The Relationships Between Negative Pore-Water Potential, Water Content, Relative Humidity and Sulfide Oxidation in Waste Rock – A Case Study

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Abstract

Acid rock drainage from mine waste is caused by the oxidation of sulfide minerals in moisture and air. In a test column filled with waste rock, oxidation was measured by oxygen consumption, moisture by weight, and negative pore-water potential indirectly by relative humidity. The results show an interesting correlation between the three.

In waste rock piles, moisture can reach areas not accessed by seepage of meteoric or ground water through vapour transport. Rocks retain/release moisture based on their water retention characteristics. This will in turn influence the relative humidity of the surrounding air space and sulfide oxidation rate.

Keywords: Sulfide Oxidation, Oxygen Consumption Test, Water (Moisture) Content, Humidity, Waste Rock

Introduction

Acid rock drainage and metal leaching (ARD-ML) is the outflow of acidic water from mine waste that often contains elevated metal(loid)s. ARD-ML is an environmental issue with potentially detrimental effects on the biota of receiving water bodies (Jennings 2008). The main source of acidity in ARD-ML is the oxidation of sulfide-containing minerals, such as pyrite (FeS_2). The overall chemical reaction for ARD-ML production from pyrite oxidation can be expressed as:

$$FeS_2 + \tfrac{7}{2} O_2 + H_2O \rightarrow Fe^{2+} + 2SO_4^{2-} + 2H^+ + heat$$

[eq. 1]
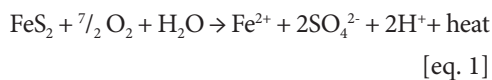
It can be seen from the equation above, that for sulfide oxidation and acid production to occur, both water and oxygen must be present. In fact, a common way to prevent sulfide oxidation of mine tailings is to submerge them under water to prevent oxygen exposure. Conversely, given the right combination of sulfide surface exposure to air and water, the ARD-ML generating reaction rate is expected to escalate.

When a waste rock pile is wetted by meteoric water (snowmelt and/or rain), or groundwater, the rocks retain some of the water based on its water retention characteristics even as the excess water drains away. Understandably, the resulting negative pore-water pressure (PWP) condition of the rocks will influence how much of the active sulfide surface area will actually be exposed to both water and air.

Oxygen consumption (OxyCon) tests, first published by Elberling *et al.* (1994), have been used to measure the kinetic rate of sulfide oxidation. In this test, an oxygen sensor monitors the drop in the oxygen level within a closed container filled with waste rocks. As sulfide oxidation occurs, the oxygen content inside the container will decrease. In the case of rocks with relatively high levels of exposed sulfides, the oxygen level inside the container will decrease more sharply. Recently, much work on OxyCon

tests has been published by Earth Systems (Schmieder *et al*. 2012). OxyCon tests have been used to investigate the effect of many rock parameters, including sulfide content, particle size and moisture content.

This study explores one aspect of ARD-ML generation by OxyCon test that is often overlooked: the role of the pore-water pressure, or suction of waste rock, as shown by Salmon *et al*. (2018). The oxygen consumption rates of relatively dry rocks (with moisture contents of ≈2.0 wt.% and lower) were measured to study the role of PWP (suction) on the sulfide oxidation rate. Measuring suction of waste rock is challenging due to their large sizes and irregular shapes, and most commercial analysers are designed for soil. Headspace relative humidity (RH) was used as a direct indication of the suction of waste rocks.

Methods

Rock samples from a mine site were crushed passed through a 0.64-cm sieve. The samples were homogenized and split into three representative portions: one portion for characterization by acid base accounting (ABA), one portion for Rietveld XRD analysis and one portion for OxyCon testing.

A 10.2 cm (d) × 20.3 cm (h) column was filled with 2.854 kg of rocks to a height of 17.8 cm as shown in fig. 1 below. The column
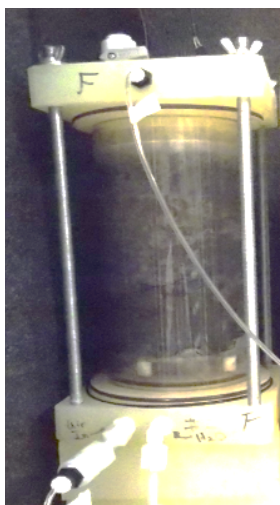

Figure 1 Photograph of the experimental setup, including custom-made columns with connections for water and gas flow.

was equipped with a water distributor at the top and a drain at the bottom for collecting water effluents. The column also has an air input line at the bottom and a corresponding output line at the top.

