

FHWA Workshop

Alkali-Aggregate Reaction

Session 02: Fundamentals of Alkali-Aggregate Reaction



Outline

- **Definitions: ASR & ACR**
- **Alkali-Silica Reaction (ASR)**
 - **Background and History**
 - **Mechanisms of ASR**
 - **Contributing Factors**
- **Alkali-Carbonate Reaction (ACR)**
 - **Summary of ACR**

In this presentation the two types of alkali-aggregate reaction – ASR and ACR will be defined.

As ASR is more widespread and better understood – the focus of the presentation will be on the background and history of ASR – with information on the mechanisms and the contributing factors (such as the source of the alkalis and the silica that participate in the reaction)

ACR – which occurs far less frequently – will be discussed only briefly – to ensure that attendees are aware of the phenomenon.

Alkali-Aggregate Reaction - AAR

Alkali-Aggregate Reaction – AAR

... chemical reaction in either mortar or concrete between alkalis (sodium and potassium) from portland cement or other sources and certain constituents of some aggregates; under certain conditions, deleterious expansion of concrete may result

ACI 116

<http://www.concrete.org/Technical/CCT/ACI-Terminology.aspx>

Read description. Point out that although these descriptions are taken – verbatim from ACI 116 committee document on terminology – this document no longer exists and terminology is now available on the ACI website – link included.

Alkali-Aggregate Reaction - AAR

Alkali-Aggregate
Reaction (AAR)

{ Alkali-Carbonate Reaction (ACR)
Alkali-Silica Reaction (ASR)

Two types: AAR = ASR and ACR

Alkali-Carbonate Reaction - ACR

Alkali-Carbonate Reaction – ACR

... the reaction between the alkalis (sodium and potassium) in portland cement and certain carbonate rocks, particularly calcitic dolomite and dolomitic limestones, present in some aggregates; the products of the reaction may cause abnormal expansion and cracking of concrete in service.

ACI 116

<http://www.concrete.org/Technical/CCT/ACI-Terminology.aspx>

Read description of AAR.

Alkali-Silica Reaction - ASR

Alkali-Silica Reaction – ASR

... the reaction between the alkalies (sodium and potassium) in portland cement and certain siliceous rocks or minerals such as opaline chert, strained quartz, and acidic volcanic glass, present in some aggregates; the products of the reaction may cause abnormal expansion and cracking of concrete in service.

ACI 116

<http://www.concrete.org/Technical/CCT/ACI-Terminology.aspx>

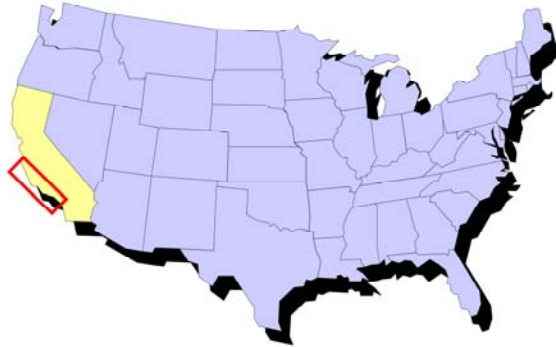
Read description.

ASR vs. ACR

- This workshop will mainly deal with **ASR**, which occurs throughout North America
- **ACR** occurs relatively infrequently and is restricted to a few isolated locations
- Methods of mitigation for **ASR** generally **NOT** suitable for controlling **ACR**
- Must avoid **ACR** rocks – e.g. by selective quarrying
- Some **ASR** test methods may **FAIL** to identify **ACR** rocks

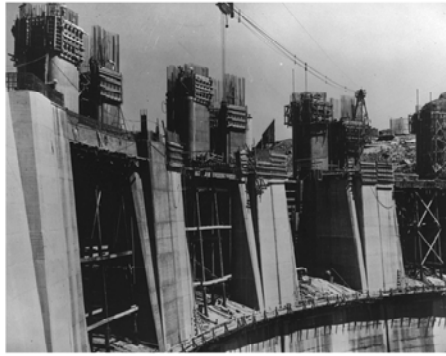
This slide contains a few important distinctions between ASR and ACR.

History of ASR



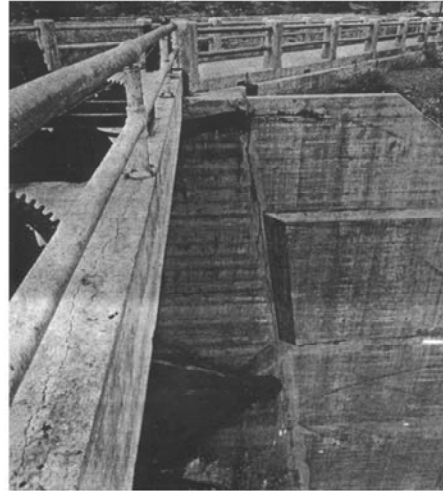
- First discovered in the late 1930s
- In Monterey County and Los Angeles County
- Thomas Stanton of California State Division of Highways

In the 1930s – unusual cracking was observed in concrete structures – particularly highway structures and pavements, and a few dams – in a number of states in western USA and the mid-west. Thomas Stanton of the California State Division of Highways was the first to diagnose the cause of the problem and presented a description of the reaction including the role of cement alkalis and reactive silica in aggregates in his seminal (or landmark) paper published in 1940.



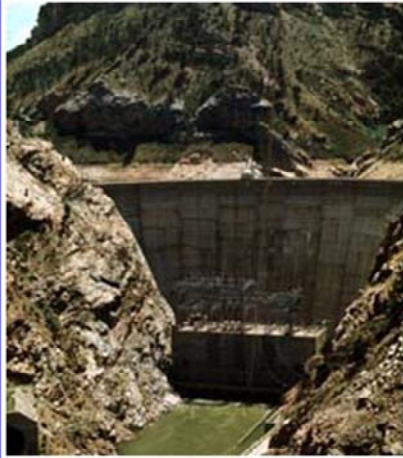
Parker Dam

Colorado River, Arizona
Completed in 1938

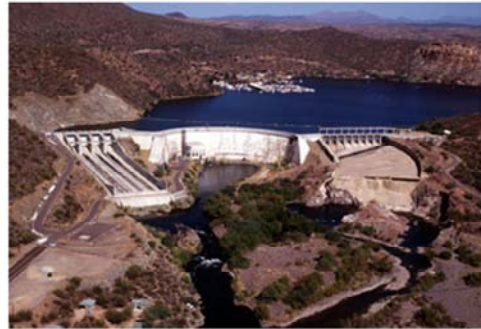


Following Stanton's discovery the US Bureau of Reclamation determined that ASR was the probably cause of expansion and cracking in the Parker Dam which is a massive arch dam crossing the Colorado River 155 miles downstream of the Hoover dam and straddling the border between Arizona and California.

