# Evaluating the Oxygen Reaction Rate Coefficient of Sulphidic Tailings using Laboratory and Field Tests

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## Abstract
The oxygen flux into exposed tailings can be assessed in the field by conducting oxygen consumption (OC) tests. Such tests can also be conducted in the laboratory using closed cells. As shown in this paper, numerical solutions can advantageously be used to interpret OC tests and evaluate the experimental values of the diffusion ($D_e$) and reaction rate ($K_r$) coefficients. These two parameters are included in modified Fick's laws that give the oxygen flux entering the surface of reactive tailings. The paper describes both types of OC tests, as performed in the field on an abandoned tailings impoundment at the Manitou mine site in north-western Quebecand in the laboratory on the Manitou tailings. The experimental results are interpreted using numerical simulations of the tests performed with commercial codes. The values of coefficient $K_r$ obtained in the field (under natural conditions) and in the laboratory (under preset conditions) are also compared and discussed.

Key Words:Fick's laws, oxygen diffusion, oxygen consumption, numerical simulations, surface flux

## Introduction
Reclamation of tailings disposal sites containing sulphidic minerals that can oxidize to produce acid rock drainage (ARD) is a high priority for many mining operations. Engineered soil coversacting as oxygen barriers can be used for that purpose in regions with a relatively humid climate, when the water balance favors long term moisture storage (Nicholson et al. 1989, Bussière et al. 2003). Evaluation of the oxygen flux consumed by the tailings is usefulto assess the efficiency of the cover, as its performance is often determined by comparing the fluxes into the reactive tailings with and without the cover. These fluxes can be obtained under transient or (pseudo) steady-state conditions usinganalytical (for simple boundary and initial conditions) ornumerical solutions, based onthe modified versions of Fick's first and secondlaws (Aubertin et al. 1999; Mbonimpa et al. 2003, 2011). These laws (Eqs. 1 and 2) provide a practical means to evaluate the diffusive oxygen flux F(z, t) atposition *z* and time t (Collin and Rasmusson, 1988; Nicholson et al. 1989) into reactive tailings. For a one-dimensional diffusion process, the Fick's first law canbe written as (Mbonimpa *et al*. 2003; 2011)

$$F(z,t) = -D_e \frac{\partial C(z,t)}{\partial z} = -\theta_{eq} D^* \frac{\partial C(z,t)}{\partial z} \qquad (1)$$

where$D_e$ is the effective oxygen diffusion coefficient; C (z, t) is the oxygen concentration (in the gasphase); $\theta_{eq}$ is the equivalent (diffusion) porosity. Parameter $\theta_{eq}$takes into account the oxygen in the air and water phases (Aubertin et al. 1999, 2000), i.e. $\theta_{eq} = \theta_a + H\theta$(where$\theta_a$is the air filled porosity, θ is the volumetric water content; H is the dimensionless Henry's equilibrium constant - H ≅ 0.03 at 20°C for oxygen). Parameter $D^*$ (= $D_e/\theta_{eq}$) is the bulk diffusion coefficient.

For sulphidic minerals, it is often assumed that the diffusing oxygen is being consumedby an irreversible first-order kinetic reaction that follows an exponential decay(e.g. Elberling and Nicholson 1996). In this case, a modified version of Fick's second law can be used to evaluate the interstitial oxygen concentration

C(z, t);for one-dimensional process, this equation can be expressedas follows(Mbonimpa et al. 2003; 2011).

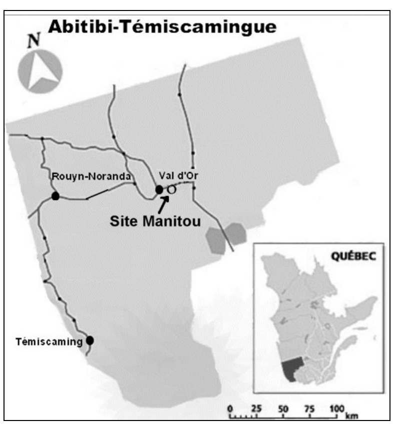
$$\frac{\partial}{\partial t}\left(\theta_{eq}C\right)=\frac{\partial}{\partial z}\left(D_e\frac{\partial C}{\partial z}\right)-K_rC=\frac{\partial}{\partial z}\left(\theta_{eq}D^*\frac{\partial C}{\partial z}\right)-\theta_{eq}K_r^*C \qquad (2)$$

In eq. 2, parameters $K_r^*$ and $K_r$ (=$\theta_{eq}$ $K_r^*$) are the bulk and effective reaction rate coefficients, respectively.

