

# Oxygen Consumption Techniques to Quantify Acidity Generation Rates

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A key aspect of acid and metalliferous drainage (AMD) prevention is predicting the AMD risk associated with various geologic materials. Prediction requires characterisation of the sulfidic materials using static and kinetic geochemical tests. Static tests assess the maximum potential of a sample to generate acidity based on its total sulfide content. Such tests, however, do not consider the rate or duration of acidity generation. In addition, AMD generation is affected by many variables that are not considered in static tests such as the availability of reactive pyrite within a rock matrix (Nicholson, 1994) and the supply of oxygen to the reaction sites (Ritchie, 1994). For these reasons, kinetic geochemical tests are carried out to estimate the rate at which AMD is generated and the longevity of issue.

Kinetic tests can be performed in the laboratory or the field. Commonly used geochemical kinetic tests include humidity cells, column leach tests, field-scale test piles and field and laboratory oxygen consumption tests. Humidity cells and column leach experiments rely on successive flushes of a sample to measure the rate of release of sulfate. Flushing cycles are generally carried out over 3-24 months and data interpreted to estimate the acidity generation characteristics of geologic materials. Significant errors may occur in the interpretation of this data, especially in colder climates where the difference between the actual climate and the induced climate in the humidity cell is significant (Comarmond, 1997).

Oxidation rates that rely on sulfate release rates can be underestimated if sulfate precipitates in the column or test pile (eg. gypsum, schertmannite, jarosite) or overestimated by progressively dissolution of residual sulfate or sulfate-bearing secondary minerals if they are present in the sample prior to the commencement of testwork.

Oxygen consumption experiments can be used to measure the pollution generation rate of a material directly, overcoming the limitations of column leach tests and humidity cells. Laboratory based oxygen consumption testwork generally consists of a sealed sample chamber containing sulfidic material, and subsequent measurement of gas concentrations in the headspace inside the chamber over time to determine the oxygen consumption rate.

This paper reviews published information relating to laboratory based oxygen consumption techniques and presents an oxygen consumption testwork approach developed by Earth Systems. The benefits of such testwork and implications for mines and acid sulfate soils management are discussed.

## OXYGEN CONSUMPTION TECHNIQUES

#### **Overview of Existing Oxygen Consumption Techniques**

Oxygen consumption testwork requires a gas impermeable chamber for storing a sulfidic sample (Bennett et al., 2005; Anderson et al., 1999; Eidsa et al., 1997; Scarek et al., 2006; Hollings et al., 2001; Jerz et al., 2004; Elberling, 2005; Andersen et al., 2001). Over time, gas concentrations can be measured by: a) gas chromatography (Elberling, 2005; Andersen et al., 2001); b) direct measurement inside the vessel using electrochemical gas sensors (Anderson et al., 1999; Hollings et al., 2001; Bennett et al., 2005; Eidsa, 1997); or c) by measurement of pressure changes in the vessel (Jerz et al., 2004) assuming all pressure change is attributed to oxygen consumption.

Carbon dioxide generated from neutralisation reactions or bacterial oxidation of organic carbon (in samples containing organic carbon such as acid sulfate soil material) can also be measured using carbon dioxide sensors (Eidsa et al., 1997; ANSTO, 1997) or by gas chromatography. Carbon dioxide generation rates can then be used to readjust oxygen consumption rates, and can assist in identifying the acid neutralisation capacity or bacterial activity of a sample (Hollings et al., 2001). Leachate water quality can be obtained after testing, allowing comparison between oxidation rates based on sulfate release and oxidation rates based on oxygen consumption (Hollings et al., 2001).

Test times varied in the literature, with most testwork conducted over 0.5-5 days (Elberling et al., 2005; Hollings et al., 2001; Anderson et al., 1999; Bennett et al., 2004; Sracek et al., 2006). However, some experiments lasted for 2-8 weeks (Eidsa et al., 1997; Andersen et al., 2001).

#### New Approach to Oxygen Consumption Testwork

Oxygen Consumption testwork is a geochemical kinetic testwork methodology that measures oxygen consumption to determine the pyrite oxidation rate (and pollution generation rate) of a sample. The new OxCon (oxygen consumption) test procedure developed by Earth Systems is based on similar oxygen consumption test methods developed and used by other researchers.

