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Physical Salt Attack on Concrete, Part 2

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Physical Sulfate Attack on Concrete

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Types of External Sulfate Attack

Being covered in new draft revision to C201.2R

- Ettringite, gypsum formation
- Magnesium sulfate attack
- Thaumasite sulfate attack (TSA)
- Physical sulfate attack (PSA)—a subset of physical salt attack involving Sodium Sulfate

Define the Exposure Conditions
(ACI 318-11 Classifications)

Severity of Potential Exposure	Water-Soluble Sulfate (SO_4) in Soil, % mass	Sulfate (SO_4) in water, ppm
S0	$SO_4 < 0.10$	$SO_4 < 150$
S1	$0.10 \le SO_4 \le 0.20$	$150 \le SO_4 \le 1500$ and Seawater
S2	$0.20 \le SO_4 \le 2.00$	$1500 \le SO_4 \le 10000$
S3	$SO_4 > 2.0$	$SO_4 > 10000$

But sulfates also become concentrated by evaporation so in arid regions, all concentrations can become a concern for PSA

US (ACI) and Canadian (CSA) Code Limits

Exposure	ACI 318-11		CSA A23.1-09		
	w/cm max.	cement type*	w/cm max.	min. strength (MPa)	cement type*
Class S1: moderate 150-1500mg/L SO_4	0.50	II, IP, IS	0.50	30	MS, MSb HS, HSb
Class S2: severe 1,500-10,000 mg/L	0.45	V	0.45	32	HS, HSb
Class S3: very severe >10,000 mg/L	0.45	V+ pozzolan	0.40	35	HS, HSb

* or alternative binders using ASTM C1012 performance limits

What part of 318 addresses Physical Sulfate Attack

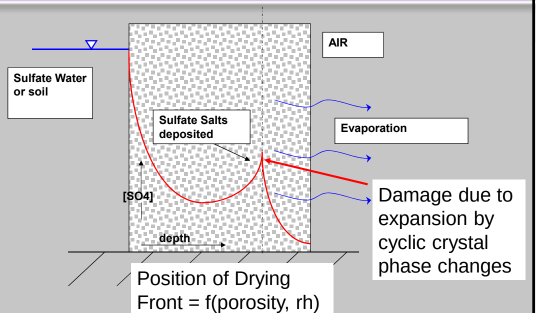
- Current standards do not address it by name but cover deal it by limiting the W/CM of concrete .
- At W/CM < 0.45, as in ACI 318, the rate of evaporative transport rapidly diminishes.
- At W/CM <0.40 it is better still (CSA A23.1)

PCA photo

Intro to Draft C201Chapter 6

1. Sulfate salts in solution enter the pore spaces of concrete and have to potential to chemically attack the cementing materials.
2. If evaporation takes place from a surface exposed to air, the sulfate ions can concentrate near that surface and increase the potential for causing deterioration.
3. In addition, especially in arid conditions, evaporation can precipitate sulfate salts which then may undergo subsequent phase changes due to fluctuations in temperature and relative humidity resulting in expansive cracking and spalling, referred to as physical sulfate attack.

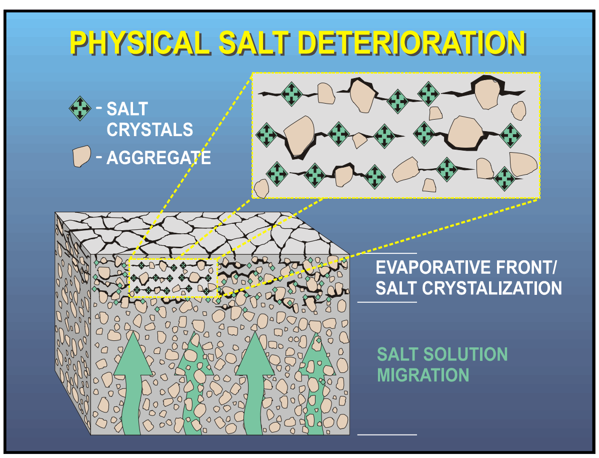
Evaporative Transport (Wick Action)



Mechanism of Physical Sulfate Attack

Folliard and Sandberg (1994), Haynes et al (1996)

1. Groundwater enters the concrete by capillary action and diffusion.
2. When pore water evaporates from above-ground concrete surfaces, the salt concentrates until it crystallizes, sometimes generating pressures large enough to cause cracking.
3. Changes in ambient temperature and relative humidity cause some salts to undergo cycles of dissolution and crystallization, or hydration-dehydration.
4. When crystallization or hydration is accompanied by volumetric expansion, repeated cycles can cause deterioration of concrete similar to that caused by cycles of freezing and thawing.