Various laboratory and field testing methods were developed to characterize reactive tailings and determine the value of parameters $D_e$ and $K_r$. New interpretation procedureshave been proposed by the authors for oxygen consumption tests in closed reservoirs, based on numerical simulations of the oxygen migration intoreactive tailings. This paper recalls briefly the testing methodologies and interpretation procedures, and then compares the results obtained from laboratory tests carried out on tailings from the Manitou sitewith those obtained using field oxygen consumption (OC)tests on the Manitou site.

## Site Description and Tailings Sampling

The tailings were sampled at the Manitou mine site, located about 10 km east of the city of Val-d'Or in north-western QC, Canada.The overall site plan is shown in Figure 1.During the mining operation (from 1942 to 1979), about 11 million tons of zinc, copper and lead oreweretreated on this site. The tailings were first deposited inanatural valley, and later in tailings impoundments A and B (see Figure 1). Dike breaches lead to partial tailings discharge around the impoundments, while wind and water erosion contributed to further spreading. At the time of this experimental study (2006), the tailings occupied about 185 hectares on three main areas: impoundments A and B (43 ha), the originaldischarge area and spill zone (90ha), and the delta along the Bourlamaqueriver(52 ha). The relatively coarse grained texture (sandy silt) of the tailings favors natural drainage. The water table was fairly deep (about 8 meters) in impoundment A, which was the focus of this investigation.



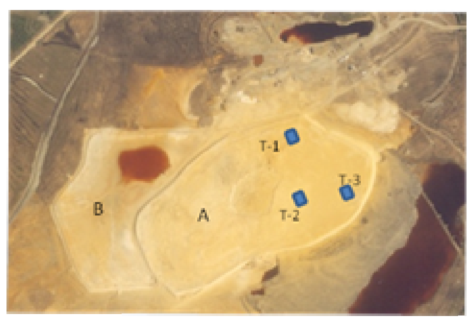




Figure 1.Plan showing the location of the Manitou mine site (left) and aerial view of the Manitou site and approximate locations of the three trenches T1 to T3 wherethe tailings were sampled and field OC tests performed (right).

The Quebec Ministry of Natural Resources and Fauna (MRNF) took over the site, following the bankruptcy of the mining rights owners in 2003. A progressive rehabilitation plan was about to be implemented at the time of this experimental investigation. As part of this ongoing plan, tailings from the Agnico Eagle Mines (AEM) Goldex project, located west of Val-d’Or, QC, are being used to cover the acid generating Manitou tailings; new dikes constructed on the site are also expected to raise the water table. The rehabilitation program is planned to continue for many years (Émond et al. 2011).

A sampling campaign was carried out in June 2006. Three trenches (T-1, T-2, and T-3) with a depth of 1.5 to 1.8 m were excavated in impoundment A; locations are indicated in Figure 1.Visual observations in these trenches indicatedphysical and chemicalheterogeneities (stratifications) with variable alteration conditions. The tailingswere generally more oxidizedclose to the surface (up to about 1.2 m deep), and remained relatively intact (grey) at larger depth. Tailings samples were collected at the bottom of each trench. The three samples were mixed to obtain a composite sample (about 240 kg). These“unoxidized” tailings were put in buckets and kept under water to minimize contact with oxygen.

Basic physical and geochemical characterisation was performed on the tailings sample. The grain-size distribution is fairly typical of hard rock tailings (sandy fraction) with a $D_{10}$of about 0.015 mm,$D_{30}$near 0.080 mm and $D_{60}$ of 0.200 mm.According to the unified (USCS)system, these tailings are classified as silty sand (SM). The relative density of the solid particles is about 2.8.The chemical and mineralogical analysis indicated that pyrite was the main sulfide mineral, with a content of about 7% (w/w). The net neutralisation potential (NNP) is about -142 (kg $CaCO_3$/t), confirming the acidic nature of these tailings.

## Laboratory Tests in Closed Cells

The main experimentalprocedureto determine parameters $D_e$ and $K_r$ in the laboratory is basedonthe oxygen diffusion and consumption (ODC) test, developed progressively over the years (Aubertin et al. 1995, 1999, 2000; Aubertin et Mbonimpa, 2001; Mbonimpa et al. 2003). Thistest is conducted in a closed cell with two reservoirs, initially purged with nitrogen, located on both sides of the sample. The source reservoir is then filled with air from which oxygen diffuses through the material where it is partially consumed. The flow through is collected in thereceptor reservoir. The change in oxygen concentration measured directly in both reservoirs is used to obtain$D_e$ and $K_r$. Such tests were included in this investigation (results not shown here) to assess materials properties and to help validate other types of measurements.

