Evolving kinetic testing methods to incorporate key dynamic waste rock dump parameters ⌾

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Abstract

Kinetic testing of reactive mine waste material is a key step for characterising acid and metalliferous drainage (AMD) risk. The recently developed Advanced Customisable Leachate Columns (ACLCs) allow control of key parameters that significantly influence oxidation rates and pore water chemistry in the field. Gas flowrate and composition, temperature, and the water addition regime can be adjusted to better approximate conditions within a waste rock dump. Results of dynamic ACLC testing are compared to free draining leach columns using the AMIRA (2002) method. Data from ACLCs will better inform AMD risk assessment and optimisation of management strategies, while also limiting the need for scaling factors typically required when interpreting kinetic tests for predicting commercial scale seepage water quality.

Keywords: kinetic testing, acid and/or metalliferous drainage, waste rock dumps, geochemistry

Introduction

Exposure of sulfide-bearing mine waste material to atmospheric oxygen may lead to production of AMD. Risk assessment for a site's water quality typically involves subjecting site materials to a series of standardised tests, which focus on geochemical properties of the material, including the oxidation rate of the material (typically expressed in $kgO_2/m^3/s$). Results of such kinetic testing are used in both conceptual and predictive (quantitative) models of how water quality at mine sites will evolve over time.

The two main methods for estimating sulfide oxidation rates are the sulfate release method and the oxygen consumption method (Elberling 1993; Elberling et al. 1994; Hollings et al. 2001; Kempton et al. 2010):

- Sulfate release method – Utilises the relationship between measured sulfate production rate and the necessary oxygen required to enable stoichiometric oxidation of the sulfide mineral (usually pyrite) to estimate the oxidation rate (Elberling et al. 1994; Maest and Nordstrom, 2017).
- Oxygen consumption method – Estimates the sulfide oxidation rate by measuring the decrease in oxygen concentration over time (Hollings et al. 2001).

The sulfide oxidation rate determined by both methods is often presented as the intrinsic oxidation rate (IOR) of a material and is expressed in kg $O_2/m^3/s$.

Current standard kinetic testing methods (humidity cells, ASTM 2012; free draining leach columns, AMIRA 2002) involve assessment via the sulfate release method. However, there are a number of ways in which the experimental conditions for these tests can limit extrapolation of the results to field conditions:

- The reaction rates may be overestimated if there is accumulated sulfate present (e.g., gypsum) in the sample at the start of the experiment or underestimated if flushing events do not release all the sulfate generated (e.g., due to formation of jarosite-type minerals).
- A key control on the reaction is the availability of oxygen throughout the sample during the test; this is rarely measured or

controlled.

- The sample is crushed; this may alter water retention characteristics of the material, which in turn changes oxygen availability, as oxygen diffusion through water is four orders of magnitude slower than through air.
- Crushing of the sample also exposes more mineral surface area for reaction than would be otherwise be available.

Experimental conditions may therefore differ significantly to those that the material will be exposed to in the field, to a degree that is rarely monitored or even considered. Mine wastes at many sites also contain reactive organic matter, which may compete with sulfide minerals for oxygen. The standard testing methods do not allow assessment of this potentially ameliorating effect.

The alternative approach to assessing the reaction rate, through the measurement of oxygen consumption, is the basis of the newly developed Advanced Customisable Leachate Columns (ACLCs). The ACLC configuration specifically allows testing of how materials will respond with different oxygen concentrations and water flow. Irrespective of the way in which the rate is measured, the physical conditions of the kinetic testing can be as important as the geochemical properties of the material in controlling the overall reaction rate. This is because the physical material properties, combined with the water balance over the column, affect the water content in material porespaces, which in turn affects oxygen availability, which is the main driver of the geochemical processes. In ACLCs, physical properties such as the matric potential (suction), humidity, and airflow are controlled and monitored continuously, allowing interpretation with respect to physical as well as geochemical controls on the reaction rates. The ACLCs also have the capacity to hold a larger amount of material with larger particle sizes, which allows the tests to be run using material with hydraulic properties that are the same as, or closer to, those in the field.

This testing is highly relevant for assessing AMD management options for mine sites, as these typically involve altering the physical controls on the reaction rate, through reducing the availability of oxygen for reaction, for example through increasing the degree of water saturation of the material, and/or reducing water fluxes to reduce export of weathering products. In the field this can be achieved by altering waste rock dump (WRD) construction methods and drainage, or placing a cover system on the WRD to limit oxygen and/or water ingress. The information obtained from the ACLC method is therefore directly relevant for assessing impacts of different AMD risk mitigation strategies.

