Proposed Testing and Research Approach for Pyrrhotite-Induced Concrete Deterioration

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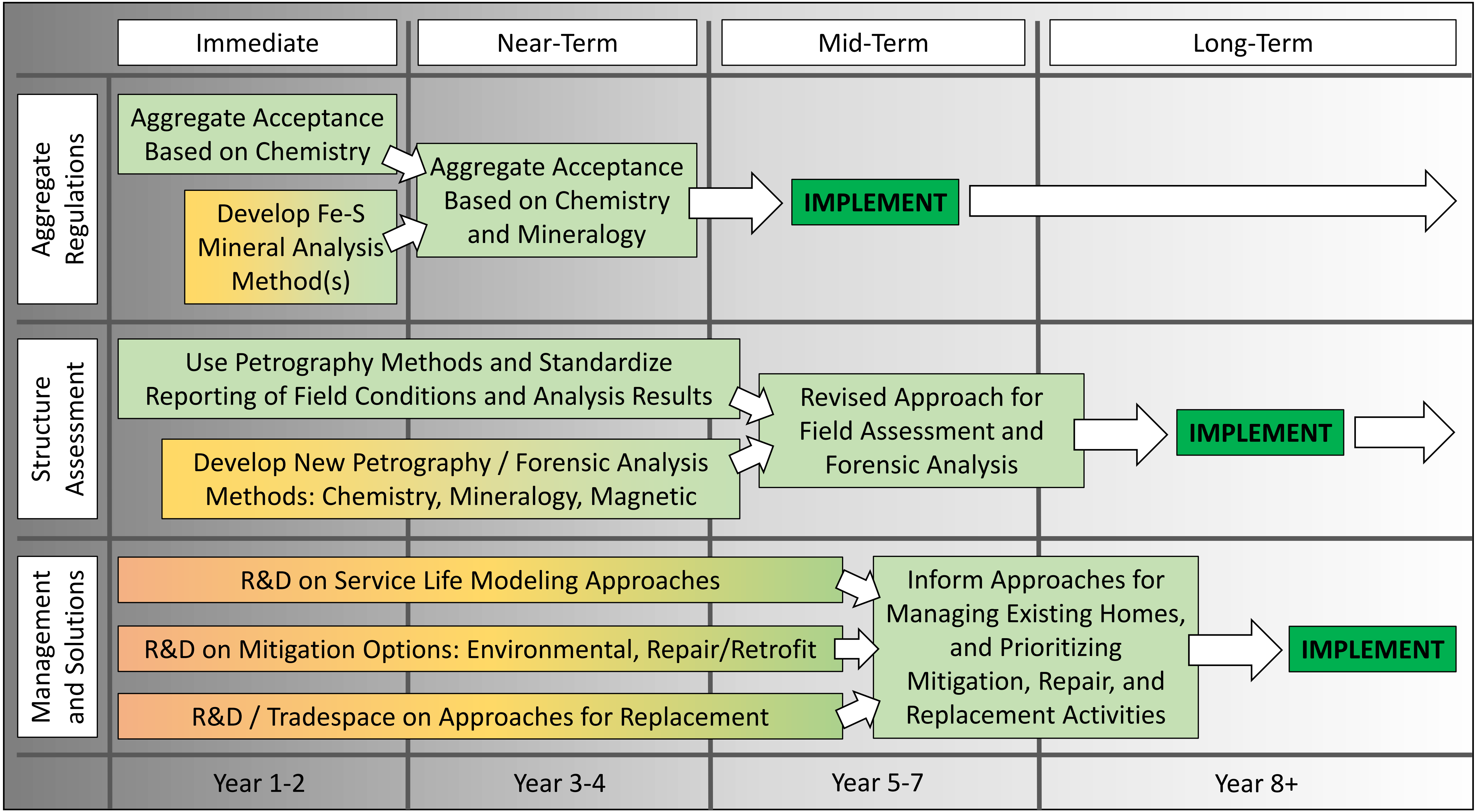
This briefing presents recommendations for test methods and approaches for addressing pyrrhotite-induced expansion in concrete. There is no standard procedure to apply or guidance available. Almost all of the recommendations require R&D ranging from months to years to develop a solution.

