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Concrete damage due to oxidation of sulfide-bearing aggregate: a review of recent advances and limitations

Josée Duchesne[1]*, Andrea Rodrigues[1], Benoit Fournier[1]

[1] Centre de Recherche sur les Infrastructures en Béton (CRIB), Université Laval, 1065 ave de la Médecine, Québec, QC, Canada, G1V 0A6

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Abstract

Oxidation of sulfide-bearing aggregates is one of the major causes of concrete damage in numerous buildings in Trois-Rivières in Canada and Connecticut in the USA. In the presence of moisture and oxygen, pyrrhotite oxidizes to generate iron-and sulfate-rich secondary minerals that cause internal sulfate attack. Iron sulfides are accessory minerals of different rock types. The distribution of sulfides is often very heterogeneous in terms of aggregate particles, even at the level of the quarries in which some areas may contain copious amounts than others, which complicates the sampling method. Pyrrhotite is a complex mineral with varying chemical composition, crystallographic structure, and specific surface area. These factors influence the reactivity of pyrrhotite. Therefore, it is challenging to control the quality of the aggregate sources.
In this study, recent advances in the identification and quantification of pyrrhotite to diagnose complicated cases are presented, and a performance-based approach for the quality control of new sources of aggregates is introduced. The performance-based approach is preferred because it eliminates the influence of the oxidation of pyrrhotite.

Keywords: Sulfide minerals; Pyrrhotite; Oxidation; Internal Sulfate Attack; Diagnosis

1 Introduction

Fine and coarse aggregates typically make up 60 to 75 % of concrete material. Therefore, it is not surprising that their composition and physicomechanical properties impact the mechanical behavior and durability of concrete.

Iron sulfides, mainly pyrite (Fe_2S) and pyrrhotite ($Fe_{1-x}S$) are common and widespread accessory minerals in rocks. Pyrrhotite is of non-stoichiometric composition with x varying from 0 to 0.125 [1]. These sulfide minerals are unstable in the presence of oxygen and water and tend to oxidize. Pyrrhotite is known as one of the most reactive sulfide minerals for oxidation [2–4]. The oxidation of pyrrhotite is a highly studied subject in the field of mining engineering because it is often the cause of acid-rock drainage.

In concrete, the oxidation of iron sulfides causes chain reactions. Pyrrhotite, in the presence of an oxidizing agent (oxygen or ferric ions), oxidizes to form acidic, iron, and sulfate-rich by-products according to equation 1 [5]:

$$Fe_{1-x}S\ (s) + \left(1 - \frac{x}{2}\right) O_2 + \ x(H_2O) \longrightarrow (1-x)Fe^{2+} + \ SO_4^{2-} + 2xH^+ \quad (1)$$

Pyrrhotite can also reacts with acid forming Fe^{2+} and H_2S, thus consuming acid according to equation 2 [2]:

$$Fe_{1-x}S\ (s) + 2H^+ \longrightarrow (1-x)Fe^{2+} + \ H_2S \quad (for\ x = 0) \quad (2)$$

The oxidation of ferrous iron (Fe^{2+}) produces ferric iron (Fe^{3+}), which can precipitate into iron hydroxide or ferric oxy-hydroxide, mainly ferrihydrite represented here by one of several possible compositions ($Fe_2O_3{\cdot}0.5(H_2O)$) and goethite (FeOOH). Under alkaline conditions, such as in a concrete environment, ferrihydrite is more stable [6]. The sulfuric acid generated through this process provokes an internal sulfate attack. Sulfuric acid reacts with the solid phases of the cement paste, particularly the portlandite ($Ca(OH)_2$) to form gypsum ($CaSO_4 \cdot 2H_2O$), ettringite ($Ca_6Al_2(SO_4)_3(OH)_{12}{\cdot}26H_2O$), and thaumasite ($CaSiO_3{\cdot}CaCO_3{\cdot}CaSO_4{\cdot}15H_2O$) [7]. These chain reactions can cause the affected concrete to expand and crack very quickly. It is important to note that thaumasite replaces the cement paste matrix and does not normally involve significant expansion, in contrast to the effect of gypsum and ettringite. Examples of deteriorated concrete foundations are shown in Fig. 1. Sulfate attacks are, by far, the most expansive reactions [8] compared to oxidation reactions; for instance, during the formation of gypsum, the volume of the precipitated product is a little over twice that of the starting solids.

* Corresponding author: Josée Duchesne, E-mail: josee.duchesne@ggl.ulaval.ca

There are some documented cases in literature that relate the damage in concrete structures to the presence of iron sulfide-bearing aggregates or granular base materials [9–17]. In the analyzed cases, problematic aggregates consisted mainly of limestone and schist, porous and mechanically weak rocks.

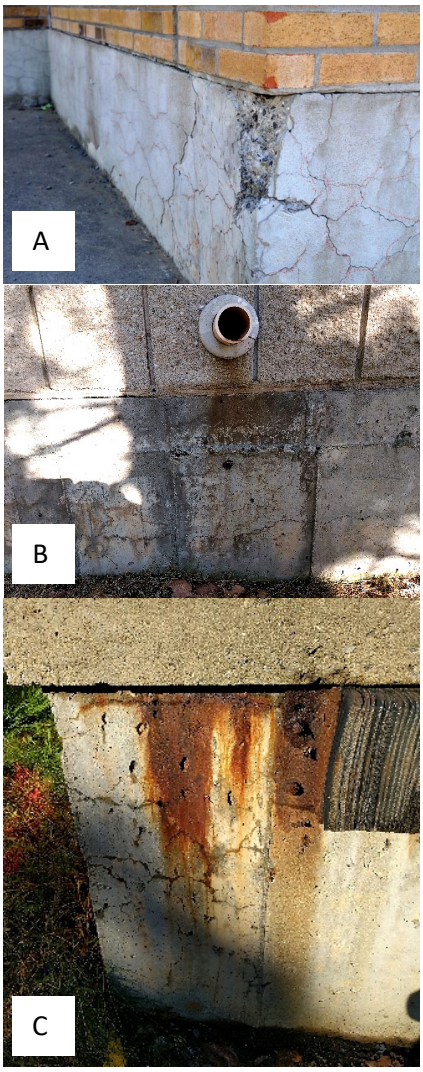

Figure 1. Typical signs of deterioration observed in a building containing iron-sulfide-bearing aggregates. A) Trois-Rivières, Canada. B and C) Connecticut, USA.

