# Alkali-Aggregate Reactions

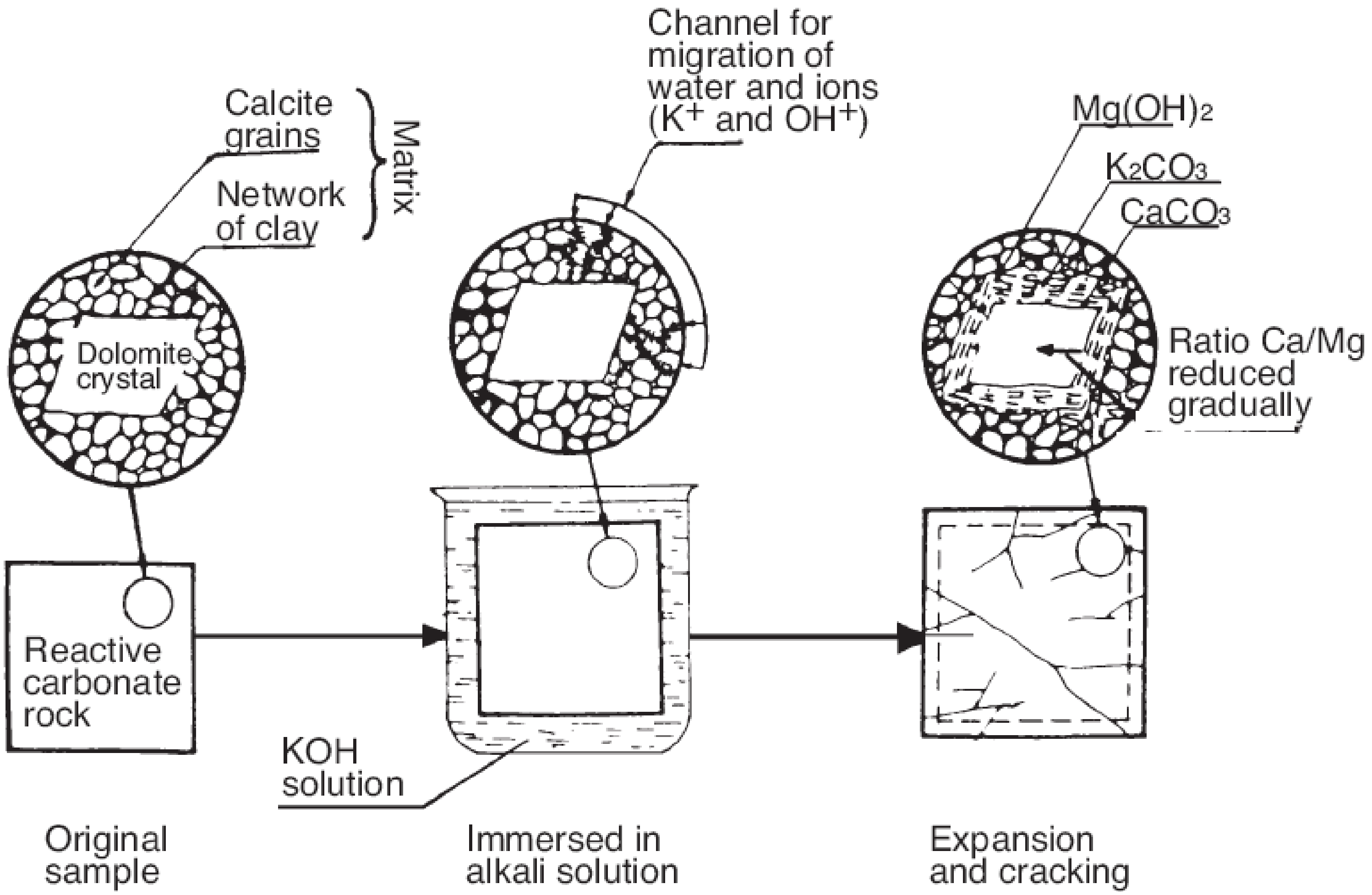
**Alkali-Aggregate Reaction (AAR)**

- **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

*SHRP-C-315*

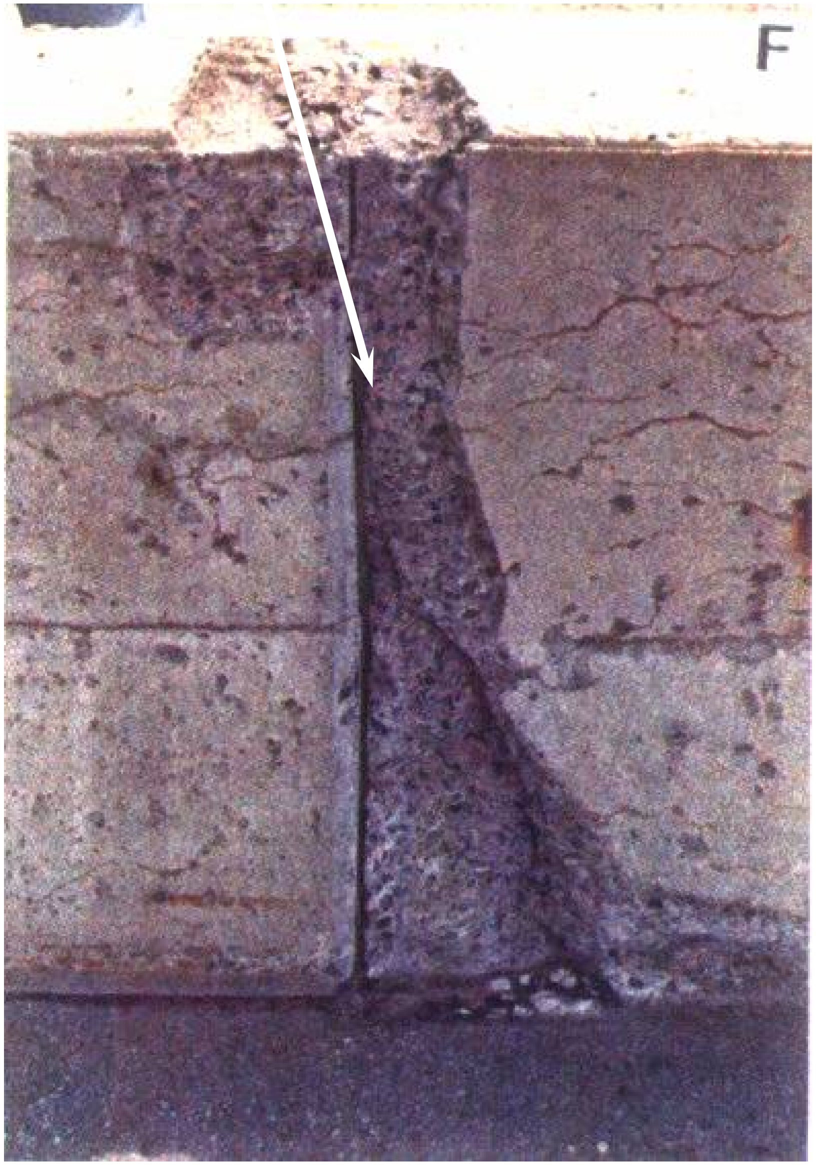
# Misalignment of Sections

SHRP-C-315

# Closing of joints or loss of clearance between members

# Extrusion of joint-sealants

# Concrete crushing

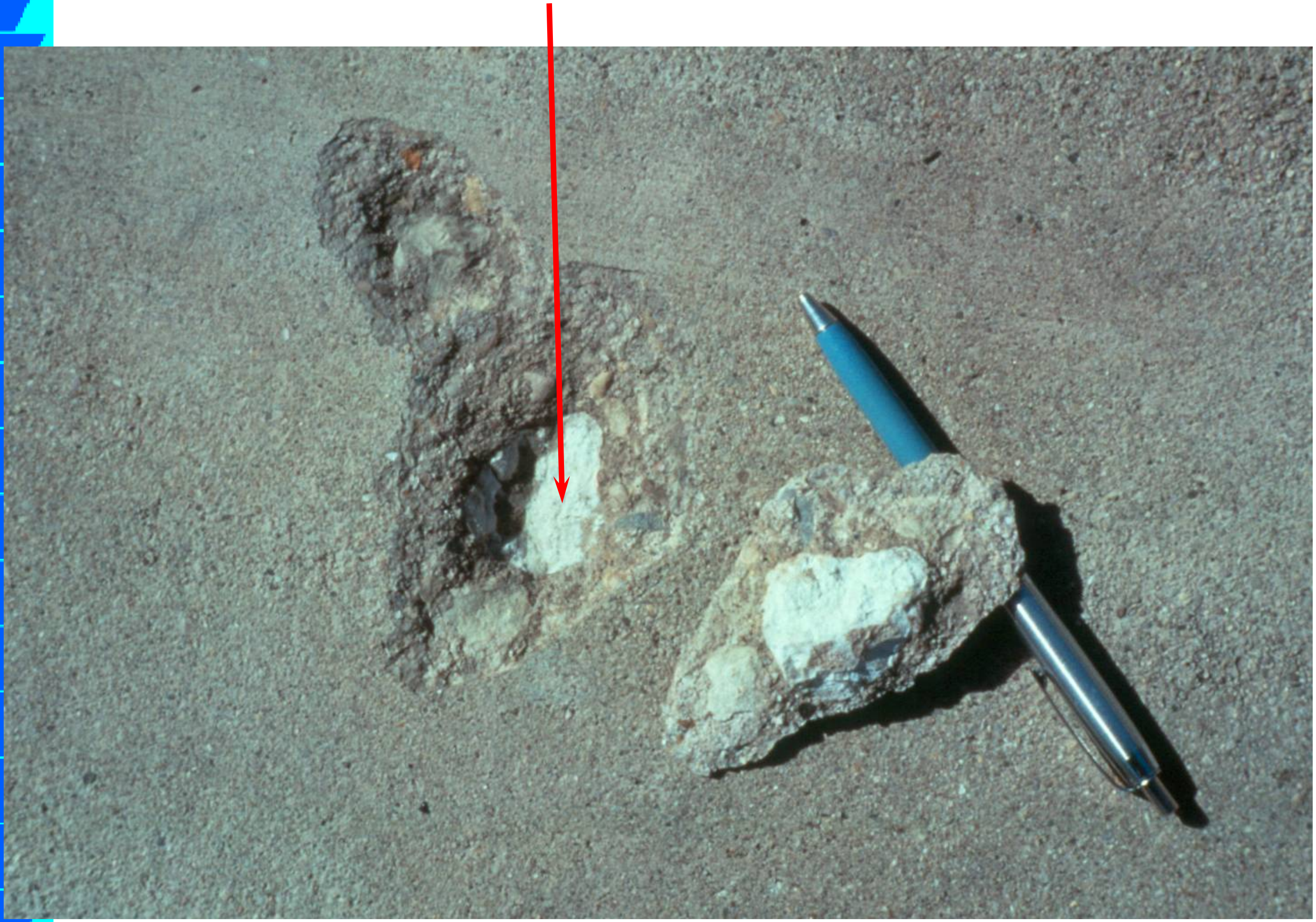


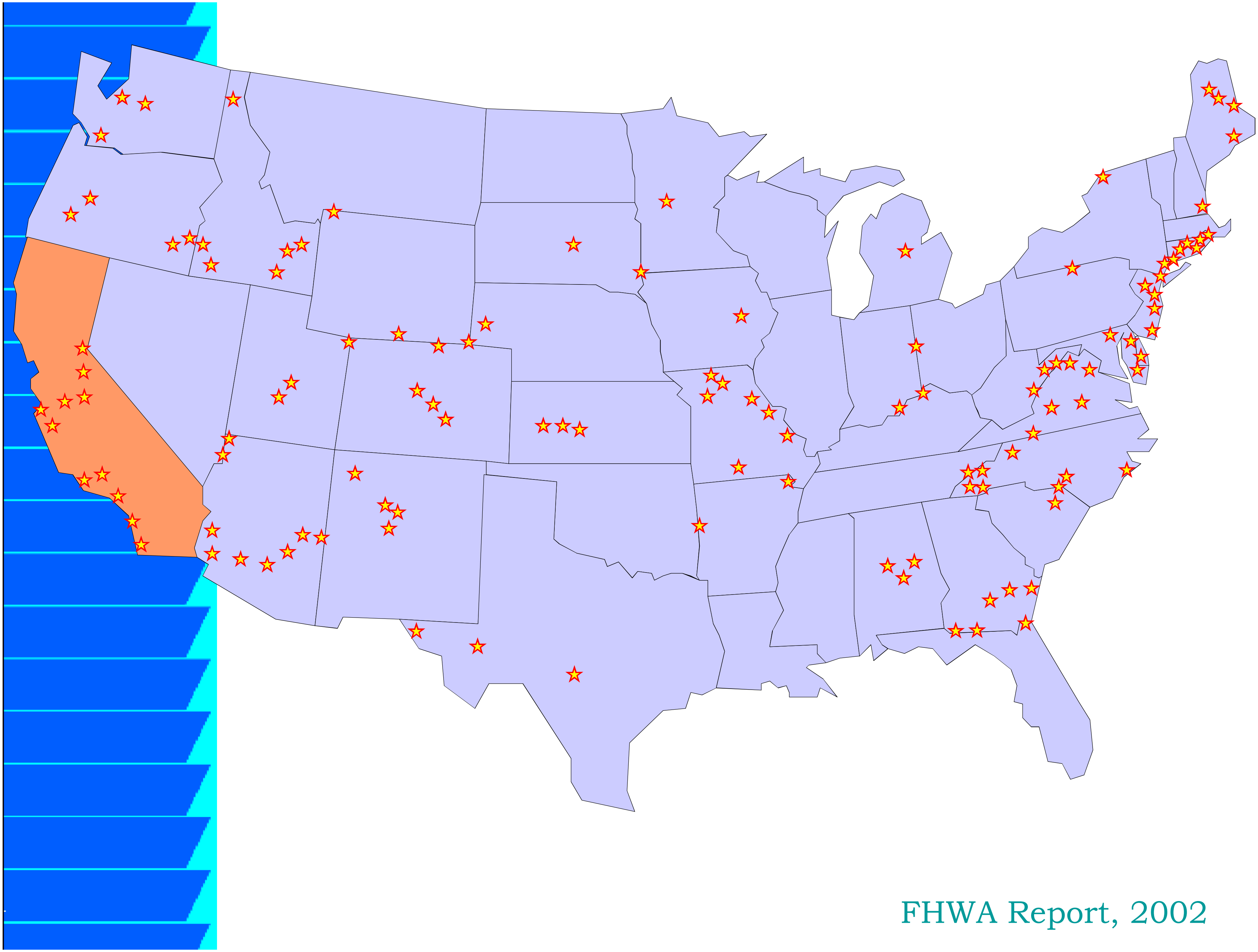
*CSA A864-00*

# Operational difficulties

# Discoloration or "gel staining" around cracks

# Popouts

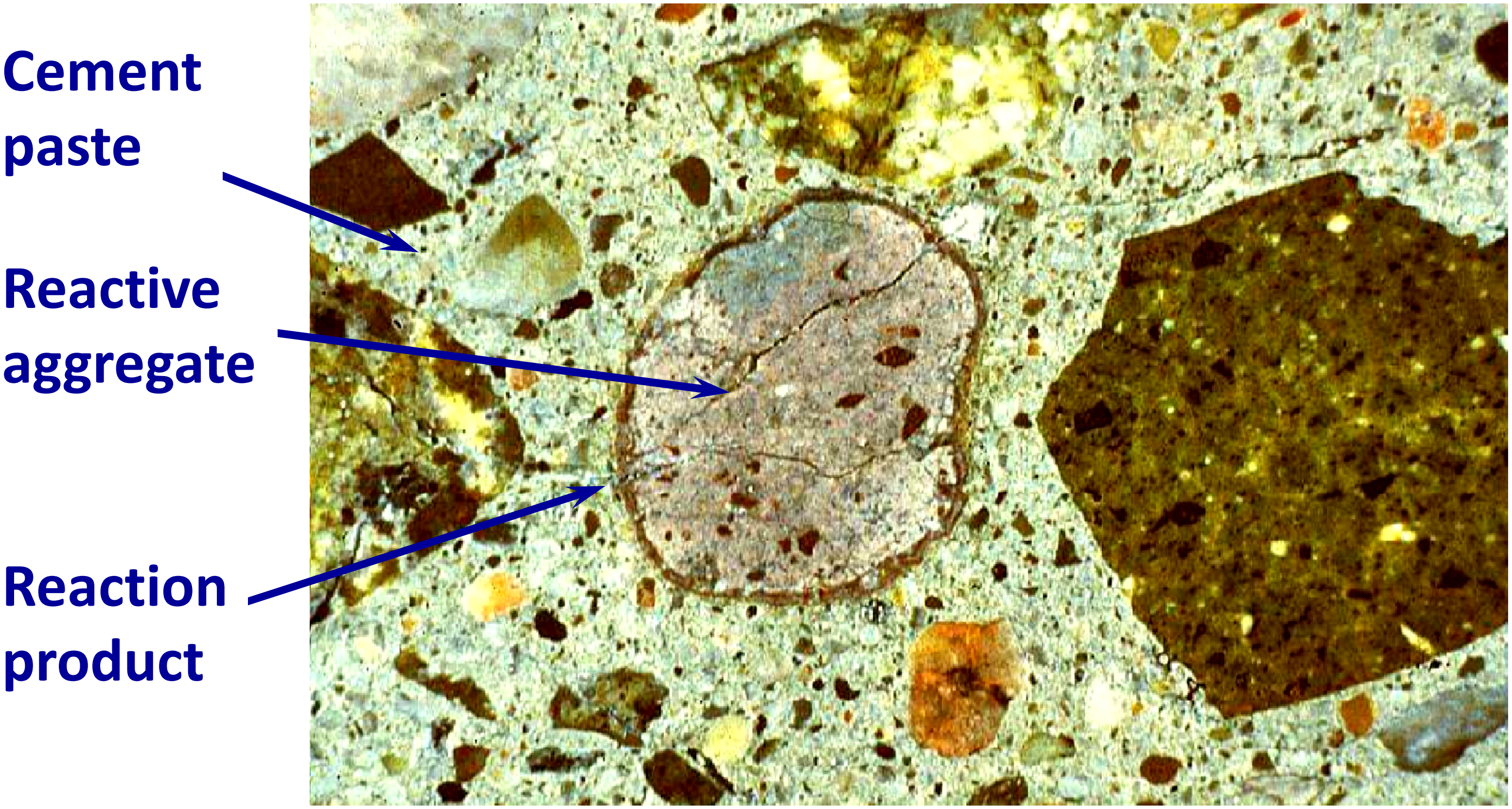




