## Proceedings

First International Conference on Iron Sulfide Reactions in Concrete May 2024

10 A 10

Edited by: Benoît Fournier, Josée Duchesne, Rodolfo Castillo Araiza, Andreia Rodrigues, and Pierre-Luc Fecteau





### Cracking and crumbling of concrete blocks in County Donegal, Ireland: A holistic approach from case studies on deleterious effects of open microstructure of blocks, phyllite aggregate, pyrrhotite Oxidation, paste carbonation, lime leaching, and internal sulfate attacks

#### Dipayan Jana<sup>1</sup>

(1) Construction Materials Consultants, Inc. and Applied Petrographic Services, Inc., Greensburg, USA, info@cmc-concrete.com

#### Abstract

Two different mechanisms are offered for extensive cracking and crumbling of an estimated 5000 properties in County Donegal in Ireland. One mechanism, known as the 'mica crisis' is reported to be from the use of defective concrete blocks containing excessive (free) mica in the mortar fractions derived from micaceous aggregates (mostly phyllite with subordinate mica schist, quartzite, etc.). Excess mica from abraded phyllite in paste has reportedly caused many known mica-related issues, e.g., increased water demand at a given workability, increased water absorption, increased microporosity, loss of compressive strength, reduced resistance to frost attack from high water demand, increased leaching, etc. Subsequent studies have established evidence of iron sulfides mostly in the form of pyrrhotite in the aggregates, which have caused oxidation and related expansions in the presence of moisture and oxygen followed by internal sulfate attacks (ISA) from reactions between sulfates released from pyrrhotite oxidation and cement hydration products resulting in formation of gypsum, ettringite, and thaumasite causing expansions and cracking to softening and crumbling of paste from decomposition of calcium silicate hydrate (CSH) from thaumasite attack and severe carbonation and leaching of paste. The present report has taken a holistic approach from case studies of moderately to severely crumbled blocks to sound cast-in-place foundation of homes in County Donegal to evaluate deleterious roles of open microstructure of blocks, phyllite aggregates, pyrrhotite oxidation, paste carbonation and leaching, and internal sulfate attacks for the catastrophic distress.

Keywords: cracking, Donegal, ISA, phyllite, pyrrhotite

#### 1. INTRODUCTION

The so-called 'mica crisis' in Ireland [1, 2, 3] is rightfully confirmed to be the case of internal sulfate attacks (ISA) from oxidation of iron sulfide minerals (mostly pyrrhotite, sometimes along with pyrite) in aggregates used in the defective concrete blocks [4, 5]. Studies of 1800 distressed properties from 1995 to 2010 in County Donegal found deleterious roles of pyrrhotite-bearing phyllite as the main cause of distress [5]. From the independent case studies of author on the severely crumbled down to 'powder' to moderately crumbled 'fragments' of blocks from some of the most distressed homes (Fig. 1.1 Photos 1-20), along with 'sound' cast-in-place concrete foundation of a house (Fig. 1.1 Photos 21-25) all containing same crushed pyrrhotite-bearing phyllite aggregate reportedly sourced from the same Buncrana quarry as the aggregate source for the other defective blocks, a preliminary holistic approach is taken to evaluate relative roles of: (1) open microstructure of blocks as opposed to denser microstructure of cast-in-place foundation for deeper penetration of moisture, oxygen, and CO<sub>2</sub> in blocks during service than in foundation, (2) easy abrasion of phyllite to expose more pyrrhotite grains to oxidation than other hosts during block manufacturing, (3) advanced pyrrhotite oxidation in blocks starting from steam curing process to easy access to moisture/oxygen during service through open microstructure of blocks, (4) deeper, pervasive carbonation through open-structured block than limited (max. 15 mm) carbonation in denser foundation, (5) preferential internal sulfate attacks (ISA) in the paste of distressed blocks but not in the sound foundation from sulfate release from pyrrhotite oxidation to cause (5a) deleterious ettringite formation (E-ISA) in the denser confined spaces of less/non-carbonated regions to cause expansions and cracking to (5b) deleterious thaumasite formation (T-ISA) in the porous, moderately carbonated regions to cause decomposition of calcium silicate hydrate (CSH) with softening and disintegration to (5c) gypsum form of ISA (G-ISA) in severely carbonated paste by replacing calcium carbonate, and (6) leaching of lime and products of ISA from continued moisture circulation throughout the open-structured block during service to re-precipitate lime and ISA products in voids and turn the paste into a silica-alumina-magnesia-based gelatinous mass with little or no cementitious property, which was already started with T-ISA to cause catastrophic crumbling of blocks across County Donegal.

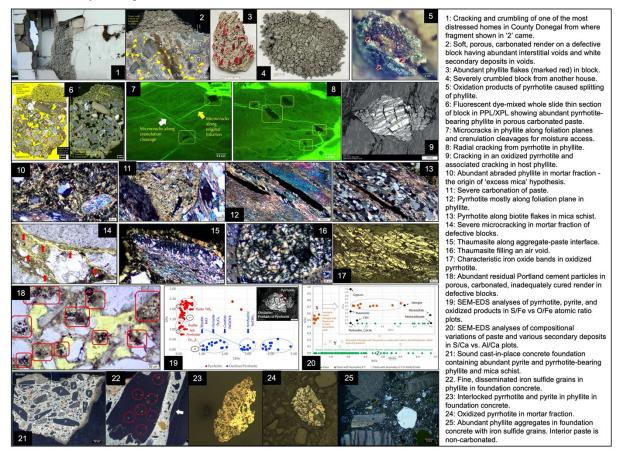


Figure 1.1: A microstructural collage of defective concrete blocks (Photos 1 to 20) and sound cast-inplace foundation (Photos 21 to 25) from County Donegal, Ireland.

### 2. METHODOLOGIES

All samples were examined by: (1) polarized-light microscopy (reflected-light microscopy of polished thin and solid sections, transmitted-light microscopy of polished thin sections) for iron sulfide minerals, oxidation products, aggregates' mineralogies/textures, paste compositions/microstructures/alterations, and secondary deposits, (2) SEM-EDS studies of polished thin/solid sections for further characterization of phases detected in optical microscopy, (3) XRD studies of bulk samples and extracted aggregates for detection and quantifications of iron sulfide minerals, aggregate mineralogies, and ISA products, (4) XRF and combustion IR for major element oxide compositions and total sulfur content ( $S_T$ ), (5) thermal analysis for sulfate/carbonate phases, and (6) ion chromatography of filtrates of deionized water-digested samples for water-soluble sulfate contents. Details can be found in Jana [6].

#### 3. RESULTS

Crumbling in one of the most distressed homes in County Donegal (Fig. 1.1 Photo 1) examined by author was the result of multiple episodes that started with the use of defective concrete blocks having: (1) abundant easily splitable phyllite aggregates (as high as 80% by volume of coarse aggregate, Fig.

1.1 Photos 2, 6), along with (2) overall porous, high water-cement ratio (w/c), and low cement content (4% [3]) nature of blocks leaving a lot of interstitial spaces for migration of moisture, oxygen and CO<sub>2</sub> through the renders to the blocks especially at the outer leaf to cause pyrrhotite oxidation, paste carbonation, ISA, and leaching/re-precipitation.

Phyllite occurred as low-grade, fine-grained metamorphic rock of Precambrian Dalradian Supergroup consisting of major amounts of interlayered muscovite, chlorite and subordinate amounts of very fine-grained silty quartz and alkali feldspar all in parallel layered arrangements to form the typical foliation or sheet-like flakes and characteristic crenulation cleavages of deformed flakes (Fig. 1.1 Photos 10-12). Weak zones along foliation planes and crenulation cleavages provided crisscross intersecting pathways for migration of moisture and oxygen to pyrrhotite (Fig. 1.1 Photo 7). Muscovite and chloride are non-swellable sheet silicates but their presence as easily breakable foliated sheets in phyllite along with their inherent finer grain size than schist have contaminated the mortar fractions of blocks with abraded phyllite flakes (>10% to as high as 50%, by paste volume) to increase the water demand at a given workability and reduce the compressive strength. After phyllite, coarser-grained mica schist is detected at subordinate (15-20%) amount consisting of parallel alignments of muscovite mica, biotite, chlorite, deformed quartz, and alkali feldspar grains (Fig. 1.1 Photo 13). Only a minor (1-5%) amount of noticeably denser and non-foliated coarse-grained metaquartzite aggregate is found, which, if were used as the primary aggregate would have drastically reduced the observed disintegration of blocks let alone to expose pyrrhotite grains to oxidize.

Abundant pyrrhotite grains in phyllite (sizes from < 1 mm at long to <0.5 mm at short directions, Fig. 1.1 Photos 6-9) have acted as the effective sites for expansion from oxidation during service especially at the moist and alkaline (pH >10, less to non-carbonated) conditions of blocks. Some prior oxidations, however, may have occurred in geologic formation and during storage in the aggregate stockpile. Pyrrhotite grains are detected mostly in phyllite as opposed to mica schist or metaguartzite as (a) finegrained isolated disseminated irregular-shaped to subhedral equant grains (Fig. 1.1 Photo 7) to (b) mostly elongated grains aligned along the dominant foliation planes (Fig. 1.1 Photo 12), which shows extensive reddish-brown oxidation products (e.g., goethite, ferrihydrite, Fig. 1.1 Photo 5) causing further cracking, splitting, and disintegration of phyllite. In situ oxidation of pyrrhotite has caused further splitting and crumbling of phyllite (Fig. 1.1 Photos 8,9) especially since most pyrrhotite grains have crystallized along the prevailing foliation planes where the inherent phyllitic texture of foliation and deformed (crenulation) cleavage planes provided pathways for ready migration of moisture to facilitate oxidation. Additionally, spectacular radial cracks are often seen from oxidized pyrrhotite grains in phyllite (Fig. 1.1 Photos 8, 9) as a testament of in situ expansion from pyrrhotite oxidation. Reddish-brown oxidized pyrrhotite products are preferentially noticed between the greenish sheened (from chlorite) foliated sheets where expansive oxidation reactions have further disintegrated the phyllite. Pyrrhotite contents in phyllite aggregates varied from 0.75 to 1.5 percent, by volume. Pyrrhotite is associated with pyrite though no evidence of oxidation of pyrite, or its subsequent sulfate attack (as found in the neighboring County Mayo from framboidal pyrite) was found in the present study.

 $S_T$  varied from 0.5 to 1% by mass in distressed blocks and sound foundation depending on the pyrrhotite and pyrite contents, which after converting to aggregate sulfide contents for appropriate aggregate contents are a factor of 5 to 10 times higher than the maximum allowable sulfur content of 0.1% as per EN 12620 specification. At least for the foundation, a high  $S_T$  did not necessarily transform to high risk, which amongst various reasons is due to the abundance of non-reactive (blocky) form of pyrite, which has contributed to the lion's share of  $S_T$ , and non-reactive finely disseminated form of pyrrhotite.

Fig. 1.1 Photos 19 and 20 show SEM-EDS analysis of compositional variations of pyrrhotite with oxidation products, and paste with secondary deposits, respectively. XRD studies showed both pyrite and pyrrhotite in blocks and foundation but higher amounts of pyrrhotite in blocks leading to higher risk along with indication of potential variations in pyrrhotite contents across the quarry.

Along with aggregate disintegration, mortar fractions of blocks (Fig. 1.1 Photos 10, 11, 14) became the junkyard of (1) abundant abraded fractions of phyllite, (2) oxidized pyrrhotite grains, (3) products of carbonation, (4) lime-poor silica-alumina-magnesia gel from carbonation to decalcification (magnesia was from chlorite decomposition), (5) scattered products of E/T/G-forms of ISA either in least leached/carbonated paste, or as (6) innocuous secondary deposits lining air voids and pores from dissolution and reprecipitation in the decalcified regions of paste. All these products are initially characterized from optical microscopy but best diagnosed during subsequent SEM-EDS studies.

Since pyrrhotite-bearing phyllite occupied much larger volumes (80%) of blocks than the mortar fractions (<10%), distress from aggregate disintegration by pyrrhotite oxidation contributed to the larger part of distress at the initial stage to cause initial cracking, which was followed by subsequent disintegration of the lower volume mortar fraction mostly from carbonation, ISA, and leaching to cause eventual softening and crumbling of blocks.

For the sample from cast-in-place foundation, nonreactive pyrite is more abundant than pyrrhotite, where the former contributed to the lion's share of  $S_T$  and the latter mostly occurred as nonreactive fine disseminated grains in phyllite (Fig. 1.1 Photo 22) instead of along foliations, and lesser in the mortar fractions where it shows some oxidation (Fig. 1.1 Photo 24), which is consistent with lesser amount of abraded phyllite in the mortar fraction (Fig. 1.1 Photo 25) than found in defective blocks. Characteristic 'striated' appearance of oxidized pyrrhotite grains having iron oxide bands in iron sulfide body so common in the blocks (Fig. 1.1 Photos 9, 17) are virtually absent in the foundation (Fig. 1.1 Photo 23). Carbonation was restricted to the top 15 mm mostly in a porous cementitious coating on concrete, where secondary ettringite is found in voids. Evidence of E-ISA, T-ISA, or G-ISA are not found in the interior concrete, nor any cracking, which are due to the inherent denser microstructure of concrete along with the absence of moisture during service. Cases from Canada and US, however, showed that denser microstructure alone cannot prevent the distress if foundation were exposed to moisture during service.

