Preventing Pyrrhotite Damage in Concrete

Proposal for a performance-based testing protocol

by Dipayan Jana

Pyrrhotite has been associated with the destruction of thousands of concrete structures in the United States, Canada, and Ireland.[1-6] Even at a level of less than 0.5% by mass of aggregate, this iron sulfide mineral can cause extensive cracking to crumbling of concrete from two forces of expansion—first from oxidation and formation of iron sulfates and iron oxyhydroxides (goethite, ferrihydrite) in aggregates, and second, from internal sulfate attacks in paste from released sulfuric acid resulting in expansive formation of gypsum and ettringite to the decomposition of calcium silicate hydrate (C-S-H) in the formation of thaumasite. The crystal structure, along with grain size, electrochemical reactions with pyrite or other sulfides, alkaline environment of paste, availability of oxygen, qualities of host aggregates and concrete, and, above all, the direct hit by moisture, can make pyrrhotite 100 times more reactive than pyrite.

From North America to Ireland

Fortunately, it is not difficult to locate the potential sources of the problem in the United States. Sulfide-bearing igneous and metamorphic rocks, the potential hosts for pyrrhotite, are located along a narrow belt of the Appalachian Mountain range, in different sporadic locations in the western United States,[7] and they are not present in the central United States. Timing of the occurrence of distress, however, has varied widely—from 3 to 5 years in Canada to 10 to 15 years in the United States and Ireland—indicating the complexity of forecasting future distress. Experiences from North America and Ireland have shown that damage has been associated with schist/gneiss aggregate in cast-in-place concrete foundation walls in the United States,[1,2] anorthositic aggregate in cast-in-place concrete foundation walls and slabs-on-ground in Canada,[5,6] and abradable foliated rock phyllite and mica schist in porous, absorptive concrete blocks in Ireland[5,6] (shown in Fig. 1; Fig. 2 is included in the online appendix to this article).

Lack of a Performance-Based Testing Protocol

Because such damage and property loss are rather new, only becoming serious in the past 10 to 15 years, and regional in scale, most national standards, codes, and specifications for construction aggregates did not pay attention to it until after the damage had occurred. Even then, case-based regional (Connecticut[8] and Massachusetts[9]) legislative actions in the United States or national codes (European[10] along with Irish and Norwegian adaptations) are either insufficient or unnecessarily restrictive to suggest premature rejection without a proper testing protocol to forecast potential damage in concrete.

First-Stage Screening from Pyrrhotite Distribution Map and Quarry

To take a performance-based approach for a meaningful test protocol, the first step is to locate the quarries that would potentially have iron sulfide minerals to search deeper for pyrrhotite and examine any potential sign of unsoundness in its moist exposure, as it is the durability of quarry rocks in a moist environment that determines the future performance of its aggregate in concrete. As mentioned, the United States Geological Survey has done just that with their map[7] of the distribution of "potentially" pyrrhotite-bearing rocks (not necessarily having pyrrhotite), with a lot of work still left to nail down detection of pyrrhotite, along with more common pyrite and rare marcasite, the two other "reactive" iron sulfides in the quarried aggregates. From a traditional geological map to tools such as a simple, handheld X-ray fluorescence spectrometer (XRF), a portable laser-induced breakdown spectroscopy (LIBS) unit, or a high-end core logger, we already have the necessary means in our arsenal to detect iron sulfide-bearing rocks in a quarry before subsequent in-depth examination in a laboratory.

