

Investigation of Presence of Pyrrhotite in A Residential Concrete Foundation In Mansfield Center, Connecticut



154 Coventry Road
Mansfield Center, Connecticut

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CMC 0718143



EXECUTIVE SUMMARY

Widespread outbreak of deterioration of many residential concrete foundations due to oxidation of an iron sulfide mineral 'pyrrhotite' in the quarried aggregate stones has occurred in the state of Connecticut with many thousands of homes being affected. Pyrrhotite (from Greek *pyrrhos* i.e. flame-colored or redness) commonly occurs in many mafic igneous, sedimentary, and metamorphic rocks, or in high temperature hydrothermal and replacement veins as a minor accessory mineral having a chemical formula of $Fe_{1-x}S$, where x varies from 0 to 0.125. It is commonly associated with pyrite (FeS_2) but is distinguished by its bronze rather than brass color of pyrite, its lower hardness, decomposition in HCl (Deer et al., 2008), lower S/Fe ratio, and weakly magnetic nature. All these features along with X-ray diffraction of rocks containing both iron sulfide minerals help to determine the pyrrhotite content, whereas XRF analysis of rocks determine the sulfur (as SO_3) content from all iron sulfide minerals. Currently, much of the information available on pyrrhotite-related concrete deterioration in northeastern Connecticut is limited to news media but the cause of deterioration has been attributed by an investigation conducted at the University of Connecticut (Wille and Zhong, 2016) and Jana (2017) as oxidation of pyrrhotite present in the coarse aggregate in the presence of moisture and oxygen in concrete. Manifestation of the damage has taken as much as 10 to 20 years. Typical visual deterioration is in the form of map cracking, some causing deformation of the wall, reddish-brown discoloration as rust stains, whitish formation of sodium sulfate salts (thenardite and mirabilite) in the vicinity of surface cracking, and in some severe cases crumbling of concrete. Most of the damage to date has been linked to aggregates supplied from one square-shaped quarry (Becker's quarry) in Willington, CT that sits in a weathered hydrothermal vein of metamorphic rocks containing significant pyrrhotite mineralization. The geology in the vicinity of the quarry is made up of metamorphic rocks predominately from two to three formations consisting predominantly of foliated schists and gneissic rock, granofels, and foliated quartz diorite. Quartz, plagioclase or oligoclase are primary minerals with micas, and noted are garnet and pyrrhotite as common accessory minerals. Most findings of concrete deterioration around the world due to pyrrhotite oxidation, including the ones in northeastern Connecticut (e.g., Moum and Rosenqvist 1959 from Norway, Tagnit-Hamou, et.al. 2005 and Rodrigues et al. 2012 from Canada, Oliveira, et al. 2014 from Spain, and Wille and Zhong, 2016 and Jana 2017 from USA) indicated the following two-stage mechanisms of distress due to: (a) primary expansions associated with oxidation of pyrrhotite in the presence of oxygen, moisture, and high pH in concrete to form ferric oxy-hydroxides, e.g., ferrihydrite $[Fe(OH)_3]$ causing cracking of the unsound aggregates, followed by (b) secondary expansions from internal sulfate attacks by the sulfates released from pyrrhotite oxidation to cement hydration and carbonation products forming secondary ettringite and thaumasite, respectively causing further cracking in the paste. The former expansion is contributed from the pyrrhotite-bearing aggregates, whereas, the latter expansion is contributed from internal sulfate attacks within the confined spaces of the released sulfate-contaminated hydrated cement paste.

In light of this known problem of pyrrhotite in concrete aggregate from around the world, and particularly from the Becker's quarry in CT, and the resulting distress in many residential foundations in northeastern Connecticut, a concrete core from a foundation wall at the residence of Rogers and Swaminathan at 154 Coventry Road in Mansfield Center, Connecticut i.e. within the known area of 'pyrrhotite epidemic' was provided with the concern of: (a) whether or not the concrete foundation contains pyrrhotite in its aggregate, and, if detected, (b) if pyrrhotite has played the role for deterioration of concrete foundation, if any, as in the case of other residential foundations from eastern Connecticut that have shown widespread cracking from pyrrhotite oxidation and resultant sulfate attacks in concretes.

Contrary to other occurrences of pyrrhotite-related deterioration of residential foundation, however, field photographs of the subject foundation wall at Rogers and Swaminathan's residence do not show any map cracking or any other type of cracking *at the time of this investigation* as those found in other pyrrhotite-related cracking from distressed residences. Consistent with field photos, an 8 in. (200 mm) long and $3\frac{5}{8}$ in. (92 mm) diameter hardened concrete core drilled from near the base of a foundation wall provided for detailed laboratory investigation does not show any visible cracking. Laboratory investigation was conducted for determination of possible presence of pyrrhotite in concrete, and, its potentially deleterious role in concrete deterioration, if any. Pyrrhotite's presence along with overall condition of concrete and aggregates were examined by detailed petrographic examinations (optical microscopy) *a la* ASTM C 856, whereas possible roles of pyrrhotite, its potential oxidation products and sulfate levels, and microstructures of deteriorated concrete around pyrrhotite-bearing aggregates were examined by



scanning electron microscopy and energy-dispersive X-ray microanalysis (SEM-EDS) of multiple thin sections of concrete (*a la* ASTM C 1723), X-ray diffraction (XRD) and X-ray fluorescence (XRF) of multiple pyrrhotite-bearing coarse aggregate particles extracted from the concrete, and ion chromatography (IC *a la* ASTM D 4327) of extracted aggregate particles digested in a strong oxidant of 35% hydrogen peroxide solution in an accelerated oxidation test, then diluted in distilled water to determine levels of sulfates released by these aggregates in relation to a control aggregate without any iron sulfide mineral. Detection of pyrrhotite by optical microscopy and XRD, along with detection of its oxidation products by SEM-EDS and XRD, reaction microstructures and evidence of distress by SEM-EDS, and measurement of release of sulfate levels by IC have provided a good assessment of potential role of pyrrhotite in causing the observed distress.

Petrographic examinations have determined the concrete to be made using: (a) crushed stone coarse aggregate, which is a mixture of a predominant dark gray metamorphic garnetiferous quartzo-feldspathic and micaceous gneiss and a subordinate light brown quartz-feldspar-mica gneiss (having a higher quartz content than the dark gray gneiss) both having a nominal maximum size of $\frac{3}{4}$ in. (19 mm) showing the typical gneissose texture of alternating bands of quartz-albitic feldspar and micaceous (mostly biotite and less muscovite) minerals that often contain pyrope garnet poikiloblast; (b) natural siliceous sand fine aggregate having a nominal maximum size of $\frac{3}{8}$ in. (9.5 mm) and containing major amounts of quartz and quartzite, and subordinate amounts of feldspar, mica, ferruginous rock, and mafic minerals; (c) a hardened paste of Portland cement as the sole cementitious component having an estimated cement content of 6 to $6\frac{1}{2}$ bags per cubic yard and an estimated water-cement ratio (*w/c*) of 0.45 to 0.50, and (d) an estimated air content of 6 to 7 percent; the concrete is air-entrained. Overall composition of concrete, including the crushed gneiss coarse aggregate particles present in the examined concrete is similar to the concretes (including similar crushed gneiss coarse aggregates) found in other foundations from eastern Connecticut that were examined by this laboratory and detected pyrrhotite-oxidation-related cracking of foundation.

Contrary to other pyrrhotite-related cracking of residential foundations, petrographic examinations of current concrete core has failed to detect any cracking in the foundation wall core that is not only absent in the core when received, but also during subsequent examinations of lapped and saw-cut cross sections of core, even after impregnating the cross sections with a fluorescent dye-mixed epoxy and viewed in an ultraviolet light where any cracking is revealed due to penetration of fluorescent epoxy into the cracks and then become highlighted in UV light. Only a few crushed gneiss coarse aggregate particles show some internal cracking, which may or may not be due to oxidation of pyrrhotite but for the most part, most of the crushed gneiss coarse aggregate particles as well as the concrete lack any visible or invisible cracking. By contrast, cores examined by this laboratory from other residential foundation walls from eastern Connecticut showed extensive cracking in the cores received, as well as on lapped, saw-cut and fluorescent impregnated cross sections of cores where not only the pyrrhotite-bearing unsound crushed gneiss coarse aggregates have shown cracking but also the surrounding concrete due to extension of cracks from unsound pyrrhotite-bearing gneiss to the concrete. No such cracking is observed for this core at the time of this investigation. Absence of any visible and invisible cracking in the core examined is responsible for the sound condition of foundation found in the field photos of this residence.

Petrographic examinations detected two types of crushed gneiss coarse aggregate particles – (a) a dominant dark gray crushed gneiss that contains alternating bands of quartz-feldspar and micaceous (mostly biotite less muscovite) minerals (defining the gneissose texture) and pyrope garnet poikiloblast, and lesser quartz than the other (b) less predominant light colored crushed gneiss. Both gneiss types contained iron sulfide minerals (but more common in the predominant dark gray gneiss particles) as small equant to irregular-shaped to elongated particles with characteristic metallic luster appearance and optically opaque natures. Multiple lapped cross sections of core show many such iron sulfide inclusions mostly concentrated in the dark gray crushed gneiss and lesser in light coarse aggregate throughout the entire depths of the cross sections. Clearly, abundant iron sulfide mineralization in the quarried stone coarse aggregate is established in the concrete, as was reportedly found in many other foundations from the northeast CT that has shown pyrrhotite-oxidation related cracking.

Therefore, despite the lack of any cracking in the core, or in the foundation wall from field photos, crushed gneiss coarse aggregate particles present in this core are found to contain pyrrhotite, similar to the other pyrrhotite-bearing crushed gneiss coarse aggregate particles from other residential foundations that have shown cracking due to oxidation of pyrrhotite in those gneiss aggregates. It is, therefore, suspected that the crushed gneiss found in the



present core is compositionally similar to crushed gneiss found in other coarse aggregates from other distressed residential foundations and probably derived from the same aggregate quarry (Becker's quarry) that is known to supply unsound pyrrhotite-bearing gneiss to other distressed concretes.

XRD analyses of coarse aggregate particles extracted from the core have confirmed the iron sulfide minerals to be pyrrhotite, along with ferrihydrite as its oxidation product, which are, again, in line with previous findings from other deteriorated foundations (Wille and Zhong, 2016, Jana 2017). XRD and XRF studies of both crushed gneiss types showed characteristic difference in mineralogy and chemistry between these types, e.g., having higher quartz in lighter brown particle, higher pyrrhotite in darker gray particles, higher iron oxide and sulfate in dark gray particle in XRF, etc.

Sulfate contents (as SO_3) in five crushed gneiss coarse aggregate particles extracted from the core are wide, e.g., from almost none to as high as 1 percent (determined from X-ray fluorescence analyses). These sulfate levels, however, are less than the sulfate (SO_3) levels found in similar crushed gneiss coarse aggregate particles from other residential foundations in eastern Connecticut where as high as 10 percent or more sulfur (SO_3) was detected in the similar dark gray crushed gneiss coarse aggregate, which was 10 times higher than the minimum 1 percent SO_3 limit by mass of aggregates established in many codes and guidelines. Clearly, there is a large range of sulfate contents in crushed gneiss coarse aggregate particles in the concrete where gneiss was supposedly quarried from the Becker's quarry, which is due to similar large range of iron sulfide mineral contents in this gneiss in the quarry, which is probably responsible for finding deleterious reactions and unsoundness of gneiss coarse aggregate in some residential foundation walls (where sulfate in aggregate were high), but not in all. Although only five crushed gneiss coarse aggregate particles were extracted from the present core for XRF analyses of sulfates, and it is quite possible that there may be some crushed gneiss particles still present in this concrete that have much higher sulfate (and pyrrhotite) levels than 1 percent SO_3 , perhaps as high as 10 percent SO_3 or more as found in other similar gneiss coarse aggregates from distressed foundations, but based on the observed sulfate levels in five extracted coarse aggregate particles it is possible that perhaps lack of cracking and pyrrhotite-related distress in the present foundation is due to low sulfate (and pyrrhotite) level of crushed gneiss coarse aggregate in this concrete compared to other similar gneiss from other distressed foundations. It is important to note that sulfate is commonly contributed not only from pyrrhotite but also from its close cousin, pyrite, and other sulfide minerals that may be present in gneiss, but for the present gneiss from Becker's quarry, as is found in other distressed foundations from eastern Connecticut it is mostly contributed from pyrrhotite.

Contrary to the extracted crushed gneiss coarse aggregate particles, XRD analysis of bulk concrete, however showed 1.8 percent pyrrhotite, with a total sulfate level of 0.678 percent which has not only confirmed the presence of pyrrhotite in the concrete and that it was contributed from crushed gneiss coarse aggregate but also its potential to cause oxidation-related distress in concrete as found in other similar gneiss coarse aggregates in distressed concretes. Despite the potential for distress, absence of any visible or invisible cracking in the core indicates absence of moisture – the essential player for oxidation of pyrrhotite and subsequent release of sulfate to cause internal sulfate attack in concrete.

Microcracking within many pyrrhotite-bearing crushed gneiss coarse aggregates occurs due to pyrrhotite oxidation, which is often associated with reddish brown oxidation products of pyrrhotite, and microcracks often extend from unsound aggregates to paste – this is the first microstructural evidence of distress due to primary expansion of unsound aggregate *per se* that are distinct in numerous photomicrographs of thin sections of concretes from other residential foundations of eastern Connecticut studied by the present laboratory. Many times, microcracks simply follow the micaceous bands in gneiss due to the internal plane of weakness along the micaceous bands of gneissose-textured rock. The gneissose texture of crushed gneiss coarse aggregate particles consisting of alternating bands of denser quartzo-feldspathic minerals and flaky (cleavable) biotitic mica provide additional inherent planes of weaknesses (foliation) in the aggregate that are susceptible to develop cracking along the internal planes of weakness along the biotite bands during expansions from pyrrhotite oxidation. As a result, a lot of cracks within the gneiss coarse aggregate particles are found along the weak bands of mica flakes. In many particles, however, no such preferential path of aggregate cracking was noticed. Detailed examinations of crushed gneiss coarse aggregate particles in the present core, both from stereomicroscopical examination of lapped cross section and petrographic



microscopical examination of thin section have failed to detect similar microcracking and associated reddish brown oxidation product of pyrrhotite.

Petrographic examinations of distressed residential foundations from other homes of eastern Connecticut has also detected abundant secondary ettringite crystallization lining or filling many air voids and occasionally lining some microcracks that are indicative of prolonged presence of moisture in those concretes during service, which, as mentioned, is an essential pre-requisite for pyrrhotite oxidation. Presence of moisture also indicates availability of sulfates to be released from pyrrhotite-oxidation and for subsequent ettringite crystallization, which, however, may or may not have necessarily derived from pyrrhotite oxidation since ettringite-filled air-voids are a very common microstructural feature in a concrete exposed to moisture without even any iron sulfide contaminant. Any Portland cement concrete exposed to moisture during service forms secondary ettringite deposits lining and filling air voids. To establish the source of secondary ettringite i.e. from Portland cement's sulfate and/or from oxidation of pyrrhotite-bearing aggregates require determination of sulfate levels in concrete i.e. if the level is higher than that expected from a typical Portland cement concrete where sulfate (as SO_3) content in cement is around 3 weight percent i.e. giving about 0.45 percent sulfate in concrete for a usual cement content of 15 percent by mass of a normal weight concrete. Excess sulfate in concrete above 0.45 percent from cement's contribution would then correspond to the pyrrhotite-aggregate source if no other sulfate source were present. To determine the sulfate (SO_3) level of bulk concrete, a thin slice of concrete was sectioned through the entire length of the core traversing the full thickness of the foundation wall and pulverized for XRF analysis, which showed 0.678 percent bulk sulfate (SO_3) by weight of concrete, which is higher than that normally contributed from Portland cement. Clearly, observed sulfate content of concrete indicates a sulfate source other than Portland cement, which is most likely sourced from pyrrhotite in coarse aggregate.

Despite the high sulfate content of concrete (i.e. higher than that contributed from Portland cement), however, petrographic examinations of paste in the present core did not detect any potentially deleterious secondary ettringite, which was found in other distressed foundations, indicating, again that the moisture, the essential ingredient for release of sulfate from pyrrhotite to the paste, was not present for the present concrete during its service.

To establish secondary expansion of paste from internal sulfate attacks by reactions between sulfates released from pyrrhotite oxidation and cement hydration products, microstructural evidence for expansion of the sulfate-contaminated hydrated cement paste has to be established. A common microstructural evidence of paste expansion commonly attributed to delayed ettringite formation (DEF) in many steam-cured precast concrete elements is gaps or separations around aggregates due to direct expansion of paste relative to aggregate (Jana 2008), where widths of the gaps are usually proportional to the size of the aggregates around which the gaps are formed from paste expansion. Optical microscopy did not detect any such gaps around aggregates, or, similar features as found in many cracked precast concrete members deteriorated by delayed ettringite formation. Another feature common in sulfate attacks from internal or external sulfates is ettringite filled cracks, which was found in other distressed foundations but was absent in the present concrete. Therefore, the possibility of paste expansion from an internal sulfate attack by reactions between excess (i.e. beyond cement's contribution) sulfates released from pyrrhotite oxidation and cement hydration products are not diagnosed for the present foundation.

Therefore, contrary to other pyrrhotite-oxidation-related cracking in residential foundations from eastern Connecticut, examined core from the foundation of Rogers and Swaminathan's residence has failed to show any microstructural evidence of (a) primary expansion of concrete due to oxidation of pyrrhotite in crushed gneiss coarse aggregate to cause cracking within the unsound aggregate particles or their extension into paste, and (b) secondary expansion of paste due to formation of poorly crystalline (perhaps also colloidal formed) secondary ettringite in relatively confined areas in sulfate-contaminated paste (called ettringite infested paste) that are the breeding ground for internal sulfate attack causing paste expansion and associated cracking in other distressed foundations.

In accelerated pyrrhotite oxidation test, multiple crushed gneiss coarse aggregate particles are extracted from the core, cleaned of adhered paste remains, crushed, then immersed in a 35% hydrogen peroxide (strong oxidant) solution for 24 hours. Sulfates released from aggregates to the filtrates are measured (as SO_4^{2-}) in an anion exchange chromatograph. All particles show release of sulfates as opposed to no sulfate released from a control gneiss



aggregate in previous studies containing no pyrrhotite. The high pH environment of Portland cement concrete is also known to enhance pyrrhotite oxidation (Divet and Davy 1996).

Case studies on pyrrhotite-oxidation-related distress of concrete foundations from eastern Connecticut by the present laboratory have confirmed and provided clear mechanisms of the common consensus that the observed cracking and reported crumbling of many concrete foundation walls in eastern Connecticut is due to: (a) oxidation of pyrrhotite in crushed garnetiferous quartzo-feldspathic gneiss coarse aggregate particles *in the presence of oxygen and moisture during service in concrete* with the formation of ferrihydrite causing expansion of the unsound aggregates and formation of cracks from unsound aggregates to paste, which was then followed by (b) additional expansion in the paste from reactions between sulfates released from pyrrhotite oxidation and cement hydration products (internal sulfate attack) and formation of poorly crystalline or perhaps colloidal ettringite within the confined spaces in paste. The present examined concrete core from the foundation of Rogers and Swaminathan's residence, however, failed to provide similar evidence of pyrrhotite-oxidation-related distress or its manifestation as cracking – this indicates that the moisture, the essential ingredient for pyrrhotite-oxidation and subsequent internal sulfate attack of concrete was not present in this foundation at least *at the time of this investigation*.

