# Sulfate Attack: Are We Missing the Mechanism Causing Most Concrete Damage?

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# Many Types of Sulfate Attack

# Types of External Sulfate Attack

- **Ettringite:** related to $C_3A$ in cement, from AFm forming AFt→ expansion & cracking.
- **Thaumasite:** Less common, low-temperature attack, attacks cement matrix.
- **Physical:** Wick action concentrates $Na_2SO_4$ + $Na_2SO_4.10H_20$ in pores as water evaporates (in arid zones) → progressive cracking and spalling of concrete surfaces due to cyclic phase changes.

# Sulfate Soils in Western USA

Reportedly, sulfate concentrations can exceed 30,000 ppm.

And the west is mostly arid, which concentrated salts

Ref: USBR soils map, where alkalinity = alkali sulfates

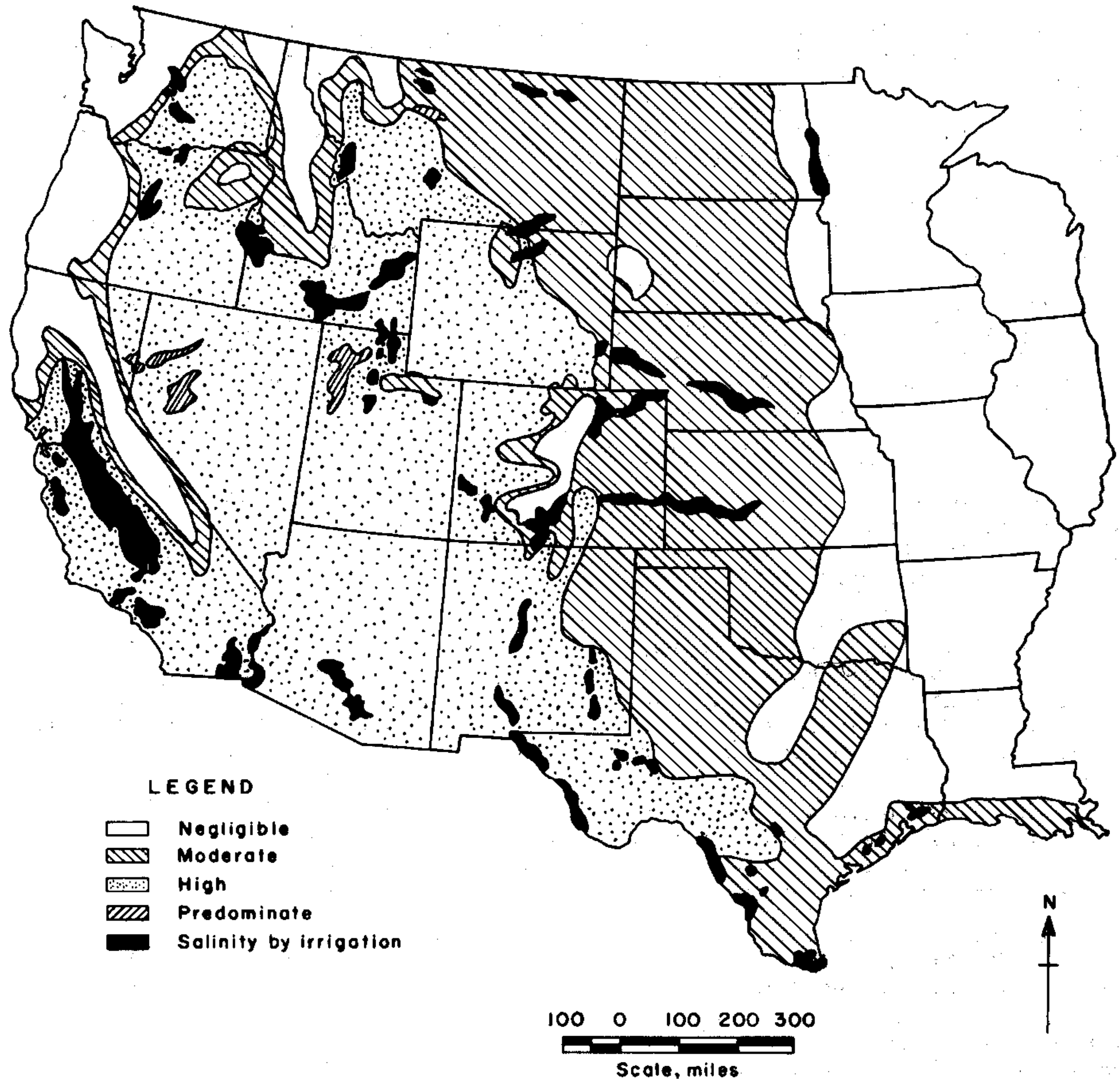
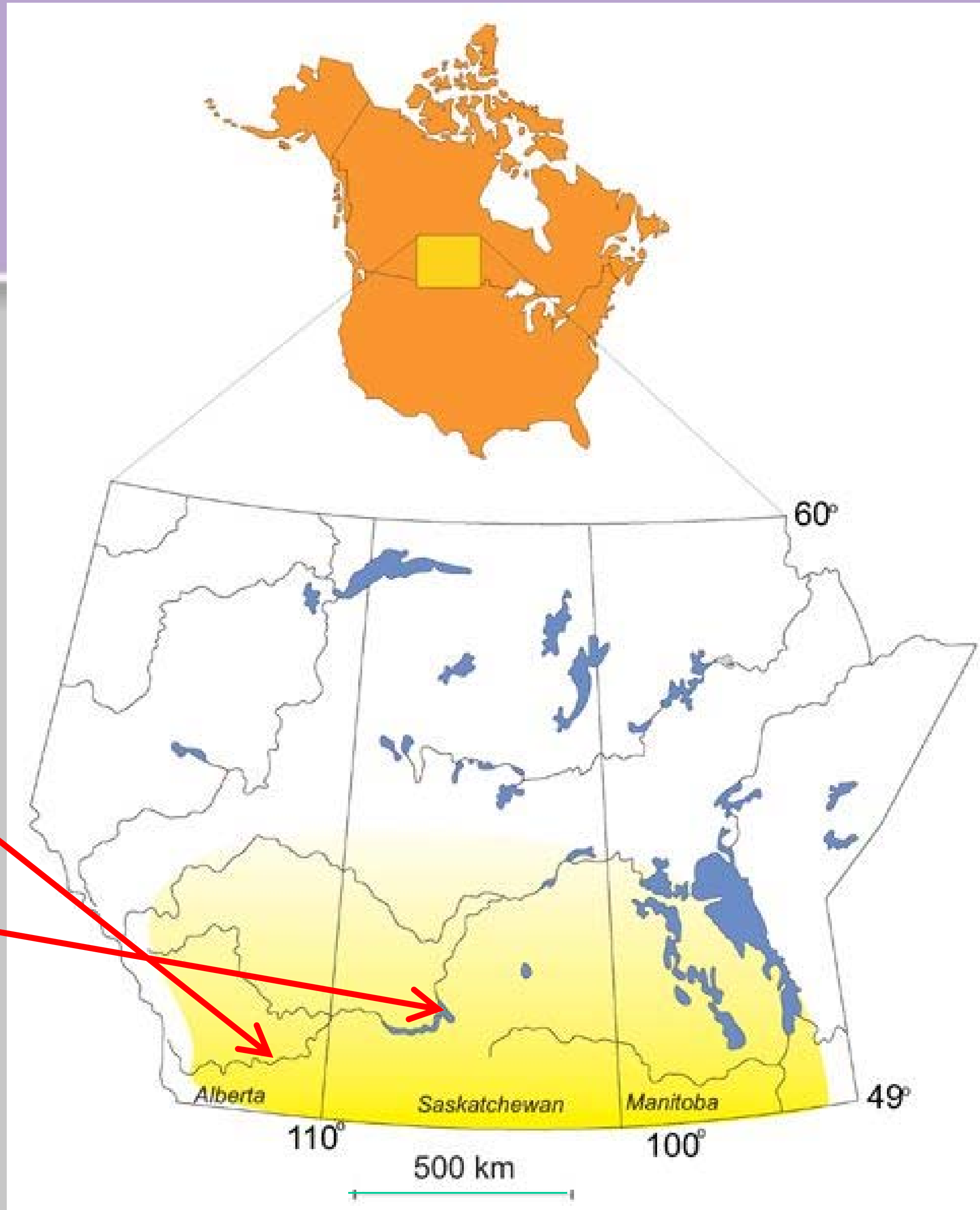



FIGURE 2. - Map of Alkali and High Salinity Soils in Western United States (2).

