Localized Sulfide Oxidation Limited by Oxygen Supply in a Full-Scale Waste-Rock Pile

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Open-pit mines produce large amounts of waste rock that is placed on-site, often in tall, mixed-composition piles. These waste-rock piles pose environmental risks because their weathering (i.e., sulfide oxidation) may generate acidic and metal-laden drainage. However, the reaction and transport limitations controlling sulfide oxidation remain poorly described at field scales. Here, we present comprehensive multiyear data from two instrumented boreholes in an operational waste-rock pile at the Antamina mine in Peru. Localized but significant (~20 m) sections of reactive waste rock with up to 20% (w/w) sulfide existed at depths of up to 100 m in the pile, and their oxidation with rates of up to $1 \times 10^{-7}$ kg S m$^{-3}$ s$^{-1}$ completely consumed pore-gas O$_2$ and generated temperatures >40°C. Using mass-transport calculations, we show that advective rather than diffusive O$_2$ ingress controlled the sulfide oxidation rates in reactive regions of the waste-rock pile. Sulfide weathering rates in the less reactive zones of the pile were not limited by O$_2$ ingress, independent of the gas transport mechanism, with the exception of fine-grained waste rock at or near complete water saturation. Our results demonstrate the pronounced effects of physical and mineralogical heterogeneity on O$_2$ supply to waste-rock piles and controls of gas transport on waste-rock weathering rates.

Waste rock is typically the largest waste fraction produced by open-pit mines, with millions of tonnes produced around the world annually (Lottermoser, 2010). Waste rock is often stored on-site in mixed-composition, heterogeneous piles or “dumps” that can be hundreds of meters high. The weathering of these exposed waste-rock piles bears significant environmental risks because the oxidation of reactive sulfide minerals, if present, can produce acidic drainage with high metal concentrations (Amos et al., 2015; Dold, 2017) The rate of waste-rock weathering, and thus ultimately the drainage quality from waste-rock piles, is determined by a number of intricately coupled processes, including chemical-reaction kinetics (Singer and Stumm, 1970; Strömberg and Banwart, 1994), biological catalysis (Johnson and Hallberg, 2003; Blackmore et al., 2018), gas transport (Ritchie, 2003), and hydrological flow (Amos et al., 2015; Nordstrom et al., 2015).

During waste-rock weathering, the oxidation of sulfidic gangue minerals consumes O$_2$ and H$_2$O and releases acidity and heat, whereas the acid-buffering dissolution of carbonate minerals (when present) releases CO$_2$. It has been previously observed that sulfide oxidation in waste-rock piles can lead to locally elevated temperatures >60°C (Lefebvre et al., 2001b), virtually complete O$_2$ depletion (Dold, 2017; Parbhakar-Fox and Lottermoser, 2015), and, in carbonate-rich waste-rock piles, to CO$_2$ levels >2% (v/v) (Lorca et al., 2016). Fast reaction kinetics and relatively slow mass- and heat-transport mechanisms in unsaturated waste-rock piles can thus lead to pore-gas and pore-water conditions that are substantially different from ambient atmospheric conditions (Lorca et al., 2016) and elevated internal pile temperatures (Amos et al., 2015).

Previous studies have identified O$_2$ supply as a major factor limiting sulfide oxidation rates in waste-rock piles (Strömberg and Banwart, 1994; Lefebvre et al., 2001b; Molson et al., 2005; Demers et al., 2013). The abovementioned gradients in pore-gas pressure and
composition between the unsaturated waste rock and the atmosphere can trigger gas transport (Fig. 1): the supply of $O_2$ to and release of $CO_2$ from waste rock can occur by diffusion (i.e., described by Fickian diffusion, Knudsen diffusion, or multicomponent diffusion models such as the “dusty gas model”) (Molins and Mayer, 2007; Thorstenson and Pollock, 1992), by advection driven by pressure gradients (barometric pumping or wind-driven advection) (Massmann and Farrier, 1992; Elberling et al., 1998; Kuang et al., 2013; Amos et al., 2009) and compositional changes of the gas phase (Kuo and Ritchie, 1999), and by thermal convection (“chimney effect”) (Kuo and Ritchie, 1999; Sracek et al., 2004; Ning and Zhang, 1997). In contrast, the contribution of dissolved $O_2$ transport by percolating water is limited, and diffusion of $O_2$ through the pore water is orders of magnitude slower than through pore gas (Ritchie, 2003). Unfortunately, the contribution of each of these different gas transport mechanisms to $O_2$ resupply into waste-rock piles varies from site to site and greatly depends on the waste-rock grain size, porosity, pore-water saturation, and meteorological conditions, among others (Lefebvre et al., 2001b; Molson et al., 2005; Lahmira et al., 2017). For instance, using field observations and numerical models, previous studies have concluded that sulfide oxidation rates in waste rock were controlled by either diffusion (Sracek et al., 2004; Pantelis et al., 2002; Gunsinger et al., 2006), pressure- and temperature-driven advection and convection (Amos et al., 2009; Ritchie, 1994; Chi et al., 2013), or both (Lefebvre et al., 2001b; Lahmira et al., 2016). Typically, advection and temperature-driven convection are the main $O_2$ supply mechanisms in coarser material, whereas diffusion dominates the $O_2$ supply in lower permeability material where moisture content is high (Pantelis et al., 2002).

Major complications for the evaluation of gas transport mechanisms in waste-rock piles include: (i) the nonlinear interactions between reaction kinetics and mass and heat transport (e.g., thermal autocatalysis through exothermal energy release from sulfide oxidation, or kinetic limitation of sulfide oxidation through $O_2$ depletion [Lefebvre et al., 2001b; Molins and Mayer, 2007; Lahmira et al., 2016]), and (ii) the poor parameter constraints that arise from the physical and chemical heterogeneity of the waste rock (site specificity) and limited field verification. Engineering efforts aimed at minimizing the impact of environmental loadings from waste-rock piles typically rely on a reduction of drainage or on a deceleration of oxidation rates by limiting the $O_2$ resupply, e.g., through cover construction (Aubertin et al., 2000; Pabst et al., 2017; Romano et al., 2003). However, the relevance and parameterization of water- and gas-transport mechanisms cannot be generalized across sites. Thus, a successful prediction of the overall drainage quality from waste-rock piles requires identification of the rate-limiting processes for sulfide weathering and an understanding of the effects of physical and chemical heterogeneities of the waste-rock pile and prevailing in situ conditions.

