

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

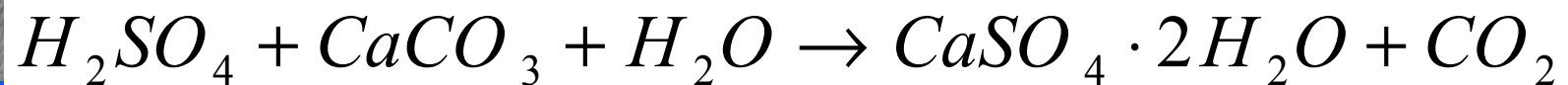
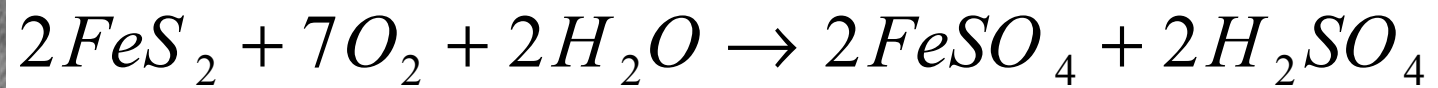
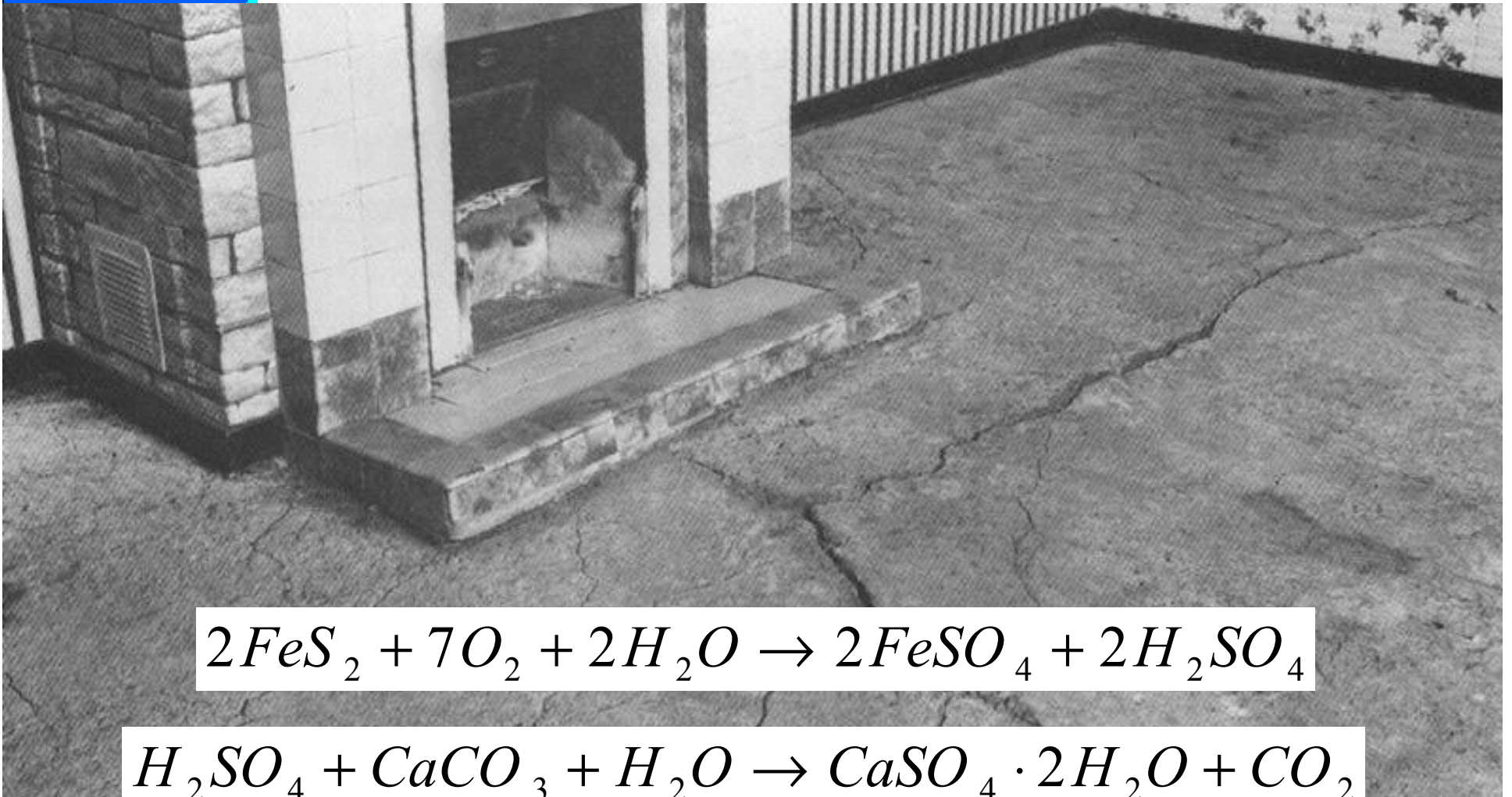
3. Thaumasite



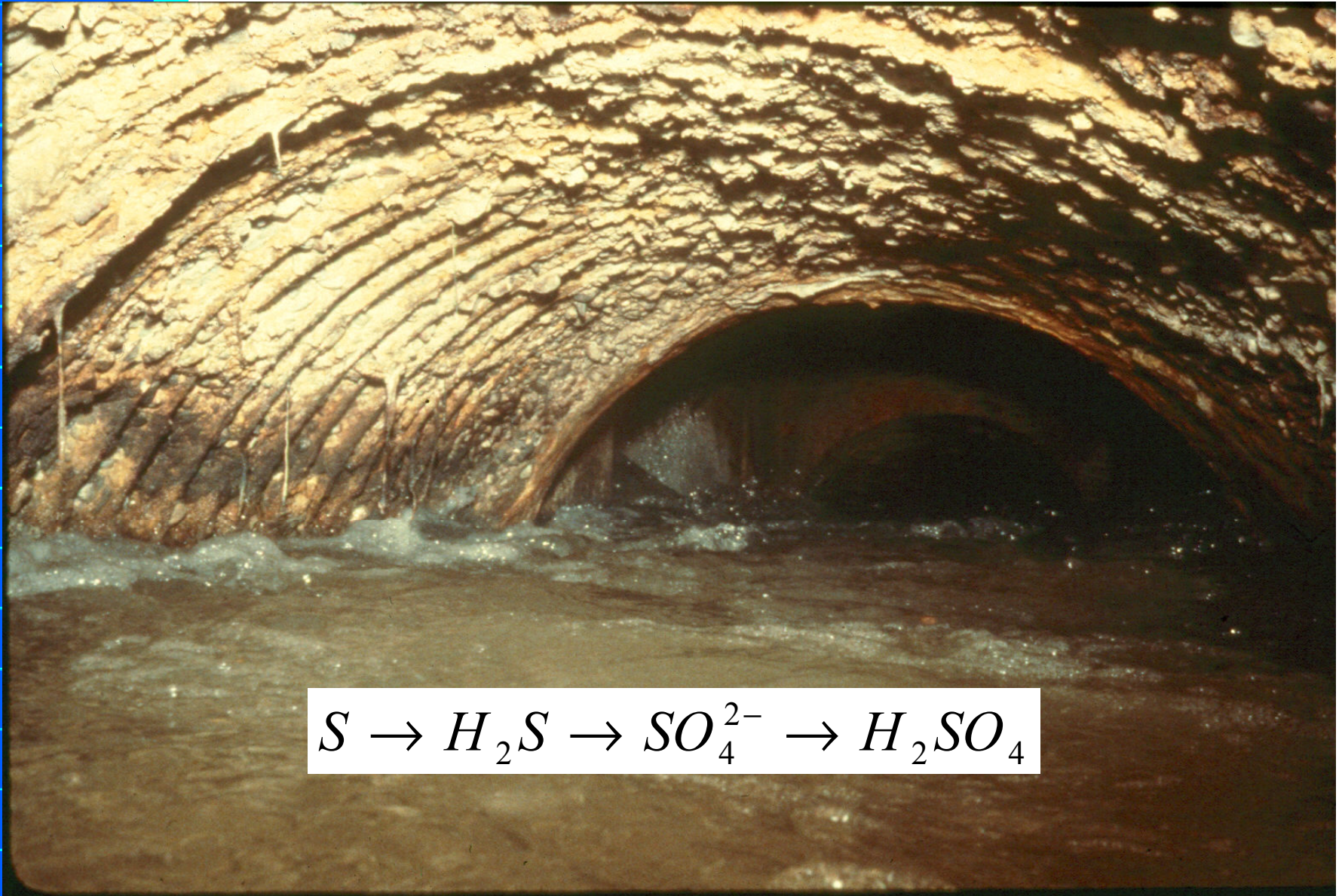
Classical Sulfate Attack



Slab on Pyritic Fill



Courtesy of BRE



Crown Sewer Corrosion

Courtesy David Fowler, 2001

Salt Crystallization (Physical Salt Attack)