# Sulfate soils in Western Canada




Up to 14,600 ppm $SO_4$ found in Alberta soils

11,000 ppm at Gardiner Dam

Map: W. M. Last and F. M. Ginn, U. Manitoba

# Define The Exposure Conditions

## (ACI & CSA Classifications)

| Severity of Potential Exposure<br>ACI 318 CSA A23.1 | Water-Soluble Sulfate ($SO_4$) in Soil, % mass | Sulfate ($SO_4$) in water, ppm |
|---|---|---|
| S0 negligible | $SO_4 < 0.10$ | $SO_4 < 150$ |
| S1 S3 | $0.10 \leq SO_4 \leq 0.20$ | $150 \leq SO_4 \leq 1500$<br>and Seawater |
| S2 S2 | $0.20 \leq SO_4 \leq 2.00$ | $1500 \leq SO_4 \leq 10000$ |
| S3 S1 | $SO_4 > 2.0$ | $SO_4 > 10000$ |

But sulfates can become concentrated by evaporation, etc.

EN206 exposures also include pH and cation exposures

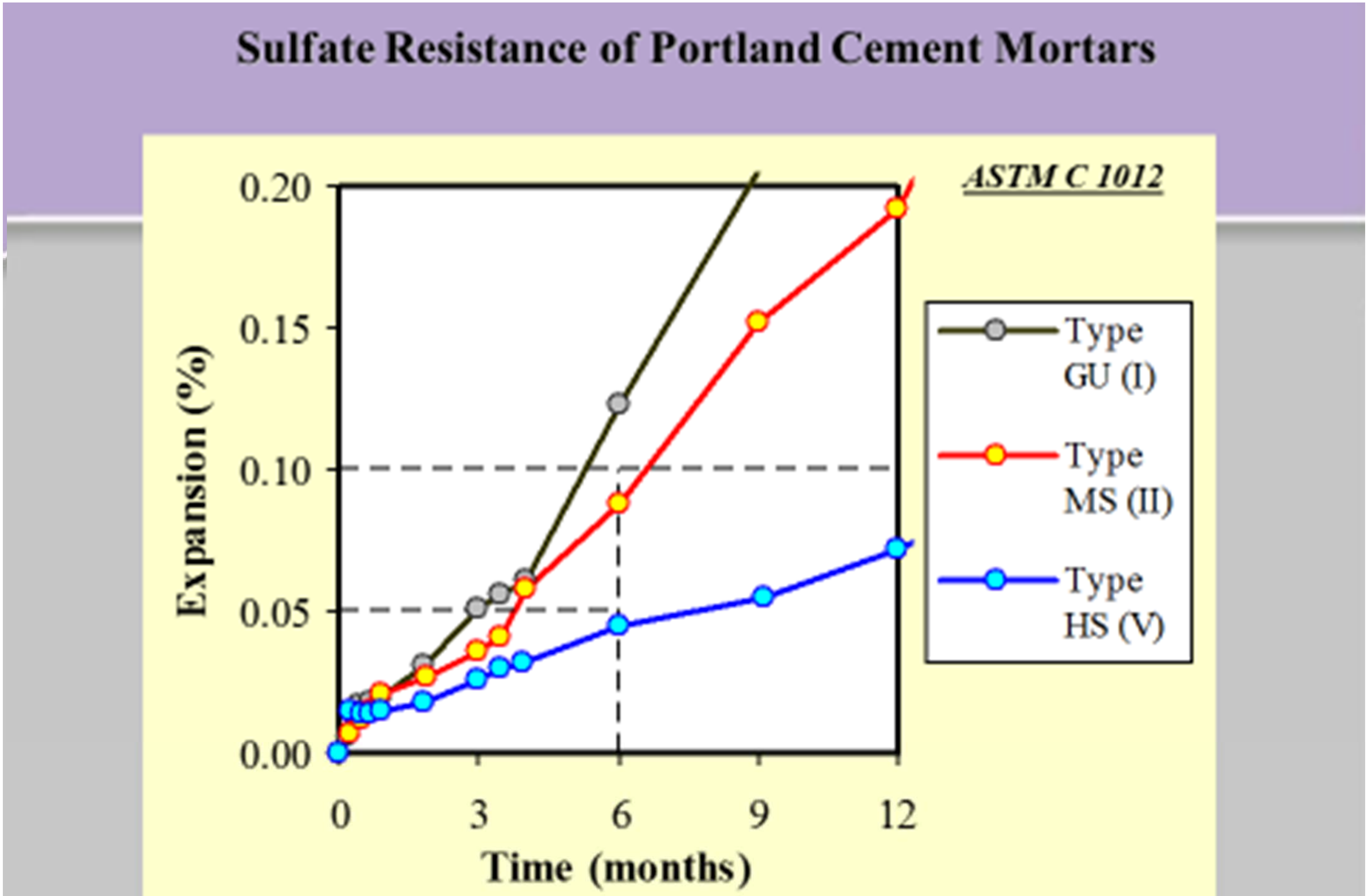
# $C_3A$ & Sulfate Resistant Cements

- In 1919, Thorbergur Thorvaldson, at the University of Saskatchewan, in Canada initiated studies and in 1927 reported that $C_3A$ was responsible for the deterioration of cements exposed to sulfate solutions, and later that high-iron cements were more resistant since they suppressed $C_3A$ (In 1928, Hansen, Brownmiller, and Bogue identified the iron phase as $C_4AF$).

- The Canada Cement Co., that had funded the research, then patented the first Type V sulfate resistant cement, Kalicrete, in 1933.

# Effect of $C_3A$: The mechanism given in textbooks

- Typically the role of cement $C_3A$ content is discussed along with expansion due to formation of ettringite at later ages.
- Hence, in severe exposures Type V sulfate resistant cement or use of SCMs are required along with control of w/cm (0.45 in ACI 318) (0.40 in CSA A23.1).
- But how typical is this mechanism of the damage that occurs in the field?




ASTM C1012 is used to evaluate sulfate resistance of SCMs and blended cements in ACI 318

