Funded by the Office of Provost and the
Office of the Vice President for Research

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Development, Verification and Validation of a Test Method for Pyrrhotite in Concrete

PI: Kay Wille
Associate Professor, Director of ACMC lab

PI: Maria Chrysochoou
Associate Professor and Department Head
Department of Civil & Environmental Engineering

Co-PI: Jim Mahoney
Director, Connecticut Transportation Institute

Concrete affected by pyrrhotite containing aggregates

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Investigating the Deterioration of Basement Walls made of concrete in CT - PAST

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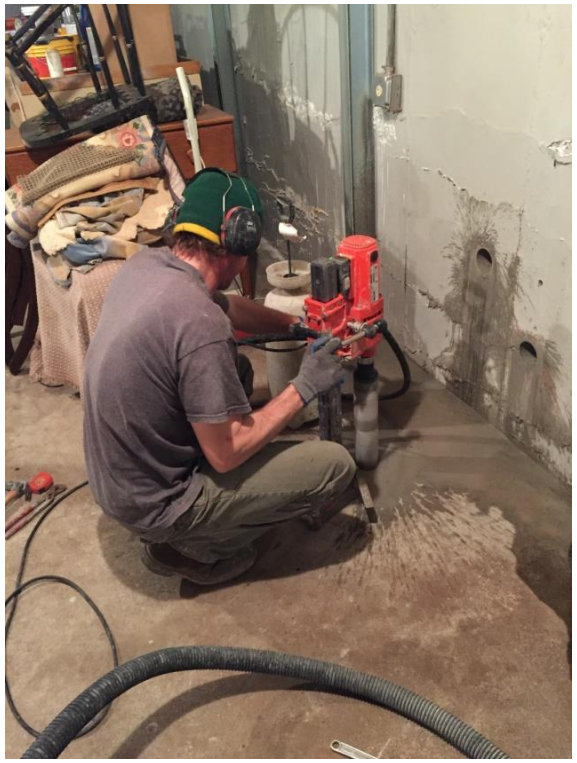


Nov 2015 – August 2016

Attorney General Office

Department of Consumer Protection

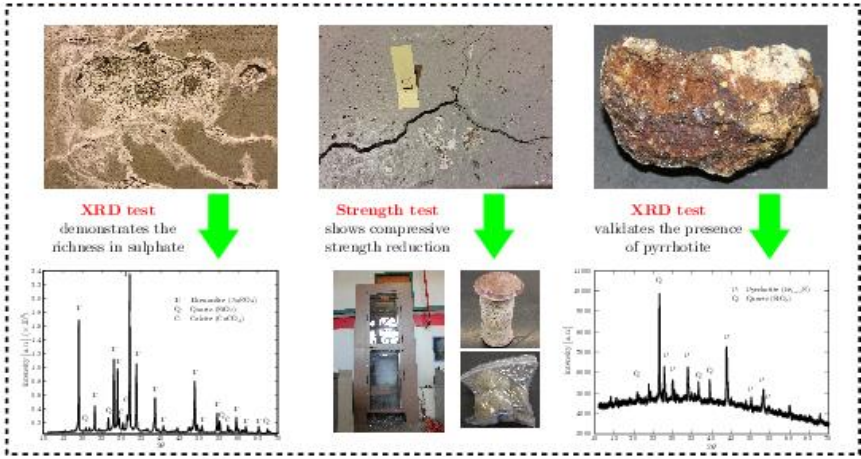
observation

hypothesis: DFE

test

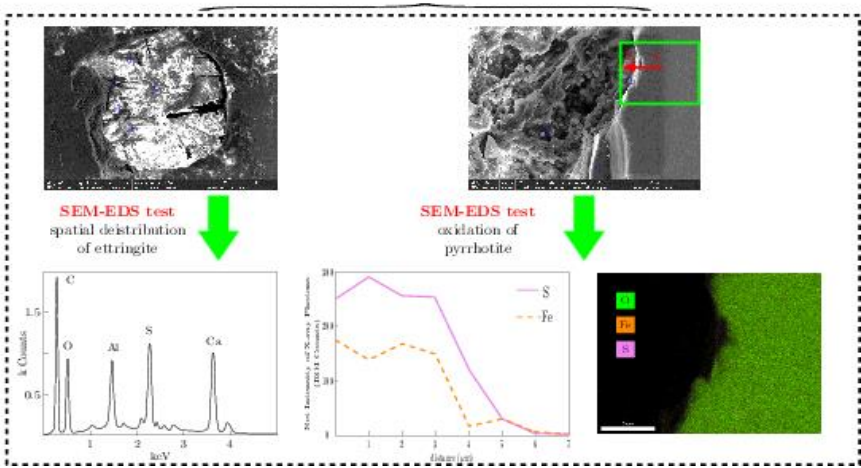
Validation of the hypothesis: spatial distribution of ettringite, oxidation of pyrrhotite

science



macro properties

micro structure



What we know vs. what we don't know

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We know

- Pyrrhotite oxidation causes damage
- Vertical foundation walls are impacted, not horizontal slabs
- Moisture control prevents or slows down damage

We don't know

- How much pyrrhotite causes how much damage damage? How fast?
- Why?
- How can we use that to protect impacted houses?

What will it take to answer these questions?

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Step 1

- **Identify** and **quantify** pyrrhotite with an **standardized**, reproducible **method** (measure is correct and always the same)

Phase I – funded by UCONN
12 months - $300K

Step 2

- We apply the method to a **large number of houses** under different conditions AND do lab testing under controlled conditions

Future work

Step 3

- We use the data to develop a **tiered system** for **risk assessment**

Step 4

- We evaluate options (**replace, repair, retrofit, do nothing**) based on risk

Test Method for Pyrrhotite in Concrete - NOW

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Goal: Develop a rapid and cost-effective test method

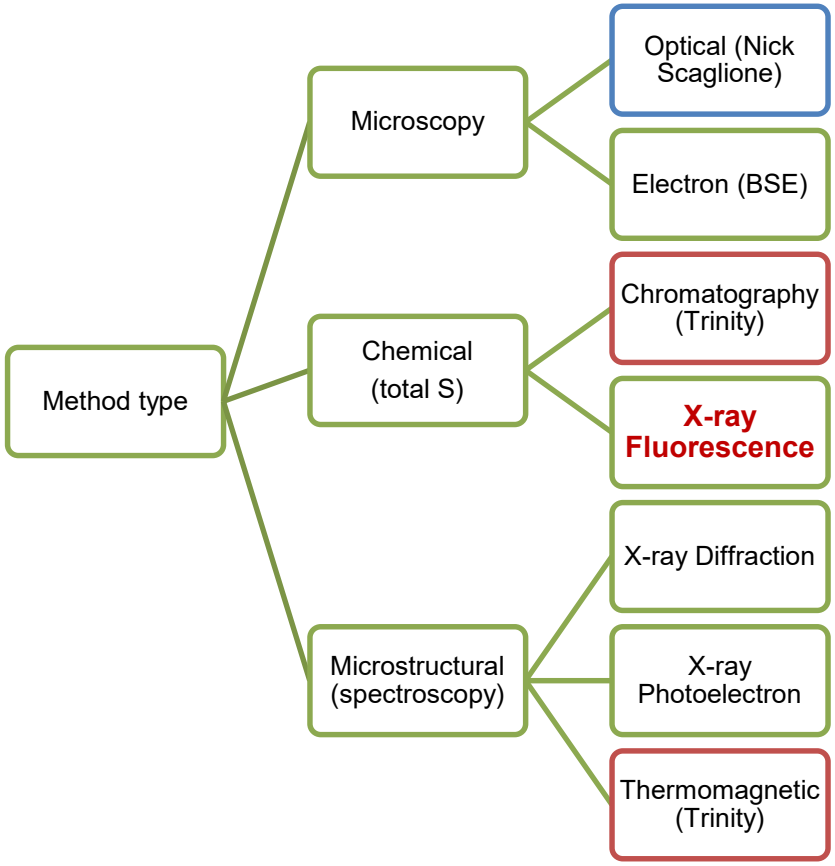
For what: Identify and quantify the presence of pyrrhotite in concrete (challenging)