FHWA Report, 2002

# ASR EXPANSION MECHANISM

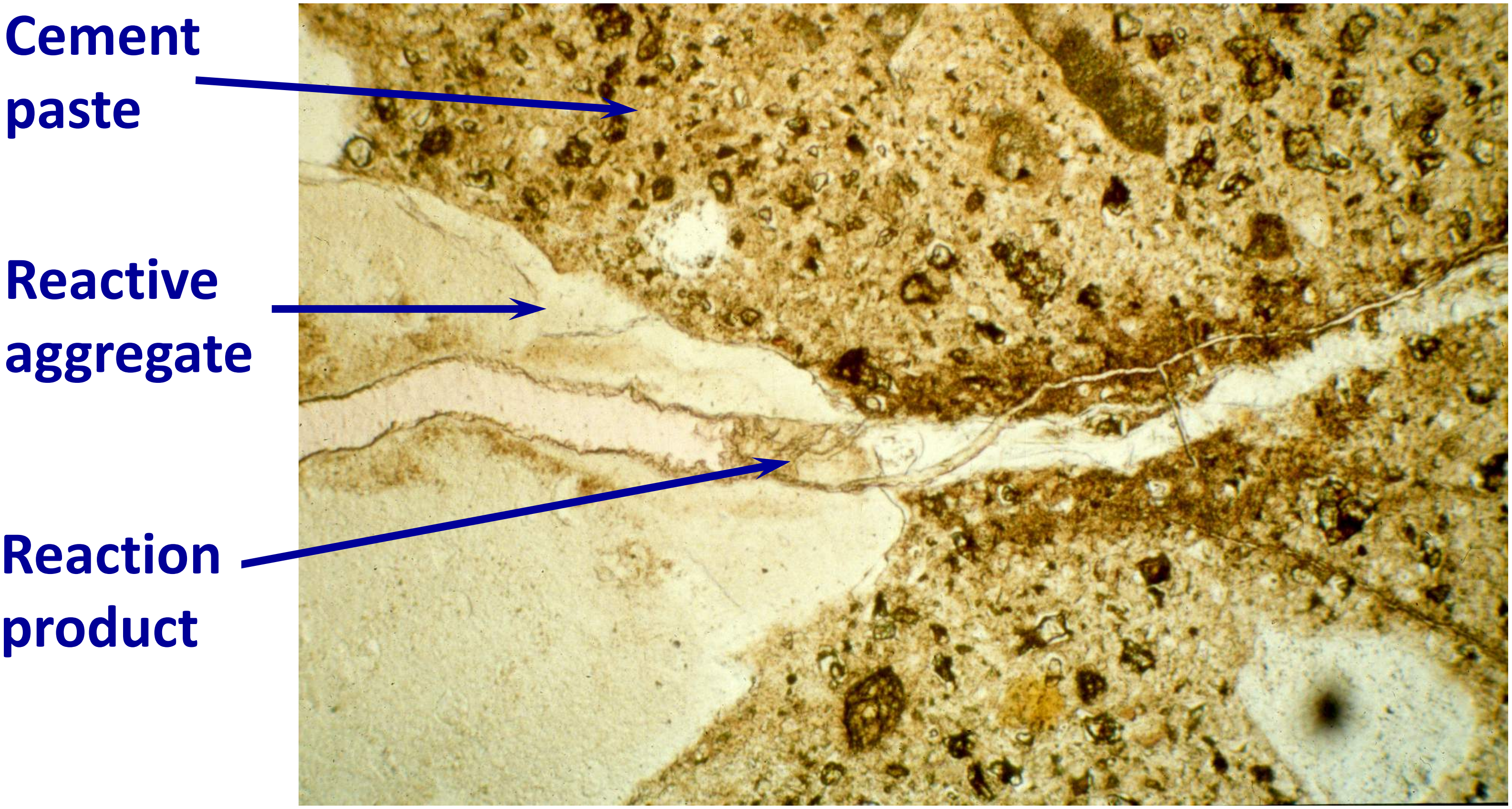
# ASR in Concrete Polished Section


**Cement paste**

**Reactive aggregate**

**Reaction product**

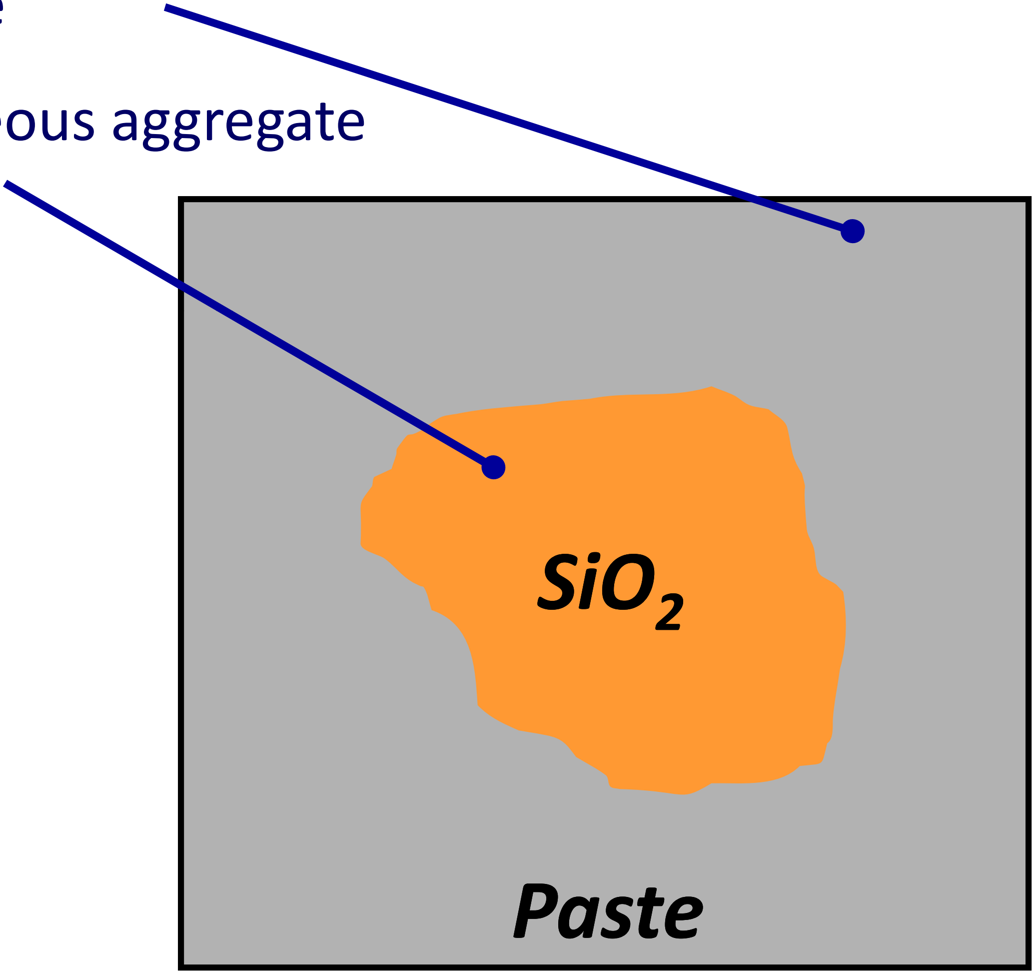
# ASR in Concrete Thin Section



# ASR Mechanism

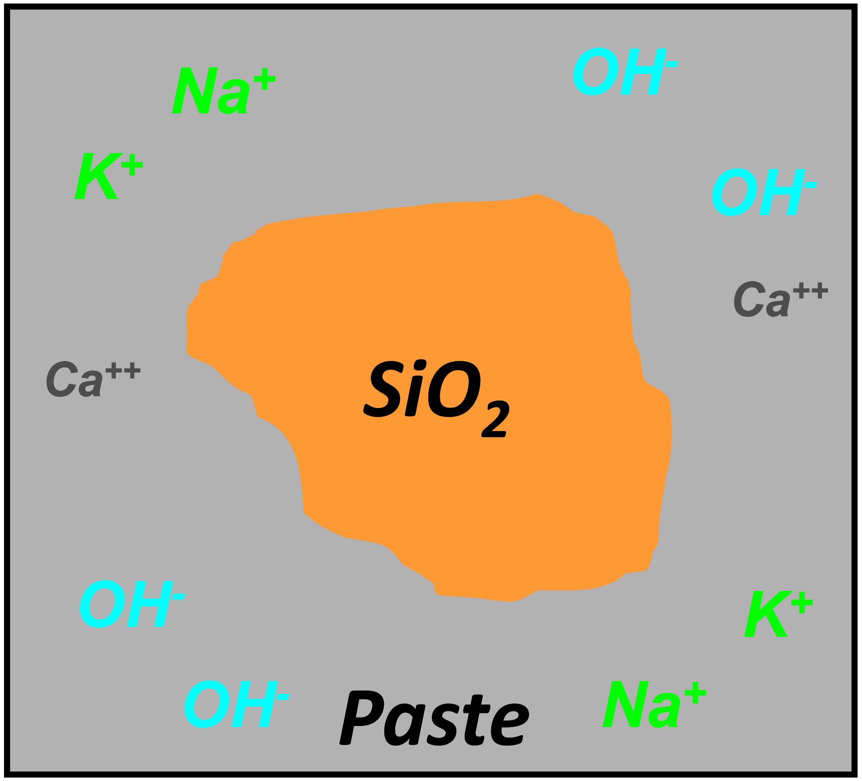
Concrete “model” showing:

- cement paste
- reactive siliceous aggregate



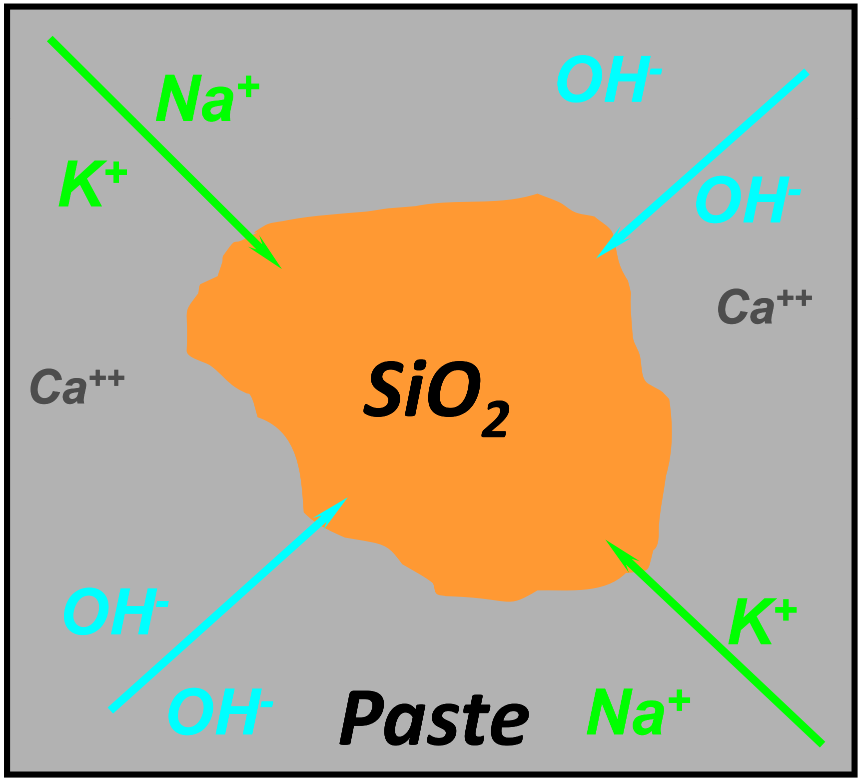
# ASR Mechanism

- 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 . . .