An alternative measurement method, which involves the use of a closed cell with a single reservoir, leads to a more precise determination of $K_r$(Gosselin 2007; Gosselin et al. 2007). This OCtest uses the experimental setup shown in Figure 2.

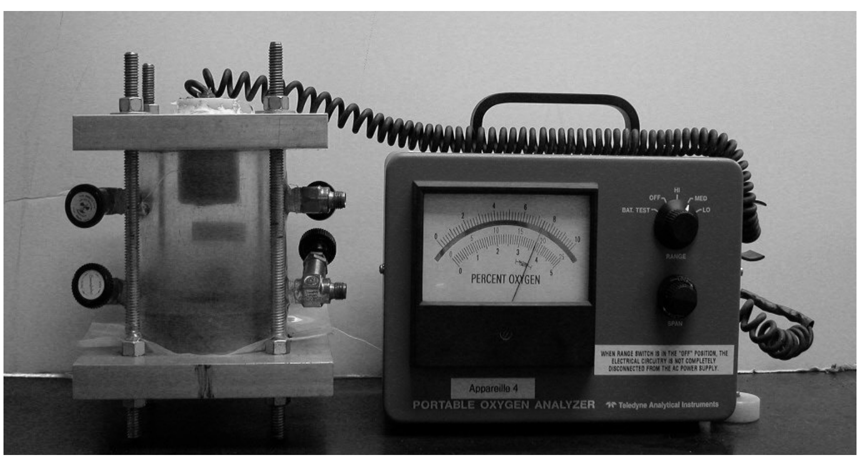


Figure 2.The laboratory OCtestcell with a single reservoir

In this case, the tailings are put in place, at the desired porosity n and water content$\theta$, at the base of a Plexiglas cylinder with a diameter of 8 cm. The specimen thickness is about 2 cm, while the height of the reservoir above varies from 5 to 10 cm. An oxygen sensor (Teledyne 320 P/D) measures the concentrationof oxygen. This sensor is calibrated for each test. Before starting a test, the cell is purged with humidified nitrogen. The cell filled with nitrogen is left standing 24 hours to make sure that it is airtight. The top reservoir is then filled with air under atmospheric conditions.Oxygen migrates inside the tailings(due to the concentration gradient in the closed cell) where it is consumed by the oxidation of sulphidic minerals. The evolution of the oxygen concentration in the reservoir ismonitored and used to back calculate the values of $D_e$ and $K_r$. The test ends when the oxygen concentration has decreased significantly (i.e. down to 15 % or less).A series of 10 tests were conducted on the Manitou tailings at various degrees of saturation ($S_r$). The tailings (initially kept under water)were previously dried under a nitrogen atmosphere before the first test.

The interpretationapproach for the laboratory ODC and OC tests is based on numerical solutionsto the modified Fick's lawspresented above (e.g. Mbonimpa et al. 2003, 2011). The software POLLUTE (Rowe et al. 1994) was used for thenumerical simulations of these tests. POLLUTE has been used for many years tosimulate oxygen diffusion in unsaturated media. The evolution of the oxygen concentration in the reservoir(s) is calculated for given (preset) values of D* and $K_r$*. Iterative calculations areperformed to adjust the calculated and measured oxygen concentrationsand thus obtain the most representative values of D* and $K_r$* (and the corresponding values of $D_e$ and $K_r$). This approach assumes that the material characteristics (volumetric water content θ, porosity n, $D_e$ and $K_r$) are uniform and constant during a test.

## Field OC Tests

Seven field OC tests were carried out on the Manitou tailings site, following the approach proposed by Elberling et al. (1994, 1996), and illustrated schematically in Figure 3. These authors have demonstrated the use of the field oxygen consumption (OC) test to estimate the steady-state surface oxygen flux into tailings exposed to the atmosphere. The test consists of driving an aluminum cylinder into the tailings, leaving an empty space at the top that forms the oxygen reservoir (by closing the cylinder with a tight lid). The progressive decrease of oxygen concentration in the closed chamber is monitored over time,i.e C (z = 0, t>0), where z is the depth from the surface of the tailings. The initial oxygen concentration C (z = 0, t=0) = $C_0$ corresponds to the atmospheric concentration ($C_0$ = 20.9% or about 8.65 mole /$m^3$ or 276 g/$m^3$).

