Stacked Field Cells as a Means for Studying Metal Attenuation by Waste Rock Mixing at the Antamina Mine in Peru

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Abstract
This work focuses on the use of a novel stacked field cell technique to study the geochemical attenuation of molybdenum in leachate from waste rock at the Antamina mine in Peru. Two stacked (double barrel) field cells were installed at the Antamina site to explore the geochemical effects waste rock mixing: one containing Mo-bearing intrusive rock on top of Pb-bearing black marble, and the other containing Pb-bearing black marble on top of Mo-bearing intrusive rock. Single field cells of the same material types were also studied for comparison. Results indicated that contact with Pb-bearing marble waste rock considerably reduced Mo concentrations in leachate, likely due to wulfenite ($PbMoO_4$) precipitation. Mo-attenuation was only observed when Mo-rich leachate flowed through Pb-bearing black marble, and not when the leachate from the Pb-bearing black marble flowed into Mo-bearing intrusive rock. This study provides insight into the use of layering to attenuate metals in leachate before it drains from waste rock dumps. Strategic waste rock layering could be used to attenuate Mo in waste rock dumps at other mines that exhibit neutral drainage.

Key words: Neutral Mine Drainage, Molybdenum, Aqueous Geochemistry, Stacked Field Cells, Attenuation, Wulfenite.

Introduction
Environmental ore deposit models, where knowledge of ore body geology and mineralogy play a role in planning mine waste disposal, represent a means of predicting and mitigating metal leaching at mine sites (Kwong 2003). A possible application of environmental ore deposit models is to mix different types of waste rock to create favourable geochemical conditions. Previous research on waste rock mixing has included studying the effects of blending carbonates with acid generating waste rock at the Grasberg Mine in Indonesia (e.g. Andrina *et al*. 2006; Rusdinar 2006). Research at the Grasberg Mine was carried out using an instrumented waste rock pile, where distinct waste rock blending techniques were applied to different sections of the pile (Andrina *et al.* 2003). The geochemical effects of mixing distinct waste rock types in a neutral mine drainage is also being explored in experimental waste rock piles at the Antamina mine in Ancash, Peru (Blackmore *et al.* 2012). This paper focuses on the use of stacked double barrel field cells as a lower cost alternative for studying the attenuation of metals of concern through waste rock mixing.

Molybdenum is a metal of concern in some neutral mine drainage (NMD) systems, including at the Antamina Mine (Golder Associates 2010). The focus of this paper is to evaluate whether reactions caused by mixing different types of waste rock could attenuate Mo concentrations in leachate from waste rock dumps at the mine site. Molybdenum attenuation is investigated using stacked field cells that are designed such that the leachate from the waste rock in the top cell flows into the lower cell, which contains a distinct rock type.

Antamina site

Located approximately 270 km northeast of Lima, at an average elevation of 4300 m above sea level, the Antamina mine is one of the world´s ten largest mines in terms of production volume (Antamina 2011). Inaugurated in 2001, Antamina produces copper and zinc, along with smaller quantities of molybdenum and lead, from a skarn deposit formed by a series of quartz monzonite intrusions into carbonate country rock (Redwood 1999; Love *et al.* 2004). The mine currently mills on average 104,000 tonnes of ore and about 340,000 tonnes of waste rock daily, and is expected to close in 2029 (Klohn Crippen Berger Ltd, 2010). Metal leaching from the mine's waste rock dumps is of concern given the dumps´ location at the top of the watershed and proximity to permeable karst features (Evans *et al.* 2005). Antamina receives ~1200 mm precipitation per year, most of which falls as rain during the region´s six or seven month wet season. Very little precipitation occurs between May and September. Mean annual temperature at the mine site ranges between 5.4 and 8.5 °C (Klohn Crippen Berger Ltd, 2010).

