Spatial and Temporal Variations of O_2 and CO_2 Pore Gas Concentrations in an Experimental Waste Rock Pile at the Antamina Mine, Peru

O. Singurindy[1,2], M.E. Lorca[1,*], H.E. Peterson[1], T. Hirsche[1], M. Javadi[1], S. R. Blackmore[1],C. Aranda[3],K.U. Mayer[1], R.D. Beckie[1], and L. Smith[1]

[1]Earth and Ocean Sciences, University of British Columbia, 6339 Stores Road, Vancouver, BC, V6T 1Z4, Canada, mlorca@eos.ubc.ca, hpeterson@eos.ubc.ca, dthirsch@interchange.ubc.ca, mjavadi@eos.ubc.ca,sblackmore@eos.ubc.ca,umayer@eos.ubc.ca, rbeckie@eos.ubc.ca, lsmith@eos.ubc.ca
[2]now at:Tripol Canada Inc., 999 Canada Place, Suite #404, Vancouver, BC, V6C 3E2, Canada, olgasing22@yahoo.com
[3]Compañía Minera Antamina, Av. El Derby 055, Torre 1, Oficina 801, Santiago de Surco, Lima L-33, Peru, caranda@antamina.com

Abstract
An automated gas analysis system was used to measure the spatial and temporal distribution of O_2 and CO_2in a 10 m high experimental waste rock pile at the Antamina Mine, Peru.The analysis system was connected to 62 observations ports and gas measurements were collected daily over a time period of one year. The results reveal that oxygen becomes locally depleted to less than 50% of atmospheric values, while CO_2 becomes locally enriched to values exceeding 2%. The highest degree of O_2-depletion was observed near the front of the pile, which contains the most reactive material and near the top of the pile, which is composed of the most fine-grained and compacted waste rock. Temporal analyses demonstrate strong correlations between pore gas composition, seasonal variations in precipitation, and internal moisture contents. The results suggest that oxygen-limited conditions may develop in the full scale piles at Antamina.

Key Words:Waste Rock; Sulfide Oxidation; Pore Gas Composition; Oxygen, Carbon Dioxide, Seasonal Fluctuations

Introduction
The oxidation of sulfideminerals in mine waste leads to the generation of acidity, the liberation of metals, and the release of sulfate, negatively affecting the composition of drainage water:

$$FeS_2 + 3.5O_2 + H_2O \rightarrow 2H^+ + Fe^{2+} + 2SO_4^{2-} \qquad (1)$$

Oxygen derived from the atmosphere is required to sustain the oxidation reactions and its availability provides a major control on the progress and extent of sulfide mineral weathering. If carbonate minerals are abundant, the dissolution of these phases effectively neutralizes acidity, leading to a release of CO_2, which tends to partition into the gas phase:

$$2H^+ + CaCO_3 \rightarrow CO_2 + H_2O + Ca^{2+} \qquad (2)$$

These processes lead to characteristic changes in pore gas composition within mine waste deposits, resulting in a decline of O_2 relative to atmospheric concentrations, combined with an increase in CO_2. Monitoring the gas composition in space and time may reveal zones of enhanced reactivity and provide important information on the development of oxygen-limited conditions.

Possible transport mechanisms to supply O_2 and release CO_2include diffusion, advection, and convection through the unsaturated mine waste material (Pantelis et al., 2002, Wels et al., 2003). Diffusion is caused by gas concentration gradients, while advection may be induced by atmospheric pumping (Wels et al., 2003), wind effects (Amos et al., 2009), or gas production and consumption (Molins and Mayer, 2007). Convection is caused by the exothermic nature of sulfide mineral oxidation (Lefebvre et al., 2001, Pantelis et al., 2002), which may result in substantial internal temperature increases and enhanced O_2 supply to waste rock due to the 'chimney effect' (Lefebvre et al., 2001, Wels et al., 2003). The analysis of pore gas composition, together with temperature, may therefore provide important clues on the contribution of the various transport mechanisms and the role of internal heating.

In addition, it is well known that gas transport in mine waste is strongly affected by increases in moisture content, which reduce the gas-filled pore space and connectivity of gas migration pathways, inhibiting O_2 ingress and CO_2 loss to the atmosphere (e.g. Shaw et al., 2003). As a result, the grain size distribution of waste rockand seasonal variations in precipitation patterns mayhave a considerable influence on gas mobility and sulfide mineral weathering. The measurement of moisture contents is beneficial to provide a more complete picture of gas migration, O_2 consumption, and CO_2 generation within rock piles.