Why: No test standard with known accuracy and precision exists

How:

- ✓ Prepare standard specimens with **known** pyrrhotite content AND obtain various field specimens
- ✓ Investigate sample volume and preparation requirements *(how much sample do I need to make sure it represents the whole foundation)*
- ✓ Apply a host of methods to both sample types and determine which combination has optimum performance in terms of
  - ✓ Accuracy
  - ✓ Speed
  - ✓ Cost

Methods for pyrrhotite analysis



Field and lab method

Photo: Courtesy Tennessee DOT

Measure Elements such as **S**

Photo: Courtesy Maine DOT

Sulfide (S^{2-}) vs Sulfate (SO_4^{2-})

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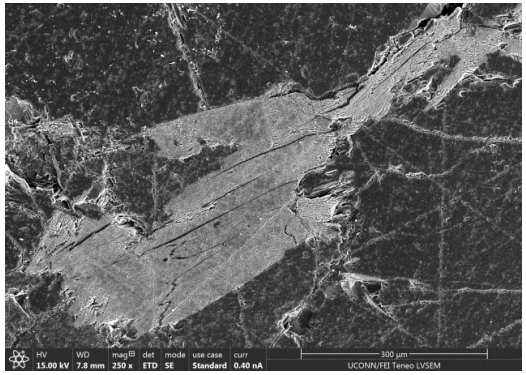
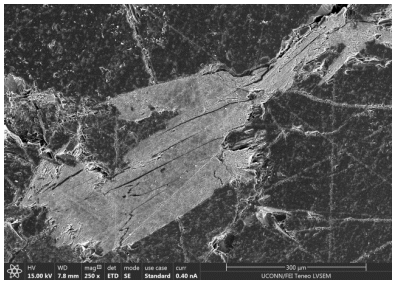
- **Sulfate (SO_4^{2-})** → **gypsum (cement) / limestone (aggregates)**

- **Sulfide (S^{2-})** → **pyrrhotite in aggregates**



Mechanisms of Deterioration



SEM – streaks of FeS

Pyrrhotite Oxidation **(FeS)**

Products

SO_4^{2-} → Sulfate attack
Delayed ettringite formation
Volume expansion

H^+ → Acid attack, dissolution of paste
Formation of gypsum, **expansion**

$Fe(OH)_3$ → **Volume expansion**

Consumption

O_2 → During freezing, negative pressure can be induced in large voids acting as vacuum pump sucking in aggressive solution from surroundings

Sulfide vs Sulfate using WD-XRF

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Chemical composition of Kamin™ 35 used as a carrier for sulfide-sulfate-mixtures

Constituent	SiO_2	Al_2O_3	Fe_2O_3	CaO	K_2O	TiO_2	P_2O_5	S
Concentration (% by weight)	62.1	26.4	0.44	0.08	0.06	0.69	0.59	0.03

Concentrations of FeS and CuSO4*1/2H2O in prepared calibration samples for measurement by WD-XRF

	$CaSO_4$	mix	mix	mix	mix	mix	mix	mix	mix	mix	FeS
m(FeS) [g]	0	0.45	0.9	1.35	1.8	2.25	2.7	3.15	3.6	4.05	4.5
m($CaSO_4$) [g]	4.5	4.05	3.6	3.15	2.7	2.25	1.8	1.35	0.9	0.45	0
m(kaolin) [g]	4.5 g for each sample										
Total S(S^{2-})/Total S	0	0.144	0.275	0.394	0.503	0.603	0.695	0.779	0.858	0.932	1
Total S(S^{6+})/Total S	1	0.856	0.725	0.606	0.497	0.397	0.305	0.221	0.142	0.068	0

Total Sulfur Content using WD-XRF
(Wavelength Dispersive X-ray Fluorescence)

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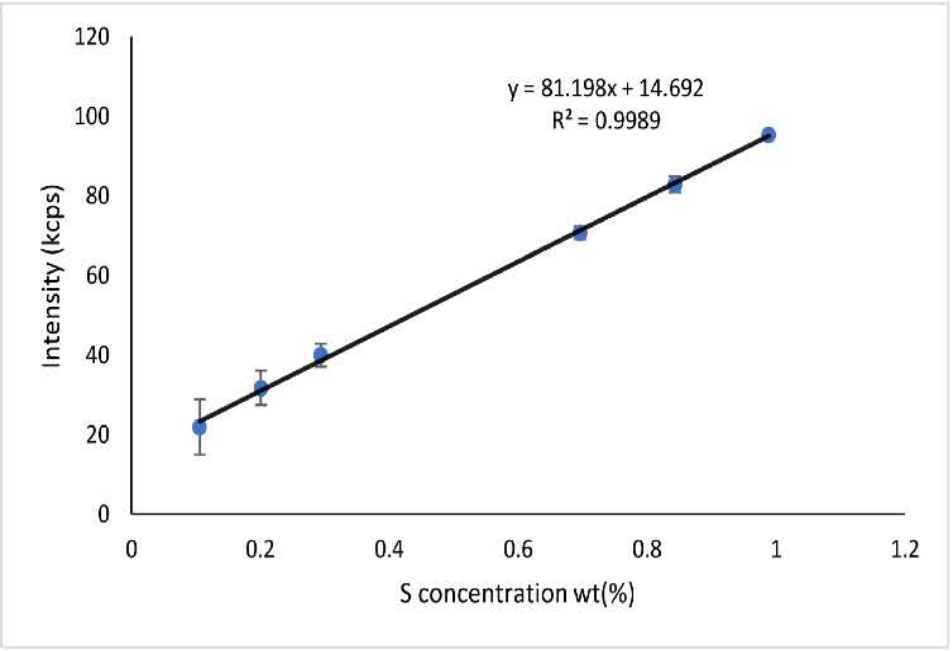
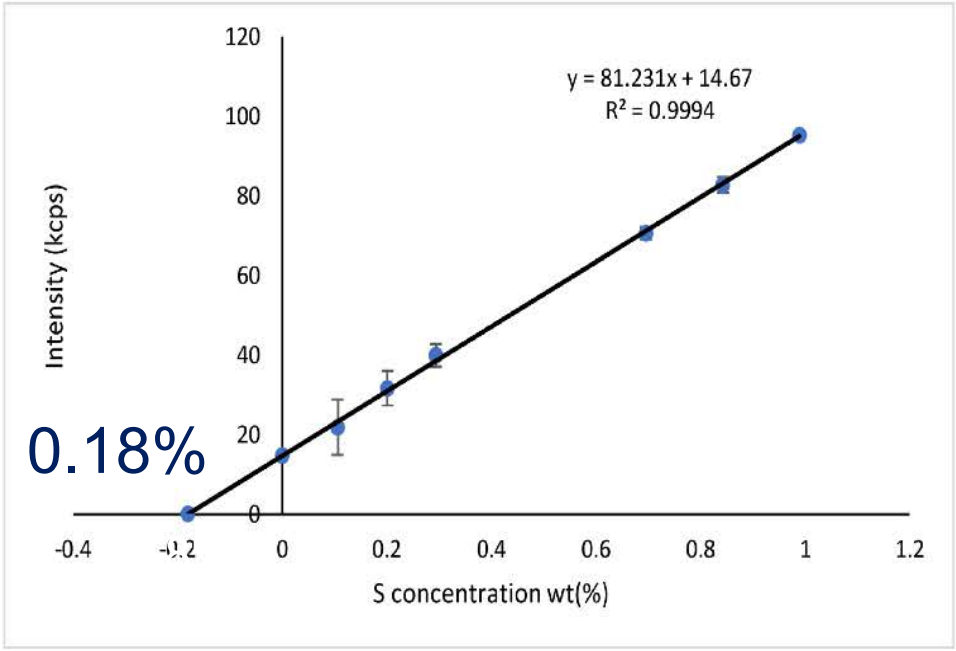
WD-XRF allows us to distinguish between **sulfate (gypsum)** and **sulfide (pyrrhotite)**.