Key features of the flexible ACLC configuration include:

- Up to 25 kg of sample is placed in the column (Figure 1) with, or without, prior further particle size reduction, and flushed with water at a user-defined rate.
- The columns are run in a temperature-controlled enclosure; testing can therefore be performed at conditions that are relevant to the field.
- The gas phase composition in the column headspace/outlet is monitored over time, including for example O_2 and CO_2 concentrations.
- The columns can be flexibly configured to have constant or intermittent airflow, or reaction progress monitored under sealed conditions.
- Critical physical parameters such as the air flowrate, matric potential (suction), humidity, pressure, and temperature are continuously controlled and logged.
- Leachate collection allows assessment via the sulfate release method and oxygen consumption method in parallel. However, as the oxygen consumption method is not dependent upon leachate collection, experiments can be run at much lower liquid:solid ratios, with associated longer residence times, and greater potential for oxygen ingress into partially saturated porespaces, which more closely reproduces the conditions inside many WRDs.

Methods

For this paper, waste rock material (100 kg) was composited (2.9 wt% total S; 1.4 wt% acid soluble sulfate; 88 kg H_2SO_4/t maximum potential acidity; 10 kg H_2SO_4/t acid neutralising capacity) and then divided into ACLCs and AMIRA leach columns. Results in this paper are presented from ACLCs with varied

Figure 1 Advanced customisable leachate columns (ACLCs).

air flowrates as summarised in Table 1. The range of airflow values were selected to represent different oxygen availabilities inside a WRD, based on the WRD construction methodology, for example, low airflow represents lower WRD lift heights (e.g. less than 5 m to 10 m such that material segregation is reduced and/or density of the material is increased); the intermediate (control) airflow represents higher WRD lift heights where the propensity for material segregation increases and density can decrease; and, the high airflow represents relatively unrestricted oxygen supply.

Table 1 ACLC conditions tested

ACLC	Airflow (L/min)
ACLC_10	0.008
ACLC_11	0.06
ACLC_15	0.2

Temperature in the ACLC enclosure was maintained at 35-38°C. Water was added at the start of the experiments, with a target water content similar to that in the field (8-12 wt%). Additional flushing events occurred after 41 weeks and at the end of the experiment (≈65 weeks). Leachate was sent for analysis in order to facilitate geochemical equilibrium calculations, which give an indication as to whether typical secondary minerals are controlling aqueous concentrations. Detailed static geochemical characterisation was also completed on the materials before and after the kinetic tests (not shown).

During the first stages of the column tests the experimental conditions were adjusted as the methodology was fine-tuned, including adjustment of air flow rates and installation of a fan in the temperature-controlled enclosure to allow even heat distribution. Continuous monitoring of the physical and geochemical parameters allows responses to changing experimental conditions to be captured and analysed as the experiment progressed. The results presented below demonstrate that ACLCs can provide insight into how the material may behave under dynamic conditions in the field.

Free draining leach columns based on the AMIRA (2002) method were run on the same material, after crushing of the sample to < 6 mm, compared to 42% >6.7 mm in the original sample placed in the ACLCs. Airflow cannot be varied for AMIRA columns. The AMIRA columns were run at room temperature with heat lamps (150 W) operated for eight hours a day for five consecutive days each week.

Results

Oxygen consumption by organic carbon

In mine waste material that contains organic carbon (e.g., shale) the overall rate of oxygen consumption is a combination of consumption by pyrite and by organic matter. The organic matter oxidation releases CO_2, which was monitored in the control column. Assuming typical stoichiometry of 1 mole CO_2

produced for each mole of oxygen consumed, the CO_2 concentrations indicate that the rate of consumption of oxygen by organic carbon in these samples was more than an order of magnitude lower than the total oxygen consumption rate. For the purpose of this assessment, the oxygen consumption rate was therefore assumed to be predominantly due to pyrite oxidation.

Effect of varied air flowrate

The time series results of suction, oxygen concentration, airflow, and calculated IOR are shown in Figure 2. The suction in all three columns increased over time between wetting events. For these experiments the air entering the columns was passed through a moisture trap, and therefore there was a net export of moisture from the ACLCs. For future experiments, the moisture trap can be replaced with a humidifier, as required.

In the column with the lowest airflow, the water content was still sufficiently high that after the second wetting event, water pooled on the surface of the material in the column, until the standing water was carefully removed some weeks later (Figure 2). The oxidation rate was calculated on the basis of a mass balance over the column as a function of the air flow rates (oxygen resupply). The rate of oxygen consumption is also expected to be a function of the water content, as it affects the oxygen ingress into pore spaces. The causes of the low oxidation rate in the low air flowrate column are therefore likely twofold: low oxygen supply, and water-filled porespaces limiting oxygen transport to sulfide mineral surfaces. By comparison, in the ACLCs with higher airflow and less water in porespaces (as indicated by higher suction), the oxidation rates were higher.

