Sulfate Attack

What is Sulfate Attack?

- A form of chemical attack
- Internal or external

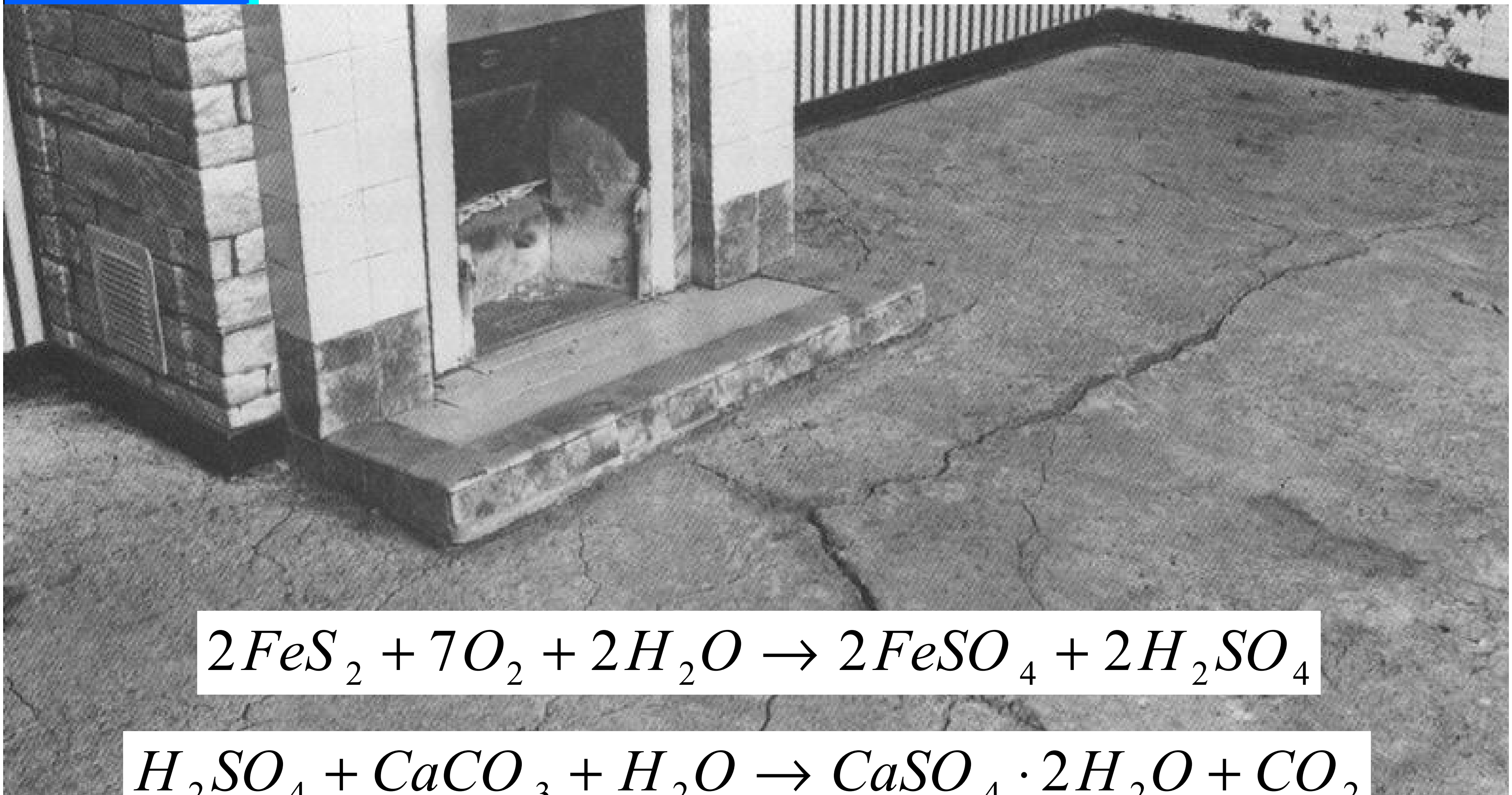
Visual Rating → 1.1 2.5 5.0

External Sulfate-Related Deterioration Issues

1. "Classical" sulfate attack
   - Soil
   - Groundwater
2. Salt crystallization
3. Thaumasite

