Wall Wash Samples to Predict AMD Longevity at Coal Mines in New Zealand

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Abstract

Wall wash samples were collected at man-made coal measures exposures between 3 days and 138 years old to understand to evolution of wall wash chemistry with time. Acidity in the wall wash solutions decreased rapidly from a maximum of >1000mg/l H_2SO_4 to <1mg/l H_2SO_4 as the age of the exposure increases. The composition of acidity also changes, at young exposures (≤1y) Fe Lewis acidity is the most abundant form of acid, at sites 3-18y old Al Lewis acidity is most abundant and at sites 45-130y old, proton acidity is most abundant. Trace element concentrations in wall wash (Zn, Ni, Co, Cd & Mn) also decrease 3-4 orders of magnitude with increasing age of exposure.

Keywords: Wall wash, AMD, Lewis acid, trace element.

Introduction

Wall wash samples were collected from man made Brunner Coal Measures exposures between 3 days old and 138 years old at mine sites on the West Coast of the South Island of New Zealand. The Brunner Coal measures are regionally extensive and contain high quality coking coal seams within PAF (potentially acid forming) mudstones and sandstones. There are several active mines and many abandoned mines hosted within these coal measures and the longevity of acid release related to mining disturbances is not quantified.

The solution chemistry of the acid mine drainage is from Brunner Coal Measures is well characterised, pH is low (2-4.5), Fe and Al are abundant Lewis acids, the most elevated trace elements Zn, Ni & Mn, and occasionally Cu, As or Co are present at elevated concentrations (Pope et al., 2010a; Pope et al., 2010b; Weber et al., 2006). However, the long term evolution of AMD chemistry is not well understood. Our objective is to measure changes in wall wash chemistry with the age of exposure and use this information to develop a predictive relationship for:

- decrease in acid release rate from pit walls with time and the time taken for acidity in pit wall run off to return to natural levels
- decreases in trace element release rate from pit walls with time
- evolution of mine drainage chemistry with time

Methods

Samples of wall wash were collected from Brunner Coal Measures outcrops at the high walls of 4 mine sites one road cutting and one rail cutting. Wall wash was generated by rapid (~10 seconds) application of 500ml of distilled water to an area about 50cm by 50cm and collection of as much run off as possible in a large plastic sampling bag sealed to the outcrop with duct tape (Figure 1). About 40 to 80% of the wall wash was retrieved in the sampling bag with some lost due to rough surfaces and wetting. Wall wash samples were transferred into chilled 500ml sample bottles (unpreserved and un filtered) for subsequent processing in the laboratory. The samples often included a small amount of solid material (sediment, precipitates ± organic material). The sample collection process is similar to field conditions where solid material is washed off along with runoff mine drainage water and all material is discharged from the high-wall area with dissolved and suspended material included.

Application of this volume of water to ~ ¼m^2 reflects a 6-10 mm rainfall event depending on the slope of the high-wall which is between 70° & 80° at the sites selected. This size of rainfall event was selected because it is relatively common on the West Coast (weekly) along with much larger rainfall events (annual rainfall 2-6m per year).

Sample sites

Site A is at a mine in the Buller Coalfield that has been operating for about 4 years where wall wash samples were collected from pit wall exposures that were 3 days old and 1 year old at the time of sampling.

Site B is an operational mine in the Garvey Creek Coalfield and includes a sequence of complexly folded and faulted Brunner Coal Measures. Pit walls where access was possible were between 3 & 5 y old at the time of sampling.

Site C is a road cutting through Brunner Coal Measures that occurs on the road close to the entrance of Stockton mine in the Buller Coalfield. The cutting was exposed about 10 years prior to the time of wall-wash sampling.

Site D is at a mothballed mine in Brunner Coal Measures within the Garvey Creek Coalfield. Access is available to the coal measures sequence in the mine high-wall which was 18 years old (pers. com. Phil Lindsay) at the time of sampling.

Site E is at a cutting for the portal of an abandoned underground mine in the Buller Coalfield. The cutting was about 62 years old at the time of wall wash sampling.