Gas composition has been monitored previously in full scale waste rock piles (Harries and Ritchie, 1985, Garvie et al., 1997, Smolensky et al., 1999, Lefebvre et al., 2001, Shaw et al., 2002, Birkham et al., 2003, Milczarek et al., 2009).In these cases, multilevel monitoring wells were installed in boreholes, providing depth-discrete information on pore gas composition and related parameters. At the Diavik diamond mine, the construction of experimental waste rock piles facilitated the emplacement of a multilevel monitoring system with a more comprehensive spatial coverage. In addition, an automated gas measurementsystem was used to provide temporal information on the distribution of internal gas composition and pressure (Amos et al., 2009). Although O_2 and CO_2concentrationsremained near atmospheric levels in this waste rock pile due to low sulfide mineral weathering rates and a high degree of gas mobility, detailed information was obtained on wind-inducedgas migration through the pile(Amos et al., 2009).

More recently, a comprehensive research project including five experimental waste rock piles of different rock composition and variable sulfide and carbonate contents was initiated at the Antamina mine, Ancash, Peru (see Bay et al., 2009 and Hirsche et al., 2012 for a project overview). Antamina is one of the largest polymetallic skarn deposits in the world, producing a substantial volume of waste rock, which is placed in piles up to 300 m high. Two distinct seasons occur at the site: a rainy season, which lasts from October to April, and a dry season between May and August.Total yearly rainfall at the site averages approximately 1 200 mm/yr. Both size of the waste rock piles and climate are suspected to have an effect of O_2-ingress of sulfide weathering.

In this paper we present spatial and temporal distributions of O_2, CO_2, temperature, and moisture content within one of the experimental waste rock piles at the Antamina mine. The study focuses on Pile 2, composed of intrusive material that is relatively fine grained, has substantial sulfide content, and exhibits a high degree of reactivity(Peterson et al., 2012). We presentO_2 and CO_2distributionscontinuously monitored over a time period of one year using an automated gas analysis system similar to the one used by Amos et al. (2009).The key questions that we want to address are: a) Forthe material investigated, is O_2 depletion and CO_2 accumulation observed?andb) Dothe pronounced wet and dry seasons have an effect on the temporal evolution of pore gas composition? The investigationof gas chemistry contributes to a broader study designed to provide information on the geochemistry and hydrogeology of the waste rock dumps at Antamina mine (Bay et al., 2009, Hirsche et al., 2012).

Methods

Pile 2 completion details

The large-scale experimental pile (36 m (*l*) x 36 m (*w*) x 10 m (*h*)) was constructed by end dumping. The pile contains approximately 24000 tonnes of waste rock,has a volume of about 12000 m^3 and is composed of Class A intrusive material (see Bay et al. (2009), and Hirsche et al. (2012)for descriptions of Antamina's waste rock classification system). The pile was built in four phases, including a protective layer across the bottom of the pile and three end-dumped tipping phases. The elemental composition and grain size distribution of the rock varies significantly among the tipping phasesand isdocumented in Peterson et al. (2012).Basic information on NP/AP, sulfur content and carbonate content are shown in Table 1.Materials emplaced during tipping phases 2and3are significantly finer grained than waste rock from tipping phase 1.

Table 1: Select results for Pile 2 materials. NP/AP refers to the neutralizing potential – acid producing potential ratio. S refers to mass percent of sulphur and C is the mass percent of carbon.

Tipping Phase	**NP/AP**	**S (%)**	**C (%)**
Protective layer	1.49	0.62	0.17
Tipping phase 1a	1.90	0.20	0.15
Tipping phase 1b	0.06	4.26	0.09
Tipping phase 2	0.40	0.64	0.08
Tipping phase 3	0.14	1.56	0.05

The phased construction allowed installation of six instrumentation lines above the protective layer and between the tipping phases. We focus here on four instrumentation lines (1, 2, 4 and 6) located in the center of the pile (Figure 1).The instruments installed in the lines allow for in situ measurement of temperature, volumetric water content, and electrical conductivity of the matrix pore water (EC), as well as pore water and gas sampling (Peterson et al., 2012).The gas sampling ports are connected to an automated gas analysis systeminside an instrumentation hut located adjacent to the pile.

