#### **Materials Related Distress of PCC**



U.S. Department of Transportation

**Federal Highway Administration** 



IOWA STATE UNIVERSITY Institute for Transportation

#### Introduction

- Concrete pavements are inherently durable, having a history of exceptional long-term performance
- In some instances, pavement service life has been adversely affected by the concrete's inability to maintain its integrity in the environment in which it was placed
- These distress manifestations are categorized as materials-related distress (MRD)

#### What is Materials-Related Distress?

- MRD is commonly associated with the "durability" of the concrete
- Durability is not an intrinsic material property
  - Concrete that is durable in one application may rapidly deteriorate if placed in another application
  - "Durability" can not be measured directly.
    Potential durability can be inferred
- It is not related to loading, although loading can exacerbate the distress

#### **MRD Manifestations**

- Fine pattern cracking
  - Isolated to joints or over entire surface

Progressive in nature, getting worse over time

- Degradation such as spalling or scaling
- Often accompanied by staining and/or exudate
- Evidence of expansion is also common with some types of MRD

#### **Are These MRDs?**



## And This?



#### What About This One?



#### **Important Considerations**

- The concrete constituents, proportions, and construction all influence MRD
- Water is needed for deleterious expansion to occur
- Severe environments (e.g. freezing and thawing, deicer applications, high sulfate soils, etc.) are major contributors
- Strength does not equal durability

#### Materials Basics - Hardened Cement Paste (HCP)

 Combination of cement, supplementary cementitious materials (SCMs), water, and admixtures to form hydration products and entrained air

> HCP provides cohesion to the concrete mixture

- Comprised (primarily) of calcium silicate hydrate (CSH) and calcium hydroxide (CH)
- CSH provides strength and is desirable
- CH provides little strength and plays a role in many MRD mechanisms
  - ≻CH is soluble in water; solubility maximum at 0 °C (32 °F)

➢Pozzolans (e.g., fly ash) consume CH and yield CSH

#### Materials Basics - Aggregates

 Natural gravel, quarried rock, and sand, or manufactured mineral filler (e.g., air-cooled blast furnace slag and manufactured sand)

> 65 - 80 % volume of the concrete

- Less expensive than components of the HCP
- Provide the load-carrying capacity of concrete
- Provide dimensional stability
- Generally considered inert but not always the case
- Aggregate quality significantly impacts concrete quality
- Local sources used (shipping considerations) so poor quality is often accepted but needs to be mitigated

#### **Mechanisms of MRD Common in Pavements**

#### Physical Mechanisms

- Freeze-thaw deterioration of hardened cement paste
- Deicer scaling/deterioration
- Freeze-thaw deterioration of aggregate

### Chemical Mechanisms

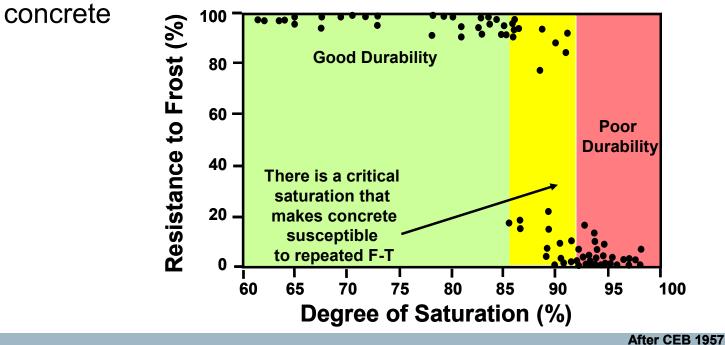
- > Alkali–aggregate reactivity
  - ➢Alkali–silica and alkali–carbonate reactivity
- Sulfate attack
  - External and internal sulfate attack
- Corrosion of embedded steel

#### Freeze-Thaw Deterioration of Hardened Cement Paste

- Overview
  - Deterioration of saturated HCP due to repeated freeze-thaw cycles
  - > Manifests as scaling, spalling, or map cracking
  - > Typically appears within 1 to 5 years after construction
  - Prevented through the use of air entraining admixtures which create a protective air-void system

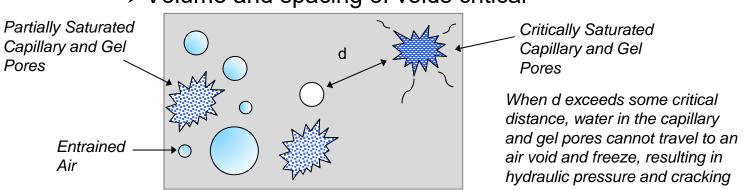
#### **Freeze-Thaw Deterioration of Hardened Cement Paste**

- Mechanism
  - Results when the HCP becomes "critically saturated" and concrete under goes F-T cycles
  - The expansion of ice causes tensile forces that crack

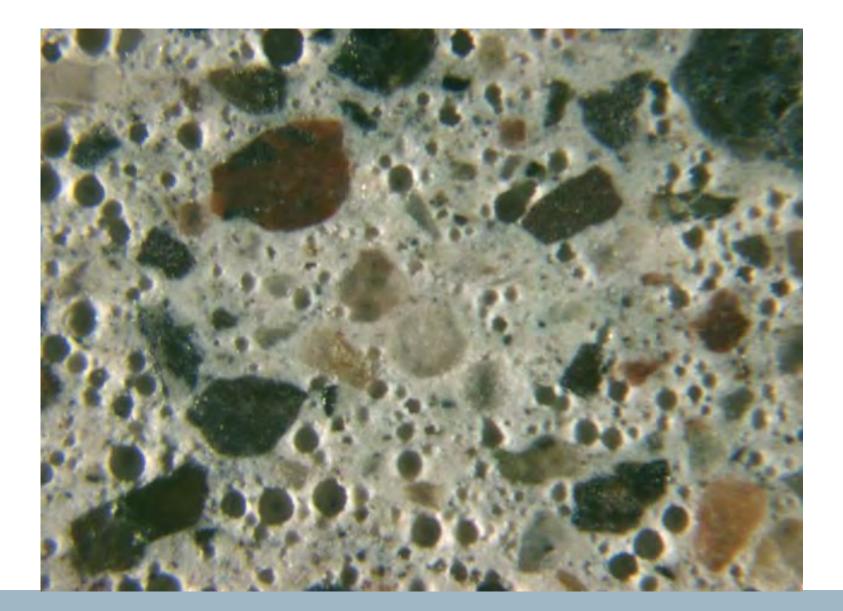


#### Freeze-Thaw Deterioration of Hardened Cement Paste

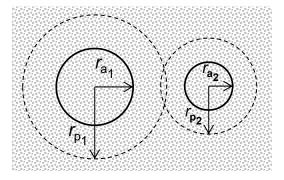
- Prevention
  - Entrained air-void system
    - Delays the time to critical saturation
    - ➢ Provides space for ice formation
    - >Allows for water movement (minimizing hydraulic pressure)



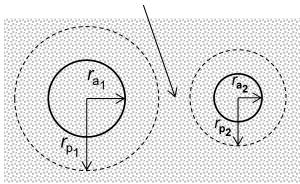
Volume and spacing of voids critical



- Testing
  - ASTM C231 (pressure meter), ASTM C173 (roller meter), and ASTM C138 (unit weight bucket) all measure <u>ONLY</u> the air content (A)
  - Air content is the volumetric air content, typically 4 8 % volume by specification
  - > For QC purposes it is sufficient to measure the volume of air
  - To fully establish F-T durability other air-void system (such as spacing factor) parameters are more important



unprotected paste



 $r_{a_n}$  = radius of air void n  $r_{p_n}$  = radius of FT protection

F-T durability requires adequate air void system

## > Spacing Factor $(\overline{L})$ :

> Approximates the constant distance from the surface of each air void surface, which would encompass some large fraction of the paste<sup>†</sup>.