#### 4. DISCUSSIONS

Sulfates released from pyrrhotite oxidation as sulfuric acid create an ideal scenario for ISA from deleterious formation ettringite (E-ISA) in the confined spaces in paste from reactions with monosulfates and associated expansions and cracking. E-ISA, however, is more common in the denser and less carbonated concrete, e.g., as seen in numerous residential concrete foundations in the eastern Connecticut [6,7] than in the defective concrete blocks that are inherently porous with a high void content (for use of a low cement content mix), and a porous, high *w/c* paste (for the high-water demand of abraded phyllite). Extent of distress from pyrrhotite oxidation and subsequent forms of ISA are essentially controlled by the host rock for pyrrhotite and whether the distress is occurring in a dense concrete microstructure (e.g., cases in eastern Connecticut or Canada [6,7,9]), or in an inherently porous microstructure of concrete block as in the present case.

In the distressed blocks, sulfates released from pyrrhotite oxidation did cause E-ISA but mostly in the moist condition in initial non-carbonated low-volume porous paste, and in intergranular void spaces and air voids as the first form of ISA, whose remains became limited as the porous paste became dried and carbonated when thaumasite-form of ISA (T-ISA) became evident especially during the cold weather conditions (at 5 to 15°C). Localized occurrence of gypsum is reported in the severely carbonated paste by reaction with calcite as the final form of ISA (G-ISA) at the high sulfate areas [4]. Though not detected in the presently examined block fragments probably for advanced dissolution, but G-ISA is found in the study of other distressed blocks by Leemann et al. [4] and is, indeed, very common in many other cases in Ireland, e.g., causing cracking of defective blocks in County Mayo containing framboidal pyrite in limestone aggregates [1] or devastating building heaves in Dublin constructed on carbonate mudstone fill containing framboidal pyrite where reactions between sulfates released from pyrite oxidation and calcite in the host rock have caused expansive formation of gypsum [8].

High intergranular void contents and low volume, porous, high *w/c* paste of blocks have caused effective carbonation of paste especially when relative humidity was in the range of 60-80% to convert original calcium hydroxide and CSH components to fine-grained calcite and hydrated silica-alumina gel thereby providing the seeds for T-ISA. Carbonation occurred more effectively in the relatively drier inner leaf and during intermittent dry periods in the outer leaf, which itself at the advanced stage can cause severe loss of strength from decomposition of CSH. Deleterious effects of carbonation-induced T-ISA, however, are more pronounced at the early stages of carbonation and in the least decalcified regions. Severe carbonation (pH <10) and lime leaching to the point of silica-alumina-gel formation from original CSH either prevent T-ISA or restrict secondary thaumasite formation mostly in the porous regions and as linings in air voids and cracks simply from dissolution, redistribution, and reprecipitation of available dissolved sulfate and carbonate ions – as seen in the severely disintegrated blocks. Such three-stage alterations of CSH, i.e., first by carbonation, then by subsequent T-ISA, and finally by severe leaching/decalcification has caused severe disintegration and crumbling of blocks. T-ISA, however, is more pronounced in the distressed blocks than in the foundation sample (as also not seen in distressed foundations in eastern Connecticut, USA [6,7]), which is directly related to much denser microstructure

of foundation concrete to prevent severe carbonation (or any other source of carbonates). Carbonates released from paste carbonation during drier periods (at 60-80% relative humidity) along with sulfates released from pyrrhotite oxidation during wet periods have caused T-ISA preferentially in the outer leaf to cause its higher extent of damage than the inner leaf.

Distresses from E/T-ISA, however, are less evident in the severely carbonated, porous, silica-aluminarich gelatinous regions of paste where products of ISA are mostly found as secondary deposits in coarse voids (as interlayered secondary ettringite and thaumasite fibers, Fig. 1.1 Photo 16) from dissolution and re-participation, whereas in the least de-calcified regions E/T-ISA products are often found mixed within the paste to implant seeds for potential expansions. Distresses from E/T-ISA, however, are inherently restricted for the low (<10%) paste volumes of blocks and even more so only in the moderately carbonated and less decalcified paste regions. The outcome, however, is severe crumbling of blocks.

Abundant pyrrhotite provided the starting ingredients for ISA, foliated nature of phyllite provided ideal pathways for entry of moisture and oxygen to release sulfates for E/T-ISA, porous microstructure of blocks provided pervasive carbonation and released carbonates and silica gel for T- ISA, but the extent of distress from E/T-ISA are controlled by the abundance of pyrrhotite (for sulfates) in the phyllite host, paste volume, and the degree of leaching and carbonation (for carbonate and silica source for thaumasite). Moist conditions in the outer leaf promoted pyrrhotite oxidation and sulfate release to cause E-ISA distress from expansive ettringite formation in the noncarbonated paste leading to initial cracking, whereas subsequent T-ISA at moderately carbonated paste at colder and relatively drier conditions mostly contributed to crumbling. Relatively drier conditions in the inner leaf promoted advanced carbonation but intermittent drier conditions between moist seasons in the outer left promoted cyclic formation of E-ISA during moist conditions to T-ISA during intermitted carbonation at drier and colder conditions. The end results of carbonation and T-ISA are a paste of little or no cementitious property eventually causing mass-scale crumbling of blocks. Effects of pyrrhotite oxidation are more towards initial cracking and crumbling of blocks, whereas that of carbonation and T-ISA are towards eventual decomposition of paste to cause large-scale crumbling of blocks. Not one single factor alone has had the lion's share for catastrophic failure of houses - as many as six different factors are discussed here, which have worked together to cause the progressive damage. Pyrrhotite was the undoubted 'cancer cell' in the blocks whose deleterious effect was initiated with moisture and spread rapidly through interactions of other five factors mentioned in the title and discussed here. It is time to take a holistic approach in Ireland instead of polarized views of wrongfully advertised mica-only to rightfully determined ISA-only theories.

*Acknowledgments*: Debbie MacCoy (US), Deirdre McLaughlin (Ireland), Paddy Diver (Ireland), Sharon Moss (Ireland), and Shubham Mahajan (CMC) are thanked for various contributions.

#### 5. **REFERENCES**

- 1. McCarthy D, Kane N, Lee F, Blaney D (2017) Report of the Expert Panel on Concrete Blocks, Department of Housing, Local Government and Heritage. https:// www.gov.ie/en/publication/0218freport-of-the-expert-panel-on-concrete-blocks/.
- 2. Irish Standard I.S. 465:2018 (2018) Assessment, testing and categorization of damaged buildings incorporating concrete blocks containing certain deleterious materials.
- 3. Eden M Vickery, Sandberg LLP. (2019) Investigating the causes of deterioration in concrete blocks in Southern Ireland. 17th EMABM, University of Toronto, Toronto, Canada.
- 4. Leemann A, Lothenbach B, Münch B, Campbell T, Dunlop P (2023) The "mica crisis" in Donegal, Ireland A case of internal sulfate attack? Cem. Concr. Res. 168, 107149.
- 5. Brough C, Staniforth B, Garner C, Garside R, Colville R, Strongman J, Fletcher J (2023) High risk concrete blocks from County Donegal: The geology of defective aggregate and the wider implication. Construction and Building Materials, V. 408, 133404.
- 6. Jana D (2023) Concrete Deterioration from the Oxidation of Pyrrhotite: A State-of-the-Art Review. In: Maher MLJ (ed) Pyrite and Pyrrhotite, Nova Science Publishers, Inc, pp. 137-221.
- 7. Jana D (2020), Pyrrhotite Epidemic in Eastern Connecticut: Diagnosis and Prevention. ACI Materials Journal V 117, No. 1.
- 8. Hawkins AB (2014) Implications of Pyrite Oxidation for Engineering Works. Springer International Publishing Switzerland.
- 9. Duchesne J, Rodrigues A, Fournier B (2021) Concrete damage due to oxidation of pyrrhotite-bearing aggregate: a review of recent advances and limitations. RILEM Tech. Lett. 6, pp. 82–92.

1<sup>st</sup> International Conference on Iron-Sulfide Reactions in Concrete Quebec City | Université Laval Campus | Canada | May 14<sup>th</sup> – May 17<sup>th</sup> 2024

## After CT-MA in US and Quebec, Canada

# **Ireland has become the Epicenter of Pyrrhotite Nightmare!**

Map Cracking - Pattern Cracking - Disintegration of Blocks - Outward Bowing of Outer Leaf -Wide Vertical/Horizontal Cracks - Window/Door Displacement - Blown Render



Crumbled block samples from Houses 1 to 3 and a sound foundation sample from House 3

www.cmc-concrete.com

An estimated 5,000 properties are affected in County Donegal





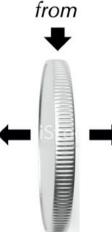
Some severely distressed homes in County Donegal, Ireland from where samples for this study were retrieved

# **Two Different Notions for Distress**



Excessive Mica in the Blocks (Expert Panel's Report 2017)

**Mica Action Group** 



Internal Sulfate Attacks (ISA) of Paste from Oxidation of Iron-Sulfide Minerals in Blocks (Leemann et al. 2022) No Pyrite-Pyrrhotite-

ISA Action Group?

- Loss of Compressive Strength
- High Water Demand from Excess Mica
- High Water Absorption
- Expansion from Wetting and/or Freezing of Water-Saturated Blocks
- Low cement, high void contents in mix

- Expansion from Oxidation of Iron Sulfide (pyrrhotite, framboidal pyrite)
- Paste Disintegration from ISA from Sulfates Released from Iron Sulfide Oxidation Causing Formation of Ettringite, Thaumasite, and Gypsum





Field Distress

**Culprits Presented** 

Interpretations Offered

1<sup>st</sup> International Conference on Iron-Sulfide Reactions in Concrete Quebec City | Université Laval Campus | Canada | May 14<sup>th</sup> – May 17<sup>th</sup> 2024



www.cmc-concrete.com



A Holistic Approach

On investigation of: Cracking and Crumbling of Concrete Blocks in County Donegal, Ireland

- Open Microstructure of Blocks The Porous Body!
   Easily Abradable Phyllite Aggregate The Weak Organ!
- 3. Oxidation of Pyrrhotite
- 4. Carbonation, Leaching and The Polluted Blood! Internal Sulfate Attacks (ISA) of Paste
- 5. Poor Quality Sand-Cement Render The Weak Skin!

## Dipayan Jana

Construction Materials Consultants, Inc. and Applied Petrographic Services, Inc., Greensburg, PA USA info@cmc-concrete.com

Entire Presentation along with results of research on Distressed Blocks of Ireland and Distressed Foundation of Connecticut can be downloaded from www.cmc-concrete.com/pyrrhotite-crumbling-foundations



The Cancer Cell!

#### **2024** International Conference on Iron Sulfide Reactions in Concrete

1<sup>st</sup> International Conference on Iron-Sulfide Reactions in Concrete Quebec City | Université Laval Campus | Canada | May 14<sup>th</sup> – May 17<sup>th</sup> 2024



## Acknowledgments

- 1. ICISR Organizer Kudos to the Laval Group for their Extensive Research!
- 2. My Industry Clients The Backbone Behind Building One of World's Largest Petrographic Labs in Pennsylvania
- 3. Debbie MacCoy The 'Concrete Queen' of Connecticut
- 4. This work is dedicated to the Homeowners - Deirdre McLaughlin (Ireland), Paddy Diver (Ireland), Sharon Moss (Ireland)
- 5. Petrographer and Lab tech at CMC

## Dedication



Michael L.J. Maher (1951-2022)

#### www.cmc-concrete.com



Entire Presentation along with results of research on Distressed Blocks of Ireland and Distressed Foundation of Connecticut can be downloaded from www.cmc-concrete.com/pyrrhotite-crumbling-foundations



1st International Conference on Iron-Sulfide Reactions in Concrete Quebec City | Université Laval Campus | Canada | May 14th - May 17th 2024

#### ACI MATERIALS JOURNAL MS No. M-2018-524.R1

Pyrrhotite Epidemic in Eastern Connecticut: Diagnosis and Prevention 2020 by Dipayan Jana

Editor's note: Due to length restrictions, blue hard copy version of his paper does not have its figures included in the paper. For a complete version of the paper that includes the fall other figures, please examine for and decondend the paper from trapecitores means are methodications interactional encoder.

urity crucking in showands of residential concrete found Sine in eastern Connecticut is found to be due to two stege expan-tions associated with oxidation of pyrrhotic in creathed guests course aggregate of concrete used from a local quarry that sits on a photoconal vois of significant perioditic correlations, persona-tion of the study of the study of the study of the second per-pendition and the study of the study of the study of the valence of perioditis establishes and the resultant burned indifici-tion in the second perioditis of the study of the study of the study tending protocol is suggested for ascenario of aggregates using tending postocol is suggested for ascenario of aggregates on the areas as provident periodic disclosed discoversion for future tends to converse perioditis characterized discoversion for future