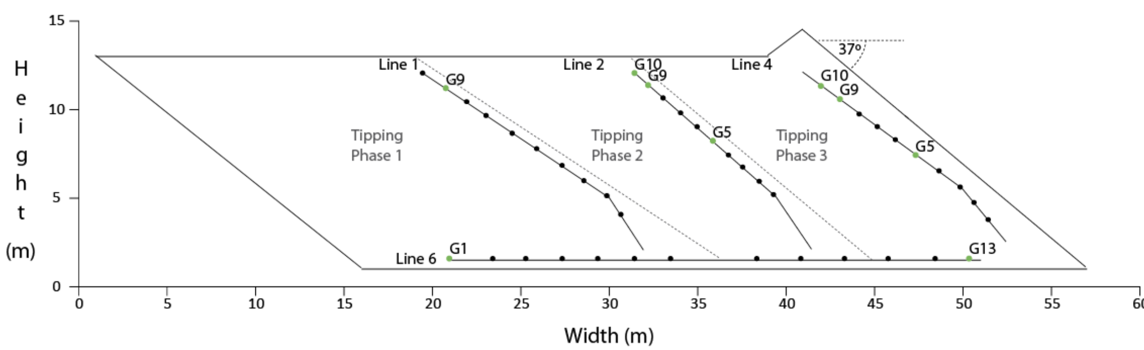

Figure 1: Location of end-dumped tipping phases, instrumentation lines, and select gas sampling portsin Pile 2.

Automated gas analysis system

A simplified schematic of the automated gas analysis system is shown in Figure 2.The system consists of an analysis module and four sampling modules. In total, the system is able to analyze gas pressures, O_2 and CO_2 composition from 64 monitoring ports (16 per sampling module). An array of solenoids is used to connect thegas ports in the pile (Figure 1) to either a pressure transducer or a peristaltic pump which routes the gas to CO_2 and O_2 analyzers. This set-up allows monitoring anyone of the ports in the pile at any instant in time for either differential gas pressure or gas concentrations. Differential pressure between a selected port and ambient air is measured under no-flow conditions, cycling continuously between the ports (about four times per hour). The pressure measurements are interrupted once per day for CO_2 and

O_2analysis from each port, after purging sufficiently long to ensure that representative samples are collected for analysis by the instruments.

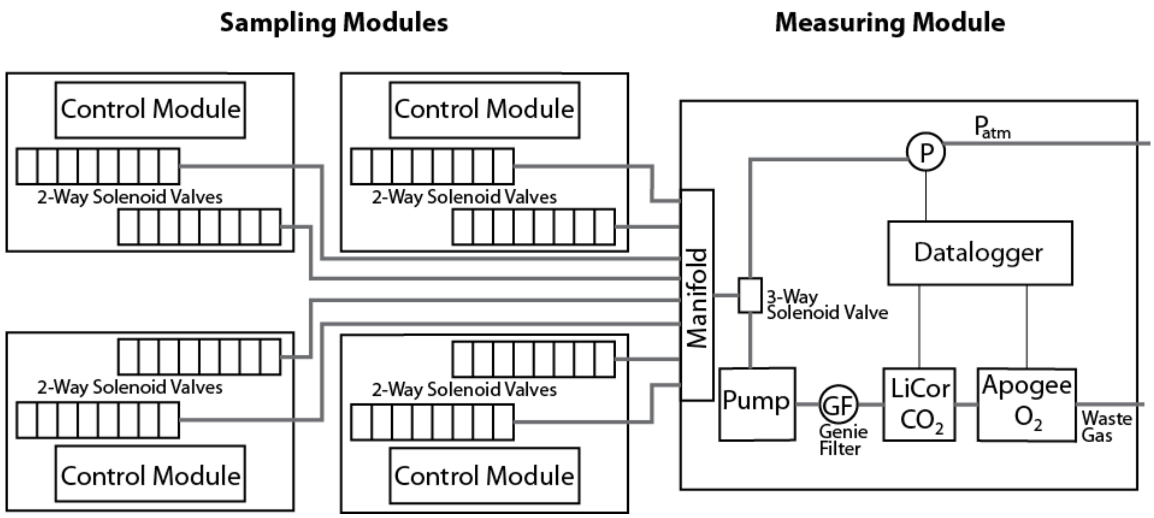

Figure 2: Schematic diagram for the automated measuring system.

