Pyrrhotite Legislation in Massachusetts

North**E**astern **S**tates **M**aterials **E**ngineers' **A**ssociation

100th Annual Meeting

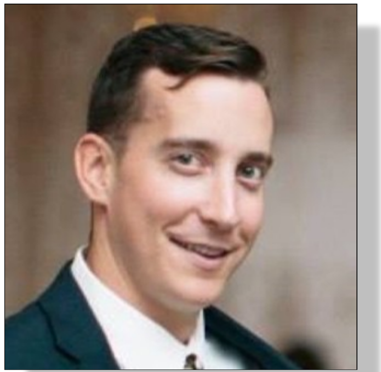
Springfield, MA

October 15, 2024

massDOT
Massachusetts Department of Transportation
Highway Division

North**E**astern
States **M**aterials
Engineers'
Association

Presenters



Richard Mulcahy, P.E.
Materials Research and Evaluation Engineer
MassDOT Research and Materials Section
Richard.Mulcahy@dot.state.ma.us

Jason M. Robertson
Director of Research and Materials
MassDOT Research and Materials Section
Jason.Robertson@dot.state.ma.us

Learning Outcomes

- ❑Homeowner Concrete Foundation Deterioration
- ❑Mechanism of Iron Sulfide Reaction (Pyrrhotite)
- ❑MGL Part I, Title II, c.6C § 79 (2023)
- ❑Geological Sourcing, Sampling, and Testing Protocols
- ❑MassDOT & UConn Research Project

Homeowner Concrete Foundation Deterioration

Pyrrhotite Legislation in Massachusetts

massDOT Massachusetts Department of Transportation Highway Division

NESMEA 100th Annual Meeting

Source of Video: Foundation Solutions of NE, LLC

YouTube Hyperlink: https://youtu.be/OIHL-kxnwRk

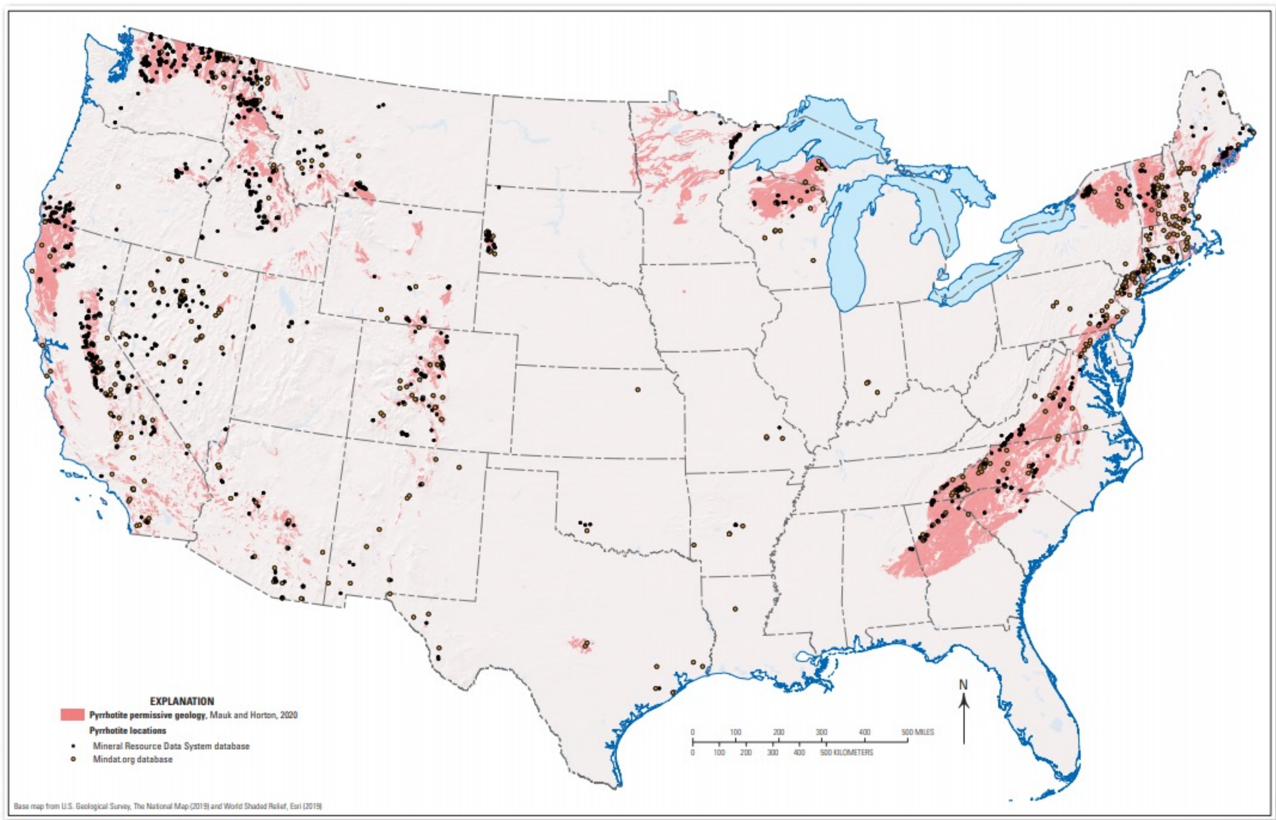
Homeowner Concrete Foundation Deterioration

Overview

- ❑Central and Eastern Connecticut
  - ❑Thousands of homes constructed between 1983 to 2015 affected
  - ❑Originated from one aggregate source in CT
  - ❑July 1, 2021: CT Legislation signed into law
- ❑Western, Central, and Northeastern Massachusetts
  - ❑Thousands of homes also affected in MA
  - ❑Originated from same aggregate source in CT, one aggregate source in MA, and another source of unknown origin (looking into it)
  - ❑December 31, 2019: MA Final Report of the Special Commission to Study the Financial and Economic Impacts of Crumbling Concrete Foundations due to the Presence of Pyrrhotite
  - ❑October 17, 2023: MA Legislation signed into law