Classical Sulfate Attack

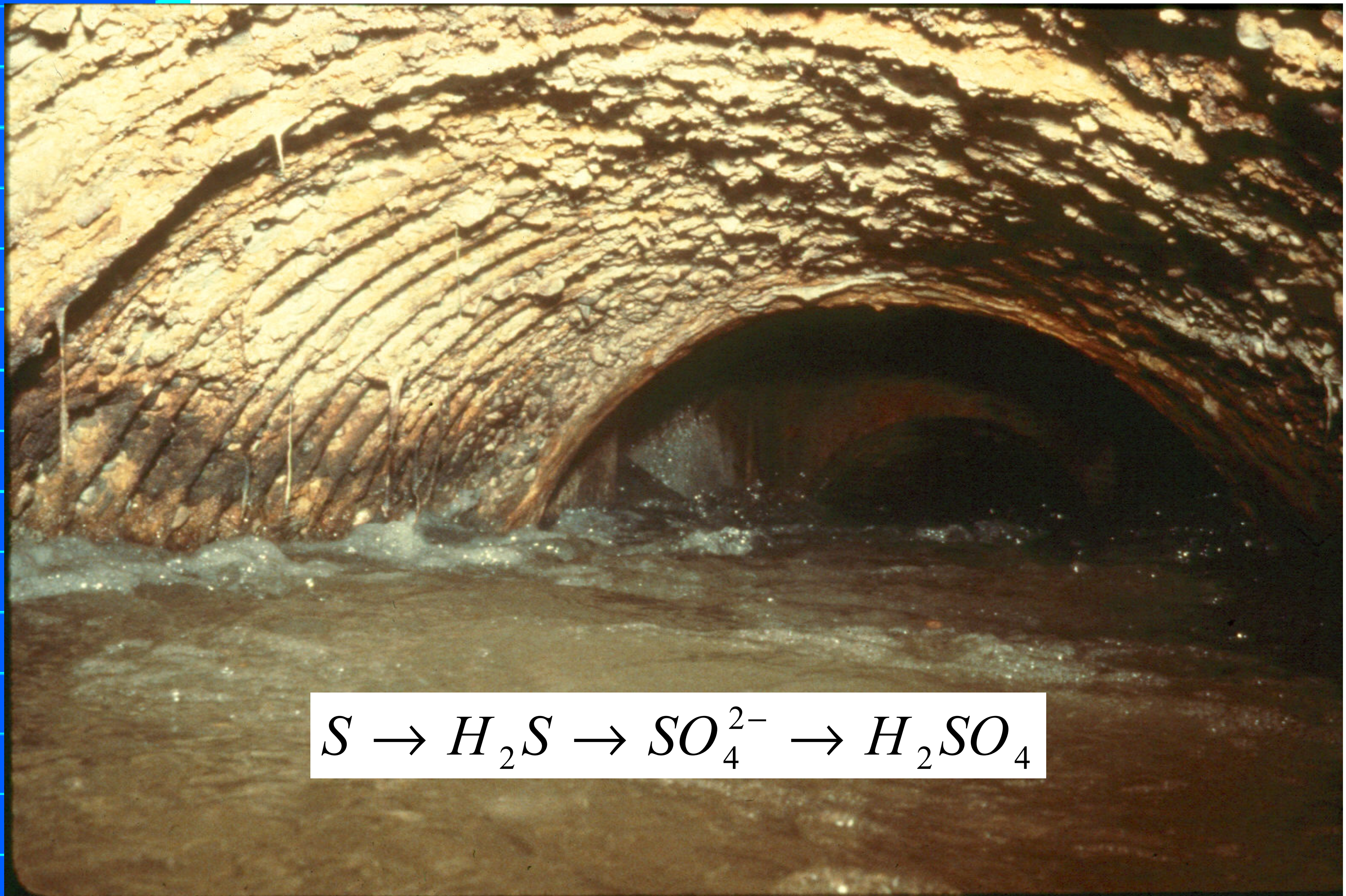
Slab on Pyritic Fill



$$2FeS_2 + 7O_2 + 2H_2O \rightarrow 2FeSO_4 + 2H_2SO_4$$

$$H_2SO_4 + CaCO_3 + H_2O \rightarrow CaSO_4 \cdot 2H_2O + CO_2$$

Courtesy of BRE



Crown Sewer Corrosion

Courtesy David Fowler, 2001

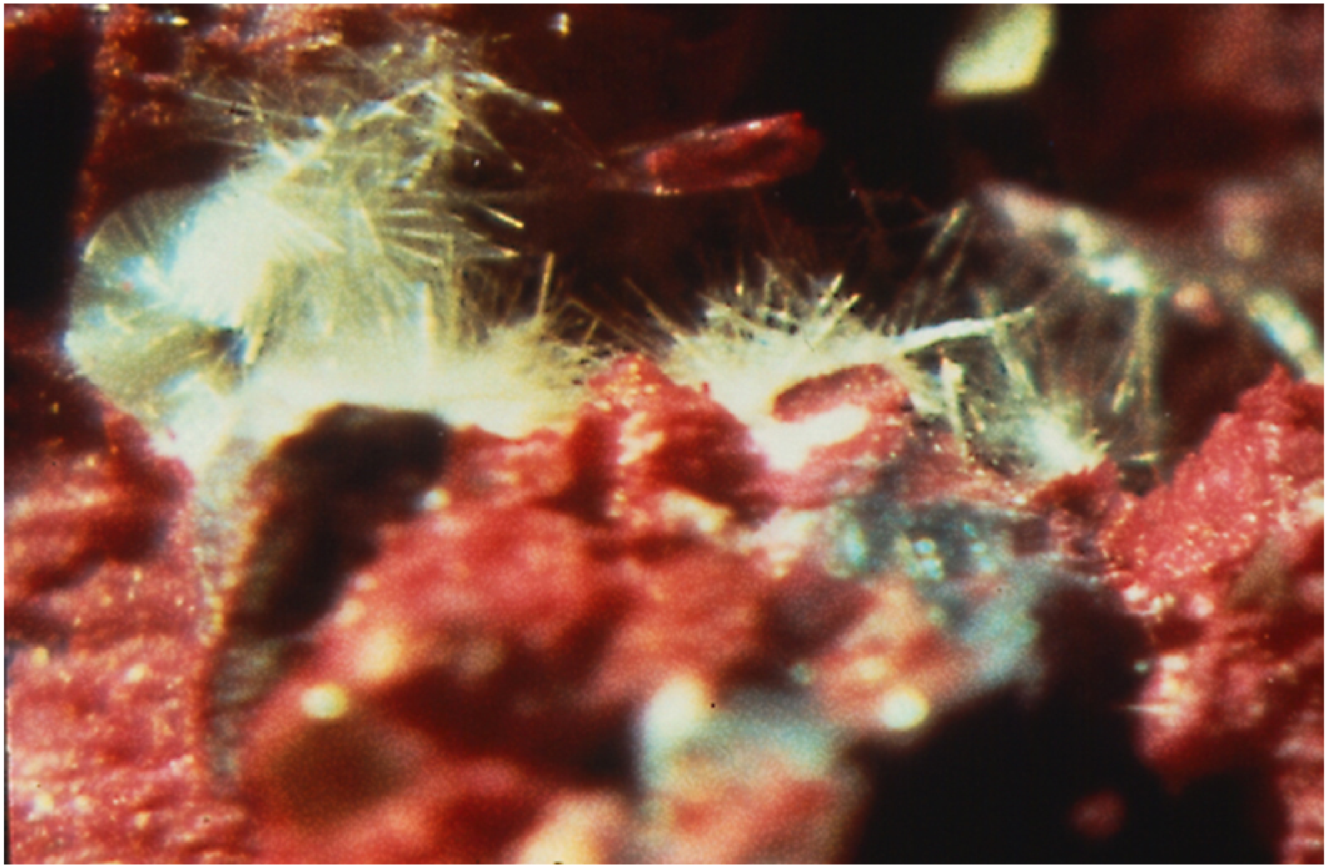
Salt Crystallization (Physical Salt Attack)

Internal Sulfate-Related Deterioration Issues

1. Excess sulfates (over-sulfated system)
2. Potential for DEF
   - Curing temperature history and RH
   - Effects of cement chemistry
   - Interaction with ASR, freeze-thaw, etc.
3. “Clogging” of entrained air voids

Delayed Ettringite Formation

Secondary Ettringite

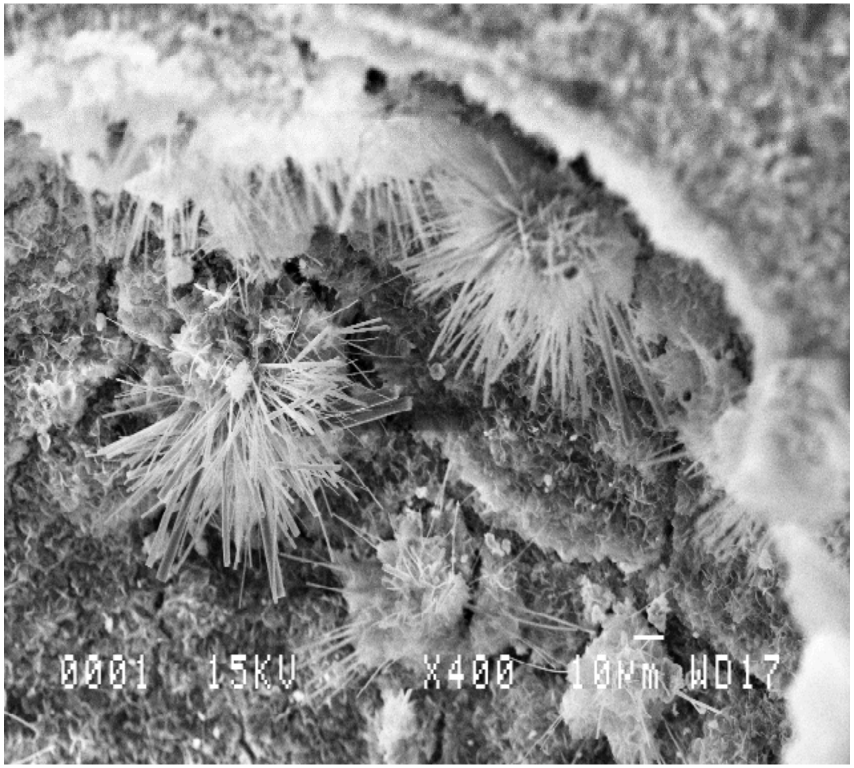


Mechanisms

Role of Ettringite in Cement Hydration

$$C_3A + 26H + 3C\bar{S}H_2 \rightarrow C_6A\bar{S}_3H_{32}$$

Tricalcium aluminate + Water + Gypsum → Calcium sulfoaluminate (Ettringite)



Role of Ettringite in Cement Hydration

$$2C_3A + 4H + C_6A\bar{S}_3H_{32} \rightarrow 3C_4A\bar{S}H_{12}$$

Tricalcium aluminate + Water + Ettringite → Calcium monosulfoaluminate

$$3C_3A + 12H \rightarrow C_3AH_{12}$$

$$3C_3A + 12H + CH \rightarrow C_4AH_{13}$$

Sulfate Attack

Sodium (or potassium) sulfate from soil or groundwater + Calcium hydroxide in concrete → Gypsum

Gypsum + Calcium aluminate hydrate in concrete → Ettringite

Reactions accompanied by volumetric expansion of cementitious matrix!

Magnesium Sulfate Attack

In addition to reacting with the aluminates and calcium hydroxide, magnesium sulfate will also react with the hydrated calcium silicates (C-S-H):

Magnesium sulfate from soil or groundwater + Calcium silicate hydrate in concrete → Gypsum + brucite + silica gel

Reactions accompanied by volumetric expansion of cementitious matrix!

Calcium Sulfate Attack

$$C_3A\left(C\overline{S}\right)H_{12} + 2C\overline{S}H_2 + 16H \rightarrow C_3A\left(C\overline{S}\right)_3H_{32}$$

Calcium Monosulfoaluminate + Gypsum + Water → **Ettringite**

$$C_3AH_{12} + 3C\overline{S}H_2 + 6H \rightarrow C_3A\left(C\overline{S}\right)_3H_{32}$$

Calcium Aluminate Hydrate + Gypsum + Water → **Ettringite**

Alkali Sulfate Attack

$$CH + N_2\bar{S}H_{10} \rightarrow C\bar{S}H_2 + 2NH + 8H$$

Calcium Hydroxide + Sodium Sulfate → Gypsum + Sodium Hydroxide + Water

$$2C_3AH_{12} + 3N_2\bar{S}H_{10} \rightarrow C_3A\left(C\bar{S}\right)_3H_{32} + 2AH_3 + 6NH + 17H$$

Tri-Calcium Aluminate Hydrate + Sodium Sulfate → **Ettringite** + Aluminum Hydroxide + Sodium Hydroxide + Water