Maximum: less than 0.2 mm (0.008 in.) (ACI 201)

## > Specific Surface (α):

Surface-to-Volume Ratio

➢ Defines the surface area associated with a unit volume of void space – smaller voids (i.e., more voids per unit volume) result in a higher specific surface

Minimum: 24 mm<sup>2</sup>/mm<sup>3</sup> (600 in.<sup>2</sup>/in.<sup>3</sup>)

#### ≻Air Content (A)

- Measured on hardened & fresh concrete
- > L and  $\alpha$  assumed proportional to A in fresh concrete

† Snyder, K., N. Natesaiyer and K. Hover (2001). The Stereological and Statistical Properties of Entrained Air Voids in Concrete: A Mathematical Basis for Air Void System Characterization. <u>Materials Science of Concrete. S. Mindess and J. Skalny.</u> <u>Westerville, OH USA., American Ceramic Society.</u> **VI:** 129-214.

- Testing
  - To measure spacing factor, specific surface, and other air-void system parameters, it is necessary to analyze hardened concrete using ASTM C457
    - >Requires special equipment and skilled operator (petrographer)
    - Because only hardened concrete can be analyzed, can only be used as a QA tool
  - AASHTO TP 118 (SAM meter) is an emerging technique that measures a combined parameter (SAM number) on fresh concrete that correlates to F-T performance in a manner similar to ASTM C457

- Testing
  - Measurement of F-T performance of a concrete mixture is measured using ASTM C666 Standard Test Method for Resistance of Concrete to Rapid Freezing and Thawing
  - Measures the loss in dynamic modulus after undergoing up to 300 cycles of freezing (either in air or water) and thawing (in water)
  - Test is severe and does not always correlate with field performance, but serves as a mixture screening test
  - Performed as part of mixture design, not as part of a QC/QA program (typically)

## **Deicer Scaling**



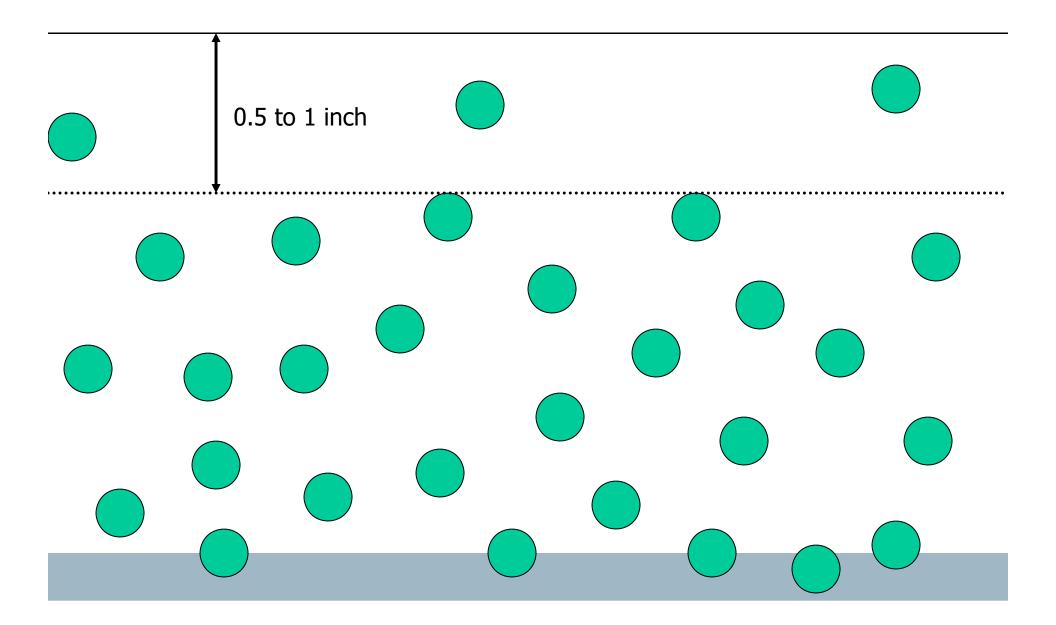
#### **Deicer Scaling/Deterioration**

- Overview
  - Deicer chemicals can amplify paste freeze-thaw deterioration and may also chemically react with or degrade hydrated paste constituents
  - Manifests as scaling, spalling, or map cracking with possible staining near joints
  - > Typically appears within 1 to 5 years after construction
  - Prevented through the use of air entraining admixtures and a relatively low water-to-cement ratio
  - Minimize finishing, which can reduce air content at surface

## **Deicer Scaling/Deterioration**

- Mechanism
  - Not well understood
  - Current research indicates scaling is due to tensile forces developed in the surface layer of concrete due to expansion of the ice layer<sup>†</sup>
  - The expansive forces of the ice are at a maximum when the solution freezing on the surface contains ~3% dissolved salt, and the type of salt is not a factor<sup>†</sup>
  - Often seen when the concrete is over finished, working the air out of the surface layer

# Impact of Poor Finishing



#### **Deicer Scaling/Deterioration**

- Prevention
  - Do not over finish
  - ➢ Good air-void system to begin with
  - Avoid salts especially at early ages (i.e., one year or less)
  - Proper curing
  - Penetrating sealers to reduce water ingress

### **Deicer Scaling/Deterioration**

- Testing
  - Scaling performance of a concrete mixture is measured using ASTM C672 Standard Test Method for Scaling Resistance of Concrete Surfaces Exposed to Deicing Chemicals
  - Assesses (by visual inspection only) the loss of material from the concrete surface after ponding dilute salt solution on the surface and exposing the samples to 50 cycles of F-T
  - Test is widely criticized for its subjectivity; modifications include measuring the mass loss from the sample
  - Test very susceptible to how specimens are finished

#### F-T Deterioration of Aggregate (D-cracking)

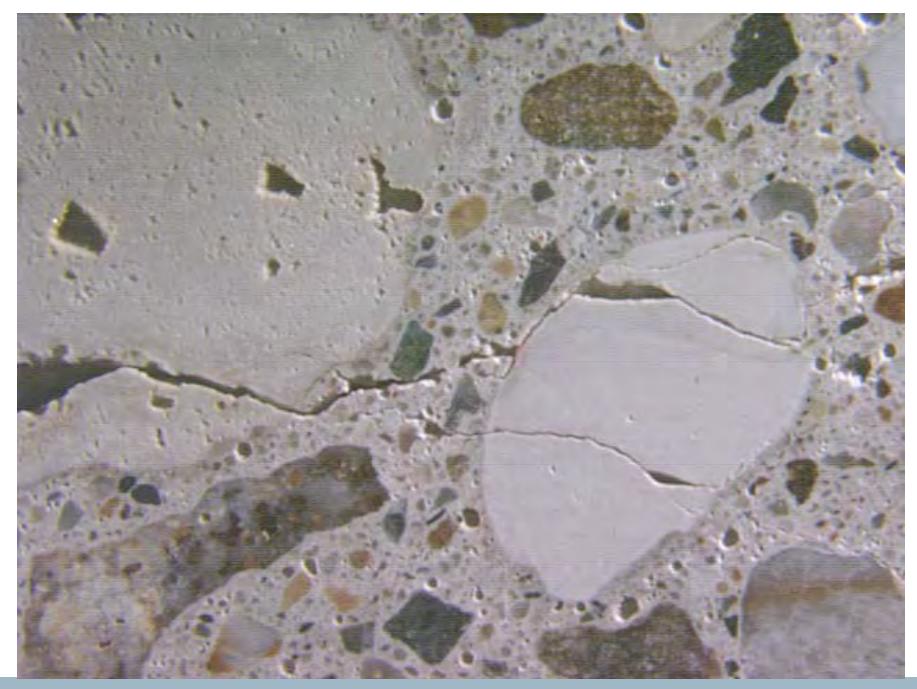
- Overview
  - Caused by the fracturing or dilation of coarse aggregate under freeze-thaw cycling in a saturated state
  - Manifests as cracking and staining parallel to joints and cracks that may eventually spall
  - Commonly manifests within 10 to 15 years
  - Prevented through the use of non-susceptible aggregates or reduction in the top size of the coarse aggregate