Fig. 2 shows schematic representations of the OxyCon test procedures. Before beginning of the OxyCon test, the columns were wetted with deionized water at 16 mL/min, as shown in Fig. 2a, until 600 mL of effluents were collected. After the leaching process, the column was purged with dry air for two weeks as shown in Fig. 2b. The direction of air flow was from the bottom up—opposite to the direction of water flow and consistent with the belief that air mostly enters covered waste rock dumps from the toe (Pearce *et al*. 2016). This leaching process was repeated three times to condition the sample. The pH of the effluent was close to neutral as expected from ABA analysis.

Oxygen consumption test was performed as shown in Fig. 2c. In our version of the OxyCon test, air was circulated from the columns to external sensors, which measured the concentrations of O_2 and RH. After each OxyCon test cycle, the column was again purged with dry air (Fig. 2b) to remove moisture from the waste rocks. The weight of the column was then recorded, and moisture content for the next round of OxyCon test was calculated. While rocks in the column were being dried, sensor lines were isolated from the columns for calibration and performance validation. Seven OxyCon-drying cycles were performed until the oxygen consumption slowed down appreciably. As a final quality control procedure, the rocks were humidified again with water-saturated air using the same configuration as in fig. 2b. The OxyCon rate was measured to ensure that retardation of oxygen consumption did not arise simply from of the depletion of active sulfide surfaces. This is reported as the 8th cycle in the results below.

Results and Discussion

Representative portions of the rock sample underwent ABA analysis and Rietveld analyses. The results are shown in tab. 1 and 2, respectively. As can be seen in tab. 2, this waste rock sample contains a substantial
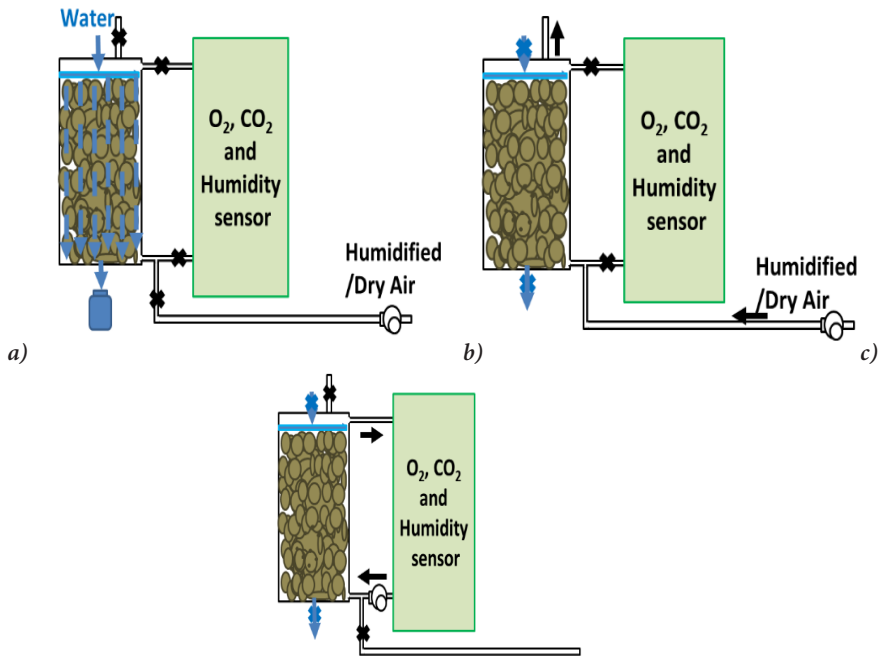
Figure 2 Experimental processes: a) column wetting, b) column drying or humidification and c) oxygen consumption, carbon dioxide generation and humidity monitoring. "X" indicates where valves were closed. Black arrows indicate the direction of air flow while blue arrows indicate the direction of water flow.

Table 1 Results of acid base accounting analysis.

Parameter	Unit	Result	Parameter	Unit	Result
Paste pH		7.0	Non-Extractable S	wt.%	0.31
CO_2	wt.%	2.7	Acid generation potential	kg $CaCO_3$/t	51.9
$CaCO_3$ equiv.	kg $CaCO_3$/t	61.4	Mod. ABA neutralization potential	kg $CaCO_3$/t	50.5
Total S	wt.%	2.02	Fizz rating		SLIGHT
HCl Extractable S	wt.%	0.05	Net neutralization potential	kg $CaCO_3$/t	-1.4
HNO_3 Extractable S	wt.%	1.66	Neutralization potential ratio		1.0

Table 2 Results of Rietveld XRD quantitative phase analysis.