Alkali Sulfate Attack

$$CH + N_2\bar{S}H_{10} \rightarrow C\bar{S}H_2 + 2NH + 8H$$

Calcium Hydroxide + Sodium Sulfate → Gypsum + Sodium Hydroxide + Water

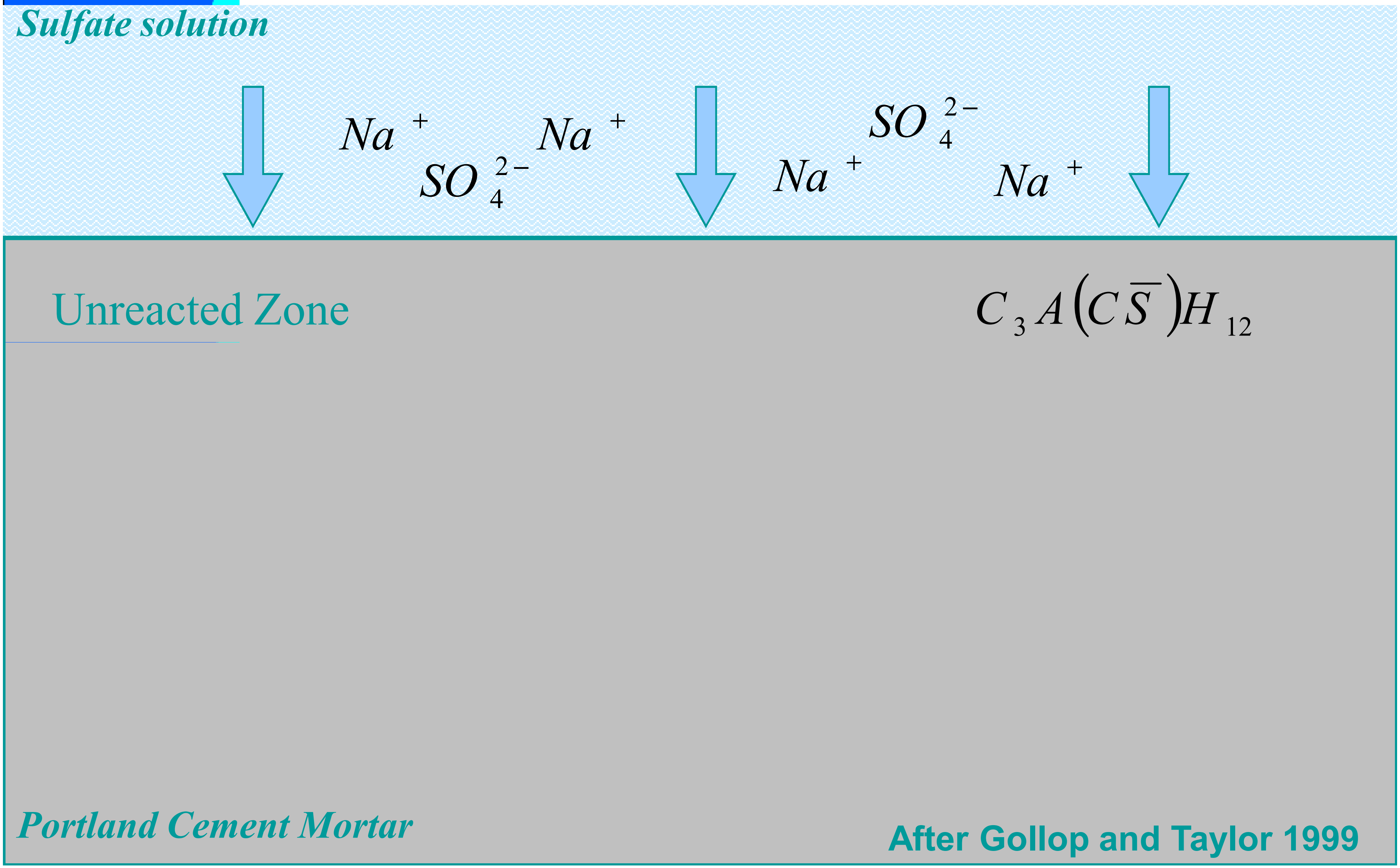
Calcium Silicate + Sodium Sulfate →

$$3CaO \cdot 2SiO_2 + 3N_2\bar{S}H_{10} \rightarrow$$

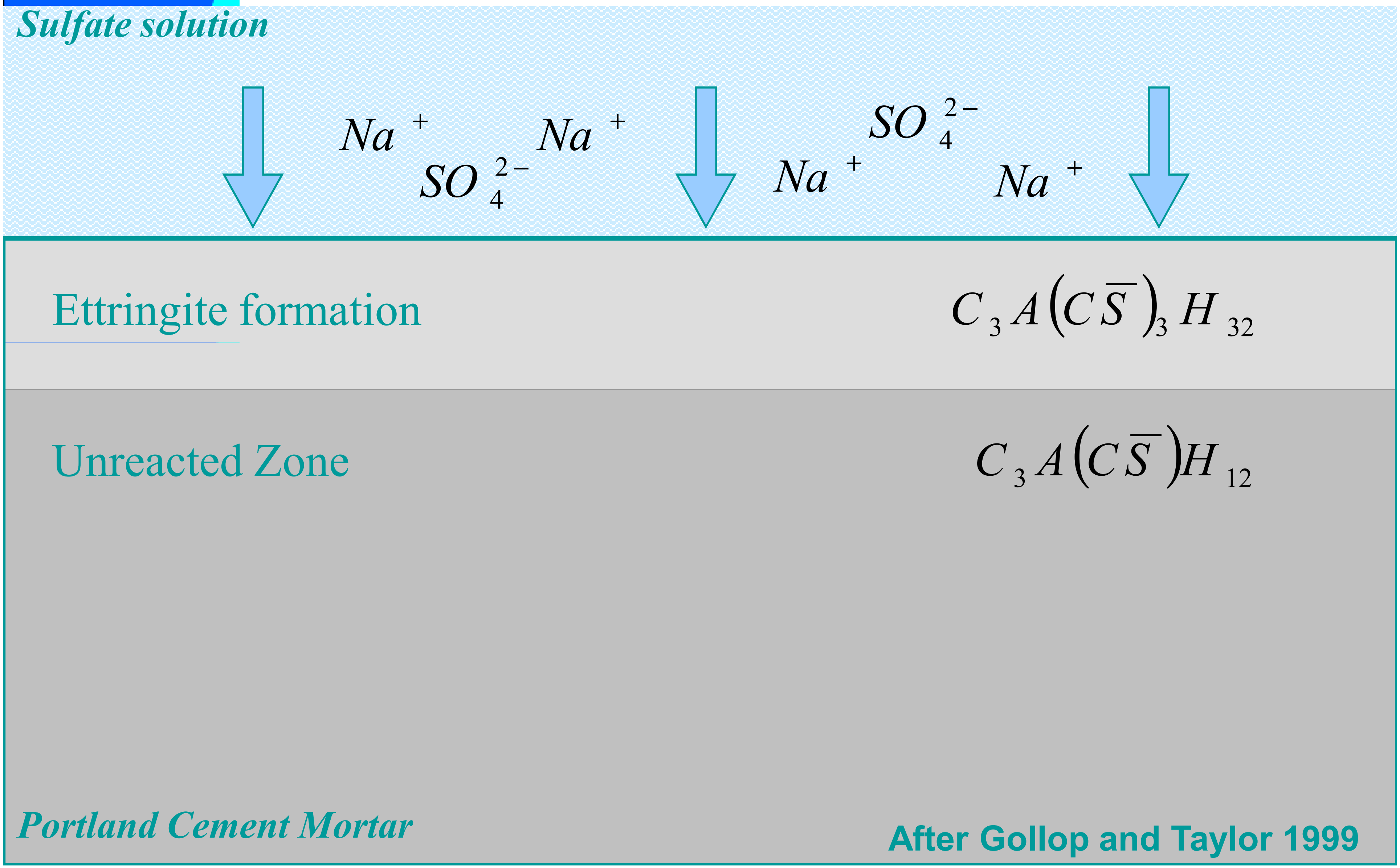
$$3C\bar{S}H_2 + 6NH + 2SiO_2 \cdot aq + 18H$$

Gypsum + Sodium Hydroxide + Silica Gel + Water

Zones of Attack in Portland Cement Mortar



Zones of Attack in Portland Cement Mortar



Zones of Attack in Portland Cement Mortar

Sulfate solution

Na^+ SO_4^{2-} Na^+ Na^+ SO_4^{2-} Na^+

Gypsum formation & reduced $Ca(OH)_2$	$C\overline{S}H_2$ $C_3A\left(C\overline{S}\right)_3H_{32}$
Ettringite formation	$C_3A\left(C\overline{S}\right)_3H_{32}$
Unreacted Zone	$C_3A\left(C\overline{S}\right)H_{12}$

Portland Cement Mortar

After Gollop and Taylor 1999

Zones of Attack in Portland Cement Mortar

Sulfate solution

Na^{+} SO_4^{2-} Na^{+} Na^{+} SO_4^{2-} Na^{+}

Gypsum formation & decalcification of C-S-H	$SiO_2 \cdot aq$, $C\bar{S}H_2$, $C_3A(C\bar{S})_3H_{32}$
Gypsum formation & reduced $Ca(OH)_2$	$C\bar{S}H_2$, $C_3A(C\bar{S})_3H_{32}$
Ettringite formation	$C_3A(C\bar{S})_3H_{32}$
Unreacted Zone	$C_3A(C\bar{S})H_{12}$

Portland Cement Mortar

After Gollop and Taylor 1999

Magnesium Sulfate Attack

Calcium Silicate + Magnesium Sulfate →

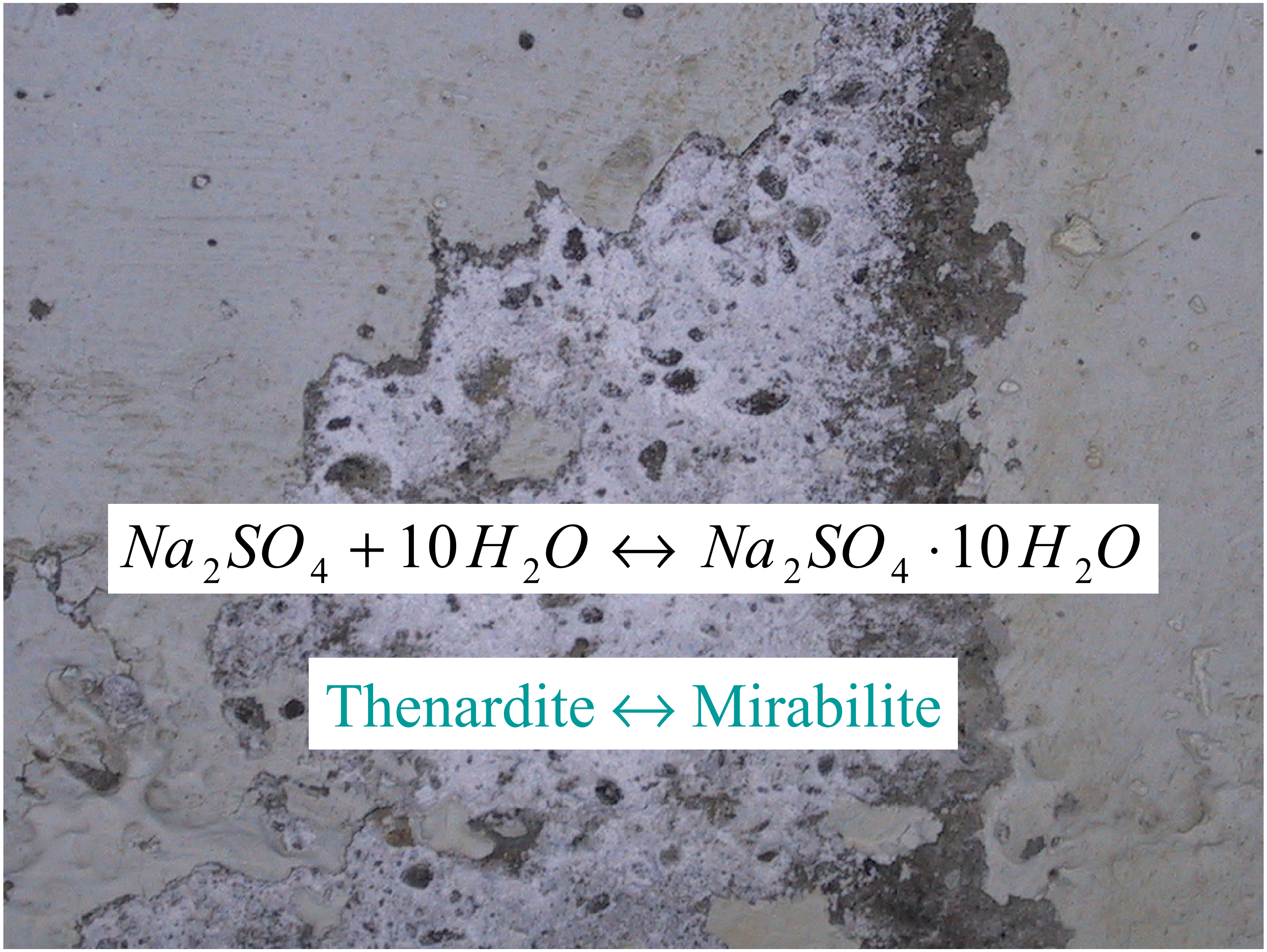
$$3CaO \cdot 2SiO_2 + MgSO_4 \cdot 7H_2O \rightarrow$$