# Aggregate Freeze-Thaw Deterioration





- Mechanism
  - > Aggregates are porous and absorb water
  - The rate of water absorption and the rate of water expulsion is a function of the pore size distribution of the aggregates
  - D-cracking aggregates have a pore size distribution that does not allow for rapid expulsion of water as a freezing front moves through an aggregate
  - The resulting hydrostatic pressure forces can exceed the tensile strength of the aggregate



# 18.1 x 13.6 mm

Photo credit K. Peterson, University of Toronto

• Prevention

> Avoid the use of susceptible aggregates

>D-cracking aggregates are best identified by experience

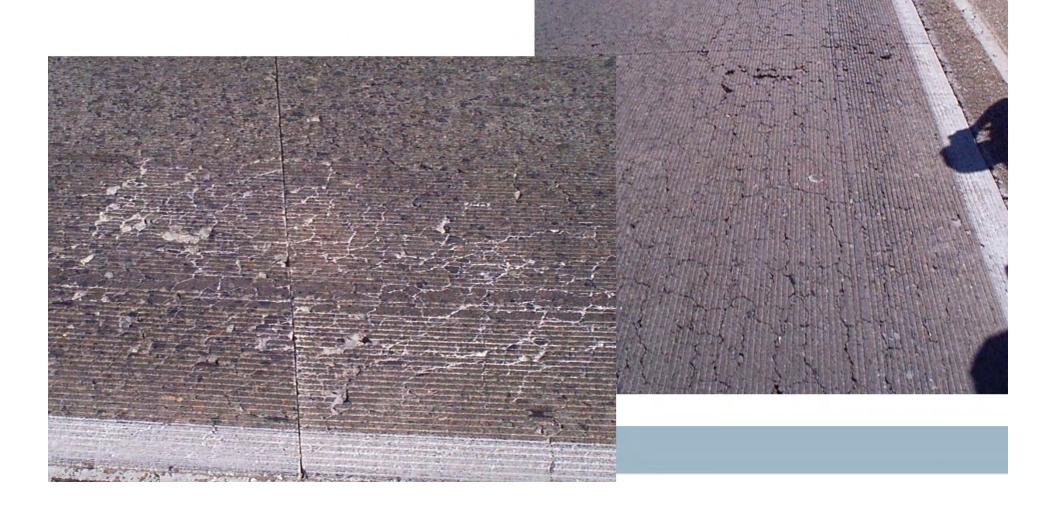
When it is necessary to use susceptible aggregates, limit the aggregate top size

A smaller aggregate particle diameter allows for more rapid expulsion of absorbed water

- Testing
  - ➢ Iowa Pore Index Test (IPIT)
    - Measures the amount of water absorbed by aggregates under pressure (241 kPa, 35 psi) in a prescribed time
      - Water absorbed 0-1 minutes  $\infty$  macropores (Primary Load)
      - Water absorbed 1-15 minutes  $\infty$  micropores (Secondary Load)
      - Secondary Load > 27 mL is associated with D-racking susceptible aggregates
  - IPIT results are more representative of the parent rock because of the large sample volume used (9000 g)
  - Variable/erroneous results for aggregates with rapid rates of early absorption
  - > No discernible trends in the results from gravels

- Testing
  - Washington Hydraulic Fracture
    - Measures the amount of particle fracture that occurs after pressurizing aggregate (7930 kPa, 1150 psi) submerged in water
      - Start with n particles retained on a 12.5 mm (1/2 inch) sieve. After 10 cycles of pressure and release, report the increase in the number of particles retained on a #4 sieve as a percentage of n (percent fracture)
      - From these measurements determine the number of pressurization cycles required to create a percent fracture of 10% - low values indicate more Dcracking susceptibility
    - ➤Can identify aggregates likely to fail due to hydraulic pressures
    - Does not simulate the confining effect of the HCP

# Alkali-Silica Reactivity



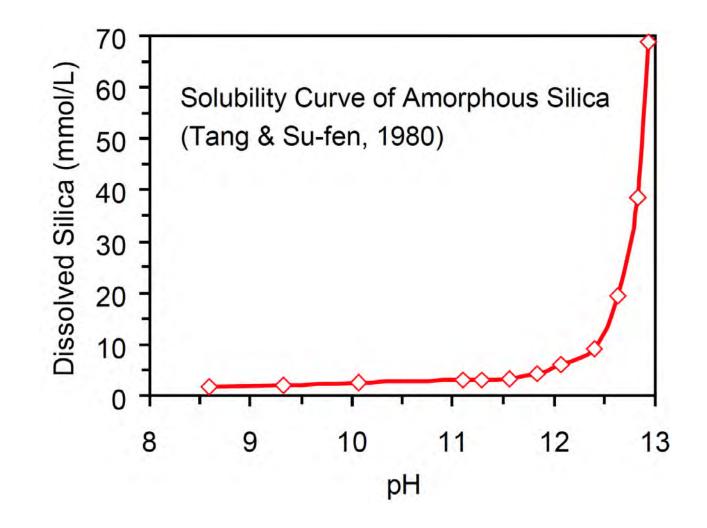
#### **Alkali-Silica Reactivity**

- Overview
  - Caused by a reaction between alkali hydroxides in the paste pore solution and reactive silica in aggregate that forms expansive reaction product
  - Manifests as map cracking over the entire slab area. Exudate is common, as is expansion related distress
  - Commonly occurs within 5 to 15 years
  - Prevented through the use of non-susceptible aggregates, limiting total mixture alkalinity, and addition of pozzolans

#### **Alkali-Silica Reactivity**

- Mechanism
  - In the presence of pore solution (i.e., H<sub>2</sub>O, Na<sup>+</sup>, K<sup>+</sup>, Ca<sup>2+</sup>, OH<sup>-</sup>, and H<sub>3</sub>SiO<sub>4</sub><sup>-</sup> ions), reactive silica undergoes depolymerization, dissolution, and swelling
  - Depends on pH of the solution, not on alkalis per se, although they control the pH
  - > The higher the pH, the more soluble the silica
  - Attack is more aggressive when the silica is not crystalline (i.e., amorphous or crypto-crystalline) as in cherts or opaline shales

#### **Alkali-Silica Reactivity**

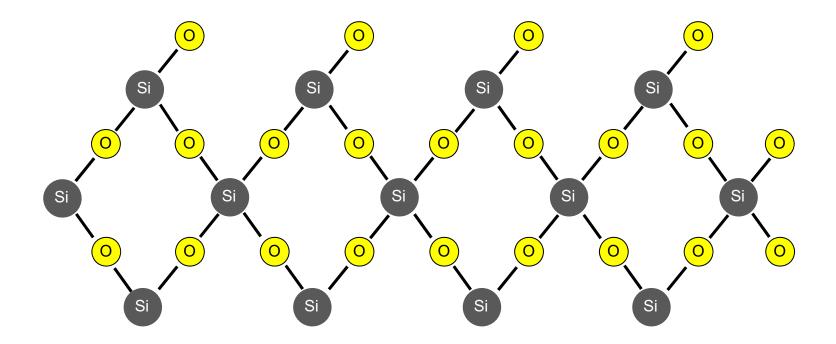


Tang, M.S. and Su-Fen, H. (1980), 'Effect Of Ca(OH)<sub>2</sub> On Alkali-Silica Reaction', *Eighth International Congress of Cement Chemistry* (2; Paris, France), 94-99.