Carbon dioxide concentrations are measured with an LI-820 (Li-Cor Biosciences) infra-red gas analyzer (IRGA), and oxygen content is measured using a SO-200 galvanic sensor (Apogee Instruments) with flow-through head. Both instruments and the solenoid arrays are controlled by a CampbellScientific datalogger (CR1000).The CO_2analyzer can measure in the range of 0 to 20,000 ppm (2%). The O_2 analyzer has a wide range of measures covering from 0 to 100% of oxygen.

Twoof the 64 ports are dedicated to gases of known concentrationswhich are alsosampled dailyto ensure that the instrumentation is working correctly and to facilitate calibration of gas composition measurements. These ports sample atmospheric air (380 ppm CO_2, 20.95% O_2) and a fixed-composition calibration gas (1.5% CO_2, 98.5% N_2). During the measurement period of one year, the observations at these two ports remained stable, which demonstrates the reliability of the analyzers.

Measurement of moisture content and internal temperature

A total of 22 ECHO-TE probes (Decagon Devices Inc.)were installed along the six instrumentation lines (Figure 1). The TE probes measure moisture content, electrical conductivity and temperature. Additional internal temperature measurements are obtained with 10 thermistors (RST Instruments), located at locations where no TE probes were installed.TE probe and thermistor measurements are also automated and collectedat 30-minute intervals using a Campbell Scientific data logger (CR 1000). Additional detail about sensors installation and measurements can be found in Bay et al. (2009).

Results and Discussions

Spatial distribution

Figure 3 shows spatial variations for all the parameters in April 2010, i.e. at the beginning of the measurement period, and approaching the end of the wet season. Regions of high oxygen depletion and CO_2 accumulation are observed near the front and the top of the pile. In end-dumped waste rock piles, the top of the pile contains material with the smallest grain size (Smith and Beckie, 2003), which can also be compacted due to the presence of a traffic surface. These characteristics lead to reductionsin gas diffusivity and permeability, inhibiting O_2 ingress and causing CO_2 accumulation. The highest degree of

O_2 depletion is found near the front of the test pile, which contains the most reactive and fine grained material.