$$3(CaSO_4 \cdot 2H_2O) + 3Mg(OH)_2 + 2SiO_2 \cdot aq$$

Gypsum + Magnesium Hydroxide + Silica Gel

Skalny et al, 2002

Physical Salt Attack

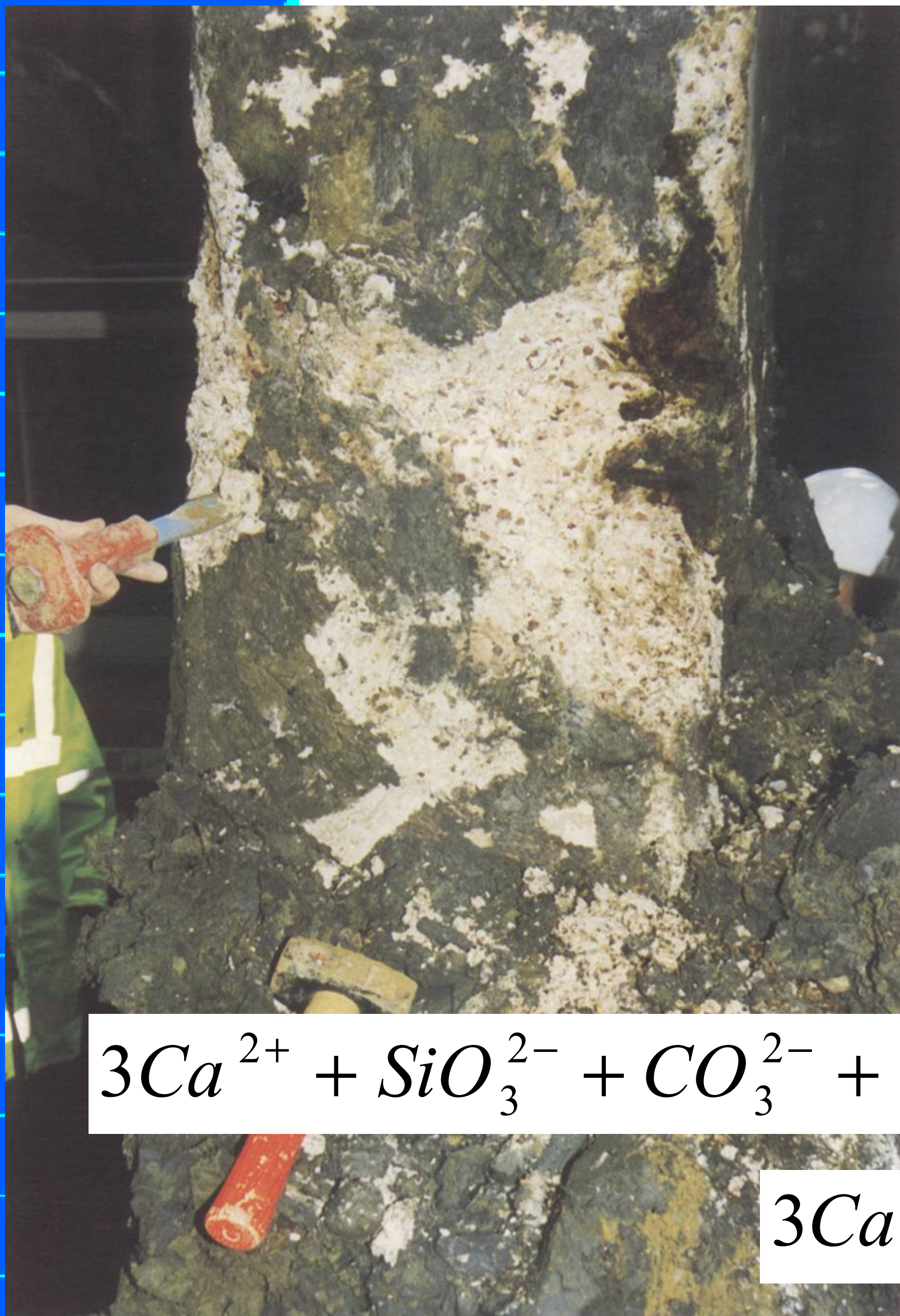


$$Na_2SO_4 + 10H_2O \leftrightarrow Na_2SO_4 \cdot 10H_2O$$

Thenardite ↔ Mirabilite

Thaumasite

- Combination of carbonation and sulfate attack
- High RH
- Low T (5°C to 10°C)
- Rare



Thaumasite Form of Sulfate Attack

$$3Ca^{2+} + SiO_3^{2-} + CO_3^{2-} + SO_4^{2-} + 15H_2O \rightarrow$$

$$3CaO \cdot SiO_2 \cdot CO_2 \cdot SO_3 \cdot 15H_2O$$

Clark et al. 1999

Prevention

Is Sulfate Attack a Problem?

- Environment
  - Local soils
  - Groundwater
  - Other sources

Prevention

- Low permeability
  - Mix design
    - Water:cement ratio
    - Cement content
    - SCMs
      - Type
      - Content
      - Testing
  - Curing
  - Sealants?

Sulfate-Resistant CEMENTS

Moderate sulfate resistance

Types II, IP(MS), IS(<70)(MS), MS

High sulfate resistance

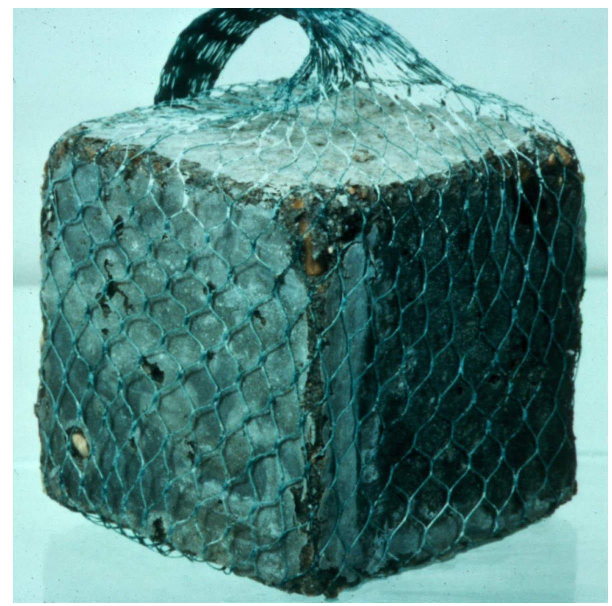
Types V, IP(HS), IS(<70)(HS), HS)

