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EFFECTS OF SAMPLE PREPARATION ON THE RESULTS OF THE OXYGEN CONSUMPTION TEST USED TO EVALUATE OXIDATION POTENTIAL OF SULPHIDE-BEARING AGGREGATE

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Abstract: In the last decade, the sulphide-bearing aggregate was reported to be responsible for a severe deterioration in concrete elements. This deterioration takes place due to the oxidation of sulphide phases in aggregate which produces sulphuric acid, then gypsum which leads to internal sulphate attack. Earlier research work came up with a test for quantifying the oxygen consumption of sulphide bearing aggregate using oxygen consumption cells. In the earlier research work, the aggregate was processed to obtain materials passing 150 μm sieve. The processed aggregate was then compacted into 100 mm layer in a cell of 200 mm height. The sample was exposed to oxygen and the O_2 consumption was monitored. This paper examines the factors that affect the test results. The results show that aggregate processing has a great effect on the oxidation. Processing the aggregate using the commercially available disk pulveriser with cast iron plates, which was not used in the earlier research work, results in the presence of iron powder in the crushed materials, and overestimation of the oxygen consumption. When ceramic plates are used, better results with almost zero O_2 consumption is obtained for aggregate with zero sulphide content. Grinding the aggregate to a particle size of 300 μm to 75 μm is found to produce slightly higher O_2 consumption compared to the same aggregate sample tested using finer particle size (passing 150 μm). Based on the obtained results, a method to process aggregate samples is recommended.

1 INTRODUCTION

The presence of iron sulphides in aggregates has been recently recognized as a problem in concrete durability. Pyrite (FeS_2) and Pyrrhotite ($\text{Fe}_{(1-x)}\text{S}$ ($x = 0$ to $x = 0.2$)) are the most common and easily oxidized sulphide minerals; they are often found in sedimentary rocks such as shales and in most ore deposits (Bryant 2003). When oxidized, sulphides release sulphuric acids that react with the calcium hydroxide causing sulphate attack. The sulphuric acid can attack the calcium hydroxide or the calcium silicate hydrate releasing calcium ions to form gypsum (Monteny et al. 2000).

The degree of aggregate oxidation leads to the identification of potential of future problems in concrete expansion as a result of sulphate attack. Sulphide problems have occurred in materials containing a very small percentage of sulphide. About 0.1% of sulphide minerals can result, when oxidized, in the production of harmful oxidation products, such as sulphates, in the form of sulphuric acid (H_2SO_4) (Nordstorm and Alpers 1999). The products of sulphide oxidation reactions are extremely less dense than the original sulphide, therefore they occupy a larger volume than the initial sulphide product. These products can occupy up to eight times of the original volume of the sulphide mineral (Dougherty and Barsotti 1972).

Oxidation tests help in identification of the expansion rate and help predicting future issues. Elberling et al. 1994 developed a series of column experiments to determine sulphide oxidation rates in mine tailings. This

test was adopted and used by (Rodrigues, Duchesne, and Fournier 2016) to evaluate the potential deleterious effects of sulphide-bearing aggregates for use in concrete.

The Oxygen Consumption Test (OCT) adopted by (Rodrigues, Duchesne, and Fournier 2016) was conducted at atmospheric pressure, room temperature (22°C), and with a 3.5-hour test duration (30 minutes for the probes stabilization in addition to 3 hours of effective oxygen consumption measurements). For aggregate crushing, jaw crusher was used followed by a roller crusher until the entire sample passed the 1.18 mm sieve. Then, a rod mill was used until the entire sample passed the 150 µm sieve. The use of disk pulveriser with iron plates was not adopted in the work of Rodrigues, Duchesne, and Fournier 2016. Testing indicated that the optimum experimental conditions, that seemed most suitable to discriminate potentially deleterious aggregates from non-sulphide aggregate, were the use of 40% saturation, a thickness of compacted ground material of 100 mm with a 100 mm headspace and a maximum particle size of 150 µm with no limit on the minimum size.

This study examines the factors that affect the test results including aggregate processing and size. The proposed sample preparation and sample gradation was adopted and used to test two concrete aggregates.