# Effect of $C_3A$: 38 years immersed in 50,000ppm $Na_2SO_4$, 0.50 portland mixes

TI
12.3%
$C_3A$

Type GU,
W/C=0.50

TII
7.1 %
$C_3A$
Type MS,
W/C=0.50

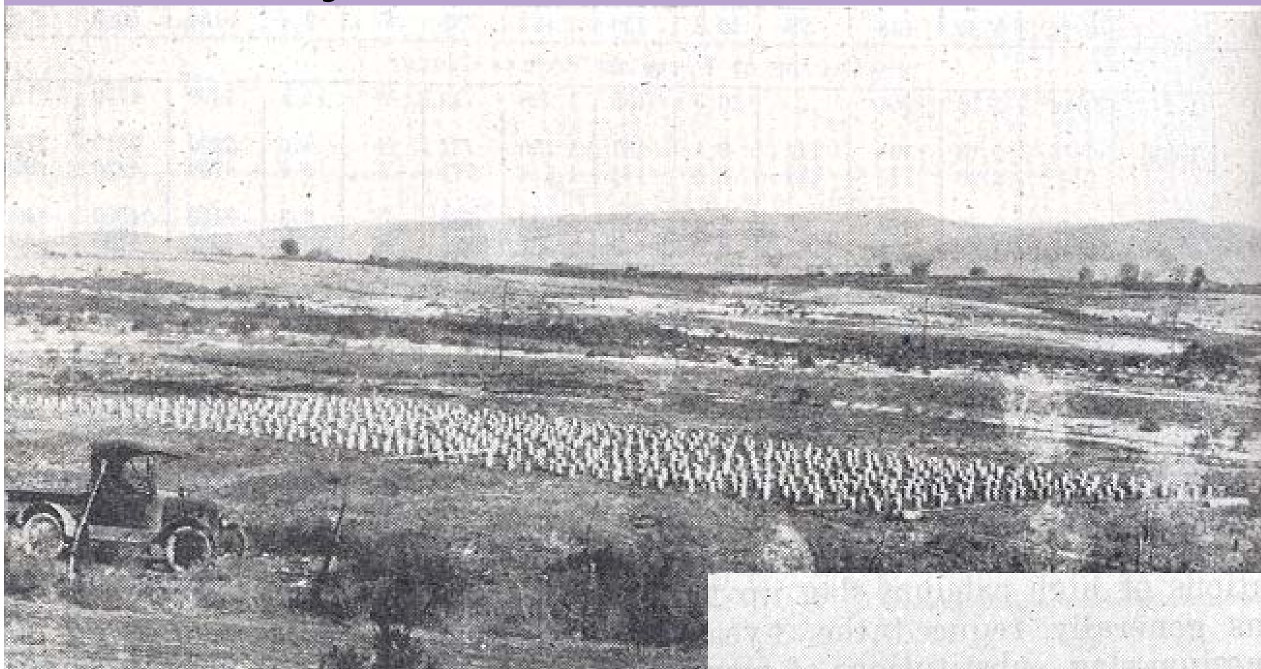
TV
Type HS,
W/C=0.50

Alapour & Hooton 2017,
ACI Mat. J.

# Effect of w/cm

- i.e. limit w/cm to keep sulfates out

# PCA Field Studies on Sulfate Attack by R. Wilson & A. Cleve, 1921-1928

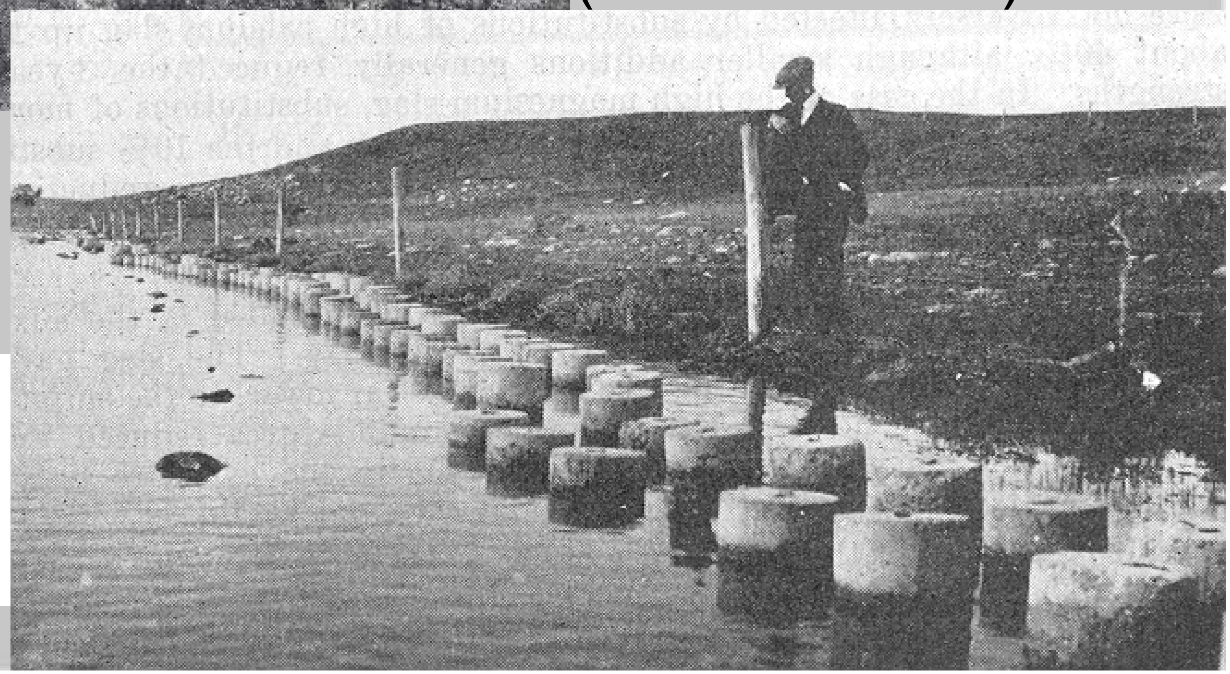


Montrose, Colorado

2000 cylinders,

10 in. x 24in. Semi-immersed

(250 x 500 mm)



Medicine Lake, South Dakota

After 7 years, concretes with w/c >0.36 were damaged

# PCA Studies on Sulfate Attack Related to W/C by R. Wilson & A. Cleve, 1921-1928

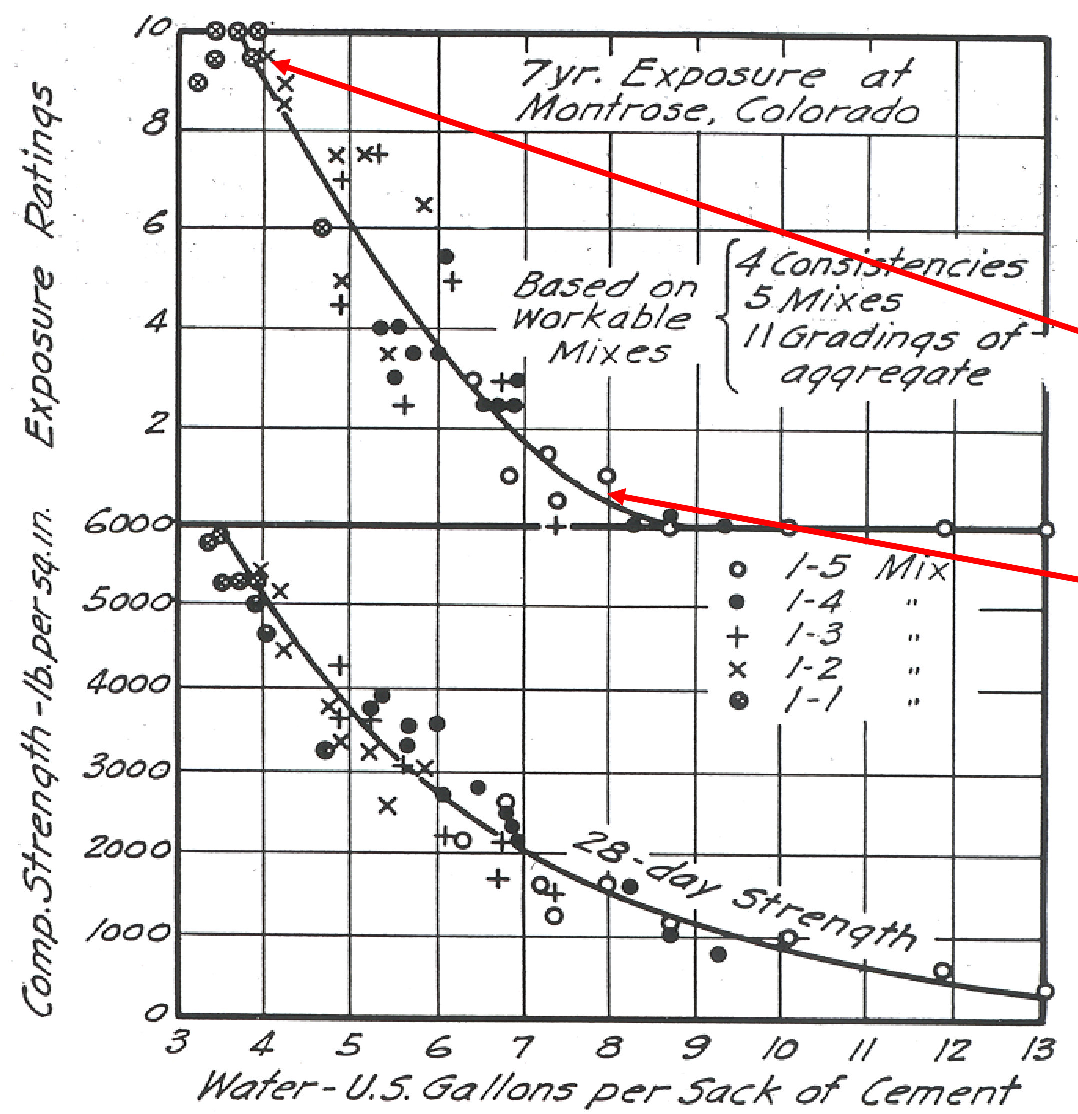



Fig. 3—Water-Cement Ratio Strength and Rating Curves.