Total Sulfur Content?





Validation Total Sulfur Content - WD-XRF

(Wavelength Dispersive X-ray Fluorescence)

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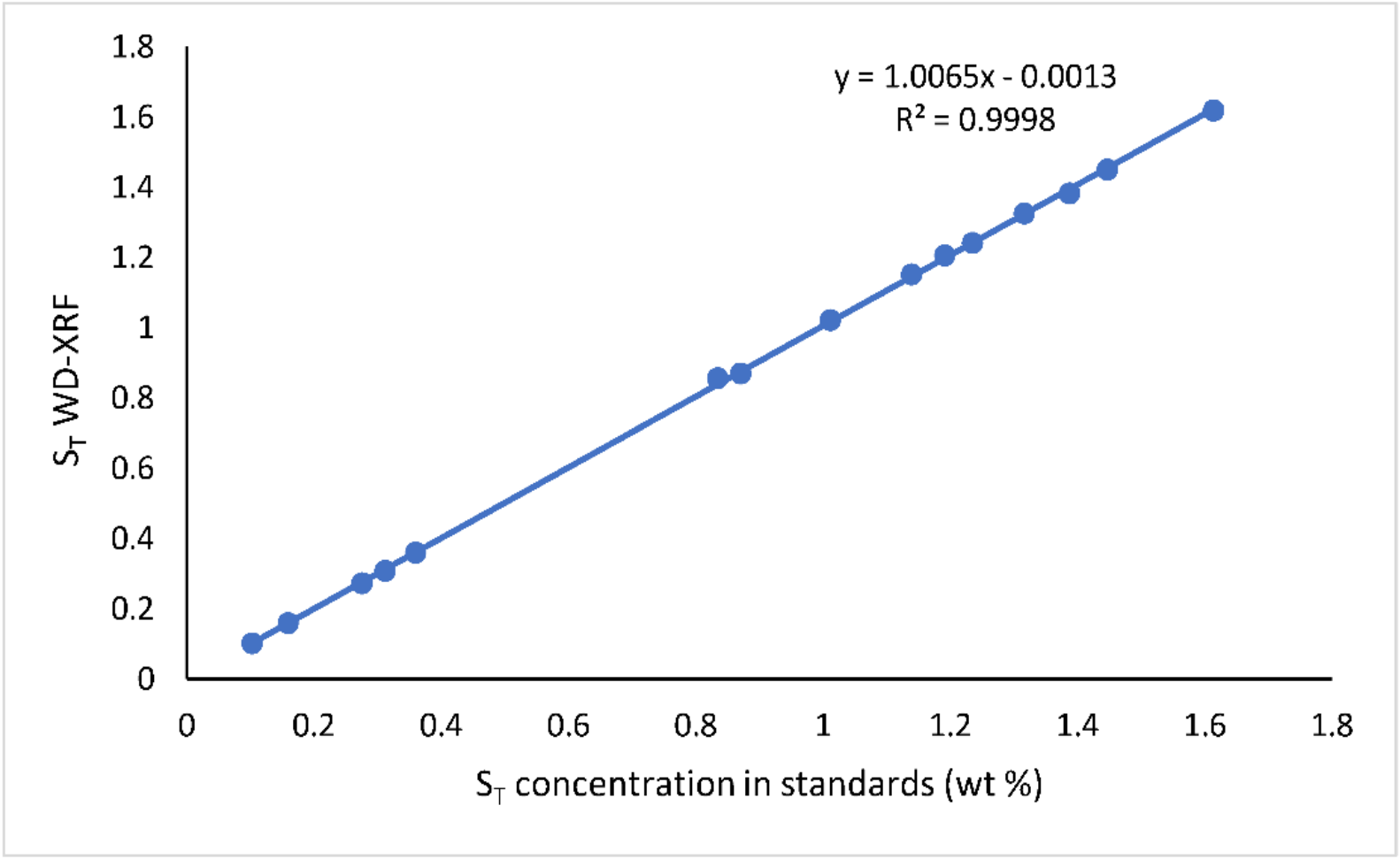

Validation with other methods and samples

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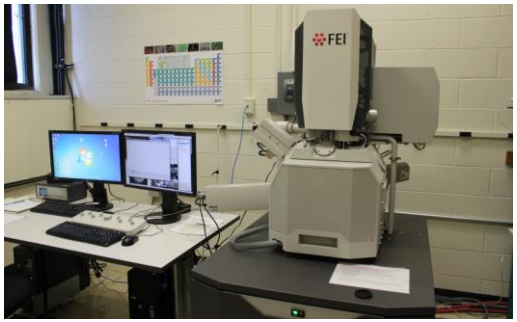
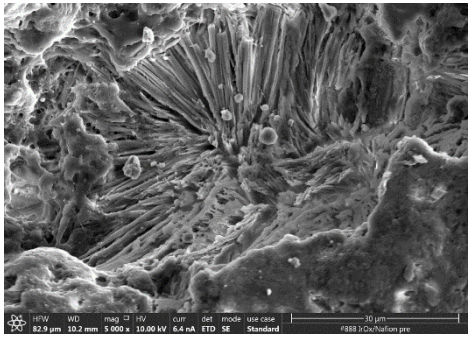
- **Elemental Analyzer**
- **Scanning Electron Microscopy (SEM) with Energy Dispersive X-ray spectroscopy (EDX)**
- **X-Ray Diffraction (XRD)**
- **Ion Chromatography (IC)**
- **PETROGRAPHIC ANALYSIS**
- **THERMOMAGNETIC ANALYSIS**