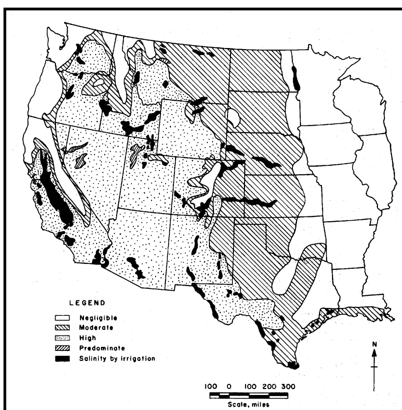


FIGURE 2. - Map of Alkali and High Salinity Soils in Western United States (2).

From ACI 201.2R

Sulfate attack is a particular problem in arid areas, such as the northern Great Plains and parts of the western United States, the prairie provinces of Canada and in the Middle East

USBR soils map, where alkalinity = alkali sulfates

T. Dolen

Sulfate-Containing Evaporite Minerals and their Formulas

List from ACI 201.2R

Mineral Name	Chemical Formula
anhydrite	$CaSO_4$
aphthtalite	$K_2SO_4 \cdot (Na,K)_2SO_4$
arcanite	K_2SO_4
bassinite	$CaSO_4 \cdot ½H_2O$
bloedite	$NaMg(SO_4)_2 \cdot 4H_2O$
epsomite	$MgSO_4 \cdot 4H_2O$
glauberite	$Na_2Ca(SO_4)_2$
gypsum	$CaSO_4 \cdot 2H_2O$
kieserite	$MgSO_4 \cdot H_2O$
mirabilite	$\mathbf{Na_2SO_4 \cdot 10H_2O}$
syngenite	$CaSO_4 \cdot K_2SO_4 \cdot H_2O$
thenardite	$\mathbf{Na_2SO_4}$
vanhoffite	$MgSO_4 \cdot 3Na_2SO_4$

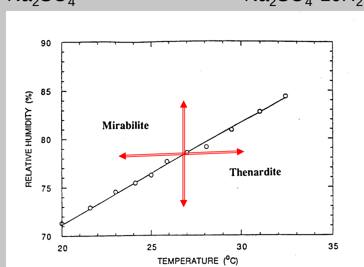
The 2 of primary concern for PSA are the sodium sulfates

Sodium Sulfate Salts

- The most common and most severe type of physical salt attack is caused by sodium sulfate salts (Folliard and Sandberg 1994, Scherer 2004).
- The changes in temperature and relative humidity can cause alternate cycles of dissolution and crystallization of sodium sulfate salts, resulting in phase changes between anhydrous sodium sulfate (thenardite, Na2SO4) and decahydrate sodium sulfate (mirabilite, Na2SO4 · 10H2O).
- Under field conditions, due to changes in ambient temperature and relative humidity, these cycles can occur several times a day.

Eg. Phase Changes in Sodium Sulfate

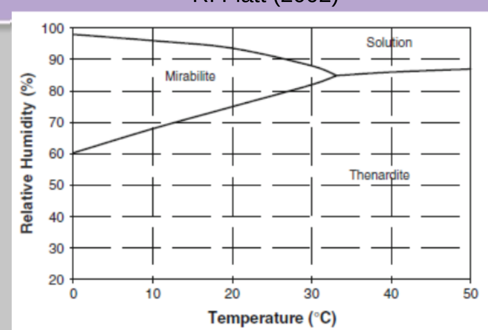
Thenardite Na_2SO_4 ↔ Mirabilite $Na_2SO_4 \cdot 10H_2O$