Montrose, Colorado

After 7 Years Exposure

4 gal./sack = 0.36 W/C

6 gal./sack = 0.55 W/C

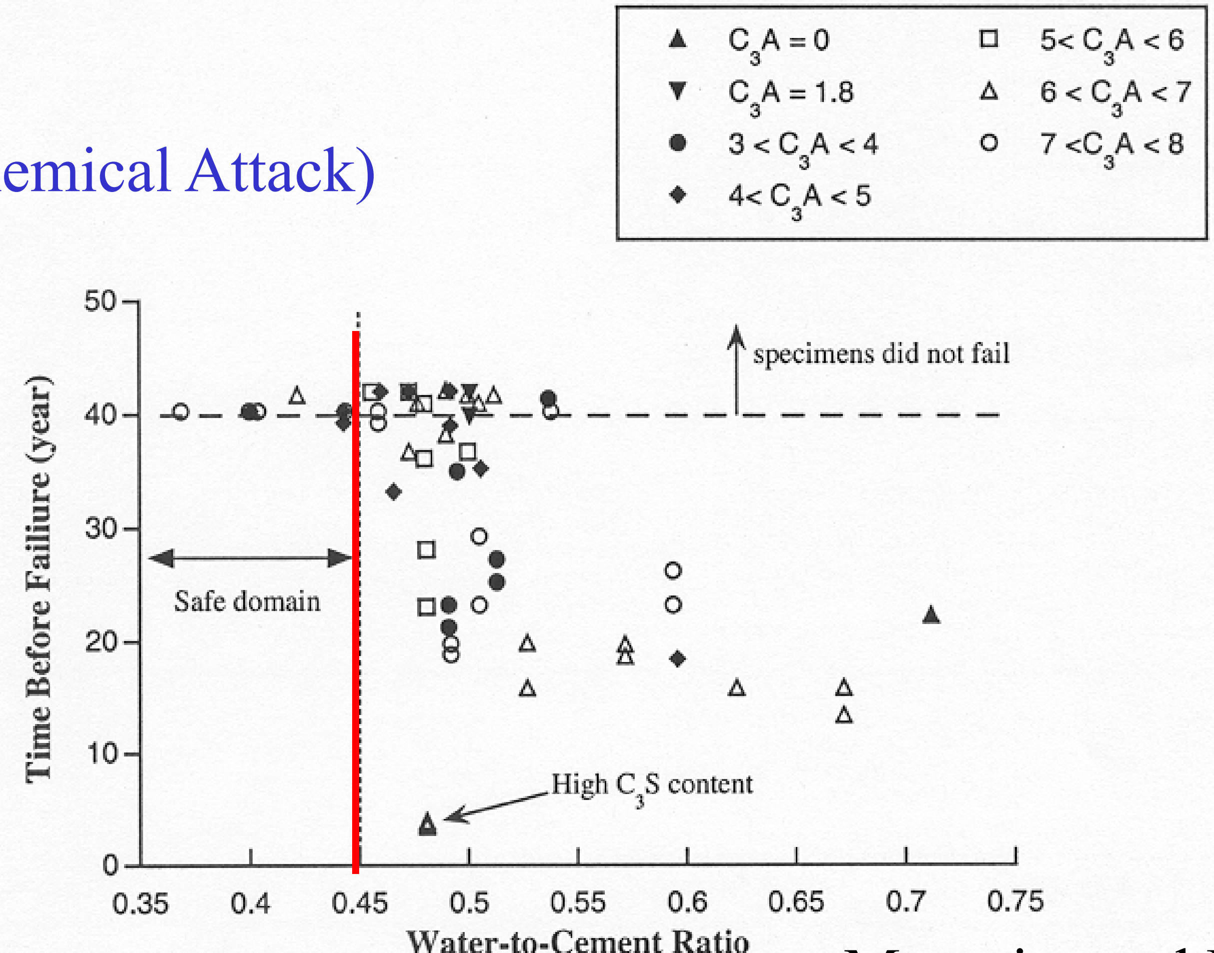
8 gal./sack = 0.73 W/C

Any concrete with W/C > 0.45 was damaged

# Effect of W/C: USBR 40-Year Data
# ($C_3A$ from 0 to 8%)

*P.J.M. Monteiro, K.E. Kurtis / Cement and Concrete Research 33 (2003) 987–993*

(Chemical Attack)




Monteiro and Kurtis, 2003

Fig. 2. Time to failure as a function of w/c ratio, with ranges of $C_3A$ content in the range 0–8% shown by the shape and color of the markers.

# ACI 318-14 Code Reqts

| Exposure Class | Max w/cm | Cement (or meet C1012 limit) | Min. 28d fc' | Max. ASTM C1012 Expn. |
|---|---|---|---|---|
| S0 | -- | -- | -- | -- |
| S1 | 0.50 | II | 4000 psi (27.5 Mpa) | 0.10% @ 6m |
| S2 | 0.45 | V | 4500 psi (31 Mpa) | 0.10% @ 12m |
| S3 | 0.45 | V+ SCM | 4500 psi (31 Mpa) | 0.10% @ 18m |

# PFRA, Gardiner Dam Saskatchewan: 30 year concrete data (from K. Lenz report, 1992)

TABLE 16
Performance of Type 10 and Type 50 Cement Concretes, with and without Fly Ash, in 0.15M Mixed Sulphate Solution

| w/cm | Years to 0.05% Expansion | | | |
|---|---|---|---|---|
| | Type 50 Cement | | Type 10 Cement | |
| | Visual Best Fit Line | Variation | Visual Best Fit Line | Variation |
| 0.7 | 8 | - | 1 | ±0.7 |
| 0.6 | 9 | ±1.2 | 2 | ±1.0 |
| 0.5 | 10 | ±1.8 | 3 | ±1.3 |
| 0.45 | 12 | ±2.5 | 4 | ±1.7 |
| 0.4 | 17 | highly variable | 5.5 | ±2.5 |
| 0.375 | 26 | highly variable | 7 | highly variable |

Numerous Type 50 (Type V or HS) and Type10 (Type I or GU) cements were used to establish this table and this data led to **CSA A23.1 dropping w/c for S1 exposure to 0.40**

# Additional Notes in CSA A23.1 on Sulfate Exposures

- *When structures are only partially immersed or are in contact on only one side with sulfate water or soils, the continuing evaporation can build up a very high concentration of sulfates within the concrete. Thus, a severe sulfate attack can occur even where the sulfate content is not initially high.*
- *Concrete wholly or permanently above the water table can be subjected to sulfate attack as a result of the migration of salts through the capillaries of the subsoil.*
- *Concretes buried in soil or completely immersed in water are under static conditions in which sulfate attack is confined to surfaces and normally is negligible.*
- *Flowing water and groundwater under a hydraulic head can lead to a more severe sulfate attack than static water containing the same concentration of salts.*

# The severity of sulfate attack depends on the mechanism of sulfate ingress

- The ingress of aggressive fluids, such as sulfate or chloride solutions, occurs through the capillary pore system in the bulk paste and the in the ITZ.
- Transport mechanisms include:

1. **Capillary suction** into unsaturated pores.----**fast**
2. **Diffusion** due to concentration gradients.----**slow**
3. **Permeation** due to hydraulic head.----**slow**
4. **Wick action** due to evaporation.----**fast at high w/cm**

The rates and relative importance of these processes are functions of the boundary conditions and the pore size distribution and continuity of the pore system as well as physical/chemical interactions of penetrating ions with the solid.

