Proposed Testing and Research Approach for Pyrrhotite-Induced Concrete Deterioration

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This briefing presents recommendations for test methods and approaches for addressing pyrrhotite-induced expansion in concrete. There is no standard procedure to apply or guidance available. Almost all of the recommendations require R&D ranging from months to years to develop a solution.
Phased approach

- Approach focused on addressing near-term regulatory needs and developing approaches to identify, prioritize, and manage structures susceptible to concrete damage from pyrrhotite-induced expansion.
- Quarry oversight / putting a “clamp” on deleterious aggregates
  - 1st phase conservative guidance based on chemistry
  - 2nd phase to consider both mineralogy and chemistry – needs short term R&D
- Forensics on existing homes
  - Near-term recommendations for improving petrographic analysis
  - Med-term improved analysis methods – needs med term R&D
- Projection of future damage – long term (5+ years) R&D needed
- Develop mitigation options – long term (1-3 years) R&D needed
- Best practices for concrete replacement - med term (1 year) R&D needed
### Aggregate Regulations
- **Aggregate Acceptance Based on Chemistry**
- **Develop Fe-S Mineral Analysis Method(s)**

### Structure Assessment
- **Use Petrography Methods and Standardize Reporting of Field Conditions and Analysis Results**
- **Develop New Petrography / Forensic Analysis Methods: Chemistry, Mineralogy, Magnetic**

### Management and Solutions
- **R&D on Service Life Modeling Approaches**
- **R&D on Mitigation Options: Environmental, Repair/Retrofit**
- **R&D / Tradespace on Approaches for Replacement**

### Year Planning
- **Immediate**
- **Near-Term**
- **Mid-Term**
- **Long-Term**

- **Year 1-2**
- **Year 3-4**
- **Year 5-7**
- **Year 8+**

**IMPLEMENT**
Quarry oversight

- Regulations on quarries for minimum testing and acceptance requirements for supply of aggregate materials to concrete production industry
- Lean on testing standards from ASTM, AASHTO currently used for aggregates, cements, etc.
- Reference acceptance / rejection requirements (i.e., limits on test results) from Canadian and European Standards
- Frequency of testing based on quantity of material that adjusts based on observed variation in results
Quarry Oversight

Phase 1 - Immediate
- Combustion IR
- ASTM C33
- Overly restrictive limits

Phase 2 – Long term
- ASTM C295
- X-ray diffraction (ASTM C1365)
- Development of pyrrhotite specific standards
  - Accurate accept/reject limits

• X-ray Fluorescence
• Testing regimen for aggregate sources
Quarry oversight – basic requirements

- Aggregate must meet minimum requirements of ASTM C33 Standard Specification for Concrete Aggregates
  - Gradations
  - Deleterious Materials
- This requirement should already be in place for materials to be used in certified ready-mix concrete plant
- Does not cover chemical and mineralogical concerns with pyrrhotite in aggregate
Quarry oversight – basic requirements

- No general standards that cover specifics of chemical and mineralogical analysis of aggregate
- Specific test method to identify pyrrhotite at relevant resolution (e.g., 0.2-0.3%) needs to be developed and vetted.
- Suggest immediate conservative focus that assumes pyrrhotite is present and uses standard test methods for chemical analysis to qualify and aggregate for use in concrete.
- 2nd phase would include mineral ID rather than conservative focus on pyrrhotite.
- Recommend using specific standards / test methods for chemistry and mineralogy.
Quarry Oversight – 1st phase sulfur content by XRF or IR combustion

- Leco infrared combustion sulfur analysis
  - Obtain elemental sulfur (S) content
- X-ray fluorescence (XRF) measurements on aggregate to identify bulk chemical composition
  - Performed on fused glass samples following procedures in AASHTO M85 for cement
    - Pulverize aggregate to produce fused glass sample
      - Pulverize sample to 90% by mass passing #325 (45 μm) sieve
  - Obtain bulk chemistry using XRF
  - Quantify elemental sulfur (S) content

<table>
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<tr>
<th>Element</th>
<th>%</th>
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<tbody>
<tr>
<td>SiO₂</td>
<td>20.0</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>5.0</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>3.1</td>
</tr>
<tr>
<td>CaO</td>
<td>63.0</td>
</tr>
<tr>
<td>MgO</td>
<td>2.9</td>
</tr>
<tr>
<td>SO₃</td>
<td>3.3</td>
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<tr>
<td>LOI</td>
<td>1.74</td>
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<tr>
<td>Na₂O</td>
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<tr>
<td>K₂O</td>
<td>0.5</td>
</tr>
<tr>
<td>TiO₂</td>
<td>0.25</td>
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<tr>
<td>P₂O₅</td>
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<tr>
<td>C₃A</td>
<td>8</td>
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<tr>
<td>C₃S</td>
<td>67</td>
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<tr>
<td>C₂S</td>
<td>6</td>
</tr>
<tr>
<td>C₄AF</td>
<td>9</td>
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Quarry Oversight – 1st phase accept / reject limits for aggregate

- Assume that pyrrhotite is present in aggregate
  - Accept aggregate if sulfur (S) content <0.1%
  - Otherwise, reject aggregate for use in concrete
- Suggest that CT State Geologist has input on this and if it is possible to just apply this analysis regionally. However, pyrrhotite geological maps are for non-trace compositions. Relevant amounts of pyrrhotite likely extend far beyond mapped regions.