INVESTIGATION METHODS – SEM + EDX



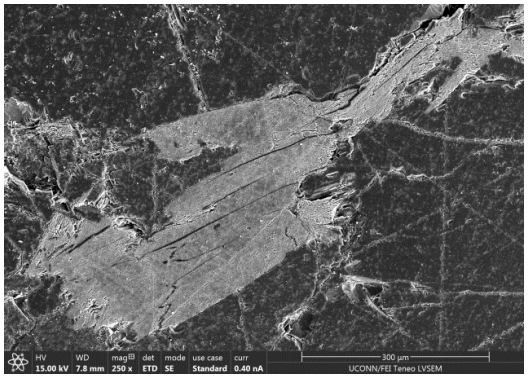
Teno field emission SEM + EDX

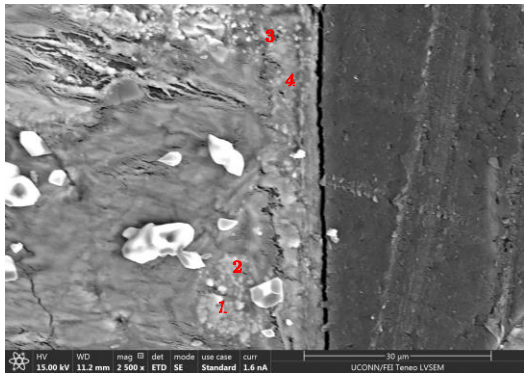


Scanning Electron Microscopy (SEM)

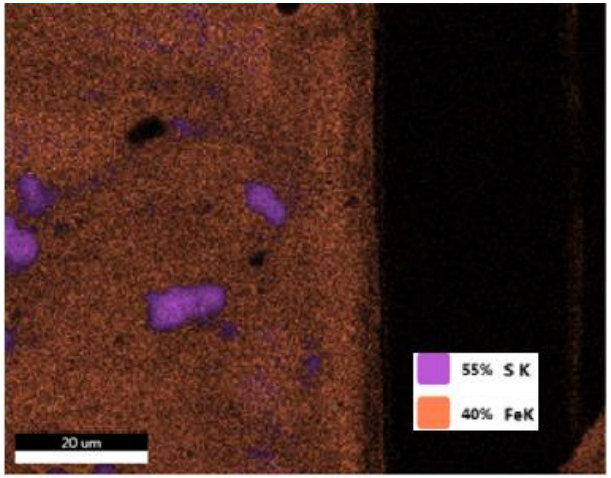
Energy Dispersive X-ray spectroscopy (EDX)

Microstructure (SEM)

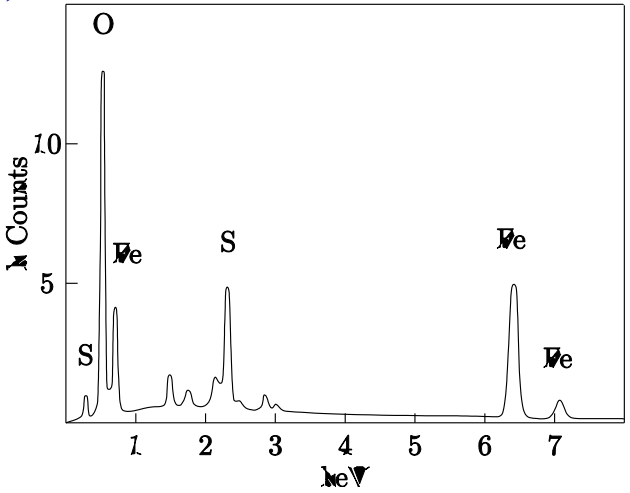




Elementary Composition (EDX)

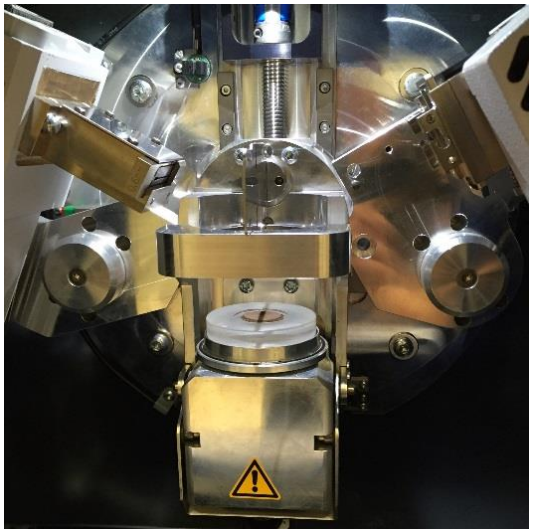


Mapping



Point analysis (Point 2)

INVESTIGATION METHODS - XRD



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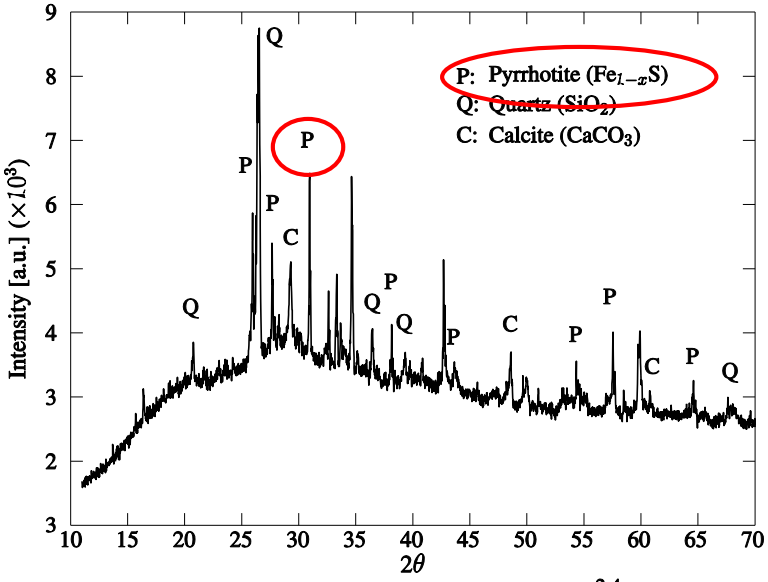
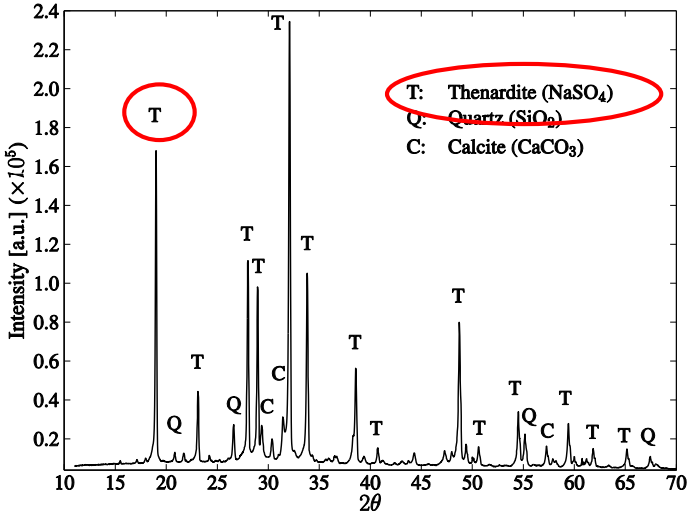