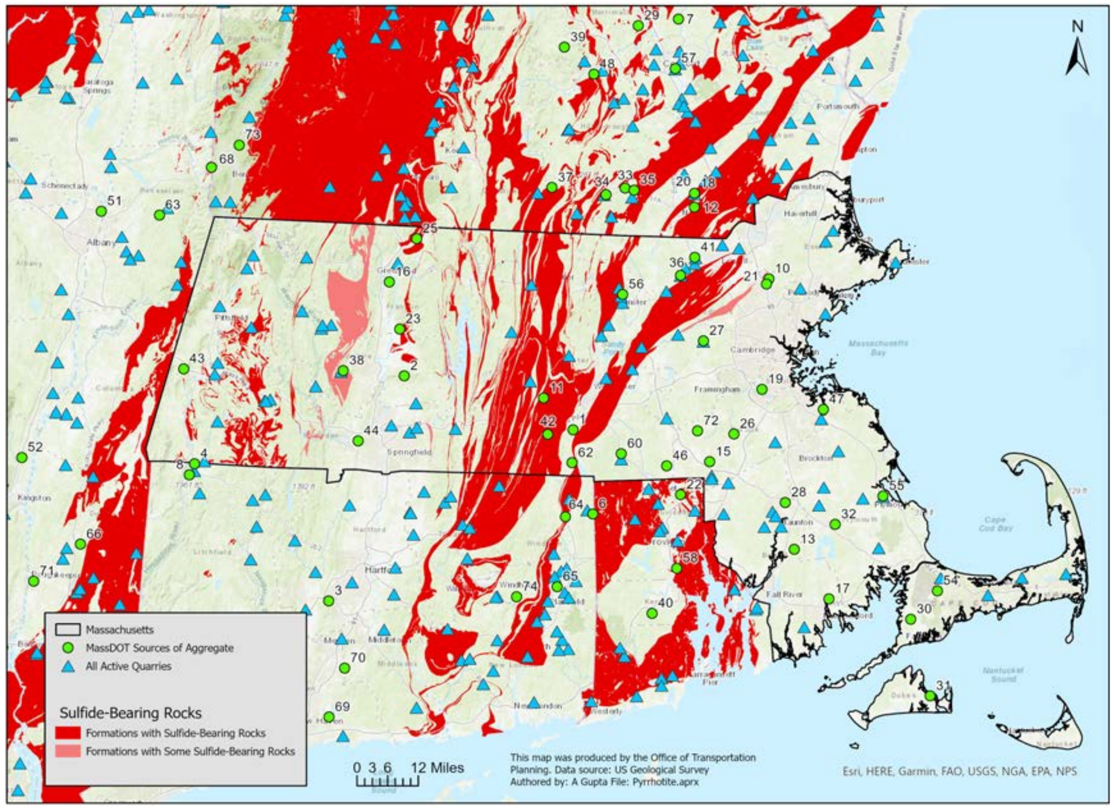
Homeowner Concrete Foundation Deterioration

USGS Iron Sulfide Bearing Aggregate



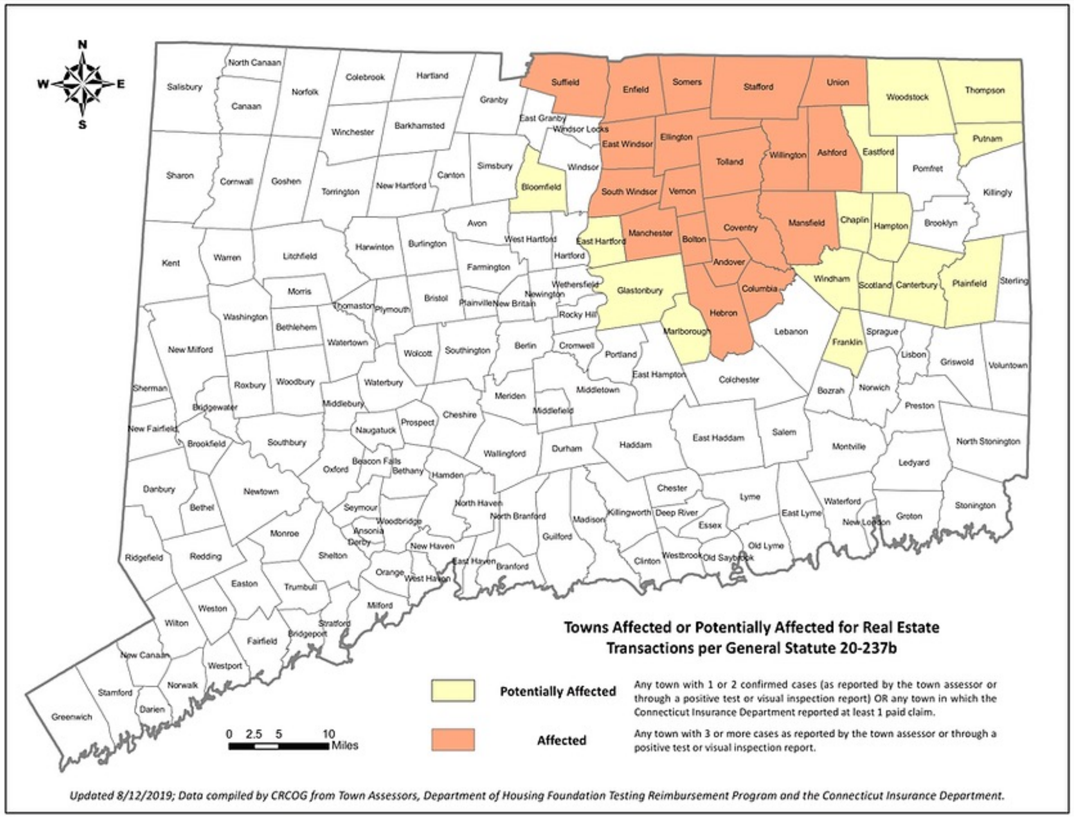
Homeowner Concrete Foundation Deterioration