Waste rock at Antamina is divided into three categories based on its degree of visible oxidation and its sulfide, zinc, and arsenic contents (Table 1). Reactive (class A) and slightly reactive (class B) waste rock is placed in the East dump, while the least-reactive rock (class C) is placed in the Tucush waste rock dump or used for construction of the tailings dam and other structures at the mine. Some class B rock has also been placed in the Tucush dump. Waste rock is categorized as reactive or slightly reactive if it exceeds the limits listed in Table 1 for one or more of the four criteria.

Table 1: Antamina waste rock classification criteria as of 2010. Waste rock is classified in the more reactive class if one or more of the criteria are met. From Golder Associates 2010.

Class	Reactivity	Description	Zn (mg/kg)	As (mg/kg)	Visual Sulphide (%)
A	Reactive	Endoskarn, exoskarn, and intrusive rocks. Also hornfels, marble, or limestone with high Zn, As, or sulfide.	>1500	>400	>3
B	Slightly reactive	Hornfels, marble and limestone with moderate zinc	700-1500	<400	>3
C	Non-reactive	Hornfels, marble and limestone with low Zn, As, and sulfides	<700	<400	<3

Study background

Since 2006 the University of British Columbia (UBC) has been working collaboratively with NSERC, Antamina and Teck ART on a multi-scale study of the hydrology and geochemistry of waste rock at the Antamina mine site. The study includes five 36 m by 36 by 10 m tall experimental waste rock piles (Bay *et al.* 2009). Each of the five piles is composed of a different waste rock type, or combination of waste rock types. The leaching behavior of smaller-scale samples of the individual material types placed in each pile is also being examined at the mine site using barrel-sized field cells. The UBC research team has also established a cover study, which will investigate several options for limiting metal loadings by reducing water infiltration into waste rock material.

This study of Mo attenuation through waste rock mixing was motivated by observations from two distinct experiments. Results from single-barrel field cells show that some waste rock types from the mine produce leachate with molybdenum concentrations of over 30 mg/L (Golder Associates 2010. These concentrations are more than 100 times higher than the CCME Mo guideline for the protection of aquatic life of 0.073 mg/L (CCME 2007). A laboratory study by Conlan *et al.* (2011) has shown that the addition of lead (Pb) to Mo-rich water samples can reduce Mo concentrations in water through the precipitation of wulfenite ($PbMoO_4$). Some waste rock at Antamina contains significant quantities of Pb-minerals, though Pb and Mo do not occur in the same rock type. Pb and Mo-bearing rocks are co-mingled in the East Dump at Antamina, so it is possible that wulfenite precipitation may affect Mo concentrations. The aim of this research is to determine if Mo attenuation through wulfenite precipitation as identified by Conlan *et al.* (2011) could act as a sink for Mo under field conditions in a NMD setting.

Methods

The field cells at Antamina consist of 205 L plastic drums filled with coned and quartered waste rock material that was passed through a 10 cm sieve (Figure 1). The plastic drums are open at the top allowing them to collect natural precipitation, and are fitted with a sloping bottom to direct basal drainage to a leachate sample collection system (Aranda *et al.* 2009). The sloping bottom is protected by a 10 cm thick layer of #60 mesh silica sand covered by a piece of Geotextile. Refer to Aranda *et al.* (2009) for a more detailed description of the field cell installation procedure.

Leachate from field cells is sampled regularly throughout the wet season, provided sufficient volume is produced over the sampling interval for laboratory analysis. The volume of leachate produced, and the conductivity and pH of each sample is measured in the field. Water samples are collected in plastic bottles and taken to the laboratory at Antamina for filtration through 0.45 µm filter membrane. Trace metals and cation samples are acidified with nitric acid to below pH 3 for preservation. Samples are then stored below $4^{o}C$ and shipped to ALS laboratories in Lima for chemical analysis.

Figure 1: Some of the UBC single field cells installed at Antamina. Each barrel is 90 cm tall with a diameter of 48 cm. The buckets placed in front of the barrels collect leachate.