If the pyrrhotite-bearing crushed gneiss coarse aggregate found in this concrete was indeed from the Becker's quarry as reported for other foundations undergoing pyrrhotite-oxidation-related distress, then due to the known geology of pyrrhotite mineralization in the hydrothermal vein in which this quarry is situated, and its known devastating effects when used in concrete from case studies of multiple homes (Wille and Zhong 2016, Jana 2017), use of crushed stone from this quarry for concrete aggregate should be abandoned, or should only be used after extensive evaluation of aggregates for the presence of pyrrhotite (e.g., from magnetic test, total sulfur test from XRF, XRD detection of pyrrhotite amount) and its potential release of sulfate in an accelerated oxidation test of aggregates.

Aggregate to be used in a new foundation from other quarries must be evaluated for the possible presence of any unsound constituents, including iron sulfide minerals, e.g., (a) from XRD analysis of quarried stones to detect the amount and speciation of iron sulfide minerals present, (b) from XRF analysis to detect the total sulfur (as SO_3) content of quarried stones, (d) from accelerated oxidation test to detect the rate and level of sulfates that can be released from aggregates, and (e) even from a magnetic test to separate weakly magnetic pyrrhotite grains from other non-magnetic iron sulfide minerals.

Since there is no industry specification on the threshold pyrrhotite limit above which potential for oxidation-related distress can occur, and, in fact as low as 0.3% pyrrhotite by mass of aggregate in the host rock has reportedly shown severe distress in concrete (e.g., in Quebec Canada), the best solution is to avoid aggregates containing pyrrhotite for its known damaging affects without further laboratory verification of its potential unsoundness in concrete (e.g., from expansion of mortar bar or concrete prism tests similar to those used for ASR-expansion).

Absence of visible or invisible cracking in the present foundation and absence of evidence of pyrrhotite-oxidation-related distress in concrete at the time of this investigation only confirms possible absence of moisture in this foundation concrete since moisture is the essential ingredient for the distress to occur, or perhaps, slow uptake of moisture through the wall in which case moisture-induced oxidation and related distress may occur in future considering the fact that most of pyrrhotite-related distress in residential foundations of eastern Connecticut has surfaced after 10 to 20 years of construction, the time period within which the present foundation reportedly falls.



INTRODUCTION

Reported herein are the results of detailed laboratory studies of a hardened concrete core reportedly retrieved from an existing foundation wall of a residential home located at 154 Coventry Road in Mansfield, Connecticut. The concrete wall is reportedly sound and crack free, however, the homeowner plans to sell the home and due to the known pyrrhotite-related distress in many concrete foundation walls from the area, detailed laboratory analyses were requested to investigate the presence and amount of pyrrhotite and its potential to cause deterioration of concrete.

PURPOSE OF PRESENT INVESTIGATION

Based on the background information, the purposes of the present investigation, therefore, are to determine: (a) the composition, quality, and overall condition of concrete in the wall as represented by the core; and particularly (b) detection of any possible physical or chemical deterioration of concrete that may have contributed to the reported cracking or spalling of the foundation wall; and (c) detection of any pyrrhotite presence in the concrete aggregates, and, if such mineral has caused the reported distress due to its known deleterious effects on durability of concrete from other studies in the region.

BACKGROUND INFORMATION

The following information was received in a letter of transmittal with the sample from Ms. Rogers:

“The owners are planning to sell and need a report documenting the condition of the foundation, the extent to which pyrrhotite is present, and the likelihood of future deterioration.

The foundation is currently in good condition with no visible horizontal cracking on the exterior or interior. There are small vertical cracks in a few places possibly due to settlement.

The foundation was poured in July/August of 2005.

The sample was taken from the western wall of the foundation. Pictures are attached.

Mix design unknown.”

Figure 1 shows field photographs of the subject foundation wall that *does not* show random and/or closed polygonal-shaped map cracking that are common and found in many other homes from the neighborhood from pyrrhotite-related distress in concrete. The top left photo in Figure 1 shows the core location from a wall extracted from near the ground-level along with the core of this study after extraction. The retrieved 8 in. (200 mm) length of the core represents partial thickness of the wall. The wall in all photos appears to be present in sound condition without any cracking, except some long striation marks that are judged unrelated to any concrete distress.

FIELD PHOTOGRAPHS



Figure 1: Field photographs showing the overall sound condition of the foundation walls, and the location on the wall from where the core for the present study was reportedly retrieved (top left photo).



METHODOLOGIES

OPTICAL MICROSCOPY (FOR OVERALL CONDITION OF CONCRETE AND AGGREGATES)

The core was tested and examined by following the methods of ASTM C 856 “Standard Practice for Petrographic Examination of Hardened Concrete.” Details of petrographic examinations and sample preparation are described in Jana (2006). The steps of petrographic examinations include (Jana 2006):

- i. Visual examinations of the core, as received to trace all visible cracks, if any;
- ii. Low-power stereomicroscopical examinations of as-received, saw-cut and freshly fractured sections, and lapped cross sections of core for evaluation of concrete composition, condition, extent of cracking (if any), detection of iron sulfide minerals, etc.;
- iii. Low-power stereomicroscopical examinations of air content and air-void system of concrete as well as detection of iron sulfide minerals (amount and distribution) in the lapped cross sections;
- iv. Examinations of oil immersion mounts in a petrographic microscope for mineralogical compositions of specific areas of interest;
- v. Examinations of un-treated and fluorescent-dye-mixed (to highlight open spaces, cracks, etc.) epoxy-impregnated treated lapped cross sections of concrete in a stereomicroscope for detailed compositional and microstructural analyses;
- vi. Examinations of fluorescent dye-mixed (to highlight open spaces, cracks, etc.) epoxy-impregnated large area (50 mm × 75 mm) thin sections of concrete in a stereomicroscope and in a petrographic microscope for detailed compositional and microstructural analyses;
- vii. Photographing sample as received, and during preparation with a digital camera and a flatbed scanner;
- viii. Photomicrographs of full-length lapped cross sections and thin sections of core taken with stereomicroscope and petrographic microscope, respectively to provide detailed compositional, microstructural, and mineralogical information of concrete;
- ix. Detailed compositional, mineralogical, and microstructural examinations of concrete in a petrographic microscope from thin sections;
- x. Selection of areas of interest in the thin sections for subsequent examinations in scanning electron microscope;
- xi. A Nikon Eclipse 600 POL petrographic microscope attached to a Jenoptik Progres GRYPHAX high-resolution digital camera were used for petrographic examinations and collecting photomicrographs of thin sections of concretes (Figure 2). A Nikon SMZ-10A stereomicroscope (Figure 2) and an Olympus SZH stereo zoom microscope (equipped with transmitted polarizing light facilities) were used for examinations of fresh fractured and lapped sections and transmitted-light examinations of thin sections, respectively.



Figure 2: Optical Microscopy: Left - A Nikon Eclipse E600 POL polarizing (petrographic) microscope at left with reflected, transmitted, polarized-light, and fluorescent-light capabilities; Middle – An Olympus SZH reflected/transmitted/polarized-light Stereozoom microscope; and Right – A Nikon SMZ-10A Stereozoom microscope. All microscopes are equipped with Jenoptik Gryphax and Lumenera Infinity digital cameras.

X-RAY DIFFRACTION (FOR MINERALOGY OF UNSOUND AGGREGATE, IDENTIFICATION OF IRON SULFIDE PHASES & THEIR OXIDATION PRODUCTS)

A few crushed stone coarse aggregate particles containing metallic-lustered iron sulfide minerals (as detected from the core as received, and from its lapped cross section) were extracted from the core, pulverized, and used for X-ray diffraction to determine the iron sulfide species (e.g., pyrite, pyrrhotite) present in the aggregate.



Figure 3: XRD: Siemens D5000 X-ray diffractometer and MDI Jade search/match software used for determination of mineralogical compositions of extracted concrete aggregates. Left to right: Rocklab pulverizer for initial grinding of aggregate with anhydrous alcohol; McCrone micronizing mill for final grinding; Spex 25-ton press for pellet preparation; Siemens D5000 X-ray diffractometer; and custom-made sample holder to place a 32-mm diameter pellet on sample stage.



A Rocklab pulverizer was used to grind the extracted aggregate particles down to finer than 100 microns. Usually, a few drops of anhydrous alcohol are added to reduce decomposition of any hydrous phases from the heat generated from grinding. Approximately 10 grams of sample was ground first in the Rockland pulverizer, from which about 8.0 grams of sample was selected, mixed with three binder tablets (total binder weight of 0.6 grams, for a fixed binder proportion of 7.5%), the mixture is then further ground in Rocklab pulverizer and in a McCrone micronizing mill down to finer than 44 micron size. Approximately 7.0 grams of binder-mixed pulverized sample thus prepared was weighed into a stainless steel die to prepare the sample pellet. A 25-ton Spex X-press was used to prepare 32 mm pellet from the pulverized sample. The same pellet is used for XRD to determine the mineralogy and XRF to determine the chemical composition.

X-ray diffraction was carried out in a Siemens D5000 Powder diffractometer (θ - 2θ goniometer, Figure 3) employing a long line focus Cu X-ray tube, divergent and anti-scatter slits fixed at 1 mm, a receiving slit (0.6 mm), diffracted and incident beam Soller slits (0.04 rad), a curved graphite diffracted beam monochromator, and a sealed proportional counter. Generator settings used are 40 kV and 30mA. Sample was placed in a custom-made circular sample holder and excited with the copper radiation of 1.54 angstroms. Tests were scanned at 2θ from 4° to 64° with a step of 0.02° 2θ integrated at 1 sec. step^{-1} dwell time.

The resulting diffraction patterns were collected by DataScan 4 software of Materials Data, Inc. (MDI), analyzed by Jade software of MDI with ICDD PDF-4 (Minerals 2017) diffraction data. Phase identification, and quantitative analyses were carried out with MDI's Search/Match, Easy Quant, and Rietveld modules, respectively.

SCANNING ELECTRON MICROSCOPY AND ENERGY-DISPERSIVE X-RAY SPECTROSCOPY (SEM-EDS) (FOR MICROSTRUCTURE & COMPOSITION OF DETERIORATED CONCRETE & UNSOUND AGGREGATE)

Products of oxidation of iron sulfide minerals and associated possible secondary ettringite/thaumasite reaction products and reaction microstructures were examined in detail by SEM-EDS. Procedures for SEM examinations are described in ASTM C 1723.

Polished and gold-palladium coated thin sections of core already examined by optical microscopy were selected for SEM-EDS studies and examined in a Cambridge CamScan Series II scanning electron microscope equipped with a backscatter detector, a secondary electron detector, and x-ray fluorescence spectrometer (Figure 4) to observe pyrrhotite or other potentially unsound constituents in concrete and aggregate and their effect on the performance and durability of concrete, as well as evidence of internal sulfate attack and secondary ettringite formation in the paste from released sulfate.



Figure 4: SEM-EDS: Cambridge CamScan Series II Scanning Electron Microscope and 4Pi Revolution software, backscatter detector, secondary electron detector, and energy-dispersive X-ray fluorescence spectrometer used for microstructural and microchemical analyses of concrete and aggregate.

ENERGY-DISPERSIVE X-RAY FLUORESCENCE SPECTROSCOPY (ED-XRF) (FOR OXIDE COMPOSITION & SULFUR (SO₃) LEVEL OF UNSOUND AGGREGATE & CONCRETE)

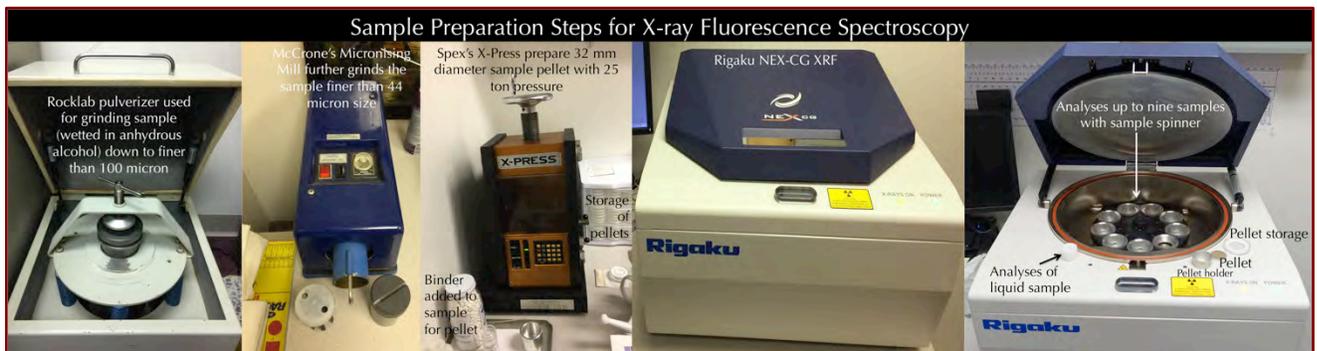


Figure 5: XRF: Rigaku NEX-CG bench-top ED-XRF unit used for bulk chemical compositions of aggregates.

An energy-dispersive bench-top X-ray fluorescence unit from Rigaku Americas Corporation (NEX-CG, Figure 5) was used for determination of bulk chemical (oxide) composition and sulfur (as SO₃) content of unsound aggregate particles, and concrete. The instrument is calibrated by using various certified (CCRL, NIST, GSA, and Brammer) reference standards of rocks. The sample pellet prepared for X-ray diffraction is used for X-ray fluorescence studies as well. The main focus of this analysis was to determine the sulfur content (as SO₃) in the aggregate particles as well as sulfate content (as SO₃) in concrete.

ION CHROMATOGRAPHY (FOR RELEASED SULFATES FROM UNSOUND AGGREGATES)

Pyrrhotite-bearing coarse aggregate particles extracted from the core were pulverized to pass No. 20 sieve, then digested in a hydrogen peroxide (35%) solution for various days for accelerated oxidation, then filtered through 0.45-micron micro-filter paper under vacuum.

The filtrate was then diluted to 250 mL with distilled water to be analyzed by Metrohm's 861 Advanced Ion Chromatograph (Figure 6) for determination of released sulfates from oxidation of sulfides.

Procedures followed in Ion chromatography are described in ASTM D 4327 "Standard Test Method for Anions in Water by Chemically Suppressed Ion Chromatography." The IC was calibrated against six (6) different custom-made Metrohm anion standard solutions having sulfate from 0.1-ppm to 100-ppm levels.



Figure 6: IC: Metrohm 861 Advanced IC used for analysis of sulfate released from aggregate.

SAMPLE

PHOTOGRAPHS, IDENTIFICATION, INTEGRITY, AND DIMENSIONS

Received was one concrete core identified as 71318W. Figure 7 shows the exposed formed surface of the core on the left that represents the foundation wall's interior surface, the fresh fractured inside surface on the right due to partial-depth extraction of the core from the wall, and, the cylindrical side views of the core in the middle column. The core is 8 in. (200 mm) in total length, and 3⁵/₈ in. (92 mm) in nominal diameter.

END SURFACES

The exposed surface of core (wall) is a smooth flat formed surface of wall with no visible cracking (Figure 6, top left photo of core). The opposite surface is fresh fractured.



Figure 7: Shown are the location on the foundation wall from which the sample was taken (left), the formed exposed surface (right column top left), fresh fractured inside surface (right column top right), and cylindrical side view of the core (right column bottom), as received. Arrows in the right column photo indicate the exposed surface.

CRACKING & OTHER VISIBLE DISTRESS

There are no visible cracks or signs of distress in the core as-received; the core was received in intact condition.

EMBEDDED ITEMS

There is no evidence of any fibers, wire mesh, reinforcing steel or other embedded items found in the core.

RESONANCE

The core has a ringing resonance, when hammered.

LABORATORY STUDIES

LAPPED, SAW-CUT, AND FLUORESCENT CROSS SECTIONS OF CORE

Figures 8 through 10 show: (a) two lapped cross sections (Figure 8 left and middle photos), (b) one saw-cut cross section after treatment with a phenolphthalein alcoholic solution to highlight non-carbonated concrete that has turned pink after treatment and carbonated concrete at the exposed surface region that has remained gray or light pink due to atmospheric carbonation of concrete (Figure 8 right photo), (c) two additional fluorescent dye-mixed epoxy-impregnated cross sections of core (Figure 9 left and 2nd from left photos) to highlight voids and cracks, if

any in the cross sections of core that are prominent when such sections are viewed in a short wavelength ultraviolet (UV) light in a dark room as shown in the 3rd and 4th from left photos in Figure 9.

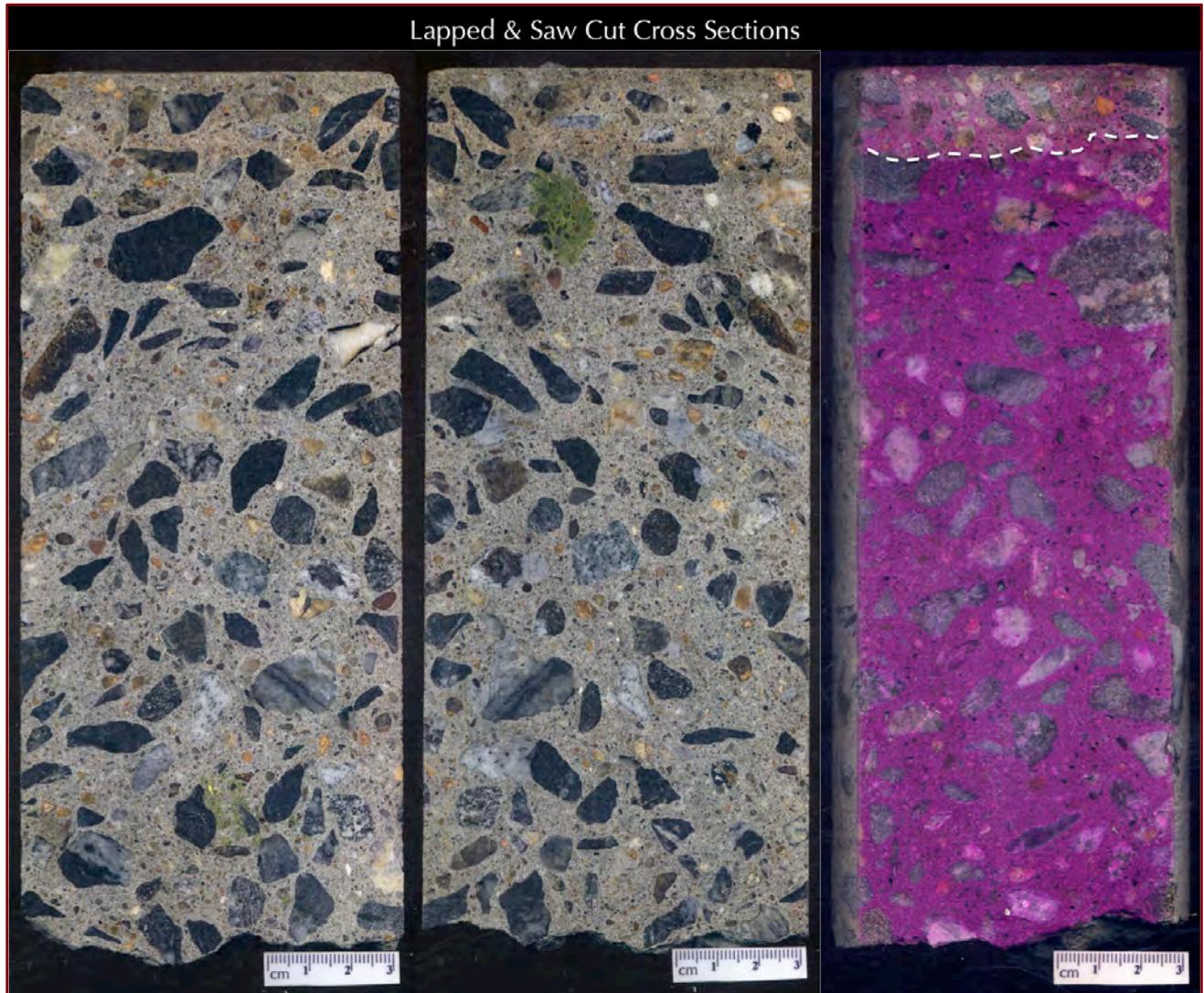


Figure 8: Lapped cross sections of the core showing: (a) no cracking in concrete as opposed extensive cracking found in many other foundation walls from eastern Connecticut that are affected by pyrrhotite-related distress in concrete; and (b) a saw-cut cross section at right after treatment with a phenolphthalein alcoholic solution to highlight non-carbonated concrete that has turned pink after treatment and carbonated concrete at the exposed surface region that remained gray or light pink to a depth of 20 to 30 mm from the exposed surface due to atmospheric carbonation of concrete. Notice good grading and well-distribution of the crushed stone coarse aggregate particles in all cross sections.