#### INTRODUCTION

Pyrite (FeS<sub>3</sub>, 46.6% Fe and 53.5% S) and pyrthotite (Fe<sub>1</sub>, 5, 0 < x < 0.125, polytypes Fe<sub>2</sub>S<sub>3</sub>, Fe<sub>1</sub>S<sub>35</sub>, Fe<sub>1</sub>S<sub>12</sub>) are two mon iron sulfide minerals that occur as minor acces common ions salide minerals that occur as minor acces-sory minerals in many gincoux, oblematry, and metamor-phic recki.<sup>1</sup> Pyrite also occurs as a major phase in many salida or bodies, and pyritoritia as a scendary mineral in high-emperator hydrohymmi and replacement veisa, occurring the anthropyrin, and with-thoris malidlea-fred<sub>3</sub>. Inagentic (FeA), and calassient (SeA), and Calassient (FeA), angentic (FeA), and calassient (SeA), and Calassient (SeA), and the feed of glat and a characteristic section. Pyrite in a scolar-mousted interpis minard with a yelfor-ial-where orden interleaf light and a characteristic section. uster.<sup>1</sup> Pymbotite is a monoclinic (stable below 254°C) or tesagonal (stable above 254°C) anisotropic mineral with a braxgnud (table these 254%) anisotropic microil with a pile-reare nr sin does in a reflected given that has an attribution in the second given. The second results are realised with the second results of the second results are related to the second results are related to the second results. The relation is a second results are related to the second results. The second results are related to the relation of the second results are related to the relation of ines the total sulfur (as 50,) erce mahsis deter

thueencerce analysis determines the total militar (as 90), content contributed from all iron sulfide minerals. Concrete aggregates containing these iron sulfide specie are known to cause various deteriorations from: a) unsightly ACI Materials, Income

6.34

Case study

Dipayan Jana

Contents lists available at Science

Cracking of residential concrete foundations in eastern

ABSTRACT

Connecticut, USA from oxidation of pyrrhotite

unter Mantali Considers. In: and Applied Personality Services. In: Considers PA 1954

**Case Studies in Construction Materials** 

stains, poposts of near-surface unsound aggregates, and associated local fracturing from oxidation of iron salide minerals in the presence of moisture and oxygen to, and b) in extreme cases, severe cacking, microsencking, and loss of strength and structural atshifting of concerns when sulfates ( soffuric acid) released from the exidation rencess react with sulture acid) released trem the exidation process react with cornent hydratron products resulting in cognasis reactions frem internal sullate attacks? Concerns regarding possible im sulfale-related distruss in a concerne reviewire require proper identification of the type(s) of iron sulfder mineral responsible for the distruss, quantification of the unsund constituent(s), oxidation products, and microstructural and schemical evidences of estent and relative roles of exidation and internal sulfate attacks on concrete durability Table 1 summarizes literatures on occurrences of conc distress around the world from exidation of northetite dutters around the world from existing of probability, followed by a few world.hown cases from pertiveriated dutters. Pythonise-related courses deteined in the hown sponted in challs, howeys in 1997 from solidation an acquerging in the Torito-Review around the the the argengesis; in the Torito-Review around a in Quebec, Canada is 2009<sup>100</sup>. from pythonise in anothenise gathere course aggregates: in a down fram in 2014 from synthesis in solid argengesis; and in performant Connection from monthetic in permitted antice scores tensors? Allowed allowed anothenistic in the second antice scores tensors? Allowed allowed anothenistic in the second antice scores tensors? Allowed allowed and the second antice scores tensors? Allowed allowed and the scores of the second and the second allowed and the scores tensors? Allowed allowed and the scores tensors? Allowed allowed and the scores and the scores of the scores of the score scores of the score score scores and the score scores and the score scores and the score sc

TECHNICAL PAPER

n aggregate, and in northeastern Connection non-hotite in crushed gneiss coarse aggregate.<sup>2</sup> Almost all e distresses are contributed to the two-stage mecha-of (fin. 1): a) reference commission of mecha-of (fin. 1): a) reference commission of mecha-terior. these dista nim of (Fig. 1): a) primary expansion gates associated with oxidation of py gates associated with oxidation of pyrthetite or pyrite in the presence of oxygen, moisture, and high pH in concrete to form ferric oxy-hydroxides—for example, formhydrite [Fe(OH),]\_ goethite FeO(OH), and limorite—causing staining, popout, or cracking of the unseand aggregat and concrete, followed by b) secondary expansions fro and cor internal sulfate attacks by the sulfates released from pyrth tite oxidation to coment hydration and carbonation re ferming secondary entringite and thaumanite, respectively causing further exacting. Total sulfur (as 50.3) content e unseened aggregates varied form as low as 0.2% to as hig as 6%, and pyrthetite content showed even more variation-from less than 5% to higher than 75% by volume of all ion withdu. There are have ability in identifying outfor content rulfides. Due to such variability is cher and mineralogy instentially deliterious part proper detection of: a) the type of iron sulfide phase(s)

BC Ristrich Asseud V. 107. Nr. 1. Strong 2028. SS Nr. & S2314-DAEL, and 1114305-5514609, maximal Dassether 13, 2017 Nr. et al. 2018 A sight retrocking of control of the strong of the series and retrocking of the strong stro

2022

Interive enough as thousands of moderial inclusions as eases: Councefort is from the top responsion from which and protection to only plants more segments to assume the origination of the council of the council plants more segments processes that in allocations and the first expansions. There are sengle expansion processes to also leave that is allocated in the processes of the processes of the plants of the plants countiling. The sense of product the sense of the plants are plant of Obderia countiling the processes of the processes of the plants countiling. The sense of product the sense of the plants of the p

one concerns of similar distress of many honors with urgers need for standardized test acobs to control perhective endated distress. A five-stage testing protocol is proposed in stearially deleterious psychotic busing aggregates for miligating this distress in

Widespread cracking and crumbling of many residential concrete foundations have occurred in the eastern United States of Wedgered caching and crambing of many resolution incorrect foundations have accurate in the sames Tabuis of formation of Massachine due to sociation in a son addre mater, granter, and the same and the same of the same and same of the same and same comparison of the same of the same

aber 2021: Received in revised form 23 December 2023: Accessed 21 January 2022 headable soline 22 January 2022 2214-5095/90 2022 Published by Elsevier Inti. This is an open access article under the CC BY-NC-ND license

2023 Concrete Deterioration from the Oxidation of Pyrrhotite: A State-of-the-Art Review

#### Dipayan Jana<sup>\*</sup>

Construction Materials Consultants, Inc. and Applied Petrographic Services, Inc., Greensburg, PA, USA

#### Abstract

Chapter 5

After pyrite, pyritetite is a common accessory mineral found in many inneous sedimentary, and metamorphic rocks used as aggregates in concrete. In most exposures oxidation of pyrthotite has caused distress ranging from miner cracking to extensive cracking, crumbling, and disintegration of concrete structures. In almost all cases, distress is found to be due to two-stage expansions associated with oxidation of pyrrhotite forming goethite, limonite, ferrihydrite, and other oxidation products in aggregates, followed by internal sulfate attacks in paste by reactions between the sulfater released from pyrthoite oxidation with the alaminous phases in paste, Orginally discovered in a concrete tunnel in Oslo, Norway, subsequently many other parts of the world showed similar distress, e.g., in numerous foundations in the Treis-Rivières area in Québec, Canada, in concrete dams in Central and Catalan Pyrenees in Spain, in a dam in Switzerland, in many houses in Penge, South Africa, "mundic" problems of pyrite and pyrthotite oxidation in many buildings in Beauer efficient and Desone, Englished and pyrote many pyroteline extensions in time of summarge management and the second se the cases examined by the author, perhaps at the epicenter of such distress in the eastern US where an estimated 35,000 residential concrete foundations in Connecticut and 10,000 more in Massachusetts are in danger of potential collapse from slow and progressive cracking due to pyrrhotite oxidation in the crushed gneiss coarse aggregates. Time of occurrence varied from less than a year in Norway to 5 years in Canada to 20 years in the US. A detailed review is provided on various field and laboratory testing procedures, e.g., petrography, SEM-EDS, XRD, XRF, uXRF, chemical analyses for sulfur content. thermomagnetic susceptibility, oxygen consumption rate, mortar bar expansion, etc., for detection of pyrthetite and measuring exidation-related distress. Also discussed are mechanisms of distress, problems in detection of pyrrhotite in aggregates, factors influencing pyrrhotite oxidation, and various microstructural evidence of distress. Finally,

\* Corresponding Author's Email: info@cmc-concrete.com

In: Pyrite and Pyrrhotite Editor: Michael L. J. Mahe ISBN: 979.8.88697.179.7 O 2023 Nova Science Publishers. Inc.

#### Preventing Pyrrhotite 2024 **Damage in Concrete**

Proposal for a performance-based testing protocol

by Dipoyon Jone

Production of the second with the destruction of theorem of concrete structures in the United States, Canada, and located <sup>11</sup> Bern at a fewel of loss than 5% by mass of aggregate, this iton sulfide mineral can cause intensive crucking to crumbling of concrete from two forces of requestion—first from availation and fermation of item of requestion. sulfates and iron oxyhydroxides (gosthite, fortibydeite) in aggregates, and second, from internal sulfate attacks in paste from referent utilistics from released sulfaric acid resulting in expansive formation proxim and entringine to the decomposition of calcium silica gpour and entrippive to the decomposition of calcium silican hydrate (C-S-H) in the formation of faustrankie. The crystal structure, along with grain size, decetochemical reactions with gryite or other still des, staking environment of paste, availability of oxyges, qualities of host aggregates and concerne, and, above all, the direct bit by mointant, ear make grythedit [10] times more reactive than grithe.

#### From North America to Ireland

Fortunately, it is not difficult to locate the potential source of the problem in the United States. Sulfide-bearing igneous and metamorphic rocks, the potential hosts for pyrthotite, are located along a narrow belt of the Appalachian Mountain rangs, in different apendie locations in the waters United Stand, and they are not present in the courted United States. Timing of the occurrence of distants, however, has writed widel—dross 1 a loyous in Canadoo to 10 ke 15 years in the United States and Indand—indicating the complexity of forewarding fature of givens. Experiences may how how how the and helman have shown that damage has been another works and helman have shown that damage has been another works while in the United States, <sup>14</sup> anothersitic aggregate in cash-log-tatice acourted from their sendoward to the sense the innt aroundic locations in the weatern United place concerns fromdation walls and slabs-on-ground in Canada.<sup>14</sup> and abradable foliated rock phyllite and mica schist Second-Stage Screening from Total Sulfur

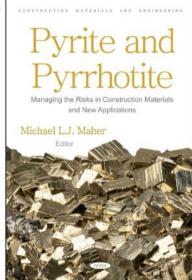
s, absorptive concrete blocks in Ireland's (shown in Fig. 1; Fig. 2 is included in the online appendix to this article). Lack of a Performance-Based Testing Protocol

such-damage and property loss are rather in ing serious in the past 10 to 15 years, and i

in scale, most national standards, codes, and specifications for construction aggregates did not pay attentions to it smill after the damage had occurred. Even then, case-based miglional (Connecticut? and Manaschusett?) legislative actions in the United States or national codes (European'' along with Irish and Norwegian adoptational are either insufficient or or anly restrictive to surrest premature relewithout a proper testing protocol to forecast potential damage

First-Stage Screening from Pyrcholite Distribution Map and Quarry To Usks a portionarchaol approach for a maningful screptoreact, the first exp is to locat the quarter that would portatility have insolitor monitories in the source of the pyrcholite and cuarties are potential sign of useondores in a most exponent, as it in the durafile (quarty rock in a most environment that determines the future performance of its unserverse in courses, as a mesh one of the Valual States. its aggregate in concrete. As mentioned, the United States Geological Survey has done just that with their map' of the distribution of "potentially" porthotite-bearing rocks (not necessarily having pyrhotite), with a lot of work still left to nail down detection of pyrhotite, along with more common notice and are marcaile, the two other "mactive" iron pyrite and rare marcaaler, the two other "matrixe" iron satifdes in the quartied aggregates. Firms a traditional geological map to book wath as a simple, handheld X-ray fluorescores spectrometers (XP), a partable laser-induced breakdown spectrometers (XP), a partable laser-induced breakdown spectroscopy (LBB) unit, et a high end core logger, we already have the necessary means in our anneal to detect iron satified-beating rocks in a quarry before subsequent induced essentiation in a fabbration. in-depth ena

Total sulfar content (S-) is the most convenient and commonly used parameter to evaluate combined sulfide selfate/themental/organic forms of selflar without secons separating them. Various techniques, from classical wet chemistry to XRF or more traditional infrared combustic



