Concrete Deterioration due to Oxidation of Pyrrhotite-Bearing Aggregate: A Case Study in CT and MA

Kay Wille, Marisa Chrysochoou and James Mahoney

University of Connecticut
Goals and Objectives

- Provide an overview of **concrete deterioration** due to the presence of the **sulfide-bearing mineral pyrrhotite** in the aggregates.

- Share information about the **field sampling & testing program** and current **results**
Typical Signs of Deterioration

- Map cracking
- Darkening
- Mineral Deposit
- Deformation
- Red-brownish Discoloration

> 40,000 homes potentially affected in CT and MA
What is the Issue?

**Presence** of Iron-Sulfide
(Pyrrhotite containing aggregates in concrete)

**Exposure** to O₂, H₂O and high pH

**Oxidation** of Iron-Sulfide

**Expansion** of Oxidation Products and Release of Sulfuric Acid

Release of Sulfates → **Internal Sulfate Attack**

Formation of **Expansive Minerals** (Ettringite and Thaumasite)

Cracking and **Premature Deterioration** → Significant Deformations, Water ingress, Structural Deficiency
Field Testing Overview

Lifted Condo Complex in CT

UConn testing showing pyrrhotite in concrete foundations as of 04/2024 (https://crumblingconcrete.engr.uconn.edu/)
Field Testing Program

To Date We Have Sampled 200+ Foundations – at no cost

40+ Foundation Replacements
(90% CT, 10% MA)

160+ Foundations in Use with Drilling Technique
(70% CT, 30% MA)

Giving back to our community - savings in fees for Service/Testing → $0.4 Mio
Field Testing Program – Sample Processing

40+ Foundation Replacements
(90% CT, 10% MA)

160+ Foundations in Use with Drilling Technique
(70% CT, 30% MA)

- 5 holes from the inside
- 1 inch in diameter, ~5 inches deep
- No damage of any waterproofing
- Cleaning + patching holes
- Entire process 60 min
- No water is used
- Report with photos

over 4000 tests in the lab
Laboratory Testing - Report

Table 1: Sulfur analysis results for the collected samples

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Total Sulfur (S\textsubscript{T}) average % by weight</th>
<th>Sulfate (S\textsuperscript{6+}) average % by weight</th>
<th>Sulfide (S\textsuperscript{2-}) average % by weight</th>
<th>Pyrrhotite (Fe\textsubscript{7}S\textsubscript{8}) average % by weight**</th>
</tr>
</thead>
<tbody>
<tr>
<td>W1 (wall)</td>
<td>0.34 ± 0.00</td>
<td>0.18</td>
<td>0.17</td>
<td>0.42</td>
</tr>
<tr>
<td>W2 (wall)</td>
<td>0.28 ± 0.01</td>
<td>≤0.28</td>
<td>&lt;0.1</td>
<td>&lt;0.25*</td>
</tr>
<tr>
<td>W3 (wall)</td>
<td>0.21 ± 0.00</td>
<td>≤0.21</td>
<td>&lt;0.1</td>
<td>&lt;0.25*</td>
</tr>
<tr>
<td>W4 (wall)</td>
<td>0.31 ± 0.00</td>
<td>0.21</td>
<td>0.10</td>
<td>0.25</td>
</tr>
<tr>
<td>W5 (wall)</td>
<td>0.30 ± 0.00</td>
<td>0.20</td>
<td>0.10</td>
<td>0.25</td>
</tr>
<tr>
<td>W6 (wall)</td>
<td>0.46 ± 0.01</td>
<td>0.17</td>
<td>0.28</td>
<td>0.71</td>
</tr>
</tbody>
</table>

* calculated based on the 0.1 wt.% quantitation limit for sulfide
** Assumes sulfides are in the form of pyrrhotite

Along with other information:
- Testing method
- Pictures
- Basement floor plan
How to sign up for testing? (at no cost)

Google: “UConn crumbling concrete”

Other information available on the website:
- Research team
- Test Methods
- Live Map
- Results
Laboratory Testing - Method

Wavelength Dispersive X-Ray Fluorescence (WD-XRF)

Elemental Total Sulfur Analyzer

Spectroscopy Letters - 2024
APPLICATION OF X-RAY PRINCIPLES TO QUANTIFY SULFUR OXIDATION STATES IN CONCRETE

Leana Santos, Kay Wille, Maria Chrysochoou
Why do we need to distinguish between Sulfates and Sulfides?