Therefore, we investigated the weathering rates and factors limiting sulfide oxidation in a previously uncharacterized, full-scale operational waste-rock pile at the Antamina mine, Peru. We present integrative geochemical and pore-gas data collected from >100-m-deep instrumented boreholes during four consecutive years, which we used to determine waste-rock weathering rates and their spatial distribution as well as gas transport mechanisms.

Methods and Materials

Site Description

The Antamina mine is a large and productive open-pit mine, located approximately 270 km northeast of Lima, Peru (Fig. 2). The Cu–Zn–Mo-rich skarn deposit at Antamina was formed by the intrusion of a quartz monzonite body into a limestone host rock (Love et al., 2004). Located in the Andes at an elevation of ~4200 m above sea level, the mean annual temperature at the

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Fig. 1. Conceptual overview of major physical water- and gas-transport mechanisms in heterogeneous, composite waste-rock piles.
The site is approximately 5°C, and Antamina receives approximately 1200 mm precipitation per year, 80% of which falls during the wet season from October to April (Blackmore et al., 2014). The mine operates two on-site waste-rock storage facilities: the Tucush Dump and the East Dump, both of which are currently hundreds of meters tall, several kilometers wide, and growing. The mine is expected to have produced 2.2 billion tonnes (Mg) of waste rock by the proposed mine closure (Harrison et al., 2012).

Waste rock generated at Antamina is segregated into reactivity classes based on its geochemical and lithological properties (Harrison et al., 2012). The relatively heterogeneous East Dump receives both acid-generating and non-acid-generating waste rock with variable lithology and size, ranging from friable intrusive material to blocky limestone, marble, hornfels, and skarn assemblages. The East Dump is progressively constructed by end-dumping batches of waste rock over the pile’s edge, which creates additional physical heterogeneity from sorting effects (i.e., coarse basal layers and fining-upward layers; Fig. 1 and 2). Compacted traffic surfaces separate distinct end-dumping terraces or “lifts” that dip at an ~37° angle of repose roughly every 60 m vertically (Fig. 2). Drainage from the East Dump is continuously monitored, collected in the tailings pond, and subsequently treated as part of the on-site water management plan.

**Borehole Drilling and Sensor Installation**

Between 2013 and 2015, two pairs of one deep and one shallow borehole each were drilled in the East Dump. Located at two sites on flat traffic terraces (Fig. 2), the deep and shallow boreholes were drilled approximately 10 m apart. Whereas the shallow boreholes were ~20 m deep, the deep boreholes penetrated the entire depth of the East Dump, into the underlying bedrock >120 m below ground surface (bgs) (Fig. 2). The boreholes were drilled using a vibratory percussion hammer (Casagrande C3 drill rig) equipped with an air-driven reverse circulation drill cyclone to prevent mineral alteration by drilling fluids. Composite waste-rock samples from each 1.5-m drill-cut interval were pneumatically retrieved from the borehole in welded-steel casings and collected in trays. The drill cuttings, as grab samples from individual lithological intervals as identified by Antamina’s geologists (Supplemental Fig. S1), were collected in plastic bags and homogenized, aliquoted, and stored in the dark until further use.

The four boreholes were instrumented by installing 80-mm-thick polyvinyl chloride or steel center stocks that were equipped with air piezometers to collect pore-gas samples and with various...
sensors to measure (in situ) moisture content (ECH2O 10HS probes), O2 concentration (KE-50 Figaro probes), temperature (thermocouples and thermistor strings, Geokon and RST Instruments), soil matric potential (heat dissipation sensors, Campbell Scientific Model 229-L), phreatic water level (vibrating wire piezometers, RST Instruments), and gas pressure (Vaisala PTB110 differential air pressure sensors coupled to Campbell CS106 barometers at the top of the boreholes to record atmospheric pressure). The positioning of these piezometers and probes within the boreholes, as well as the backfill materials used, is illustrated in Supplemental Fig. S1. All probes were calibrated according to the manufacturer’s specifications, and the probes were automated to collect measurements at 4-h intervals between January 2015 and January 2018 using Campbell Scientific CR 1000 dataloggers.

Collected and quality-checked sensor data were aggregated to plot depth profiles of monthly average values, thereby eliminating dynamics of, e.g., barometric fluctuations; only a selection of recorded time-series data is referred to below and provided in the Supplemental Material. Depth profiles of the recorded parameters are shown only for January of each year, at the height of the wet season at Antamina; this month yielded the highest quality data and was considered representative for long-term evolution because the annual variation of the recorded parameters was typically <30% for near-surface sensors and <10% for sensors below the 10-m depth (data not shown). For data visualization, the depth profiles of each pair of one shallow and one deep borehole are combined for the two drilling sites, and hereafter referred to simply as Borehole 1 and Borehole 2.

**Geochemical Characterization of the Waste Rock**

A selection of homogenized 1.5-m-interval drill-cutting aliquots and collected grab samples (both ∼500 g each) was sieved to <2 mm, air dried at room temperature for 1 wk, and submitted to an external laboratory for analyses of elemental composition and acid–base accounting parameters. Total S content of the waste rock was determined using a Leco CNS analyzer (Leco Corp. Model NS-1000) and HCl-leachable sulfate content was determined by heating in dilute HCl followed by precipitation as barium sulfate. Subsequently, sulfide-S concentrations were calculated by subtracting HCl-leachable sulfate from the total S content. Elemental composition (As, Cu, Mo, Pb, Zn, Al, Ca, Fe, and Mn) was determined by inductively coupled plasma–mass spectrometry and –optical emission spectrometry (ICP-MS and ICP-OES) after sample digestion using a four-acid method (i.e., HCl, HNO3, HF, and HClO4). Acid-production potential (AP) and neutralization potential (NP) were measured using the modified Sobek method with siderite correction (Skousen et al., 1997; Dold, 2017), in which AP was determined from sulfide-S and NP was determined using an HCl digestion at ambient temperature and using measurements of inorganic Ca as CO2 using ALS Chem internal method C-GAS05, respectively. Whereas sulfide-S concentrations were measured in the majority of collected waste-rock samples, other parameters were analyzed with a reduced vertical resolution of, on average, one analysis every 7 m. Because the percussion hammer used for the drilling crushed the waste rock into smaller pieces, the particle-size distributions of borehole samples were not determined. Instead, average values for waste-rock porosity and particle-size distributions (Table 1) were obtained from earlier work with Antamina waste rock (Vriens et al., 2019; Blackmore et al., 2014).