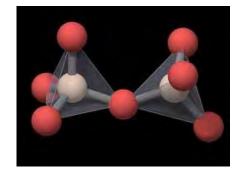
• Mechanism

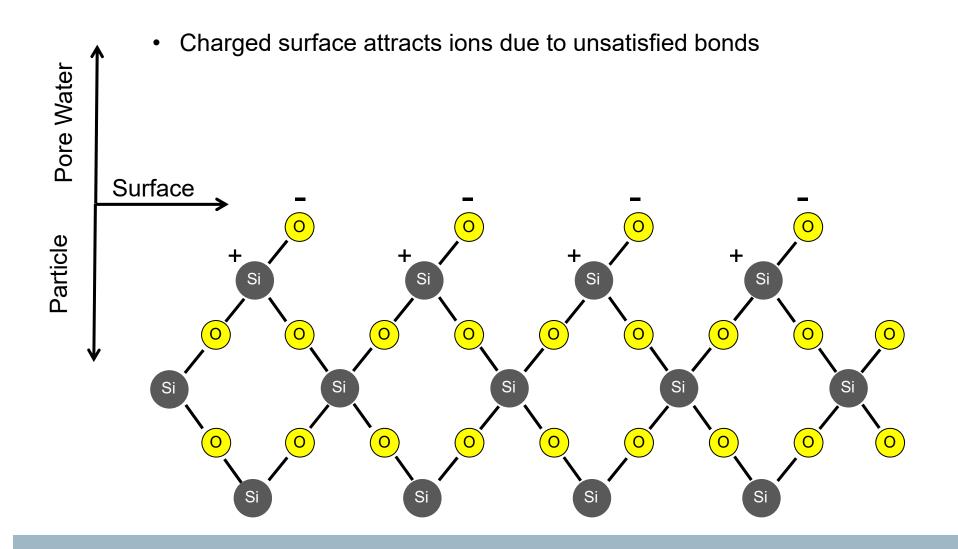
Silica tetrahedra forming siloxane bond<sup>†</sup>

- Silicon and oxygen prefer to combine in "tetrahedral coordination"
- > Four (4) oxygens surround each silicon open surface structure

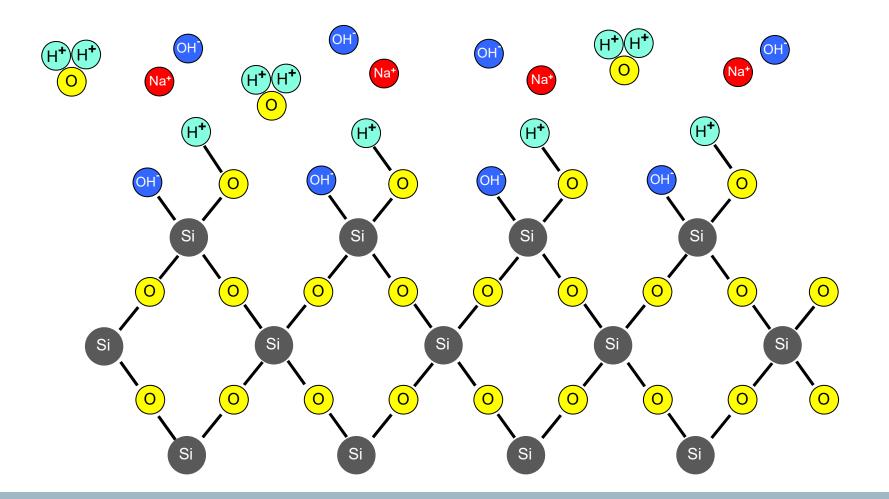


+ http://www.quartzpage.de/gen\_struct.html

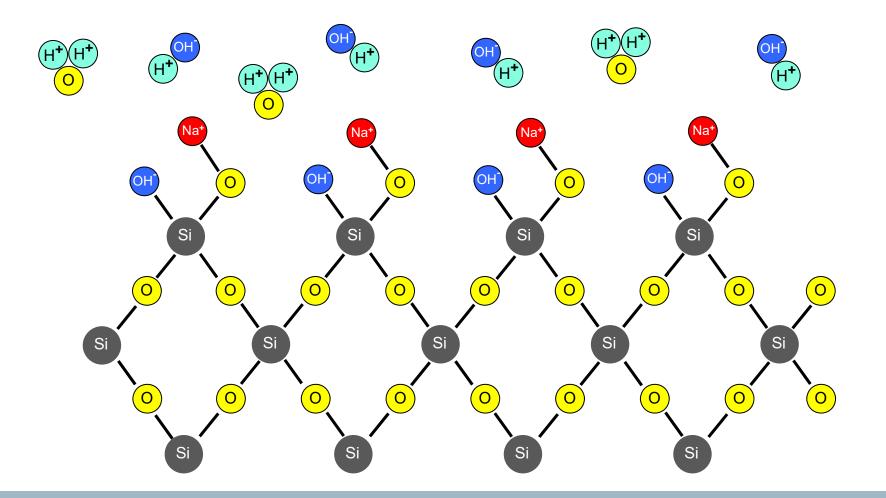




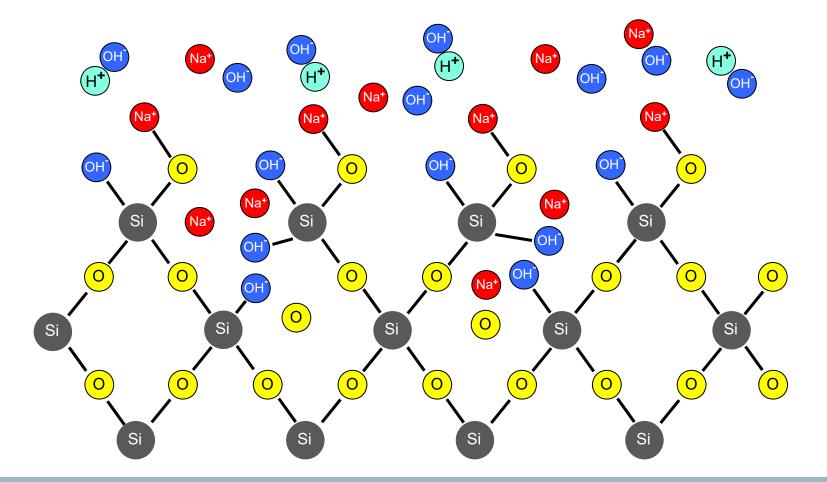
- Charged surface attracts  $H^{^{+}}$  and  $OH^{^{-}}$  ions from alkali pore water



