

Alkali-Aggregate Reactions





Alkali-Aggregate Reaction (AAR)

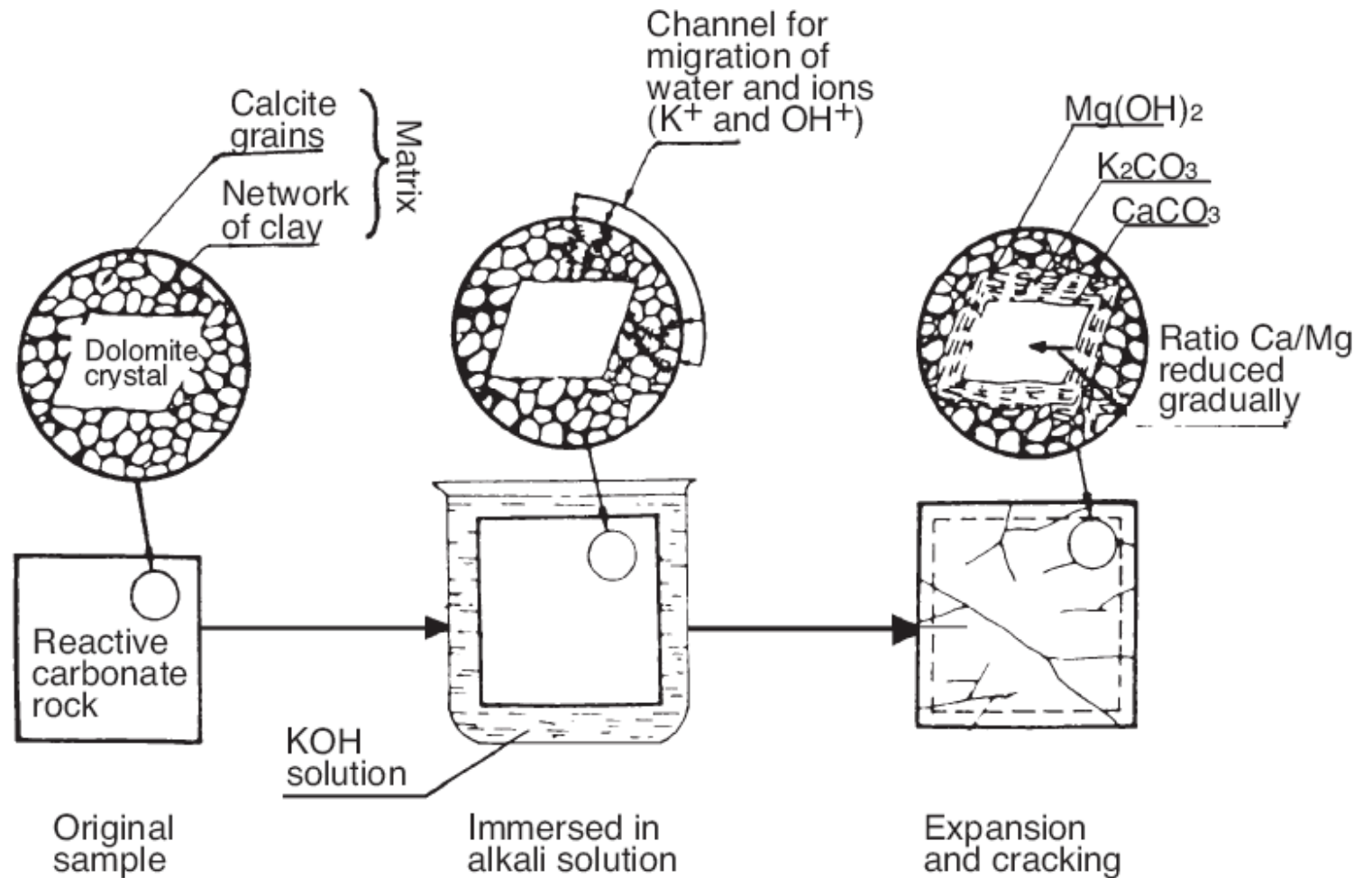
Alkali-Carbonate Reaction (ACR)

Alkali-Silica Reaction (ASR)

Alkali-Carbonate Reaction (ACR) – is related to a dedolomitization of dolostones and dolomitic limestones, and the associated expansion of the coarse aggregate particles. ACR is a serious, but fortunately rare, variety of AAR.

Alkali-Silica Reaction (ASR) – is associated with the dissolution of silica (SiO_2) in the aggregate and the subsequent formation of alkali-silica gel in the aggregate and concrete.

ACR Mechanism



Tang, Liu, and Han 1987



ACR Prevention

- Selective quarrying
- Blending aggregate
- Reducing aggregate size
- Not effective
 - ◆ Use of pozzolans
 - ◆ Low-alkali cement
 - ◆ Lithium?



ASR EXAMPLES

Cracking



Cracking



Misalignment of Sections



SHRP-C-315

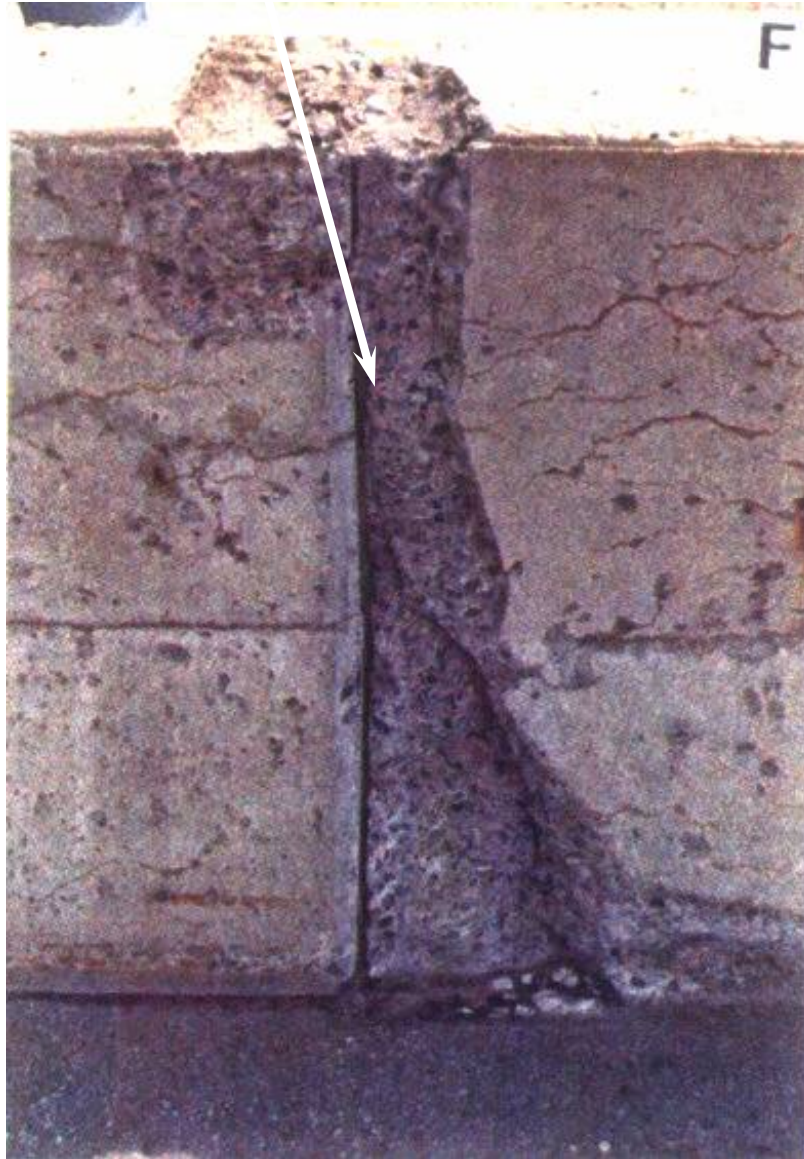
Closing of joints or loss of clearance between members