2 MATERIALS AND METHODOLOGY

2.1 Methodology

For sample preparation, three methods of aggregate processing were used:

1. Jaw crusher followed by disk pulveriser with cast iron plates,
2. Jaw crusher followed by grinding mill with stainless steel balls (micro-deval apparatus), and
3. Jaw crusher followed by disk pulveriser with ceramic plates (Figure 1).

In the three cases, aggregate samples were initially crushed in the jaw crusher until the whole samples passed sieve #16 (1.18 mm). Samples were then introduced to the secondary mode of crushing until the whole sample reached the required size.

It should be noted that the authors understand that using micro-deval apparatus may not produce representative samples; however, it is used here with a non-sulphide aggregate sample to examine the effects of using disk pulveriser with iron plates.



Figure 1. Disk pulveriser with ceramic plates.

The test configuration is adopted from the work of Rodrigues, Duchesne, & Fournier (2016). The cells are made of Plexiglas columns that are sealed with Plexiglas cap in their upper part allowing a headspace above the ground material. Each cell has a 200 mm height and an internal diameter of 141.7 mm (Figure 2). During the experiment, the columns were sealed using a gasket of 3 mm thickness to avoid any leaks or entry of oxygen into the system.

Oxygen consumption was monitored for 3.5 hours (includes 30 minutes for oxygen sensor probe stabilization) as originally proposed by (Rodrigues, Duchesne, and Fournier 2016), and extended to 16.0 hours in addition to the 30 minutes for the oxygen sensor probe stabilization. The ground aggregate was tested at 40% degree of saturation and 100 mm headspace were left at the top of the cell. A galvanic-cell type oxygen sensor (Apogee SO-100 & 200 series) was inserted through the Plexiglas cap and connected to a 4 channel Quad-Volt data Logger (OM-CP-IFC200), as shown in Figure 2.

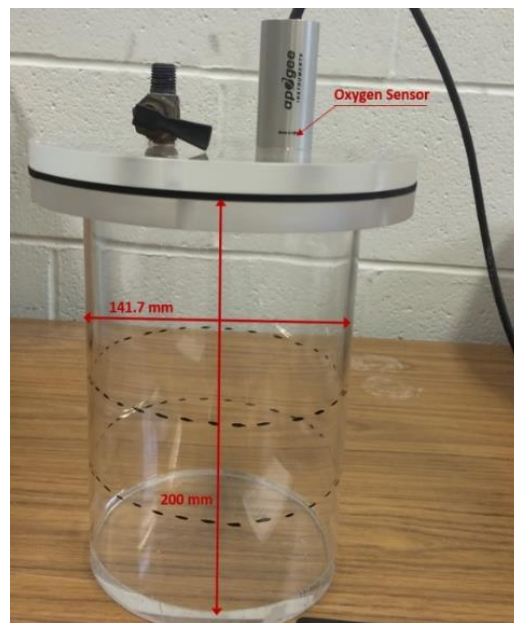


Figure 2. Oxygen consumption cell dimensions.

2.2 Materials

In the proposed experimental program, a compacted aggregate layer of 100 mm thickness of crushed aggregates was tested in different gradation compared to the gradation used by (Rodrigues, Duchesne, and Fournier 2016). In order to investigate the applicability of the test, samples were prepared by mixing an aggregate containing no sulphides and an aggregate with very high level of sulphide. The zero-sulphide aggregate is natural river sand (S) that was quarried from the Caledon area near Toronto, Ontario, Canada. This sand is used in commercial concrete in the southern Ontario area, and has a good track record of past performance. The sulphide bearing aggregate is a sulphide ore (Ore) coarse aggregate from Sudbury area. It is mainly pure pyrite and pyrrhotite which is used in this study as a source of sulphides

The test was also conducted on the following aggregates:

1. A sulphide-bearing aggregate from Quebec, Maskimo (MSK) which consists mainly of Pyrrhotite. This aggregate is considered responsible for severe deterioration in concrete foundation in Trois-Rivieres area, Quebec, Canada (Rodrigues, Duchesne, and Fournier 2012; Rodrigues et al. 2012; Duchesne and Fournier 2013; Rodrigues, Duchesne, and Fournier 2016).

