used before – blocks expand in the field with less than four pounds per cubic yard of alkali – but concrete prisms from the same mix do not expand in the laboratory

Preventing ASR – Limiting Alkali Content of Concrete



Concrete alkali content $< 3 \text{ kg/m}^3 \text{ Na}_2\text{Oe}$

Examples of ASR in concrete structures produced with low-alkali content



Concrete alkali content $< 2 \text{ kg/m}^3 \text{ Na}_2\text{Oe}$



Concrete alkali content $< 2 \text{ kg/m}^3 \text{ Na}_2\text{Oe}$

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 U.S. Department of Transportation
Federal Highway Administration

Here are some more examples of ASR in a dam with less than 3 kg or 5 pounds of alkali

-another dam with less than 2 kg or just slightly more than 3 pounds

-And a pavement with less than 2 kg or 3 and a half pounds of alkali per cubic metre of concrete

In Canada – a range of alkali limits are used depending on the type of aggregate and the nature of the structure and its exposure condition

Preventing ASR – Limiting Alkali Content of Concrete

Methods for Evaluating the Effect of Cement Alkalis
on Expansion due to ASR

- Laboratory-size specimens require more alkali to initiate ASR expansion than large field-exposed blocks (or structures) to compensate for alkali leaching during test
- Currently there is no standard test method for evaluating job mixes containing low-alkali cement
- Many specifications and guidelines impose limits based on field experience

AASHTO PP65 alkali limit: 3.0 to 5.0 lb/yd³ Na₂O_e

Depending on “Risk of ASR” & “Class of Structure”

As a consequence of this ... specifications such as the Canadian spec and the more recent AASHTO (ash-toe) recommended practice base alkali limits largely on field experience – in AASHTO the actual limit varies from 3 to 5 pounds depending on the risk of asr and the nature of the structure – this will be explained later

Preventing ASR – Limiting Alkali Content of Concrete

Methods for Evaluating the Effect of Cement Alkalis
on Expansion due to ASR

- Laboratory-size specimens require more alkali to initiate ASR expansion than large field-exposed blocks (or structures) to compensate for alkali leaching during test
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AASHTO PP65 alkali limit: 1.8 to 3.0 kg/m³ Na₂O_e

Depending on “Risk of ASR” & “Class of Structure”

SI alternative to previous slide

As a consequence of this ... specifications such as the Canadian spec and the more recent AASHTO (ash-toe) recommended practice base alkali limits largely on field experience – in AASHTO the actual limit varies from 1.8 to 3 kilograms depending on the risk of asr and the nature of the structure – this will be explained later

Preventing ASR – Use of SCMs

SCM – Supplementary Cementing Materials

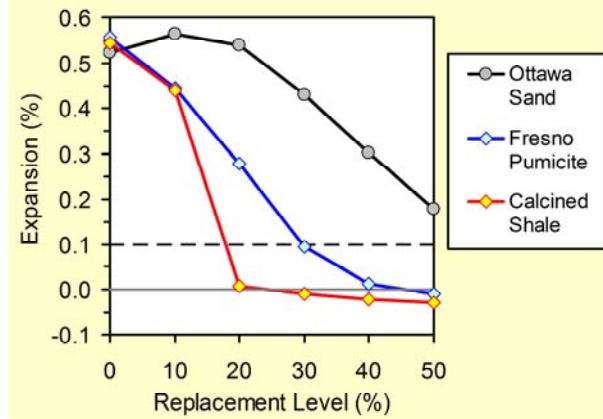
- Fly Ash
- Slag
- Silica Fume
- Natural Pozzolans

Ok so what about s-c-m's (ess-see-ems)

Commonly used SCMs in North America include fly ash – ground granulated (iron) blast-furnace slag – silica fume and various natural pozzolans such as calcined clay or shale – such as metakaolin ... and occasionally some volcanic ash and other materials

Preventing ASR – Use of SCMs

Effect of Natural Pozzolans (Stanton, 1940; 1952)



Pozzolans had an effect beyond that of an inert diluent

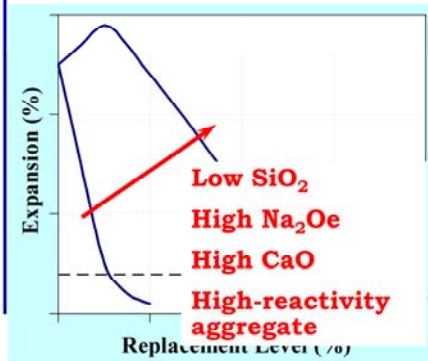
Thomas Stanton recognized the possibilities of using pozzolans to control ASR in his seminal paper in 1940. In this and later work he showed that the impact of pozzolans went beyond the effect of merely diluting the cement alkalis in the mix.

Preventing ASR – Use of SCMs

Fly Ash
Slag
Silica Fume
Natural Pozzolans

Almost all sources of these materials are effective in controlling ASR

Providing they are used in sufficient quantity



Amount of preventive required depends on:-

- Composition of material (esp. Na_2Oe , SiO_2 , CaO)
- Available alkali in the system
- Nature of the reactive aggregate

[Not to instructor: animation used in the slide]

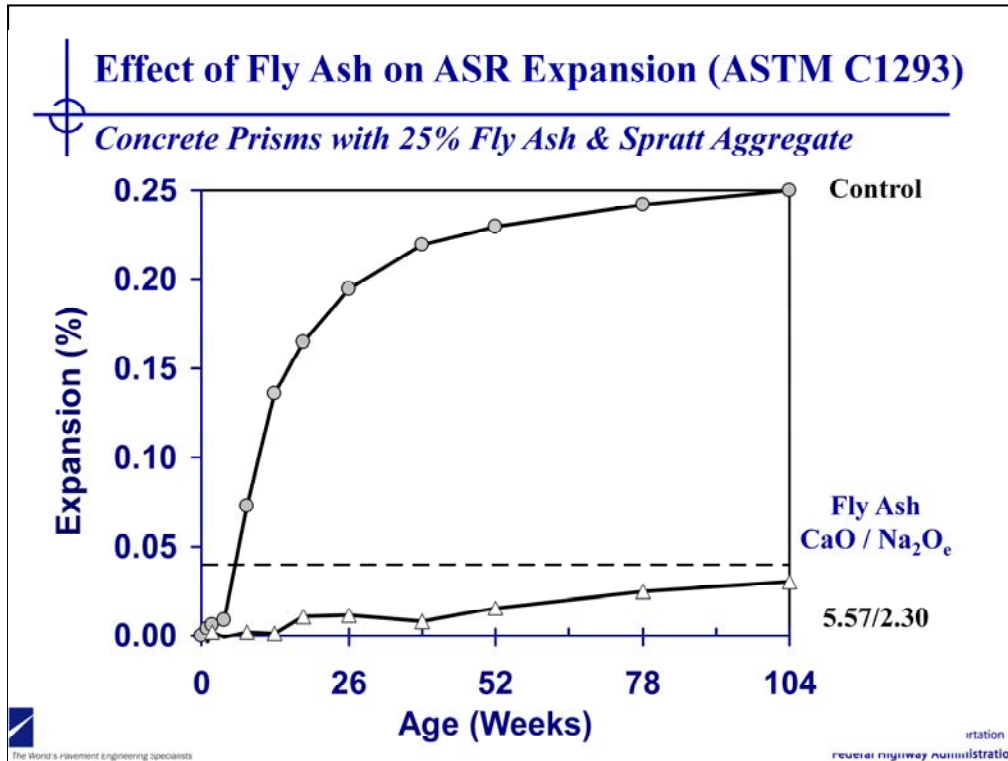
SCMs include fly ash, slag, silica fume and natural pozzolans and almost all sources of these materials can be used to control ASR provided they are used in sufficient quantity – so the question is – “How much is enough?” – to which the answer is ... “It depends!”

What does it depend on? Well of course it depends on – among other things – the composition of the SCM itself.

