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
   ➢ 42
**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 °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 undergoes F-T cycles
- The expansion of ice causes tensile forces that crack concrete

![Graph showing the relationship between degree of saturation and resistance to frost](image)

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

Partially Saturated Capillary and Gel Pores

Critically Saturated Capillary and Gel Pores

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

- 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 ($\alpha$):
  
  ► 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 $\alpha$ assumed proportional to $A$ in fresh concrete

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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/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

Impact of Poor Finishing

0.5 to 1 inch
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
**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
**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 minutes µ macropores (Primary Load)
      − Water absorbed 1–15 minutes µ 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$_2$O, Na$^+$, K$^+$, Ca$^{2+}$, OH$^-$, and H$_3$SiO$_4^-$ 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

• 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\textsuperscript{-}) 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**

• \( \text{Si-O-Si} + 2\text{OH}^- + 2\text{Na}^+ \rightarrow 2(\text{Si-O-Na}) + \text{H}_2\text{O} \)
**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 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 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
**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 undergo 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

\[
\text{CaMg(CO}_3\text{)}_2 + 2(\text{Na,K})\text{OH} \rightarrow \text{Mg(OH)}_2 + \text{CaCO}_3 + (\text{Na,K})\text{CO}_3
\]

- Dolomite
- Alkali Hydroxide
- Brucite
- Calcite
- Alkali Carbonate

Recycle Alkalis – leads to carbonate halos

\[
\text{Na(K)}_2\text{CO}_3 + \text{Ca(OH)}_2 \rightarrow \text{CaCO}_3 + 2\text{Na(K)}\text{OH}
\]

- Alkali Carbonate
- CH
- Calcite
- Alkali Hydroxide

Recycling of alkalis makes mitigation ineffective
**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 reported to be ACR susceptible
  - **IMPORTANT**: Requires a specific dolomite rock type – *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)*

- **Prevention – Avoid ACR susceptible aggregates**
Alkali-Carbonate Reactivity

- Testing – Reject aggregates based on chemistry
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

\( \bar{S} = \text{sulfate ion} \ (\text{SO}_4^{2-}) \)

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

\( \text{AFm} = \text{monosulfate} \ \left(3\text{CaO} \ ± \text{Al}_2\text{O}_3 \ ± \text{CaSO}_4 \ ± 12\text{H}_2\text{O}\right) \)

\( \text{AFt} = \text{ettringite} \ \left(3\text{CaO} \ ± \text{Al}_2\text{O}_3 \ ± 3\text{CaSO}_4 \ ± 32\text{H}_2\text{O}\right) \)

Ettringite Formation with Calcium Hydroxide Dissolution

\[
4(\text{Na,K})^+ + 2\bar{S} + 2\text{CH} + \text{AFm} \rightarrow 4(\text{Na,K})^+ + \text{AFt} + 4\text{OH}
\]
External Sulfate Attack

- Mechanism – Example Reactions

Symbols Used

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

\( CH \) = calcium hydroxide \((Ca(OH)_2)\)

\( CS \) = calcium sulfate, gypsum \((CaSO_4 \cdot 2H_2O)\)

Gypsum Formation with Calcium Hydroxide Dissolution

\((Na,K)^+ + \bar{S} + CH \rightarrow 4(Na,K)^+ + CS + 4OH\)
External Sulfate Attack

• Mechanism – Example Reactions

Symbols Used

\( \bar{S} = \text{sulfate ion (SO}_4^{2-}) \)

\( \text{CSH} = \text{calcium silicate hydrate (1.7Ca\text{SiO}_2 \cdot 4H_2O)} \)

\( \text{CSH}_D = \text{decalcified calcium silicate hydrate (<1.7Ca\text{SiO}_2 \cdot 4H_2O)} \)

\( \text{AFm} = \text{monosulfate (3CaO\cdotAl}_2\text{O}_3 \cdot Ca\text{SO}_4 \cdot 12H_2O)} \)

\( \text{AFt} = \text{ettringite (3CaO\cdotAl}_2\text{O}_3 \cdot 3Ca\text{SO}_4 \cdot 32H_2O)} \)

Decalcification of CSH Due To Ettringite Formation

\( n\text{CSH} + \text{AFm} + 4(Na,K)^+ + 2\bar{S} \rightarrow n\text{CSH}_D + \text{AFt} + 4(Na,K)^+ + 4OH^- \)
External Sulfate Attack

• Mechanism – Example Reactions

Symbols Used

\( \bar{S} = \text{sulfate ion (SO}_4^{2-} \) \\
CSH = \text{calcium silicate hydrate (1.7CaSiO}_2 \cdot 4H_2O) \\
CSH_D = \text{decalcified calcium silicate hydrate (<1.7CaSiO}_2 \cdot 4H_2O) \\
C\bar{S} = \text{calcium sulfate, gypsum (CaSO}_4 \cdot 2H_2O) \\

Decalcification of CSH Due To Gypsum Formation

\[
n\text{CSH} + 2(\text{Na, K})^+ + \bar{S} \rightarrow n\text{CSH}_D + C\bar{S} + 2(\text{Na, K})^+ + 2\text{OH}^{-}
\]
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 °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
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 \([\text{Fe}_{(1-x)}\text{S} \ (x = 0 \text{ to } 0.2)]\) 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
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.

\[
\begin{align*}
\text{Anode} & : \quad \text{Fe} \rightarrow \text{Fe}^{2+} \\
\text{Cathode} & : \quad \text{electrons} \rightarrow \text{OH}^{-} \\
\text{ions (OH}^{-}) & : \quad \text{O}_2 + \text{H}_2\text{O} \\
\end{align*}
\]
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$_2$O) limits corrosion

\[
\begin{align*}
\text{Anode} & : \text{Fe} \rightarrow \text{Fe}^{2+} \\
\text{Cathode} & : \text{O}_2 + 2\text{H}_2\text{O} + 4\text{e}^- \rightarrow 4\text{OH}^- \\
\end{align*}
\]
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 **cannot** 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.