The startling feature from such exercises, especially after viewing two fluorescent epoxy-impregnated cross sections of core in UV light in Figure 9 is the absence of any cracking either in the crushed stone coarse aggregate particles or in the mortar fraction of concrete, which is the common microstructural manifestation of pyrrhotite-related distress in concrete. Concrete from other foundation walls from Eastern Connecticut areas that are affected by pyrrhotite-related cracking showed extensive cracking during such fluorescent treatments. Absence of such cracking in this examined core indicates sound condition of concrete at least during the time of this investigation. Air voids

in concrete as well as many coarse voids are highlighted in fluorescent treatment under UV light. Crushed stone coarse aggregate particles appear dark with no prominent cracking to be highlighted by absorption of fluorescent epoxy.

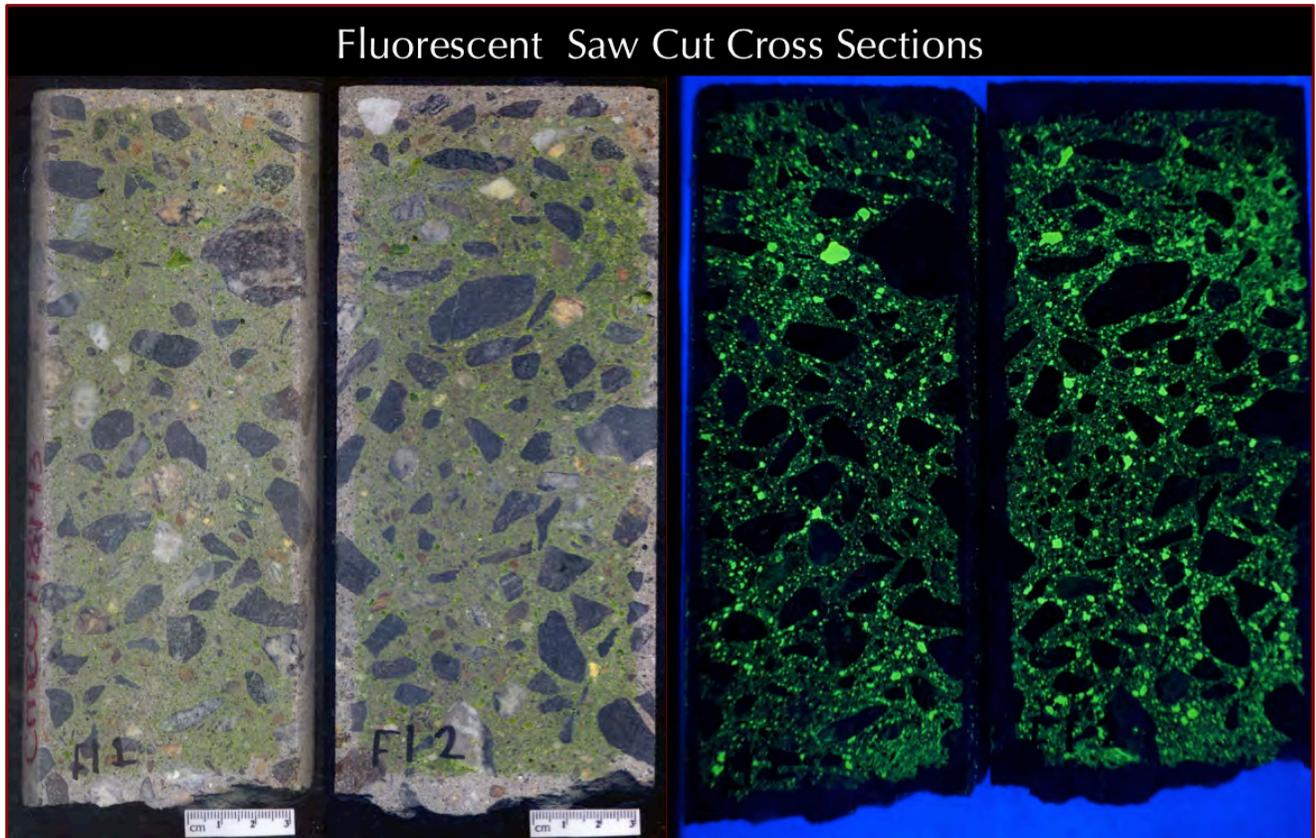


Figure 9: Fluorescent dye-mixed epoxy-impregnated cross sections of core (left and 2nd from left photos) to highlight voids and cracks, if any in the cross sections of core that are prominent when such sections are viewed in a short wavelength ultraviolet (UV) light in a dark room as shown in the 3rd and 4th from left photos.

Saw-cut cross section in Figure 8 shows non-carbonated nature of the interior concrete where the phenolphthalein-treated section has turned pink but carbonated portion at the 20 to 30 mm of exposed surface region has remained light grey to light pink color tone of paste. The dashed line separates the interior non-carbonated concrete from the carbonated exposed end of the wall. Depth of carbonation is measured to be a distance of 20 to 30 mm from the exposed face of the wall. Densification of paste due to carbonation at the exposed end of the core (foundation Wall) is clear in all cross sections.

Figure 10 shows photomicrographs of lapped cross section of core where metallic lustered golden or brown color tone iron sulfide minerals are marked with arrows for some individual dark gray to black crushed stone coarse aggregate particles (boxed). Many of these tiny particles marked with arrows are determined to be pyrrhotite-based iron sulfide minerals consistent with pyrrhotite found in similar coarse aggregate from other foundation walls in eastern Connecticut homes affected by pyrrhotite-related cracking. The present pyrrhotite inclusions did not show

any cracking or reddish brown oxidation products common in other homes, which indicate an absence of moisture that is necessary for oxidation of pyrrhotite and related cracking.

IRON SULFIDE MINERALS IN CRUSHED GNEISS COARSE AGGREGATE IN LAPPED CROSS SECTION

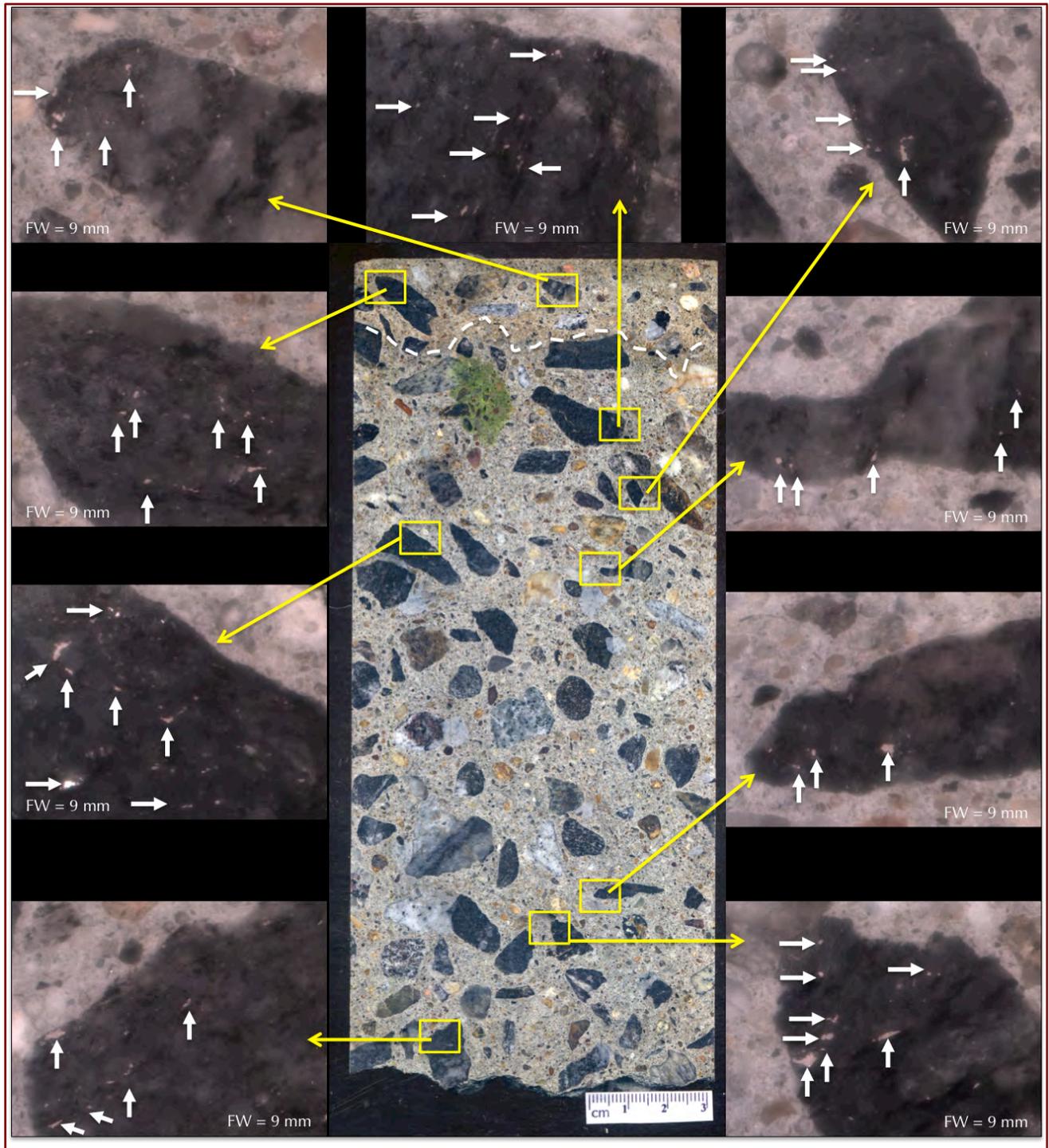


Figure 10: Lapped cross section of core and photomicrographs taken from various locations showing metallic lustered iron sulfide inclusions (arrows) in dark gray to black crushed stone coarse aggregate particles (boxed).

PHOTOMICROGRAPHS OF LAPPED CROSS SECTION

Figure 11 shows six (6) photomicrographs of lapped cross section of core from various depths, taken by using a stereomicroscope to depict the overall air-entrained nature of concrete.

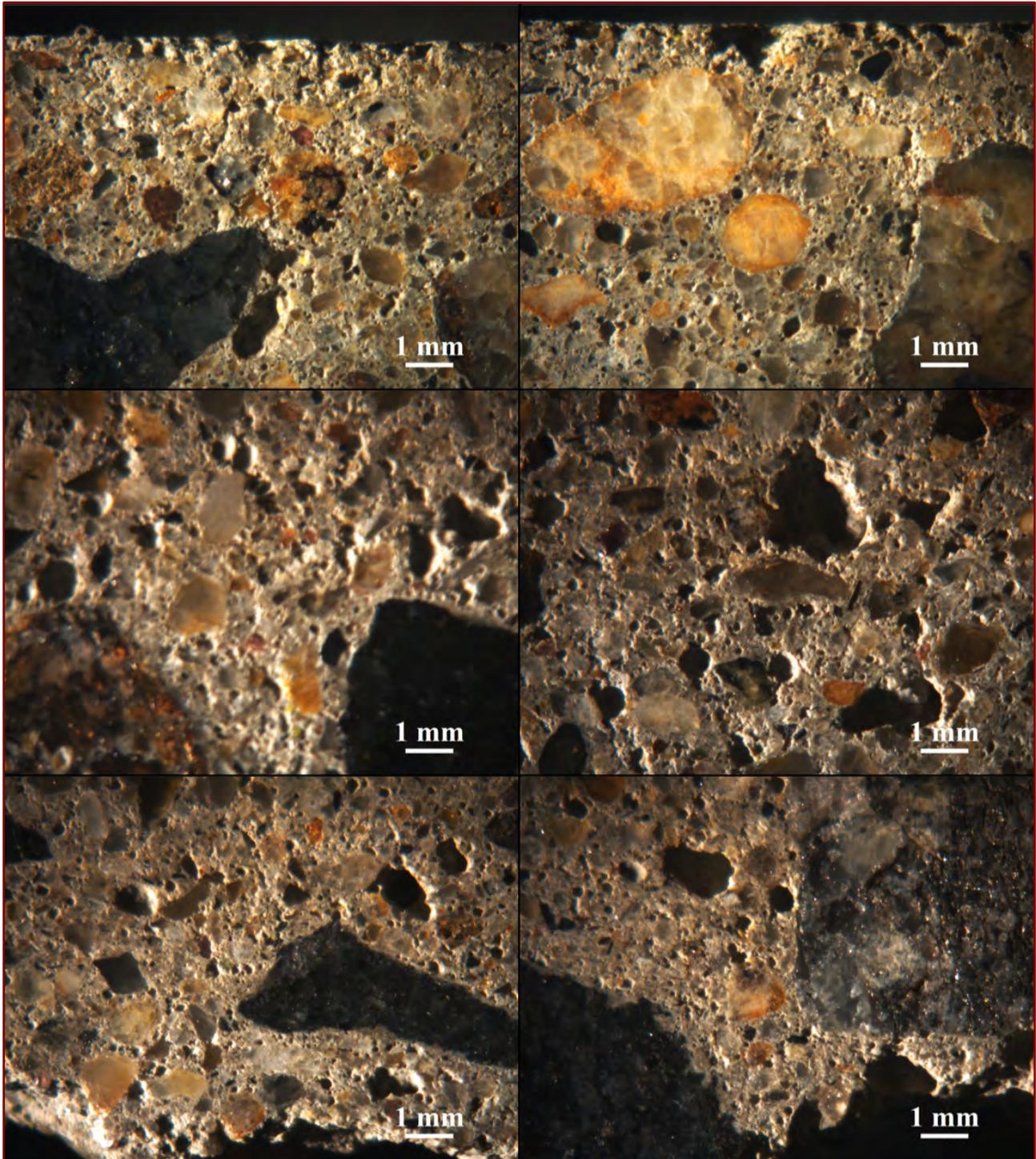


Figure 11: Photomicrographs of lapped cross section showing the air-entrained nature of concrete and many fine to coarse spherical and irregularly-shaped air-voids.

THIN SECTIONS

Figure 12 shows fluorescent dye-mixed epoxy-impregnated thin sections of core prepared from exposed surface region and interior of core to highlight voids, pore spaces, and cracks in concrete and aggregates.

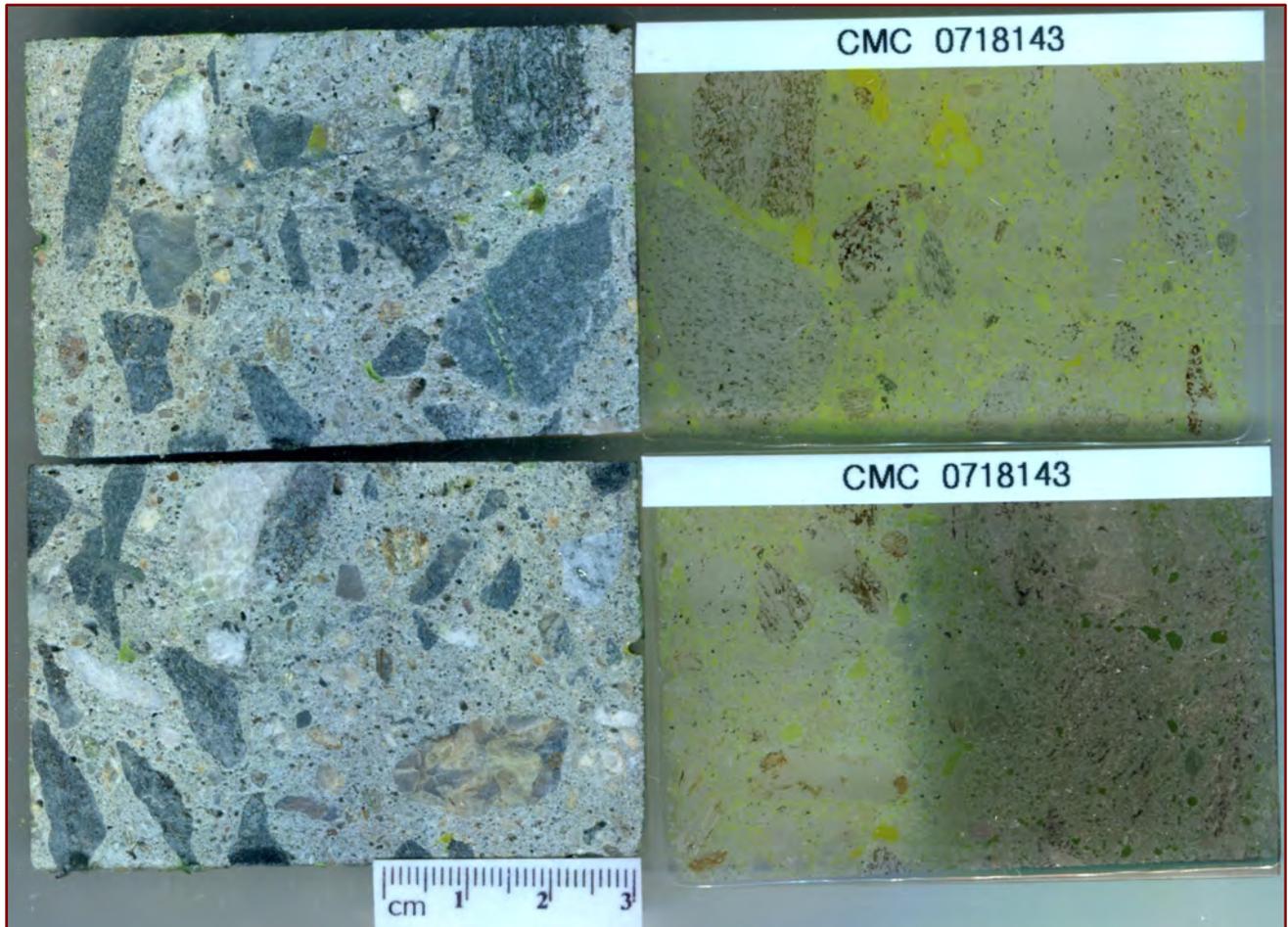


Figure 12: Fluorescent dye-mixed epoxy-impregnated thin sections (30 micron thickness) and corresponding residues left from thin sections. These thin sections are examined: (a) in a stereozoom microscope, in transmitted and reflected light modes along with UV light attachment to highlight pores, air voids, and cracks, and, (b) in a petrographic microscope to examine the microstructural features at higher magnifications than that from stereomicroscope. The bottom thin section at right was partially coated with thin film of gold for SEM-EDS studies.

REFLECTED-LIGHT PHOTOMICROGRAPHS OF FLUORESCENT THIN SECTIONS

Figure 13 shows photomicrographs of fluorescent-epoxy impregnated thin sections of core viewed in a reflected-light Stereozoom microscope equipped with UV light facilities to examine the fluorescent thin section in such light.