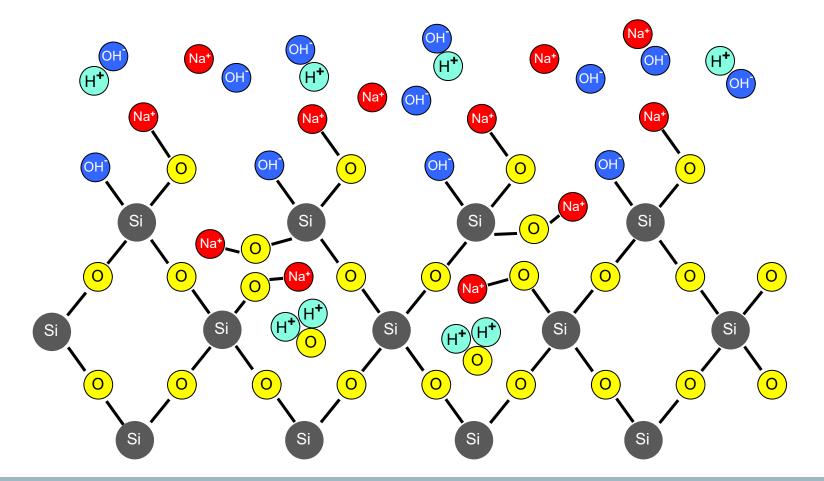
• With alkalis in pore water,  $Na^+$  substitutes for  $H^+$ 



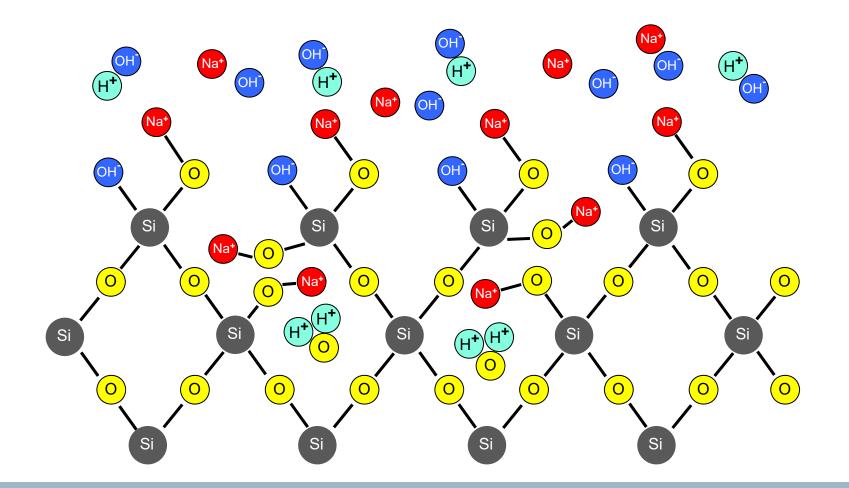
 If any excess alkalis still exist, the associated hydroxyl (OH<sup>-</sup>) breaks the Si-O-Si bond and free an oxygen

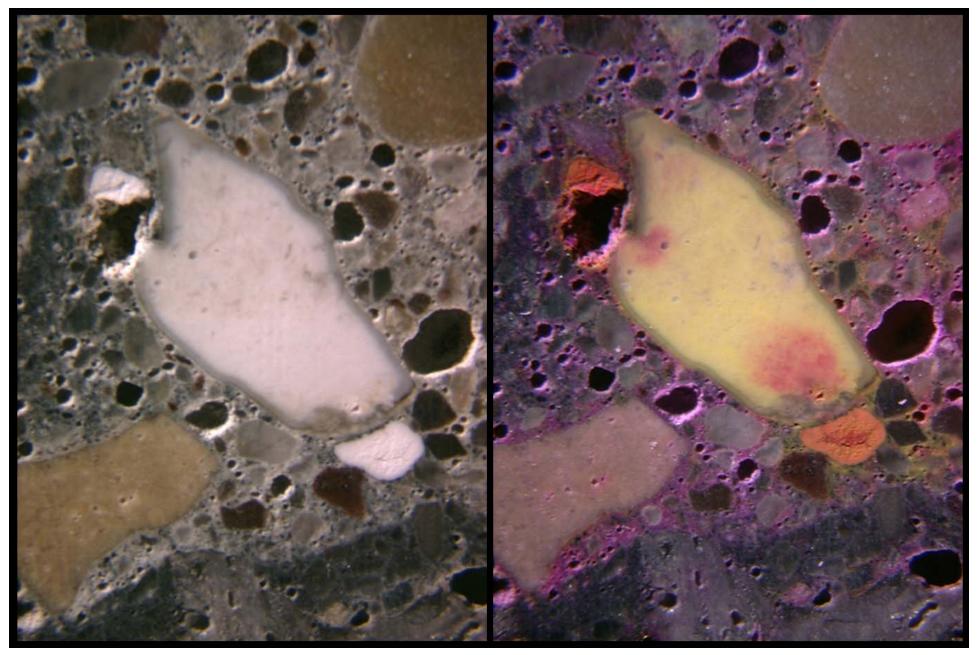


Hydrogen dissociates from OH<sup>-</sup>, combines with O<sup>2-</sup> to form water.
 Na<sup>+</sup> substitutes for H<sup>+</sup> and the attack has progressed



• Si-O-Si + 2OH<sup>-</sup> + 2Na<sup>+</sup> -> 2(Si-O-Na) + H<sub>2</sub>O





7.2 x 5.4 mm

Photo credit K. Peterson, University of Toronto

- Prevention
  - Avoid use of reactive aggregates
  - Limit alkalis in the concrete mixture
- Mitigation
  - ➤ Use of SCMs
    - ≻Fly Ash
    - ≻Slag Cement
  - ➤ Use of Lithium

### Guidance

- ASTM C1778 Standard Guide for Reducing the Risk of Deleterious Alkali-Aggregate Reaction in Concrete
- AASHTO PP-65 Standard Practice for Determining the Reactivity of Concrete Aggregates and Selecting Appropriate Measures for Preventing Deleterious Expansion in New Concrete Construction

Performance Approach

- Demonstrate performance (ASTM C1260 and ASTM C1293)
- Prescriptive Approach
  - Limit the alkali content of the concrete mixture
  - Mitigate with SCMs

- Testing
  - Various Screening Methods
    - ASTM C295 Standard Guide for Petrographic Examination of Aggregates for Concrete
    - ASTM C1260 Standard Test Method for Potential Alkali Reactivity of Aggregates (Mortar-Bar Method)
    - ASTM C1567 Standard Test Method for Determining the Potential Alkali-Silica Reactivity of Combinations of Cementitious Materials and Aggregate (Accelerated Mortar-Bar Method)
    - ASTM C1293 Standard Test Method for Determination of Length Change of Concrete Due to Alkali-Silica Reaction

- Testing
  - ≻ ASTM C295
    - Outlines procedures for the petrographic examination of materials proposed for use as aggregates in cementitious mixtures or as raw materials for use in production of aggregates
    - Can identify, and approximate the quantity of, potentially ASR reactive aggregates
    - ➤Useful way to screen potential sources
    - If an aggregate is identified as potentially reactive by petrography, expansion testing is still required to identify if the aggregate exhibits deleterious ASR or to identify mitigation strategies

