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

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## Abstract

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

Keywords: cracking, Donegal, ISA, phyllite, pyrrhotite

#### 1. INTRODUCTION

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



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

## 2. METHODOLOGIES

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

## 3. RESULTS

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

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

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

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

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

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

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

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

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

## 4. DISCUSSIONS

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

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

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

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

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

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

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## 5. **REFERENCES**

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