SULPHATE AND DELAY ETTRINGITE FORMATION

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M50-03-12
References

2. Fundamentals of Durable Reinforced Concrete, M.G. Richardson, Spon Press, 2002
Learning Outcome

• At the end of the course student should be able to understand
  – Mechanism of sulphate attack
  – Factors that influence
  – Method of rectification
INTRODUCTION

• Sulphate attack is a chemical breakdown mechanism where sulphate ions attack components of the cement paste.

• The compounds responsible for sulphate attack are water-soluble sulfate-containing salts, such as alkali-earth (calcium, magnesium) and alkali (sodium, potassium) sulphate that are capable of chemically reacting with components of concrete.
Sulphate attack might show itself in different forms Depending on:

• The chemical form of the sulphate

• The atmospheric environment which the concrete is exposed to
SULPHATE SOURCES

1. Internal Sources:

Originates from such concrete-making materials as hydraulic cements, fly ash, aggregate, and admixtures.

- portland cement might be over-sulfated.

- presence of natural gypsum in the aggregate.

- Admixtures also can contain small amounts of sulphate.
2. External Sources:

External sources of sulphate are more common and usually are a result of high-sulfate soils and ground waters, or can be the result of atmospheric or industrial water pollution.

- **Soil** may contain excessive amounts of gypsum or other sulphate.
- **Ground water** be transported to the concrete foundations, retaining walls, and other underground structures.
- **Industrial waste waters**.
What happens when sulphate get into concrete?

- It combines with the C-S-H, or concrete paste, and begins destroying the paste that holds the concrete together. As sulphate dries, new compounds are formed, often called ettringite.

- These new crystals occupy empty space, and as they continue to form, they cause the paste to crack, further damaging the concrete.
Nature of reaction: (chemical, Physical)

SULFATE ATTACK processes decrease the durability of concrete by changing the chemical nature of the cement paste, and of the mechanical properties of the concrete.
Chemical process:

- the sulphate ion + hydrated calcium aluminate and/or the calcium hydroxide components of hardened cement paste + water = *gypsum* (calcium sulphate hydrate)

- \( \text{Na}_2\text{SO}_4 + \text{Ca(OH)}_2 + 2\text{H}_2\text{O} = \text{CaSO}_4.2\text{H}_2\text{O} + 2\text{NaOH} \)

- \( \text{MgSO}_4 + \text{Ca(OH)}_2 + 2\text{H}_2\text{O} = \text{CaSO}_4.2\text{H}_2\text{O} + \text{Mg(OH)}_2 \)
Two forms of Chemical reaction depending on

- Concentration and source of sulphate ions.
- Composition of cement paste in concrete.
Physical process:

• The complex physico-chemical processes of "sulphate attack" are interdependent as is the resulting damage.

• Physical sulphate attack, often evidenced by bloom (the presence of sodium sulphate Na$_2$SO$_4$ and/or Na$_2$SO$_4$.10H$_2$O) at exposed concrete surfaces.

• It is not only a cosmetic problem, but it is the visible displaying of possible chemical and microstructural problems within the concrete matrix.
DIAGNOSIS

• Spalling due to sulphate attack.
• Spalling due to sulphate attack.
• Spalling due to sulphate attack.
Microscopical examination
Main factors affecting sulphate attack:

1. Cement type and content:

   The most important mineralogical phases of cement that affect the intensity of sulphate attack are: C₃A, C₃S/C₂S ratio and C₄AF.
1. Cement type and content:

![Graph showing the effect of C₃A content on the rate of deterioration of concrete exposed to sulphate bearing soils.](image)

**Fig. 9.5.** Effect of the C₃A content in Portland cement on the rate of deterioration of concrete exposed to sulphate bearing soils. (Adapted from Ref. 9.14.)
2. Fly ash addition

- The addition of a pozzolanic admixture such as fly ash reduces the C₃A content of cement.

Fig. 9.8. Sulphate expansion of concrete containing low-calcium fly-ash of different compositions marked 1 to 4. (Adapted from Ref. 9.19.)
3. Sulphate type and concentration:

- The sulphate attack tends to increase with an increase in the concentration of the sulphate solution up to a certain level.