Second-Stage Screening from Total Sulfur

Total sulfur content (S_T) is the most convenient and commonly used parameter to evaluate combined sulfide/sulfate/elemental/organic forms of sulfur without necessarily separating them. Various techniques, from classical wet chemistry to XRF or more traditional infrared combustion furnace in an elemental analyzer, can successfully measure S_T
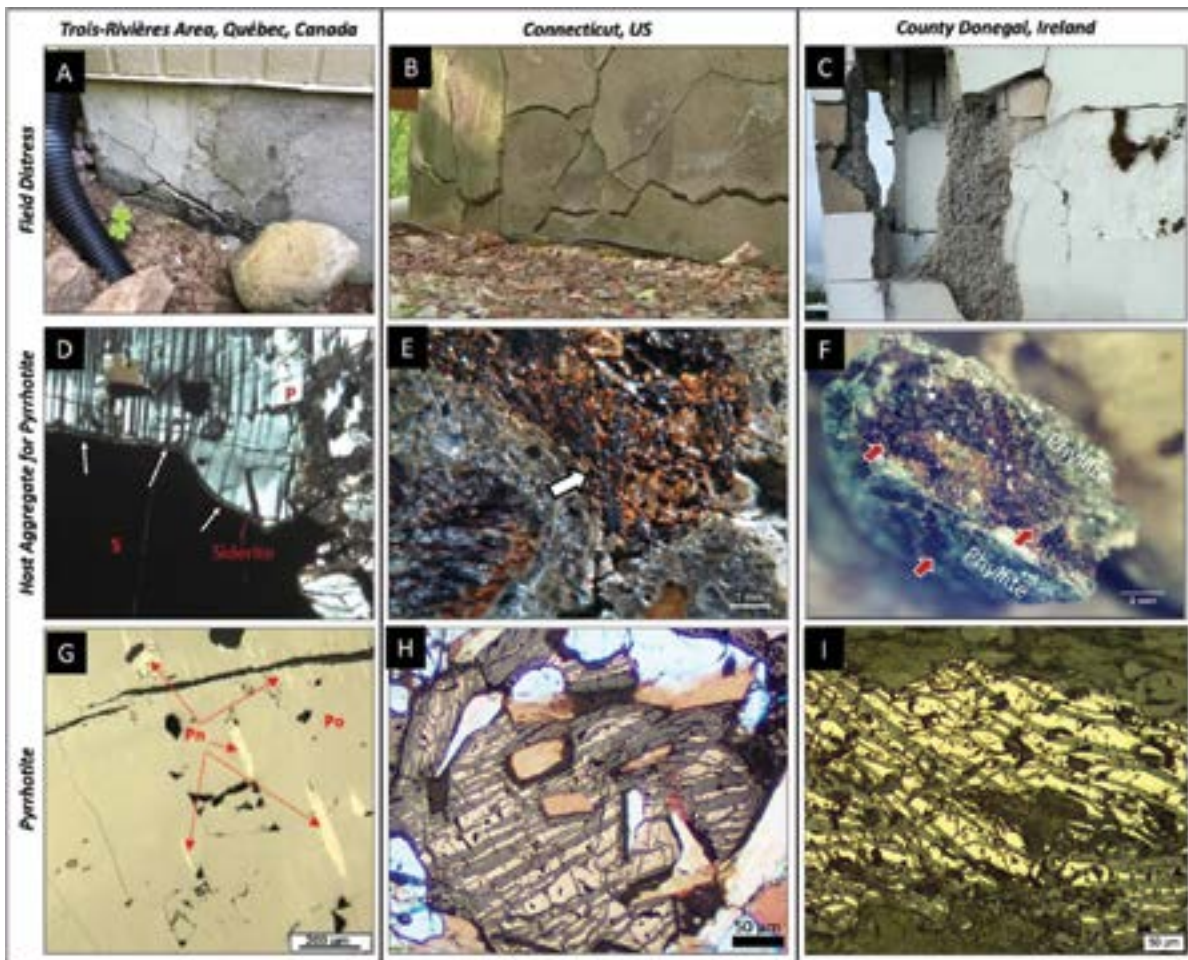
Fig. 1: Pyrrhotite distress (top row) in Canada (left), United States (center), and Ireland (right), host aggregates (middle row) and pyrrhotite (bottom row): (a) major cracks in a residential foundation wall are mostly at the corner next to rain downspouts, indicating role of water in distress; (b) extensive cracking and crumbling of a residential foundation wall in Connecticut; (c) an extreme case of crumbling of a house in Ireland; (d) anorthosite host for pyrrhotite, where an iron carbonate (siderite) rim (arrows) around sulfide promoted thaumasite attack in concrete; (e) rust stain from oxidized pyrrhotite and cracking of host garnetiferous quartzo-feldspathic schist and gneiss from Brimfield Schist formation in Connecticut; (f) similar rust stains and cracking/crumbling of foliated muscovite-chlorite-quartz-based phyllite aggregate in distressed concrete block in Ireland; (g) main pyrrhotite (Po) and other minor pentlandite (Pn) phases in Canada; and (h) and (i) characteristic bands of oxidized iron in pyrrhotite in Connecticut and Ireland. Left-column photos are reproduced with permission from Nova Science Publishers from Duchesne at al.[4]

for screening—depending on $S_T < 0.1\%$, between 0.1% and 1.0%, and > 1.0% by mass of aggregate traditionally used in most European,[10] Canadian,[11] Irish, Norwegian, and U.S. codes[8,9] as parameters for accepting, further testing, or rejecting aggregate, respectively, for potential pyrrhotite distress in a moist exposure condition. Stringent reliance on S_T alone, usually tested on less than a gram of sample, can unnecessarily reject aggregates that do not contain pyrrhotite, marcasite, or reactive forms of pyrite (for example, framboidal clusters of pyrite microcrystals) or accept ones that do have those perhaps at low amounts to be registered in a small mass, or missed for known heterogeneous distribution of pyrrhotite in a quarry.

Third-Stage Screening from Petrography, SEM-EDS, XRD, WDXRF, and XPS

This stage is most crucial because it nails down detecting pyrrhotite along with all other potentially unsound iron sulfides. Petrography is the most convenient method[12] because, after all, the issue with pyrrhotite is, first and foremost, an issue with rocks, and petrography can detect pyrrhotite, pyrite, their oxidation products, and resultant sulfate attacks in concrete (Fig. 2 to 4, shown in the online appendix to this article), and thus offer an assessment of the extent of damage in a structure, or in a laboratory sample undergoing performance-based testing.

To enhance petrography, X-ray diffraction (XRD) can

quantify pyrrhotite content down to 0.05% by mass level with the latest silicon drift detectors and high-resolution XRD units with synchrotron radiation. Wavelength dispersive XRF technique (WDXRF) can separate and quantify sulfide and sulfate phases, though it still cannot separate pyrrhotite per se from other sulfides. Micro-XRF technique can quickly detect iron sulfide phases in a cross section of a quarried core or epoxy-encapsulated slab of aggregates from iron and sulfur elemental maps. Due to pyrrhotite's weak magnetism (unlike pyrite), a thermomagnetic test can measure the drop in magnetic susceptibility during heating across its Curie temperature (at 325°C [617°F], where it loses its magnetism) and quantify that drop at different pyrrhotite (or S_T) contents in a calibrated set of standards to detect and quantify pyrrhotite in an unknown aggregate or concrete down to 0.1% by mass level simply from S_T and the susceptibility drop. X-ray photoelectron spectroscopy (XPS) not only detects sulfide and sulfate but actually separates pyrite and pyrrhotite contents. Raman spectroscopy, LIBS, Auger electron spectroscopy, thermal analysis, and nuclear magnetic resonance spectroscopy are now being tested at various research laboratories for pyrrhotite detection. We have more than enough tools to detect and quantify pyrrhotite, though not all are equally accessible or extensively researched to include in a standardized testing protocol.[1]