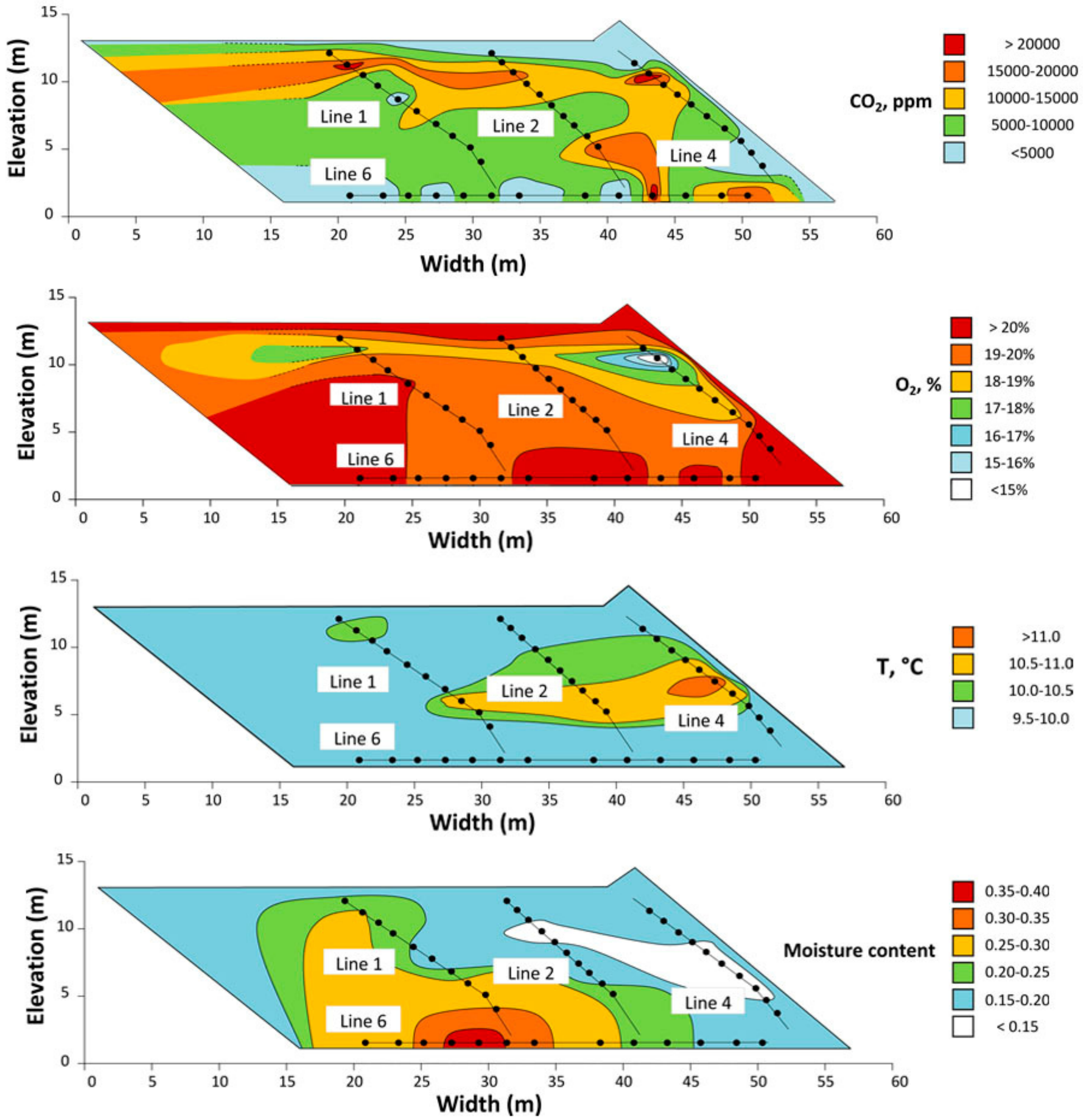

Figure 3: Contour plots for the experimental pile in April 2010.

Regions with the most reactive material are also characterized by the most significant temperature increases. Overall, internal temperatures are elevated relative to average yearly temperatures and average daily surface temperatures in the month of April, despite the modest size of the pile. Material heterogeneities may be responsible for hot spots within the waste rock pile, as the one observed near the front of the pile.

Moisture content is highest near the bottom of the pile(Figure 3) and a correlation to O_2 depletion and CO_2 accumulation is not apparent. However, it must be emphasized that moisture content without knowledge of the porosity distribution is ineffective in predicting gas diffusivities and air permeability. Although lower moisture contents were measured near the top of the pile, it is conceivable that decreased porosities in the fine grained and compacted material leads to higherpore water saturations, providing a potential explanation for the observed gas compositions. The coarse grained material, located at the bottom layer, is expectedto have near to atmospheric values for CO_2 and O_2 composition. In general this is observed within the experimental pile, but the area with higher moisture content in this region of the pile also has lower than atmospheric O_2 pore gas composition.

Temporal variations

O_2 and CO_2 concentrations, temperatures and moisture contentsare shown in Figure 4 at selected monitoring points for a time period of one year from April 2010 to April 2011 (locations are highlighted in Figure 1). A strong seasonal effect on pore gas concentrations is observed, which can be correlated to variations in precipitation intensity (Figure 4). The measurement period begins at the end of the 2009/2010 wet season and O_2 concentrations increase throughout the pile until October 2010. During the same time period, CO_2 concentrations decline substantially. This period corresponds to the dry season, when drain-down of the pile occurs as evidenced by the outflow hydrograph (see Peterson et al., 2012, Javadi et al., 2012) and declining internal moisture contents (Figure 4).

With the onset of the 2010/2011 wet season, CO_2 accumulation and O_2 depletion is occurring as the waste rock pile wets up. In addition to the feedback with seasonal precipitation patterns, several short-term responses to significant precipitation events can be identified clearly (Figure 4). Observed moisture contents at different depths reveal the advancement of a wetting front through the pile (Figure 4). Monitoring locations closest to the surface of the pile, represented by Line 1 Gas Port 9(L1 G9), Line 2 Gas Port 9 (L2 G9) and Line 4 Gas Port 5 (L4 G5) increased significantly in moisture content by the end of October. The wetting front reached the center of the pile (L2 G5) by mid-December. Gas composition is also observed to vary at a later time in the lower areas of the experimental pile. This suggests that moisture content within the waste rock pile might be responsible for "partial sealing" the gas migration pathways and inhibiting transport of O_2 and CO_2 through the waste rock.