Paradoxically – the main parameter that effects the efficiency of an SCM in terms of controlling ASR is the amount or reactive silica in the SCM. Those with a lot of silica – like silica fume – will behave like the left hand curve reducing expansion to a safe level at relatively low levels of replacement – such as 10 to 15% for silica fume. Those SCMs with lower amounts of silica and more calcium – such as Class C fly ash or slag – have to be used at much higher replacement levels (maybe 50% or more) to control expansion – like the right hand curve.

The alkali content of the SCM is also important – those with higher alkali contents tend to be less effective.

In addition to the composition of the SCM itself – the other parameters that affect the amount of SCM you need are the reactivity of the aggregate and the amount of alkali in the system – basically as the aggregate reactivity increases or as the amount of alkali in the system increases – so too does the level of SCM required.



OK – lets look at some real data – this shows the expansion with time – up to 2 years – for concrete prisms produced with a reactive siliceous limestone – the Spratt aggregate.

The control samples with no SCM expand rapidly exceeding the commonly-used expansion limit of zero-point-zero-four percent after a month or so. Partial replacement of 25% of the cement with a typical low-calcium Class F fly ash is extremely effective in reducing expansion even though the fly ash itself contains more alkali than the portland cement it replaces.

Effect of Fly Ash on ASR Expansion

Long-Term Performance of Fly Ash Well-Established by Exposure-Site Studies

Control Concrete (no Fly Ash)



Concrete with 25% Fly Ash



Appearance of 1 cubic-yard blocks after 18 years on exposure site at the Building Research Establishment (BRE) in the U.K.

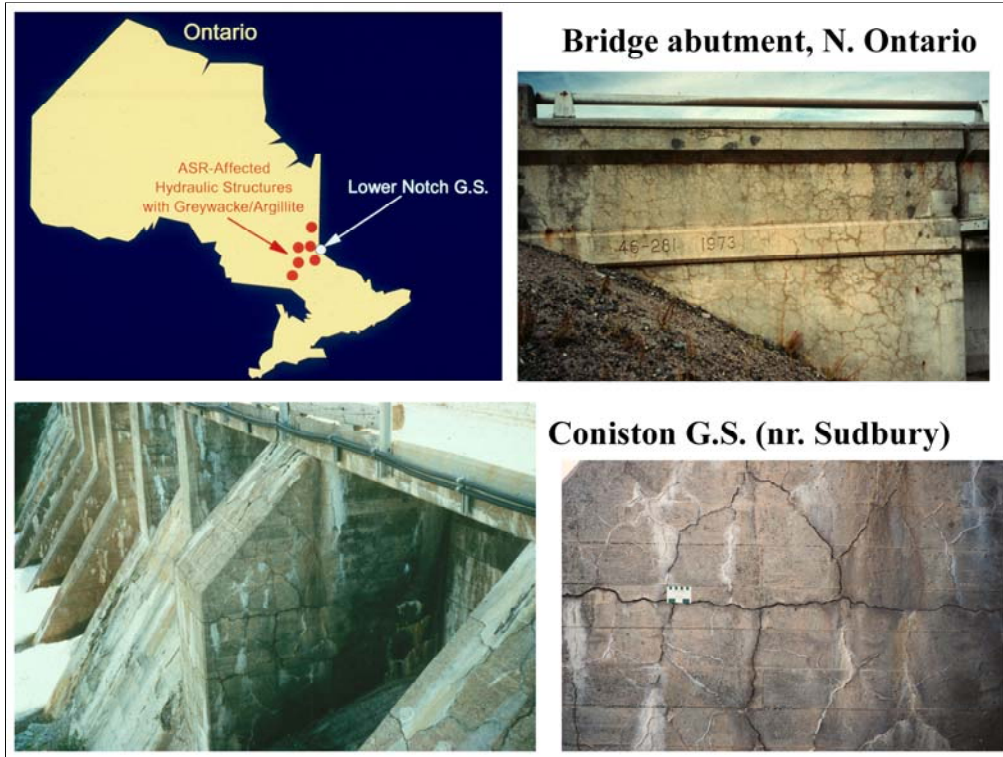
The efficacy of low-calcium, Class F fly ash has also been well-established by exposure site studies ... such as this one in the UK. These blocks are each a cubic yard of concrete – the control sample on the left exhibited deleterious expansion and cracking after about 5 years and was extensively cracked at 18 years. The block on the right has the same amount of portland cement plus 25% fly ash – no expansion or cracking was in evidence when it was inspected at 18 years.

Preventing ASR – Use of Fly Ash

Lower Notch Dam, Built ~ 1970

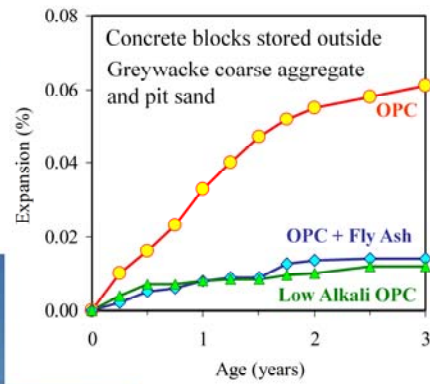


The long-term beneficial effect of fly ash has also been established by field performance. This slide shows the Lower Notch Dam in Ontario – which was complete around 1970

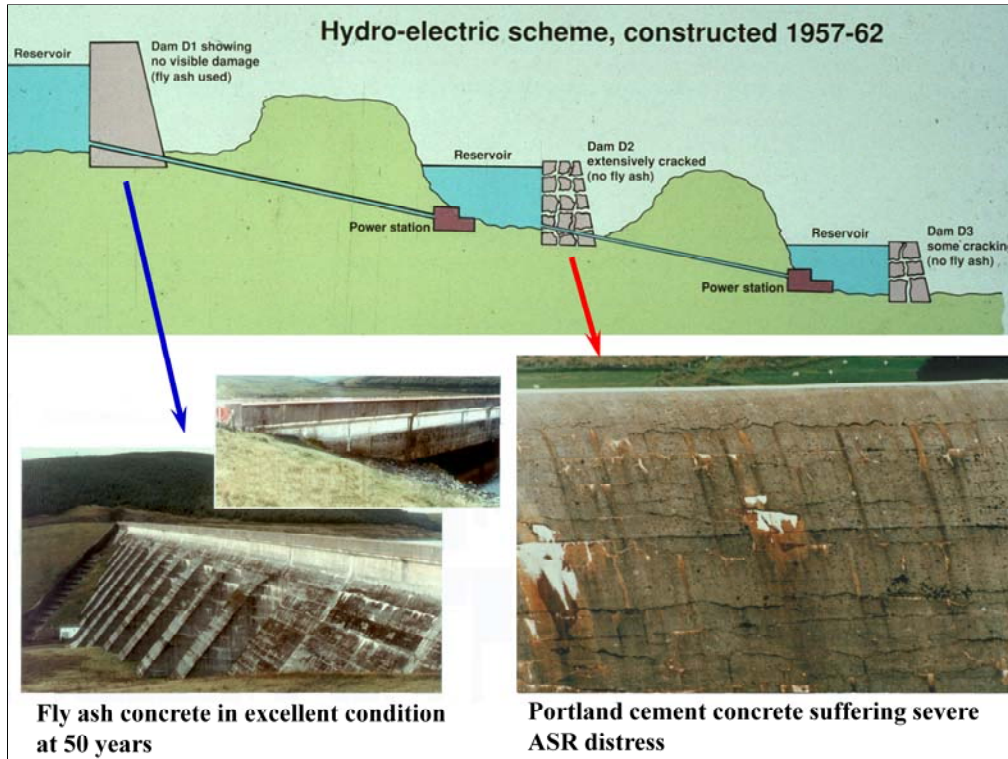


When it was built – it was known that the aggregate was reactive as it has caused deleterious expansion and cracking in a great many highway and hydraulic structures in the same location as the new dam

20% to 30% fly ash used with high-alkali cement (1.09% Na_2Oe) and reactive aggregate
Current condition (at 40 years) is excellent