4. Chloride ions
Other factors:

• The level of the water table and its seasonal variation

• The flow of groundwater and soil porosity

• The form of construction

• The quality of concrete
CONTROL OF SULPHATE ATTACK

• 1. The *quality of concrete, specifically a low permeability*, is the best protection against sulphate attack.

• Adequate concrete thickness
• High cement content
• Low w/c ratio
• Proper compaction and curing
Effect of w/c ratio

Fig. 9.6. Effect of W/C ratio on rate of deterioration of concrete made of ordinary Portland cement and exposed to sulphate bearing soils. (Adapted from Ref. 9.14.)
2. The use of sulphate resisting cements provide additional safety against sulphate attack

<table>
<thead>
<tr>
<th>Exposure</th>
<th>Concentration of water-soluble sulphate</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>In soil per cent</td>
</tr>
<tr>
<td>Mild</td>
<td>&lt;0.1</td>
</tr>
<tr>
<td>Moderate</td>
<td>0.1 to 0.2</td>
</tr>
<tr>
<td>Severe</td>
<td>0.2 to 2.0</td>
</tr>
<tr>
<td>Very severe</td>
<td>&gt;2.0</td>
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Evolution of Amtrak’s Concrete Crosstie and Fastening System Program
Presentation Outline

• Why Concrete Ties?
• Timeline of Concrete Tie Manufacture
• Concrete Tie Problems
• Concrete Tie Design Changes
• Elastic Fasteners
• Shoulders
• Tie Pads and Insulators
• Switch Ties
• Future Considerations
Why Concrete Ties?

• Manufactured Product
  – Uniformity
  – Better control of tolerances in rail seat leading to better track geometry
  – Well adapted for elastic fasteners

• Better Track Stability
  – Weighs 790 pounds compared to 240 for hardwood tie
  – Elastic fasteners control longitudinal rail forces better
  – Stiffer track promotes better track geometry

• Track Renewal Installation Benefits
  – High quality track with fewer track occupancies
  – Facilitate rail change in the process of tie replacement
Timeline of Manufacture

- First concrete tie manufactured & installed – 1978
- Manufacturers:
  - Santa Fe San Vel: 1978 to 1983 ~ 1.0 million
  - Lonestar: 1983 to 1986 ~ 0.3 million
  - Rocla: 1990 to 2000 ~ 1.4 million
  - Rocla: 2003 to 2011 ~ 1.3 million
- Total concrete ties purchased to date ~ 4.0 million
Concrete Tie Problems – ASR

ASR results when cement alkalis react with certain soluble forms of silica in the aggregate component of a concrete, forming an alkali-silica gel at the aggregate’s surface. This formation, often referred to as “reaction rim” has a very strong affinity for water, and thus has a tendency to swell. These expanding compounds can cause internal pressures sufficiently strong to cause cracking of the paste matrix which can then result in a compromised concrete having an open door to additional moisture and an increasing rate of deterioration.
Concrete Tie Problems – DEF

Delayed Ettringite Formation (DEF) is a type of internal sulfate attack that occurs in concrete that has reached certain high temperature thresholds in the first few hours of placement. At these temperatures, normal formation of ettringite (calcium sulfoaluminate hydrate) is impeded until after concrete has hardened. When ettringite does form, it can cause deleterious expansion, resulting in cracking.
Greater Tensile Strength also Reduces Cracking

**MgO Changes Surface Charge as the pH Rises.** This could be the reason for the greater tensile strength displayed during the early plastic phase of tec-cement concretes. The affect of additives is not yet known.
Reducing Cracking as a Result of Volume Change caused by Delayed Reactions

An Alkali Aggregate Reaction Cracked Bridge Element
Photo Courtesy Ahmad Shayan ARRB
Types of Delayed Reactions

• There are several types of delayed reactions that cause volume changes (generally expansion) and cracking.
  – Alkali silica reactions
  – Alkali carbonate reactions
  – Delayed ettringite formation
  – Delayed thaumasite formation
  – Delayed hydration or dead burned lime or periclase.