Phased approach

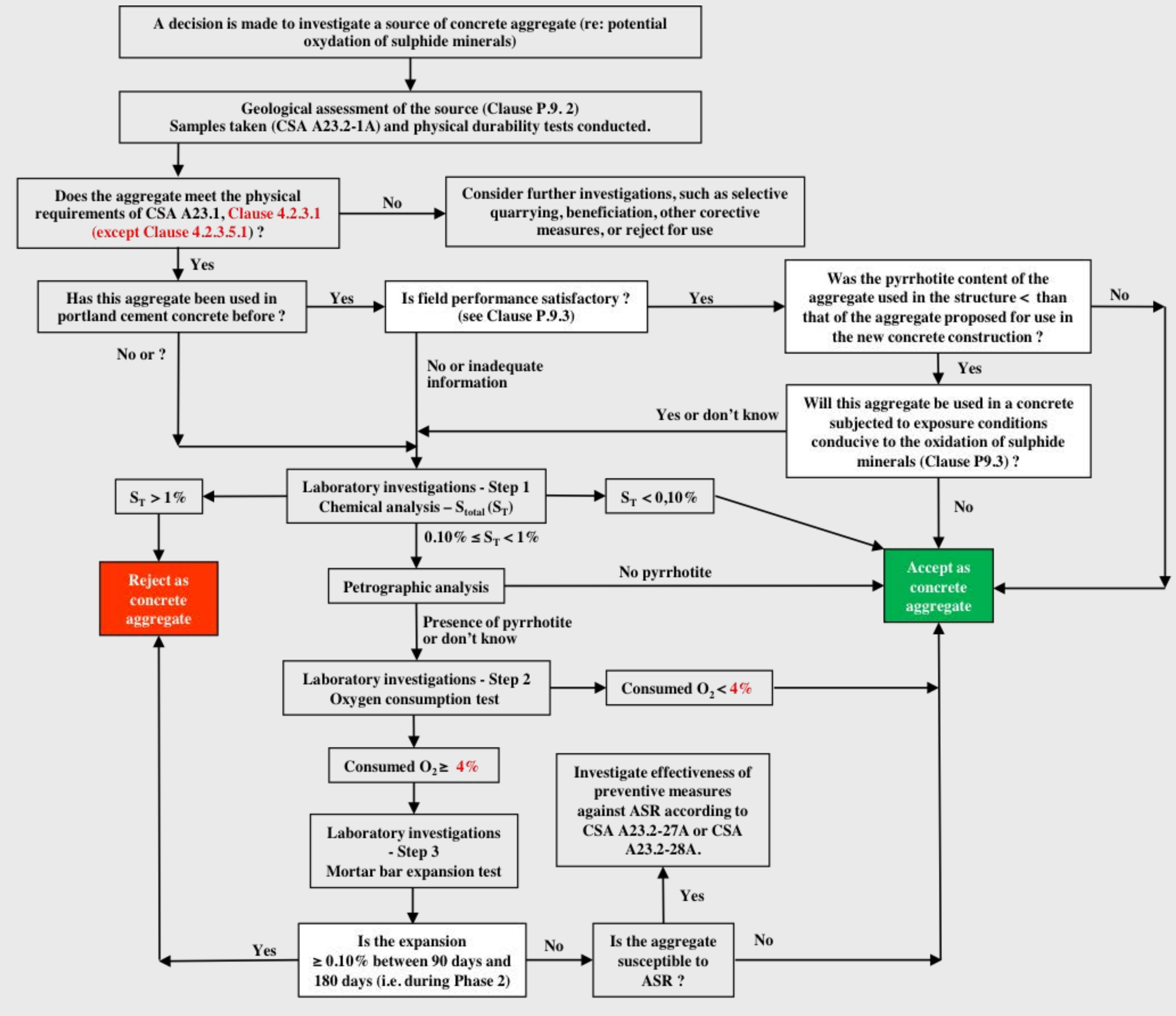
- Approach focused on addressing near-term regulatory needs and developing approaches to identify, prioritize, and manage structures susceptible to concrete damage from pyrrhotite-induced expansion.
- Quarry oversight / putting a "clamp" on deleterious aggregates
  - 1st phase conservative guidance based 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



Immediate
Near-Term
Mid-Term
Long-Term
Aggregate Regulations
Aggregate Acceptance Based on Chemistry
Develop Fe-S Mineral Analysis Method(s)
Aggregate Acceptance Based on Chemistry and Mineralogy
IMPLEMENT
Structure Assessment
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
IMPLEMENT
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
Inform Approaches for Managing Existing Homes, and Prioritizing Mitigation, Repair, and Replacement Activities
IMPLEMENT
Year 1-2
Year 3-4
Year 5-7
Year 8+

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

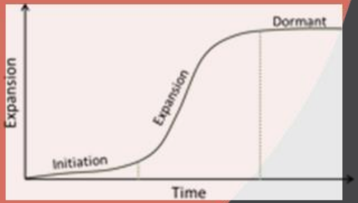
Phase 1 - Immediate

- Combustion IR
- ASTM C33
- Overly restrictive limits

- X-ray Fluorescence
- Testing regimen for aggregate sources

Phase 2 – Long term

- ASTM C295
- X-ray diffraction (ASTM C1365)
- Development of pyrrhotite specific standards
  - Accurate accept/reject limits