Prior to testing, representative samples of sulfidic material are analysed for various relevant parameters including moisture content and total sulfur.

The OxCon apparatus (shown in Plates 1 and 2) operates by permitting a known mass of sulfide bearing material to react

with a known volume of oxygen inside a sealed vessel. Once testwork is instigated, oxygen consumption proceeds via sulfide oxidation (see Reaction 1) causing the internal pressure of the system to decrease. Pressure decreases are datalogged and related to oxygen consumption via Boyle's Law to calculate an oxygen consumption rate (eg. mol/day/mass of sulfide).

The measured oxygen consumption rate is assumed to be proportional to the mass of pyrite in the sample and is converted into a pyrite oxidation rate using the stoichiometry in Reaction 1 (ie. 3.75 moles of oxygen are consumed to oxidise 1 mole of pyrite). This assumes that all sulfur present is in the form of reactive pyrite and that Reaction 1 is driven to completion. The pyrite oxidation rate is reported as a weight percent of pyrite exposed to atmospheric oxygen that will be oxidised to ferric hydroxide (Fe(OH)<sub>3</sub>) and sulfuric acid (H<sub>2</sub>SO<sub>4</sub>) per year. This study reports sulfide oxidation rate results in units of weight percent of pyrite (exposed to atmospheric oxygen) that is converted to sulfuric acid per year. (wt.% FeS<sub>2</sub> converted / year). This is a convenient unit that facilitates the rapid determination of acidity generation data for individual waste rock piles or entire mine sites.

Alternatively, OxCon data can be reported as intrinsic sulfide oxidation rates (IOR). IOR's are reported in units of kilograms of oxygen consumed per kilogram of material per second (kg  $O_2$  / kg (material) / second). As these units do not normalize the oxidation rate to unit sulfide content, it is difficult to apply them broadly to the behaviour of a waste rock pile. Other workers use units of kilograms of sulfur oxidised per tonne of material per year (kg S / tonne (material) / year), and these units are also difficult to apply broadly to a site.

With knowledge of the pyrite oxidation rate of a sulfidic material (normalised to the sulfur content) and the mass and average sulfur content of the material, it is possible to estimate the annual acidity generation rate of a material (kg  $H_2SO_4$  / tonne (material) / year), regardless of its sulfide content. For example; if 1.0 million tonnes of waste rock with an average pyrite content of 3 wt.% FeS<sub>2</sub> and a pyrite oxidation rate of 0.5 wt.% FeS<sub>2</sub> per year (ie. 0.5 weight percent of all FeS<sub>2</sub> exposed to atmospheric oxygen that will convert to sulfuric acid per year) were exposed to atmospheric oxygen, the estimated acidity generation rate would be approximately 150 t  $H_2SO_4$  per year, or 0.15 kg  $H_3SO_4$  per tonne of rock per year.

Once OxCon testwork is completed, the sample can be flushed with deionized water and analysed. The leachate chemistry can be used to provide indicative information on likely water quality and key elements of concern.

Carbon dioxide generated a) as a result of bacterial oxidation of organic carbon (e.g. for acid sulfate soils or coal samples) or b) from carbonate neutralisation reactions, can be measured using a carbon dioxide absorbent located inside the sample chamber during oxygen consumption testing. The mass change in absorbent can be used to estimate the



Plate 1: OxCon apparatus vessels including (from left to right) sample chamber, displacement chamber and fluid reservoir.



Plate 2: OxCon apparatus depicted with data logger, temperature transmitter and power supply

rate of organic carbon oxidation or to estimate the extent of neutralisation that occurred during testing. The effects of CO<sub>2</sub> gas release during OxCon testwork is routinely quantitatively accounted for in the calculation of FeS<sub>2</sub> oxidation rates.

#### SULFIDE OXIDATION RESULTS FROM OXCON TESTWORK

The calculated change in oxygen concentration within an OxCon apparatus containing a pyrite/marcasite sample from a brown coal mine is shown in Figure 1 below. The sample had a total sulfur content of 29 wt.% S (equivalent to 54 wt.% pyrite)

and the sample was finely milled (grain size minus 100  $\mu$ m) prior to the commencement of OxCon testwork. The oxygen concentration within the OxCon vessel decreased from an initial value of 20.95 vol. % O<sub>2</sub> to 0 vol.% O<sub>2</sub> after approximately 14 days.