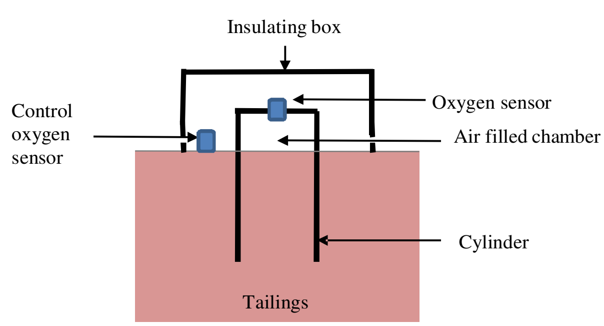



Figure 3.Schematic view of a vertical section for a typical setup of the field OC test.

A conventional (analytical) interpretationapproach was usedby Elberling et al. (1994) for short duration OC tests, assuming that asteady-state condition existed before the test and was maintained during the short test. It also assumes that the depth of oxygen penetration in the tailings was infinite, i.e. C (z, t) = 0 at z → ∞. Under these conditions, the evolution of the oxygen concentration C follows therelationshipgiven by Eq. 3 (Elberling et al. 1994).

$$\ln(\frac{C}{C_0}) = -t\sqrt{K_r D_e}\frac{A}{V} \qquad (3)$$

In this equation, A is the area of the air reservoir and V is its volume. The slope of theln($C/C_0$) versus time t plot provides the value of $(D_eK_r)^{0.5}$. The individual values of $K_r$ and $D_e$cannot be explicitly determined by this approach. The steady-state oxygen flux into the tailings can be calculated by substituting the term $(D_eK_r)^{0.5}$in Equation 4(Elberling et al. 1994, 1996; Mbonimpa et al. 2003).

$$F_s(z=0) = C_0\sqrt{K_r D_e} \quad (4)$$

Several studies have used this interpretation approachfor short OC tests(e.g. Tibble and Nicholson 1997;Elberling and Langdahl 1998; Bussière et al. 2004).Different authors have proposed an alternative approach based on a numerical interpretation, which is also applicable to long duration tests (e.g. Mbonimpa et al. 2000, 2002; 2011; Bussière et al. 2002; Dagenais et al. 2005;Martin et al. 2006; Demers et al. 2009), which are particularly appropriate for relatively low oxygen flux. Dagenais et al. (2012) have also shown how to use this approach to evaluate the oxygen flux through layered covers.

Mbonimpa et al. (2011) have recently shown that this alternative interpretation approach is more representative in many cases, as the conventional interpretation method often tends to underestimate the corresponding flux $F_s$.One of the main advantages of thenumerical interpretation procedure is that it becomes possible to distinguish the values for the two independent parameters D* and $K_r$* (or $D_e$and $K_r$) from a single OC test, contraryto the conventional interpretationwhichonly provides a lumped value($D_eK_r$).The same numerical solutions can also be applied to calculate theoxygen fluxes to the tailings surface, under transient or steady-state conditions.

The value of $D_e$is known to depend strongly on the volumetric water content θ(or degree of saturation$S_r$= θ / n); this dependency is represented here using the $D_e(S_r)$ relationship proposedby Aachib et al. (2004), based on the work of Millington and Shearer (1971) and Collin and Rasmuson (1988); this relationship can be written as:

$$D_e = \frac{1}{n^2}\left\{D_a^0\left[n\left(1-S_r\right)\right]^{p_a} + HD_w^0\ \left(n\,S_r\right)^{p_w}\right\} \quad (5)$$

In this equation, $D_a^0$ is the diffusion coefficient of oxygen in air (≈ 1.56 $m^2$/day) and $D_w^0$ is the diffusion coefficient of oxygen in water (≈ 2.16 × $10^{-4}$ $m^2$/day). Precise values for exponents $p_a$ and $p_w$can be obtained explicitly from the volumetric air and water contents, but in most cases it if sufficient to assume that $p_a$= $p_w$~ 3.5.

The value of $D_e$ obtained from Eq. 5 serves to initiate the iterative calculations with POLLUTE to determine the best fit values corresponding to OC test results. To obtain the starting value of $K_r$, the authors use the simple model proposed byCollin (1987). When the specific surface of the tailings is expressed from the grain-size distribution, this model can be expressed as follows (Mbonimpa et al. 2003; Gosselin et al. 2007).

$$K_r = K'\frac{6}{[1+1.17\log(C_U)]D_{10}}(1-n)C_p \quad (6)$$

whereK′ is the reactivity of pyrite with oxygen (K′= 4.33 x $10^{-5}$$m^3$ $O^2$/$m^2$pyrite/day) and$C_p$ is the pyrite content over mass of dry tailings (kg/kg).One drawback of this model is that it doesn't take into account the influence of $S_r$on $K_r$;this effect is not yet well understood (Gosselin et al. 2007).