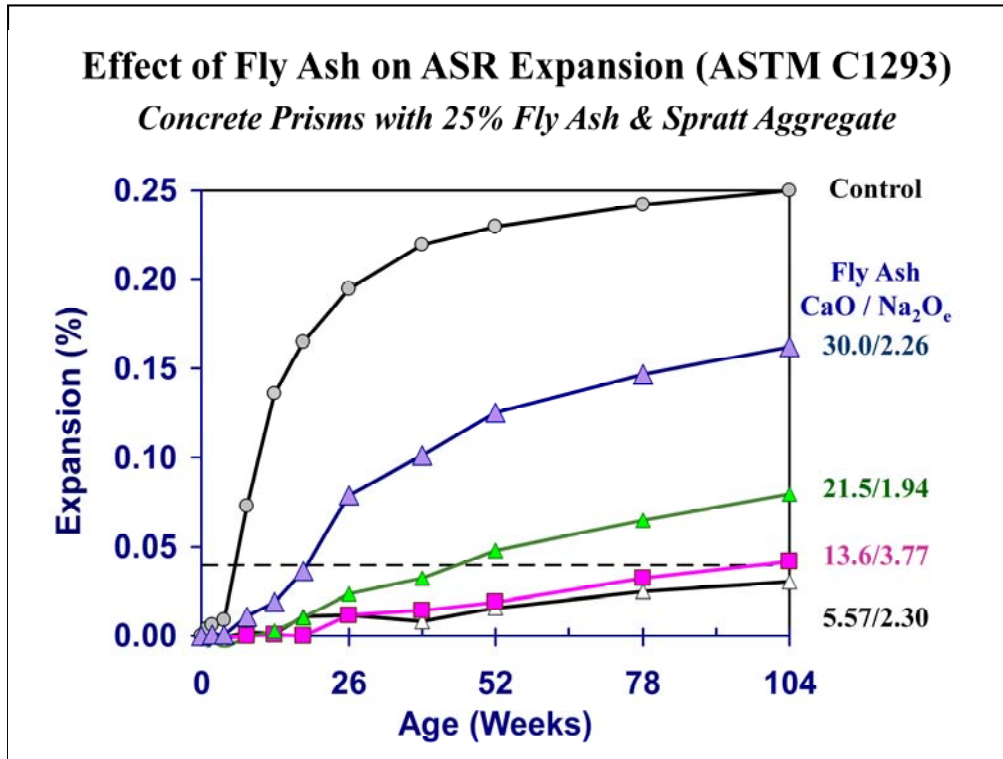


Expansion testing prior to construction showed that the combination of the local cement which was high in alkalis and fly ash performed as well as a low-alkali cement – since the low-alkali cement was from out-of-province – a decision was made to go ahead with the high-alkali cement plus fly ash combination. A recent inspection revealed no signs of ASR as the structure reached its fortieth birthday



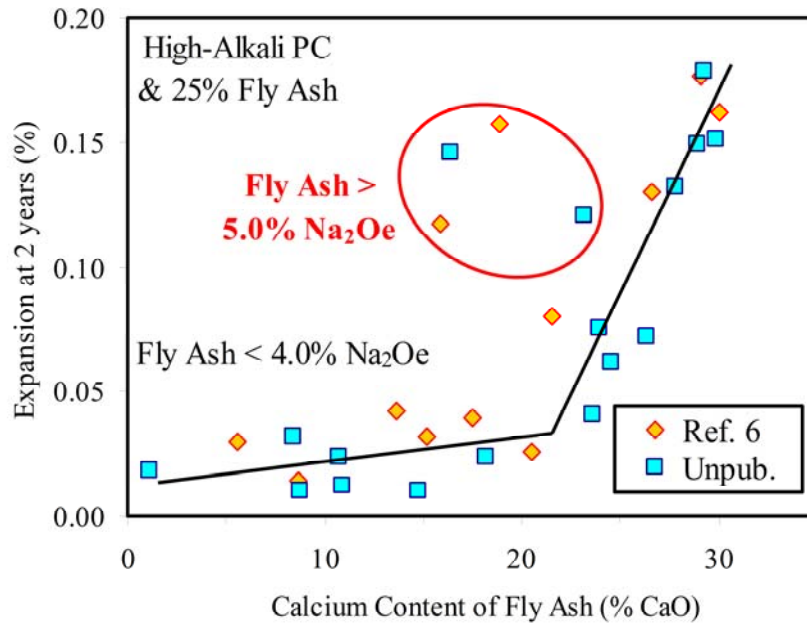
[Animated slide]

This slide shows two dams that were built as part of the same hydroelectric scheme around 1960 – the middle structure – an arch dam is extensively cracked and has required structural stabilization to prevent the arch moving upstream as it expanded – the structure upstream – a gravity dam – used the same aggregate and a cement of similar alkali content but also incorporated 25% fly ash to control heat – the fly ash has effectively staved off ASR expansion for more than 50 years now.



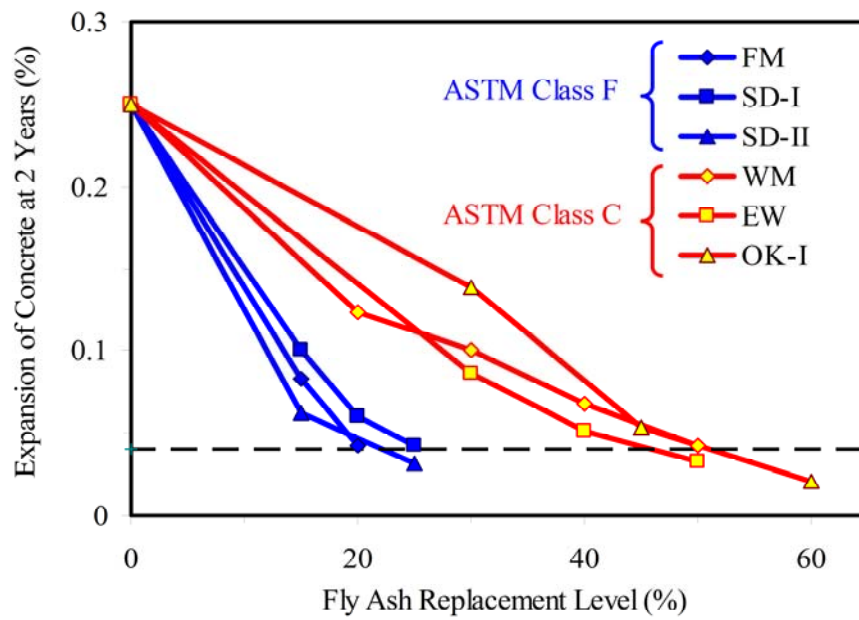
Not all fly ashes behave the same way. This slide shows that fly ashes with higher calcium contents do not completely suppress expansion when used at a replacement level of 25%

**Effect of Calcium Content of Fly Ash (ASTM C1293)
Concrete Prisms with 25% Fly Ash & Spratt Aggregate**



Indeed – the 2-year expansion of concrete prisms containing 25% fly ash is strongly dependent on the calcium content of the fly ash. Fly ashes with less than 20% calcium are generally effective unless they have a high alkali content. As the calcium content of the fly ash increases above 20% the efficacy of the fly ash decreases

Effect of Fly Ash Replacement Level (ASTM C1293)
Concrete Prisms with 25% Fly Ash & Spratt Aggregate

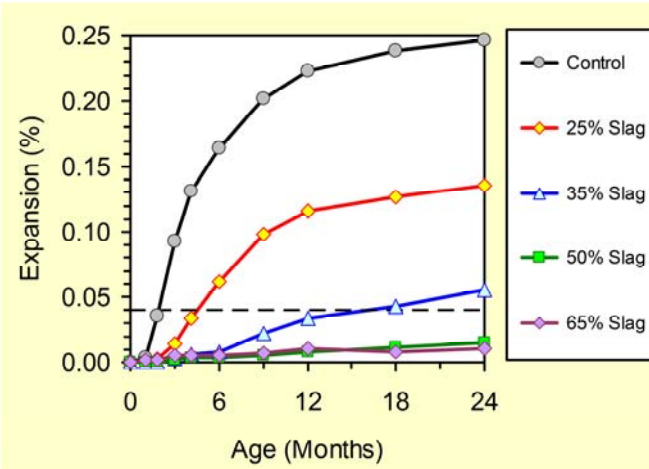


High-calcium Class C fly ashes can be used ... but have to be used at a much higher replacement rate as shown here.

