A Review of Static Tests and Recent Studies

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Abstract: Problem statement: Acid mine drainage from waste rocks, tailings and other mine components, is one of the most important environmental concerns at mining sites. To attempt to determine the balance between the acid and neutralization potentials of the material and evaluate the possible acid-forming potential of mine waste, many static prediction tests have been developed to evaluate the acid-forming potentials of samples in recent years. Approach: This study attempts to highlight and summarize their essential issues and collates the mining projects that have used such static tests. Results: The advantages and disadvantages of each technique are compared to formulate and present guidelines for the appropriate selection and application of these tests. According to many studies, although several test methods have been modified in recent years, the ABA, NAG and paste pH methods are the most commonly static tests reported for initially indicating the acid-generating and neutralizing potential of samples. Conclusion/Recommendations: To provide confident acid-forming predictions and consequently, the best waste management plans, at least several different techniques needs to be applied together in order to classify the acid generating potential of a sample more reliably.

Key words: Acid-forming potential, neutralization potential, acid mine drainage, mining areas, Acid Mine Drainage (AMD), sulfide minerals, Modified Acid Base Accounting (MABA), Acid Buffering Characteristics Curve (ABCC), acid-forming potentials, acid generation

INTRODUCTION

Mining industries are associated with Acid Mine Drainage (AMD), which is formed when sulfide minerals are oxidized on exposure to air and water in mine areas. The resultant acidification of the water from sulfur oxidation, coupled with oxidation itself, can lead to both chemical and microbial release of other pollutants and so mining areas can contain relatively high levels of toxic substances, such as cyanide, sulfate and potentially toxic heavy metals (i.e., Pb, Zn, Cu, Cd, Fe, Mn and Al), which can pose adverse long-term impacts on animals, human health and ecosystem degradation (Ardejani et al., 2010; Liang-qi et al., 2010; Perez-Lopez et al., 2007; Silvia and Zanetti, 2009; Unruh et al., 2009). Under an AMD situation, the release of such toxic substances can severely pollute the soil, surface and ground water systems (Alligui and Boutaleb, 2010; Mossad and Aral, 2010; Oprea et al., 2010; Ouangrawa et al., 2010; Rani and Chen, 2010). Although this process occurs naturally, mining industries may significantly accelerate AMD through disturbing the sulfide mineral and promoting their expose to water and oxygen. Moreover, some bacteria can naturally promote AMD generation, such as Thiobacillus, which is capable of catalyzing iron oxidation at pH levels of 3.5-4.5 (Liang-qi et al., 2010; Jennings et al., 2008). The reactions of acid generation from the oxidation of pyrite (FeS₂), which is one of the most common sulfide minerals and precipitation of Fe hydroxides are shown in Eq. 1-4 below:

\[
\begin{align*}
2\text{FeS}_2 + \frac{7}{2}\text{O}_2 + \text{H}_2\text{O} & \rightarrow \text{Fe}^2+ + 2\text{SO}_4^{2-} + 2\text{H}^+ \\
\text{Fe}^{2+} + \frac{1}{4}\text{O}_2 + \text{H}^+ & \rightarrow \text{Fe}^{3+} + \frac{1}{2}\text{H}_2\text{O} \\
\text{Fe}^{3+} + 3\text{H}_2\text{O} & \rightarrow \text{Fe(OH)}_3(s) + 3\text{H}^+ \\
2\text{FeS}_2 + 14\text{Fe}^{3+} + 8\text{H}_2\text{O} & \rightarrow 15\text{Fe}^{2+} + 2\text{SO}_4^{2-} + 16\text{H}^+
\end{align*}
\] (1)

As shown above, oxygen is an important oxidant of pyrite. The dissolved \( \text{Fe}^{2+} \), \( \text{SO}_4^{2-} \) and \( \text{H}^+ \) represent an increase in the total dissolved solids and acidity of the water and sequentially induce a decrease in the pH.

Due to variations in the mineralogy and geological formations from site-to-site and other factors affecting
AMD generation, predicting the potential for AMD can be exceedingly challenging and costly (USEPA, 1994; Sapsford et al., 2009). Nevertheless, the prediction of AMD plays an important role in planning for mine waste management (Hesketh et al., 2010b) as the control of AMD to prevent or to inhibit acid production, by control of the acid migration or by treatment of AMD, can minimize the risk of any ongoing environmental liability from mining operations. Recently, various techniques have been developed to predict the Acid-Forming Potential (AFP) of mine waste materials, such as geological assessment, geochemical static tests and geochemical kinetic tests (Liao et al., 2007; Komnitsas et al., 2009; Hesketh et al., 2010b). Amongst these techniques, the static tests are popular as they are simple, rapid and inexpensive.