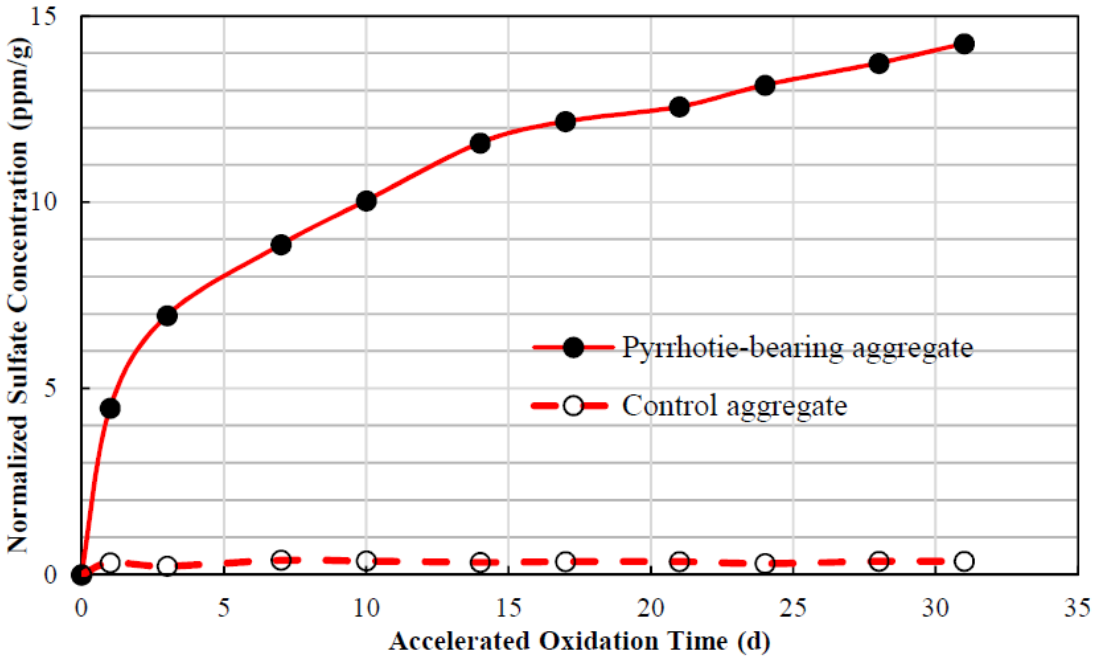


X-Ray Diffraction (XRD)

INVESTIGATION METHODS – IC

DIONEX ICS-1100 ion chromatography

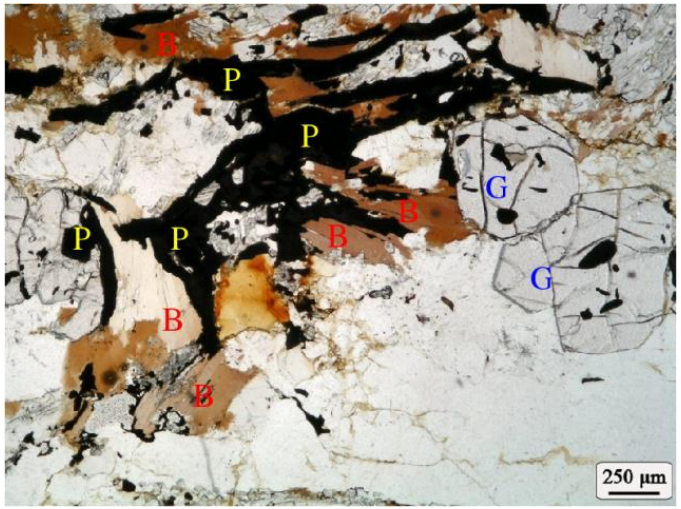
Release of sulfate ions – accelerated oxidation



Ion Chromatography (IC)

PETROGRAPHIC ANALYSIS

Pyrrhotite Inclusion in Coarse Aggregate
(photo courtesy of Nick Scaglione)



Thin Sections of Coarse Aggregate Under the View of Plane Polarized Light (B: Biotite, P: Pyrrhotite, G: Garnet)
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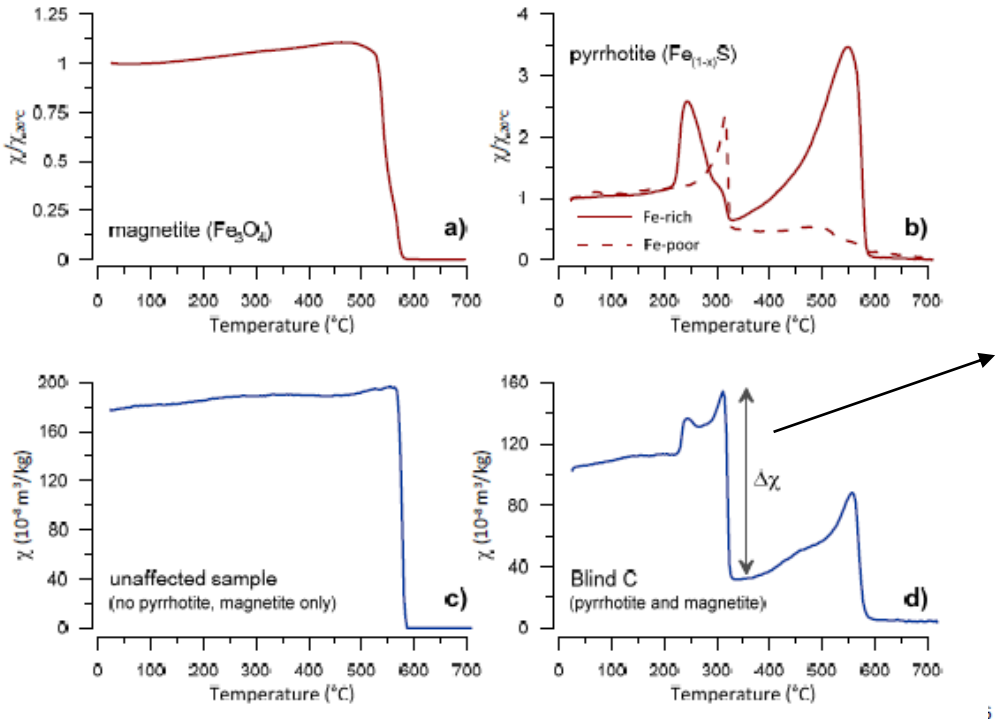
INVESTIGATION METHODS – THERMOMAGNETIC ANALYSIS