Geological Map of Connecticut
Quarry Oversight – 1st phase qualification of laboratories

- Certification programs for laboratories to conduct this testing are recommended:
  - AASHTO Accredited
  - ISO 17025
  - Participate in Cement and Concrete Reference Laboratory (CCRL) testing proficiency sample program.
- Sulfur (S) content measurements are less than typically present in cement. New low S content calibrations will need to be performed by laboratories to calibrate/verify instruments.
Quarry Oversight – 1st phase frequency of testing

- Recommend testing for every 25k tons or 3 months, whichever is most frequent
  - Based on making testing less than 1% of operating cost
  - Assumed testing cost $5k and rock price $25/ton
- Perform this testing four times
  - If variability in results is less than +/-10% of mean of four test results, switch to conducting once per year
  - If higher variability observed, continue at testing frequency specified above
- NOTE: CT State Geologist should have input on this. The frequency / weight for each interval of testing should be based on the strata / heterogeneity in the formation.
Quarry oversight – 2nd phase mineralogy + sulfur content

- A 2nd phase of implementation to also consider mineralogy to understand Fe-S mineral present
- Fe-S mineral identification would guide selection of acceptable limits on sulfur content
- Recommend optionally using either thin section petrography by ASTM C295 or X-ray diffraction (or other undiscovered) to qualitatively identify Fe-S minerals
- Recommend using specific standards / test methods for chemistry and mineralogy.
- Recommend a quality materials consultant / laboratory services laboratory perform short-term research to develop method rather than university.
Quarry Oversight – 2nd phase X-ray diffraction for mineral ID

- X-ray diffraction (XRD) measurements on aggregate to identify deleterious minerals
- No specific procedures to apply. Can lean on ASTM C1365 and D934
- Example recommended operating procedures
  - Pulverize sample to 90% by mass passing #325 (45 μm) sieve
  - Random powder pack sample preparation
  - Scan resolution of <0.1° 2θ
  - Scan speed to achieve >10k counts on 100% peak
    - Modern XRDs can do this with a 2hr scan / 0.67 °/min
  - Scan between 20-100° 2θ
    - Applicable to Cu and Co K-α sources
    - Scan correlated to d-space between approx. 1-5 Å
  - Identify if pyrrhotite and/or pyrite are present
    - Using ICDD verified powder diffraction reference patterns
    - If no pyrrhotite or pyrite is detected, no additional testing (i.e., XRF) is required
- Recommend a short study by quality analysis laboratory to run through method and “tweak” any parameters
Quarry Oversight – 2nd phase X-ray diffraction for mineral ID

<table>
<thead>
<tr>
<th>Phase ID (4)</th>
<th>Chemical Formula</th>
<th>PDF-#</th>
<th>NA</th>
<th>NR</th>
<th>NP</th>
<th>Wt% (ed)</th>
<th>RR</th>
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<tbody>
<tr>
<td>Calcite</td>
<td>Ca(CO₃)₂</td>
<td>01-083-0578</td>
<td>12</td>
<td>14</td>
<td>26 (0)</td>
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<tr>
<td>Quartz</td>
<td>SiO₂</td>
<td>98-001-0369</td>
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<td>34</td>
<td>7</td>
<td>1 (0)</td>
<td>4.29</td>
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<tr>
<td>Anorthite, ordered</td>
<td>CaAl₂Si₂O₈</td>
<td>00-041-1486</td>
<td>58</td>
<td>7</td>
<td>0</td>
<td>0 (0)</td>
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<tr>
<td>Dolomite</td>
<td>MgCa(CO₃)₂</td>
<td>01-083-1756</td>
<td>15</td>
<td>14</td>
<td>73 (1)</td>
<td>2.53</td>
<td></td>
</tr>
</tbody>
</table>

XRF Wt%: CaO=36.7%, SiO₂=15.0%, Al₂O₃=6.1%, MgO=16.0%, CO₂=48.3%

Refinement Converged (R/E=1.53), Round=3, Iter=5, P=42, R=6.3% (E=4.12%, EPS=0.5)
Quarry Oversight – 2nd phase sulfur content by XRF or IR combustion

- Leco infrared combustion sulfur analysis
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X-ray fluorescence (XRF) measurements on aggregate to identify bulk chemical composition
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- Obtain bulk chemistry using XRF
- Quantify elemental sulfur (S) content
Quarry Oversight – 2nd phase Accept / reject limits for aggregate

- If pyrrhotite is observed by XRD and/or ASTM C295
  - Accept aggregate if sulfur (S) content <0.1%
  - Otherwise, reject aggregate for use in concrete
- If pyrrhotite is not observed but other Fe-S minerals are (e.g., pyrite) by XRD and/or ASTM C295
  - Accept aggregate if XRF sulfur (S) content <1%
  - Otherwise, reject aggregate for use in concrete
- If no Fe-S minerals (i.e., pyrrhotite, pyrite) are observed by XRD and/or ASTM C295, no objection to acceptance based on chemistry and mineralogy