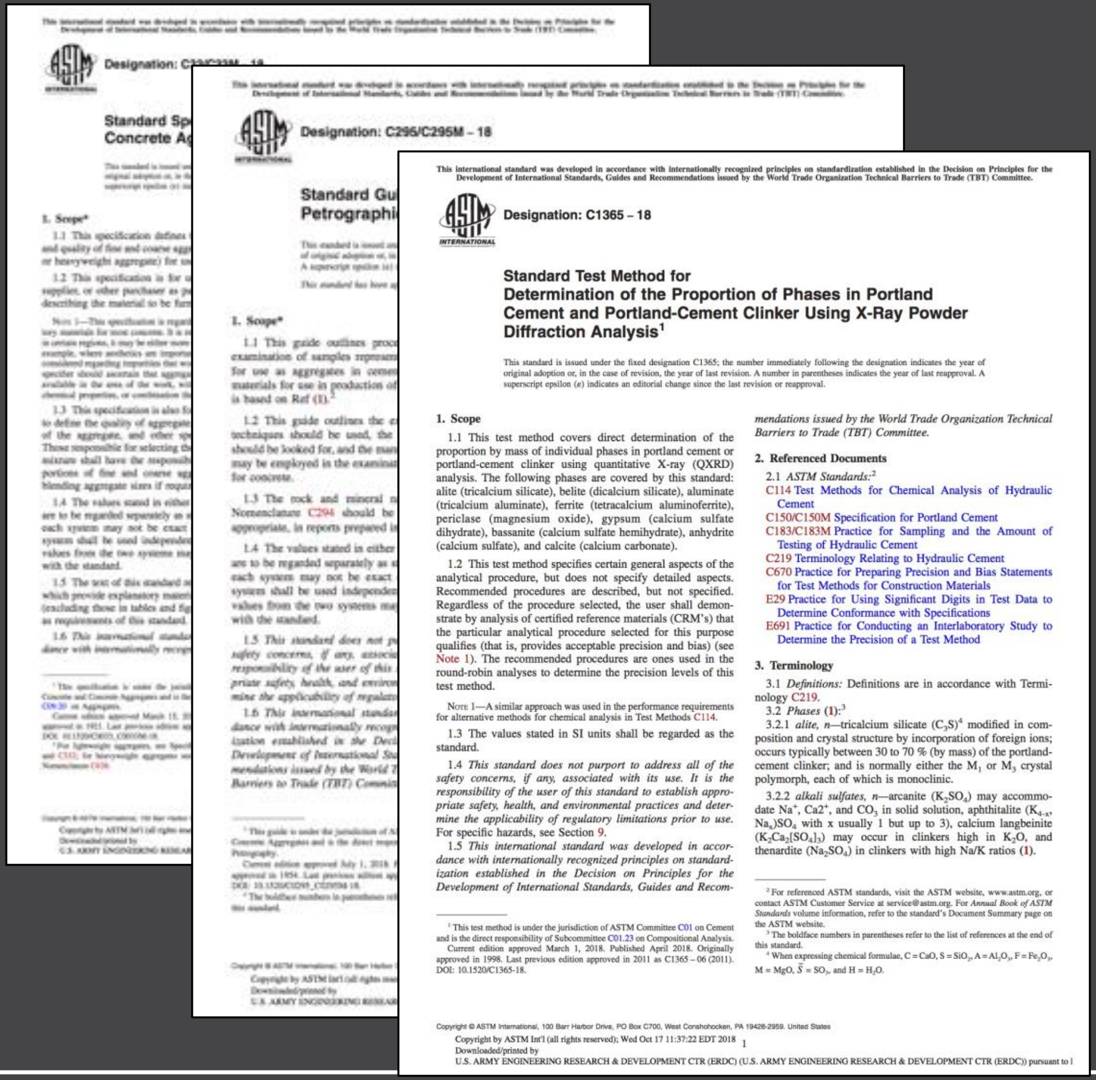


Quarry oversight – basic requirements

- 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.



Designation: C295/C295M – 18

This international standard was developed in accordance with internationally recognized principles on standardization established in the Decision on Principles for the Development of International Standards, Guides and Recommendations issued by the World Trade Organization Technical Barriers to Trade (TBT) Committee.

ASTM INTERNATIONAL

Designation: C1365 – 18

Standard Test Method for Determination of the Proportion of Phases in Portland Cement and Portland-Cement Clinker Using X-Ray Powder Diffraction Analysis[1]

This standard is issued under the fixed designation C1365; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

1. Scope

1.1 This test method covers direct determination of the proportion by mass of individual phases in portland cement or portland-cement clinker using quantitative X-ray (QXRD) analysis. The following phases are covered by this standard: alite (tricalcium silicate), belite (dicalcium silicate), aluminate (tricalcium aluminate), ferrite (tetracalcium aluminoferrite), periclase (magnesium oxide), gypsum (calcium sulfate dihydrate), bassanite (calcium sulfate hemihydrate), anhydrite (calcium sulfate), and calcite (calcium carbonate).

1.2 This test method specifies certain general aspects of the analytical procedure, but does not specify detailed aspects. Recommended procedures are described, but not specified. Regardless of the procedure selected, the user shall demonstrate by analysis of certified reference materials (CRM's) that the particular analytical procedure selected for this purpose qualifies (that is, provides acceptable precision and bias) (see Note 1). The recommended procedures are ones used in the round-robin analyses to determine the precision levels of this test method.

NOTE 1—A similar approach was used in the performance requirements for alternative methods for chemical analysis in Test Methods C114.

1.3 The values stated in SI units shall be regarded as the standard.

1.4 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety, health, and environmental practices and determine the applicability of regulatory limitations prior to use.* For specific hazards, see Section 9.

1.5 *This international standard was developed in accordance with internationally recognized principles on standardization established in the Decision on Principles for the Development of International Standards, Guides and Recommendations issued by the World Trade Organization Technical Barriers to Trade (TBT) Committee.*

2. Referenced Documents

2.1 *ASTM Standards:*[2]

C114 Test Methods for Chemical Analysis of Hydraulic Cement

C150/C150M Specification for Portland Cement

C183/C183M Practice for Sampling and the Amount of Testing of Hydraulic Cement

C219 Terminology Relating to Hydraulic Cement

C670 Practice for Preparing Precision and Bias Statements for Test Methods for Construction Materials

E29 Practice for Using Significant Digits in Test Data to Determine Conformance with Specifications

E691 Practice for Conducting an Interlaboratory Study to Determine the Precision of a Test Method

3. Terminology

3.1 *Definitions:* Definitions are in accordance with Terminology C219.