Temperatures within the waste rock pile are variable near the surface (L2 G10, L4 G10 and L4 G5), and are closely correlated to atmospheric temperature variations measured at thenearby Yanacancha weather station (Figure 4).In contrast, monitoring points located inside the pile (L2 G5, L6 G1 and L6 G13) show a more stable trend. L6 G1, located at the bottom and near the back of the pile shows the most constant temperature over the measurement period. Figure 4 also reveals that temperatures decrease inside the pile during the wet season, in particular near the surface of the pile. These results suggest that infiltrating rain water has the ability to "cool down" the pile.

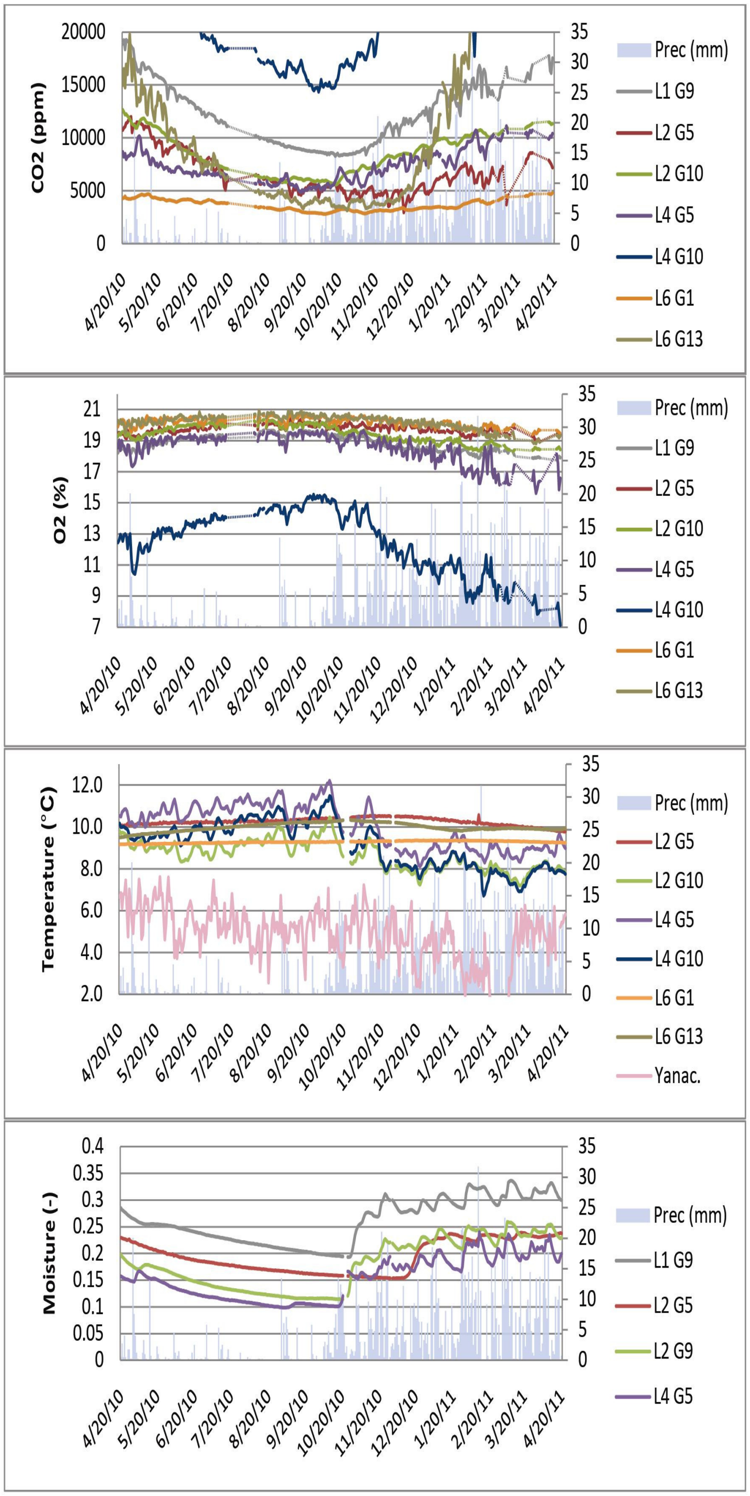

Figure 4: CO_2, O_2, temperature and moisture content variations over time at selected monitoring locations(Location of measuring points within the pile are shown in Figure 1. Precipitation and surface temperature data are from the Yanacancha weather station. Top of pile: L1 G9, L2 G9 and L2 G10; front of pile: L4 G10, L4 G9 and L4 G5; interior of pile: L2 G5; bottom of pile: L6 G1and L6 G13)

