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New Zealand Coal Acid Mine Drainage, Mineral Control of Acidity and Downstream Chemical Evolution

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Abstract Modelling Al concentrations in acid coal mine drainages in New Zealand demonstrates mineral control of maximum concentrations for Fe and Al in the seep zones by schwertmannite and basaluminite respectively. An unidentified mineral process operates between pH 3-4.5 to reduce the concentrations of Fe and Al. When AMD is neutralised by addition of limestone, schwertmannite is again important for Fe, but boehmite controls Al concentrations. The modelling presented here allows prediction of mine drainage chemistry and is useful for planning mine drainage treatment.

Keywords acid mine drainage (AMD), modelling, saturation, aluminium, iron,

Introduction

Acid coal mine drainages from New Zealand contain a characteristic suite of dissolved components, Fe + Al ± Mn >> Zn > Ni > other trace elements (Cr ± Co ± Cu) (Pope et al., 2010a). This chemical pattern is consistent upstream of treatment systems at all active coal mine sites that disturb acid forming rocks and at abandoned historic mines where drainages are untreated. At a regional scale, chemistry is predictable based on geological correlations and trends in the relative abundance of these dissolved components are related to mine type (underground or open cast) and hydrogeology (Pope et al. 2010b). Detailed study of sulphide mineralogy (de Joux and Moore 2005; Weber et al. 2006; Weisener and Weber 2010) and interpretation of silicate mineralogy (Pope et al. 2010a) indicate the source minerals for many of these dissolved components. However, predicting the presence of these components and understanding the sources is not adequate for planning treatment because the concentrations of the components are highly variable and span three to five orders of magnitude.

We use geochemical modelling of data from column leach tests, analyses of mine drainage seeps and analyses of streams impacted by mine drainage to assess the downstream chemical evolution of Fe and Al in New Zealand's acidic coal mine drainages. Minerals identified through this modelling approach enable prediction of dissolved concentrations and total acid loads which can then be used for planning mine drainage treatment.

Methods

Column leach data selected for this study is obtained from a free draining method using open Buchner funnels with a known mass (usually 1-2 kg) of crushed (-4 mm) rock, a mass-normalised distilled water weekly rinse and a mass-normalised distilled water four-weekly flush (Smart et al. 2002). The funnels are arranged in racks under heat lamps on a 12-hour cycle to encourage oxidation and capillary processes. Following the flush, all leachate is measured, sampled and analysed. Analyses used in this study are from samples that produce acid rapidly.

Filtered (0.45 µm) acidified samples were collected from ~ 30 seeps at active and historic coal mines that are hosted in acid forming rocks in New Zealand. Similar samples were collected at AMD impacted streams downstream of the seeps. Two neutralisation experiments were completed on 1L AMD samples from seeps using incremental addition of limestone and collection of small subsamples at intervals for analysis during the reaction.

Analysis of metal concentrations was completed by ICP-MS. Charge balanced analyses including major cations and anions were completed on most seep samples, whereas selected analytes without charge balance were completed on most stream samples and subsamples from the neutralization experiments.

Modelling was completed using PhreeqC (Parkhurst and Appelo 1999) with additional solubility information for schwertmannite (Bigham et al. 1996).

Results

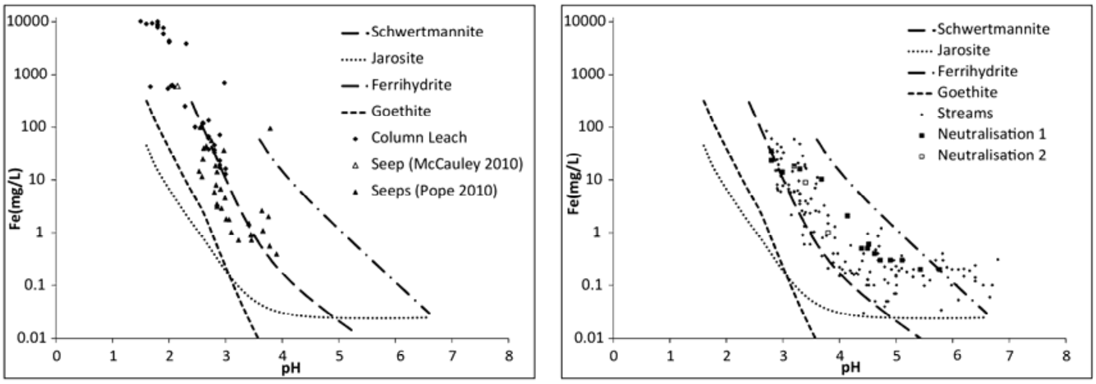
The concentrations of Fe and Al in column leach tests, seeps and streams impacted by AMD span several orders of magnitude (table 1).

