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Acid Base Accounting Criteria Used in the Prediction of Drainage Chemistry

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- Prediction of whether sulphidic geologic materials are capable of producing acidic drainage is a key component of sound environmental and fiscal management.
- The most cost-effective means of predicting ARD potential typically uses the results of acid base accounting.

Acid Base Accounting (ABA)

ABA is a series of compositional analyses and calculations.

- analysis of pH
- analysis of sulphur species and calculation of the Acid Potential (AP)
- analysis of Neutralization Potential (NP)
- calculation of NP/AP (NPR) and NP-AP (NNP)

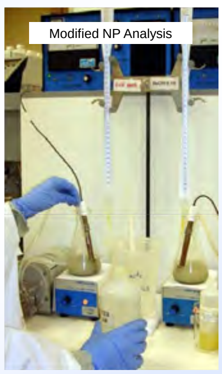
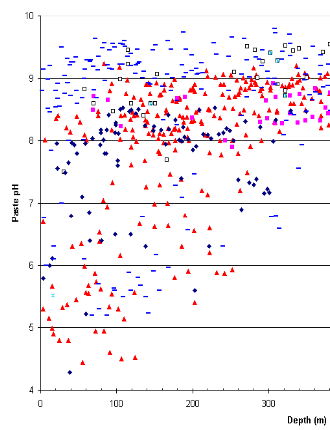


Photo from Maxxam Analytical



pH indicates if a sample is presently able to produce acidic drainage.

pH analysis indicated that a significant portion of this deposit was already acid.

The future potential for acidic drainage 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 ratio of NP/AP (Neutralization Potential Ratio or NPR).

AP is reported as kg $CaCO_3$ equivalents/tonne so it can be compared with the NP.

AP = 31.25 (% acidic sulphide-S + % acidic sulphate-S)

31.25 converts % S to kg $CaCO_3$ equivalents/tonne based on the assumption that:

- 1 mole of S produces 2 moles of H^+
- 1 mole of calcite ($CaCO_3$) neutralizes 2 moles of H^+.

Pyrite - $FeS_2 + O_2 + H_2O \rightarrow Fe(OH)_3 + 2SO_4^{2-} + 4H^+$

Calcite - $CaCO_3 + 2H^+ \rightarrow Ca^{2+} + H_2CO_3^0$

However, there are two neutralization reactions for calcite.

1. $CaCO_3 + \underline{2H^+} \rightarrow Ca^{2+} + H_2CO_3^0$ pH < 6.3
2. $CaCO_3 + \underline{H^+} \rightarrow Ca^{2+} + HCO_3^-$ pH > 6.3

Reaction 1, used in the calculation of AP predominates below pH 6.3.

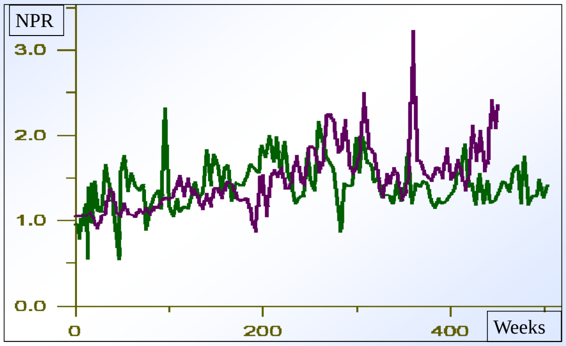
Reaction 2, which requires twice as much NP to neutralize each mole of H^+, predominates at higher pH.

With reaction 1, an NPR < 1 is required to produce ARD.

With reaction 2, an NPR > 2 is required to prevent ARD.

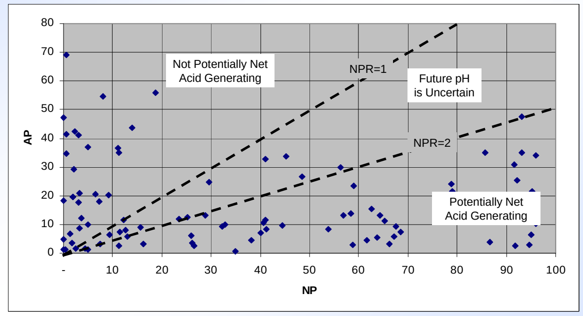
Under near-neutral pH conditions, micro-sites with both reactions 1 and 2 are likely to occur. Consequently, the NP/AP (NPR) required to generate ARD will be between 1 and 2.

This is why the ratio of NP depletion (moles Ca + Mg) to acid generation (moles sulphate) measured in humidity cells is typically between 1 and 2.