More recently, major cases involving thousands of foundations have shown that this phenomenon can also affect concrete, incorporating hard and rather massive rocks, such as anorthositic gabbro (Trois-Rivières region, Canada) [7] or gneisses (Connecticut, USA) [18]. These important cases have affected several buildings and attracted the attention of lawmakers behind large-scale research projects. This article aims to illustrate the problem, identify scientific bottlenecks, and present recent scientific advances.

2 Comparison of recent cases—Trois-Rivières (Canada) and Connecticut (USA)

Between 1996 and 2008, the owners of many single-family homes, apartment buildings, and commercial buildings in the Trois-Rivières area (Quebec, Canada) faced serious problems with their concrete foundations. In all cases, the aggregate used to make the concrete was anorthositic gabbro with various metamorphic degrees, originating from an intrusive rock body in the Saint-Boniface region, containing different proportions of iron sulfides, including pyrite and pyrrhotite. The aggregate is mainly composed of calcium plagioclase feldspar ($(Ca_{0.542}Na_{0.464}K_{0.008})$ $(Al_{1.544}Si_{2.438})O_8$) with lesser amounts of biotite ($K(Mg, Fe)_3AlSi_3O_{10}(F, OH)_2$) and orthopyroxene from the enstatite-ferrosilite series ($Fe_{0.67}$ $Mg_{1.28}$) ($Si_{1.95}$ $Al_{0.05}$) O_6) (Fig. 2E–H). The rock also contains varying amounts of pyrite and pyrrhotite associated with lesser amounts of chalcopyrite ($CuFeS_2$) and pentlandite ($(Fe, Ni)_9S_8$). Sulfur contents were measured in several aggregate particles, and the range obtained extended from 0.0 to 2.15 % S [19]. In many cases, cracking and deformation problems appeared in affected structures within five years after construction. Rodrigues et al. [7] presented a detailed mineralogical assessment of deteriorated concrete from the Trois-Rivières area.

More recently, hundreds to thousands of homes in northeastern Connecticut (USA) have developed significant signs of damage between 10 and 20 years after construction [18]. More precisely, the foundations of these homes were built between 1983 and 2015 in the states of Connecticut and Massachusetts, with aggregates coming from Becker's Quarry, Willington, Connecticut. According to the Connecticut State Department of Housing [20] "*Upwards of 35, 000 homes … are facing the potential for a failed concrete foundation due to the possible presence of a naturally occurring iron sulfide, pyrrhotite, in their concrete foundation*." Aggregates were supplied from a weathered hydrothermal vein of metamorphic rocks containing significant pyrrhotite mineralization. Secondary weathering minerals observed include thenardite (Na_2SO_4) and aphthitalite ($(K,Na)_3Na(SO_4)_2$) [16]. According to Jana [21], geology in the vicinity presents foliated schists, gneissic rocks, granofels, and foliated quartz diorite. Crushed gneiss coarse aggregate is a common lithology and is composed of quartz (SiO_2), plagioclase feldspar, mica, and pyrope garnet ($Mg_3Al_2Si_3O_{12}$) (Fig. 2A–D). Zhong and Willie [18] and Jana [21] presented a detailed mineralogical study of deteriorated concrete from Connecticut.

Figs. 2 and 3 compare the mineralogical composition of aggregates from quarries in Trois-Rivières and Connecticut. These figures show images under a polarizing microscope in transmitted (A, B, E, F) and reflected light (C, D, G, H). The samples presented in Fig. 2 are particularly rich in sulfides (minerals appearing black in transmitted light and colored in reflected light). The Connecticut samples come from a much-deteriorated concrete sample, while the Trois-Rivières samples are from a fresh sample taken directly from the quarry. The pyrrhotite from Connecticut is highly oxidized, as shown in gray ferrihydrite (e.g. Fig. 2D). The major difference observed between the two samples is the presence of pyrite, which is found only in the aggregates of Trois-Rivières. This is supported by Jana's descriptions of the Connecticut aggregate [21], which does not report pyrite in petrographic

or X-ray diffraction analyses. Fig. 4 shows scanning electron microscope micrographs of the sulfides from a Connecticut sample. The oxidation of pyrrhotite (ferrihydrite) is depicted in Fig. 4A and is confirmed using energy-dispersive X-ray spectroscopy (EDS) (no data is given). Fig. 4B shows very fine pentlandite flames in pyrrhotite.

In both cases, pyrrhotite was the mineral responsible for the failure of the concrete. Pyrrhotite can be blamed for the damage as the examination of a large number of deteriorated concrete samples from the Trois-Rivière area show that the pyrrhotite grains were mainly oxidized, while pyrite grains remain practically intact [5]. In the case of Connecticut, pyrrhotite is by far the most predominant sulfide mineral with only traces of pentlandite and chalcopyrite, pyrite has not been observed. Oxidation of pyrrhotite can occur by geological processes leading to the formation of secondary weathering minerals. Weathering can also occur in concrete in contact with cement paste leading to the generation of secondary products, including ferric oxi-hydroxide (mainly ferrihydrite), gypsum, ettringite, and thaumasite, the last three being generated on contact with the cement paste. Mineral pyrrhotite cannot be considered a single mineral because of the variability in chemical composition, crystallographic structure, and other factors. A detailed description of iron sulfides is required to understand these issues.