USGS Iron Sulfide Bearing Aggregate



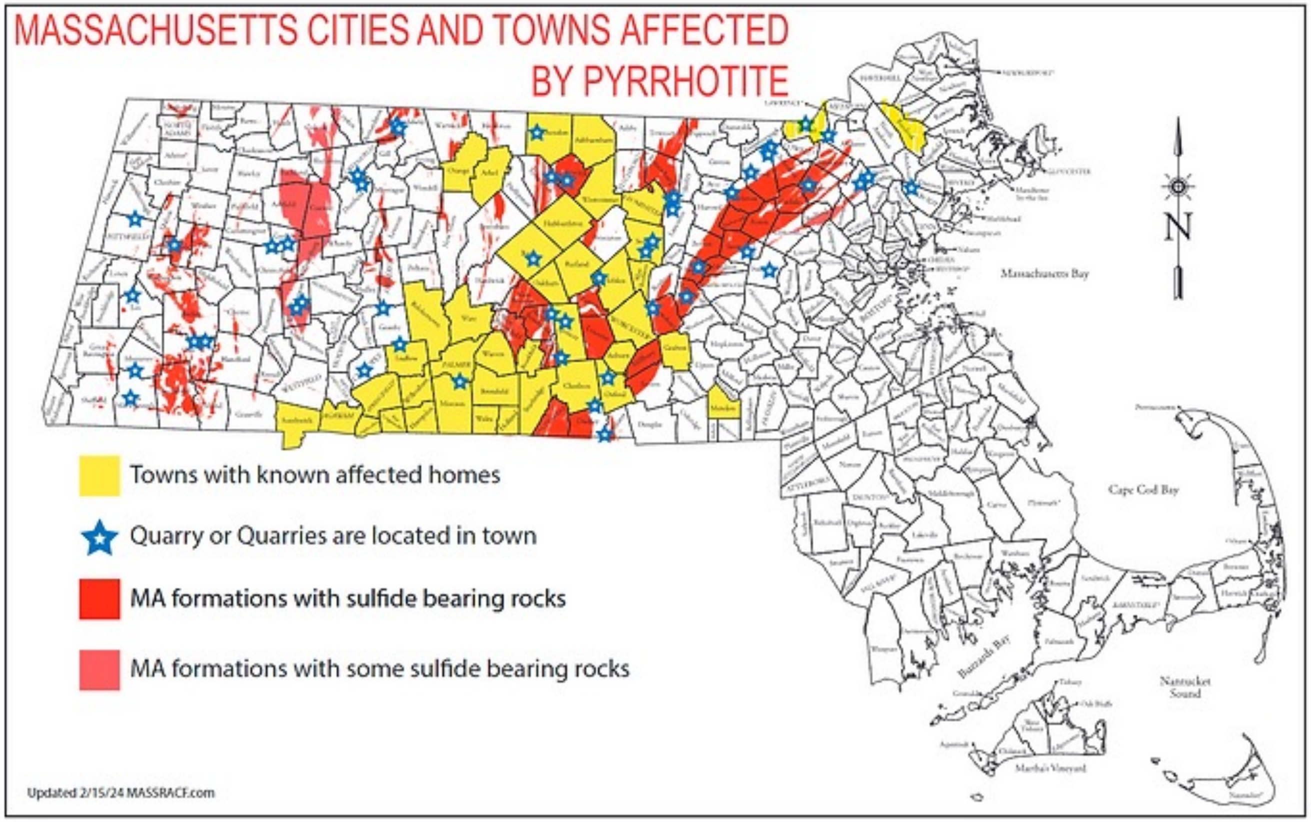
Homeowner Concrete Foundation Deterioration

Known CT Affected Homes



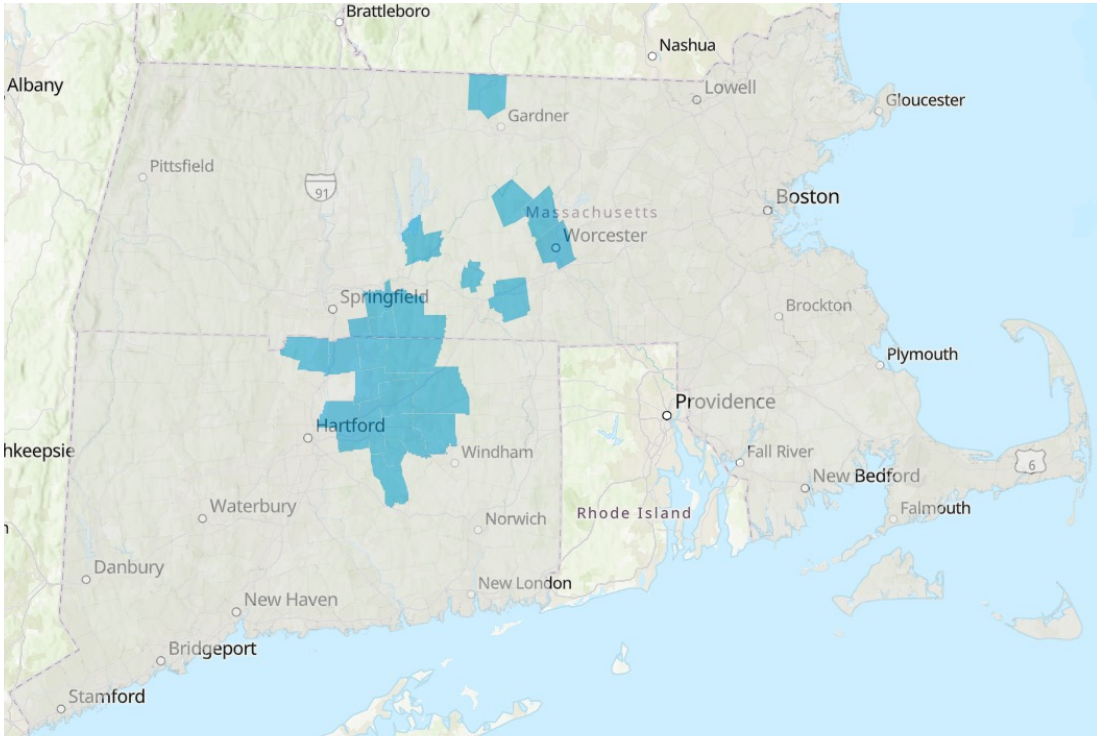
Homeowner Concrete Foundation Deterioration

