Acid Base Accounting Criteria Used in Prediction of Drainage Chemistry

William (Bill) Price

CANMET- Mining and Mineral Sciences Laboratories.Natural Resources Canada

Abstract Acid Base Accounting (ABA) consists of a series of compositional analyses and calculations. ABA is used to guide decisions regarding the potential for acidic drainage and is a key component of sound environmental and fiscal management. Challenges include limitations of the analyses and calculations and the many parameters and processes potentially contributing to drainage pH. ABA analyses and criteria may enable cost effective prediction but users need to consider whether ABA results and predictions are compatible with the mineralogy, elemental concentrations, weathering rates, weathering and leaching conditions, and other inputs of acidity and alkalinity.

Key Words Acid base accounting, acidic drainage, acid potential, prediction

Acronyms acid base accounting (ABA); acid potential (AP); acid rock drainage (ARD); acidic drainage (AD); neutralization potential (NP); NP-AP or Net Neutralization Potential (NNP); NP/AP or Neutralization Potential Ratio (NPR); not potentially net acid generating (non-PAG) and potentially net acid generating (PAG)

Introduction

The future potential for neutral or alkaline sulphidic geologic materials to produce acidic drainage (AD) if exposed to oxygen and water depends on the relative concentration and reaction rates of acid generating sulphur minerals (AP) and neutralizing minerals (NP). The relative magnitude of the NP and AP is indicated by the NP/AP or Neutralization Potential Ratio (NPR). AP and NP are reported as kg $CaCO_3$ equivalents/tonne so they can be compared. A factor of 31.25 converts % S to kg $CaCO_3$ equivalents/ tonne based on the assumption that 1 mole of S produces 2 moles of H^+ (Reaction 1 and 2) and 1 mole of calcite ($CaCO_3$) neutralizes $2H^+$ (Reaction 3).

$$AP = 31.25\ (\%\ \text{sulphide-S} + \%\ \text{acid sulphate-S})$$

Sulphide (pyrite) oxidation: $FeS_2 + O_2 + H_2O \rightarrow Fe(OH)_3 + 2SO_4^{2-} + 4H^+$ (1)
Acidic sulphate (melanterite) dissol.: $FeSO_4 \cdot 7H_2O + O_2 \rightarrow Fe(OH)_3 + SO_4^{2-} + H_2O + 2H^+$ (2)
Acid neutralization by calcite: $CaCO_3 + 2H^+ \rightarrow Ca^{2+} + H_2CO_3 \quad pH < 6.3$ (3)
Acid neutralization by calcite: $CaCO_3 + H^+ \rightarrow Ca^{2+} + HCO_3^- \quad pH > 6.3$ (4)

There are two neutralization reactions for calcite. Reaction 3 predominates below pH 6.3. Reaction 4, which requires twice as much NP to neutralize each mole of H+, predominates at higher pH. Reaction 3 is assumed in the calculation of AP (%S x 31.25). With reaction 3, an NPR < 1 is required to produce ARD. With reaction 4, an NPR > 2 is required to prevent ARD. Under near-neutral pH conditions, micro-sites with both reaction 3 and 4 are likely to occur. Consequently, the NP/AP (NPR) required to generate ARD will be between 1 and 2. This is why the ratio of NP depletion (moles Ca + Mg) to AP depletion (moles sulphate) measured in humidity cell drainages is typically between 1 and 2 (Figure 1).

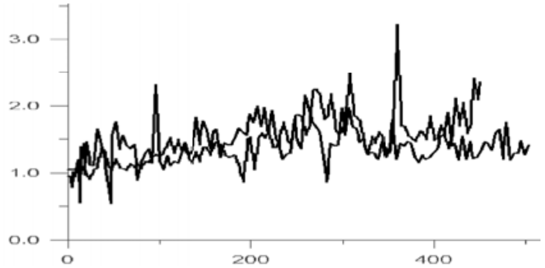

***Figure 1** Molar ratio of $(Ca+Mg)/SO_4$ versus time in weeks for two humidity cells from a Cu mine*

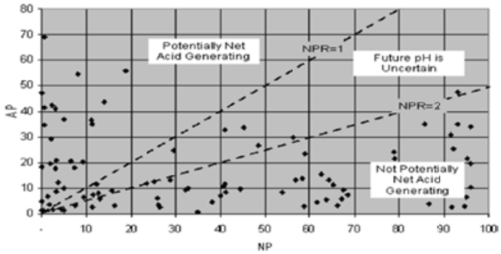

Figure 2 *An example of AP versus NP data*

As illustrated in Figure 2, assuming the correct AP and NP, the future drainage pH is:

- potentially net acid generating (PAG) if NP/AP < 1
- not potentially net acid generating (non-PAG) if NP/AP > 2
- uncertain if NP/AP is between 1 and 2

Safety factors may need to be added to these criteria to address limitations in the precision or accuracy in sampling, material handling or prediction of the NP and AP. There are many possibilities for over or under estimating the AP and NP. Reasons the actual AP might be significantly higher than the predicted AP are outlined below (Price, 2005a and 2009).