# Severe Sulfate Damage in the Field

- **The most severe cases** appear to have been have been where there have been **wetting/drying** or an **evaporative front** allowing **rapid salt crystallization** followed by chemical degradation.
- Old PCA sites in Colorado and S. Dakota USA
- PCA Sacramento California test site USA
- USBR exposure site, water retaining structures in SW USA
- PFRA exposure site in Western Canada
- Australia
- Middle East
- China

# Phase Changes in Sodium Sulfate can occur with daily changes in RH & Temp.

Thenardite ⟷ Mirabilite

$Na_2SO_4$ ⟷ $Na_2SO_4 \cdot 10H_2O$

Not a big problem with $MgSO_4$ or $CaSO_4$

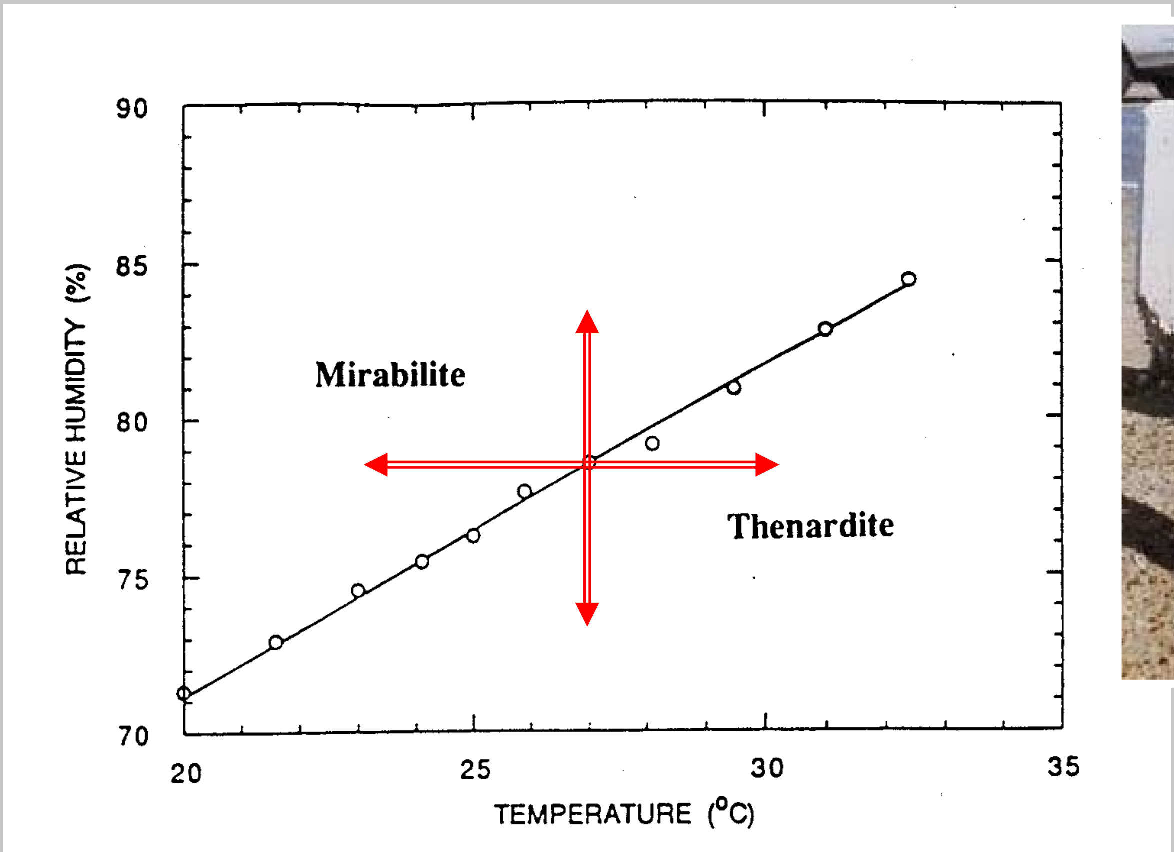
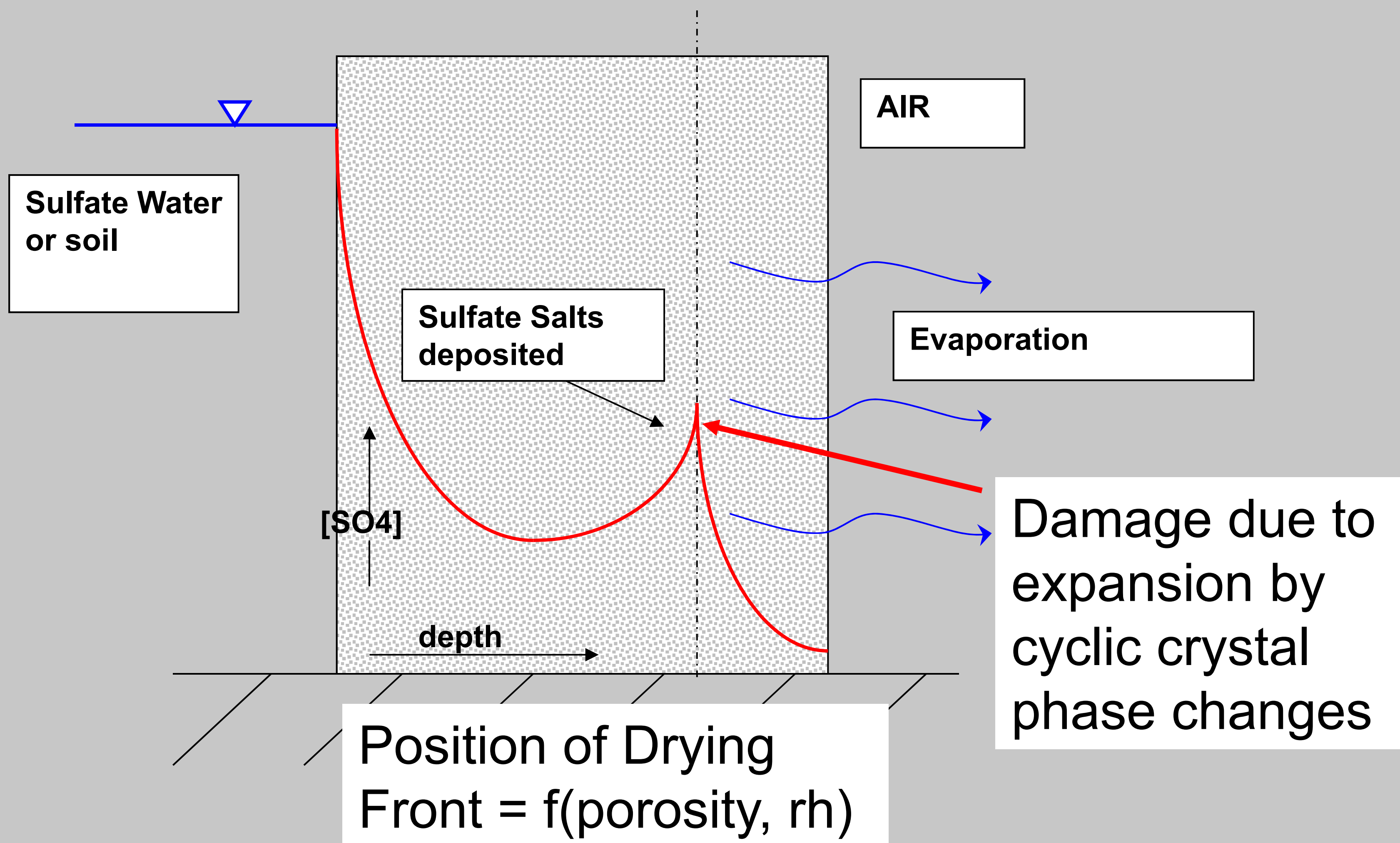
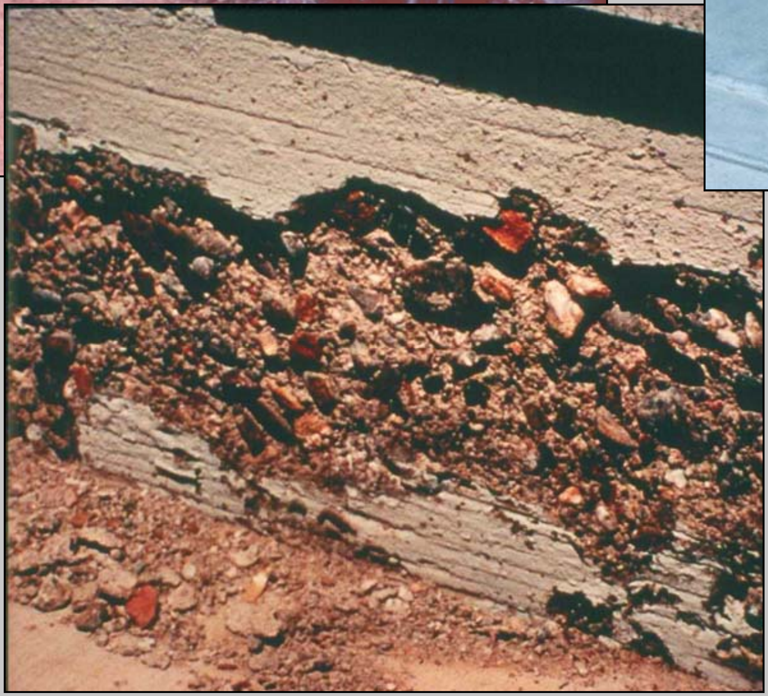