Therefore, this study consists of a brief review of recent static tests, one of the AMD prediction techniques, in the literature by comparing their advantages and disadvantages and the reagents used in each technique. The study also attempts to summarize recent studies in acid-forming prediction using static tests in mine sites between 1998 and early 2010.

**Acid generation prediction technique: Static tests**

Static tests are usually measured over a short time period of hours or days and are relatively low cost. They evaluate the balance between the acid generating and acid neutralizing capacity of a sample. Seven techniques are reviewed in this study, which determine the sample’s maximum Acid Production Potential (APP) with its maximum Neutralization Potential (NP). These seven methods are (i) Acid-Base Accounting (ABA), (ii) Modified ABA (MABA), (iii) paste pH, (iv) Net Acid Generation (NAG), (v) Sequential NAG test (SNAG), (vi) Kinetic NAG test (KNAG) and (vii) Acid Buffering Characteristics Curve (ABCC) test (Ehinola and Adene, 2008; Komnitsas et al., 2009; Hesketh et al., 2010b; Huges et al., 2007; Miller et al., 1991; Pope et al., 2010; Shu et al., 2001; Weber et al., 2004). Each test uses separate methods to evaluate the capacity for acid generation and neutralization.

The assumption of static tests is the instant of acid production and neutralization potential. These tests are not used to predict the rate of acid-generating and acid-consuming minerals, but are only used for prediction of the APP. However, despite this limitation, static tests are quick and economical to perform and additionally have been reliably used as a tool for the evaluation of the AFP in mining areas in recent years. The seven selected static tests mentioned above are described as follows.

**Acid-Base Accounting (ABA) method:** The ABA test was developed in 1974 to evaluate coal mine waste and later was modified by Sobek et al. (1978). In the main, the ABA test has been applied in the United States and Canada. ABA methods are widely applied as a screening procedure for classifying samples according to their predicted AFP. The Maximum Potential Acidity (MPA) is determined from multiplication of the total sulfur contents by 30.59 (Bester and Vermeulen, 2010), which of course assumes that all of the sulfur present is reactive (i.e., pyritic sulfur). The Acid-Neutralization Capacity (ANC) was determined by a modified Sobek method (Sobek et al., 1978). Here, Hydrochloric Acid (HCl) is added to the sample and then boiled until the reaction stops. The resulting cooled solution is back titrated to pH 7 with NaOH to determine the amount of acid remaining and from this the amount of acid consumed in the reaction between HCl and the sample is deduced. A fizz test rating of the neutralization potential is used to select the HCl strength.

In Australia the ABA test is determined as the net acid producing potential (NAPP). This value is determined by subtracting the ANC from the MPA and is a measure of the difference between the NP and the AFP (Bester and Vermeulen, 2010). The NAPP is expressed in the units of kg H2SO4/t of sample (Weber et al., 2004) and may be either negative or positive. The NAPP and/or the ratio of acid-NP to APP, is then compared with criteria values of classification to divide samples into categories. Materials with sulphide minerals, which have a NAPP (MPA-ANC) value of higher than 20 are likely to be an acid drainage source.

**Advantages:**

- It is a simple technique, takes a short time to perform, requires no special equipment, is easy to interpret and many samples can be tested (Bradham and Caruccio, 1990)
- It is relatively inexpensive and with a relatively high throughput can be used for processing large sample numbers

**Disadvantages:**

- The total sulfur is evaluated by Leco furnace, which measures all sulfur-bearing forms, including sulfides, sulfates and the organic sulfur in the sample. So, the MPA in the sample may be over-estimated. Thus, there is the need to determine the organic sulfur, sulfate, sulfur and pyritic sulfur
separately so as to be able to estimate the APP of each sample

- This method does not account for a kinetic rate (Bradham and Caruccio, 1990)
- If the MPA and ANC values are close, it is hard to interpret (Deopker and O'Connor, 1991)
- Different particle sizes are not reflected (Deopker and O'Connor, 1991)
- The ANC is affected by Fe carbonates, such as siderite (FeCO_3) and its presence may result in over estimation of the effective acid neutralization mineral content in that sample

**Modified Acid Base Accounting (MABA) method:**

(Ehinola and Adene, 2008). This MABA method calculates the MPA based on the sulfide content, which is different from the total sulfur analyzed in the ABA test above in that the sulfur contribution from non-sulfide sources is excluded. The ANC is determined by using a longer (24 h) acid digestion at room temperature. Then, the sample is back titrated with sodium hydroxide to determine the acid consumed in the digestion, but with an endpoint of pH 8.3 instead of the pH 7 used in the ABA method.

