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Quantitative assessment of the oxidation potential of sulfide-bearing aggregates in concrete using an oxygen consumption test

Andreia Rodrigues*, Josée Duchesne, Benoît Fournier

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

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In the presence of oxygen and humidity, the iron sulfide minerals present in some concrete aggregates can oxidize creating damage to concrete infrastructure. An oxygen consumption test was developed to assess the oxidation potential of concrete aggregate. A compacted layer of aggregate material is exposed to oxygen (O_2) in a hermetic cell, and the O_2 consumption is monitored. Optimized parameters included a 10 cm compacted layer of aggregate material with particle size <150 μm kept at 40% saturation degree with a 10-cm headspace left at the top of the cell. The consumption of the O_2 present in the headspace is monitored over a 3-h testing period at 22 °C. The test was able to discriminate the eight sulfide-bearing and control aggregates selected when using a threshold limit of 5% O_2 consumed. This draft limit will, however, require to be confirmed through the testing of a larger number of aggregates.

1. Introduction

Concrete deterioration due to sulfide-bearing aggregates is not a new subject in the world of civil and geological engineering. Since the 1950's, numerous cases, such as the one reported by Moum and Rosenqvist [1] in the Oslo region (Norway), involving the deterioration of concrete structures due to the presence of iron sulfide minerals (pyrrhotite and pyrite) in the aggregates, have been published [2]. One of the recent cases is the one in the Trois-Rivières area (Quebec, Canada), where the deterioration of concrete foundations and slabs in private houses and commercial buildings was caused by the oxidation of iron sulfides (mainly pyrrhotite) in coarse aggregates followed by internal sulfate attack leading to thaumasite formation [3–6].

Even if this problem has been known for many years, there are currently no laboratory tests capable of satisfactorily predicting the potential deleterious character of sulfide-bearing aggregates. A full chemical analysis including the measurement of the total sulfur content, although allowing identifying the presence and, to some extents, the total sulfide mineral content within the aggregate material, will however not differentiate the different mineral forms present, e.g. pyrite from pyrrhotite. This could potentially be done by X-Ray diffraction; however, the method is generally sensitive only for mineral forms in excess of 5% in the rock sample. A detailed petrographic characterization of the aggregates is one of the best ways to identify the various iron sulfides, but various limitations are affecting this technique. For example, in this particular case, the examination needs to be carried out by petrographers with an appropriate experience in reflected light petrography, a challenge that can be even enhanced since sulfide minerals are often sparsely and/or finely disseminated within concrete aggregate particles. Also, unless specific measures are used (e.g. using point-counting methods), the proportions of sulfide minerals in polished thin sections or slabs are often obtained by visual estimate, which can generate significant variations from one petrographer to another. Combined chemical and petrographic characterization of the aggregate material has the potential of providing semi-quantitative or even quantitative (when using advanced methods such as the Mineral Liberation Analysis (MLA) by scanning electron microscopy (SEM) analysis of ground rock/aggregate samples) measurements of the mineral contents within aggregate materials. However, the above still cannot readily assess the deleterious character of the sulfide minerals present since the latter can be influenced by factors such as the mineral types present, the mineral crystallinity and crystallographic characteristics (e.g. for pyrrhotite), porosity, grain size, and galvanic effects between the distinct associated mineral

* Corresponding author.
E-mail addresses: andreia.oberon81@gmail.com (A. Rodrigues), josee.duchesne@ggl.ulaval.ca (J. Duchesne), benoit.fournier@ggl.ulaval.ca (B. Fournier).

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phases [7,8].

There is consequently an obvious need for a performance test for reliably assessing the oxidation potential of concrete aggregate materials. The mechanisms of iron sulfides oxidation are well-known in the mining environment literature because these reactions are the source of acid rock drainage (ARD) that is a major concern for the mining industry [9–12]. It occurs when the iron sulfides are in the presence of oxygen and humidity forming acidic, iron and sulfate-rich by-products as seen in the following Equation (1) for the pyrrhotite oxidation:

$$Fe_{1-x}S + (2\text{-}(1/2)x)O_2 + xH_2O \rightarrow (1-x)Fe^{2+} + SO_4^{2-} + 2xH^+ \quad (1)$$

where x varies between 0.0 and 0.125 depending on the pyrrhotite crystallography [13].