Stacked field cells, where one rock type is placed above another, are used to study of metal attenuation caused by mixing. The stacked field cells were constructed by placing a second barrel on top of a conventional barrel field cell used at the site to form a single, 1.8 m tall field cell. A wooden frame was constructed to hold the field cells in place and to prevent toppling (Figure 2). Distinct waste rock types were placed in the top and bottom half of each field cell, such that at the midpoint of the cell the two rock types were in direct contact with each other, as would occur in the experimental piles or full scale waste rock dumps.

Figure 2: The seven stacked field cells installed at Antamina. Each stacked field cell contains 2 to 3 different material types arranged to approximate geochemical conditions in UBC's experimental piles at Antamina, or the dumps themselves. The grey PVC tubes visible on the sides of the barrels channel drainage from the lysimeters.

Drainage collected from the bottom of a stacked field cell flows through both rock types contained in the field cell. In each field cell, samples representative of leachate from the material in the top half of the stacked cell were collected using three mini-lysimeters installed above the contact between the two material types (Figure 3). The mini-lysimeters were made by cutting the bottoms out of 1 L polyethylene sample bottles and covered a total of about 6.5% of the surface area of the field cells. All three mini-lysimeters drained to the same sample bucket. Holes were drilled into the sides of the plastic field cell barrels prior to the installation of the waste rock material to allow the mini-lysimeter drainage hoses to pass through the sides of the plastic barrels. These holes were sealed with silicone after the installation of the mini-lysimeters.

Figure 3: The mini-lysimeters used to sample leachate from the top material (material 1) in the stacked field cells prior to mixing with the bottom material (material 2). The mini-lysimeters are labeled 1, 2 and 3 in the diagram. L in the diagram indicates the bucket that collects water from the lysimeters, whereas B represents the bucket that collects water from the base of the field cell, where the geochemical effects of mixing will be more apparent.

The waste rock used in this study was selected based on three criteria: propensity to leach metals of interest, the hypothesized ability to attenuate metals of interest, and previous use in UBC's experimental waste rock piles. This paper deals with results from field cells containing two distinct materials: Pb-bearing black marble from pile 1, UBC-1-3A; Mo-bearing intrusive from pile 2, UBC-2-0A.The single field cells, each with one rock type, containing Pb-bearing black marble and Mo-bearing intrusive rock were installed in August 2006 and October 2007, respectively. Additional samples from this waste rock were stored at ambient temperatures in plastic bags under a roof or tarps until they were placed in the stacked field cells UBC-Mo-T1 and UBC-Mo-T2 (Table 2). Approximately 350 Kg of a distinct rock type was placed in each half of the stacked cell.

Although the single field cells UBC-1-3A and UBC-2-0A were installed shortly after their contents had been sampled, the same materials were not installed in the stacked field cells until June 2009, meaning that they had been in storage for 33 and 19 months, respectively.

Data from the first rainy season after installation are presented for all 4 field cells, starting at 10 days before the first samples were collected from each cell. Data from single field cells were included on the graphs for comparison with data from the stacked field cells given that very few data points were available from the stacked field cell's mini-lysimeters.

Table 2: Contents of the 4 field cells installed to study Mo attenuation at Antamina. UBC-Mo-T1 and UBC-Mo-T2 are stacked field cells with two different material types, whereas UBC-1-3A and UBC-2-0A are single field cells.

Field Cell Code	Materials Used	Purpose
UBC-1-3A	Pb-bearing black marble waste rock – one of the material types used in UBC-Mo-T1 and UBC-Mo-T2.	Determine composition of unmixed leachate from Pb-bearing black marble
UBC-2-0A	Mo-bearing intrusive waste rock – one of the material types used in UBC-Mo-T1 and UBC-Mo-T2.	Determine composition of unmixed leachate from Mo-bearing intrusive rock
UBC-Mo-T1	Pb-bearing black marble on top of Mo-rich intrusive rock	Investigate possible Mo attenuation by co-precipitation with Pb
UBC-Mo-T2	Mo-rich intrusive on top of Pb-bearing black marble	Investigate possible Mo attenuation by co-precipitation with Pb