Extrusion of joint-sealants

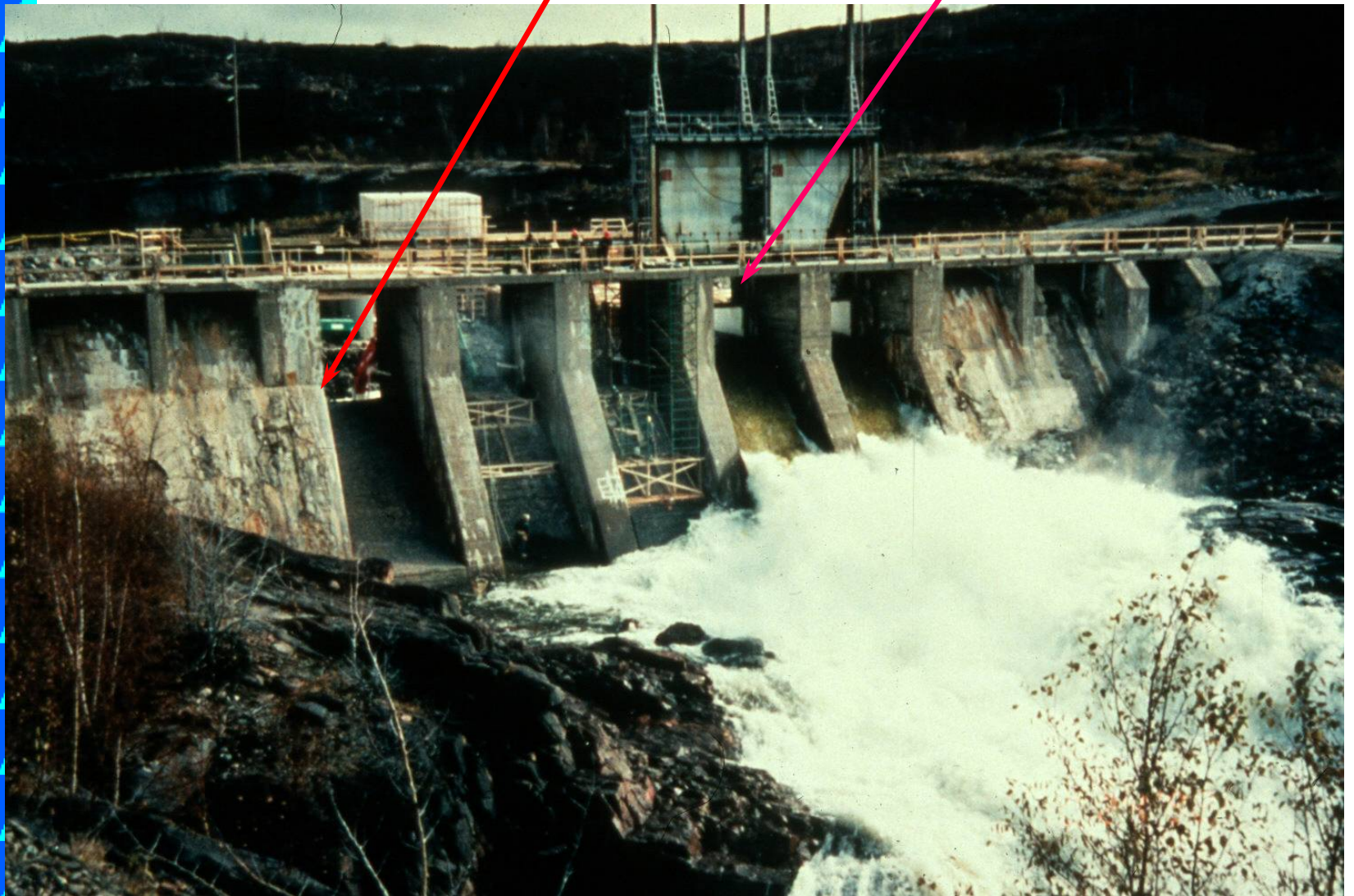


Concrete crushing



CSA A864-00

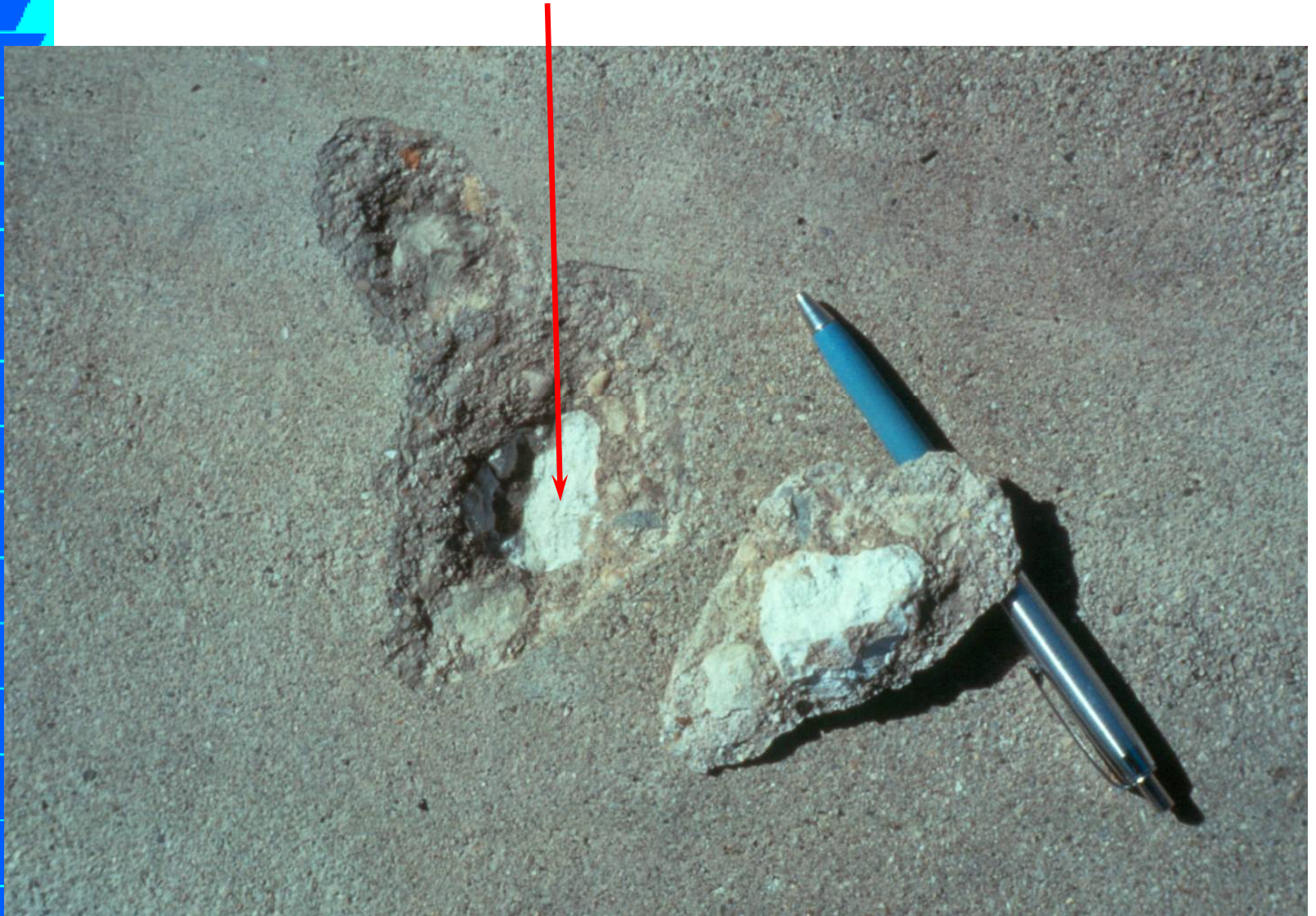
Operational difficulties

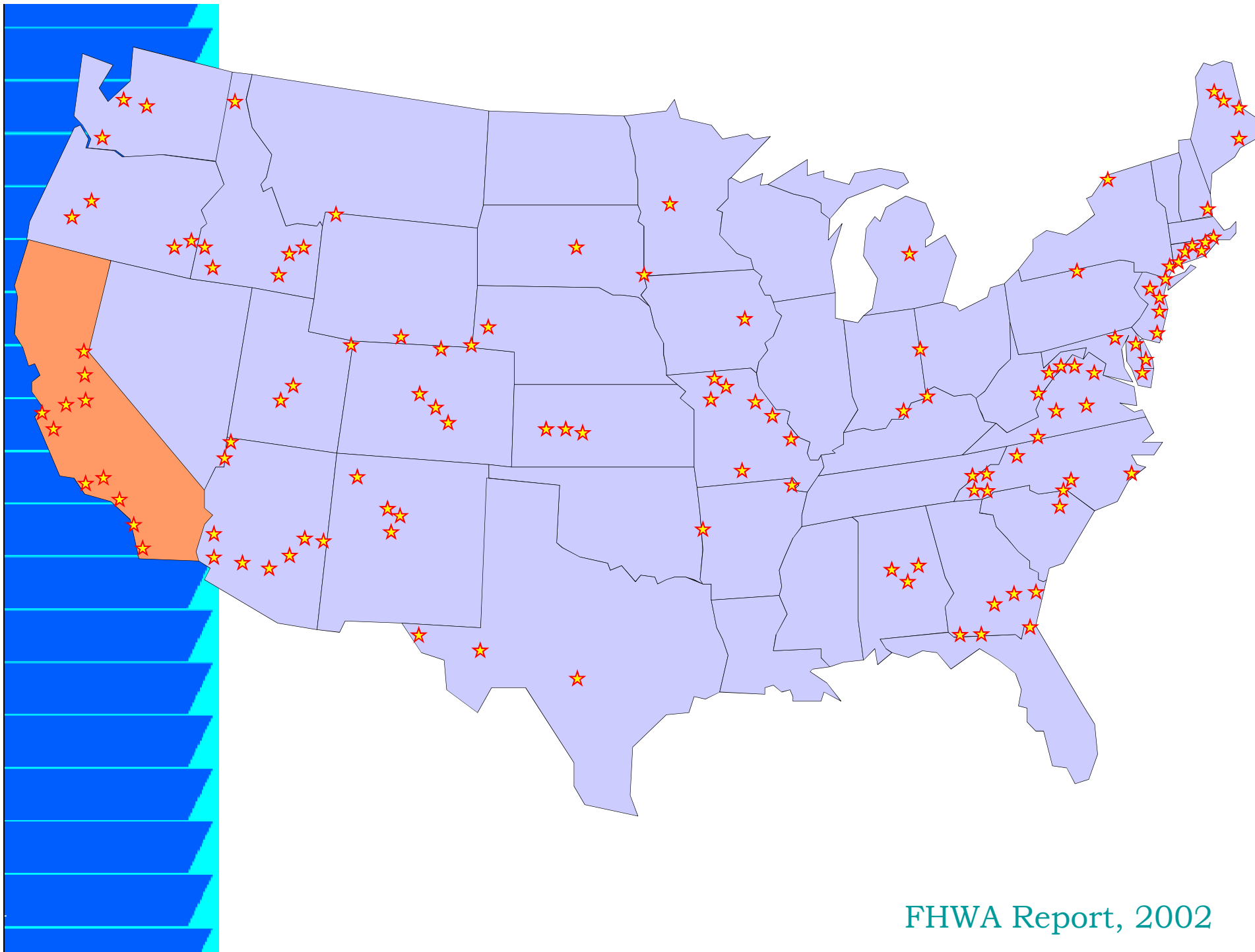


Discoloration or “gel staining” around cracks



Popouts





FHWA Report, 2002

ASR EXPANSION MECHANISM

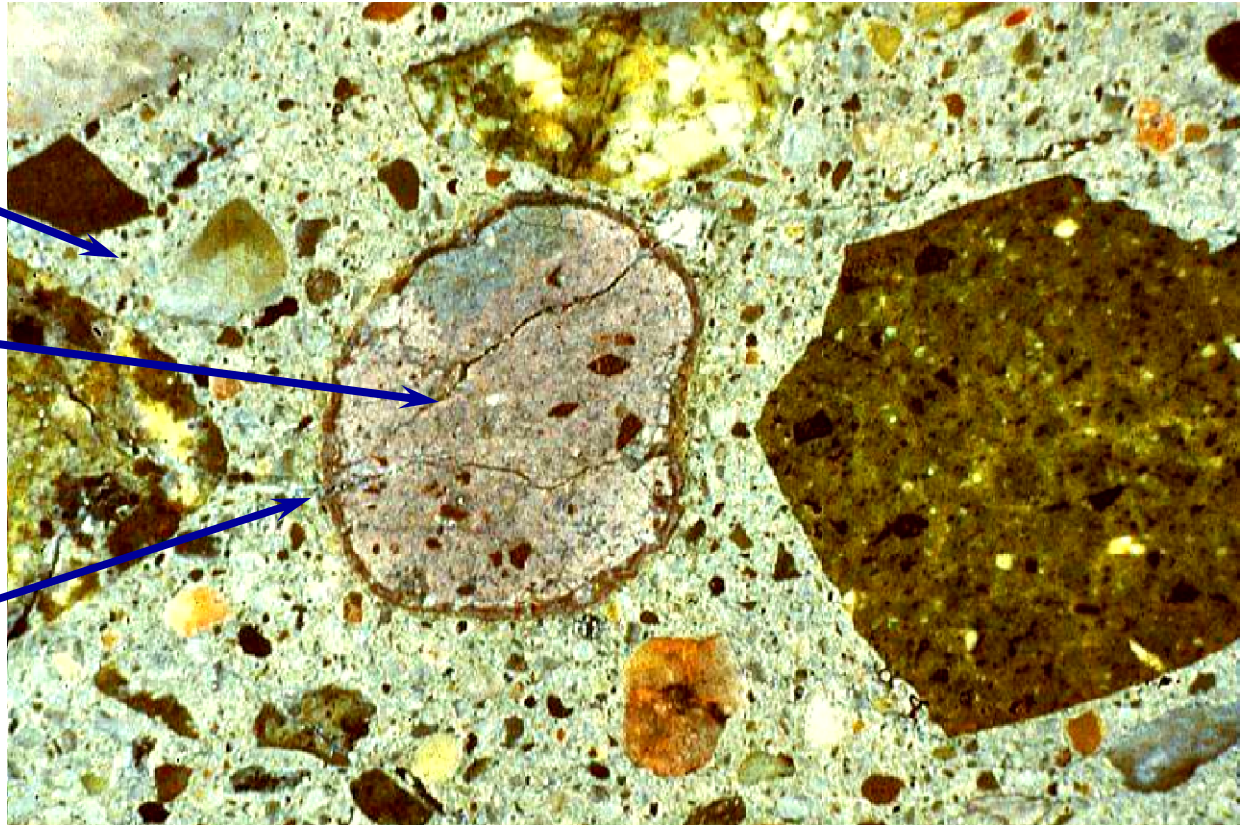


ASR in Concrete Polished Section

Cement
paste

Reactive
aggregate

Reaction
product



ASR in Concrete Thin Section

Cement
paste

Reactive
aggregate

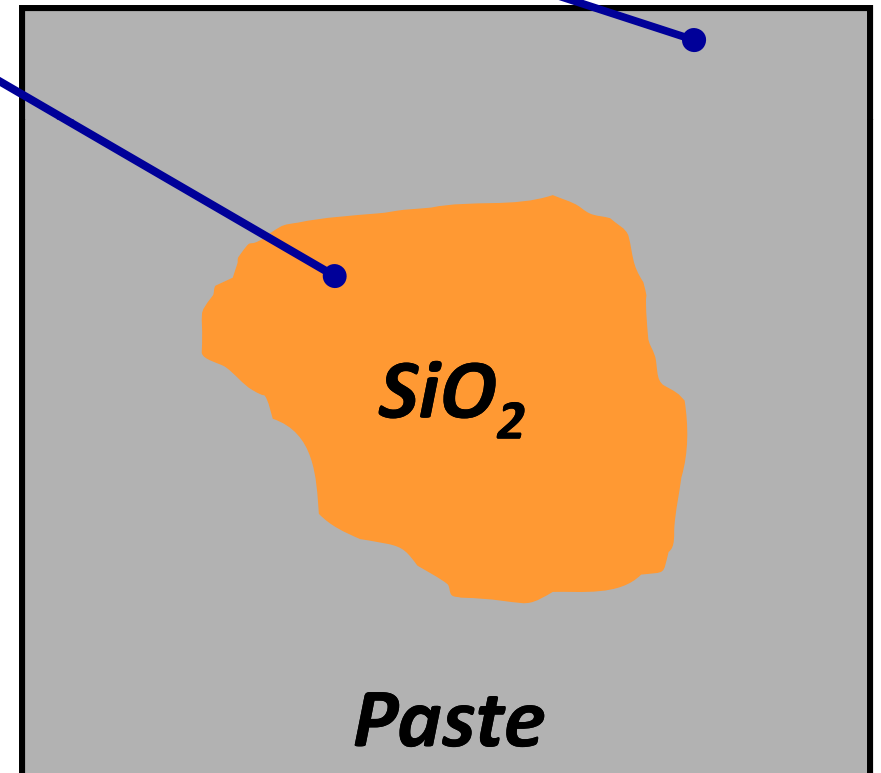
Reaction
product



ASR Mechanism

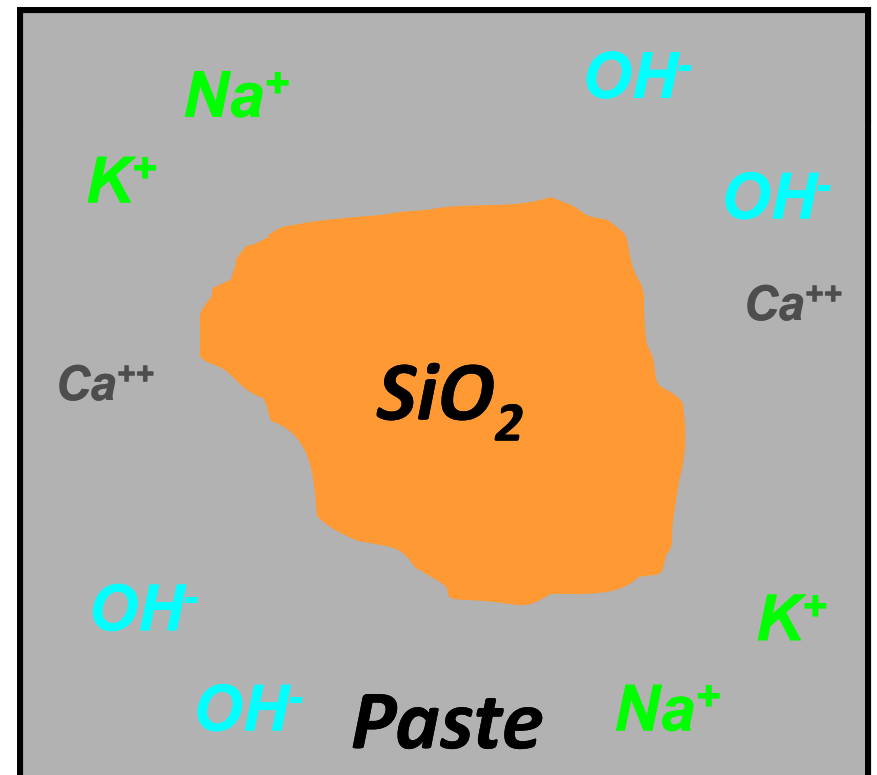
Concrete “model” showing:

- cement paste
- reactive siliceous aggregate



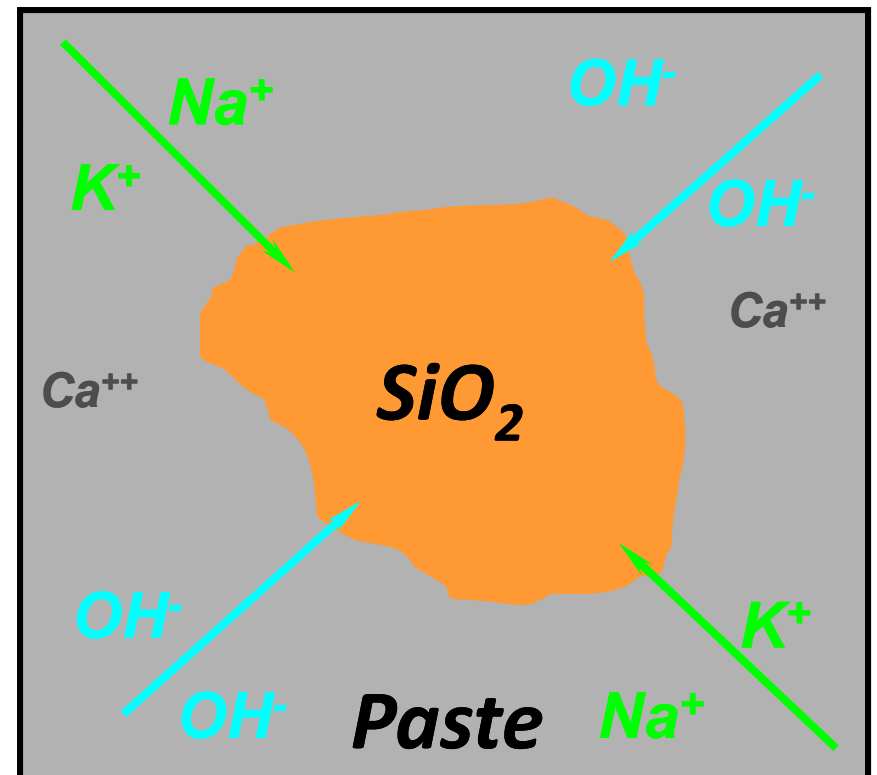
ASR Mechanism

- Pore solution dominated by:
 - sodium, Na^+
 - potassium, K^+
 - hydroxyl, OH^-
 - minor amounts of calcium, Ca^{++} and other ionic species



ASR Mechanism

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



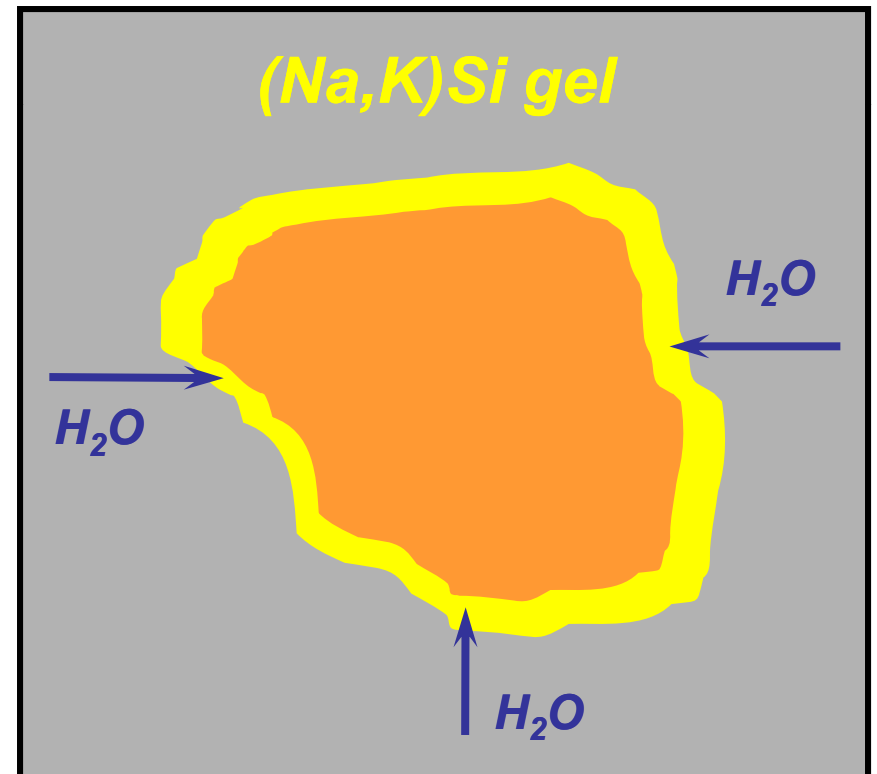
ASR Mechanism

- Forming an alkali-silica gel composed predominantly of Na , K & Si .



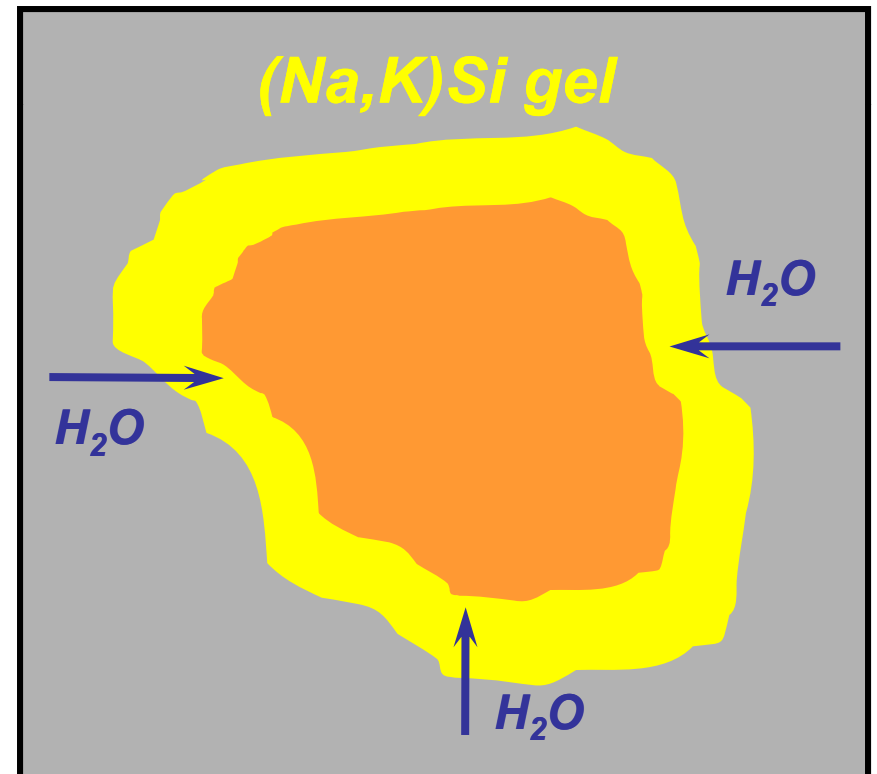
ASR Mechanism

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



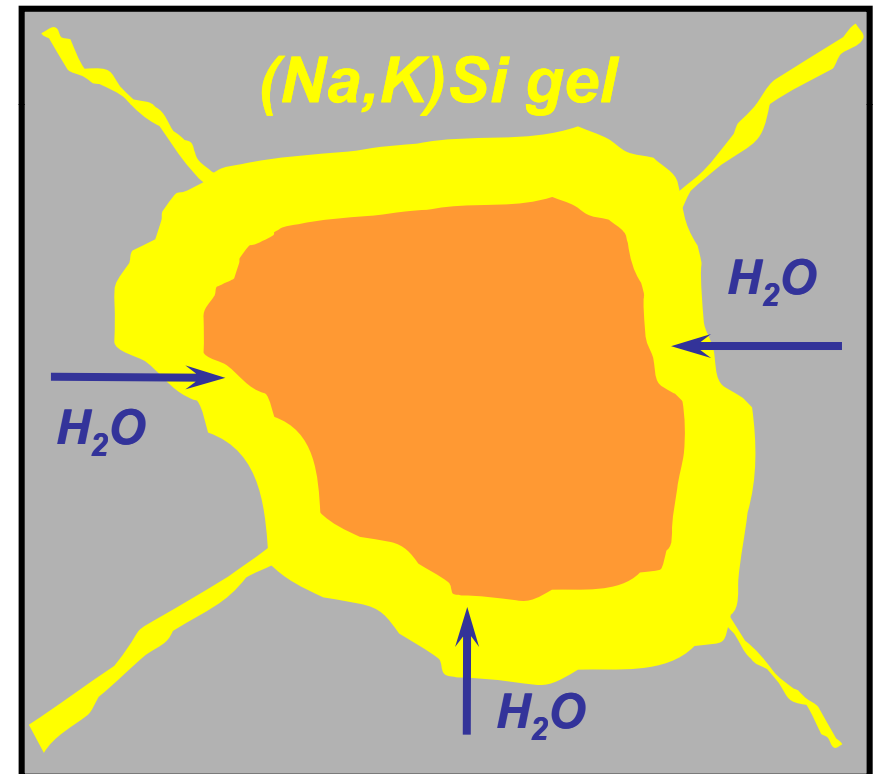
ASR Mechanism

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



ASR Mechanism

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



ASR Mechanism

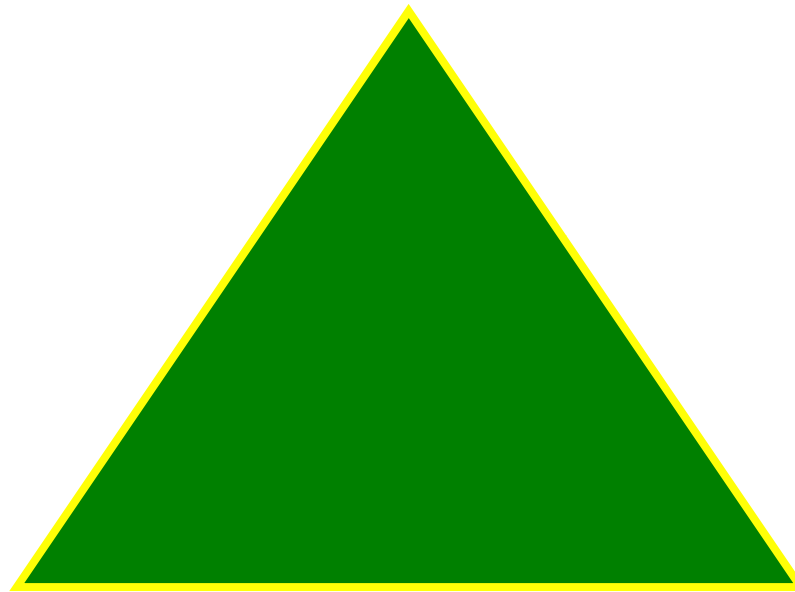


Three Necessities for ASR

Reactive Silica

Sufficient
Alkali

Sufficient
Moisture





ASR-Susceptible Rocks and Minerals

Rocks

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

Reactive Minerals

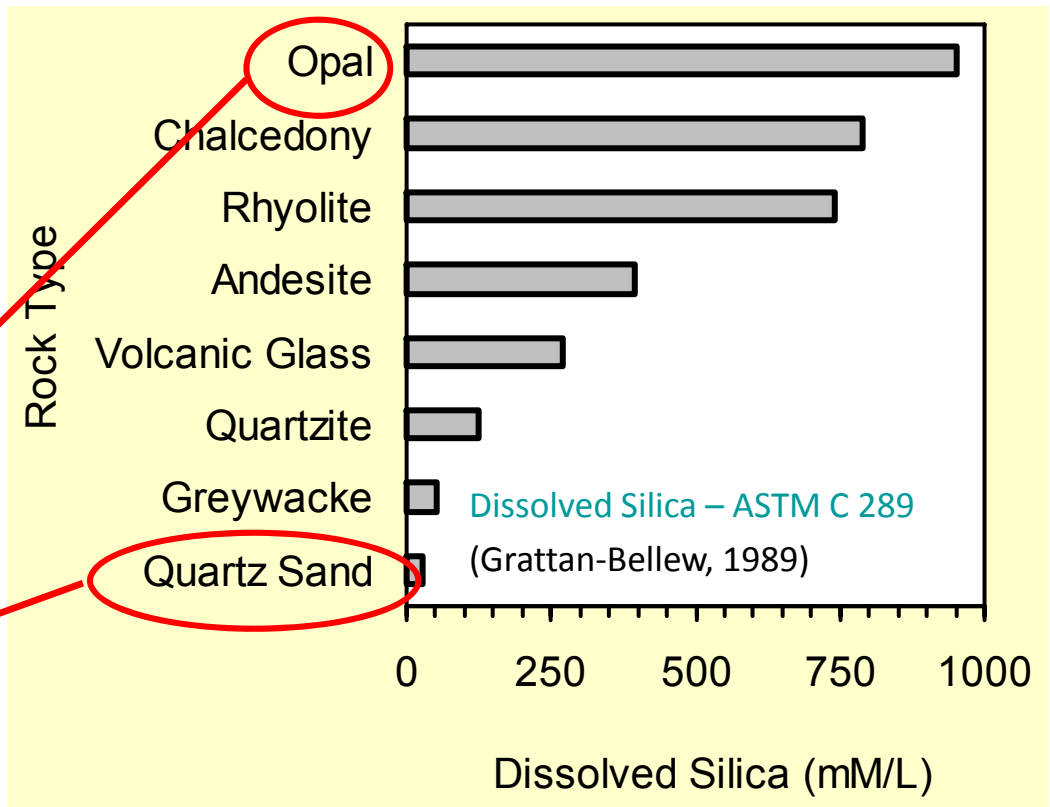
Opal
Tridymite
Crisobalite
Volcanic glass
Cryptocrystalline
(or microcrystalline) quartz
Strained quartz



ASR-Susceptible 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 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 a highly reactive aggregate.