**Gas Sample Collection and Analyses**

Pore-gas samples were collected in January 2015 from various depths in the boreholes through 30-cm slotted air piezometers that were connected to the surface with high-density polyethylene and stainless steel tubing. Stainless steel gas-sampling cylinders (50 cm3, Swagelok, equipped with gas-tight Thermolite septa, Restek) were filled with pore gas at ~10 kPa by connecting them between a valved sampling-tube exit at the borehole surface and a valved connector to a vacuum pump. The air piezometers, borehole tubing, and gas cylinders were purged for 2 min to ensure that pore-gas samples were representative of in situ conditions within the pile. To measure O2 and CO2, 10 µL of pore-gas sample was extracted from the sampling cylinders using a Luer-lock fitted gas-tight syringe (Hamilton) and injected into a gas chromatograph (Agilent 490 MicroGC, equipped with a micro-thermal conductivity detector). Oxygen and CO2 were separated on a 30-m by 0.53-mm i.d. Carboxen-1010 PLOT column (Sigma-Aldrich) using He as a carrier gas. The instrument was regularly calibrated with a fixed-composition ambient air standard (3.8 × 10−2% [v/v] CO2, 20.95% [v/v] O2) and a fixed-composition calibration gas (1.5% [v/v] CO2, 98.5% [v/v] N2, 0% [v/v] O2, Praxair).

**Results and Discussion**

**Distribution of Reactive Waste Rock within the Full-Scale Pile**

The elemental concentrations and acid–base accounting parameters measured in the waste rock from both boreholes show similar concentration ranges (Fig. 3), indicating that the waste rock from the two drilling locations approximately 1.2 km apart (Fig. 2) has a comparable geochemistry. Waste rock from both boreholes generally has a low (<2% w/w) sulfide content down to 140- and 120-m depths in Boreholes 1 and 2, respectively. However,
Fig. 3. Depth profiles of sulfide-S, Fe, Ca, Cu, and Zn content, as well as acid production potential (AP) and neutralization potential (NP) (kg CaCO$_3$/tonne waste rock) of the waste rock from Boreholes 1 (top) and 2 (bottom) in the East Dump at Antamina. The gray shading indicates the approximate location of the reactive (high-sulfide) zones; legends are indicated in each panel.
both boreholes also contain zones with elevated sulfide content: in Borehole 1, up to 20 and 13% (w/w) sulfide is present at \( \sim 40- \) and \( \sim 70-90 \) m depths, respectively, whereas up to 14 and 10% (w/w) sulfide is observed at \( \sim 20-40 \) and \( \sim 80-100 \) m depths, respectively, in Borehole 2 (Fig. 3). These zones also display an elevated AP that exceeds the corresponding NP, indicating that substantial net-acid-production potential is present in these high-sulfide regions. Furthermore, zones with elevated sulfide content often display higher Fe concentrations and, to a lesser extent, higher Cu and Zn concentrations in their waste rock. These correlations confirm that the majority of waste-rock sulfides stem from pyrite, pyrrhotite, and other Fe-rich primary sulfidic ore minerals like chalcopyrite \( ([Cu,Fe]S_2) \) and sphalerite \( ([Zn,Fe]S) \) that occur at Antamina (Love et al., 2004; Harrison et al., 2012). Similarly, the depth profiles of NP show trends comparable to those of Ca, which corroborates research showing that NP in Antamina waste rock mainly originates from CaCO\(_3\) and Ca-rich silicates (Love et al., 2004; Harrison et al., 2012). The measured depth profiles of the waste-rock chemistry illustrate that significant chemical heterogeneity is unrelated to the method of deposition or existence of traffic surfaces and only poorly reflects the distribution of primary lithological rock types documented in the borehole logs (Supplemental Fig. S1). The latter illustrates the importance of chemical evaluation of waste rock in addition to a geological classification prior to end-dumping, as is conducted by Antamina already. In summary, the East Dump waste-rock pile thus contains multiple and considerable (up to 20 m thick) zones with potentially reactive waste rock buried at depths of up to 100 m bgs.

**Hydraulics and Pore-Gas Composition in the Waste-Rock Pile**

From 2015 to the end of 2017, the top of the phreatic zone oscillated between 139 and 142 m bgs in Borehole 1 and between 121 and 125 m bgs in Borehole 2 (data not shown), demonstrating that the East Dump waste-rock pile remained largely unsaturated. The average moisture content in both boreholes (ranging between 0.05–0.46 in January, at the height of Antamina’s wet season) varied irregularly among years and with depth (Fig. 4). Although particle-size distributions and porosities of the borehole waste rock were not determined, a comparison of the measured average moisture content with the average porosity of bulk Antamina waste rock obtained from previous studies (Vriens et al, 2019; Blackmore et al., 2014) shows that the average pore-water saturation in the boreholes was 0.77 (Table 1). The lack of response to seasonal recharge (i.e., reflecting pore-water infiltration) may be explained by the physical heterogeneity of the waste rock (i.e., variable particle-size distributions due to end-dumping sorting effects and traffic surface compaction) and by the overlapping of annual infiltration fronts (estimated flow velocities of \( \sim 11 \) m yr\(^{-1} \)) indicate that precipitation requires \( >10 \) yr to penetrate the current height of the continuously expanding waste-rock pile; Vriens et al., 2019; Blackmore et al., 2018).