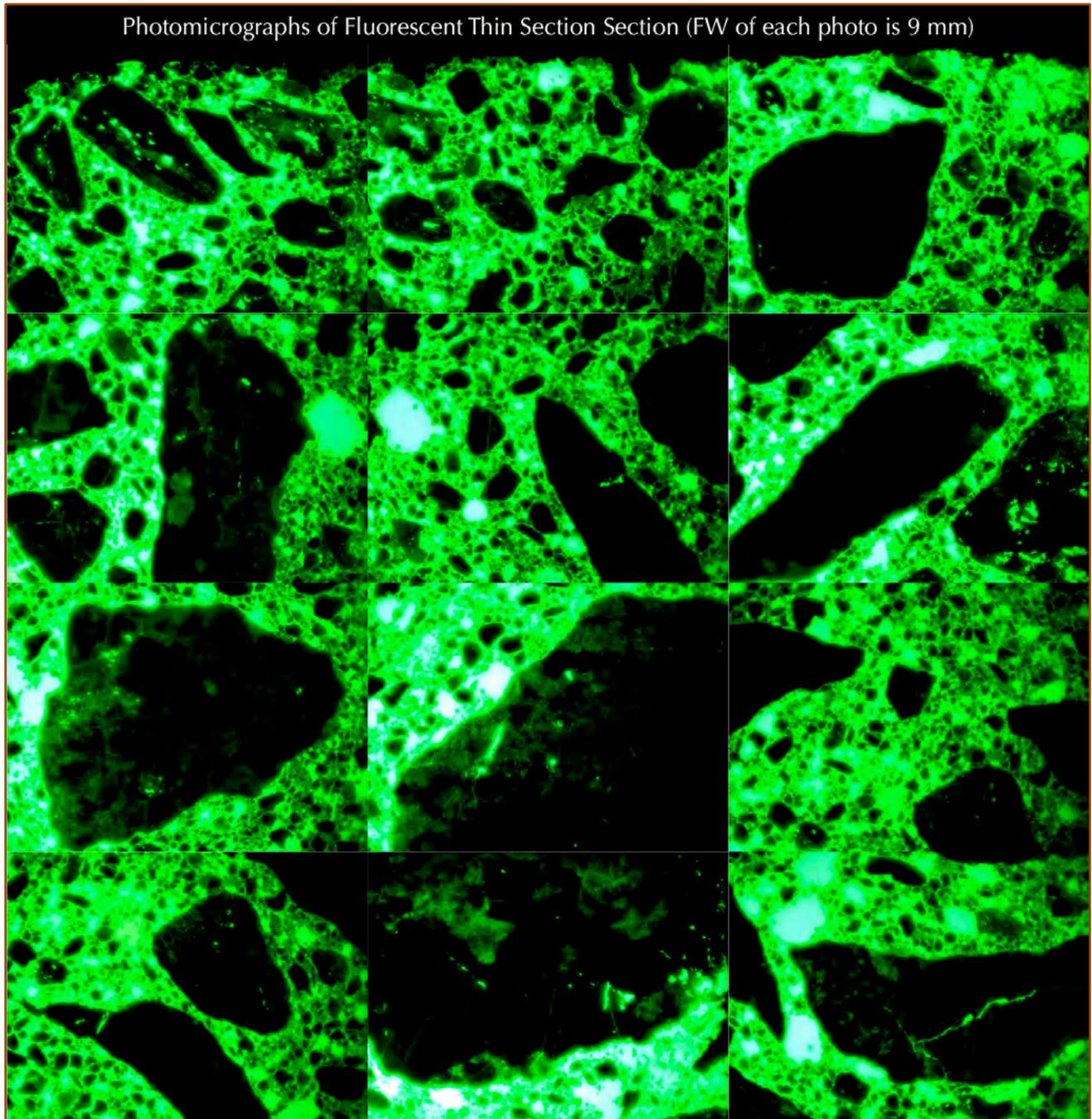


Figure 13: Photomicrographs of fluorescent-epoxy impregnated thin section of core viewed in a reflected-light Stereozoom microscope equipped with UV light facilities to highlight porous areas, air voids, and cracks in aggregates and concrete.

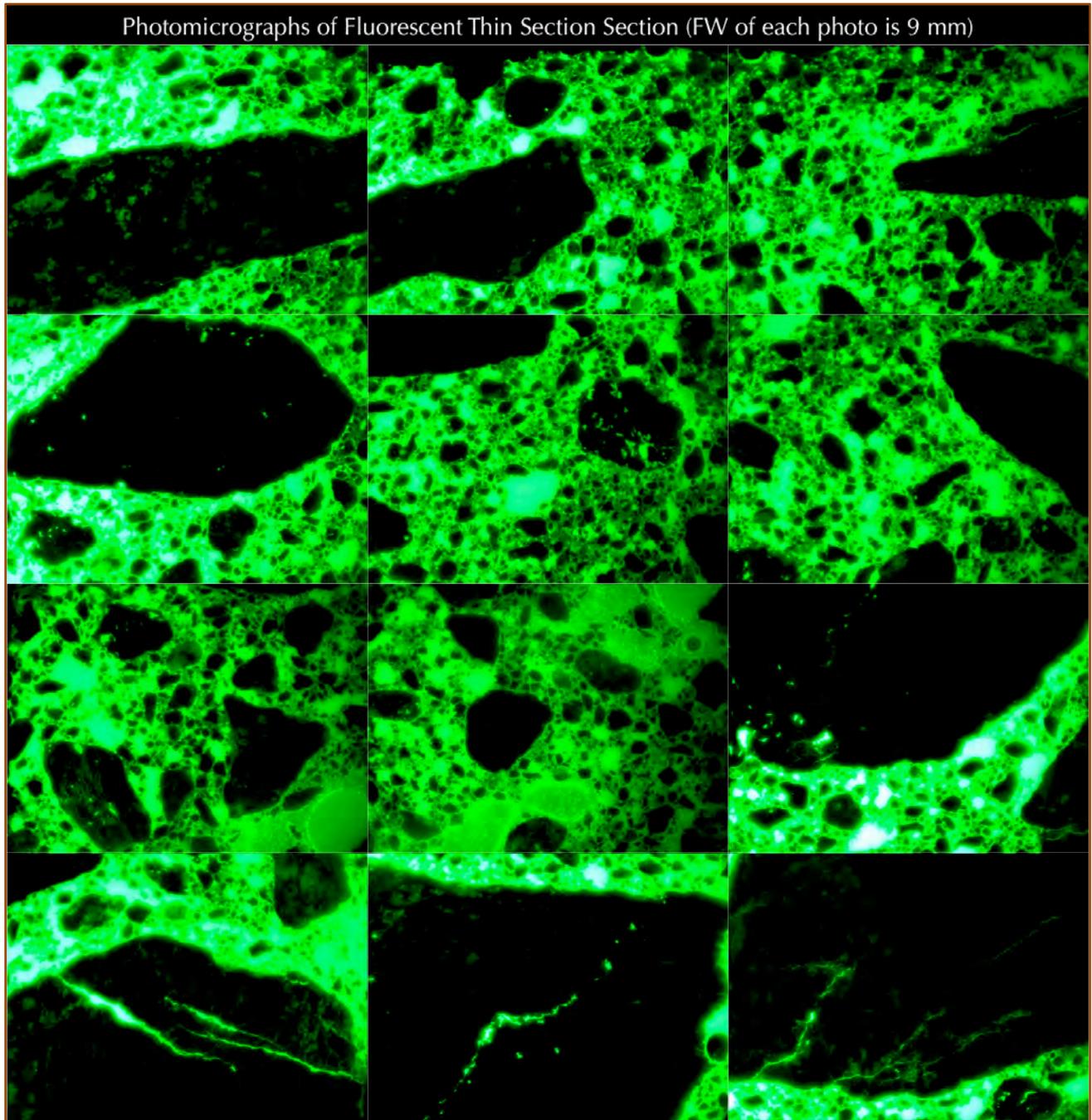


Figure 14: Photomicrographs of fluorescent-epoxy impregnated thin section of core viewed in a reflected-light Stereozoom microscope equipped with UV light facilities to highlight porous areas, air voids, and cracks in aggregates and concrete.

This UV-light examination of fluorescent thin sections at high magnification in a stereomicroscope shows the overall sound condition and absence of cracking in the concrete and in its aggregates, except for some minor areas (e.g., the bottom row in Figure 14) where a few crushed stone particles show some cracking highlighted by the absorbed fluorescent epoxy.

PHOTOMICROGRAPHS OF FLUORESCENT THIN SECTIONS

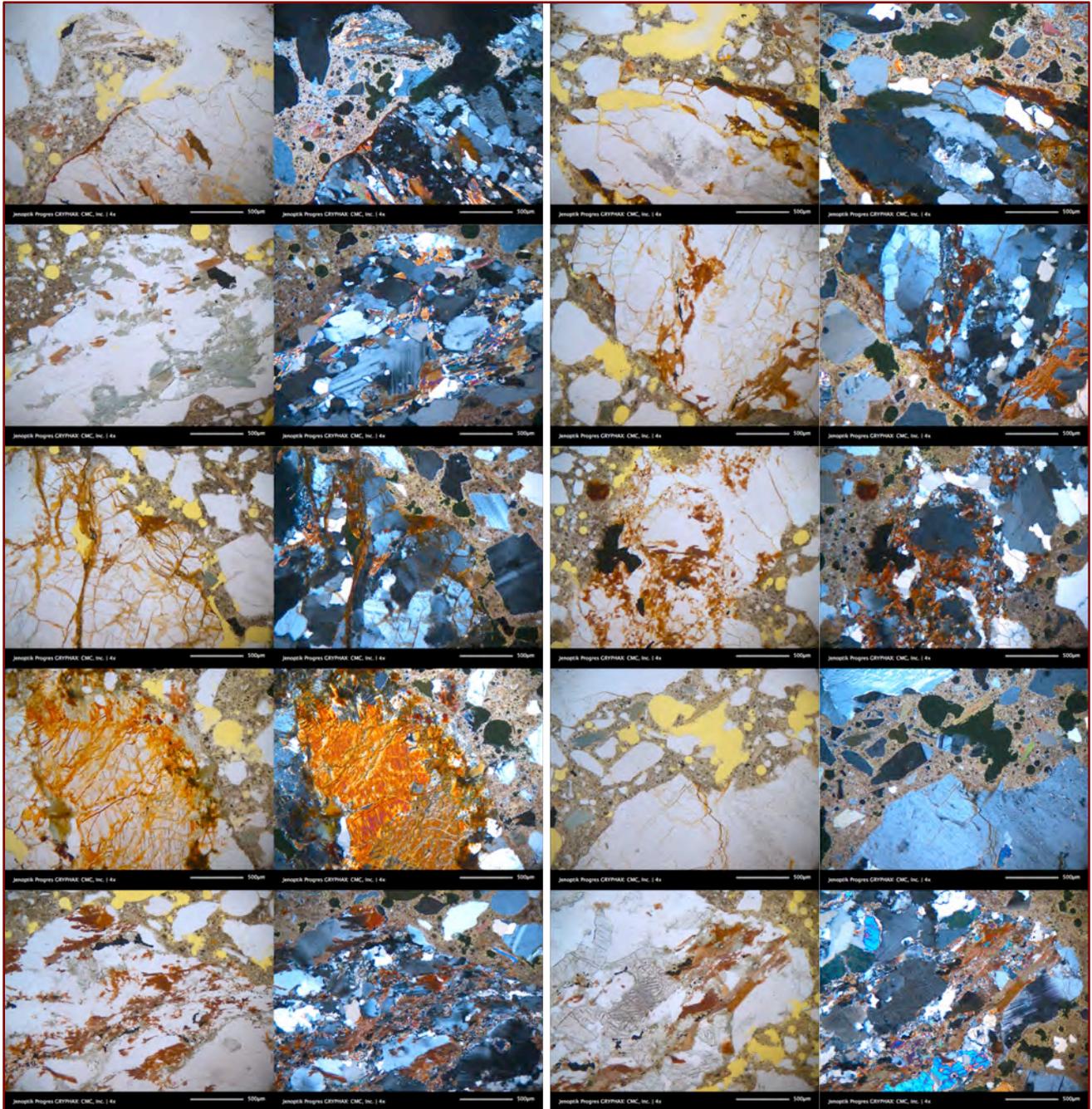


Figure 15: Photomicrographs of blue dye-mixed epoxy-impregnated thin section (30 micron thickness) of core showing: (a) crushed gneiss coarse aggregate having alternating bands of light-colored quartzo-feldspathic and dark brown colored pleochroic biotite and light-colored muscovite/chlorite micaceous minerals defining the gneissose texture common in these crushed gneiss coarse aggregate particles, (b) dark opaque iron sulfide and iron oxide minerals, (c) poikiloblastic garnet grains with mineral inclusions in gneiss, and (d) the absence of cracking or reddish brown oxidation of iron sulfide inclusions in gneiss coarse aggregate. Air voids are highlighted by fluorescent-dye-mixed epoxy. Right column photomicrographs were taken in crossed-polarized light mode and left column in corresponding plane polarized mode in a petrographic microscope.

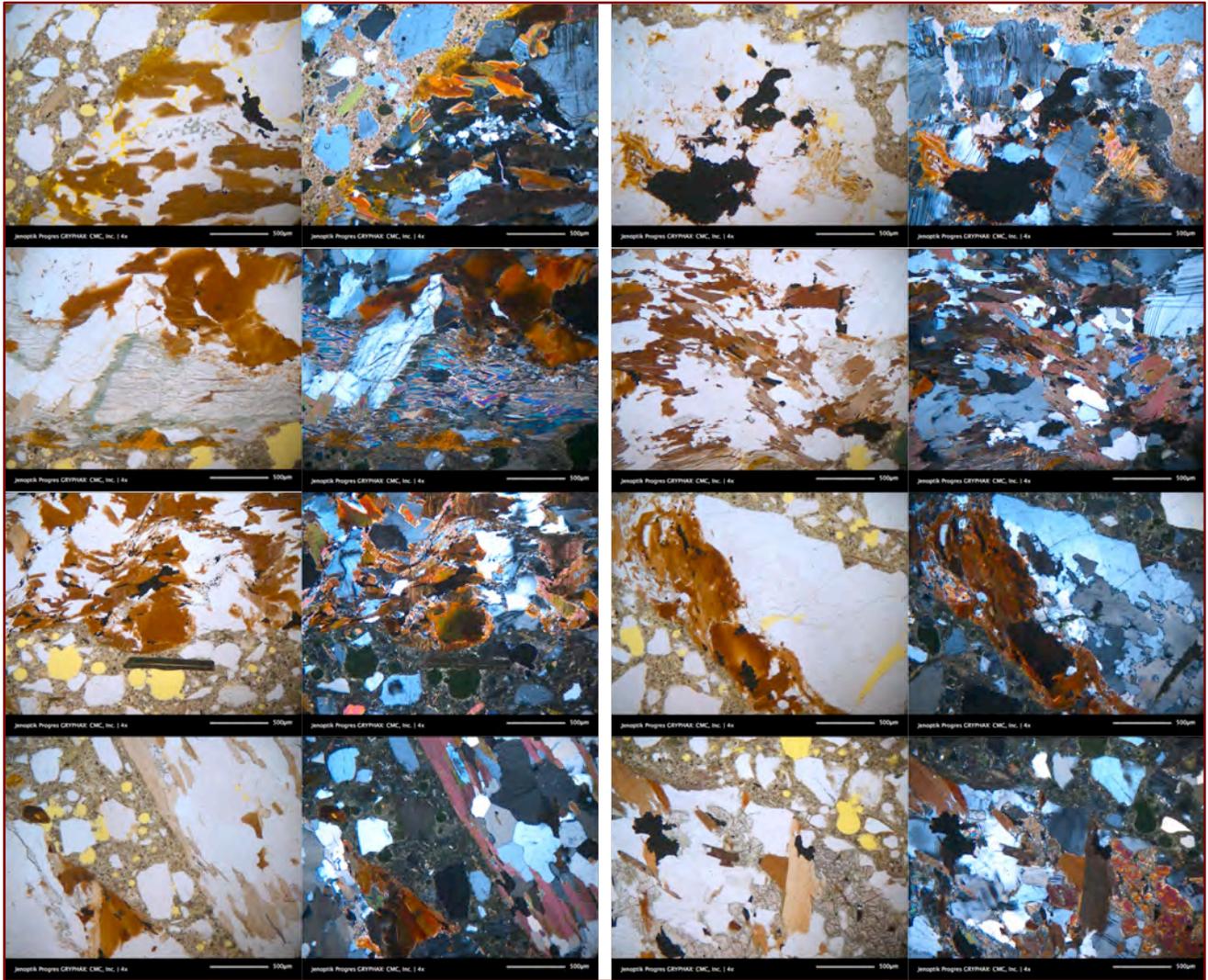


Figure 16: Photomicrographs of blue dye-mixed epoxy-impregnated thin section (30 micron thickness) of core showing: (a) crushed gneiss coarse aggregate having alternating bands of light-colored quartzo-feldspathic and dark brown colored pleochroic biotite and light-colored muscovite/chlorite micaceous minerals defining the gneissose texture common in these crushed gneiss coarse aggregate particles, (b) dark opaque iron sulfide and iron oxide minerals, (c) poikiloblastic garnet grains with mineral inclusions in gneiss, and (d) the absence of cracking or reddish brown oxidation of iron sulfide inclusions in gneiss coarse aggregate. Air voids are highlighted by fluorescent-dye-mixed epoxy. Right column photomicrographs were taken in crossed-polarized light modes and left column in corresponding plane polarized modes in a petrographic microscope.



COARSE AGGREGATE

Coarse aggregate is crushed stone which is a mixture of a predominant dark gray metamorphic garnetiferous quartzo-feldspathic and micaceous gneiss and a subordinate light brown quartz-feldspar-mica gneiss (having a higher quartz content than the dark gray gneiss) both having a nominal maximum size of ³/₄ in. (19 mm) and showing the typical gneissose texture of alternating bands of quartz-albitic feldspar and micaceous (mostly biotite and less muscovite) minerals that often contain pyrope garnet poikiloblast. Particles are angular, dense, hard, and medium to dark gray, gneissose-textured, equidimensional to elongated, variably altered, uncoated, and variably cracked. Coarse aggregate particles are well-graded and well-distributed. There is no evidence of alkali-aggregate reactions of coarse aggregate particles in the concrete. Despite finding similar particles in other homes that have been unsound during their service in the concrete due to observed cracking and microcracking in many of those particles often extending into paste that are determined to be due to oxidation of pyrrhotite minerals in those particles, particles in the present core, despite similar mineralogy, texture, and rock-type as the other deleterious ones, however, show no such cracking to indicate absence of oxidation of pyrrhotite or moisture to cause such oxidation.

FINE AGGREGATE

Fine aggregate is natural siliceous sand having a nominal maximum size of ³/₈ in. (9.5 mm). Particles contain major amounts of quartz and quartzite, and subordinate amounts of feldspar, mica, ferruginous rock, and mafic minerals. Particles are variably colored, subangular to subrounded, dense, hard, equidimensional to elongated, unaltered, uncoated, and uncracked. Fine aggregate particles are well-graded and well-distributed. There is no evidence of alkali-aggregate reaction of fine aggregate. Particles are sound during their service in the concrete.

| Properties and Compositions of Aggregates | Core from Rogers & Swaminathan Residence |
|---|---|
| Coarse Aggregate | |
| Types | Crushed Stone |
| Nominal maximum size (in.) | ³ / ₄ in. (19 mm) |
| Rock Types | Mixture of a predominant dark gray metamorphic garnetiferous quartzo-feldspathic and micaceous gneiss and a subordinate light brown quartz-feldspar-mica gneiss |
| Angularity, Density, Hardness, Color, Texture, Sphericity | Angular, dense, hard, medium to dark gray, massive textured, equidimensional to elongated |
| Cracking, Alteration, Coating | Variably altered, Uncoated, and variably cracked |
| Grading & Distribution | Well-graded and Well-distributed |
| Soundness | Sound |
| Alkali-Aggregate Reactivity | None |
| Fine Aggregate | |
| Types | Natural siliceous sand |
| Nominal maximum size (in.) | ³ / ₈ in. (9.5 mm) |



| Properties and Compositions of Aggregates | Core from Rogers & Swaminathan Residence |
|---|--|
| Rock Types | Major amounts of quartz and quartzite, and subordinate amounts of feldspar, mica, ferruginous rock, and mafic minerals |
| Cracking, Alteration, Coating | Variably colored, subangular to subrounded, dense, hard, equidimensional to elongated |
| Grading & Distribution | Well-graded and Well-distributed |
| Soundness | Sound |
| Alkali-Aggregate Reactivity | None |

Table 1: Properties of coarse and fine aggregates of concrete.