Sandberg & Folliard, 1994

Larger range of Temperature and RH

R. Flatt (2002)



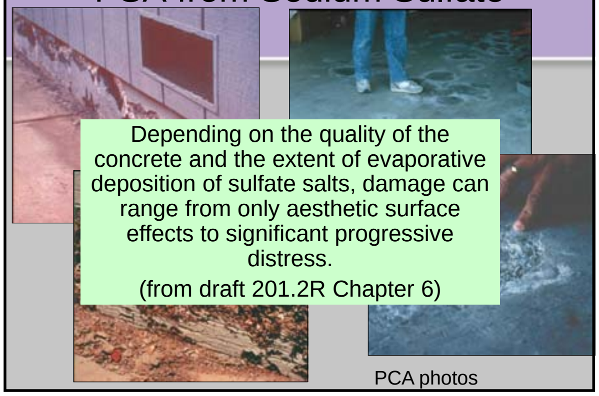
Crystallization Pressures

Salt	Formula	Pressure at 0°C
Gypsum	$CaSO_4 \cdot 2H_2O$	28 MPa
Halite	NaCl	56 MPa
Mirabilite	$Na_2SO_4 \cdot 10H_2O$	7.6 MPa
Thenardite	Na_2SO_4	30 MPa

PSA from Sodium Sulfate

PCA photos

PSA from Sodium Sulfate

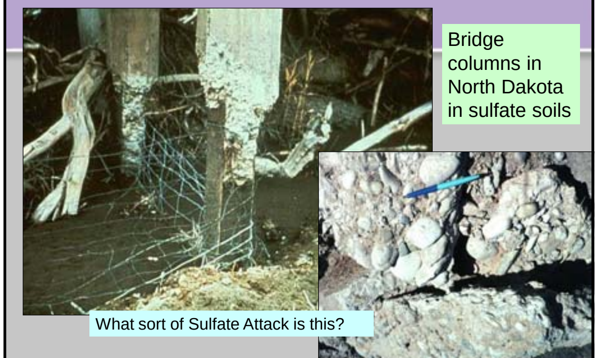


Depending on the quality of the concrete and the extent of evaporative deposition of sulfate salts, damage can range from only aesthetic surface effects to significant progressive distress.

(from draft 201.2R Chapter 6)

PCA photos

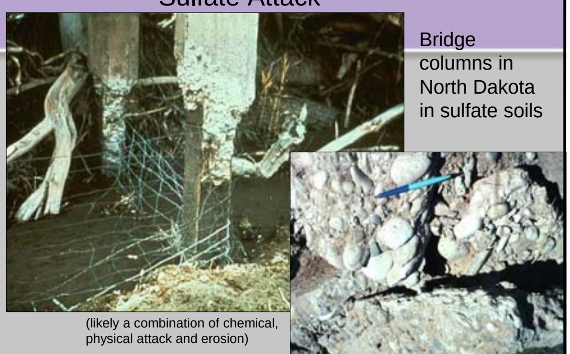
Sulfate Resistance



Bridge columns in North Dakota in sulfate soils

What sort of Sulfate Attack is this?

Combined Physical and Chemical Sulfate Attack



Bridge columns in North Dakota in sulfate soils

(likely a combination of chemical, physical attack and erosion)

S. Dakota US 18-43 Bridge Piers

Built 1960's, inspected in 2003.

In Severe Sulfate soils and low humidity

Piers were jacketed in 2004 due to damage

D. Johnston

Early Research on Sulfate Attack

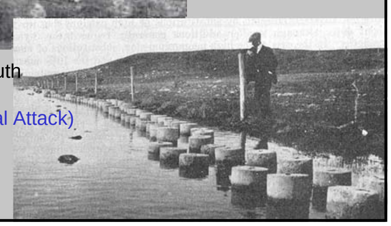
- Much of the early research did not distinguish the difference and simply referred to both chemical and physical sulfate attack as simply "sulfate attack".
- But many of the early exposure programs used partial immersion tests or wet/dry cycles, thus combining both types of attack.

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

Montrose, Colorado

2000 cylinders,

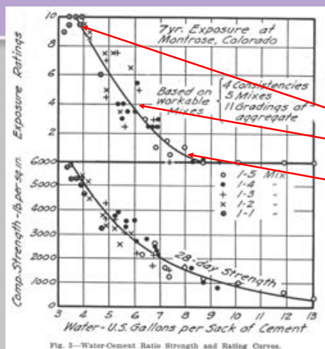
10 in. x 24in. Semi-immersed



Medicine Lake, South Dakota

(Physical and Chemical Attack)