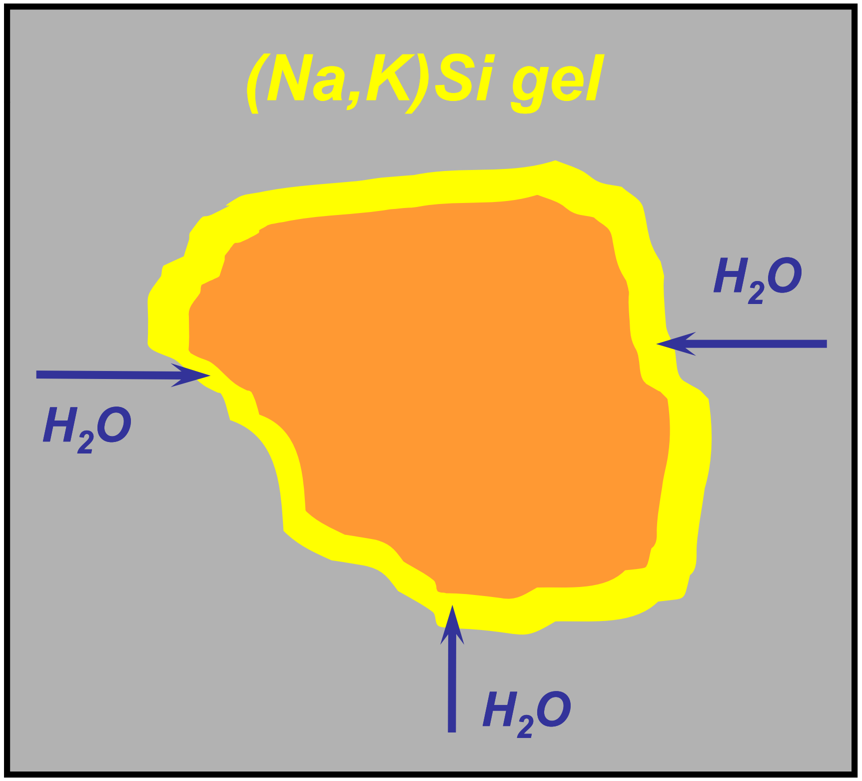


# ASR Mechanism

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

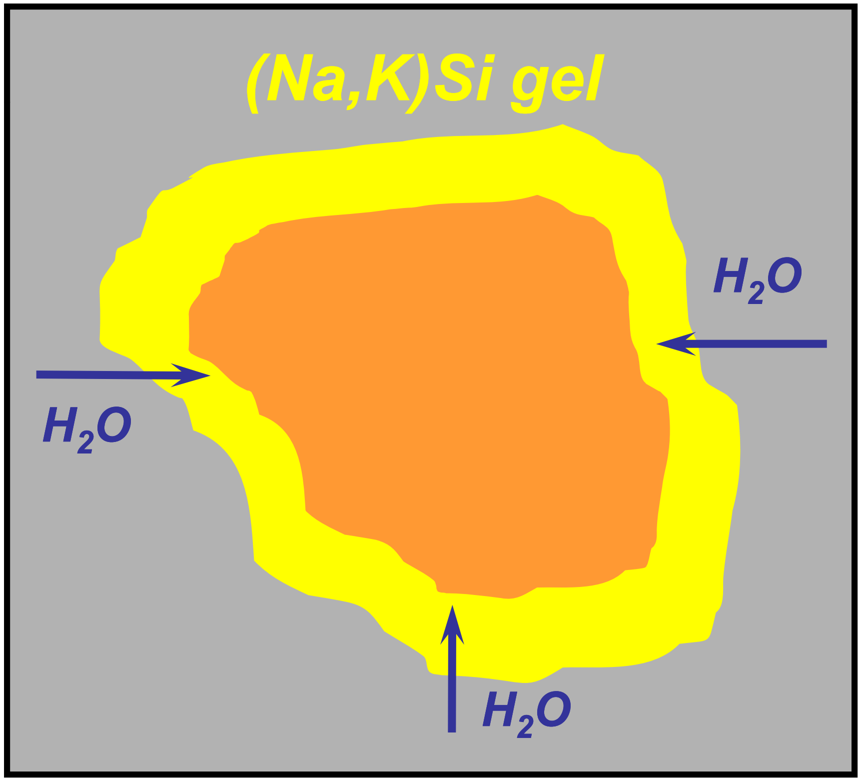
# ASR Mechanism

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



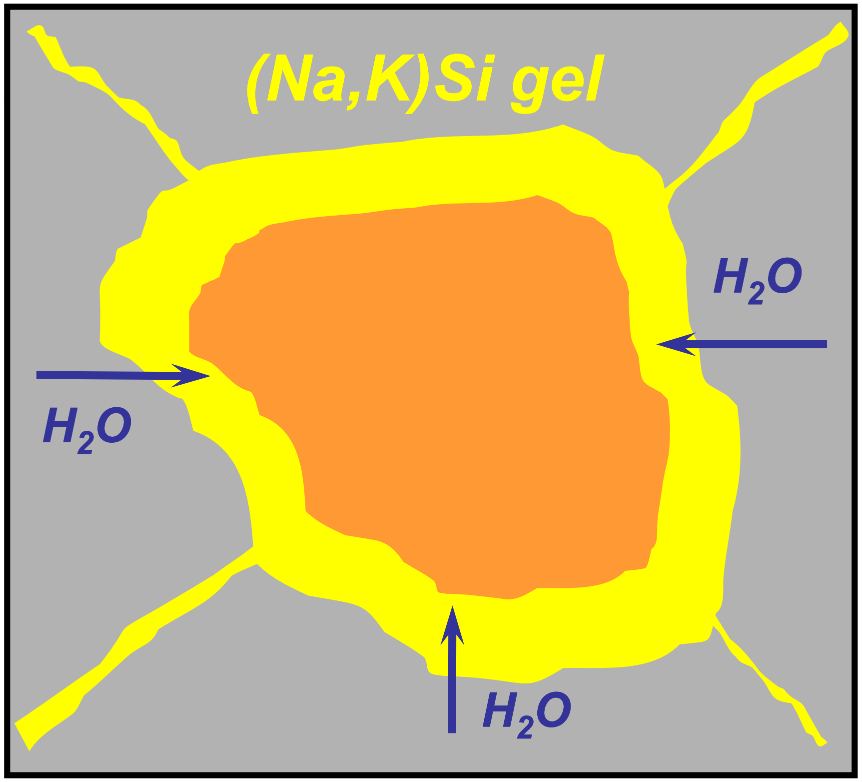
# ASR Mechanism

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



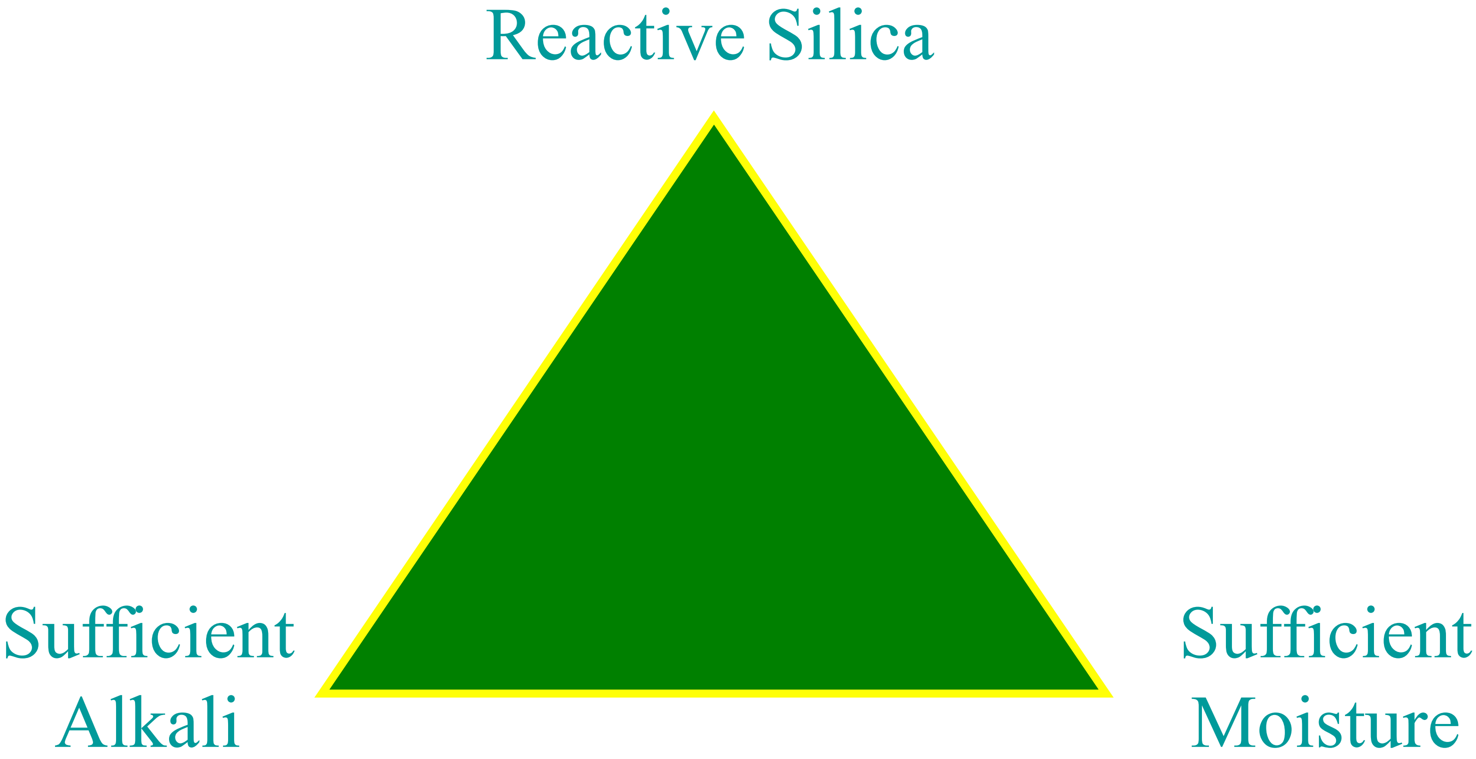
# ASR Mechanism

- 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

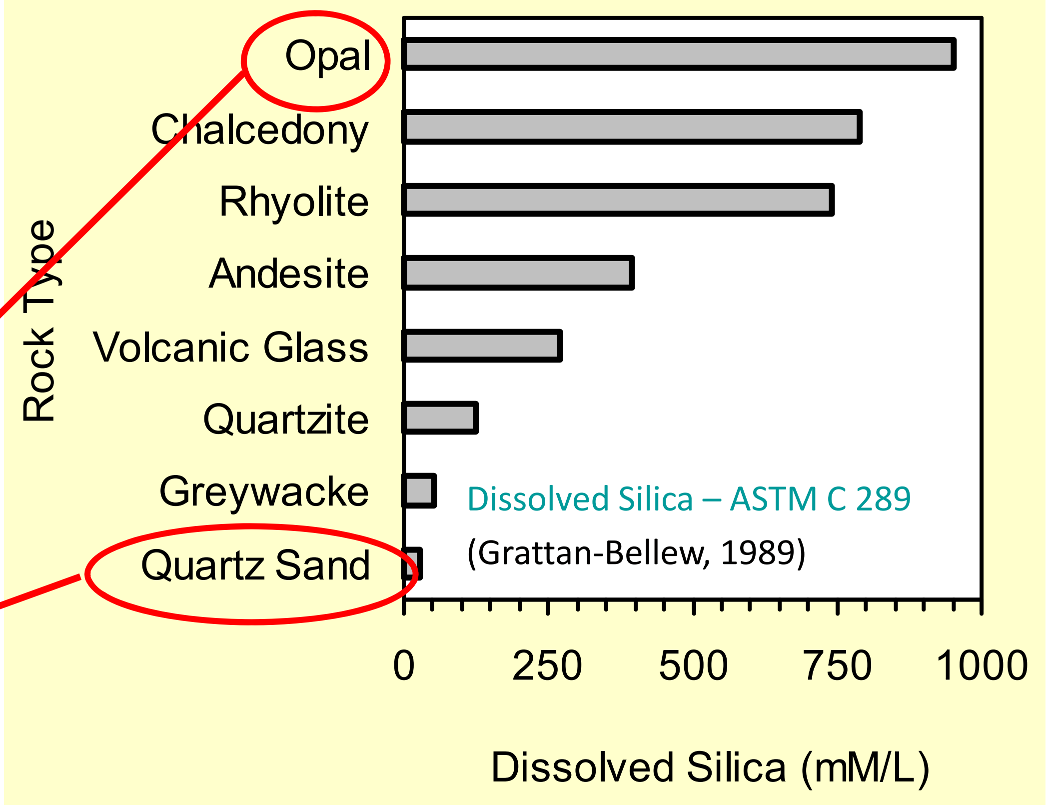
# ASR-Susceptible Rocks and Minerals

- **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 →



Dissolved Silica – ASTM C 289

(Grattan-Bellew, 1989)

| **Mineral** | | **Chemical composition** |
|---|---|---|
| Opal | → | $SiO_2$ |
| Quartz | | $SiO_2$ |

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

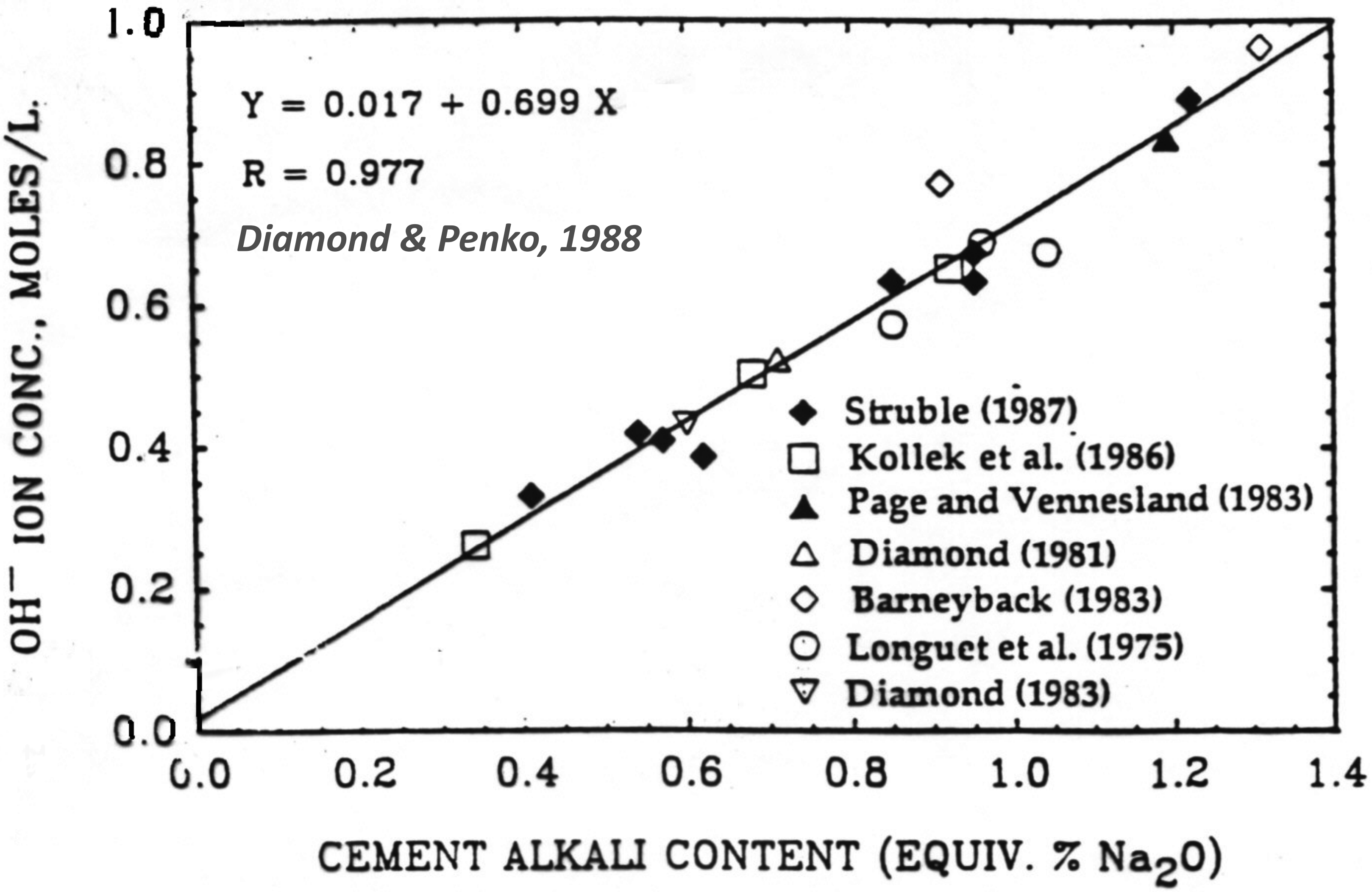
| Oxide | OPC |
|---|---|
| $SiO_2$ | 20.55 |
| $Al_2O_3$ | 5.07 |
| $Fe_2O_3$ | 3.10 |
| CaO | 64.51 |
| MgO | 1.53 |
| $K_2O$ | 0.73 |
| $Na_2O$ | 0.15 |
| $SO_3$ | 2.53 |
| LOI | 1.58 |

+ other trace elements

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

$$K_2O + H_2O \rightarrow 2K^+ + 2OH^-$$
$$Na_2O + H_2O \rightarrow 2Na^+ + 2OH^-$$

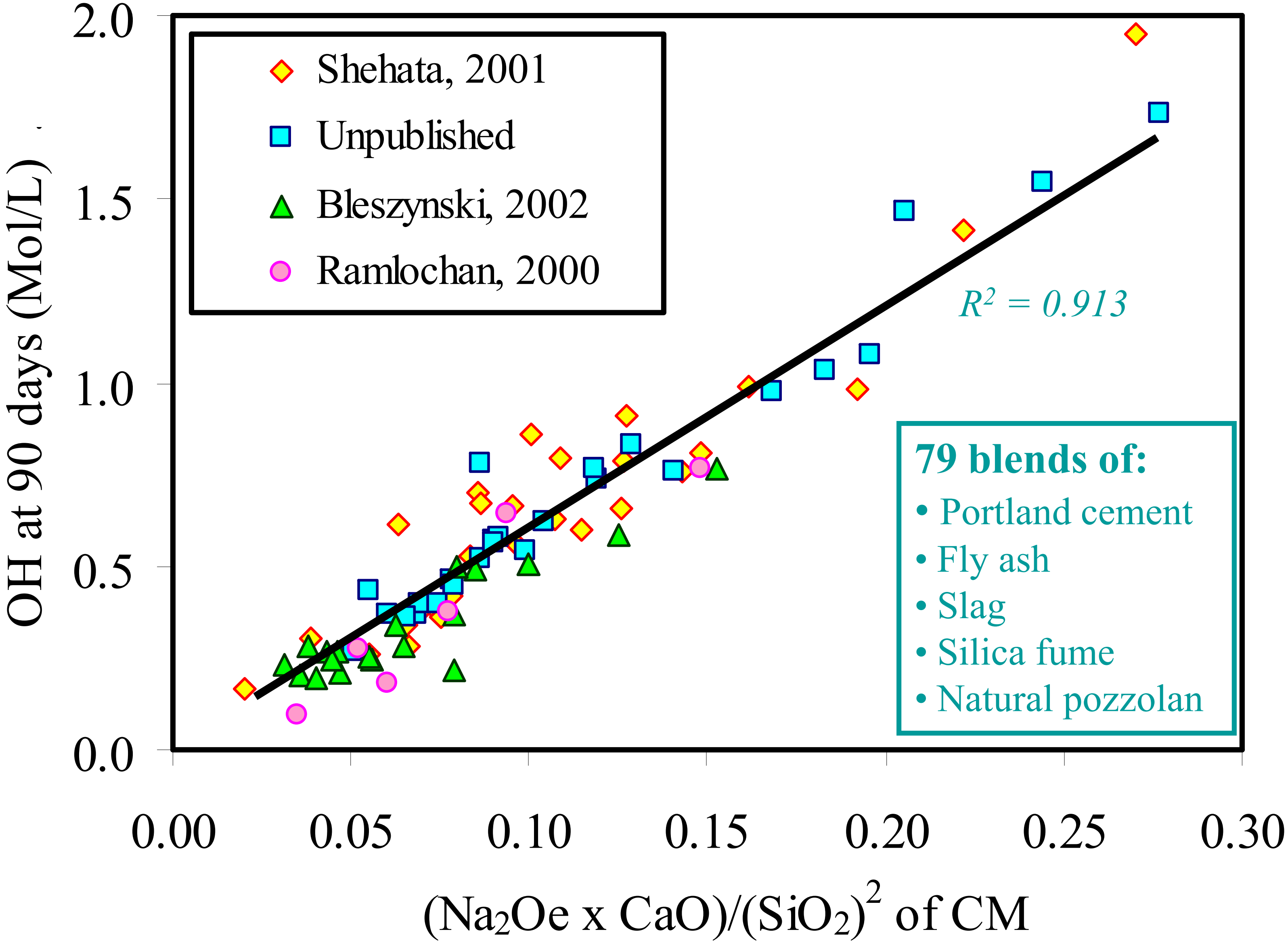
Most of the alkalies end up in the pore solution and the associated OH concentration is sufficient to produce a pH in the range of 13.2 to 14.0



*Diamond & Penko, 1988*

Example: A paste with w/c = 0.50 produced with a high-alkali portland cement with 1.00% $Na_2O_e$ will have a pore solution with ~ 0.7 mol/L OH- ions (~ pH 13.85)

# Cement Composition & Pore Solution Alkalinity

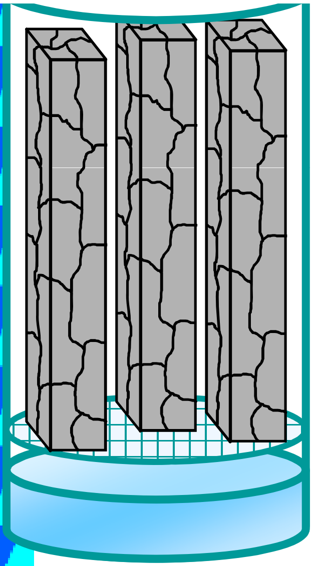


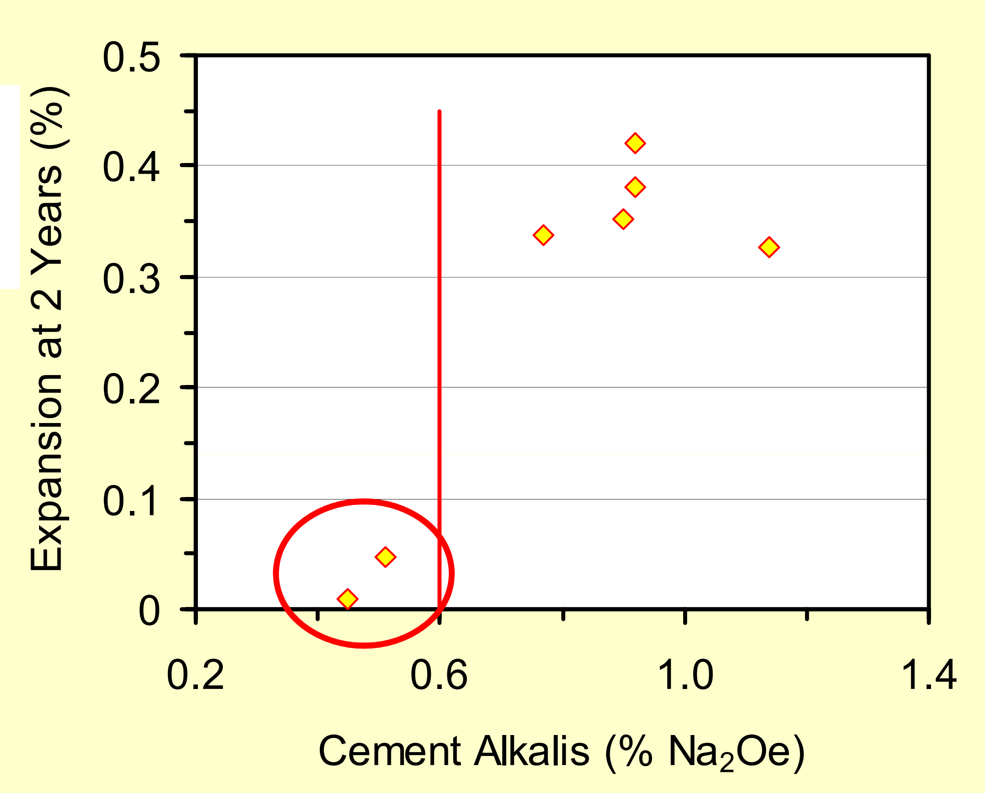
**79 blends of:**

- Portland cement
- Fly ash
- Slag
- Silica fume
- Natural pozzolan

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

**Expansion unlikely if cement alkalies < 0.60% $Na_2Oeq$**





**WRONG!**

# Cement vs. Concrete Alkali

$$\underset{\text{kg/m}^3\ \text{Na}_2\text{Oeq}}{\text{Concrete alkali content}} = \underset{\text{kg/m}^3}{\text{Cement content}} \times \underset{\%\ \text{Na}_2\text{Oeq}}{\text{Cement alkalies}} \times \frac{1}{100}$$

Example:

If a concrete contains 350 kg/m$^3$ of Portland cement and the cement has an alkali content of 0.78% Na$_2$Oe 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:

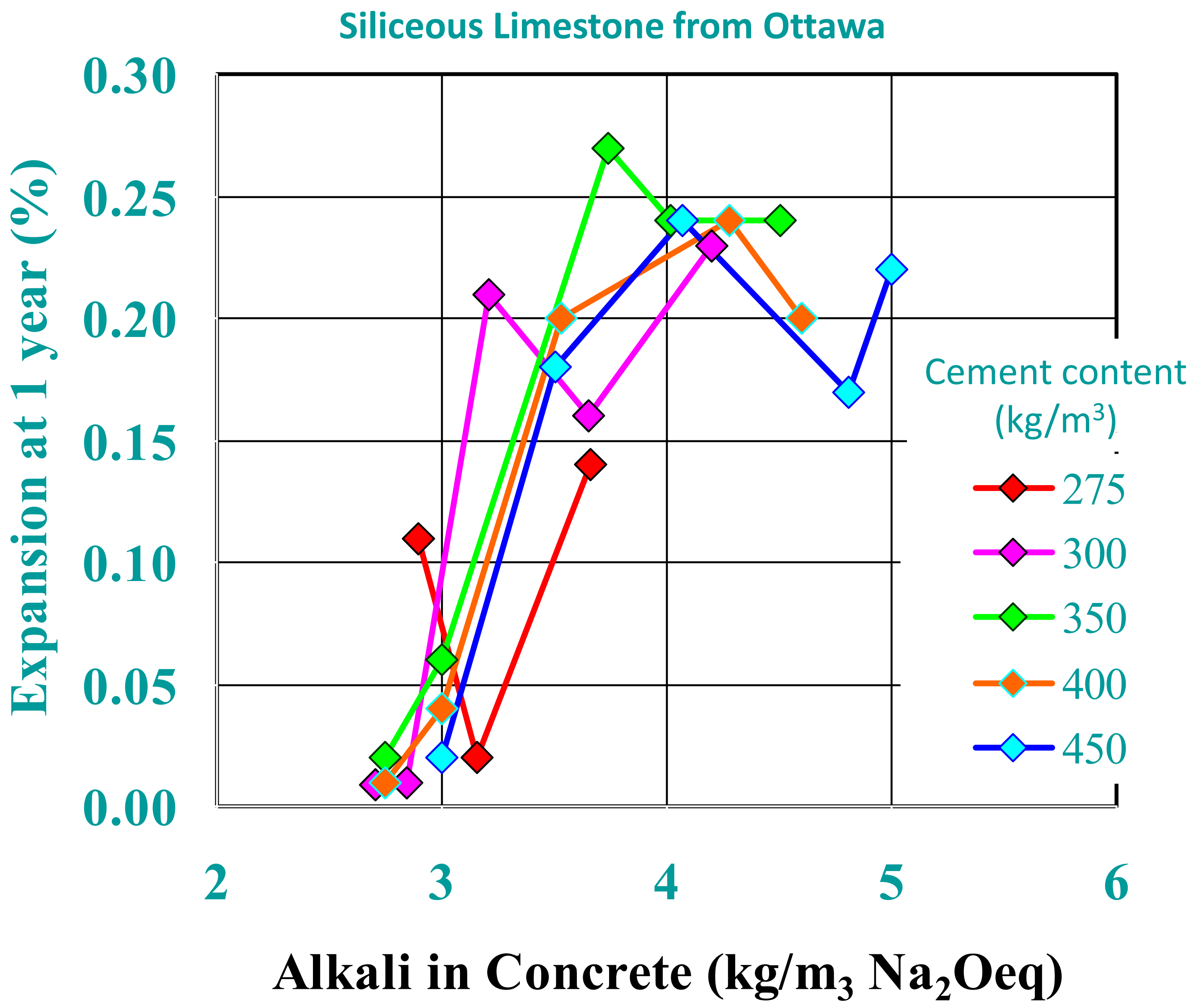
- $Na_2Oeq$
- $CaO$
- $SiO_2$

In the cementitious system

(i.e. including portland cement and all supplementary cementing materials)

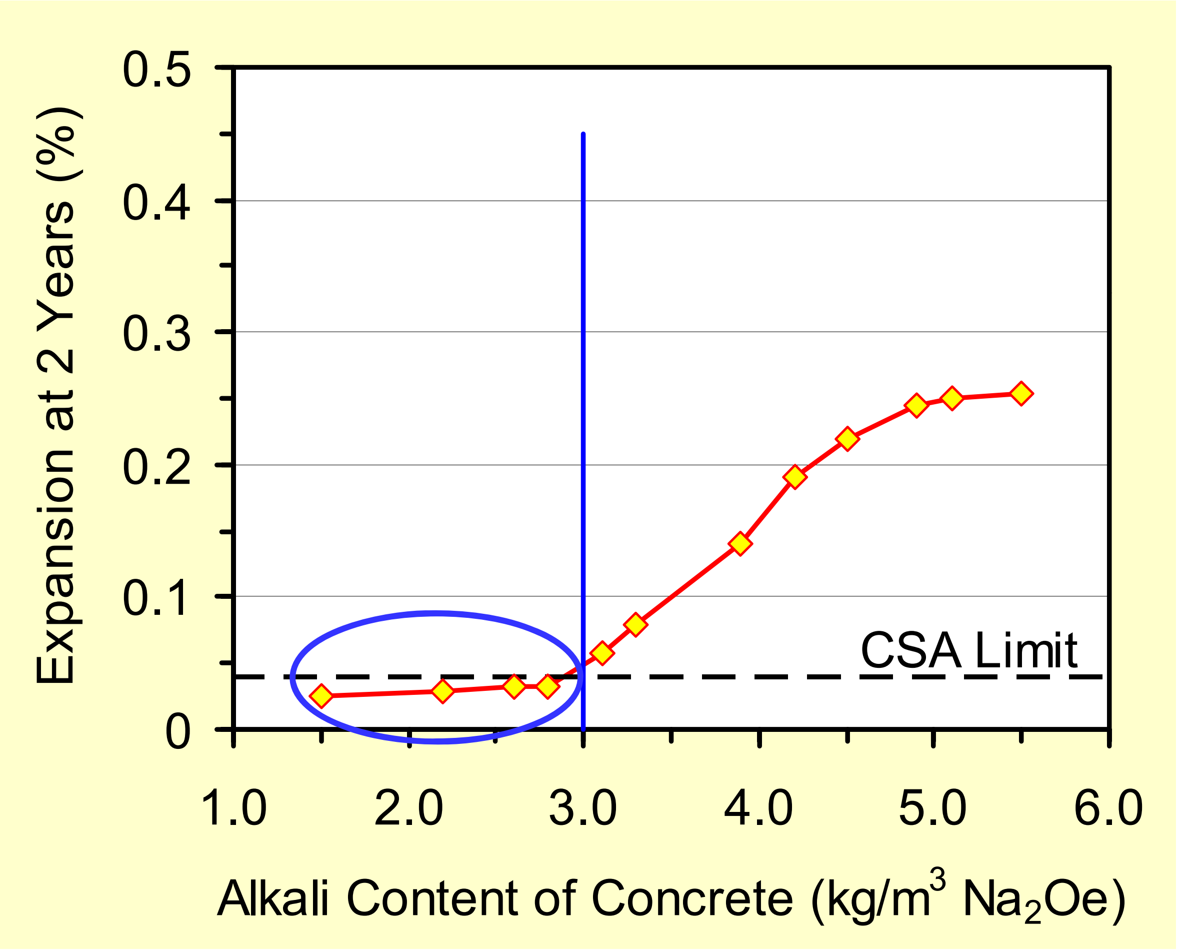
Concentration of Na, K & OH in pore solution ↑ as $Na_2Oeq$ $CaO$ ↑ & $SiO_2$ ↓

# Effect of Concrete Alkali

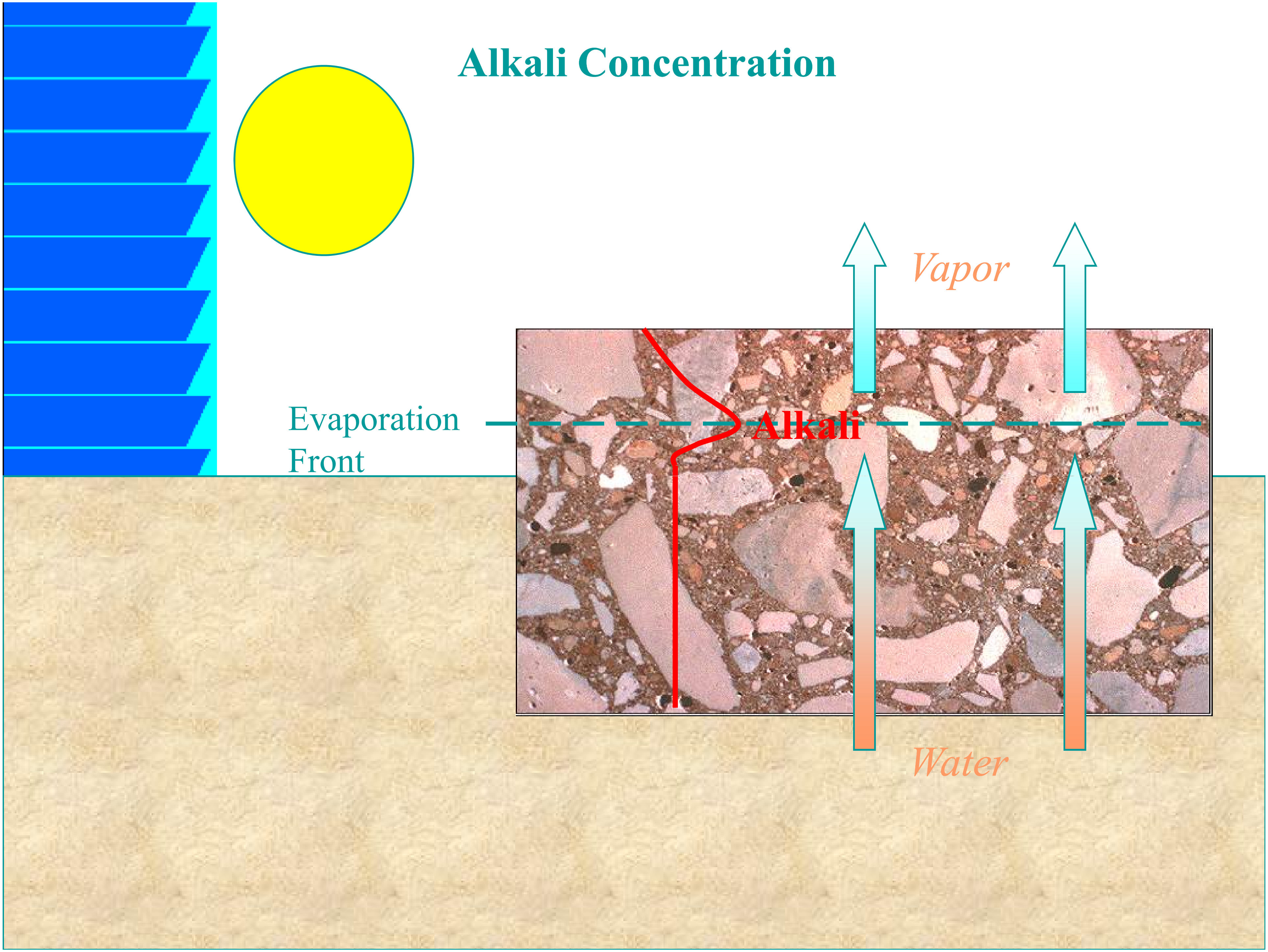


# Effect of Concrete Alkali Content

**Expansion unlikely if alkali content of concrete < 3.0 kg/m$^3$**



# Alkali Concentration



# Eq. Alkali Contents of North American Cements

| Cement Type | ≤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*

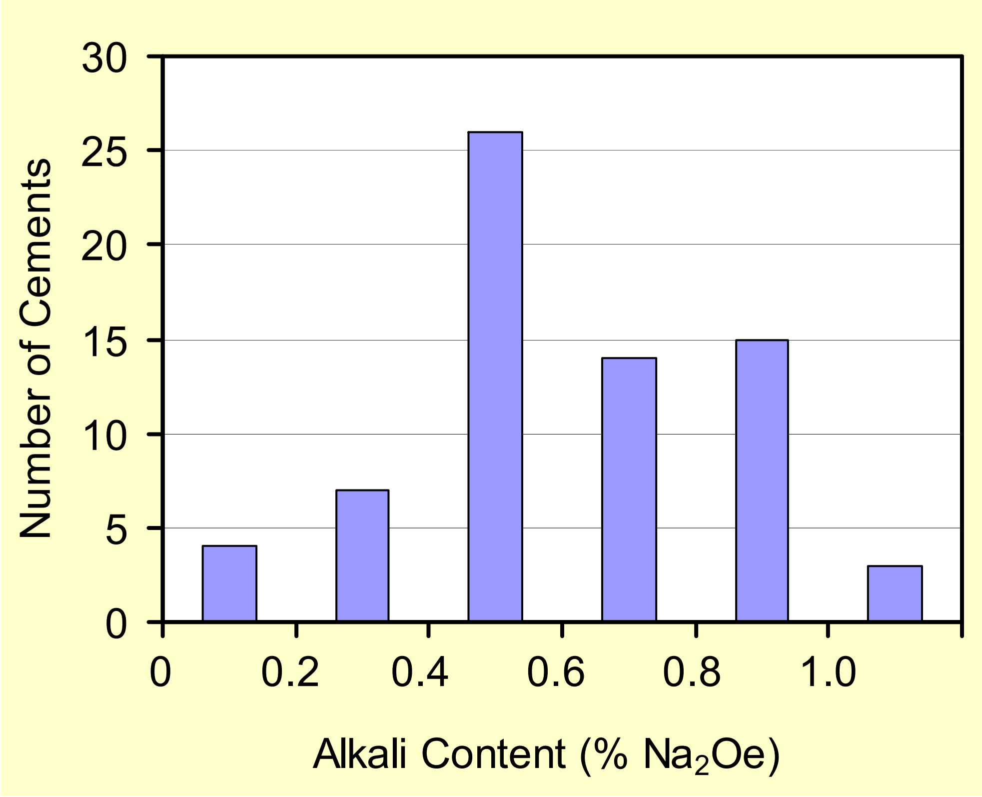
# Eq. Alkali Contents of North American Cements

Alkali contents of 69 sources of

Type I cement in North America

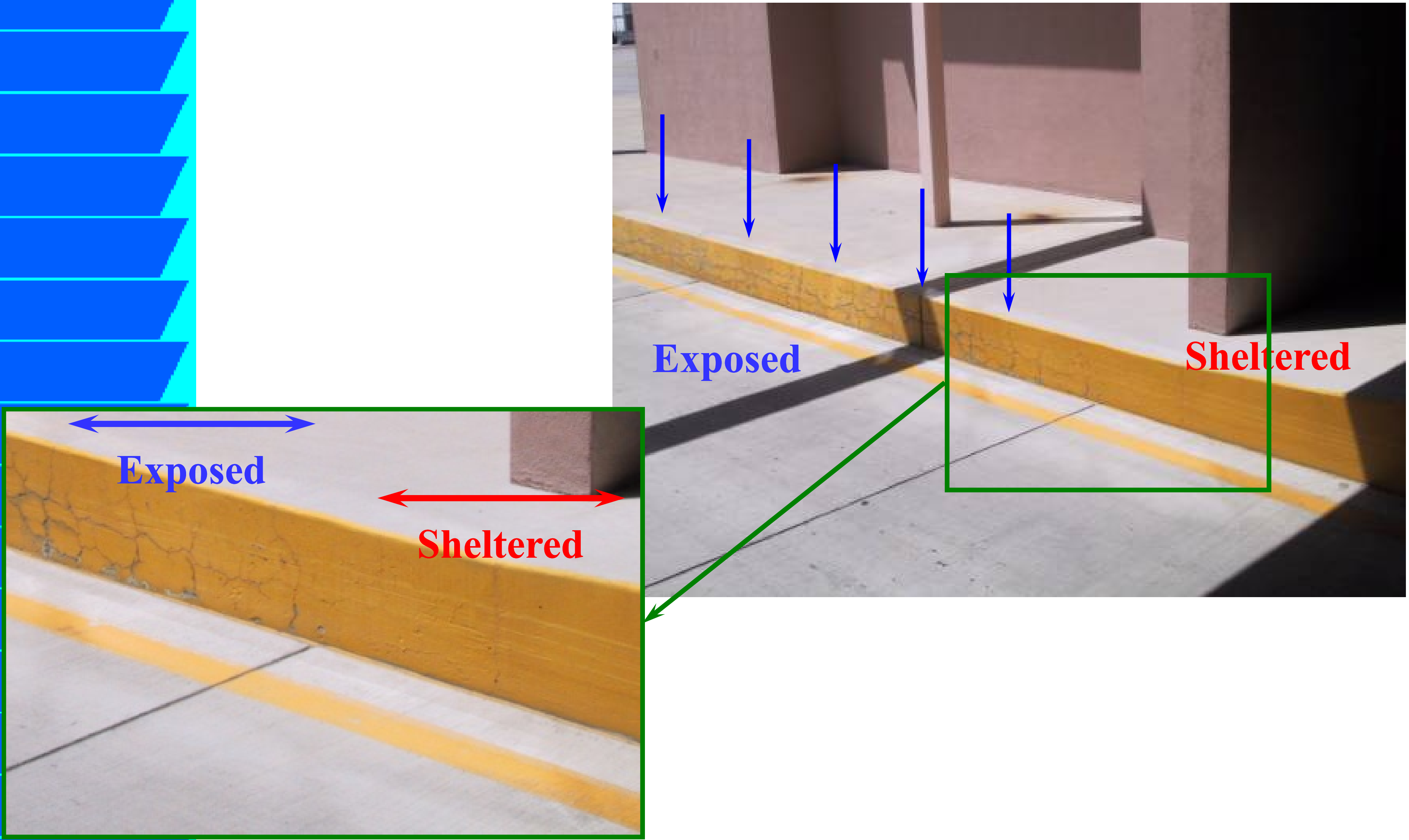
37 of 69 cements < 0.60% $Na_2Oeq$

32 of 69 cements > 0.60% $Na_2Oeq$



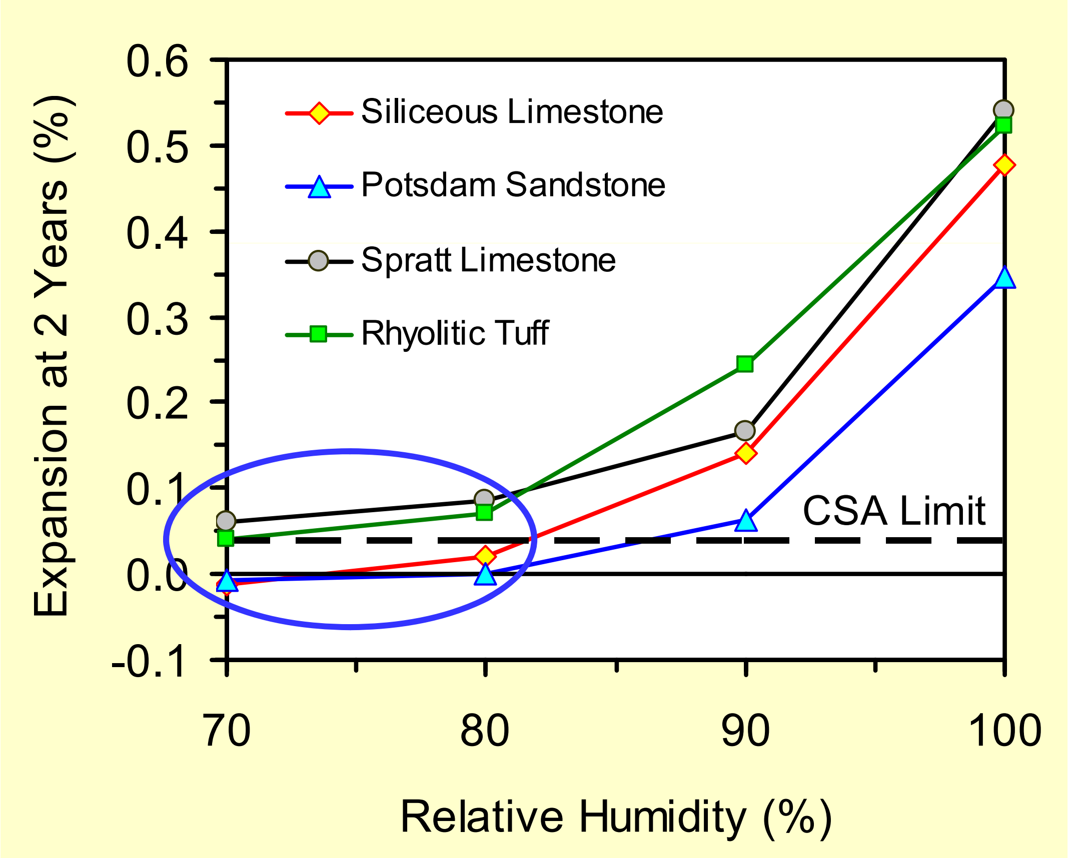
*Bhatty and Tennis 2008*

# 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**

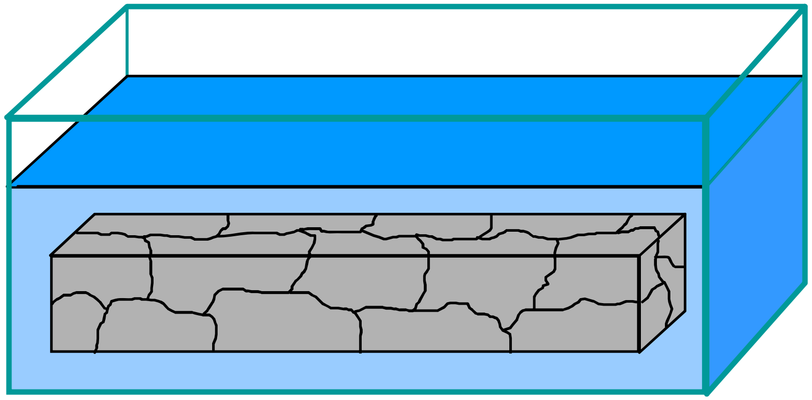
# The BEST ASR "Test"

- 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?