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.

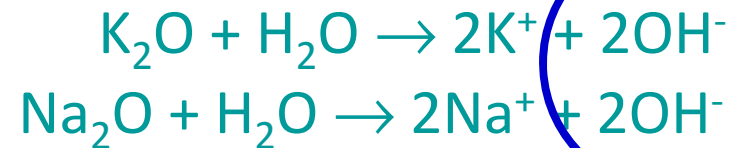
Composition of Portland Cement

Oxide Analysis

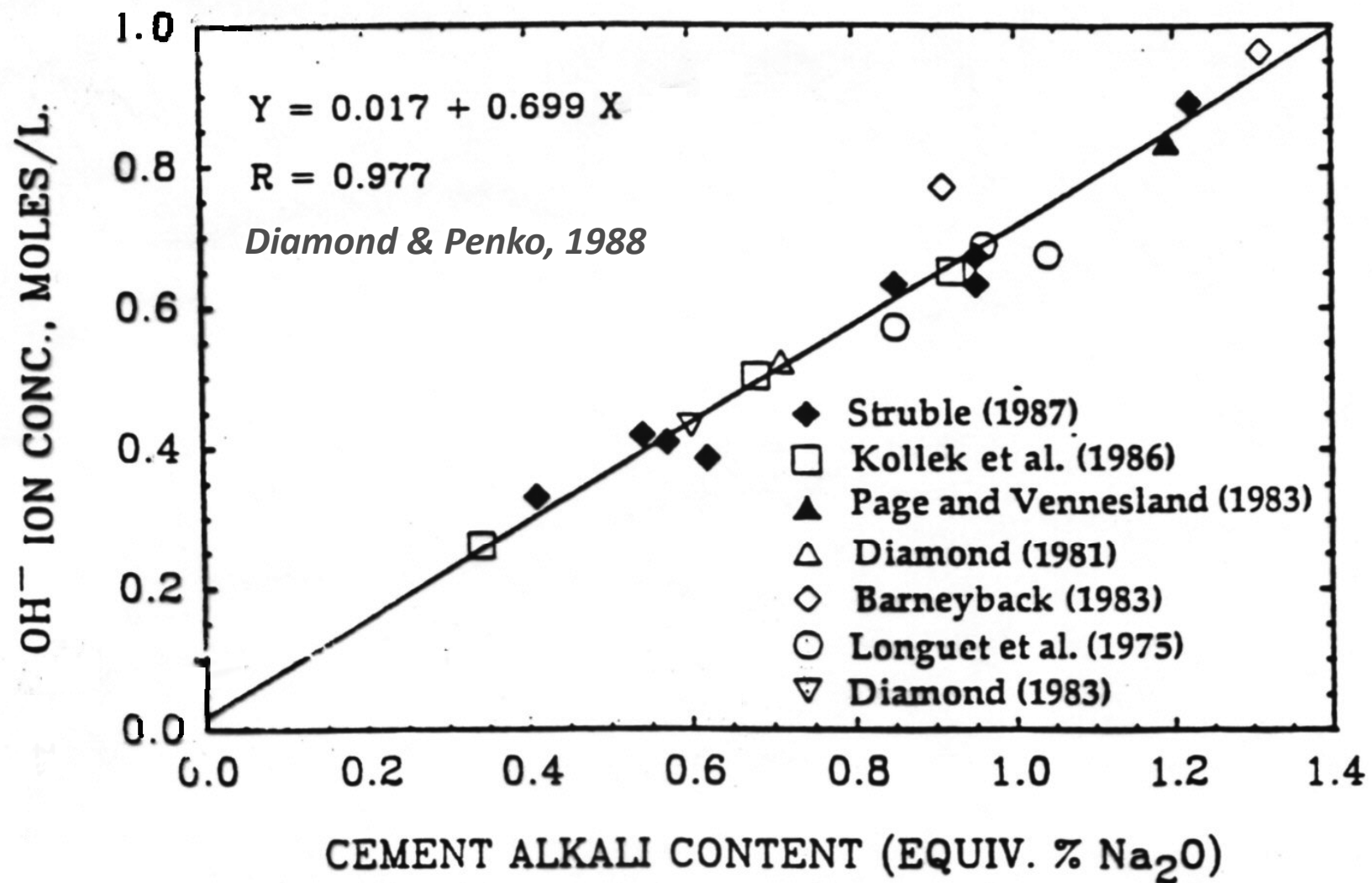
Oxide	OPC
SiO ₂	20.55
Al ₂ O ₃	5.07
Fe ₂ O ₃	3.10
CaO	64.51
MgO	1.53
K ₂ O	0.73
Na ₂ O	0.15
SO ₃	2.53
LOI	1.58

+ other trace elements

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

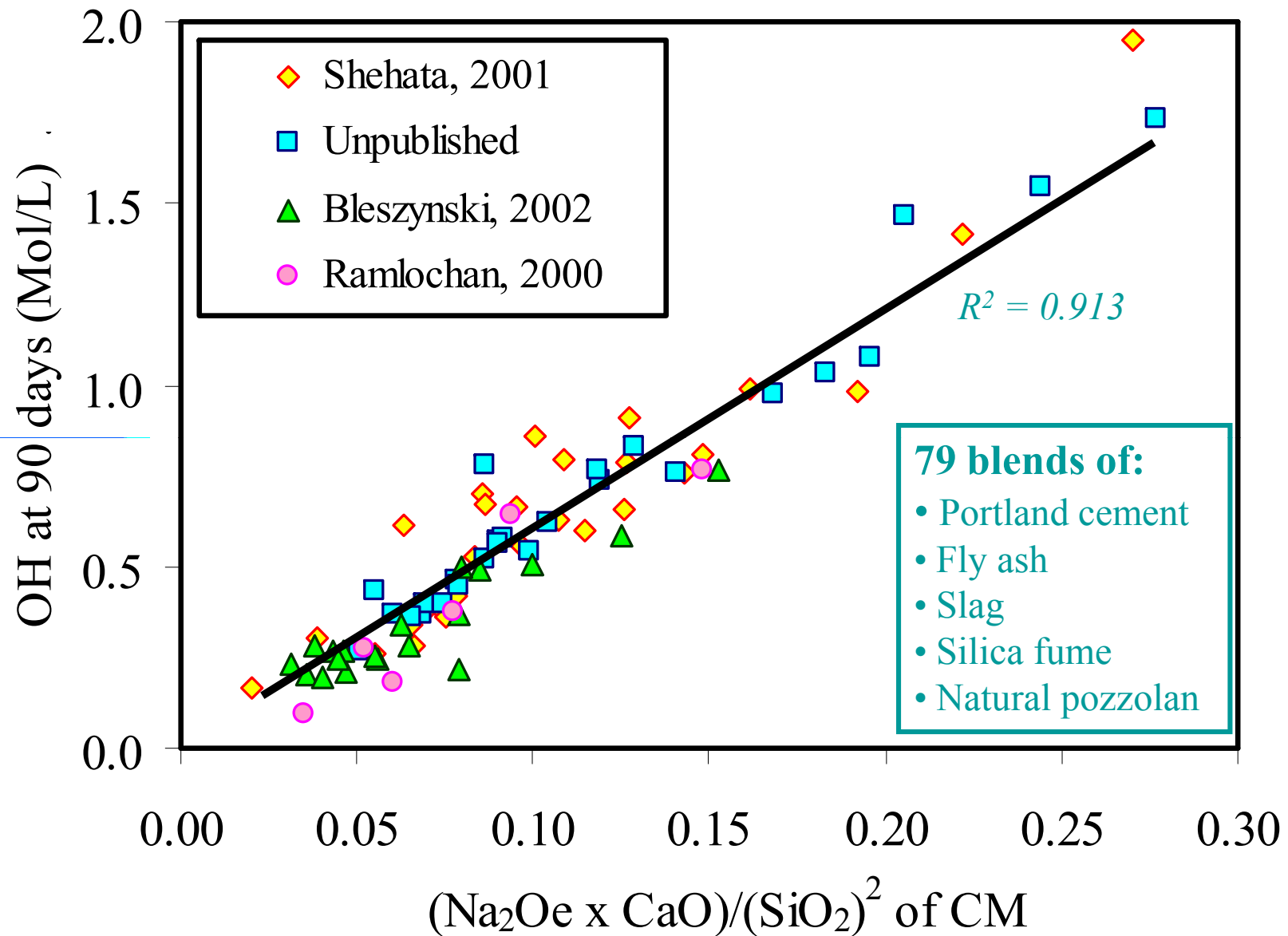


Most of the alkalies end up in the pore
solution and the associated OH
concentration is sufficient to produce a
pH in the range of 13.2 to 14.0



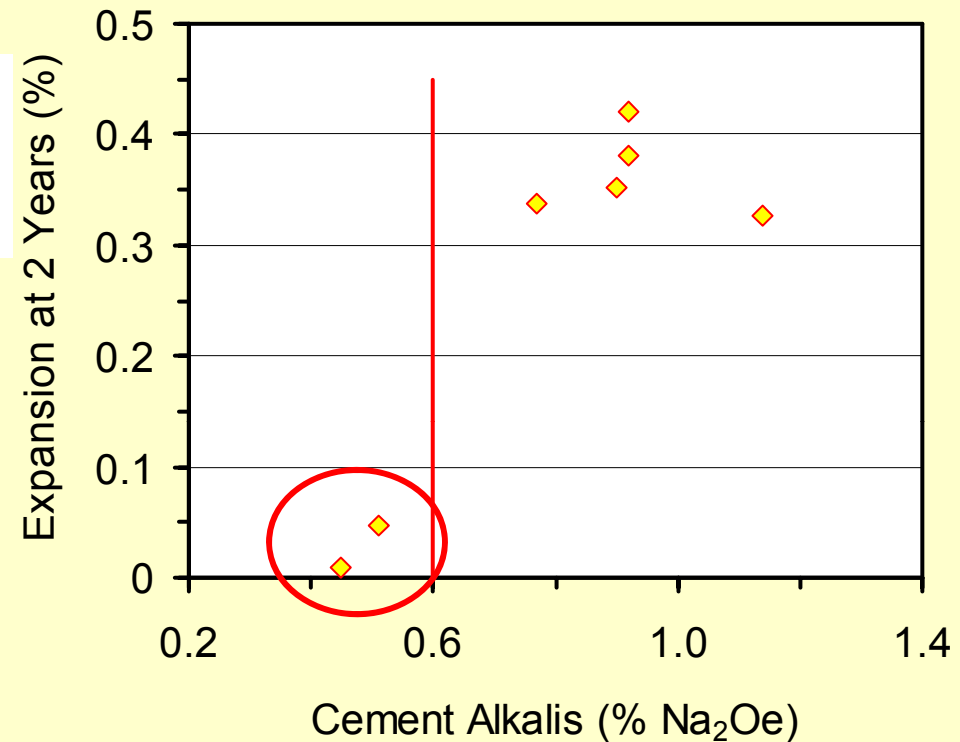
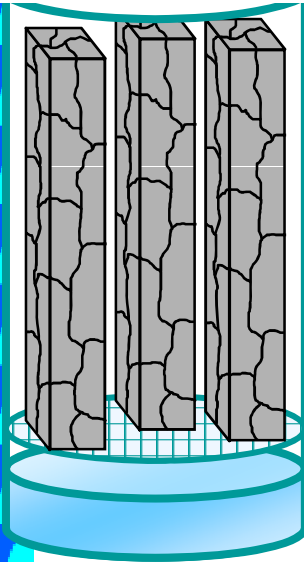
Example: A paste with $w/c = 0.50$ produced with a high-alkali portland cement with 1.00% Na₂O_e will have a pore solution with ~ 0.7 mol/L OH⁻ ions (\sim pH 13.85)

Cement Composition & Pore Solution Alkalinity



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

Expansion unlikely if cement
alkalies < 0.60% Na₂Oeq



WRONG!

Cement vs. Concrete Alkali

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

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

Example:

If a concrete contains 350 kg/m³ of Portland cement and the cement has an alkali content of 0.78% Na₂Oe then the alkali content of the concrete is:

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

Cement Composition & Pore Solution Alkalinity

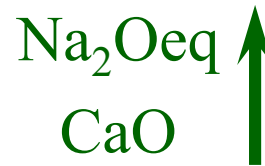
Alkali concentration in the pore solution is dependent on:

- $\text{Na}_2\text{O}_{\text{eq}}$
 - CaO
 - SiO_2
- } In the cementitious system
(i.e. including portland cement and all supplementary cementing materials)