• Delayed reactions cause dimensional distress, cracking and possibly even failure.
Reducing Delayed Reactions

• Delayed reactions do not appear to occur to the same extent in TecEco cements.
  – A lower long term pH results in reduced reactivity after the plastic stage.
  – Potentially reactive ions are trapped in the structure of brucite.
  – Ordinary Portland cement concretes can take years to dry out however the reactive magnesia in Tec-cement concretes consumes unbound water from the pores inside concrete.
  – Magnesia dries concrete out from the inside. Reactions do not occur without water.
Concrete Tie Problems
Concrete Tie Problems
Concrete Tie Problems
Concrete Tie Problems – Lone Star

- Approx. 300,000 ties manufactured between 1982 and 1986
- Cracking first detected in 1986
- Spider cracking with slow progression to failure within a few years
- Attributed to an alkali-silicone reaction (ASR) and low air entrainment
- All ties installed in stretches replaced between 1990 & 1995
- Others similarly afflicted (CSX, LIRR, Transit Systems)
Concrete Tie Problems – Rocla

• Approximately 1,400,000 ties manufactured between 1990 and 2000

• Population of cracking ties & year of first detection:
  – 1990 to 1992: 360,000 ties / cracks detected in 1999 (7+ years from manufacture)
  – 1993 to 1994: 323,000 ties / cracks detected in 2006 (12+ years from manufacture)
  – 1996: 133,000 ties / cracks detected in 2007 (11 years from manufacture)
  – 1997: 118,000 ties / cracks detected in 2001 (4 years from manufacture)
  – 1998 to 1999: 314,000 ties / cracks detected in 2007 (8+ years from manufacture)

• Most ties exhibit hairline cracking with a slow propagation rate

• Some ties exhibit spider cracking with a more rapid propagation rate (predominantly the ties manufactured in 1997)

• Tie cracking attributed to ASR and DEF, result of contamination in the fine aggregate and possible high curing temperatures

• Others similarly afflicted (Metro North, LIRR, MBTA)
Concrete Ties Problems – Operations

• Severity of speed drops
  – 1 failed tie – can run 150 MPH
  – 2 consecutive failed ties – track slow ordered to 60 MPH
  – 3 consecutive failed ties – track slow ordered to 15 MPH
  – 4 consecutive failed ties – track out-of-service
• Ties often fail quickly, spread to adjacent ties
• Cracks on side and cannot be seen without removing ballast
• Cast shoulder and tie depth make removal/insertion difficult
• Track with tie failures are difficult to surface
Concrete Tie Problems - Operations

• Amtrak has contracted with HNTB for tie evaluation by qualified inspectors
• Tie evaluation done by walking with Amtrak
• Ties are graded based on visual inspection:
  – Ties replaced with concrete and interlaced wood ties are noted
  – Cracked ties are graded 2 thru 5 in order of extent of cracking
  – Grades 3 and above are marked
• Data accumulated to track trends, identify critical areas, program replacement programs
• UICU under contract to the Law Dept., also to assist with design changes
• CTL used for periodic testing and monitoring
Concrete Tie Design Changes

- Santa Fe San Vel 1978-83
- Lonestar 1983-86
- Rocla 1990-2000
- New Rocla 2003 to present
- In 1992, increased air entrainment from 2%-5% to 4%-6%
Concrete Tie Design Changes
Concrete Tie Design Changes

MATERIAL SPECIFICATIONS

CONCRETE TIES
Concrete shall meet the following specifications:
- Strength: 7200 PSI at 28 days
- Durability shall meet ASTM C33
- Aggregate shall meet ASTM C33" and C200
- Air entrained: 2 to 5%
- cured 7 days at 75°F
- Finish: Steel Form Finish except at location of tie which will have rough finish with 3/4" coated edge.
- Preservatives shall consist of eight (8) 1/8" diameter / wire distended strands conforming to ASTM A616-61. Ultimate strength (at) shall be 700-5 PSI and initial tension 15-68 Kips per strand (0.725") of projection.

HARDWARE
- Cables shall be made of SAE 5130H heat treated steel.
- Finished cables shall be tempered within the hardness range of 40 to 44 Rockwell "C".
- Shoulder shall be made of acid case-hardened conforming to ASTM A536-72 Grade 45-45-12.
- Stirrups shall be made of cold drawn carbon steel for concrete reinforcement conforming to ASTM A320.
- Stirrups shall be made of U.H. Heat Stabilized Grade reinforced A36.
- Rods shall be made of (2) stainless steel 430 (3.5) stabilized color blane.