The experimental data indicate that the oxidation of pyrite as a function of oxygen concentration is consistent with a first order reaction with a rate constant of 0.351 day<sup>-1</sup>. Figure 1 shows that oxygen consumption rate, and hence pyrite oxidation rate, remained relatively constant until oxygen concentrations fell below approximately 15 vol.%. Pyrite oxidation rates were still significant between 5 and 2.5 vol.%  $O_{2^{\prime}}$  but substantially lower than at atmospheric oxygen concentration levels.

In general, the trend described by the data during the initial stages of the testwork approximate a straight line, whose slope represents the oxygen consumption rate for the given time interval. The oxygen consumption rate obtained from the linear fit of the data can be used to derive the "initial pyrite oxidation rate".

Based on this approach, the initial pyrite oxidation rate for the milled pyrite/marcasite sample shown in Figure 1 was calculated to be 2.3 wt.% (FeS<sub>2</sub>) / year. The same material yielded an oxidation rate of 2.13 wt.% (FeS<sub>2</sub>) / year using conventional column leach experiments (McIllwaine, 1997). This study reports sulfide oxidation rate data in units of weight percent of pyrite (exposed to atmospheric oxygen) that is converted to sulfuric acid per year (wt.% FeS<sub>2</sub> converted / year) as shown in Table 1 below.

A comparison of the decrease in oxygen concentrations over time for two samples of pyrite/marcasite from the same brown coal mine (both approximately 54 wt.% pyrite) is shown in Figure 2. The two samples differed in grainsize only. One sample was milled to a grain size of less than 100  $\mu$ m while the other sample comprised of minus 30 mm aggregate. After 7 days the milled sample had consumed almost all of the oxygen in the apparatus. After approximately 60 days the oxygen concentration in the apparatus containing the minus 30 mm aggregate sample was approximately 16 vol.% O<sub>2</sub>.

The decrease in oxygen concentration over time for a sample of Proterozoic Mount McRae (pyritic) Shale from the Pilbara region of Western Australia is also shown in Figure 2. The pyrite content of the shale was 12.6 wt. % FeS<sub>2</sub>. Despite the large difference in geologic histories and pyrite contents of the Mount McRae Shale (12.6 wt.% FeS<sub>2</sub>) and the pyrite/marcasites sample from the Brown Coal mine (75 wt.% FeS<sub>2</sub>), the normalised pyrite oxidation rate of both minus 30 mm aggregate samples was similar.

The sulfide oxidation rates determined using oxygen consumption techniques for a broad range of geologic materials are displayed in Figure 3. Some of this data has been generated from OxCon testwork, and other oxidation rate data obtained from published literature (Anderson et al., 1999; Borma et



Figure 1: Oxygen concentration (volume %) decreasing over time (days) as a result of the oxidation of a pyrite/marcasite sample from a coal mine (grain size <100  $\mu$ m).



Figure 2: Oxygen concentration (volume %) decreasing over time (days) as a result of sulfide oxidation in pyrite/marcasite samples from a brown coal mine (grain sizes <100  $\mu$ m and -30 mm aggregate) and Mount McRae Shale (-30 mm aggregate). The oxidation rate is based on initial reductions in oxygen concentration (i.e. down to approximately 19 vol.% O<sub>2</sub>)

al., 2003; Di Nanno et al., 2007; Eidsa et al., 1997; Hollings et al., 2001; Morse, 1991; Rigby et al., 2006)., is provided for comparison. Samples include sulfidic metal and coal mine wastes and acid sulfate soils. Oxidation rates vary over approximately 8 orders of magnitude, with sandy acid sulfate soil materials providing some of the most rapid oxidation rates (eg. 1-3 wt.% FeS<sub>2</sub>/day). The oxidation rates of some of these materials have been tested as a function of sample moisture content. For both pyritic mine wastes and sandy acid sulfate soil materials, an increase in gravimetric moisture content is directly related to a decrease in sulfide oxidation rate.

#### **BENEFITS OF OXCON PROCEDURE**

The OxCon procedure offers significant benefits relative to other geochemical testwork methods. These include:

- The OxCon procedure is more accurate, reproducible, low cost and very rapid relative to all other kinetic test methods that quantify sulfide oxidation rates.
- · The OxCon procedure avoids all complications

associated with the precipitation or dissolution of secondary sulfate-bearing mineral phases that are unavoidable with both column leach and humidity cell testwork.