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



Montrose, Colorado

After 7 Years Exposure

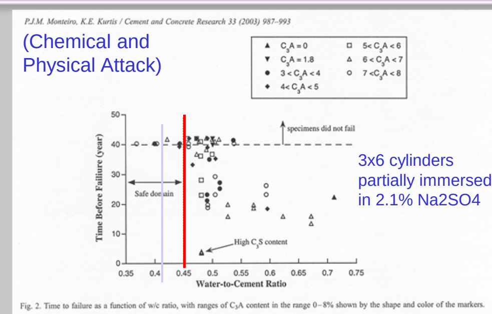
4 gal./sack = 0.36 W/C

6 gal./sack = 0.55 W/C

8 gal./sack = 0.73 W/C

All concretes with W/C > 0.45 were damaged

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

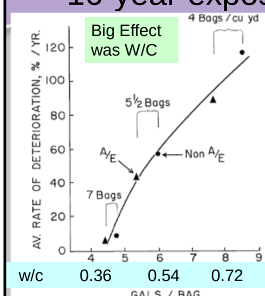


Monteiro and Kurtis, 2003

PCA Exposure Site, Sacramento

- Several long-term studies were done using partial immersion and W/D cycles in soil saturated with Na_2SO_4.
- G. Verbeck, 1968: 10% sodium sulfate
- D. Stark, 1982, 1990, 2002: 6.5% sodium sulfate

G. Verbeck 1968
16-year exposure (PCA RD227)



EFFECT OF CEMENT CONTENT AND AIR ENTRAINMENT ON DETERIORATION OF CONCRETES EXPOSED TO SULPHATE SOIL
(basin 1)

Cement Type	Deterioration (% per yr) 4 bags	5½ bags	7 bags
I—non-A/E	117	56	8
I—A/E	88	45	6

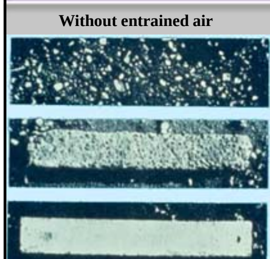
AE- Mixes had reduced rates of deterioration (f'c, E, visual) but this was attributed to reduced w/c.

EFFECT OF CEMENT TYPE, CEMENT CONTENT, AND AIR ENTRAINMENT ON DETERIORATION IN SULPHATE SOIL
(basin 1, 16 years)

Cement Type	No.	Av. C_3A (%)	Deterioration (% per yr) 5½ bags	7 bags
II non-A/E	5	3.72	1.8	0.5
II—A/E	5	3.72	0.8	0.3
V—non-A/E	5	1.54	1.0	0.6
V—A/E	5	1.54	0.5	0.4

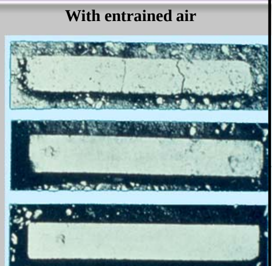
Concrete with Type II Moderate Sulfate Resisting Cement after 5 years exposure on-grade in sulfate soil in California (Chemical + Physical Attack)

Without entrained air



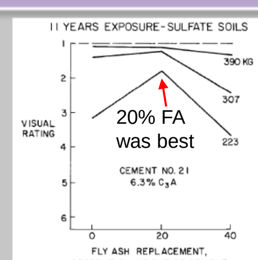
Increasing W/C

With entrained air



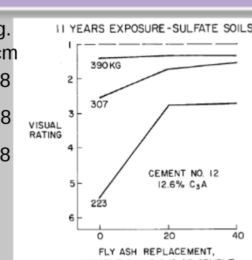
PCA

Old PCA Sacramento Site
D. Stark 1982 (PCA RD086)



Effect of Class F Fly Ash on Type II Cement

Avg. w/cm
0.38
0.48
0.68



Effect of Class F Fly Ash on Type I Cement

PSA: Effect of W/C Ratio

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

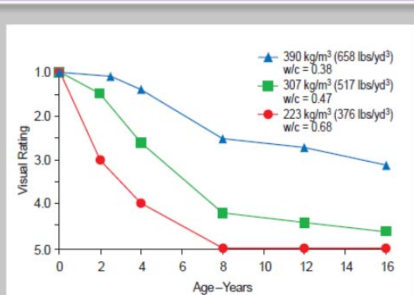
Rating of Concrete: 2 @ 16 yrs
Type V Cement
W/C = 0.39

D. Stark PCA, Sacramento Site 1990

D. Stark 2002 PCA Sacramento (PCA RD129)

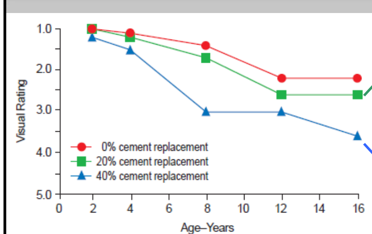
- 16 years of severe outdoor exposure consisting of partial immersion in a 6.5% sodium sulfate concentration (65,000 ppm) with alternate wetting and drying.
- 3 concrete beams – 152x152x762 mm (6x6x30 in.)