Known MA Affected Homes



Homeowner Concrete Foundation Deterioration

Affected Homes Tested by UConn



x = 0 to 0.125

$$Fe_{1-x}S + \left(\frac{10-3x}{4}\right)O_2 + \left(\frac{4-3x}{2}\right)xH_2O \rightarrow$$

$$(1-x)Fe(OH)_3 + SO_4^{2-} + H^+$$

1. Aggregate Expansion from Oxidation
2. Internal Sulfate Attack of Cementitious Matrix

Mechanism of Iron Sulfide Reaction (Pyrrhotite)

Mechanism of Iron Sulfide Reaction (Pyrrhotite)

Overview

- Pyrrhotite + Oxygen + Water = Extreme Expansion
  - Oxidation reaction of pyrrhotite **ONLY** occurs when oxygen and humidity are present
- Slow moving deterioration (20 to 30 years)
  - Speed of deterioration likely dependent on the permeability (quality) of the concrete (research being conducted)
- Caused by a chain of reactions, generating numerous expansive mineralogical phases
- Deterioration of the concrete is due to a combination of primary and secondary reactions
  - 1st: Aggregate Expansion from Oxidation
  - 2nd: Internal Sulfate Attack of Cementitious Matrix

Mechanism of Iron Sulfide Reaction (Pyrrhotite)

1st: Aggregate Expansion from Oxidation

1. Oxidation of pyrrhotite (x = 0 to 0.125)

Pyrrhotite + Oxygen + Water → Ferric Hydroxide + Sulfate + Hydrogen

$$Fe_{1-x}S + \left(\frac{10-3x}{4}\right) O_2 + \left(\frac{4-3x}{2}\right) xH_2O \rightarrow (1-x)Fe(OH)_3 + SO_4^{2-} + H^+$$

2. Formation of expansive minerals (ΔV = cm^3/mole of S^{2-})

Pyrrhotite + Oxygen + Water → **Ferrous Sulfate** + Sulfate + Hydrogen

$$8Fe_{1-x}S + \left(\frac{31}{2}\right) O_2 + 8H_2O \rightarrow FeSO_4 \cdot H_2O + SO_4^{2-} + 2H^+$$

ΔV = 209.96

Pyrrhotite + Oxygen + Water → **Goethite** + Sulfate + Hydrogen

$$8Fe_{1-x}S + \left(\frac{67}{4}\right) O_2 + \left(\frac{25}{2}\right) H_2O \rightarrow 7FeO(OH) + 8SO_4^{2-} + 16H^+$$

ΔV = 0.64

Pyrrhotite + Oxygen + Water → **Ferrihydrite** + Sulfate + Hydrogen

$$8Fe_{1-x}S + 21O_2 + 11H_2O \rightarrow 7Fe(OH)_3 + 8SO_4^{2-} + H^+$$

ΔV = 6.04

Mechanism of Iron Sulfide Reaction (Pyrrhotite)

1st: Aggregate Expansion from Oxidation

Ferrous Sulfate

Ferrihydrite

Goethite

Mechanism of Iron Sulfide Reaction (Pyrrhotite)

2nd: Internal Sulfate Attack of Cementitious Matrix

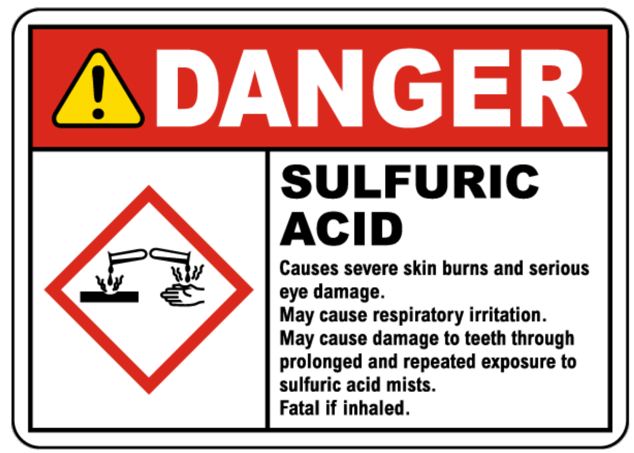
3. Release of sulfuric acid

Ferric Hydroxide + Sulfate + Hydrogen + Water → Ferrous Sulfate + **Sulfuric Acid**

$$(1-x)Fe(OH)_3 + SO_4^{2-} + H^+ + H_2O \rightarrow FeSO_4 \cdot H_2O + H_2SO_4$$

Ferrous Sulfate + Water → Ferrous Hydroxide + **Sulfuric Acid**

$$FeSO_4 \cdot H_2O + H_2O \rightarrow Fe(OH)_2 + H_2SO_4$$



Mechanism of Iron Sulfide Reaction (Pyrrhotite)

2nd: Internal Sulfate Attack of Cementitious Matrix

4. Formation of expansive sulfates ($\Delta V = cm^3/\text{mole of } S^{2-}$)

Calcium Hydroxide + Sulfate + Water → **Gypsum**

$CH + \overline{S} + 2H^{+} \rightarrow C\overline{S}H_2$

ΔV = 41.63

Calcium Hydroxide + Tricalcium Aluminate + Sulfate + Water → **Monosulfoaluminate**

$CH + C_3A + \overline{S} + 11H \rightarrow C_4A\overline{S}H_{12}$

ΔV = 182.89

Calcium Hydroxide + Tricalcium Aluminate + Sulfate + Water → **Ettringite**

$3CH + C_3A + 3\overline{S} + 29H \rightarrow C_6A\overline{S}_3H_{32}$

Monosulfoaluminate + Gypsum + Water → **Ettringite**

$C_4A\overline{S}H_{12} + 2\ C\overline{S}H_2 + 16\text{H} \rightarrow C_6A\overline{S}_3H_{32}$