USBR STRUCTURES

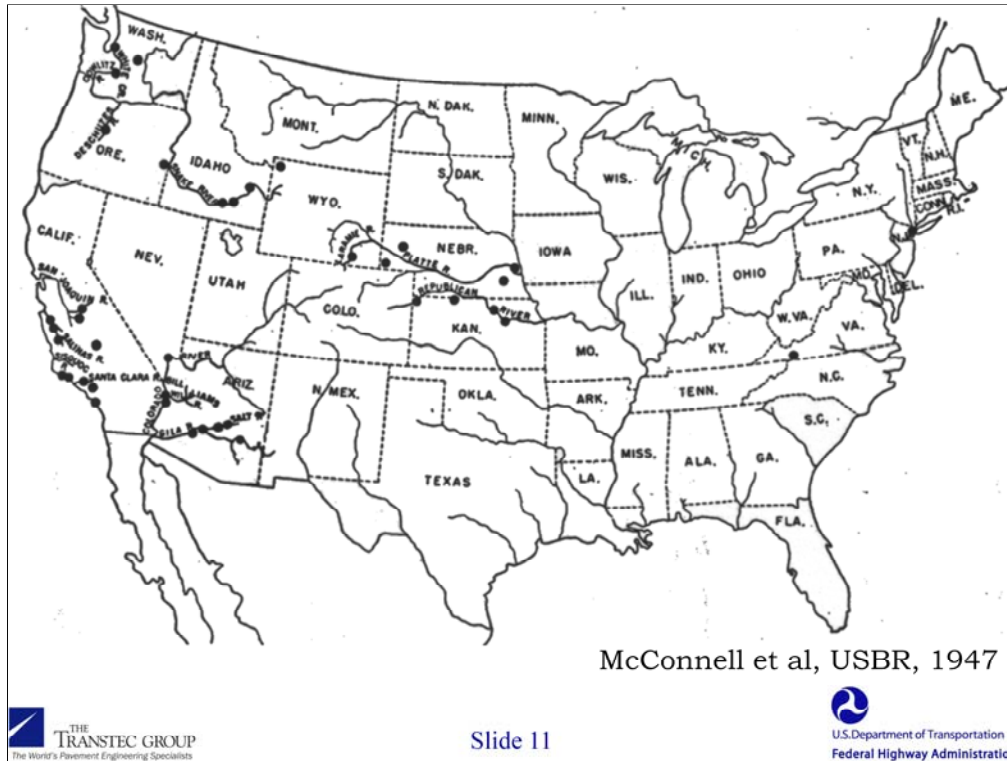


Seminole Dam



Stewart Mountain Dam

About the same time – the US bureau determined that other dams – such as the Stewart Mountain Dam near Phoenix, AZ, built between 1928 and 1930 and the Seminole Dam on the North Platte River in Wyoming which was completed in 1938.



By 1947 – just 7 years after the publication of the first paper describing the reaction – ASR was confirmed in a number of states in the west including more cases in California and Arizona and a number of cases along the Snake river in Idaho. In the mid-west more cases were discovered along the Platte River and the Republican river – and a few isolated locations were discovered in the east (for example Virginia).

This is a map produced by the US bureau of reclamation that appeared in a publication on asr in 1947.

Occurrences of ASR in U.S.A.



- Field cases of ASR in most (if not all) states of USA.

This is an old map produced by FHWA ago 10 years ago now (i.e. around the beginning of this millennium). Each star represents not just one case of asr – but a location where reactive aggregates have been identified and have been implicated as the cause of damage in a number of structures in that location. Since this map was produced ASR has been detected in most of the states that were missing a star ten years ago and it is probably safe to say that ASR has caused problems in all 48 of the contiguous states of the US. As far as we are aware – both Hawaii and Alaska are still free of the problem.

It is interesting note that although ASR appeared to start in the west of the US – it slowly spread east and there are now probably just as many – if not more – cases in the east. This may have something to do with the population – or rather infrastructure – density – but is also probably a function of the cements being higher in alkali content in the east

Occurrences ASR in Canada



- Field cases of ASR in all provinces of Canada

ASR has occurred in all of the provinces in Canada – again with a higher concentration in the east – largely due to cements being higher in alkali. There are no reported cases in the northern territories – probably due to a combination of there being very little infrastructure and very low temperatures – ASR being a chemical reaction and the rate of reaction being very strongly dependant on temperature.

ASR-Affected Structures

ASR affects all types of structures and has been implicated as a main or contributory cause of distress in thousands of concrete structures in North America.

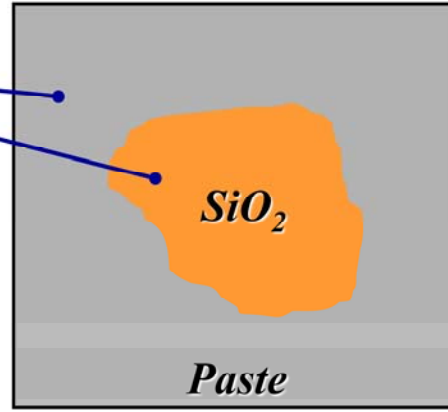


All types of concrete structure can be affected by ASR – provided moisture is available.

ASR Mechanism

Concrete “model” showing:

- cement paste
- reactive siliceous aggregate

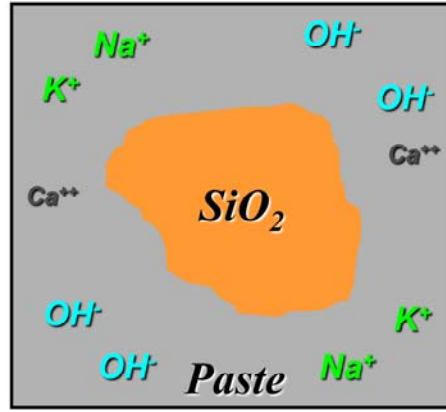


Let's discuss the mechanism – by considering concrete to consist of aggregate – in this case a reactive silica aggregate - surrounded by cement paste. It should be noted that not all siliceous aggregates are reactive.

ASR Mechanism

Concrete “model” showing:

- cement paste
- reactive siliceous aggregate
- pore solution dominated by:
 - sodium, Na^+
 - potassium, K^+
 - hydroxyl, OH^-
 - minor amounts of calcium, Ca^{++} and other ionic species



The paste is in fact porous and if the concrete is exposed to moisture the pores will be completely or partially saturated with solution. We call this the pore solution – which in concrete is composed predominantly of positively-charged alkali ions – these being sodium (N-a-plus) and potassium (K-plus) ions – balanced by an equal number of negatively-charged hydroxyl (or O-H-minus) ions. There is also a very small amount of calcium in solution as C-a-two-plus ions

ASR Mechanism

If the silica is reactive it may be “attacked” first by OH^- and then by Na^+ and K^+ ions



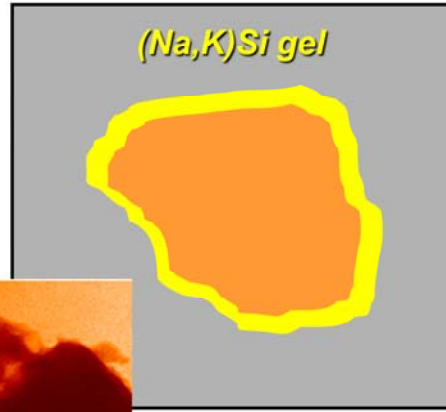
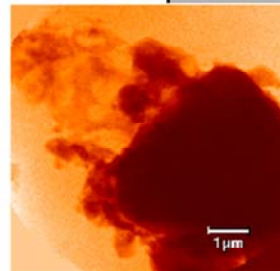
Despite its name – alkali-silica ions – it is the hydroxyl ions that first attack the reactive silica – the silica goes into solution and then combines with the sodium and potassium ions

ASR Mechanism

If the silica is reactive it may be “attacked” first by OH^- and then by Na^+ and K^+ ions -

forming an alkali-silica gel composed predominantly of Na , K & Si with minor amounts of Ca

X-ray image showing
ASR gel formation



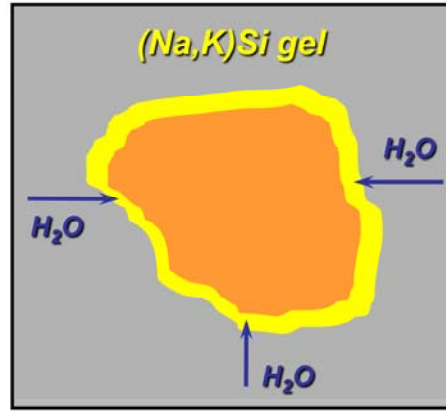
The reaction product is an alkali-silicate solution or gel with minor amounts of calcium (the calcium content increases with time).

ASR Mechanism

If the silica is reactive it may be “attacked” first by OH^- and then by Na^+ and K^+ ions -

forming an alkali-silica gel composed predominantly of Na , K & Si with minor amounts of Ca

The gel absorbs water from the surrounding cement paste and ...