All these published articles along with this entire presentation can be downloaded from www.cmc-

concrete.com/ pyrrhotite-crumblingfoundations



#### Pyrrhotite Research at CMC was not funded by any external groups

www.cmc-concrete.com



www.petrography.net

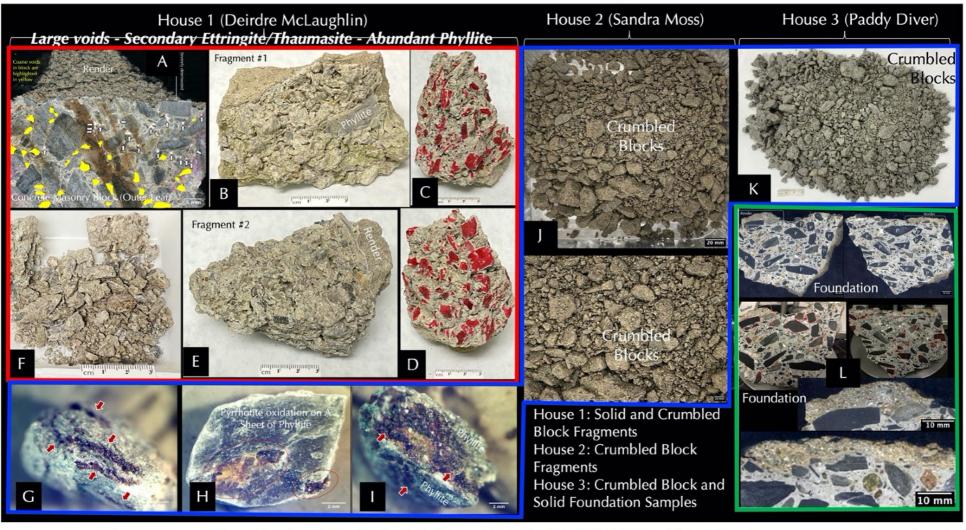
 1st International Conference on Iron

 Sulfide Reactions in Concrete

 1st International Conference on Iron

 1st International Conference on Iron

## From Solid Fragments to Completely Disintegrated Samples of Blocks and A Sound Cast-in-Place Foundation Sample Received



www.cmc-concrete.com



Some Results of Blocks: S<sub>T</sub> 0.5-1% >> 0.1% limit of EN 12620 with Pyrrhotite; 80% Phyllite, 15-20% Mica Schist; up to 50% abraded phyllite in mortar fraction; 0.75-1.5 vol.% Pyrrhotite in Phyllite; < 10 vol.% Mortar Fraction; 5 vol.% Paste



1<sup>st</sup> International Conference on Iron-Sulfide Reactions in Concrete Quebec City | Université Laval Campus | Canada | May 14<sup>th</sup> – May 17<sup>th</sup> 2024

## **Extensive State-of-the-Art Laboratory Facilities For Iron Sulfide Research**

**Optical Microscopy Lab** 

**Petrographic Sample Preparation Lab** 



Bruker D2 Phase

**SEM-EDS Lab** 



www.cmc-concrete.com



XRD Lab

Siemens D5000





Applied Petrography.net

# For Regular Aggregate Evaluation for Iron Sulfide

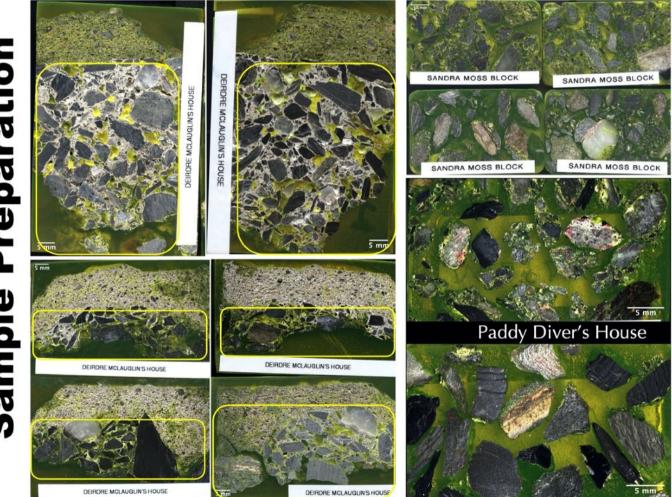


www.cmc-concrete.com





# Fluorescent Epoxy-Impregnated Polished Solid Sections of BlocksRL Stereo-MicroscopyOre MicroscopySEM-EDS



Preparation Sample

**ICCISER**<sup>2024</sup> International Conference on Iron Sulfide Reactions in Concrete

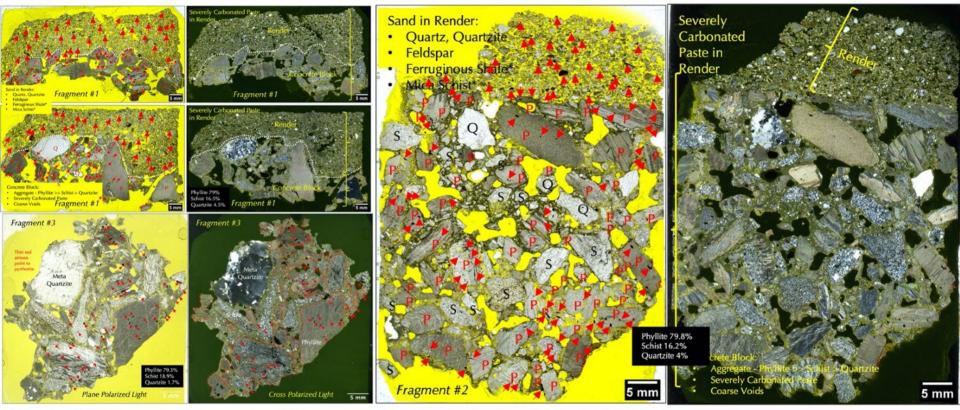
www.cmc-concrete.com



Fluorescent epoxy encapsulated polished sections for examination in reflected-light stereozoom microscope, epifluorescent stereo/petrographic microscope, and SEM-EDS



### Fluorescent Dye-Mixed Epoxy-Impregnated Three Thin Sections of Blocks from House 1 PPL Scans - Abundant Coarse Voids + Abundant Finely Disseminated Pyrrhotite XPL Scans - Phyllite > Mica Schist + Widespread Carbonation



- 1. Phyllite is the most abundant aggregate, which is a metamorphosed claystone/mudstone/shale, which is followed by schist (mica-chlorite-schist, mica-schist), and metaquartzite.
- 2. Pyrrhotite, mostly occurring as disseminated grains are mostly concentrated in phyllite (all thin red arrows point to pyrrhotite).
- 3. Fine grain size of muscovite-chlorite-quartz in phyllite, foliation planes from parallel arrangement of grains to form planes of weakness (cleavage) and further deformation of cleavage to form 2<sup>nd</sup> series of weak planes (crenulation cleavage) make phyllite susceptible to flaking, water absorption and expansion during wetting or freezing to create microcracking (shown later in fluorescent images).

www.cmc-concrete.com

**ICCISER**<sup>2024</sup> International Conference on Iron Sulfide Reactions in Concrete



Fluorescent dye-mixed epoxy-impregnated thin sections of defective blocks scanned on transparent flatbed scanner with one or two perpendicular polarizing filters for PPL & XPL Views

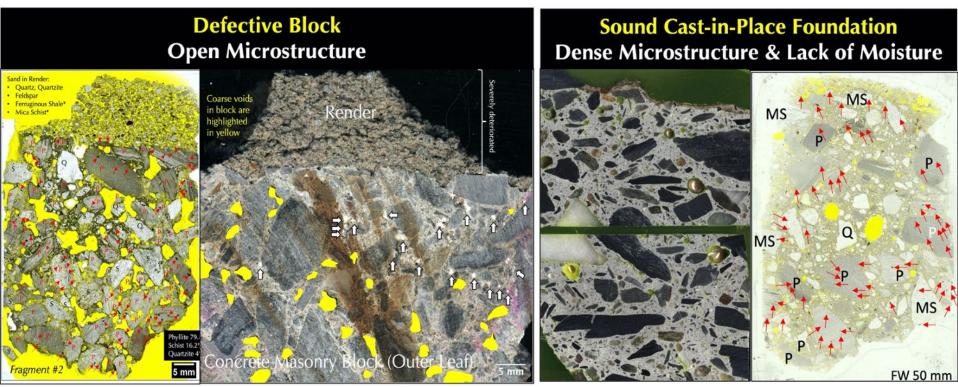
www.petrography.net



1<sup>st</sup> International Conference on Iron-Sulfide Reactions in Concrete Quebec City | Université Laval Campus | Canada | May 14<sup>th</sup> – May 17<sup>th</sup> 2024

## 1<sup>st</sup> Culprit! - Open Microstructure of Blocks for Easy Moisture Entry

Defective Blocks (High Void Content, High w/c of Paste) vs. Sound Cast-in-Place Foundation (Low Void Content, Dense low w/c Paste)



Needed Full Block Epoxy-Encapsulation to Improve Integrity

Sample was Dense Enough for just Surface Impregnation

www.cmc-concrete.com



### Defective Blocks & Sound Foundation Contained - Pyrrhotite (and Pyrite) as well as Phyllite-Mica Schist

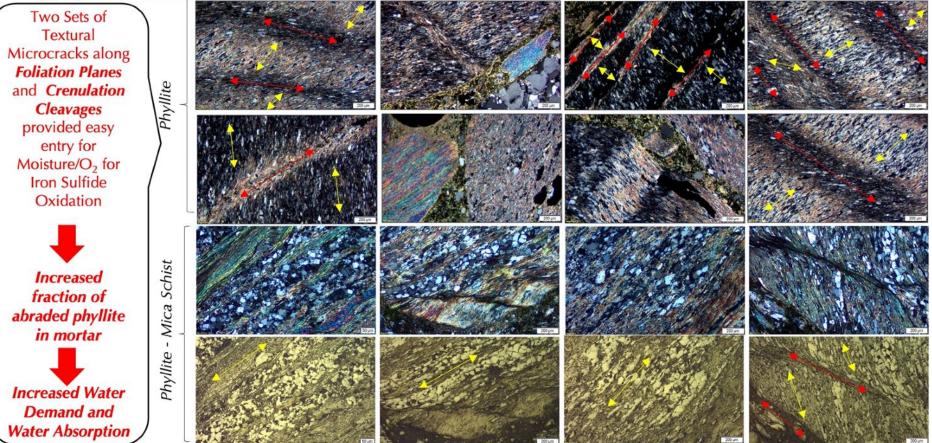


Fluorescent dye-mixed epoxy-impregnated whole-slide scans of thin sections of defective blocks and cast-in-place foundation

1<sup>st</sup> International Conference on Iron-Sulfide Reactions in Concrete Quebec City | Université Laval Campus | Canada | May 14<sup>th</sup> – May 17<sup>th</sup> 2024

# 2<sup>nd</sup> Culprit - Abundant Easily Abradable Phyllite - The Weak Organ!

Aggregates from the Dalradian Supergroup from 700 Ma old Mountain Building Event (Grenvillian Orogeny)



- Phyllite is the most abundant aggregate, around 80% by volume, which are noticeably finer-grained than mica schist or quartzite and shows foliation planes, and folded/crenulation cleavages from two-stage deformation of shale/mudstone by grinding actions of mother Earth during Grenvillian Orogeny.
- Fine grain size of muscovite, chlorite, and quartz grains in phyllite and the internal planes of weakness (cleavages and folded/crenulation cleavages) make phyllite highly susceptible to flaking, expansion from moisture absorption, which can aggravate during exposures to subfreezing temperatures.
- The texture of phyllite makes it more unsuitable for use as concrete aggregate than the mineralogy.

www.cmc-concrete.com



More than 80% of houses at **high-risk** contained **phyllite** (Brough et al. 2023)

www.petrography.net



Transmitted (XPL) and Reflected-light micrographs of polished thin sections of defective blocks

1<sup>st</sup> International Conference on Iron-Sulfide Reactions in Concrete Quebec City | Université Laval Campus | Canada | May 14<sup>th</sup> – May 17<sup>th</sup> 2024

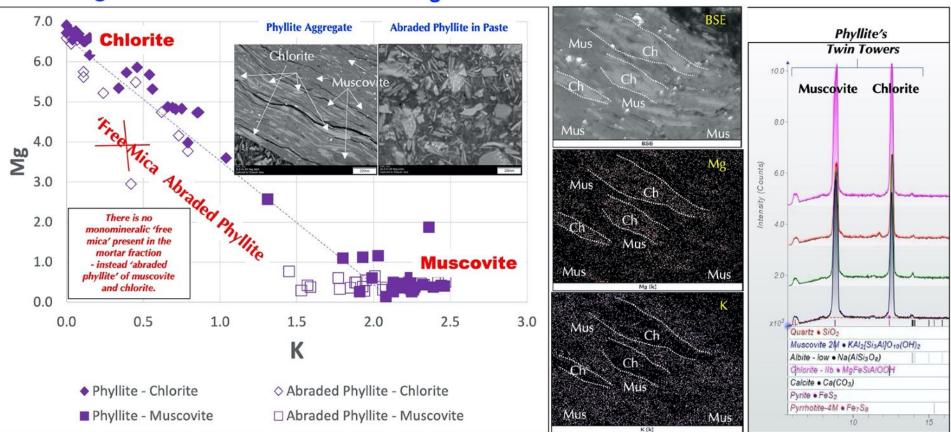
## It is NOT Free Mica but Juxtaposed Layers of Intimately Mixed Mica and Chlorite

