Materials-Related Distress

BEST PRACTICES
WORKSHOP

U.S. Department of Transportation
Federal Highway Administration

National Concrete Pavement Technology Center

IOWA STATE UNIVERSITY
Institute for Transportation

Outline

- Why are we here
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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?

How About These?

And This?

What About This One?

How About Here?

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 ºC (32 ºF)
    - 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

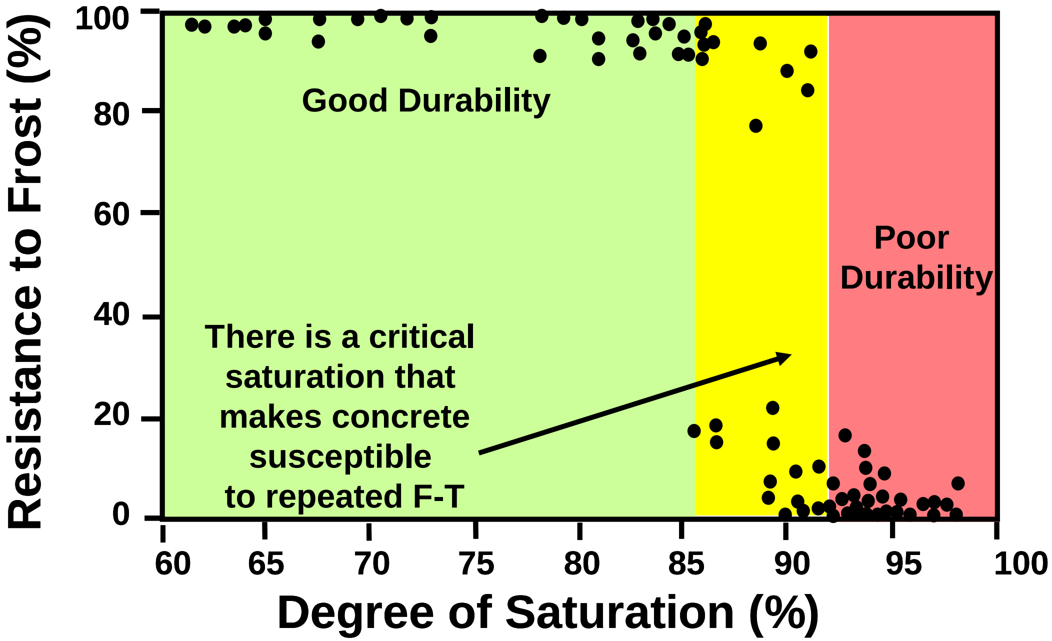
- **Physical Mechanisms**
  - Freeze-thaw deterioration of hardened cement paste
  - Deicer scaling/deterioration
  - Freeze-thaw deterioration of aggregate
- **Chemical Mechanisms**
  - Alkali-aggregate reactivity
    - Alkali-silica and alkali-carbonate reactivity
  - Sulfate attack
    - External 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 concrete

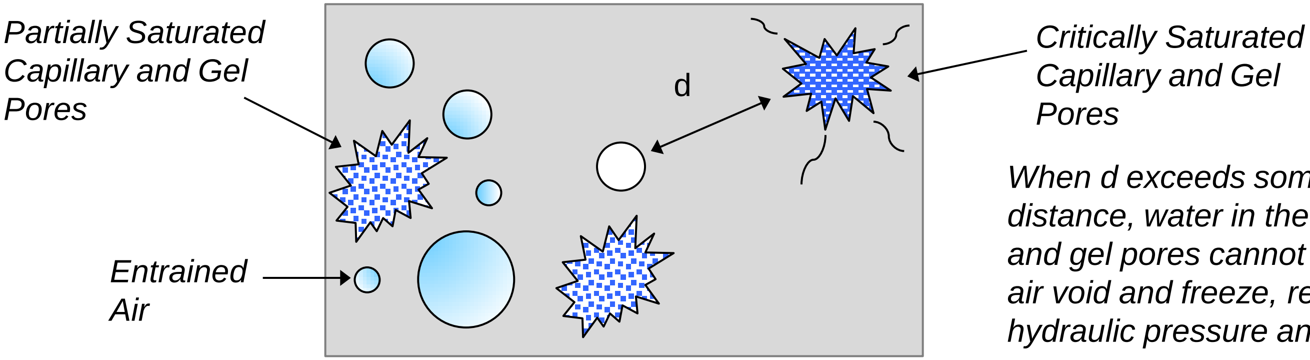


There is a critical saturation that makes concrete susceptible to repeated F-T

After CEB 1957

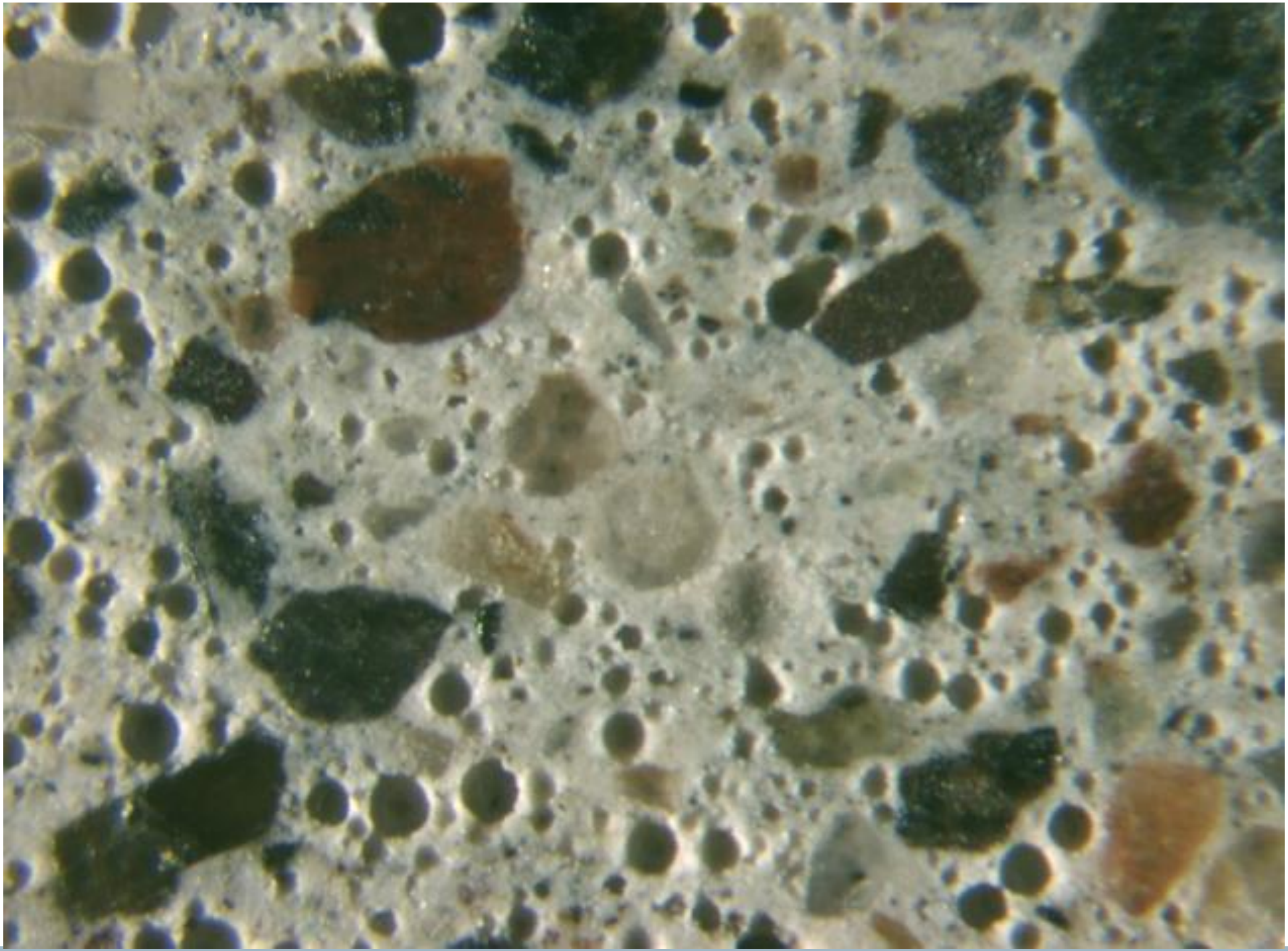
Freeze-Thaw Deterioration of Hardened Cement Paste

- 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



When d exceeds some critical distance, water in the capillary and gel pores cannot travel to an air void and freeze, resulting in hydraulic pressure and cracking

Air-Void System



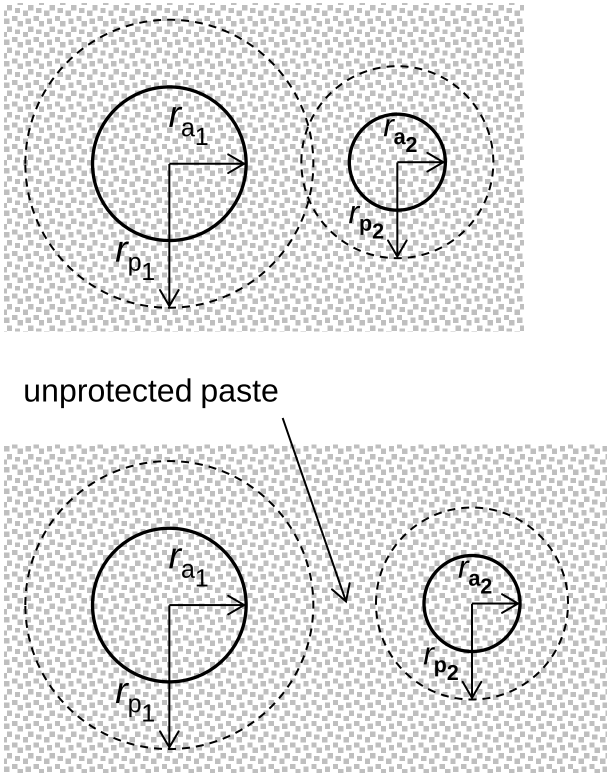
Air-Void System

- Testing
  - The air-void system can be evaluated using various tests
    - ASTM C231 - *Standard Test Method for Air Content of Freshly Mixed Concrete by the Pressure Method*
    - ASTM C173 - *Standard Test Method for Air Content of Freshly Mixed Concrete by the Volumetric Method*
    - ASTM C138 - *Standard Test Method for Density (Unit Weight), Yield, and Air Content (Gravimetric) of Concrete*
    - ASTM C457 - *Standard Test Method for Microscopical Determination of Parameters of the Air-Void System in Hardened Concrete*
    - AASHTO TP 118 - *Characterization of the Air- Void System of Freshly Mixed Concrete by the Sequential Pressure Method*

Air-Void System

- Testing
    - ASTM C231 (pressure meter), ASTM C173 (roller meter), and ASTM C138 (unit weight bucket) all measure **ONLY** 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

Air-Void System



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 ($\bar{L}$):
    - Approximates the constant distance from the surface of each air void surface, which would encompass some large fraction of the paste[†]
    - 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^2/mm^3 (600 $in.^2/in.^3$)
  - Air Content (A)
    - Measured on hardened & fresh concrete
    - *L* and α 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. *Materials Science of Concrete VI*. Eds. S. Mindess and J. P. Skalny. American Ceramic Society, Westerville, OH. pp. 129–214.