Type I - 14.1% C_3A

***W/C* = 0.50**

Type V - 1.2% C_3A

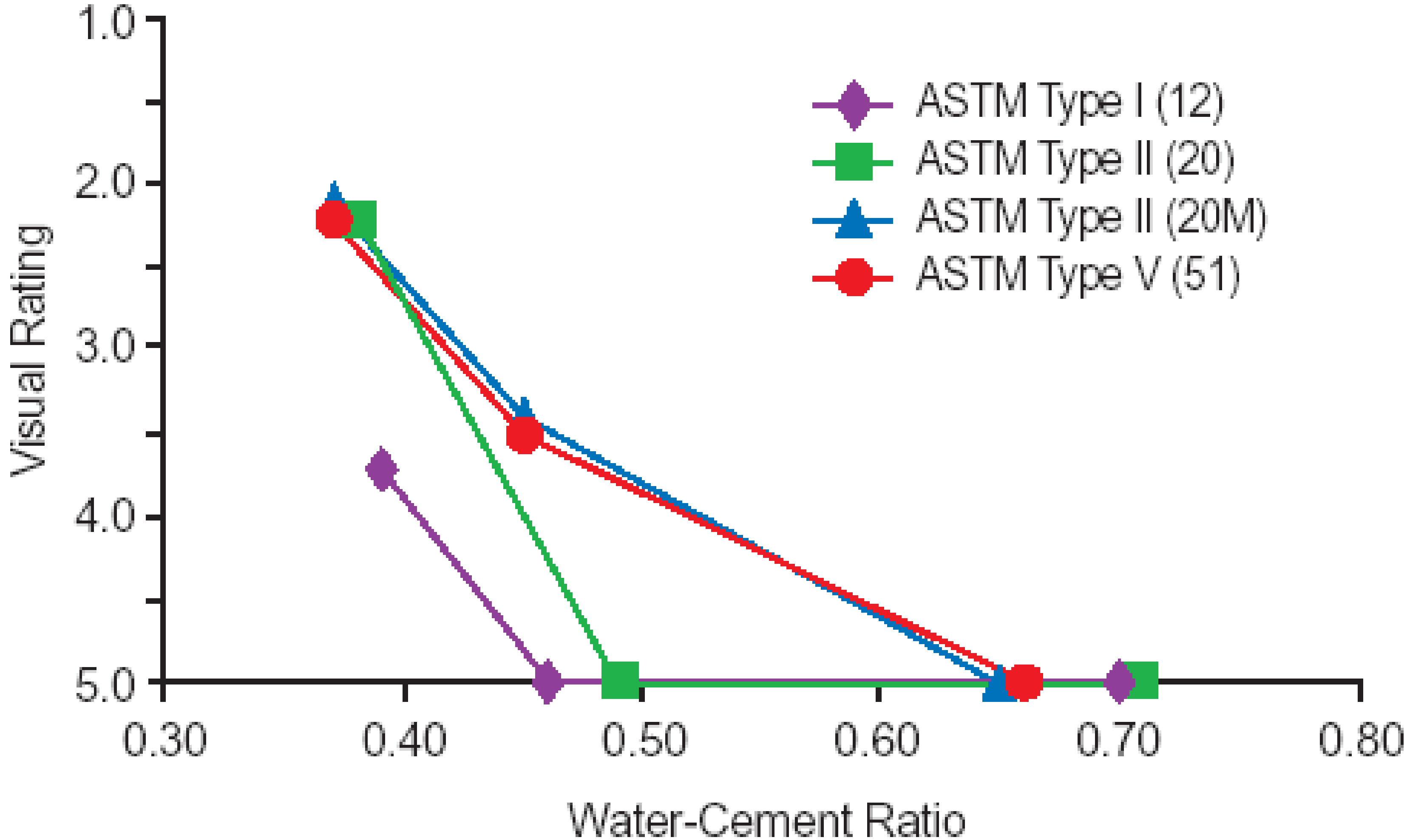
***W/C* = 0.51**



After immersion in sulfate solution for 5 years

Courtesy of BRE

Portland Cement Type



PCA RD129

Sulfate-Resistant CONCRETES

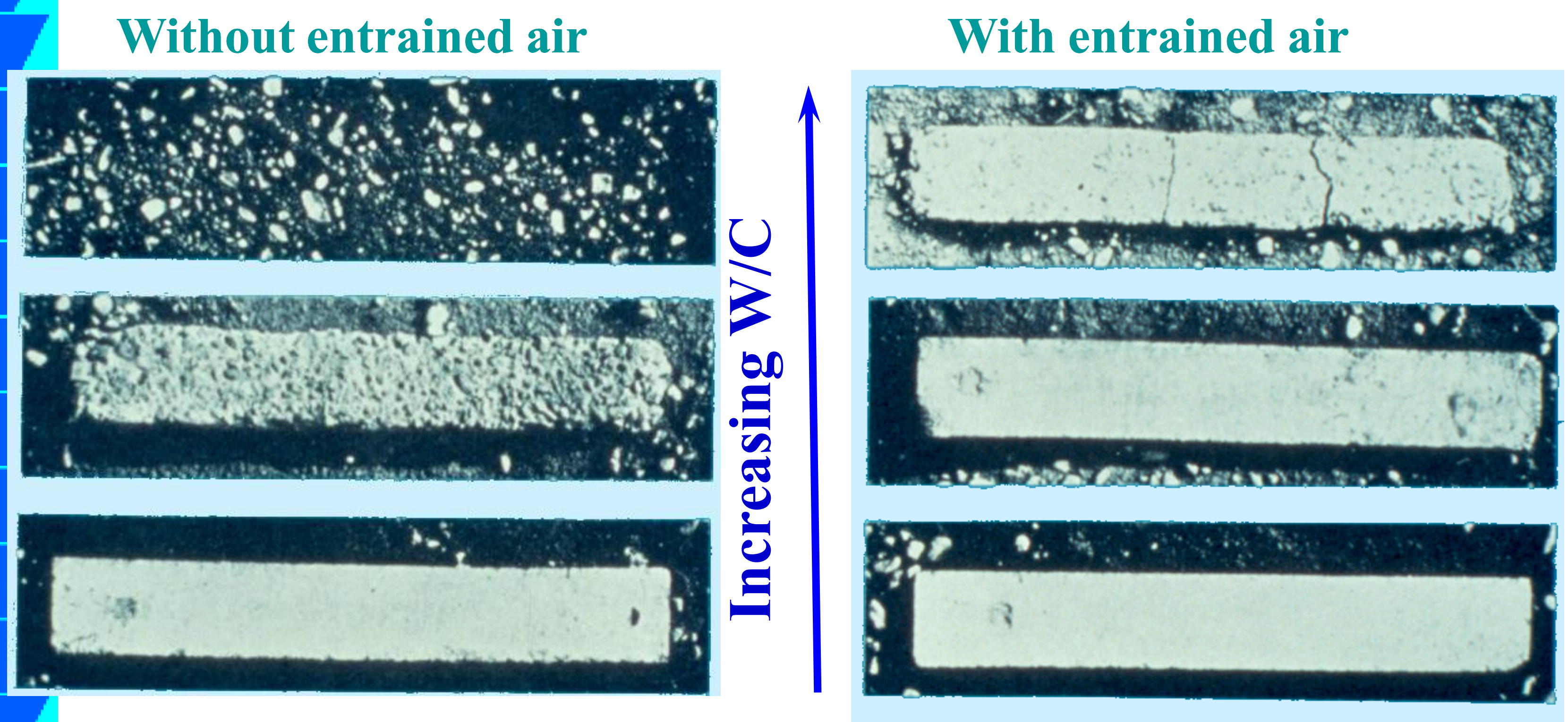
The resistance of **concrete** to sulfate attack can be improved by:

- Sulfate resistant cement AND
- Use of low W/CM (to reduce permeability)
- Use of most supplementary cementing materials

Type V Cement: W/C = 0.65

Type V Cement: W/C = 0.38

Entrained Air



Use of Supplementary Cementing Materials

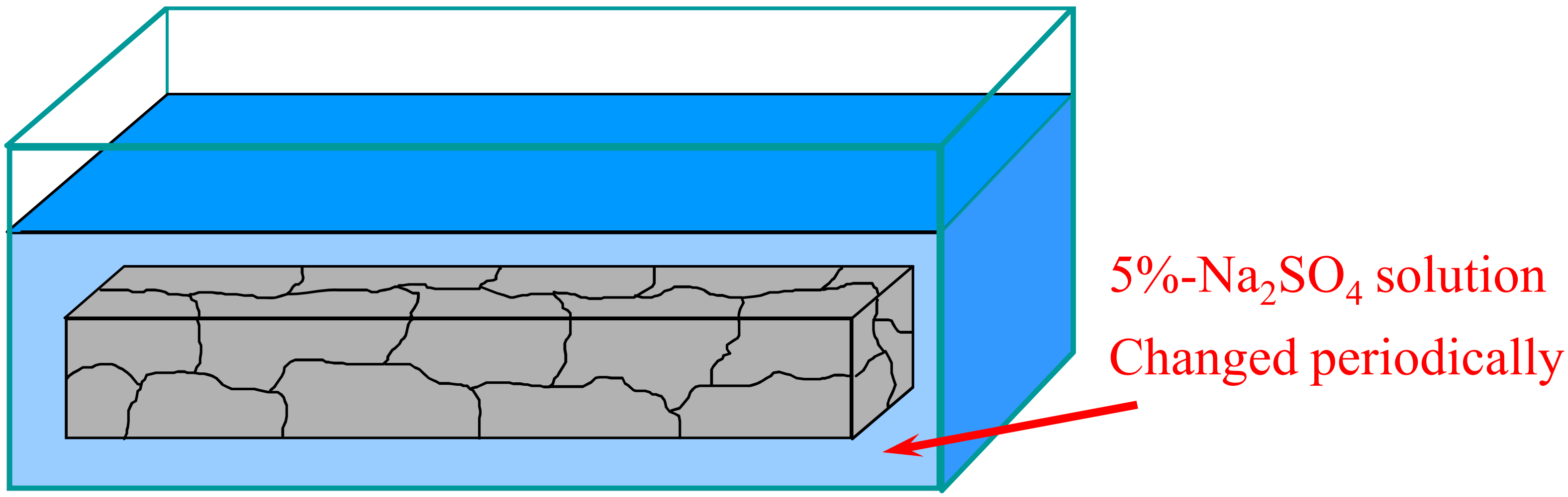
- Silicates in SCMs react with calcium hydroxide (CH)
- More C-S-H, less CH formation!
- Lower permeability

Not All SCMs!