**Advantages:** It is a simple technique, takes a short time, requires with no special equipment, is easy to interpret and many samples can be tested (Bradham and Caruccio, 1990).

**Disadvantages:**

- This method does not account for a kinetic rate (Bradham and Caruccio, 1990)
- If the MPA and ANC values are close, it is hard to interpret (Deopker and O'Connor, 1991)
- Different particle sizes are not reflected (Deopker and O'Connor, 1991)
- If jarosite or other acid producing sulfate minerals is present, this test may underestimate the available MAP (USEPA, 1994)

**Paste pH method:** The paste pH method is used to measure a mixture of soil and deionized water that form a slurry or paste together (Pope et al., 2010). The air-dried sample is mixed with deionized water at a 1:1 (w/w) ratio and the pH is then measured with a pH meter, calibrated at pH 4.00-7.00. Commonly, the paste conductivity, redox potential and Total Dissolved Solid (TDS) contents are also measured simultaneously with the paste pH. Samples with a paste pH of less than 4.0 are considered as potentially APP.

**Advantages:**

- It is relatively inexpensive and can be used to assay a large amount of samples
- It is a simple and common field and bench scale test
- It takes a short time (ca. 15 min.) to determine the acid generation (Pope et al., 2010; Hughes et al., 2007)

**Disadvantages:**

- This method does not account for a kinetic rate (Bradham and Caruccio, 1990; Nugraha et al., 2009)
- This method needs to be combined with other techniques for estimating the acid-forming potential (Hughes et al., 2007)

**Net Acid Generation (NAG) or net acid production test:** In the NAG test, hydrogen peroxide (H_2O_2) is used to accelerate the oxidation of sulfide (Saria et al., 2006; Nugraha et al., 2009). The reaction generates both acid and acid neutralization simultaneously. The final result represents the net acidic amount generated by the sample. This test differs from the ABA method described above in that it does not determine separately both the MPA and ANC, but rather determines a single value, NAPP.

To determine the NAG, 2.5 g of sample is oxidized by suspension in 250 mL of 15% (v/v) H_2O_2, placed inside a fume hood for 24 h and then boiled for 1 h. After cooling to ambient temperature, the final NAG pH is then measured and titrated using 0.1 mol/l NaOH to pH 4.5 and pH 7. The NAG is calculated in terms of kg H_2SO_4/t of sample (Shu et al., 2001). Commonly, a NAG pH of less than 4.5 indicates the sample is acid producing and the amount of acid is determined by back-titration and expressed in terms of kg H_2SO_4 /t of sample, similar to the ABA technique.

The NAG and ABA tests are usually used together to classify the acid generating potential of a sample (Hesketh et al., 2010b; Nugraha et al., 2009).

**Advantage:** This test is relatively inexpensive for determination and can be applied to a large numbers of samples.
**Disadvantage:** The complete decomposition of H$_2$O$_2$ in the test may occur before all the reactive sulfides have oxidized. Subsequently, the acidity potential may underestimate the APP. Therefore, the use of the NAG test alone may not reveal the actual total APP of samples (USEPA, 1994).

**Sequential NAG test (SNAG):** The SNAG test was developed to overcome the effect of the incomplete oxidation of sulphide, which typically occurs when the pyritic sulfur content is greater than 0.7-1% of the total sulfur content and simply involves a series of additions of 15% (v/v) H$_2$O$_2$ to the same sample. At the end of each NAG test stage, the mixture sample is filtered and then the NAG pH and titrated acidity are measured. The NAG test is then repeated in the same manner until the NAG pH is $\geq$ 4.5. All of the individual NAG acidities are summed to estimate a total SNAG acidity in the terms of kg H$_2$SO$_4$/t of sample. Then, the SNAG solutions are filtered, pooled and made up to the original 250 ml with deionized water in order to account loss by evaporation, prior to being analyzed for sulfur content by ICP-OES (Hesketh *et al.*, 2010a).

**Advantages:**

- It provides a better estimation of the total APP of samples than the NAG test
- It provides a snapshot of the balance between the acid production and acid neutralization during the procedure

**Disadvantage:** It takes a much longer time than the NAG test.

**Kinetic NAG test (KNAG):** The KNAG test is applied to evaluate the lag time that may be experienced by any given material type before acid generation begins. To carry out the KNAG test, 250 mL of 15% (v/v) H$_2$O$_2$ is added to the sample (1 g) and the pH and temperature of the NAG liquor are monitored throughout the test. The Electrical Conductivity (EC) of the NAG liquor may also optionally be monitored.