Preventing ASR – Use of Slag

ASTM C 1293

- Concrete prism test
- Siliceous limestone
- 1.25% Na_2O_e
- 100°F (38°C) over water



Thomas and Innis, 1998

This graph shows data from laboratory expansion tests using concrete prisms in accordance with ASTM C 12-93.

The data show expansion curves for 5 concretes with varying levels of slag. The expansion decreases as the amount of slag in the mix increases.

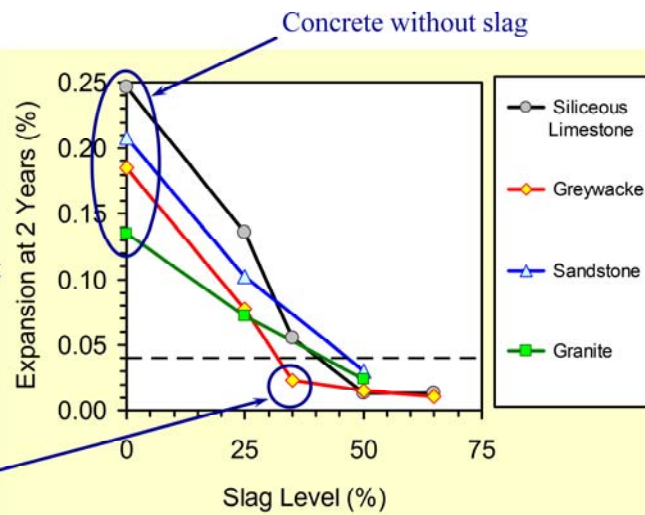
More than 35% slag is required to meet typical specification limits of zero-point-zero-four % at 2 years when combined with this highly reactive aggregate.

Effect of Aggregate Reactivity (Example for Slag)

ASTM C 1293

- Concrete prism test
- 4 aggregates
- 1.25% Na_2O_e
- Stored over water at 100°F (38°C)

Moderately-reactive aggregate with 35% slag



Thomas and Innis, 1998

This graph shows test results for four different reactive aggregates – in this case the expansion at 2 years is plotted against the level of slag.

As can be seen – when there is no slag in the mix – all of the 2-year expansion results are greater than 0.04%

The expansion decreases with increasing slag content in all cases.

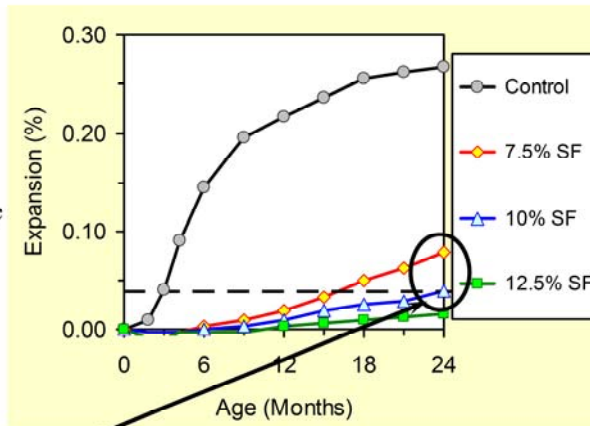
Although 50% slag is needed to reduce the expansion to less than zero-point-zero-four percent in the concrete with the highly-reactive siliceous limestone – only 35% slag is required with the moderately reactive greywacke aggregate.

Generally, the amount of slag required to control expansion increases as either the reactivity of the aggregate or the amount of alkali in the mix increases.

Preventing ASR – Use of Silica Fume

Laboratory Test Results

- ASTM C1293 (Concrete Prism Test)
- Cement = 1.25% Na₂Oe
- Siliceous limestone aggregate
- Concrete at 100°F (38°C) over water
- Test for 2 years



Amount required to meet expansion limit at 2 years maybe > 10% silica fume

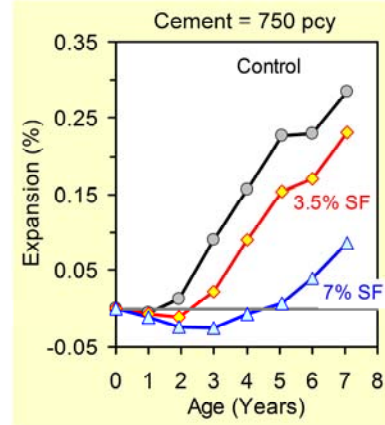
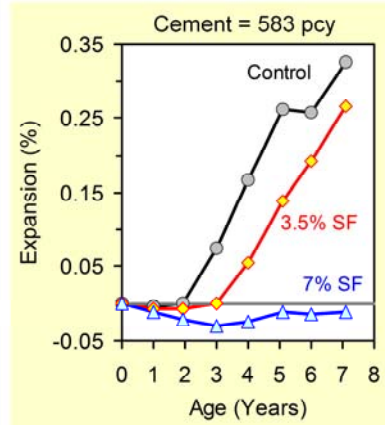
These data show that silica fume is very effective in controlling expansion due to ASR at relatively low levels compared with fly ash or slag. However, in the standard test conditions – the amount of silica fume required to control expansion with a highly-reactive aggregate is around 10% or more. This level of silica fume is higher than that typically used in concrete and can lead to problems with placing and finishing.

The efficacy of silica fume appears to be strongly dependent on the alkali available in the concrete system and other studies have shown that lower amounts of silica fume can be used when the alkali content of the concrete is lower than typically used in these concrete prism tests

Effect of Alkali Content (Example for Silica Fume)

'Active' alkalis ~ 6.7 lb/yd³ Na₂Oe

'Active' alkalis ~ 8.3 lb/yd³ Na₂Oe

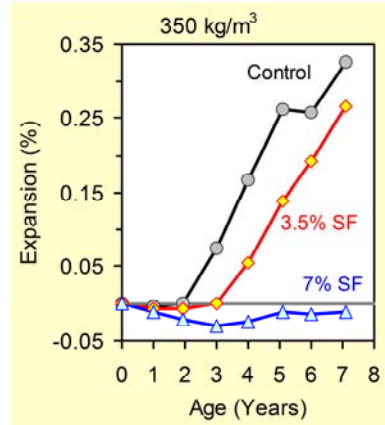


Concrete cubes (12-inch) exposed outdoors in S. Africa
 Reactive aggregate = "Malmesbury" Hornfels
 Expansion measured to 8 years

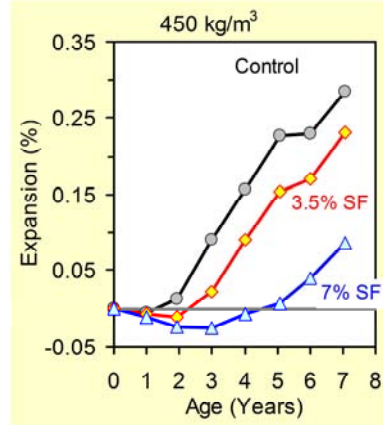
This is demonstrated in this slide. These are data for 12-inch concrete cores stored outdoors in South Africa. The graph on the left show expansion curves for concrete with a lower alkali content – under 7 pounds – and it would seem that 7% silica fume is effective in controlling expansion – at least to 7 years. On the right are data for concrete with a greater alkali loading – above 8 pounds – and it can be seen that 7% silica fume was not effective in the long term.