**NOTE:** Other methods for mineralogy and chemistry may be available such as examination of magnetic properties.
Quarry Oversight – 2\textsuperscript{nd} phase qualification of laboratories for testing

- Certification programs for laboratories to conduct this testing are recommended:
  - AASHTO Accredited
  - ISO 17025
  - Participate in Cement and Concrete Reference Laboratory (CCRL) testing proficiency sample program.
- Sulfur (S) content measurements are less than typically present in cement. New low S content calibrations will need to be performed by laboratories to calibrate / verify instruments.
Quarry Oversight – 2nd phase frequency of testing

- Recommend testing for every 25k tons or 3 months, whichever is most frequent
  - Based on making testing less than 1% of operating cost
  - Assumed testing cost $5k and local rock price $25/ton
- Perform this testing four times
  - If variability in results (max vs. min) <10%, switch to conducting once per year
  - If higher variability observed, continue at testing frequency specified above
- NOTE: CT State Geologist should have input on this. The frequency / weight for each interval of testing should be based on the strata
Forensics – Using current procedures ASTM C856

- Currently ASTM C856 Standard Practice for Petrographic Examination of Hardened Concrete
- Need to standardize sample collection
  - Sample from consistent location (i.e., basement wall with maximum soil elevation)
  - Report site conditions: water table, waterproofing systems, sump present, dehumidifier, HVAC in basement
  - Report environmental conditions: internal temperature and relative humidity in basement
  - Report damage: standard “classes” of damage with visual rating guidance, note efflorescence, etc.
Forensics – Using current procedures ASTM C856 (cont’d)

• Need to standardize reporting:
  • Note presence of Fe-S minerals: pyrrhotite, pyrite, or others
  • Note if present in coarse and/or fine aggregate
  • Note any other relevant features: SCMs used, rough estimate of water-to-cement ratio, large voids and air entrainment observations
  • Provide semi-quantitative estimate of composition. Below is an example potential binning:
    ► <0.1% / minor
    ► 0.1%-1% moderate
    ► 1%-10% high
    ► >10% very high
    ► Can base off of visual estimators applied to thin sections
    ► The resolution in these bins is difficult to obtain w/ current analytical methods

• Would require some short term trials with concrete from affected structures to refine method.
Forensics – New method development, med term R&D needed

- Full concrete petrography by ASTM C856 is expensive and low resolution
- Need better method with high resolution to quantify Fe-S content in existing concrete
- Ideally coring would not be required
- Many potential options:
  - On-site forensic analysis using handheld instruments
  - Collection of powders for laboratory-based analysis
  - Improved petrographic analysis procedures to apply to cores to improve resolution and speed of analysis
- Would recommend medium term R&D conducted by quality materials consultant with expertise in concrete materials, petrography, and unique test methods
Service Life Prediction for Infrastructure

Current State of Distress → Future State of Distress → Influence on the Structure

Risk-informed decisions for prioritizing funding for future maintenance and repair activities.
Projecting future concrete deterioration, long term R&D needed

- To project how concrete damage will occur in future
- Map space of material, construction, exposure:
  - Different pyrrhotite contents, coarse and/or fine aggregate
  - Different construction / basement types
  - Different environments: water table, RH, etc.
- Laboratory testing:
  - Simulate different variables with accelerated laboratory-based expansion testing
- Goal would be to correlate observations from forensic analysis and “bins” structure types to project future damage
  - Minimal expansion capacity, moderate, high, very-high, etc.
Develop potential mitigation options, long term R&D needed

- Focus on R&D to understand if there’s anything that can be done to help mitigate expansion
  - French drains, upstream waterproofing, dehumidifiers, or other (more outside-the-box) ways
  - Results from the service life modeling research would provide information to guide potential mitigation options
- Would be tied to “bins”
  - 1: Minimal damage anticipated, no mitigation needed
  - 2: Mitigation can actually help to extend life of concrete
  - 3: Nothing you can do – full replacement needed
Best practices for full concrete replacement, med term R&D needed

- Need to generate some best practices for remediation / replacement of basements
  - Engineered solutions for typical basements
  - Jack up house vs. wall-by-wall replacement
  - Other innovative construction approaches
- In future, this guidance would roll into the high risk “bin” for structures where full replacement is needed
Aggregate Acceptance Based on Chemistry

Develop Fe-S Mineral Analysis Method(s)

Aggregate Acceptance Based on Chemistry and Mineralogy

Use Petrography Methods and Standardize Reporting of Field Conditions and Analysis Results

Develop New Petrography / Forensic Analysis Methods: Chemistry, Mineralogy, Magnetic

Revised Approach for Field Assessment and Forensic Analysis

R&D on Service Life Modeling Approaches

Inform Approaches for Managing Existing Homes, and Prioritizing Mitigation, Repair, and Replacement Activities

R&D on Mitigation Options: Environmental, Repair/Retrofit

R&D / Tradespace on Approaches for Replacement

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