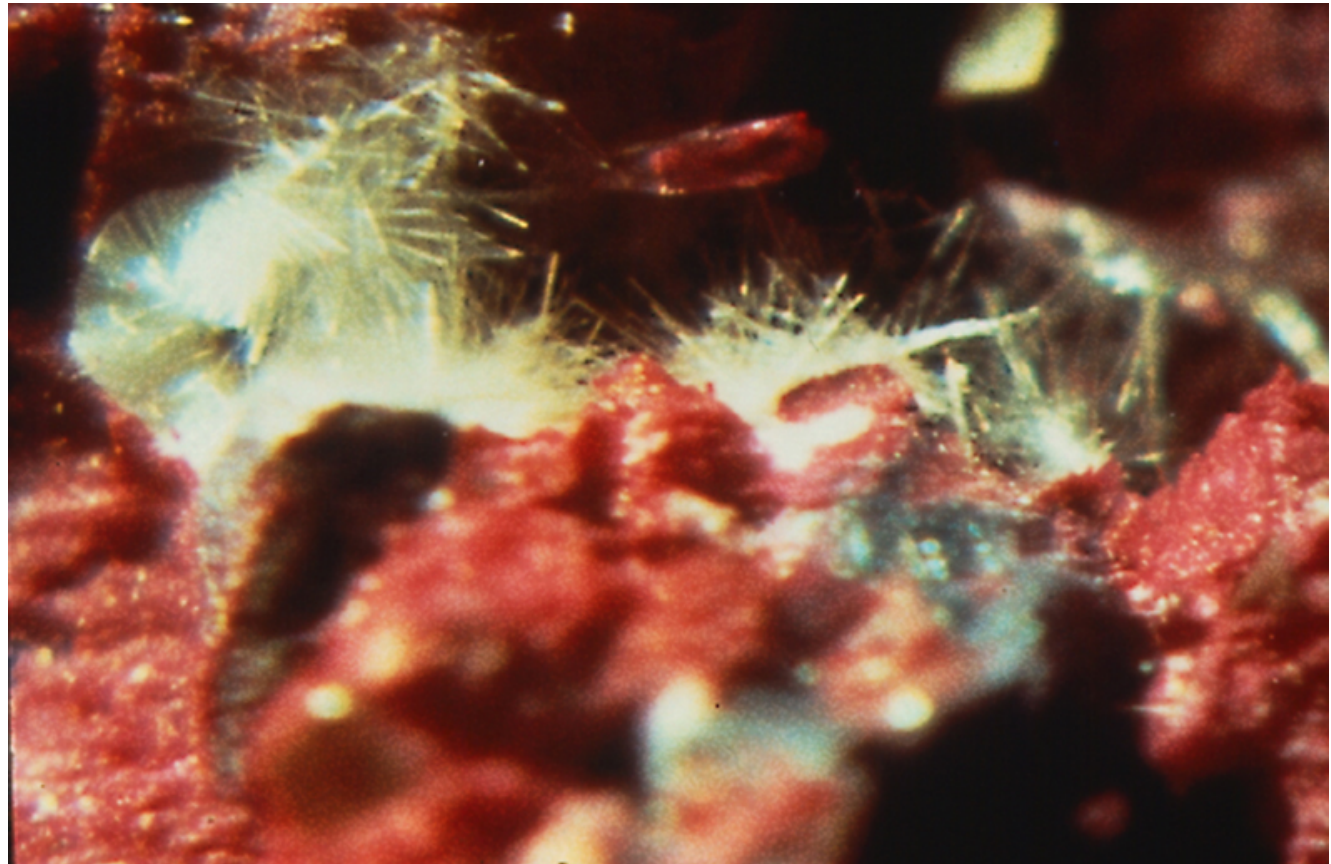
Internal Sulfate-Related Deterioration Issues

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



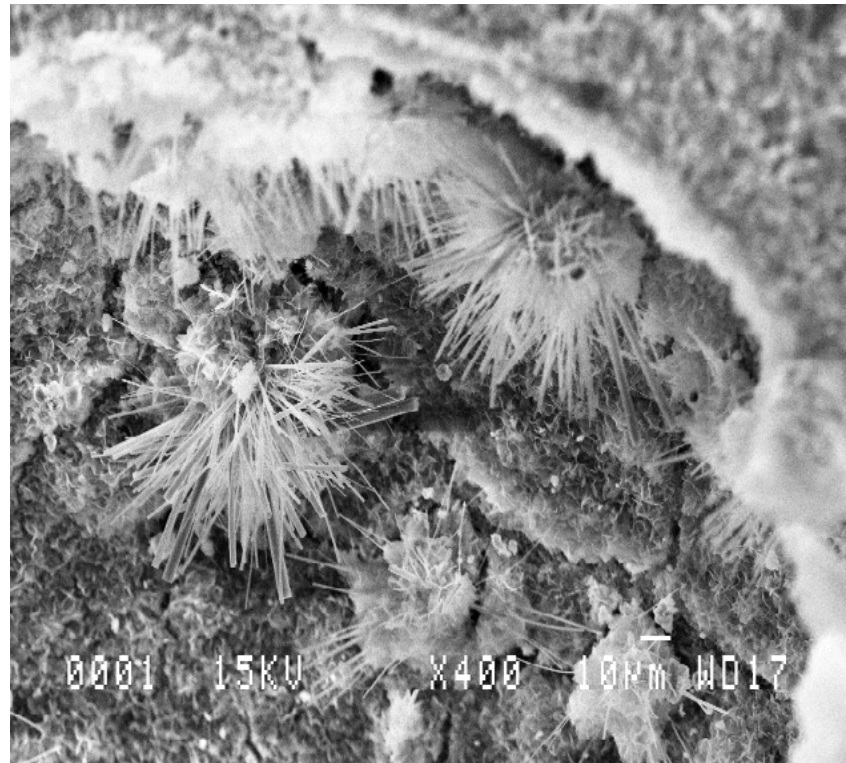
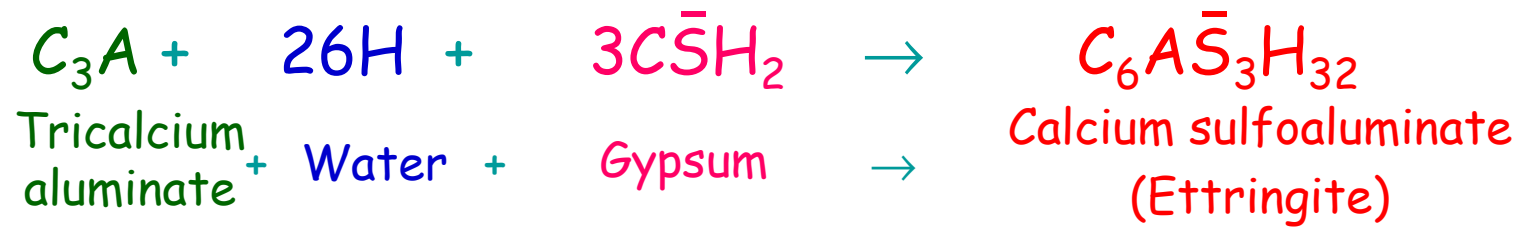
Secondary Ettringite



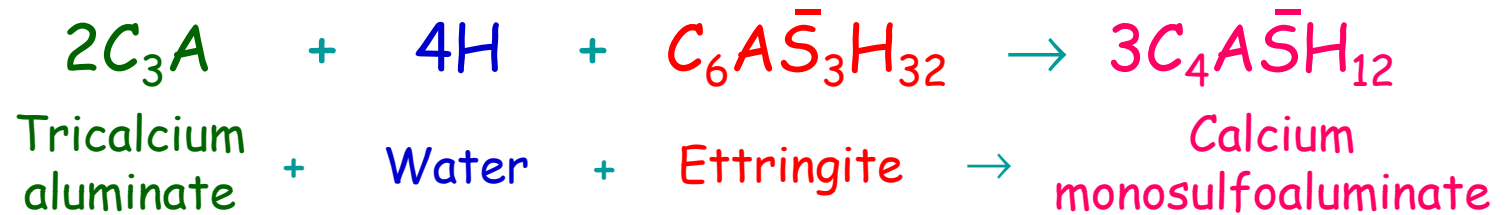
Mechanisms



Role of Ettringite in Cement Hydration



Role of Ettringite in Cement Hydration



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

+

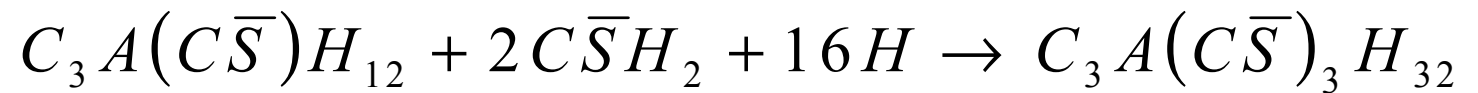
Calcium silicate
hydrate in concrete

→

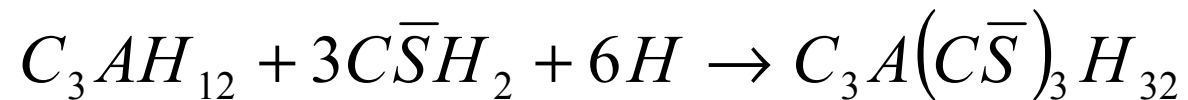
Gypsum +
brucite +
silica gel

Reactions accompanied by volumetric expansion of cementitious matrix!