Effect of Alkali Content (Example for Silica Fume)

'Active' alkalis ~ 4 kg/m³ Na₂O_e



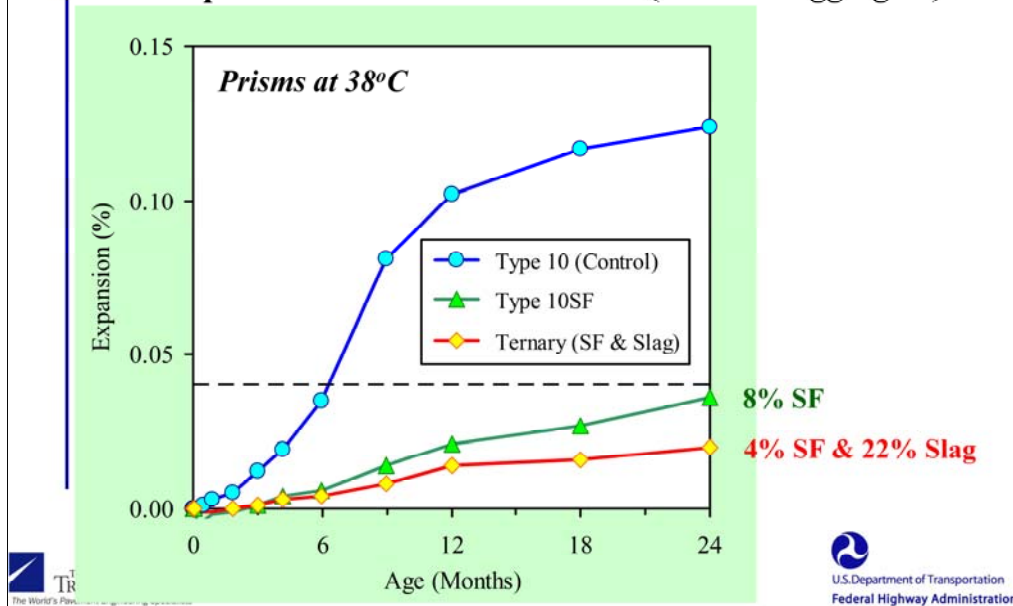
'Active' alkalis ~ 5 kg/m³ Na₂O_e



Concrete blocks (300-mm, 12-inch cubes) exposed outdoors in S. Africa
 Reactive aggregate = "Malmesbury" Hornfels
 Expansion measured to 8 years

Preventing ASR – Ternary Blends

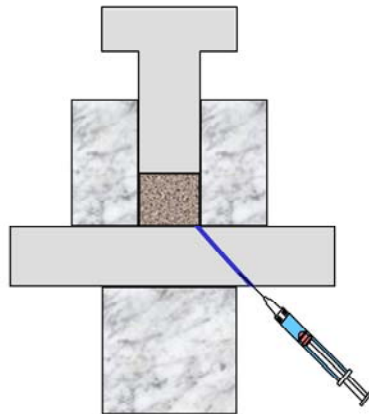
ASR Expansion – Concrete Prism Test (Sandhill Aggregate)



Ternary blends containing two SCMs can also be effective measures for controlling ASR. Generally the effects of each SCM are additive. So you could use half the safe level of one SCM combined with half the safe level of a second SCM – or a third of one plus two thirds of the other – etcetera

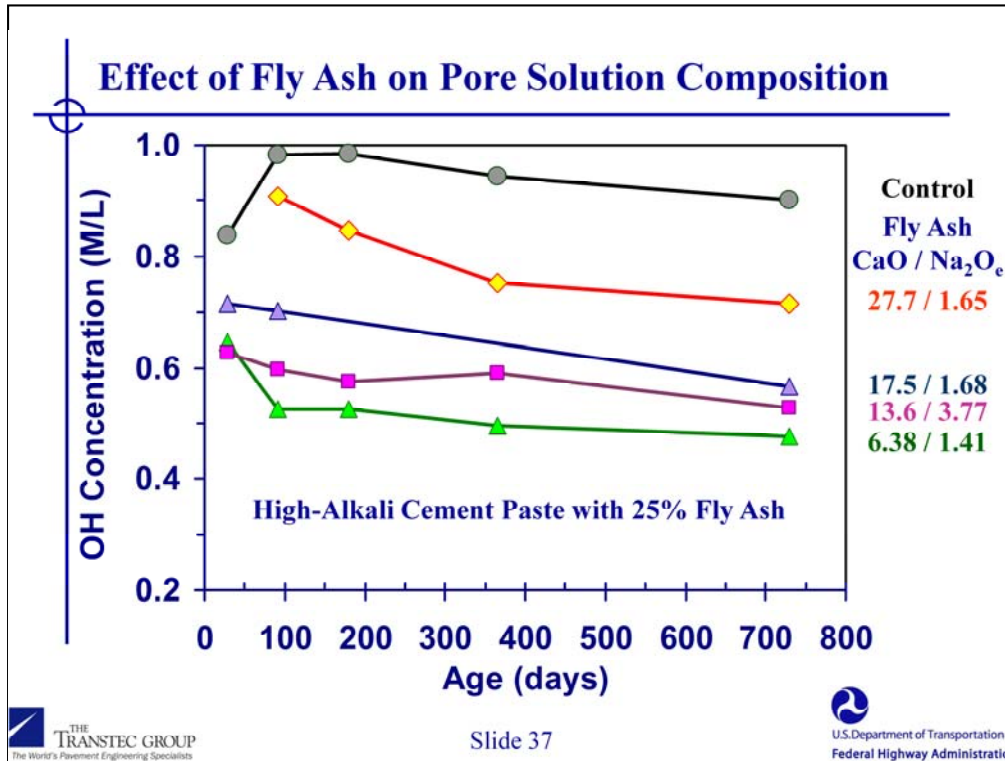
SCM & ASR – Mechanism of Action

Pore Solution Expression & Analysis



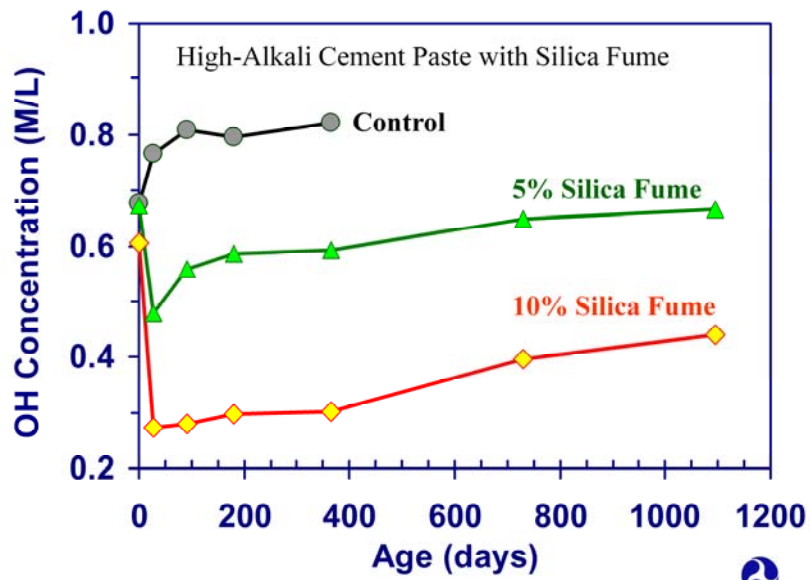
- Solution extracted from hydrated pastes, mortars or concretes using pressures of ≥ 450 MPa
- Extracted solution analyzed for various species

So ... how do scms work. Well to understand this we have to go to pore solution studies – the pore solution of concrete can be extracted by squeezing the concrete using very high pressures of 450 MPa or more – that is 65 thousand psi or more – once extracted the solution can be analyzed to determine how much alkali is in solution and therefore available for reaction with the aggregate.



In this slide it can be seen that the pore solution extracted from a control cement paste is very rich in hydroxyl ions (remember these are the negatively charged ions that balance the positively charged sodium and potassium ions) – the concentration is almost most one mole per litre – which produces a pH of 14 – very caustic if you remember your pH scale. The incorporation of fly ash reduces the amount of alkali in solution – this means that even though fly ash itself contains alkalis – the use of fly ash reduces the amount of alkali that is AVAILABLE to the pore solution and ABLE to react with the aggregate. In effect the fly ash – like other SCMs consumes alkalis. The higher calcium fly ashes are less effective in this role and are also less effective in controlling ASR expansion.