Three OC tests were conducted in the field on the tailings surface. Tests 1 and 2 were performed close to trench T-1 and test 3 close to trench T-2. Four tests were made at the base of the trenches:test 4 at the bottom of trench T-1, test 5 at the bottom of trench T-2 and tests 6 and 7 at the bottom of trench T-3. Figure 4illustrates tests conducted on the tailings surface and at the base of the trenches. The aluminum cylinders used for these tests had an internal diameter of 14.5 cm and a total length of 50 cm. The reservoir created by placing the lid on top of the cylinder had a height between 1.5 and 4.0 cm. The cylinder was driven into the tailings with a sledge hammer or pushed with a small excavator. The entire system was covered with an insulating box during the tests to limit the effect of varying meteorological conditions. The decrease in oxygen concentration over time within the reservoir was measured using a GC Industry sensor. Another oxygen sensor was left outside the cylinder in the insulating box to monitor the atmospheric concentration during the test; these measurements are used to correct oxygen concentration readings in the source reservoir, which may fluctuate with ambient conditions (Tibble and Nicholson 1997). The water content w, relative density of solid grains $D_r$, and wet density $\rho_{wet}$ of the tailings were determined and used to evaluate the total porosity n and degree of saturation $S_r$. As with the laboratory tests, it is assumed that these the tailings characteristics within the cylinder are uniform and constant during a field test.

Figure 4. Images of field OC tests conducted on the tailings surface (left) and at the base of the trenches (right)

Two approaches wereused (and compared) for the field tests interpretation: a computational interpretation with the finite element software VADOSE/W (GEO-SLOPE International2005) and the conventional (analytical-graphical) approach proposed byElberling et al. (1994, 1996).

The interpretation with VADOSE/W follows somewhat similar lines as with the POLLUTE calculations described above. It is based on an axisymmetric numerical model representing the OC test configuration.Constant values of n and $S_r$ are imposed for the tailings within the cylinder (theseparameters aregiven in Table 2). The volumetric water content at saturation $\theta_s$, considered equal to the measured porosity n, is imposed below the water table.The average volumetric water content $\theta$ measured *in situ* is used above the water table.VADOSE uses these hydrogeotechnicalcharacteristics toestimate the value of D*(and $D_e$) from the model of Collin and Rasmuson (1988; see also Aachib et al. 2004).

It is assumed also that an equilibrium concentration exists before the start of the test. The estimated value of $K_r$(based on Equation 6)is used to start the simulation with VADOSE/W (see Mbonimpa et al. 2003, 2011). The oxygen concentration profile at equilibrium in the exposed tailings is obtained from a transient analysis performed over a long period (up to 10 days).The variation of the oxygen concentration in the closed reservoir during the field OC test is then obtained from a new transient simulation, where the equilibrium oxygen profile from the previous step is used as initial condition.The change in oxygen concentration calculated by VADOSE/W is compared with the values measured in the field. Iterative calculations are used to adjust the calculated and measured oxygen concentration curves and thus to obtain the actual (or most representative)value $K_r$.

## Results from LaboratoryTests

Figure 5shows the result of one ofthe OC tests performed in the laboratory on the Manitou tailings. The testing period lastedup to 27 days for these tests. Table 1 presents the main characteristics of each test and the values $D_e$and $K_r$ resulting from the interpretation with POLLUTE. It is seen that the degree of saturation $S_r$ of the specimens ranged from 3 to 83% (for a porosity between0.42 and0.54). The adjusted $K_r$ values vary between 0.057$d^{-1}$ and 0.093$d^{-1}$.

It is seen that the predicted and adjusted values of $D_e$ are very close to each other in all cases, but some significant differences are obtained for $K_r$.