Calcium Sulfate Attack

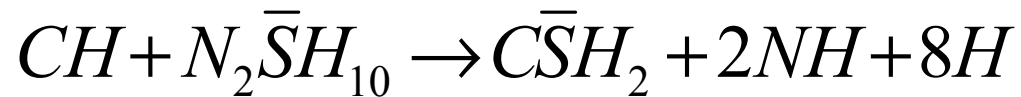


Calcium
Monosulfoaluminate + Gypsum + Water \rightarrow **Ettringite**

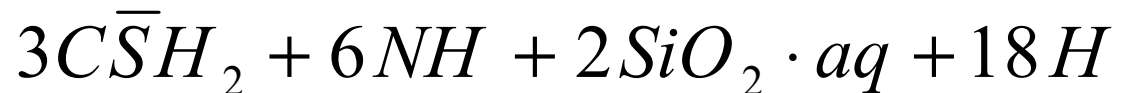
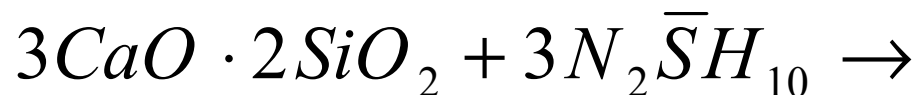
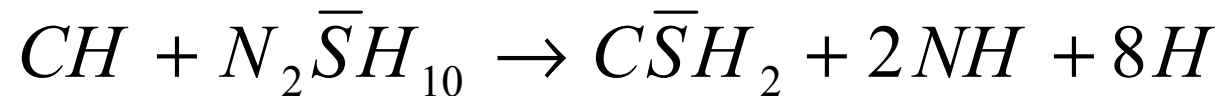


Calcium
Aluminate
Hydrate + Gypsum + Water \rightarrow **Ettringite**

Alkali Sulfate Attack

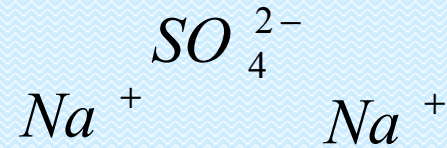
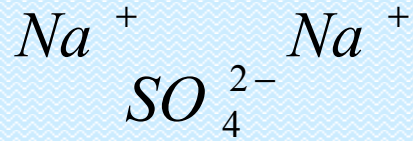


Alkali Sulfate Attack

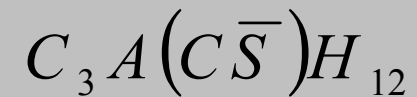


Zones of Attack in Portland Cement Mortar

Sulfate solution



Unreacted Zone

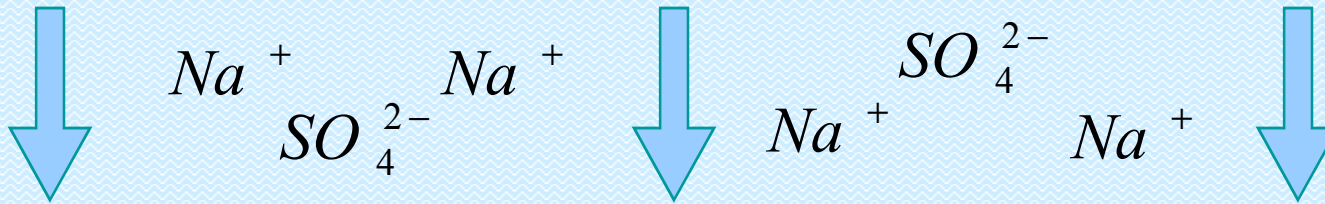


Portland Cement Mortar

After Gollop and Taylor 1999

Zones of Attack in Portland Cement Mortar

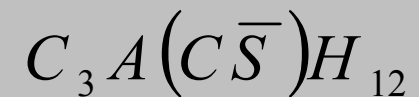
Sulfate solution



Ettringite formation



Unreacted Zone

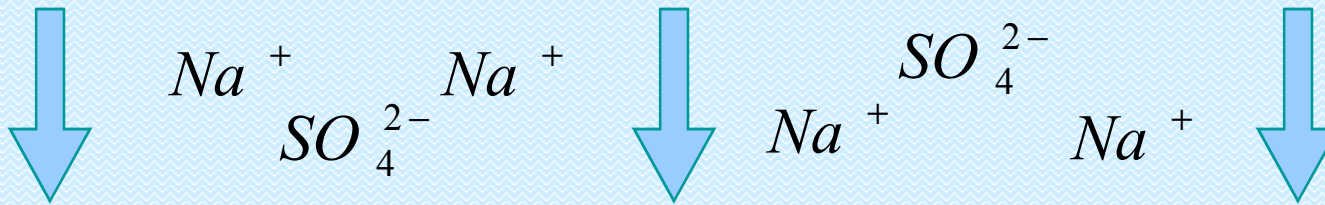


Portland Cement Mortar

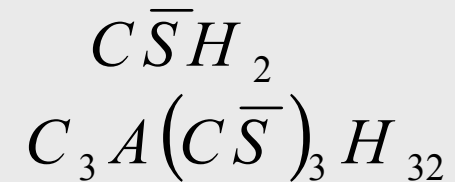
After Gollop and Taylor 1999

Zones of Attack in Portland Cement Mortar

Sulfate solution



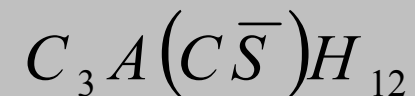
Gypsum formation & reduced $Ca(OH)_2$



Ettringite formation



Unreacted Zone

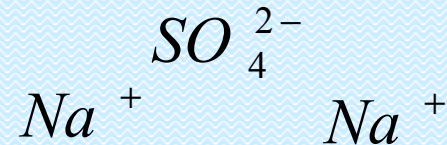
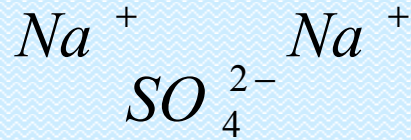