Mg-K SEM-EDS Plot

## **BSE Image**

### Mg-K Elemental Map

XRD



# **Phyllite (Pyrrhotite) Action Group** would have been the right group to form instead of *Mica Action Group*!

www.cmc-concrete.com

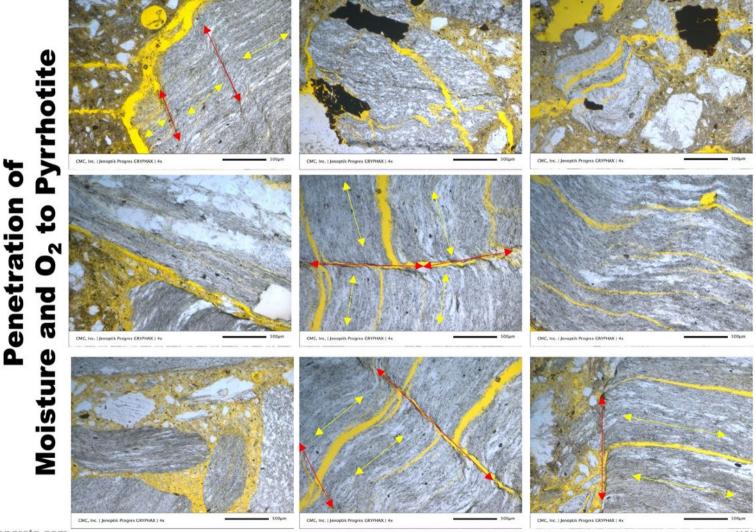


Backscatter electron image, Elemental Maps, and EDS Analyses of Phyllite in Aggregate and Abraded Phyllite in Mortar Fraction of Defective Blocks



1<sup>st</sup> International Conference on Iron-Sulfide Reactions in Concrete Quebec City | Université Laval Campus | Canada | May 14<sup>th</sup> – May 17<sup>th</sup> 2024

# Textural Microcracks in Phyllite - Along Foliation Planes & Crenulation Cleavage Planes In and around Phyllite Grains Highlighted by Fluorescent Epoxy





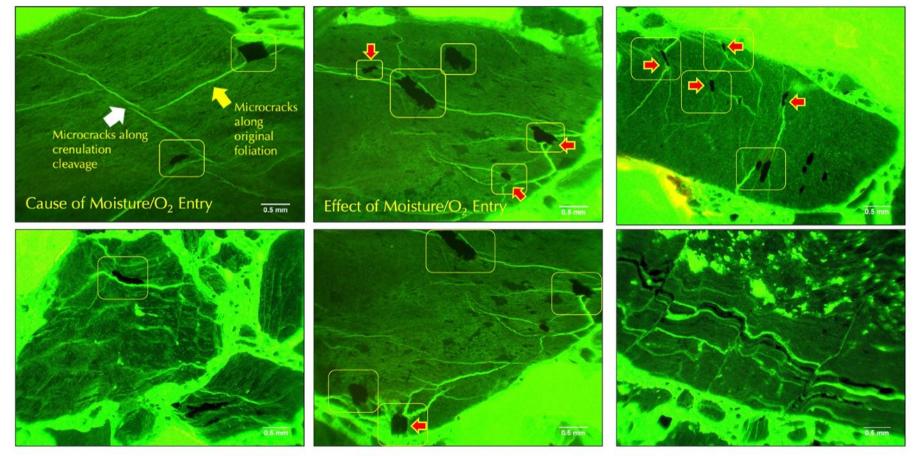
**Excellent Pathways** 

Transmitted light (PPL) micrographs of polished thin sections of defective blocks



1<sup>st</sup> International Conference on Iron-Sulfide Reactions in Concrete Quebec City | Université Laval Campus | Canada | May 14<sup>th</sup> – May 17<sup>th</sup> 2024

## Two Types of Microcracks in Phyllite Inherent Textural Microcracks Following Foliation Planes & Crenulation Cleavage Planes & Radial Microcracks from Oxidized Pyrrhotite Grains



## Both Types of Microcracks are responsible for Abundant Abraded Phyllite in Mortar Fraction

www.cmc-concrete.com

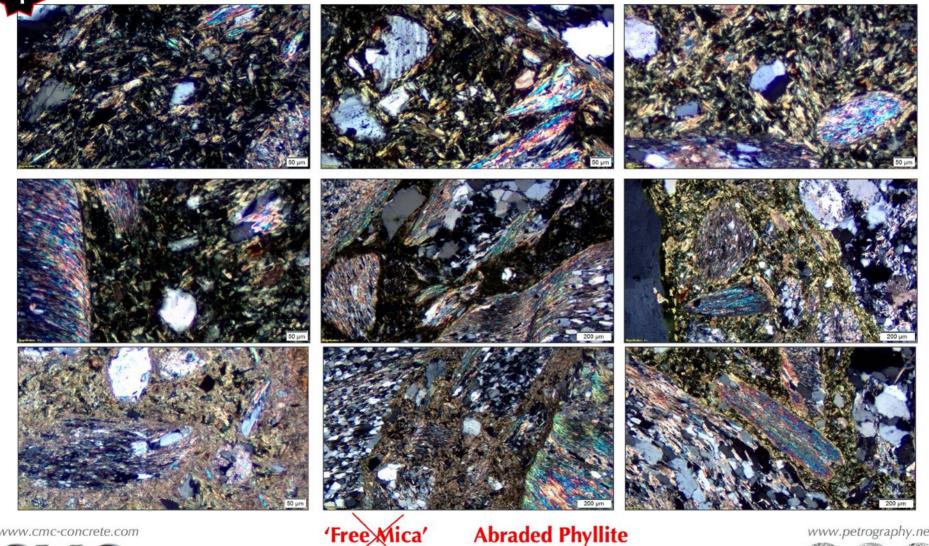


Micrographs of fluorescent dye-mixed epoxy-impregnated thin sections of defective blocks

Applied Petrographic Servicer. Inc.

1st International Conference on Iron-Sulfide Reactions in Concrete Quebec City | Université Laval Campus | Canada | May 14th - May 17th 2024

## Abundant Abraded Phyllite in Mortar Fraction (up to 50% by volume of mortar) Phyllite Action Group would have been the right group to form than Mica Action Group!



.cmc-concrete.com



Transmitted-light (XPL) micrographs of polished thin sections of defective blocks



1<sup>st</sup> International Conference on Iron-Sulfide Reactions in Concrete Quebec City | Université Laval Campus | Canada | May 14<sup>th</sup> – May 17<sup>th</sup> 2024

## Abundant Abraded Phyllite in Mortar Fraction (up to 50% by volume of mortar) Phyllite Action Group would have been the right group to form than Mica Action Group!

All and a start		1	Probes	0	Na	Mg	Al	Si	S	к	Ca	Ti	Fe	Phase
$\gamma$	$\overline{2}$	a state	1	62.81	0.64	0.49	12.35	20.83	0.00	2.23	0.56	0.06	0.03	Muscovite
	$\frac{1}{9}$ $\left( \begin{array}{c} 1 \\ 1 \end{array} \right)$	Probe 23	2	62.69	0.70	0.47	12.59	20.51	0.00	2.31	0.56	0.07	0.11	Muscovite
			3	62.72	0.61	0.49	12.62	20.61	0.00	2.42	0.46	0.04	0.04	Muscovite
	Persta 3	15	4	62.51	6.03	0.00	6.68	24.71	0.00	0.05	0.02	0.00	0.00	Muscovite
Trote 29	2 Prebe 22	$\begin{pmatrix} 2 \\ -2 \end{pmatrix}$	5	62.50	6.00	0.00	6.86	24.58	0.00	0.04	0.02	0.00	0.00	Muscovite
		$\sqrt{3}$	6	62.73	0.69	0.31	13.07	20.30	0.00	2.26	0.42	0.11	0.10	Muscovite
		0	7	66.57	0.19	0.00	0.00	33.23	0.00	0.00	0.00	0.00	0.00	Quartz
3	$\begin{pmatrix} 8 \end{pmatrix}$ · · · · · (2)	$\begin{pmatrix} 2 \end{pmatrix}$	8	61.71	0.20	6.59	11.70	17.63	0.00	0.00	0.59	0.03	1.54	Chlorite
		-51/	9	61.73	0.09	6.45	12.73	17.15	0.00	0.03	0.01	0.00	1.81	Chlorite
Anna Ali		Jan.	10	63.08	0.34	2.95	6.70	23.19	0.00	0.42	3.02	0.00	0.30	Paste
Probe Drobe 5		Probe 23	11	61.60	0.03	6.55	12.87	16.82	0.00	0.07	0.04	0.00	2.00	Chlorite
Probe 6		Star 1000	12	61.83	0.24	5.49	12.43	17.73	0.00	0.45	0.12	0.05	1.65	Chlorite
h.	$(\mathbf{N}_{1}, 7_{2})$ $(8)$ $(0)$	2	13	62.86	0.66	0.55	11.97	21.02	0.00	1.95	0.88	0.02	0.08	Muscovite
-bashe in		2 1	14	62.53	5.68	0.00	7.18	24.34	0.00	0.06	0.16	0.00	0.04	Muscovite
	Traces	U TRates	15	61.99	0.19	5.75	11.75	18.19	0.00	0.11	0.45	0.05	1.52	Chlorite
$\left( \begin{array}{c} 1 \end{array} \right) $		12.13	16	62.90	0.70	0.49	11.22	21.39	0.00	1.89	1.21	0.09	0.10	Muscovite
		12.3	17	63.34	0.53	1.74	8.18	23.16	0.00	0.66	2.04	0.02	0.34	Paste
	$\left( 6 \right)$	Tomba 40	18	61.55	0.28	7.31	6.59	19.98	0.00	0.33	3.19	0.12	0.63	Chlorite
$\begin{pmatrix} 1 \\ \end{pmatrix} \rightarrow \begin{pmatrix} 1 \\ \end{pmatrix}$		A. WA	19	63.46	0.66	0.36	9.90	23.17	0.00	1.85	0.43	0.06	0.12	Muscovite
$\begin{pmatrix} 4 \\ \end{pmatrix}$		7.9.00	20	66.56	0.19	0.00	0.00	33.19	0.00	0.00	0.02	0.01	0.03	Quartz
Probe 14		1200	21	62.47	6.08	0.00	6.86	24.53	0.00	0.02	0.01	0.03	0.00	Muscovite
Pabe 15		Trabe 24	22	62.77	0.77	0.37	12.29	20.77	0.00	2.08	0.81	0.05	0.08	Muscovite
Probe 17		1	23	62.85	0.84	0.28	12.41	20.77	0.00	1.94	0.79	0.11	0.02	Muscovite
		27	24	62.27	0.58	3.77	11.71	19.29	0.00	0.79	0.64	0.08	0.88	Chlorite
$\begin{pmatrix} 1 \\ \end{pmatrix}$ $\begin{pmatrix} 1 \\ \end{pmatrix}$ $\begin{pmatrix} 1 \\ \end{pmatrix}$	1 - (0) - (2) (8)		25	66.44	0.21	0.00	0.73	32.61	0.00	0.00	0.00	0.00	0.00	Quartz
	6	4	26	62.98	0.66	0.39	11.56	21.36	0.00	1.93	0.89	0.10	0.14	Muscovite
			27	63.02	1.56	0.29	11.05	21.58	0.00	1.53	0.36	0.48	0.13	Muscovite
CMC, Inc.			28	62.93	0.66	0.65	11.56	21.28	0.00	1.81	0.94	0.04	0.12	Muscovite
20.0 KV EM Mag 490X		200nm	29	62.56	5.61	0.00	6.89	24.56	0.00	0.19	0.15	0.01	0.02	Muscovite
Captured by Dipayan Jana	Atomic Weight Percent of:	2001111	30	62.25	0.20	4.16	11.82	19.04	0.00	0.73	0.56	0.01	1.24	Chlorite
Prightor flakos ara Chla	rito and darker flakes are Muscovite													

Brighter flakes are Chlorite and darker flakes are Muscovite

www.cmc-concrete.com



Backscatter Electron Image (Left) and X-ray Microanalysis (Right) of Phyllite in Mortar Fraction in Block from House 1

**Abraded Phyllite** 

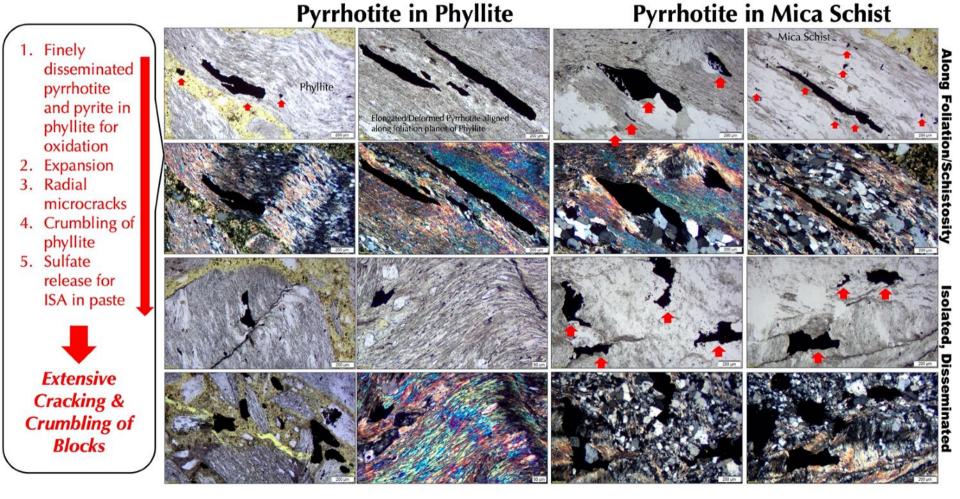
'Free Mica'





1<sup>st</sup> International Conference on Iron-Sulfide Reactions in Concrete Quebec City | Université Laval Campus | Canada | May 14<sup>th</sup> – May 17<sup>th</sup> 2024