3.2 *Phases* (1):[3]

3.2.1 *alite, n*—tricalcium silicate (C_3S)[4] modified in composition and crystal structure by incorporation of foreign ions; occurs typically between 30 to 70 % (by mass) of the portland-cement clinker; and is normally either the M_1 or M_3 crystal polymorph, each of which is monoclinic.

3.2.2 *alkali sulfates, n*—arcanite (K_2SO_4) may accommodate Na^+, Ca2$^+$, and CO_3 in solid solution, aphthitalite (K_{4-x}, $Na_x)SO_4$ with x usually 1 but up to 3), calcium langbeinite ($K_2Ca_2[SO_4]_3$) may occur in clinkers high in K_2O, and thenardite (Na_2SO_4) in clinkers with high Na/K ratios (1).

[1] This test method is under the jurisdiction of ASTM Committee C01 on Cement and is the direct responsibility of Subcommittee C01.23 on Compositional Analysis.
Current edition approved March 1, 2018. Published April 2018. Originally approved in 1998. Last previous edition approved in 2011 as C1365 – 06 (2011). DOI: 10.1520/C1365-18.

[2] For referenced ASTM standards, visit the ASTM website, www.astm.org, or contact ASTM Customer Service at service@astm.org. For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

[3] The boldface numbers in parentheses refer to the list of references at the end of this standard.

[4] When expressing chemical formulae, C = CaO, S = SiO_2, A = Al_2O_3, F = Fe_2O_3, M = MgO, $\bar{S}$ = SO_3, and H = H_2O.

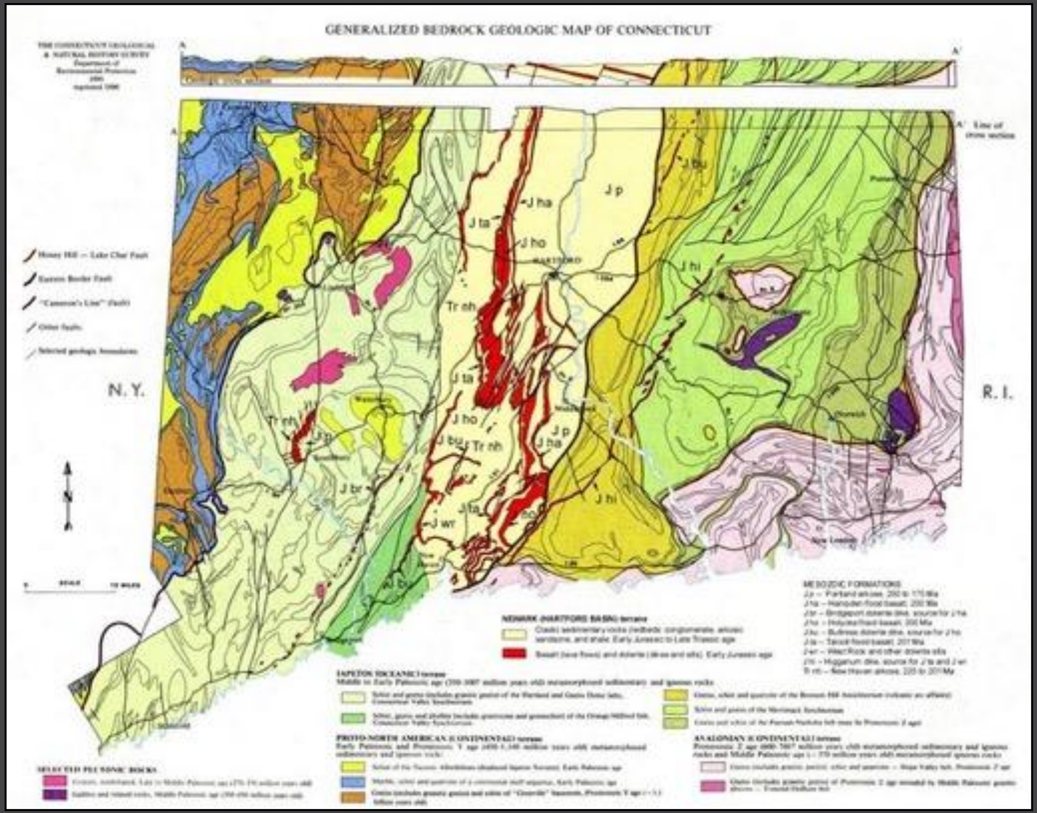
Quarry Oversight – 1st phase sulfur content by XRF or IR combustion

- 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

SiO_2, %	20.0
Al_2O_3, %	5.0
Fe_2O_3, %	3.1
CaO, %	63.0
MgO, %	2.9
SO_3, %	3.3
LOI, %	1.74
Na_2O, %	0.15
K_2O, %	0.5
TiO_2, %	0.25
P_2O_5, %	0.05
C_3A, %	**8**
C_3S, %	**67**
C_2S, %	**6**
C_4AF, %	**9**

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.