Mortar bars with high-C_3A cement + 40% high-CaO Fly Ash after 2 years in ASTM C1012 (5% Na_2SO_4 Solution)

ASTM C1012 *Standard Test Method for Length Change of Hydraulic-Cement Mortars Exposed to a Sulfate Solution*

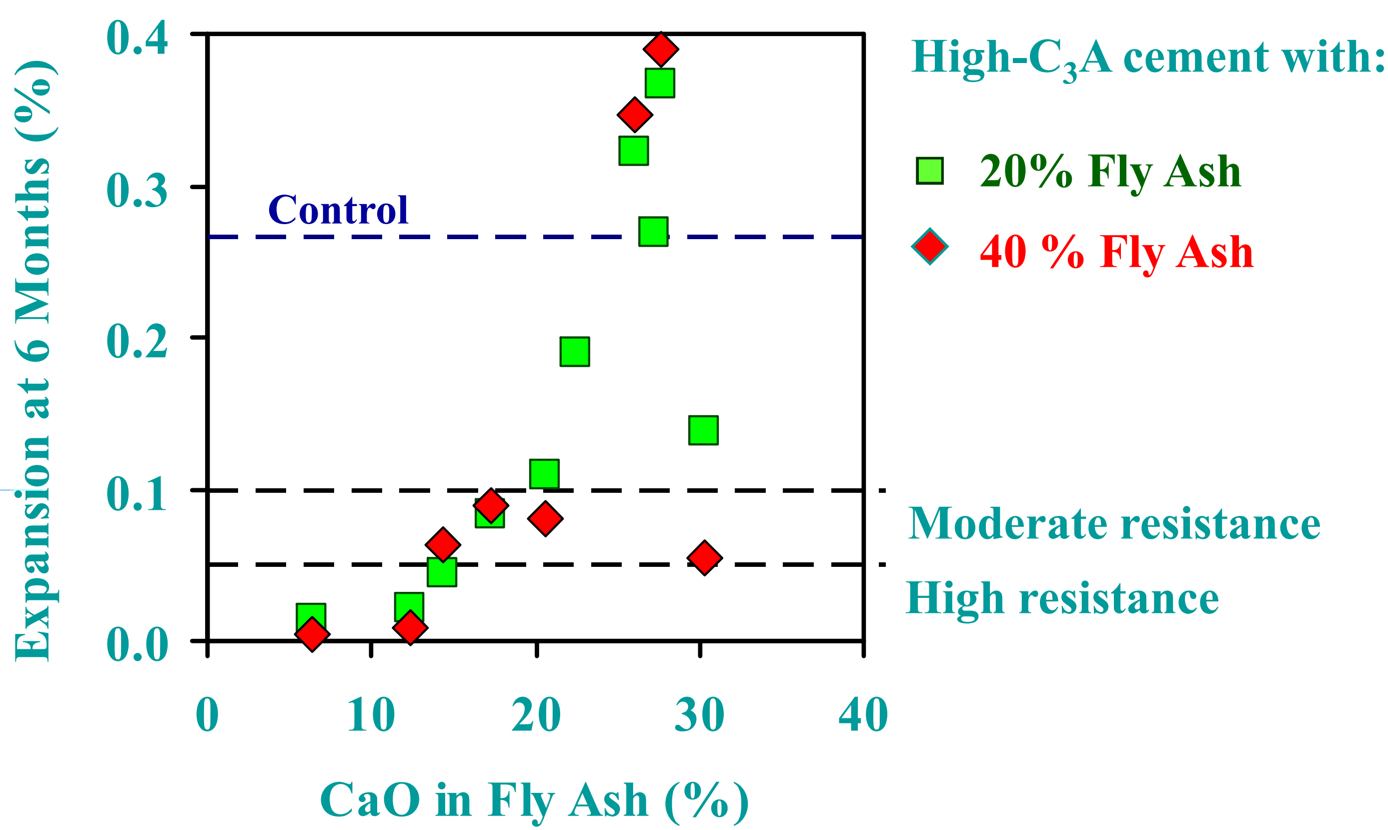
1. Aggregate/cementitious material = 2.75 & W/CM = 0.485
2. Mortars stored in limewater until a strength of 20 MPa is attained
3. Mortar bars (25 x 25 x 250 mm) then immersed in a 5% solution of sodium sulfate for 6 months or 1 year ~ length change monitored during storage



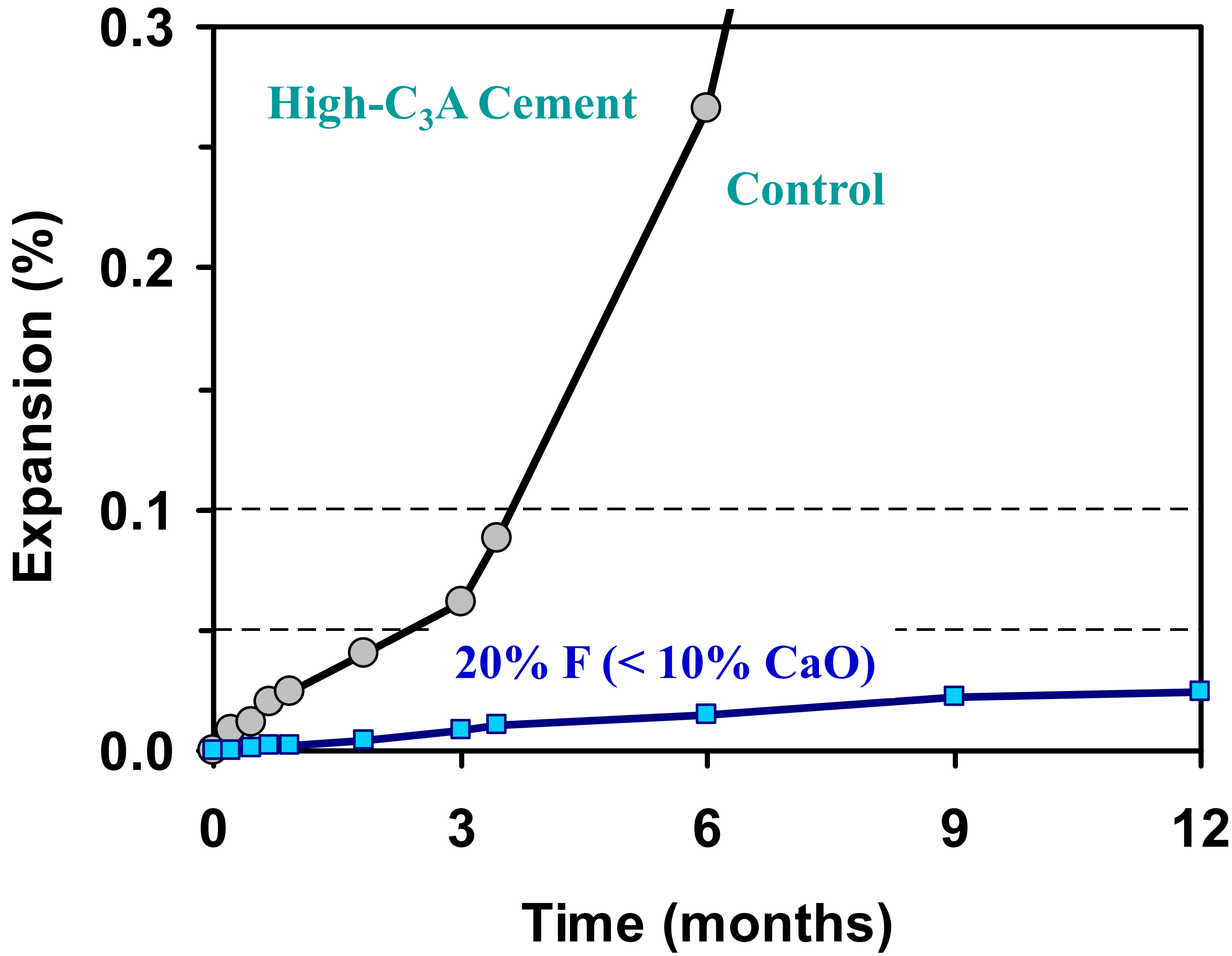
ASTM C1012 – Interpretation of Results

Material Specification	Sulfate Resistance	Maximum expansion (%)	
		6 Months	12 Months
ASTM C 618 Fly Ash & Pozzolans ASTM C 989 Slag	Moderate	0.10	-
	High	0.05	-
ASTM C 1240 Silica Fume	Moderate	0.10	-
	High	0.05	-
	Very High	-	0.05
ASTM C595 and C1157 Blended & Hydraulic Cements	Moderate	0.10	-
	High	0.05	0.10