3 Iron sulfides occurrence and reactivity

According to Vaughan and Corkhill [22], out of the hundreds of known sulfide minerals, only five of them are sufficiently abundant to be referred to as rock-forming minerals. Pyrite and pyrrhotite are two of these accessory minerals.

3.1 Pyrite

Pyrite is the most common and widespread sulfide mineral and is found in a wide variety of geological formations. It normally occurs in the form of large masses or veins of hydrothermal origin. It can be well crystallized in the form of cubes, octahedra, and dodecahedra, but it often occurs in a framboidal form in sedimentary rocks such as shale and limestone in which the framboids tend to be recrystallized. Framboidal pyrite has a large specific surface area and is subject to oxidation, which causes rock heave problems [23]. Pyrite also occurs as recrystallized grains of irregular shapes for example in gneisses and gabbroic rocks.

3.2 Pyrrhotite

Pyrrhotite is a complex sulfide mineral with structures that have distinct degrees of Fe deficiency. The most iron-deficient end-member, Fe_7S_8, has a monoclinic superstructure that results from vacancy ordering. Further, the structure of hexagonal pyrrhotite (Fe_9S_{10}, $Fe_{10}S_{11}$, and $Fe_{11}S_{12}$) is more complex and can be also described as monoclinic or orthorhombic structures. Pyrrhotites are characterized by distinct composition, crystal symmetry, mineral stability, reactivity, and magnetic characteristics [24–28]. Monoclinic pyrrhotite is magnetic, while hexagonal pyrrhotite is non-magnetic. This variability is due to the presence of metal cation vacancies in the structure and their stacking sequence [26]. The natural forms of pyrrhotite and their main characteristics are listed in Table 1.

Pyrrhotite rarely exists as a pure phase mineral but usually consists of mixtures of hexagonal and monoclinic phases [30], which means that non-magnetic and magnetic varieties can occur simultaneously, forming complex intergrowth textures [25–26]. Identifying the co-existing types of pyrrhotite is vital for understanding their oxidation potentials. The proportion of ferric ions in the structure of pyrrhotite indicates the oxidation reactivity of the given pyrrhotite. The ferric ions act as internal oxidizing agents [30], which explains why 4C pyrrhotite is more prone to oxidation than the 5C type. Consequently, the proportion of ferric ions relative to total iron is positively correlated with the oxidation rate. These characteristics demonstrate the large variations that pyrrhotite can take.

Pyrrhotite is mainly associated with pentlandite ($(Fe, Ni)_9S_8$) in basic igneous rocks, such as veins in different types of rocks and metamorphic rocks. Pyrrhotite is also associated with pyrite, marcasite, magnetite, and chalcopyrite [2, 31]. In direct response to the issue of crumbling foundations in Connecticut and Massachusetts, the U.S. Geological Survey (USGS) published a map of the possible distribution of pyrrhotite in the United States to help assess the national risk of pyrrhotite in aggregates [32]. This map was built from the data available on rock units in which pyrrhotite had been reported, rock units containing sulfide minerals, and rocks moderately to highly metamorphosed.

Table 1. Characteristic of naturally occurring pyrrhotite (modified from [27])

Type	Ideal composition	Structure	Vacancy (%)	Proposed formula for charge neutrality	$\frac{Fe^{3+}}{Total\ Fe}$ (%)	Ideal atomic (%)		Ideal Weight (%)		Magnetic properties
						Fe	S	Fe	S	
6C	$Fe_{11}S_{12}$	Hex Ortho Mon*	8.3	$Fe^{3+}_2Fe^{2+}_9S^{2-}_{12}$	18.2	47.83	52.17	61.49	38.51	Antiferromagnetic
11C	$Fe_{10}S_{11}$		9.1	$Fe^{3+}_2Fe^{2+}_8S^{2-}_{11}$	20.0	47.62	52.38	61.29	38.71	
5C	Fe_9S_{10}		10.0	$Fe^{3+}_2Fe^{2+}_7S^{2-}_{10}$	22.2	47.37	52.63	61.05	38.95	
4C	Fe_7S_8	Mon	12.5	$Fe^{3+}_2Fe^{2+}_5S^{2-}_8$	28.6	46.67	53.33	60.38	39.62	Ferromagnetic

* Pyrrhotite superstructures are complex and are described with different symmetries or structures depending on the authors [29].