Results

Results from UBC-Mo-T1U and UBC-Mo-T2U serve to better understand whether Mo can be attenuated by contact with lead under field conditions at Antamina. Data from the upper lysimeters in the stacked field cells, supplemented by data from related single field cells were used to determine leachate composition prior to mixing. Data from the single field cells were appropriate for this purpose since they were installed with the same Mo- and Pb-bearing materials as are present in the stacked fields. All of the data reported in this section are from the first rainy season after the installation of each field cell.

Results from UBC-Mo-T1U showed that high Mo concentrations persisted in basal leachate even though water passed through Pb-bearing black marble before making contact with the Mo-bearing intrusive (Figure 4). The time scale in the horizontal axis of the graphs in this section refer to the number of days since the first leachate from the field cell appeared in the sample bucket, usually during the first rainy season after the field cell was installed. Mo concentrations from the base of field cell UBC-Mo-T1U reached a level of 10.2 mg/L. As the rainy season progressed, Mo concentration leveled off at about 3.4 mg/L (Figure 4). The single data point available from top black marble prior to mixing with the Mo-rich intrusive material had a Mo concentration of 0.03 mg/L, suggesting that nearly all of the Mo originated from the intrusive material at the bottom of the stacked field cell. Data from the single field cell with the same black marble also confirmed that less than 0.1 mg/L of Mo leached from this material.

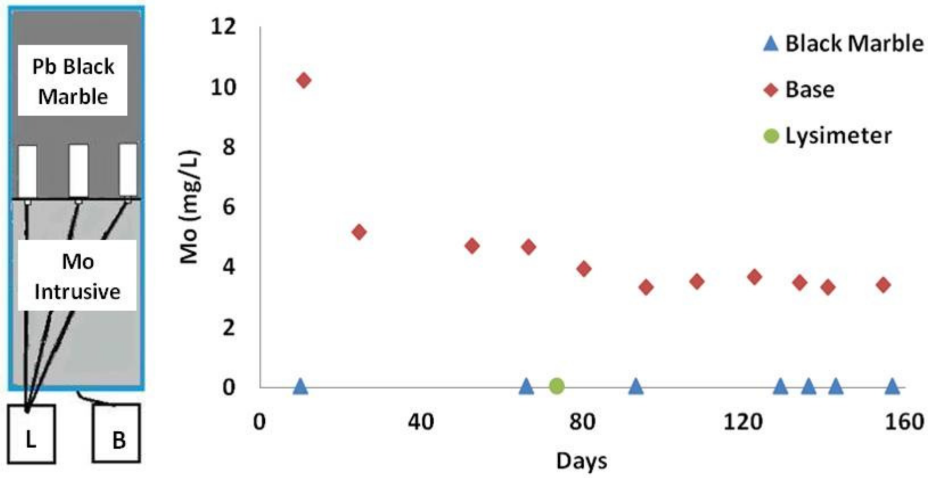

Figure 4: Mo-concentrations as a function of days since the initiation of flow in the field cells (the first significant precipitation since installation) from the UBC-Mo-T1 stacked field cell showing Mo concentrations as a function of time. The diagram to the left shows the configuration of waste rock material in this field cell. L refers to drainage from the upper lysimeters (the 'Lysimeter' series in the graph), and B refers to drainage from the base of the stacked cells (the 'Base' series in the graph). The 'Black Marble' series Mo concentrations in leachate from a single field cell containing the same Pb-rich black marble as was installed in the stacked field cell.

Results from the UBC-Mo-T2U revealed that contact with Pb-rich black marble removed Mo from leachate. Compared to leachate from the base of UBC-Mo-T1, leachate from UBC-Mo-T2 had very low Mo-concentrations, consistently less than 0.03 mg/L (Figure 5).The single sample available from the lysimeter had a concentration of 6.7 mg/L, confirming that the Mo-rich intrusive material was indeed leaching Mo in the stacked field cell. Mo concentrations in leachate from a single field cell containing the same Mo-rich intrusive material reached 0.75 mg/L shortly after installation, before falling to 0.24 mg/L a week later, and then gradually increasing to about 1.7 mg/L by the end of the first rainy season.