Concentration of
Na, K & OH
in pore solution



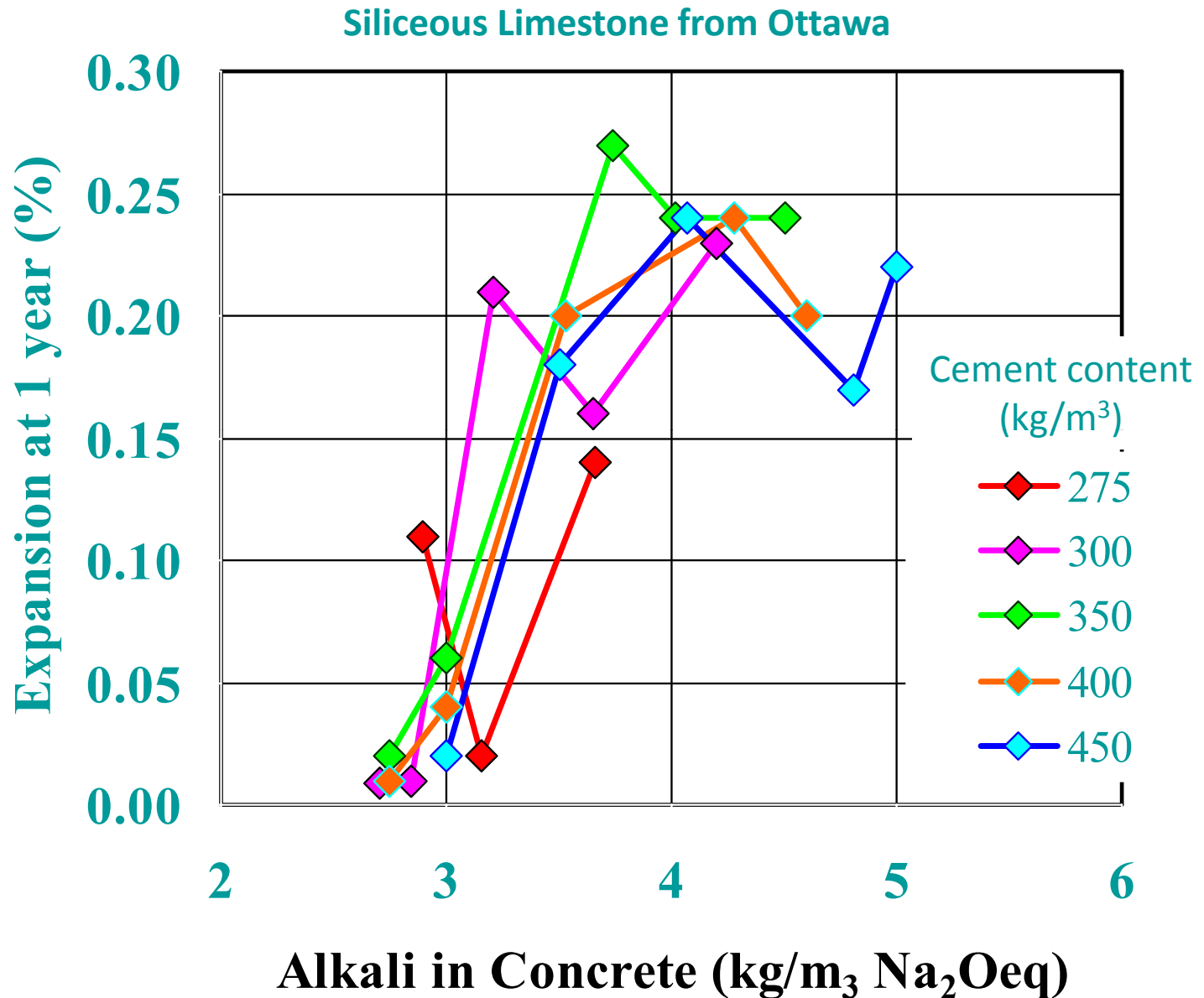
as



&

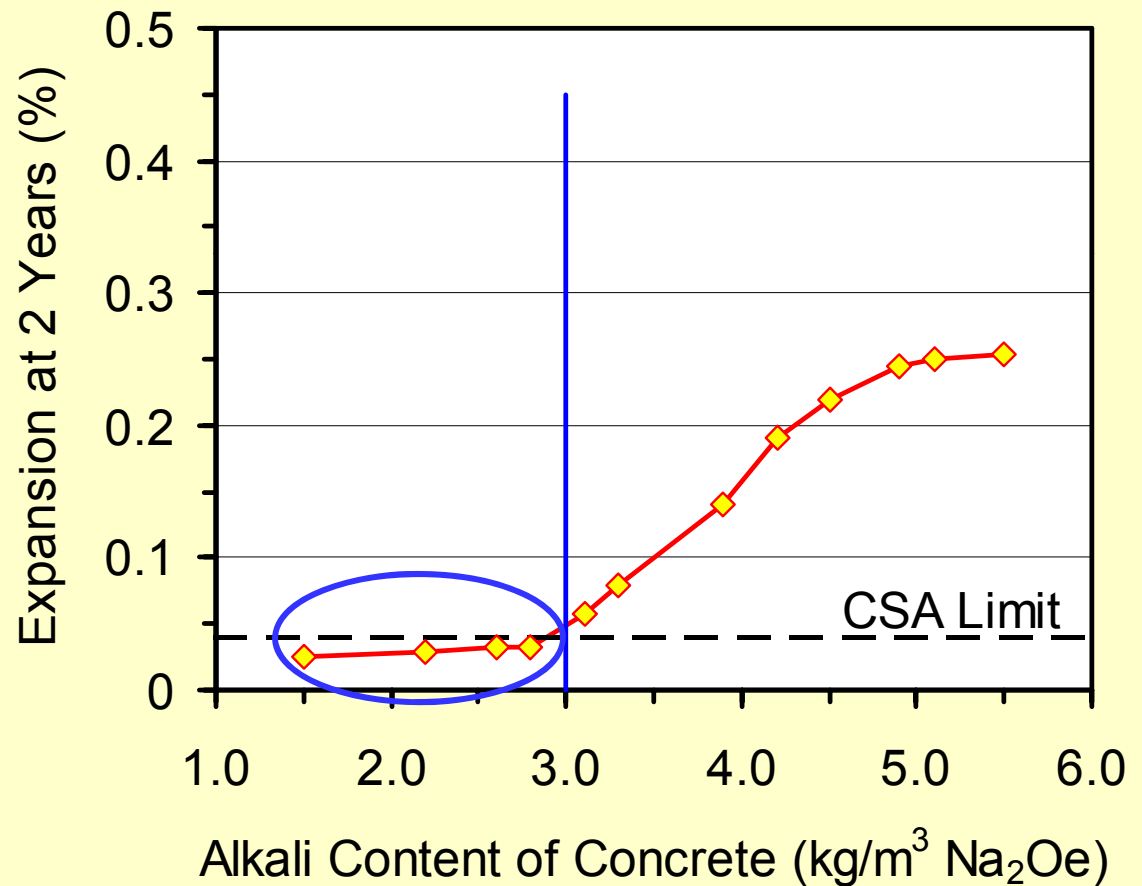


Effect of Concrete Alkali

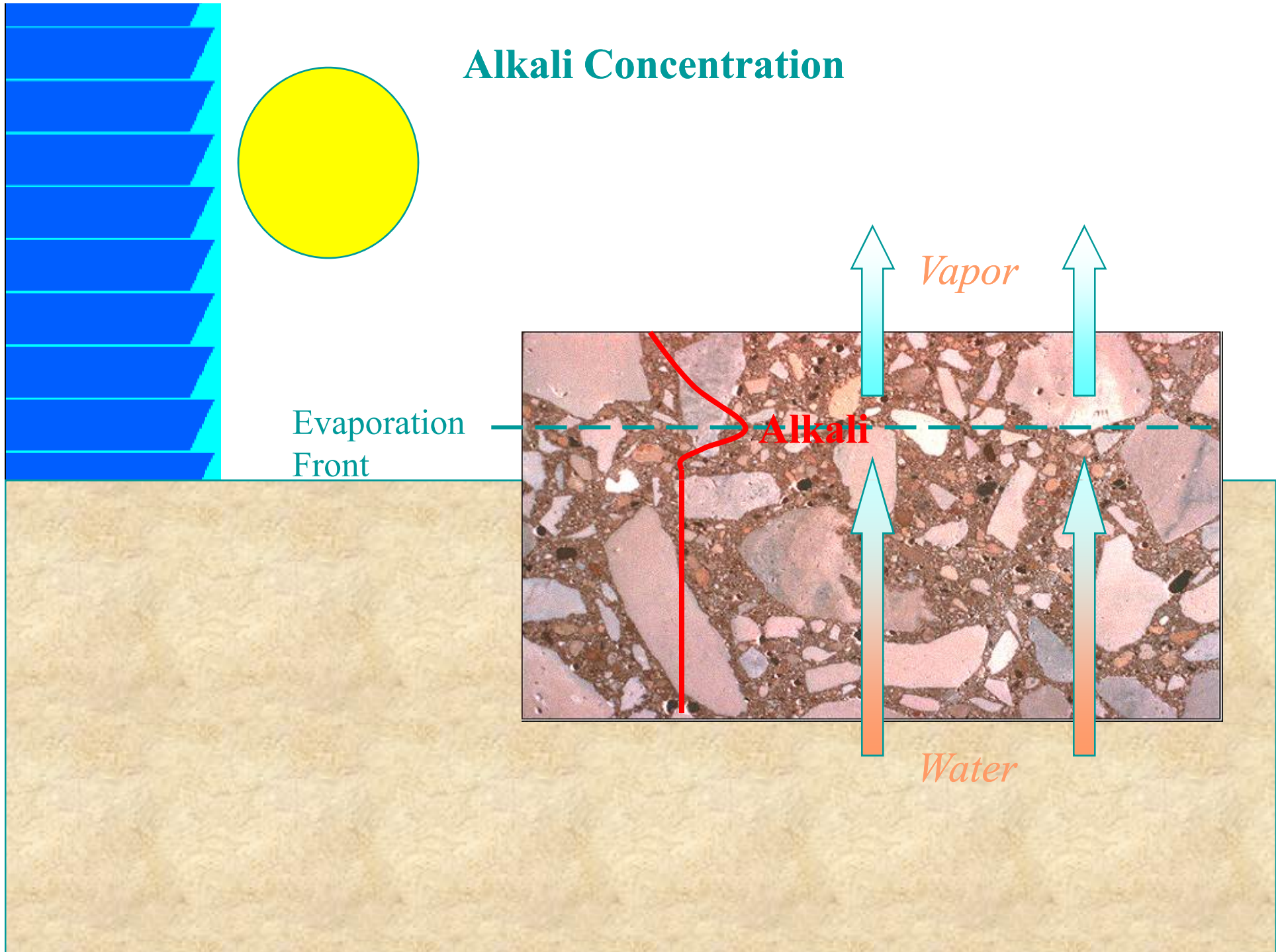


Effect of Concrete Alkali Content

Expansion unlikely if alkali content of concrete $< 3.0 \text{ kg/m}^3$



Alkali Concentration





Eq. Alkali Contents of North American Cements

Cement Type	$\leq 0.60\%$	$> 0.60\%$	% Low Alkali
I	22	29	43%
II	51	28	65%
III	37	20	65%
V	25	1	96%
Total	135	78	63%

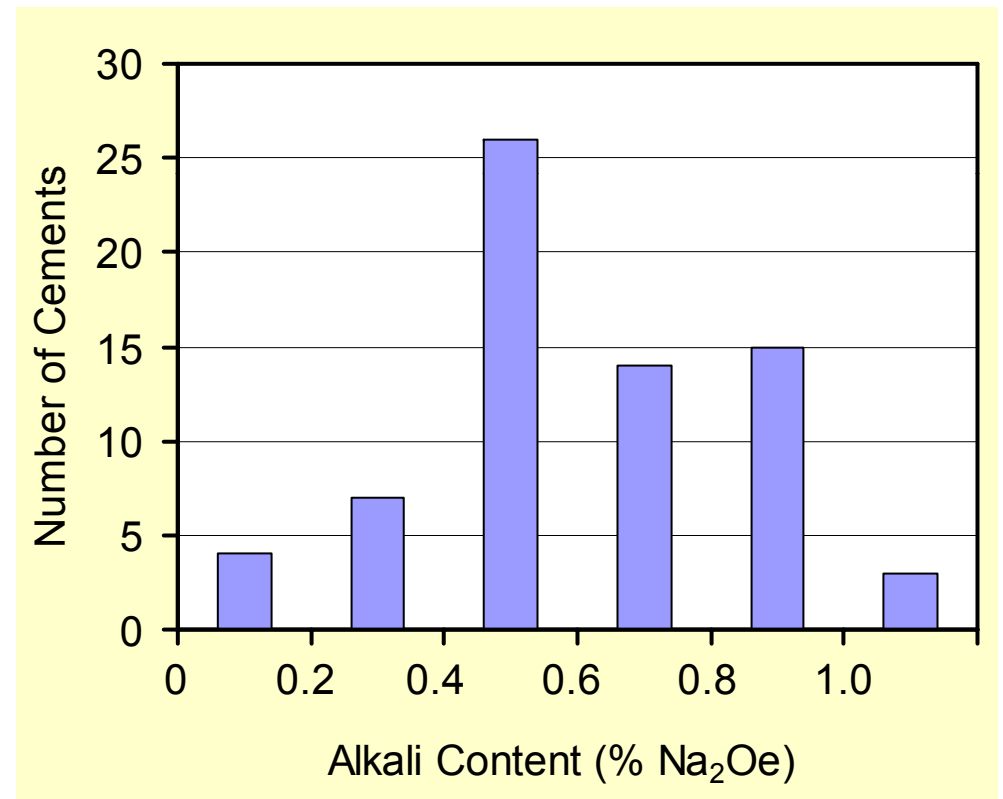
Bhatty and Tennis 2008

Eq. Alkali Contents of North American Cements

Alkali contents of 69 sources of
Type I cement in North America

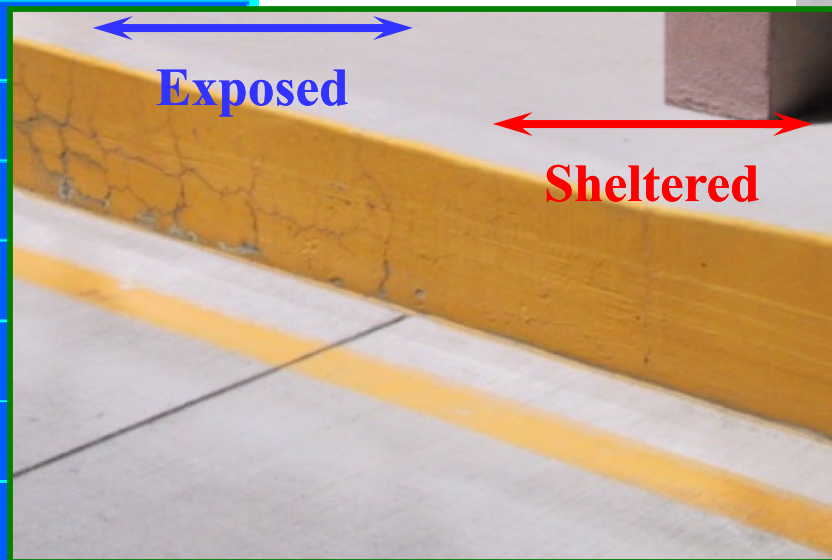
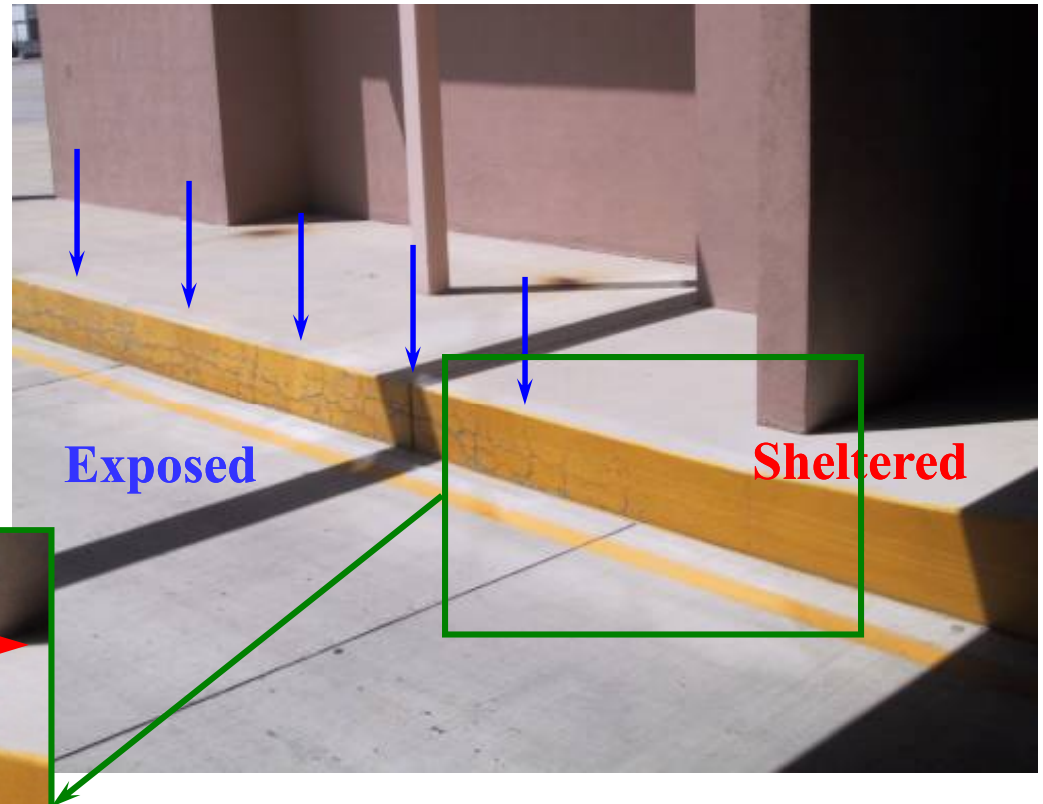
37 of 69 cements $< 0.60\%$ $\text{Na}_2\text{O}_{\text{eq}}$

32 of 69 cements $> 0.60\%$ $\text{Na}_2\text{O}_{\text{eq}}$



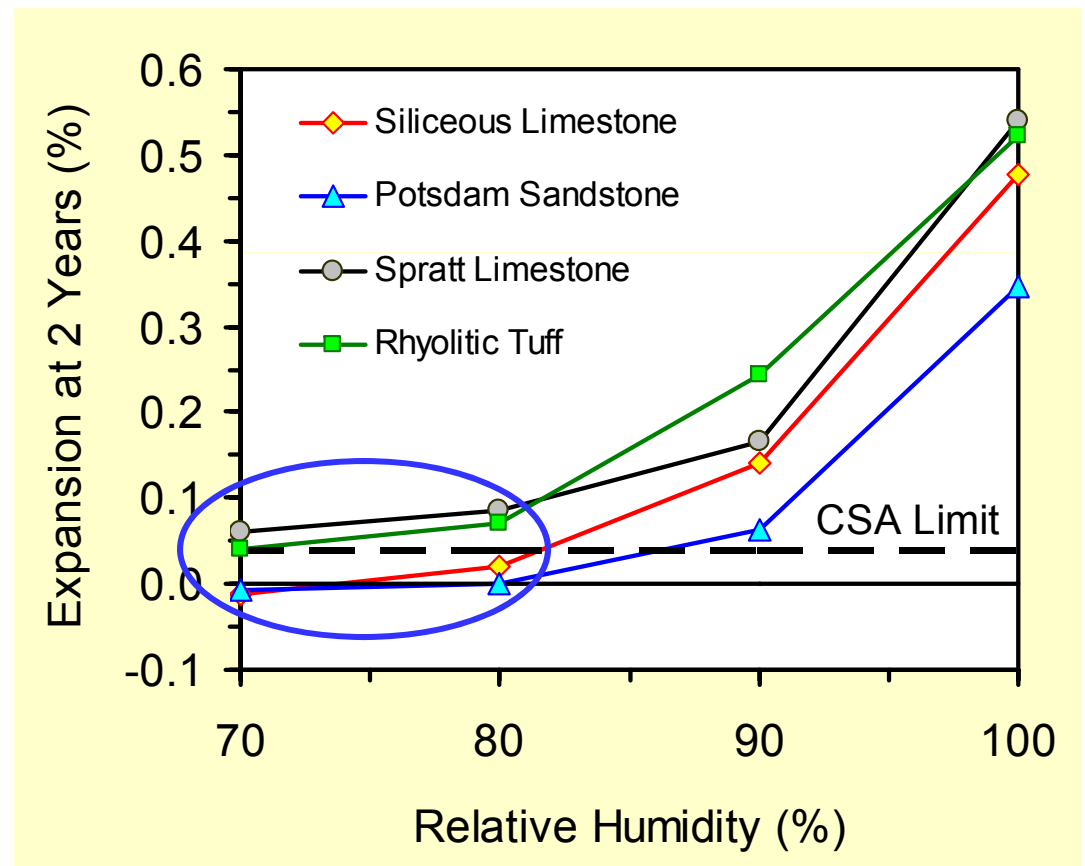
Bhatty and Tennis 2008

The Role of Moisture



Effect of RH on Expansion

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



Pedneault 1996



ASR TESTING AND MITIGATION



Preview:

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
- Test



ASR Test Methods

- Desires
 - ◆ Fast
 - ◆ Accurate
 - ◆ Aggregate & mitigation



Requirements of test method for measuring preventive measures

- Capable of evaluating efficacy of mineral & chemical admixtures – i.e. determining quantity required to suppress expansion in a given system
- Measures effect of aggregate reactivity
- Measures impact of cement alkalies
- Short duration (i.e. rapid test)

Reliable – correlates with field performance

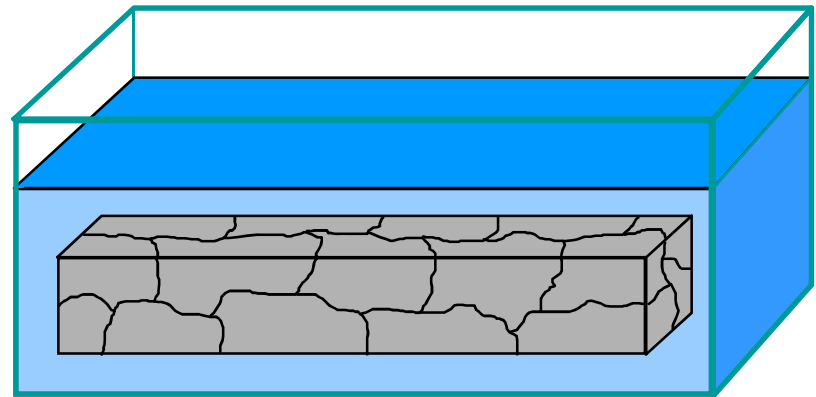
The BEST ASR “Test”

- The most accurate test for determining deleterious ASR potential is **Field History**
 - **However**
 - ◆ Structures >15 years old?
 - ◆ Same aggregate?
 - ◆ Same cement/concrete alkali ?
 - ◆ Same SCMs (brand, type, amount)?
 - ◆ Same water content?
 - ◆ Same exposure conditions?



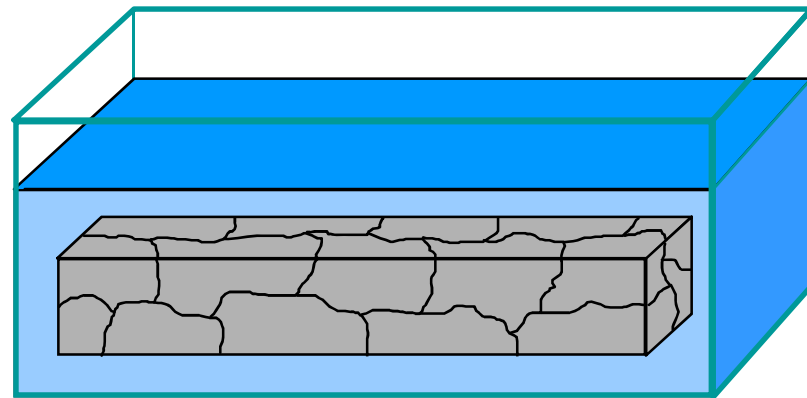
Accelerated Mortar Bar Test – ASTM C1260

- Originally developed at NBRI in South Africa – Oberholster & Davies, 1986
- Now used in many countries for testing aggregates.
- Mortar bars stored immersed in 1 N NaOH solution at 80°C for 14 days.