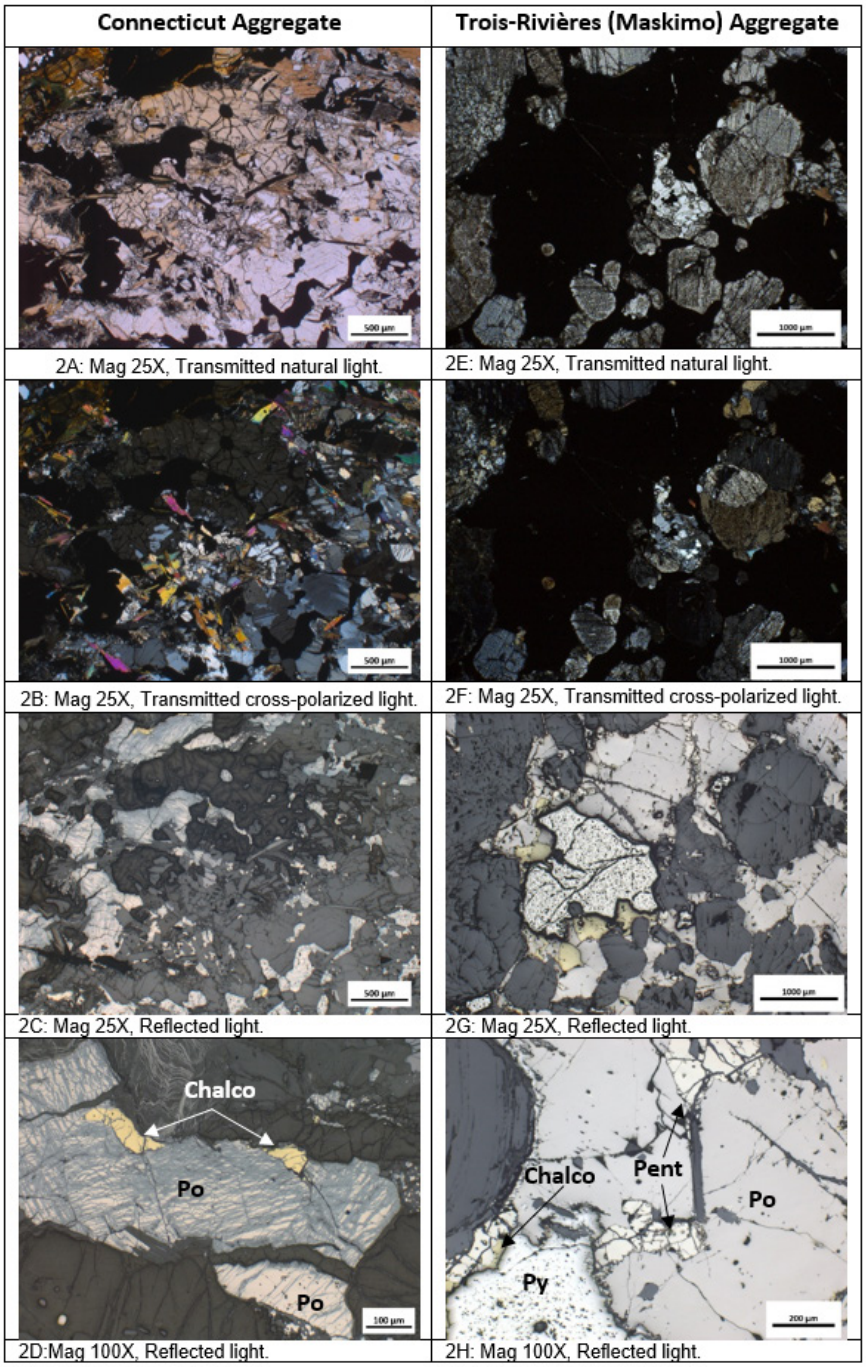

Figure 2. Comparison of the mineralogical composition of aggregates from Connecticut (left) and Trois-Rivières (right). Note: the samples are very rich in sulfides. Po: pyrrhotite; Py: pyrite; Chalco: chalcopyrite; Pent: pentlandite. Figs. 2C-2D show highly oxidized pyrrhotite. Fig. 2H shows small intergrowths of pentlandite.