PASTE

Properties and composition of hardened cement paste are summarized in Table 2. Paste at the near-surface carbonated zone is beige-toned, but interior body is medium gray, dense and hard; freshly fractured surfaces have subvitreous lusters and subconchoidal textures. Residual and relict Portland cement particles are present and estimated to constitute 8 to 10 percent of the paste volume. Hydration of Portland cement is normal. The textural and compositional features of the paste are indicative of a cement content estimated to be 6 to 6¹/₂ bags of Portland cement per cubic yard. The concrete has an estimated water-cement ratio (w/c) more or less similar throughout the body and is estimated to be from 0.40 to 0.45. There is no evidence of deleterious secondary ettringite deposits that are found in the cores from other homes that have shown distress due to oxidation of pyrrhotite. Bonds between the coarse and fine aggregate particles and paste are tight. There is no evidence of microcracking due to deleterious reactions. The overall quality and condition of the concrete in the wall core is judged to be sound at the time of this investigation with no evidence of chemical deterioration due to internal sulfate attack that is common in other homes affected by pyrrhotite-oxidation-related cracking. The interior concrete is moderately dense, consolidated, and present in sound condition.

| Properties and Compositions of Paste | Core from Rogers & Swaminathan Residence |
|--|--|
| Color, Hardness, Porosity, Luster | Gray, dense and hard, Subtranslucent vitreous |
| Residual Portland Cement Particles | Normal, 8 to 10 percent by paste volume |
| Calcium hydroxide from cement hydration | Normal, 10 to 14 percent by paste volume |
| Pozzolans, Slag, etc. | None |
| Water-cement ratio (w/c), estimated | 0.40 to 0.45 |
| Cementitious materials contents, estimated (equivalent to bags of cement per cubic yard) | 6 to 6 ¹ / ₂ |
| Secondary Deposits | No evidence of poorly crystalline secondary ettringite infested paste (EIP) or relatively well crystalline secondary ettringite lining and filling many air-voids and sometimes in cracks found in other homes affected by pyrrhotite-oxidation-related distress |
| Depth of Carbonation, mm | 20 to 30 mm from exposed surface of foundation wall |
| Microcracking | Not present in concrete except some in some crushed stone |



| Properties and Compositions of Paste | Core from Rogers & Swaminathan Residence |
|--------------------------------------|---|
| Aggregate-paste Bond | Tight to moderately tight |
| Bleeding, Tempering | None |
| Chemical deterioration | No evidence of internal sulfate attack or ettringite infested paste at the time of this investigation, found in other homes from eastern Connecticut due to oxidation of pyrrhotite in crushed gneiss coarse aggregate during service |

Table 2: Composition and properties of paste.

AIR

Air occurs as: (a) numerous fine, discrete, spherical and near-spherical voids having sizes of 1 mm; and (b) a few coarse near-spherical and irregularly shaped voids that are characteristic of entrapped air. Concrete is air-entrained having an estimated air content of 6 to 7 percent (Figure 11).

SEM-EDS STUDIES

Figures 17 through 20 provide SEM-EDS analyses of concrete to investigate the following:

1. Composition of iron sulfide minerals in aggregates – from backscatter electron image and energy-dispersive x-ray fluorescence spectroscopy - Figures 17 and 18;
2. Composition of paste to determine sulfur (SO₃) level from infestation of poorly crystalline ettringite in paste from released sulfates from aggregates, if any – Figure 19;
3. Microstructure of unsound pyrrhotite-bearing aggregate including cracking and extension of cracks from unsound aggregates to paste, if any – Figure 18;
4. Secondary ettringite crystallization along aggregate-paste interfaces, if any – Figure 19;
5. Secondary ettringite crystallization in air-voids, if any – Figure 19;
6. Gaps around aggregate due to expansion of sulfate-contaminated paste, if any – Figure 19

All these microstructural and microchemical studies are helpful for:

1. Identifying iron sulfide mineral present in aggregate, e.g., lower S/Fe atomic ratio than pyrite to indicate pyrrhotite – Figure 18 confirmed the presence of pyrrhotite in aggregate;
2. Evidence of oxidation of pyrrhotite from low S/Fe atomic ratio compared to non-oxidized stoichiometric S/Fe ratio of pyrrhotite – Figure 18 confirmed no noticeable oxidation of pyrrhotite;
3. Evidence of unsoundness of pyrrhotite-bearing aggregate from expansion and cracking – Figure 18 confirmed no noticeable cracking or unsoundness of aggregate;
4. Evidence of internal sulfate attack in paste from high sulfur (as SO₃) level of paste compared to normal Portland cement paste, due to secondary ettringite infestation in confined areas in paste – Figure 19 confirmed no such sulfate attack in paste or any noticeable release of sulfate from aggregate to paste.
5. Evidence of internal sulfate attack in paste from gaps around aggregates due to expansion of paste and secondary ettringite crystallization along aggregate-paste interfaces – Figure 19 confirmed no expansion or secondary ettringite crystallization in the present core.

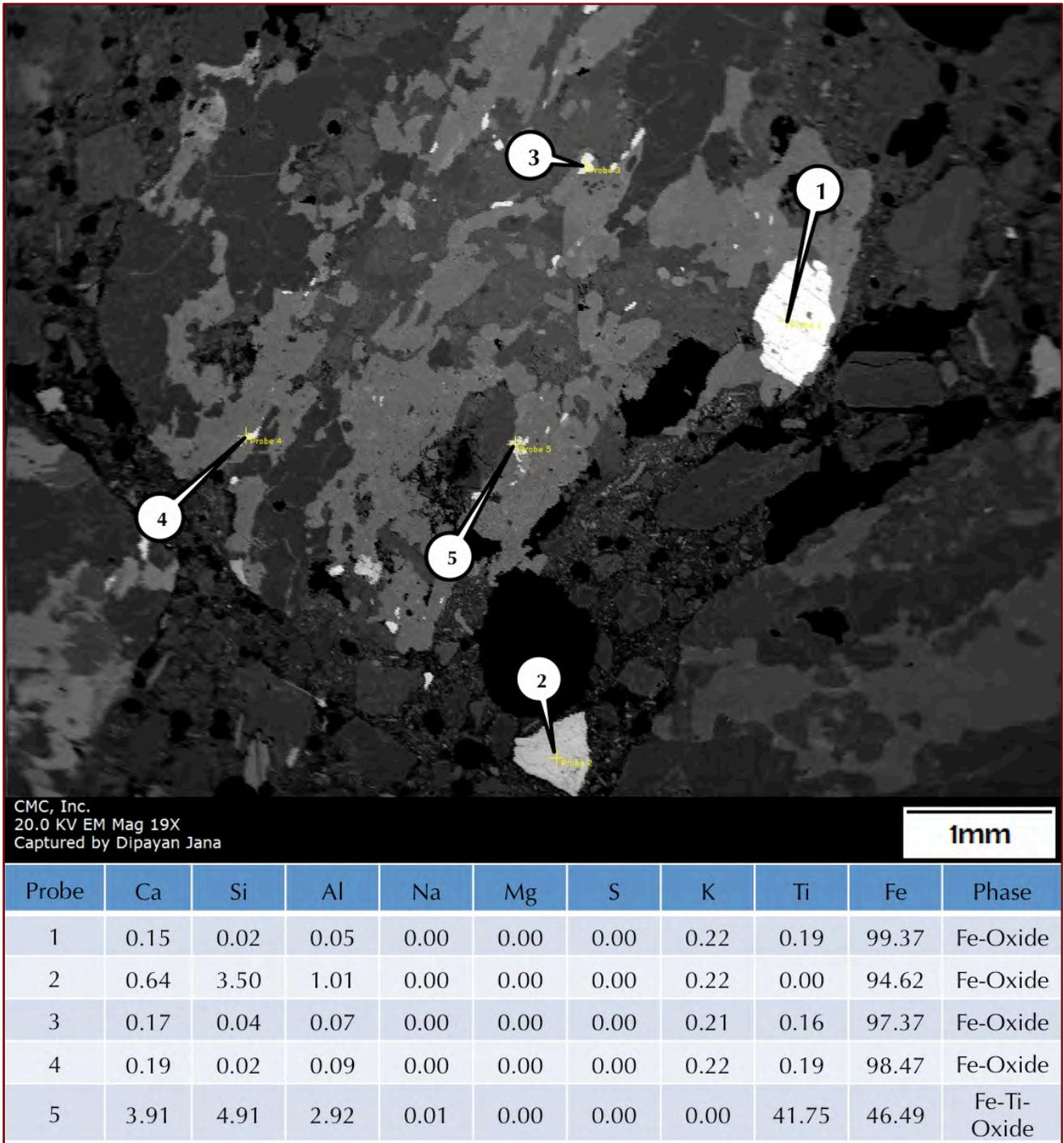


Figure 17: Backscatter electron image and X-ray elemental analysis of various bright iron-bearing minerals in a crushed geniss coarse aggregate particle showing the iron oxide and iron-titanium oxide compositions of these minerals, as opposed to iron sulfide. Magnetite (iron oxide) and ilmenite (iron titanium oxide) are commonly associated with iron sulfide minerals as contaminants in many rocks, including geniss.

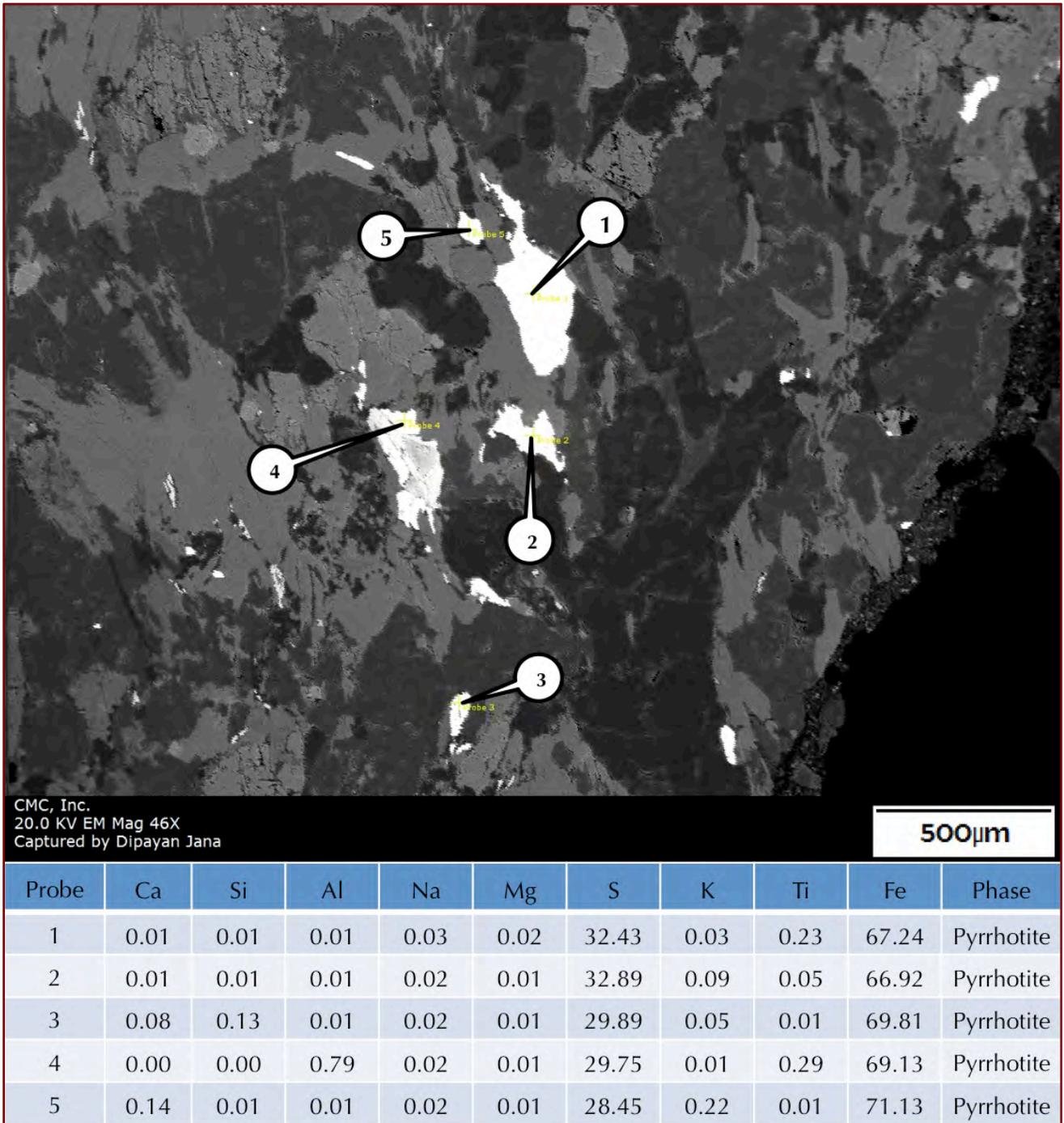


Figure 18: Backscatter electron image and X-ray elemental analysis of various bright iron-bearing minerals in a crushed geniss coarse aggregate particle showing the iron sulfide mineral - pyrrhotite.

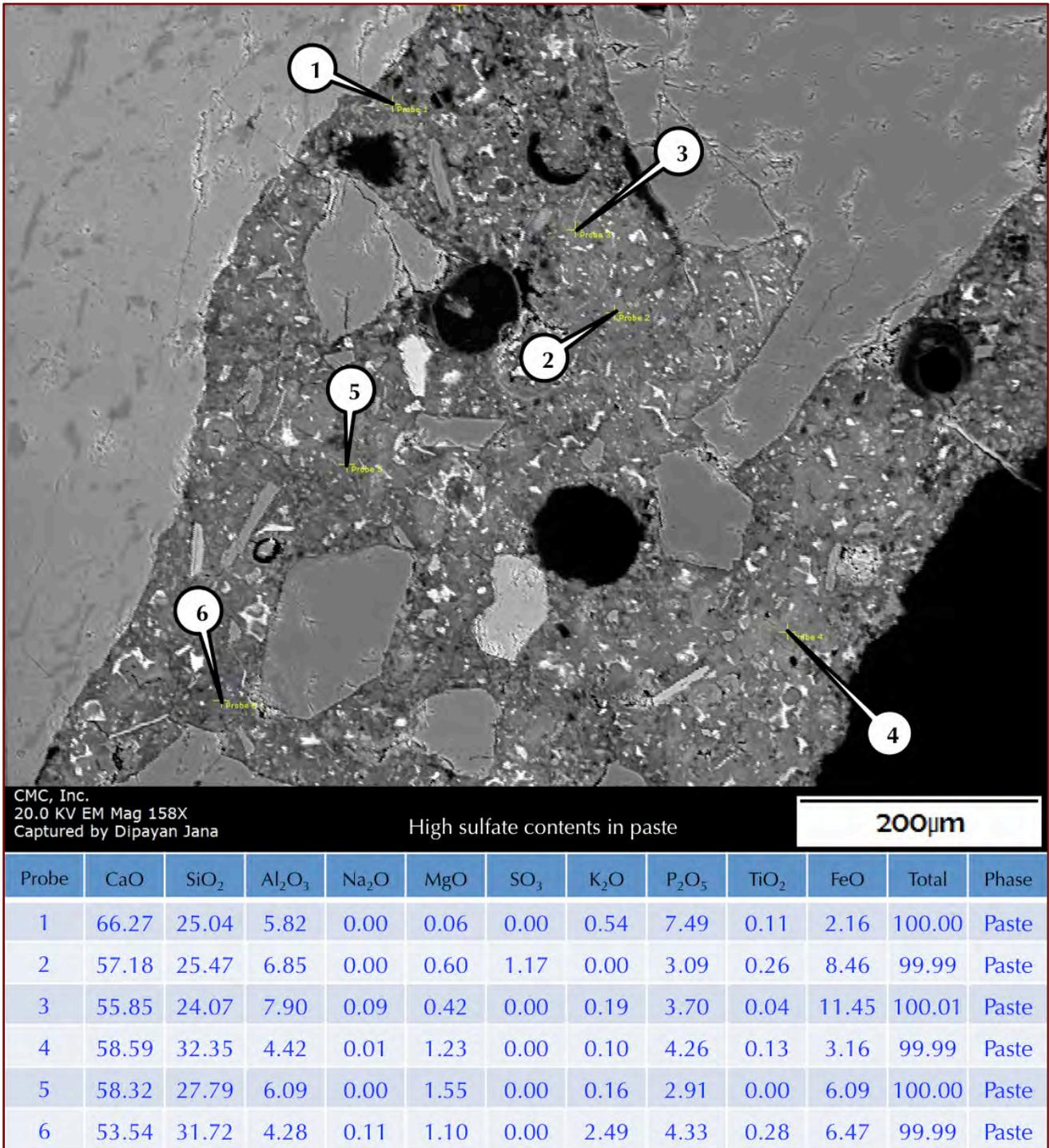


Figure 19: Backscatter electron image and X-ray elemental analysis of paste in concrete showing the absence of cracking, absence of any secondary ettringite crystallization in the paste or along aggregate-paste interfaces, which were found in other distressed foundations, and low sulfate levels in paste, as opposed to high sulfate found in the paste in other distressed foundations – this confirms absence of moisture and no noticeable release of sulfate from pyrrhotite-bearing gneiss to the paste.