The experiments revealed an unexpected control on the oxidation rate in the higher air flowrate experiment. The oxidation rate began to decease as the suction increased to around 1,000 kPa. Upon replenishment of moisture after the wetting event, the rate increased back to the maximum observed. The process of the rate decreasing as suction increased was repeated during the second drying cycle. Our experience indicates that the suction required to reduce the rate of oxygen consumption in this experiment was greater
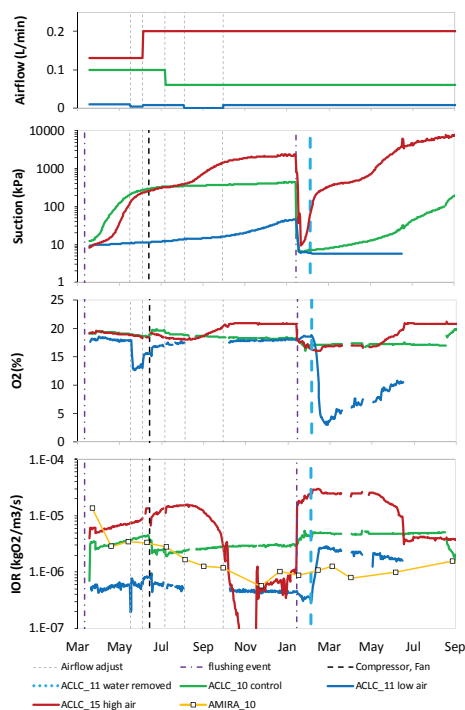

Figure 2 Time series from (top): Air flowrate, suction, oxygen concentration, and oxidation rate (IOR) for the three ACLCs. Also shown is an oxidation rate for an AMIRA column with the same material (see text for explanation). Vertical lines indicate airflow adjustments, water flushing events, points where the compressor temporarily stopped and a temperature-levelling fan was installed in the enclosure, and when pooled water was removed from the top of ACLC_11 after the second flushing event.

than those likely to exist in WRDs, which indicates that the rate limitation due to very low water availability (as indicated by high suction) is unlikely to occur in the field.

Comparison with AMIRA column oxidation rates

The oxidation rates determined from the AMIRA column are also show in Figure 2. Similar results were obtained for all AMIRA columns on this material. The decreasing rate over the first part of the experiment may be due to either a gradual release of pre-existing sulfate in the sample or the crushing process may have exposed fresh mineral surface area, the reactivity of which decreases over time (or as very fine particles are depleted); a com-

monly observed phenomenon in mineral weathering experiments.

For the majority of the duration of the experiment, the rate obtained from the AMIRA column was lower than the rates observed in the ACLCs with intermediate and high air flowrate, other than when the high flowrate experiment was limited by other factors. Given the higher surface area of the crushed material in the AMIRA column, with all else being equal, a higher oxidation rate would be expected in the AMIRA columns than in the ACLCs. However, there are a number of possible explanations for this, including:

- The AMIRA columns had a higher water content, and therefore less oxygen availability.
- Sulfate precipitation occurred within the column, leading to underestimation of IOR.
- Temperature as measured in one of the AMIRA columns varied considerably on a daily basis as a result of the heat lamp cycles, ranging from between below 20 °C to almost 50 °C. However, the daily average was 5-10 °C lower than the ACLC enclosure temperature; temperature is a key factor in geochemical rates.

Calculations with geochemical equilibrium software indicate that leachate from all AMIRA columns were close to solubility equilibrium, with the common sulfate mineral gypsum, indicating that this mineral may be dissolving or precipitating within the column. The oxidation rate, based on the assumption that the sulfate release rate is solely affected by the rate of pyrite oxidation, may therefore be over- or underestimating the true rate, respectively. Changes to the geochemical characteristics of the material before/after the experiment are being further investigated in order to elucidate the processes that have occurred.

Discussion and Conclusions

The new ACLC methodology can capture dynamic responses of geochemical process rates to physical controls (e.g., oxygen availability, water flushing rates) as well as geochemical controls (e.g., S content). The experimental methodology is being continually improved through OKC's R&D team. For example, experiments are currently being run at lower temperature (10°C) on materials from a site with a low annual average temperature; methods are being refined to allow accurate measurement of the correspondingly lower oxygen consumption rates. The flexibility of the ACLC allows experiments to be tailored to best approximate conditions relevant to the field in a range of different climate zones and under a range of different waste rock management options. The ACLC method therefore provides another powerful tool to complement existing methods of kinetic testing for assessment and mitigation of AMD risks.

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