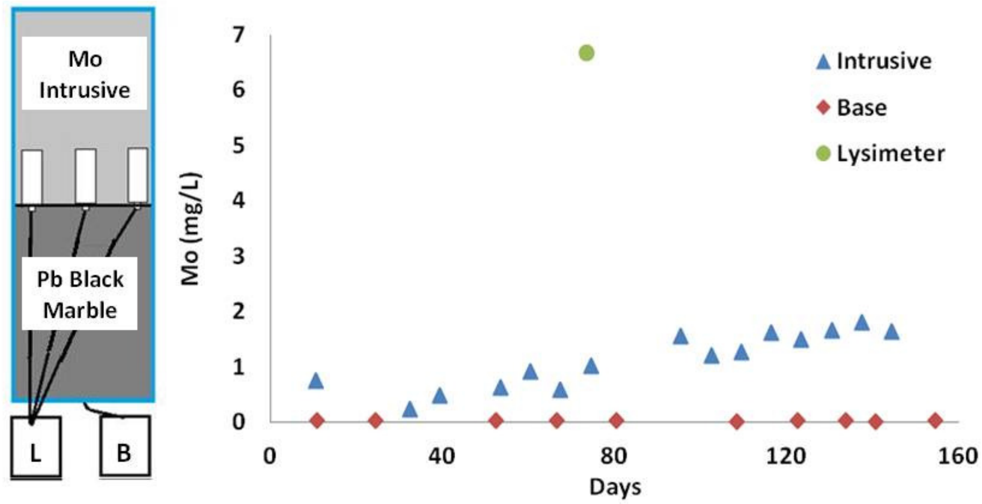

Figure 5: Mo-concentrations as a function of days since the initiation of flow in the field cells (the first significant precipitation since installation) from the UBC-Mo-T2 stacked field cell showing Mo concentrations as a function of time. The diagram to the left shows the configuration of waste rock material in this field cell. L refers to drainage from the upper lysimeters (the 'Lysimeter' series in the graph), and B refers to drainage from the base of the stacked cells (the 'Base' series in the graph). The 'Intrusive' series Mo concentrations in leachate from a single field cell containing the same Mo-rich intrusive as was installed in the stacked field cell.

Discussion

Molybdenum attenuation

Results from the first rainy season since the stacked field cells were installed at Antamina demonstrate that Mo attenuation is occurring in UBC-Mo-T2, where Mo-rich intrusive waste rock is placed on top of Pb-rich black marble. Considering that the concentration of leachate from the Mo-rich intrusive single field cell was more than 1.1 mg/L in the first rainy season and the basal leachate from UBC-Mo-T2 was less than 0.03 mg/L, it appears that at least 97% of the Mo in the leachate from the intrusive rock is removed before it reaches the base of the stacked field cell. The Mo removal efficiency may be as high as 99%, given that the single available pure leachate sample from the Mo-rich intrusive rock in the stacked field cells contained 6.7 mg/L Mo.

Direct contact between Pb-rich materials and Mo-rich materials, however, was not enough to guarantee Mo attenuation. The average Mo concentration in leachate from the base of UBC-Mo-T1 was 4.5 mg/L during the first rainy season, indicating that minimal, if any, attenuation took place in this stacked field cell. The lack of attenuation when the Pb-rich black marble was placed on top of the Mo-rich intrusive rock could be explained by the low mobility of lead in this stacked field cell. Lead concentrations from the base of UBC-Mo-T2 and from the lysimeter in UBC-Mo-T1 were both less than 0.03 mg/L. This low concentration implies that virtually no lead from the top half of the UBC-Mo-T1 field cell had contact with the Mo-rich intrusive material at the base of the cell. The apparent relationship between lead and Mo attenuation, where Mo was only removed in the case where it came in direct contact with Pb-bearing minerals, supports Conlan *et al.*'s (2011) hypothesis that Wulfenite ($PbMoO_4$) precipitation is a potentially important mechanism for Mo attenuation in Antamina waste rock.