Assuming accurate AP and NP measure, future drainage pH is:

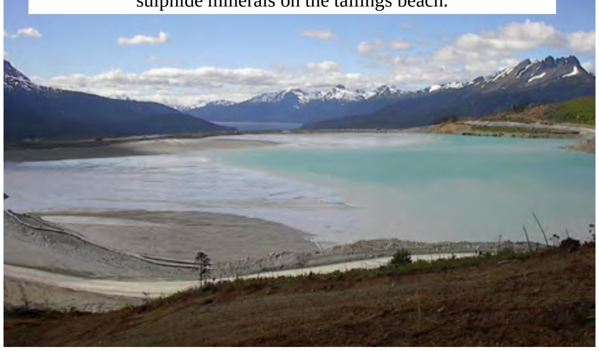
– potentially net acid generating if NP/AP < 1
– not potentially net acid generating if NP/AP > 2
– uncertain if NP/AP is between 1 and 2



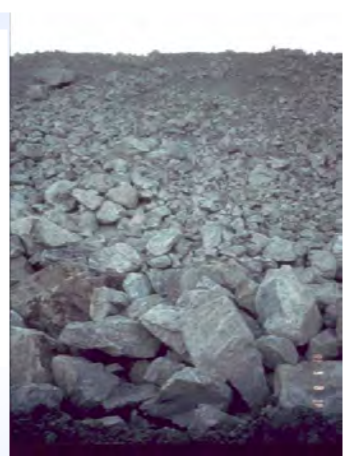
Errors in prediction of the NP/AP may occur due to errors or omissions in sampling, analysis and material handling.

The following are examples of how the AP may be underestimated resulting in acidic drainage despite an NP/AP > 2.

In tailings, the AP next to the disposal location may be higher than predicted from the analysis of tailings leaving the processing plant due to preferential deposition of the heavy sulphide minerals on the tailings beach.



In waste rock, the majority of the weathered surface area and therefore the drainage chemistry depends on the composition of fine-sized particles that are typically less than 30% of the mass and may have a different AP from the 'whole rock'.

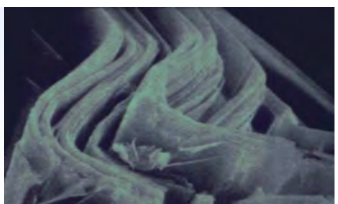


The AP of waste rock is commonly predicted from the analysis of drill core or blast hole chips, which are 'whole rock' analyses.

Post-blast waste rock monitoring is needed to check if sulphides preferentially report to waste rock fines. In this example, post-blast monitoring indicated the preferential accumulation of AP was 2x higher than NP in < 2 mm particles of a volcanic waste rock.

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

If there is no consideration of surface area, the AP in waste rock fines may be underestimated in a waste rock dump in which the largest AP source is highly sericitic rock that opens like the pages of book, exposing much of the AP, while the majority of the NP occurs in a more indurate rock type.



- The AP may also be underestimated if there are external sources of acid. These include acid from the:
  - thiosalts;
  - ammonium;
  - underlying soils;
  - precipitation; and
  - groundwater or runoff.
- The oxidation of thiosalts produced by mineral processing has been responsible for the acidification of drainage associated with tailings at a number of mines.

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

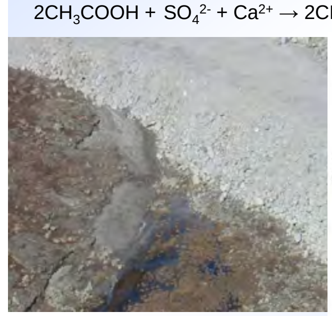
The decrease in pH and subsequent increase in Cu in this water cover was primarily attributed to oxidation (nitrification) of ammonium, a by-product of cyanide decomposition.

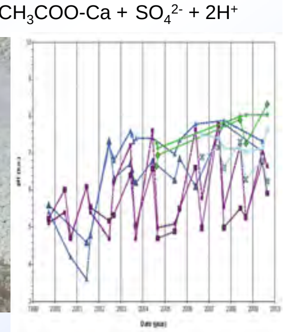
$$NH_4^+ + 2O_2 \rightarrow NO_3^- + 2H^+ + H_2O$$

NH_4^+ may also come from blasting powder and fertilizer.

An initial decline in seepage pH despite a large excess of NP at the Ekati diamond mine resulted from exchange of Ca^{2+} in basic mine drainage for H^+ in organic soils below the waste rock dump.

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





Although I don’t have time to provide examples:

– acidic drainage may also occur in the future despite an NP/AP > 2 if there is a large enough overestimation of the NP and

– future drainage pH may remain neutral despite an NP/AP < 1 if there is a large enough overestimation of the AP or underestimation of the NP.