Air-Void System

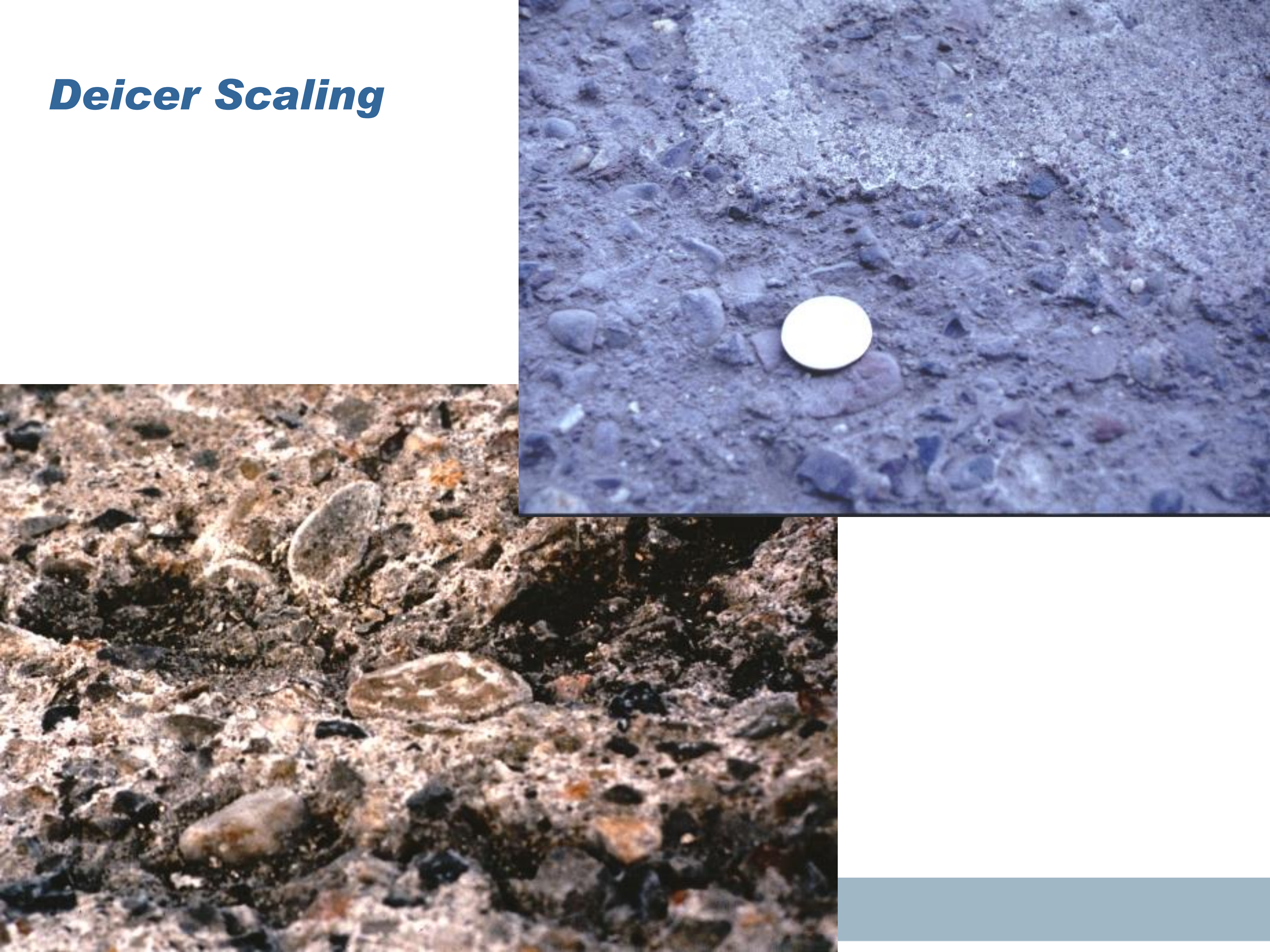
- Testing
  - To measure spacing factor, specific surface, and other air-void system parameters, it is necessary to analyze hardened concrete using ASTM C457
    - Requires special equipment and skilled operator (petrographer)
    - Because only hardened concrete can be analyzed, can only be used as 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

Air-Void System Analysis – ASTM C457

Air-Void System

- 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

Deicer Scaling

Deicer Scaling/Deterioration

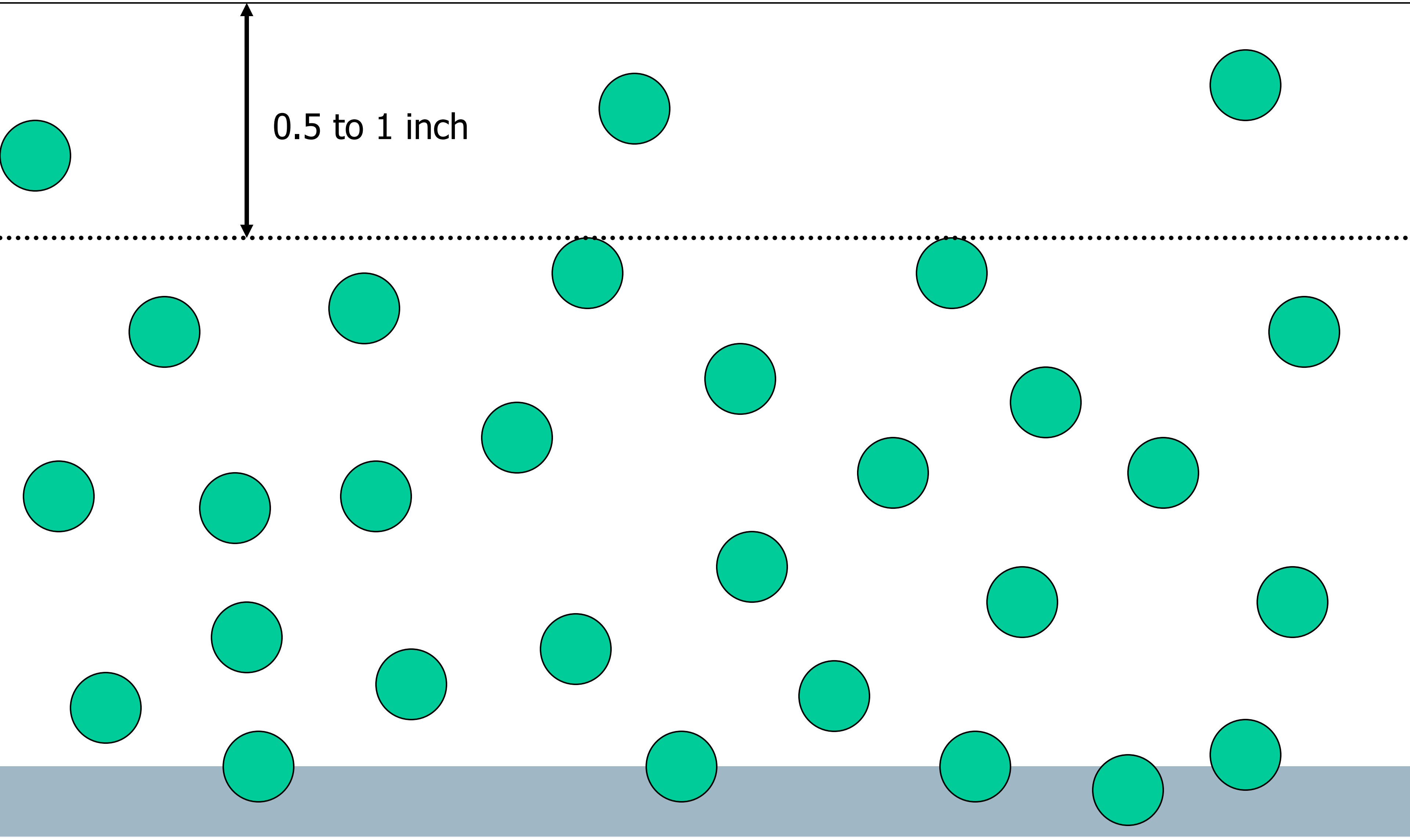
- Overview
    - ➢ Deicer chemicals can amplify paste freeze-thaw deterioration and may also chemically react with or degrade hydrated paste constituents
    - ➢ Manifests as scaling, spalling, or map cracking with possible staining near joints
    - ➢ Typically appears within 1 to 5 years after construction
    - ➢ 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[†]
  - 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[†]
  - Often seen when the concrete is over finished, working the air out of the surface layer

[†] Valenza, J. J. and G. W. Scherer. 2007. A Review of Salt Scaling: II. Mechanisms, *Cement and Concrete Research*. Vol. 37, No. 7, pp. 1022–1034.