Stacked field cell performance

The results of this study also provided an opportunity to evaluate the performance of the stacked field cells as means of collecting data on the geochemical effects of waste rock mixing. Of particular importance was the performance of the upper lysimeters, since they provide a direct means of comparison between pre-mixing leachate chemistry and the mixed leachate that flows out of the base of the field cell. The stacked field cells were designed such that just over 6% of the total flow would be intercepted by the upper lysimeters. During the first rainy season after their installation, 3.5% of the total flow was captured by the upper lysimeters in UBC-Mo-T2, whereas only 0.4 % of the total flow was captured by UBC-Mo-T1's upper lysimeters. Capillary breaks in the upper lysimeters may help explain why the lysimeters' performance was less efficient in UBC-Mo-T1, where they were situated in the relatively coarse, Pb-bearing black marble. The better performance in UBC-Mo-T2 may have been related to the upper lysimeters' placement in fine-grained Mo-bearing instrusive rock.

It should be noted that the low number of data points from the upper lysimeters was not just a result of the low water volume that the upper lysimeters captured. A second important issue that limited the amount of data that could be collected from these upper lysimeters was that the commercial laboratory where the samples were analyzed required at least 1L of sample for their analysis to comply with QA/QC procedures.

The relatively few leachate samples from the upper lysimeters meant that data from the single field cells was essential for interpreting the results of this study. We believe that the single field cell leachate results are valid surrogates for the upper lysimeters of the stacked field cell, since they were composed of the same homogenized waste rock. As the data from this study indicate, there were some important differences in leachate composition between the stacked and the single field cells, such as the fact that the average Mo concentration in leachate from the intrusive single field cell was only 1.1 mg/L, whereas it was 4.5 mg/L in the stacked field cell.

Conclusions and recommendations

This study leads to two important conclusions that have implications for waste rock management in neutral drainage systems: 1) Wulfenite precipitation through contact with Pb-bearing rock can serve as a means to attenuate Mo in neutral systems 2) Simply putting the two rock types in contact is not enough to ensure attenuation; the Mo-rich leachate must flow through the Pb-bearing rock itself. Future work will focus on confirming the presence of Wulfenite in waste rock from the bottom of UBC-Mo-T2, and continuing to run the study over several more rainy seasons in order to gain a better understanding of the attenuation mechanism and determine if it can be relied on over the long term. Similar work is also underway to evaluate the attenuation of Zn and As in leachate from Antamina waste rock.

Preliminary results highlighted the importance of using geochemistry data from single field cells to support the results obtained from stacked field cells, given that performance of the upper lysimeters may always be a risk. Single field cells also allow for a better understanding of the pre-mixing leachate composition from the material in the bottom of the stacked field cell.

The discrepancies in leachate composition between the single field cells and stacked field cells highlight that material heterogeneity, or simply differences in sample storage and handling can have important effects on leachate composition. This demonstrates the complications inherent in relying solely on surrogate single field cells for waste rock mixing studies and the importance of installing lysimeters at the boundary between different materials in the stacked field cells as a means to sample unmixed leachate directly. These lysimeters should be designed to capture as much flow as possible and not cause capillary breaks. To this end, a possible strategy may be to have a single large lysimeter rather than three small ones. The larger lysimeter diameter would allow for larger waste rock clasts to fit inside the lysimeters and therefore could be more representative of the overall waste rock texture.

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Abbreviations

Neutral Mine Drainage – NMD, Canadian Council of Ministers of the Environment – CCME, University of British Columbia – UBC, Polyvinyl Chloride – PVC.