Preferential deposition of heavier sulphide minerals may result in a tailings beach with a higher AP than predicted from the analysis of tailings leaving a processing plant. The exposed AP of waste rock may be higher than predicted by analysis of pre-mine drill core or pre-blast hole chips, if sulphides preferentially report to waste rock fines (< 2 mm; Table 1). Rock types differ in their surface area and therefore their relative contribution to the overall waste rock composition. At several sites, PAG waste rock is highly sericitic and opens up like a book exposing all its AP. In contrast, non-PAG waste rock with most of the NP may be very hard with relatively little reactive surface area. The net result is far more exposed AP than predicted by the relative masses of the two rock types.

There are other sources of acid in addition to sulphide and acidic sulphate minerals, such as naturally acidic groundwater and runoff from surrounding areas of sulphide mineralization (Price, 2005b). In addition, oxidation of thiosalts produced during mineral processing may acidify a tailings water cover (Reaction 5). Oxidation of ammonium (NH_4^+) from blasting powder, fertilizer and cyanide decomposition may also acidify a tailings water cover (Reaction 6 and Figure 3). An initial decline in seepage pH may result from the exchange of cations in near-neutral or alkaline mine drainage for H^+ in acidic organic soils below a waste rock dump (Reaction 7 and Figure 4).

$$S_2O_3^{2-} + 2O_2 + H_2O \rightarrow 2SO_4^{2-} + 2H^+ \tag{5}$$

$$NH_4^+ + 2O_2 \rightarrow NO_3^- + 2H^+ + H_2O \tag{6}$$

$$2CH_3COOH + SO_4^{2-} + Ca^{2+} \rightarrow 2CH_3COO\text{-}Ca + SO_4^{2-} + 2H^+ \tag{7}$$

Minimum %S Capable of Producing ARD

The ‘minimum %S capable of causing ARD depends on the type of S and the magnitude of the NP. Mined rock often has an extremely low NP. At the East Kemptville Mine in Nova Scotia, humidity cell samples with 0.07 to 0.19% sulphide-S, NPR of 1 to 2 and NNP > 0 produced acidic drainage (Morin and Hutt, 2006). Great care is required when working with materials containing low AP

Table 1 *AP and NP of > 2 mm and < 2 mm waste rock particle size fractions from a Cu mine*

	> 2 mm	< 2 mm	< 2 / > 2
AP (kg/t)	86	257	3.0
NP-Sobek (kg/t)	32	44	1.4

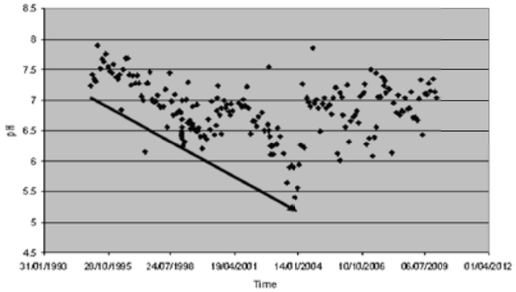

__Figure 3__ A decline in drainage pH from a flooded impoundment resulting from oxidation of ammonium

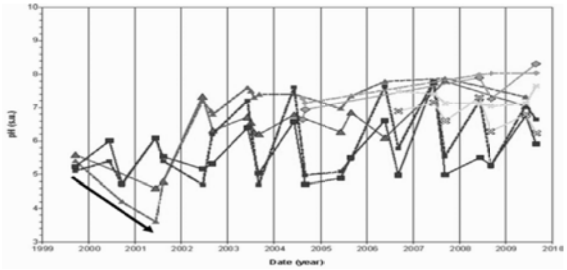

__Figure 4__ An initial decline in seepage pH from exchange of cations in near-neutral or alkaline mine drainage for H+ in acidic organic soils below a waste rock dump

and NP levels because minor variations can significantly alter the predicted and resulting drainage chemistry.

A % S cut-off should not be used to assess the ARD potential unless the minimum NP value is known. Even low levels of sulphide can produce ARD if the NP is insufficient to neutralize the resulting acid.

Maximum Delay Prior to Acidic Drainage

Absence of acidic drainage up to now no matter how long the time of exposure does not prove acidic drainage will not occur in the future. Depletion of NP may take 10s to 100s of years. It took more than 15 years before acidic drainage was observed from waste rock with only a moderately sized NP at the Island Copper mine (Morin and Hutt, 1997).