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

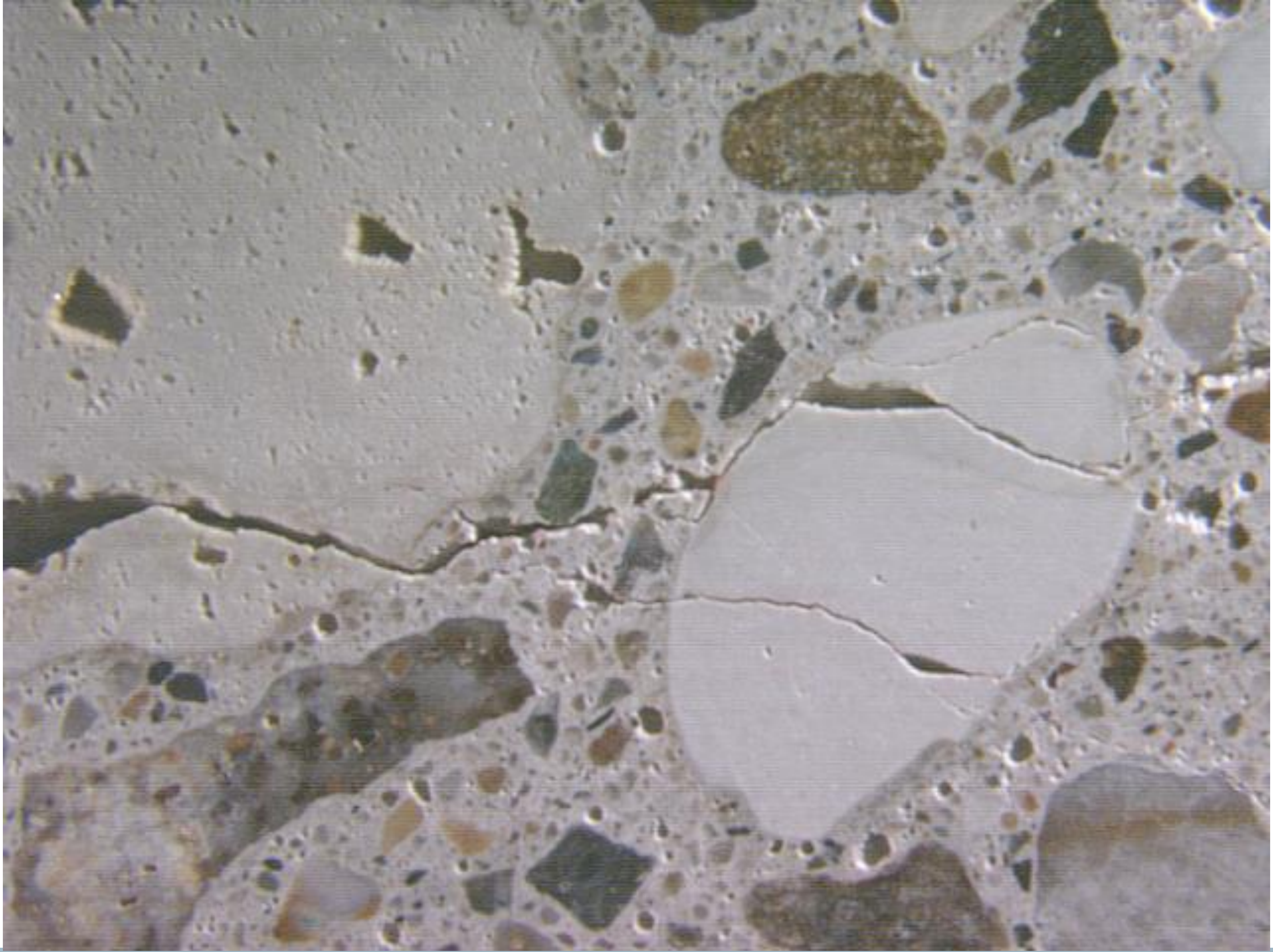
F-T Deterioration of Aggregate (D-cracking)

- 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

F-T Deterioration of Aggregate

- 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

Image: Karl Peterson, University of Toronto

F-T Deterioration of Aggregate

- 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

F-T Deterioration of Aggregate

- 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 minutesμ macropores (Primary Load)
      - – Water absorbed 1–15 minutesμ 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

F-T Deterioration of Aggregate

- 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 D-cracking susceptibility
    - Can identify aggregates likely to fail due to hydraulic pressures
    - Does not simulate the confining effect of the HCP
    - Cannot identify aggregates that cause cracking due to excessive water expelled from aggregates

Alkali–Silica Reactivity

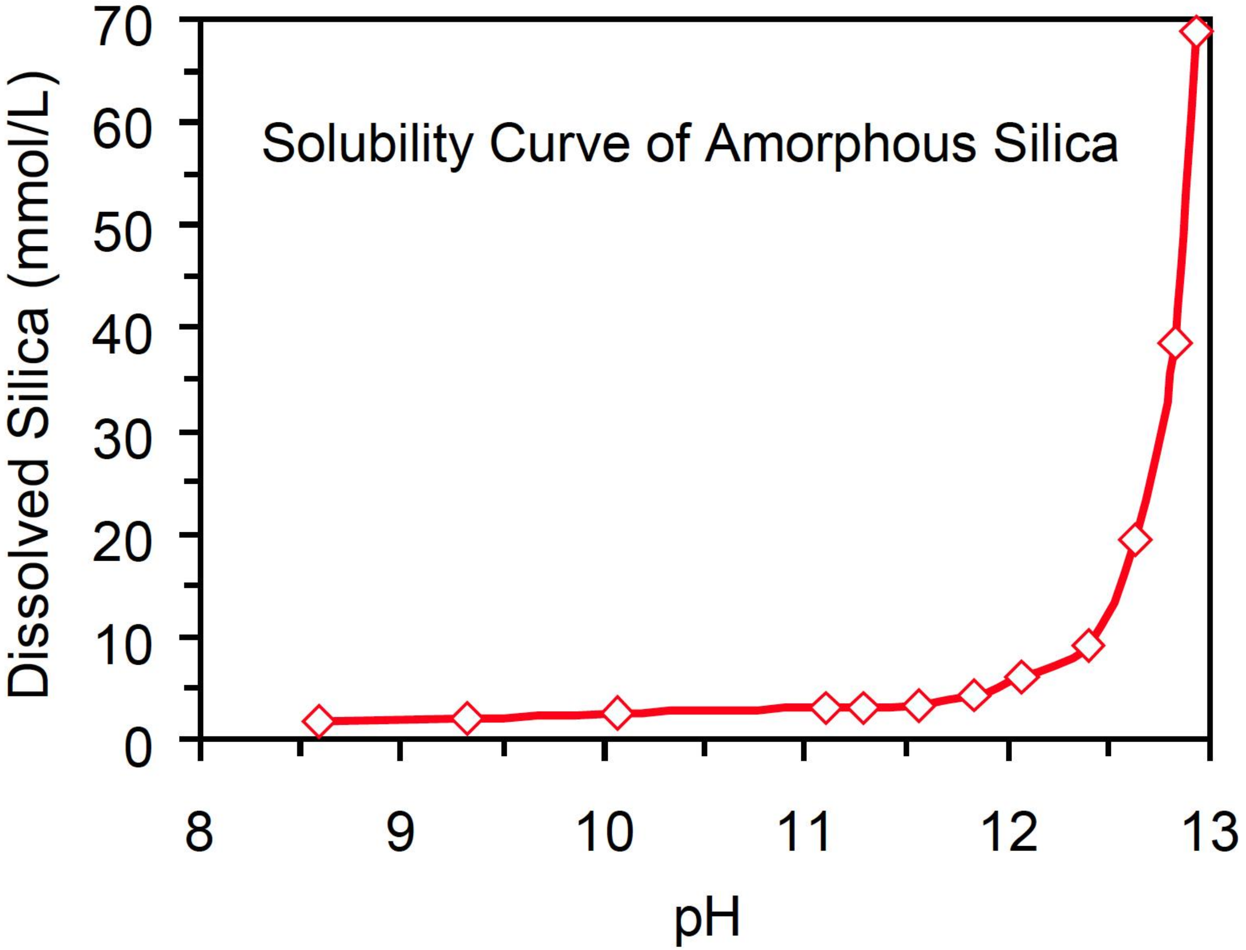
Alkali–Silica Reactivity

- Overview
  - Caused by a reaction between alkalis 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

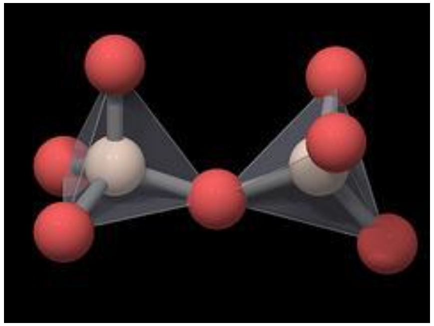
- Mechanism
  - In the presence of pore solution (i.e., H_2O, Na^+, K^+, Ca^{2+}, OH^-, and $H_3SiO_4^-$ ions), reactive silica undergoes depolymerization, dissolution, and swelling
  - Depends on pH of the solution, not on alkalis per se, although they control the pH
  - The higher the pH, the more 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



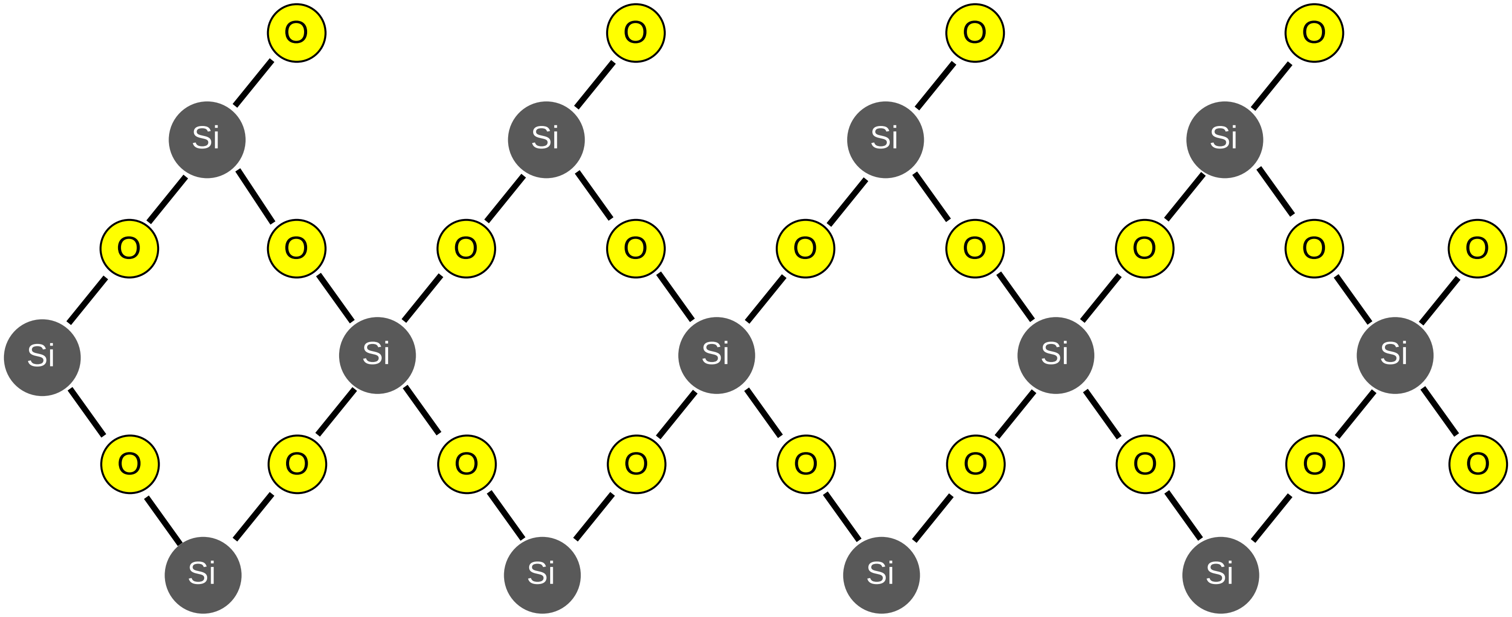
Ming-shu, Tang and Su-feng Han. 1980. Effect of $Ca(OH)_2$ on Alkali-Silica Reaction, *Proceedings of the 7th International Congress on the Chemistry of Cement*, Session II, pp. 94–99. June 30–July 5, Paris, France).