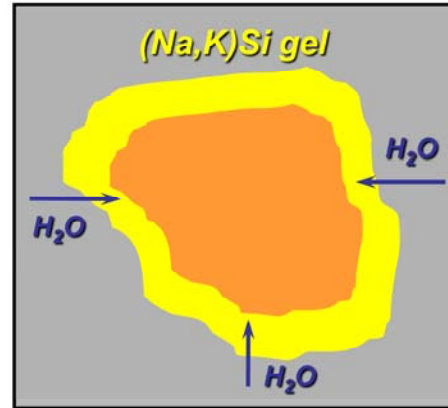
The gel is hygroscopic and absorbs water from the surrounding paste and as it takes in water it expands ...

ASR Mechanism

If the silica is reactive it may be “attacked” first by OH^- and then by Na^+ and K^+ ions -

forming an alkali-silica gel composed predominantly of Na , K & Si with minor amounts of Ca

The gel absorbs water from the surrounding cement paste and expands ...



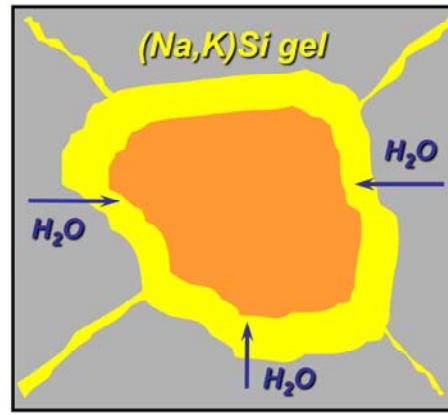
... and eventually causes expansion ...

ASR Mechanism

If the silica is reactive it may be “attacked” first by OH^- and then by Na^+ and K^+ ions -

forming an alkali-silica gel composed predominantly of Na , K & Si with minor amounts of Ca

The gel absorbs water from the surrounding cement paste and expands – causing internal stresses and eventually leading to cracking



... and cracking of the surrounding paste. The aggregate itself may expand and crack in many cases – the cracks in the aggregate often being filled or partially filled with gel

ASR Mechanism

If the silica is reactive it may be “attacked” first by OH^- and then by Na^+ and K^+ ions -

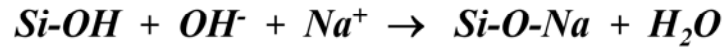
forming an alkali-silica gel composed predominantly of Na , K & Si with minor amounts of Ca

The gel absorbs water from the surrounding cement paste and expands – causing internal stresses and eventually leading to cracking

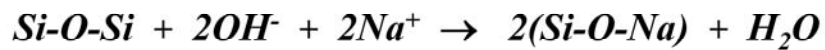


The internal expansion and cracking eventually becomes visible on the concrete surface.

Alkali-Silica Reaction: Chemistry



(Silanol group)

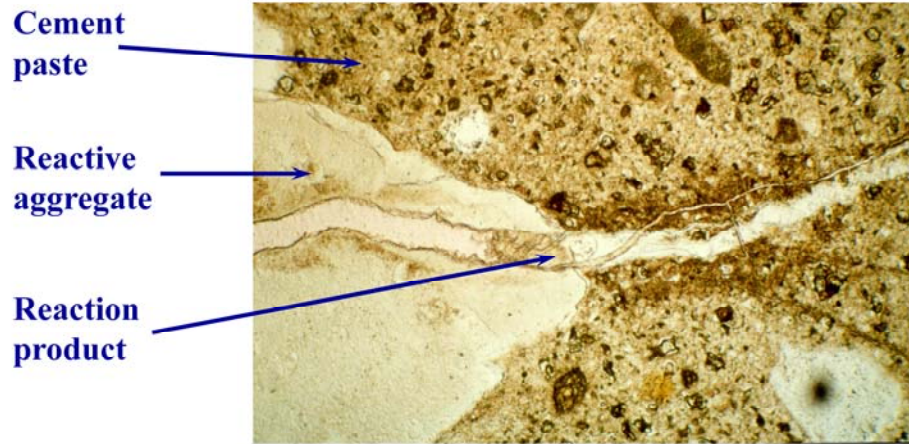


(Siloxane group)

The chemistry of the alkali-silica reaction can be represented by these two equations. These are discussed in some detail in the reference manual and in more detail in the “facts book”.

They are shown here to underline the importance of the hydroxyl ions. Without the OH ions – the breakdown of the Si-O-H groups at the surface or the main Si-O-Si groups that hold the silica together do NOT occur. In other words strong solutions of other alkali compounds – such as sodium carbonate or potassium chloride for example – will not attack the silica.

ASR in Concrete Thin Section



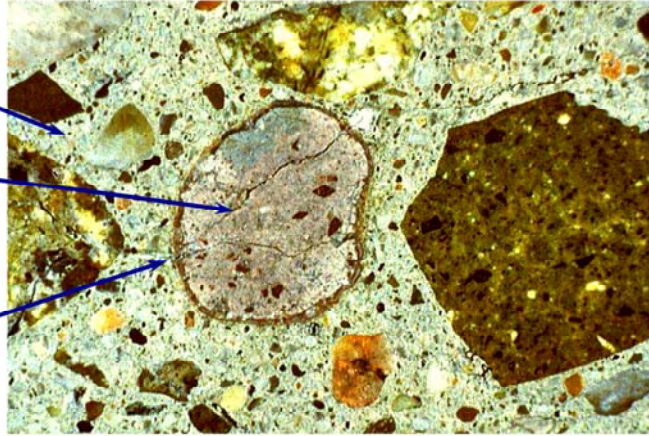
This shows a thin-section prepared from a concrete undergoing ASR. To the left is a reactive chert particle that has reacted, expanded and cracked – the crack extends into the surrounding paste and is partially filled with reaction product – that is – alkali-silica gel. The chert is what we call a “site of expansive reaction” – such features are helpful in the diagnosis of the cause of damage.

ASR in Concrete Polished Section

Cement
paste

Reactive
aggregate

Reaction
product



This is a polished section viewed in reflected light with a stereo binocular microscope. At the center is a reactive coarse aggregate particle consisting of rhyolite – the particle is cracked and as with the previous example the cracks extend into the surrounding paste making this another “site of expansive reaction”.

Expansion Mechanisms



Failure of Jersey barrier due to expansion of concrete

Expansion mechanisms are presented in the workshop reference manual with further detail provided in the facts book

Requirements for ASR

Reactive Silica

Sufficient Alkali

Sufficient Moisture

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From our simplistic description of the mechanisms of ASR we can see that the three requirements for alkali-silica reaction are:

1. A sufficient quantity of reactive silica ... provided by the aggregate
2. A sufficient concentration of alkalis ... mainly contributed by the cement
3. And moisture ... provided by the environment

Rocks and Minerals

Rocks

Shale
Sandstone
Limestone
Chert
Flint
Quartzite
Quartz-arenite
Gneiss
Argillite
Granite
Greywacke
Siltstone
Arenite
Arkose
Hornfels

Reactive Minerals

Opal
Tridymite
Cristobalite
Volcanic glass
Cryptocrystalline (or microcrystalline) quartz
Strained quartz

Examples of Non-Reactive (Rock-Forming) Minerals

Calcite
Halite
Pyrite
Feldspar
Olivine
Topaz

And thousands more!

The following shows a list of rock types that are commonly used as concrete aggregates. Such rock types may or may not cause deleterious reaction in concrete – each source has to be evaluated separately. For example, most types of granite do not lead to damaging ASR in concrete, but a few isolated sources in North America have been implicated as the cause of damage in a limited number of ASR-affected structures. It depends on the composition of the rock.

Rocks are composed of minerals. An individual rock may be composed of many different minerals. Unlike rocks, minerals have a specific chemical composition and crystal structure. There are literally thousands of different minerals that go together to form the rocks that make up the earth's surface deposit. Only a few of these minerals are associated with causing damaging alkali-silica reaction in concrete. Common reactive minerals are listed.

Rocks and Minerals

Limestone is predominantly composed of the mineral calcite.

The chemical composition of calcite is calcium carbonate – CaCO_3

Calcite is chemically inert in concrete and pure limestone is not reactive.