Site F is a cutting for historic rail operations near Denniston in the Buller Coalfield. The cutting was about 136 years old at the time of sampling and the surfaces were ~60% lichen covered.

Laboratory methods

In the laboratory, the pH was measured in each sample using a calibrated (buffers 2,4 & 7) pH metre. Samples were filtered through 0.45μm syringe filters, then acid preserved using analytical grade HNO_3 and dispatched for element analyses. Analyses were conducted for major cations, and trace elements by APHA method 3125 B. The analysis suite included K, Na, Ca, Mg, Al, Fe, As, Sb, Cu, Cr, Co, Mn, Ni & Zn at Hills Laboratory by ICP-MS.

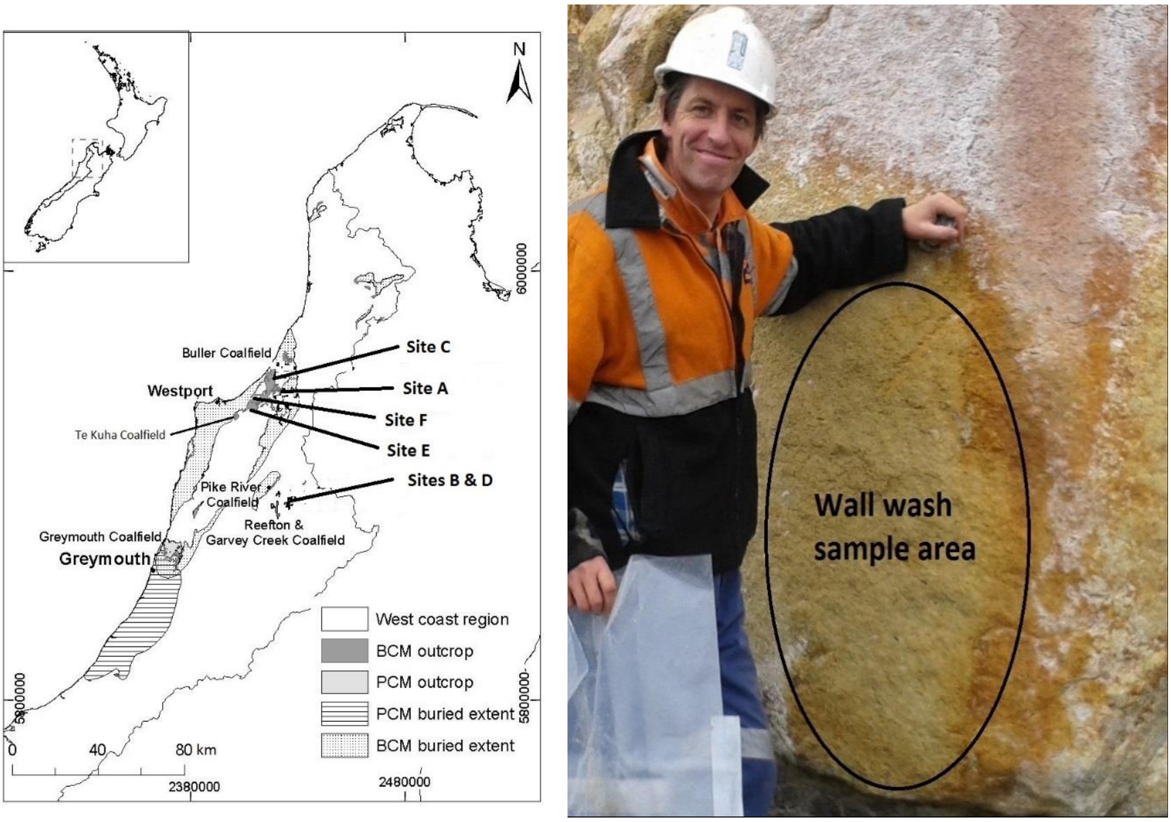

Figure 1 *Location map and example wall wash sample site.*

Results and Discussion

The chemistry of wall wash was variable at each site and between sites (Pope et al., 2018). However, in general the characteristics of wall wash at sites <60 years old match with previous studies of Brunner Coal Measures AMD, pH is commonly between 2.5 and 4, Fe and Al are typically abundant Lewis acids, and trace elements are enriched, Zn, Mn > Ni > Co, Cu, Cd > As, Sb and others (Pope et al., 2010a; Weber et al., 2006; Weisener and Weber, 2010). The total acidity (mg/l H_2SO_4) calculated from pH, Fe and Al concentrations is within the range between 0.05mg/l and just over 10000mg/l, similar to the range of acidity concentrations that occurs in leachate samples from Brunner Coal Measures column testing (Olds et al., 2016; Pope and Weber, 2013). The maximum concentration of trace elements in wall wash samples is often higher than the concentrations found in AMD or column leach analyses, Mn up to 90mg/l, Zn up to 31mg/l, Ni up to 43mg/l and Co up to 31mg/l (Pope et al., 2018). At sites < 60 years old the pH is often circum-neutral and concentrations with low acidity, although trace element concentrations can remain relatively high compared to the acid load at some sites.

Acidity trends

The acidity data collected are variable and this reflects the nature of the sampling method and coal measures rocks that have been washed. The sampling method is difficult to standardise because each outcrop has a different slope, roughness and wetting characteristic. The rocks have variable lithology and secondary minerals that store acid and trace elements are not uniformly distributed. Despite the variability in acidity that can be washed from different sample sites, there are consistent trends in acid release compared to the age of the exposure.