2. Crushed quarried dolomitic limestone coarse aggregate (C1). This aggregate has a very good history as a non-reactive aggregate and is used in concrete in Toronto, Canada. The sulphide content in this aggregate is negligible.
3. A dolostone Coarse Aggregate (C20) which is being used as concrete aggregate sources. This aggregate has a total sulphur content of 0.151% and contains gypsum in small quantities.
4. A limestone aggregate (P) from Quebec which has no sulphide minerals. Table 1 shows some physical and chemical properties of the tested aggregates.

Table 1. Physical and chemical properties of tested aggregates

Aggregate	Relative density	St (%)
Sand	2.693	0.0
P	2.87	0.04 to 0.06
C1	2.571	0.09-0.19
Ore	2.697	13.86-14.46
MSK	2.888	0.73-1.28
C 20	2.696	0.151

In addition to the previous samples, and in to examine the sensitivity of the test method to detect different levels of sulphide in aggregates, mixtures of the sand (S), and different percentage of sulphide ore aggregate (Ore) were tested. Samples were first processed in the jaw crusher, then introduced in the micro-deval abrasion machine for eight hours until a size passing 150 μm and retained on 75 μm was reached. The tested samples were:

- S (100): 100% sand
- S/Ore (1%): Sand contains 1% of sulphide ore aggregate
- S/Ore (2%): Sand contains 2% of sulphide ore aggregate
- S/Ore (5%): Sand contains 5% of sulphide ore aggregate
- S/Ore (10%): Sand contains 10% of sulphide ore aggregate

In addition to the previous samples, a sand sample with 5% iron powder collected from Ryerson's machine shop was tested to investigate the effect of iron impurities on the oxygen consumption.

To test the effect of grinding size, aggregates (MSK) and (C20) were also tested in two gradations. As shown in Table 2. These sample gradations and proportion was chosen in an attempt to have a control on the tested gradation, especially the fine fraction.

Table 2. Gradation of the tested samples

Gradation # and description	Sieve size		
	600 μm – 300 μm	300 μm -150 μm	150 μm – 75 μm
1 (coarse)	50%	50%	--
2 (fine)	--	50%	50%

3 RESULTS

The two aggregates P and C1 were prepared using jaw crusher and disk pulveriser with cast iron plates. The oxygen consumption test results showed both aggregates - P ($S_{i=}$ 0.04-0.06 (%)) and C1 ($S_{i=}$ 0.09-0.19 (%)) - to have high oxygen consumption (Figure 3). Even when aggregate (P) was ground using the same method to a coarser size - between 600 μm and 300 μm - it has shown a high consumption (about 94%), despite the anticipated lower oxidation associated with larger particle size. When the sample was left in the cell for two days, rust appeared in the aggregate as shown in Figure 4.

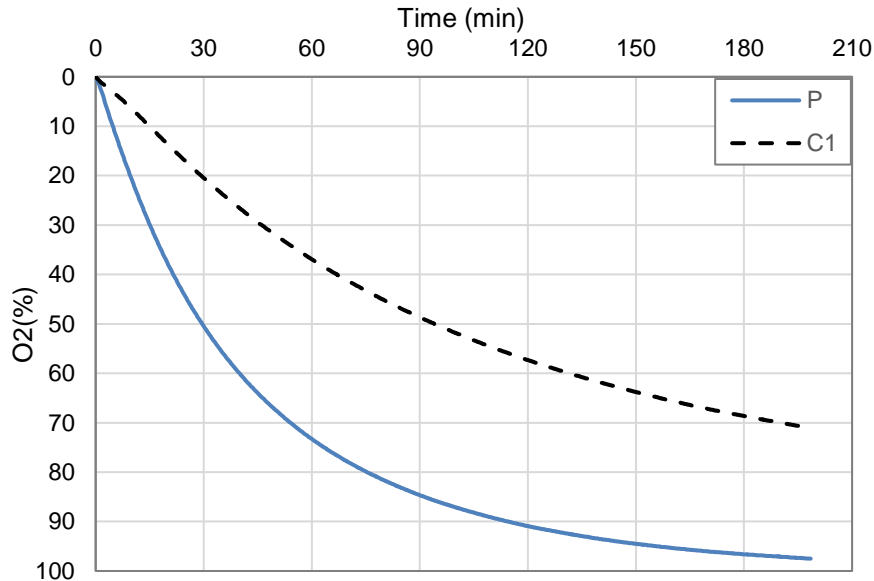


Figure 3. Oxygen consumption for samples crushed by the disk pulveriser with cast iron plates.



