# A critical review of static geochemical test methods applied to mining wastes, including their applicability to field conditions

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## Abstract

Assessments for Acid Mine Drainage (AMD) and metal leaching potential for mining projects use several static geochemical test methods to measure different parameters. These tests are generally developed in a laboratory and are often subject to uncertainty and are representative of closed systems.

Issues commonly ignored or misunderstood during ARD assessments, related to acid base accounting (ABA), net acid generation (NAG) and leach tests are discussed along with some of the practical implications for sample classification under field conditions.

These issues are implicitly recognised in several review and guideline documents, but are often not adequately evaluated for mining projects.

**Keywords**: static geochemical testing, acid base accounting (ABA), Net Acid Generation (NAG), Synthetic Precipitation Leaching Procedure (SPLP), Acid Mine Drainage (AMD).

## Introduction

Static geochemical testing is used as an important part of characterising mine wastes. Several screening tools are used in an attempt to rapidly and cheaply measure inherent geochemical properties of the materials of interest, including the potential to release acidity, metals or salinity. Generally a suite of methods is recommended, as no one method is considered reliable on its own (Price 2009, Morin & Hutt 2001, White et al. 1999, Maest & Kuipers 2005, GARD Guide).

This paper focuses on Acid Base Accounting (ABA), Net Acid Generation (NAG) Testing and leach testing for metals, as these tests are frequently the point of departure for an AMD assessment but can easily lead to erroneous conclusions by inappropriately qualified or inexperienced practitioners.

Despite most guideline documents recommending specific test methods and classification criteria, almost all of them agree that both the acid potential (AP) and the neutralising potential (NP) (or NAG potential) of a sample are unlikely to be accurately measured without a good understanding of sample mineralogy. Some of these limitations are discussed, along with the implications of currently used classification criteria and the effect of field conditions on the ABA classification criteria.

## Methods

Several guideline documents and reviews were evaluated for this paper, including Price 2009, Morin & Hutt 2001, Maest & Kuipers 2005, White et al. 1999, Jambor 2003 and INAP 2012.

## Discussion

The methods used for ABA testing rely on the measurement of different sulphur species to quantify the sample AP. All methods assume that acidity originates exclusively from the mineral pyrite. This can be an accurate assumption, but particularly in hard rock mining environments several other sulphide minerals may be present, which can produce variable amounts of acidity per mole of sulphide, less than or equal to pyrite. These other minerals can have a bearing on the result but are often ignored as the assumption that pyrite is present is considered to be conservative from an environmental point of view. From an economic point of view, however, if they make up a significant proportion of a sample, it may be erroneously classified as potentially acid forming (PAF).

The NP of a sample is measured by titrating it against an acid (different strengths of HCl are used for the most commonly used methods). The oldest, most common method in current use is the Sobek (1978) method, which is favoured due to its low cost, short timeframe and long history. The "modified method" is favoured by many practitioners currently (Price 2009) as it is considered more accurate and less likely to overestimate NP than the Sobek (1978) method. According to data presented by Lawrence and Wang (1997), overestimation of NP by more than 50% can occur by the Sobek (1978) method. Jambor 2003 reported that the modified method can yield higher NP than the Sobek (1978) method if a final pH <2 occurs, although such results are excluded by the method description.

Both the Sobek (1978) and modified methods use HCl to dissolve the test samples (between 0.1N and 1N, depending on the "fizz ratings). These acid solutions would have a pH of between 0.08 and 1.1 according to speciation calculations carried out for this paper with Geochemist's Workbench (thermo.dat database). This implies that any minerals that buffer acidity between the pH of the acid and the back titration could contribute to the measured ANC, depending on the sample mineralogy. The risk is limited somewhat for the modified procedure, as a final target pH of >2 is required, however, this pH is still well below pH 6, which would be considered environmentally acceptable (Price 2009, Jambor 2003, Morin & Hutt 2001). The modified method has a titration pH of 8.3, which is considered to provide a more reliable NP than the pH 7 endpoint of the Sobek (1978) test because $Fe^{2+}$ can remain in solution below pH 8.3. At the pH 7 titration endpoint of the Sobek (1978) test, peroxide oxidation can be used to oxidised remaining $Fe^{2+}$ in solution, although this is a modification of the standard procedure (Price 2009).

Procedures, which are considered more conservative and reliable for measuring effective neutralising capacity above pH 6 are the Lapakko (White et al. 1999) method and the acid buffering characteristic curve (AMIRA 2002) method. The latter test also has the advantage of being indicative of mineralogy. These tests are more time consuming and more costly than the more commonly used tests and thus are not normally run in large quantities. No reference was found to the effect of $Fe^{2+}$ on these tests, although their acidic pH endpoints may result in some acidity not being measured.