There are two general trends in acidity released from the coal measures pit walls in this study. High acid loads are released for the first year and decreasing acid loads for subsequent years. When pit walls are fresh (3 days to ~1 year in this study) the acid release rate is relatively rapid average 2032mg/l(H_2SO_4) from 3 day old pit walls, and 4187mg/l(H_2SO_4) from 1y old pit walls.

As pit walls age (1 year to 62 years in this study) the release rate of acid decreases with increasing age of pit exposure. Average acidity is 159mg/l(H_2SO_4) for 3-5y old exposures, decreasing to 79 and 55mg/l(H_2SO_4) for exposures 10 and 18y old respectively. Exposures that are 62y old produce wall wash average acidity with 4mg/l(H_2SO_4) and the exposure that is 138 years old produces wall wash with average acidity of 0.1mg/l(H_2SO_4). The changes in average concentration of acidity as a function of time can be fitted with a power law.

Different processes controlling acid release from mines at different times have been noted in other studies. In a long term study of closed underground coal mine drainage from the United Kingdom two phases of acid production also occur, vestigial acidity related to flushing of partial oxidation products in mine impacted areas and juvenile acidity related to ongoing pyrite oxidation in host rocks which decreases with time. (Younger, 1997). Although the hydrogeology in underground workings is very different to a pit wall, the concepts of juvenile and vestigial acidity can be applied. Wall-wash only measures vestigial acidity, acidity that can be rinsed off the pit wall by rainwater, juvenile acidity is released as pyrite oxidises this leads to the secondary minerals that store acid and build up on the pit wall until the next rainfall.

Chemical trends

In the wall wash samples the contribution of H^+, Fe^{3+} and Al^{3+} to the total acidity varies with the age of the pit wall. At the youngest pit walls (3 days and 1 year old) where acidity values are much higher dissolved Fe^{3+} is the largest component of acidity and Al^{3+} > than H^+. At the older pit walls (3 years to 18 years,) dissolved Al^{3+} is the most important component of acidity and H^+ is more significant than Fe^{3+}. At the oldest sites (62 years and 138 years), H^+ is the largest component of acidity, Al^{3+} acidity remains abundant and there is no detectable dissolved Fe^{3+}.