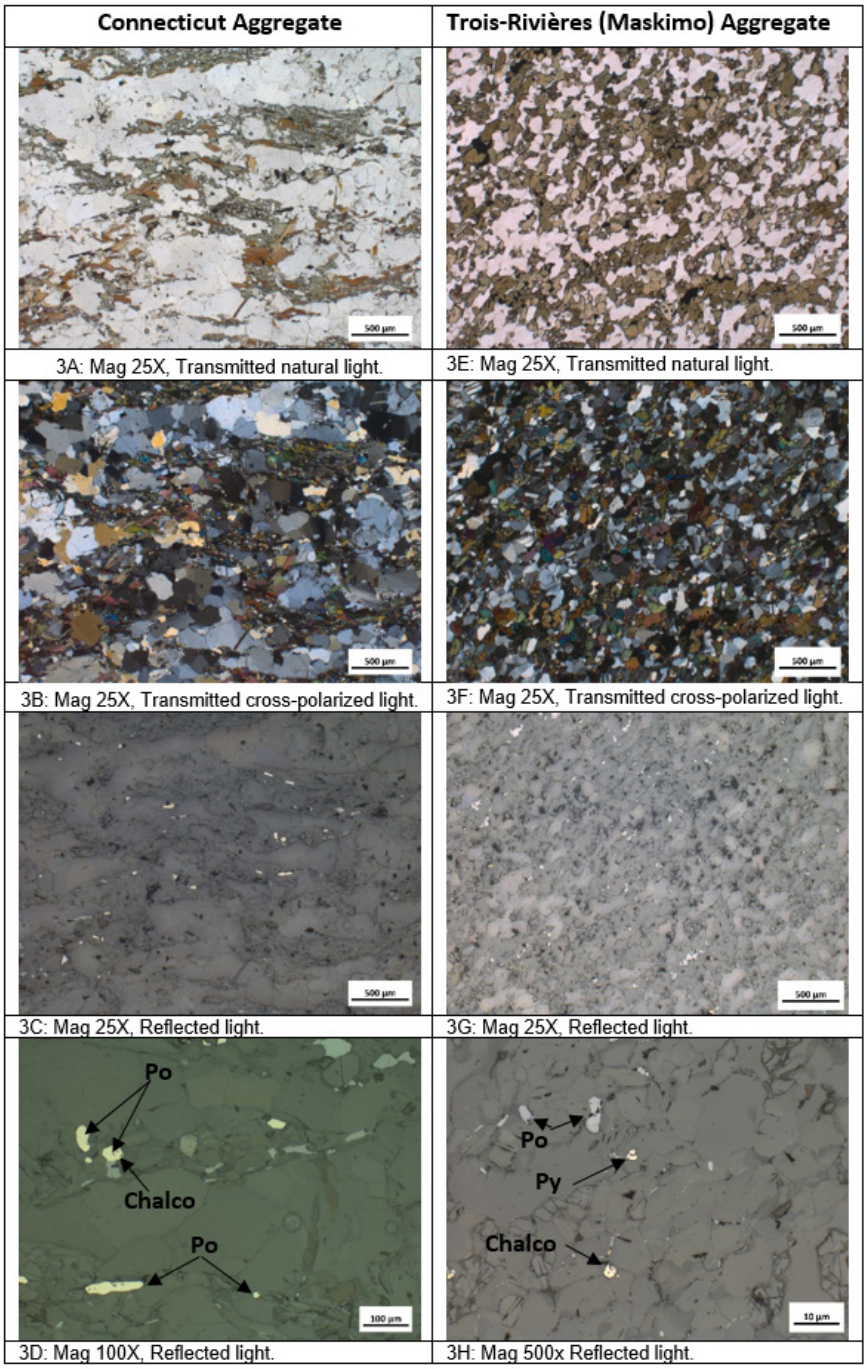

Figure 3. Microscopic images of aggregate samples with disseminated sulfides from Connecticut (left) and Trois-Rivières (right). Po: pyrrhotite; Py: pyrite; Chalco: chalcopyrite.

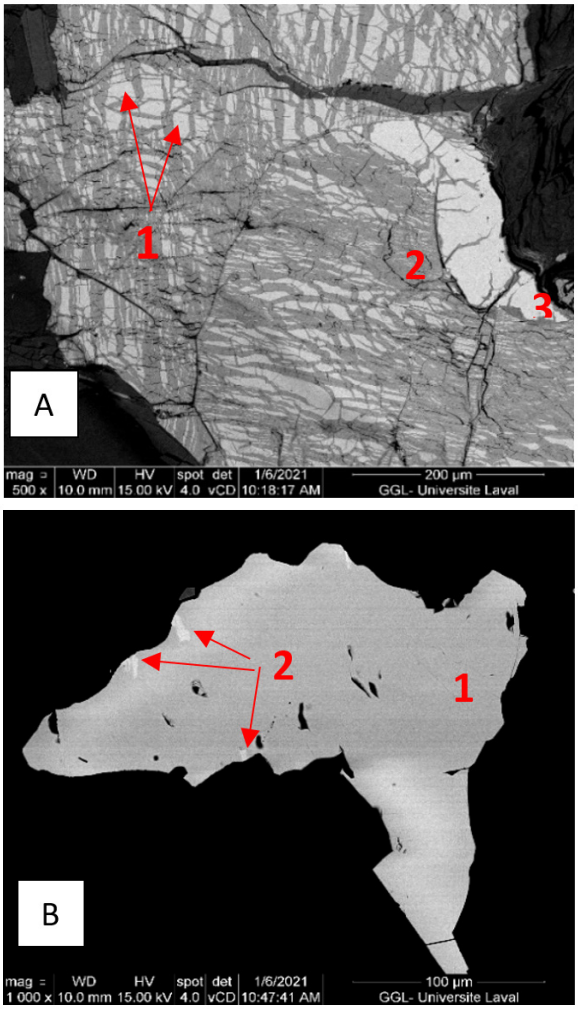

Figure 4. Secondary electron (SE) images of the sulfide from the Connecticut concrete sample. A) Strongly oxidized pyrrhotite grain. 1. pyrrhotite 2. ferrihydrite, 3. chalcopyrite. B) Pyrrhotite grain with pentlandite flames. 1. pyrrhotite 2. pentlandite.

4 Effects of pyrrhotite characteristics on oxidation potential

Pyrrhotite is known to be a highly reactive mineral, especially with oxygen. Exposure of a freshly fractured pyrrhotite surface to air for a few seconds would lead to an oxidation reaction [33,34]. The surface of pyrrhotite is complex and gives rise to different oxidation mechanisms. Because of the deficiency of Fe atoms at the pyrrhotite surface, oxidation proceeds via the formation of a sulfur-rich layer [35], whereas in the Fe-rich surface layers of pyrite, ferric oxyhydroxide forms during the initial oxidation. Janzen et al. [30] studied the oxidation kinetics of 12 well-characterized pyrrhotite samples using oxygen and ferric iron. The crystal structure varied from pure hexagonal to monoclinic. The specific surface areas of the samples also varied considerably and were unrelated to the crystal structure. The mean oxidation rate of the pyrrhotite samples by oxygen was $4 \times 10^{-9} \pm 6 \times 10^{-10}$ mol·m^{-2}·s^{-1}. Oxidation by ferric iron was faster at a value of $3.5 \times 10^{-8} \pm 1.5 \times 10^{-9}$ mol·m^{-2}·s^{-1}. The authors concluded that neither pyrrhotite crystal structure nor trace metal content had a consistent or systematic effect on the pyrrhotite oxidation rates. On the other hand, according to Belzile et al. (2004) [1], there is a trend of decreasing reaction rates with increasing trace metal contents and therefor a need for more research because there is no statistical basis to prove it.

According to Multani et al. [27], although there are disagreements as to which superstructure is more reactive, the overall trend is that 4C magnetic pyrrhotite is more reactive than its 5C non-magnetic counterpart. Therefore, it is more susceptible to surface oxidation. Pyrrhotite is often accompanied by other sulfides, which enhance galvanic interactions and accelerate the oxidation of pyrrhotite. According to these authors, 4C pyrrhotite is expected to oxidize faster than 5C not only because it contains a higher percentage of vacancies (12.5 % compared to 10 % for 5C) and higher proportion of Fe^{3+} (~29 % of total iron compared to ~22 % for 5C) but also because it is commonly found with pyrite, and is therefore subject to galvanic interactions. Galvanic interactions occur when two sulfide minerals are in contact with each other in an electrolyte solution and is characterized by their rest potentials. There is a preferential oxidative dissolution of sulfide minerals with low rest potentials. Among the common sulfide minerals, pyrite has a high rest-potential and it is the least likely to oxidize while pyrrhotite has a much lower potential [27, 36]. Galvanic interactions certainly play an important role in oxidation and should be investigated because the majority of the data come from studies in acidic medium (flotation and acid mine drainage) whereas concrete is a very basic medium.