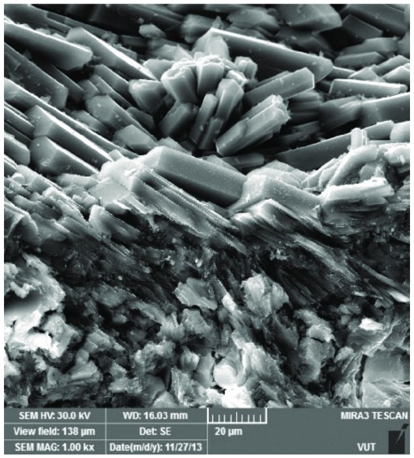
ΔV = 172.19

5. Formation of thaumasite and its decomposition of calcium silicate hydrate

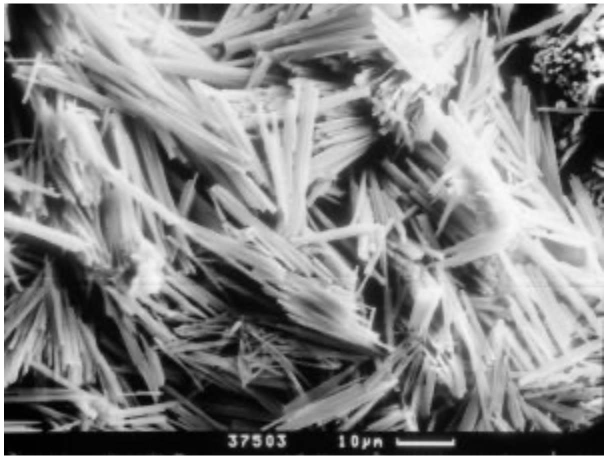
Sulfate + Carbonate + Calcium Silicate Hydrate + Water → **Thaumasite**

$SO_4^{2-} + CO_3^{2-} + 3CaO \cdot 2SiO_2 \cdot 4H_2O + H_2O \rightarrow CaSiO_3 \cdot CaCO_3 \cdot CaSO_4 \cdot 15H_2O$

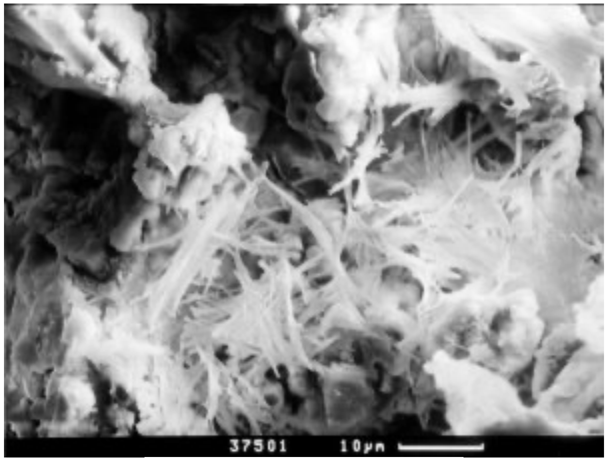
2nd: Internal Sulfate Attack of Cementitious Matrix



Gypsum



Ettringite



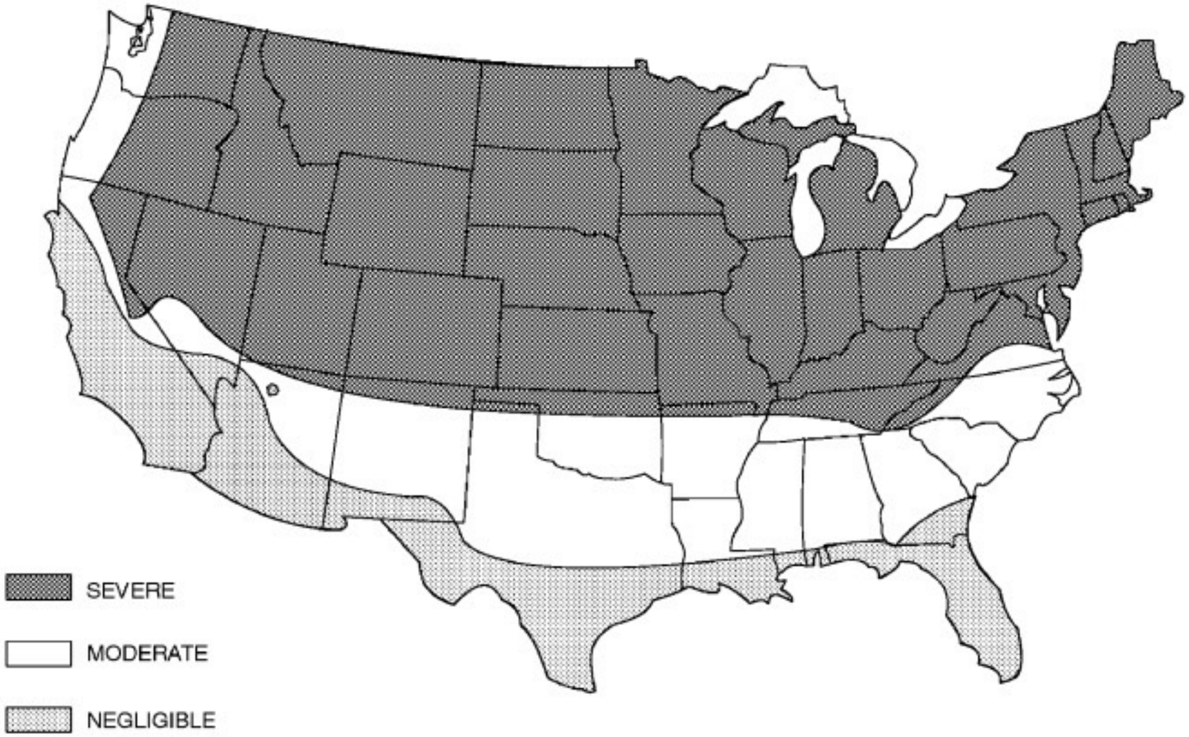
Thaumasite

Making Matters Worse for Residents

- Non-compliant residential foundation concrete
  - Cored specimens show very high water-cementitious ratios (high permeability = low durability)
- Insufficient / non-existent…
  - Application of proper curing methods
  - Application of proper waterproofing materials and sealers
  - Incorporation of supplementary cementitious materials and chemical admixtures into the concrete
  - Quality control inspection and testing
  - Review of mix design formulations and batch tickets