- Testing
  - ≻ ASTM C1260
    - Used to detect the potential for deleterious alkali-silica reaction of aggregate in mortar bars
    - Samples are exposed to NaOH solution for 14 days (cement alkali content not a factor) and expansion measured
    - Accepted expansion limit (0.1 at 14 days) chosen empirically to correlate with an ASTM C1293 expansion of 0.04
    - Performing the test with modifications (e.g., exposure time other than 14 days, expansion limit other than 0.1 or any other changes undermines the validity of the test

- Testing
  - ≻ ASTM C1567
    - Used to detect the potential for deleterious alkali-silica reaction of <u>combinations of cementitious materials and aggregate</u> in mortar bars
    - Samples are exposed to NaOH solution for 14 days and expansion measured
    - Accepted expansion limit (0.1 at 14 days) chosen empirically to correlate with an ASTM C1293 expansion of 0.04
    - Mitigation of expansion can be evaluated by the test, but the actual SCM replacement level required must be confirmed by ASTM C1293 or field experience

Testing

### ≻ ASTM C1293

- Estimates the susceptibility of an aggregate, or combination of an aggregate with pozzolan or slag, for participation in expansive ASR by measurement of length change of concrete prisms
- Samples are spiked with alkali to create any possible ASR and expansion is monitored for 1 – 2 years, depending on the test intent - accepted expansion limit (0.04 at 1 year)
- Pozzolan replacement levels established by ASTM C1293 should be treated as the minimum required
- The "gold standard" of ASR testing not without incorrect results but the best test available
- Concerns with the test include alkali leaching from the specimens over time

- Overview
  - Caused by a reaction between alkalis in the paste pore solution and <u>specific</u> carbonate/dolomitic aggregates that under go dedolomitization and brucite formation
  - Manifests as map cracking over entire slab area with accompanying expansion related distress
  - Commonly manifests in 5 to 15 years
  - Only sure prevention is to avoid susceptible aggregates, although blending and sizing aggregates and/or significantly reducing total alkalinity may be effective
  - Mitigation is not possible

• Mechanism

Dedolomitization

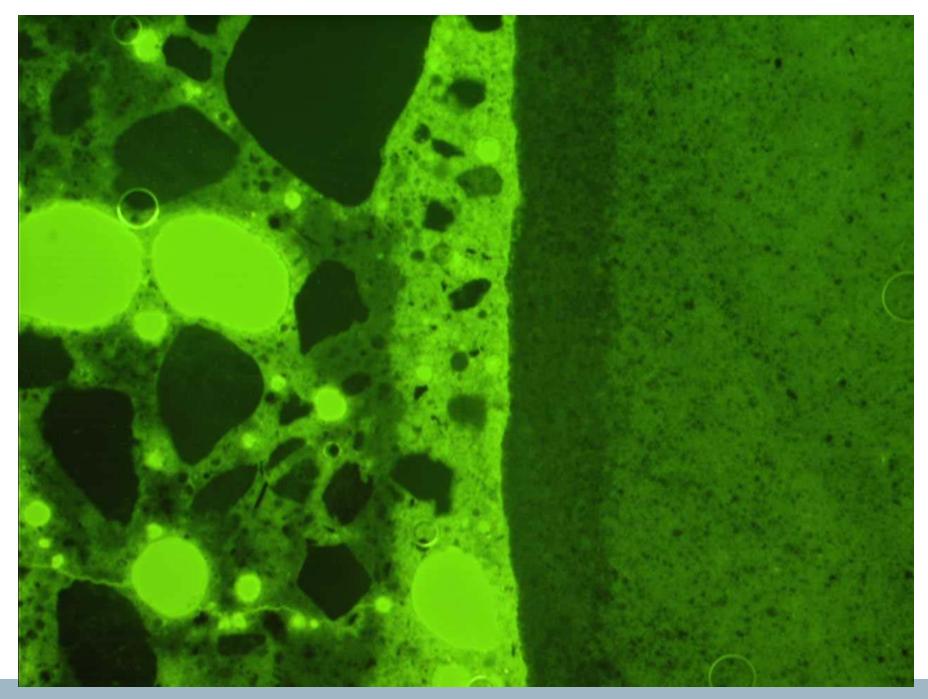
 $\begin{array}{ccc} CaMg(CO_3)_2 + 2(Na,K)OH \twoheadrightarrow Mg(OH)_2 + CaCO_3 + (Na,K)CO_3 \\ Dolomite & Alkali Hydroxide & Brucite & Calcite & Alkali Carbonate \end{array}$ 

Recycle Alkalis – leads to carbonate halos

 $Na(K)_2CO_3 + Ca(OH)_2 \rightarrow CaCO_3 + 2Na(K)OH$ 

Alkali Carbonate CH Calcite Alkali Hydroxide

Recycling of alkalis makes mitigation ineffective



1.24 x 0.93 mm

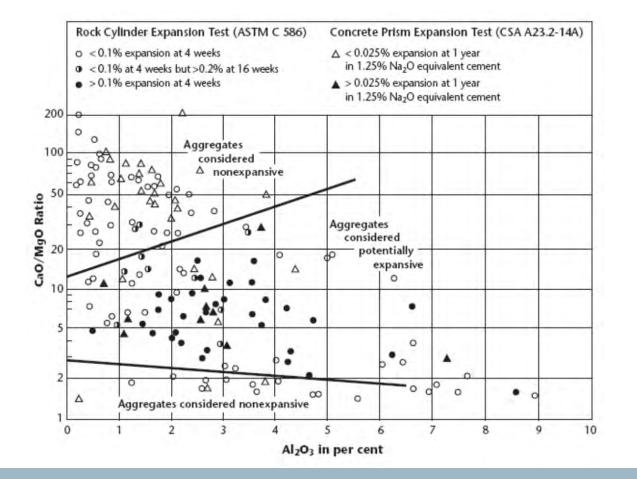
Photo credit K. Peterson, University of Toronto

- Mechanism Possible Reasons For Expansion
  - Swelling of clay minerals in dolomite
    - > Dedolomitization increases permeability, more water ingress, possible swelling
  - Crystal growth in dolomite matrix
    - Brucite formation
  - Increased alkalis leading to ASR

> Microcrystalline silica is present in many aggregates reported to be ACR susceptible

- IMPORTANT: Requires a specific dolomite rock type <u>Only a very</u> <u>slight fraction of dolomite rocks are ACR reactive – specific geologic</u> <u>deposits/locations (i.e., argillaceous dolomitic limestone, fine grained</u> <u>matrix with dolomite crystals embedded</u>)
- Prevention Avoid ACR susceptible aggregates

Testing – Reject aggregates based on chemistry



CSA A23.2-26A)

- Testing
  - ASTM C586 Standard Test Method for Potential Alkali Reactivity of Carbonate Rocks as Concrete Aggregates (Rock-Cylinder Method)

➤Used to screen rock materials for potential ACR reactivity

ASTM C1105 Standard Test Method for Length Change of Concrete Due to Alkali-Carbonate Rock Reaction

Determines the susceptibility of cement-aggregate combinations to expansive alkali-carbonate reaction for certain calcitic dolomites and dolomitic limestones

Aggregates passing ASTM C1105 should be evaluated for ASR potential using ASTM C1260 or C1293, as appropriate