Alkali–Silica Reactivity



Silica tetrahedra forming siloxane bond†

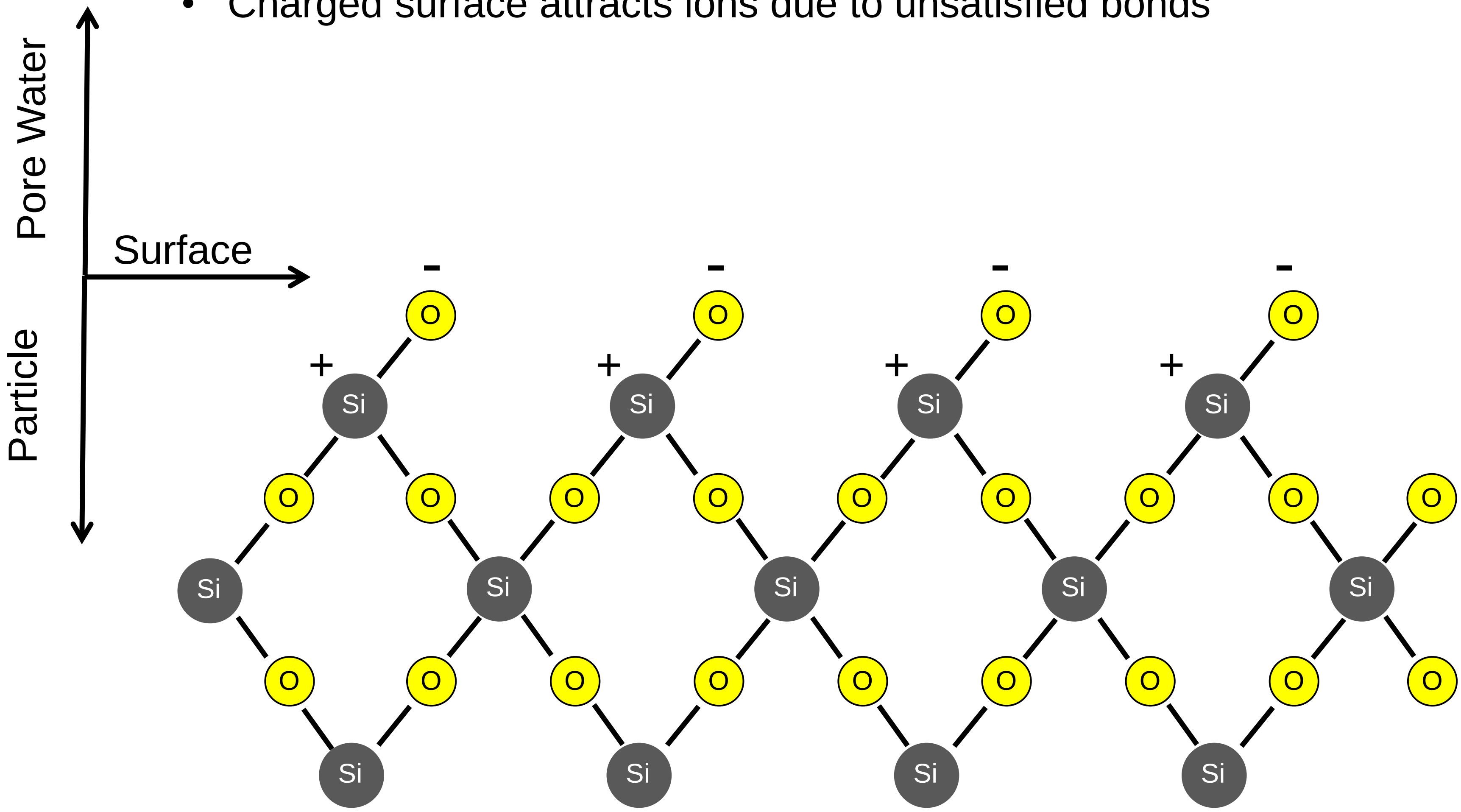
- Mechanism
  - Silicon and oxygen prefer to combine in “tetrahedral coordination”
  - Four (4) oxygens surround each silicon – open surface structure