Figure 4. Rust in aggregate crushed in the disk pulveriser with iron plates.

For more evaluation of this behaviour, the sand (S) was processed in a very similar manner in the disk pulveriser with cast iron plates. Also, another sample was crushed by the micro-deval abrasion machine for comparison. A third sample was prepared by mixing the sand processed by the micro-deval with 5% by mass of iron powder. Results of these tests are shown in Figure 5: the first sample have shown high oxygen consumption, while the sample crushed in the micro-deval have shown very little or no consumption. A 5% by mass iron powder added to the sand crushed in the micro-deval showed a high oxygen consumption that is close to the measured consumption of the sand crushed in the disk pulveriser. These results indicate

that the measured oxygen consumption in the samples tested and presented in Figure 5 was not a result of sulphide oxidation, but was due to inclusion of iron impurities within the sample either from the iron plates or through adding the iron powder.

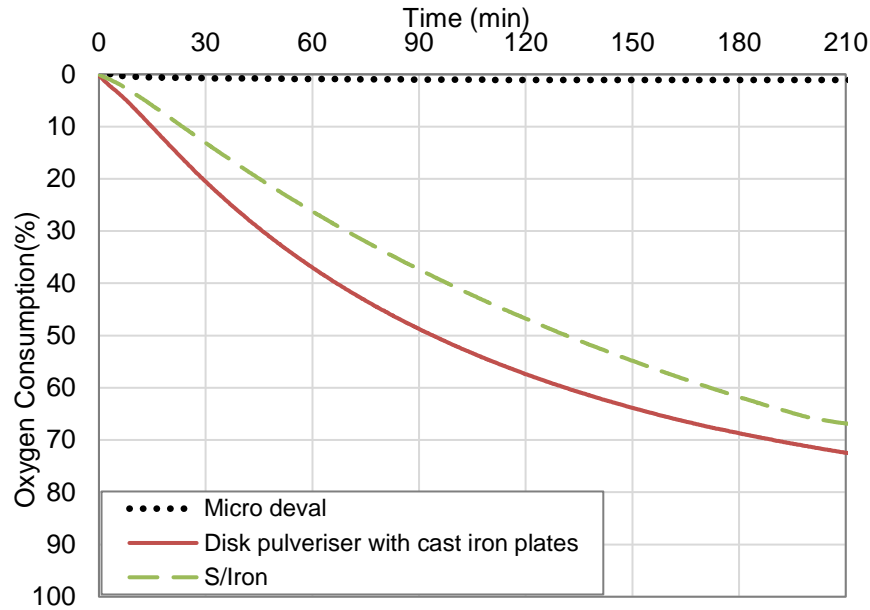


Figure 5. Oxygen consumption for sand crushed by the micro-deval abrasion machine and disk pulveriser with cast iron plates and a sample with crushed with the micro-deval and has 5% iron powder.

Figure 6 shows the results of testing sand (S) with different sulphide ore (Ore) content. The sand sample was crushed in the micro-deval abrasion machine, while the (Ore) sample was introduced first to the jaw crusher until the sample reached 1.18 mm, then the sample was crushed in the micro-deval. The oxygen consumption for sample (S) was about 1% O₂. This percentage increased to 7% O₂ when using 1% of Ore, and about 30% O₂ when mixed with 10% of Ore during the 3.5 hours' test period.