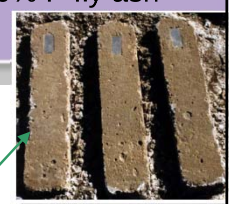
D. Stark 2002: Visual Ratings over 16 Years for w/c = 0.38, 0.47. 0.68



PCA RD129

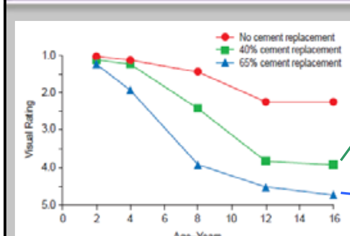
Non-air entrained 20 and 40% F-fly ash mixes, w/cm = 0.38, 0.41





D. Stark 2002

Non-air Entrained Slag mixes at w/cm = 0.37, 0.39



D. Stark 2002

Silica fume (No-air) (D. Stark 2002)

Mixture Variables	28-day Compressive Strength MPa (psi)	Cement Content kg/m³ (lbs/yd³) (ASTM Type II Cement No. 2)	Water to cement ratio	Rating at Age (years) 2	5	7	9
8% silica fume + HRWR	46.9 (6795)	282 (476)	0.52	1.2	3.7	4.0	4.0
8% silica fume, no HRWR	37.8 (5485)	205 (335)	0.56	1.3	4.2	4.3	5.0

Silica fume reduces permeability but won't prevent PSA at w/cm = 0.52-0.56.

Likely high absorption combined with no air.

PCA Conclusions 2002 (D. Stark, RD129)

1. Use of low ratios of water to total cementitious materials provided the greatest resistance to sulfate attack on the concrete.
2. Composition of portland cement was less important as it relates to performance in sulfate solutions.
3. The salt crystallization process was a major cause of concrete distress compared with the traditional hypothesis of chemical reaction of aluminates from cement hydration and sulfates from external sources.

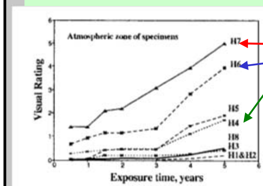
Irassar et al 1996

6x12 cylinders semi-immersed in 1% Na2SO4 at 28d for 5 years.

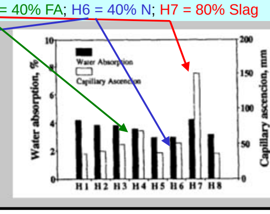
28d Strengths 16-31 MPa, w/cm = 0.53

Chem. Attack where immersed + PSA above

Poor PSA resistance of high-SCM mixes due to high capillary rise/absorption



H4 = 40% FA; H6 = 40% N; H7 = 80% Slag



28-day Sorption Data

Binder	W/CM	Initial Rate of Absorption (10-5 m/sec-1/2)	ASTM C1202 (Coulombs)
Type I PC	0.40	0.78	4510
20% Fly Ash	0.40	1.40	3420
35% Slag	0.40	1.06	1040
7% Silica Fume	0.40	0.88	850
Type I PC	0.55	1.08	5670
Type I PC	0.70	1.27	6400

PCA exposure site concretes were cured 28 days

Nokken & Hooton 2004

Bassuoni & Nehdi 2008

Cyclic W/D cyclic exposure to 5% Na2SO4 over 24m (>100 cycles)

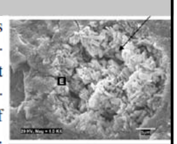
- 8% silica fume mix and 5% silica fume+ 45% slag mix at w/cm = 0.38 performed better than PC mix in both air and non-air entrained mixes.
- Air-entrained mixes at same w/cm performed better in all cases than non-air mixes.
- Salts precipitated in air voids (and filled small <50um air voids)

Effect of air entrainment on SCC in 24m Cyclic Wet/Dry Na2SO4

Bassuoni and Nehdi 2008

Non-air-entrained SCC specimens made from quaternary binders (with or without limestone filler) had a very fine pore structure, which made them vulnerable to severe damage and/or fracture under conditions that promote salt crystallization.