The average pore-gas pressure in Borehole 1 is approximately 2 kPa lower than that of Borehole 2, consistent with its 200 m higher elevation (Fig. 4). The recorded pore-gas pressures in Borehole 1 decrease in the top 40 m to pressures approximately 2 kPa below atmospheric levels, and depth profiles are similar for all years except 2016. In contrast, pore-gas pressures in Borehole 2 have been similar to atmospheric levels throughout the entire depth profile in all years, with the exception of up to 2 kPa lower pressures recorded at approximately 30- and 83-m depths. These pressure gradients of up to 2 kPa observed at depths \( >40 \) m in both boreholes are substantial, considering that diurnal or seasonal barometric pressure variations at the surface were typically on the order of 0.5–1.0 kPa (Supplemental Fig. S3). In Borehole 2, zones with lower pressure coincide with elevated temperatures of up to 25°C recorded at these depths in all years (Fig. 4). In contrast, temperature profiles in Borehole 1 do not appear to be related to low-pressure anomalies, but they are also consistent across the years and indicate elevated temperatures of up to 41°C at the 38-m depth and up to 22°C at the 84-m depth.

The depth profiles of O\(_2\) concentrations measured with sensors indicate that severely O\(_2\)-depleted zones (\( \leq 5\% \text{ v/v} \)) were sustained in both Borehole 1 (at \( \sim 15-38 \) - and \( \sim 80-\text{m depths} \)) and Borehole 2 (at \( \sim 32-45 \) - and \( \sim 82-\text{m depths} \)) throughout the four monitored years (Fig. 4). Except for these low-O\(_2\), the other regions of both boreholes, even at depths below 100 m bgs, appear to be well oxygenated with (near-) atmospheric O\(_2\) levels. The O\(_2\) profiles deduced from actual pore-gas analyses accurately mirror those measured by sensors, both in terms of trends as well as absolute values (Fig. 4). The pore-gas samples further show that CO\(_2\) levels may reach \( >75\% \text{ v/v} \) in the low-O\(_2\) zones and that CO\(_2\) concentrations are strongly anticorrelated with O\(_2\) concentrations (Fig. 4). The pore-gas composition in the waste rock, particularly in zones with elevated temperatures, is thus substantially different from the atmospheric composition, and the strong inverse correlation between the depth distributions of O\(_2\) and CO\(_2\) indicates fast reaction kinetics in comparison to relatively slow atmospheric exchange rates.

The consistently O\(_2\)-depleted zones identified from the sensor and pore-gas sample data coincide, with little vertical offset, with the reactive zones identified from the waste-rock geochemistry (compare shading in Fig. 3 and 4): in Borehole 1, elevated sulfide contents in the waste rock at \( \sim 40-\) and \( \sim 80-\text{m depths} \) coincide with higher temperatures, O\(_2\) depletion, and elevated CO\(_2\) levels, whereas high-sulfide zones at the 20- to 40- and 80- to 100-m depths in Borehole 2 similarly exhibit elevated temperatures and CO\(_2\) levels and a low O\(_2\) content. However, low O\(_2\) and high CO\(_2\) concentrations also extend beyond reactive zones, e.g., at \( \sim 18-\text{m depth} \) in Borehole 1, where the waste rock is less reactive (\( <3\% \text{ w/w} \) sulfide). This may be explained by the fact that oxidation of waste rock with \( <3\% \text{ sulfide} \) may still generate O\(_2\) depletion if the waste rock is well confined or finer grained, and by the fact that the pore-gas and geochemical depth profiles have a different vertical sample resolution so that an isolated fraction of sulfidic waste rock may not appear in the chemical depth profile (i.e., drill-cutting samples were homogenized, limiting resolution to 1.5 m) but still create O\(_2\) depletion around the local sensor environment on oxidation. Similar to the distribution of chemical reactivity, the depth profiles of pore-gas composition and
moisture content in the waste-rock pile do not indicate a large effect of compacted, lower permeability traffic surfaces (expected every ~60 m vertically, hence at 0 m and approximately -60- and -120-m depths, Fig. 2) or particle sorting from end-dumping. Yet, physical waste-rock heterogeneity may still explain the oxygenated conditions at deeper regions of the pile, e.g., via (lateral) O\textsubscript{2} supply through coarse basal layers (Fig. 1), and further investigation of the local particle-size distribution and moisture content at a higher vertical depth.

Fig. 4. Depth profiles of the in situ conditions and pore-gas composition of the waste rock in the instrumented Boreholes 1 (top) and 2 (bottom) in the East Dump at Antamina. Sensor-based temperatures, water contents, pore-gas pressures, and pore-gas O\textsubscript{2} contents were measured for 4 yr and averaged for January, whereas sample-based pore-gas O\textsubscript{2} and CO\textsubscript{2} levels were measured in January 2015 only. The gray shading indicates the approximate location of the reactive (high-sulfide) zones from Fig. 3; the legend applies to all frames.
resolution is therefore required. In conclusion, O2 consumption from sulfide oxidation clearly exceeds the O2 supply in zones with reactive waste rock, and this occurrence of localized O2 depletion appears to be dominantly related to waste-rock geochemistry rather than the physical heterogeneity of the waste rock.

**Estimation of Sulfide Oxidation Rates**

Several rapid O2 concentration changes in the waste rock could be observed from the sensor data, i.e., when pore-gas O2 levels decreased from ~15 to 0% (v/v) in a time span of maximally 8 h (see examples in Supplemental Fig. S2). It can be assumed that these decreases in pore-gas O2 were related to O2 consumption and not displacement, e.g., due to an infiltrating water front, because the moisture content recorded by adjacent sensors was virtually constant during that time (Supplemental Fig. S2). Therefore, it can be estimated that for dry air at 60 kPa and 20°C (Fig. 4), using the average properties of Antamina waste rock (Table 1), such rapid decreases equal an O2 consumption rate of at least $2 \times 10^{-7}$ kg O2 m$^{-3}$ s$^{-1}$, considering that the observed decrease may have been faster than the sensor resolution of 4 h. Assuming a molar stoichiometry of 2:1 between O2 consumption and S oxidation on congruent oxidation (Amos et al., 2015; Vriens et al., 2019), this O2 consumption rate equals a sulfide oxidation rate of at least $1 \times 10^{-7}$ kg S m$^{-3}$ waste rock s$^{-1}$.