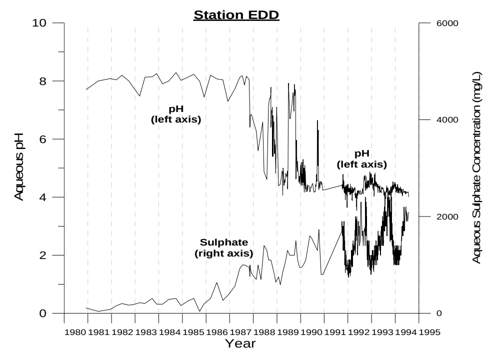
Minimum %S Capable of Producing ARD

- 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.
- Mined rock often has an extremely low NP.
- At the East Kemptville Mine in Nova Scotia, samples with as low as 0.07 to 0.19% sulphide-S produced acidic drainage.
- Great care is required when working with materials containing low AP and NP levels because minor variations can significantly alter the predicted and resulting drainage chemistry.

Maximum Delay Prior to Acidic Drainage

- Absence of acidic drainage up to now does not prove it 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 at Island Copper, a mine with only a moderately sized NP (from Morin and Hutt, 1997).



The initial magnitude plus the rate of NP removal provide rough estimates of the time to NP depletion.

A humidity cell provides a lab measurement of the rate of NP removal and the time to NP depletion.

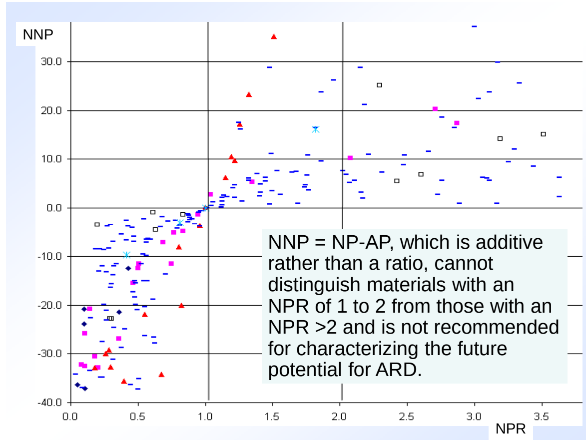
Field test tests should be constructed to measure site-specific NP depletion rates.

Other Considerations:

- 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.

$CaCO_3 + H^+ \rightarrow Ca^{2+} + HCO_3^-$

- Notably, East Kempville tailings samples that produced acidic drainage had an NPR of 1 to 2 and NNP > 0.



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Conclusions

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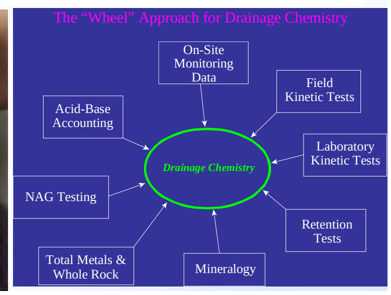
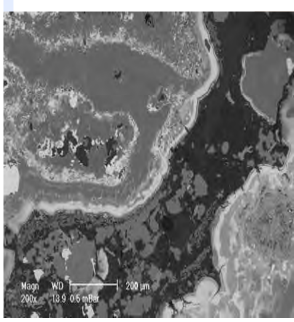
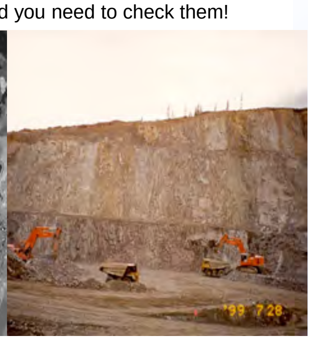
- ABA criteria used to classify materials should be based on practical and theoretical (scientific) considerations.
- ABA criteria may provide short cuts, but practitioners always need to check the underlying assumptions and site-specific limitations.



- Mineralogical, elemental and humidity cell data are required to check assumptions about the chemical species contributing to ABA analysis and calculated results.
- The devil is in the details and you need to check them!





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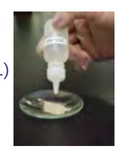
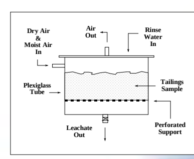
More information on ABA Criteria can be found in the MEND Prediction Manual

Prediction Manual for Drainage Chemistry from Sulphidic Geological Materials (MEND Report 1.20.1)



- Manual provides the comprehensive, in-depth level of understanding needed to conduct a prediction program and review the results.
- Available electronically at: http://www.abandoned-mines.org/mend-e.htm
- Available for purchase in hard copy at: mend-nedem@nrcan.gc.ca



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