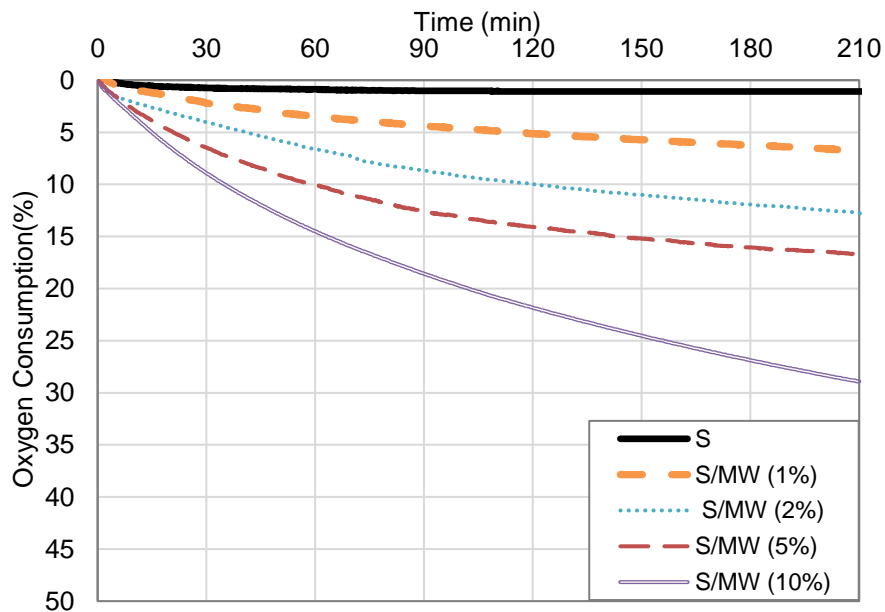


Figure 6. Oxygen consumption for samples crushed by the micro-deval abrasion machine and contain the indicated sulphide bearing aggregates percentages.

Based on the obtained results, and to avoid the effect of the abraded iron from grinding, the cast iron plates were replaced with ceramic plates. After crushing the sample in the jaw crusher until the whole samples passed sieve #16 (1.18 mm), the samples were introduced to the disk pulveriser with ceramic plates. Figure 7 shows the oxygen consumption for three aggregate samples crushed using the ceramic plates (S, C1 and MSK) to particle size (300 μm to 75 μm). S and C1 are concrete aggregates that have an excellent record in concrete with very minimal sulphate content, these aggregates had shown consumptions of 2-5% and 2-7 % after 3:30 and 16:30 hours respectively (includes 30 minutes for probe stabilization). The third sample (MSK), which contains total sulphur between 0.73 and 1.28%, had shown consumption of about 28% and 65% after 3:30 and 16:30 hours respectively.

The effect of grinding size is shown in **Error! Reference source not found.**. In this test, (MSK) and (C20) aggregates, were crushed into two different sizes (300 μm to 75 μm) and (600 μm to 150 μm). Processing the aggregate to a larger particle size (600 μm to 150 μm) gave less oxygen consumption. The higher consumption in case of smaller grinding size likely attributable to the increase of surface area of iron sulphide, hence, a greater surface is exposed to moisture and oxygen.

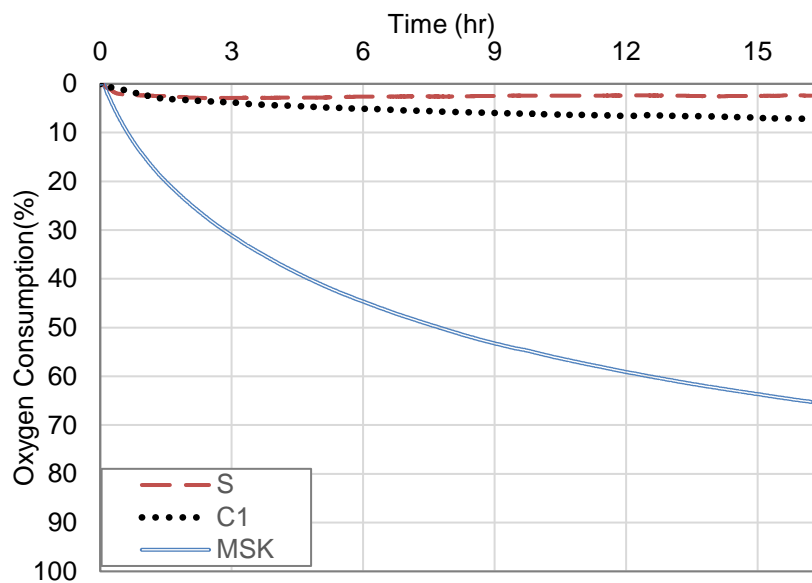


Figure 7. Oxygen consumption for samples crushed by the disk pulveriser with ceramic plates.