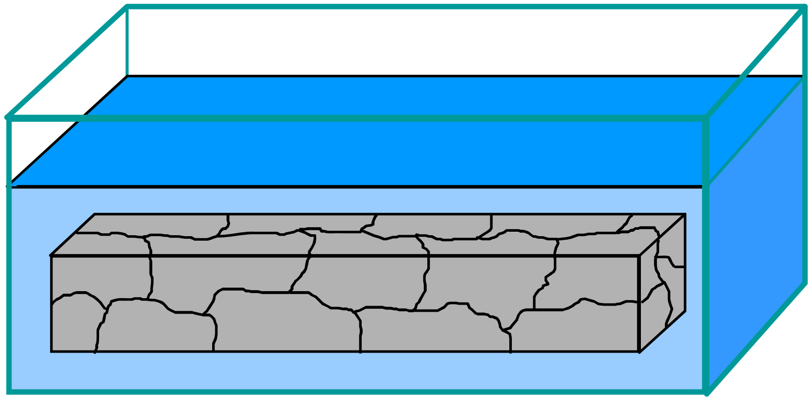
# Accelerated Mortar Bar Test – ASTM C1260

- 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.

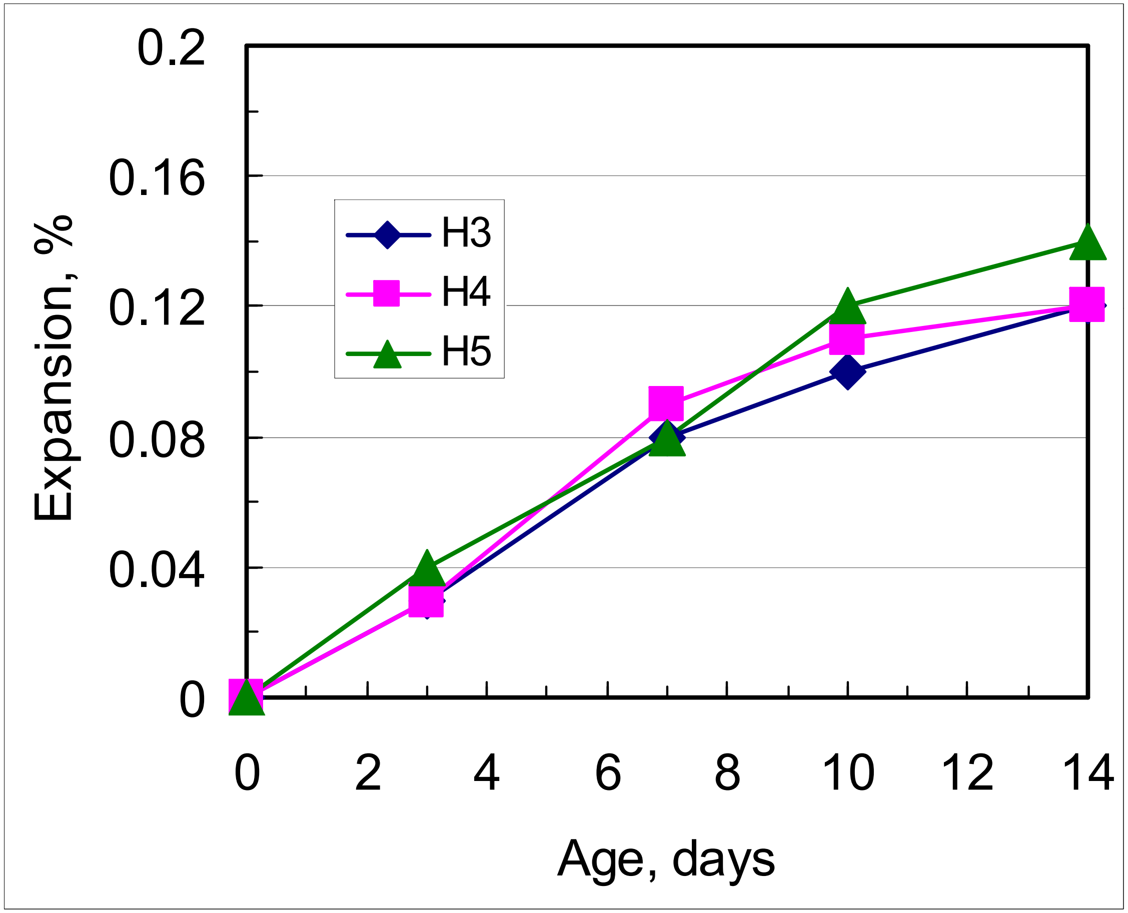


# Accelerated Mortar Bar Test 2 – ASTM C1567

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



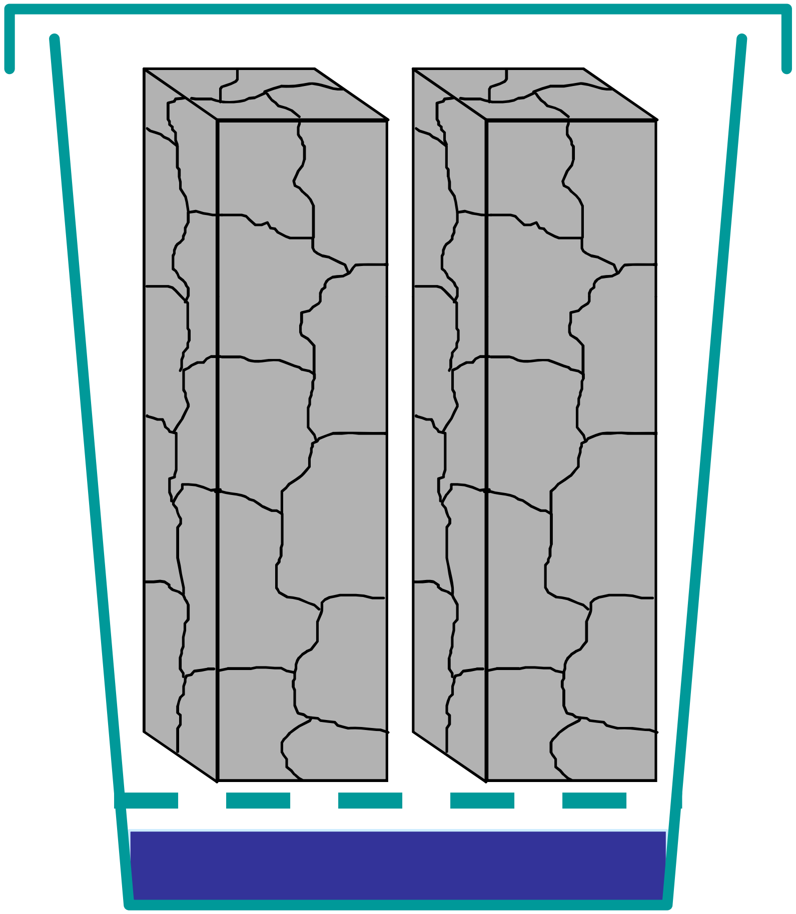
# AMBT



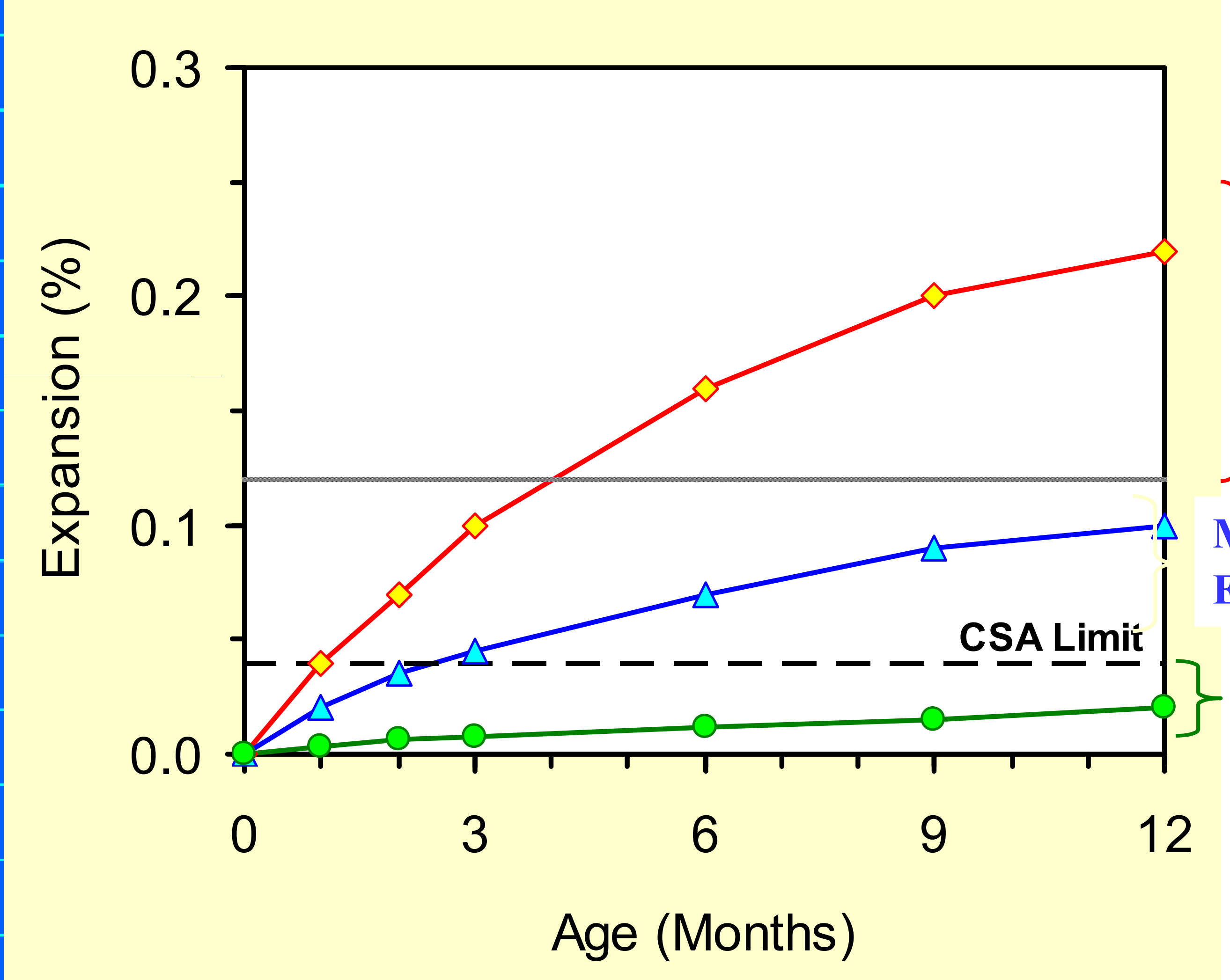
# Concrete Prism Test

## CSA A23.2-14A ASTM C1293

- 420 kg/m$^3$ cementitious material
- NaOH added to yield 1.25% $Na_2O_{eq}$ 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

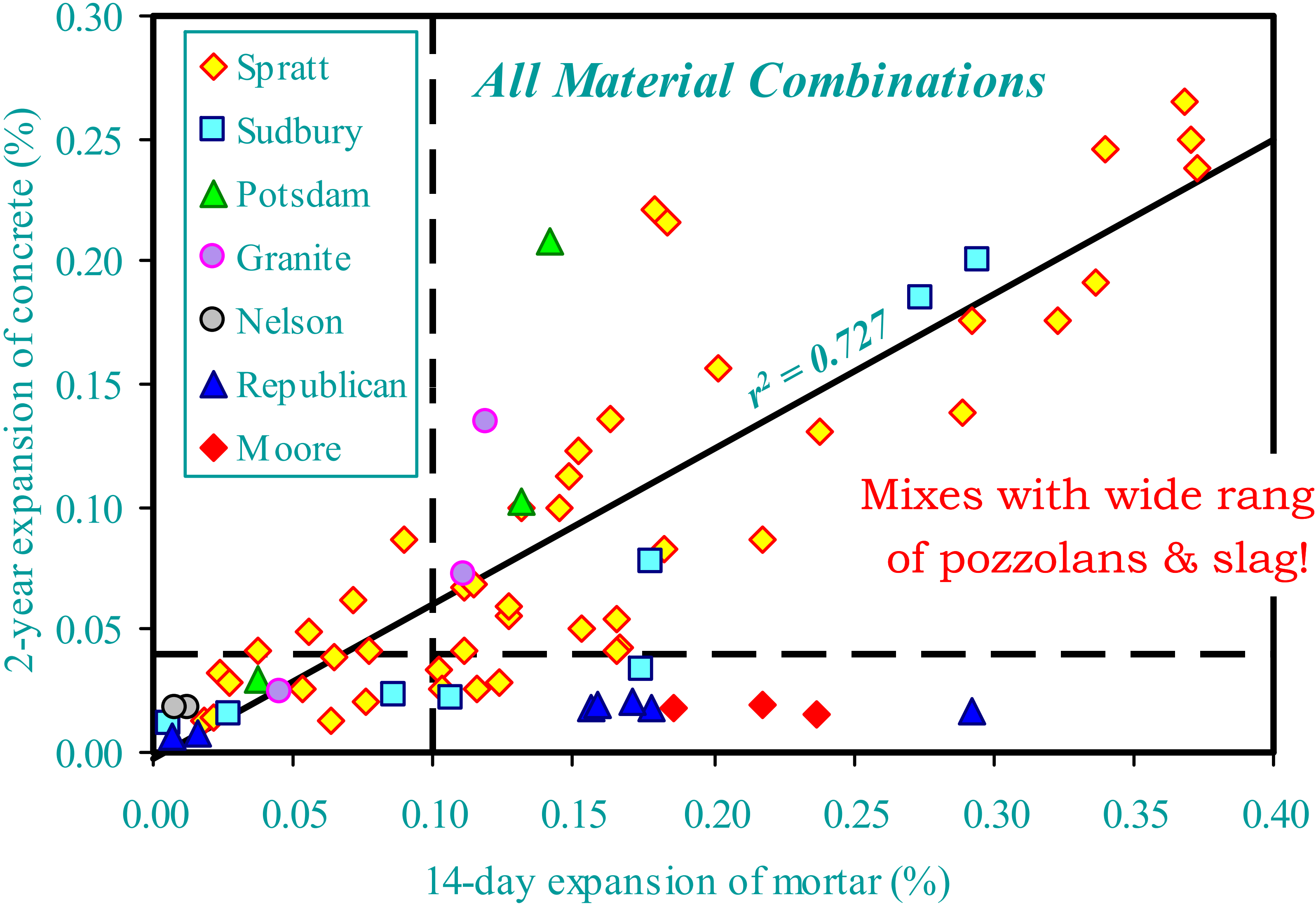


**Highly-reactive**
**Expansion > 0.12%**

**Marginally-reactive**
**Expansion = 0.04 to 0.12%**

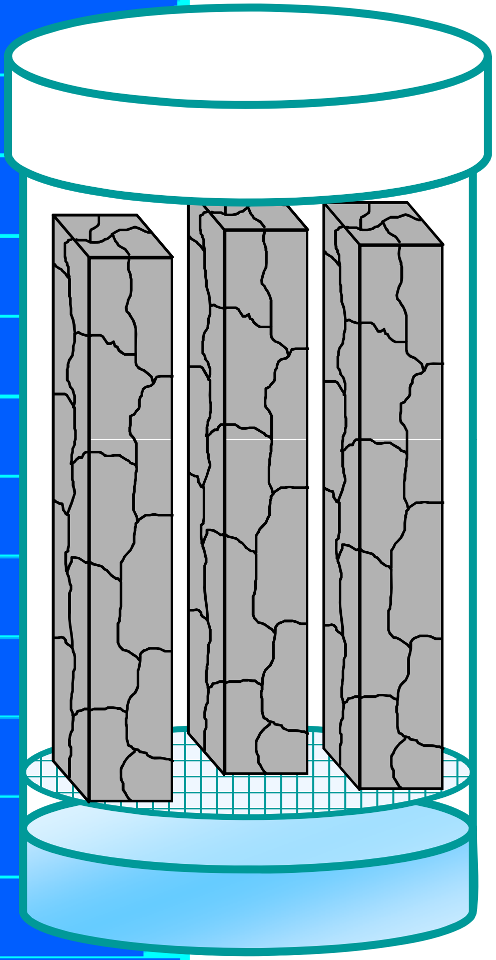
**Non-reactive**
**Expansion < 0.04%**

# Accelerated Mortar Bar vs. Concrete Prism Test



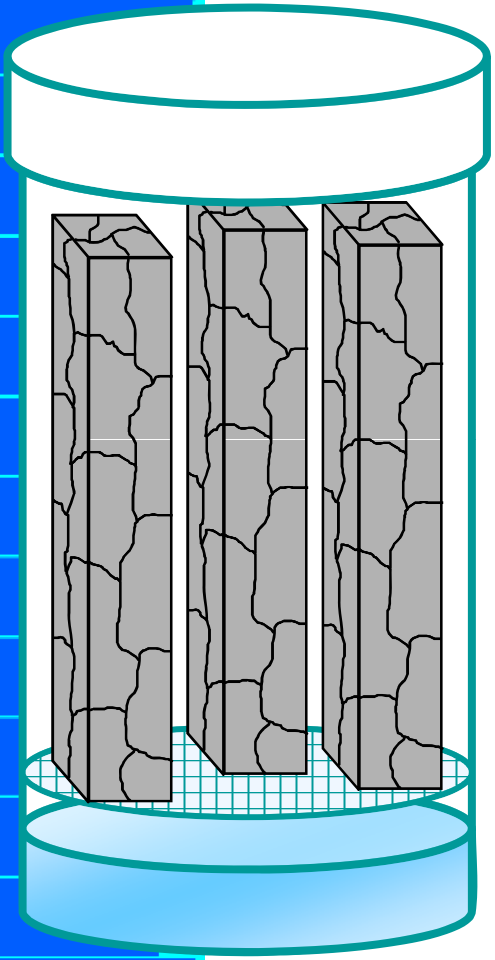
Mixes with wide range of pozzolans & slag!