# 3<sup>rd</sup> Culprit - Pyrrhotite & Other Iron Sulfides - The Cancel Cell!



## Pyrrhotite Action Group would have been the right group to form than Mica Action Group!

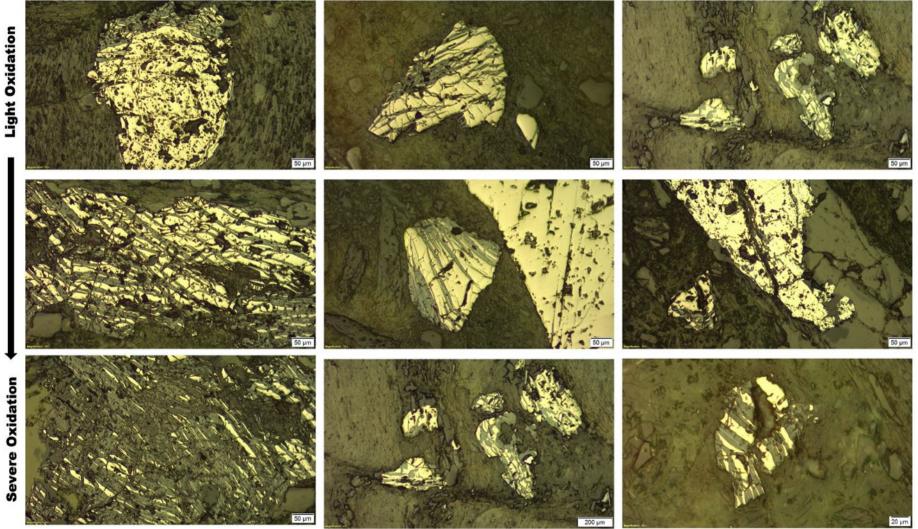
www.cmc-concrete.com



Disseminated & Elongated/Deformed Pyrrhotite Grains in Phyllite and Mica Schist Aggregates Aligned along the Plane of Foliation in Phyllite or Schistosity in Schist Applied Petrographic Service/, Inf. www.petrographic.aet

1st International Conference on Iron-Sulfide Reactions in Concrete Quebec City | Université Laval Campus | Canada | May 14th - May 17th 2024

## **Ore Microscopy** - Best Method to Detect Oxidized Pyrrhotite in Defective Blocks Characteristic 'Striated' Appearance of Dark Fe-O Bands in Bright Fe-S Matrix of Oxidized Pyrrhotite



-concrete.com

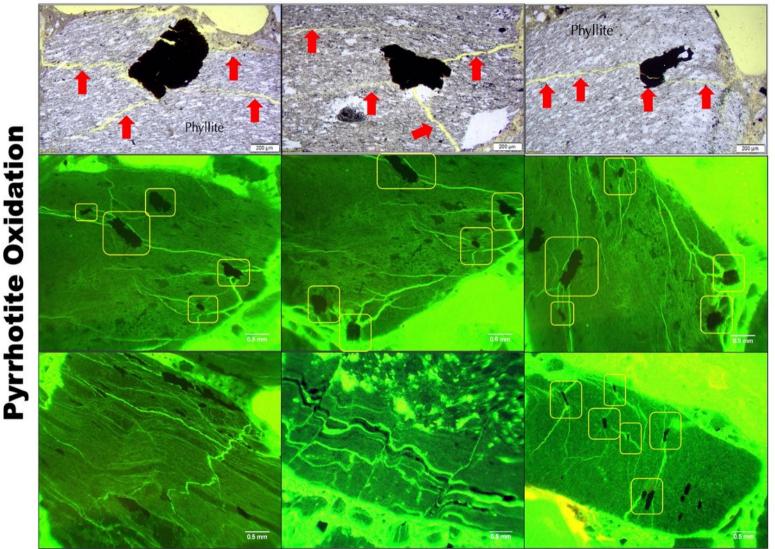


Reflected-light micrographs of polished thin sections of defective blocks



1st International Conference on Iron-Sulfide Reactions in Concrete Quebec City | Université Laval Campus | Canada | May 14th - May 17th 2024

## Fluorescent Microscopy - Best Method to Detect Radial Microcracks



www.cmc-concrete.com



Result

rom

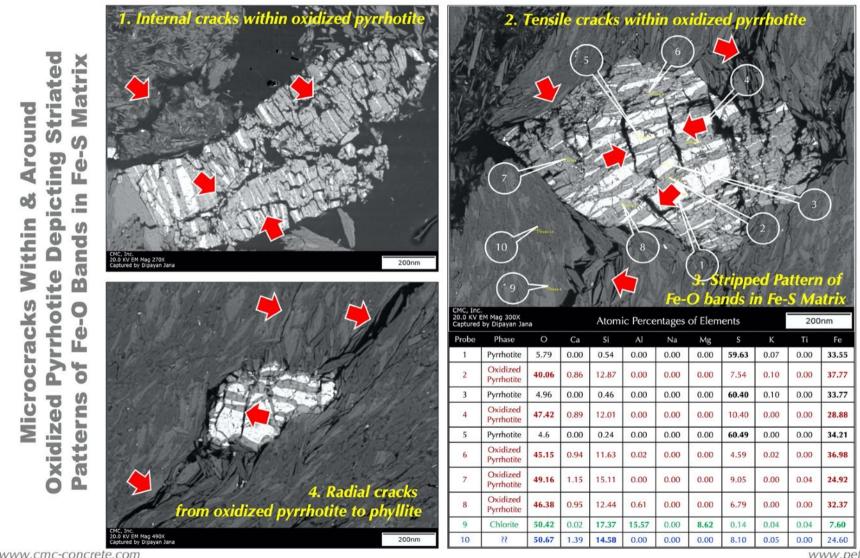
Radial Microcracks sult of Expansion f

Transmitted (PPL) and UV-light micrographs of polished thin sections of defective blocks

www.petrography.net pplied Petrographic Servicer. InC. www.petrography.net

1st International Conference on Iron-Sulfide Reactions in Concrete Quebec City | Université Laval Campus | Canada | May 14th - May 17th 2024

## **BSE Imaging** - Best Method for Detecting Expansion from Pyrrhotite Oxidation



EM-EDS 0-0 and Π nal P to < S PS 0 3 2 th

www.petrography.net

lied Petrographic Services, IAC.

www.petrogrophy.net



C

ð

Striat

cting

1 1000 00

õ

ţ

Pyrrhoti

dized

OXIC

Around

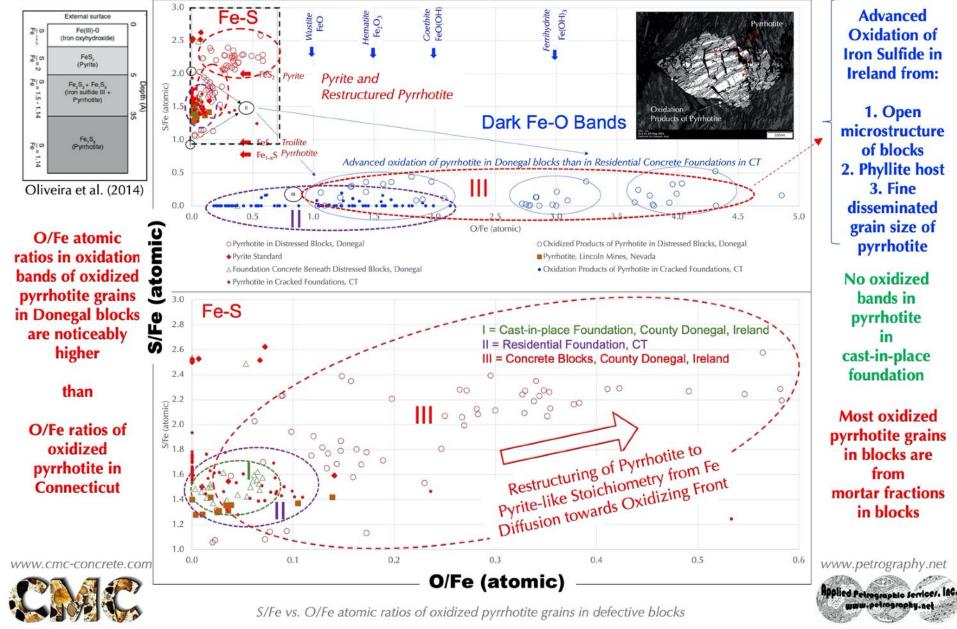
Within

Microcracks

Backscatter electron images and SEM-EDS analyses of oxidized pyrrhotite grains in host phyllite

1<sup>st</sup> International Conference on Iron-Sulfide Reactions in Concrete Quebec City | Université Laval Campus | Canada | May 14<sup>th</sup> – May 17<sup>th</sup> 2024

## S/Fe vs. O/Fe Atomic Plots - Oxidized Pyrrhotite from Ireland and Connecticut



1<sup>st</sup> International Conference on Iron-Sulfide Reactions in Concrete Quebec City | Université Laval Campus | Canada | May 14<sup>th</sup> – May 17<sup>th</sup> 2024

## In CT - Coarse Pyrrhotite Grains Allowed Direct In-Situ XRD by Micro-Drilling



Hexagonal

Monoclinic

Type 5C Fe<sub>9</sub>S<sub>10</sub>

Type 4M, 4C Fe<sub>7</sub>S<sub>8</sub>

www.cmc-concrete.com



Pyrrhotite dust collected by direct in situ micro drilling a grain and spread across a zero background silicon wafer sample holder over a thin film of petroleum jelly for XRD analysis at a slow scan rate

Debbie's Daughter's Home

Pyrrhotite • Fe<sub>9</sub>S<sub>10</sub> Pyrrhotite-4M • Fe<sub>7</sub>S<sub>8</sub> Quartz • SiO<sub>2</sub>

Four main

peaks of

pyrrhotite \_\_\_\_\_ 29.98°, 33.88° 43.82°, 53.17°

inalyzed Drilled directly with 9 zero-background silicon 9 micro-drill and wafer dust

1 mm

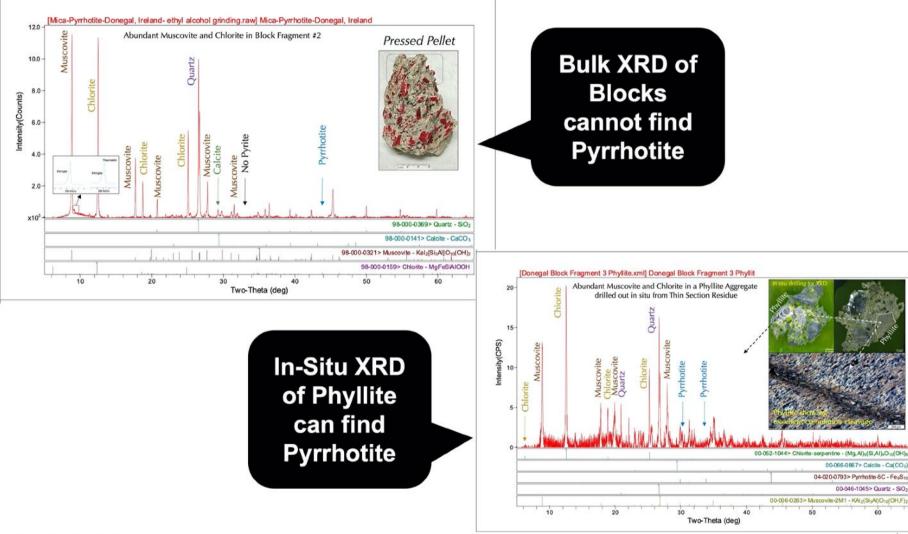
Quartz: Q

Pyrrhotite (4M, 5C): P



1<sup>st</sup> International Conference on Iron-Sulfide Reactions in Concrete Quebec City | Université Laval Campus | Canada | May 14<sup>th</sup> – May 17<sup>th</sup> 2024

## But In Ireland - Due to Finely Disseminated Forms, Direct XRD of Pyrrhotite is Difficult



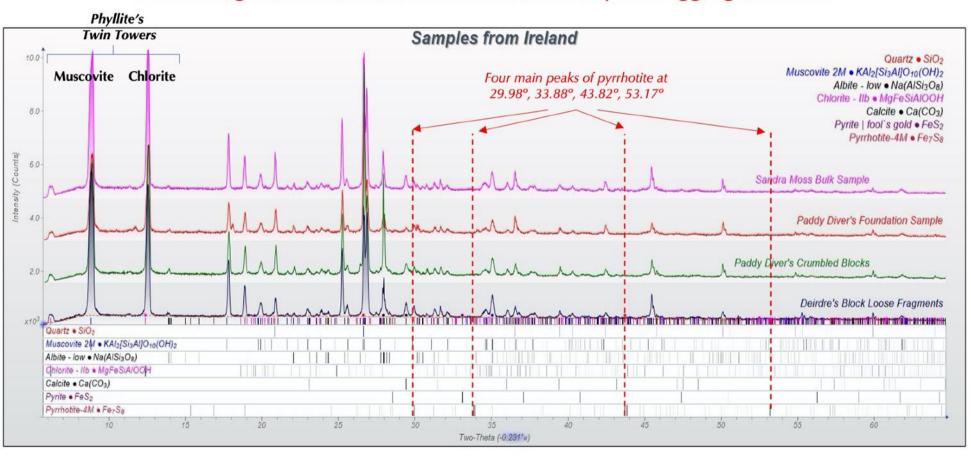
www.cmc-concrete.com



Powder finer than 44-micron from bulk sample was side-loaded in a sample holder (not pressed) for XRD whereas an aggregate grain was analyzed directly with some dust collected by drilling