International Residential Code (IRC)

Weathering Probability Map for Concrete



Water-Cementitious (w/cm) Ratio

Transportation Infrastructure (MassDOT Specifications)

Exposure Class	Severity	Condition	Maximum w/cm Ratio
F1	Moderate	Exposed to freezing and thawing cycles; Not exposed to accumulation of snow, ice, and de-icing chemicals; Limited exposure to water	0.55
F2	Severe	Exposed to freezing and thawing cycles and accumulation of snow and ice; Not exposed to de-icing chemicals; Frequent exposure to water; Direct contact with soil	0.45
F3	Very Severe	Exposed to freezing and thawing cycles and accumulation of snow, ice, and de-icing chemicals; Frequent exposure to water	0.40

[1] For exterior slab concrete without steel reinforcement, the w/cm ratio shall be less than or equal to 0.45.

Mechanism of Iron Sulfide Reaction (Pyrrhotite)

Water-Cementitious (w/cm) Ratio

Residential Foundation Concrete (MA Building Code)

Exposure Class	Severity	Condition	Maximum w/cm Ratio
RF1	Moderate	Exposed to freezing and thawing cycles; Exposed to moisture but not likely to be in a saturated condition	0.55
RF2	Severe	Reinforced Concrete; Exposed to freezing and thawing cycles; Exposed to moisture with potential to be in a saturated condition	0.45
RF3	Very Severe	Plain Concrete; Exposed to freezing and thawing cycles; Exposed to moisture and de-icing chemicals with potential to be in a saturated condition	0.45
RF4	Most Severe	Reinforced Concrete; Exposed to freezing and thawing cycles; Exposed to moisture and de-icing chemicals with potential to be in a saturated condition	0.40

[1] Table based on ACI 332 Code Requirements for Residential Concrete (MA Building Code).
[2] With proper waterproofing and sealing, could be designated as Class RF1, but that's a stretch (my opinion).

Mechanism of Iron Sulfide Reaction (Pyrrhotite)

Water-Cementitious (w/cm) Ratio

w/cm Ratio vs. Time of Capillary Pore Discontinuity

w/cm Ratio	Time Required
0.40	3 Days
0.45	7 Days
0.50	14 Days
0.60	6 Months
0.70	1 Year
> 0.70	Impossible

So much time for water and oxygen to enter the hardened concrete and oxidize iron sulfide bearing aggregate!

[1] Powers and others (1959)
[2] Continuously moist-cured

MGL Part I, Title II, c.6C § 79 (2023)

Pyrrhotite Legislation in Massachusetts

massDOT Massachusetts Department of Transportation Highway Division

NESMEA 100th Annual Meeting

MGL Part I, Title II, c.6C
§ 79 (2023)

Overview

- Chapter 6C: Massachusetts Department of Transportation
- Section 79: Operation of Quarry, Sand or Gravel Operation; Licensure
- Effective Date: July 1, 2024
- Subsection (b): Any person seeking to mine, expand, excavate or otherwise operate a quarry, sand and gravel operation or any other aggregate source for the purpose of producing concrete aggregate for sale or use in foundations, structural elements or infrastructure, including, but not limited to, roadways and bridges, shall submit to the department and the state geologist an application for a license to conduct such activity.

MGL Part I, Title II, c.6C § 79 (2023)

Overview

- Subsection (b) (Continued): Each license application shall consist of: (i) a description of the geographic location of the aggregate source; (ii) an operations plan, including, but not limited to, mining, processing, storage and quality control methods; (iii) a geological source report, consistent with subsection (c); and (iv) the results of aggregate testing for the presence of pyrite and pyrrhotite, consistent with subsection (d). Each license application shall be accompanied by a fee as established by the department. Fees received by the department under this section shall be used to implement this section; provided, however, that any surplus fee receipts shall be deposited into the General Fund.

MGL Part I, Title II, c.6C § 79 (2023)

Challenges

- Tight timeframe to develop program
- Cost of the program (staffing and web software development)
- Fees and cost of testing and petrographic examination incurred by Aggregate Manufacturers
- No national (or international) consensus testing protocols
- Industry and building official/inspector feedback
- Pyrrhotite appears to be isolated to certain areas
- Are cities and towns properly equipped to enforce the law and building code?
- Ever-evolving research, legislation, regulations, and requirements

MGL Part I, Title II, c.6C § 79 (2023)

Challenges

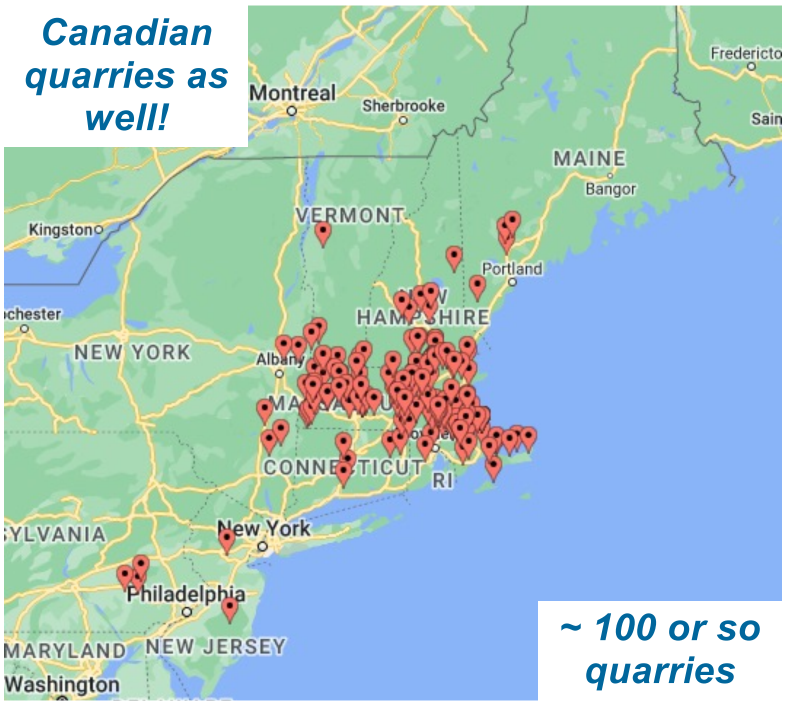
- ❑Originally thought to be a “state” program
- ❑Producing concrete aggregate for sale or use…
  - ❑Ready Mix, Precast, Volumetric, and Prepackaged Concrete
  - ❑What quarries need to be licensed?
  - ❑How is this to be tracked and policed?
- ❑Structural elements or infrastructure, including, but not limited to, roadways and bridges…
  - ❑MassDOT incorporates “High Performance Concrete” and robust sampling, testing, and inspection into its infrastructure
  - ❑Infrastructure has a defined life / replacement cycle