In an alternative approach, the recorded temperature gradient of 34°C between the 40-m depth and the surface of Borehole 1 (Fig. 4) can be used to estimate sulfide oxidation rates. One-dimensional heat conduction through unsaturated and homogeneous waste rock can be described by

$$q = -k_T A \frac{\Delta T}{\Delta x}$$

where $q$ is the heat flux (W), $k_T$ is the thermal conductivity of the bulk waste rock (W °C$^{-1}$ m$^{-1}$), $A$ is the surface area (m$^2$) perpendicular to the temperature gradient, and $\Delta T$ over $\Delta x$ is the temperature gradient over path length $x$ (m) (Pantelis et al., 2002). The average thermal conductivity of the bulk waste rock at Antamina is assumed to be constant and is estimated at 1.5 W °C$^{-1}$ m$^{-1}$, based on a range of previously reported literature values for waste rock of similar geochemistry (0.7–7.6 W °C$^{-1}$ m$^{-1}$; Ritchie, 2003; Lefebvre et al., 2001b; Blowes et al., 2003). Accordingly, the observed heat flux between the reactive zone at the 40-m depth and the surface of Borehole 1 is 1.3 W m$^{-2}$ or 1.3 J m$^{-2}$ s$^{-1}$. The exothermic energy released by sulfide oxidation equals ~1500 kJ mol$^{-1}$ pyrite (Rohwerder et al., 1998) and will be transferred both up and down a one-dimensional depth profile. Assuming that the reactive zone at the 40-m depth in Borehole 1 is 1 m$^3$ in extent (i.e., 1 m thick), the abovementioned heat flux then indicates a sulfide oxidation rate of $1 \times 10^{-7}$ kg S m$^{-3}$ s$^{-1}$ or an O2 consumption rate of $2 \times 10^{-7}$ kg O2 m$^{-3}$ s$^{-1}$. These rates agree well with the minimum sulfide oxidation rates deduced from the observed O2 concentration decreases above.

The calculated sulfide oxidation rates in the reactive zones in the East Dump waste-rock pile are similar to oxidation rates previously reported for reactive waste rock in smaller experimental piles at Antamina. For instance, oxidation rates ranging from $4.0 \times 10^{-10}$ to $1.2 \times 10^{-7}$ kg O2 m$^{-3}$ s$^{-1}$ were calculated from pore-gas monitoring in basal and exposed zones, respectively, of an experimental pile (Lorca et al., 2016), and oxidation rates ranging from $1.0 \times 10^{-9}$ to $5.5 \times 10^{-7}$ kg S m$^{-3}$ s$^{-1}$ were deduced from monitoring of drainage from experimental piles with net-neutral to strongly acid-generating waste rock (Vriens et al., 2019). This agreement indicates that high-sulfide waste rock, buried at the 40-m depth or deeper within the full-scale waste-rock pile (i.e., poorly exposed to atmospheric conditions), may exhibit reactivity similar to waste rock in more exposed, smaller scale experimental systems. The oxidation rates calculated above will be hardly representative of the overall reactivity of the heterogeneous full-scale waste-rock pile (Lahmira et al., 2017; Pedretti et al., 2017) because oxidation rates in non-reactive, low-sulfide waste rock may be orders of magnitude lower (Vriens et al., 2019) and because reactive “hotspots” with high oxidation rates need not exclusively be located in O2-depleted regions (Lorca et al., 2016). Sulfide oxidation rates in reactive waste rock located in more exposed sections of the full-scale pile may therefore be verified, e.g., by measuring dynamic O2 exchange with the atmosphere. Finally, the oxidation rates for the reactive waste rock calculated in this study fall within the broad range of reported literature values (between $10^{-5}$ and $10^{-11}$ kg O2 m$^{-3}$ s$^{-1}$; Ritchie, 2003; Bennett et al., 2000; Lefebvre et al., 2001b; Sracek et al., 2006), which illustrates how sulfide oxidation rates vary widely as a result of, e.g., waste-rock mineralogy, particle size, and local climatic conditions and should be assessed on a site-specific basis.

**Evaluation of Oxygen Transport Mechanisms**

The existence of O2-depleted zones and the inversely correlated depth distributions of O2 and CO2 in the waste-rock pile indicate that the atmospheric gas exchange rates may be slow compared with the sulfide oxidation rates and that the O2 supply may thus limit sulfide oxidation in the full-scale waste-rock pile. To test this, the potential diffusive and advective O2 fluxes into the reactive zones of the full-scale dump are estimated below using mass-transport estimates.

**Diffusion**

A single-component, one-dimensional, purely Fickian diffusive O2 flux $J_{\text{diff}}$ (kg O2 m$^{-2}$ s$^{-1}$) through homogeneous waste rock can be described by (Thorstenson and Pollock, 1992)