Applied Petrography.net

## XRD Patterns of Distressed Blocks from Three Homes and One Sound Foundation Showed Mineralogical Similarities from Abundant Phyllite Aggregate in All



www.cmc-concrete.com



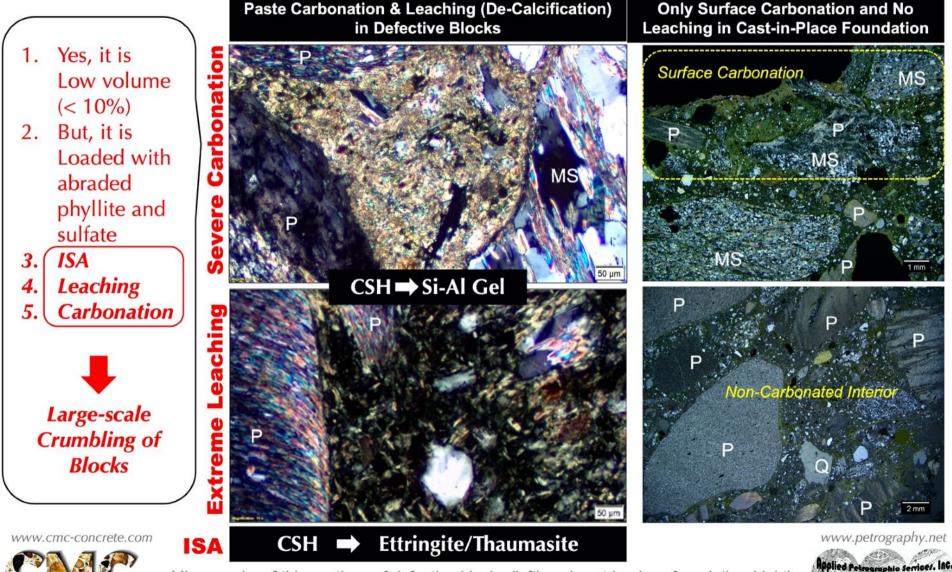
www.petrography.net



1<sup>st</sup> International Conference on Iron-Sulfide Reactions in Concrete Quebec City | Université Laval Campus | Canada | May 14<sup>th</sup> – May 17<sup>th</sup> 2024

www.petrogrophy.net

# 4<sup>th</sup> Culprit - Paste - The Sulfate/Carbonate Contaminated Blood!

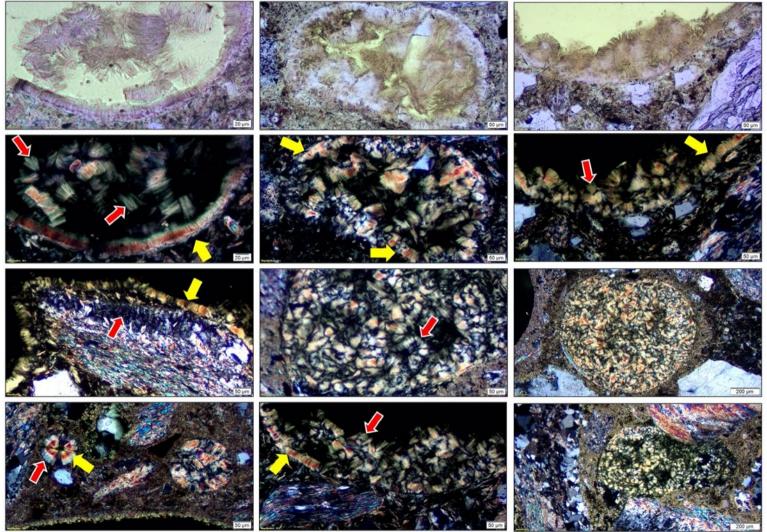




Micrographs of thin sections of defective blocks (left) and cast-in-place foundation (right)

1<sup>st</sup> International Conference on Iron-Sulfide Reactions in Concrete Quebec City | Université Laval Campus | Canada | May 14<sup>th</sup> – May 17<sup>th</sup> 2024

Telltale Signs of ISA - Profuse Secondary Ettringite and Thaumasite in Voids and Pore Spaces Precipitated Products of Internal Sulfate Attacks (E-ISA & T-ISA)



www.cmc-concrete.com

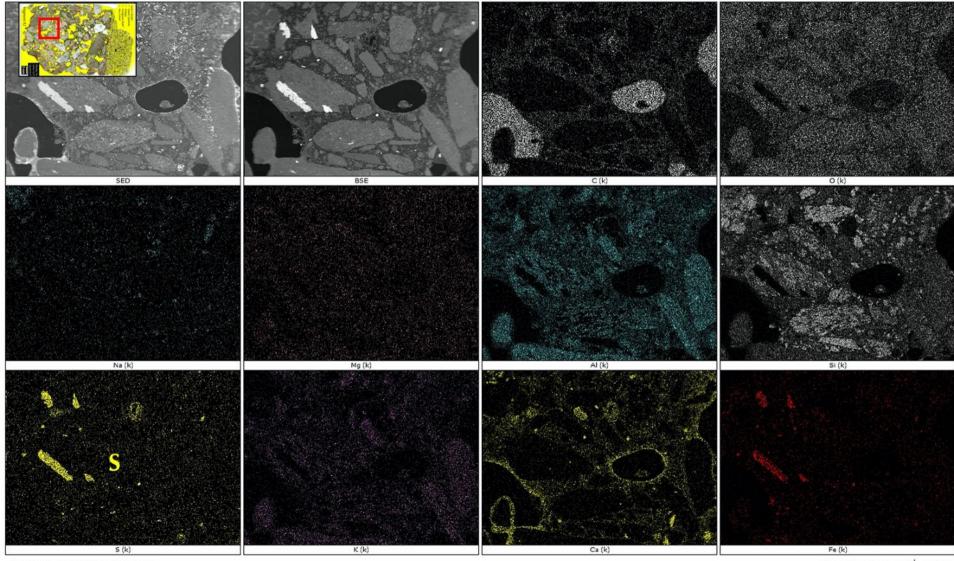


Plane and Corresponding Cross Polarized Light Images from a Petrographic Microscope

www.petrography.net

# 1st International Conference on Iron Sulfide Reactions in Concrete 1st International Conference on Iron 1st International Conference on Iron

## In Search of ISA - Scavenged Entire Thin section for S-rich areas in Elemental Mapping



www.cmc-concrete.com



Scavenging a thin section through rasters of elemental maps for S, Ca, Si, Al, Mag, Na, C, O



1<sup>st</sup> International Conference on Iron-Sulfide Reactions in Concrete Quebec City | Université Laval Campus | Canada | May 14<sup>th</sup> – May 17<sup>th</sup> 2024

## SEM-EDS Analysis of Leached Paste of Si-Al Gel

(Notice Abundant Phyllite Flakes in Mortar)

	Probes	о	Na	Mg	Al	Si	S	к	Ca	Ti	Fe	Phase
Tirata 2	1	53.05	1.78	2.11	7.31	30.49	0.00	0.16	4.06	0.29	0.74	Paste
Protes (1)	2	50.62	1.95	1.03	7.55	32.79	0.00	0.17	4.70	0.30	0.91	Paste
	3	50.19	0.51	1.13	8.08	33.24	0.00	0.44	5.67	0.00	0.74	Paste
	4	54.72	0.88	0.61	7.12	22.53	0.00	0.77	12.74	0.15	0.48	Paste
	5	55.30	0.44	1.05	8.38	26.21	0.00	0.70	6.74	0.08	1.10	Paste
	6	60.46	0.52	1.07	7.68	24.95	0.00	0.47	4.08	0.15	0.61	Paste
	7	54.78	0.61	1.58	7.11	24.24	0.00	0.27	10.17	0.18	1.05	Paste
	8	55.01	0.62	0.79	8.35	27.89	0.00	0.70	6.03	0.02	0.60	Paste
TPmbs 10	9	49.87	0.74	0.55	12.58	31.21	0.00	2.01	2.30	0.11	0.63	Paste
	10	49.89	0.93	1.04	18.70	24.88	0.00	3.58	0.21	0.07	0.69	Paste
	11	50.54	0.33	4.13	10.35	28.38	0.00	1.04	3.40	0.09	1.73	Paste
CMC, Inc. 20.0 KV EM Mag 660X Captured by Dipayan Jana Atomic Weight Percent of: 200nm	12	56.51	0.49	0.43	6.57	26.65	0.00	0.18	6.32	2.44	0.42	Paste

Backscatter Electron Image

SEM-EDS Analyses at the tips of Callouts

Si-Al Gel (No S)

Applied Petrographic Services. In uww.petrographic Services. In

www.cmc-concrete.com



Backscatter electron image and SEM-EDS analyses of paste in the mortar fraction of defective blocks

1<sup>st</sup> International Conference on Iron-Sulfide Reactions in Concrete Quebec City | Université Laval Campus | Canada | May 14<sup>th</sup> – May 17<sup>th</sup> 2024

## SEM-EDS Analysis of ISA-Affected S-Rich Regions in Paste

CMC, Inc.	The second secon			Atom	ic Perce	3	of Elem	-le Fents	4	-5-							r 3		2:			トトリート	
Probe	Phase	0	Ca	Si	Al	Na	Mg	s	К	Ti	Fe		Support of							and the second	-	-	
1	Paste	46.91	20.97		5.49	0.00	1.47	11.08	0.14	0.13	1.04	CMC, Inc. 20.0 KV EM	1 Mag 1490X y Dipayan Jai	-		Atom	ic Perce	entages	of Elem	ents		200	nm
2	Paste	41.56	8.55	31.74	8.16	0.00	5.60	1.50	0.66	0.10	1.82				6								
3	Paste	38.01	2.22	40.90	11.16	6.32	0.02	0.30	0.68	0.06	0.25	Probe	Phase	0	Ca	Si	Al	Na	Mg	S	К	Ti	Fe
4	Paste	47.31	10.15	23.90	7.08	0.43	7.63	1.45	0.14	0.15	1.46	1	Paste	65.50	15.65	8.52	0.98	0.00	0.00	8.85	0.03	0.00	0.33
5	Paste	37.36	7.48	36.91	11.30	0.60	2.37	0.76	2.14	0.17	0.84	2	Paste	62.32	16.29	11.56	0.76	0.00	0.00	8.56	0.00	0.00	0.28
6	Paste	30.76	8.16	38.87	13.40	0.76	1.64	1.45	3.52	0.16	0.96	3	Paste	52.22	17.04	13.99	5.34	0.00	0.22	9.93	0.20	0.00	0.74
7	Paste	19.64	5.45	43.00	20.75	0.10	0.96	1.41	7.19	0.15	0.90	4	Paste	65.71	15.96	9.38	0.25	0.00	0.00	8.29	0.02	0.00	0.10
			1	1				1							1	1				1			

High calcium, silica, and sulfur in paste are from carbonation followed by thaumasite alteration



www.cmc-concrete.com

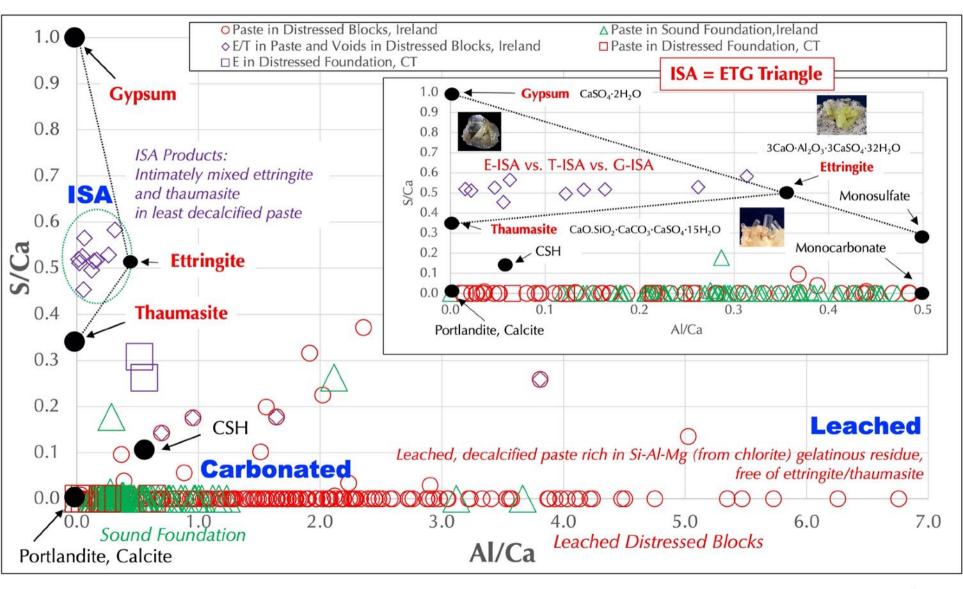
www.petrography.net

1<sup>st</sup> International Conference on Iron-Sulfide Reactions in Concrete Quebec City | Université Laval Campus | Canada | May 14<sup>th</sup> – May 17<sup>th</sup> 2024

www.petrography.net

www.petrography.net

ed Petrographic Service/. IAG



www.cmc-concrete.com

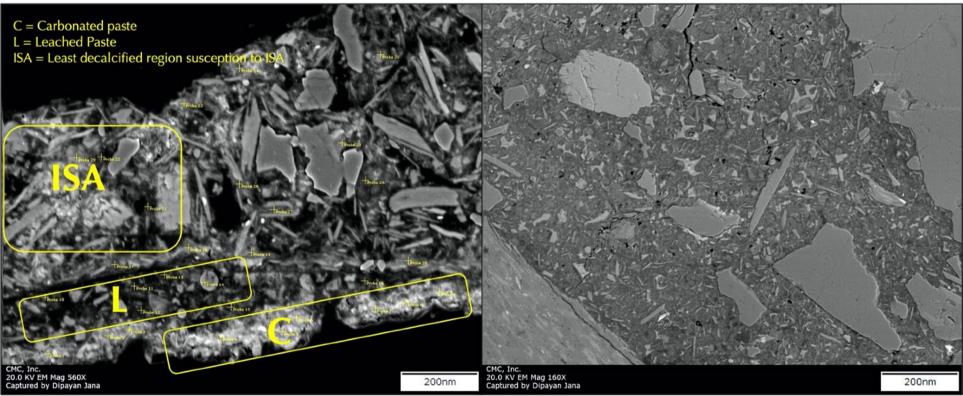


S/Ca vs/ Al/Ca plots of Variably Altered Regions of Paste

1<sup>st</sup> International Conference on Iron-Sulfide Reactions in Concrete Quebec City | Université Laval Campus | Canada | May 14<sup>th</sup> – May 17<sup>th</sup> 2024