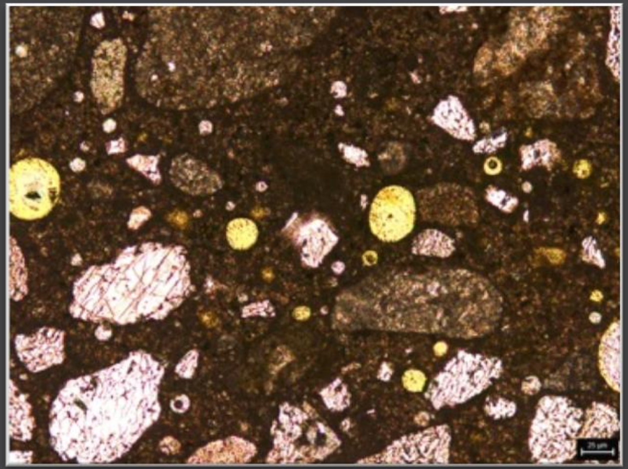
Quarry Oversight – 1st phase frequency of testing

- **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.**

Becker's Quarry, Willington CT

Quarry oversight – 2nd phase mineralogy + sulfur content

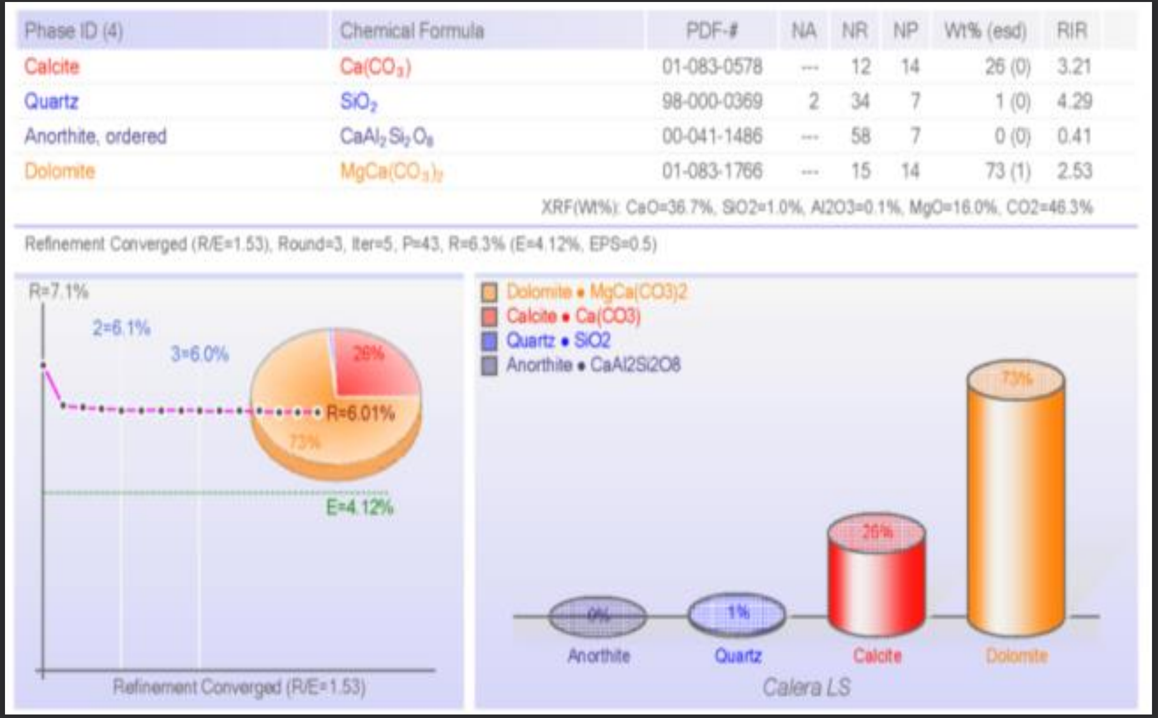
- A 2nd phase of implementation to also consider mineralogy to understand Fe-S mineral present
- Fe-S mineral identification would guide selection of acceptable limits on sulfur content
- Recommend optionally using either thin section petrography by ASTM C295 or X-ray diffraction (or other undiscovered) 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