The contributions to acidity by pH, Fe & Al in Brunner Coal Measures AMD have previously been attributed to factors such as mine type with Al^{3+} typically considered the most important Lewis acid at open cut mines (Pope et al., 2010a). However, this previous study does not consider the evolution of AMD chemistry with time. At new seeps (McCauley et al., 2010) and early in column leach testing (Pope and Weber, 2013) Fe^{2+} and Fe^{3+} is often the most important component of total acidity regardless of whether mining occurs at surface or underground. At older seeps, in column leach samples from tests that proceed for >1 y and at a regional scale Al^{3+} is the major component of Lewis acidity in Brunner Coal Measures AMD. At an active mine where pit walls might be cut back every few months to few years the pit wall chemistry will be a mix of Fe^{3+} and Al^{3+} rich AMD acidity.

Acid mine drainage from Brunner Coal Measures typically contain trace elements including Zn, Mn > Ni > Cu, Co, Cd > As, Sb and other trace elements. In the wall wash this pattern of enrichment is generally correct, however these samples contain some of the highest concentrations of trace elements occur that have been observed in Brunner Coal Measures AMD. Higher than previously recorded in seeps or leach tests (Pope et al., 2010a; Pope and Weber, 2013). In addition, the elevated concentrations of elements like Mn, Zn and Ni can occur in wall wash samples from either young or old pit walls. For example, the sample site D4 (18years old exposure) samples contains Zn 21mg/l, Ni 5.4mg/l and Mn 27mg/l. The reason for the elevated trace element concentrations in wall wash samples from both young and old pit walls is not clear.

Comparison to background

The power function correlation used to characterise the decay rate for acid release from pit walls can compared to the background acidity in streams draining Brunner Coal Measures. Background acidity concentrations are compiled from analyses of streams that drain only Brunner Coal Measures but are not impacted by mining disturbances. The range of acidity values at each site spans between 0.5 and 2.5 orders of magnitude and the total range of acidity in the data is almost 6 orders of magnitude. Extrapolating the data collected related to acid release with time indicates acid production at levels above maximum acidity level measured in streams will occur for between 10 and about 165 years. If a regression is applied to the average data, then the time taken for acid load from high walls to decline to similar levels found is streams is 45 years to meet the most acidic natural conditions and 130 years to meet low level natural acid conditions.