- Overview
  - Expansive formation of sulfate minerals resulting from an external source of sulfate ions
  - Fine cracking and deterioration near joints and slab edges and on underside of slab
  - Usually manifests within 1 to 5 years
  - Mitigated through the use of low w/c, minimizing aluminate phases in cementitious materials, or using pozzolans or ground slag

• Mechanism

Sulfate-laden solution enters concrete

> Sulfate reacts with alumina and calcia to form ettringite

>Monosulfate – normally present in HCP is converted to ettringite

>Ettringite can form in HCP or at the HCP-aggregate interface

- Conversion to ettringite results in volume increase expansion – and cracking
- Ettringite that forms in air voids does not exert expansive pressures but may compromise the air-void system

• Mechanism – Example Reactions

#### Symbols Used

$$\begin{split} \overline{\mathbf{S}} &= \text{sulfate ion} \left( \text{SO}_{4}^{2-} \right) \\ \mathbf{CH} &= \text{calcium hydroxide} \left( \text{Ca}(\text{OH})_2 \right) \\ \mathbf{AFm} &= \text{monosulfate} \left( 3\text{CaO} \square \text{AI}_2\text{O}_3 \square \text{CaSO}_4 \square 12\text{H}_2\text{O} \right) \\ \mathbf{AFt} &= \text{ettringite} \left( 3\text{CaO} \square \text{AI}_2\text{O}_3 \square 3\text{CaSO}_4 \square 32\text{H}_2\text{O} \right) \end{split}$$

#### **Ettringite Formation with Calcium Hydroxide Dissolution**

 $4(Na,K)^{+} + 2\overline{S} + 2CH + AFm \rightarrow 4(Na,K)^{+} + AFt + 4OH^{-}$ 

Mechanism – Example Reactions

#### Symbols Used

- $\overline{S}$  = sulfate ion (SO<sub>4</sub><sup>2-</sup>) CH = calcium hydroxide(Ca(OH)<sub>2</sub>)
- $C\overline{S}$  = calcium sulfate, gypsum (CaSO<sub>4</sub>  $\Box$ 2H<sub>2</sub>O)

#### **Gypsum Formation with Calcium Hydroxide Dissolution**

 $(Na,K)^{+} + \overline{S} + CH \rightarrow 4(Na,K)^{+} + C\overline{S} + 4OH^{-}$ 

Mechanism – Example Reactions

#### Symbols Used

 $\mathbf{\overline{S}} = \text{sulfate ion} (\text{SO}_4^{2-})$   $\mathbf{CSH} = \text{calcium silicate hydrate } (1.7\text{Ca} \square \text{SiO}_2 \square 4\text{H}_2\text{O})$   $\mathbf{CSH}_D = \text{decalcified calcium silicate hydrate } (<1.7\text{Ca} \square \text{SiO}_2 \square 4\text{H}_2\text{O})$   $\mathbf{AFm} = \text{monosulfate } (3\text{CaO} \square \text{Al}_2\text{O}_3 \square \text{CaSO}_4 \square 12\text{H}_2\text{O})$   $\mathbf{AFt} = \text{ettringite } (3\text{CaO} \square \text{Al}_2\text{O}_3 \square 3\text{CaSO}_4 \square 32\text{H}_2\text{O})$ 

#### **Decalcification of CSH Due To Ettringite Formation**

 $nCSH + AFm + 4(Na,K)^{+} + 2\overline{S} \rightarrow nCSH_{D} + AFt + 4(Na,K)^{+} + 4OH^{-}$ 

• Mechanism – Example Reactions

#### Symbols Used

$$\overline{\mathbf{S}} = \text{sulfate ion} (\text{SO}_4^{2-})$$

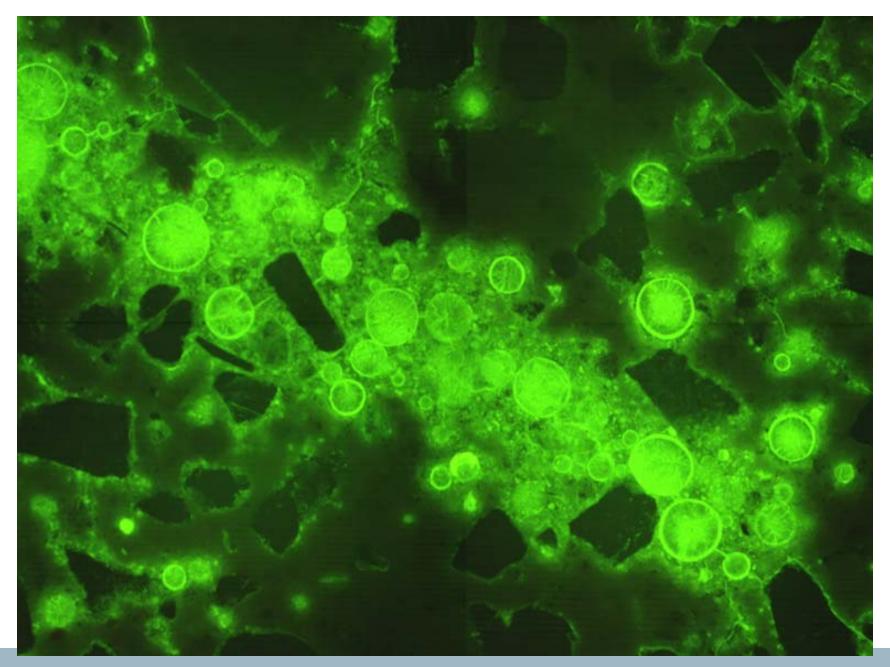
$$\mathbf{CSH} = \text{calcium silicate hydrate (1.7Ca \square \text{SiO}_2 \square 4\text{H}_2\text{O})}$$

$$\mathbf{CSH}_D = \text{decalcified calcium silicate hydrate (<1.7Ca \square \text{SiO}_2 \square 4\text{H}_2\text{O})}$$

$$\mathbf{C\overline{S}} = \text{calcium sulfate, gypsum (CaSO}_4 \square 2\text{H}_2\text{O})}$$

#### **Decalcification of CSH Due To Gypsum Formation**

$$nCSH + 2(Na, K)^{+} + \overline{S} \rightarrow nCSH_{D} + C\overline{S} + 2(Na, K)^{+} + 2OH^{-}$$



2.54 x 1.90 mm

Photo credit K. Peterson, University of Toronto

- Prevention
  - Reduce concrete permeability
    - Lower w/c see ACI 201.2R-08 Guide to Durable Concrete for guidance on w/c determination based on sulfate exposure
    - Use pozzolans or slag to densify the CSH and reduce the available CH for reaction – see ACI 201.2R-08 Guide to Durable Concrete for guidance on replacement level
  - Reduce aluminate phases in cementitious materials that can react
    - Use ASTM C150 Type II or Type V cement and limit aluminate phases in SCMs – see ACI 201.2R-08 Guide to Durable Concrete for guidance on cement selection based on exposure class and SCM composition

- Overview
  - Expansive formation of ettringite in paste due to an internal source of sulfates
    - Most commonly associated with high curing temperatures (delayed ettringite formation)
    - Can also be associated with an internal source of sulfates (e.g. aggregate, fly ash, etc.)
  - Fine cracking concentrated at joints but may effect entire slab area
  - ➤ Usually manifests in 1 to 5 years
  - Prevented by controlling internal sources of sulfate and avoiding high curing temperatures