Portland Cement Mortar

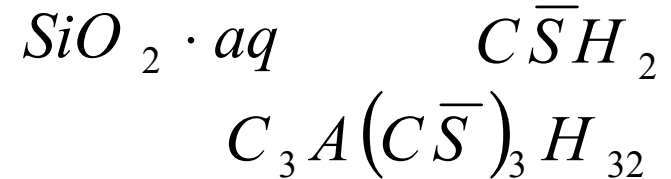
After Gollop and Taylor 1999

Zones of Attack in Portland Cement Mortar

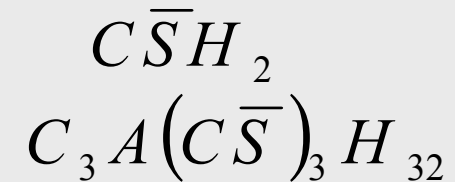
Sulfate solution



Gypsum formation &
decalcification of C-S-H



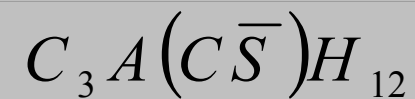
Gypsum formation & reduced $Ca(OH)_2$



Ettringite formation



Unreacted Zone



Portland Cement Mortar

After Gollop and Taylor 1999

Magnesium Sulfate Attack

Calcium
Silicate

+

Magnesium
Sulfate

→



Gypsum

+

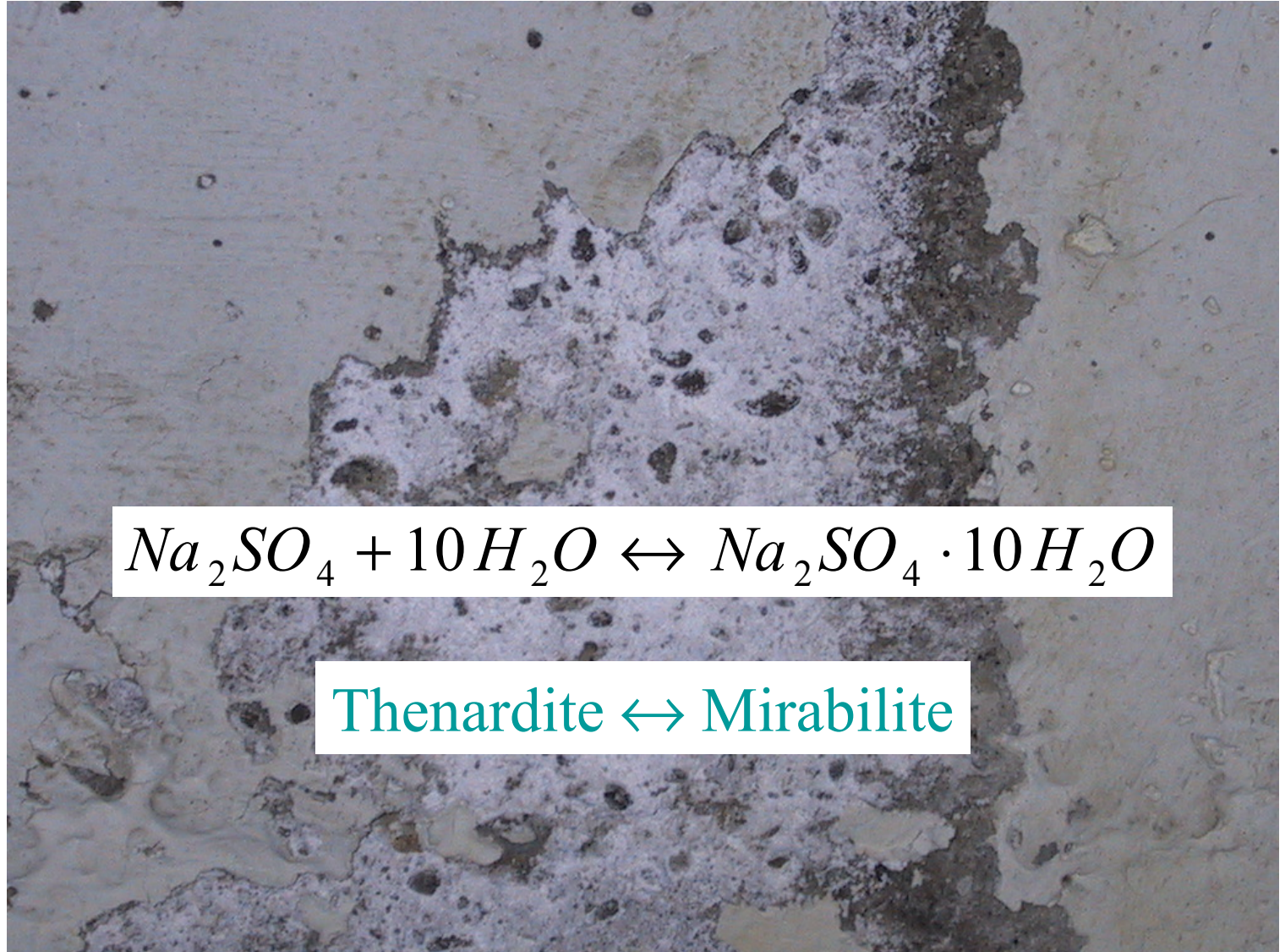
Magnesium
Hydroxide

+

Silica
Gel

Skalny et al, 2002

Physical Salt Attack



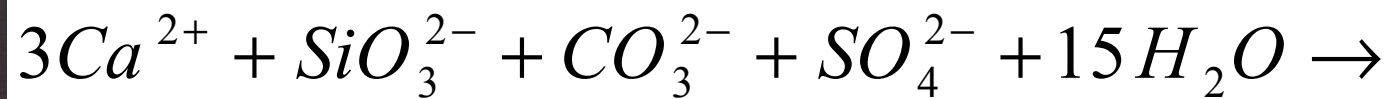


Thaumasite

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



Thaumasite Form of Sulfate Attack