XRD & XRF OF CONCRETE AND ITS COARSE AGGREGATE FOR SULFIDE MINERALOGY, OXIDATION PRODUCTS, AND SULFUR (SO₃) CONTENTS

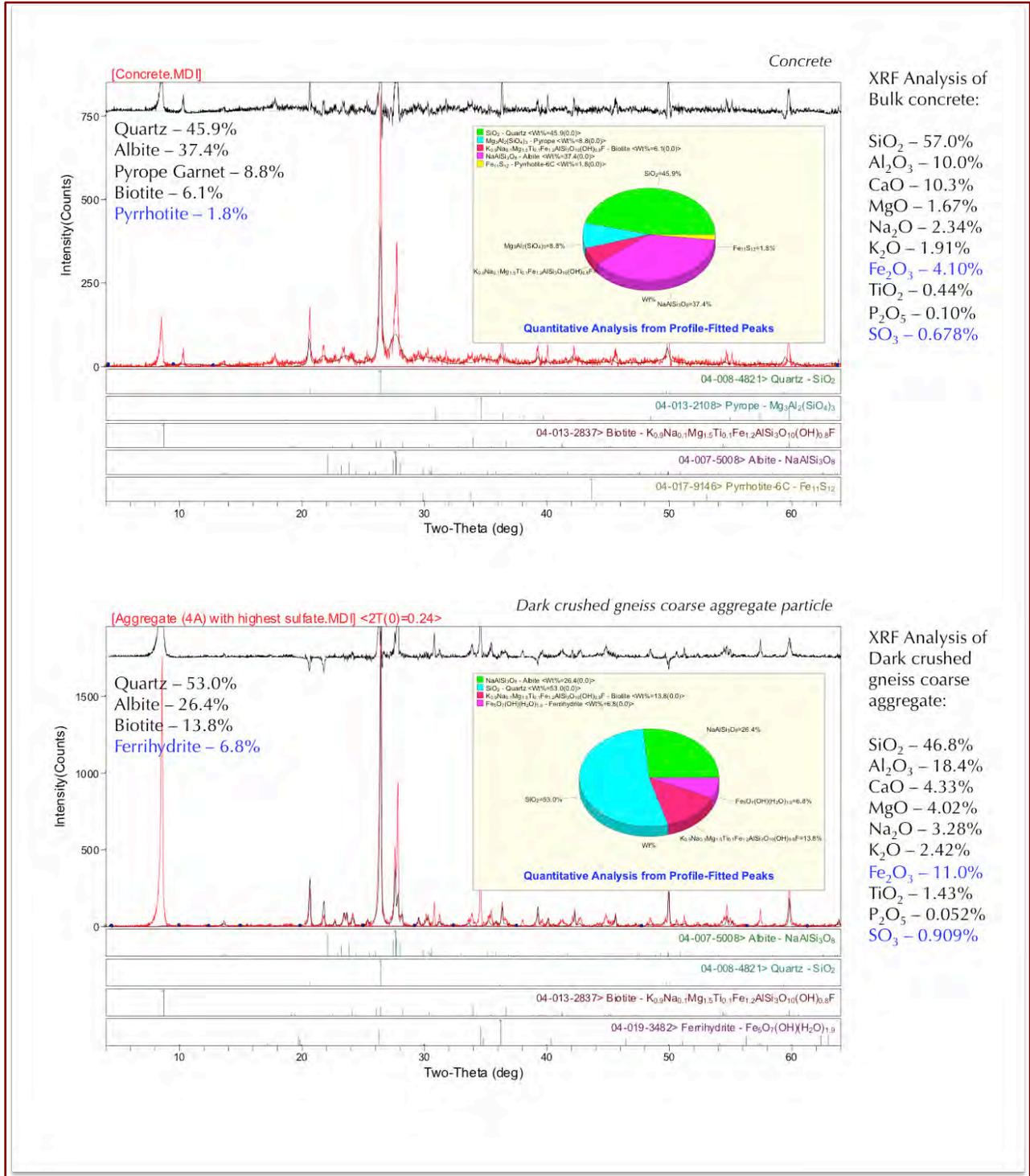


Figure 20: X-ray diffraction patterns, quantitative proportions of minerals, and X-ray fluorescence analyses of bulk concrete (top) and a representative dark gray crushed gneiss coarse aggregate (bottom) showing the presence of pyrrhotite in concrete and its oxidation product ferrihydrite in the aggregate. Insets show semi-quantitative proportions of different minerals in concrete and coarse aggregate, as well as oxide compositions from XRF.

| Oxide (wt.% from XRF) | 1A | 2A | 3A | 4A | 5A | Bulk Concrete |
|--------------------------------|--------|--------|--------|--------|--------|---------------|
| SiO ₂ | 56.90 | 63.10 | 46.80 | 57.80 | 57.90 | 57.00 |
| Al ₂ O ₃ | 11.50 | 10.70 | 18.40 | 13.00 | 13.60 | 10.00 |
| Fe ₂ O ₃ | 5.73 | 5.22 | 11.00 | 10.10 | 5.18 | 4.10 |
| CaO | 12.50 | 4.55 | 4.33 | 2.43 | 11.40 | 10.30 |
| MgO | 2.57 | 3.34 | 4.02 | 3.81 | 2.11 | 1.67 |
| Na ₂ O | 1.04 | 1.61 | 3.28 | 1.90 | 1.56 | 2.34 |
| K ₂ O | 0.27 | 1.67 | 2.42 | 2.81 | 0.66 | 1.91 |
| TiO ₂ | 0.53 | 0.68 | 1.43 | 0.95 | 0.36 | 0.44 |
| P ₂ O ₅ | 0.16 | 0.15 | 0.05 | 0.06 | 0.13 | 0.11 |
| SO ₃ | ND | 0.01 | 0.91 | ND | ND | 0.68 |
| Balance | 9.03 | 8.96 | 7.29 | 7.56 | 7.44 | 11.50 |
| Total | 100.00 | 100.00 | 100.00 | 100.00 | 100.00 | 100.00 |

Table 3: Results of XRF analyses of five crushed gneiss coarse aggregate particles extracted from the core and of the bulk concrete for sulfate (SO₃) contents, and other oxide contents. Gneiss aggregates show large sulfate contents with stone 3A showing highest sulfate as well as iron contents.

To determine the sulfate (SO₃) level of bulk concrete, a thin slice of concrete was sectioned through the entire length of the core and pulverized and pressed into a pellet to do XRF analysis, which showed 0.68 percent sulfate (SO₃) by weight of concrete which is higher than that normally contributed from Portland cement.

ION CHROMATOGRAPHY FOR POTENTIAL SULFATE RELEASE OF AGGREGATES IN ACCELERATED OXIDATION TEST

Five pyrrhotite-bearing crushed gneiss coarse aggregate particles were carefully extracted from the core and cleaned of all adhered paste to be crushed and immersed in a strong oxidant (35% hydrogen peroxide) solution. For each extracted aggregate, after crushing, one gram of pulverized aggregate was selected for determining released sulfate contents after 24 hours of immersion. Each sample was immersed in a 25-mL hydrogen peroxide (35%) solution, then at the end of run filtered all solid residues with a 25-micron filter paper, the filtrate was then re-filtered through a 0.45-micron filter paper. The filtrate thus prepared is then diluted with distilled water to 100 mL to be analyzed in IC. All coarse aggregate particles showed release of sulfates in an oxidizing environment in 24 hours. Apparently, released sulfates from these aggregate particles is possible to contaminate the paste, and form the seeds for internal sulfate attack by reactions with cement hydration products – as long as moisture is present during service.

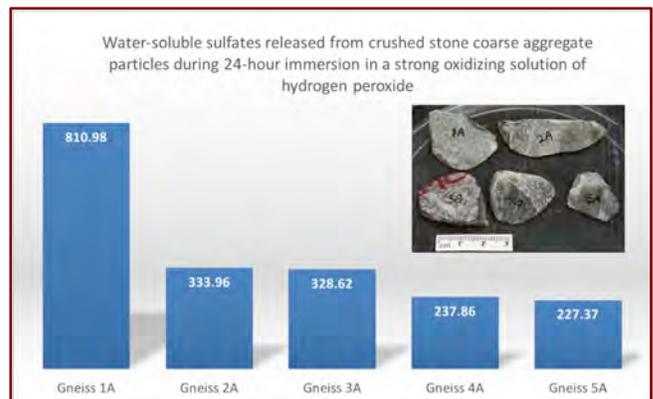


Figure 16: Results of accelerated oxidation test of five crushed gneiss coarse aggregate particles extracted from the core and cleaned of all adhering paste to be crushed and immersed in a strong oxidant (35% hydrogen peroxide) solution for 24 hours.



DISCUSSION

IRON SULFIDE MINERALS IN CONCRETE AGGREGATES¹

Iron sulfide minerals (e.g., pyrite FeS_2 , or pyrrhotite Fe_{1-x}S , x varies from 0 to 0.125) occurring mostly as ‘accessory’ minerals in many concrete aggregates are known to cause various deteriorations in concrete in service. **Oxidation of iron sulfide minerals in concrete** can cause various deteriorations from **unsightly staining** on the exposed surface to **popouts** of near-surface unsound aggregates (Jana 2008) and associated local fracturing to in extreme cases severe **cracking, microcracking, and loss of strength** of concrete from **internal sulfate attacks** by reactions between released sulfate and hydrogen ion (sulfuric acid) from oxidation reactions with cement hydration products – all resulting in expansive reactions leading to structural instability. The mineral pyrrhotite has been found to be the most reactive and detrimental to the durability of concrete. If a suspicion arises regarding a possible pyrrhotite-related distress in a concrete structure then identification of the type of iron sulfide mineral responsible for the distress, and quantification of the total sulfur content in the pyrrhotite-bearing aggregate would be prudent to determine whether the mineral may have an effect on the durability of concrete.

Background

Iron sulfide minerals occur commonly as minor, but significant accessory minerals in a variety of rocks. Pyrite is the most common of all sulfide minerals. It is a common accessory mineral in igneous, metamorphic, and sedimentary rocks, and is a major phase in many sulfide ore bodies. In hand sample, this mineral has a metallic luster and pale yellow color. Microscopically, pyrite is a cubic isotropic mineral with a yellowish-white color in reflected light (Deer et al., 1992). Pyrite, with the chemical formula FeS_2 , is composed of 46.6% Fe and 53.5% S.

Pyrrhotite is the second most common iron sulfide in nature, found as a primary accessory mineral in ultra-mafic and mafic rocks, metamorphosed igneous and sedimentary rocks, and as a secondary mineral in hydrothermal deposits. It is mostly found with other iron sulfides, particularly pentlandite ($(\text{Fe,Ni})_9\text{S}_8$), but also commonly found associated with pyrite, marcasite (orthorhombic FeS_2), magnetite (Fe_3O_4) and chalcopyrite (CuFeS_2) (Deer et al, 1992; Belzile et al, 2004). These different minerals can all coexist within a grain of pyrrhotite or in contact with the grain (Uytenbogaardt, Burke, 1971). In hand sample, this mineral has a metallic luster and bronze brown, yellow, or reddish color. Microscopically, pyrrhotite is a monoclinic or pseudohexagonal anisotropic mineral with a pink cream or skin color in reflected light (Deer et al, 1992). Pyrrhotite has an unbalanced chemical formula Fe_{1-x}S , with x ranging from 0 (FeS) to 0.125 (Fe_7S_8).

¹ Excerpts from American Concrete Institute’s technical notes on pyrrhotite-related distress in concrete, plus author’s own addition.



Mechanism of Distress by: (1) Oxidation of Iron Sulfides (Primary Expansion Causing Surface Staining, Popout, Cracking), (2) Release of Sulfates and Internal Sulfate Attack (Secondary Expansion Causing Further Cracking)

It is well known from the literature that sulfide minerals are unstable in oxidizing conditions. According to Divet and Davy (1996), high pH conditions, such as those found in concrete, enhance iron sulfide oxidation. Upon exposure to water and oxygen, sulfide minerals (pyrite, pyrrhotite) oxidize to form acidic, iron oxides/hydroxides, and sulfate-rich by-products with an increase in solid volumes from the sulfide minerals to their oxidized products (Belzile et al. 2004, Rodrigues et al. 2012). The oxidation of ferrous iron (Fe^{2+}) produces ferric ions (Fe^{3+}) that can precipitate out of solution to form ferric hydroxide, if pH is not too low. Fe^{2+} is oxidized and precipitated as ferric oxyhydroxides, principally **ferrihydrate** [$\text{Fe}(\text{OH})_3$] and **goethite** [$\text{FeO}(\text{OH})$]. The sulfuric acid (sulfate and hydrogen ion, H_2SO_4) generated through oxidation reactions reacts with cement hydration products, e.g., with the portlandite [$\text{Ca}(\text{OH})_2$], to form **gypsum** [$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$] (Grattan-Bellew and Eden 1975, Shayan 1998, Rodrigues et al. 2012), with calcium aluminate or monosulfoaluminate hydrates to form **ettringite** [$\text{Ca}_6\text{Al}_2(\text{SO}_4)_3(\text{OH})_{12} \cdot 26\text{H}_2\text{O}$], or, **thaumasite** [$\text{Ca}_6[\text{Si}(\text{OH})_6]_2(\text{CO}_3)_2(\text{SO}_4)_2(\text{H}_2\text{O})_{22}$] latter one if carbonate minerals are present. Both the processes of *oxidation of iron sulfides*, and *reactions between released sulfates and cement hydration products* are expansive in nature resulting in concrete deteriorations.

Figure 22 from various authors (e.g., Rodrigues et al. 2012, Oliveira et al., 2014, Willi and Zhoing 2016) summarizes mechanism of two-stage expansions resulting in concrete deterioration from: (a) *primary expansion due to oxidation of iron sulfide minerals to ferric oxyhydroxides, principally goethite and ferrihydrate and associated solid volumes' increases*, and (b) *secondary expansion due to internal sulfate attacks of released sulfate and hydrogen ions (sulfuric acid) from oxidation to cement hydration products, e.g., calcium hydroxide and calcium sulfoaluminate hydrate to form gypsum (with a solid volume increase of 42) or more commonly due to formation of ettringite (with a solid volume increase of 172).*

The above expansive mineral formation results in **rust staining and pop-outs at the aggregate site in milder cases most commonly associated with pyrite, to severe cracking and decreased strength due to internal sulfate attack in paste from released sulfates in the most severe cases associated with pyrrhotite.**

In the case of pyrrhotite, the degree of cracking damage correlates with the deterioration of the mineral and the quantity of resultant expansive sulfates in the paste. **Not all concretes with pyrrhotite in aggregates, however, result in deterioration.** As shown in the case studies in Table 4, the rate and extent of damage can be variable. The rate and severity of damage are dependent on a number of factors including: (a) the interaction between the particle and the surrounding host rock that forms the aggregate (Oliveira et al. 2014) and the concrete paste, (b) the concrete quality, (c) the environmental conditions to which the concrete element is exposed to (exposure to oxygen, moisture, and temperature), (d) crystal structure, (e) the mineral associations (more than one sulfide minerals present), (f) concrete pH, (g) trace metal content, and (h) bacterial activity (Belzile et al. 2004). The extents of controlling factors are not yet fully understood in light of the limitations of reproducing the deterioration in the laboratory.

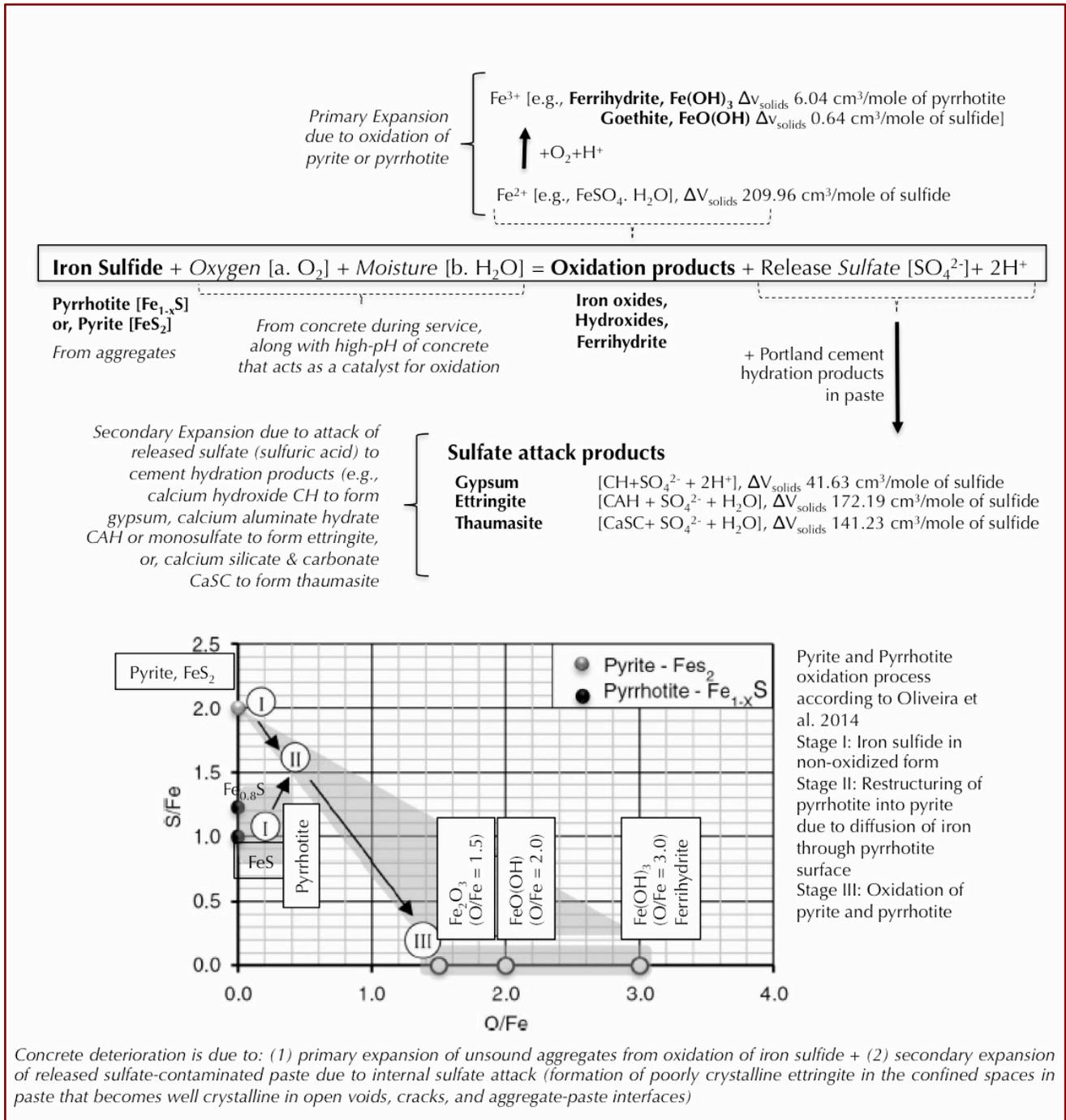


Figure 22: Mechanisms of oxidation of iron sulfide minerals in concrete according to various authors, and primary expansion due to oxidation of iron sulfide to various forms of iron oxides, hydroxides, ferrihydrite, followed by secondary expansions due to reactions between the released sulfates and hydrogen ions from oxidation reactions (sulfuric acid) and cement hydration products (calcium hydroxide, calcium aluminat, and monosulfoaluminat hydrate) to form ettringite (or thaumasite if carbonate ions are present).



Pyrrhotite Limit

Standardization of the amount of iron sulfide minerals that are considered acceptable in concrete aggregates is not well established. American, Canadian, British, and French standards for concrete aggregates mention iron sulfides and their related problems with use in concrete, but have not established acceptable limits of iron sulfide contents in aggregates. Limits have been established for total sulfur (S_T) by mass in French at 0.4%, European at 1%, or 0.1% if pyrrhotite is present. The limits as to the amount of pyrrhotite that would lead to damage has not been identified to date; this may be quite difficult because the reactivity of pyrrhotite may vary according to its crystallographic characteristics, while many factors are involved in this deleterious mechanism. No precise guidelines or methods have been proposed to evaluate the potential reactivity of sulfide containing aggregates.

Recently, an extensive investigation was carried out over a four-year period by researchers from four Canadian organizations aimed at developing an evaluation protocol for iron sulfide bearing aggregate (Rodrigues et al., 2016). The resulting recommended protocol involved a three-phase testing program including (a) measurement of total sulfur, (b) oxygen consumption determination, and (c) accelerated mortar bar expansion test. Limits are proposed for each phase of the protocol, but are in need of additional validation. These tests can be used as a general screening, but would need to be supplemented by further testing to identify the sulfate sulfur and the sulfate mineral type. Significant research is still needed to identify appropriate limits.

CASE STUDIES OF CONCRETE DETERIORATION DUE TO OXIDATION OF IRON SULFIDE MINERALS IN AGGREGATES

Examples of deterioration of concrete structures due to oxidation corrosion of iron sulfate minerals, with pyrrhotite date back to 1955, and span a range of aggregate types. Structural damage to buildings due to pyrite or pyrrhotite breakdown has been observed in many places around the world since the mid-1950s, including Ireland, Wales, Spain, Canada, Namibia, and Japan. In the United States, pyrite-induced swelling has been observed in Ohio, West Virginia, Pennsylvania, Missouri, Kansas, and Kentucky, and more recently thousands of homes in Connecticut have been affected by pyrrhotite in concrete foundations.