However, limestone as a rock type may contain other minor minerals in addition to calcite.

For example, Spratt limestone (discussed later) contains about 9% silica (SiO_2) some of which is present as a highly disordered opaline material

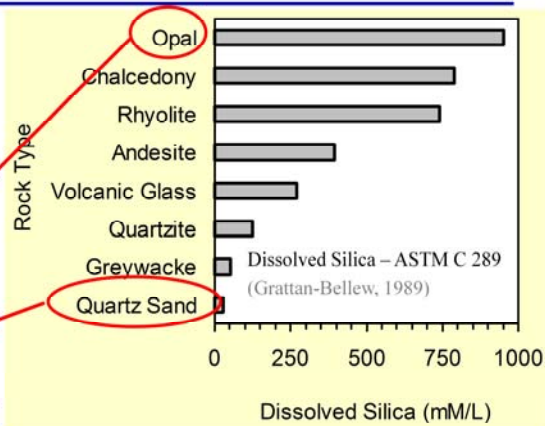
The presence of the opaline material renders Spratt rock a highly alkali-silica reactive aggregate (not alkali-carbonate reactive).

Care should be taken when distinguishing between rocks and minerals and when discussing reactive rock types. For example, limestone is one of the most widely used aggregate types. In its pure form it is composed entirely of the mineral calcite which chemically is calcium carbonate. Calcite is not on the list of minerals shown because it is chemically inert in concrete. Most limestones are NOT deleteriously reactive.

However, certain types of limestone may contain small quantities of silica. An example of such a rock is the Spratt limestone from Ontario. This rock is been used in a great number of research studies and much of the data shown later in this course come from studies using this material as a reactive aggregate. Spratt contains approximately 9% silica by mass – that is 9% silicon dioxide or S-I-O-2. This silica happens to be in a very reactive mineral form – it is opal. The presence of this opaline material renders the Spratt rock a highly reactive aggregate and its use in concrete has virtually ceased (apart from for research applications).

Rocks and Minerals

Amount of silica dissolved when a sample of crushed rock is immersed in a solution of NaOH (1 molar) at 80°C →



Mineral

Opal

Quartz

Chemical composition

SiO₂

SiO₂

Not all siliceous minerals react to a significant degree in concrete.

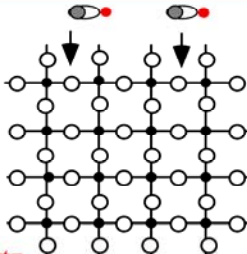
In fact, most siliceous aggregates do NOT cause deleterious reaction.

One of the methods commonly used to determine the reactivity of silica-containing or siliceous aggregates is the ASTM C 289 Quick Chemical Test. This test involves immersing a sample of crushed rock in a hot alkaline solution and determining the quantity of silica or SiO₂ that goes into solution (in other words how much dissolves).

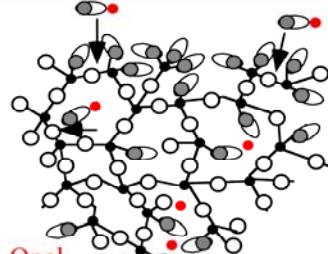
The bar chart shows data for a number of siliceous rock types. It can be seen that the quantity of soluble silica varies widely between rock types. Indeed the solubility of silica is strongly dependent on its crystal structure – in other words it is a function of its mineralogy.

This can be demonstrated by comparing the results for opal and quartz sand. Both of these rocks are composed of silica minerals and their chemical composition is predominantly silica – which is silicon dioxide or SiO₂.

Rocks and Minerals




Quartz



Opal


• Si ○ O ◐ OH ● Na or K

<u>Mineral</u>	<u>Chemical composition</u>	<u>Structure</u>
Opal	SiO ₂	Disordered, amorphous
Quartz	SiO ₂	More crystalline, ordered



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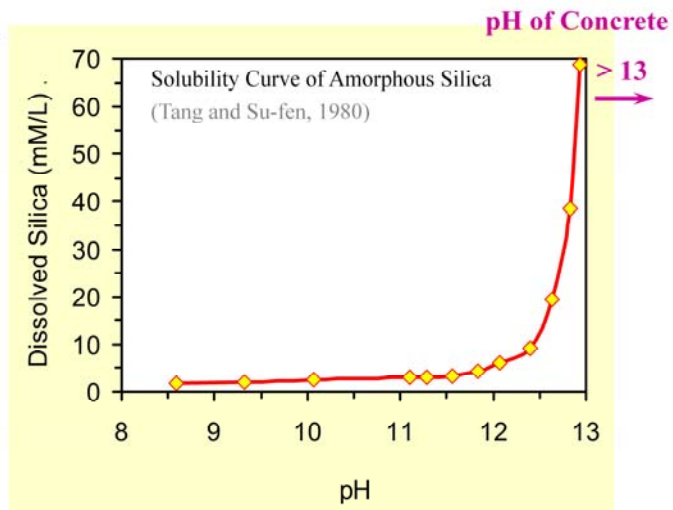
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The difference between the minerals is that quartz has a highly ordered crystal structure which makes it very stable in an alkali environment – whereas opal has a highly disordered structure and is thermodynamically unstable in concrete – in other words it dissolves.

It is important to understand that not all silica-bearing minerals are reactive and that not all siliceous rock types cause problems in concrete. Indeed, it can be said that most siliceous aggregates do NOT lead to damaging ASR in concrete.

Role of pH

Effect of the pH of the alkali solution on the solubility of amorphous silica →



This graph shows that the solubility of silica is not just dependent on the form and structure of the silica mineral, but also on the composition of the solution. Even highly amorphous silica will not dissolve unless the pH of the solution is sufficiently high – in other words unless the solution is sufficiently alkaline.

This goes back to our original requirements for ASR – moisture – reactive silica – AND sufficient alkali. As we introduce more and more alkali then the pH inside the concrete will increase – this will be explained in the following section.

Requirements for ASR



Sources of Alkali in Concrete

- **Portland cement**
- Other cementing materials
 - Fly ash
 - Slag
 - Silica fume
- Chemical admixtures
- Wash water (if used)
- Aggregates
- External sources
 - Seawater
 - Deicing chemicals

In most cases, the main source of alkali in concrete is the Portland cement. However, there are other potential sources including other cementing materials such as fly ash, slag or silica fume, certain types of chemical admixtures, recycled wash water, and some aggregates. Additionally, alkalis may be contributed from external sources such as when concrete is exposed to seawater or deicing chemicals such as rock salt.

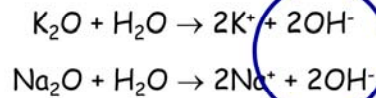
Alkalis in Portland Cement

Typical Oxide Analysis

Oxide	%
SiO ₂	20.55
Al ₂ O ₃	5.07
Fe ₂ O ₃	3.10
CaO	64.51
MgO	1.53
K ₂ O	0.73
Na ₂ O	0.15
SO ₃	2.53
LOI	1.58

+ other trace elements

Alkalis (sodium & potassium) represent a small proportion of the cement



Most of the alkalis end up in the pore solution and the associated OH concentration is sufficient to produce a pH in the range of 13.2 to 14.0

A typical oxide analysis is shown for portland cement. The main component of portland cement is calcium oxide followed by silica, alumina and iron. These four compounds are responsible for producing the main clinker compounds of portland cement – the calcium silicates, calcium aluminate and ferrite minerals. Sulfate – in the form of calcium sulfate (for example gypsum) is added to the clinker during grinding to control setting. The raw materials used to manufacture portland cement contain many other compounds albeit in relatively low quantities – these include magnesia (or M-G-O) and the alkalis sodium and potassium. The oxide form of sodium is written as N-A-2-O and that of potassium as K-2-O.