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

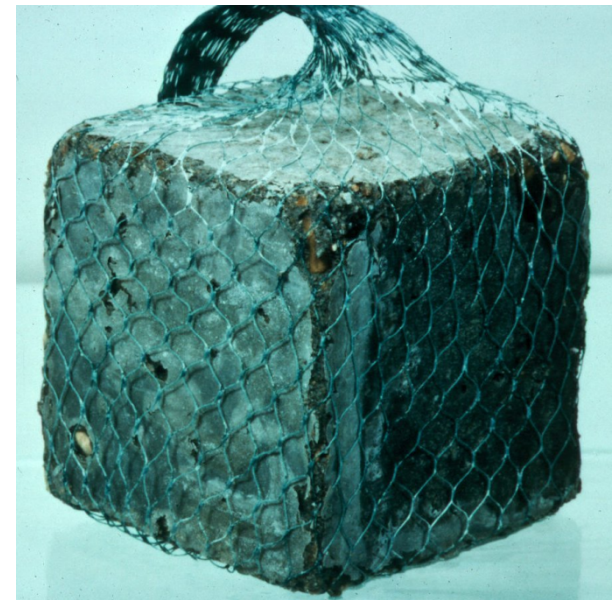
W/C = 0.50



After immersion in sulfate solution for 5 years

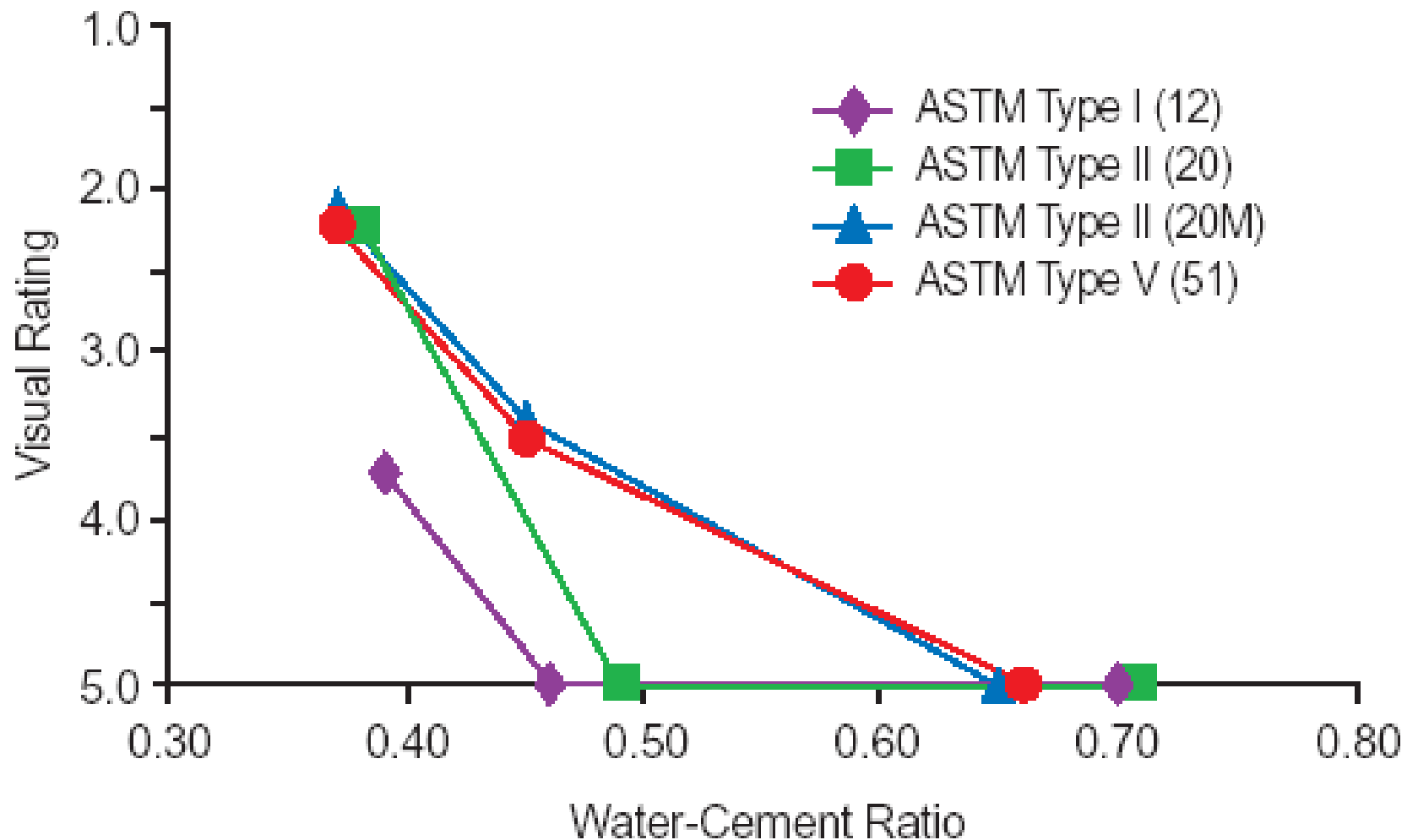
Type V - 1.2% C_3A

W/C = 0.51



Courtesy of BRE

Portland Cement Type



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



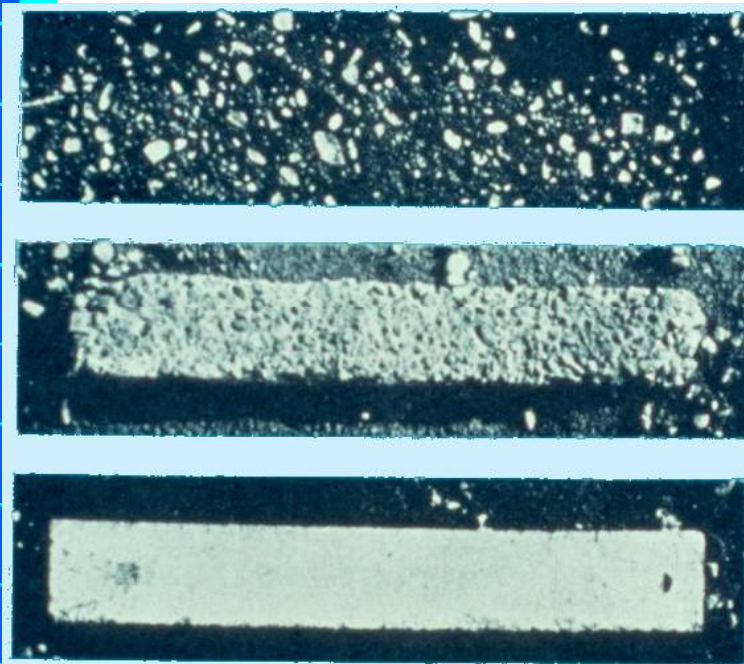
Type V Cement: W/C = 0.65



Type V Cement: W/C = 0.38

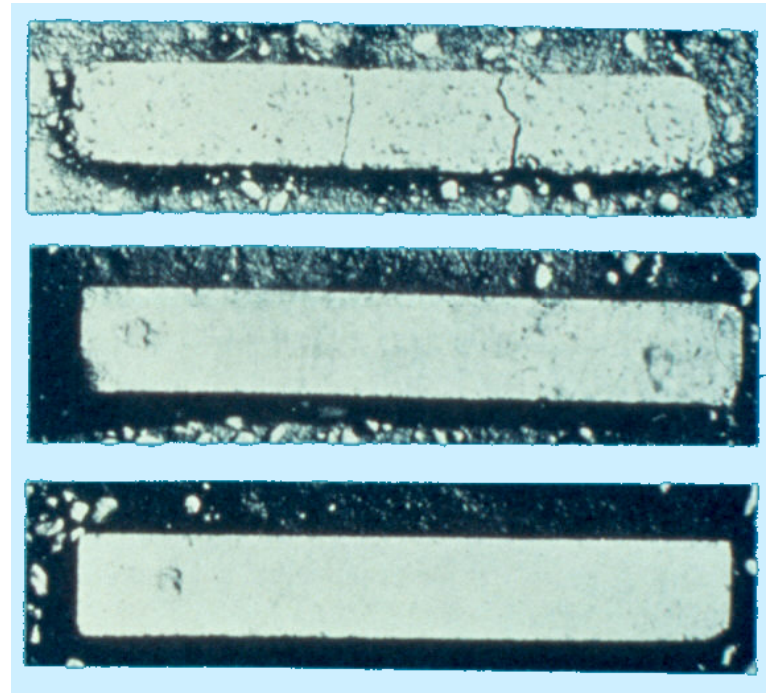
Entrained Air

Without entrained air

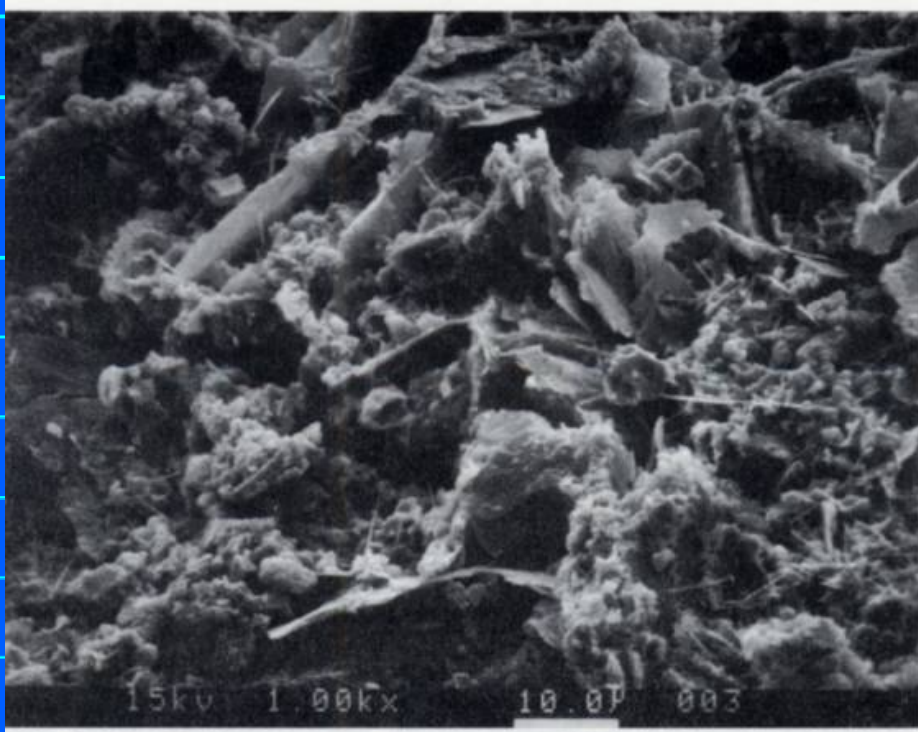


Increasing W/C

With entrained air



Use of Supplementary Cementing Materials



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

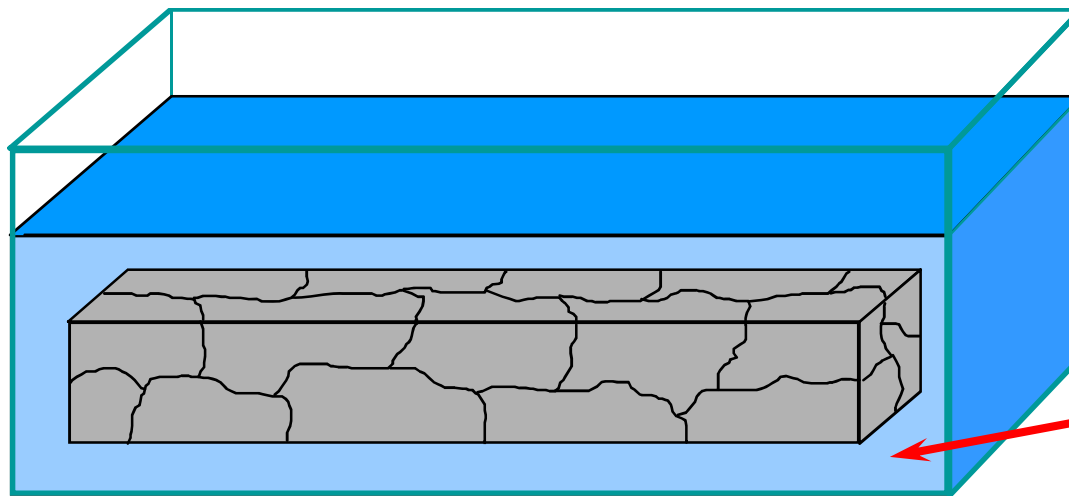
Not All SCMs!