Following are summaries of cases studies on concrete deterioration around the world that are described due to unsoundness of aggregates containing iron sulfide minerals, all of which have concluded that expansions associated with oxidation of iron sulfide minerals followed by additional expansions associated with internal sulfate attacks between the released sulfates and cement hydration products have caused the deterioration in form of map cracking, heaving, displacement of affected elements, and in severe cases crumbling of concrete elements. The last row is for oxidation of pyritic shale in the substrate causing heaving of structural elements, or, blistering of floor tiles when pyritic is present in the concrete aggregates at the surface of floor slab, but all other case studies are from pyrrhotite-oxidation related damages.



| <ul style="list-style-type: none"> • Locality (References) | <ul style="list-style-type: none"> • Pyrrhotite containing rocks • Associated sulfide minerals | <ul style="list-style-type: none"> • Average sulfur content in aggregate • Pyrrhotite content | <ul style="list-style-type: none"> • Structure affected • Type of Damage • Time taken to manifest the damage | <p>Proposed Mechanisms of Distress</p> |
|---|---|--|---|--|
| <ul style="list-style-type: none"> • Oslo, Norway (Moum and Rosenqvist 1959) | <ul style="list-style-type: none"> • Sedimentary rocks (alum shales some with slight metamorphism) • Pyrite occurred with pyrrhotite | <ul style="list-style-type: none"> • 6% (highly variable), all shales that weathered 'explosively' due to oxidation contained more than 0.2% sulfur as monoclinic pyrrhotite. • Pyrrhotite content is related to rate of alteration of pyrite and rate of weathering of shale | <ul style="list-style-type: none"> • Foundation • Upheaval of foundation, cracking, crumbling, yellowish deposit of jarosite [KFe₃(OH)₆(SO₄)₂] and brown-iron oxide (Fe₂O₃·nH₂O) on weathered shales. • Within 9 months | <p>Swelling of shale due to oxidation of pyrrhotite and internal sulfate attack from released sulfate; reactivity of alum shale and resultant damage increased with increasing pyrrhotite content, with no occurrence of damage when alum shale was free of pyrrhotite; acidic and sulfate-rich water percolated through alum shale has caused acid attack and internal sulfate attack in concrete</p> |
| <ul style="list-style-type: none"> • Trois-Rivières area, Quebec, Canada (Tagnit-Hamou, et.al. 2005; Rodrigues, et.al. 2012; Duchesne and Benoit 2013) | <ul style="list-style-type: none"> • Quarried intrusive igneous rock anorthositic gabbro (norite) with different degrees of metamorphism • Pyrite and chalcopryrite. Only pyrrhotite showed signs of oxidation but pyrite and chalcopryrite were largely unaffected. A thin coating of iron carbonate (siderite) on sulfides provided carbonates to promoted thaumasite form of attack in addition to internal sulfate attack from pyrrhotite oxidation | <ul style="list-style-type: none"> • As low as 0.30% to 2.92% total sulfur by mass of aggregate in pyrrhotite-bearing coarse aggregates that have caused damage, all damaged concrete exceeded the European limit of 0.1% sulfur in aggregate when pyrrhotite is present by 3 times to as high as 30 times. • Less than 5 to 10 percent total sulfide minerals by volume, average 75% of sulfide minerals was pyrrhotite and lesser pyrite and chalcopryrite from a study of 223 house basements containing varying amounts of iron sulfide in gabbro coarse aggregate | <ul style="list-style-type: none"> • Residential foundations and commercial buildings. • Map cracking (cracks up to 40 mm in width) and yellowish or brownish staining), popouts of oxidized pyrrhotite with white rim of secondary reaction products, and open cracks more pronounced at the corners of the foundation blocks • More than 1000 to as high as estimated 4000 residential and commercial buildings were affected within 3 to 5 years after construction | <p>Oxidation of sulfide minerals (mainly pyrrhotite) in anorthositic gabbro coarse aggregate in concrete has: (a) formed various "rust" minerals (e.g., ferric oxyhydroxides such as goethite FeO(OH), limonite, and ferrihydrite) and (b) released sulfuric acid/sulfates, which then reacted with cement hydration products resulting in further expansive formation of gypsum, ettringite, and thaumasite in concrete. Oxidation of pyrrhotite followed by internal sulfate attack of cement paste is the main mechanism of concrete deterioration.</p> |
| <ul style="list-style-type: none"> • Northeastern Connecticut, USA (Wille and Zhong 2016) | <ul style="list-style-type: none"> • Foliated schist and gneissic metamorphic rocks, granofels, foliated quartz diorite in a hydrothermally altered vein from a particular quarry in Willington, CT (Becker's quarry). • Pyrrhotite as the predominant iron sulfide mineral present in metamorphic rocks containing quartz, plagioclase feldspar, micas, and garnet | <ul style="list-style-type: none"> • Average 2.54% sulfur in pyrrhotite-bearing quarry aggregate • Pyrrhotite was not detected in XRD analysis of quarry aggregate by Wille and Zhong due to possible presence below the 5% detection limit of XRD | <ul style="list-style-type: none"> • Residential foundations. • Map cracking, crumbling, deformation of wall, reddish-brown discoloration, whitish formation of secondary ettringite and thaumasite in the vicinity of surface cracks. Cores from foundation walls of houses showed noticeably lower compressive strengths (some no strength due to complete crumbling) compared to the cores from slabs, indicating possible effect of more oxidation in wall than slab and hence more damage in wall than slab • 10 to 20 years after construction, estimated 34,000 homes are at risk | <p>Primary expansion due to oxidation of pyrrhotite followed by secondary expansion due to internal sulfate attack by released sulfates</p> |



| <ul style="list-style-type: none"> • Locality (References) | <ul style="list-style-type: none"> • Pyrrhotite containing rocks • Associated sulfide minerals | <ul style="list-style-type: none"> • Average sulfur content in aggregate • Pyrrhotite content | <ul style="list-style-type: none"> • Structure affected • Type of Damage • Time taken to manifest the damage | <p>Proposed Mechanisms of Distress</p> |
|--|--|---|---|--|
| <ul style="list-style-type: none"> • <i>Catalan Pyrenees, Spain</i> (Araujo et al. 2008) | <ul style="list-style-type: none"> • Schist containing quartz, muscovite mica, chlorite and non-expansive illitic clay. • Pyrite and Pyrrhotite | <ul style="list-style-type: none"> • 2% sulfur (as SO₃ from XRF) in schist. • Predominantly pyrrhotite (S/Fe ratio 0.62 as opposed to 1.15 of pyrite) but XRD also detected some pyrite | <ul style="list-style-type: none"> • Tórán Dam • Map cracking and non-recoverable movements, more dramatic expansion in the downstream face of the dam for upstream displacement of the crest | <p>Oxidation of pyrite and pyrrhotite forming surface stains of greyish brown iron hydroxides (goethite) and lighter-green potassium iron sulfates (jarosite), gypsum efflorescence from sulfate attack; and causing expansions, e.g., 6.04 cm³/mol from primary expansion from oxidation of iron sulfides followed by 172.19 cm³/mol from internal sulfate attack by reaction between released sulfates and cement phases</p> |
| <ul style="list-style-type: none"> • <i>Central Pyrenees, Spain</i> (Ayora et al. 1998; Oliveira et al. 2014) | <ul style="list-style-type: none"> • Schist containing bands of pyrrhotite that created planes of weakness and present cracks that serve as preferential paths for entrance of oxygen thus aggregates containing pyrrhotite bands with cracks showed much more pronounced oxidation than the aggregates without cracks. • Pyrite | <ul style="list-style-type: none"> • Median sulfur (SO₃) content of 1.42% for rocks from a quarry that have known to cause severe damage when used as aggregate in dam | <ul style="list-style-type: none"> • Graus and Tavascan Dams • Map cracking, damage in downstream face and galleries of the Graus Dam due to severe cracking and movement | <p>Alteration from acidic solution produced by weathering and oxidation of pyrrhotite in aggregates followed by expansion due to internal sulfate attack and formation of ettringite and gypsum. Characteristic ratios of 2.44 for the Fe/O ratio and of 2.63 for the S/O ratio in pyrrhotite marked critical limits that produced the activation and acceleration of pyrrhotite oxidation leading to an increase of expansive reactions and risk of structural damage.</p> |
| <ul style="list-style-type: none"> • <i>Ottawa, Quebec City, Matane, and Montreal, Canada</i> (Quigley and Vogan 1970; Berard 1970; Berube et al. 1986; Penner et al. 1972) • <i>Ireland</i> • <i>Wales</i> (Hawkins and Pinches 1987) • <i>Marcellus Shale, USA</i> (Hoover and Lehmann 2009) • <i>Chattanooga Shale, Kentucky, USA</i> (Anderson 2008) • <i>SW England in Cornwall and Devon</i> | <ul style="list-style-type: none"> • Black shale containing pyrite (not pyrrhotite). Pyrite is most common in metamorphic and sedimentary rocks as either a primary mineral or a fine, widespread impregnation of subsequent origin. • Pyrite is frequently found in association with coal and shale deposits • Mundic (means mine waste) concrete blocks used in the foundations of thousands of 20th century homes in SW England, blocks were prepared using mine waste rocks as aggregates containing pyrite that has caused serious damage (Mundic decay) in foundations | <p>The minimum amount of pyrite that will cause heaving problems is not known with certainty. Some reports describe difficulties with contents as low as 0.1 per cent by weight. In the Ottawa area heaving problems have been encountered only in rock formations with much higher pyrite contents, although a systematic sampling program has not been carried out. Pyrite weathering is a chemical-microbiological oxidation process; some of the oxidation reactions are solely chemical, others are attributed to autotrophic bacteria of the ferrobacillus-thiobacillus group, and still others are both chemical and micro-biological.</p> | <ul style="list-style-type: none"> • Foundation, basement floor above weathered pyritic substrate. Pyrite weathering was identified as early as 1950 as a major foundation problem in the U.S.A. in buildings dating back to 1920. • Pyrite oxidation in the Chattanooga Shale has caused serious foundation problems in numerous buildings and structures in Estill County, KY. • Heaving of pyritic substrate causes cracking, lifting of concrete floor slabs; differences in levels across floor slabs; cracking, buckling lifting of elements resting on the concrete floor slabs, doors, stairs, fixtures; cracking, bulging, movement of internal or external walls. • Blistering and de-bonding of vinyl tile from concrete floor is reported due to oxidation of pyritic aggregates at the surface of concrete floor (Shayan 1988) | <p>Oxidation of pyrite in shale or coal causes formation of <i>gypsum</i> from reactions between (a) sulfates or sulfuric acid released from pyrite oxidation and calcium hydroxide component of cement hydration (if pyritic rock is used as aggregate in concrete), and/or (b) between sulfuric acid from oxidation and associated calcite in pyritic rocks cause heaving and associated volume changes. When calcite converts to gypsum, the volume increases by a factor of 2, but of greater importance is the force associated with the growth of gypsum crystals, which can be very high. When gypsum grows in rock under buildings it tends to form needle-like crystals that force the layers apart, resulting in much greater heave than would occur with simple volume expansion during formation. Another oxidation product found in all weathered pyritic materials is jarosite, KFe₃(SO₄)₂(OH)₆, recognized by its bright yellow-brown color. The calculated volume increase from pyrite to jarosite is 115 percent, which is another main contributor to volume increase and heaving.</p> |

Table 4: Case studies on concrete deteriorations due to oxidation of iron sulfide minerals in aggregates.



PYRRHOTITE EPIDEMIC IN EASTERN CONNECTICUT

Figure 23 shows regional spread of the latest reported incident of widespread outbreak of deterioration of concrete due to pyrrhotite oxidation in the aggregate along northeastern Connecticut with many hundreds of homes being affected. Figures 24 through 27 show various manifestations of distress in the affected homes from various sources. Typical visual deterioration was in the form of map cracking, some causing deformation of the wall, extensive longitudinal to random cracking of the wall, reddish-brown discoloration, and whitish formation in the vicinity of surface cracking most of which are shown in Figures 24 to 27. Currently, much of the information available on this problem is limited to newspaper articles but the cause of deterioration has been confirmed by an investigation conducted at the University of Connecticut (Wille and Zhong, 2016) as oxidation of pyrrhotite present in the aggregate. In contrast to the problems encountered in Quebec, manifestation of the damage in Connecticut has taken as much as 10 to 20 years.

Most of the damage to date has been linked to one quarry operating in Willington, CT. The geology in the vicinity of the quarry is made up of metamorphic rocks predominately from two to three formations. The formations are comprised predominantly of foliated schists and gneissic rock, granofels, and a foliated quartz diorite. Quartz, plagioclase or oligoclase are primary minerals with micas, and noted are garnet and graphite as common accessory minerals. Iron sulfides are found predominately as pyrrhotite.

Wille and Zhong (2016) did extensive mechanical, mineralogical, microstructural and chemical tests on the core samples taken from 7 houses and did visual inspection of 14 additional houses, from which the primary findings they found are:

- a) Ubiquitous in all cases of concrete deterioration are the presence of pyrrhotite in aggregates and their oxidation products, such as goethite $[\text{FeO}(\text{OH})]$, and ferrihydrite $[\text{Fe}(\text{OH})_3]$;
- b) Sodium sulfate and hydrated forms of sodium sulfate (thenardite and mirabilite) based white efflorescence deposits at the vicinity of surface cracks;
- c) Porous paste and aggregate-paste interfaces, abundance of secondary ettringite crystallization in aggregate-paste interfaces and other open spaces; cracking is often associated with these open spaces and either within the voids or extends into cement paste
- d) Oxidation of pyrrhotite in the presence of water and oxygen is reported to have caused the distress by expansive formation of ferrihydrite, and subsequent release of sulfate to paste, sulfate-aluminate reactions with aluminate phases in paste, and expansive formation of secondary ettringite crystals.
- e) In the presence of carbonate ions secondary thaumasite crystallization is also noted.

In light of the present study it is concluded that the above finding of Wille and Zhong (2016) are all in the same line as the present study. Additionally, this study found formation of poorly crystalline secondary ettringite in the confined areas in paste as ettringite infested paste to be the breeding ground for internal sulfate attack that has

caused the expansion and cracking. Relatively well formed secondary ettringite in voids and cracks are the result of exposure to moisture of sulfate-contaminated paste. All these information are primarily obtained from optical microscopy, which is an indispensable tool for this type of investigation, which Wille and Zhong (2016) did not do. The host rock is garnetiferous quartzo-feldspathic gneiss (again, determined from optical microscopy) containing pyrrhotite having sulfur (as SO₃) levels from 2 percent in light brown gneiss to as high as 10 percent in predominant dark gray gneiss particles, giving a total bulk sulfate (SO₃) content of 1.45 percent in the concrete, which is more than 3 times the sulfate in a normal Portland cement concrete without any iron sulfide contaminant. As high as 8 percent pyrrhotite is found from XRD analysis of dark gray gneiss. Pyrrhotite oxidation has readily released sulfates and contaminated the Portland cement paste as detected from high (4 to 6.5%) sulfate contents in paste as opposed to normal less than 1% sulfate found in the paste of a Portland cement concrete containing no iron sulfide contaminants. Ready release of sulfate has promoted internal sulfate attack and subsequent secondary expansion of paste with additional cracking.

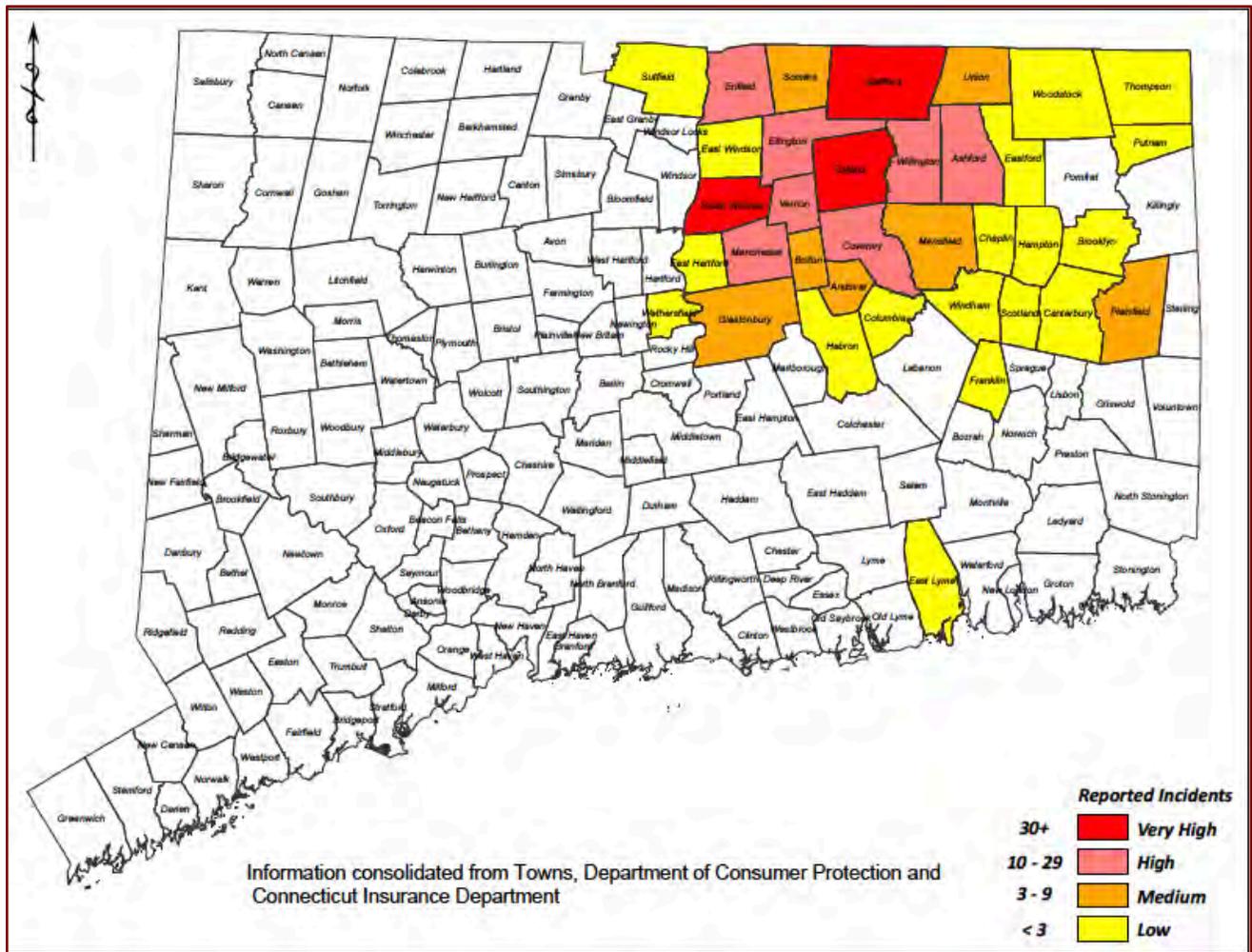


Figure 23: Reported incidences of pyrrhotite-related concrete deterioration in northeastern Connecticut. Note the present residential house in Mansfield Center falls under Medium-risk zone for concrete containing aggregates reportedly supplied from the Becker’s quarry.



Figure 24: Cracking of concrete foundations in Connecticut due to oxidation of pyrrhotite bearing aggregates in concrete. Notice wide cracks in the top row as well as a network of numerous fine cracks in the wall in the bottom right row all from pyrrhotite oxidation and associated expansion of concrete.



Figure 25: Cracking of concrete foundations in Connecticut due to oxidation of pyrrhotite bearing aggregates in concrete. Notice dark reddish brown rust staining on the wall and associated cracking in the top row from pyrrhotite oxidation and formation of ferric oxy-hydroxide oxidation products (goethite, limonite, ferrihydrite rust minerals). Notice wide cracks in the 2nd through 4th rows from pyrrhotite oxidation and associated expansion of concrete.