$$J_{\text{diff}} = -D_{\text{eff}} \frac{\Delta C}{\Delta x}$$

where $D_{\text{eff}}$ is the effective diffusion coefficient (m$^2$ s$^{-1}$) of O2 through the pore gas or pore water of the bulk waste rock (diffusion through the rock itself is assumed to be negligible), and $\Delta C/\Delta x$ is the O2 concentration gradient (kg O2 m$^{-3}$) over path length $x$ (m). The effective diffusion constants of O2 in pore gas and pore water differ from the respective intrinsic diffusion coefficients because they account for non-standard conditions and tortuosity effects caused by the waste-rock porosity and pore-water content (Pantelis
et al., 2002). Values for $D_{\text{eff}}$ can be inferred from field data or calculated using semi-empirical tortuosity models (Aubertin et al., 2000; Collin and Rasmuson, 1988; Moldrup et al., 2000; Millington and Quirk, 1961), in which $D_{\text{eff}}$ usually strongly depends on porosity and pore-water saturation (see equations in Supplemental Table S1). Using intrinsic diffusion coefficients calculated for the climatic conditions at Antamina (Table 1 and Supplemental Table S1), effective O$_2$ diffusion coefficients ranging from $7 \times 10^{-8}$ to $2 \times 10^{-6}$ m$^2$ s$^{-1}$ in air and from $1 \times 10^{-11}$ to $9 \times 10^{-10}$ m$^2$ s$^{-1}$ in water can be calculated for the average waste-rock porosity and water saturation at Antamina (Supplemental Table S1). These values fall within the wide range of previously reported values for $D_{\text{eff}}$ of O$_2$ in bulk waste rock (varying widely between $5 \times 10^{-11}$ and $5 \times 10^{-6}$ m$^2$ s$^{-1}$; Ritchie, 2003; Lefebvre et al., 2001b; Molson et al., 2005; Mbonimpa et al., 2011). When the O$_2$ concentration gradient between the surface and the reactive zone at the 40-m depth in Borehole 1 (15% [v/v] O$_2$, the highest O$_2$ concentration gradient observed in the two boreholes; Fig. 4) is taken as an example, the semi-empirical models from Supplemental Table S1, the O$_2$ concentration gradient, and Eq. [2] can be used to calculate a range of diffusive O$_2$ fluxes into this reactive zone (again assumed to be 1 m$^3$ large and 1 m thick) for various bulk porosities and degrees of pore-water saturation (Fig. 5).

Figure 5 indicates that, for the entire range of bulk waste-rock porosities observed at Antamina (Table 1), and for all degrees of pore-water saturation, the diffusive O$_2$ supply into the reactive zone at the 40-m depth in Borehole 1 is $<5 \times 10^{-8}$ kg O$_2$ m$^{-3}$ s$^{-1}$ and thus substantially lower than the calculated O$_2$ consumption rates for this zone ($2 \times 10^{-7}$ kg O$_2$ m$^{-3}$ s$^{-1}$). Considering that the same one-dimensional approach was used for this calculation and the O$_2$ consumption rate estimation discussed above, the dimensionality of different transport scenarios (e.g., lateral vs. spherical transport through the pile's outer faces) would cancel out, leaving diffusion similarly lower than O$_2$ consumption estimated from the corresponding temperature gradient. Although the presented mass-transport estimate contains an implicit uncertainty caused by unaccounted physical heterogeneities and thermal effects on diffusive mass transport, it illustrates that diffusion will probably have a small contribution to O$_2$ supply into the reactive zones of the waste-rock pile on the bulk scale, as both boreholes contained O$_2$ concentration gradients at depth that were otherwise smaller than the example used above (Fig. 4).

Advection

The potential supply of O$_2$ into the waste-rock pile by air advection can be estimated using Darcy's law for gas flow (Massmann and Farrier, 1992). Assuming the waste rock to be homogeneous and anisotropic, and air to be an ideal, noncompressible gas of constant composition, the one-dimensional, isothermal, advective air flux,

$$J_{\text{adv}} \, (\text{kg m}^{-2} \text{s}^{-1})$$

(3)

where $K_{\text{air}}$ is the intrinsic dry air permeability of the waste rock (m$^2$), $k_{\text{air}}$ is the relative coefficient of air permeability of the partially saturated waste rock (dimensionless), $\mu_{\text{air}}$ is the dynamic viscosity of air (Pa s or kg m$^{-1}$ s$^{-1}$), and $g$ is the gravitational acceleration constant (9.81 m s$^{-2}$). For the
average waste rock at Antamina (Table 1), the relative coefficient of permeability $K_{\text{air}}$ can be estimated using the Brooks and Corey formula (Supplemental Table S2; Pantelis et al., 2002; Brooks and Corey, 1966), whereas the dynamic viscosity and density of air are fixed at $1.7 \times 10^{-5}$ kg m$^{-1}$ s$^{-1}$ and 0.75 kg m$^{-3}$, respectively, for the average conditions encountered between the surface and the 40-m depth in Borehole 1 (60 kPa, 20°C; Fig. 4).

Similar to the approach used to estimate $D_{\text{eff}}$ values for $K_{\text{air}}$, this can be predicted using physico-empirical relationships (see equations in Supplemental Table S2; Wang et al., 2015). In addition, the in situ air permeability (i.e., $k_{\text{air}}$) of the waste rock can be calculated by considering the pore-gas pressure dissipation with depth in a borehole as a natural slug test, i.e., as an alternative to a controlled injection test or laboratory analysis, which are highly challenging for coarse waste rock. The value of $K_{\text{air}}$, obtained by using the physico-empirical relationships of Supplemental Table S2 and the range of waste-rock properties at Antamina (Table 1) varies between $2 \times 10^{-9}$ and $4 \times 10^{-11}$ m$^2$. The value of $K_{\text{air}}$ calculated from the borehole pore-gas pressure data is similar and ranges between $1 \times 10^{-10}$ and $9 \times 10^{-10}$ m$^2$ (details in the Supplemental Material and Supplemental Fig. S3). Both estimates of $K_{\text{air}}$ fall within the wide range of previously reported values for waste-rock air permeability ($4 \times 10^{-13}$–$5 \times 10^{-9}$ m$^2$; Amos et al., 2009; Lefebvre et al., 2001a; Lahmira et al., 2014). Taken together, the obtained range of values for $K_{\text{air}}$, Eq. [3], and the observed pressure gradient were used to calculate a range of bulk advective air fluxes (and thus O$_2$ fluxes when assuming a constant O$_2$ content of 21% v/v in air) as a function of porosity and pore-water saturation for the same example used above: a 1-m-thick reactive zone at the 40-m depth in Borehole 1 (Fig. 6). This example not only exhibited the largest O$_2$ concentration gradient but also the largest pressure gradient: 2 kPa across 40 m (or 50 Pa m$^{-1}$; Fig. 4), significantly larger than—and anti-directional to—what can be expected from the altitude difference between the surface and this reactive zone.