If only pyrite contributes acidity and calcite and dolomite contribute significant buffering capacity to a sample, then most procedures should provide reasonably accurate results, although the fizz test may result in over-estimation of NP if dolomite is the dominant mineral rather than calcite, as dolomite reacts more slowly with acid and is thus likely to result in a lower “fizz rating” for the same concentration of NP. If significant buffering capacity is derived from other carbonates or aluminosilicates, then buffering often occurs below pH 6 (Morin & Hutt 2001, Price 2009, Jambor 2003, Maest & Kuipers 2005), which is too low to ensure compliance with environmentally regulated water quality criteria.

NAG tests are based on sample oxidation by hydrogen peroxide and can be useful additional tests. They cannot be used as standalone tests and must be verified by other data (Price 2009, Morin & Hutt 2001). They provide a mechanism to measure the combined mobilisation of AP from oxidation of sulphides and of NP from easily soluble minerals. The NP can only be measured up to the amount of acidity generated, which is problematic if non stoichiometric consumption of NP is anticipated. NAG tests are considered to be of limited accuracy (although this is inherent in most static tests) and are subject to uncertainty due to potential catalysis of peroxide by metals and interference associated with organic acid generation from carbon-rich samples. They also require sequential extractions for samples containing > 1%S, thus compounding uncertainties. They should thus be used with caution.

Leach tests are used to evaluate samples for their propensity to leach acidity, metals and / or salts. No specific static test is recommended for such purposes at this stage, although multiple extractions are perhaps the most useful generally available option, along with specifically tailored solutions that are adequately justified based on sample composition. The use of distilled water to evaluate contact water pH is useful to test for leachablity of soluble salts and to detect acidity in materials which are already weathered. They are not useful tests for metal leaching potential or acid potential in unoxidised sulphidic mine rock samples.

Besides the abovementioned considerations regarding static tests, different assessment criteria are used to evaluate the results and thus the potential for AMD.

The Net Potential Ratio (NPR) is generally used as the main classification criterion internationally when interpreting ABA results, whereas Net Acid Production Potential (NAPP) is normally used in Australia. NAPP is the difference between AP and NP, compared with the NPR ratio, which is defined as NP / AP. Differences in classification criteria can result in very different classifications. In Figure a plot of selected NPR and NAPP criteria vs Total S (and equivalent pyrite) concentration is provided to illustrate these differences. According to most guidelines, an NPR of >3 (Nevada >1.2 and Price 2009 >2, with several conditions attached) is considered to be safe. According to the NAPP approach (DoITR 2007), an NAPP below 0 is non acid forming (NAF) and below -100 kg $H_2SO_4$/tonne is acid consuming. NAPP equivalent units of $H_2SO_4$ differ from $CaCO_3$ by about 2%, so are directly comparable. The use of criteria that require excess NP in a sample are to allow for armouring, differences in kinetics and contact area and non-stoichiometric dissolution (discussed further below).

Figure 1 shows that the NAPP method is very conservative compared with the NPR classification at low sulphide concentrations and falls below the NPR classification criteria when sulphur concentrations increase above 2% to 4%, depending on the criteria used. Assessing such material as "acid consuming" is thus potentially risky. Ultimately chemical reactions are stoichiometric and should thus be evaluated in terms of ratios, rather than differences to avoid such biases.

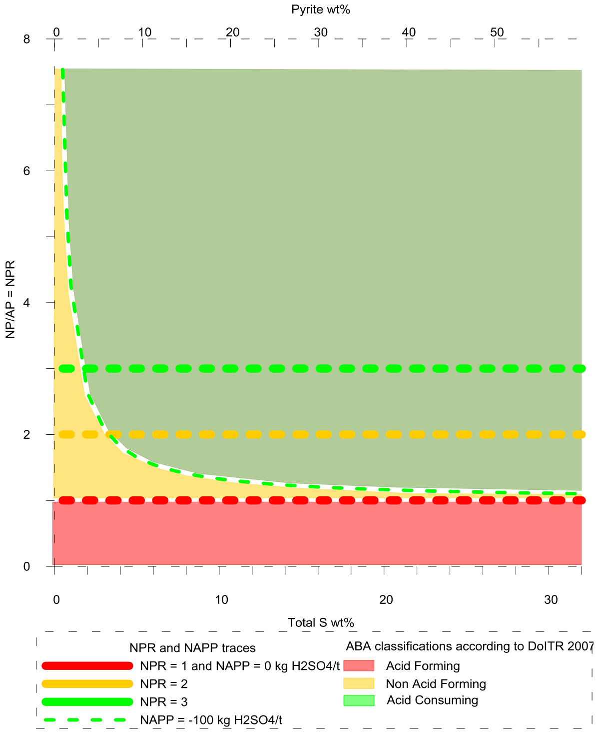

***Figure 1*** *Comparison of classification criteria using NP/AP ratios (NPR) vs. difference (NAPP or NNP).*

Some influences under field conditions on non-stoichiometric reaction of NP with AP are mentioned in guidelines, although they generally focus on mineral reactions, rather than the physical characteristics of the mine water system. These mineralogical factors include considerations such as occlusion, armouring, differences in mineral reactivity, preferential leaching, solid solution properties, etc.