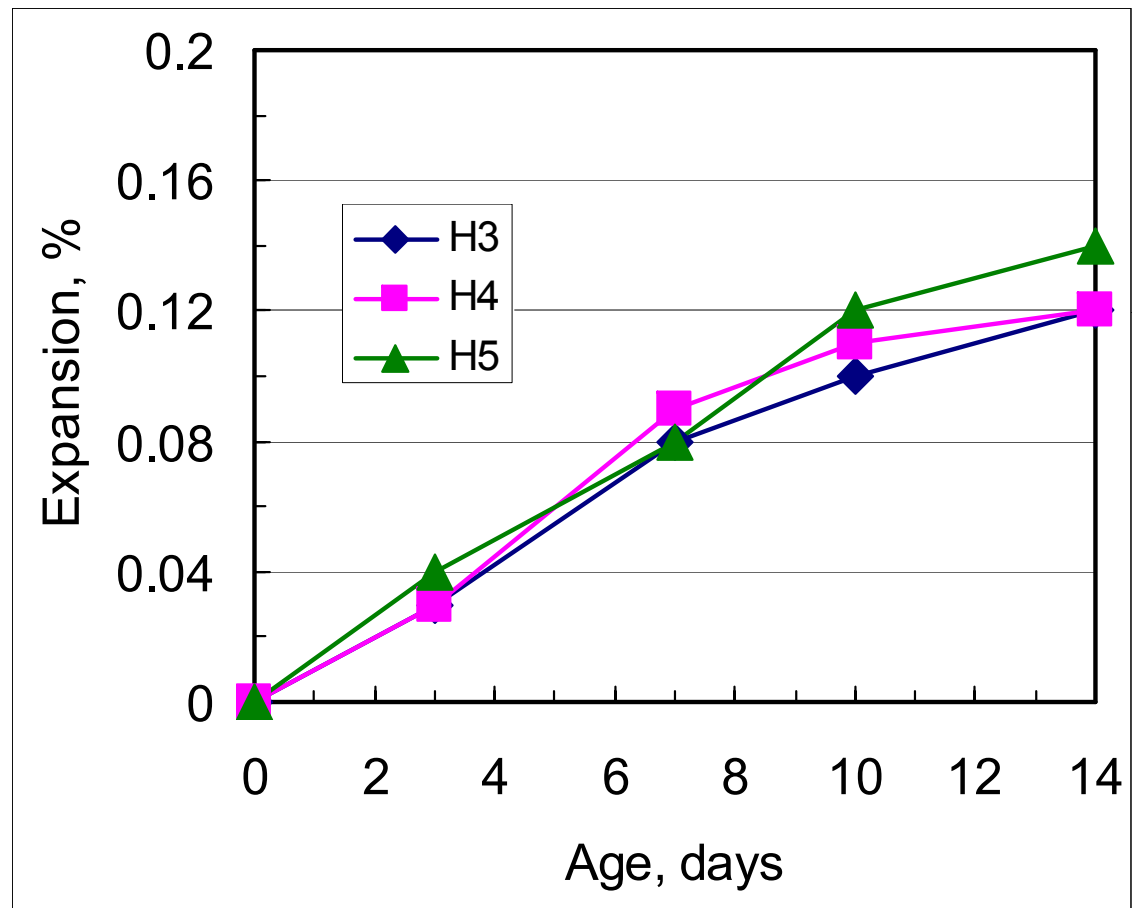


Accelerated Mortar Bar Test 2 – ASTM C1567

- Used for the evaluation of pozzolans and slag
- Many agencies now use the test for this purpose
- Same conditions as C1260, but include SCMs



AMBT

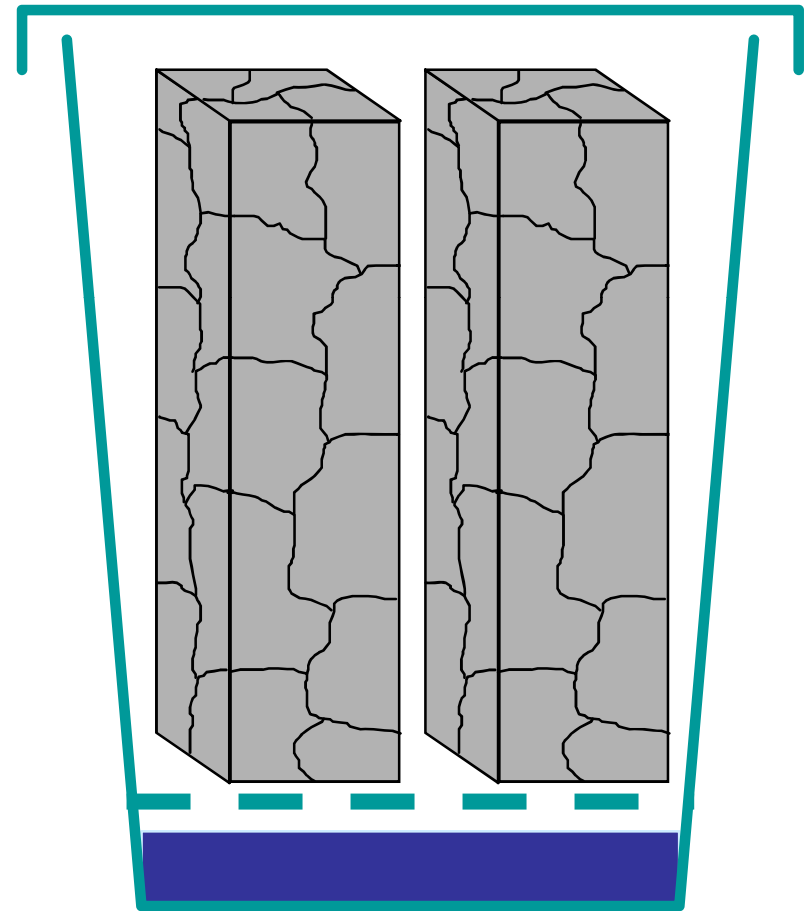


Concrete Prism Test

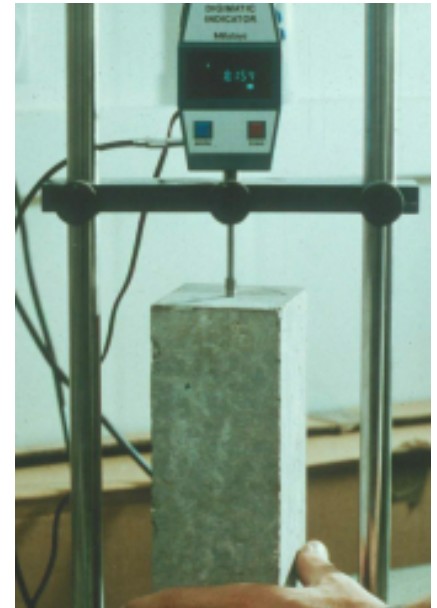
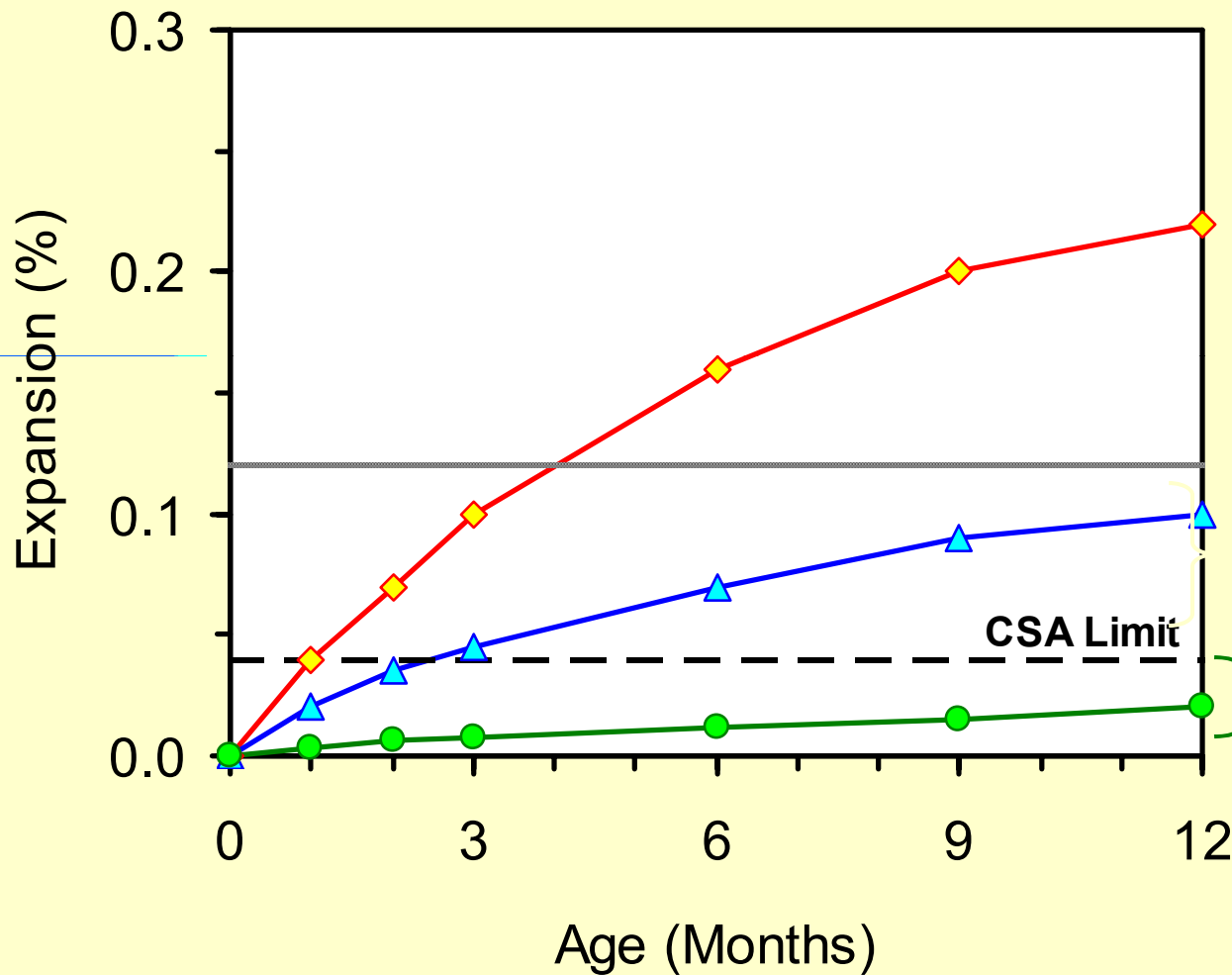
CSA A23.2-14A

ASTM C1293

- 420 kg/m³ cementitious material
- NaOH added to yield 1.25% Na₂O_{eq} by mass of portland cement
- $0.42 \leq W/CM \leq 0.45$
- Concrete prisms
 - 75 x 75 x 250 mm (min)
- Stored over water at 38°C (and nominally 100% RH) for 2 years



Concrete Prism Test

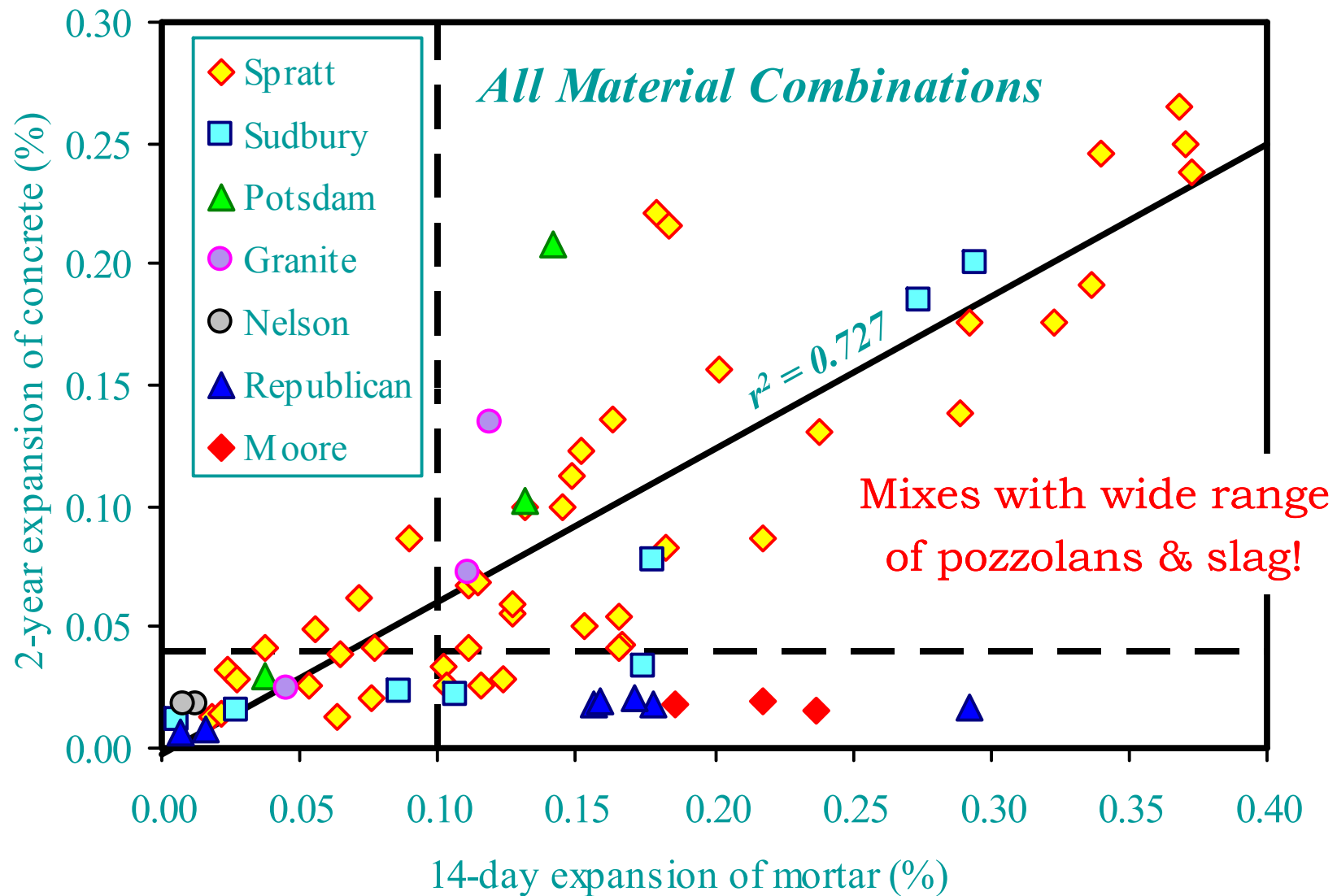


Highly-reactive
Expansion > 0.12%

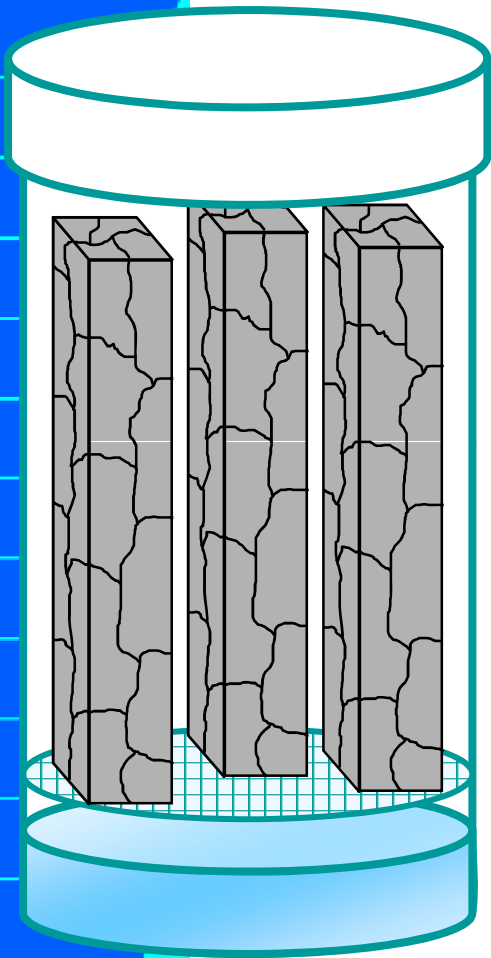
Marginally-reactive
Expansion = 0.04 to 0.12%

Non-reactive
Expansion < 0.04%

Accelerated Mortar Bar vs. Concrete Prism Test

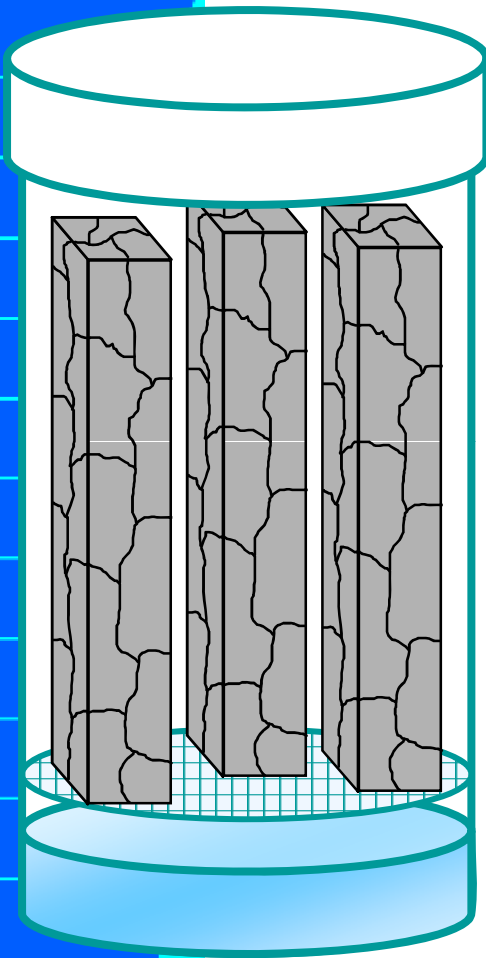


ASTM C441 Pyrex Mortar Bar Test



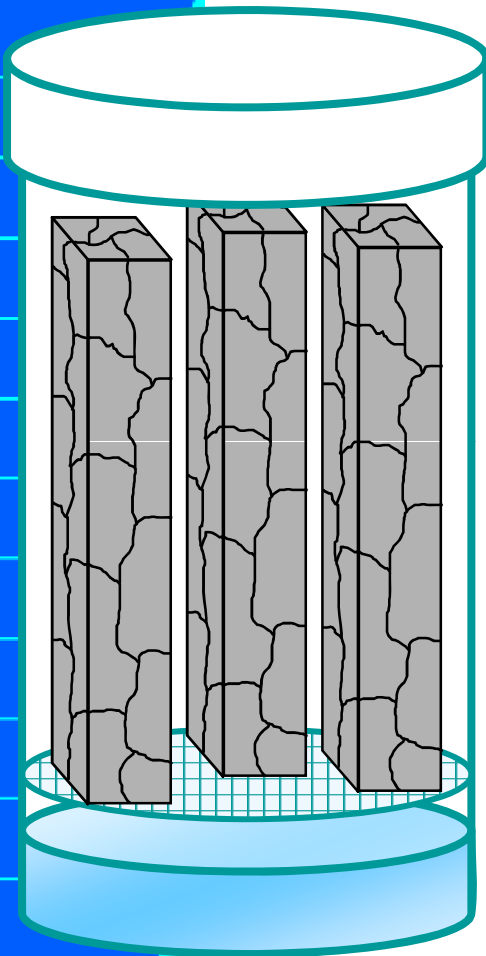
- Developed to test ability of SCMs to mitigate expansion
- Mortar bars made with Pyrex glass as model aggregate
- ASR-suppression characterized by reduction in expansion compared to low-alkali control

Problems with C441 Pyrex Mortar Bar Test



- Pyrex contains significant alkali
- Pyrex behavior varies from source to source
- Doesn't account for influence of aggregate reactivity
- Overestimates level of SCM required for many aggregates

Limits for ASTM C 441 Pyrex Mortar Bar Test



C618 Fly Ash & Natural Pozzolans

- Exp. @ 14 days \leq Control with low-alkali cement

C989 Slag

- Job mixture $\leq 0.02\%$ at 14 days
- Exp. @ 14 days $\leq 25\%$ of control with high-alkali cement (0.95 to $1.0\% Na_2O_{eq}$)

C1240 Silica Fume

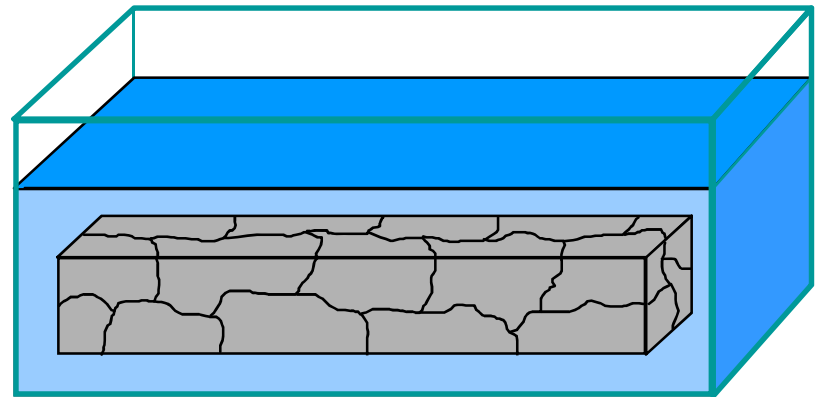
- Exp. @ 14 days $\leq 20\%$ of control with high-alkali cement (*HAC - not defined*)

C1157 Performance Specification for Hydraulic Cement

- Option R - *Low Reactivity with Reactive Aggregates*
- Exp. @ 14 days $\leq 0.02\%$
- Exp. @ 56 days $\leq 0.06\%$

C1567-Based Approach?