MGL Part I, Title II, c.6C § 79 (2023)

Challenges

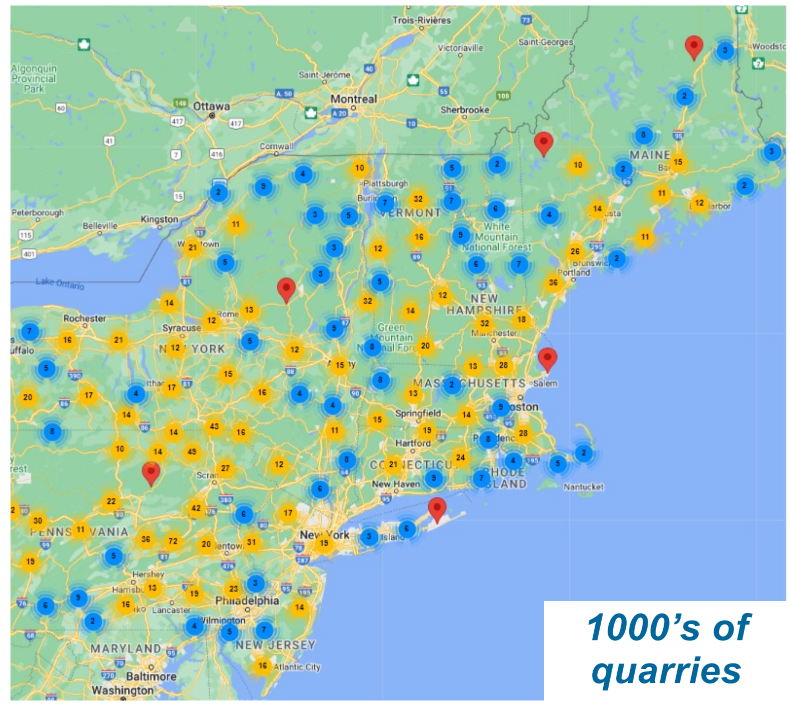
MassDOT Quarries

Canadian quarries as well!



~ 100 or so quarries

Northeast Quarries

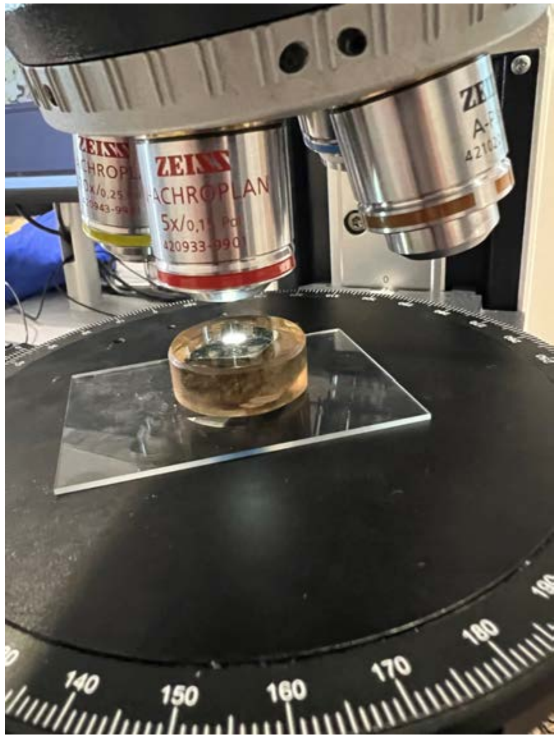


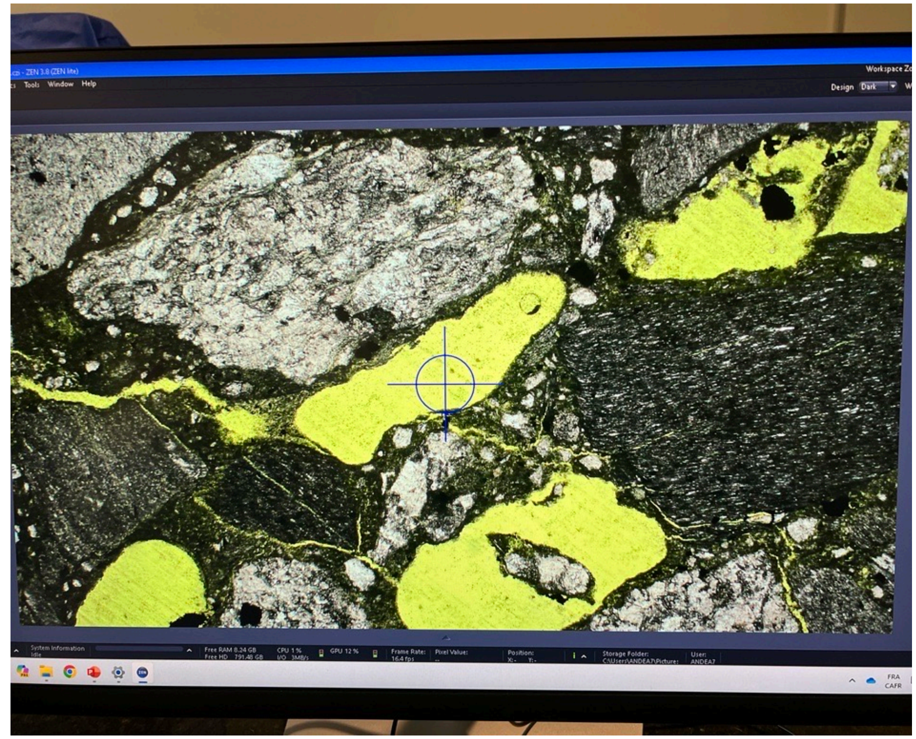
1000's of quarries

MGL Part I, Title II, c.6C § 79 (2023)