Effect of Fly Ash on Pore Solution Composition

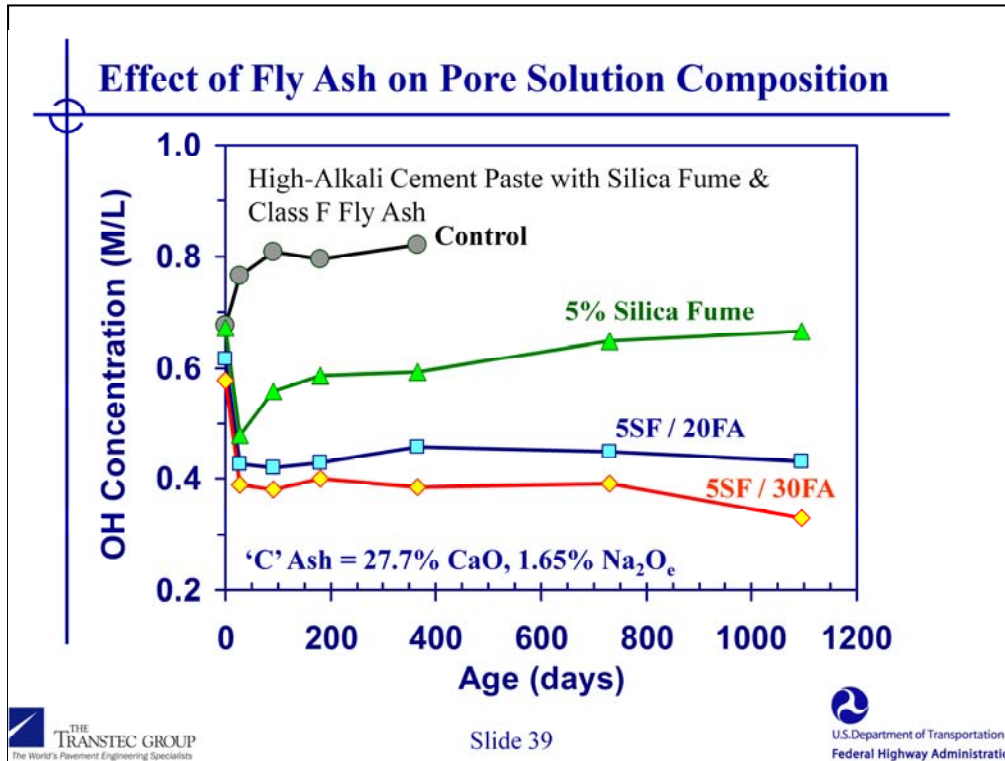


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Slide 38

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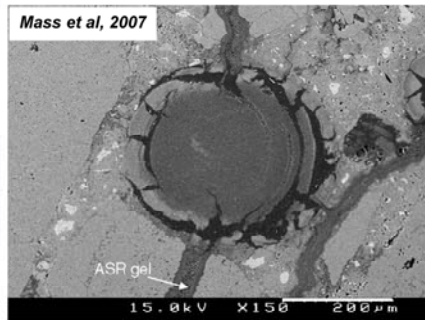
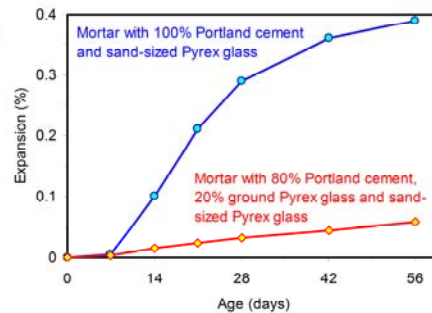
Silica fume reduces the alkalinity of the pore solution very early on but there is some evidence that some of this alkali may be released later



We can prevent this later release by using silica fume together with fly ash (or slag) – relying on the faster reacting silica fume to consume the alkalis at early age and the fly ash to maintain a low alkalinity long term

How Do SCM's Work to Control ASR Expansion?

Finely-ground reactive aggregate can behave like a pozzolan and reduce expansion due to ASR →



← Agglomerates of silica fume (or other SCM) behave like reactive aggregates and can lead to deleterious ASR

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Slide 40

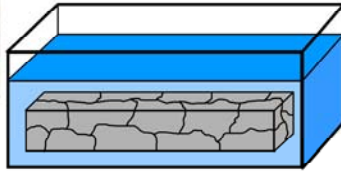
U.S. Department of Transportation
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In essence what is happening is that the silica in the SCM is reacting with the alkalis in much the same manner as the aggregate will – but because the SCM is so fine – it reacts faster and consumes the alkalis before they can react with the aggregate. Any reaction product that is formed is finely dispersed throughout the paste and large accumulations that may cause local swelling and expansion of the concrete do not occur. We can achieve the same effect by grinding reactive aggregate very finely – this is shown in the graph. The blue line shows the expansion of mortar bars produced with sand-sized Pyrex glass and high-alkali cement. The red line shows the same mix but with some of the Pyrex ground very finely and used as part of the cement. The ground Pyrex prevents reaction with the sand-sized Pyrex by consuming the alkalis first – in fact, the ground Pyrex behaves like a pozzolan. In much the same way that ground silica behaves like a pozzolan – a coarse pozzolan can act like reactive aggregate. This is shown in the photograph – the reacting aggregate particle causing damaging is in fact an agglomeration of silica fume – literally millions of silica fume particles are stuck together to form one sand-size particle of reactive silica.

Methods for Evaluating SCMs for Preventing ASR

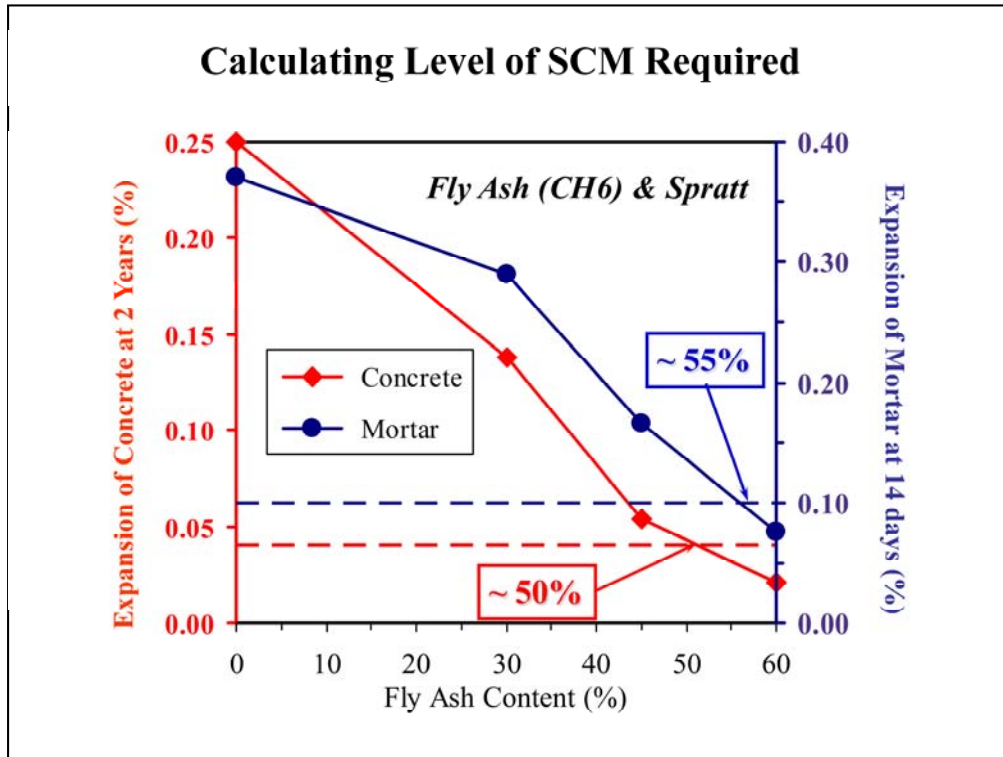


- Large blocks
- Concrete prisms
- Mortar bars



RELIABILITY VS RAPIDITY ??