Assessing Oxidation and Sulfate Attack

Petrography[12] provides the first-hand detailed anatomy of an aggregate (mineralogy/texture) for concrete or of concrete in a distressed structure, including where the pyrrhotite grains are, in which forms and other sulfide associations, their products of oxidation, sulfate attacks, and the extent of damage. To evaluate performance of a pyrrhotite-bearing aggregate in field concrete, laboratory tests must be conducted. We have tests that measure oxygen consumption of aggregates from pyrrhotite oxidation either by directly measuring loss of O_2 in air above pulverized aggregates in a sealed container with an O_2 probe[4] or by indirectly detecting the water-soluble sulfate level in a filtrate by ion chromatography from a pulverized aggregate digested in a highly oxidizing solution like hydrogen peroxide.[2]

Expansion Tests

The last step is to measure potential expansion of some laboratory-made mortar bars or concrete prisms containing aggregates that are confirmed to have pyrrhotite, before rejecting them entirely from use in a moist environment. We have at least four different tests, all of which were originally devised for (or derived from) tests proposed for assessing expansion potential of alkali-silica reactive aggregates, which are not necessarily reactive to pyrrhotite. In the absence of a standardized expansion test for pyrrhotite, these are the best options available, at least to start with. Ranging from as fast as 16 days for the ASTM accelerated mortar bar test (AMBT),[13] to 180 days for the Canadian mortar bar test

(CMBT),[14] to 8 to 12 weeks for the AASHTO miniature concrete prism test (MCPT),[15] to as long as 2 years for the ASTM concrete prism test (CPT),[16] potential expansion of pyrrhotite-bearing aggregates can be tested without necessarily paying attention to their imposed threshold expansion limits for acceptance, for example, < 0.10% for AMBT and CMBT and < 0.04% for MCPT and CPT, which were (except CMBT) proposed strictly for two-stage expansions from alkali-silica reaction (ASR) gel formation and moisture absorption of gel during ASR, and not for two-stage expansions from pyrrhotite oxidation and subsequent internal sulfate attack.

Field Lessons to Develop a Performance-Based Protocol

To assess expansion potential of pyrrhotite-bearing aggregates from oxidation and sulfate attack, we must first incorporate the lessons learned from North America and Ireland. There are too many variables and seemingly complex and rather confusing scenarios in field cases that need to be evaluated and implemented in a performance-based expansion test.

Aggregate: Whether the host aggregate is as dense as an igneous rock (anorthosite) in Canada, a deformed metamorphic rock (schist and gneiss) in the eastern United States, or a highly foliated and easily abradable phyllite and mica schist in Ireland, none provided the necessary protection to its pyrrhotite from oxidation. The texture of aggregate, however, did play a role, at least for metamorphic aggregates, such as phyllite in Ireland, in breaking down easily during mixing and preparation of concrete blocks to not only expose more pyrrhotite grains to O_2 and moisture but also enrich pyrrhotite in the mortar fraction for rapid oxidation in an alkaline medium. Foliations or weak planes in phyllite, schist, or gneiss provided easy access of moisture to pyrrhotite, not just in the United States or Ireland but also in Spain, where pyrrhotite preferentially aligned along schistosity planes defined by parallel arrangements of deformed minerals were preferentially oxidized. These aggregates and others similar to them, therefore, require special attention to the role of aggregate texture in a performance-based test.

Concrete mixture: Perhaps one reason for the relatively faster appearance of distress in Canada, despite having a dense anorthosite host for pyrrhotite, is the 0.7 water-cement ratio (w/c) of concrete, which is far higher than any industry specification for durability of concrete in a moist outdoor environment. Without bringing other variables for pyrrhotite oxidation, and just comparing cases between the United States and Canada, a w/c of 0.7 in Canada versus a w/c of 0.45 to 0.50 in the eastern United States can theoretically accelerate pyrrhotite oxidation in Canada. The real situation, however, is not that simple, as can be seen from very different host aggregates. Incorporation of supplementary cementitious materials (SCMs) should restrict moisture/O_2 ingress from pore size and grain size refinements and cement type. For

example, ASTM C150 Type IV (low C_3A content and low heat of hydration) or Type V (high sulfate resistance) portland cement should provide additional protection from sulfate attacks. This has already been confirmed from laboratory tests by the Canadian group, where a 50 to 85% reduction in expansion was noted from these beneficial effects of SCMs and sulfate-resistant cement, a necessary preventive measure to be taken when pyrrhotite-bearing aggregate is detected.

