

Effect of Water Addition Frequency on Oxygen Consumption in Acid Generating Waste Rock

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Abstract: The oxygen decay coefficient is a key parameter used to predict the distribution of oxygen concentrations spatially and temporally in a waste rock pile. The present study proposes a new equation to calculate the oxygen decay coefficient based on the oxidation rate (sulfate release rate) of the waste rock, dry density, and equivalent porosity for oxygen transport. The equation gave oxygen decay coefficients that were of the same order of magnitude as those obtained from a semianalytic solution to the modified Fick's law with an oxygen consumption term. Values were in the range of $3.74 \times 10^{-8} \text{ s}^{-1}$ for air dry waste rock and $3.99 \times 10^{-7} \text{ s}^{-1}$ for moist waste rock. The effect of water addition frequency on the oxidation rate and the oxygen decay coefficient was investigated through four column experiments with various flushing rates and a laboratory case simulating actual precipitation at a specific site. The results indicated that the oxygen decay coefficient was dependent on not only the oxidation rate but also on the physical characteristics of the waste rock, such as porosity and dry density. The flushing rate had a significant influence on the oxidation rate of the waste rock and the calculated oxygen decay coefficient. The oxidation rate of the waste rock decreased from 1.19×10^{-6} to $5.32 \times 10^{-7} \text{ s}^{-1}$ with an increase in flushing intervals from 1 week to 4 weeks. When the drying period was longer than 3 weeks, the oxidation rate decreased very slowly with an increase in drying period for the tested waste rock.

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Introduction

Engineered soil covers placed above mine waste rock piles can minimize gaseous oxygen influx and significantly reduce the production of acid rock drainage, depending on the design adopted (Yanful et al. 1993; Weeks and Wilson 2005). Oxygen flux into the waste rock through a soil cover is usually used to evaluate the performance of the soil cover (Nicholson et al. 1989; Yanful 1993). In order to calculate this oxygen flux, the oxygen concentrations in the cover and the waste rock should be known. The oxygen decay coefficient and oxygen diffusion coefficient are two critical parameters employed to predict the spatial and temporal distribution of oxygen concentrations in the waste rock dump or pile.

The oxygen diffusion coefficients of porous media are usually measured using a chamber (or column) with source and base reservoirs (Yanful 1993; Cabral et al. 2000; Jones et al. 2003). This kind of device was also employed to measure oxygen decay coefficients for reactive materials (Mbonimpa et al. 2003). Fick's

second law and its modified form with a reaction term provide the theory for analyzing these measurements and estimating the relevant parameters. Some empirical equations have also been developed to estimate the oxygen diffusion coefficient and decay coefficient (Reardon and Moddle 1985; Collin 1987, 1998; Aachib et al. 2004). In general, mine tailings have been studied more extensively than waste rock because of the complexity of waste rock dump characteristics. For example, gaseous oxygen transport in tailings is usually considered to be mainly by diffusion, while convection may play a significant role in gas transport in the batters of waste rock dumps (Pantelis and Ritchie 1992) or in dumps in which the air permeability is larger than 10^{-9} m^2 (Pantelis and Ritchie 1991). Fortunately, the most basic underlying principles and equations can still be applied to waste rock despite the obvious differences between waste rock and tailings.

The oxygen decay coefficient is also called the reaction rate constant (Cabral et al. 2000) or the reaction rate coefficient (Mbonimpa et al. 2003). It is directly related to the oxidation rate of the waste rock. However, little work has been done to estimate the oxygen decay coefficient from the oxidation rate of the waste rock even if the measurement of the oxidation rate is necessary during routine characterizations of waste rock piles (Price 2005). Collin (1987, 1998) proposed a model to calculate the oxygen decay coefficient based on pyrite oxidation, but the reactivity of the pyrite was considered constant; thus differences in oxidation rates for various waste rock materials are not taken into account in the model.

In general, there are three kinds of models used to describe the oxidation rate of pyritic waste rock (Ritchie 1994): simple constant-rate model, simple homogeneous model (Davis and Ritchie 1986), and shrinking core model (Davis and Ritchie 1986;

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Gerke et al. 1998; Mayer et al. 2003; Ritchie 2003; Molson et al. 2005). The simple constant-rate model assumes that the intrinsic oxidation rate is independent of gaseous oxygen concentration, and that oxidation is confined to a region that decreases with each step; so the global oxidation rate decreases with time (Ritchie 1994). The simple homogeneous model assumes that the oxidizable material is homogeneous in the dump, and gaseous oxygen diffusion through the pore space of the dump controls the oxidation rate of pyrite in the dump. As a result, the oxidation front in the dump will move from the surface to the base of the dump (Davis and Ritchie 1986). The shrinking core model considers the heterogeneity and microstructural phenomena within the dump and assumes that the oxidation of pyrite is limited by both availability of gaseous oxygen and oxidizable material. Oxygen diffusion in the shrinking core model is considered a two-stage process which includes oxygen diffusion through pore space of the dump and through the oxidized rim of the pyrite particles.

Several methods for measuring the oxidation rate of sulfide minerals in waste rock have been proposed and employed in the laboratory and in field tests (Hollings et al. 2001; Bussi re et al. 2004; Sracek et al. 2006; Gosselin et al. 2007). Compared with the measurement of oxygen consumption rate in a sealed chamber, the sulfate release rate is more frequently measured from kinetic cell tests including humidity cell tests and column tests (Price 2005). The humidity cell test accelerates the oxidation rate by providing optimum environmental conditions such as ample oxygen and water, but the resulting oxidation rate does not reflect the actual oxidation rate of the waste rock since the field waste rock is not always under optimum conditions. The column test used to obtain the sulfate release rate has advantages because it can easily simulate field conditions, such as the precipitation at the site.