Moving Forward

- ❑Adhere to the law as it is currently written
- ❑Conduct hearing for regulations (700 CMR 19.00)
- ❑Continue to conduct research
- ❑Stay current with the latest information, data, and testing protocols
- ❑Focus on the concrete structure where the problem resides (residential foundations only)
- ❑Focus testing on quarries that fall in the “red zones” of the USGS iron sulfide map
- ❑Allow independent geologist to conduct site geology analysis to rule out the presence of pyrrhotite in the quarry, without additional testing
- ❑Update and enforce MA Building Code (780 CMR)
- ❑Provide training and education
- ❑Apply updates to law/regulations as new research and information become available





Geological Sourcing, Sampling, and Testing Protocols

Pyrrhotite Legislation in Massachusetts

massDOT
Massachusetts Department of Transportation
Highway Division

NESMEA 100th Annual Meeting

Geological Sourcing, Sampling, and Testing Protocols

Overview

- ❑Conducted extensive vetting of protocols, in consultation with:
  - ❑Connecticut and Massachusetts State Geologists
  - ❑Massachusetts Concrete and Aggregate Producers Association (MaCAPA)
  - ❑Massachusetts Aggregate and Asphalt Pavement Association (MAAPA)
  - ❑National Stone, Sand, and Gravel Association (NSSGA)
  - ❑American Concrete Institute (ACI)
  - ❑International Conference on Iron Sulfide Reactions in Concrete (ICISR)
  - ❑Independent Laboratories
  - ❑Academia: University of Connecticut (UConn), Trinity College, Université Laval
  - ❑Numerous research papers and conferences

Geological Sourcing, Sampling, and Testing Protocols

Geological Source Report (GSR)

- Prepared by a certified professional geologist, licensed professional geologist or an equivalent acceptable to the State Geologist
- Regional Geology
- Site Geology
  - Analysis of drilled cores
- Test Results
  - 1st: Total Sulfur Content
  - 2nd: Petrographic Examination

Geolgogical Sourcing, Sampling, and Testing Protocols

Sampling and Testing

Level 1: Total Sulfur Content Testing Requirements

Method	Quality Characteristic		Limits
ASTM D4239	Total Sulfur Content (%)	Acceptable: Permitted for use in Concrete	< 0.1
		Additional: Level 2 Petrographic Examination for Pyrrhotite and Framboidal Pyrite Content Required	0.1 to < 1.0
		Rejectable: Prohibited from use in Concrete	≥ 1.0

[1] ASTM D4239 Standard Test Method for Sulfur in the Analysis Sample of Coal and Coke Using High-Temperature Tube Furnace Combustion shall be modified for the testing of aggregate accordingly.

Level 2: Petrographic Examination

Method	Quality Characteristic		Limits
ASTM C295	Pyrrhotite and/or Framboidal Pyrite	Acceptable: Permitted for use in Concrete	No Presence
		Rejectable: Prohibited from use in Concrete	Presence

Evaluation and Mitigation Methods for the Prevention of Cement Concrete Deterioration due to Pyrrhotite

MassDOT & UConn Research Project

Pyrrhotite Legislation in Massachusetts

massDOT
Massachusetts Department of Transportation
Highway Division

NESMEA 100th Annual Meeting

MassDOT & UConn Research Project

Objectives

- Identify pyrrhotite evaluation and test method protocols, including total sulfur content, pyrrhotite content, expansion, and cement concrete performance.
- Testing of the effectiveness of concrete mix design mitigation methods on the evolution of deterioration of cement concrete containing pyrrhotite reactive minerals.

MassDOT & UConn Research Project

Scope of Work

- ❑ Literature Review
- ❑ Analysis of Pyrrhotite Affected Structures
- ❑ Concrete Mix Design Mitigation Methods
- ❑ Total Sulfur Content Testing
- ❑ Electrochemical Accelerated Testing

MassDOT & UConn Research Project

Scope of Work

Mix Designs

Mix Type	w/cm Ratio	f'$_{CM}$ (psi)	NMAS (in.)
HP	0.40	5000	3/4
RF4	0.40	5000	3/4
RF3	0.45	4500	3/4
RF2	0.45	4500	3/4
RF1	0.55	3500	3/4
RF0	0.70	2500	3/4

SCMs and Admixtures

Material	Type	Spec.
Slag	Grade 120	M 302
Air Entrainer	AEA	M 154
HR Water Reducer	F	M 194
Water Reducer / Retarder	D	M 194
Corrosion Inhibitor	CIA	C1582
Permeability Reducers	S-PRA	M 194

MassDOT & UConn Research Project

Scope of Work

Reduction of Permeability using Type S-PRAs

PRA Type	Coefficient of Permeability of Reference	Coefficient of Permeability with PRA Type	Reduction in Permeability (%)
Crystalline	4.29×10^{-14}	1.28×10^{-14}	70
Colloidal Silica	1.98×10^{-13}	1.61×10^{-13}	19
Hydrophobic Pore Blocker	2.23×10^{-12}	1.14×10^{-12}	49

[1] Table from ACI 212.3-R10 Report on Chemical Admixtures for Concrete

Questions and Discussion

Special thanks to the many experts, researchers, and academics (and now friends) at the International Conference on Iron Sulfide Reactions in Concrete (ICISR), University of Connecticut (UConn), Trinity College, and Université Laval!

UCONN

ICISR 2024 International Conference on Iron Sulfide Reactions in Concrete