Iron sulfide: Pyrrhotite is far more reactive than pyrite, but its reactivity increases when pyrite is also present to engage in electrochemical reactions. Cracked foundations from Canada showed a close association of pyrrhotite with pyrite, pentlandite, and chalcopyrite, which can potentially increase the rate of oxidation of pyrrhotite. Even without other sulfides, oxidation rate of pyrrhotite can vary considerably from crystal structures (% Fe vacancies and % Fe^{3+}), moisture conditions, pH, and oxygen contents. Pyrrhotite's distribution is also quite heterogeneous in a quarry. A thin rim of iron carbonate (siderite) around iron sulfide was enough to cause thaumasite attack in Canada, which is also seen at a larger scale in Ireland, though not from a separate carbonate source but from pervasive carbonation through an open structure of blocks to cause severe crumbling. Therefore, a carbonate source can potentially be detrimental to aggravating the damage from expansive gypsum/ettringite-based to corrosive thaumasite-based sulfate attacks by decomposing C-S-H. Similar to faster oxidation of clustered pyrite microcrystals in framboids than the cubic/blocky ones, pyrrhotites in elongated forms preferentially aligned along weak planes in the host or coarser grains in the mortar fraction are more susceptible to oxidation than scattered finely disseminated ones in aggregates.
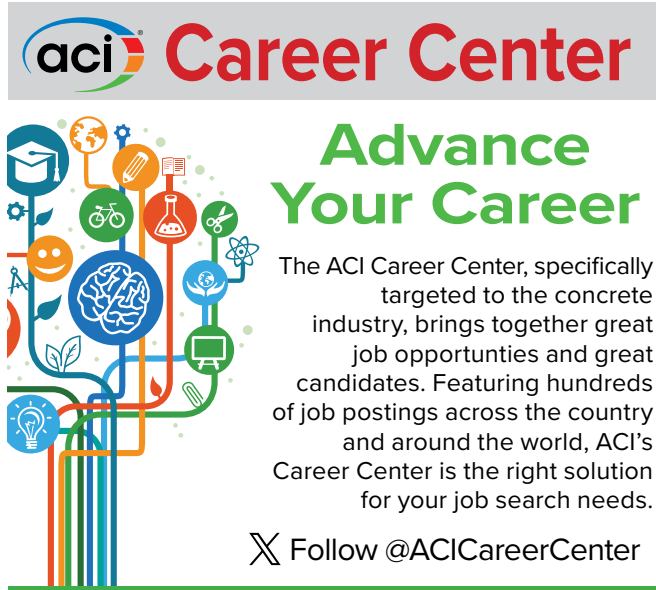
Cast-in-place concrete versus manufactured blocks: Cases of cracked foundation walls and slabs in North America and crumbled walls of defective concrete blocks in Ireland are two end scenarios of pyrrhotite distress irrespective of how dense or porous the concrete or the host aggregate is. The inherent porous microstructure of defective blocks in Ireland (with high interstitial void contents along with a low-volume, high *w/c* paste) has undoubtedly caused deeper penetration of moisture, O_2, and CO_2 during service, leading to pervasive oxidation of pyrrhotite grains, gypsum/ettringite-based internal sulfate attack, carbonation of paste with subsequent thaumasite attack, and eventual leaching of lime—where the blocks worsened to the point of crumbling to fine powder and falling from the walls. The inherent denser microstructure of concrete foundations in Connecticut, however, could not combat the damage even though a denser microstructure with SCMs does have a positive influence. The author recently examined a foundation slab from a house located in County Donegal, where crumbled blocks in the walls were to be removed, and the slab was found sound despite finding the same pyrrhotite (plus pyrite)-bearing phyllite aggregate as in the block, reportedly supplied by the same contractor and installed at the same time. Only a few pyrrhotite grains,

mostly in the mortar fraction, showed oxidation for exposure to a highly alkaline environment of paste during mixing and service, but pyrrhotite grains within phyllite were mostly unaffected. The mortar fraction of the slab was rich in abraded phyllite flakes from mixing and placement, as also seen, quite ubiquitously, in the defective blocks. The paste, however, was considerably denser in the well-consolidated slab, and it had a higher volume and lower *w/c* than the altered paste in the blocks. Hence, no carbonation of the interior slab was noticed, except at the top exposed 15 to 20 mm (0.6 to 0.8 in.) depth compared to severely carbonated and leached paste in the porous blocks. Clearly, the reported lack of a moist exposure condition of the slab has helped it survive the damage from pyrrhotite. Steam curing of blocks may have accelerated pyrrhotite oxidation at the early stage compared to oxidation in an alkaline medium in the slab.

Conclusions

The following factors are important to incorporate in a performance-based test protocol:
- Evaluation of a quarry for its geology, structure, and field durability of potentially sulfide-bearing rock formations after initial screening of drilled cores or quarry beds with handheld XRF/LIBS units for collecting samples for laboratory testing of aggregates;
- Total sulfur contents (S_T) of field-screened sulfur-bearing aggregates can then be tested only for a rough screening of aggregates of low, intermediate, and high S_T, for example, at the conventional < 0.1%, 0.1 to 1.0%, and > 1.0% S_T by mass, respectively, but without necessarily imposing those limits as criteria for acceptance/rejection/further testing, only for the sole purpose of prioritizing the members to test for pyrrhotite;

Workflow of Test Protocols

This chart describes the assessment of aggregate from field evaluation of a quarry (Phase 1) through short-term (within a month) laboratory tests (Phases 2 to 4) to detect pyrrhotite/pyrite to, finally, a long-term (from 2 weeks to 2 years) expansion test (Phase 5) guided by lessons from field distress to mitigate pyrrhotite distress in concrete (modified from Jana[1]). Relevant standardized methods are mentioned. Threshold limits are subjected to validation from long-term tests and field performance. Total sulfur (S_T) is universally suggested by British, Irish, Canadian, and United States agencies to be followed by petrography[12] for aggregates having S_T values between 0.1 and 1.0% to evaluate the presence of reactive pyrite and pyrrhotite (which is best done by a combination of reflected-light optical microscopy of polished sections, often with ancillary XRD and scanning electron microscopy and energy dispersive X-ray spectroscopy [SEM-EDS]). Suggestions from United States and Canadian agencies varied when reactive sulfide was found, where the Canadian standard suggested an intermediate oxygen consumption test before the final long-term expansion tests of mortar bars or concrete prisms. Two long-term expansion tests suggested are CSA A23.1:19 for Canadian aggregates[11] and ASTM C1293/C1293M-20a [17] for U.S. aggregates. Based on field evidence, however, a performance-based expansion test should incorporate variables from aggregate types, individual sulfide types, mixture proportions, porous block versus dense concrete preparation, various pre-conditioning, and storage temperatures and relative humidity.