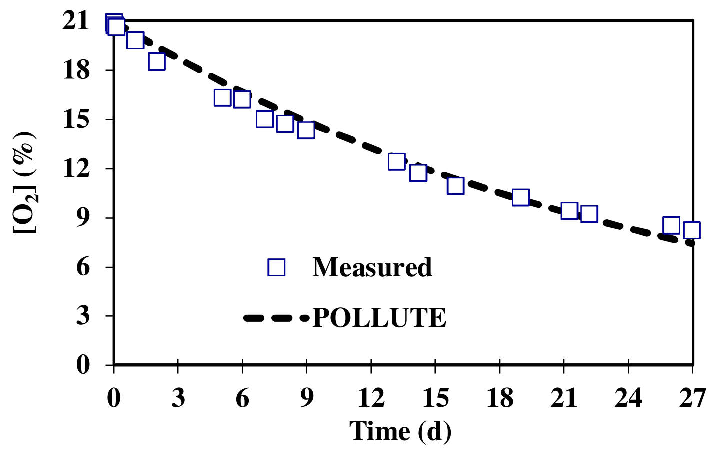


Figure 5. Comparison betweenthe oxygen concentration measureddduring an OC teston Manitou tailings and those obtained from the numerical calculations with POLLUTE,withadjusted values of $D_e$ and $K_r$

Table 1. Characteristics of the laboratory OC tests conducted on the Manitou tailings, with the predicted(pred) and adjusted (adj) values of $D_e$ and $K_r$.

| Test | $S_r$ (%) | n (-) | $\theta_{eq}$ (-) | $D_{e\text{-}pred}$ ($m^2$/d) | $K_{r\text{-}pred}$ ($d^{-1}$) | $D_{e\text{-}aj}$ ($m^2$/d) | $K_{r\text{-}adj}$ ($d^{-1}$) |
|---|---|---|---|---|---|---|---|
| L1 | 2.7 | 0.54 | 0.53 | 0.60 | 0.24 | 0.59 | 0.058 |
| L2 | 10.5 | 0.44 | 0.40 | 0.36 | 0.29 | 0.36 | 0.076 |
| L3 | 16.8 | 0.47 | 0.39 | 0.31 | 0.28 | 0.31 | 0.094 |
| L4 | 26.1 | 0.49 | 0.36 | 0.22 | 0.27 | 0.22 | 0.057 |
| L5 | 37.2 | 0.47 | 0.30 | 0.12 | 0.28 | 0.12 | 0.094 |
| L6 | 46.3 | 0.46 | 0.25 | 0.074 | 0.28 | 0.075 | 0.16 |
| L7 | 54.4 | 0.45 | 0.21 | 0.043 | 0.29 | 0.043 | 0.37 |
| L8 | 63.6 | 0.42 | 0.16 | 0.020 | 0.30 | 0.020 | 0.13 |
| L9 | 74.4 | 0.43 | 0.12 | 0.007 | 0.30 | 0.007 | 0.056 |
| L10 | 82.5 | 0.42 | 0.08 | 0.002 | 0.30 | 0.002 | 0.26 |

## Results from FieldTests

Table 2 summarizes the main characteristics of the seven OC tests conducted on the Manitou tailings site. As mentioned above, the porosity n and degree of saturation $S_r$ required for the simulations were obtained from the water content w and the dry density $\rho_d$measured in field.The value of $S_r$ ranged from 13 to 31% for the surface OC test and from 20 to 30% for the OC test performed at the bottom of the trenches.Figure6illustrates the comparison between measured and calculated oxygen concentrations in the reservoir duringa test conducted in one of the trenches.It was observed that tests F1 to F3 performed on the surface showed a slower decrease in oxygen concentration than those made in the trenches (Tests F4 to F7).

Table 2 shows that the adjusted values of $K_r$ranged between 0.0024$d^{-1}$and 0.033 $d^{-1}$ for the tests conducted at the surface (tests F1 to F3) and between 0.11$d^{-1}$and 1.27 $d^{-1}$ for the tests in trenches (F4 to F7). This difference is deemed to be related totailings oxidation (and sulphide depletion) close to the surface.

Table 2.Characteristics of the OC tests conducted on the Manitou tailings site,with thepredicted (pred) and adjusted (adj) values $D_e$ and $K_r$.

| Test Nr | F1 | F2 | F3 | F4 | F5 | F6 | F7 |
|---|---|---|---|---|---|---|---|
| Location | T-1 | T-1 | T-2 | T-1 | T-2 | T-3 | T-3 |
| Depth (cm) | 0 | 0 | 0 | 150 | 150 | 180 | 180 |
| w (%) | 18.4 | 7.8 | 7.3 | 10.0 | 12.2 | 10.9 | 10.9 |
| n (-) | 0.54 | 0.51 | 0.57 | 0.50 | 0.41 | 0.47 | 0.47 |
| $S_r$ (%) | 34.1 | 15.3 | 12.8 | 20.0 | 29.7 | 23.2 | 23.2 |
| $\theta_{eq}$ (-) | 0.36 | 0.43 | 0.50 | 0.40 | 0.29 | 0.36 | 0.36 |
| $D_{e\text{-}pred}$ ($m^2$/d) | 0.170 | 0.356 | 0.457 | 0.288 | 0.152 | 0.234 | 0.234 |
| $K_{r\text{-}pred}$ ($d^{-1}$) | - | - | - | 0.26 | 0.31 | 0.28 | 0.28 |
| $D_{e\text{-}adj}$ ($m^2$/d) | 0.178 | 0.351 | 0.457 | 0.314 | 0.155 | 0.195 | 0.234 |
| $K_{r.\text{-}adj}$ ($d^{-1}$) | 0.033 | 0.0055 | 0.0024 | 1.27 | 0.11 | 0.86 | 0.76 |