Water plays an important role in the oxidation rate of sulfide minerals. First, water is one of the reactants in sulfide oxidation and water content of waste rock affects the oxidation rate of sulfide-bearing minerals. For example, Hollings et al. (2001) and Le n et al. (2004) found that the oxidation rate of pyrite attained a maximum value at a certain water content when oxygen was sufficiently available. In these studies, Hollings et al. (2001) kept the water content of the pyrite constant during the tests. However, the water content of waste rock in the field seldom remains unchanged due to varying precipitation events, particularly for uncovered waste rocks. Gosselin et al. (2007) also reported that the effective reaction rate coefficient tended to increase with increased degree of saturation in tailings when the saturation was not too high. Second, water flushing frequency may affect the availability of fresh surfaces of sulfide minerals for contact with air, hence affecting the oxidation rate. Song and Yanful (2008) found that partially covered waste rock pile (pilot tests) produced less acid due to reduced flushing compared to uncovered waste rock pile. Therefore it is important to know how the flushing rate affects the oxidation rate of waste rock because different precipitation frequencies or flushing rates can change the water content of the waste rock, as it is often the case in the field.

In the present work, the oxidation rate of waste rock from the Mattabi Mine site near Ignace, Ont., Canada was investigated through the measurement of sulfate release rates in laboratory columns. The oxygen decay coefficient of the waste rock was then estimated from the measured sulfate release rate. The effect of flushing frequencies on the oxidation rates was evaluated based on prescribed regular flushing rates and on a specific laboratory case with field simulated rainfall events. The overall goals of the study were to: (1) develop a method to calculate the oxygen decay

coefficient based on sulfate (SO_4^{2-}) release rate; and (2) demonstrate the effects of flushing rates on the oxidation rate and oxygen decay coefficients of the waste rock. The study also contributes to the literature on the effect of water content on waste rock oxidation, which has, until now, been sparse.

Materials and Methods

Waste Rock Material

The waste rock used in the experiment was obtained from the Mattabi Mine site, located approximately 70 km northeast of Ignace, Ont. The Mattabi deposits were identified as Archean volcanogenic massive sulfide (Franklin et al. 2005). Zinc, copper, and silver were the main metals mined and extracted at the Mattabi Mine.

Waste rock from the Mattabi Mine was first sent to a stone quarry near the University of Western Ontario, Ont. to be crushed; the crushed waste rock was then taken to the laboratory and sieved through 12.5 mm opening sieve (No. 1/2 in.). Only waste rock finer than 12.5 mm was used in the experiment. After sieving, the waste rock was washed with tap water to remove debris and any coatings on the particle surfaces before the rock was used in the experiment.

Experimental Setup and Measurements

The columns used in the experiments had a bottom diameter of 20.2 cm, top diameter of 22.2 cm, and a height of 28.1 cm. Each column was sealed at the base with a 6 mm diameter opening in the middle for effluent collection. A dome shaped cap with an opening was placed on top of each column to keep air balance inside the column and to decrease evaporation from the waste rock in the column.

Two layers of geotextile were installed at the bottom of each column to filter effluent. The height of the waste rock installed in each column was 25 cm. Two oxygen sampling ports were installed in each column at distances of 10 and 20 cm from the surface of the waste rock. These oxygen sampling ports, equipped with rubber septa to seal automatically after sampling, were similar to those described by Yanful (1993) and Yanful et al. (1999). After the waste rock was placed in the columns, it was rinsed with distilled water and drained several times before measurement began. The weight of each empty column and the total mass including the wet mass of the waste rock and the mass of the column were also recorded prior to the measurement. The dry mass of the waste rock in each column was calculated based on the wet mass and measured gravimetric water content of the waste rock. Four columns (Columns 2 to 5) were used in the experiments under different flushing frequencies, namely, weekly flushing in Column 2, biweekly flushing in Column 3, triweekly flushing in Column 4, and monthly flushing in Column 5. Table 1 presents the data for the setup of the column tests. These flushing frequencies were selected to include the weekly flushing used in the standard humidity cell test and to determine whether flushing frequency has an influence on oxidation rate.

The column tests were run for 24 weeks, from February 25, 2008 to August 11, 2008. Each flushing cycle involved the use of 2,000 mL of distilled water which was kept in the packed column for two hours before it was discharged. The 2,000 mL was close to one pore volume of waste rock in the column and could flood the waste rock. Effluents from the columns following flushing

Table 1. Data for Setup of Column Tests

Column number	Mass of column (g)	Mass of dry waste rock (g)	Total mass after initial measurement (g)	Height of waste rock (cm)	Porosity	Flushing frequency
Column 2	1,080	18,424	20,895	25	0.25	Weekly
Column 3	1,075	18,500	20,920	25	0.25	Biweekly
Column 4	1,080	18,726	21,055	25	0.24	Triweekly
Column 5	1,100	18,487	21,015	25	0.25	Monthly

were collected to measure volumes. Water samples were also taken during the drainage. Water samples were filtered through 0.45 μm filters. Each water sample was analyzed for pH, electrical conductivity (EC), acidity, alkalinity, and sulfate. Other water samples were acidified with nitric acid to pH less than 2, stored at 4°C and later analyzed for dissolved metals using inductively coupled plasma (ICP) optical emission spectroscopy. Approximately 2 mL of gas was withdrawn through the sampling port with a syringe and injected into an oxygen analyzer (Model 905V, Quantek Instruments) to measure gaseous oxygen concentration. The analyzer was calibrated in the atmosphere prior to sampling each port. The oxygen concentration in each column was recorded every three days. The measured air temperature in the laboratory during the test was $23 \pm 2^\circ\text{C}$, and the measured daily temperature change was $2\text{--}3^\circ\text{C}$. In general, the distilled water used to flush the waste rock was acclimatized to laboratory temperature before use. The change in temperature in the laboratory was relatively small compared to that in the field.

In order to select the amount and frequency of water addition, a special experimental case study was conducted. Since the Mat-tabi Mine is closed and no precipitation data was available, site data from the Whistle Mine (near Capreol, Ont.), was used as a guide. Using the Whistle site data also allowed us to compare our current results to those reported by Song and Yanful (2008).

This specific laboratory case had the same setup procedure, equipment, and waste rock as those of the column tests described above. The case was labeled as Column 1 and had the following characteristics: height of the water rock=25 cm and dry density =2.06 g/cm^3 . The measurements made in this column were the same as those conducted for the previous column tests, but the water addition events were different from those of the column tests (Columns 2 to 5). The amount and frequency of water added to Column 1 was selected to approximately represent precipitation at the Whistle Mine site in 2002, which had an annual precipitation of 956 mm. Specifically, the waste rock in Column 1 was subjected to six continuous days of water addition after 18 days of drying, followed by a long drying period (61 days) and then by a 7-day wetting event. This designed wetting-drying pattern was considered to be much closer to the wetting-drying process at the site in summer than the regular flushing cycles used in the column tests. The purpose of this specific laboratory case was to find which flushing rates better represented the actual rainfall events at the site. The findings from this specific laboratory case should be helpful in understanding trends in oxidation rates and oxygen decay coefficients in situations with similar precipitation and drying events.