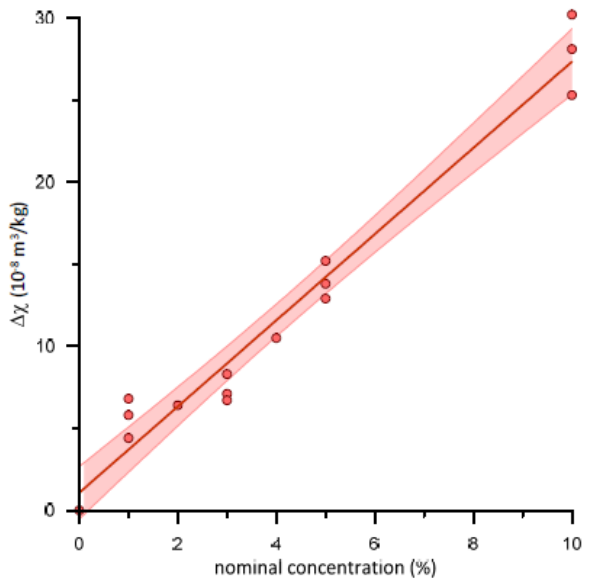


Fig. 3: Drop in magnetic susceptibility Δχ between 310° C and 325°C for a series of cement-pyrrhotite mixtures. Δχ can be considered a semi-quantitative measure of Pyrrhotite content if the investigated pyrrhotites have similar chemical compositions and crystallographic superstructures.

Gneiss and Gurley, 2018 (Trinity College, CT)

Research on Pyrrhotite in Concrete - FUTURE

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Long-term Goal:

- Predict deterioration of concrete and structural integrity of basement walls and other structures
- Determine acceptable pyrrhotite limits
- Develop prevention methods

Challenges:

- Highly complex mechanism and various interconnecting parameters
- Laboratory testing at small and large scale at various conditions over longer time periods is needed
- Funding for data collection, testing, forensic analysis and fundamental research is needed

(e.g. research on pyrrhotite in the amount of $5 million over 4 years just recently funded by the National Research Council Canada, the Quebec government and University Laval, Canada)

Thank you.

Questions?

Special Thanks to UConn, SOE
Yusniel Cruz-Hernandez and Douglas Hendrix

Oxidation of Pyrrhotite

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Sulfate attack - **Volume expansion**

Gypsum + Tricalcium aluminate → Ettringite

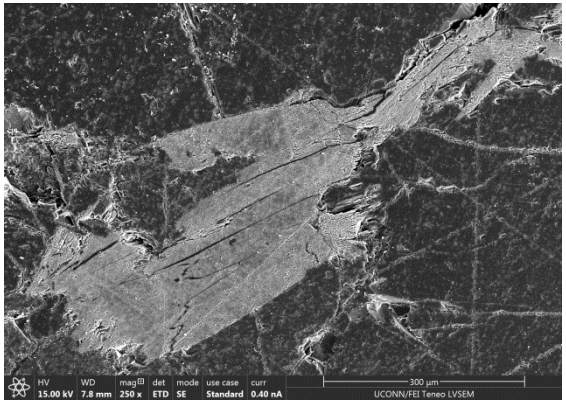
$$3CaSO_4 \bullet 2H_2O + 3CaO \bullet Al_2O_3 + 26H_2O \rightarrow 3CaO \bullet Al_2O_3 \bullet 3CaSO_4 \bullet 32H_2O$$

delayed ettringite formation

Pyrrhotite

$$Fe_{1-x}S + \left(\frac{10-3x}{4}\right)O_2 + \left(\frac{4-3x}{2}\right)H_2O \rightarrow (1-x)Fe(OH)_3 + SO_4^{2-} + H^+$$

Ferrihydrite



SEM – streaks of FeS in aggregate

Volume expansion

3.05 cm^3/mol

Acid attack+

Formation of gypsum

$$Ca(OH)_2 + H_2SO_4 \rightarrow CaSO_4 \bullet 2H_2O$$

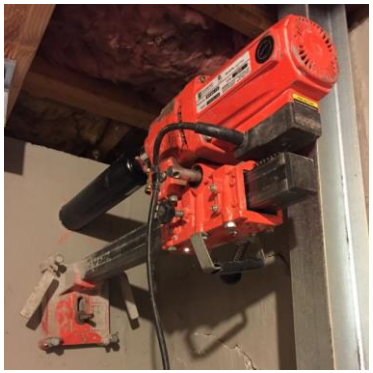
Portlandite → Gypsum

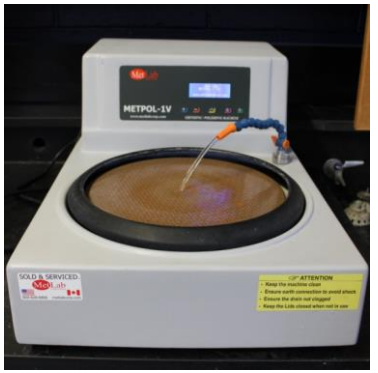
Investigation Methods – Compressive Strength

400 kip load

frame

Specimen Preparation





compressive strength reduction of concrete foundation wall **27% to 100%**

INVESTIGATION METHODS – SEM + EDX

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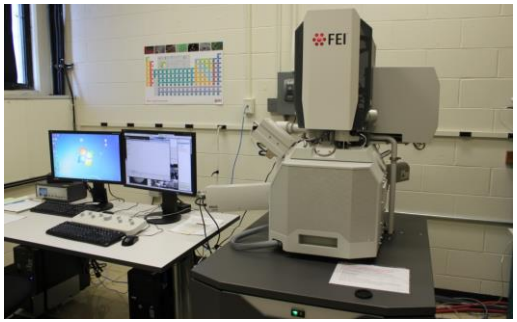

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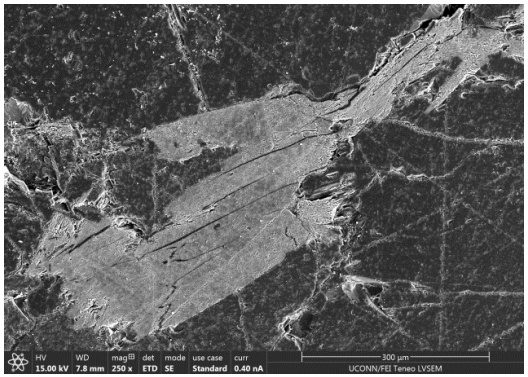