Evidently, from comparing Fig. 5 and 6, the potential advective O$_2$ transport is orders of magnitude larger than the potential diffusive O$_2$ transport: Péclet numbers are >>1 until >>95% pore-water saturation, i.e., when the pore-gas phase is discontinuous (Supplemental Fig. S4). The observed significance of O$_2$ advection supports previous work showing that even small pressure gradients (<1 Pa m$^{-1}$) can cause significant viscous fluxes in porous media (Elberling et al., 1998) and that advection can be a dominant O$_2$ supply mechanism in coarse waste rock (Amos et al., 2009; Pantelis et al., 2002; Lahmira et al., 2014; Pantelis and Ritchie, 1991). At the same time, the advective O$_2$ transport appears to more strongly depend on waste-rock porosity and pore-water saturation than diffusion (e.g., diffusion and advection vary 5 and 10 orders of magnitude, respectively, as a function of saturation), which is a reflection of the fact that the effective air permeability, like $D_{\text{eff}}$, varies greatly with particle size and pore-water saturation (Supplemental Table S2).

At average pore-water saturation and porosity (Table 1), the potential advective O$_2$ transport into a 1-m-thick reactive zone at the 40-m depth in Borehole 1 (i.e., $1 \times 10^{-7}$ kg O$_2$ m$^{-3}$ s$^{-1}$; Fig. 6) is orders of magnitude larger than the diffusive O$_2$ transport (Fig. 5) and practically similar to the O$_2$ consumption rate calculated for that zone ($2 \times 10^{-7}$ kg O$_2$ m$^{-3}$ s$^{-1}$). This suggests that advection may be the limiting O$_2$ supply mechanism and ultimately controlling sulfide oxidation rates in the reactive O$_2$-depleted zones of the full-scale waste-rock pile. Considering that the highest observed pressure gradient was used for the example calculation above, advection into deeper regions of the pile, even via lateral transport through the batters, will be correspondingly lower and may similarly be controlling sulfide oxidation rates. However, Fig. 6 also implies that the oxidation of less reactive, low-sulfide waste rock may only be limited by advective O$_2$ ingress in waste rock with low permeability and a high pore-water saturation.

The important role of advection in regulating pore-gas O$_2$ concentrations is further supported by the observation that temporal variations in pore-gas O$_2$ concentrations, albeit being relatively small (<2%) in the short term, strongly correlate with fluctuations in barometric pore-gas pressure and temperature measured at adjacent depths (see example in Supplemental Fig. S5). As described previously (Ritchie, 2003), the observed fluctuations in pore-gas O$_2$ mimic pressure and temperature variations on both diurnal timescales as well as on the timescales at which weather patterns are relevant (i.e., weeks). At Antamina, the role of additional processes that may enhance advective O$_2$ influx into the waste-rock pile (e.g., wind-induced pressure gradients [Amos et al., 2009], aerodynamic dispersion, or gas composition changes [Pantelis et al., 2002]) may be the topic of future study.

**Thermal Convection**

Thus far, the diffusive and advective mass transfer of O$_2$ was considered under isothermal conditions. However, previous studies have shown that temperature gradients caused by heat release from sulfide oxidation can significantly enhance gas transport into waste-rock piles (Kuo and Ritchie, 1999; Ning and Zhang, 1997). Unfortunately, the identification and quantitative isolation of a convective effect on mass transfer is challenging due to the large degree of (nonlinear) coupling between mass- and heat-transfer processes in multiphase, unsaturated, porous media (Pantelis et al., 2002; Ritchie, 2003). For instance, temperature gradients in a waste-rock pile will simultaneously affect the density, viscosity, and heat conductivity of pore gas and pore water, the diffusivity of heat and mass (i.e., O$_2$) through pore gas and pore water, and, through the evaporation and condensation of pore water, the saturation and permeability of the waste rock. In addition, temperature increases may also accelerate biological sulfide oxidation rates by reducing activation energies (Rohwerder et al., 1998). Such complexity clearly advocates for the use of reactive transport models for the investigation of convective effects in waste-rock systems.

The advective O$_2$ transport calculated above under isothermal assumptions inherently includes a thermal component, as the pneumatic head between the surface and reactive zones in the boreholes is also affected by the coinciding temperature gradient (see Eq. [S6] in the Supplemental Material [Massmann and Farrier, 1992]). This is illustrated, e.g., by correlations between temperature gradients...
and O2 concentrations recorded in the waste-rock pile (see example in Supplemental Fig. S5). On the other hand, an advective O2 supply—equaling the O2 consumption rate—was already achieved under isothermal assumptions in the calculations above, so that the contribution of thermal air convection to O2 supply into the waste-rock pile at Antamina may be minor. In fact, the ideal gas law and equations in Supplemental Tables S1 and S2 can be used to show that the temperature gradients observed at Antamina (i.e., <34°C) will change the density, viscosity, or diffusion coefficients by <200% at most, which is small compared with the orders-of-magnitude changes induced by variations in waste-rock porosity or pore-water saturation. Further study is thus required to investigate whether the relatively moderate temperature maxima (i.e., maximum 42°C in the studied pile vs. >65°C in other waste-rock piles; Lefebvre et al., 2001a) are sufficient to trigger effective convection.

Implications for the Management of Full-Scale Waste-Rock Piles

In addition to limiting the drainage water flow, waste-rock covers may also be designed to reduce sulfide oxidation rates by lowering the O2 supply. Most effective in reducing air ingress are low-permeability and highly water saturated cover materials, but maintaining a cover at high water saturation at Antamina may be difficult (Nicholson et al., 1989; Aubertin et al., 2016), especially during the dry season. This is illustrated by the fact that the pore-water saturation of surficial waste rock in the East Dump is roughly reduced by 50% during the dry season (Supplemental Fig. S6). As a "worst-case scenario," a waste-rock cover must therefore have an air permeability that, even at half the average pore-water saturation observed at Antamina (i.e., 0.39, from Table 1), is low enough to limit the O2 supply and therefore reduce sulfide oxidation rates. Using a reversed approach to the mass transport calculations presented above but using the same O2 and pressure gradients and sulfide oxidation rates, the penetration depth of a total O2 flux (i.e., advection + diffusion) into the waste-rock pile can be estimated as a function of the waste-rock air permeability (Fig. 7). These calculations show that a cover material, at an average pore-water saturation of 0.39 during the dry season, will need to have a $K_{\text{air}}$ smaller than $1 \times 10^{-13}$ m$^2$ to restrict O2 ingress into the waste-rock pile to the top 10 m (Fig. 7). This reasonable value is in the range of commonly used cover materials in the silty-clay particle-size region (Switzer and Kosson, 2007). However, because the performance of any cover is also affected by other design factors and prevailing weather conditions (e.g., variable pore-water saturation; Aubertin et al., 2000), this should be the topic of further dedicated study.