Oxygen Decay Coefficient Calculation from Measured Sulfate Release Rate

Oxygen concentration change with time can be related to the oxygen consumption rate [Eq. (1)] in a closed chamber when oxygen diffusion is negligible and $t \leq t_{1/2}^*$ (Song and Yanful 2009)

$$\partial C / \partial t = -\rho_d R_{O_2} / \theta_{eq} \quad (1)$$

where ρ_d =dry density of the waste rock in the chamber; R_{O_2} =oxygen consumption rate of the waste rock; and θ_{eq} =equivalent porosity for oxygen transport. The negative symbol in the right hand of Eq. (1) indicates that the oxygen concentration would decrease due to the oxygen consumption. The solution for Eq. (1) is

$$C = -\rho_d R_{O_2} t / \theta_{eq} + C_0 \quad (2)$$

C_0 =oxygen concentration in the chamber at the start of the test (that is, at $t=0$). From the definition of half-life, when $t=t_{1/2}^*$, $C = 1/2C_0$, which yields

$$t_{1/2}^* = \theta_{eq} C_0 / 2\rho_d R_{O_2} \quad (3)$$

Substituting Eq. (3) into the definition of bulk decay coefficient [Eq. (4)], the relationship between the bulk oxygen decay coefficient and oxygen consumption rate can be presented as Eq. (5)

$$\lambda^* = \ln(2) / t_{1/2}^* \quad (4)$$

$$\lambda^* = 1.386\rho_d R_{O_2} / \theta_{eq} C_0 \quad (5)$$

where λ^* =bulk oxygen decay coefficient and $t_{1/2}^*$ =half-life time, at which the oxygen concentration is half of the oxygen concentration at the beginning. The effective oxygen decay coefficient, λ , and the equivalent porosity, θ_{eq} , are defined in Eqs. (6) and (7), respectively (Aubertin et al. 2000; Mbonimpa et al. 2003)

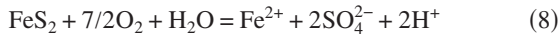
$$\lambda = \lambda^* \theta_{eq} \quad (6)$$

$$\theta_{eq} = \theta_a + K_H \theta_w \quad (7)$$

where λ =effective oxygen decay coefficient; K_H =dimensionless Henry's equilibrium constant (K_H is approximately 0.03 at 20°C); θ_a and θ_w =volumetric air and water content in waste rock, respectively (with $n=\theta_a+\theta_w$ and n =porosity of the waste rock; θ_a is also called the air-filled porosity).

In a recent publication (Song and Yanful 2009), decay coefficients calculated from Eq. (5) were compared to values estimated from a semianalytic solution to the modified Fick's law with an oxygen consumption term. The results showed that the two sets of values were close and of the same order of magnitude (2.61×10^{-8} and $3.74 \times 10^{-8} \text{ s}^{-1}$ for "air dry" waste rock with a gravimetric water content of 0.14% and 3.92×10^{-7} and $3.99 \times 10^{-7} \text{ s}^{-1}$ for "moist" waste rock with a gravimetric water content of 5.13%).

The relation between the oxygen consumption rate and the sulfate release rate can be established through the stoichiometry reaction of the oxidation of sulphide minerals. Pyrite is usually used to illustrate the oxidation of sulfide minerals because it is the most abundant sulfide mineral in mine waste. The oxidation of pyrite can be expressed as (Stumm and Morgan 1996)



Eq. (8) shows that generating 2 mol of sulfate will consume 3.5 mol of gaseous oxygen. Eq. (8) does not reflect all the processes involved in pyrite oxidation and acid generation. For instance, it does not account for biotic or microbial enhanced oxidation. In addition, secondary mineral precipitation, such as the formation of gypsum, can complicate the amount of sulfate produced versus what is measured in solution. Despite these limitations, Eq. (8) can still be used as a reasonable approximation to evaluate oxygen consumption during pyrite oxidation. For example, Hollings et al. (2001) used this stoichiometric relationship to compare the oxygen consumption rate to sulfate release rate, and found that the oxygen consumption rates were comparable to the sulfate release rates in kinetic cell tests. Lefebvre et al. (2001) also employed this relationship [Eq. (8)] to evaluate the oxygen consumption in waste rock piles.

Based on Eq. (8), the oxygen consumption rate (mass of oxygen over time per unit mass of dry waste rock) can be expressed as a function of the sulfate release rate, R_{SO_4} , as shown in

$$R_{\text{O}_2} = 7/12 R_{\text{SO}_4} \quad (9)$$

where R_{SO_4} = mass of sulfate over time per unit mass of dry waste rock. Substituting Eq. (9) into Eq. (5) yields

$$\lambda^* = 0.8085 \rho_d R_{\text{SO}_4} / \theta_{\text{eq}} C_0 \quad (10)$$

Eq. (10) builds the relationship between sulfate release rate and the oxygen decay coefficient in the waste rock when oxygen diffusion is not the dominant transport mechanism. When using this equation to calculate the oxygen decay coefficient, the basic characteristics of the waste rock, such as dry density and water content, should be known in advance. As the waste rock in the column was 25 cm thick, its moisture content and, hence, reactivity was probably not uniform. Consequently, the oxygen decay coefficient reported here would be a bulk rate. In the field, moisture distribution in a waste rock pile (a few meters high) may also not be uniform. As would be seen in the equations that follow, the bulk or average water content of the waste rock in the column is estimated and then used in the calculation of the decay coefficient.