Table 1 *Range of Fe and Al concentrations in samples*

Sample Type	pH range	Fe range (mg/L)	Al range (mg/L)
Column leachate	1.6 – 3.0	10 – 10 000	1-1000
AMD seeps	2.2 – 4.0	0.5 - 500	0.1 - 100
AMD impacted streams	3.0 – 5.0 +	0.05 - 50	0.05 - 100

Secondary minerals that control Fe and Al concentrations in AMD include hydroxides, oxy-hydroxides and hydroxy-sulphates (Nordstrom and Alpers, 1999). These minerals can be poorly crystalline or amorphous and they may be difficult to identify by X-ray diffraction.

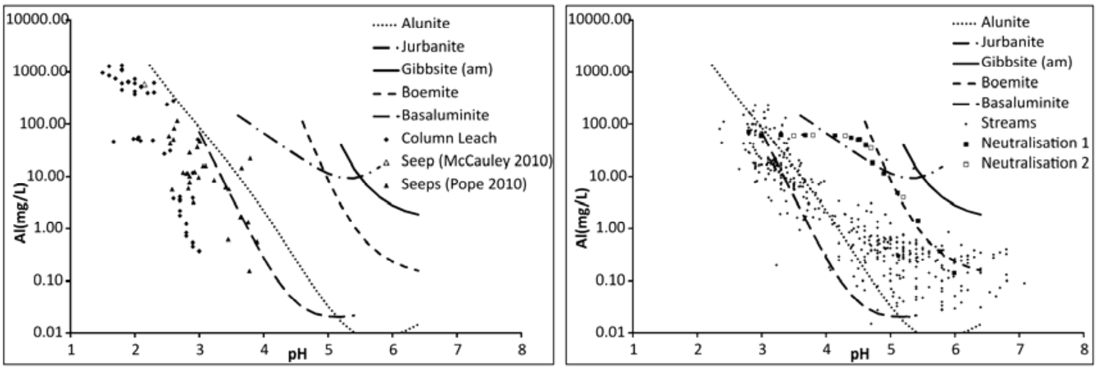
Modelling of Fe data indicates control of Fe concentration by schwertmannite ($Fe_8O_8(SO_4)OH_6$) in seeps (fig. 1a), but mineral associations for leachate cannot be interpreted with certainty at high concentrations. Fe concentrations in stream samples decrease in a pattern parallel to the schwertmannite solubility curve throughout the pH range 3-4.5, but many samples are over-saturated. At pH greater than 4.5 mineral associations are difficult to interpret (fig.1b). Fe concentrations in neutralisation experiments decrease along the schwertmannite solubility curve initially (~ pH 3 and ~50 mg/L Fe) and then in parallel with the schwertmannite solubility curve but at oversaturated concentrations.



(a) (b)

Fig. 1 *(a) Fe concentrations in leachate and seeps plotted over solubility curves for common Fe AMD minerals. (b) Fe concentrations in streams and neutralisation experiments over solubility curves for common Fe AMD minerals.*

Modelling of Al data indicate that maximum concentrations in leachate could be controlled by alunite ($KAl_3(SO_4)_2(OH)_6$) (however, the salinity of some of these samples is high for standard aqueous modelling) (fig. 2a). Maximum concentrations of Al in seeps is controlled by basaluminite ($Al_4(SO_4)OH_{10}\cdot 5H_2O$). Concentrations in streams (fig. 2b) are over saturated with respect to alunite and basaluminite, but a general decrease in concentration of Al in streams between pH 3-4.5 could reflect an alunite or basaluminite-like mineral phase. At pH greater than 4.5 in the stream samples, there is no interpretable mineral association. When AMD is neutralised with limestone, boehmite controls the concentration of dissolved Al (fig.2b).