Functionality of the system

Overall, the gas analyzing system proved reliable and collected data on a daily basis with limited maintenance. Between July 20th and August 9th the gas sampling line became blocked due to a mechanical obstruction and gas composition data could not be collected. Towards the end of the measurement period, stable gas compositions could not be achieved during short time intervals. This was attributed to the ingress of moisture into the gas sampling modules following intense precipitation events in February 2012 (Figure 4). The gas analyzers are protected by a genie filter that removes moisture from the gas stream; however, the sampling modules are directly connected to the monitoring ports inside the pile to minimize friction losses and vacuum upstream of the peristaltic pump. The CO_2 analyzer was chosen on purpose to provide a good resolution between atmospheric concentrations and 2% CO_2. However, given the significant accumulation of CO_2 in sections of the experimental pile, several measurements were out of range (i.e. > 2%) and the maximum CO_2 concentration in the pile could not be determined. In the future, we will consider an additional analyzer to cover the full range of CO_2-concentrations.

Implication forsulfide mineral oxidation in full scale piles

Results show that substantial oxygen depletion occurs at the scale of the experimental test pile. Concentrations of O_2 vary from atmospheric composition (20.95%) down to one third of atmospheric oxygen content (7%). CO_2 concentrations range from atmospheric concentrations (380ppm) to greater than 20000ppm (Table 2).

Table 2: Minimum and maximum of measured the parameters (all monitoring points).

	CO_2 (ppm)	O_2 %	T (°C)	Moisture (-)
Min	380	7	6.6	0.094
Max	>20000	20.95	13.3	0.372

Zones of greatest oxygen depletion were identified near the top of the pile, where truck traffic during pile construction led to compaction of the surface of the waste rock, and also in regions where the most reactive and fine grained materialswere placed.Based on these results, it may be hypothesized that complete O_2depletion occurs in thefull-scale piles at Antamina. Full-scale piles are much larger, will have more compacted and thicker traffic surfaces, and may contain larger volumes of fine grained reactive materials. On the other hand, if coarse grained and fine grained waste rock alternate, it is possible that the coarse grained materials act as preferential gas migration pathways, bringing oxygen deep into the piles. Although the size of the experimental piles is very modest in comparison to the full scale piles at Antamina, there is evidence that the exothermal nature of sulfide mineral oxidation has led to a temperature increase of approximately 3-4°C in average. This finding indicates that temperature increases may be more substantial in the full scale piles due to the difference in spatial scale, large piles having relatively lower heat loss rates compared to the experimental waste rock piles investigated here.

Conclusions and Outlook

We measured gas composition (O_2 and CO_2), temperature and moisture content within an experimental waste rock pile usingan automated gas monitoring system. Analysis over a one-year time period showed a consistent inverse relationship between O_2 and CO_2 concentrations and a clear correlation between oxygen depletion and increased waste rock moisture contents during the wet season. Together with temperature measurements, O_2 and CO_2 concentrations proved useful in identifying reaction hotspots. Waste rock moisture content data proved most useful to explain seasonal variations in gas composition within the pile and to trace the advancement of infiltration fronts during the wet season. We will continue gas composition measurements in Pile 2 and initiate analysis of gas pressure data. Recently, we have installed similar automated gas analysis systems at two additional waste rock piles containing different waste rock materials. These experiments will help to identify the role of material composition and grain size on gas composition and migration patterns.

Acknowledgements

Funding for this project has been provided by the Natural Sciences and Engineering Research Council of Canada (NSERC), Teck ART, and the Compañía Minera Antamina. We would like to express special thanks to Edsael Sanchez and Janeth Vizconde for their help during system installation and on-site maintenance at Antamina.