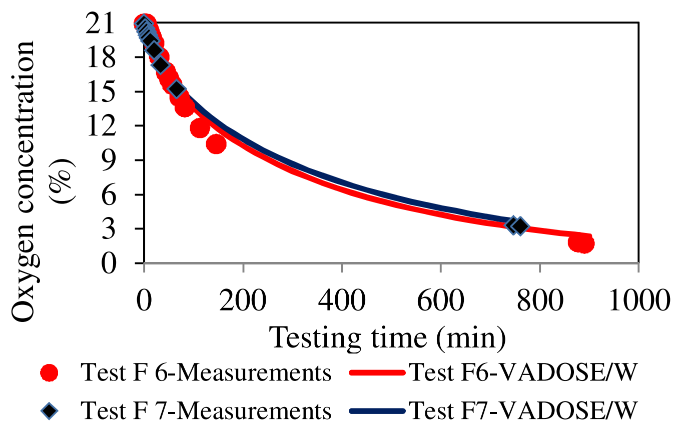



Figure 6.Evolution of the oxygen concentration measured in the reservoir during two OC tests conducted on the Manitou tailings site, with the simulated curves obtained with VADOSE/W for theadjusted value of $K_r$.

As withthe laboratory tests, predicted and adjusted values of $D_e$ are close to each other, while the corresponding values of $K_r$ can be quite different.

## Analysis andDiscussions

### *Comparison of $K_r$values obtained from laboratory and field tests*

The results presented above indicate that the values of $K_r$obtained from the laboratory cell tests using“unoxidized”tailings (sampled at thebase of the trenches, with $0.057d^{-1} \leq K_r \leq 0.093d^{-1}$) are lower than those obtained from field tests conducted at the sampling location (F4 to F7). This difference may be due tovariations in the tailings characteristics, and also to passivation of the grains surface during sampling and handling.It was observed that these tailingswere originally grey when the trenches were excavated, but they took an orange colour within hours when exposed to atmospheric conditions. It was therefore not possible to completely prevent alteration of thesetailings before conducting the laboratory tests. This constitutes an additional justification to conduct OC tests in the field.

Figure 7illustrates how the value of $K_r$seems to varywith respect to the degree of saturation$S_r$for the laboratory and field tests results. As the tailings porosity variesfrom one test to another, the valuesare normalized (as $K_r/(1-n)$) for comparison purposes. Results from Gosselin et al. (2007) on different tailings indicate that an increase in $S_r$generally tends to increase$K_r/(1-n)$ at low water content, until a plateau is reached; this trend is not clear from the results obtained herewith the Manitou tailings. The comparisonbetween the values of $K_r/(1-n)$ obtained from the predictive Collin (1987) model (Eq.6) and the experimental data indicates that the laboratory values are generally lower than the predicted ones. The observed surface alteration may explain this difference, assome passivation of pyrite grains could have reducedthe apparent reactivity of thesetailings. It is also seen that three of the four values of $K_r/(1-n)$ obtained from the field OCtests conductedin trenches (i.e. F4, F6 and F7) are higher than those predicted by Eq. 6.

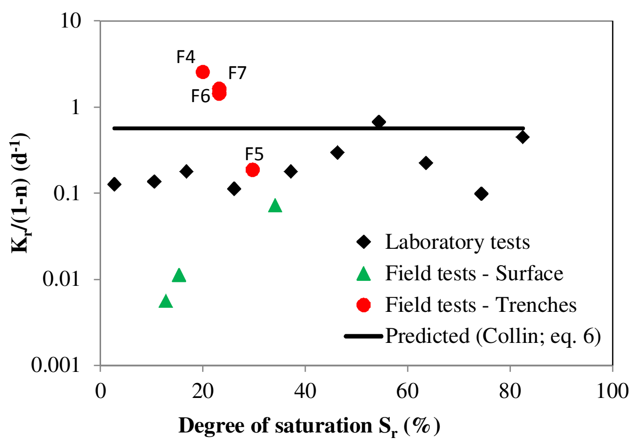



Figure 7.Effect of the degree of saturation on the normalizedreaction rate coefficient $K_r/(1-n)$; the values of $K_r$shown here were obtained from the laboratoryusing OC tests in closed cells with a single reservoir, and in situ from OC tests on the surface and in trenches.