† Amir C. Akhavan, The Quartz Page.
www.quartzpage.de/gen_struct.html

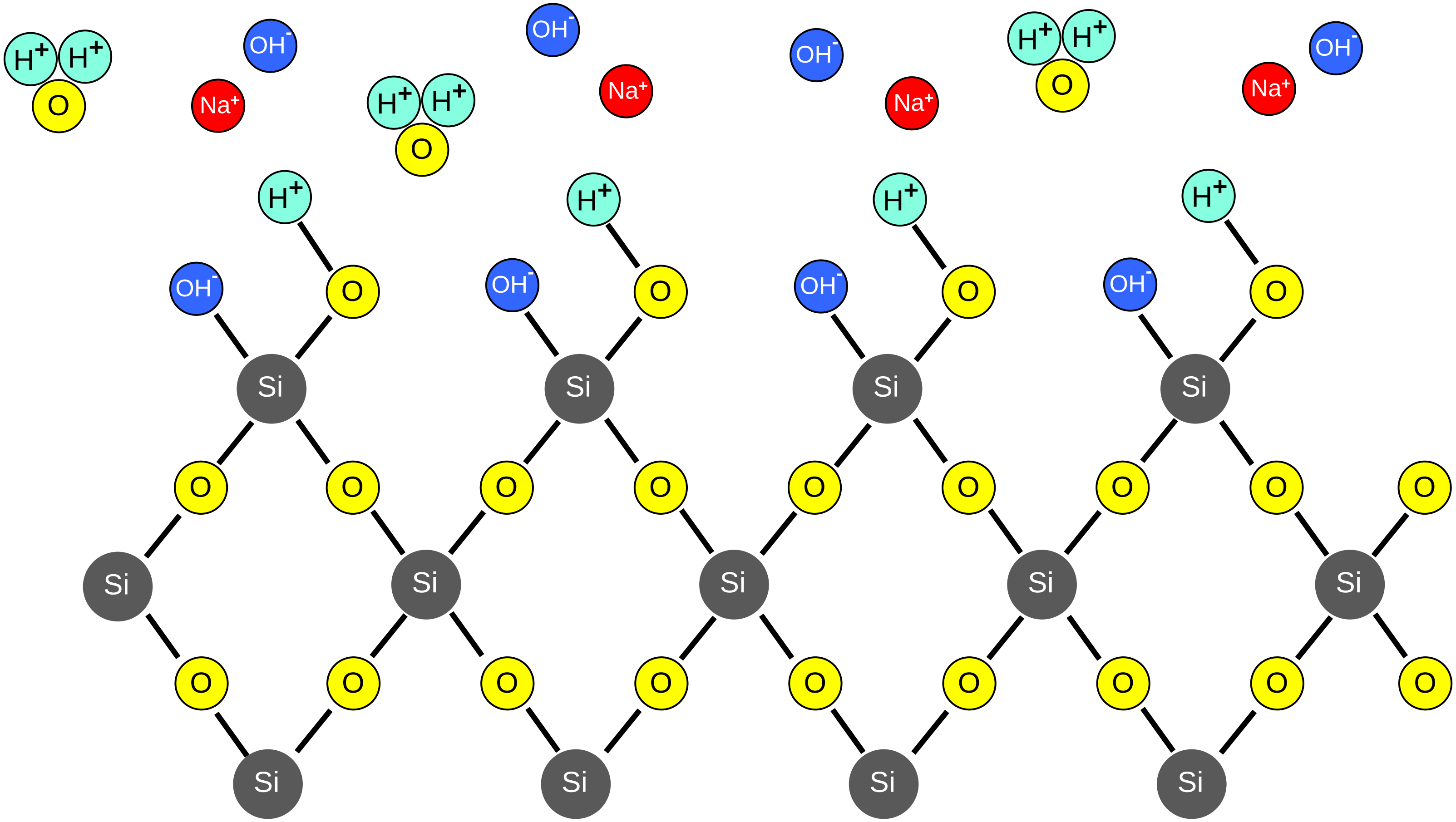
Alkali–Silica Reactivity

- Charged surface attracts ions due to unsatisfied bonds



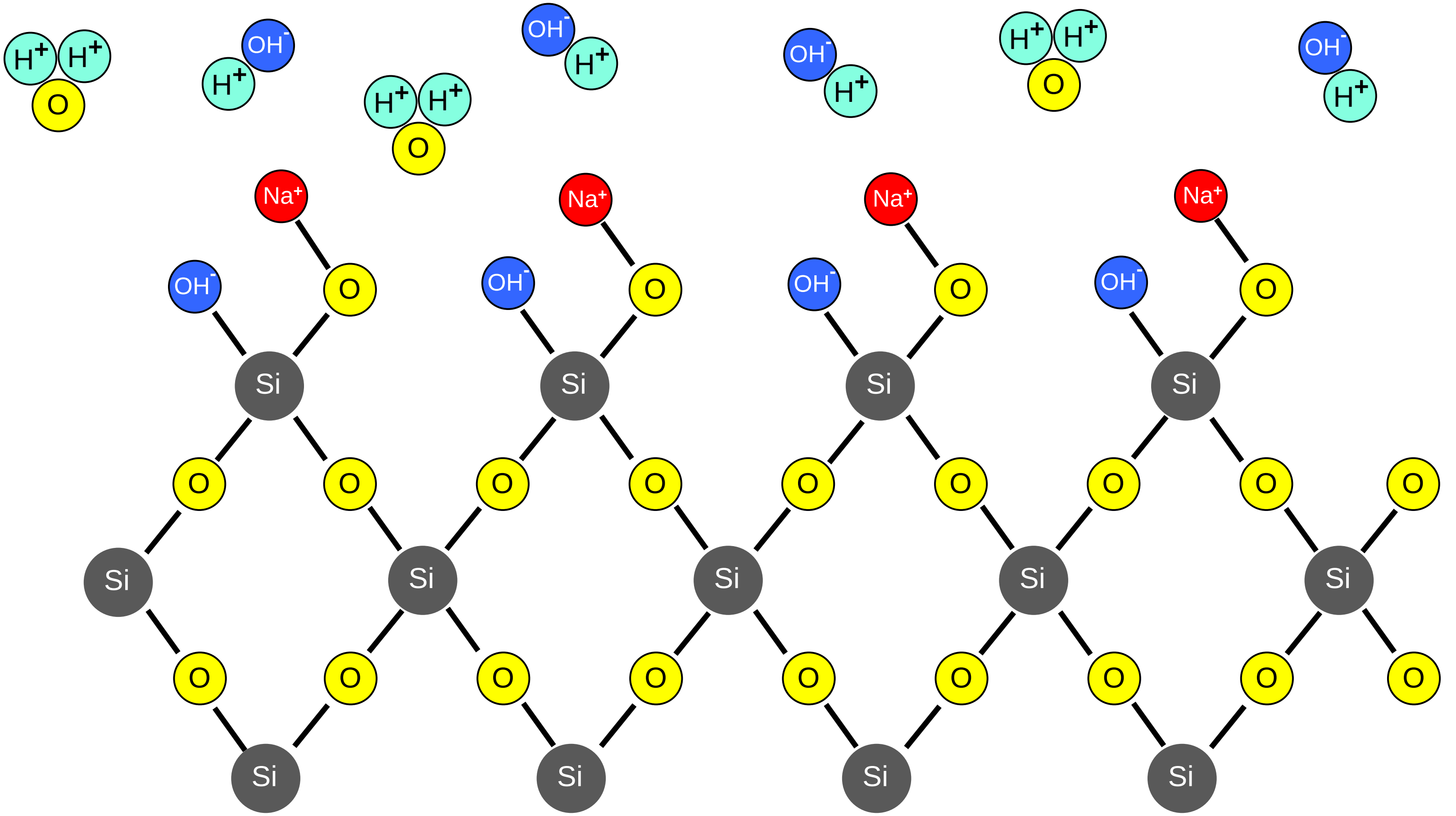
Alkali–Silica Reactivity

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



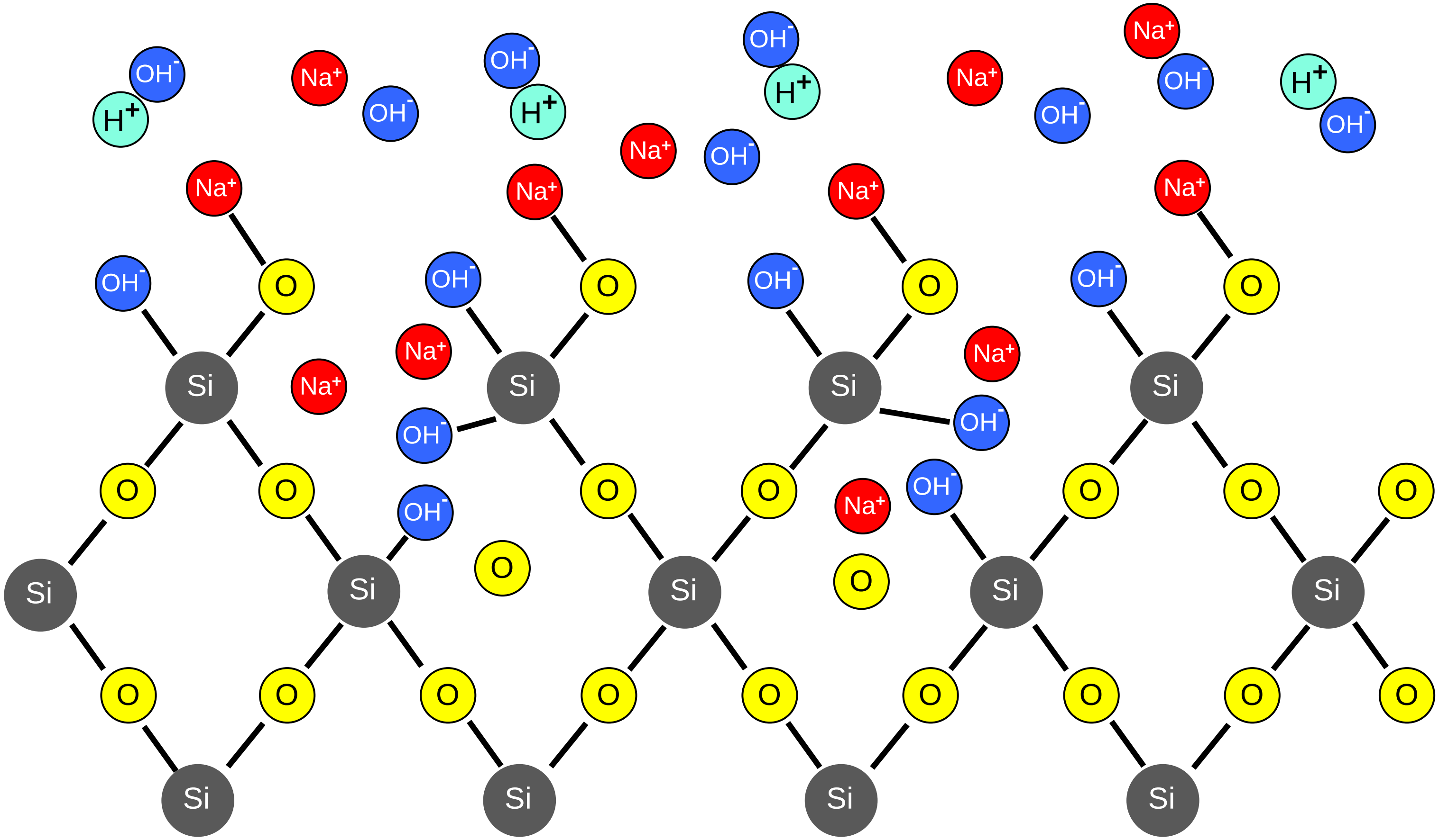
Alkali–Silica Reactivity

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



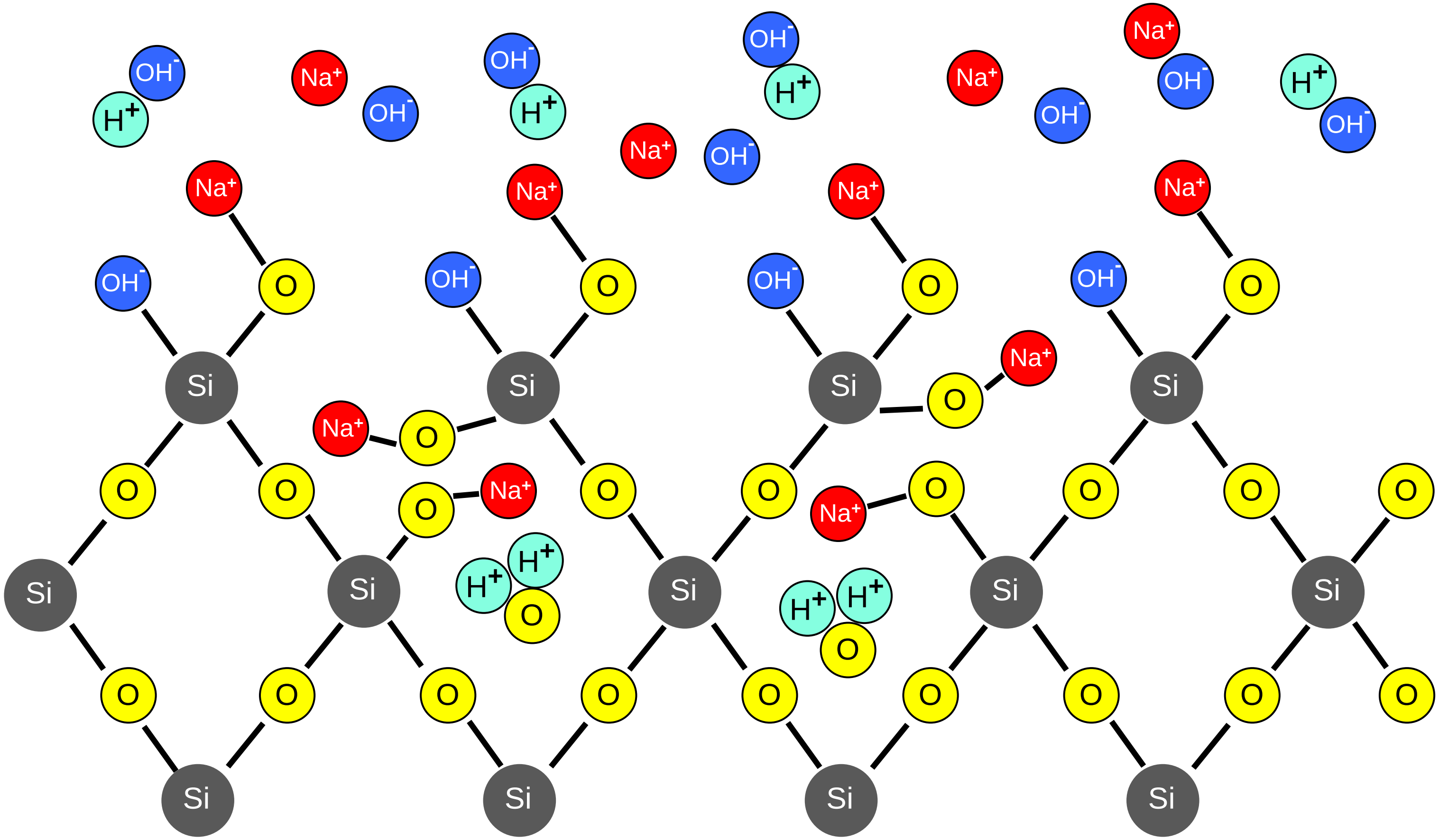
Alkali–Silica Reactivity

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



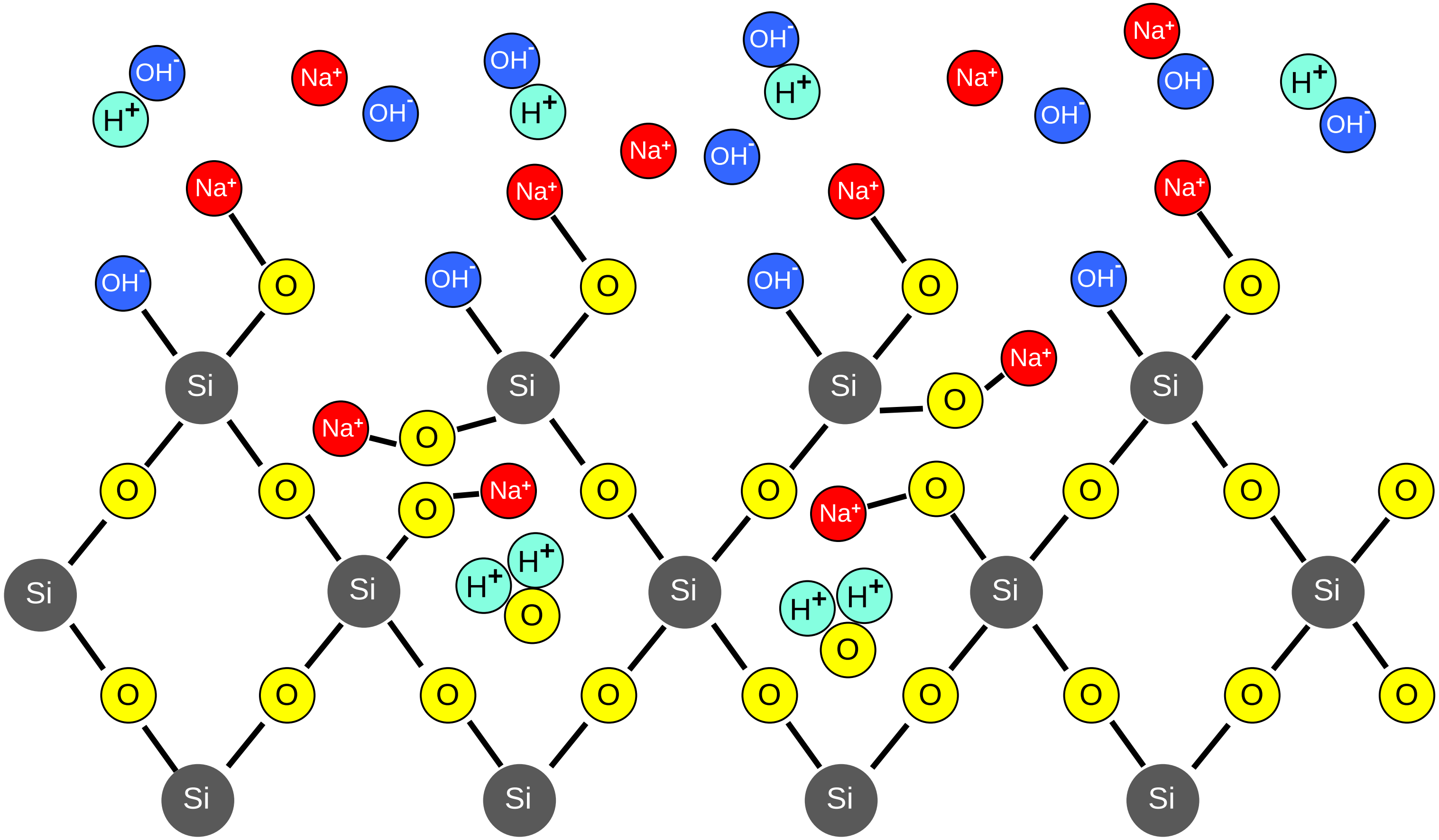
Alkali–Silica Reactivity

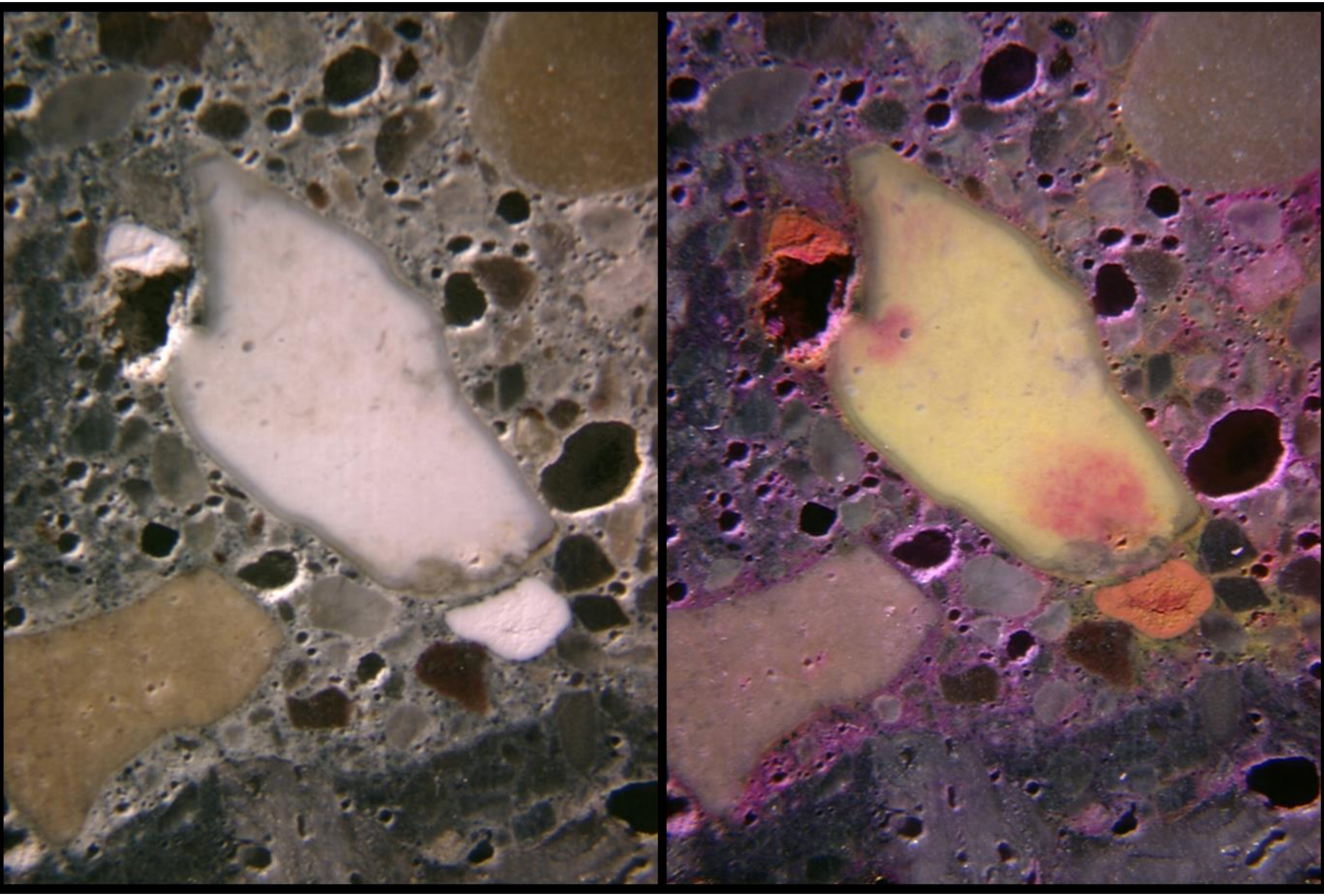
- Hydrogen dissociates from OH^-, combines with O^{2-} to form water. Na^+ substitutes for H^+ and the attack has progressed



Alkali–Silica Reactivity

- Si-O-Si + $2OH^- + 2Na^+$ -> 2(Si-O-Na) + H_2O





7.2 x 5.4 mm

Images: Karl Peterson, University of Toronto

Alkali–Silica Reactivity

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

Alkali–Silica Reactivity

- 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