- Oxygen consumption testwork is the only kinetic testwork procedure that permits accurate quantification of the effect of moisture on the inhibition of sulfide oxidation.
- Oxygen consumption is the only kinetic testwork procedure that permits the determination of sulfide oxidation rates as a function of the different oxygen concentrations likely to be encountered in a broad range of geologic settings (eg. tailings and waste rock accumulations).
- OxCon testwork also enables easy and independent assessment of sulfide oxidation rates as a function of sulfide type, sulfide concentration, grainsize, temperature, metamorphic terrain / geologic history.
- The OxCon procedure is the only kinetic testwork method that permits simultaneous but independent assessment of carbon oxidation rates, or quantifies carbonate neutralization reactions during the test.
- Like column leach or humidity cell testwork, OxCon testwork also permits an assessment of the leachate water quality, and thereby independently checks sulfate release rates. In providing a comparison between oxygen consumption rates and sulfate release rates, it is also possible to quantify the role of secondary sulfate salts in acidity generation.
- OxCon apparatus design is simple, cost effective and flexible, and can be scaled or customised for different applications (eg. in-situ highwall sulfide oxidation rates).

Based on these benefits, it is concluded that oxygen consumption methods should become a standard geochemical kinetic test to complement existing geochemical characterisation procedures.

### CONCLUSIONS

- Key conclusions from OxCon data available to date include:
- For the materials tested to date, pyrite oxidation rates does not decrease significantly with oxygen concentration until the oxygen concentration falls below approximately 15 vol. %.
- Sulfide oxidation continues at significant rates even at very low oxygen concentrations.
- The pyrite oxidation rate increases substantially with a decrease in the grain size of the sulfidic material.
- The pyrite oxidation rate decreases with an increase in moisture content, presumably largely due to the impact of moisture on retarding oxygen diffusion.
- · Acid sulfate soils have far higher oxidation rates than



Fig 3. Sandy acid sulfate soil. Earth Systems internal data

- ◊ Lagoon sediments. Borma et al. (2003)
- Acid sulfate soil. Rigby et al. (2006)
- + Sediments with microbial and nutrient innoculation. Di Nanno et al. (2007)
- △ Marine sediments. Morse (1991)
- · Sulfidic interseam material from a brown coal mine. Earth Systems internal data
- Gold mine tailings. Earth Systems internal data
- $\times$  Sulfidic waste rock (Mine 1). Earth Systems internal data
- Sulfidic waste rock and tailings mixture (Mine 2). Earth Systems internal data
- Nickel mine waste rock (pyrrhotite). Anderson et al. (1999)
- + Base metal mine ore. Eidsa et al. (1997)
- + Uranium mine waste rock. Hollings et al. (2000)

Figure 3: Pyrite oxidation rates as a function of moisture content for acid sulfate soils and sulfidic mine wastes from various mine sites world-wide. Where gravimetric moisture content data was unavailable, 10 wt.% water was assumed.

the metamorphosed pyritic material common to most metal and coal mines, but also display a much finer grainsize.

#### IMPLICATIONS FOR MANAGING SULFIDIC MATERIALS

- The implications of OxCon testwork for the management of sulfidic materials include:
- The OxCon apparatus can be used to construct and quantify the effectiveness of various waste storage facility designs and remediation scenarios.
- The OxCon apparatus can be used to quantify the effectiveness of various water cover scenarios for a tailings storage facility or waste rock dam.
- Accurate quantification of the likely acidity generation rates from various site domains (e.g. waste rock piles, tailings storage facilities or highwalls) assists with planning for operations and closure.
- The role of the moisture content of sulfidic materials to retard oxidation can be more accurately quantified, and hence the moisture retention benefits of paste tailings, paste rock and other co-disposal options can be quantified. This quantification will be comparable to measuring the influence of moisture on decreasing "air

entry values" into sulfidic materials.

- It is important to note that decreases in oxygen concentration have little effect on pyrite oxidation until concentrations fall below 15 vol.%. This places significant challenges on management or remedial methods that rely on oxygen consumption.
- The available data suggests that oxygen concentrations need to fall well below 5 vol.% in underground mines with GaRDS installations (Taylor and Waring, 2001) before substantial reductions in acidity generation can be expected.

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