- Based on CSA approach
- Use an aggregate with $>0.30\%$ expansion in C1260
- Mitigate down to $<0.10\%$ expansion in C1567





SUMMARY: Test Methods

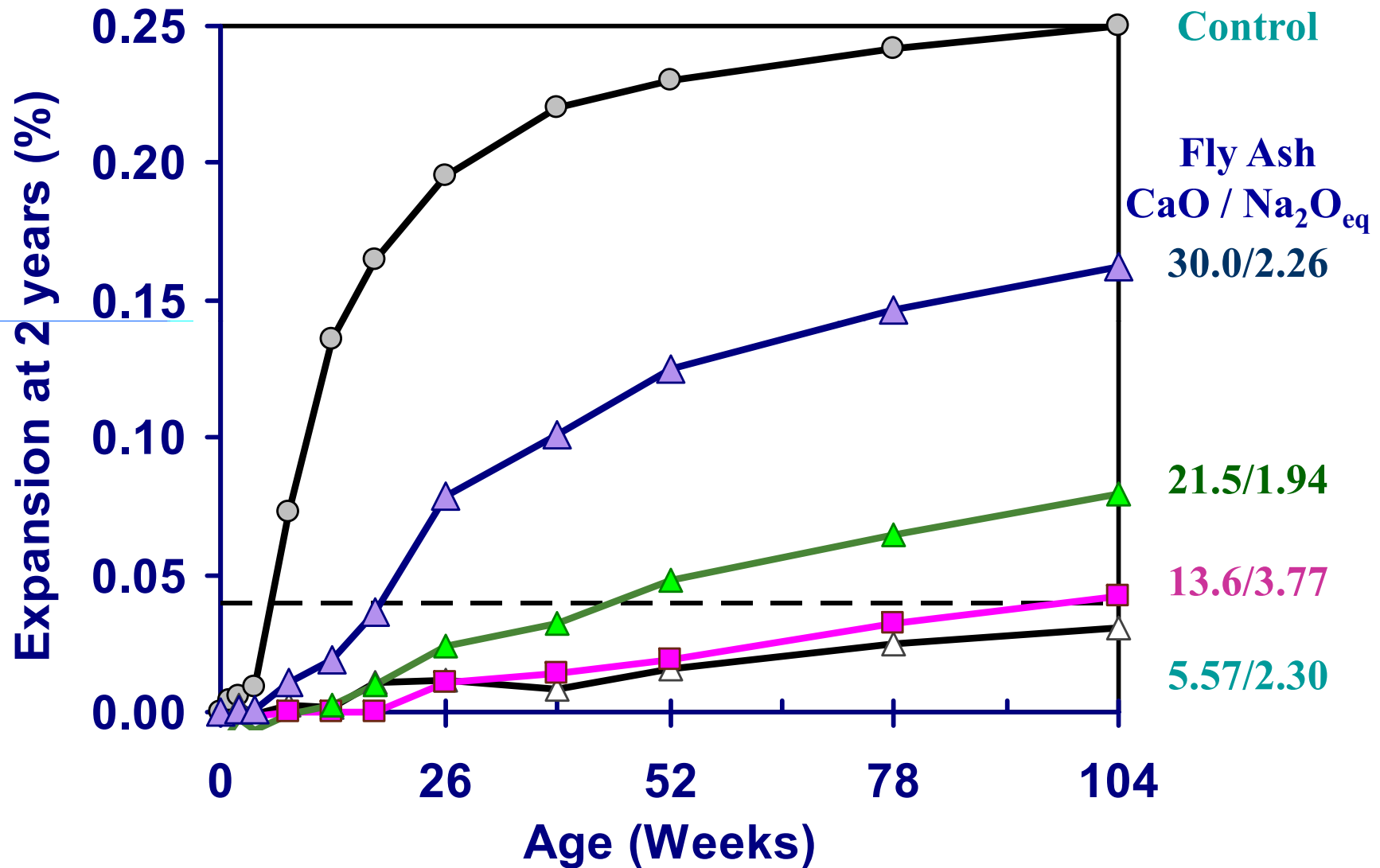
- Most reliable “test” is field history
- “Long-term” concrete prism test provides a reliable prediction of expansion with high-alkali cement – but difficult to predict role of cement alkalies
- Accelerated mortar bar test is generally preferred for its speed, but some addition risk involved.
- (Accelerated concrete prism test requires further study to determine if it can provide a reliable indication of behavior under field conditions)



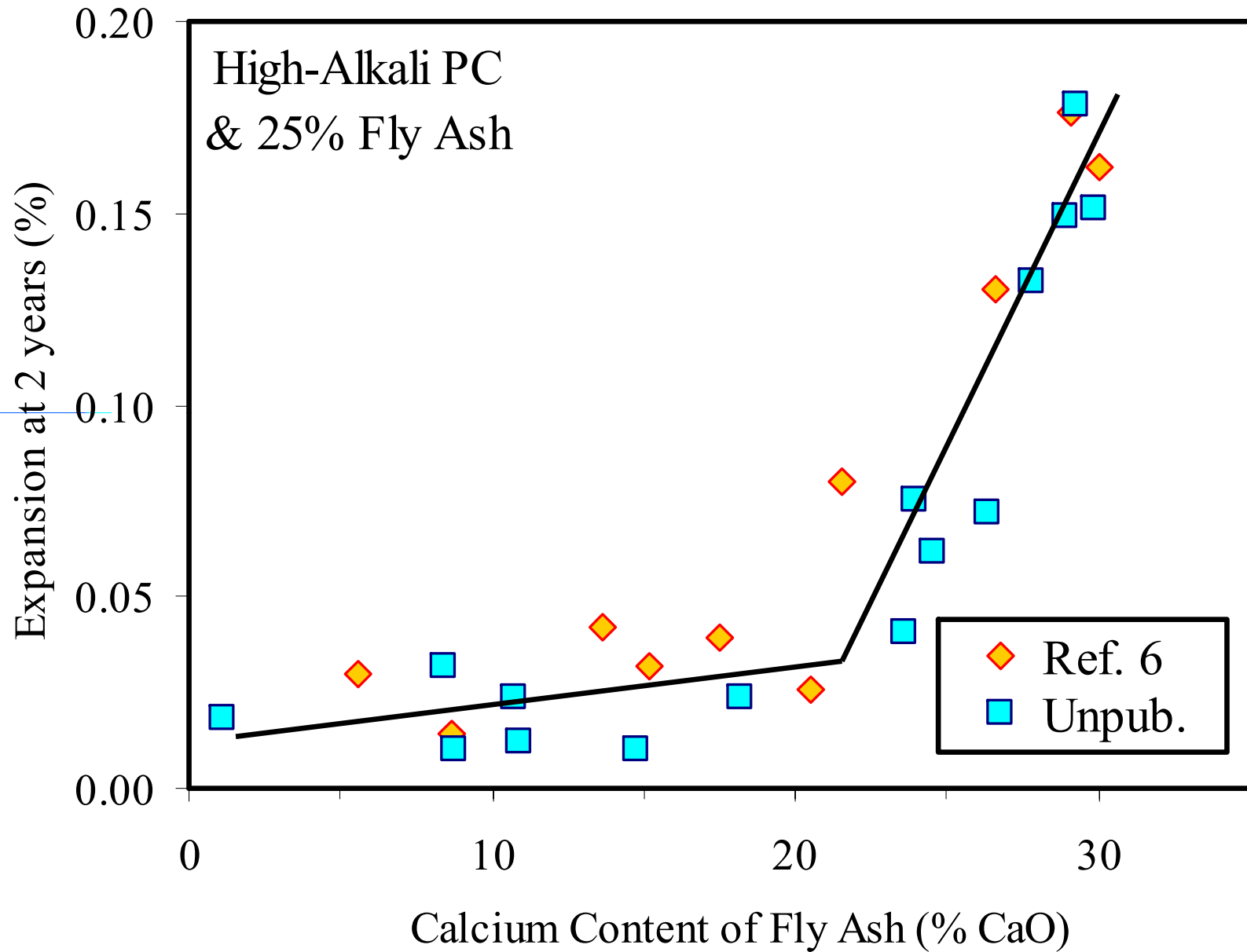
ASR MITIGATION

Effect of Fly Ash on ASR Expansion

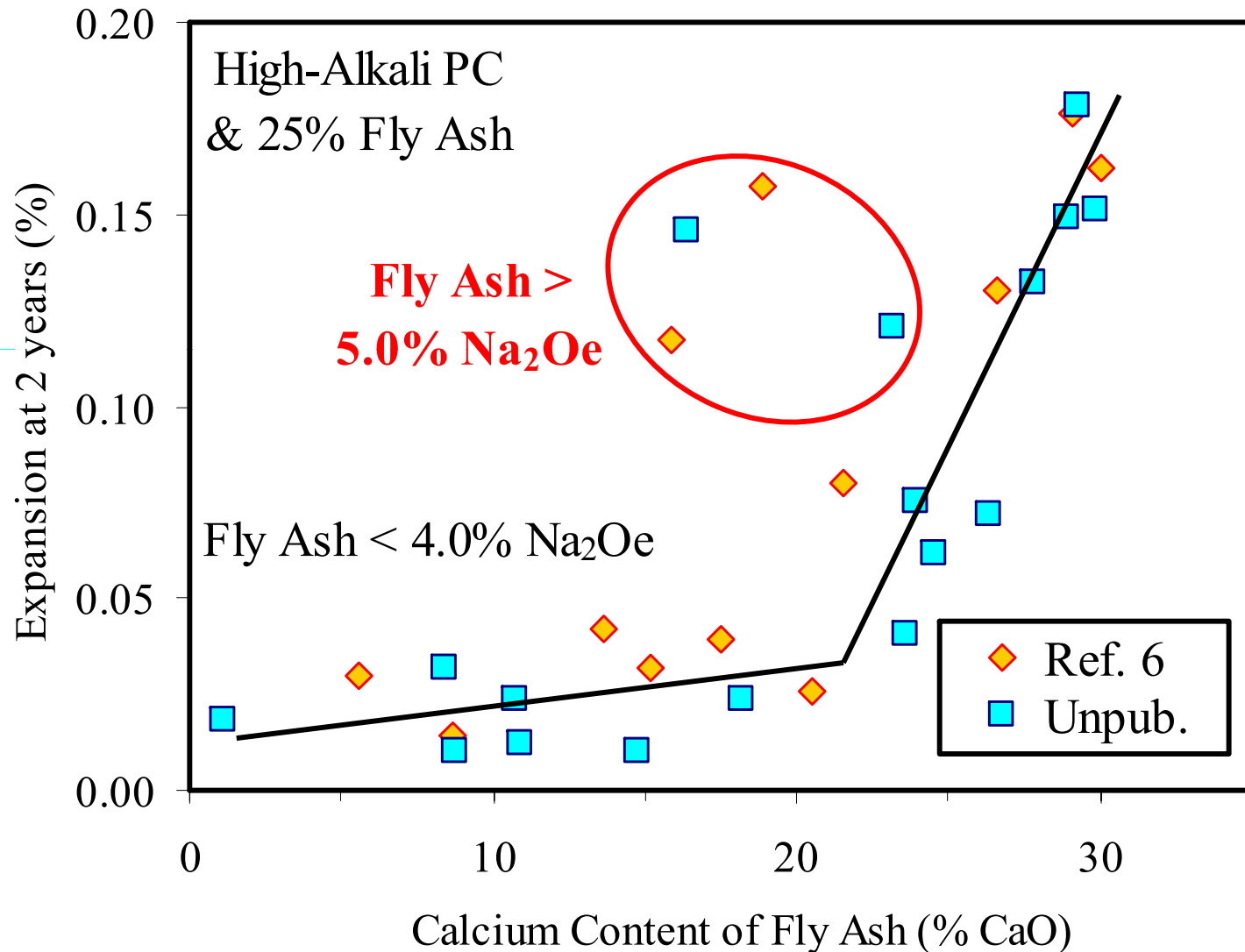
Concrete Prisms with 25% Fly Ash & Spratt Aggregate



Effect of Calcium Content of Fly Ash



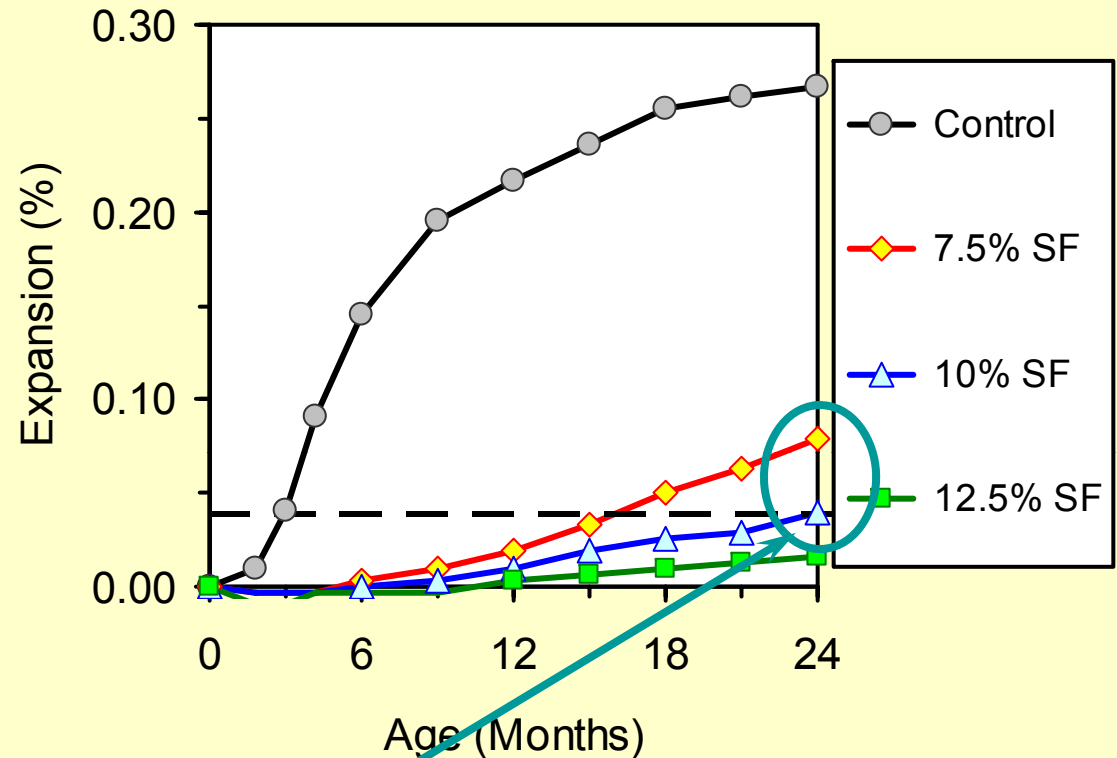
Effect of Calcium & Alkali Content of Fly Ash



Effect of Silica Fume

Laboratory Test Results

- ASTM C1293 / CSA A23.2-14A
- Cement = 1.25% $\text{Na}_2\text{O}_{\text{eq}}$
- Siliceous limestone aggregate
- Concrete at 38°C over water
- Test for 2 years

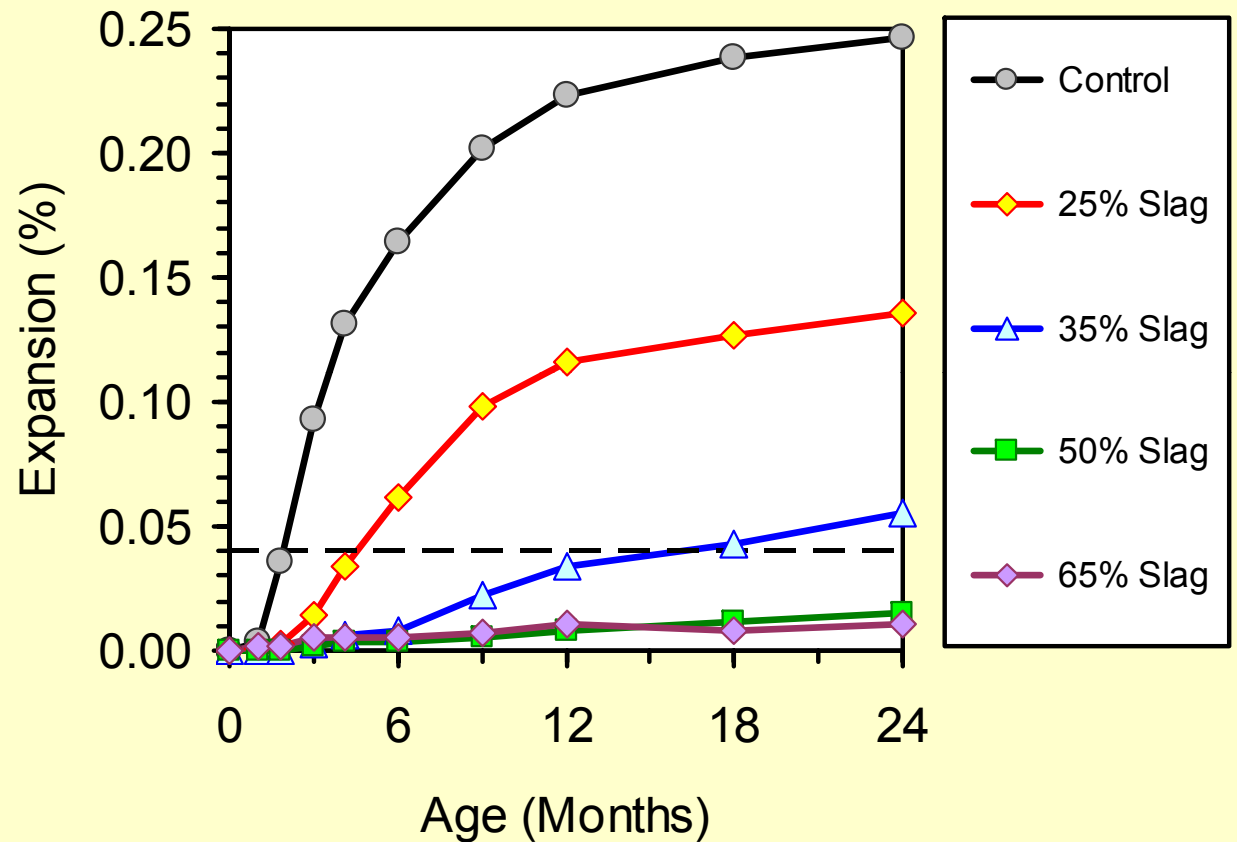


Amount required to meet CSA limit
at 2 years maybe > 10% silica fume

Effect of Slag

ASTM C1293

- Siliceous limestone
- 1.25% $\text{Na}_2\text{O}_{\text{eq}}$
- 38°C and 100% RH