Alkali–Silica Reactivity

- 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*

Alkali–Silica Reactivity

- 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

Alkali–Silica Reactivity

- 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 emperically 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

Alkali–Silica Reactivity

- Testing
  - ASTM C1567
    - Used to detect the potential for deleterious alkali-silica reaction of combinations of cementitious materials and aggregate 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

Alkali–Silica Reactivity

- 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

Alkali-Carbonate Reactivity

- Overview
  - ➢ Caused by a reaction between alkalis in the paste pore solution and ***specific*** 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

Alkali-Carbonate Reactivity

- Mechanism

Dedolomitization

$$CaMg(CO_3)_2 + 2(Na,K)OH \rightarrow Mg(OH)_2 + CaCO_3 + (Na,K)CO_3$$

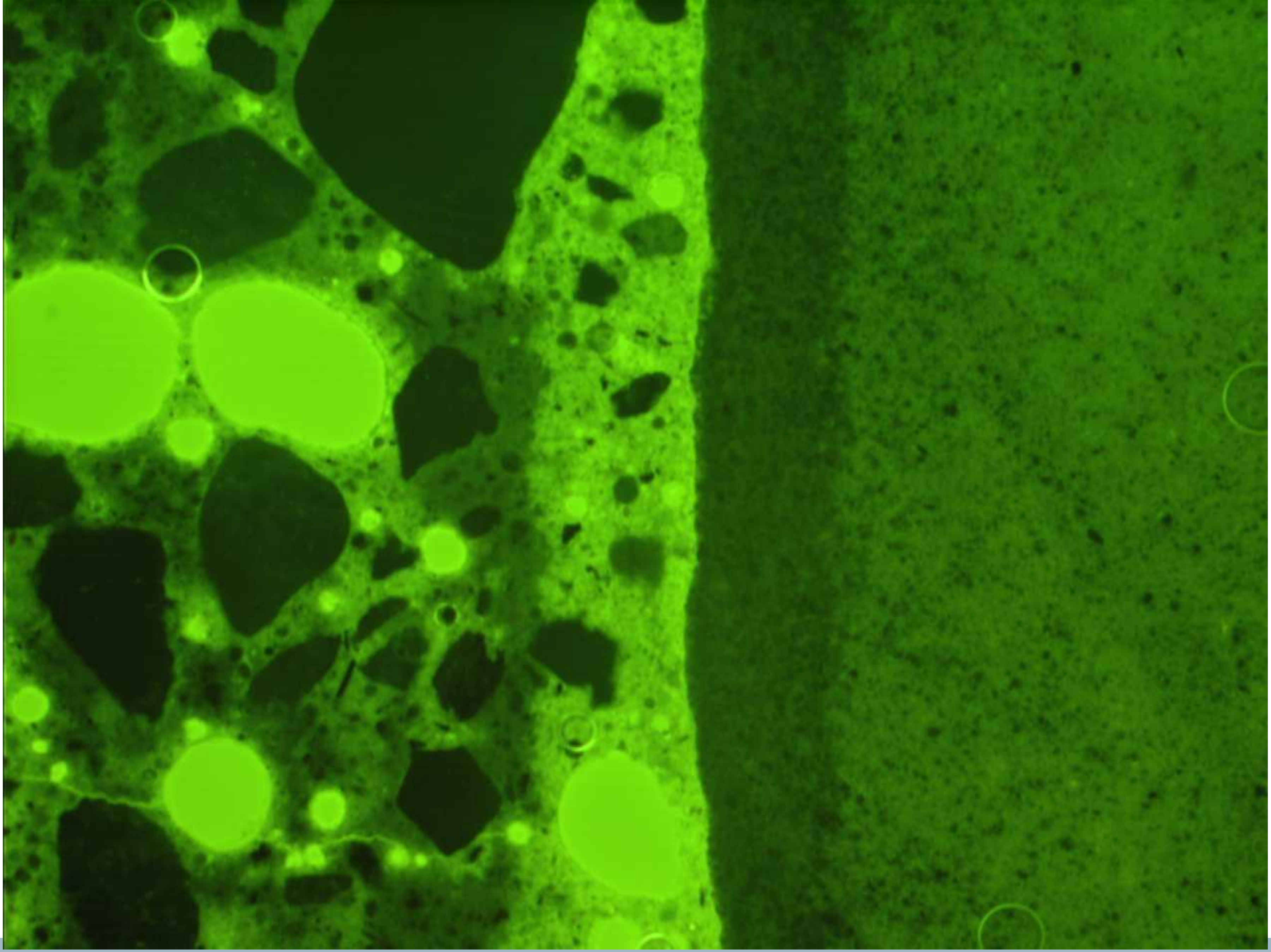
Dolomite *Alkali Hydroxide* *Brucite* *Calcite* *Alkali Carbonate*