Phase 1: Field Evaluation of Quarry for Iron Sulfide Aggregates and Durability

US, Canadian, and European Testing Protocols for Acceptance/Rejection Criteria of Aggregates For Potential to Cause Iron Sulfide Attacks in Concrete

Short-Term Tests / *Long-Term Tests (When Reactive Pyrite or Pyrrhotite is Detected)*

Phase 2: Detecting Total Sulfide & Sulfate Contents

Laboratory Test Step 1
Total Sulfur Content, S_T (%)
EN 12620, ASTM D 4239, IS 465, CSA A23.1:19
- IR Combustion, XRF, Gravimetry

$S_T < 0.10$-0.15% | 0.10-$0.15\% \leq S_T < 1.0\%$ | $S_T > 1.0\%$

Laboratory Test Step 4
Mortar Bar or Concrete Prism Expansion Tests for Aggregate
- Length Change Measurements at Controlled Environment

Phase 3: Detecting and Quantifying Pyrrhotite, along with its association, e.g., with Reactive Pyrite, Marcasite

Accept

Laboratory Test Step 2
Petrography, XRD, SEM
ASTM C 295, BS 812-104
CSA A23.2-15

Reject

Reject or accept if $S_T < 0.1\%$

Reactive Pyrite or Pyrrhotite Not Found | Reactive Pyrite or Pyrrhotite Found

ASTM C 1260/C 1567
Accelerated Mortar Bar Test for 16 days | Expansion < 0.10% | Expansion ≥ 0.10%

or *CSA A23.1:19 Annex P* **Mortar Bar Test** for 90 (Phase I, high-T) to 180 days (Phase II, low-T) | Expansion < 0.10% | Expansion ≥ 0.10%

or *AASHTO T380* **Miniature Concrete Prism Test** for 8 to 12 weeks | Expansion < 0.04% | Expansion ≥ 0.04%

or *ASTM C 1293, CSA A23.2-14A* **Concrete Prism Test** for 1 or 2-year (pozzolanic mix) *CA & MA Laws* | Expansion < 0.04% | Expansion ≥ 0.04%

Phase 5: Long-Term Expansion Tests of Pyrrhotite-bearing Aggregates

Phase 4: Lab-specific tests for pyrrhotite and its oxidation potential

Lab-Specific Tests Step 3 *(Optional)*

Oxygen Consumption Test CSA A23.1:19 | *Thermo-magnetic Studies* | *WD-XRF* | *Accelerated Oxidation*

CT & MA Laws

$O_2 < 4.0\%$ | $O_2 \geq 4.0\%$

Accept | Proceed to Expansion Tests

Proceed to Expansion Tests

Accept only with a low *w/cm* (≤ 0.45) mix and moisture protection of concrete element | Restrict from use in concrete especially in a moist exposure without a field performance record

S_T ➡ Positive ID of Reactive Sulfides ➡ Expansion Tests
% Reaction Products vs % Expansion ➡ Cracking

All Threshold values are subjected to validation from field performances

Variables to Incorporate in *Performance-Based Tests* Mortar Bar/Concrete Prism Expansion Tests for Concrete Aggregate

Phase 5: Incorporation of Variables in Long-Term Expansion Tests of Pyrrhotite-bearing Aggregates

Lessons from Field Distress for Variables to Include in a Long-Term Expansion Test

Aggregate Type	Iron Sulfide Type and S_T	Mix Proportions	Preparation	Pre-Conditioning	Storage T/RH
For Mortar Bar/Concrete Prism Expansion Test • Non-schistose/Non-foliated Igneous/Metamorphic Aggregate (Granite, Amphibolite) • Schistose (Metamorphic) Aggregate (Schist, Gneiss) • Foliated, Abradable (Metamorphic) Aggregate - Phyllite, Mica Schist	For Mortar Bar/Concrete Prism Expansion Test • Pyrite-only • Pyrrhotite-only • Pyrite-Pyrrhotite Mix • Each at $S_T > 0.1$, 0.1-1.0 and >1.0%	For Mortar Bar/Concrete Prism Expansion Test • Coarse/fine aggregate ratios • *w/c* and *w/cm* ratios, 0.40 vs 0.70 • PC vs. sulfate-resistant vs Blended cement • Limestone filler/cement	For Mortar Bar/Concrete Prism Expansion Test • CMU-type low-cement high-void mix in mold with open/porous nature • Dense well-compacted mix in mold	For Mortar Bar/Concrete Prism Expansion Test • 1-day steam curing • 1-day lime water curing • 1-day tap water curing	For Mortar Bar/Concrete Prism Expansion Test • 30°C/100%RH • 80°C/60%RH • 4°C/100%RH

Continuation of Test with Petrographic Check of Progress of Deleterious Reactions Until Cracking