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

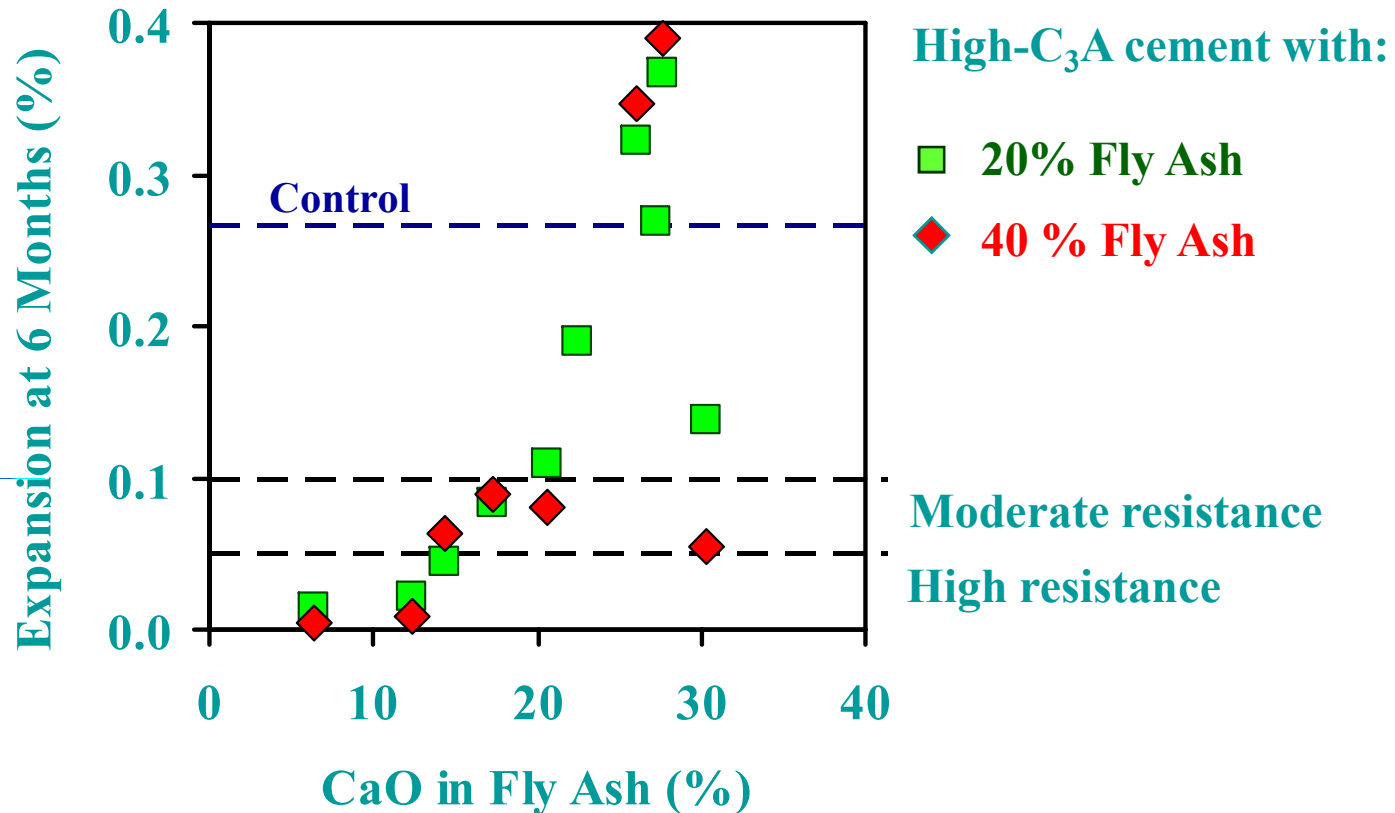


5%-Na₂SO₄ solution
Changed periodically

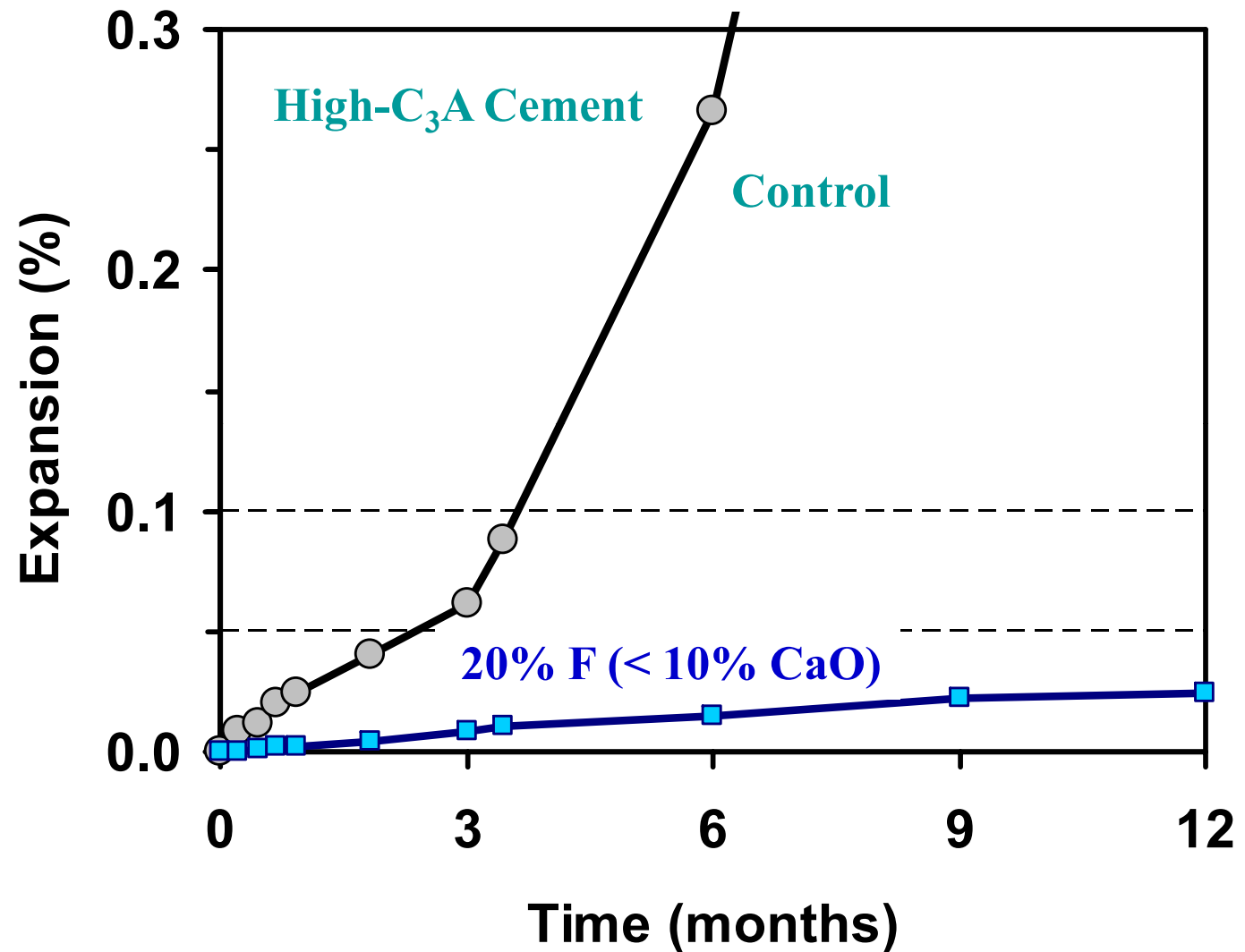
ASTM C1012 – Interpretation of Results

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

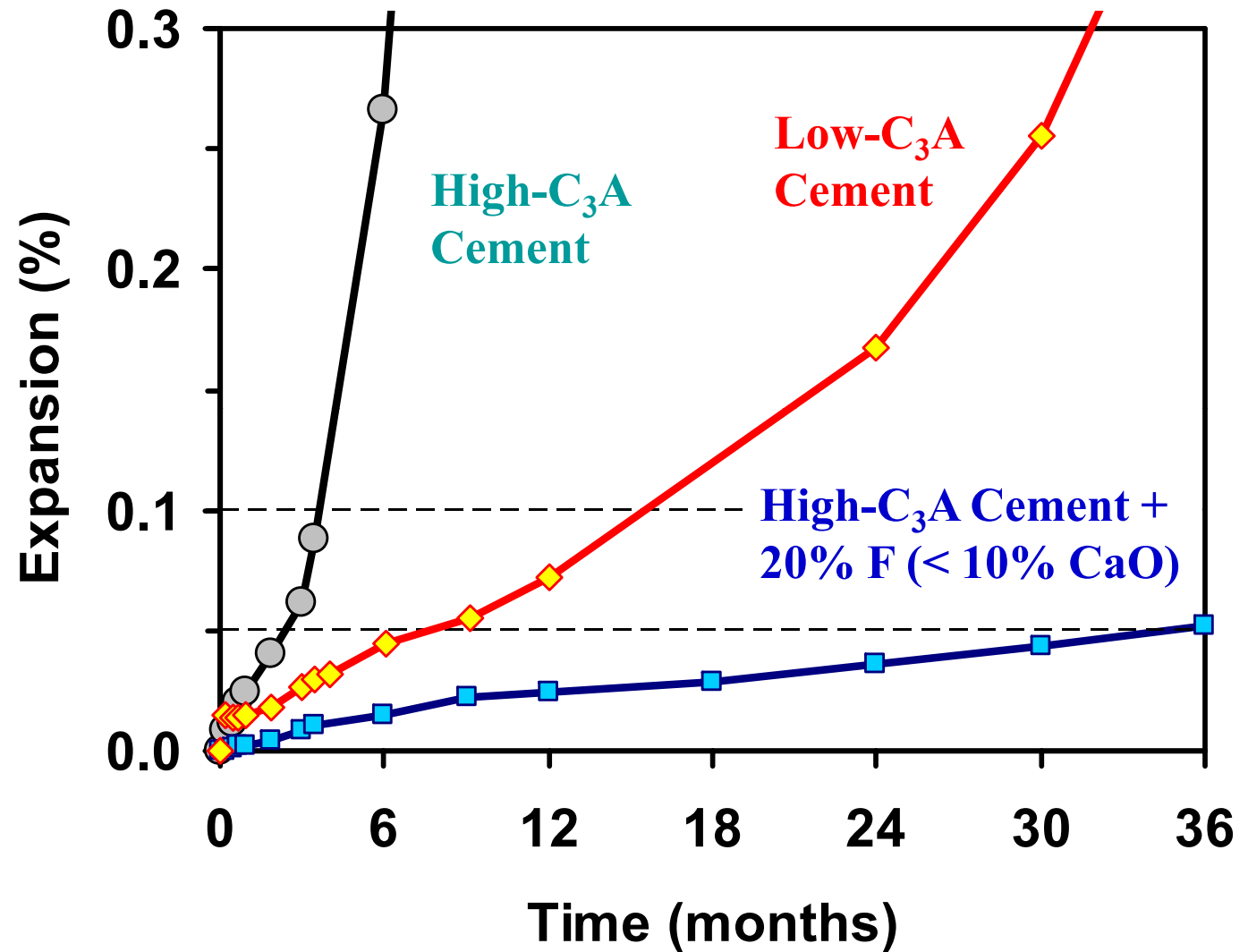
Effect of Fly Ash Composition