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

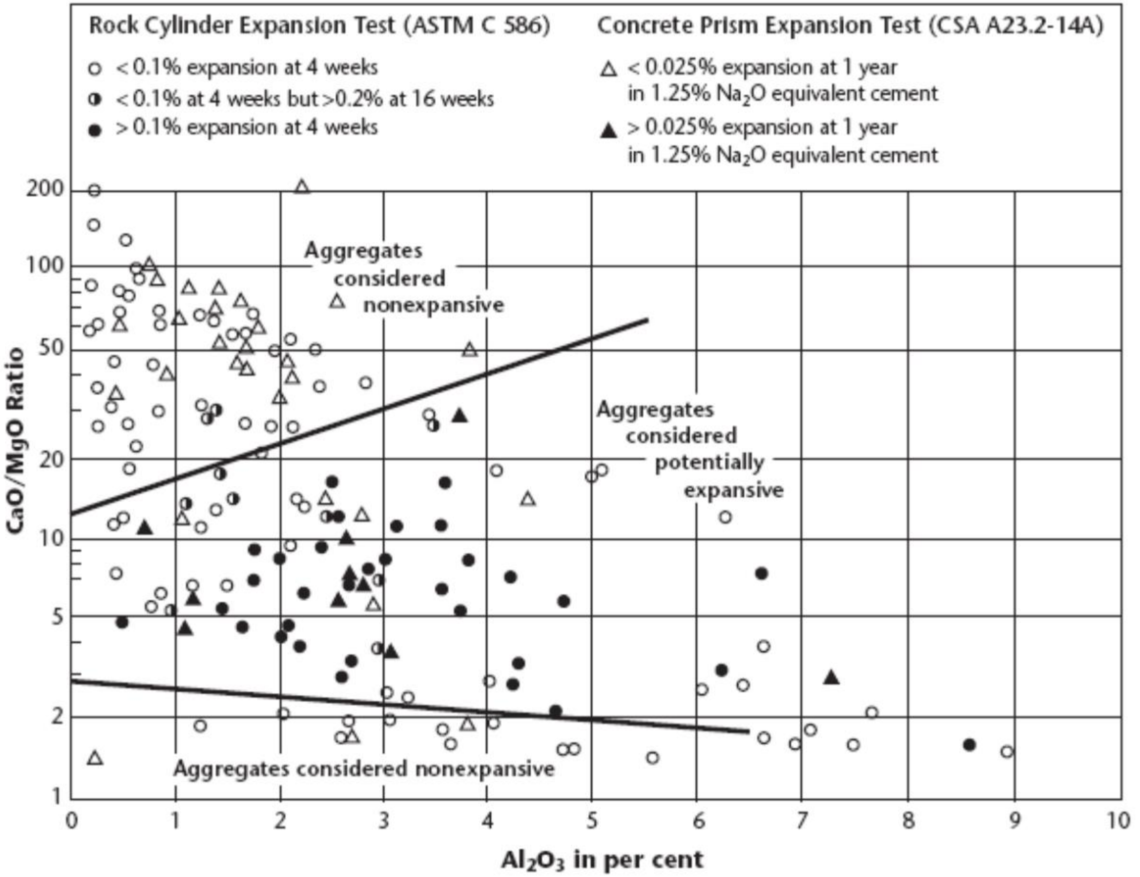
Image: Karl Peterson, University of Toronto

Alkali-Carbonate Reactivity

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

Alkali-Carbonate Reactivity

- Testing – Reject aggregates based on chemistry



CSA A23.2-26A)

Alkali-Carbonate Reactivity

- 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

External Sulfate Attack

- 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

External Sulfate Attack

- 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

External Sulfate Attack

- Mechanism – Example Reactions

Symbols Used

$\overline{\mathbf{S}}$ = sulfate ion (SO_4^{2-})

CH = calcium hydroxide $\left(Ca(OH)_2\right)$

AFm = monosulfate $(3CaO \cdot Al_2O_3 \cdot CaSO_4 \cdot 12H_2O)$

AFt = ettringite $(3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot 32H_2O)$

Ettringite Formation with Calcium Hydroxide Dissolution

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

External Sulfate Attack

- Mechanism – Example Reactions

Symbols Used

$\mathbf{\bar{S}}$ = sulfate ion (SO_4^{2-})

$\mathbf{CH}$ = calcium hydroxide $\left(Ca(OH)_2\right)$

$\mathbf{C\bar{S}}$ = calcium sulfate, gypsum ($CaSO_4 \cdot 2H_2O$)

Gypsum Formation with Calcium Hydroxide Dissolution

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

External Sulfate Attack

- Mechanism – Example Reactions

Symbols Used

$\bar{S}$ = sulfate ion (SO_4^{2-})

CSH = calcium silicate hydrate ($1.7Ca \cdot SiO_2 \cdot 4H_2O$)

$\mathbf{CSH}_D$ = decalcified calcium silicate hydrate ($< 1.7Ca \cdot SiO_2 \cdot 4H_2O$)

AFm = monosulfate ($3CaO \cdot Al_2O_3 \cdot CaSO_4 \cdot 12H_2O$)

AFt = ettringite ($3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot 32H_2O$)

Decalcification of CSH Due To Ettringite Formation

$$n\mathbf{CSH} + \mathbf{AFm} + 4(\mathrm{Na,K})^+ + 2\bar{S} \rightarrow n\mathbf{CSH}_D + \mathbf{AFt} + 4(\mathrm{Na,K})^+ + 4OH^-$$

External Sulfate Attack

- Mechanism – Example Reactions

Symbols Used

$\bar{\mathbf{S}}$ = sulfate ion (SO_4^{2-})

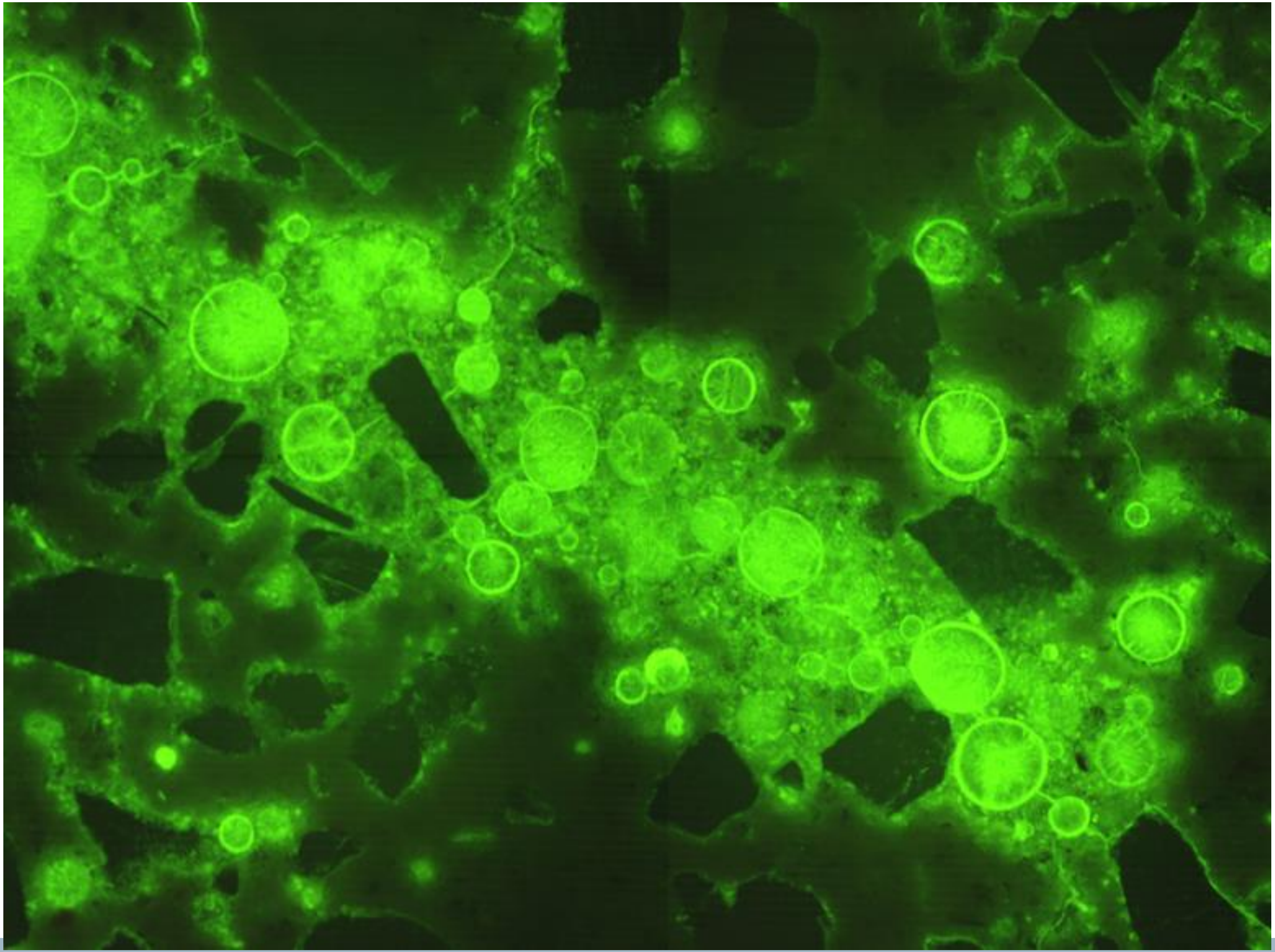
$\mathbf{CSH}$ = calcium silicate hydrate $(1.7Ca \cdot SiO_2 \cdot 4H_2O)$