So how do we test to determine how much SCM we need? Well I think we already covered this in the previous presentation

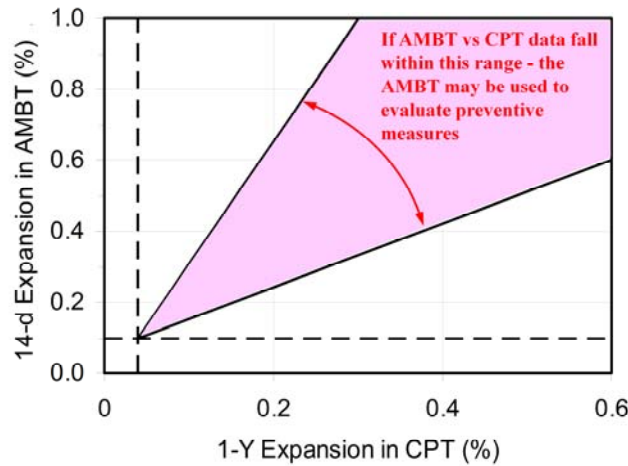


But as a reminder – what we would like is to have aggregates that behave well in our accelerated tests so that when we use the rapid 14-day test to determine the safe level of SCM we get a similar result to that obtained by the longer-term concrete test in 2 years

AASHTO – Performance Approach

Performance Testing using the AMBT

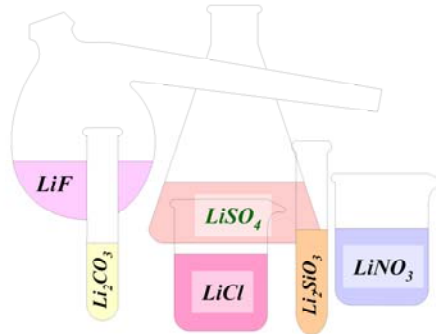
First establish correlation between AMBT & CPT for aggregate



In the AASHTO spec – it is strongly recommended that you calibrate the rapid mortar test with the concrete test for each aggregate – for this aggregates that give similar results in both tests – it is acceptable to use the rapid tests to evaluate the efficacy of preventive measures.

Preventing ASR – Use of Lithium

First work on the use of lithium to counteract ASR dates back almost 50 years!



McCoy & Caldwell, 1951

Expansion tests with Pyrex glass and more than 100 different chemical compounds to determine whether the reaction between alkalis and silica could be chemically inhibited

Lithium compounds were found to be the most promising.

The potential for lithium-based chemicals to control expansion due to ASR dates back half-a-century to the work of McCoy and Caldwell at the Portland Cement Association in Chicago.

They evaluated the effect of more than 100 chemicals on the expansion of mortars containing Pyrex glass – which serves as a highly reactive artificial aggregate – they discovered a number of lithium compounds including – lithium carbonate, sulfate, chloride, silicate, fluoride and lithium nitrate – to be the most effective.

Preventing ASR – Use of Lithium

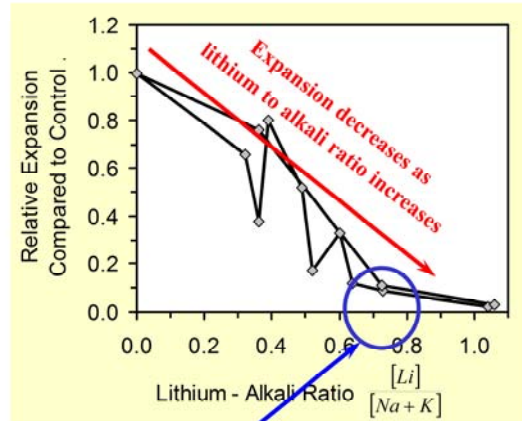
Effect of Lithium Compounds

McCoy & Caldwell, 1951

Mortar Bars with Pyrex Glass

Expansion decreases as the ratio of lithium to alkalis increases

$$\text{Lithium to alkali molar ratio} = \frac{[Li]}{[Na + K]}$$



$$\text{Expansion controlled when: } \frac{[Li]}{[Na + K]} \geq 0.74$$

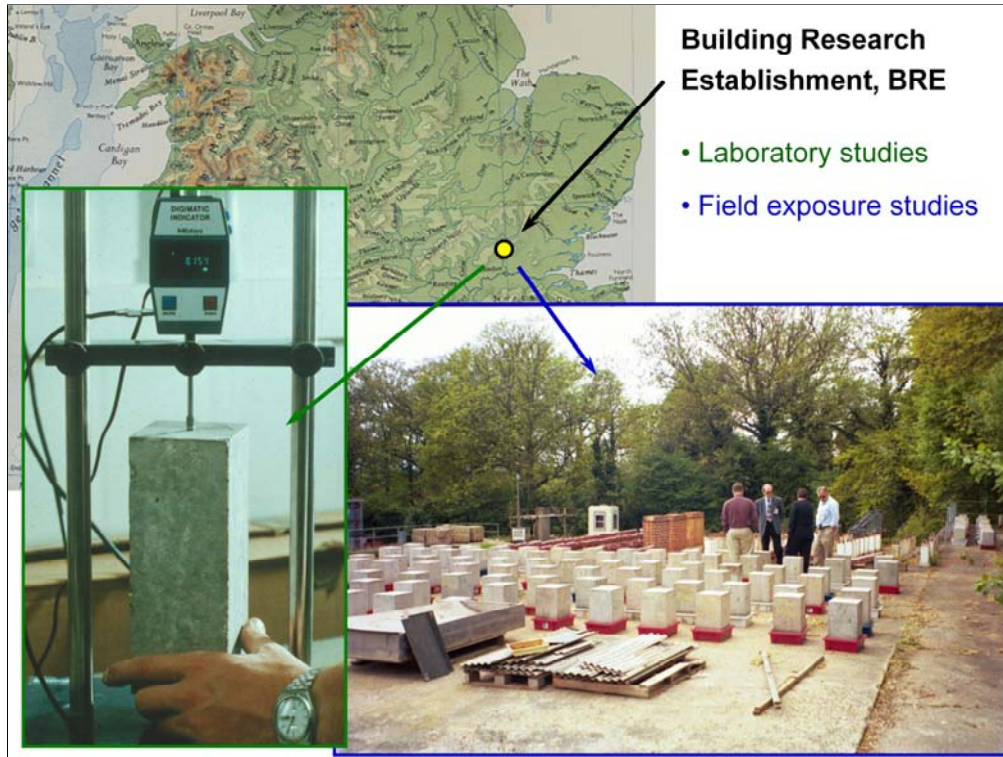
The graph shows some of the data from this early study.

The expansion of mortar bars with lithium are plotted on the vertical (or y) axis relative to the expansion of the mortar bars without lithium – so a value of 1 on this axis means that the mortar expanded the same amount as the control – in other words there was no reduction.

On the horizontal (or x-) axis of the graph the lithium content of the mortar is plotted as a ratio of the sum of sodium and potassium alkalis. In fact the number of moles of lithium is plotted as a ratio of the number of moles of sodium plus potassium.

As this molar ratio increases – in other words as the content of lithium increases compared to the sum of the sodium and potassium – the relative expansion of the mortar bars decreases,

McCoy and Caldwell's data indicate that a molar ratio of 0.74 might be sufficient to suppress expansion to a suitable level



Since this early work using Pyrex mortar bars – numerous researchers have confirmed the efficacy of lithium in controlling ASR in concrete with natural aggregates. One such study was a comprehensive research program conducted in the UK using a large number of aggregates and concrete mixes with various SCMs stored under laboratory and field conditions

Preventing ASR – Use of Lithium

Effect of Lithium Compounds

Building Research Establishment U.K.

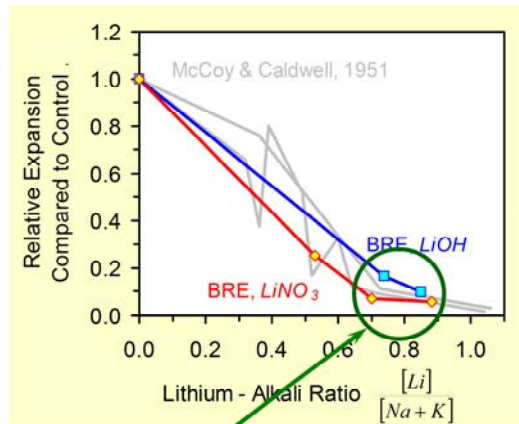
Concrete prisms

Highly-reactive siltstone aggregate

Lithium hydroxide (LiOH) or lithium nitrate (LiNO₃) admixtures

Concrete stored at 100°F (38°C) and 100% RH for three years

Expansion expressed relative to control without lithium



LiNO₃ slightly more effective than LiOH

LiNO₃ does not increase pH

Thomas et al, 2000

Most of the data generally follow the trends shown earlier and an example of this is shown in this graph.