It is useful to mention here that a complementary OC test was performed in the laboratory using a large column filled with Manitou tailings. Measurements were interpreted with VADOSE/W. The results (not presented in details here) indicated that $K_r/(1-n)$ was about $0.11d^{-1}$for$S_r \approx 0.39$ (Gosselin 2007). This value is close to the results obtained in the laboratory OC tests in closed cells.

### *Oxygen fluxes*

The daily oxygen fluxentering in the exposed tailings can be estimatedusingEquation 4, based on a steady-state hypothesis andassuming that thecoefficients$D_e$ and $K_r$are uniform throughout the tailings. Figure 8summarizes the oxygen flux results obtained from the laboratory tests (Table 1) and field tests (Table 2).

As expected, the flux would be larger for fresh (unoxidized) tailings exposed to atmospheric conditions, while it would usually be smaller for tailings near the surface that have been preoxidized, The composite laboratory tailings specimenscollected at the bottom of the trencheswould give intermediate fluxes, and this flux appears to decline when $S_r$ approaches full saturation (which is expected, considering the reduced diffusion coefficient at a large water content).

The field OC tests were also interpreted using the analytical method proposed by Elberling et al. (1994) (Eq. 3). The resulting factors $(D_eK_r)^{0.5}$were then used to estimate the surface flux with Eq. (4). This flux was compared with the oxygen flux calculated using values $D_e$ and $K_r$ obtained from the numerical interpretation of the field tests. The result of this comparison (not shown here) indicates that the conventional (analytical) interpretation method generally underestimates the flux (for 6 of the 7 field tests), by as much as 80%, confirmingother recent results presented by Mbonimpa et al. (2011). Hence, it is deemed more appropriate to interpret the field OC tests using the numerical procedure described briefly above, and presented in more details in Mbonimpa et al. (2002, 2011).

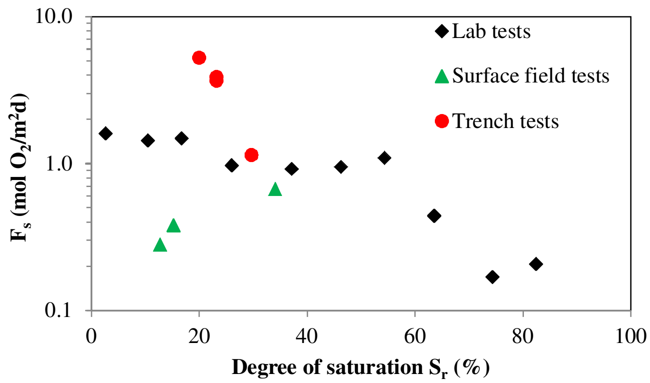



Figure 8.Oxygen fluxes entering exposed tailings, as calculated with Eq. 4 and with the parameters obtained from the laboratory and field OC tests.

## Conclusions

Oxygen consumption (OC) tests, as described by Elberling et al. (1994),were performed on the Manitou tailings site at the surface and at the baseof three trenches where the tailings were (assumed to be)unoxidized. OC tests were also conducted in closed cellsin the laboratory on Manitou tailings samples collected at the bottom of the trenches.Field and laboratory tests results were interpreted using numerical simulations. The ensuing diffusion ($D_e$) and reaction rate ($K_r$) coefficients were then used to estimate the daily oxygen flux ($F_s$) entering tailings exposed to the atmosphere. The main findings indicate that the values of $K_r$ (and $F_s$) obtained from the field tests conducted at the tailings surface are lower than those from tests in trenches; the difference is attributed to the(pre)oxidation of sulphidic minerals close to the surface. The values of $K_r$ (and $F_s$) obtained from the laboratory tests are larger, but fairly close to those obtained from the field tests performed at the tailings surface; these are lower than those from the field tests performed at the base of the trenches. This would indicatethat tailings used in the laboratory tests may have been altered during sampling and preparation (despite the precautions taken in this regard). The $K_r$ values obtained in the trenches also show that the Manitou tailings can be highly reactive, as the reaction rate coefficient measured at depth largely exceeds the value predicted from the pyrite content.

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