Effect of Low-Calcium Fly Ash



Effect of Low-Calcium Fly Ash

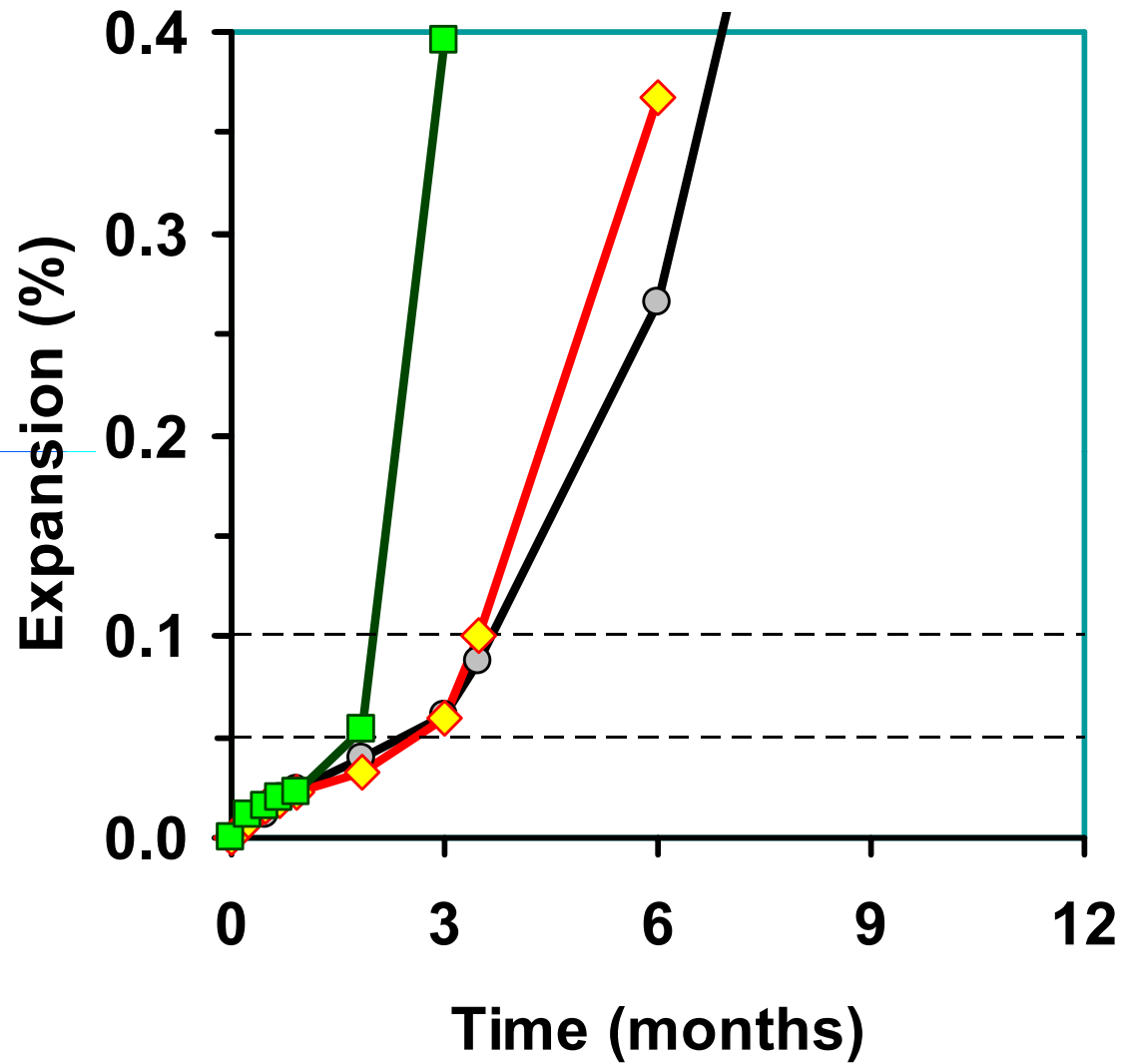




Mechanism of Improvement with Low-CaO Fly Ash

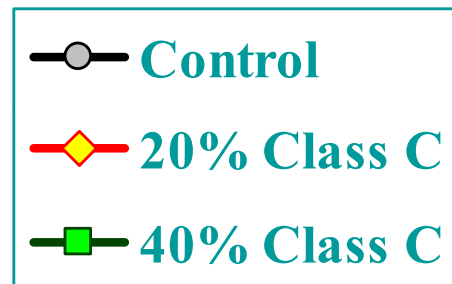
- Dilution of portland cement (C_3A and CH)
- Consumption of lime by pozzolanic reaction
- Increased resistance to SO_3 ingress/transport (lower permeability)