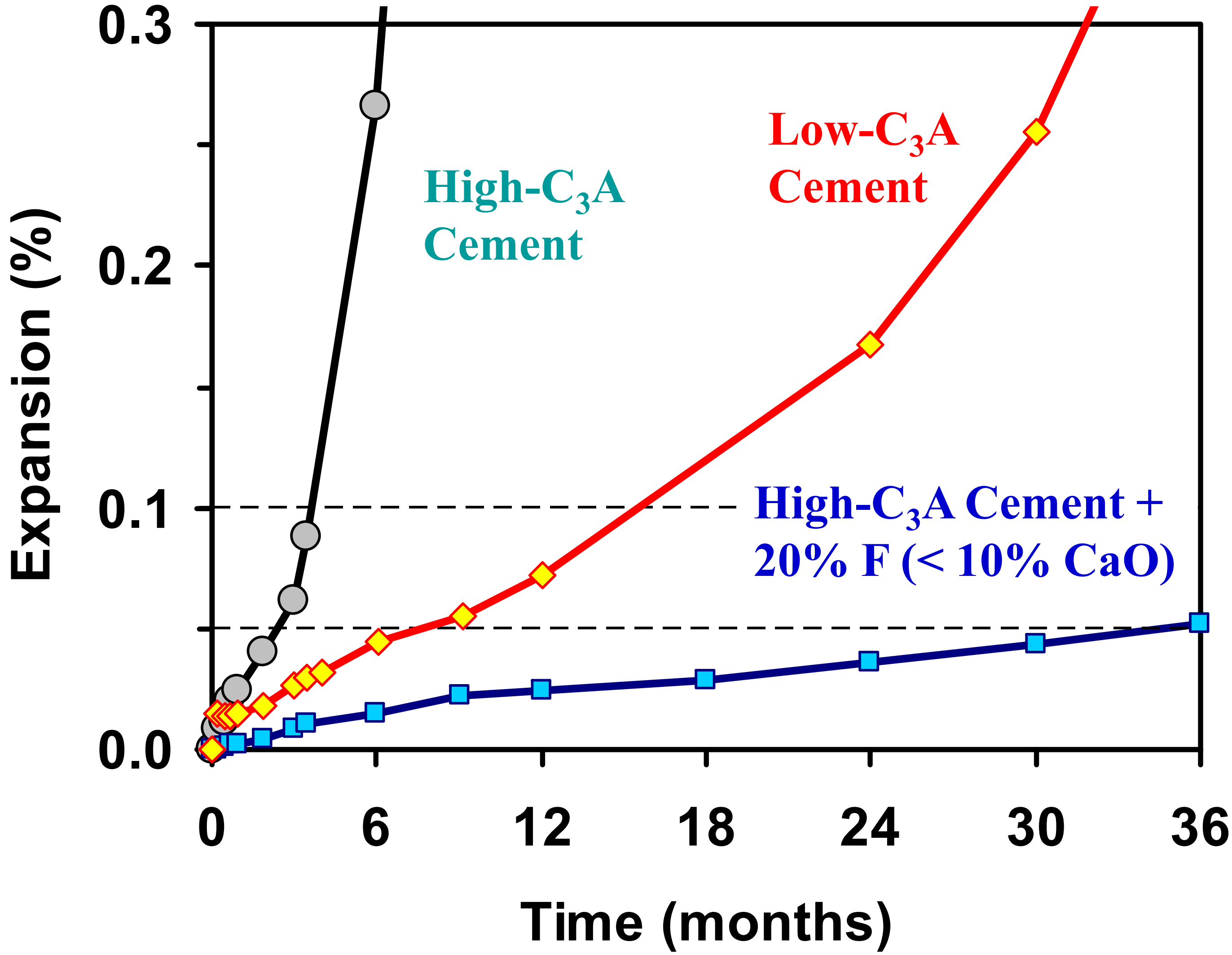
Effect of Fly Ash Composition



Effect of Low-Calcium Fly Ash



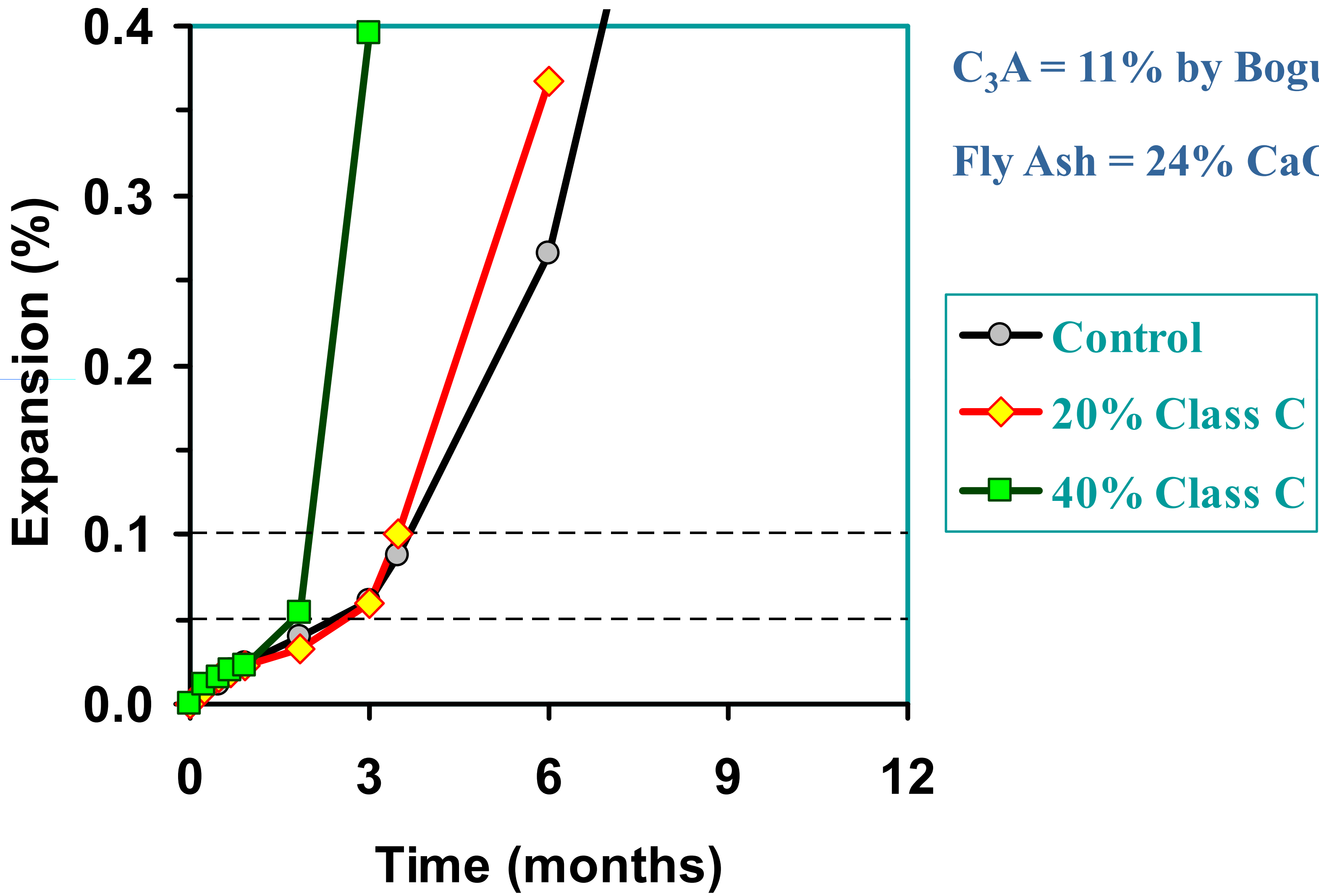
Effect of Low-Calcium Fly Ash



Mechanism of Improvement with Low-CaO Fly Ash

- Dilution of portland cement (C_3A and CH)
- Consumption of lime by pozzolanic reaction
- Increased resistance to SO_3 ingress/transport (lower permeability)