In large-scale waste-rock piles, spatial and temporal variations in porosity and pore-water saturation will occur as a result of structural heterogeneities (e.g., compaction of traffic surfaces and vertical sorting effects from waste rock end-dumping), precipitation of secondary minerals, or the advancement of pore water infiltrating the pile. For instance, push-dumped and end-dumped waste-rock piles can have low-permeability zones (e.g., compacted traffic surfaces) with sulfide oxidation rates limited by negligible O2 diffusion and advection, as well as coarser

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Fig. 6. Calculated potential advective O2 transport (logarithmic y axis) between the surface and a 1-m-thick reactive zone at the 40-m depth in Borehole 1 for various waste-rock porosities as a function of pore-water saturation. The colored shading along each colored line indicates the variability resulting from the different semi-empirical methods used to calculate air permeability (Supplemental Table S2). The average pore-water saturation at Antamina is indicated by the dashed vertical line; the O2 consumption rate in the reactive zone at the 40-m depth deduced from the O2 and temperature depth profiles is indicated by the dashed horizontal line.
grained (basal) regions where advective air ingress may sustain higher sulfide oxidation rates. Because both diffusion and advection ultimately critically depend on particle size and pore-water saturation, the spatial distribution of particle sizes and prevailing in situ conditions in the full-scale waste-rock pile should therefore ideally be known and monitored, e.g., using pumping tests to measure air permeability or (near-)surface geophysical techniques such as ground-penetrating radar. Furthermore, the distribution of waste-rock reactivity may be at least equally as important as the physical heterogeneity of a waste-rock pile: in this study, high-sulfide waste rock induced severe \( \text{O}_2 \) depletion seemingly irrespective of waste-rock porosity and pore-water saturation, and previous work has shown that small fractions of reactive waste rock may dominate the overall drainage quality from composite piles (Vriens et al., 2019; Pedretti et al., 2017). Therefore, both the geochemical characteristics and the spatial distribution of reactive waste rock (hotspots) within the full-scale pile should be known to effectively optimize waste-rock storage and pile construction (e.g., using blending strategies; Parbhakar-Fox et al., 2018) for improved control of (long-term) drainage quality. This is particularly true for complex waste-rock piles that exhibit a high degree of physical and geochemical heterogeneity, for which even complex reactive transport models may not adequately capture the spatial distribution of reactivity and gas transport on the bulk scale.

**Summary**

Multyear experimental data from two instrumented boreholes in an operational, full-scale waste-rock pile show that localized, buried sections of reactive, high-sulfide waste rock are prone to rapid oxidation. Their weathering generates elevated temperatures and pore-gas pressures and compositions significantly different from atmospheric conditions. The pore-gas distribution in the bulk waste-rock pile was more strongly related to waste-rock reactivity than to physical heterogeneity (i.e., particle-size distribution and moisture content). Mass-transport estimates show that the observed \( \text{O}_2 \) and pressure gradients can induce significant \( \text{O}_2 \) ingress tens of meters into the waste-rock pile, whereby bulk \( \text{O}_2 \) transport via advection largely outweighs that via diffusion and likely ultimately controls sulfide oxidation rates. The mass-transport estimates further show that a reduction of the advective \( \text{O}_2 \) influx, or a more important role for diffusive \( \text{O}_2 \) transport, may only be expected for poorly permeable waste rock with low porosity and a high pore-water saturation. In summary, this study demonstrates how site-specific information on the spatial distribution of waste-rock reactivity and pore-gas composition can be applied in fully uncoupled gas-transport estimates to inform waste management decisions aimed at reducing the long-term environmental impacts of waste-rock weathering.

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**Conflict of Interest**

The authors declare no conflicts of interest.

**References**


Johnson, D.B., and K.B. Hallberg. 2003. The microbiology of acidic mine wa-


Blackmore, S., L. Smith, K.U. Mayer, and R.D. Beckie. 2014. Comparison of

Bennett, J.W., M.J. Comarmond, and J.J. Jeffery. 2000. Comparison of


Kuo, E.Y., and A.I.M. Ritchie. 1999. The impact of convection on the overall


Lahmira, B., R. Lefebvre, M. Aubertin, and B. Bussière. 2011. Oxygen consump-


Mbonimpa, M., M. Aubertin, and B. Bussière. 2011. Numerical modeling of con-


Moldrup, P., T. Olesen, J. Gamst, P. Schjønning, T. Yamaguchi, and D.E.


Ning, L., and Y. Zhang. 1997. Onset of thermally induced gas con-

Kuo, E.Y., and A.I.M. Ritchie. 1999. The impact of convection on the overall

Kuo, E.Y., and A.I.M. Ritchie. 1999. The impact of convection on the overall

Kuo, E.Y., and A.I.M. Ritchie. 1999. The impact of convection on the overall

Kuo, E.Y., and A.I.M. Ritchie. 1999. The impact of convection on the overall

Kuo, E.Y., and A.I.M. Ritchie. 1999. The impact of convection on the overall

Kuo, E.Y., and A.I.M. Ritchie. 1999. The impact of convection on the overall

Kuo, E.Y., and A.I.M. Ritchie. 1999. The impact of convection on the overall

Kuo, E.Y., and A.I.M. Ritchie. 1999. The impact of convection on the overall