High-Calcium Fly Ash



$C_3A = 11\%$ by Bogue

Fly Ash = 24% CaO

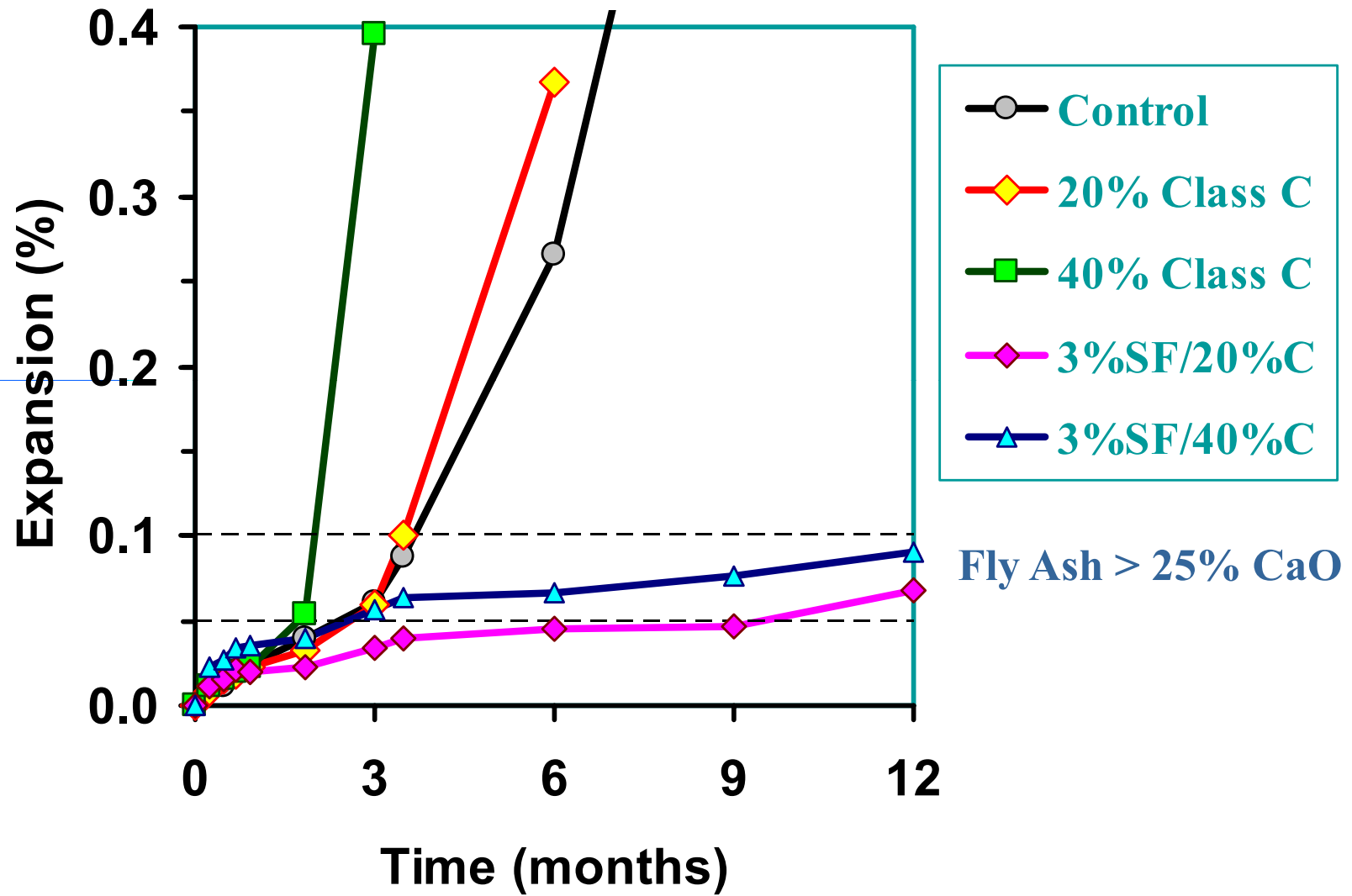




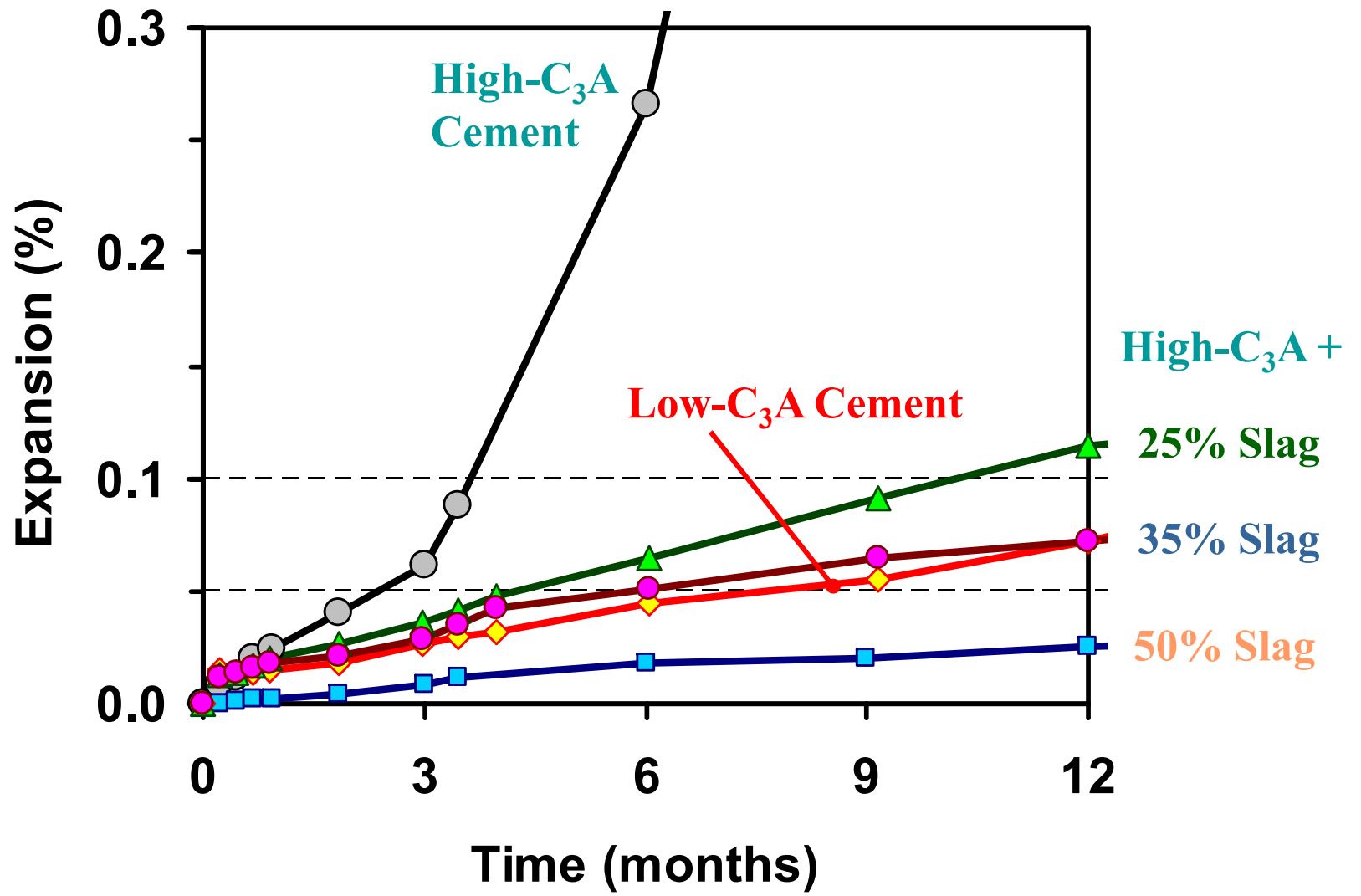
Mechanism of Reduced Resistance of High-CaO Fly Ash

- 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

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Guide to Durable Concrete

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This guide describes specific types of concrete deterioration. Each chapter contains a discussion of the mechanisms involved and the recommended requirements for individual components of concrete, quality considerations for concrete mixtures, construction procedures, and influence of the exposure environment. All important considerations to ensure concrete durability. Some guidance as to repair techniques is also provided.

This document contains substantial revisions to Section 2.2 (chemical sulfate attack) and also includes a new section on physical salt attack (Section 2.3). The remainder of this document is essentially identical to the previous "Guide to Durable Concrete." However, all remaining sections of this document are in the process of being revised and updated, and these revisions will be incorporated into the next published version of this guide.

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Both terms water-cement ratio and water-cementitious materials ratio are used in this document. Water-cement ratio is used (rather than the newer term, water-cementitious materials ratio) when the recommendations are based on data referring to water-cement ratio. If cementitious materials other than portland cement have been included in the concrete, judgment regarding required water-cement ratios have been based on the use of that ratio. This does not imply that new data demonstrating concrete performance developed using portland cement and other cementitious materials should not be referred to in terms of water-cementitious materials. Such information, if available, will be included in future versions.

Keywords: abrasion resistance; adhesives; adhesion; aggregate; air entrainment; alkali-aggregate reaction; bridge deck; carbonation; calcium chloride; cement paste; coating; corrosion; curing; fabric; demarcation; durability; epoxy resins; dry ash; mixture proportion; petrography; plastic; polymer; potassium; reinforced concrete; repair; resin; salt; sulfate; shrink resistance; spalling; strength; sulfate attack; water-cement ratio; water-cementitious materials ratio.

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 201.2R-2 (approved ACI 201.2R-2) (Reapproved 1997) and became effective September 6, 2003.

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201.2R-1

design and construction of concrete nuclear power plant and which have but does not cover concrete reactor structure (as defined by ACI-ASME

do include concrete structures inside and applied subject to agreement later Authority.

on the "Building Code Requirement for Structural Concrete (ACI 318-92)" and incorporates recent revisions of that standard, except for Chapter 12, which is based on ACI 318-99.

Keywords: admixtures; aggregates; anchorage (structural); beam-column frame; beams (support); building codes; cement; cold weather construction; columns (support); combined stress; composite construction (concrete and steel); composite construction (concrete to concrete); compressive strength; concrete construction; concrete; concrete slabs; construction joints; continuity (structural); cover;

cracking (fracturing); creep properties; curing; deep beams; deflection; drawings (drafting); earthquake resistant structures; edge beams; embedded service ducts; flexural strength; floors; folded plates; footings; formwork (construction); frames; hot weather construction; inspection; joints; loads (force); load tests (structural); mixing; mix proportioning; modulus of elasticity; moments; nuclear power plants; nuclear reactor containment; nuclear reactors; nuclear reactor safety; pipe columns; pipes (tube); placing; precast concrete; prestressed concrete; prestressing steel; quality control; reinforced concrete; reinforcing steel; roofs; safety; serviceability; shear strength; shearwalls; shells (structural forms); splices; specifications; splicing; strength; strength analysis; structural analysis; structural design; T-beams; temperature; torsion; walls; water; welded wire fabric.

ACI 349-01 supersedes ACI 349-97 and became effective February 1, 2001.

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ACI 349-01

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

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Exposure Class



Designation: C 1580 – 05

Standard Test Method for
Water-Soluble Sulfate in Soil¹

	Exposure class	Water-soluble sulfate in soil, % by mass	Dissolved sulfate in water, ppm
Not applicable	S0	$\text{SO}_4 < 0.10$	$\text{SO}_4 < 150$
Moderate*	S1	$0.10 < \text{SO}_4 < 0.20$	$150 < \text{SO}_4 < 1500$
Severe	S2	$0.20 < \text{SO}_4 < 2.00$	$1500 < \text{SO}_4 < 10,000$
Very severe	S3	$\text{SO}_4 > 2.00$	$\text{SO}_4 > 10,000$

*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	<u>0.45*</u>	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

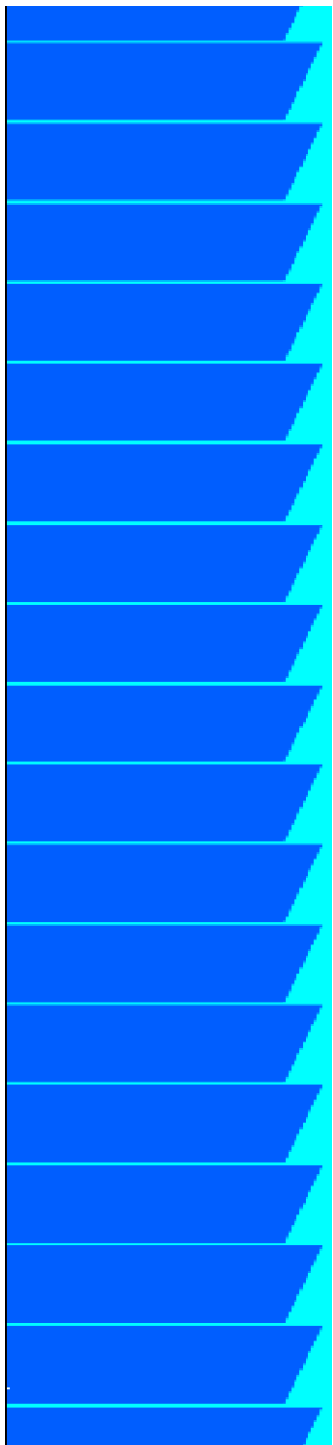
- Keep water:cement ratio low to achieve low permeability
- Cure properly
- Use appropriate (testing!) pozzolans and slags
- Use sulfate resistant cements (Type II or V, MS or HS)



References

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





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