Estimating Average Water Content of the Waste Rock during the Column Tests

Because the initial masses of the columns and volumes of influent and effluent for each flushing event were recorded, the cumulative evaporation from each column could be estimated assuming that the field capacity of the waste rock in each column after every flushing remained unchanged during the test

$$E^n = M_w^n - w_{\text{fc}} \quad (11)$$

where E^n = cumulative evaporation (in mass) after n th flushing; M_w^n = cumulative water mass in the column after the n th flushing assuming no evaporation from the column; and w_{fc} = field capacity (the maximum capacity to hold water without effluent resulting from gravitational drainage) of the waste rock in the column. M_w^n and w_{fc} can be calculated as Eqs. (12) and (13), respectively

$$M_w^n = M_w^{n-1} + M_{\text{in}}^n - M_{\text{ef}}^n \quad (12)$$

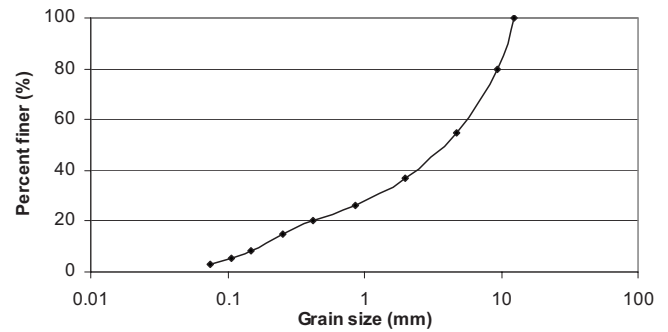


Fig. 1. Particle size distribution of waste rock used in the experiment

$$w_{\text{fc}} = M_T - M_R - M_C + M_{\text{in}}^0 - M_{\text{ef}}^0 \quad (13)$$

where M_w^{n-1} = cumulative water mass in the column after $(n-1)$ th flushing assuming no evaporation from the column (with $M_w^0 = w_{\text{fc}}$); M_{in}^n and M_{in}^0 = n th influent and the initial (zeroth) influent (in mass); M_{ef}^n and M_{ef}^0 = n th effluent and the initial (zeroth) effluent (in mass), respectively; M_T = initial total mass of the column including moist waste rock and the column itself; M_R = measured dry mass of waste rock in the column; and M_C = mass of the empty column.

With the cumulative evaporation over time data for the column, the average daily evaporation (M_E^d) from the waste rock can be obtained from the fitted slope in the cumulative evaporation over time figure. The average evaporation in one flushing cycle can then be estimated from

$$M_E = M_E^d * t_F \quad (14)$$

where M_E (in mass) = average evaporation from the waste rock in one flushing cycle; M_E^d (in mass) = average daily evaporation; and t_F = flushing interval of the column test.

When the average evaporation from the waste rock in one flushing cycle is known, the mass of water in the column before flushing can be calculated as Eq. (15) and the average water content of waste rock in the column can be defined as Eq. (16)

$$M_{\text{bf}} = w_{\text{fc}} - M_E \quad (15)$$

$$W_w = (w_{\text{fc}} + M_{\text{bf}}) / (2M_R) \times 100\% \quad (16)$$

where M_{bf} = water mass of waste rock in the column before flushing and W_w = average gravimetric water content of the waste rock in the column.

After the final flushing, the total mass of each column (including moist waste rock and column) was measured. This measured total mass is close to the initially measured total mass of the column (with a maximum relative error of 0.5% for all columns), indicating that the assumption of unchanged field capacity of the waste rock after each flushing in the column is reasonable. The calculated field capacity values were 1,459 g for Column 2, 1,382 g for Column 3, 1,246 g for Column 4, and 1,438 g for Column 5. Relative to the mass of waste rock, these corresponded to gravimetric water contents of 7.9, 7.2, 6.7, and 7.8%, respectively, and a range of degree of saturation of 60–65%.

Results

Fig. 1 shows the particle size distribution of the waste rock used in the experiment. The d_{10} diameter is 0.16 mm and d_{60} is 6 mm.

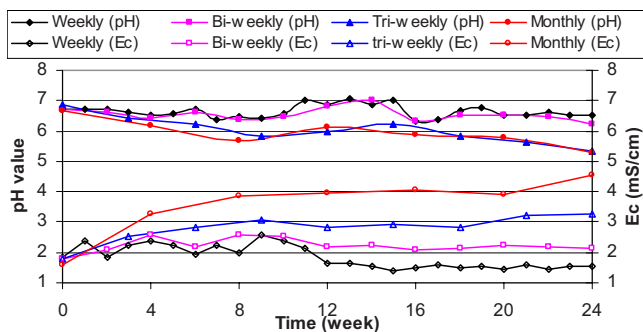
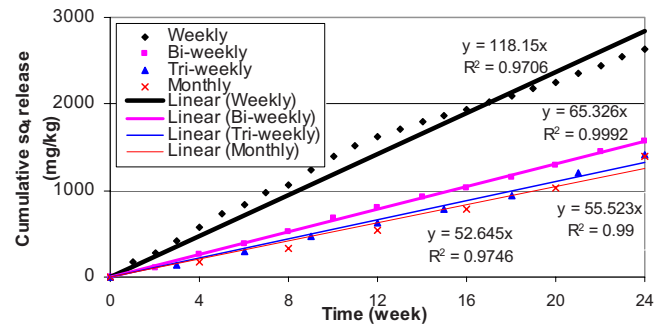
Table 2. Bulk and Trace Elemental Composition of Waste Rock Material

Major oxides	% by weight	Trace elements	$\mu\text{g/g}$
SiO ₂	26.78	Al	5654.4
TiO ₂	0.43	As	680.8
Al ₂ O ₃	9.30	B	97.9
Fe ₂ O ₃	30.98	Ca	8500.4
MnO	0.18	Cd	146.7
MgO	2.31	Cr	5.4
CaO	1.30	Cu	1726.3
K ₂ O	1.38	Fe	186491.3
Na ₂ O	2.27	Mn	1196.0
P ₂ O ₅	0.04	Ni	22.3
L.O.I.	17.29	Pb	4248.6
Total	92.26	S	176130.4
		Zn	35971.0

The elemental composition obtained from X-ray fluorescence analysis for major oxides and by ICP atomic emission spectroscopy for trace metals is presented in Table 2. As indicated, the sulfur content of the waste rock was 17.6%.

Powder X-ray diffraction analysis indicated that sulfide-bearing minerals in the waste rock are pyrite (15%), sphalerite (5%), and chalcocite and pyrrhotite (3–4%). Gangue minerals include quartz (31%), clinocllore (24%), muscovite (6%), mica (6%), and others.