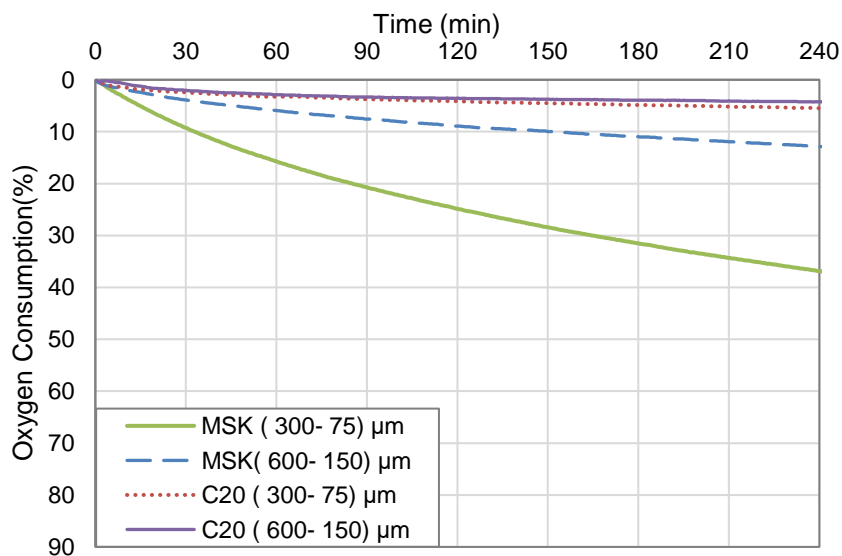


Figure 8. Effect of grinding size on oxygen consumption for MSK samples.

Table 3 summarizes the oxygen consumption for all the tested samples. The oxygen consumption for aggregates crushed using the ceramic plates indicated that the highest values of oxygen consumption were obtained for the aggregates with the highest total sulphur content (MSK with 0.73- 1.28). Adding 10% of (Ore) to the sand (S) gave high oxygen consumption similar to the consumption of (MSK). The table also shows the oxygen consumptions for samples tested by (Rodrigues, Duchesne, and Fournier 2016). The values obtained in their study are slightly lower than the values obtained in the current research. However, this is the case for only two aggregates that were available for comparison.

Table 3. Oxygen consumption for tested samples

Aggregate	Tested sample gradation (μm)	St (%)	O ₂ at 3.5 hr (%)	O ₂ (Rodrigues, Duchesne, and Fournier 2016) (%)
Sand	150-75	0.0	1.08	
S/Ore (1%)	150-75	0.13-0.14	6.75	
S/Ore (2%)	150-75	0.26-0.28	12.79	
S/Ore (5%)	150-75	0.69- 0.72	16.67	
S/Ore (10%)	150-75	1.38-1.44	28.91	
C1	150-75	0.09	4.0	3.0 (Sample <150 μm)
MSK	300-75	0.73-1.28	28.05	21.7 (Sample <150 μm)
	600-300		9.99	
20	300- 75	0.15	4.07	
	600- 300		3.36	

4 Conclusions

Based on the limited aggregate samples tested in this study, the following conclusions can be made:

1. Processing the aggregate using the commercially used disk pulveriser with cast iron plates produces samples with overestimated oxygen consumption due to eroded iron from the plates. The oxygen consumption for a sample that was ground using the cast iron plates equals the oxygen consumption for a sample that contains 5% by mass iron powder.
2. Using ceramic grinding plates produces samples without eroded iron and provided a better estimation of oxygen consumption.
3. Using samples consisting of 50% by weight passing sieve #50 (300 μm) and retained on sieve #100 (150 μm) and 50% by weight passed sieve #100 (150 μm) and retained on sieve #200 (75 μm) produces slightly higher oxygen consumption compared to the case with the whole sample passing 150 μm . Although the difference is not large, it is thought that controlling the minimum grain size of the sample will provide more consistency in the tested samples and perhaps the results.
4. Using aggregate samples of coarser size - between 600 μm and 150 μm - produces less oxygen consumption when tested for three hours.

5. The results produced here are based on limited number of aggregate. The main objective of this research is to investigate the effects of sample preparation and grain size on the obtained results. The applicability of this test to a wide range of aggregates is not carried out in this research, and is recommended.

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