Figure from Sandberg & Folliard, 1994

# Wick Action due to Evaporation



# Sulfate Salt Crystallization Damage



PCA photos

# S. Dakota US 18-43 Bridge Piers

Built 1960's, inspected in 2003.

In Severe Sulfate soils and low humidity

Pier was jacketed in 2004

D. Johnston

# Sulfate Resistance

Bridge columns in North Dakota in sulfate soils

# Sulfate Attack at Crack at Fort Peck Dam, Montana @ 33 years

Ref. Mehta & Montiero


10,000 mg/L $SO_4$ (as $Na_2SO_4$) groundwater

Type I PC, w/c = 0.49, 335 kg/m$^3$

# Port Pirie, South Australia

Courtesy of James Aldred

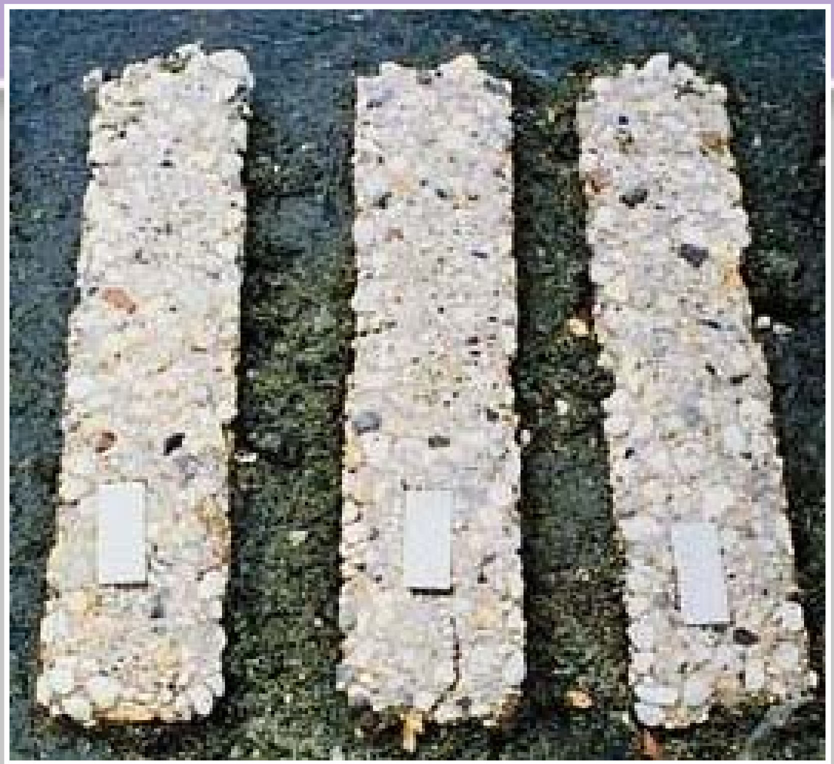
# Effects of Wetting and Drying in $Na_2SO_4$ saturated sand

PCA Exposure Site
Sacramento, California

Stark 2002

# PCA, Sacramento California Site

## Effect of W/C Ratio



Rating of Concrete: 5 @ 12 yrs
Type V Cement
W/C = 0.65

Rating of Concrete: 2 @ 16 yrs
Type V Cement
W/C = 0.39

(Physical and Chemical Attack)

Stark 2002

# PCA Sacramento Exposure Site

1. Surfaces or portions of virtually all concrete beams stored in the outdoor sulfate soils exposure displayed major to serious scaling and deterioration. Continuously immersed (buried) portions of these same beams displayed virtually no deterioration.

2. A major mechanism of deterioration in these concrete specimens appeared to be cooling and heating, and wetting and drying, with cyclic crystallization of sodium sulfate salts.

3. The traditional explanation of expansion of concrete due to chemical reaction of sulfate ion with alumina bearing cement hydration products was of minor significance in these tests.

Recommendation #1: **Reduce water-cement ratios as a primary means of improving the sulfate resistance of concrete in field structures.**

D. Stark 2002

# Current North-American Standards for Sulfate Resistance of Concrete

Covered by:
ASTM C452 and
ASTM C1012
standard test methods

**Cementitious Materials**:

- Limits on $C_3A$
- Use of Supplementary Cementitious Materials.

**Concrete:**

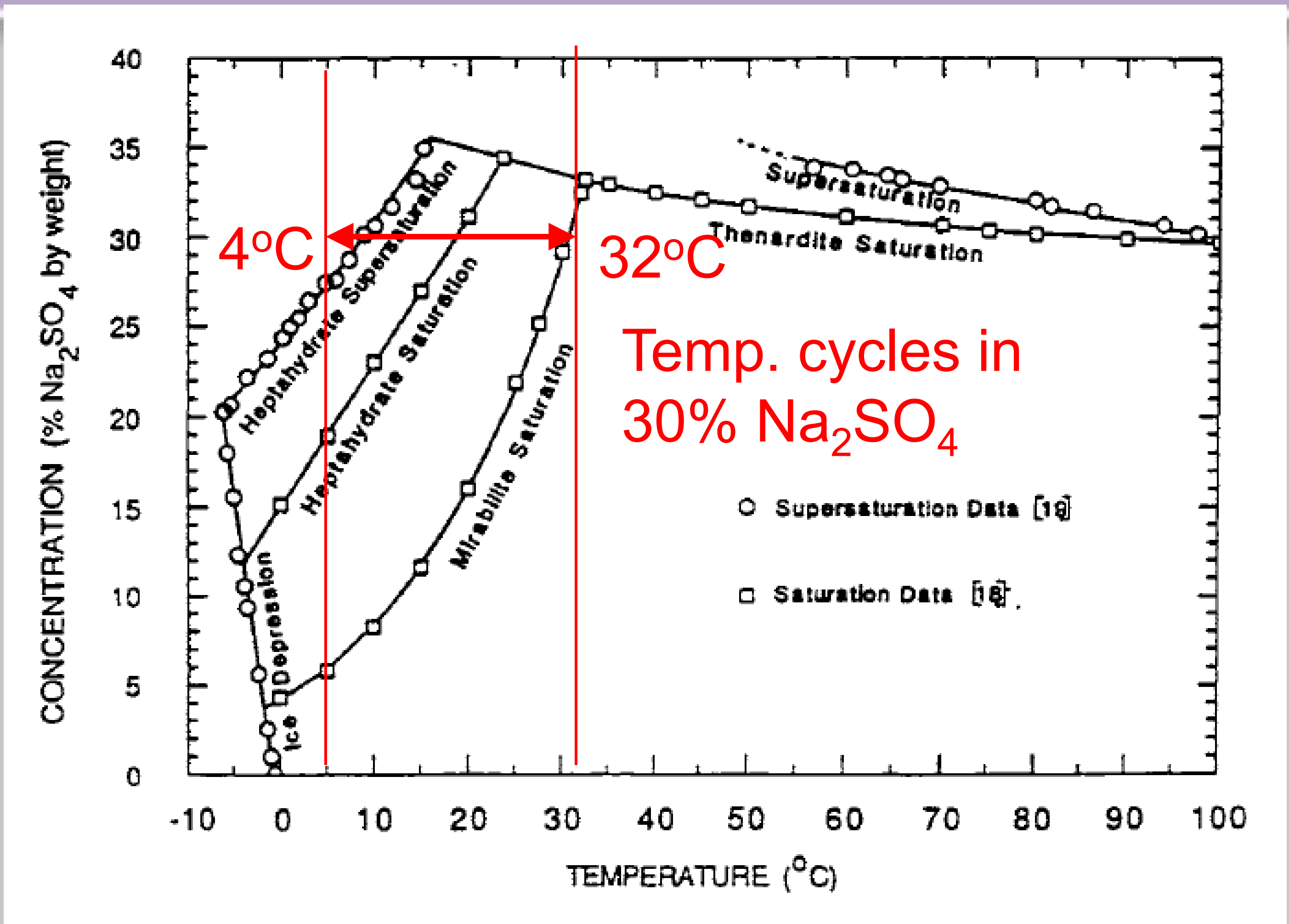
**Not Covered by standard test methods**