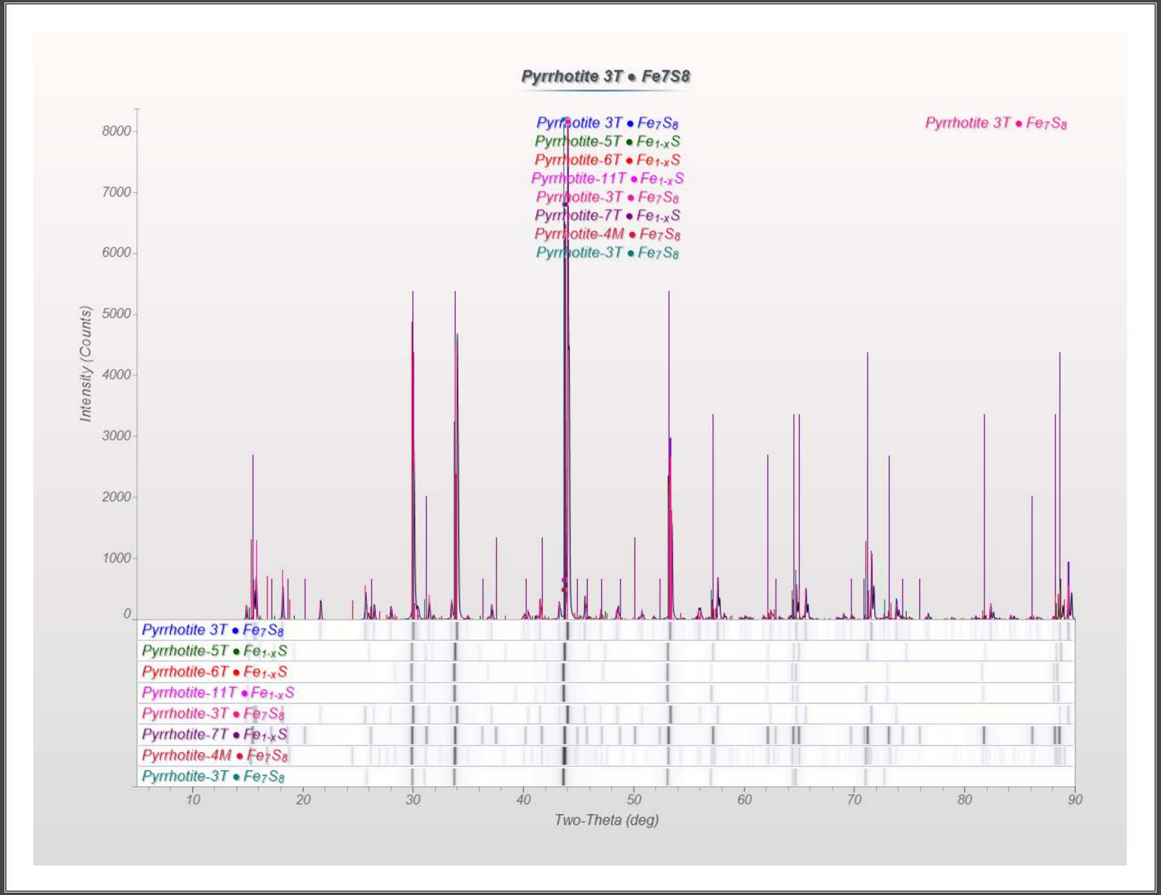
Quarry Oversight – 2nd phase X-ray diffraction for mineral ID



Phase ID (4)	Chemical Formula	PDF-#	NA	NR	NP	Wt% (esd)	RIR
Calcite	$Ca(CO_3)$	01-083-0578	---	12	14	26 (0)	3.21
Quartz	SiO_2	98-000-0369	2	34	7	1 (0)	4.29
Anorthite, ordered	$CaAl_2Si_2O_8$	00-041-1486	---	58	7	0 (0)	0.41
Dolomite	$MgCa(CO_3)_2$	01-083-1766	---	15	14	73 (1)	2.53

XRF(Wt%): CaO=36.7%, SiO2=1.0%, Al2O3=0.1%, MgO=16.0%, CO2=46.3%

Refinement Converged (R/E=1.53), Round=3, Iter=5, P=43, 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
  - 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

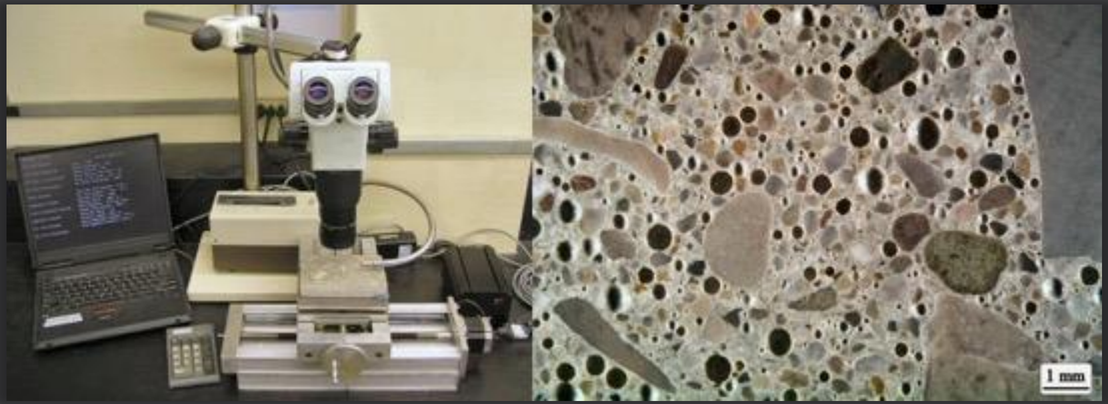
Quarry Oversight – 2nd phase Accept / reject limits for aggregate

- 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 – 2nd 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

Stony Creek Quarry – Branford, CT

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.

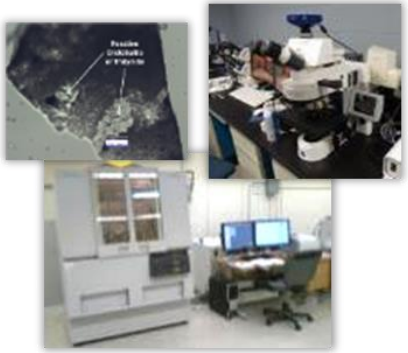
Forensics – Using current procedures ASTM C856 (cont'd)

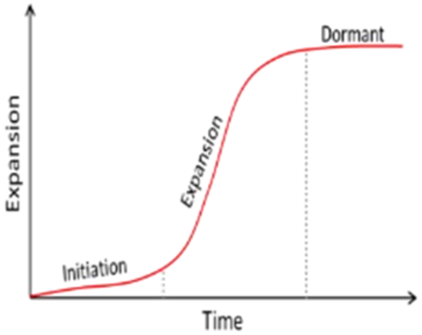
- Need to standardize reporting:
  - Note presence of Fe-S minerals: pyrrhotite, pyrite, or others
  - Note if present in coarse and/or fine aggregate
  - Note any other relevant features: SCMs used, rough estimate of water-to-cement ratio, large voids and air entrainment observations
  - Provide semi-quantitative 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.

