



# A new accelerated mortar bar test to assess the potential deleterious effect of sulfide-bearing aggregate in concrete



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## ARTICLE INFO

### Article history:

Received 1 December 2014

Accepted 9 February 2015

Available online 20 March 2015

### Keywords:

Deterioration

Testing method

Internal sulfate attack

Pyrrhotite oxidation

Concrete

## ABSTRACT

Deterioration of concrete structures incorporating sulfide bearing aggregates has been reported in Trois-Rivières area, Québec, Canada. In this case, iron sulfide oxidation and internal sulfate attack were observed.

The present study aims at developing a performance test that will reproduce, in the laboratory, the deterioration mechanisms observed on site. A two-phase accelerated mortar bar test was developed that consists 90 days of storage at 80 °C/80% RH, with two 3-h wetting cycles in a 6% bleach solution (Phase I) followed by up to 90 days of storage at 4 °C/100% RH (Phase II). Aggregates with oxidation potential presented an expansion over 0.15% during Phase I, while thaumasite formation potential is detected by rapid regain of expansion followed by destruction of the samples during Phase II. The control aggregates without sulfide mineral did not show any signs of deterioration in both phases of the testing program.

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## 1. Introduction

In the last few years, problems affecting concrete structures incorporating sulfide bearing aggregates have been reported in the Trois-Rivières area (Quebec, Canada). In most cases, the affected structures are house foundations; however, cases involving commercial buildings have also been identified. A large proportion of the house foundations were built between 2004 and 2008 and started to show deterioration within 3–5 years after construction. Visual signs of concrete deterioration consist of map-cracking (with some cracks reaching up to 40 mm in width) often showing yellowish/brownish staining. Pop-outs are also found exposing oxidized aggregate particles sometimes surrounded by a white rim of secondary reaction products [1].

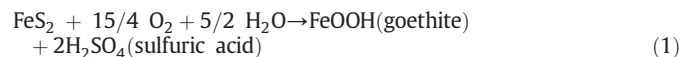
### 1.1. Mechanisms of deleterious oxidation reactions and factors influencing the reaction

Recent investigations carried out by the authors [1–4] related the concrete deterioration to the use of a hypersthene gabbro coarse aggregate containing various proportions of sulfide minerals, including pyrrhotite [Fe<sub>1-x</sub>S], pyrite [FeS<sub>2</sub>], pentlandite [(Fe, Ni)<sub>9</sub>S<sub>8</sub>] and chalcocopyrite [CuFeS<sub>2</sub>]. In addition to biotite [K(Mg,Fe)<sub>3</sub>AlSi<sub>3</sub>O<sub>10</sub>(F,OH)<sub>2</sub>] and plagioclase feldspar [NaAlSi<sub>3</sub>O<sub>8</sub>–CaAl<sub>2</sub>Si<sub>2</sub>O<sub>8</sub>], a thin layer of an iron carbonate (siderite–FeCO<sub>3</sub>) was often found surrounding those sulfide minerals. The petrographic examination of deteriorated

concrete specimens obtained from house foundations revealed that the pyrrhotite was often deeply oxidized, while pyrite showed only traces of oxidation or was perfectly sound. The rust products associated to the “unstable” aggregate particles typically consisted of iron oxide/hydroxide/oxyhydroxide; secondary products resulting from subsequent internal sulfate attack, namely gypsum [CaSO<sub>4</sub> · 2H<sub>2</sub>O], ettringite [Ca<sub>6</sub>Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>(OH)<sub>12</sub> · 26H<sub>2</sub>O] and thaumasite [Ca<sub>3</sub>Si(OH)<sub>6</sub>(CO<sub>3</sub>)(SO<sub>4</sub>) · 12H<sub>2</sub>O], were also identified.