Fig. 2 shows measured pH and EC values of effluent samples obtained from the column tests. The measured pH values of the effluents from weekly flushing (Column 2) and biweekly flushing (Column 3) were close and near-neutral. At the same time, pH values measured in the effluents from triweekly flushing (Column 4) were similar to those of the effluents from monthly flushing (Column 5), but the triweekly and monthly flushing frequencies produced effluents with much lower pH values compared to the weekly and biweekly flushing frequencies (Fig. 2). These results would suggest that the weekly and biweekly flushing had significant dilution effect on the effluents because of the greater flushing frequencies. Since pH measures the H⁺ concentration in solution, the measured pH values in Fig. 2 indicate that the waste rock samples flushed weekly and biweekly produced similar H⁺ concentration in the leachates. Similar inference may be made for the waste rock flushed triweekly and monthly. The data on the relationship between measured pH values and flushing frequencies suggest that a minimum of three weeks of drying under laboratory conditions is probably enough to oxidize the exposed surface of waste rock grains and provide a reliable oxygen decay coefficient

**Fig. 2.** Measured pH and EC in the effluents from column tests using various flushing rates**Fig. 3.** Cumulative mass of sulfate released in the effluents and their fittings of oxidation rates for the waste rock using different flushing frequencies

for modeling and analysis. Due to differences in waste rock type, this period (3 weeks) may not be applicable to other waste rocks; however, the methodology presented could be applied to waste rock from other sites to obtain oxidation rate.

The measured EC values in the effluents show different trends compared to the measured pH in the effluents (Fig. 2). The results show that the longer the flushing interval, the higher the measured EC of the effluent, implying that longer flushing interval produce more dissolved ions in solution. The different trends between measured EC and pH also underscore the complexity of waste rock weathering. This weathering include not only acid production resulting from the oxidation of sulfide minerals present in the waste rock, but also mineral dissolution reactions since flushing at various frequencies produced effluents with different EC values but similar pH. For example, in the 24th week, the effluent from the waste rock flushed triweekly (Column 4) had an EC of 3.29 mS/cm, while the effluent from the monthly flushed waste rock (Column 5) had an EC of 4.55 mS/cm, although both effluents had a pH close to 5.3 (Fig. 2). The relationship between EC and flushing frequency for the tested waste rock shows that the drying period has significant influence on waste rock weathering.

The waste rock with the longer flushing interval (lower flushing rate) produced lower sulfate release rate (Fig. 3). However, when the flushing interval was sufficiently long, the decrease in sulfate release rate was not significant. For example, the sulfate release rate of the waste rock flushed weekly was 118 mg (SO₄²⁻)/kg/week; the waste rock flushed biweekly released 65 mg (SO₄²⁻)/kg/week of sulfate; and the sulfate release rates for the waste rock flushed triweekly and monthly were 56 and 53 mg (SO₄²⁻)/kg/week, respectively, as shown in Fig. 3. These measured sulfate release rates show good agreement with the measured pH of the effluents. As predicted from measured pH values in Fig. 2, the sulfate release rate of the waste rock flushed weekly (Column 2) was almost double that of waste rock flushed biweekly (Column 3), while the waste rock flushed triweekly and monthly (Columns 4 and 5) generated similar sulfate release rates. The short flushing interval (i.e., weekly flushing) resulted in a high infiltration rate and the long flushing interval (such as monthly flushing) implied small infiltration rate because the volume of water used in each flushing event was the same. The measured sulfate release rate data suggest that a high infiltration rate resulted in high oxidation rate because more fresh sulfide mineral surfaces could be exposed for further oxidation after flushing out of previous oxidation products. However, the oxidation rate could also decrease (or increase marginally or slowly) if the infiltration rate is higher than a certain value (and corresponding flushing interval). The reason is that very high saturation of

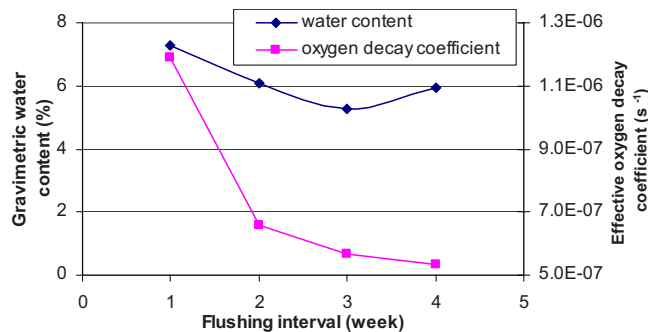


Fig. 4. Calculated effective decay coefficients and estimated average water content under different flushing intervals (flushing rates)

the waste rock can reduce gaseous oxygen transfer to sulfide mineral surfaces. In the current study, this value and the corresponding flushing interval was not identified, but the study found the optimal flushing interval (triweekly flushing) after which period the oxidation rate decreased slowly with a decrease in infiltration rate (increase in flushing interval).

Fig. 4 shows the oxygen decay coefficients calculated from the sulfate release rates and the average water content of the waste rock estimated from the water balance of the experimental columns with various flushing rates. Generally, with an increase in the flushing intervals, the water content of the waste rock decreased. The waste rock with the triweekly flushing rate (Column 4) had a water content slightly lower than the waste rock with the monthly flushing rate (Column 5). This may be attributed to the small difference in the configuration and measurement. Fig. 4 also shows that the oxidation rate decreases with water content in the range of water content used in the study (i.e., gravimetric water content of 5.3–7.3%). The relationship between the oxidation rate (sulfate release rate) and the water content of the waste rock samples found in the present study is similar to those of Hollings et al. (2001) and Gosselin et al. (2007). Similar to the relationship between sulfate release rates and flushing intervals (Fig. 3), the oxygen decay coefficients decreased with increase in flushing intervals (Fig. 4). The waste rock with the weekly flushing rate (Column 2) had the largest decay coefficient in the experiments ($1.19 \times 10^{-6} \text{ s}^{-1}$), and the triweekly flushing and monthly flushing rates generated similar decay coefficients ($5.68 \times 10^{-7} \text{ s}^{-1}$ and $5.32 \times 10^{-7} \text{ s}^{-1}$, respectively).

Determination of the Oxygen Decay Coefficient for a Specific Laboratory Case Study

Measured Sulfate Release Rate

Fig. 5 presents the measured cumulative effluents from Column 1. The data show that the effluents were very close to the influents during the continuous flushing (daily flushing) period; but the long drying period (Day 24 to Day 84) between rainfall events caused the waste rock to lose water by evaporation, which resulted in a significant difference in the measured volumes of influents and effluents during later, continuous rainfall events. The evaporation that occurred during the dry period had an important effect on the overall oxidation of the waste rock.