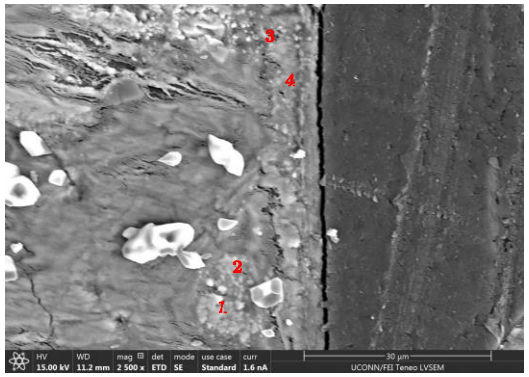

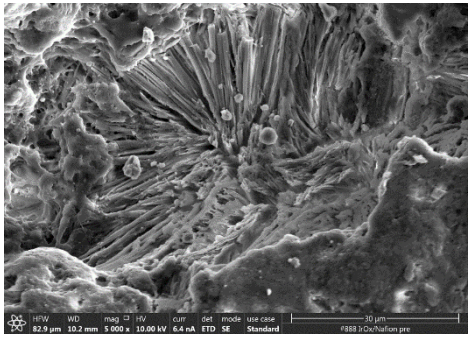

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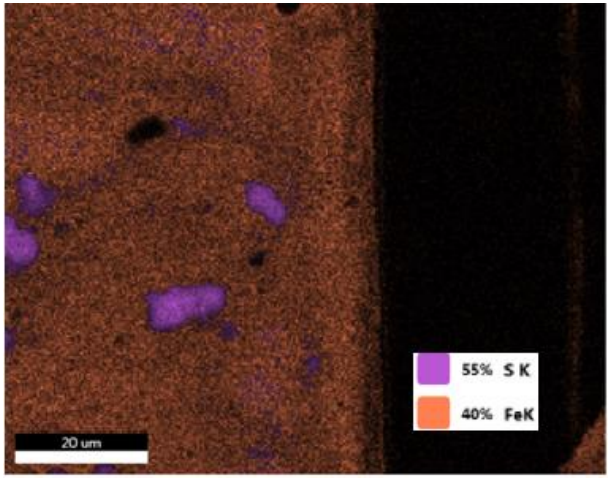

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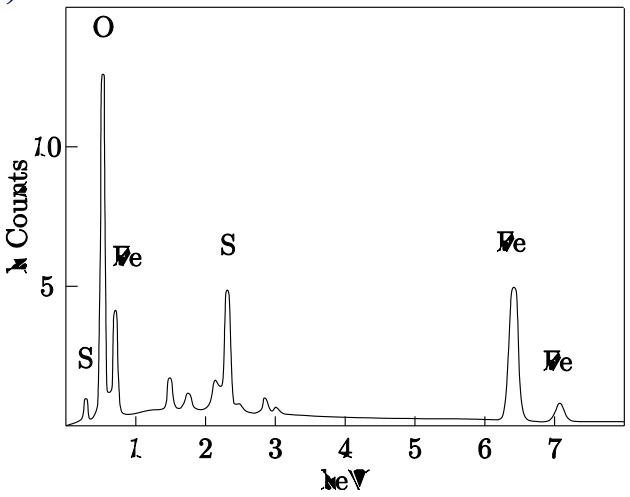
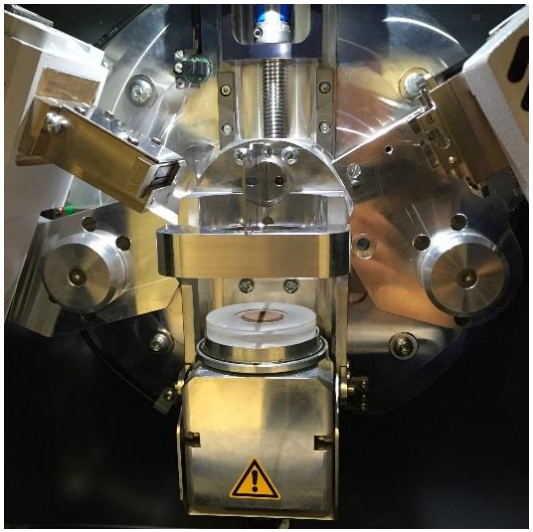


Point analysis (Point 2)

INVESTIGATION METHODS - XRD



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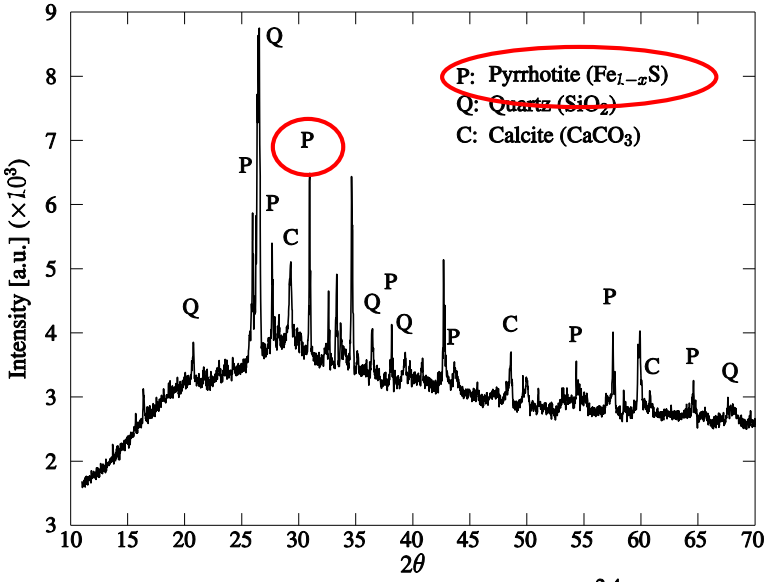
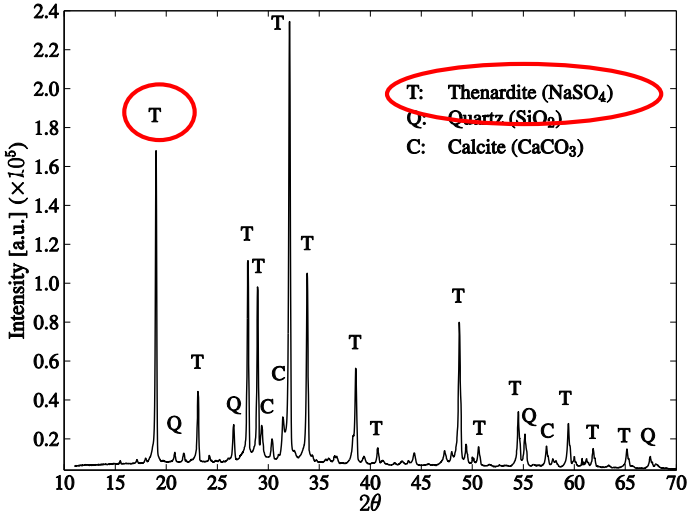




X-Ray Diffraction (XRD)