TOLERANCES

CONCRETE TIES
- Length: -1/2", -1/2" Drill 2/0.015 unless otherwise specified.
- Width: +1/8", -0.015
- Height: +1/8", -0.015
- Weight of tie: 760 lbs. net (including shoulder and hardware)

HARDWARE
- 5/8" to 1-1/4" unless otherwise specified.
- 1-1/8" to 2" unless otherwise specified.
- 2-1/8" to 2-1/4" unless otherwise specified.
Concrete Tie Design Changes
Concrete Tie Design Changes

MATERIAL SPECIFICATIONS

CONCRETE TIE:

Concrete tie shall meet the following specifications:

- Compressive Strength of 8000 psi at 28 days.
- Material shall be high strength concrete.
- Durability and resistance to freezing and thawing shall be maintained.
- Details shall be such that the tie will withstand the expected loads.

FACIAL STEEL:

Finish steel, form finish except on bottom of tie which will have rough finish with 3/8” radius corners.

PRESTRESSED STRAND:

Prestressed strand shall consist of seven 1/4” diameter I WIRE with a maximum modulus of 400,000 psi. Details shall be such that the tie will withstand the expected loads.

HARDWARE:

Clips shall be made of the same high tensile steel. Finish clips shall be incorporated into the tie design. Hardware shall be galvanized according to the manufacturer’s recommendations.

SHAPES:

Shapes shall be made of cold rolled steel, for concrete bridge preparation, conforming to ASTM standards.

TOLERANCES:

Concrete tie: +0, -3/8” dimension over unless otherwise specified.

Prestressed strand: +0.25, -0.10” dimension over unless otherwise specified.

Section 0-0:

1-1/4” to 2-1/4” dimension over unless otherwise specified.

2-1/2” to 3-1/2” dimension over unless otherwise specified.
Concrete Tie Design Changes
Concrete Tie Design Changes

- Major changes to Amtrak Tie Specification in 2003
- Design change from 8 7-strand reinforcing wires to 24 individual indented reinforcing wires to increase tensile strength
- Established tighter limitations on pre-set curing temperatures and new control system installed to closely monitor curing temperatures
- Use of manufactured sand (fine aggregate) to eliminate most all potential reactive contaminants that could contribute to ASR/DEF reactivity
- Use of up to 20% but not less than 15% fly ash in the cementitious portion of the mix for even greater resistance to formation of ASR and DEF
- Additional third party (CTL) testing of materials and hardened concrete
- Increase Q/C process
- Increase air entrainment from 4%-6% to 4%-7%
Concrete Tie Design Changes
Concrete Tie Design Changes
Elastic Fasteners

- 1978-1986 PR 601-A
- 1990-1995 e 2055
- Mid 1995 to present Fast
Cast Shoulders

- 1983-1995 Single bi-axial ragged stem
- 2003 Single button stem
- 2010 Double stem FastClip

Approx. Weight: 3.0 lbs.
Tie Pads and Insulators

- 5 mm Ohio rubber pad
- 6 1/2 mm irradiated EVA pad
- 6 1/2 mm polyurethane pad (KD, WB)
Switch Ties

- Dapped concrete ties
- Steel tie extensions
- Hollow steel ties
FUTURE CONSIDERATION

• Continue increased Q/C program
• Continue third party concrete tie testing
• Continue project with UICU on tie design
• Consider possible tie design change
• Continue FRA project with FRA and Volpe Center
• Continue other FRA projects concerning concrete ties; NDT, for example
Acknowledgement

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Joseph A. Smak
Director of Track Standards and Specifications

Concrete Crosstie & Fastening System Symposium
June 7, 2012
Pre-Election Fireworks, the Israeli way

Year 1996: Lebanon

Year 2008-09: Gaza

Year 2012: Gaza

Vote

Vote Likud

PARESH CAI/NYTS
We know too well that our freedom is incomplete without the freedom of the Palestinians.

- NELSON MANDELA
WHO YOU ARE ALL STARTS IN YOUR HEAD, NELSON.

REMEMBER, YOU ARE WHAT YOU THINK, NOT WHAT YOU THINK YOU ARE.

ARE YOU CONFUSED, OR DO YOU JUST THINK YOU'RE CONFUSED? IS CONFUSED WHAT YOU ARE, OR IS CONFUSED WHAT YOU THINK YOU ARE?

I THINK I'M GOING TO WATCH TV.