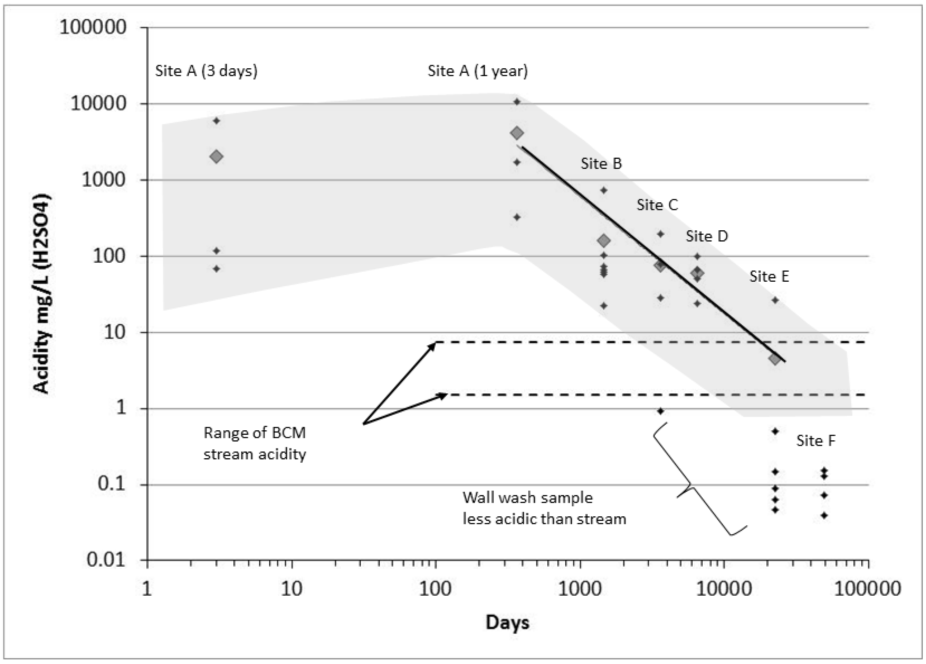

Figure 2 *Trends in acidity in wall wash at sites with different ages.*

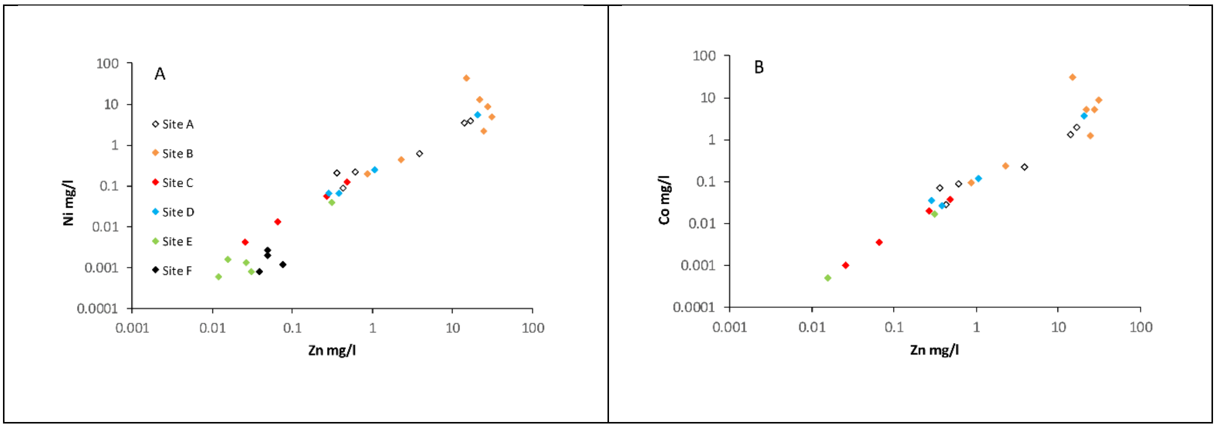

Figure 3 *Trends in trace element concentrations in wall wash at sites with different ages.*

Conclusions

Wall wash samples from mine pit walls that range in age from 3 days to 138 years have been collected and show two trends in the concentration of acidity. Pit walls exposed to weathering for 3 days to 1 year release high concentrations of acid that is comparatively Fe rich whereas older pit walls (3 – 18 years) release acid at lower concentrations and that is relatively Al rich. Pit walls that are older still release mostly proton acidity with some dissolved Al.

The average acidity concentration released from the pit walls greater than 1 year old decreases rapidly with time and can be fitted with a power function expression with data spanning 4 orders of magnitude. There is some uncertainty in the data related to the exact age of the pit wall samples and the nature of the sampling which is biased toward areas where samples can be collected easily (smooth with appropriate slope and limited debris). However, the correlation to the averaged data is relatively strong. The dataset indicate that acidic runoff from pit walls will continue at concentrations above background for a range between 10 and 165 years where background is defined by un-impacted streams draining only Brunner Coal Measures. If the averaged wall wash acidity data and power function fit is used for extrapolation, then the pit walls will release acid at concentrations above the maximum measured acidity in streams for about 45 years.

Maximum trace element concentrations in wall wash samples are higher than concentrations in AMD or column leach experiments on Brunner Coal Measures. Trace element enrichment is strongly cross correlated for elements that are typically abundant in Brunner Coal Measures AMD (Zn, Ni & Mn) as well as minor elements (Co, Cu, Cd), trace element concentrations are not as strongly correlated with acid release probably due to selective co-precipitation into different secondary minerals controlling acidity. In addition high concentrations of trace elements occur in wall wash samples from pit walls of all ages. The variability in trace element concentrations in wall wash samples indicates that the distribution of trace elements in Brunner Coal Measures is not uniform and trace elements could continue to be released as acidity declines.

This wall wash study can be used to predict acidity concentrations and loads from pit walls and other areas where unlimited oxygen and water are freely available to react Brunner Coal Measures. With this information, remediation, and treatment obligations for AMD from these types of sources can be predicted and built into mine operational and closure or rehabilitation plans.

Acknowledgements

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