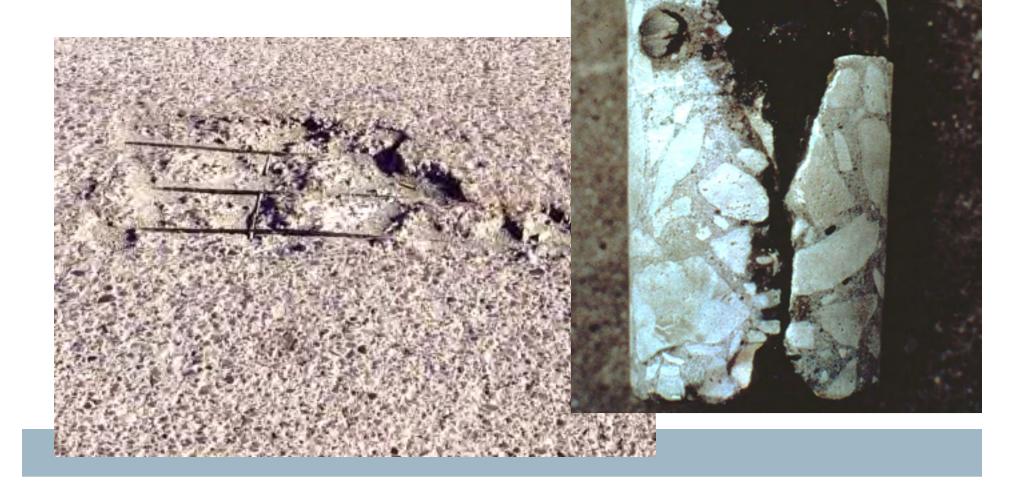
- Mechanism
  - Internal attack is most commonly associated with steam cured concrete
    - If concrete is cured at temperatures above 70-80 °C (158-176 °F) the formation of ettringite during the initial set is "delayed" and monosulfate is formed
    - The monosulfate later converts to ettringite after the concrete hardens resulting in expansion and cracking
  - Other forms of internal sulfate attack involve sources of sulfate from the constituent materials leading to the same reactions observed with external sources of sulfate

- Prevention
  - Fortunately not a distress associated with cast in place concrete
  - > For steam cured concrete observe proper curing temperatures
  - > For all concrete limit sulfate contents in constituent materials
    - ➢Portland cement is typically sulfate balanced and not an issue
    - SCMs and aggregates can be likely sources of sulfate
    - >Problems with sulfide-bearing aggregates have been reported
      - Pyrrhotite  $[Fe_{(1-X)}S (x = 0 \text{ to } 0.2)]$  weathering/oxidizing to provide sulfate internally

### **Sulfate Attack**

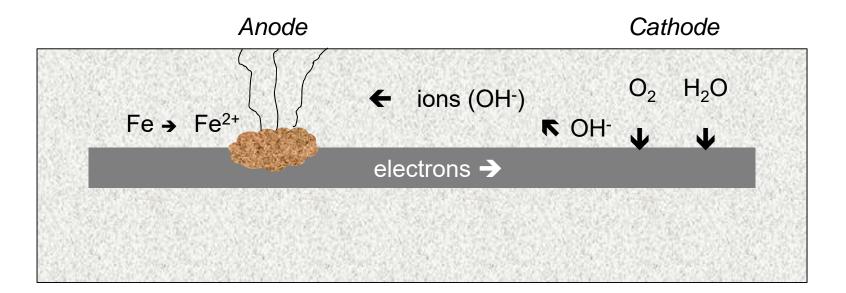
- Testing
  - Internal sulfate attack can be addressed by monitoring the chemical composition of the concrete materials
  - ASTM C1012 Standard Test Method for Length Change of Hydraulic-Cement Mortars Exposed to a Sulfate Solution
    - Used to evaluate combinations of materials for susceptibility from external sulfate attack by monitoring the length change of mortar bars immersed in a sulfate solution
    - Test duration a minimum of twelve (12) months, or eighteen (18) months in the case of ACI 201 defined Class 3 exposure
    - ➤Test exhibits considerable variation

- Overview
  - Associated most often with chloride ingress, which destroys passivity film protecting steel
  - Appears as cracking and spalling above and around embedded steel
    - ➢Rust staining
  - Commonly manifests in 3 to 10 years
  - Prevented by providing adequate concrete cover, reducing concrete permeability, protecting steel, or using corrosion inhibitors



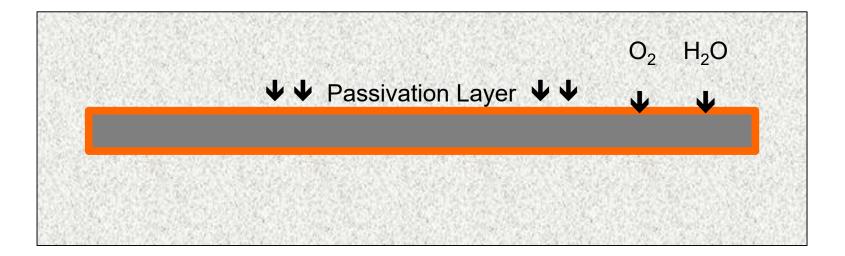
#### • Mechanism

- > At the anode iron is oxidized and combines with OH<sup>-</sup> to form corrosion product
- > At the cathode electrons, oxygen, and water combine to form OH-
- Both reactions must occur simultaneously



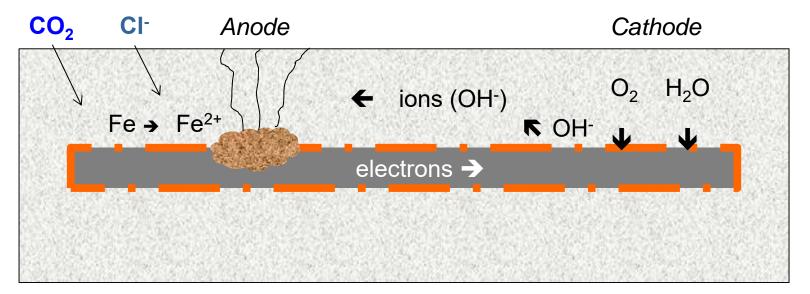
#### • Mechanism

- Under normal conditions the high pH of the concrete creates a corrosion layer on the steel that protects it from corrosion – passivation layer
- Passivation layer blocks the diffusion of water and oxygen to the steel and the cathode reaction is shut down, stopping the overall corrosion reaction



#### • Mechanism

- Carbon dioxide (CO<sub>2</sub>) lowers the pH of the concrete and the passivation layer breaks down
- > Chloride (Cl<sup>-</sup>) attacks the passivation layer directly *mechanism unclear*
- > Limiting fluid ingress (CO<sub>2</sub>, O<sub>2</sub>, Cl<sup>-</sup>, and H<sub>2</sub>O) limits corrosion



- Prevention
  - Provide adequate cover (concrete) over steel to reduce/slow the ingress of fluids
  - Reduce concrete permeability (low w/c, penetrating sealers)
  - Use corrosion inhibiting chemicals in the concrete to counteract the effects of chlorides or CO<sub>2</sub>
  - > Minimize cracking in the concrete cover

# Final Thoughts

- Many manifestations of MRD look similar, and therefore identification can not be made based on visual assessment alone
- Water is necessary for deleterious expansion to occur
- Severe environments (freezing and thawing, deicers, sulfates, etc.) exacerbate the problem
- Durable materials are typically low shrinkage and relatively impermeable