# ASTM C441  Pyrex Mortar Bar Test



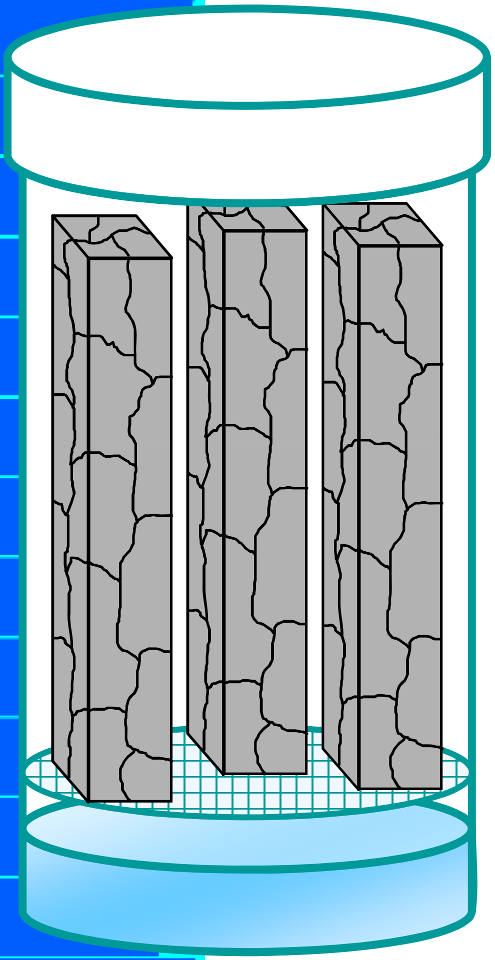
- Developed to test ability of SCMs to mitigate expansion
- Mortar bars made with Pyrex glass as model aggregate
- ASR-suppression characterized by reduction in expansion compared to low-alkali control

# 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 ≤ Control with low-alkali cement

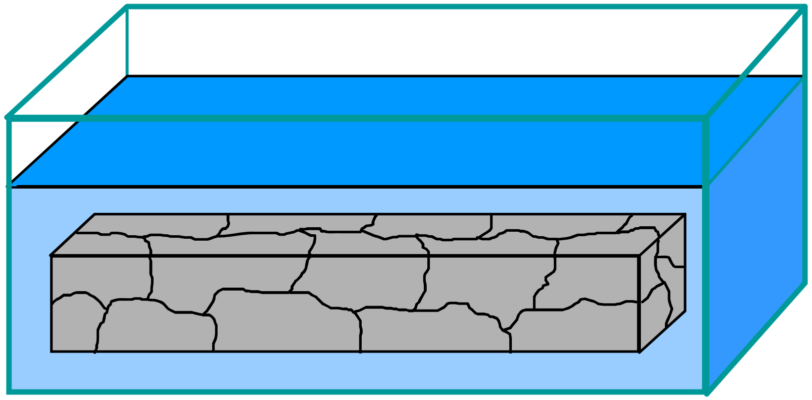
**C989 Slag**
- Job mixture ≤ 0.02% at 14 days
- Exp. @ 14 days ≤ 25% of control with high-alkali cement *(0.95 to 1.0 % $Na_2O_{eq}$)*

**C1240 Silica Fume**
- Exp. @ 14 days ≤ 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 ≤ 0.02%
- Exp. @ 56 days ≤ 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



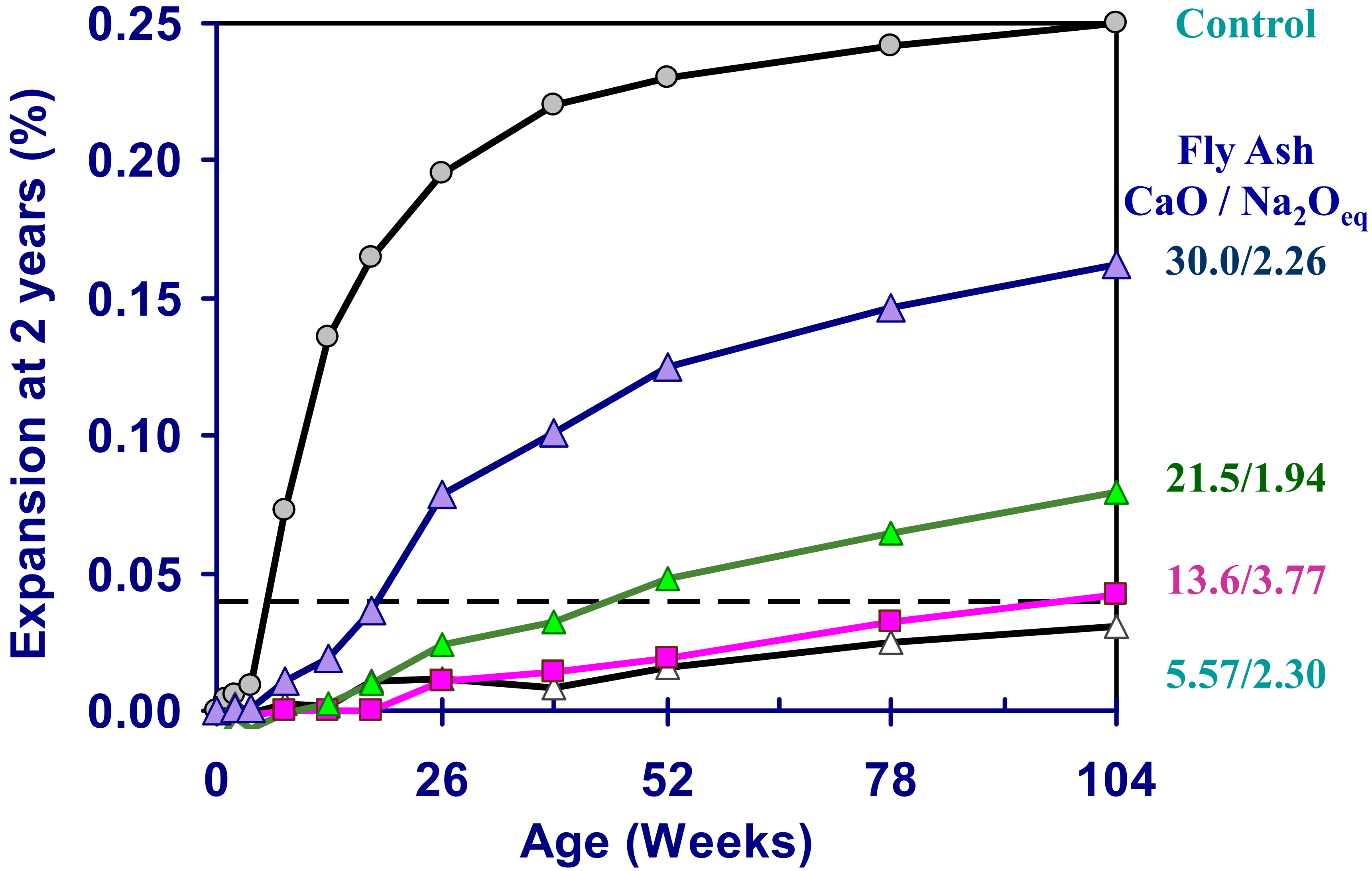
# SUMMARY: Test Methods

- 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)

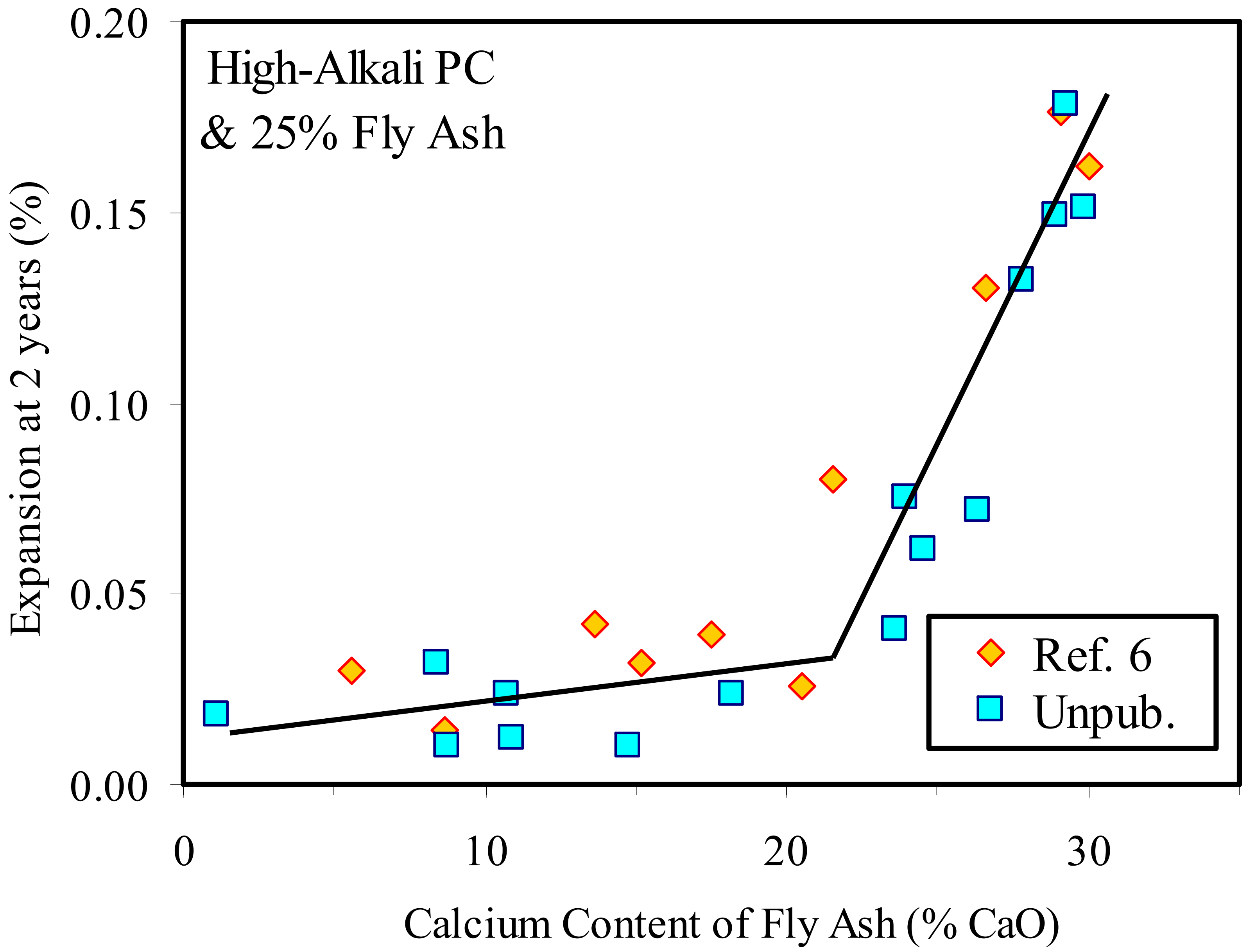
# ASR MITIGATION

# Effect of Fly Ash on ASR Expansion

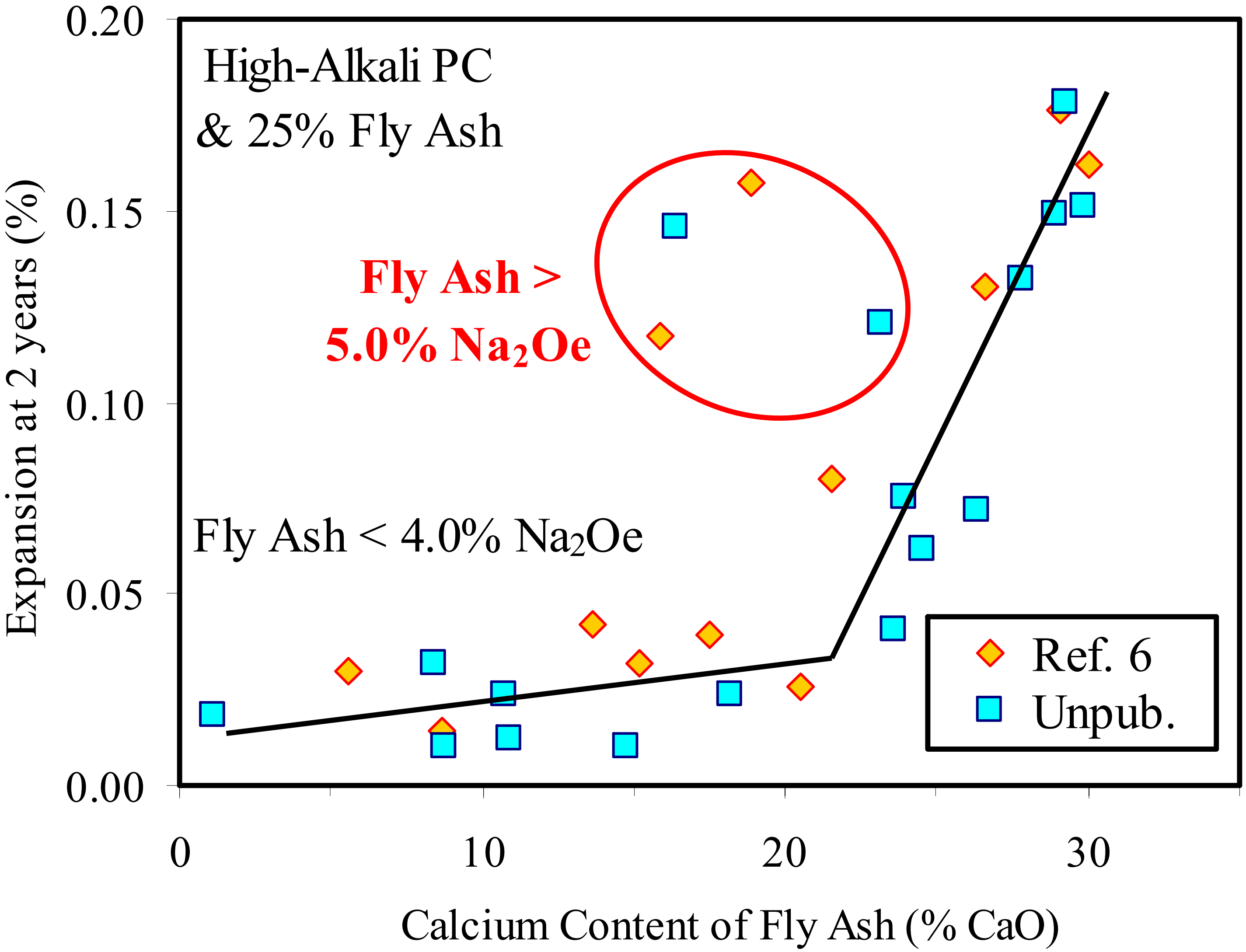
## *Concrete Prisms with 25% Fly Ash & Spratt Aggregate*



# Effect of Calcium Content of Fly Ash



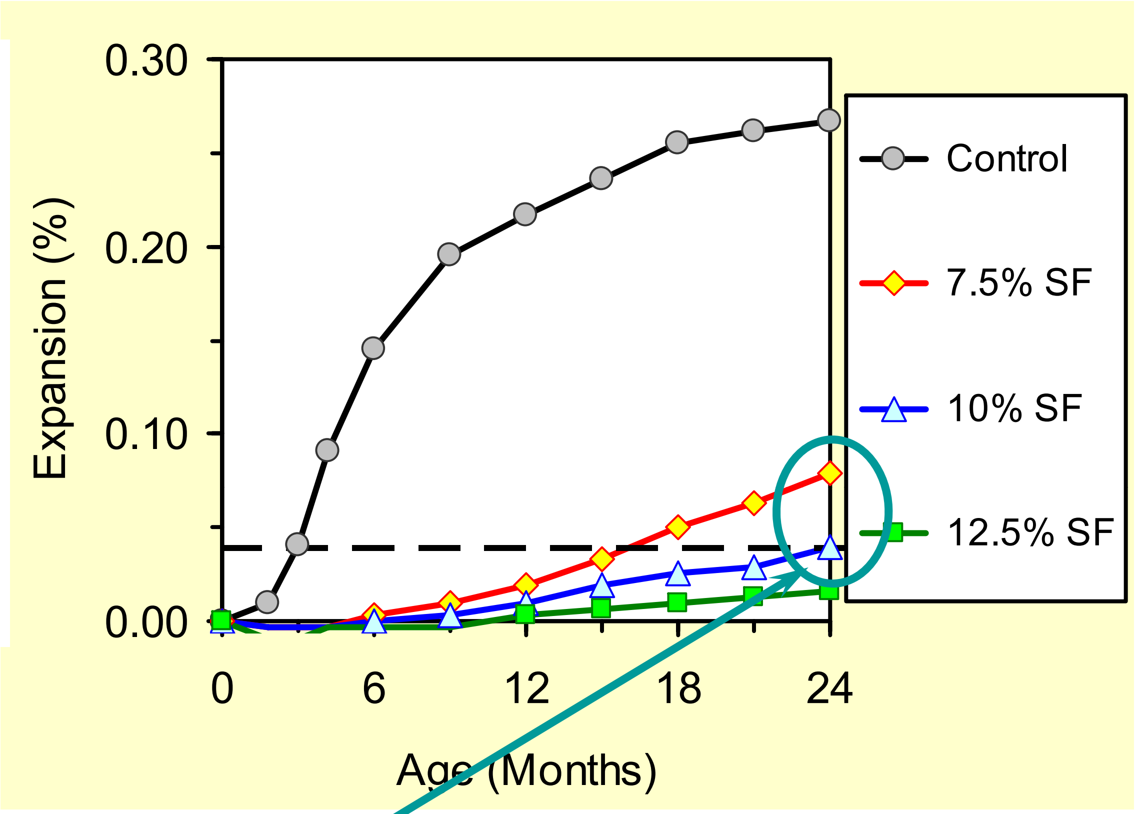
# Effect of Calcium & Alkali Content of Fly Ash



# Effect of Silica Fume

**Laboratory Test Results**

- ASTM C1293 / CSA A23.2-14A
- Cement = 1.25% $Na_2Oeq$
- Siliceous limestone aggregate
- Concrete at 38°C over water
- Test for 2 years