Cases of concrete deterioration involving sulfide bearing black shales, shists or sedimentary rocks were reported in the literature [5–13]. Tagnit-Hamou et al. [13], studied deteriorated concrete house foundations incorporating a sulfide bearing gray anorthosite with some amounts of sulfide minerals very similar to the Trois-Rivières aggregate investigated in this study. Secondary products identified in deteriorated concretes incorporating sulfide-bearing aggregates consisted of jarosite [KFe<sub>3</sub>(OH)<sub>6</sub>(SO<sub>4</sub>)<sub>2</sub>] [12,14,15], iron oxides and hydroxides [11,13,16], halotrichite [FeAl<sub>2</sub>(SO<sub>4</sub>)<sub>4</sub> · 22H<sub>2</sub>O] [13], gypsum [10,14,15], ettringite [10–13], and thaumasite [15,17,18].

The oxidation of sulfide minerals in the presence of water and oxygen results in the formation of various rust products and sulfuric acid, such as the case presented herein for pyrite (Eq. (1)).



Steger [19] concluded that the oxidation rate of sulfide minerals increases directly with increasing relative humidity (RH) values between 37% and 75%. In 1995, Knipe and coworkers [20] studied the interactions between pyrite and pyrrhotite and water vapor. They

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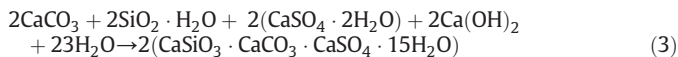
concluded that oxygen is the primary oxidant, and that the iron sulfides do not oxidize when exposed to deoxygenated water. The amount of oxygen that can diffuse is limited by the maximum concentration of  $O_2$  in water, ( $C_w \approx 9.2$  mg/L), which is about 30 times less than the equilibrium concentration of oxygen in air ( $C_a \approx 276.7$  mg/L) at 20 °C [21]. Consequently, a sample of iron sulfide immersed in water or kept at 100% relative humidity will not oxidize or the oxidation rate will be really slow. According to Bussi ere [22], an expert in the field of mining environment, the optimum relative humidity for sulfide oxidation is between 60% and 80% (personal communication).

The oxidation of pyrite and pyrrhotite can also be promoted and catalyzed by the *Thiobacillus ferrooxidans* bacteria. These bacteria occur at low pH [6], in the range 1.0–2.5, deriving their energy from redox reactions where  $Fe^{2+}$  or reduced sulfur compounds serve as electron donor and oxygen as electron acceptor [23]. The specific surface area of the iron sulfides is increased by fracturing and surface roughness that consequently increase the oxidation reaction, because more surface is exposed to moisture and oxygen [24,25]. Divet and Davy [24] and Steger [19] showed that the sulfide oxidation rate increases significantly with increasing temperature, in accordance with the Arrhenius Law. The iron sulfide morphology can also influence the oxidation reaction. Divet and Davy [24] concluded that framboidal pyrite oxidizes much faster than massive pyrite. The authors also found that the high  $OH^-$  ion concentration in the alkaline pore solution of concrete plays a major role in the pyrite's oxidation. For a pH greater than 12.5, the oxidation rate increases exponentially and reaches about 50 times its initial value for a pH of 13.7.

When the sulfuric acid generated in Eq. (1) reacts with the solids of the cement paste, mainly with the portlandite  $[Ca(OH)_2]$ , the formation of gypsum occurs according to Eq. (2) [14,26].



When the right conditions have been met, such as temperature, pH, humidity, other sulfates such ettringite and thaumasite can also be formed. The resulting internal sulfate attack (causing the formation of gypsum, ettringite and thaumasite), however, requires other conditions and is influenced by factors other than those affecting iron sulfide oxidation. In the case of internal sulfate attack with thaumasite formation, a source of water and of carbonate, sulfate and silicate ions is required (Eq. (3)).



The source of sulfates can be the cement or the aggregates [27–30]. The carbonate source is generally the aggregate [29,30], the limestone filler in certain cements or the atmospheric  $CO_2$  [30]. The silicate ions are usually provided by the silicates present in the C–S–H, thus leading to the disintegration of the cement paste and, consequently, of the concrete [30]. The favorable conditions for thaumasite formation are temperatures below 15 °C [30–33], the ideal conditions being between 0 and 5 °C [34]. However, cases of thaumasite formation were also reported at room temperature [35].