The high reactivity of pyrrhotite is often attributed to its high specific surface area compared to that of other sulfide minerals, such as pyrite. The specific surface area has been reported to be a controlling factor in the reaction kinetics of pyrite [37] and pyrrhotite [38, 39].

These data show that the oxidation of pyrrhotite is a complex phenomenon with several influencing factors.

5 Difficulties in determining the pyrrhotite content of concrete aggregates

The main challenge for accurately characterizing the aggregate lies in the uneven distribution of pyrrhotite within the aggregate material. Some aggregate particles are very rich in pyrrhotite (Fig. 2), while others are not (Fig. 3). This heterogeneity is often related to variations within the rock body that is subjected to the quarrying operations, which may contain areas richer than others in iron sulfides. The sampling method can also contribute to the observed variability.

This effect is well documented in the field of mining and mineral exploration as the "nugget effect" In fact, the nugget effect is a geostatistical term used to reflect the substantial differences that may be found between neighboring samples. This effect occurs due to random errors accumulated during sampling and some inherent short-scale variability in the phenomenon studied. According to Clarke [40], the nugget effect includes any random sampling variation in the method selected, the adequacy of the sample size, the analysis process, and other factors.

As stated by Minkkinen [41, 42], "an *error in sampling cannot be compensated for, later, even if the most sophisticated methods and instruments are used for the actual analysis*." The errors introduced during sampling are well addressed by Gy's theory of sampling of particulate materials [43, 44].

Significant sampling and modeling measures must be taken to overcome this effect. These measurements are very laborious in terms of data acquisition, sampling, analysis, and cost, and are difficult to apply in the case of granular material quarries for several reasons. First, the value of concrete aggregates is very low compared to that of the base or precious metals. Further, it is much easier to characterize and quantify minerals containing rarer metals such as Au, Ni, and Co within a sample than to quantify iron sulfides, of which iron is a common element present in several abundant mineral phases. Iron is the fourth abundantly available chemical element in the earth's crust, with an average content of 5.6 % (percentage by weight of the earth's crust). Further, iron sulfides are common minor constituents of many rock types. Therefore, concrete aggregates may contain a certain amount of iron sulfide minerals, mainly pyrite and pyrrhotite.

The issue related to the number and size of samples needed to overcome sampling errors is also very important for the owners of affected concrete structures, who are often individuals or small businesses with limited capital for investigations. For instance, to illustrate the variability in the aggregate sulfur content, Duchesne et al. [45] analyzed 15 core samples distributed at different locations in the foundations of two houses affected by pyrrhotite oxidation in Trois-Rivières, Canada. Three samples were cored in each wall of the foundation and three on the floor. Data showed the heterogeneity of the sulfur content distribution with a variation of 0.4 and 0.7 wt%, respectively, while the mean values were 1.1 wt% for both foundations. Likewise, Geiss and Gourley [46] recommended analyzing more than one core per structure as varying pyrrhotite concentration was found while evaluating the Connecticut samples for magnetic susceptibility measurements.

For all these reasons, indirect measurements (application of a chemical threshold), such as the sulfur content, are used to obtain a quick overview of the presence or absence of sulfide in the aggregate material.

5.1 Indirect method—Elemental analysis of sulfur (S)

The European Standardization NF EN 12620 [47] specified that the total sulfur content (S) of the aggregate must not exceed 1 % S by mass. If the presence of pyrrhotite is proven, a maximum total sulfur content of 0.1 % S by mass should be applied. These tools could be used for the basic screening of concrete aggregates, but they need to be supplemented by other test methods when the total sulfur content is above 0.1 %.

Various analytical methods are available to determine the total sulfur content. A distinction must be made between the total sulfur content $[S]_T$, which measures both sulfate $[S^{6+}]$ and sulfide$[S^{2-}]$ sulfur contents. Determination of total sulfur content is often obtained using carbon/sulfur elemental analyzers based on combustion technology that ignites the sample in an oxygen stream and determines the released SO_2 gases with infrared cells. Size reduction is the only sample preparation needed. The advantage of this method is that the elemental content of sulfur can be determined to be in the ppm range up to 100 %. The disadvantage is that only the total sulfur content is determined. To determine the sulfate content, other methods such as gravimetry could be used. Rodrigues et al. [48] used this method to determine the total sulfur content in concrete housing foundations in Trois-Rivières, Canada. The sulfate content in the concrete specimens analysed was estimated from the sulfate content of the Portland cement and the usual cement dosage used for residential foundations. This estimate is possible because the only source of sulfur in the aggregate is from sulfide minerals.

Cruz-Hernandez et al. [49] proposed a new wavelength dispersive X-ray fluorescence method to determine individual sulfur species contents, sulfide and sulfate, in cementitious materials from Connecticut, USA. This technique estimates the sulfide sulfur content of aggregates by subtracting the sulfate contribution from Portland cement and other sources. The authors reported that for a $[S]_T$ content of 1 %, $[S^{2-}]$ can be detected down to 0.037 % by weight. This method is site-specific because it uses a calibration curve that can be influenced by the matrix effect. However, as with other sulfur analysis methods, it cannot identify the presence of pyrrhotite.

5.2 Identification and Quantification of pyrrhotite

Different approaches have been proposed to identify and quantify the pyrrhotite content in the aggregates. Some methods are site-specific, semi-quantitative or quantitative. The following sections present the methods and their limitations.

5.2.1 Petrography

Elemental analysis of the sulfur content cannot identify the type of sulfide minerals present in the aggregate tested. The most popular method for identifying pyrrhotite is a petrographic analysis using a reflected light polarizing microscope [50, 51]. However, the precise identification of small quantities of sulfide minerals could present a significant challenge for petrographers.