In the sulfide oxidation reaction, the oxygen is one of the reactants and the monitoring of its concentration can be used to determine the oxidation potential of sulfide-bearing aggregates. This process was first proposed by Elberling and coworkers [14] and Elberling and Nicholson [15] to evaluate the rate of oxidation of mine tailings containing sulfide minerals. In the technique developed by Elberling and coworkers [14], the oxygen flux into tailings exposed to the atmosphere is evaluated using oxygen consumption assuming steady state flux prior to making any measurements [16,17]. The oxygen fluxes are calculated based on the second Fick's law (Equation (2)):

$$V\frac{dC}{dt} = AC\left(kD_{eff}\right)^{0.5} \quad (2)$$

where V is the headspace volume, A is the area of the container, C is oxygen concentration, t is the time, k is the reaction-rate constant for the sulfides and Deff is the effective diffusion coefficient, which is $1.8 \times 10{-}5\ m^2/s$ for air at 25 °C [14]. Considering the initial condition: C═C0 at t = 0, the solution of the previous equation will be (Equation (3)):

$$ln\left(\frac{C}{C_0}\right) = -t\left(kD_{eff}\right)^{0.5}\frac{A}{V} \quad (3)$$

The slope of the graph C/C0 versus time gives the value of $(kDeff)^{0.5}$ when A/V is known.

During the test, the oxygen diffuses through the tailings where it is consumed by the oxidation of sulfide minerals. The progressive decrease of oxygen concentration in the close volume is monitored over time and is used to determine Fick's laws parameters [17]. According to these authors, this interpretation can only be valid for short-duration tests and a more sophisticated approach using numerical modelling is proposed. This is important in the field of ARD where the oxygen consumption test is also used to assess the effectiveness of remediation schemes involving the use of water covers and engineered soil covers to minimize ingress of oxygen into tailings.

2. Objectives and scope of work

The oxygen consumption method seems to have a great potential to evaluate the oxidation potential of concrete aggregates containing iron sulfide minerals. First, because of the direct measurement of one of the reactants necessary for the oxidation reaction (oxygen) and, second, because the results obtained are quantitative, so less susceptible to erroneous interpretations and variations between operators, as it is the case for petrographic examination.

The present work aims at adapting the oxygen consumption test developed by Elberling and coworkers [14] to evaluate the potential deleterious character of sulfide-bearing aggregates for use in concrete. A parametric testing program was carried out to optimize testing conditions. The “optimized” test was then applied to assess the oxidation potential of ten iron sulphide-bearing and control aggregates. Finally, the precision of the test was evaluated.

3. Materials and methods

In order to optimize the oxygen consumption test, a series of experiments were carried out to identify the most reliable conditions with respect to the aggregate particle size (obtained by grinding of sulfide-bearing and control aggregates) and moisture condition, as well as the thickness of compacted ground material (Fig. 1).

Based on the experience of Prof. Bruno Bussière's research team at the Université du Québec en Abitibi-Témiscamingue (UQAT) on the use of the *Oxygen consumption test* for mine tailings, it was decided that all measurements would be performed at atmospheric pressure, room temperature (22 °C), and with a 3.5-h test duration (30 min for the probes stabilization plus 3 h of effective oxygen consumption measurements). Preliminary tests carried out in Prof. Bussière's laboratory indicated that the headspace (air volume) above the compacted ground material had a significant impact on the test results; this parameter was thus further investigated as part of this study (see Fig. 2).

3.1. Sulfide-bearing and control aggregates

A total of ten aggregates were used in the different parts of this experiment; their properties are summarized in Table 1. They consisted of 7 sulfide-bearing aggregates (MSK, B&B, GGP, SBR, PHS and WS), one mainly composed of iron sulfide minerals (SDBR) and finally three control aggregates with no (PKA, HPL) or only traces of iron sulfides (DLS). A sample of each aggregate tested was taken prior to test in order to analyse the total sulfur (% by mass) content (Table 1). MSK, the problematic aggregate used in the construction of the Trois-Rivières house foundations, is a hypersthene gabbro containing various proportions of pyrite [FeS_2], pyrrhotite [$Fe_{1-x}S$], pentlandite [$(Fe,Ni)_9S_8$] and chalcopyrite [$CuFeS_2$] [3]. The percentage of sulfur (% S_T by mass) obtained from different MSK subsamples tested varied from 0.73 to 1.28%.

The B&B is an aggregate with the same characteristics and basically the same mineralogy of MSK aggregate, but with higher sulfur content. In fact, these aggregates come from quarries that are only about 500 m apart. The B&B sample was obtained by hand-picking rock fragments (from the 100-mm stockpile) with particularly high sulfide minerals contents.

GGP is a granitic gneiss from Central Quebec (Canada) with a mineralogical composition somewhat similar to the MSK aggregate, especially regarding the iron sulfide minerals present, i.e. pyrrhotite, pyrite and chalcopyrite.

SBR is a fine-grained hornfels from the greater Montreal area (Canada). This aggregate is not used in concrete; however, it was selected due to its mineralogical composition and the presence of iron sulfide minerals (Table 1). This aggregate is also an alkali-silica reactive aggregate.

WS is mica schist aggregate from Switzerland. This aggregate was used in the construction of a large concrete dam back in the early 1970s and that started to show signs of expansion in the early 1980s [18]. The dam structure showed signs of concrete elements displacement and deposits of rust in the galleries of the dam. The authors related the concrete deterioration to the oxidation of the iron sulfide minerals present in the aggregate (Table 1).

PHS is a phyllite containing iron sulfide minerals. This aggregate