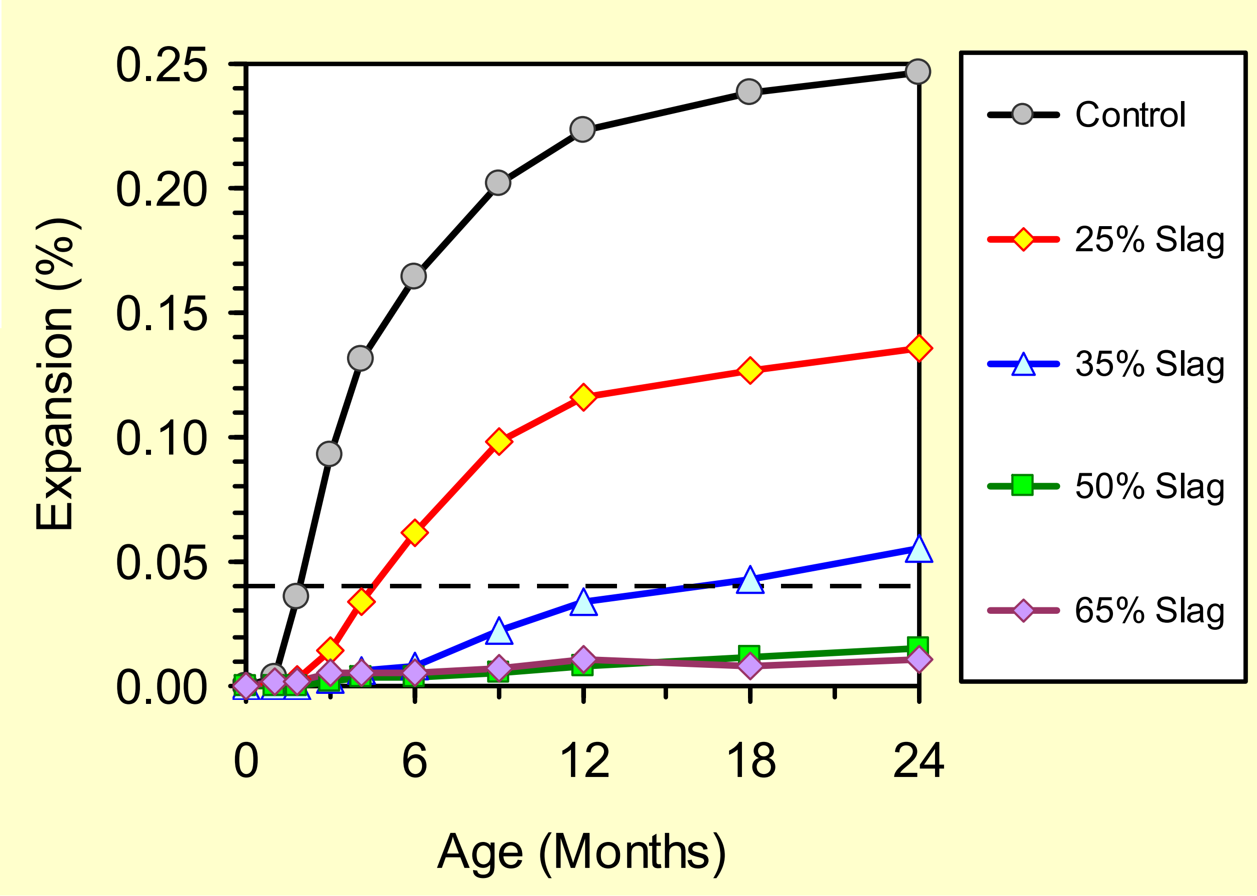
Amount required to meet CSA limit at 2 years maybe > 10% silica fume

*Fournier et al. 1995*

# Effect of Slag

ASTM C1293

- Siliceous limestone
- 1.25% $Na_2O_{eq}$
- 38°C and 100% RH



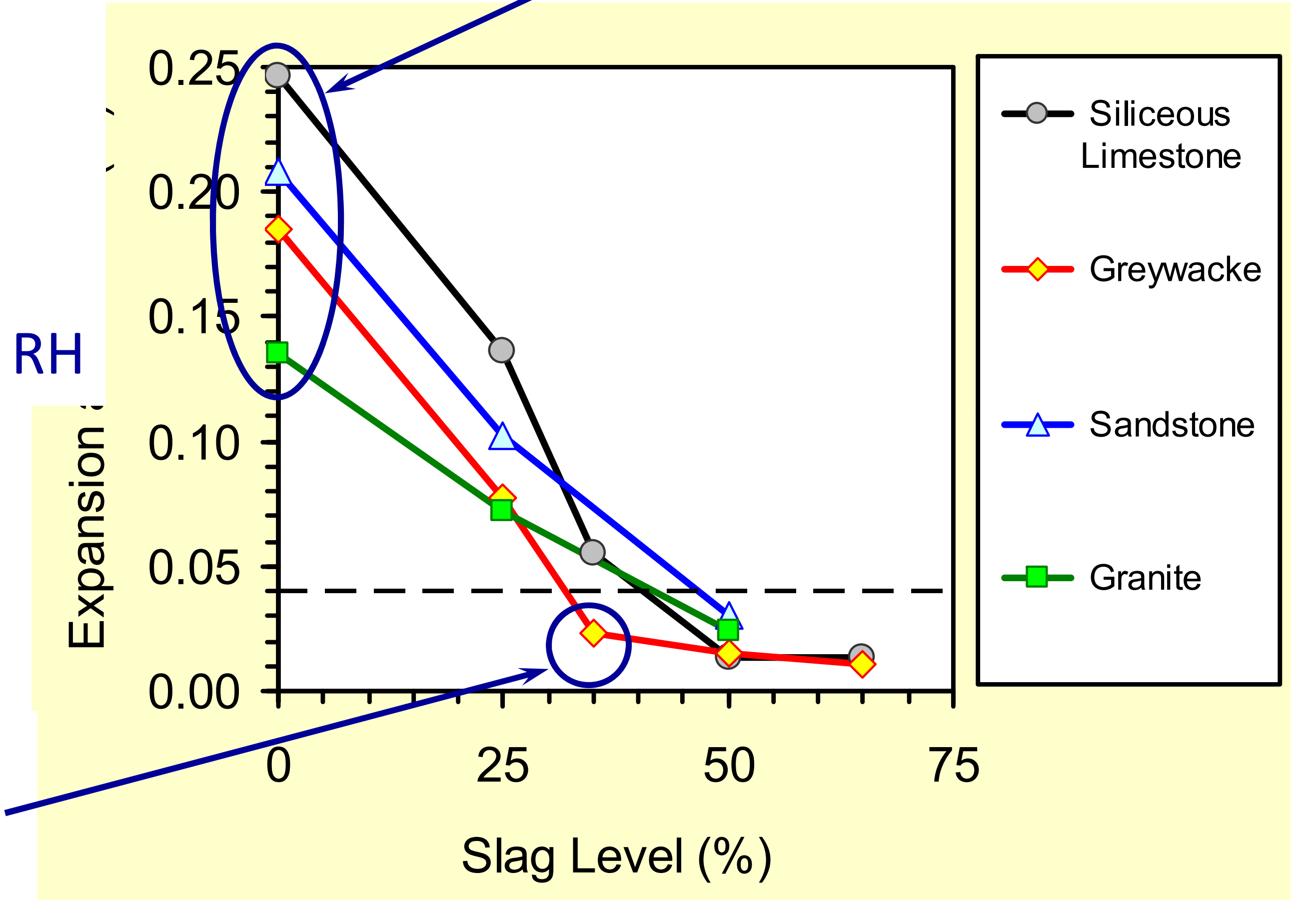
*Thomas and Innis, 1998*

# Effect of Slag

ASTM C 1293

- 4 aggregates
- 1.25% $Na_2O_{eq}$
- 38°C and 100% RH

Concrete without slag



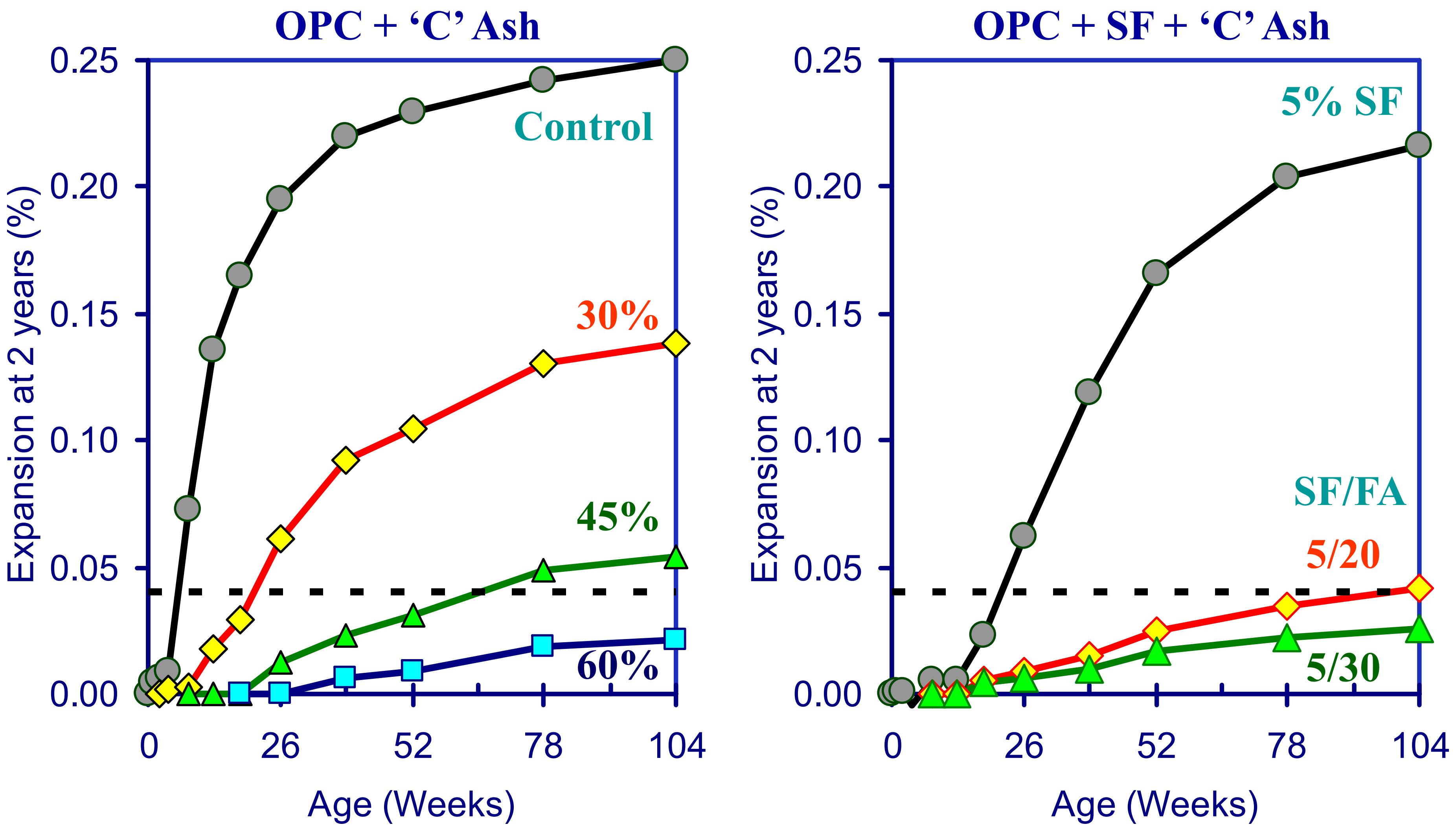
Moderately-reactive aggregate with 35% slag

***Thomas and Innis, 1998***

# Effect of Silica Fume & Fly Ash

## *Concrete Prisms with 'C' Fly Ash*

(27.7% CaO, 1.65% $Na_2O_{eq}$)

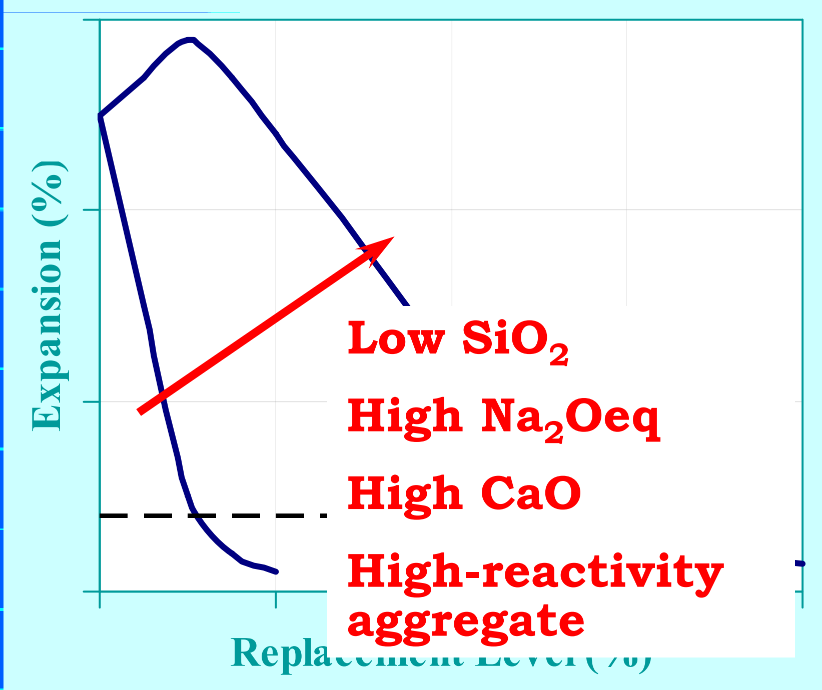


# SUMMARY: Effect of SCMs

- Fly Ash
- Slag
- Silica Fume
- Natural Pozzolans

Almost all sources of these materials are effective in controlling ASR

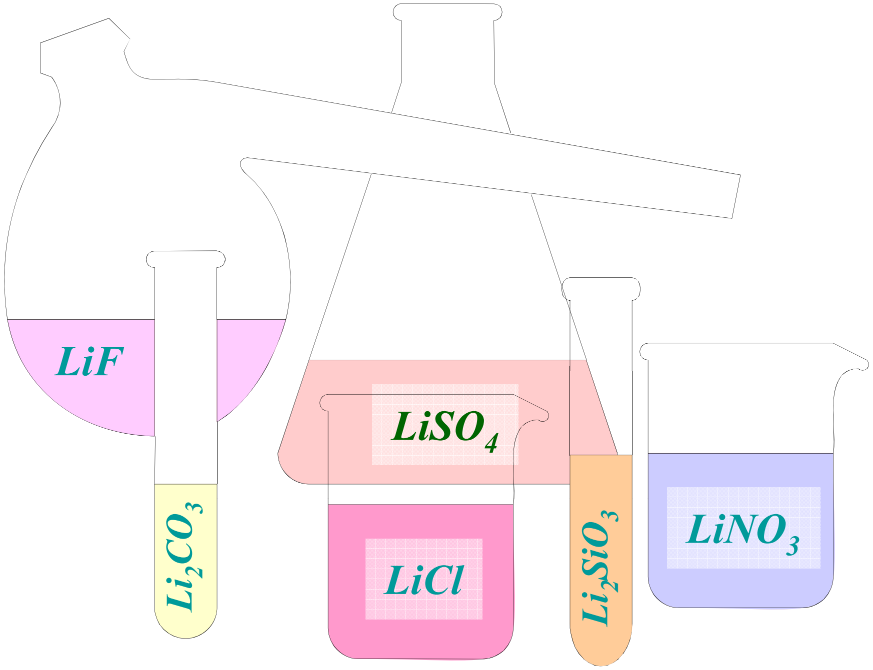
Providing they are used in sufficient quantity



**Amount of preventive required depends on:**

- Composition of material (esp. $Na_2Oeq$, $SiO_2$, CaO)
- Available alkali in the system
- Nature of the reactive aggregate

# Using Chemical Admixtures



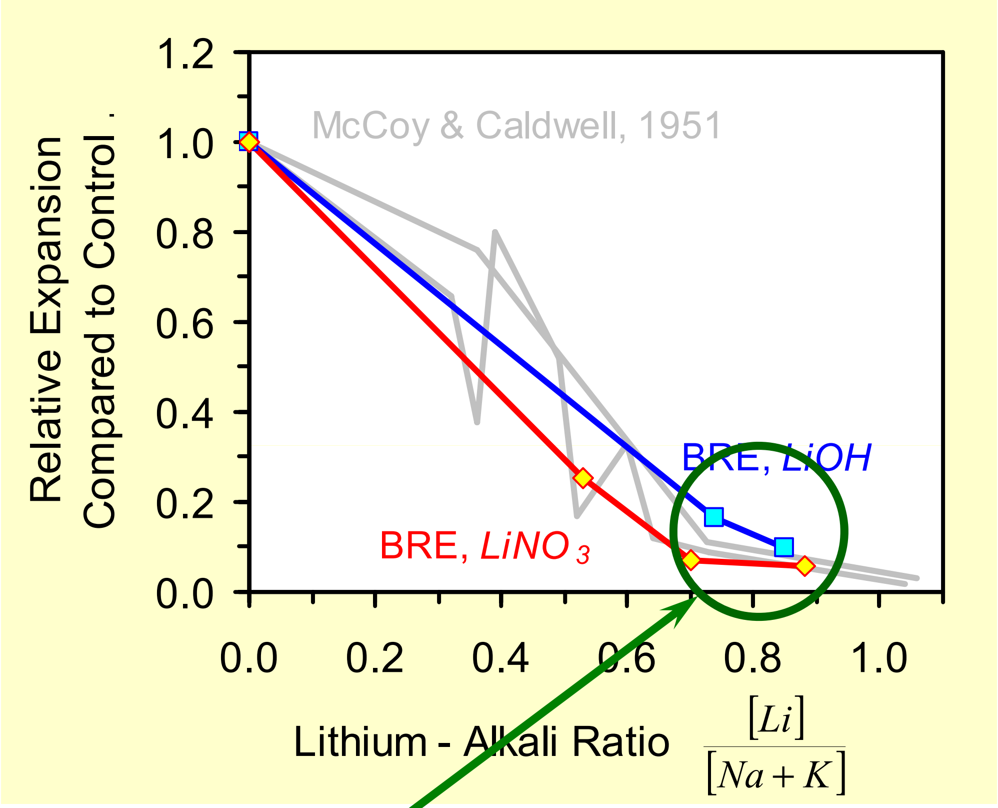
***__McCoy & Caldwell, 1951__***

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

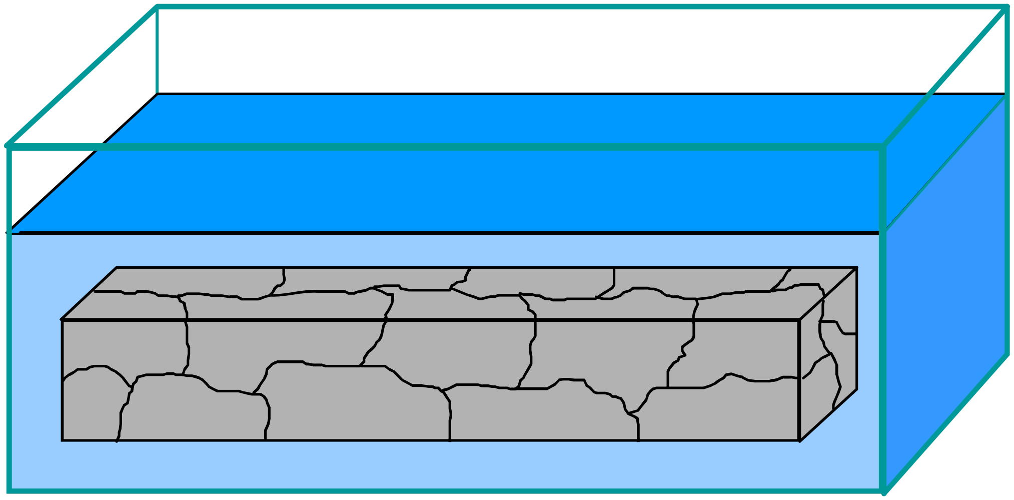
*Thomas et al. 2000*

# Modified C1260/C1567 for Lithium

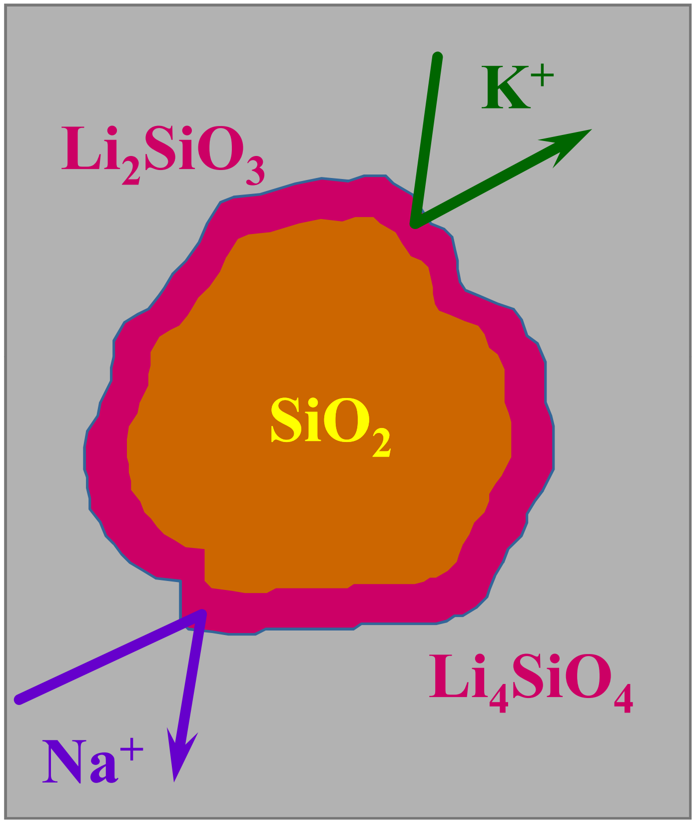
## PRELIMINARY

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

Na + K (M/L) = 0.7 x $Na_2Oeq$ (% 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*