- Determine the presence of pyrrhotite, along with the detection of pyrite, marcasite, and other sulfide minerals, mostly by petrography, with the option to exercise other lab-specific tests,[1] such as thermomagnetic studies, WDXRF, or oxygen consumption;
- Irrespective of any testing route followed for detection of pyrrhotite, especially along with pyrite at any level, it is enough for a decision of whether to restrict aggregate use only in moderate/mild/dry exposure regimes with adequate moisture protection, entirely reject the aggregate for moist outdoor exposures, or engage in a long-term performance-based expansion test, with appropriate modifications after incorporating all the variables of pyrrhotite distress that are known to affect rate of oxidation of pyrrhotite and resultant distress. Instead of paying attention to the threshold limits for acceptance/rejection originally implemented for ASR-related expansions, emphasis should be given to the time of occurrences of the products of oxidation and internal sulfate attacks in relation to cracking of the tested bars/prisms by regular checks with petrography;
- Such a protocol, which was built upon the conventional scheme along with the incorporation of factors that have effects on pyrrhotite distress in concrete, is shown in the sidebar "Workflow of Test Protocols"; and
- Modification of the concrete mixture to densify the microstructure and make it sulfate resistant and adequate moisture protection of structural elements are two mandatory requirements to mention before the use of aggregates having pyrrhotite at any level.

Acknowledgments

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Selected for reader interest by the editors.