$\mathbf{CSH}_D$ = decalcified calcium silicate hydrate $(<1.7Ca \cdot SiO_2 \cdot 4H_2O)$

$\mathbf{C\bar{S}}$ = calcium sulfate, gypsum $(CaSO_4 \cdot 2H_2O)$

Decalcification of CSH Due To Gypsum Formation

$$n\mathbf{CSH} + 2(Na,K)^+ + \bar{\mathbf{S}} \rightarrow n\mathbf{CSH}_D + \mathbf{C\bar{S}} + 2(Na,K)^+ + 2OH^-$$



2.54 x 1.90 mm

Image: Karl Peterson, University of Toronto

External Sulfate Attack

- 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

Internal Sulfate Attack

- 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

Internal Sulfate Attack

- Mechanism
  - Internal attack is most commonly associated with steam cured concrete
    - If concrete is cured at temperatures above 70-80 ºC (158-176 ºF) 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

Internal Sulfate Attack

- 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 [$Fe_{(1-X)}S$ ($x = 0$ 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

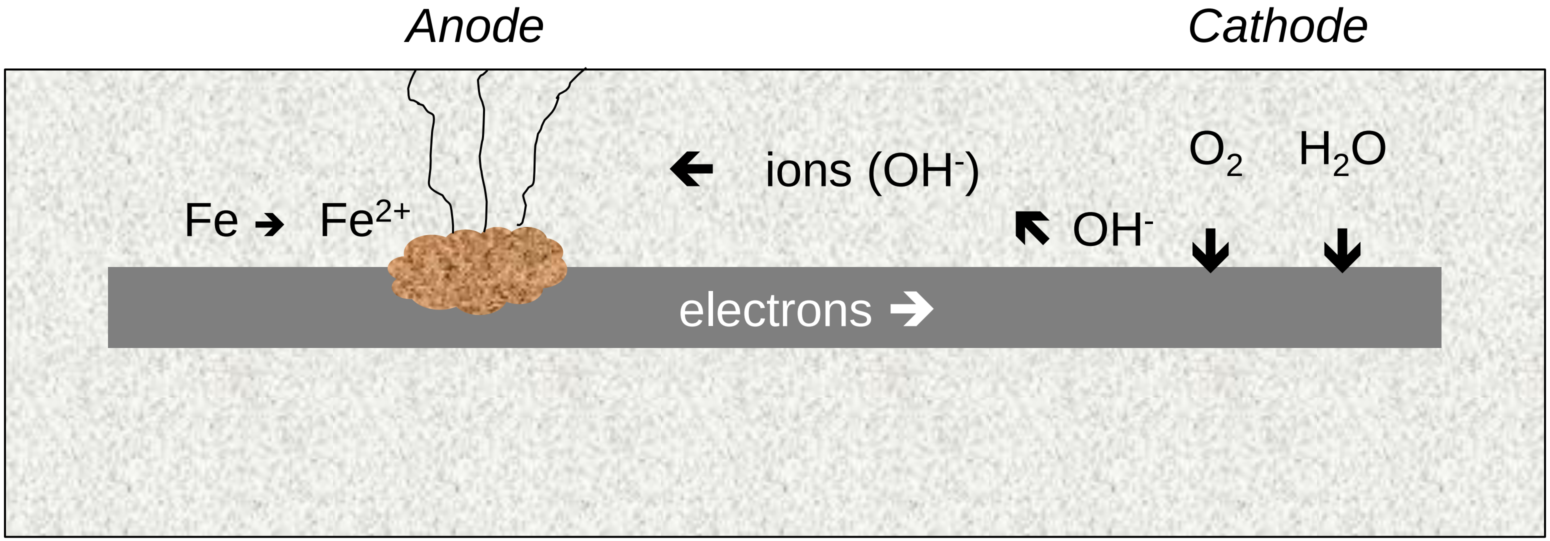
Corrosion of Embedded Steel

- 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

Corrosion of Embedded Steel

Corrosion of Embedded Steel

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



Anode

Cathode

$Fe \rightarrow Fe^{2+}$

← ions (OH^-)

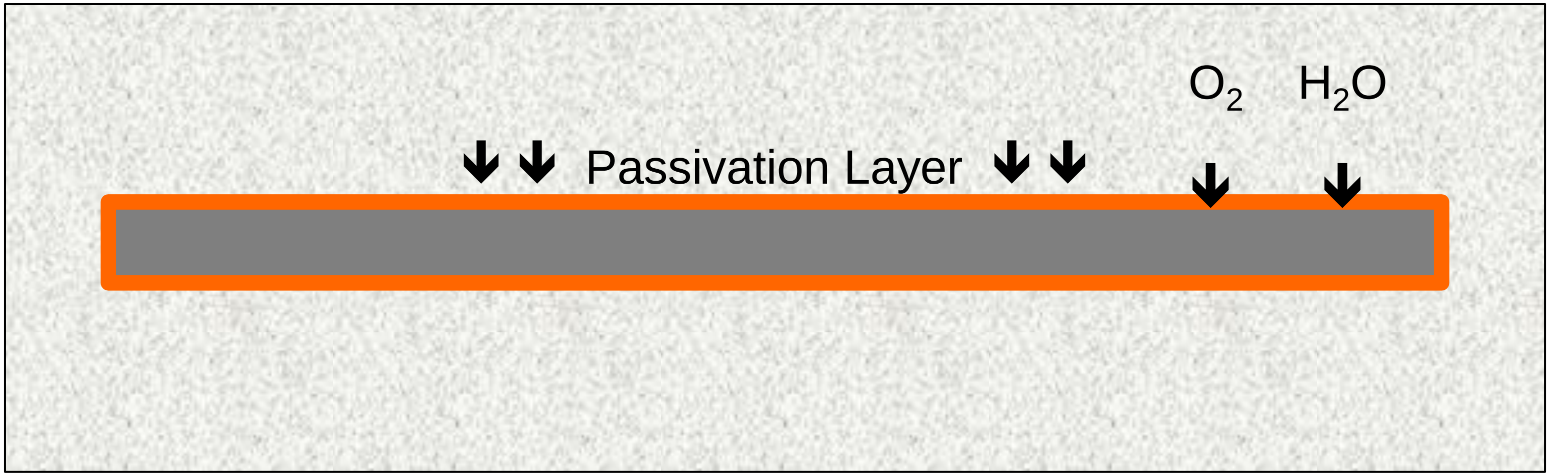
↖ OH^-

O_2 H_2O

electrons →

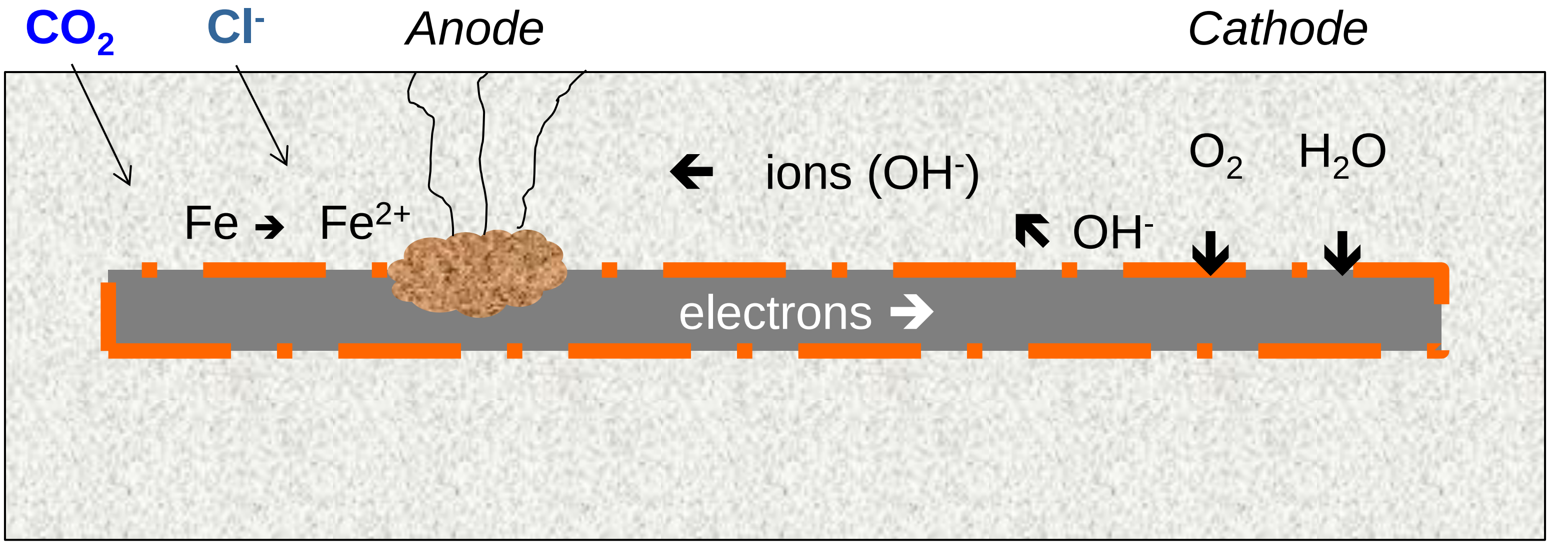
Corrosion of Embedded Steel

- 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



Corrosion of Embedded Steel

- Mechanism
  - Carbon dioxide (CO_2) lowers the pH of the concrete and the passivation layer breaks down
  - Chloride (Cl^-) attacks the passivation layer directly – *mechanism unclear*
  - Limiting fluid ingress (CO_2, O_2, Cl^-, and H_2O) limits corrosion



Corrosion of Embedded Steel

- 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_2
  - 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