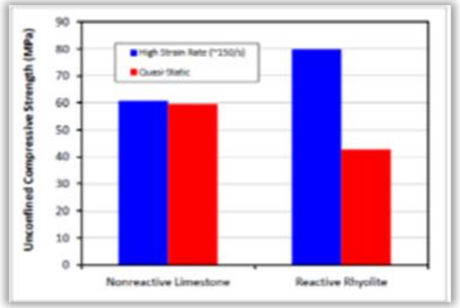
Forensics – New method development, med term R&D needed

- 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

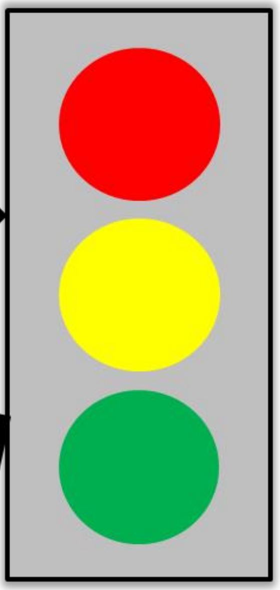
Service Life Prediction for Infrastructure







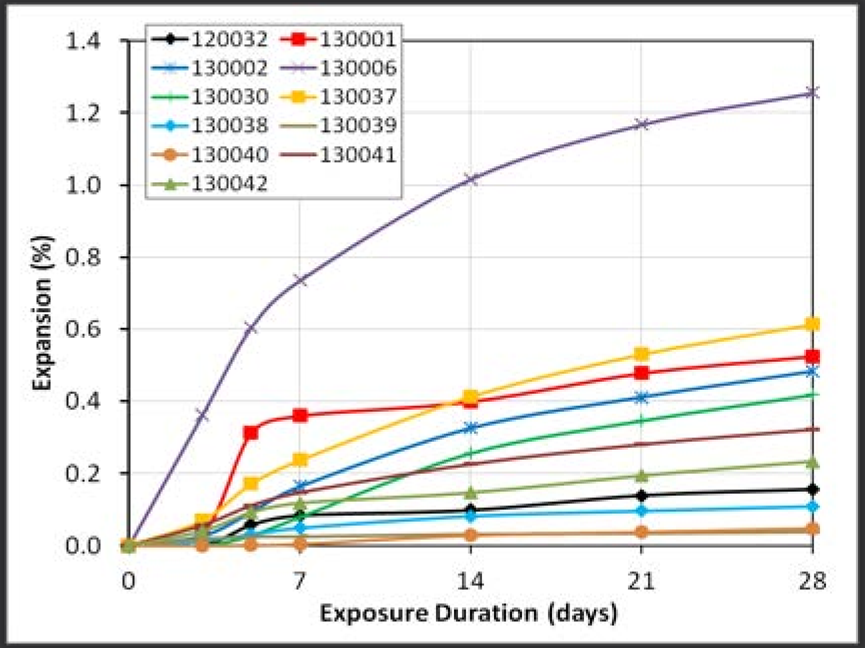
Current State of Distress → Future State of Distress → Influence on the Structure →



Risk-informed decisions for prioritizing funding for future maintenance and repair activities.

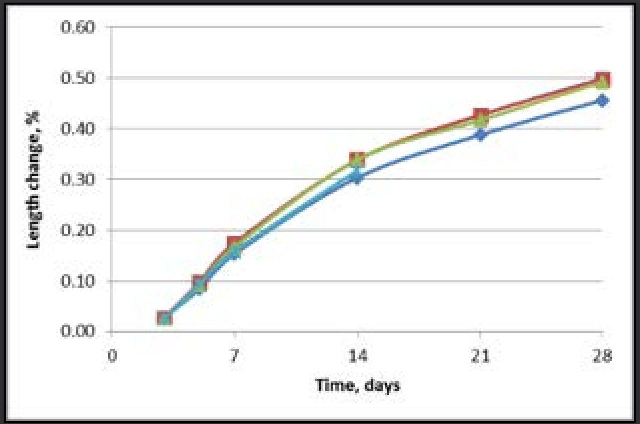
Projecting future concrete deterioration, long term R&D needed