## 1.2. Testing for evaluating the potential for deleterious reaction of sulfide bearing aggregates

Since it was found that sulfide bearing aggregates could affect concrete durability, research was carried out to develop laboratory tests to evaluate their potential deleterious reactivity [5,11,17,36–40]. Some tests aimed at determining a limit value of iron sulfides (e.g. pyrite and/or pyrrhotite) that would make concrete aggregates safe for use [5, 36,39]. Some studies also tried to recreate, in the laboratory, the conditions and mechanisms that lead to concrete deterioration in order to

identify deleterious sulfide-bearing aggregates [11,18,37,38,40]. The following subsections present a summary of the test conditions applied in the above studies and of their main findings.

### 1.2.1. Testing by Hagerman and Roosaar [36] in Sweden

Having noticed some concrete deterioration problems involving sulfide-bearing aggregates in Sweden back in the early 1950s, Hagerman and Roosaar tried to determine the maximum tolerable pyrrhotite content in concrete aggregates using rock samples from Pengfors (pyrrhotite contents of 4% and 14%), Norrforsen (21% of pyrrhotite), and Stockholm (control non sulfide-bearing granite). The authors manufactured a series of concrete beams,  $80 \times 15 \times 10$  cm and  $40 \times 15 \times 10$  cm in size, that they subjected to a range of test conditions, including weekly cycles consisting of 3 days in warm water and 4 days of air storage at 75 °C, 3 days in water and 4 days in air both at room temperature, or continuous outdoor exposure. Alternatively, some beams were subjected to steam curing in an autoclave at 225 °C for 5 h. The specimens were then allowed to cool to 100 °C in the autoclave, and then exposed to warm water to progressively bring their temperature down to 23 °C. This treatment was repeated four times at approximately 1 week intervals. Between autoclaving sessions, the specimens were stored in air at room temperature.

After 7 months of testing, the series of beams ( $80 \times 15 \times 10$  cm) made with rock samples incorporating a higher percentage of pyrrhotite (Pengfors 14% and Norrforsen 21%) and stored in warm water for 3 days followed by 4 days of air exposure at 75 °C showed the presence of rust, cracks and bending. The examination of broken surfaces of the beams made with the Norrforsen rocks (with 21% of pyrrhotite) revealed more damage at the end of testing and also that the rusty aggregate particles were limited to the first 10 mm from the surface; further petrographic examination in thin sections confirmed the presence of sulfide oxidation, together with staining in the cracks. Ettringite was however not observed.

### 1.2.2. Testing by B erard et al. [5] in Montreal (Canada)

The authors studied cases of concrete deterioration related to the presence of sulfide-bearing shale particles (4.5% pyrrhotite) in the coarse aggregate. In order to try reproduce the deleterious reaction in the laboratory, the researchers manufactured 10 concrete prisms with different proportions of shale particles recycled from the deteriorated concrete elements (maximum aggregate particle size of 2 cm), and 10 companion prisms with shale particles obtained from the original quarry (maximum aggregate particle size of 4 cm). They then subjected the concrete prisms to cycles of wetting in a moist room at 23 °C for a certain period of time, and drying in air in the laboratory for an equal period of time. All the specimens suffered shrinkage, while one specimen showed a longitudinal crack with iron oxide seeping through the crack. Although the test was unable to reproduce the distress observed in the field (expansion/cracking), the deleterious properties of the shale were somewhat highlighted since some shale particles near the surface of the test prisms generated pop-outs through the oxidation of pyrrhotite mainly visible along bedding planes.

In addition, five blocks/cubes, with an initial length of 4 cm and cut from the shale, were subjected to different test conditions and their expansion monitored over time perpendicular to the bedding. Two test cubes immersed in water expanded by more than 0.2% in less than 100 days. Two other test cubes kept outdoors expanded only slightly less than the first two cubes. A fifth specimen, kept indoors at room temperature, showed slight shrinkage. Oxidation of sulfides was visible in all the specimens and concentrated along the bedding planes.

### 1.2.3. Testing by Gomides [39] in Brazil

Gomides [39] investigated the performance of concretes incorporating sulfide-bearing aggregates and five types of cements. In stage 1 of the experimental program, concrete mixtures were prepared with

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