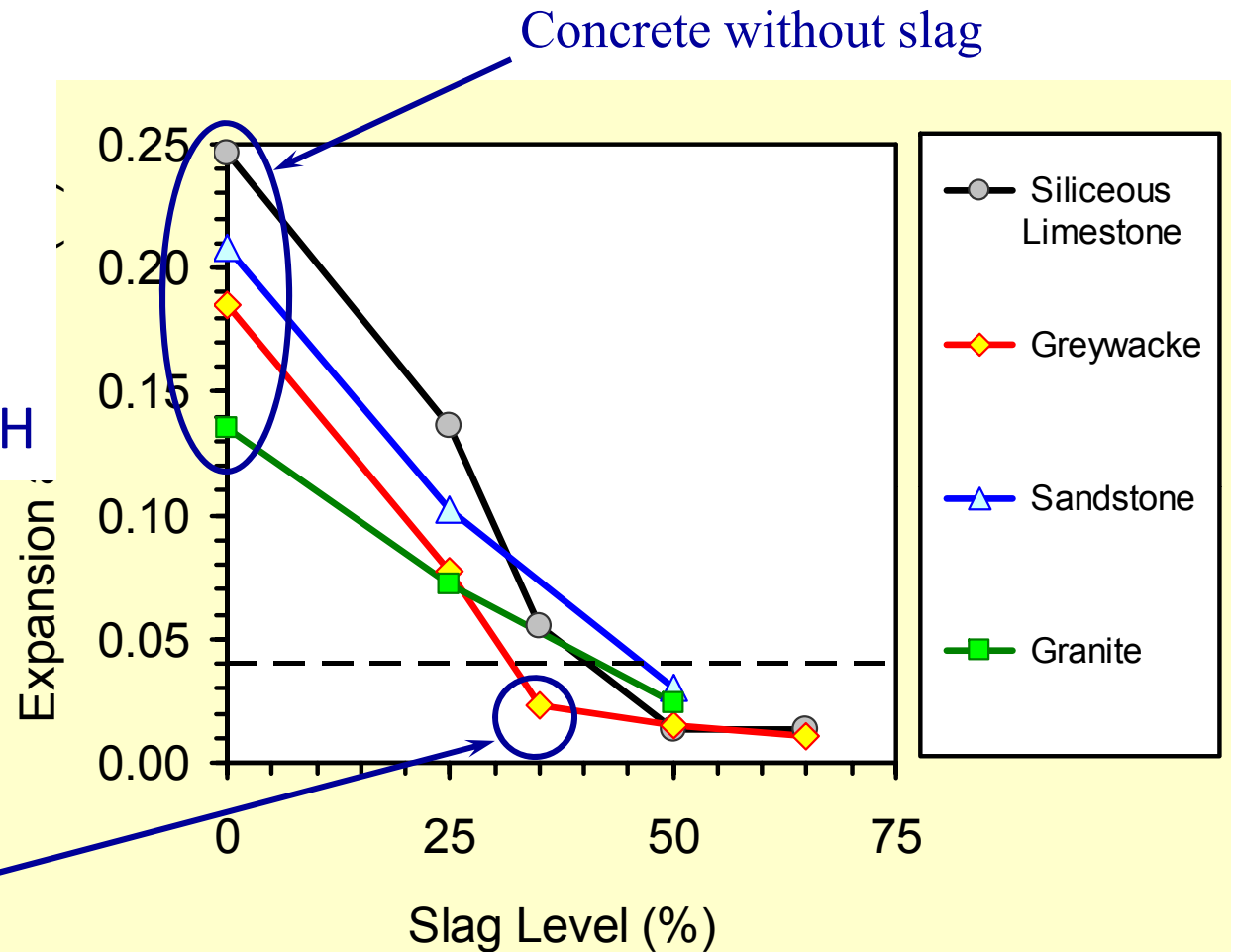
Thomas and Innis, 1998

Effect of Slag

ASTM C 1293

- 4 aggregates
- 1.25% $\text{Na}_2\text{O}_{\text{eq}}$
- 38°C and 100% RH

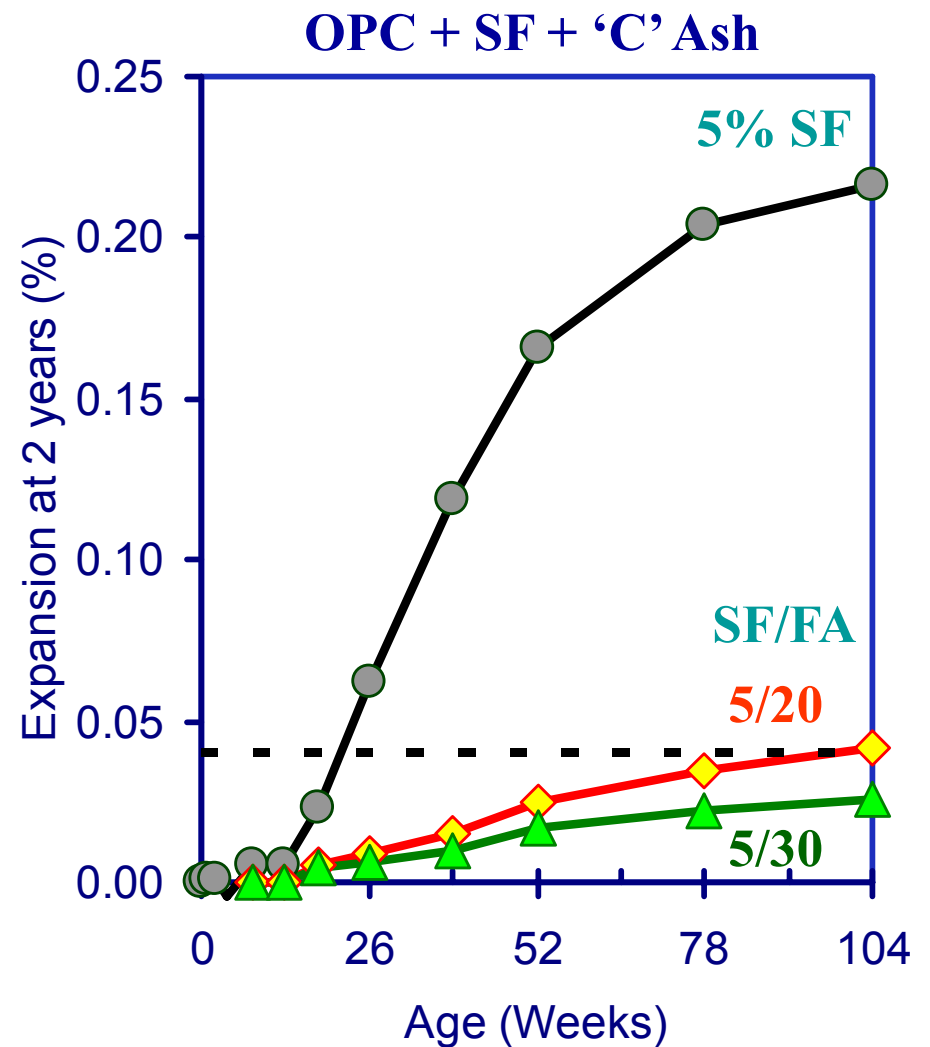
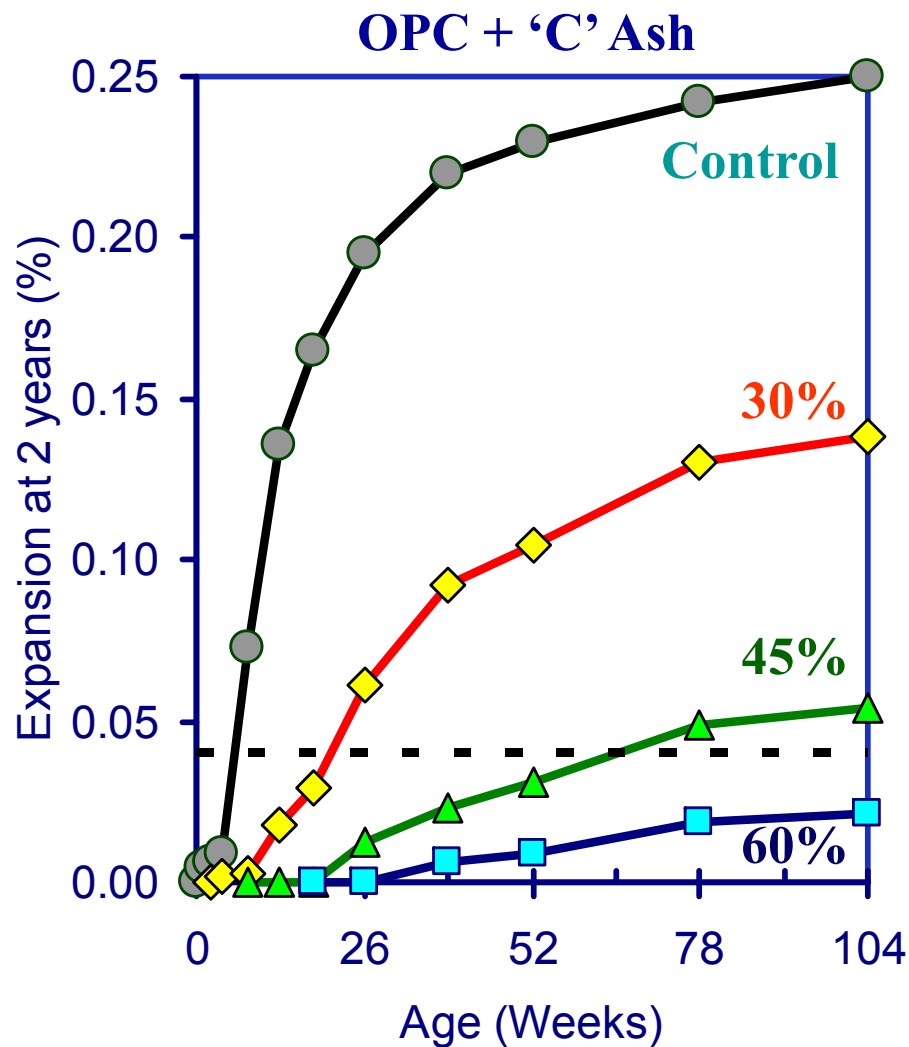
Moderately-reactive aggregate with 35% slag



Thomas and Innis, 1998

Effect of Silica Fume & Fly Ash Concrete Prisms with 'C' Fly Ash

(27.7% CaO, 1.65% Na₂O_{eq})



SUMMARY: Effect of SCMs

Fly Ash

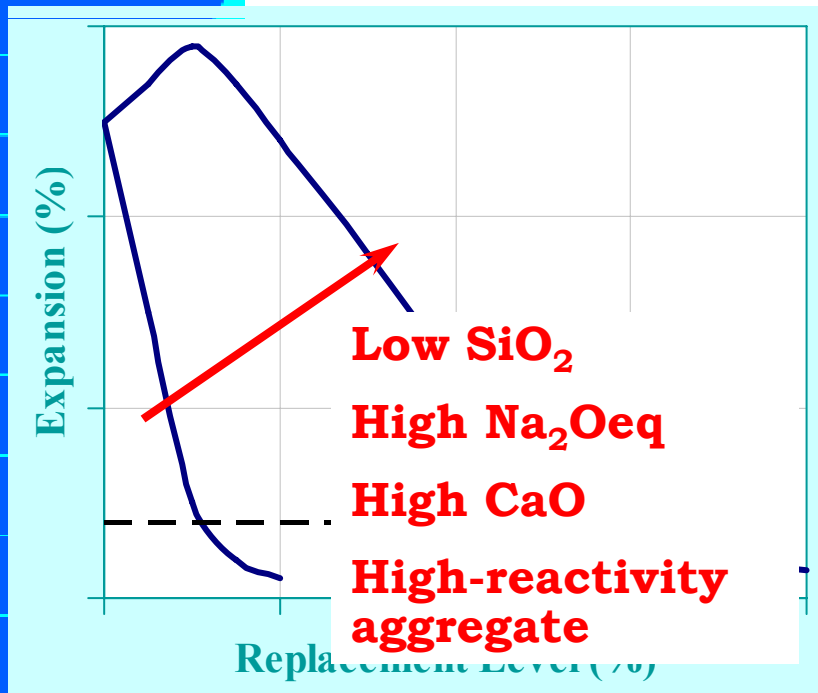
Slag

Silica Fume

Natural Pozzolans

Almost all sources of these materials are effective in controlling ASR

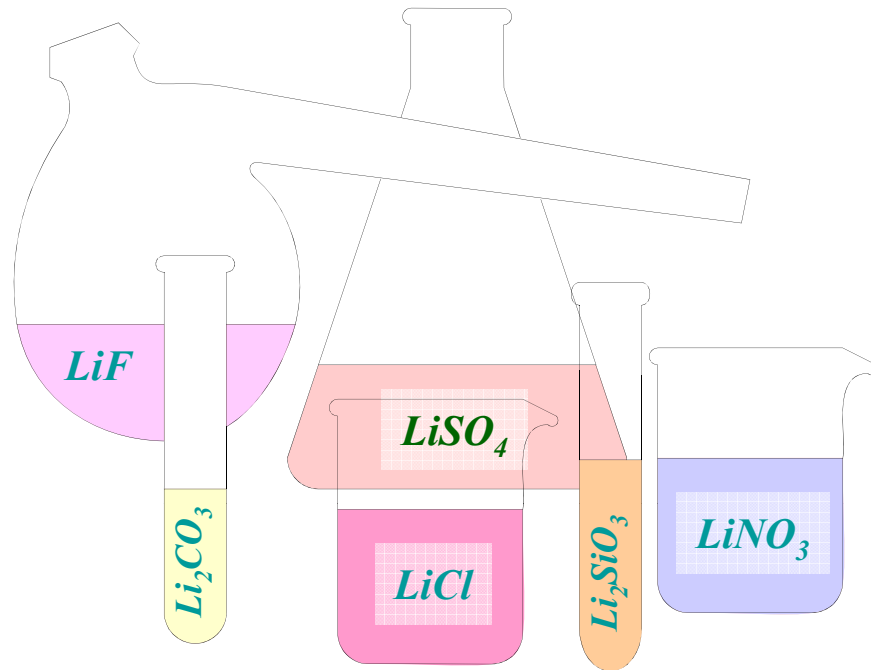
Providing they are used in sufficient quantity



Amount of preventive required depends on:

- Composition of material (esp. Na₂Oeq, SiO₂, CaO)
- Available alkali in the system
- Nature of the reactive aggregate

Using Chemical Admixtures



McCoy & Caldwell, 1951

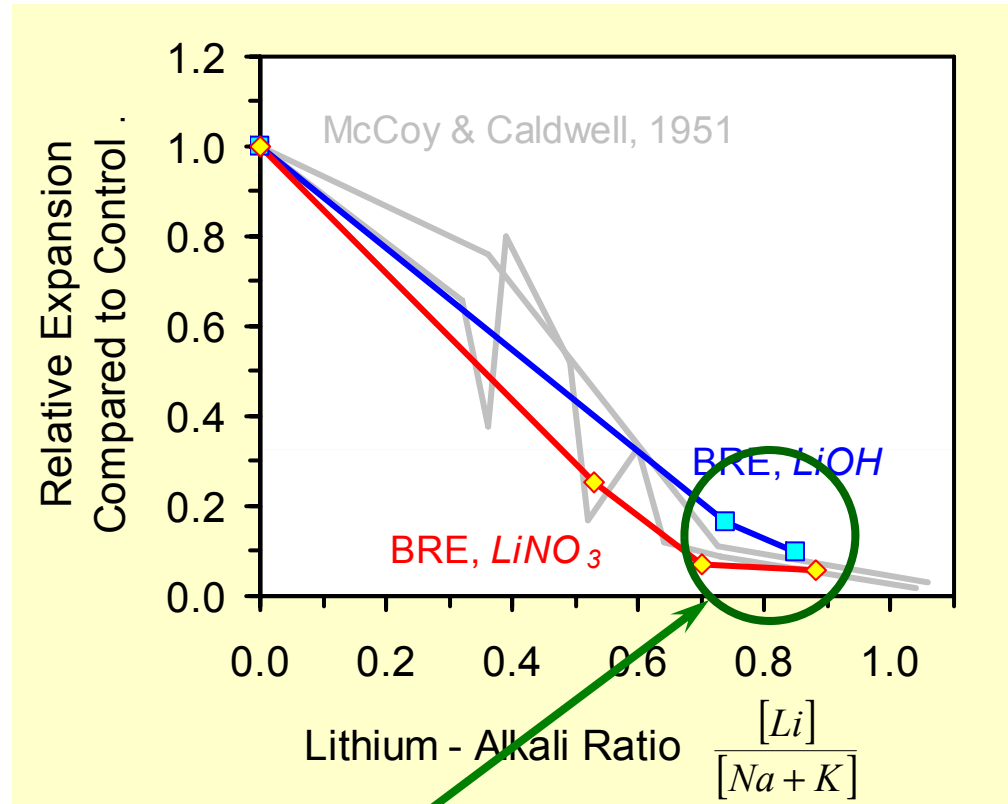
Expansion tests with Pyrex glass and more than 100 different chemical compounds to determine whether the reaction between alkalies and silica could be chemically inhibited

Lithium compounds were found to be the most promising.

Lithium Admixtures

Lithium to alkali
molar ratio

$$= \frac{[Li]}{[Na + K]}$$



$LiNO_3$ slightly more effective than $LiOH$

$LiNO_3$ does not increase pH

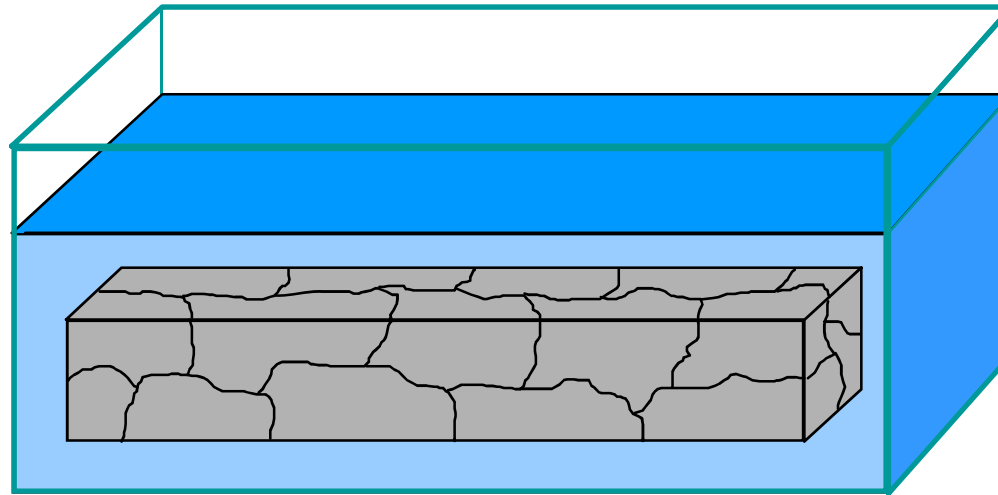
Thomas et al. 2000

Modified C1260/C1567 for Lithium

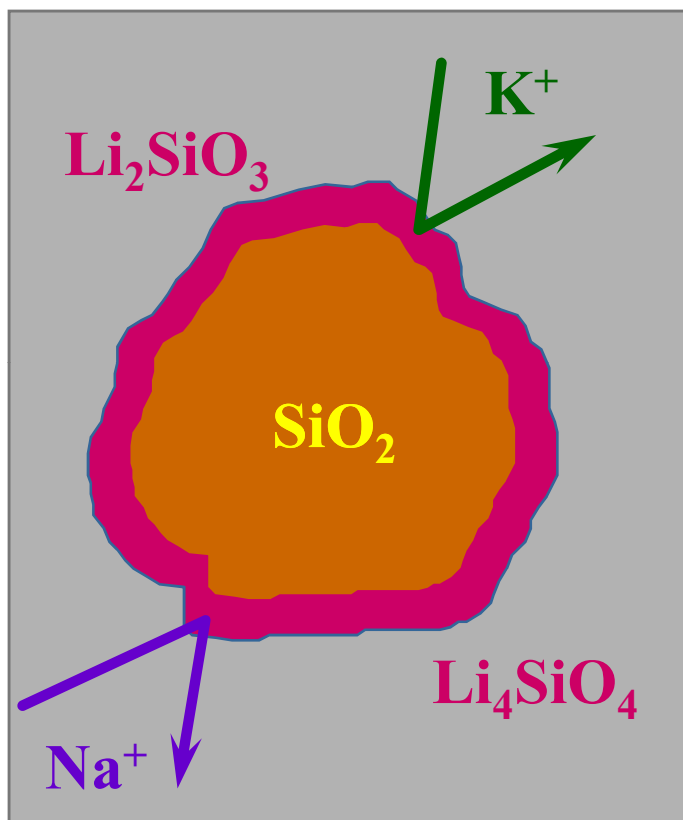
PRELIMINARY

Adjust solution molarity on the basis of the
alkalies in the portland cement

$$\text{Na} + \text{K} \text{ (M/L)} = 0.7 \times \text{Na}_2\text{O}_{\text{eq}} \text{ (\% cement)}$$



Mechanism of Lithium Effect?