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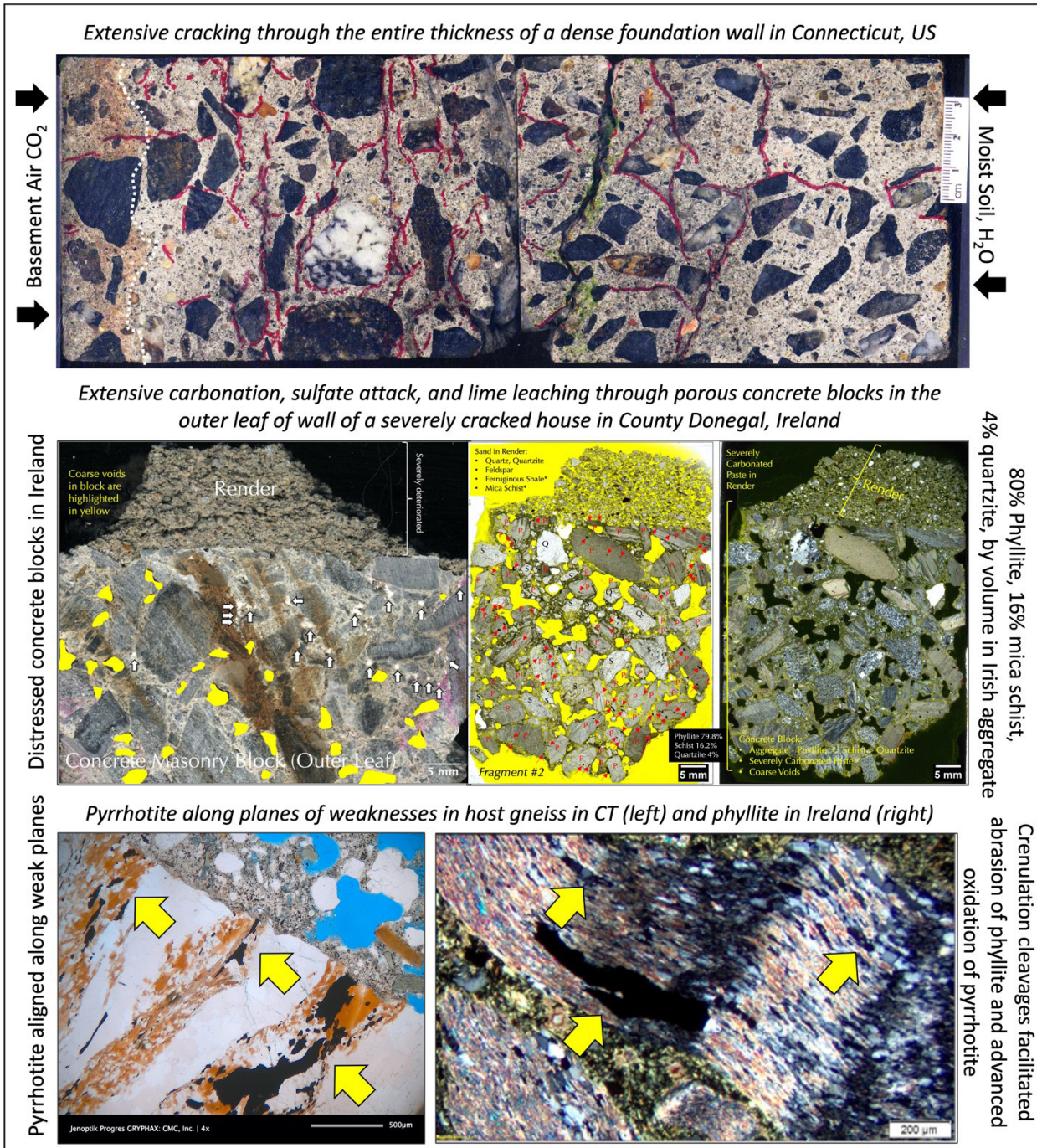
Fig. 2: At the top, extensive cracking through the entire foundation wall in a house in Connecticut shown on lapped cross section of a core, where the wall shows 15 to 20 mm carbonation from the interior surface in contact with basement air, whereas moisture entered from the outer surface from moist soil. In the middle, porous structure of low-volume paste and high interstitial void in defective concrete blocks of a wall in County Donegal, Ireland, that has facilitated migration of moisture and CO_2 for carbonation, pyrrhotite oxidation, and resultant internal sulfate attack. At the bottom, preferential alignment of pyrrhotite along the weak planes of host gneiss in association with biotite flakes in Connecticut (left) and foliation planes of phyllite in Ireland (right)
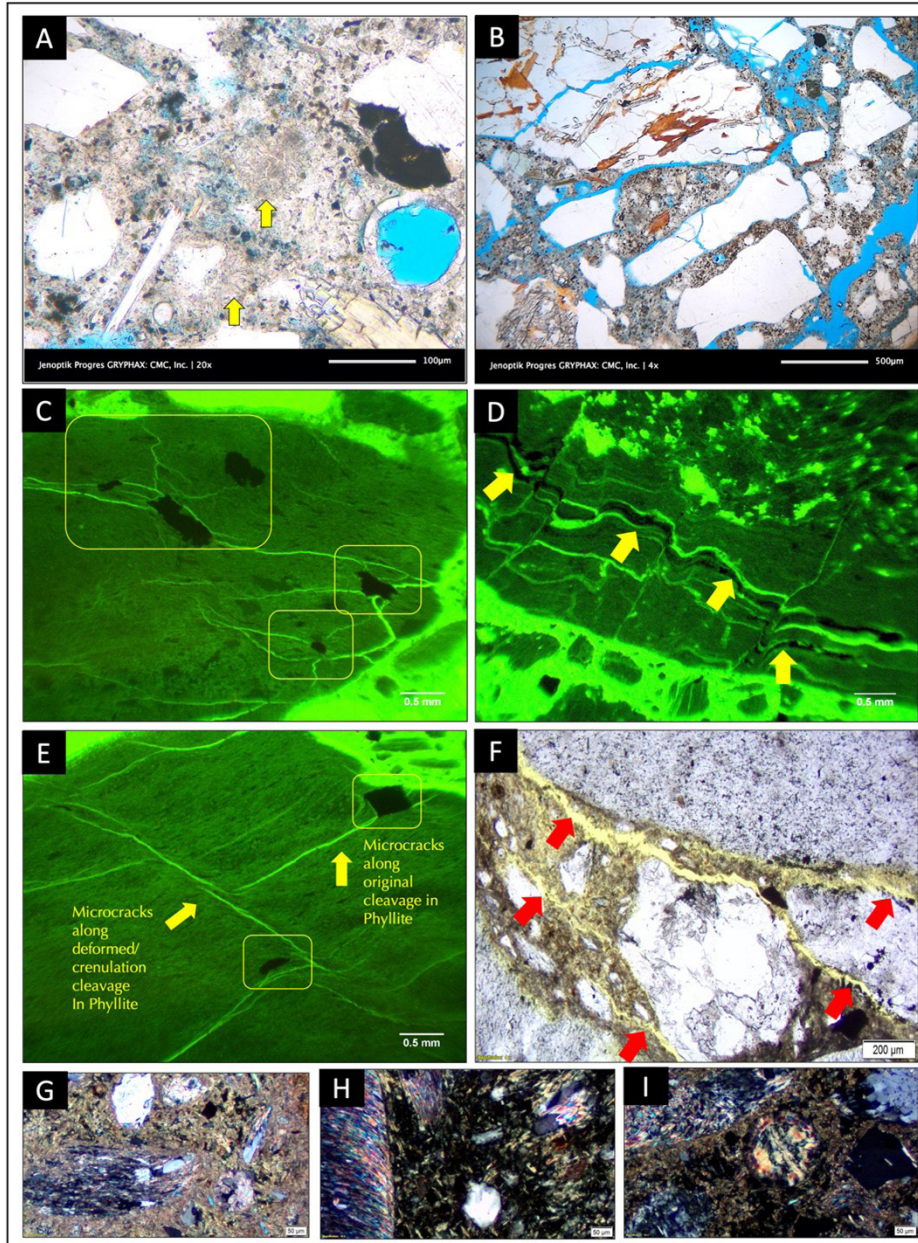
Fig. 3: Petrographic examination findings: (a) ettringite in dense, confined spaces in paste that has resulted in expansion and cracking in Connecticut,[1] whereas secondary ettringite precipitation in an air void at right is the result of dissolution and reprecipitation of ettringite from paste; (b) cracks traversing through pyrrhotite-bearing gneiss coarse aggregate, sand, and paste are highlighted by blue epoxy in a thin section micrograph of distressed concrete in Connecticut[2]; (c) fluorescent epoxy-mixed thin section micrograph of defective block from Donegal, Ireland, showing extensive cracking in phyllite aggregate with many oxidized pyrrhotite grains in phyllite showing radial cracks from expansion associated with oxidation; (d) deformation of pyrrhotite grains aligned along pre-existing foliation planes in phyllite during crenulation cleavage formation that had further enhanced its oxidation rate; (e) microcracks along two sets of cleavage planes in phyllite that has facilitated splitting and enrichment of abraded phyllite flakes in the mortar fraction as well as enhanced oxidation of pyrrhotite both within phyllite