As can be seen from the chemical analysis of this cement – the alkali oxides represent a very small proportion of the cement. However, the alkalis are the most soluble of all the phases in cement and the pore solution of hardened concrete (i.e. the solution in the pores of concrete) is dominated by the alkalis. Indeed, after about 1 day the pore solution is composed almost entirely of sodium ions – potassium ions – and hydroxyl ions. Sodium and potassium are positively charged ions called cations – and these have to be balanced by negatively charged ions or anions – in concrete the negative ions are supplied by hydroxyl ions – written as O-H-minus. It is the hydroxyl ions that create the condition of the high pH. The more sodium and potassium that is available – the more hydroxyl ions that are required to balance the solution – AND the higher the pH.

Alkalis in Portland Cement

Typical Oxide Analysis

Oxide	%
SiO ₂	20.55
Al ₂ O ₃	5.07
Fe ₂ O ₃	3.10
CaO	64.51
MgO	1.53
K ₂ O	0.73
Na ₂ O	0.15
SO ₃	2.53
LOI	1.58

+ other trace elements

Alkali Equivalent or “Equivalent Soda”

- K₂O converted to an “equivalent” content of Na₂O
- Based on respective molecular weights of sodium and potassium oxide
- Total sodium oxide equivalent is often written as Na₂O_e
- Calculated as follows:

$$\text{Na}_2\text{O}_e = \text{Na}_2\text{O} + 0.658 \text{K}_2\text{O}$$

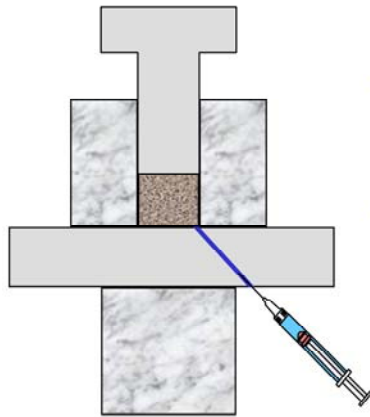
For the analysis shown the equivalent soda is:

$$0.15 + 0.658 \times 0.73 = 0.63 \% \text{Na}_2\text{O}_e$$

When discussing cement alkalis – it is convenient to combine the alkalis of sodium and potassium into a single value. This is done by introducing the concept of equivalent alkalis. The percentage value of potassium is converted into an EQUIVALENT amount of sodium oxide by applying a multiplying factor of 0.658 (this is in fact the ratio of the molecule weights of sodium and potassium oxide). The equivalent alkali content is then equal to the sum of the sodium oxide plus the converted amount of potassium oxide or the N-A-2-O content plus 0.658 times the K-2-O content. The equivalent alkali or equivalent soda as it is sometimes called is written as N-A-2-O with the letter E at the end to indicate equivalent. Sometimes the letters E-Q are used in place of the letter E.

To calculate the equivalent alkali content for the cement analysis shown – it is simply the N-A-2-O content of 0.15 plus 0.658 times the K-2-O content of 0.73 which yields 0.63 percent N-A-2-O-E.

Pore Solution Expression & Analysis



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

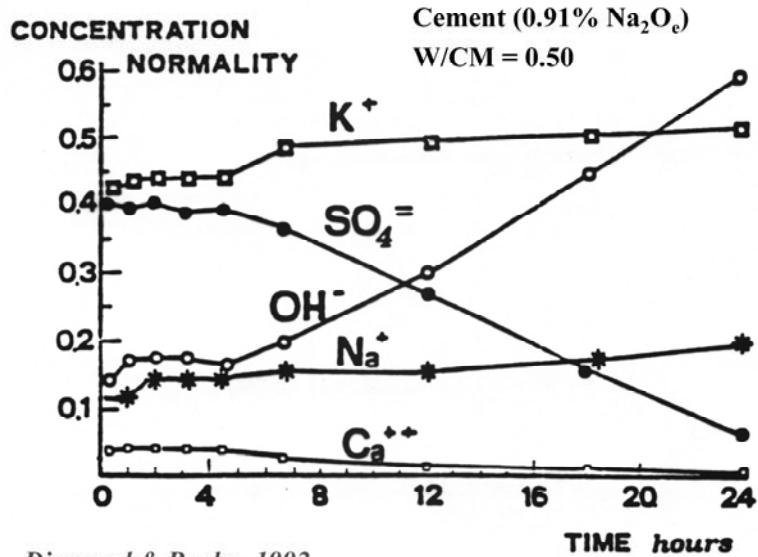
We have mentioned the term pore solution a couple of times – what exactly do we mean by this.

Concrete is a porous material and in an exposed environment the pores are filled with water containing various dissolved species – in other words the pores are filled with a solution that we call the pore solution.

There are devices that can be used to physically squeeze the pore solution out of hardened cement paste, mortar or concrete samples using very high pressures of the order of 500 megapascals or seventy thousand p-s-I

The composition of the solution can then be determined using appropriate analytical techniques

Pore Solution Composition – First 24 Hours



Diamond & Penko, 1992

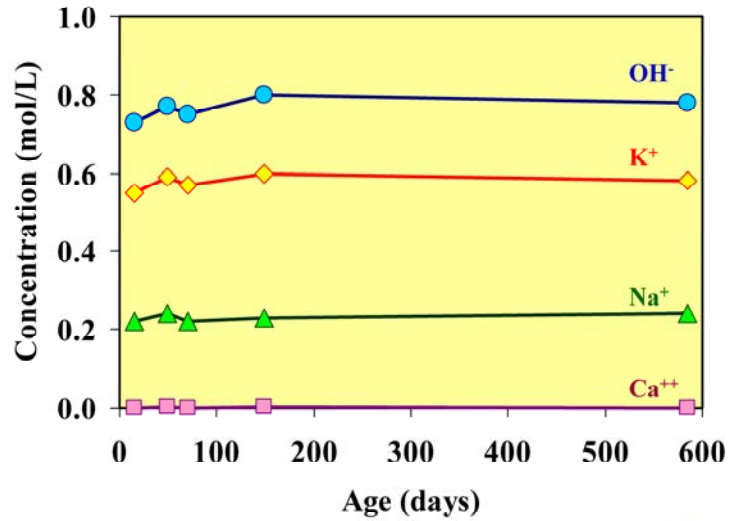
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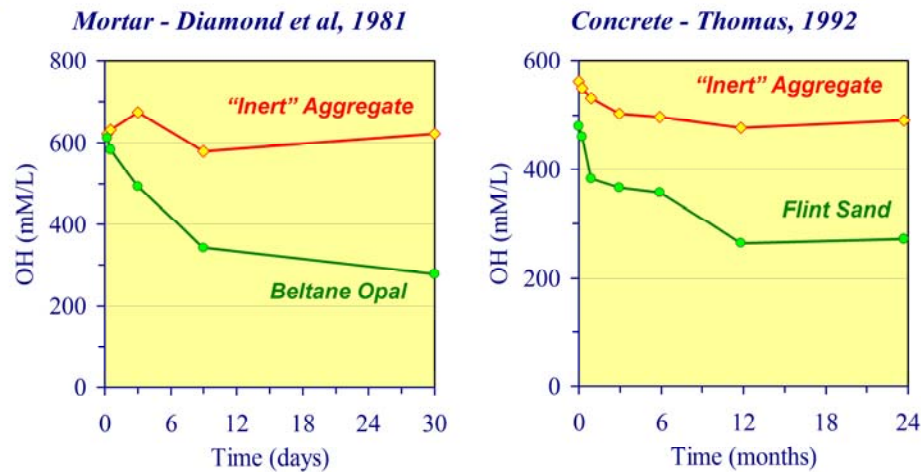
The composition of the pore solution is very dynamic during the first 24 hours. The most soluble compounds in the cement are alkali sulphates and as soon as cement and water are mixed together sodium (Na-plus), potassium (K-plus) and sulfate ions (S-O-4-2-minus) go in to solution with some small amount of calcium (C-a-2-plus). After a few hours the sulfate precipitates out as ettringite and hydroxyl ions (O-H-minus) come into solution to balance the positive Na and K ions.

Pore Solution Composition – After 24 Hours



Beyond this one day period – there is little change in the composition of the pore solution. It remains dominated by sodium, potassium and hydroxyl ions. Of course ... if there is reactive silica present ... there will be a reduction in the concentration of these ions.