Figure 26: Cracking of concrete foundation in Connecticut due to oxidation of pyrrhotite bearing aggregates in concrete. Notice wide cracks in the foundation walls, extensive cracking of walls in the top left photo all reportedly from pyrrhotite oxidation and associated expansion of concrete.



Figure 27: Cracking of concrete foundation in Connecticut due to oxidation of pyrrhotite bearing aggregates in concrete. Notice extensive cracking of foundation in all photos reportedly from pyrrhotite oxidation and associated expansion of concrete.



CONCLUSIONS

Oxidation of pyrrhotite in concrete aggregates has caused severe damage to concrete foundations in several thousands of residential and commercial buildings in Quebec, Canada, in three concrete dams in Central Pyrenees, Spain, and anticipated to have deteriorated several thousands of residential foundations in eastern Connecticut that have reportedly received concrete containing pyrrhotite-bearing aggregates from the Becker's quarry in Ellington, CT. The amount of pyrrhotite required to cause damage has been found to be as low as 0.3% (total sulfur by mass of aggregate). Recommendations in Europe limit the sulfur content of sulfide-containing aggregates to 1% sulfur by mass unless the presence of pyrrhotite is confirmed in which case the limit is just 0.1% sulfur by mass. Limits on the sulfur contents in aggregates have not yet been imposed in North America at the time of this investigation.

In light of this known problem of pyrrhotite in concrete aggregate from around the world, and particularly from the Becker's quarry in CT, and the resulting distress in many residential foundations in northeastern Connecticut, a concrete core from a foundation wall at the residence of Rogers and Swaminathan at 154 Coventry Road in Mansfield Center, Connecticut i.e. within the known area of 'pyrrhotite epidemic' was provided with the concern of: (a) whether or not the concrete foundation contains pyrrhotite in its aggregate, and, if detected, (b) if pyrrhotite has played the role for deterioration of concrete foundation, as in the case of other residential foundations from eastern Connecticut that have shown widespread cracking from pyrrhotite oxidation and resultant sulfate attacks in concretes.

Contrary to other occurrences of pyrrhotite-related deterioration of residential foundation (as shown in Figures 23 through 27), however, field photographs of the subject foundation wall at Rogers and Swaminathan's residence (Figure 1) does not show any map cracking or any other type of cracking *at the time of this investigation*. Consistent with field photos, an 8 in. (200 mm) long and 3⁵/₈ in. (92 mm) diameter hardened concrete core drilled from near the base of a foundation wall (Figure 1) provided for detailed laboratory investigation does not show any visible cracking. Laboratory investigation was conducted for determination of possible presence of pyrrhotite in concrete, and, its potentially deleterious role in concrete deterioration, if any. Pyrrhotite's presence along with overall condition of concrete and aggregates were examined by detailed petrographic examinations (optical microscopy) *a la* ASTM C 856, whereas possible roles of pyrrhotite, its potential oxidation products and sulfate levels, and microstructures of deteriorated concrete around pyrrhotite-bearing aggregates are examined by scanning electron microscopy and energy-dispersive X-ray microanalysis (SEM-EDS) of multiple thin sections of concrete (*a la* ASTM C 1723), X-ray diffraction (XRD) and X-ray fluorescence (XRF) of multiple pyrrhotite-bearing coarse aggregate particles extracted from the concrete, and ion chromatography (IC *a la* ASTM D 4327) of extracted aggregate particles digested in a strong oxidant of 35% hydrogen peroxide solution in an accelerated oxidation test, then diluted in distilled water to determine levels of sulfates released by these aggregates in relation to a control aggregate without any iron sulfide mineral. Detection of pyrrhotite by optical microscopy and XRD, along with detection of its oxidation products by SEM-EDS and XRD, reaction microstructures and evidence of distress by SEM-EDS, and



measurement of release of sulfate levels by IC have provided a good assessment of potential role of pyrrhotite in causing the observed distress.

Petrographic examinations have determined the concrete to be made using: (a) crushed stone coarse aggregate, which is a mixture of a predominant dark gray metamorphic garnetiferous quartzo-feldspathic and micaceous gneiss and a subordinate light brown quartz-feldspar-mica gneiss (having a higher quartz content than the dark gray gneiss) both having a nominal maximum size of $\frac{3}{4}$ in. (19 mm) showing the typical gneissose texture of alternating bands of quartz-albitic feldspar and micaceous (mostly biotite and less muscovite) minerals that often contain pyrope garnet poikiloblast; (b) natural siliceous sand fine aggregate having a nominal maximum size of $\frac{3}{8}$ in. (9.5 mm) and containing major amounts of quartz and quartzite, and subordinate amounts of feldspar, mica, ferruginous rock, and mafic minerals; (c) a hardened paste of Portland cement as the sole cementitious component having an estimated cement content of 6 to $6\frac{1}{2}$ bags per cubic yard and an estimated water-cement ratio (w/c) of 0.45 to 0.50, and (d) an estimated air content of 6 to 7 percent; the concrete is air-entrained. Overall composition of concrete, including the crushed gneiss coarse aggregate particles present in the examined concrete is similar to the concretes (including similar crushed gneiss coarse aggregates) found in other foundations from eastern Connecticut that were examined by this laboratory and detected pyrrhotite-oxidation-related cracking of foundation.

Contrary to other pyrrhotite-related cracking of residential foundations, petrographic examinations of current concrete core has failed to detect any cracking in the foundation wall core that is not only absent in the core when received, but also during subsequent examinations of lapped and saw-cut cross sections of core, even after impregnating the cross sections with a fluorescent dye-mixed epoxy and viewed in an ultraviolet light where any cracking is revealed due to penetration of fluorescent epoxy into the cracks and then become highlighted in UV light. Only a few crushed gneiss coarse aggregate particles show some internal cracking, which may or may not be due to oxidation of pyrrhotite but for most part, most of the crushed gneiss coarse aggregate particles as well as the concrete lack any visible or invisible cracking. By contrast, cores examined by this laboratory from other residential foundation walls from eastern Connecticut showed extensive cracking in the core received as well as on lapped, saw-cut and fluorescent impregnated cross sections of cores where not only the pyrrhotite-bearing unsound crushed gneiss coarse aggregates have shown cracking but also the surrounding concrete due to extension of cracks from unsound pyrrhotite-bearing gneiss to the concrete. No such cracking is observed for this core at the time of this investigation. Absence of any visible and invisible cracking in the core examined is responsible for the sound condition of foundation found in the field photos.

Petrographic examinations detected two types of crushed gneiss coarse aggregate particles – (a) a dominant dark gray crushed gneiss that contains alternating bands of quartz-feldspar and micaceous (mostly biotite less muscovite) minerals (defining the gneissose texture) and pyrope garnet poikiloblast, and lesser quartz than the other (b) less predominant light colored crushed gneiss. Both gneiss types contained iron sulfide minerals (but more common in the predominant dark gray gneiss particles) as small equant to irregular-shaped to elongated particles with



characteristic metallic luster appearance and optically opaque natures. Multiple lapped cross sections of core show many such iron sulfide inclusions mostly concentrated in the dark gray crushed gneiss and lesser in light gray coarse aggregate throughout the entire depths of the cross sections. Clearly, abundant iron sulfide mineralization in the quarried stone coarse aggregate is established in the concrete, as was reportedly found in many other foundations from the northeast CT that have shown pyrrhotite-oxidation related cracking.

Therefore, despite the lack of any cracking in the core, or in the foundation wall from field photos, crushed gneiss coarse aggregate particles present in this core are found to contain pyrrhotite, similar to the other pyrrhotite-bearing crushed gneiss coarse aggregate particles from other residential foundations that have shown cracking due to oxidation of pyrrhotite in those gneiss aggregates. It is, therefore, suspected that the crushed gneiss found in the present core is compositionally similar to crushed gneiss found in other coarse aggregates from other distressed residential foundations and was probably derived from the same aggregate quarry (Becker's quarry) that is known to supply unsound pyrrhotite-bearing gneiss to other distressed concretes.

XRD analyses of coarse aggregate particles extracted from the core have confirmed the iron sulfide minerals to be pyrrhotite, along with ferrihydrite as its oxidation product, which are, again, in line with previous findings from other deteriorated foundations (Wille and Zhong, 2016, Jana 2017). XRD and XRF studies of both crushed gneiss types showed characteristic difference in mineralogy and chemistry between these types, e.g., having higher quartz in lighter brown particle, higher pyrrhotite in darker gray particles, higher iron oxide and sulfate in dark gray particles in XRF, etc.

Sulfate contents (as SO_3) in five crushed gneiss coarse aggregate particles extracted from the core are wide, e.g., from almost none to as high as 1 percent (determined from X-ray fluorescence analyses). These sulfate levels, however, are less than the sulfate (SO_3) levels found in similar crushed gneiss coarse aggregate particles from other residential foundations in eastern Connecticut where as high as 10 percent or more sulfur (SO_3) was detected in the similar dark gray crushed gneiss coarse aggregate, which was 10 times higher than the minimum 1 percent SO_3 limit by mass of aggregates established in many codes and guidelines. Clearly, there is a large range of sulfate contents in crushed gneiss coarse aggregate particles in the concrete where gneiss was supposedly quarried from the Becker's quarry, which is due to similar large range of iron sulfide mineral contents in this gneiss in the quarry, which is probably responsible for finding deleterious reactions and unsoundness of gneiss coarse aggregate in some residential foundation walls (where sulfate in aggregate were high), but not in all. Although only five crushed gneiss coarse aggregate particles were extracted from the present core for XRF analyses of sulfates, and it is quite possible that there may be some crushed gneiss particles still present in this concrete that have much higher sulfate (and pyrrhotite) levels than 1 percent SO_3 , perhaps as high as 10 percent SO_3 or more as found in other similar gneiss coarse aggregates from distressed foundations, but based on the observed sulfate levels in five extracted coarse aggregate particles it is possible that perhaps lack of cracking and pyrrhotite-related distress in the present foundation is due to low sulfate (and pyrrhotite) level of crushed gneiss coarse aggregate in this concrete compared



to other similar gneiss from other distressed foundations. It is important to note that sulfate is commonly contributed not only from pyrrhotite but also from its close cousin, pyrite, and other sulfide minerals that may be present in gneiss, but for the present gneiss from Becker's quarry. as it found in other distressed foundations from eastern Connecticut it is mostly contributed from pyrrhotite.

Contrary to the extracted crushed gneiss coarse aggregate particles, XRD analysis of bulk concrete, however showed 1.8 percent pyrrhotite, with a total sulfate level of 0.678 percent which has not only confirmed the presence of pyrrhotite in the concrete and that it was contributed from crushed gneiss coarse aggregate but also its potential to cause oxidation-related distress in concrete as found in other similar gneiss coarse aggregates in distressed concretes. Despite the potential for distress, absence of any visible or invisible cracking in the core indicates absence of moisture – the essential player for oxidation of pyrrhotite and subsequent release of sulfate to cause internal sulfate attack in concrete.

Microcracking within many pyrrhotite-bearing crushed gneiss coarse aggregates occurs due to pyrrhotite oxidation, which is often associated with reddish brown oxidation products of pyrrhotite, and microcracks often extend from unsound aggregates to paste – this is the first microstructural evidence of distress due to primary expansion of unsound aggregate *per se* that are distinct in numerous photomicrographs of thin sections of concretes from other residential foundations of eastern Connecticut studied by the present laboratory. Many times, microcracks simply follow the micaceous bands in gneiss due to the internal plane of weakness along the micaceous bands of gneissose-textured rock. The gneissose texture of crushed gneiss coarse aggregate particles consisting of alternating bands of denser quartzo-feldspathic minerals and flaky (cleavable) biotitic mica provide additional inherent planes of weakness (foliation) in the aggregate that are susceptible to develop cracking along the internal planes of weakness along the biotite bands during expansions from pyrrhotite oxidation. As a result, a lot of cracks within the gneiss coarse aggregate particles are found along the weak bands of mica flakes. In many particles, however, no such preferential path of aggregate cracking was noticed. Detailed examinations of crushed gneiss coarse aggregate particles in the present core, both from stereomicroscopical examination of lapped cross section and petrographic microscopical examination of thin section have failed to detect similar microcracking and associated reddish brown oxidation product of pyrrhotite

Petrographic examinations of distressed residential foundations from other homes of eastern Connecticut have also detected abundant secondary ettringite crystallization lining or filling many air voids and occasionally lining some microcracks that are indicative of prolonged presence of moisture in those concretes during service, which, as mentioned, is an essential pre-requisite for pyrrhotite oxidation. Presence of moisture also indicates availability of sulfates to be released from pyrrhotite-oxidation and for subsequent ettringite crystallization, which, however, may or may not have necessarily derived from pyrrhotite oxidation since ettringite-filled air-voids are a very common microstructural feature in a concrete exposed to moisture without even any iron sulfide contaminant. Any Portland cement concrete exposed to moisture during service forms secondary ettringite deposits lining and filling air voids.



To establish the source of secondary ettringite i.e. from Portland cement's sulfate and/or from oxidation of pyrrhotite-bearing aggregates require determination of sulfate levels in concrete i.e. if the level is higher than that expected from a typical Portland cement concrete where sulfate (as SO_3) content in cement is around 3 weight percent i.e. giving about 0.45 percent sulfate in concrete for a usual cement content of 15 percent by mass of a normal weight concrete. Excess sulfate in concrete above 0.45 percent from cement's contribution would then correspond to the pyrrhotite-aggregate source if no other sulfate source were present. To determine the sulfate (SO_3) level of bulk concrete, a thin slice of concrete was sectioned through the entire length of the core traversing the full thickness of the foundation wall and pulverized for XRF analysis, which showed 0.678 percent bulk sulfate (SO_3) by weight of concrete, which is higher than that normally contributed from Portland cement. Clearly, observed sulfate content of concrete indicates a sulfate source other than Portland cement, which is most likely sourced from pyrrhotite in coarse aggregate.

Despite the high sulfate content of concrete (i.e. higher than that contributed from Portland cement), however, petrographic examinations of paste in the present core did not detect any potentially deleterious secondary ettringite, which was found in other distressed foundations, indicating, again that moisture, the essential ingredient for release of sulfate from pyrrhotite to the paste, was not present for the present concrete during its service.

To establish secondary expansion of paste from internal sulfate attacks by reactions between sulfates released from pyrrhotite oxidation and cement hydration products, microstructural evidence for expansion of the sulfate-contaminated hydrated cement paste has to be established. A common microstructural evidence of paste expansion commonly attributed to delayed ettringite formation (DEF) in many steam-cured precast concrete elements is gaps or separations around aggregates due to direct expansion of paste relative to aggregate (Jana 2008), where widths of the gaps are usually proportional to the size of the aggregates around which the gaps are formed from paste expansion. Optical microscopy did not detect any such gaps around aggregates, or, similar features as found in many cracked precast concrete members deteriorated by delayed ettringite formation. Another feature common in sulfate attacks from internal or external sulfates is ettringite filled cracks, which was found in other distressed foundations but was absent in the present concrete. Therefore, the possibility of paste expansion from an internal sulfate attack by reactions between excess (i.e. beyond cement's contribution) sulfates released from pyrrhotite oxidation and cement hydration products are not diagnosed for the present foundation.

Therefore, contrary to other pyrrhotite-oxidation-related cracking in residential foundations from eastern Connecticut, examined core from the foundation of Rogers and Swaminathan's residence has failed to show any microstructural evidence of (a) primary expansion of concrete due to oxidation of pyrrhotite in crushed gneiss coarse aggregate to cause cracking within the unsound aggregate particles or their extension into paste, and (b) secondary expansion of paste due to formation of poorly crystalline (perhaps also colloidal formed) secondary ettringite in relatively confined areas in sulfate-contaminated paste (called ettringite infested paste) that are the breeding ground for internal sulfate attack causing paste expansion and associated cracking in other distressed foundations.



In accelerated pyrrhotite oxidation test, multiple crushed gneiss coarse aggregate particles were extracted from the core, cleaned of adhered paste remains, crushed, then immersed in a 35% hydrogen peroxide (strong oxidant) solution for 24 hours. Sulfates released from aggregates to the filtrates are measured (as SO_4^{-2}) in an anion exchange chromatograph. All particles show release of sulfates as opposed to no sulfate released from a control gneiss aggregate in previous studies containing no pyrrhotite. The high pH environment of Portland cement concrete is also known to enhance pyrrhotite oxidation (Divet and Davy 1996).

Case studies on pyrrhotite-oxidation-related distress of concrete foundations from eastern Connecticut by the present laboratory have confirmed and provided clear mechanisms of the common consensus that the observed cracking and reported crumbling of many concrete foundation walls in eastern Connecticut are due to: (a) oxidation of pyrrhotite in crushed garnetiferous quartzo-feldspathic gneiss coarse aggregate particles *in the presence of oxygen and moisture during service in concrete* with the formation of ferrihydrite causing expansion of the unsound aggregates and formation of cracks from unsound aggregates to paste, which was then followed by (b) additional expansion in the paste from reactions between sulfates released from pyrrhotite oxidation and cement hydration products (internal sulfate attack) and formation of poorly crystalline or perhaps colloidal ettringite within the confined spaces in paste. The present examined concrete core from the foundation of Rogers and Swaminathan's residence, however, failed to provide similar evidence of pyrrhotite-oxidation-related distress or its manifestation as cracking – this indicates that moisture, the essential ingredient for pyrrhotite-oxidation and subsequent internal sulfate attack of concrete, was not present in this foundation at least *at the time of this investigation*.

If the pyrrhotite-bearing crushed gneiss coarse aggregate found in this concrete was indeed from the Becker's quarry as reported for other foundations undergoing pyrrhotite-oxidation-related distress, then due to the known geology of pyrrhotite mineralization in the hydrothermal vein in which this quarry is situated, and its known devastating effects when used in concrete from case studies of multiple homes (Wille and Zhong 2016, Jana 2017), use of crushed stone from this quarry for concrete aggregate should be abandoned, or should only be used after extensive evaluation of aggregates for the presence of pyrrhotite (e.g., from magnetic test, total sulfur test from XRF, XRD detection of pyrrhotite amount) and its potential release of sulfate in an accelerated oxidation test of aggregates.

Absence of visible or invisible cracking in the present foundation and absence of evidence of pyrrhotite-oxidation-related distress in concrete at the time of this investigation only confirms possible absence of moisture in this foundation concrete since moisture is the essential ingredient for the distress to occur, or perhaps, slow uptake of moisture through the wall in which case moisture-induced oxidation and related distress may occur in future considering the fact that most of pyrrhotite-related distress in residential foundations of eastern Connecticut have surfaced after 10 to 20 years of construction, the time period within which the present foundation reportedly falls.



Aggregate to be used in a new foundation from other quarries must be evaluated for the possible presence of any unsound constituents, including iron sulfide minerals, e.g., (a) from XRD analysis of quarried stones to detect the amount and speciation of iron sulfide minerals present, (b) from XRF analysis to detect the total sulfur (as SO_3) content of quarried stones, (d) from accelerated oxidation test to detect the rate and level of sulfates that can be released from aggregates, and (e) even from a magnetic test to separate weakly magnetic pyrrhotite grains from other non-magnetic iron sulfide minerals.

Since there is no industry specification on the threshold pyrrhotite limit above which potential for oxidation-related distress can occur, and, in fact as low as 0.3% pyrrhotite by mass of aggregate in the host rock has reportedly shown severe distress in concrete (e.g., in Quebec Canada), the best solution is to avoid aggregates containing pyrrhotite for its known damaging effects without further laboratory verification of its potential unsoundness in concrete (e.g., from expansion of mortar bar or concrete prism tests similar to those used for ASR-expansion).

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END OF REPORT²

² The CMC logo is made using a lapped polished section of a 1930's concrete from an underground tunnel in the U.S. Capitol.