and after incorporation in highly alkaline mortar fraction in Ireland; (f) extensive cracking in the mortar fraction of defective blocks in Ireland highlighted by fluorescent epoxy; (g) severe carbonation; (h) lime-leached (Si-Al-Mg rich) portions of paste; and (i) thaumasite formation in air void and paste in thin section micrographs (XPL) of defective concrete blocks from Ireland where mortar fractions in (g) to (i) are enriched in abraded phyllite flakes
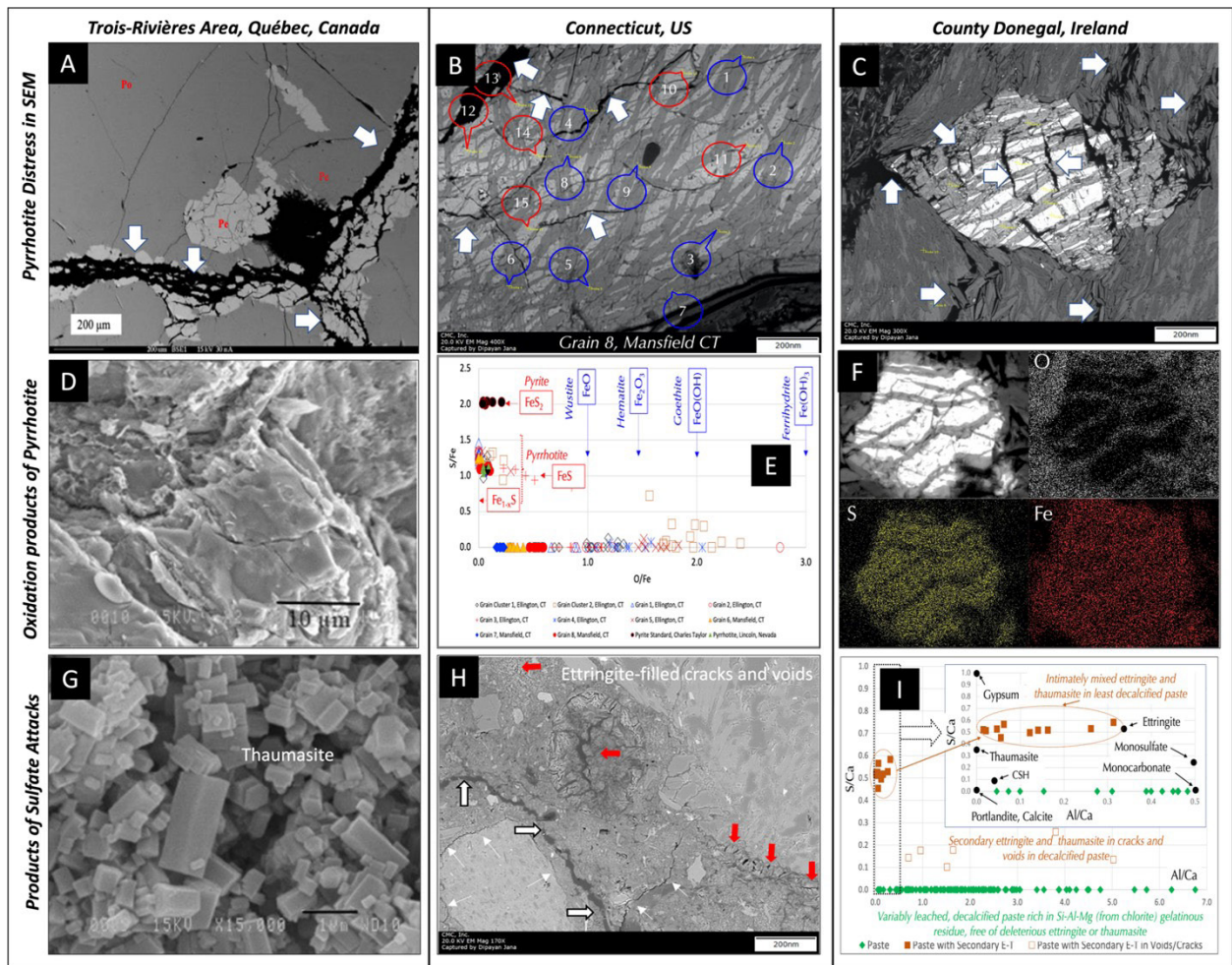
Fig. 4: In the top row, SEM-EDS studies showing cracking (arrows) from pyrrhotite oxidation in: (a) Canada, (b) United States; and (c) Ireland, forming characteristic darker gray iron oxide bands in brighter pyrrhotite in backscatter electron images Also in (c) crumbling of phyllite by pyrrhotite oxidation in Ireland. In the middle row, products of pyrrhotite oxidation: (d) iron oxy-hydroxide in secondary electron image; (e) atomic ratios of oxidized pyrrhotite from Connecticut plotting S/Fe versus O/Fe showing pyrrhotite grains at S/Fe around 1.0 and 1.5 whereas a range of oxidation products encompassing wustite to ferrihydrite; (f) X-ray elemental maps of an oxidized pyrrhotite from Connecticut showing O-rich oxidized bands in Fe,S-rich matrix. In the bottom row, products of internal sulfate attack: (g) euhedral, prismatic crystals of thaumasite from Canada; (h) ettringite formation in paste, along cracks, aggregate-paste interfaces, and within air void in Connecticut[1]; (i) atomic ratios S/Ca versus Al/Ca plots of altered paste from defective blocks in Ireland showing a linear trend of mixed secondary ettringite and thaumasite in the least decalcified but carbonated paste (solid orange squares), ettringite/thaumasite only in voids and cracks in decalcified paste (open orange squares), and Si-Al-Mg (from chlorite)-rich gelatinous residue from lime-leached areas of paste that are free of ettringite or thaumasite (green diamonds). Left column photos are reproduced with permission from Nova Science Publishers from Duchesne at al.[4]