A lithium to alkali molar ratio in the region of zero-point seven to eight seems sufficient for lithium nitrate – whilst a slightly increased lithium dose is required for lithium hydroxide. This is because lithium hydroxide affects a small increase to the pH of the concrete pore solution and presents an extra challenge.

Preventing ASR – Use of Lithium

Lithium Nitrate - LiNO_3

Most effective of lithium compounds.

Doesn't increase internal pH of concrete

Currently available on the market as a 30% solution

Recommended lithium dose:

$$\text{Molar ratio: } \frac{\text{Li}}{\text{Na} + \text{K}} = 0.74$$

For lithium nitrate solution (30%) this is equivalent to:

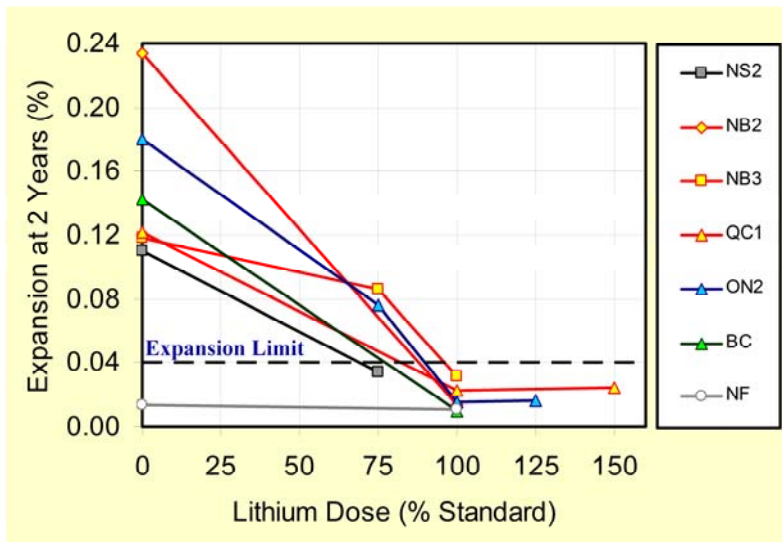
- 0.55 gallons of LiNO_3 solution per 1 lb of Na_2Oe
- 4.60 litres of LiNO_3 solution per 1 kg of Na_2Oe

Recent studies confirm that lithium nitrate is the most efficient form of lithium for controlling ASR. As such a number of admixture suppliers currently distribute a lithium nitrate as a solution – in all cases the concentration of the solution is 30% lithium nitrate by mass.

To achieve a lithium to alkali molar ratio of 0.74 requires just over half-a-gallon of 30-% lithium nitrate solution for each pound of equivalent sodium oxide in the concrete mix. This is approximately equivalent to 4.6 litres of solution for each kg of equivalent soda

The amount of lithium may be reduced when it is used in combination with other preventive measures such as Class F fly ash – in such cases, advice should be sought from the admixture supplier

Performance of Lithium with Different Reactive Aggregates

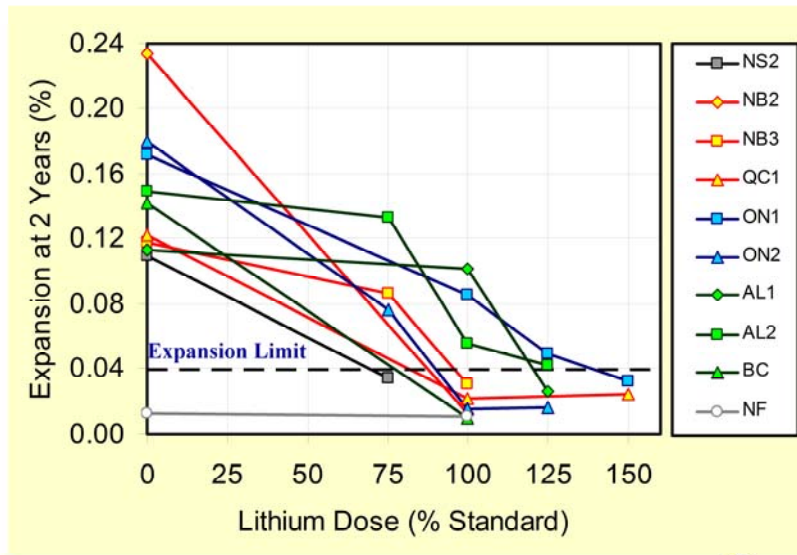


A fairly recent study conducted in Canada showed that the standard dose does not work with all reactive aggregates and that the efficacy of lithium was aggregate dependant.

This graph shows data for 6 of 12 reactive aggregates studies. Lithium works well with these aggregates and the standard dose seems to be sufficient – NOTE that 100% standard dose means a lithium-to-alkali ratio of zero-point-seven-four

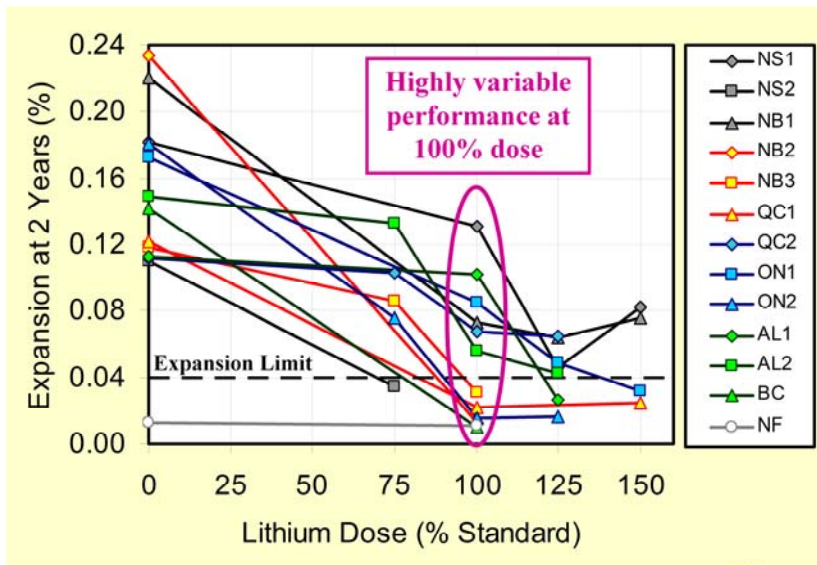
The 7th aggregate shown on the graph is a non-reactive limestone which doesn't expand even when there is no lithium in the mix.

Performance of Lithium with Different Reactive Aggregates



Unfortunately 3 of the 12 aggregates required more than the standard dose – 50% more in some cases ...

Performance of Lithium with Different Reactive Aggregates



Even this 50% increase was NOT sufficient with some aggregates and putting all the data together shows that the 100% dose gives extremely variable performance and is strongly dependent on the aggregate. Consequently ... it is not possible to prescribe a fixed dose of lithium that will work with all aggregates and the amount of lithium required must be determined by testing with the specific aggregate being used.

Performance of Lithium with Different Aggregates

- 100% lithium dose works with 6/12 reactive aggregates
- 100% lithium dose did **not** work with 6/12 aggregates
- 125% lithium dose did **not** work with 4/12 aggregates
- 150% lithium dose did **not** work with 2/12 aggregates

It is not possible at this time to recommend a “safe” lithium dose to control ASR as the amount of lithium required varies with the type of reactive and the relationship between aggregate type and lithium dose is not understood.

∴ Need a reliable performance test method to determine the “safe” dose required with a specific aggregate

[no note required - this just reinforces in writing the narration for the previous slide]

Prevention of ASR - Summary

- Use of non-reactive aggregates is most obvious choice – but may not be viable in some cases
- Limiting the alkali content of the concrete is effective provided that the “safe” level of alkali can be determined for a specific aggregate and that the concrete is not exposed to alkalis in service
- Supplementary cementing materials are effective provided they are used in sufficient quantity – the amount required depends on the composition of the SCM, the reactivity of the aggregate and the alkali loading of the system
- Lithium is effective with some but not all aggregates. The amount of lithium required has to be established for each aggregate type.

In summary [presenter to read slide]