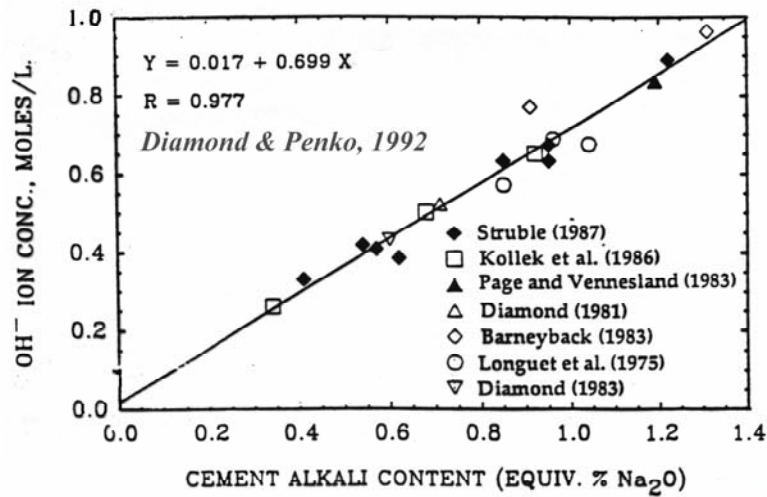
Pore Solution – Effect of ASR



It is generally agreed that $OH > 0.200$ mol/L is required to sustain ASR

This is shown here – by studying the change in the hydroxyl ion concentration. On the left we see how the OH concentration in mortar decreases with time in the presence of a highly reactive sand – Beltane Opal – the concentration dropping from about 600 millimoles per liter to about 250 in a matter of a few weeks. On the right we have a concrete with a more slowly reactive flint sand where it takes months rather than weeks for a similar reduction in OH concentration to occur.

Pore Solution – Effect of Cement Alkalis

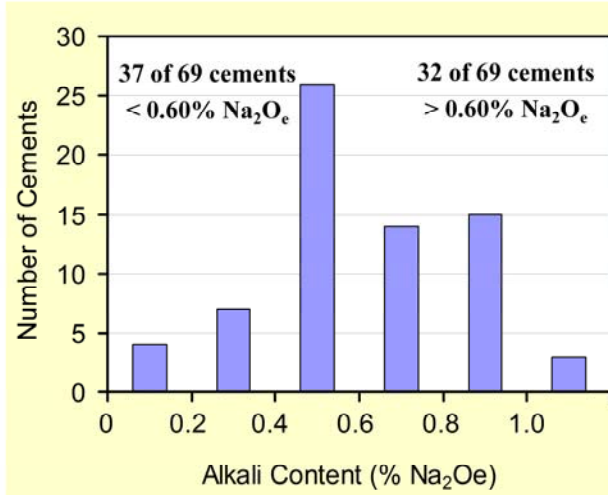


Example: A paste with $w/c = 0.50$ produced with a high-alkali Portland cement with 1.00% Na₂O_e will have a pore solution with ~ 0.7 mol/L OH⁻ ions (~ pH 13.85)

The hydroxyl ion concentration of a cement paste sample is directly related to the alkali content of the cement as might be expected. Describe example.

Alkali Contents of North American Cements

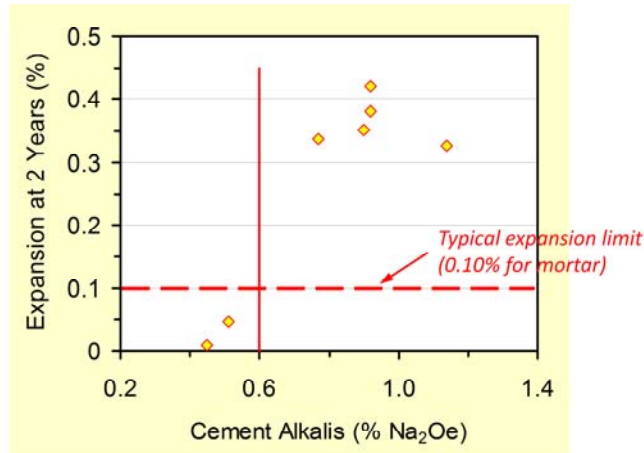
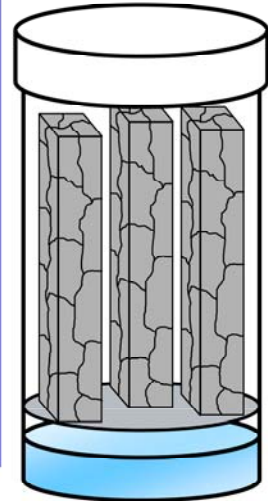
Alkali contents of 69 sources of Type I cement in North America
(Gebhardt, 1995)



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

Effect of Alkalis on Expansion

Results of Stanton's Mortar Bar Tests (*Stanton, 1940 & 1952*)



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.

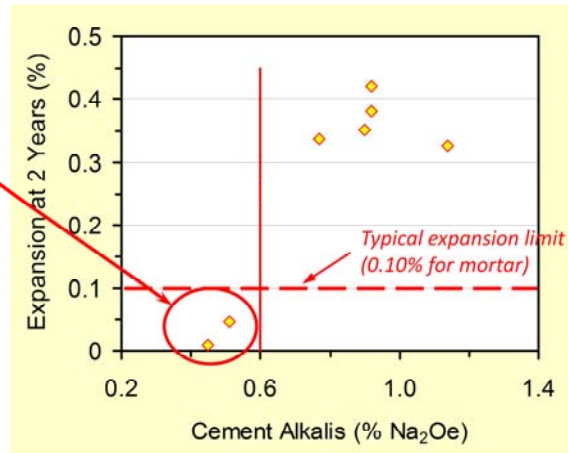
Many jurisdictions in the U.S. still specify the use of low-alkali cement as means of preventing damaging ASR. As we will see later in the course, such a measure is NOT sufficient to guarantee that damage does not occur.

Effect of Alkalis on Expansion

Results of Stanton's Mortar Bar Tests (*Stanton, 1940 & 1952*)

Expansion unlikely if
cement alkalis
< 0.60% Na₂Oe

This work defined the concept
of "low-alkali cement".
It is still generally believed
today (wrongly so) that the use
of such cement is a sufficient
measure to avoid damaging
ASR



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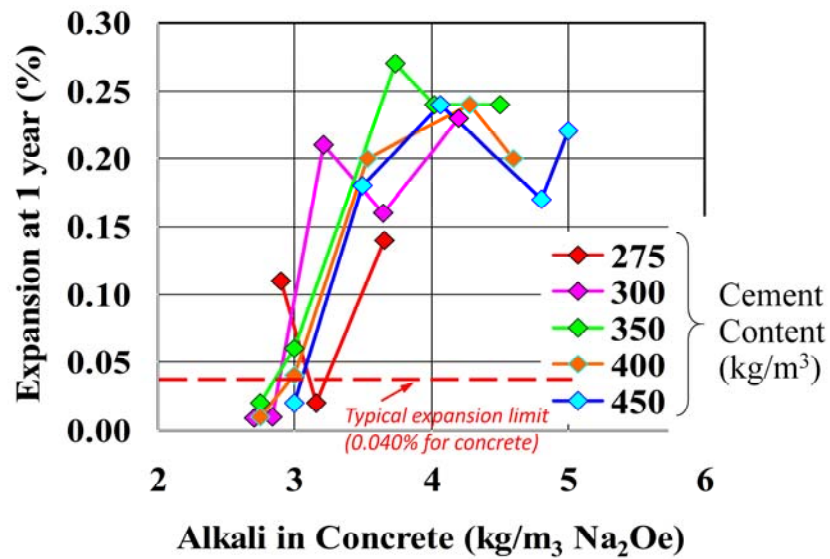
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Many jurisdictions in the U.S. still specify the use of low-alkali cement as means of preventing damaging ASR. As we will see later in the course, such a measure is NOT sufficient to guarantee that damage does not occur.