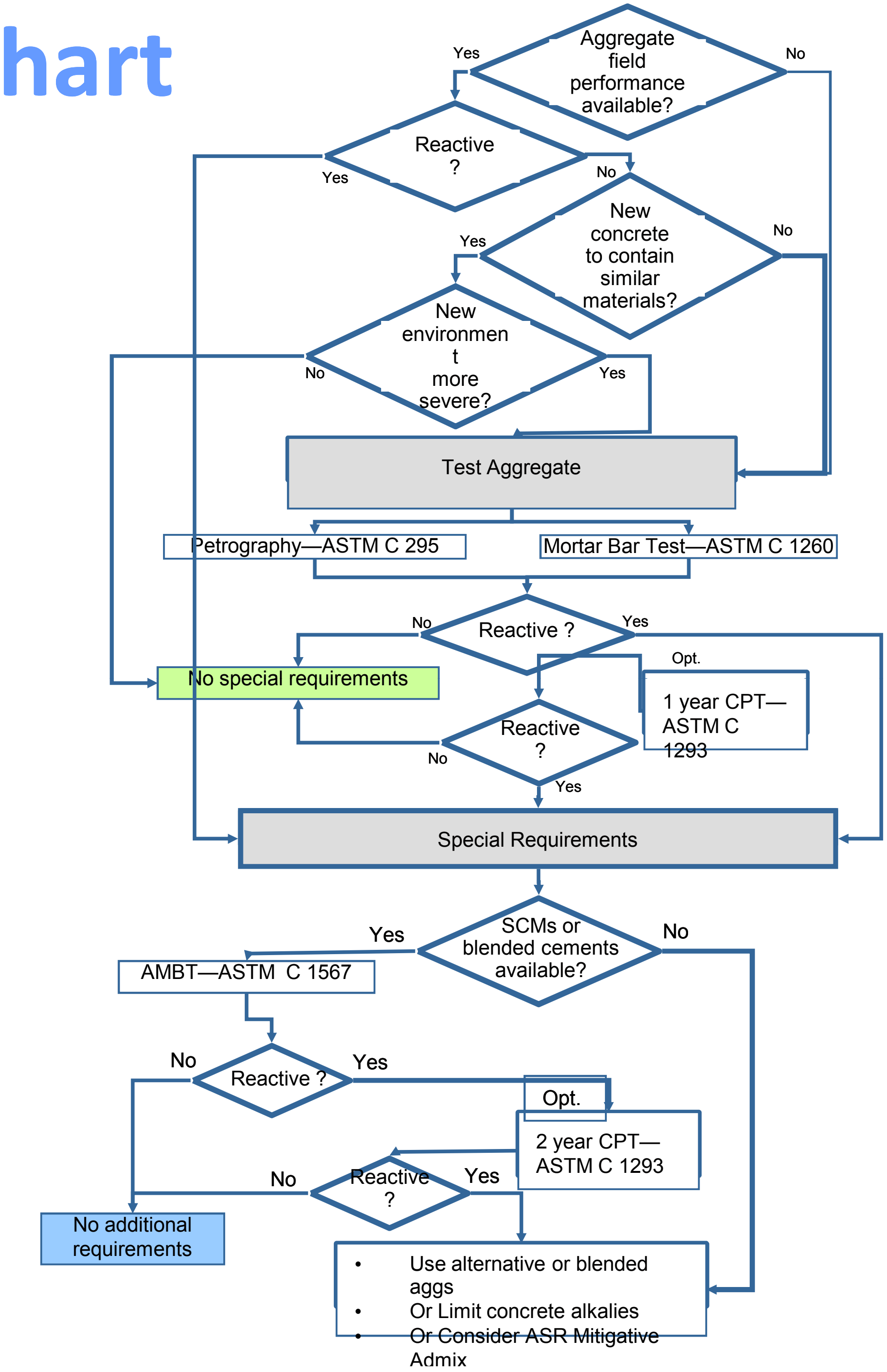
*Endorsed by*
*American Concrete Pavement Association,*
*National Ready Mixed Concrete Association*

**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 alkalies 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/gspec.stm.



Aggregate field performance available?

Yes

No

Reactive ?

Yes

No

New concrete to contain similar materials?

Yes

No

New environmen t more severe?

No

Yes

Test Aggregate

Petrography—ASTM C 295

Mortar Bar Test—ASTM C 1260

Reactive ?

No

Yes

No special requirements

Opt.

1 year CPT—ASTM C 1293

Reactive ?

No

Yes

Special Requirements

SCMs or blended cements available?

Yes

No

AMBT—ASTM C 1567

Reactive ?

No

Yes

Opt.

2 year CPT—ASTM C 1293

Reactive ?

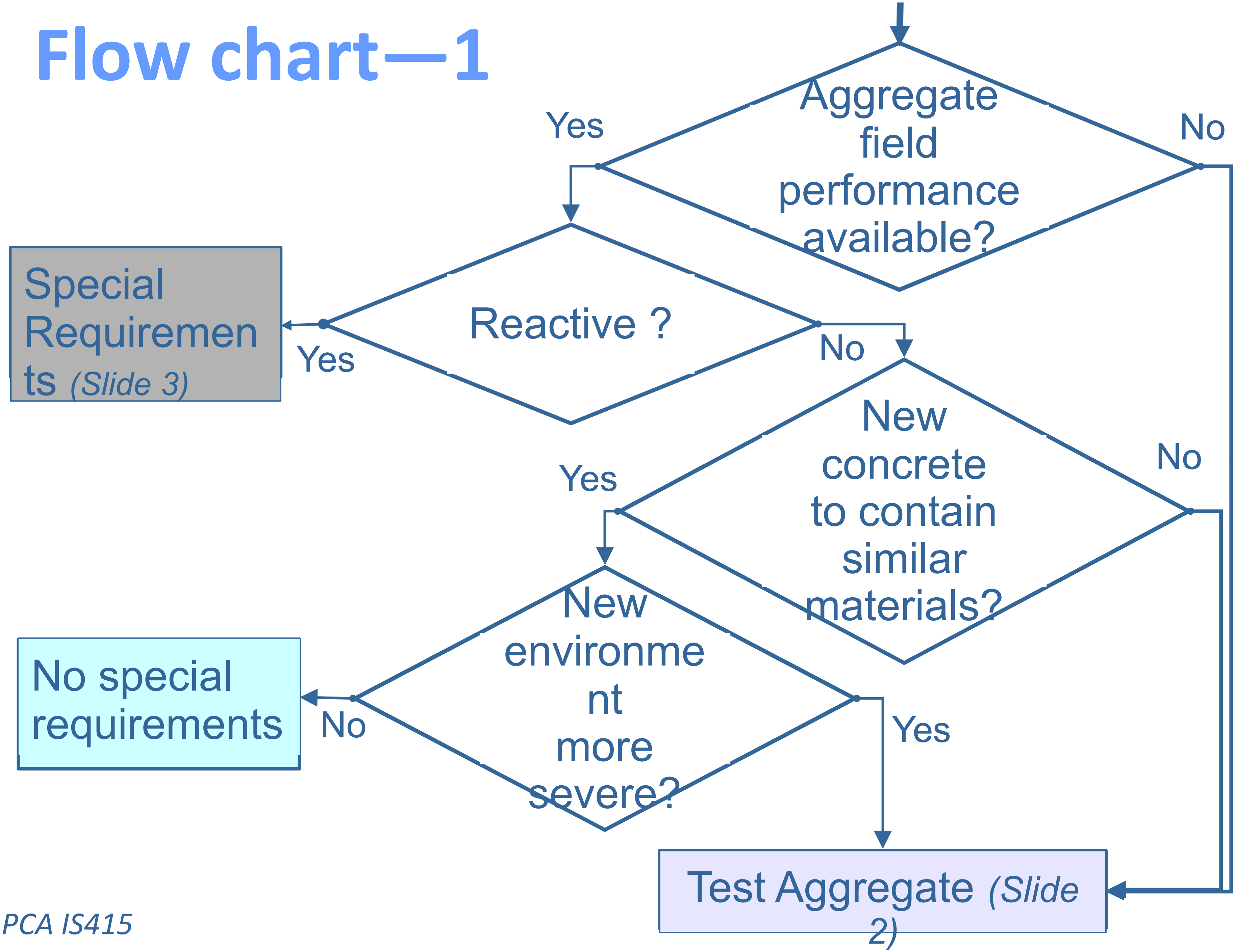
No

Yes

No additional requirements

- Use alternative or blended aggs
- Or Limit concrete alkalies
- Or Consider ASR Mitigative Admix

# Flow chart—1



Aggregate field performance available?

Yes

No

Reactive ?

Yes

No

Special Requirements *(Slide 3)*

New concrete to contain similar materials?

Yes

No

New environment more severe?

No

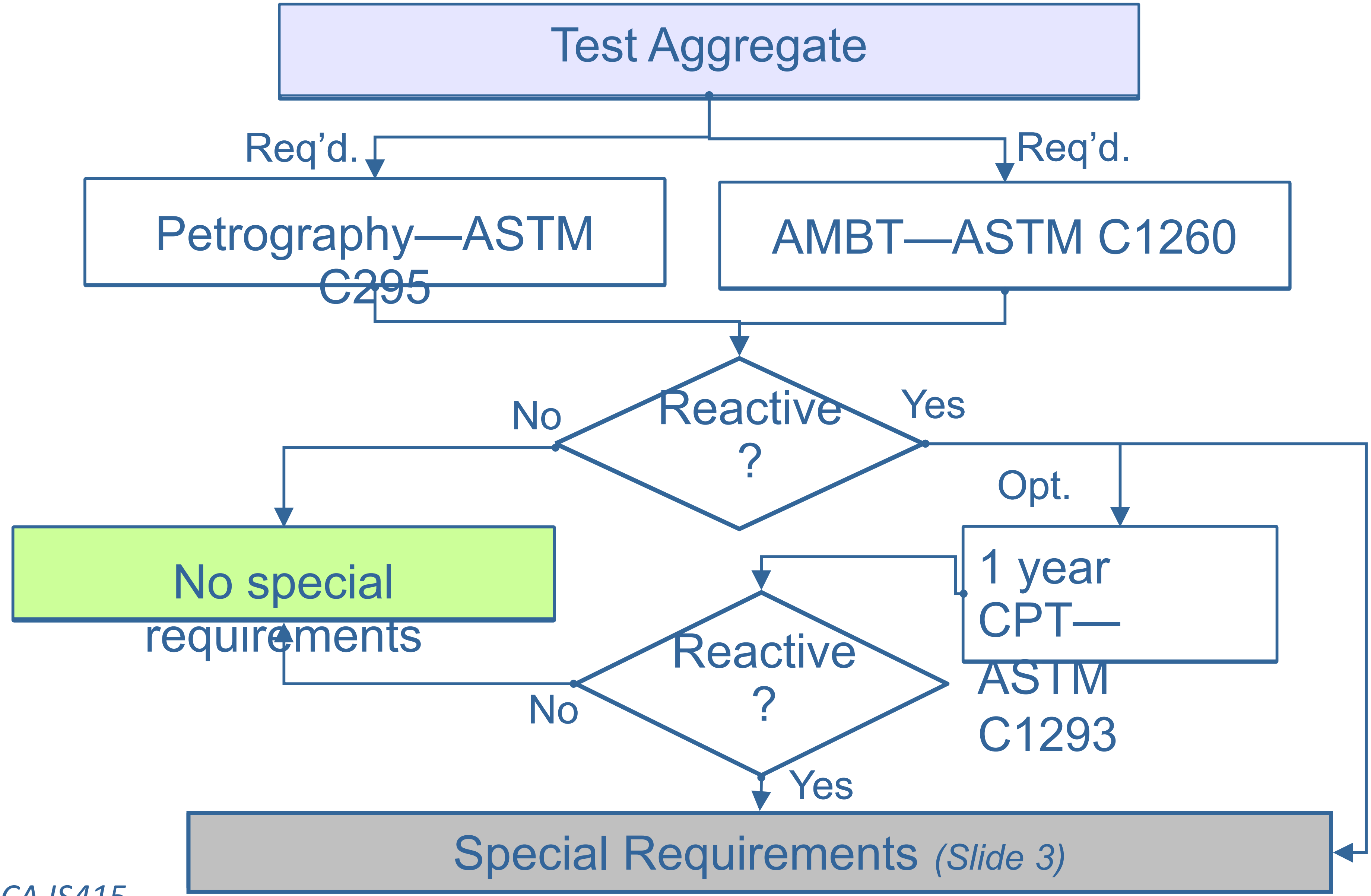
Yes

No special requirements

Test Aggregate *(Slide 2)*

*PCA IS415*

# Flow chart—2



Test Aggregate

Req’d.

Req’d.

Petrography—ASTM C295

AMBT—ASTM C1260

Reactive ?

No

Yes

Opt.

No special requirements

1 year CPT—ASTM C1293

Reactive ?

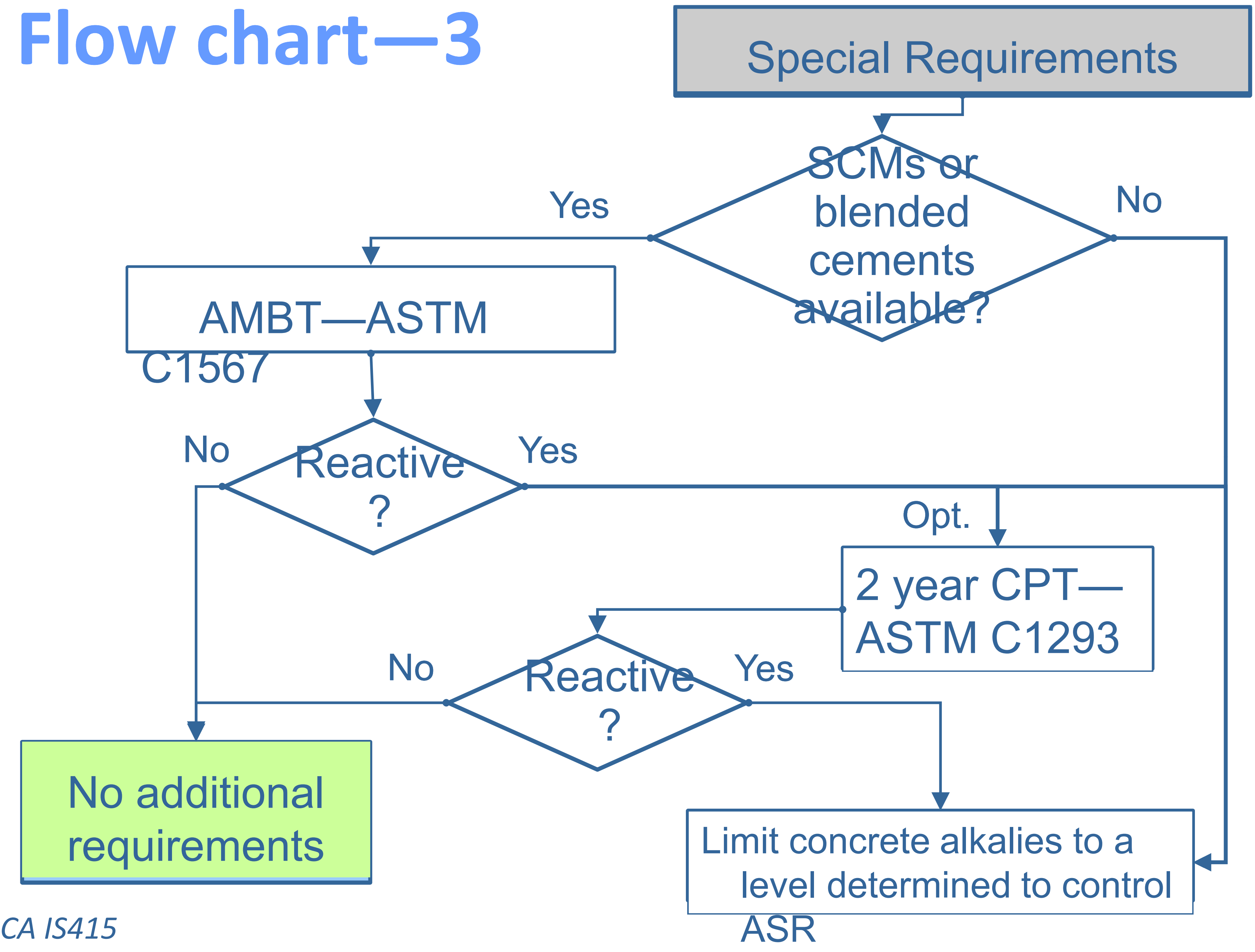
No

Yes

Special Requirements *(Slide 3)*

*PCA IS415*

# Flow chart—3



Special Requirements

SCMs or blended cements available?

Yes

No

AMBT—ASTM C1567

Reactive ?

No

Yes

Opt.

2 year CPT—ASTM C1293

Reactive ?

No

Yes

No additional requirements

Limit concrete alkalies to a level determined to control ASR

*PCA IS415*

# 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

?