Lawrence & Vivian, 1961



Conclusions (Mitigation)

Damage due to ASR can be controlled by:

- Avoiding reactive aggregates
- Controlling alkali content of the concrete
- Using suitable fly ash
- Using slag
- Using silica fume
- Using suitable natural pozzolans
- Using lithium compounds



THE FLOW CHART

ASR Guide Flow chart

PCA IS415

CONCRETE TECHNOLOGY

Guide Specification for Concrete Subject to Alkali-Silica Reactions

Developed by
the Durability Subcommittee
of the Portland Cement Association

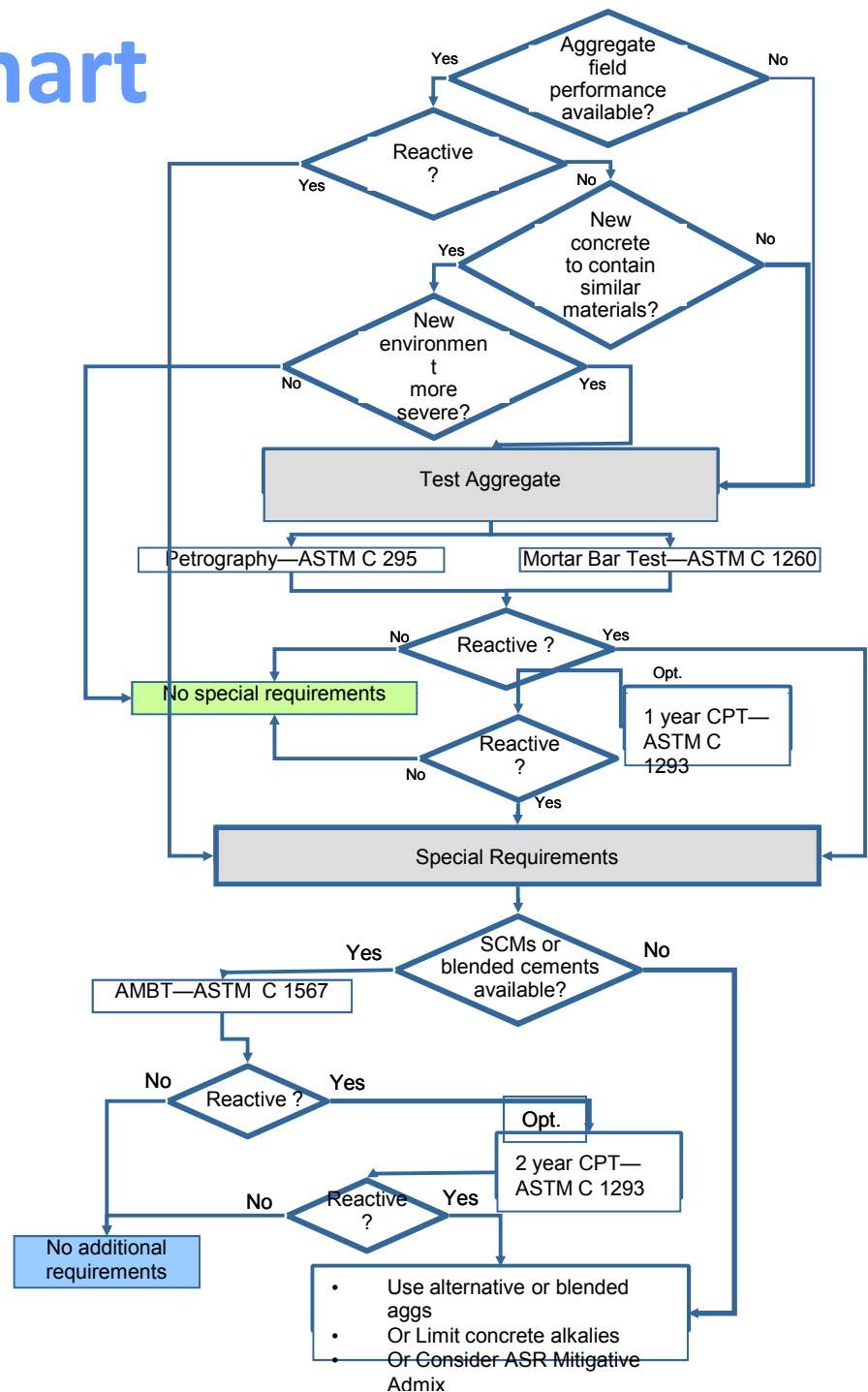
Endorsed by
American Concrete Pavement Association,
National Ready Mixed Concrete Association

Foreword

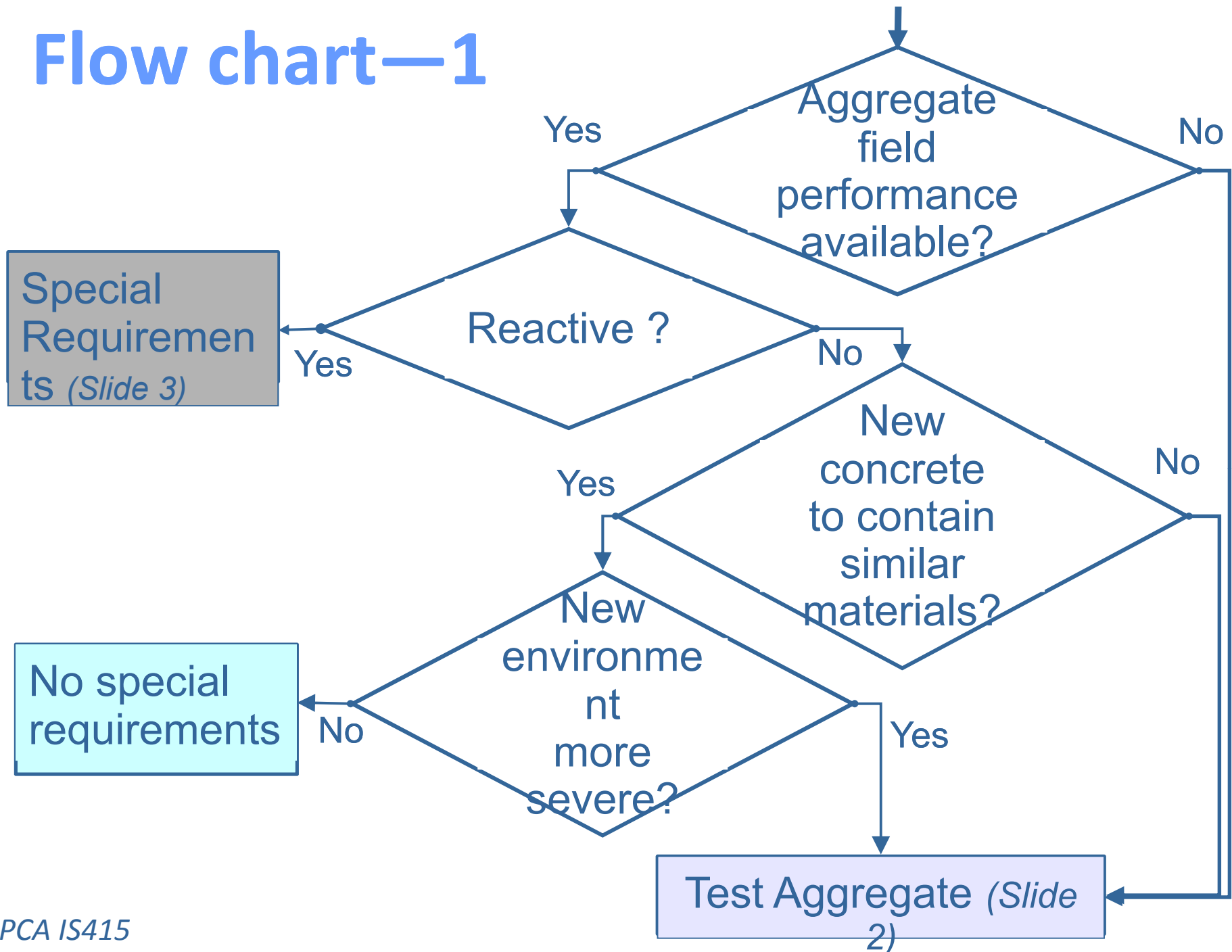
Most aggregates are chemically stable in hydraulic cement concrete, without deleterious interaction with other concrete ingredients. However, this is not the case for aggregates containing certain siliceous minerals that react with soluble alkalis in concrete, sometimes resulting in detrimental expansion and cracking of concrete structures. Alkali-silica reactivity (ASR), which was first reported in 1940, is now known worldwide. The alkali-silica reaction forms a gel that swells as it draws water from the surrounding cement paste. The presence of gel does not necessarily indicate destructive ASR. Some gels expand very little or not at all. If a gel is low-swelling, it will not create problems. High-swelling gel may cause pressures exceeding the tensile strength of concrete, which results in cracking of the concrete. Fortunately, most concrete is not affected by a destructive ASR. Although the risk of catastrophic failure and the number of affected structures are low, ASR-induced cracking can exacerbate other deterioration mechanisms such as those that occur in frost, deicer, or sulfate exposures. ASR can be controlled by the methods presented in this guide specification.

This specification is intended for use primarily by owners, transportation engineers, and structural engineers to provide safeguards against the occurrence of ASR failures. As with all specifications, this specification should be used only by qualified professionals who are competent to evaluate the significance and limitations of the specification and who will accept responsibility for the application of its requirements to the structure under consideration.

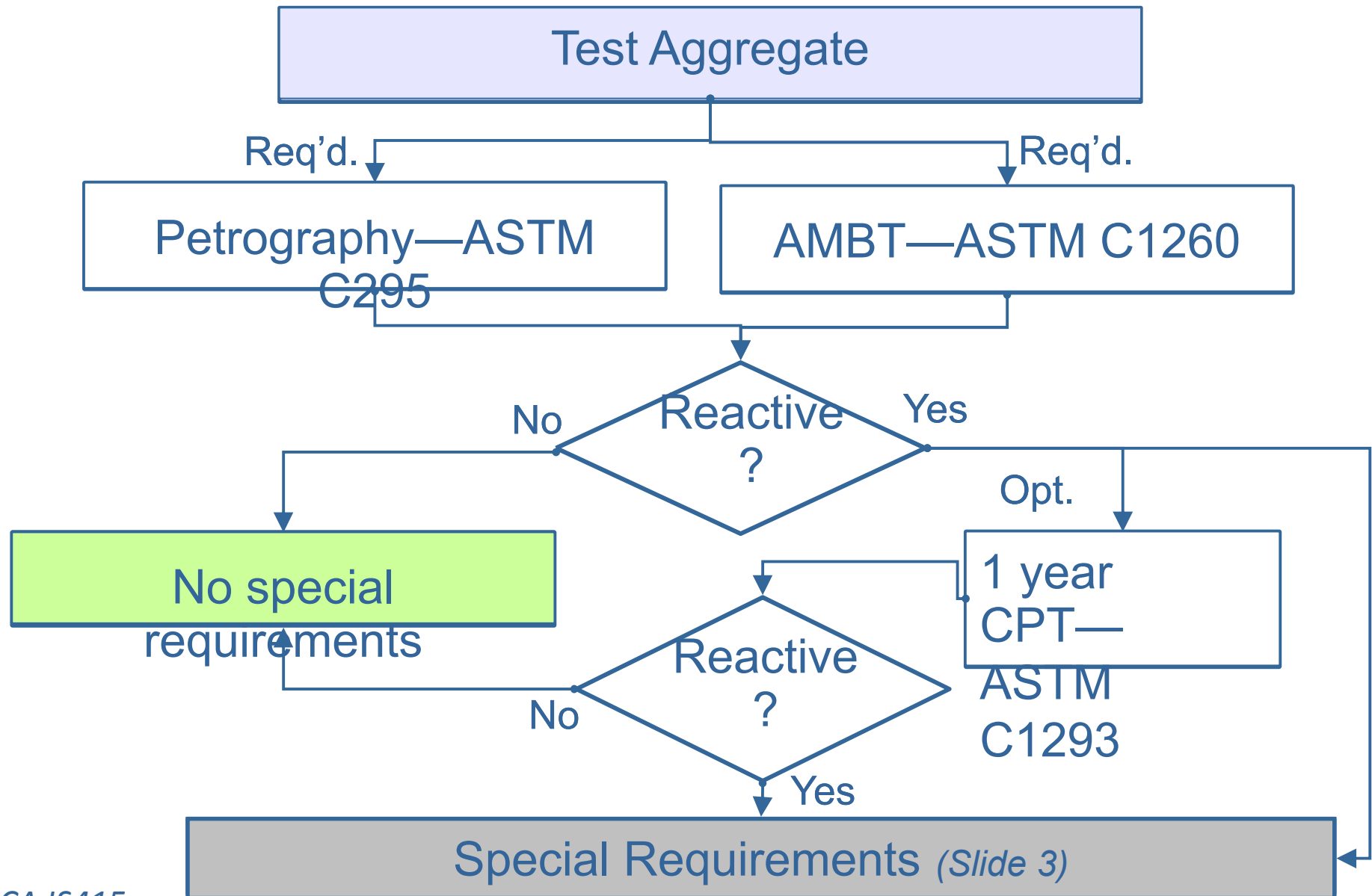
The American Association of State Highway and Transportation Officials (AASHTO) have also developed guidelines and technologies for treating and preventing ASR. An AASHTO Guide Specification on ASR-Resistant Concrete is available online at: <http://leadstates.transportation.org/asr/library/sspec.stm>.



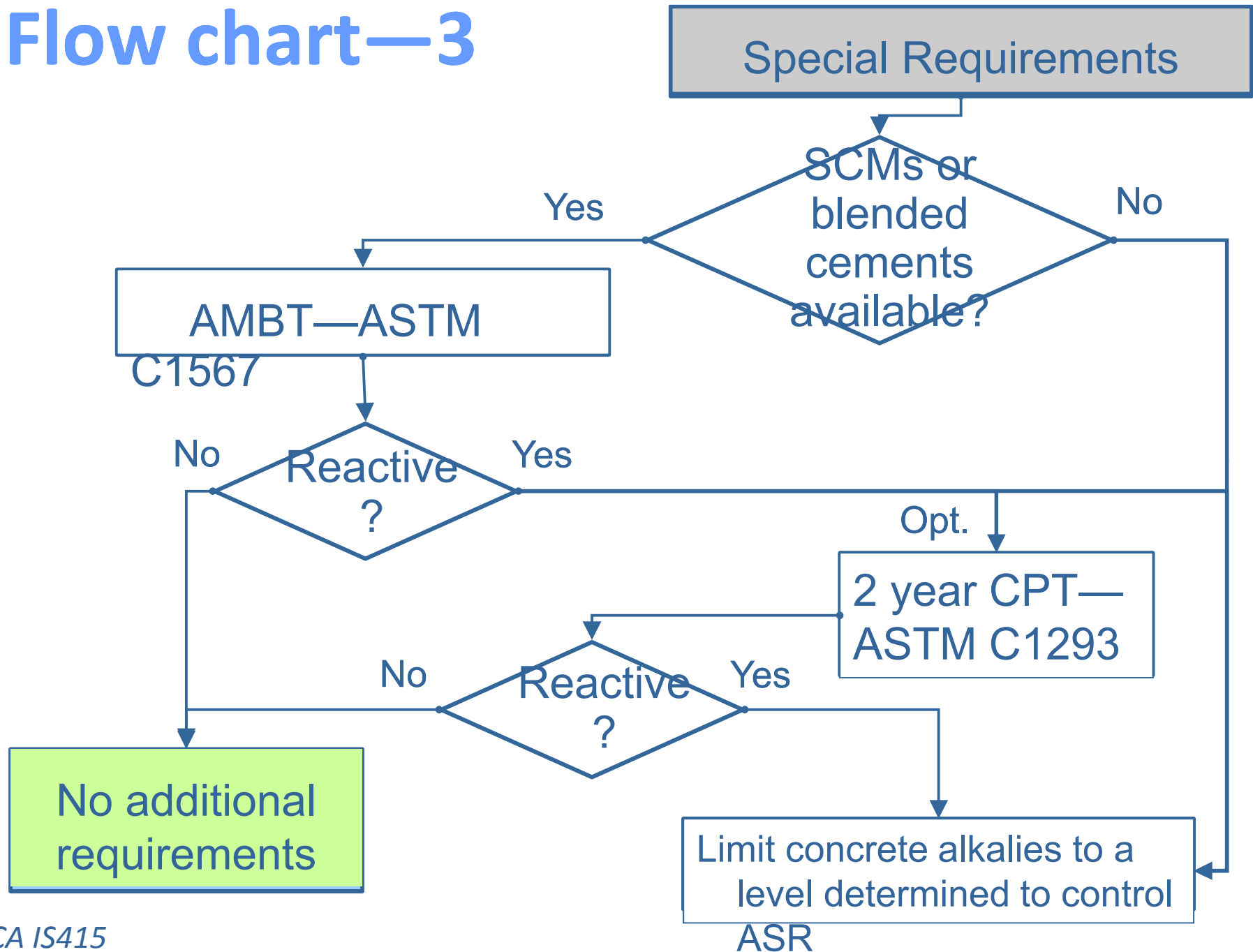
Flow chart—1



Flow chart—2



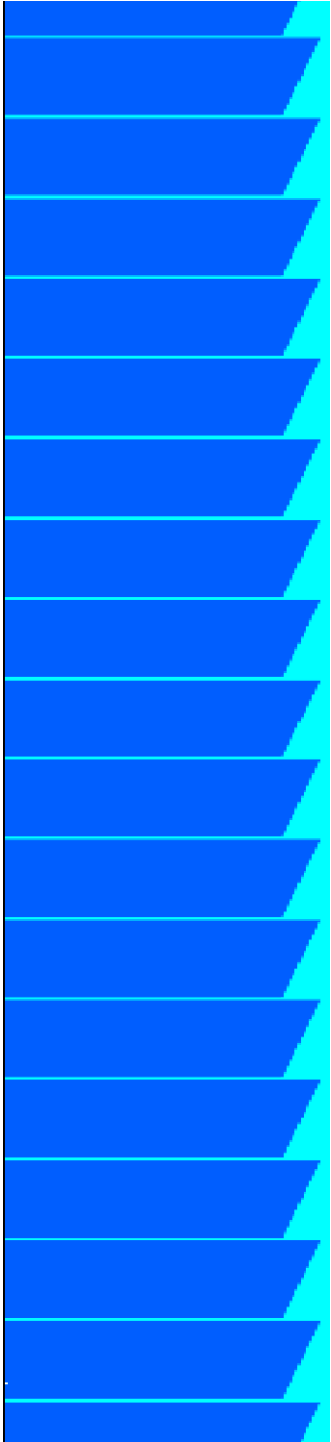
Flow chart—3





Conclusions

- ASR (and ACR) are reactions between certain aggregate particles and alkalies in concrete that can be deleterious
- Three components needed are sufficient reactive aggregate, sufficient alkalies and sufficient moisture
- A variety of test methods exist to predict ASR potential for concrete materials and mixtures
- There is no perfect test



Questions