This challenge is due to the low sulfide content of the sample and the fact that often only a small subsample is examined, which questions the representativeness of the sample. The proportion of the different iron sulfide minerals present in an aggregate material can theoretically be calculated from the total sulfur content $[S]_T$ and the detailed petrographic/mineralogical characterization of the aggregate sample. The proportions of the sulfide minerals could then be calculated based on the stoichiometry of the identified minerals. This calculation is theoretical because the majority of minerals are not 100 % pure and sometimes, depending on their concentration, cannot be detected.

5.2.2 X-ray diffraction

X-ray diffraction (XRD) is a rapid and powerful analytical technique used to identify crystalline compounds based on the determined crystal structure. The analyzed sample is finely ground and homogenized. One limitation of the XRD technique is that the detection limit is approximately 2 to 5 % by mass [30]. Rietveld refinement is a whole-pattern fitting approach for the quantification of crystalline compounds using good quality XRD patterns. Jana (2020) [21] used this technique to analyze concrete samples from Connecticut. For aggregate or concrete samples, a large volume should be ground and mixed well to obtain a representative sample. As with petrography, several samples need to be tested to estimate the actual distribution of pyrrhotite.

High-resolution X-ray diffraction with synchrotron radiation can lower the detection limit to as low as 0.1 % or less by mass on a very fine micronized powder sample (<45 μm). XRD detectors could detect pyrrhotite at levels as low as 0.05 % by mass.

5.2.3 Acid leaching method

Marcelino et al. [52] presented an acid leaching procedure to evaluate the amount of pyrrhotite in sulfide-bearing concrete samples based on the methodology developed by Lorenzen [53]. First, an aggregate sample was ground to a particle size lower than 0.15 mm. One gram of ground sample was then agitated for 1 h in 100 mL of HCl at 60 °C. Finally, the sample was filtered, washed, and oven-dried at 40 °C for 24 h. The total sulfur content was measured on a solid sample and corresponded to the pyrite content. The difference between the total sulfur content of the aggregate and the pyrite content indicated the pyrrhotite content. The result was verified by leaching pyrite in the residual solid using aqua regia (75 % HCl, 25 % HNO_3).

5.2.4 Micro X-ray fluorescence (μXRF)

Micro-XRF is a method for mapping the elemental analysis of samples. This technique characterizes and quantifies the iron sulfides present in the aggregates without differentiating between pyrite and pyrrhotite minerals [54]. These authors examined concrete core samples with aggregates containing iron sulfide minerals. The combination of elemental chemical distribution images facilitated the identification of mineral phases. Quantification was carried out using image analysis. Micro-XRF allows elementary mapping of an area up to 15 cm with a minimum beam size of 20 μm.

5.2.5 X-ray photoelectron spectroscopy (XPS)

XPS is a surface-sensitive quantitative spectroscopic technique that can distinguish sulfide types. XPS provides information about the element oxidation state and concentration with a detection limit in the parts per million (ppm) range. XPS easily detects small amounts of pyrrhotite, below 0.1% by mass of total S, in a sample [54]. However, XPS analysis requires ultra-high vacuum conditions, and the sample size is limited to a length of up to 5 cm.

5.2.6 Automated scanning electron microscopy system

Scanning electron microscopy (SEM) is routinely used with automated systems such as quantitative evaluation of minerals by scanning electron microscopy (QEMSCAN) and mineral liberation analyzer (MLA) to identify pyrrhotite through EDS using Fe/S ratios unique to pyrrhotite. However, currently, it cannot accurately quantify superstructures because their ratios are too similar [27].

The MLA transforms the raw images of particles (backscattered electron images) with the X-ray data into mineral maps and calculates different parameters such as the degree of liberation, mineral boundaries, coexistences, and other parameters, using powerful image analysis tools. Marcelino et al. [55] used MLA to determine the spatial distribution of pyrite and pyrrhotite in an aggregate sample. The oxidation of sulfide minerals is greater at the surface or in the vicinity of cracks than in the core of the particles. Thus, the exposed surface of each sulfide mineral was calculated by MLA.

5.2.7 Magnetic susceptibility (χ)

Geiss and Gourley [46] proposed a thermomagnetic technique, where magnetic susceptibility χ was monitored as the sample was heated to 700 °C to quantify the risk of concrete deterioration due to pyrrhotite. The magnetic susceptibility drop (Δχ) between 310 and 325 °C was used as a semi-quantitative measure of pyrrhotite content. However, the calibration curve is valid for pyrrhotites with similar chemical compositions and crystallographic superstructures. In the case studied, this method was used to determine the amount of pyrrhotite in deteriorated concrete from Connecticut.

5.2.8 Final considerations

The methods described above may be useful for diagnosing the affected structures. However, not all forms of pyrrhotite are equally reactive as presented in the previous sections. Therefore, other engineering tools are needed for the routine evaluation of aggregates containing iron sulfide minerals. A performance evaluation method is necessary to overcome all the factors that may influence the reactivity of pyrrhotite. In addition, further research is needed to elucidate the oxidation potential of polytypes 4C and 5C and the effect of trace metal contents of pyrrhotite.

6 Performance evaluation of the quality control of aggregate materials

Rodrigues et al. [48] proposed an innovative assessment protocol to evaluate the detrimental behavior of iron-sulfide-bearing aggregates before their use in concrete. A modified version of the protocol is included in Annex P of the Canadian standard CSA A23-2019 *Concrete materials and methods of concrete construction* [56], as illustrated in Fig 5. The protocol is divided into three successive major steps, starting with quick screening tests and then moving on to a long-term performance test on mortars. The original protocol [48] was based on the study of six sources of aggregates containing pyrrhotite and recognized to have cause damage in concrete.