Effect of Concrete Alkali on Expansion



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Slide 45

U.S. Department of Transportation
Federal Highway Administration

It is now generally accepted that the risk of asr is a function of the alkali content of the concrete rather than the alkali content of the cement. The alkali content of the concrete is – of course – a function of the alkali content of the cement BUT it also depends on the cement content of the concrete.

What this means is that concrete produced with a large quantity of low-alkali cement can still contain a sufficient quantity of alkalis to promote expansion.

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:

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

$\text{kg/m}^3 \text{ Na}_2\text{Oe}$ kg/m^3 $\% \text{ Na}_2\text{Oe}$

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

$\text{lb/yd}^3 \text{ Na}_2\text{Oe}$ lb/yd^3 $\% \text{ Na}_2\text{Oe}$

The alkali content in concrete does not depend solely on the alkali content of the Portland cement, but also on the quantity of that Portland cement. The alkali content of the concrete is the product of the cement content of the concrete and the alkali content of the cement.

To determine the alkali content of the concrete in units of kilograms of equivalent alkali per cubic meter of concrete one multiplies the cement content of the concrete (in kilograms per cubic meter) by the alkali level of the cement. This quantity is divided by one hundred because the alkali level of the cement is expressed on a percentage basis.

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Example:

If a concrete contains 350 kg/m³ of Portland cement and the cement has an alkali content of 0.78% Na₂O_e then the alkali content of the concrete is:

$$= \frac{350 \times 0.78}{100} = 2.73 \text{ kg/m}^3 \text{ Na}_2\text{O}_e$$

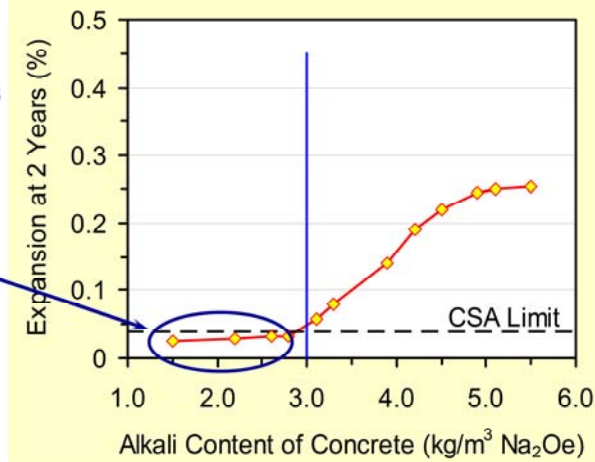
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Alkali Content of Concrete

Expansion unlikely to occur in laboratory tests if the alkali content of concrete $< 3.0 \text{ kg/m}^3$ (5.0 lb/yd^3)

Many specifications have used a 3-kg or 5-lb limit, but ...



This graph shows the expansion of concrete specimens with a reactive aggregate as a function of the alkali content in the concrete. There is a threshold alkali content below which no significant expansion occurs (in this case 3 kg per cubic metre) – above this level an increase in alkali results in increase in expansion until a certain level of alkali is reached beyond which any further increase in the alkali content does not lead to increased expansion. In this case that value appears to be around 5 kg of equivalent alkali per cubic metre of concrete.

Also shown on this graph is a broken line labelled as the CSA limit. In the Canadian Standards Association guidelines for ASR – an expansion above 0.04% is deemed to represent significant deleterious expansion. Below this value, the expansion is considered to represent non-damaging reactivity.

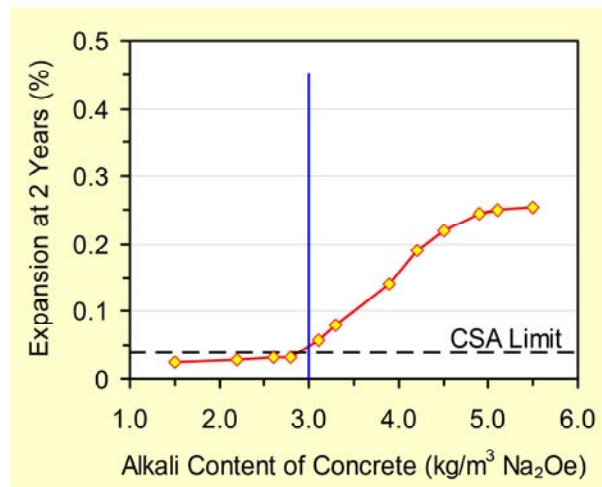
The data show that provided the alkali content in the concrete mix is kept below 3 kg of equivalent alkali per cubic metre of concrete – there will be no deleterious expansion

The actual alkali content – that is the amount of alkali required to produce damaging reaction in concrete – varies from one aggregate to another. Also, it has been observed that concrete in the field – in other words real structures – may suffer damage at a lower alkali content than that required to produce damage in the laboratory.

Alkali Content of Concrete

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 $3 \text{ kg/m}^3 \text{ Na}_2\text{O}_e$ ($5 \text{ lb/yd}^3 \text{ Na}_2\text{O}_e$)



This graph shows the expansion of concrete specimens with a reactive aggregate as a function of the alkali content in the concrete. There is a threshold alkali content below which no significant expansion occurs (in this case 3 kg per cubic metre) – above this level an increase in alkali results in increase in expansion until a certain level of alkali is reached beyond which any further increase in the alkali content does not lead to increased expansion. In this case that value appears to be around 5 kg of equivalent alkali per cubic metre of concrete.

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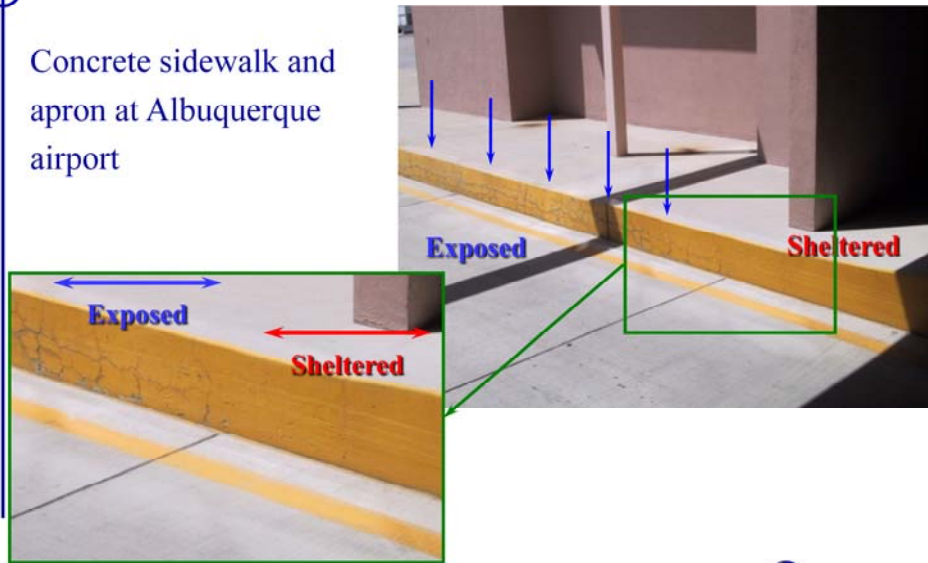
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Requirements for ASR



Role of Moisture

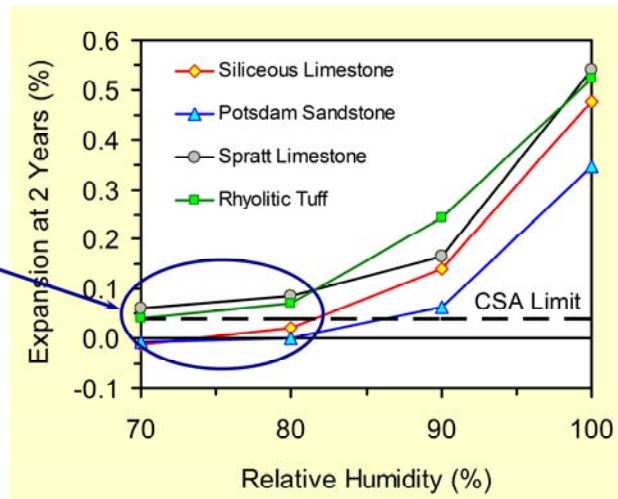
Concrete sidewalk and apron at Albuquerque airport



This slide shows cracking of a concrete sidewalk at an airport – the cracking is accentuated in the concrete that is painted yellow. The painted concrete in the left had side of the picture is severely cracked – but the same concrete to the right appears undamaged. The only difference here is the exposure condition as the concrete to the right is actually sheltered from direct precipitation by a building.