Mineral	Ideal Formula	Wt.%			
Quartz	SiO_2	68.1	Clinochlore	$(Mg,Fe^{2+})_5Al(Si_3Al)O_{10}(OH)_8$	1.5
Illite/ Muscovite 2M1	$K_{0.65}Al_{2.0}Al_{0.65}Si_{3.35}O_{10}(OH)_2$/ $KAl_2AlSi_3O_{10}(OH)_2$	15.8	Calcite	$CaCO_3$	0.5
Ankerite-Dolomite	$Ca(Fe^{2+},Mg,Mn)(CO_3)_2.\ CaMg(CO_3)_2$	7.0	Siderite	$Fe^{2+}CO_3$	0.4
Pyrite	FeS_2	3.8	Rutile	TiO_2	0.2
Kaolinite	$Al_2Si_2O_5(OH)_4$	2.5	Jarosite	$K_2Fe_6^{3+}(SO_4)_4(OH)_{12}$	0.2

Table 3 Summary of experimental results for the OxyCon tests.

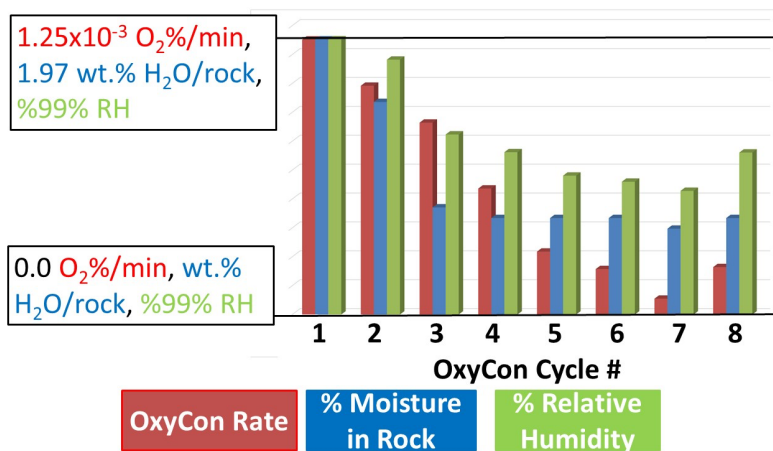| Cycle #	Wt.% H_2O	RH, +/- 0.02	PWP (kPa)	OxyCon rate (%O_2/min)
1	1.97	.99	-1.4	1.25E-03
2	1.52	.92	-11	1.04E-03
3	0.77	.65	-59	8.72E-04
4	0.69	.58	-74	5.73E-04
5	0.69	.50	-94	2.86E-04
6	0.69	.48	-1.0×10^2	2.06E-04
7	0.62	.44	-1.1×10^2	7.18E-05
8	0.69	.58	-74	2.15E-04

Figure 3 A comparison of oxygen consumption rate (O_2%/min), RH and wt.%H_2O of rock column.

amount of sulfide in the form of pyrite. The oxygen consumption was therefore expected to be easily measurable. Calcite was also present, which explains the neutralization potential measured during the ABA analysis.

OxyCon tests were subsequently performed at different levels of moisture content for a total of eight cycles, the results of which are shown in tab. 3. Between each OxyCon test cycle, dry air was used to gradually remove moisture from the rocks, and the weight of the column was recorded in order to calculate for the remaining moisture content. After seven OxyCon test cycles with progressively drier rocks, humid air was pumped through the rocks for cycle 8 to restore some moisture to the column before the eighth and final OxyCon measurement.

Fig. 3 shows the measured oxygen consumption rate versus the moisture content of the rocks and the headspace humidity.

The rate of oxygen consumption is fastest in the first cycle. Beginning at cycle four, the moisture content of the rocks no longer changes significantly, and it was observed that the rate of oxygen consumption is more correlated to the headspace humidity, which in turn is related to the suction condition of the waste rocks. RH was lowest at cycle 7 and, as expected, the rate of oxygen consumption was at its minimum. When RH was raised at cycle 8, the rate of oxygen consumption increased proportionately.