INVESTIGATION METHODS - XRF

INNOV-X Systems XRF analyzer

Promising Method to detect elemental Sulfur – part of pyrrhotite

Elemental Composition – quarry aggregate

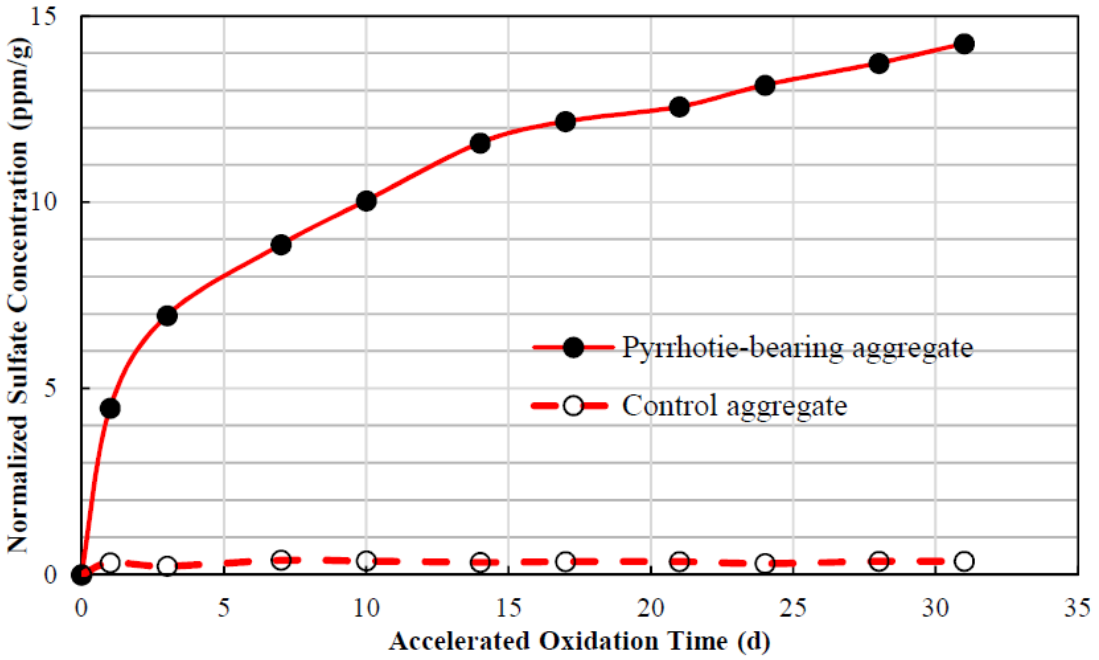
	With brown discoloring	Reference sample
	Average	Average
S	2.5%	-
Fe	6.3%	0.001%

X-Ray Fluorescence (XRF)

INVESTIGATION METHODS – IC

DIONEX ICS-1100 ion chromatography

Release of sulfate ions – accelerated oxidation



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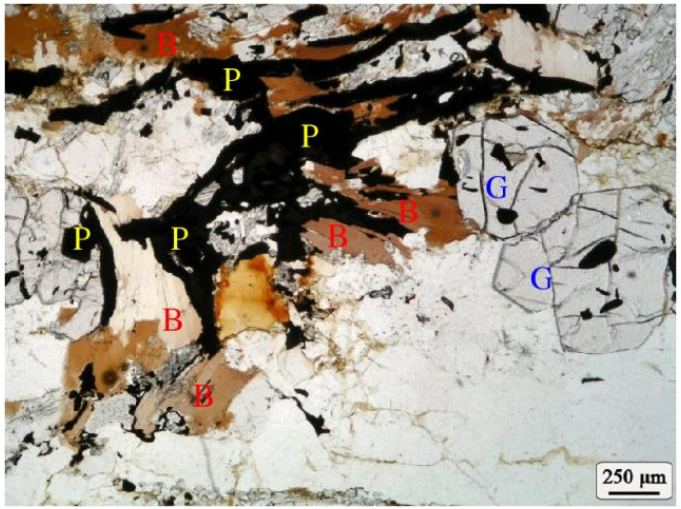

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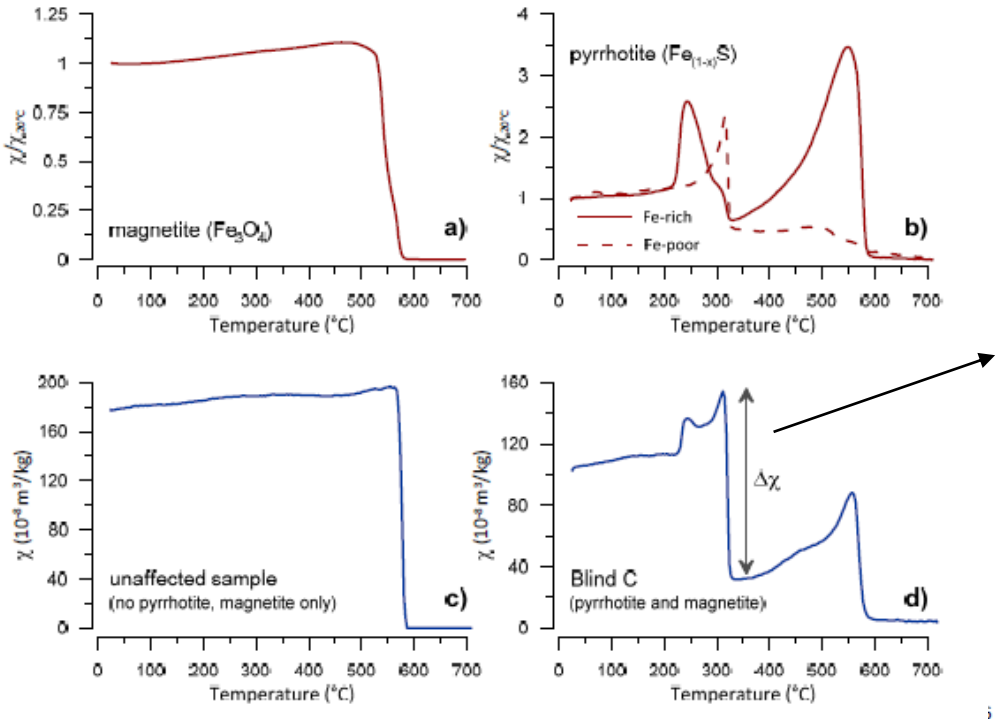
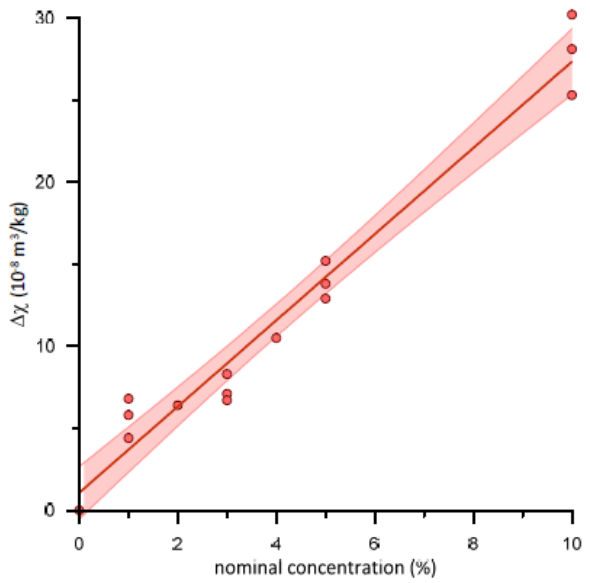
INVESTIGATION METHODS – THERMOMAGNETIC ANALYSIS





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