In exposures II and III, air-entraining bubbles could relieve possible osmotic pressures generated in the cementitious matrix and provided host locations for the growth of salt and sulfate-bearing crystals, thus discounting the rate of damage and extending the life of SCC specimens.



Air Entrainment provided additional protection

2010 PSA Tests in Toronto

- 150x150x650 mm prisms semi-immersed in 15,000ppm $SO_4^{=}$ (as Na2SO4). Solution topped up @ 3 month intervals
- 47 Mixes at 0,40, 0.50 and 0.70 w/cm.
- Mixes with Type I, II and V PC as well as portland limestone cements
- 40, 50% slag, 8% SF, 30% FA, and ternary blends
- In unheated building so temperature and humidity fluctuates.

PSA Tests in Toronto

Note capillary rise (wet front above water line) and salt crystallization on surface at drying front.

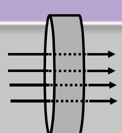
No surface damage of 0.40 and 0.50 mixes after 1 year

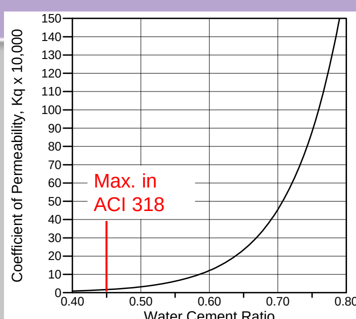
0.70 mixes were only cast in Oct. 2011

Preventing/Minimizing PSA -1

- Sulfate-resistant cements alone are not adequate to resist sulfate attack since PSA often acts faster than chemical sulfate attack.
- It is essential to limit the ability of the sulfates to enter the concrete in the first place; this is done by reducing the permeability of the concrete (minimizing the water-to-cementitious materials ratio and providing good curing) (Stark 2002).

Permeability vs w/c—used to set w/c limits in Codes

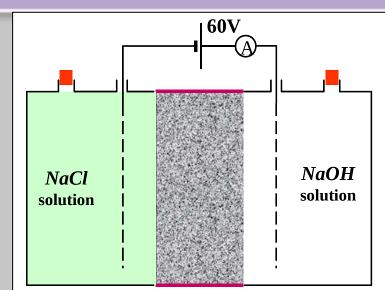




Permeability as a function of Water/Cement Ratio. Data from Bureau of Reclamation Concrete Manual, 8th Edition, 1975, Figure 17, page 37.

Rapid Chloride Permeability Test

(ASTM C1202)



Current is measured for 6h and integrated to get total charge passed in coulombs.

New draft ASTM test just measures conductivity @ 5 min.

Draft C201.2R: on Permeability and w/c

Findings from several long-term studies on resistance to sodium sulfate by the Portland Cement Association (PCA) and the US Bureau of Reclamation (USBR) confirmed that minimizing the permeability of concrete by reducing the *w/cm* was a crucial factor for providing resistance to both physical and chemical sulfate attack regardless of cement type used (Stark 1989, Stark 2002, Monteiro and Kurtis 2003).

Results from the PCA study indicate that a *w/cm* of 0.40 or lower greatly improved concrete performance when exposed to sodium sulfate, while a *w/cm* of 0.55 resulted in reduced durability (Stark, 1989, 2002).

C201: Role of SCMs

- "There is some evidence that low *w/cm* concretes containing fly ash or slag cement do not resist physical sulfate attack when exposed to sodium sulfate as well as portland cement concretes (Stark 1989; Stark 2002; and unpublished work by Folliard and Drimalis at the University of Texas at Austin)."

The reasons for this are not clear but may relate to slower hydration related to limited curing resulting in higher near-surface absorption (Irasser), or be related to altered pore size distribution.

Preventing Physical Sulfate Attack

- Best solution is to reduce capillary continuity & permeability
- Typically by w/cm < 0.45 and preferably to 0.40 and good curing
- Air–entrainment can provide space for salts as well as capillary breaks & delay/reduce damage especially with SCM mixes.

Conclusions Physical Sulfate Attack

- Use of low W/CM is essential.
- At W/CM < 0.45, the rate of evaporative transport rapidly diminishes and damage is reduced more at 0.40.
- Air entrainment is beneficial
- More work is required on SCMs and curing requirements.