Steger published a series of paper on the oxidation of sulfide minerals, such as pyrite, chalcopyrite and pyrrhotite. In the seventh paper of the series, Steger (1982) reported the results of oxidation experiments on pyrrhotite under controlled environmental conditions of 50 °C and various RH: 37%, 50%, 55%, 62% and 75%. He found that, at 37% RH, sulfate formation occurred but

oxide formation did not. This is possible because sulfate formation does not require water while hydroxides and oxides do. As RH increases, ferric oxides begin to form and the formation rate continuously increase with RH with the slope maximizing at 57-59%. The SO_4^{2-} formation also peaked at RH of 57-59%. This can be explained by further oxidation and hydrolysis reactions, and migration of species that can only occur with water molecules. Rosenbaum *et al.* (2015) observed that dried pentlandite-pyrrhotite nickel concentrate pre-weathered for 21 day at 40 °C and 30-50% RH, did not demonstrate self-heating (sulfur oxidation) capacity in a subsequent test. On the other hand, dried samples that were pre-weathered at 70 and 80% RH and otherwise similar conditions showed proportionately increasing self-heating capacity. Both studies demonstrates the importance of environmental humidity for sulfide oxidation in dry rocks. While both studies were done at elevated temperature to accelerate reaction kinetics, our study shows that such sulfide oxidation can still be observed even at room temperature (23 °C) and low % RH.

During the experiments, an interesting observation made was that dry air can be moistened when flowed through relatively dry waste rocks. Fig. 4 shows the change in the RH of the column headspace before and after flowing through a column containing waste rocks with a water content of 0.62%. The initial RH of the air was between 0.05-0.10 but its RH became 0.44 afterward purging through the column.
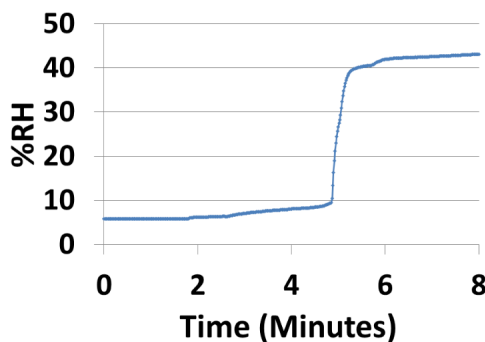

Figure 4 %RH of the headspace as a function of time during cycle seven of the OxyCon test.

Headspace relative humidity (RH) can be used as a direct indication of the suction of waste rocks, as high suction will reduce the number of water molecules (and therefore the RH) in the headspace above the sample. This relationship is given by the Kelvin equation:

$$Total\ suction = \frac{R(T+273.15)}{V_w} \ln\left(\frac{p}{p_0}\right)$$

[eq. 2]

Where R is the gas constant (8.3143 J/mol-K), T is temperature (C), V_W is the molar volume of water (1.8×10^{-5} m^{3}mol^{-1}), p_0 is the saturation vapor pressure at the sample temperature, and p is the equilibrium vapor pressure in the headspace. The term p/p_0 is the equilibrium RH of the sample (Warrick 2002).

An observation during experiments further demonstrated the relationship between rock moisture content and suction. When the lid of a test column was opened to accelerate drying, the top surface of the column appeared quite drier (bone dry) than the bottom of the column. After air recirculated throughout the column at the start of OxyCon testing, however, the top layer appeared as wet as the rest of the waste rocks in the column. This demonstrates the ability of air to redistribute moisture throughout the waste rocks. Such internal redistribution of moisture within full-scale waste rock piles and mine walls has been reported in the past (Morin and Hutt 1997 and 2001) but rarely documented in detail.

Depending on their PWP, waste rocks can act as a humidifier when the atmosphere is very dry and vice versa. In a waste rock pile, this means that moisture can reach waste rock through water vapour transport, to areas not influenced by seepage of liquid water.

Conclusion

Our study demonstrates that the suction condition of waste rock can play an important role in the sulfide oxidation process. In this case study (<2.0% moisture), it was observed that consumption of oxygen by pyrite oxidation did not slow appreciably until the moisture content of the rock was around 0.6%wt. and the RH was 0.44. There are strong positive correlations between oxygen

consumption rate, the moisture content of the waste rock and RH of the surrounding air when RH is <0.99 and the moisture content is <2.0%. Our measurements also show that waste rocks can effectively draw water from the pore-air space to drive the oxidation of pyrite. In a waste rock pile, it means that moisture can reach waste rocks through water vapour transport, to areas not influenced by seepage of liquid water. This implies that pore-air humidity may be sufficient for sustaining ARD-ML in mine waste dumps even without a fresh supply of meteoric or ground water. Since waste rocks can retain water in general, it is unlikely that rocks in commercial scale dumps can reach the level of dryness needed to stop sulfide oxidation completely.

These results are important to our understanding of ARD-ML, especially as it supports assumptions regarding water transport and acid generation in ARD-ML modeling work (Morth 1972; Liu 2017, 2018, 2019) used to design and evaluate mine waste storage facilities.

Acknowledgements

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