References

AmosRT, Blowes DW, Smith L, and Sego, DC (2009). Measurement of wind-induced pressure gradients in a waste rock pile. Vadose Zone Journal, 8:953-962.

Birkham TK, Hendry MJ, Wassenaar LI, Mendoza CA, and Lee ES (2003). Characterizing geochemical reactions in unsaturated mine waste-rock piles using gaseous O_2, CO_2, $^{12}CO_2$, and $^{13}CO_2$, Environmental Science & Technology, 37:496-501.

Bay D, Peterson HE, Singurindy O, Aranda C, Dockrey J, Sifuentes Vargas F, Mayer KU, Smith L, Klein B.and BeckieRD (2009). Assesment of neutral pH drainage from three experimental waste rock piles at the Antamina Mine, Peru. In Proceedings of the 8th International Conference on Acid Rock Drainage (ICARD), Skellefteå, Sweden.

Garvie AM, Bennett JW, and Ritchie AIM (1997). Quantifying the spatial dependence of the sulfide oxidation rate in a waste rock dump at Mt Lyell, Tasmania, In: Proceedings of 4th International Conference on Acid Rock drainage (ICARD), Vancouver, BC, May 31 – June 6 1997.

Harries JR, and Ritchie AIM (1985). Pore gas-composition in waste rock dumps undergoing pyritic oxidation, Soil Science, 140:143-152.

Hirsche T, Beckie R, Conlan M, Blackmore S, Smith L, Klein B, Mayer KU, Aranda C, Rojas LA and JamancaR (2012). Stacked field cells as a means for studying metal attenuation by waste rock mixing at the Antamina Mine in Peru. In Proceedings of the 9th International Conference on Acid Rock Drainage (ICARD), Ottawa, Ontario, Canada.

Javadi M, Peterson H, Blackmore S, Mayer KU, Beckie RD, and Smith L (2012). Evaluating preferential flow in an experimental waste rock pile using unsaturated flow and solute transport modeling. In,Proceedings of the 9th International Conference on Acid Rock Drainage (ICARD), Ottawa, Ontario, Canada.

Lefebvre R, Hockley D, Smolensky J, and Gelinas P (2001) Multiphase transfer processes in waste rock piles producing acid mine drainage 1: Conceptual model and system characterization. Journal of Contaminant Hydrology, 52:137-164.

Milczarek M, Hammermeister D, Buchanan D, Vorwaller B, and Conner D (2009). In-situ monitoring of a closed waste rock facility. In Proceedings of the 8th International Conference on Acid Rock Drainage (ICARD), Skellefteå, Sweden.

Molins S,and Mayer, KU (2007). Coupling between geochemical reactions and multicomponent gas diffusion and advection – A reactive transport modeling study, Water Resources Research, 43, W05435, doi:10.1029/2006WR005206

Pantelis G, Ritchie AIM, and Stepanyants YA (2002) A conceptual model for the description of oxidation and transport processes in sulphidic waste rock dumps. Applied Mathematical Modelling, 26:751-770.

Peterson HE, Beckie RD, Harrison B, Mayer KU, and SmithL (2012). Rapid Seasonal Transition from Neutral to Acidic Drainage in a Waste Rock Test Pile at the Antamina Mine, Peru. In Proceedings of the 9th International Conference on Acid Rock Drainage (ICARD), Ottawa, Ontario, Canada.

Shaw S, Wels C, Robertson A, and Lorinczi G (2002). Physical and Geochemical Characterization of Mine Rock Piles at the Questa mine, New Mexico. In Tailings and Mine Waste 02, Proceedings of the Ninth International Conference on Tailings amd Mine Waste, Fort Collins, Colorado, USA, 27-30 January 2002, 447-458.

Smith L,and Beckie RD (2003). Hydrological and geochemical transport processes in mine waste rock. In Environmental Aspects of Mine Wastes. Mineralogical Association of Canada.

Smolensky J, Hockley D, Lefebvre R, and Paul M (1999). Oxygen transport in the Nordhalde of the Ronneburg Mining District, Germany. In: Sudbury 99 – Mining and the Environment II, Sudbury, ON, Sept 13-15, 1999.

Wels C, Lefebvre R, and Robertson AM (2003). An overview of prediction and control of air flow in acid generating waste rock dumps,In Proceedings of the 6th International Conference on Acid Rock Drainage (ICARD), Cairns, Queensland, Australia.