- Prescribed limits on W/CM with implied limits on "Permeability" (0.45 in ACI code & 0.40 in CSA)
- Adequate Curing

# Testing for Physical Sulfate Salt Attack

- Humidity cycles
  - ➢ Change of RH inside concrete or mortar samples is slow, and significant time is required to reach RH equilibrium
- Partly-immersed
  - ➢ Damage is localized in the evaporation zone, which makes it difficult to quantify
- Fully immersed prisms with thermal cycles
  - ➢ Rapid and extensive deterioration evenly over all surfaces. Can quantify by mass loss.

# Phase Changes in 30% Sodium Sulfate between 4 and 32°C




1 cycle per day starting at 28d

Zhutovsky and Hooton 2016

Sandberg & Folliard 1994

# Deterioration due to PSA after 100 thermal cycles


Note: M50 means w/c = 0.50

effect of w/cm on sulfate resistant PC mixes

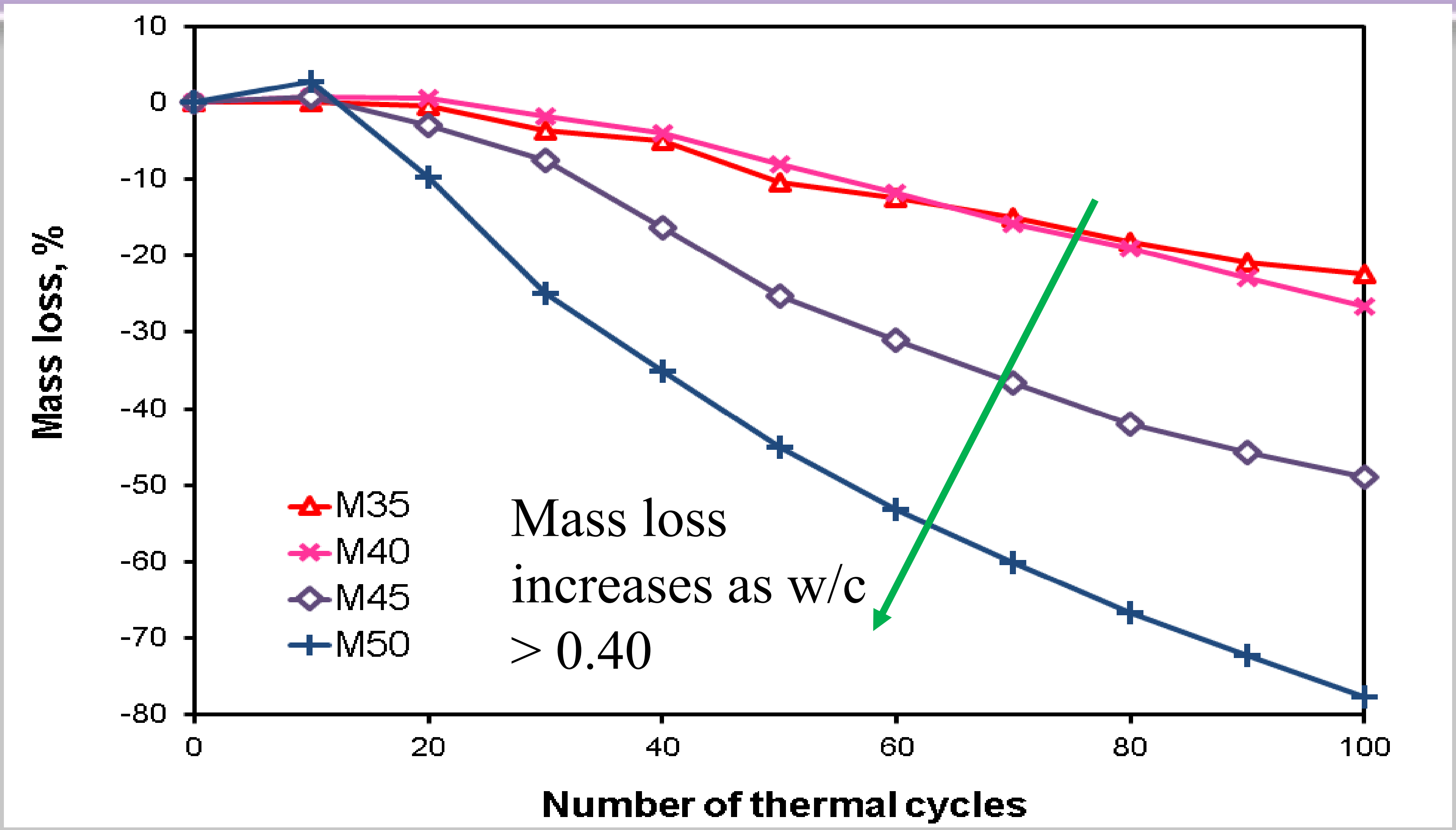
Note: from μXRF, $SO_4$ builds up only in outer 2mm before surface spalls off