Continued daily flushing did not change the pH of the effluents very much (Fig. 6), and pH values increased slightly with continuous rainfall events, indicating dilution was a dominant factor

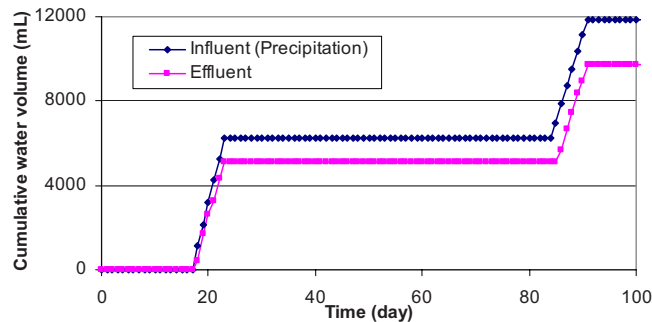


Fig. 5. Cumulative precipitation and effluent for the specific laboratory case (Column 1)

that controlled the concentration of ions in the effluents. After the long drying period, the pH of the leachate decreased sharply (close to 6) due to the longer oxidation time and less effluent volume; but this pH value was still higher than values obtained from the waste rock with the triweekly and monthly flushing rates. This could be attributed to the reduced availability of water during oxidation of the waste rock in the specific laboratory case study. The cumulative sulfate released from the waste rock showed higher oxidation rate during the continuous flushing and lower oxidation during the long drying period, which was consistent with the observation for the column tests with different flushing rates (Fig. 3). The average sulfate release rate from the waste rock with the specially designed rainfall events was a combination of these higher and lower sulfate release rates during the different rainfall intervals. In this specific laboratory case (Column 1), the long drying season had more effect on the oxidation of the waste rock than the continuous rain events. The average sulfate release rate, $8.57 \text{ mg (SO}_4\text{)}/\text{kg}/\text{d}$, for this specific case was close to the sulfate release rate from the waste rock flushed triweekly [$7.93 \text{ mg (SO}_4\text{)}/\text{kg}/\text{d}$].

Oxygen Decay Coefficient of the Specific Laboratory Case

Table 3 presents the oxygen decay coefficients for the waste rock in the specific laboratory case calculated using three different methods. In Method 1, the oxygen decay coefficient was calculated using Eq. (10) and waste rock characteristics (density and porosity) and sulfate release rate measured for the laboratory case (Column 1). This oxygen decay coefficient was assumed to be the true value for the waste rock used in the study. In Method 2, oxygen decay coefficients were computed using Eq. (10) and the

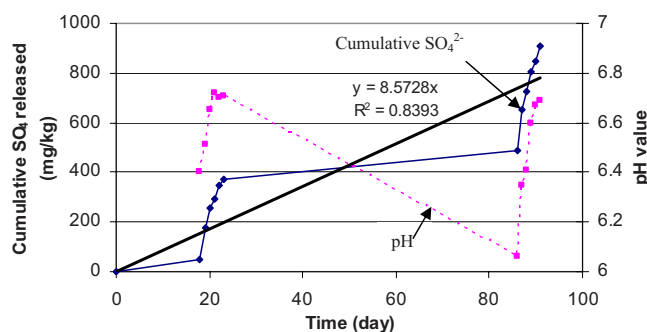


Fig. 6. Measured sulfate mass released from the waste rock and pH value in the effluent for the specific laboratory case (Column 1)

Table 3. Calculated Effective Oxygen Decay Coefficients for the Specific Laboratory Case Based on the Different Parameters

Methods	Parameters used for calculation				Effective oxygen decay coefficient (s ⁻¹)	Relative error e_r (%)
	ρ_d (g/cm ³)	θ_{eq}	SO ₄ release rate (mg/kg/d)	O ₂ consumption rate (mg/kg/d)		
Method 1	2.06	0.145	8.57	5.0	5.90×10^{-7}	0
Method 2	2.06	0.145	16.88 ^a	9.8	1.16×10^{-6}	96.8
	2.06	0.145	9.33 ^b	5.4	6.42×10^{-7}	8.8
	2.06	0.145	7.93 ^c	4.6	5.46×10^{-7}	7.5
	2.06	0.145	7.52 ^d	4.4	5.18×10^{-7}	12.3
	2.11	0.098	16.88 ^a	9.8	1.19×10^{-6}	101.5
Method 3	2.12	0.119	9.33 ^b	5.4	6.60×10^{-7}	11.9
	2.14	0.125	7.93 ^c	4.6	5.68×10^{-7}	3.8
	2.12	0.122	7.52 ^d	4.4	5.32×10^{-7}	9.9

Note: Method 1: using Eq. (10) and waste rock characteristics and sulfate release rate measured for the specific laboratory case (Column 1). Method 2: using Eq. (10) and waste rock characteristics measured for the specific laboratory case (Column 1) and various sulfate release rate obtained from the waste rock with different flushing rates (Columns 2 to 5). Method 3: using Eq. (10) and waste rock characteristics and sulfate release rate obtained from the column test with different flushing frequencies.

^aSulfate release rate obtained from the waste rock flushed weekly (Column 2).

^bSulfate release rate obtained from the waste rock flushed biweekly (Column 3).

^cSulfate release rate obtained from the waste rock flushed triweekly (Column 4).

^dSulfate release rate obtained from the waste rock flushed monthly (Column 5).

appropriate waste rock characteristics [same as those of the specific laboratory case (Column 1)] and sulfate release rates obtained from the waste rock with different flushing rates (Columns 2 to 5). In Method 3, the oxygen decay coefficients were obtained directly from the column tests with different flushing frequencies.

The relative error compares the oxygen decay coefficient obtained from Method 1 (the assumed actual value) to values obtained from Methods 2 and 3. It was evaluated using

$$e_r(\%) = \left| \frac{\lambda_1 - \lambda_2}{\lambda_1} \right| \times 100 \quad (17)$$

where e_r =relative error; λ_1 =effective oxygen decay coefficient of the waste rock for the specific case obtained in Method 1; and λ_2 =estimated effective oxygen decay coefficient of the waste rock for the specific case from Methods 2 and 3.