High-Calcium Fly Ash



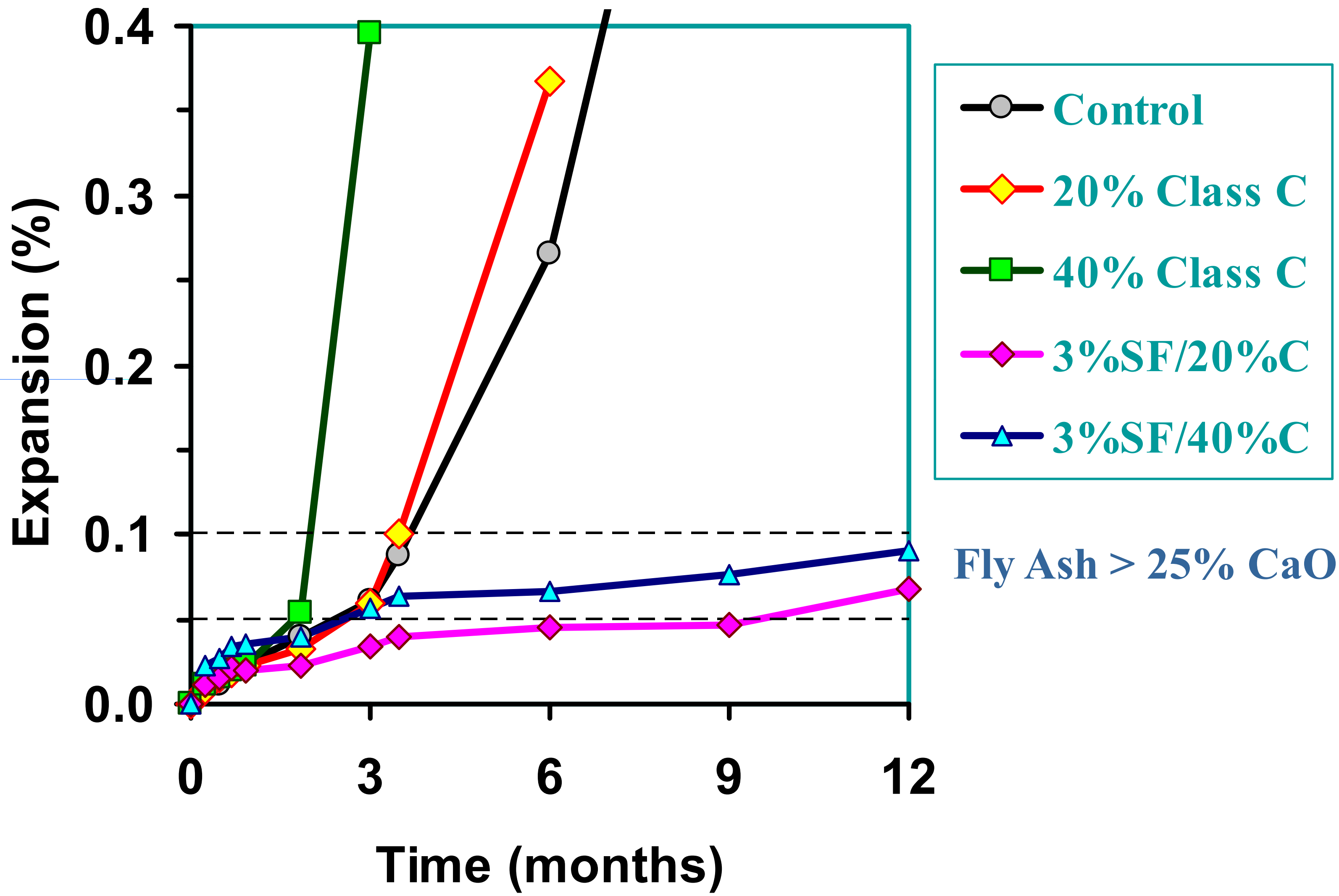
C_3A = 11% by Bogue

Fly Ash = 24% CaO

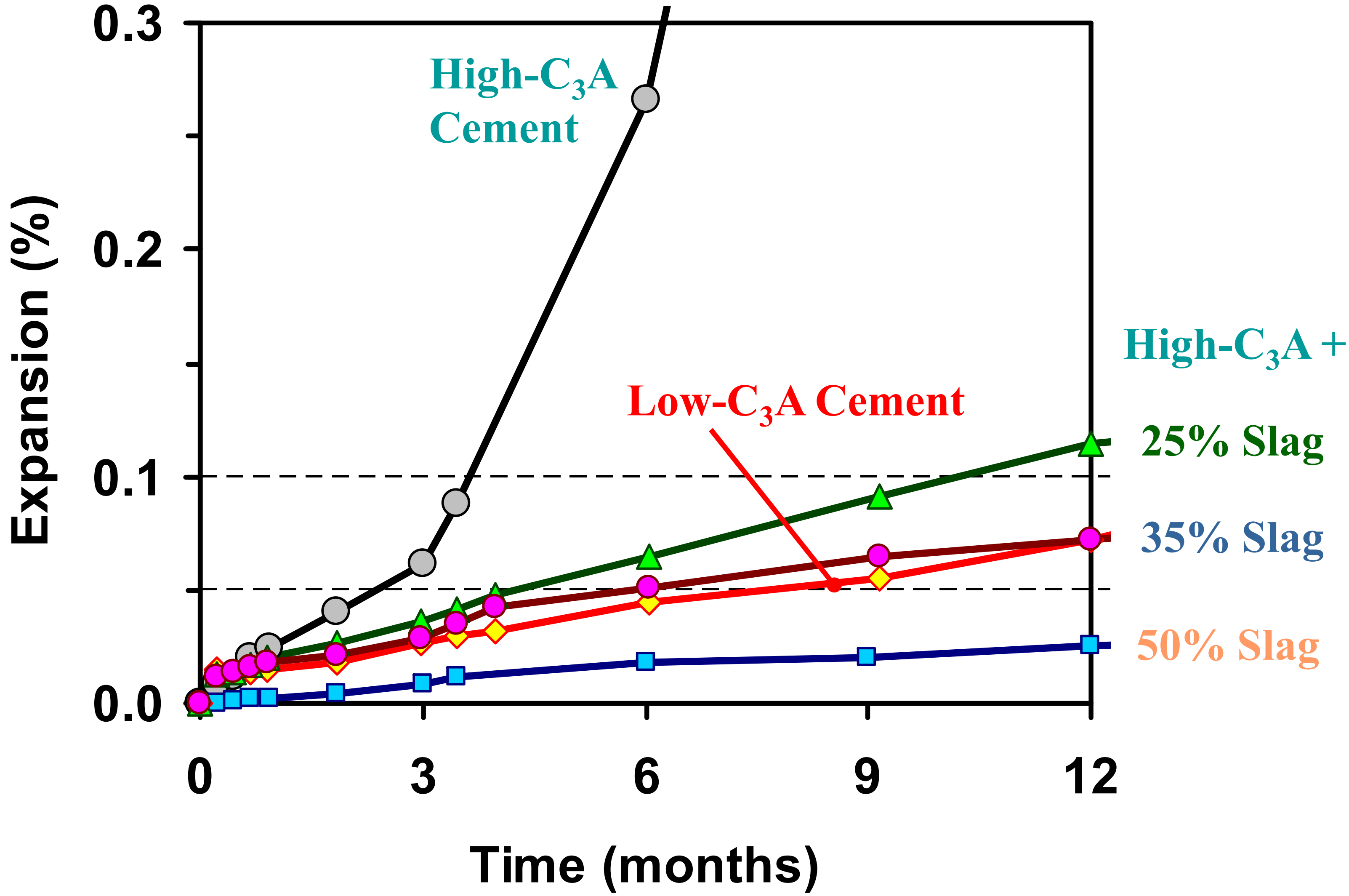
Mechanism of Reduced Resistance of High-CaO Fly Ash

- Contributes C_3A (also some CH and free lime)
- Lower consumption of lime due to reduced pozzolanicity
- Presence of reactive aluminates in glass phase

Sulfate Resistance with Ternary



Effect of Slag



Summary (Materials)

- Low C_3A cements minimize reactants
- Low permeability is more important
- SCMs can help
  - Proper dosage
  - Field history or testing
  - Curing

Code Requirements

BUILDING CODE REQUIREMENTS FOR
STRUCTURAL CONCRETE (A
COMMENTARY (ACI 3

REPORTED BY ACI COMMITTEE

ACI Committee 318
Structural Building Code

James R. Cagley
Chairman

Craig E. Barnes, Florian G. Barth, Roger J. Becker, Kenneth B. Bondy, John E. Breen, Anthony P. Chrest, W. Gene Corley, Robert A. Epifano, Catherine W. French, Luis E. Garcia, S. K. Ghosh, Hershell Gill, David P. Gustafson, James R. Harris, Neil M. Hawkins, C. Raymond Hays, Richard E. Holguin, Phillip J. Iverson, James O. Jirsa, Gary J. Klein, Cary S. Kopczynski, James Lefter, H. S. Lew, James G. MacGreg, John A. Martin, Jr., Leslie D. Martin, Robert F. Mast, Robert McCluer, Richard C. Meininge

Voting Subcommittee Members

Ronald A. Cook, Richard W. Furlong, William L. Gamble, Roger Green, Scott A. Greer, D. Kirk Harman, Terence C. Holland, Kenneth C. Hover, Michael E. Kreger, LeRoy A. Lutz, Joe Maffei, Steven L. McCabe, Gerard J. McGuire, Peter P. M. Meza, Denis Mitchell, Suzanne D. Nakaki, Randall W. Poston, Julio A., Gajana, John R, David F, Thoma

Consulting Members

Richard D. Gaynor, Jacob S. Grossman, John M. Hanson, Edward S. Hoffman, Francis J. Jacques[†], Alan H. Mattock

*Retired from committee before the final ballot.
[†]Deceased.

ACI 201.2R-01

Guide to Durable Concrete

Reported by ACI Committee 201

CONTENTS

Introduction, p. 201.2R-2

Chapter 1—Freezing and thawing, p. 201.2R-3

1.1—General

1.2—Mechanisms of frost action

ACI 349-01

Requirements for Nuclear Safety Related Concrete Structures (ACI 349-01)

Reported by ACI Committee 349

Charles A. Zalesiak
Chairman

Exposure Class

Designation: C 1580 – 05

Standard Test Method for
Water-Soluble Sulfate in Soil[1]

	Exposure class	Water-soluble sulfate in soil, % by mass	Dissolved sulfate in water, ppm
Not applicable	S0	$SO_4 < 0.10$	$SO_4 < 150$
Moderate*	S1	$0.10 < SO_4 < 0.20$	$150 < SO_4 < 1500$
Severe	S2	$0.20 < SO_4 < 2.00$	$1500 < SO_4 < 10,000$
Very severe	S3	$SO_4 > 2.00$	$SO_4 > 10,000$

*Includes seawater

ACI 318 Requirements: Cements

Class	C150	C595	C1157	Max w/cm	Min f'c (psi)	$CaCl_2$ Admixture
S0	NR	NR	NR	None	2500	NR
S1	II	IP(MS) IS(<70)(MS)	MS	0.5	4000	None
S2	V	IP(HS) IS(<70)(HS)	HS	0.45	4500	None
S3	V+SCM*	IP(HS)+SCM* IS(<70)HS+SCM*	HS+SCM	**0.45***	4500	None

*Specific SCM with service record or testing to improve sulfate resistance

ACI 318-08, PCA IS001, 2008

ACI 318: Alternative Materials

Exposure class	Maximum Expansion in C1012		
	6 months	12 months	18 months
S1	0.10%	—	—
S2	0.05%	0.10%*	—
S3	—	—	0.10%

*The 12-month expansion limit applies only when the measured expansion exceeds the 6-month maximum expansion limit.

Summary

- Sulfate attack is a family of deterioration mechanisms for concrete
- Risk based on environment
- Controlled by
  - Concrete permeability
  - Cement type, content
  - SCM type, content
  - Curing

Summary

- Keep water:cement ratio low to achieve low permeability
- Cure properly
- Use appropriate (testing!) pozzolans and slags
- Use sulfate resistant cements (Type II or V, MS or HS)

References

- PCA EB221, EB226
- PCA RD129
- PCA IS001
- PCA CD038
- ACI 318
- ACI 201
- ASTM C1012
- ASTM C150, C595, C1157

?