The magnitudes of NP with humidity cell measurement of NP removal rate provide rough estimates of time to NP depletion. NP depletion of 2.5 to 5 kg $CaCO_3$/tonne/year suggests it would take 36 to 72 years to deplete NP of 180 kg $CaCO_3$/tonne in the backfilled tailings sand in the Snip Mine (Price, 2005c). It is important to set up field test pads as soon as possible to monitor weathering rates under field conditions in various geologic materials at the site (Price, 2009).

Other Considerations

- Prediction of the ARD potential typically assumes oxidized, conditions.
- The question is not whether a sample generates acid (AP), most rock generates some acid, but whether it will become net acid because there is insufficient NP to neutralize the acid.
- The ARD potential between NPR 1 and 2 will depend on the fate of alkalinity (HCO_3^-) produced by the pH > 6.3 neutralization reaction (Reaction 4).
- NNP = NP-AP is additive rather than a ratio and cannot distinguish between materials with an NPR > 2 and an NPR 1 to 2 and is not recommended for characterizing the future potential for acidic drainage (Figure 5).
- Drainage chemistry prediction should be conducted if the NPR > 2 because contaminant concentrations at near-neutral or alkaline pH may still be above environmental guidelines (Stantec, 2004).

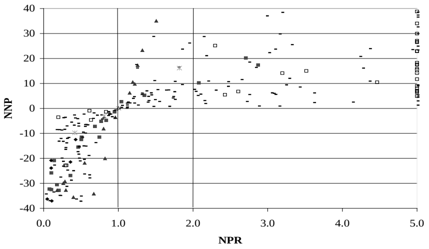

Figure 5 *NNP versus NPR data from a proposed Cu-Au deposit*

Conclusions

ABA criteria used to classify materials should be based on practical and theoretical (scientific) considerations. Criteria may provide short cuts, but one always needs to check whether the underlying assumptions or limitations apply to your specific situation. Mineralogical, elemental and humidity cell data are required to check assumptions about chemical species contributing to ABA analysis and calculation results.

Numerical ABA criteria provided in guideline documents are commonly misunderstood, used inappropriately, and inaccurately described [e.g., description of guidelines in Price (1997) by Maest et al. (2005)]. Always consider the specific situations to which criteria apply and details concerning their use.

It is important to recognize that generic numbers in ABA criteria cannot substitute for an understanding of the natural environment, project, geological materials and protection requirements. Development of site-specific criteria should be based on measurable parameters and a well-informed assessment of the limitations of the results. Practitioners need to decide what information is required to make an assessment, under what conditions are short cuts permitted, and when conditions deviate from the expected. The devil is in the details. Sensitivity analysis and risk assessment are required to determine the sufficiency of the information.

Acknowledgements

Thanks to Mike Aziz (Goldcorp), Harold Bent (Northgate Minerals), Kevin Morin (MDAG), Glenda Ferris (retired) and Kevin O'Reilly (Ekati Independent Monitoring Agency).

References

Maest AS, Kuipers JR, Travers CI, Atkins DA (2005) Predicting Water Quality at Hardrock Mines: Methods and Models, Uncertainties and State-of-the-Art. Kuipers & Associates and Buka Environmental.

Morin KA, Hutt NM (1997) Environmental Geochemistry of Minesite Drainage: Practical Theory and Case Studies. MDAG Publishing. p.333.

Morin KA, Hutt NM (2006) Is There a Solid-Phase Sulphide Level Below Which No ARD is Possible? MDAG Internet Case Study #21, www.mdag.com/case_studies/cs21.html.

Price WA (1997) Draft Guidelines and Recommended Methods for the Prediction of Metal Leaching and Acid Rock Drainage at Minesites in British Columbia, British Columbia Ministry of Energy and Mines. p. 159.

Price WA (2005a) Criteria Used in Material Characterization and the Prediction of Drainage Chemistry: "Screaming Criteria". In Price WA, Bellefontaine K (editors). Challenges in the Prediction of Drainage Chemistry: Proceedings of 12th British Columbia MEND Metal Leaching and Acid Rock Drainage Workshop, Vancouver, November 30 – December 1, 2005.

Price WA (2005b) Case Studies of ML/ARD Assessment and Mitigation: Placement of the Sulphurets Waste Rock in Brucejack Lake. MEND Report 9.1b.

Price WA (2005c) Case Studies of ML/ARD Assessment and Mitigation: Snip Gold Mine. MEND Report 9.1c.

Price WA (2009) Prediction Manual of Drainage Chemistry from Sulphidic Geologic Materials. Mend Report 1.20.1 (December 2009).

Stantec Consulting Ltd. (2004) Review of Water Quality Issues in Neutral pH Drainage: Examples and Emerging Priorities for the Mining Industry in Canada. MEND Report 10.1