May contain sulfides ($S^2$) in pyrrhotite or pyrite

Aggregate + Portland cement + Water = Concrete

0.6 – 1.8% $S$ as sulfate ($S^6$) through added gypsum

no $S$

Avg. 0.17% $S$ as sulfate from cement

+ $S$ as sulfide unoxidized pyrrhotite

+ $S$ as sulfate already oxidized pyrrhotite

\[
8Fe_{1-x}S + \frac{31}{2} O_2 + 8H_2O \rightarrow 7(FeSO_4 \cdot H_2O) + SO_4^{2-} + 2H^+ \text{ (pyrrhotite)}
\]
### Current Results - Dataset for statistical analysis

<table>
<thead>
<tr>
<th>Home Classification</th>
<th>No of homes tested</th>
<th>No of samples</th>
<th>No of ST and WD-XRF analyses each</th>
</tr>
</thead>
<tbody>
<tr>
<td>NN (No damage – No pyrrhotite)</td>
<td>57</td>
<td>260</td>
<td>780</td>
</tr>
<tr>
<td>NP (No damage – Pyrrhotite)</td>
<td>49</td>
<td>225</td>
<td>675</td>
</tr>
<tr>
<td>DP (Damage – Pyrrhotite)</td>
<td>67</td>
<td>232</td>
<td>696</td>
</tr>
<tr>
<td><strong>sum</strong></td>
<td><strong>173</strong></td>
<td><strong>717</strong></td>
<td><strong>2151</strong></td>
</tr>
</tbody>
</table>
Total Sulfur Results

NN - No Observed Damage Pyrrhotite not Detected

NP - No Observed Damage Pyrrhotite Detected

DP - Observed Damage Pyrrhotite Detected
Probability of observed Damage – Total Sulfur and Age

Probability of observed damage as a function of home age
Conclusion from Field Testing

- Effective **Sampling** Methodology (Vacuum Drilling and Pulverization)
- Testing Methodology based on **Total Sulfur** and WD-XRF developed → Distinguish between Amounts of Sulfate and Sulfides
- **Total sulfur** measured on concrete specimens obtained from housing foundations → **important parameter** in assessing the risk of damage of these concrete walls
- Concrete foundation walls with $S_T$ concentration of **less than 0.30 wt.% do not show damage** based on the collected data of 173 homes.
- Average **pyrrhotite** concentration in DP homes (visible damage and pyrrhotite present) is **higher than in NP homes** (no visible damage and pyrrhotite present).
- Based on the DP samples, if the amount of total sulfur **exceeds 0.4 wt.%** the calculated **probability of damage is 80%** or higher. In addition, the calculated probability of damage is **60%** or higher when the home age **exceeds 30 years**.
Overview Complexity – Risk Assessment

Deterioration Mechanisms → Influential Parameter → Testing Methods

- Expansion – pyrrhotite oxidation
- Expansion – Ettringite formation
- Expansion – Thaumasite formation
- Strength loss – Acid attack
- Cracking – Constrained Expansion

- Availability of reactants (Amount of pyrrhotite, …)
- Reactivity of mineral form
- Temperature
- Exposure to humidity, oxygen (inclusions, size, pore structure)
- Exposure to catalysts, oxidants

Tools
- Total Content-based
- Reactivity-based
- Sulfur, Sulfide, Pyrrhotite
- Accelerated Testing

Threshold limits → Risk Assessment

Mechanistic Approach
- Isolation of parameters & mechanisms → quantifying their time-dependent effect on failure
- Controlled lab experiments
- Time-dependent analysis → need for accelerated testing
- How to relate lab results to the foundations in the field (exposure conditions, mixture designs, time/age)
- Evaluation of failure

Empirical Statistical Approach
- Access to field samples / foundations
- Collecting samples from the field (consistent, representative, time-efficient)
- Data set of influential parameters
- Number of data sets → data base
- Empirical Data analysis
- Evaluation of failure

Data analysis – Meaning of Test Results

Failure Criterion
- min residual strength, or
- max damage parameter
Acceleration of Reaction / Expansion / Cracking

How to accelerate? Cannot wait 10-20 years in the lab

• Increase temperature
• Increase pH
• Increase oxygen concentration
• Increase reaction area (decreasing particle size)
• Increase amount of pyrrhotite in the sample
  (pyrrhotite synthesis, magnetically separate from crushed agg.)
• Using catalysts such as Cl\(^-\) in concrete or an oxidizing agent (H\(_2\)O\(_2\), NaOCl) for agg.
• Applying an electrical current (speed up redox reaction)

Before Testing

After 7 days (35V)

After 35 days (35V)
What kind of Question to you have?

**Principle Investigators**

- **Sampa**
  - Concrete Materials, Composites & Structures
  - Design, Characterization, Simulation
- **Alex**
  - Environmental Geochemistry
  - Spectroscopy
  - Earth material characterization
- **Leana**
  - Hot Asphalt, Concrete, Aggregate
  - Laboratory and Field Testing
  - Technician oversight and Training

**Co-Principle Investigator**

- **Salem**
  - Corrosion
  - Phase Transformations
  - Structure – Property – Processing Relationships
- **Meshach**
- **Hayley**
- **Ana**
- **Aagya**
- **Ryan**

**Undergraduate Students**