In open systems, outflowing mine discharge waters, affected by ARD that has reacted with carbonate minerals, can contain high concentrations of mobilised alkalinity (up to several hundred mg/L, with pH commonly >7). This dissolved alkalinity may account for a significant proportion of available alkalinity (theoretically up to 50%), implicit in pH dependent speciation of carbonate between $CO_3^{2-}$, $HCO_3^-$ and $H_2CO_3$ (Evangelou, 1998). The $fCO_2$ is a controlling variable with respect to carbonate solubility; dissolved alkalinity may therefore be transported at higher concentrations than under atmospheric $f\mathrm{CO}_2$ for solutions in equilibrium with carbonate minerals. This is particularly relevant for confined or semi-confined groundwater systems under pressure, but is also relevant in systems with near atmospheric $CO_2$ concentrations (e.g. soil profiles).

Additionally, $Fe^{2+}$ is a common constituent of partially oxidised mine waters, in contact with sulphide minerals, even at neutral pH, with the redox potential often controlled by the $Fe^{2+}/Fe^{3+}$ buffer. In open systems that theoretically contain sufficient NP to neutralise acidity that is generated, acidity released through precipitation of Fe-oxyhydroxides after oxidation of $Fe^{2+}$ by atmospheric oxygen may result in a pH <6 downstream, depending on the composition of the effluent. A schematic diagram illustrating some of the interactions between minerals and dissolved species in a pyrite-calcite driven system is included in Figure . Some aspects of open system behaviour are shown, with solutes being transported away from their site of origin.

Along with the bulk system properties that may influence the acid-base balance in open systems, aspects such as flow paths and material location can play an important role in preferential leaching of alkalinity or acidity. In high recharge environments rainfall may also leach a significant amount of available alkalinity from a waste profile, depending on mineral solubility, flow dynamics and the composition of rainwater.

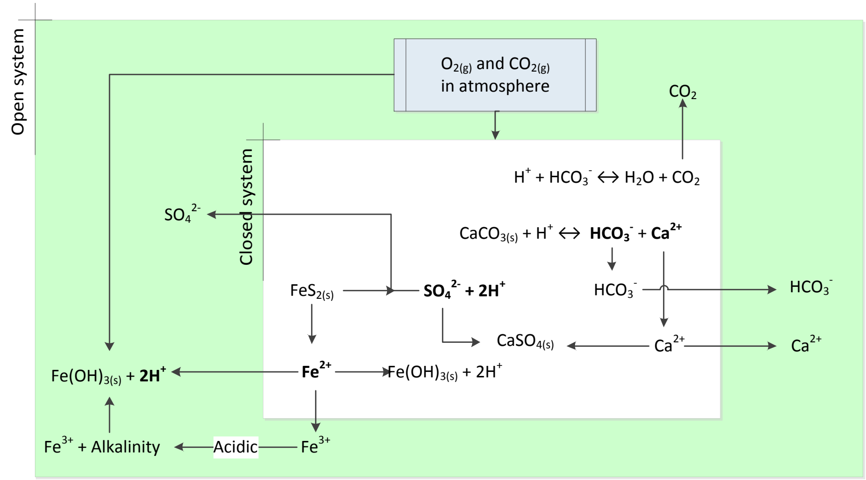

***Figure 2*** *A simplified schematic diagram illustrating the evolution of a pyrite-calcite reaction, showing closed system and open system aspects.*

## Conclusions

Static geochemical test methods generally only provide approximate results, the accuracy of which is strongly influenced by mineralogy. It is important to be aware of these uncertainties when using these methods, as erroneous conclusions can easily be reached by following guideline "criteria" without verifying the results.

Discrepancies between classification criteria, e.g. using NPR vs NAPP, can also lead to very different classifications, depending on the sulphur content of the sample. The NAPP system, although based on empirical laboratory data, should perhaps be reviewed on the basis that it penalises waste materials containing low sulphur concentrations excessively and provides excessive confidence in the neutralising capacity of high sulphur samples.

The representativeness of test data must be verified for each rock type and each test before it is, considered as definitive. This observation is particularly relevant when developing material management strategies based on geological block model total elemental geochemistry data. Since elemental abundance does not necessarily correlate with a single mineral, and thus reactivity and leaching potential, major miscalculations can be made if geochemical test data are not evaluated correctly or inappropriate tests are used for “calibration”.

In addition to uncertainties associated with static test methods, the context of the project environment should be considered when interpreting static test data and should bear in mind that open systems may behave differently to closed systems represented by static test results. This is particularly important for “flow-through” sites where carbonate minerals react with AMD, with subsequent loss of alkalinity that may otherwise prevent acidification if it were retained within the system.

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