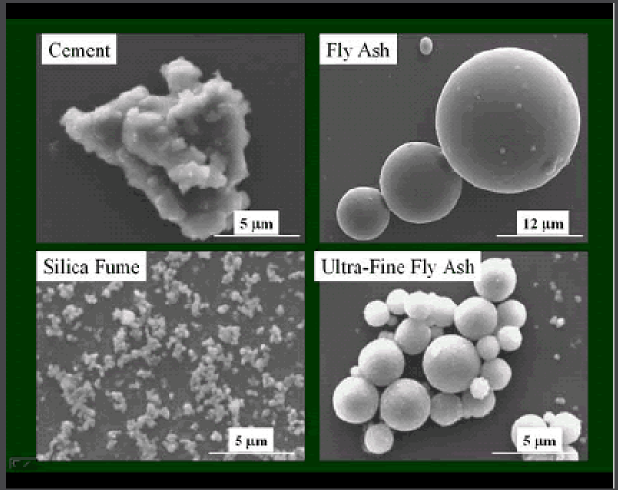
- To project how concrete damage will occur in future
- Map space of material, construction, exposure:
  - Different pyrrhotite contents, coarse and/or fine aggregate
  - Different construction / basement types
  - Different environments: water table, RH, etc.
- Laboratory testing:
  - Simulate different 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

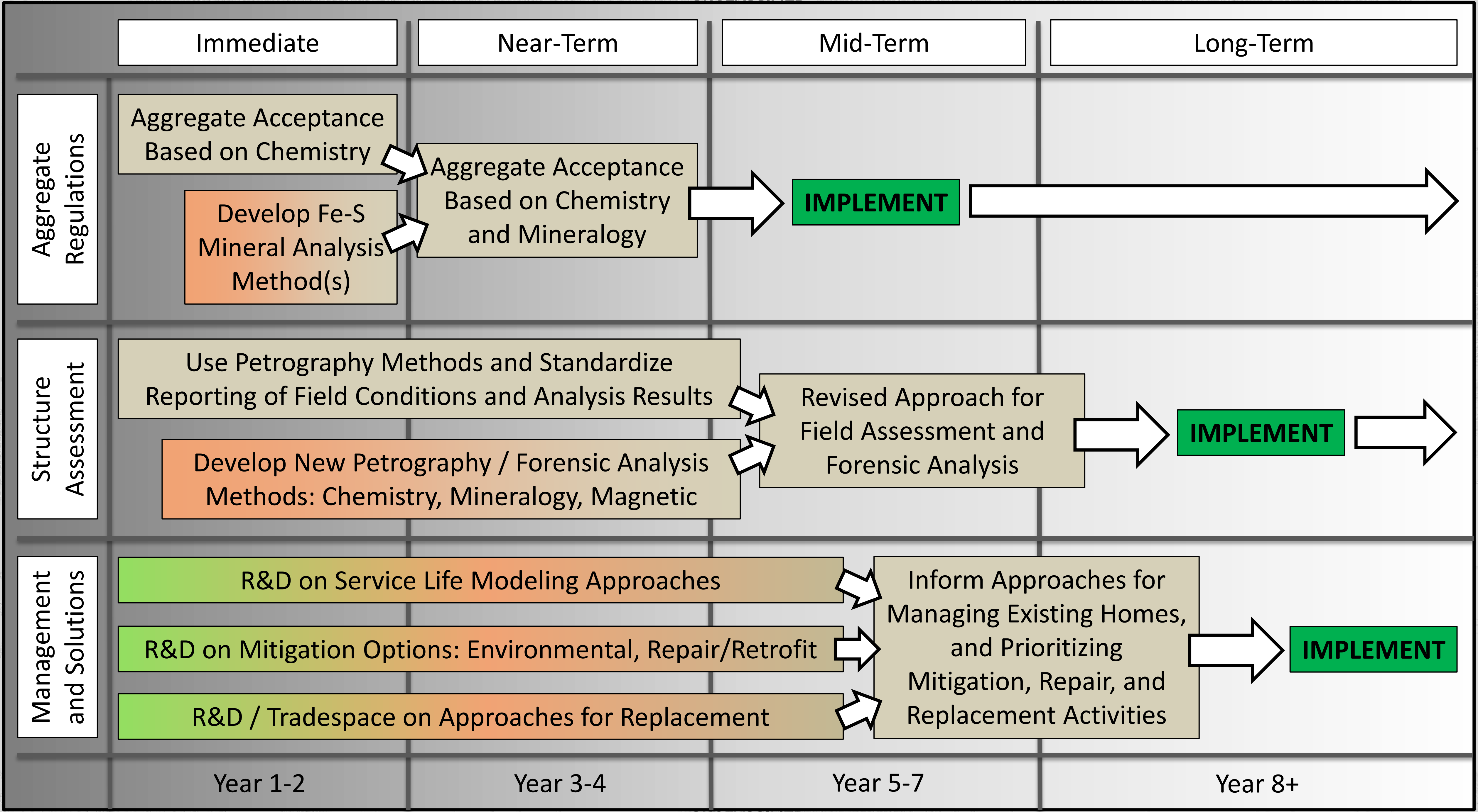
- Focus on R&D to understand if there's anything that can be done to help mitigate expansion
  - French drains, upstream waterproofing, dehumidifiers, or other (more outside-the-box) ways
  - Results from the service life modeling research would provide information to guide potential mitigation options
- 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


Immediate
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Aggregate Regulations
Aggregate Acceptance Based on Chemistry
Develop Fe-S Mineral Analysis Method(s)
Aggregate Acceptance Based on Chemistry and Mineralogy
IMPLEMENT
Structure Assessment
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
IMPLEMENT
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
Inform Approaches for Managing Existing Homes, and Prioritizing Mitigation, Repair, and Replacement Activities
IMPLEMENT
Year 1-2
Year 3-4
Year 5-7
Year 8+