Zhutovsky and Hooton 2016

Const. & Bldg. Matls

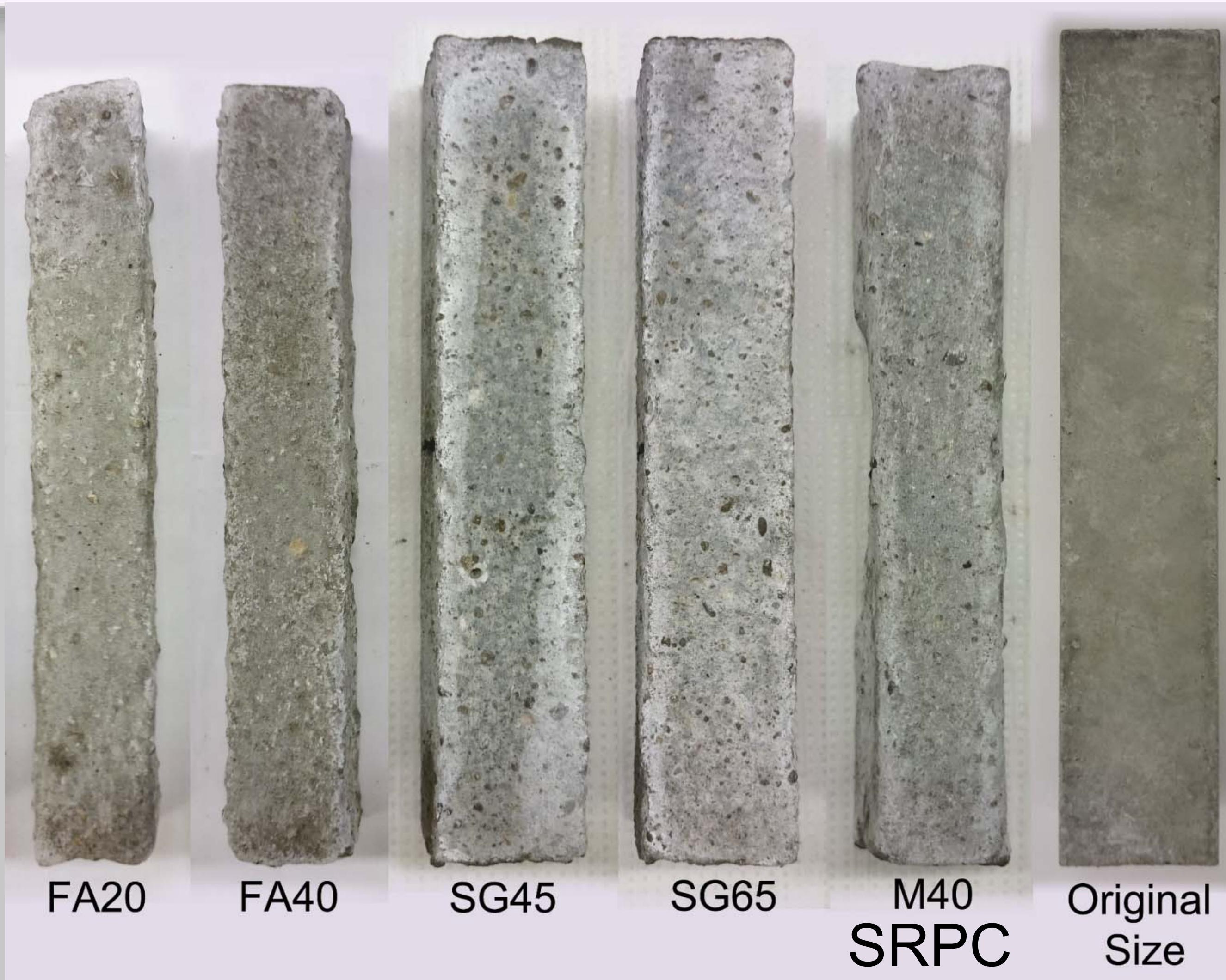
# Mass Loss due to PSA

- effect of w/cm on PC mixes




Zhutovsky and Hooton 2016

# Deterioration of 0.40 SCM mixes after 100 thermal cycles

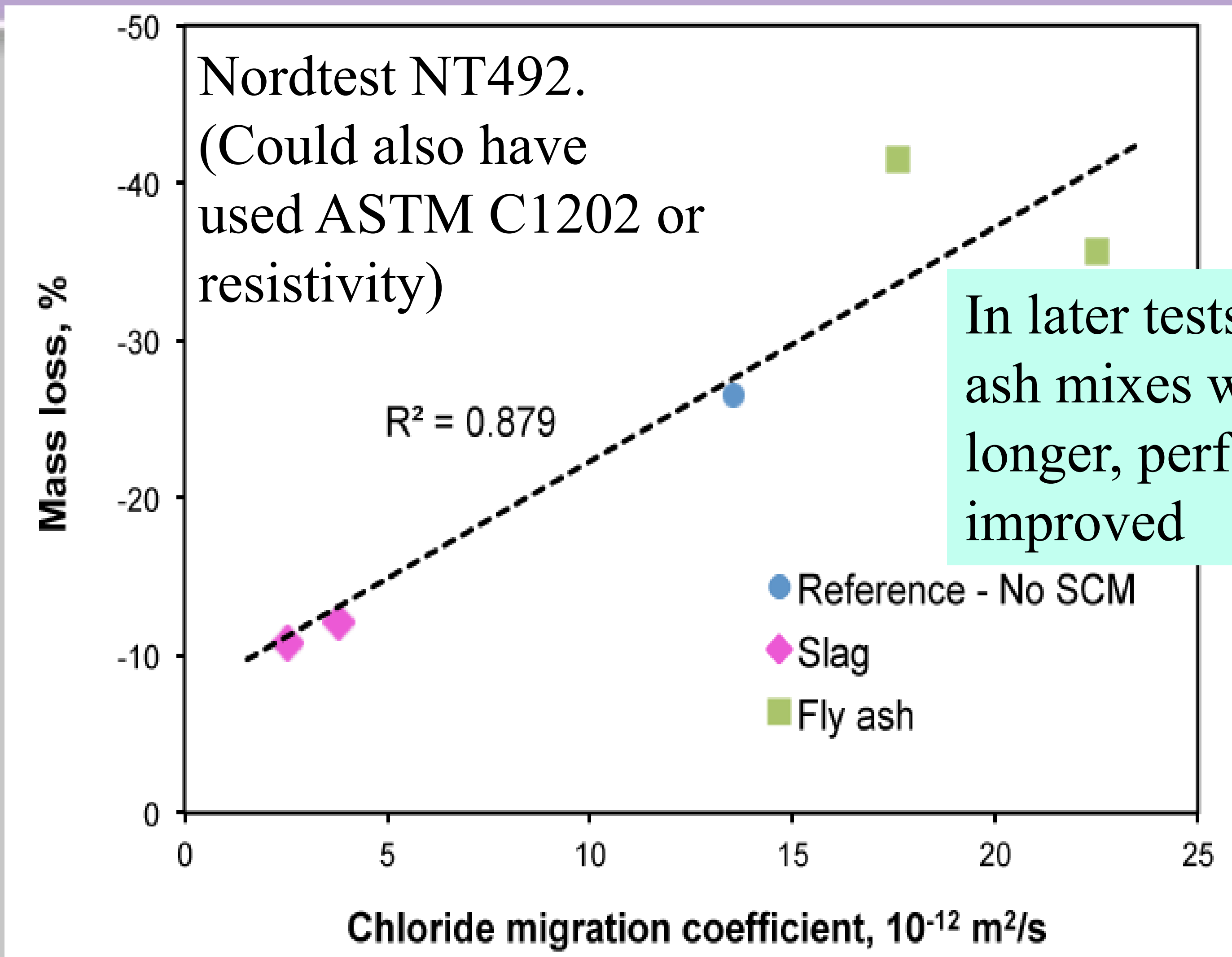



**Only 3d wet cure**—cycles started @ 28d.

More recent tests have shown that with longer curing, the FA mixes perform better (lower sorptivity)

Zhutovsky and Hooton 2016

# Correlation of transport properties and PSA mass loss




Nordtest NT492. (Could also have used ASTM C1202 or resistivity)

In later tests, when fly ash mixes were cured longer, performance improved

# Summary Regarding Resistance to Physical Sulfate Attack

- While most engineers think of using Low-$C_3A$ sulfate resistant cement, or SCMs combined with low w/cm, the chemical form of sulfate attack is not the most aggressive.
- Physical sulfate salt crystallization is much faster and more aggressive in arid climates.
  - Low-$C_3A$ cement will not prevent this.
  - **The best defense is low w/cm, well cured concrete**
- A test (or better mix design and curing criteria) is needed to evaluate resistance of concrete to <u>physical sulfate attack</u>.
- To evaluate resistance of <u>concrete mixtures</u>, it would seem logical to consider replacing strength & maximum w/cm limits with a rapid fluid penetration resistance test.

# ACI 201.2R-2016 Guidance

- Chapter 6 is on Physical Salt Attack.
- Recommendations:

Specific recommendations cannot be made to prevent physical salt attack; however, the salts of sodium sulfate and sodium carbonate are primarily responsible for physical salt attack on concrete, while sodium chloride causes less deterioration. Other common salts such as calcium sulfate and magnesium sulfate do not participate in physical salt attack.

What that means is the committee could not agree on a maximum w/cm----largely due to positions taken by some members resulting from the "California Sulfate" litigations.