Effect of Relative Humidity

Little significant expansion if the relative humidity is maintained below about 80%



Pedneault, 1996

The graph in this picture shows some data from a laboratory study conducted at the University of Laval. In the study concrete prisms were produced with 5 different reactive aggregates (including an alkali-carbonate reactive aggregate) and were then stored at a range of different relative humidities.

The graph shows the expansion of the concrete after 2 years of storage plotted against the relative humidity of the storage. It is generally considered that ASR will cease once the relative humidity within the concrete has fallen below 80%.



Except in arid climates – the vast majority of concrete elements within a civil engineering structure may be expected to be exposed – at least periodically – to sufficient levels of moisture to promote ASR expansion in concrete – provided of course that concrete contains enough reactive aggregate and alkali.

Consequently, limiting the availability of moisture is rarely a viable option for preventing ASR

History of ACR



E.G. Swenson
NRC Canada



Kingston & Cornwall, Ontario

- First discovered in the late 1950s
- Abnormal cracking in sidewalks, curbs, floors and foundation walls in Kingston, Ontario
- Reactivity not detected by ASTM C 289 *Quick Chemical Test* of ASTM C 227 *Mortar-Bar Method*

The rest of the presentation will discuss alkali-carbonate reaction – A-C-R.

The reaction was first discovered by Ed Swenson of the National Research Council of Canada as the cause of damage in sidewalks, curbs, floors and foundation walls in Kingston, Ontario.

It was also discovered that alkali-carbonate reactive rocks were not detected by the then current test methods used to detect alkali-silica reactive rocks

Occurrences of ACR in North America

- Ontario
- Indiana
- Illinois
- Iowa
- Virginia
- Kentucky

Since then A-C-R has been alleged to be the cause of damage in a few states in the USA.

Alkali-Carbonate Reactive Rock Types

- Classic rock type subjected to ACR is **argillaceous dolomitic limestone**

CaCO_3	Calcite
$\text{CaMg}(\text{CO}_3)_2$	Dolomite
MgCO_3	Magnesite

The classic rock type that causes ACR is an argillaceous dolomitic limestone. Dolomite is a mixed calcium-magnesium carbonate and usually makes good (stable) concrete aggregate – it is only argillaceous dolomites (meaning dolomites with a high clay content) that cause damaging reaction.

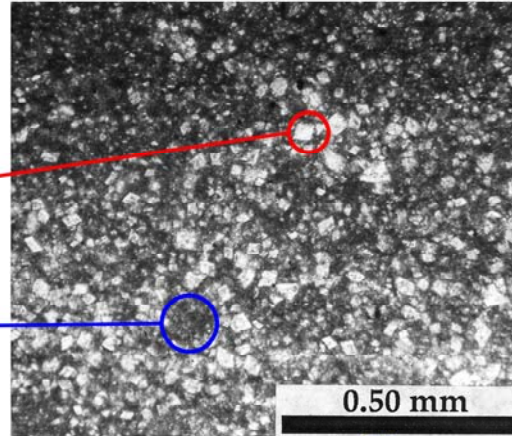
Alkali-Carbonate Reactive Rock Types

- Classic rock type subjected to ACR is **argillaceous dolomitic limestone**

Unique Petrographic Texture:

**Dolomite rhombs
(10 to 50 μm)**

**Floating in a fine-grained
matrix of clay minerals,
calcite and silica**



The classic ACR rock type also has a very specific texture being composed of small dolomite rhombs suspended in a matrix of clay minerals and fine-grained calcite and silica

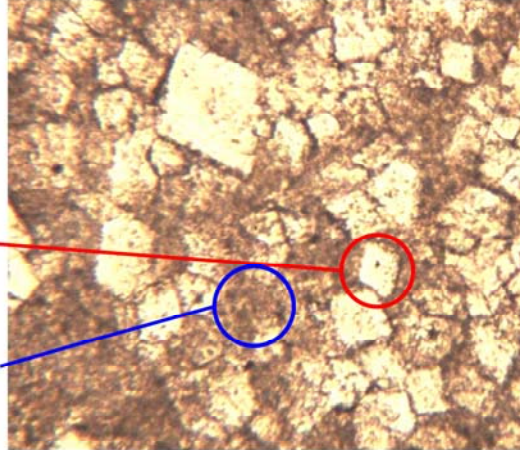
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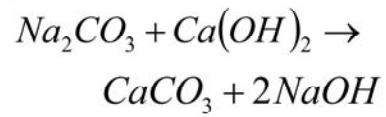
Floating in a fine-grained matrix of clay minerals, calcite and silica



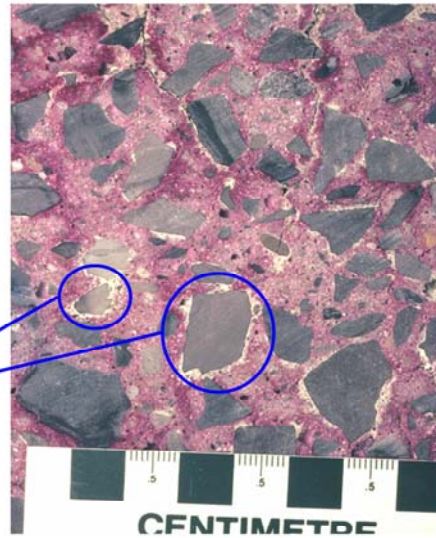
Courtesy of Chris Rogers, MTO

This slide is the same as the last – just with a different illustration of the texture

ACR Mechanisms



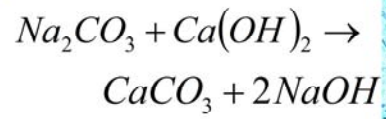
Carbonate halos



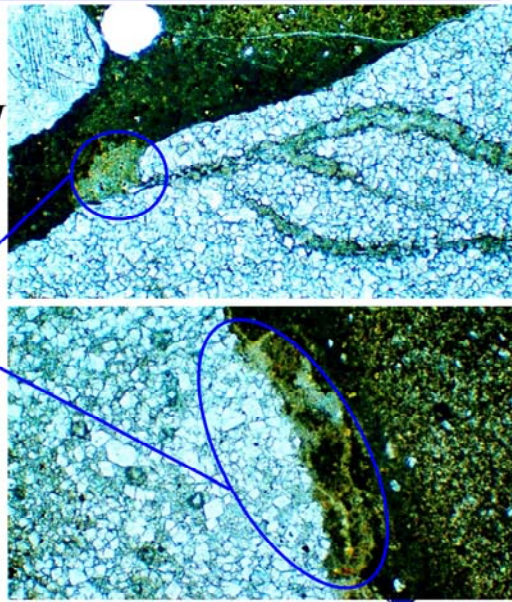
Courtesy of Chris Rogers, MTO

It is interesting that the consumption of calcium hydroxide leads to carbonated zones around reacting particles – as shown by using a phenolphthalein indicator.

ACR Mechanisms



Carbonate halos



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Slide 6
Courtesy of Benoit Fournier
U.S. Department of Transportation
Federal Highway Administration

This slide shows thin sections illustrating zones of carbonated paste around reacting aggregate particles.

ACR Characteristics

- Damage can occur very rapidly (e.g. 1 to 2 years)
- Expansion occurs with very low-alkali cement
- Pozzolans & slag generally not effective
- Lithium-based admixtures not effective

Listed are some characteristics of ACR that differentiate the reaction from ASR. These were mentioned previously.