Table 3 shows that, compared to the true effective oxygen decay coefficient ($5.9 \times 10^{-7} \text{ s}^{-1}$ in Method 1), the calculated oxygen decay coefficient had the largest relative error when the sulfate release rate of the waste rock flushed weekly was used and the least error occurred using the sulfate release rate of the waste rock flushed triweekly in both Methods 2 and 3. Specifically, if the oxygen decay coefficients obtained from the column tests with different flushing rates were employed as the oxygen decay coefficient of the specific case (Method 3), the largest error (101.5%) would be generated by the oxygen decay coefficient obtained from the weekly flushing test, and the oxygen decay coefficient obtained from triweekly flushing would have the least error (3.8%). In Method 2, the oxygen decay coefficient calculated using the sulfate release rate from the weekly flushing also produced the largest error (96.8%), and the oxygen decay coefficient calculated based on the sulfate release rate from triweekly flushing had the least error (only 7.5%). These results imply that the oxidation rate obtained from humidity cell test or column test with weekly flushing may not be the best representation of the oxidation rate occurring in waste rock in the field. The effective oxygen decay coefficient obtained directly from Column 4 using Method 3 ($5.68 \times 10^{-7} \text{ s}^{-1}$) is closer to the true value ($5.90 \times 10^{-7} \text{ s}^{-1}$) than that calculated using the physical characteristics

of the waste rock in the specific laboratory case study (Column 1) and the sulfate release rate of the waste rock flushed triweekly (Column 4) in Method 2 ($5.46 \times 10^{-7} \text{ s}^{-1}$). This indicates that the effective oxygen decay coefficient of the waste rock was dependent on both the oxidation rate (oxygen consumption rate) and the physical characteristics of the waste rock, particularly the dry density of the waste rock.

The oxygen consumption rates presented in Table 3 [4.4 to 9.8 mg (O₂)/kg⁻¹ d⁻¹] are comparable to values [3.5 to 4.2 mg (O₂)/kg⁻¹ d⁻¹] obtained by Hollings et al. (2001) for the same range of moisture content and using direct oxygen consumption measurements. The values obtained in the present study are also only an order of magnitude higher than field values reported for the Rum Jungle waste rock dumps, Australia, by Harries and Ritchie (1981). The slightly higher values obtained in the present laboratory study may be attributed to the difference in waste rock mineralogy and the finer particle size (crushed rock) compared to the coarser rock (full-scale) at Rum Jungle. The effective oxygen decay coefficients also given in Table 3 (5.18×10^{-7} to $11.9 \times 10^{-7} \text{ s}^{-1}$) are an order of magnitude higher than the values (3.1×10^{-8} to $2.2 \times 10^{-7} \text{ s}^{-1}$) reported by Mbonimpa et al. (2002) for Les Terrains Aurifères (LTA) tailings at a degree of saturation of 90%. The waste rock used in the present study was only 60% saturated and had a different mineralogy.

Although the waste rock in the specific laboratory case underwent a long drying period (approximately 60 days), which was longer than the monthly flushing interval, the oxygen decay coefficient calculated with the sulfate release rate from the triweekly flushing rate was the closest to the actual or true oxygen decay coefficient as indicated by the lowest relative error (Table 3). This implies that the oxidation of the waste rock occurring during the continuous flushing of the rainy period also affects the final oxygen decay coefficient. The final oxygen decay coefficient reflects the effects of flushing rates from both short interval and long intervals as does the oxidation rate of the waste rock. Thus it may be necessary to consider field precipitation frequency when modeling field oxidation of waste rock using laboratory column tests.

Discussion

Eq. (5) neglected oxygen diffusion in the waste rock (Song and Yanful 2009). In practice however, when the oxygen concentration in the waste rock pile is high (e.g., close to the oxygen concentration in the atmosphere), oxygen diffusion should not limit oxidation, and the measured sulfate release rate may be used to estimate the oxygen decay coefficient. The occurrence of high oxygen concentrations in mine waste rock piles is not unusual, especially for uncovered waste rock piles or dumps. For example, Adu-Wusu and Yanful (2006) reported that the measured oxygen concentrations in waste rock used in pilot tests at the Whistle Mine site (Ont.) were close to the oxygen concentration in the air because the waste rock piles were only partially covered. Linklater et al. (2005) found that the measured oxygen concentrations at some locations in the waste rock dumps remained relatively close to ambient value. Elberling et al. (1994) identified the oxidation rate of sulfide minerals to be controlled by kinetic reactions and oxygen diffusion. In the presence of kinetic reactions, diffusion was negligible. During the column tests in this study, the measured oxygen concentration in two oxygen sampling ports located 10 cm apart in each column was close to 20.7%. Further research is, however, necessary to investigate whether the calculated oxygen decay coefficient from the proposed method can be used to predict the oxygen concentration in waste rock pile for general situations.

If the oxygen concentration in the waste rock piles maintains very high and close to the atmospheric value, the oxygen concentration profile in the waste rock may not control the oxidation rate of the waste rock. In such a case, it may be advantageous to use the sulfate release rate to estimate oxygen decay coefficient. Although some researchers are of the opinion that sulfate measured in effluents does not entirely represent waste rock oxidation because sulfate in the effluent may come from the dissolution of pre-existing sulfate salts and that sulfate ion may also precipitate out of solution as gypsum, sulfate release rates from kinetic cell tests have been used extensively to determine oxidation rate (Perkins et al. 1995). In the present study, the aqueous speciation software MINTEQA2 (Allison et al. 1991) was used to analyze the possibility of gypsum precipitation from effluents obtained from the column tests (Columns 2 to 5) and from the specific laboratory case study (Column 1). The input data included measured average values of pH and dissolved species concentrations and thermodynamic data embedded in the MINTEQA2 database. In general, a saturation index greater than zero implies supersaturation of a solution with respect to a particular mineral, a saturation index less than zero suggests undersaturation while a saturation index equal to zero implies saturation. The computed saturation indices for gypsum ranged from -0.044 to -0.224 (i.e., -0.107 in Column 1, -0.224 in Column 2, -0.172 in Column 3, -0.097 in Column 4, and -0.044 in Column 5), indicating slight undersaturation of the effluents with respect to gypsum.