(a) (b)

Fig. 2 (a) Al concentrations in leachate and seeps plotted over solubility curves for common Al AMD minerals.(b) Al concentrations in streams and neutralisation experiments over solubility curves for common Al AMD minerals.

Discussion

The results of modelling indicate that the maximum concentrations of Fe and Al in AMD seeps at New Zealand's acid forming coal mines can be predicted by solubility relationships with schwermannite and basaluminite similarly to other chemical evolution of AMD studies (Espana et al. 2005). In stream environments, mineralogical control is more difficult to attribute to specific minerals because many samples are oversaturated with respect to hydroxy-sulphates and well undersaturated with respect to hydroxides and oxy-hydroxides. However, between pH 3-4.5 concentrations of Fe and Al decrease at a rate that is similar to mineral solubility curves, indicating a relationship to mineral solubility.

It is possible that the oversaturation of Fe and Al with respect to schwertmannite and basaluminite that occurs in stream samples is caused by suspended colloidal particles less than 0.45µm. For Fe there might also be unidentified dissolved FeII present. However, it is also possible that there is an unrecognised mineralogical process that influences Fe and Al concentrations through pH range 3-4.5.

Geochemical modelling of the leachate data from column experiments is difficult because many samples have salinity that exceeds the fresh water ion association assumptions used by PhreeqC. However, in column samples with low salinity, Fe and Al concentrations appear to be related to schwertmannite and basaluminite respectively, and possibly alunite for Al at low pH (~2.5).

Observations of precipitates and efflorescence's in field settings and in column samples indicate that jarosite and melanterite are present in the AMD forming environment. Current research being conducted in New Zealand focusses on the role of jarosite and melanterite in controlling Fe in coal mine AMD environments and storage of acidity by these minerals.

Neutralisation experiments indicate that there are differences in the geochemical processes that operate under environmental conditions compared to processes that operate when mine drainages are neutralised by addition of limestone. This is most apparent for Al where rapid neutralisation does not impact the concentration of Al until pH ~5 and beyond this pH, the Al concentration is controlled by boehmite (AlOOH). The behaviour of Fe during neutralisation is more complex, initially following the schwertmannite solubility curve but subsequently oversaturated with respect to schwertmannite. The differences in mineralogical control of Fe and Al between environmental processes (stream samples) compared to addition of limestone in the neutralisation experiments reflects precipitation kinetics of different mineral species and requires more study.

Summary and Conclusion

The chemistry of AMD from New Zealand coal mines is predictable. In general the same components are enriched regardless of mine site and previous studies identify trends in these concentrations and sources of the most enriched components. However predictions at this level are not useful for to identify acid loads or plan mine drainage treatment because concentrations are highly variable.

Modelling data from seeps indicates that schwertmannite can be used to predict maximum concentrations of Fe and basaluminite can be used to predict maximum concentrations of Al. Downstream of the seeps relationships are less clear but between pH 3 and 4.5 mineralogical processes appear to control Fe and Al concentrations in streams. Above pH 4.5 there is no strong mineralogical control of either Fe or Al. However, if the neutralization rate of mine drainage is increased by addition of limestone, a different mineral assemblage is likely. Schwertmannite is likely to occur at early stages of neutralization and Al is likely to remain in solution until pH 5 where boehmite precipitates.

The modelling results presented here represent part of a project that is in progress to identify which secondary minerals control acid release and storage in different parts of the mine drainage environment at coal mines in New Zealand. These studies have implications for planning mine drainage treatment, understanding storage and release of acid in the mine drainage formation zone and predicting chemical impacts downstream of mines.

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