Two to three sources of aggregates without sulfide minerals of various lithologies were used as non-reactive control aggregates. Figure 5 presents the modified version (Annex P) with slightly different limit values to consider recent results.

In Step 1, the aggregate total sulfur content is measured. The aggregate is rejected if the total sulfur content was higher than 1.00 % and accepted if it is less than 0.15 %. It is necessary to follow Step 2 if S_{total} values are higher or equal to 0.15% and lower than 1.00%. In step 2, the aggregates is subjected to an oxygen consumption test [57], in which the oxygen consumed by the oxidation of iron sulfide minerals is measured in the headspace of a sealed cell containing the ground aggregate material in the presence of specified moisture content (Fig 6). Aggregates with oxygen consumption higher or equal to the limit of 4.0% are then required to be tested in Step 3. Step 3 consists of a two-phase mortar bar expansion test. The first phase is intended to reproduce the oxidation reaction, in which the mortar bars are subjected to 90-day storage at 80 °C and 80 % RH with two 3-hour soaking periods per week in a strong oxidizing agent of 6 % bleach solution. After 90 days, the samples are transferred to 4 °C and 100 % RH for another 90 days, while maintaining the two immersion periods in bleach solution, to generate an internal sulfate attack due to ettringite and thaumasite formation [58]. If the expansion obtained in step 3 is higher or equal to 0.10% between the phase 1 at 90 days and phase 2 at 180 days, the aggregate shall be rejected for use as concrete aggregate. Tentative limits are proposed for each step, which still need to be validated by testing a wider range of aggregates. Guirguis et al. (2018) [59] and El-Mosallamy et al (2020) [60] have published results using this protocol which helped refine the limits that are currently proposed in Annex P of the Canadian A23-2019 standards.

Other rapid tests are available for the evaluation of the oxidative potential of aggregates. Ramos et al. [61] proposed a rapid staining screening test for the rapid detection of sulfide minerals that may cause staining or an oxidation reaction. The test is based on the Midgley test [62], using 6 % bleach as an oxidizing agent instead of lime water to identify the potential for the oxidation of the aggregates. Oxidation of iron sulfides by bleach creates a strongly exothermic reaction, which can be monitored by a temperature test. Guirguis and Shehata [63] also proposed a simple screening test for measuring the mass loss of aggregates immersed in an oxidizing agent. The mass loss and the change in color of the test solution are the criteria considered for the assessment of aggregate potential to oxidation. or These rapid tests are complementary and allow rapid decision-making on the relevance of undertaking other investigations.

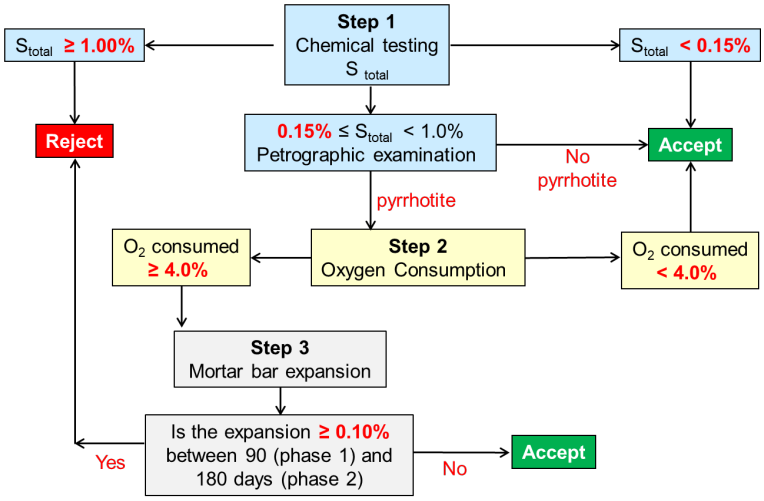

Figure 5. Simplified protocol for determining the potential reactivity of iron sulfide-bearing aggregates as presented in Annex P of CSA A23.1:19 [56] (modified from the original version proposed by Rodrigues et al. [48]. Limit values (in red) still need to be validated.

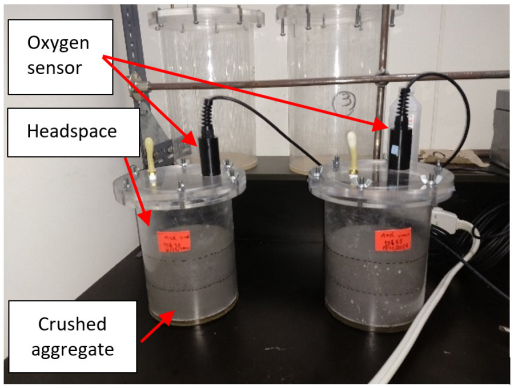

Figure 6. Cells used in the oxygen consumption test.

7 Conclusions

The presence of iron sulfides in the aggregates presents a risk of severe concrete deterioration due to oxidation, production of secondary sulfates, and subsequent generation of internal sulfate attack. Major recent advances in the development of identification and quantification methods for pyrrhotite detection, even at very low levels, enhance the diagnosis of cases where deterioration is observed.

Notably, pyrrhotite shows variable reactivity depending on several factors, including the chemical composition and crystal structure. An accurate evaluation of the new aggregate sources would need a performance-based approach to overcome these influencing factors. Evaluation protocols are currently being developed to establish accurate guidelines for the quality control of aggregates.

Recent advances have shown the importance of the specific surface area and exposed surfaces of pyrrhotite. Therefore, it is ultimately important to conduct a performance test directly on concrete samples in which aggregates are used as received from the quarry.

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CRediT authorship statement

Josée Duchesne: Conceptualization, Methodology, Visualization, Supervision, Writing – original draft, Funding acquisition.

Andrea Rodrigues: Methodology, Investigation, Resources, Visualization, Writing – review and editing.

Benoit Fournier: Conceptualization, Funding acquisition, Writing – review and editing.

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