When calculating the oxygen consumption rate from the sulfate release rate, the stoichiometry relating 3.5 mol of oxygen to 2 mol of sulfate [Eq. (8)] was used. In actual fact, the oxygen consumption calculated in this way may represent the minimum oxygen consumption from the maximum sulfate production (Hollings et al. 2001). If pyrite is not the dominant sulfide-bearing mineral in the waste rock pile, the measured oxidation rate based on the sulfate release rate and the oxygen consumption rate may not be consistent with the stoichiometry mentioned above. In such cases, it would be necessary to write appropriate oxidation reactions for the sulfide minerals involved and use the relevant stoichiometric

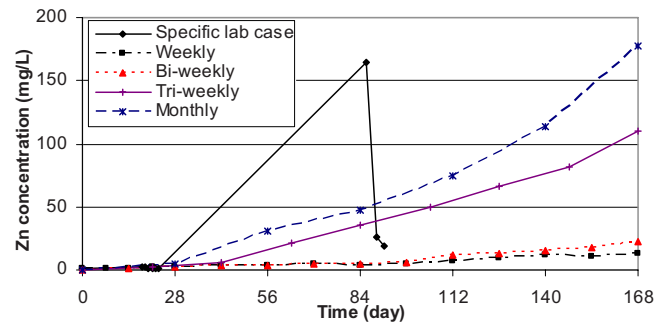


Fig. 7. Concentrations of zinc over time in the effluents from the waste rock with different water addition (flushing) frequencies

coefficients in relating oxygen consumption to sulfate production. For example, the coefficient is 0.895–0.924 for pyrrhotite (Fe_{1-x}S , $x=0$ to 0.125) and 0.924 for chalcopyrite and sphalerite. Mineralogical analysis of waste rock should help identify the sulfide minerals present in the waste rock.

The column tests with different flushing frequencies or flushing intervals provide insight to understanding the oxidation of the waste rock pile in the field because the different flushing rates approximately simulate natural rainfall processes. The different flushing intervals influence the water content of the waste rock as well as the oxidation rate. Frequent flushing could provide more fresh reaction surfaces as preoxidized material is flushed out and fresher sulfide minerals react upon exposure to air. This could accelerate oxidation. However, frequent flushing could increase the pH of solution around particles and impede reactions catalyzed by bacteria, such as *Thiobacillus ferrooxidans* (Nicholson 1994). Third, changes in flushing frequency represent real-life situations in waste rock piles in the field. Preferential flow pathways may exist in soil cover or in the underlying waste rock pile, which could change the flushing frequency in the waste rock pile. Different flushing intervals could also be produced by different climatic environments. For instance, precipitation intensities and frequencies are different among humid area, semiarid area and arid area. Thus, the relationship between flushing frequencies and oxidation rates has practical significance and application.

Preferential flow and particle migration do occur in the field, but would be minimal in this laboratory study involving prescribed flushing rate, where the rock was relatively uniform and the height of rock in the columns was small (only 25 cm) compared to the height of a field waste rock dump. Preferential flow would occur in the field waste rock due to the heterogeneity of waste rock (e.g., Stockwell et al. 2006).

The sulfate release rates obtained from the column test and the specific laboratory case study indicate that the lower the flushing rate is, the lower the oxidation rate. This finding is consistent with observations in pilot tests at the Whistle Mine site involving partially covered waste rock piles (Song and Yanful 2008). The effect of flushing frequency on oxidation rate is also reflected in the heavy metal concentrations (say, zinc) in the leachates (Fig. 7). The waste rock with lower flushing rates (e.g., triweekly and monthly flushing) produced higher effluent zinc concentrations than the waste rock with higher flushing rates (e.g., weekly and biweekly flushing) because the former had relatively longer period for oxidation and also produced smaller effluent in a flushing cycle. The zinc concentration in the effluent from the specific laboratory case (Column 1) clearly showed the effect of flushing interval. When the waste rock had the continuous flushing (rainy period), the zinc concentrations in the effluents remained low. A

much higher zinc concentration occurred after a long drying period and then decreased sharply with the following continuous flushing. The finding that the oxidation rates and heavy metal concentrations in the effluents change with precipitation frequencies should be helpful in the design of facilities to treat acid rock drainage from waste rock piles. Apart from the rainfall frequency, a number of other factors, including grain size distribution, affect the oxidation rate (oxygen consumption rate) of waste rock. The smaller the grains size of the waste rock, the larger the specific surface area, which may increase oxidation rate.

Conclusions

The oxidation rates (sulfate release rates) of waste rock from the Mattabi Mine site near Ignace, Ont. were investigated through the kinetic cell tests (column tests) in the laboratory. The oxygen decay coefficient of the waste rock was estimated. The flushing frequencies were selected to include the weekly flushing used in the standard humidity cell test and to determine whether flushing frequency had an influence on oxidation rate. Based on the results and discussion, the following conclusions are drawn:

1. The proposed method for calculating the oxygen decay coefficient of the waste rock based on the sulfate release rate showed that the oxygen decay coefficient was related to not only the oxidation rate, but also to the physical characteristics of the waste rock, such as dry density. The effect of the characteristics of the waste rock on the oxygen decay coefficient implies that the measured oxygen decay coefficient from laboratory tests (e.g., in the sealed chamber used in the present study) may have to be modified according to the actual waste rock pile configurations in practical applications.
2. When oxygen diffusion was not a dominant transport factor in waste rock, the oxygen decay coefficient could be calculated based on the measured sulfate release rate through the conversion of the sulfate release rate into the oxygen consumption rate. However, in order to convert sulfate release rate to oxygen consumption rate, the stoichiometry of the actual oxidation reaction must be known.
3. The rainfall frequency in the waste rock directly affected the oxidation of sulfide minerals. Under similar conditions, larger flushing intervals (i.e., lower flushing rates) produced lower oxidation rates (sulfate release rates) but higher heavy metal concentrations. However, the decrease in the oxidation rate declined with increase in the flushing interval.
4. The specific laboratory case study showed that the actual oxidation rate of a particular uncovered waste rock pile was affected by both frequent precipitation and sparse precipitation. The local rainfall events should be considered when simulating oxygen consumption rate (oxidation rate) of the waste rock in the laboratory. Weekly flushing (as in a humidity cell) may grossly overestimate oxidation rate.

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