## **Distressed Block** Skeletal Microstructure from Carbonation - Leaching - ISA

## Sound Cast-in-place Foundation Dense Microstructure Free from Carbonation - Leaching - ISA



Abundant Abraded Phyllite in Mortar Soft, Porous Paste, Low Paste Volume

Less Abraded Phyllite in Mortar Dense Paste, High Paste Volume



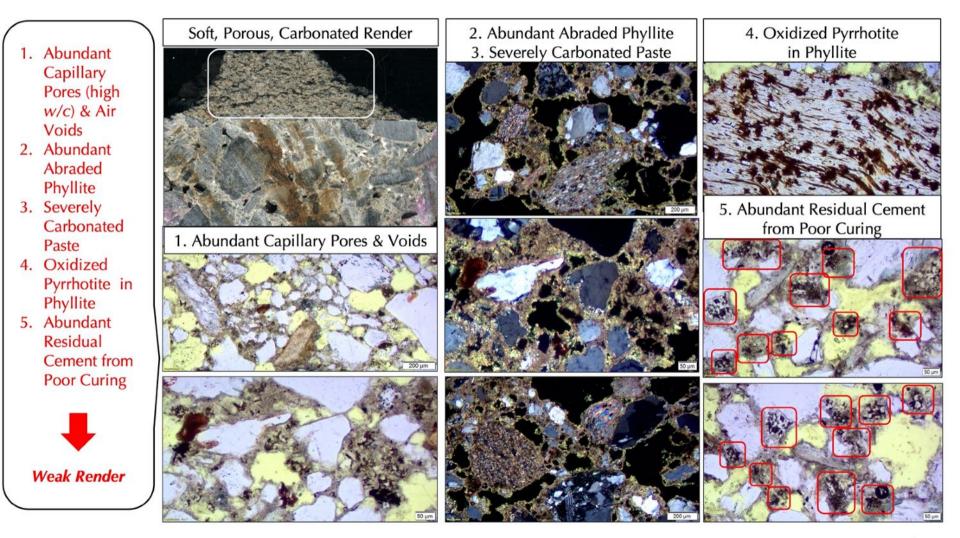
Backscatter electron images of paste in distressed block (left) vs. sound cast-in-place foundation (right)



www.cmc-concrete.com

1<sup>st</sup> International Conference on Iron-Sulfide Reactions in Concrete Quebec City | Université Laval Campus | Canada | May 14<sup>th</sup> – May 17<sup>th</sup> 2024

## 5<sup>th</sup> Culprit - Poor Quality of Sand-Cement Render - The Soft, Cracked Skin!



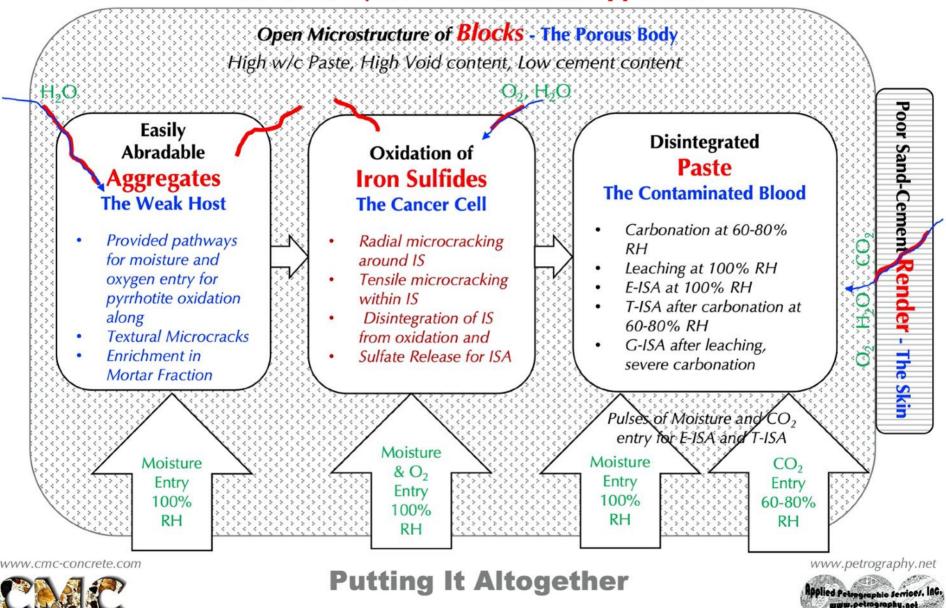
www.cmc-concrete.com





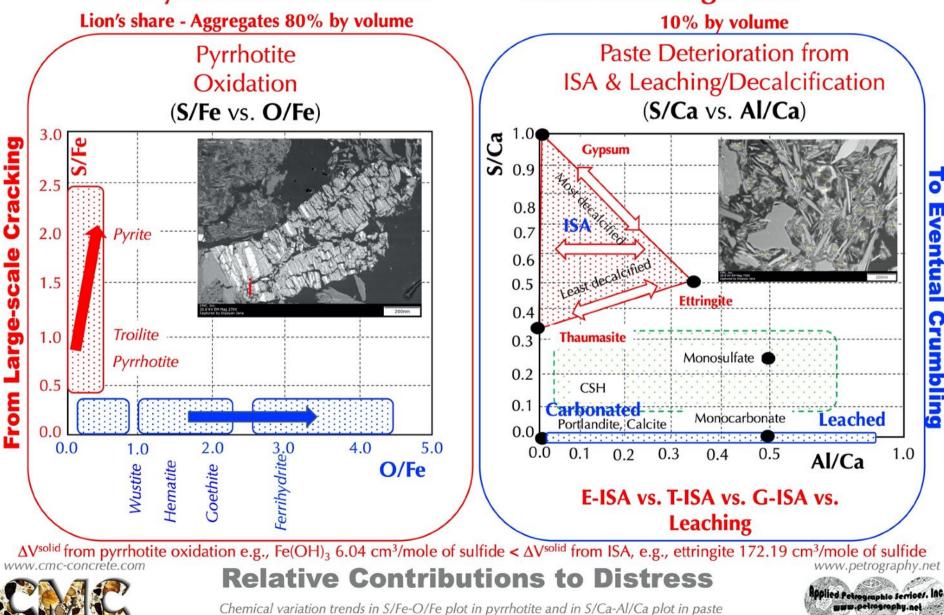
## **All Five Players in the Holistic Approach**

**ICCISER**<sup>2024</sup> International Conference on Iron Sulfide Reactions in Concrete



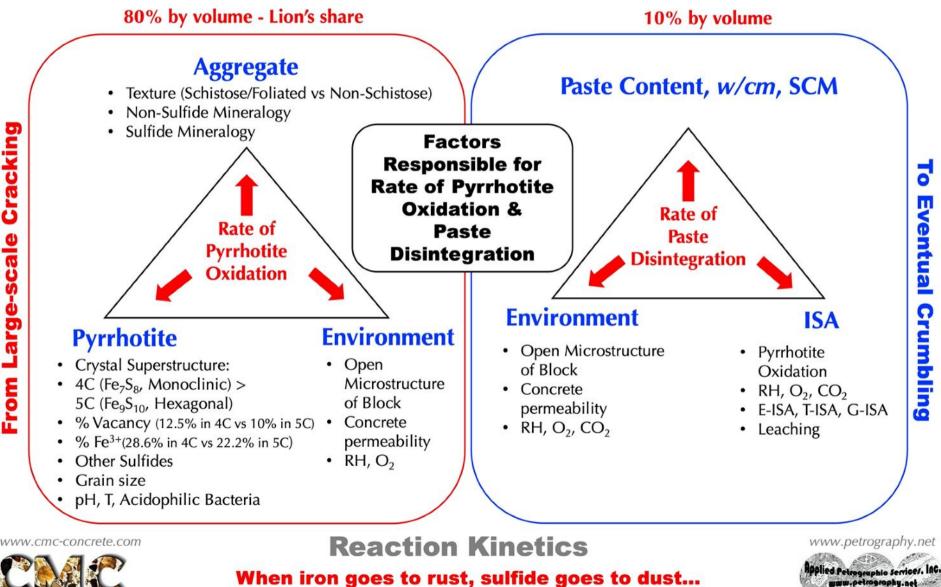
# Pyrrhotite Oxidation versus Paste Disintegration

**ICCISER**<sup>2024</sup> International Conference on Iron Sulfide Reactions in Concrete



1st International Conference on Iron-Sulfide Reactions in Concrete Quebec City | Université Laval Campus | Canada | May 14th - May 17th 2024

# **Pyrrhotite Oxidation** versus Paste Disintegration

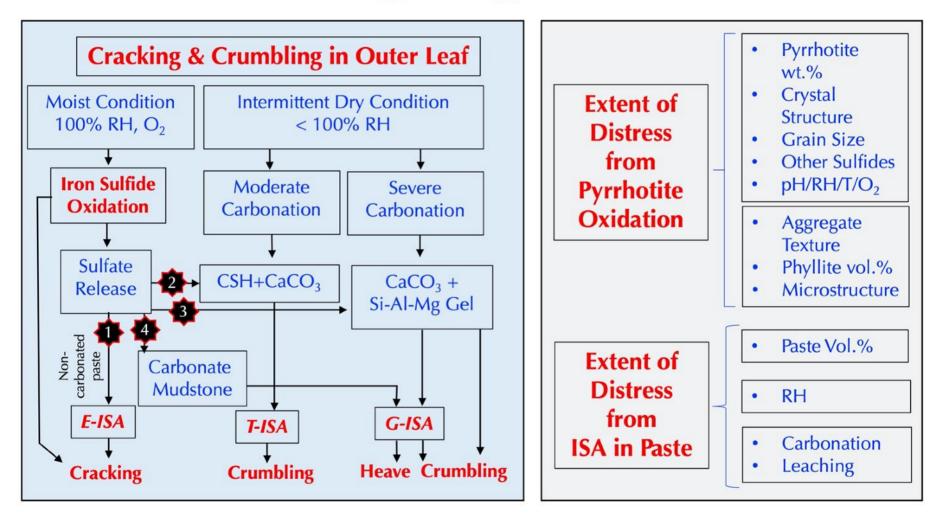


Cracking Large-scale From

**ICCISER**<sup>2024</sup> International Conference on Iron Sulfide Reactions in Concrete

1<sup>st</sup> International Conference on Iron-Sulfide Reactions in Concrete Quebec City | Université Laval Campus | Canada | May 14<sup>th</sup> – May 17<sup>th</sup> 2024

# **Putting It Altogether....**



www.cmc-concrete.com



Towards a holistic approach...from aggregate expansion and cracking from pyrrhotite oxidation to paste disintegration from ISA/Decalcification

www.petrography.net



# **Final Comments**

- Pyrrhotite was undoubted the 'cancer cell' whose deleterious effect was initiated with its presence in the weak phyllite host within the porous microstructure of block for its advanced *oxidation* and sulfate contamination of paste to trigger *ISA*, where render failed to protect the blocks from moisture/O<sub>2</sub>/CO<sub>2</sub> entry.
- Due to the *larger volume of pyrrhotite-bearing phyllite* compared to the *low-volume of paste, distress from pyrrhotite oxidation played the dominant role* in large-scale cracking, which was subsequently aggravated by crumbling of paste from *ISA*.
- It is time to take a holistic approach in Ireland instead of 'polarized' views of wrongfully advertised mica-only to rightfully but narrowed down to ISA-only theories from limited data.
- Geologists and petrographers have more important roles to play than engineers since this is, essentially, a petrographic/aggregate issue, which can only be prevented from detailed petrographic examinations of aggregates from quarries and distressed structures. Above all, we need to do good, holistic research, and faithfully transfer scientific evidence into practice.

Thank you!





Applied Petrographic Servicer. Ing.