**Advantage:** It can evaluate the lag period and oxidation rates as with leached column tests but in a shorter time.

**Disadvantages:**

- It takes a much longer time than the NAG test
- Samples in which pyrite armoring inhibits the oxidation under leach column conditions result in longer column lags than those estimated by the KNAG test
- Samples with a neutralizing phase of low reactivity, which are not ready for acid buffering in the short period of NAG tests but are available in the longer time in column tests, consequently yield longer column lag times than those predicted by the KNAG technique

**Acid Buffering Characteristics Curve (ABCC):** The ABCC test is an alternative to the ANC procedure, but takes a longer time to complete than the ANC test and involves a slow titration of a given sample with continuous monitoring of the pH values. The shape of the acid ABCC profile provides an indication on the availability for acid neutralization. When ANC values affected by siderite, the ABCC will show very shape drop with sequential acid additions. The test can be carried out as follows: the addition of water to the sample at a 2% (w/v) ratio and then the slow titration with HCl with continuous stirring until the mixture reaches pH 3. The volume and concentration of HCl at each addition is varied according to set ANC ranges and the time of successive additions is kept constant at approximately 15 min. High HCl volumes and concentrations are added for high ANC samples and low HCl volumes and concentrations are used for low ANC samples.

**Advantage:** 1. The ABCC test results effectively provide an indication of the relative resistivity of the ANC measured in waste rock samples, something not evident in ANC test results alone (i.e., Siderite).

**Disadvantage:** It takes a longer time per sample than the ANC method.

**AFP prediction using static tests in recent studies:** Evaluation of the AFP has been developed and applied for many mine projects throughout the world. A summary of the recent studies of AFP prediction using static tests is shown in Table 1.
Table 1: The mining sites used the static test methods to characterized the APP (Modified from Samuel, 2006)

<table>
<thead>
<tr>
<th>Site or Project</th>
<th>Location</th>
<th>Method</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pb - Zn mine at Lechang</td>
<td>Guangdong, People’s Republic of China</td>
<td>ABA, NAG test</td>
<td>Wong et al. (1998)</td>
</tr>
<tr>
<td>New Zealand coal mine</td>
<td>New Zealand</td>
<td>Paste pH, ABA</td>
<td>Campbell et al. (2001)</td>
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<td>INAP Rock Pile</td>
<td>Papua</td>
<td>ABA, NAG kinetic and sequential NAG</td>
<td>Rumble et al. (2003)</td>
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<tr>
<td>Ok Tedi Mine</td>
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<tr>
<td>Kaltim Prima Coal mine</td>
<td>Samarinda, Kalimantan, Indonesia</td>
<td>Paste pH, ABA and kinetic NAG</td>
<td>Weber et al. (2004)</td>
</tr>
<tr>
<td>Coal mine (Three pit mine dumps: FD, ND, OD)</td>
<td>Berau, East Kalimantan, Indonesia</td>
<td>ABA and NAG</td>
<td>Saria et al. (2006)</td>
</tr>
<tr>
<td>Questa molybdenum mine</td>
<td>Taos County, North central New Mexico</td>
<td>Paste pH, ABA, NAG</td>
<td>Samuel (2006)</td>
</tr>
<tr>
<td>Prestea and Bogoso mines</td>
<td></td>
<td></td>
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<tr>
<td>17 mine sites</td>
<td>Provinces of Guangdong, Hunan, Gansu and Shanxi, China</td>
<td>Paste pH, NAG</td>
<td>Liao et al. (2007)</td>
</tr>
<tr>
<td>Stockton coal mine</td>
<td>South Island, New Zealand</td>
<td>Paste pH, ABA</td>
<td>Hughes et al. (2007)</td>
</tr>
<tr>
<td>Nigeria coal mine</td>
<td>Benue, Nigeria</td>
<td>Modified ABA</td>
<td>Ehinola and Adene (2008)</td>
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<tr>
<td>Akara gold mine</td>
<td>Pichit Province, Thailand</td>
<td>ABA and NAG</td>
<td>Changul et al. (2009)</td>
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<tr>
<td>PT. Kaltim Prima Coal (KPC)</td>
<td>Sengata-East Kalimantan, Indonesia</td>
<td>ABA, NAG and Paste pH</td>
<td>Nugrah et al. (2009)</td>
</tr>
<tr>
<td>Atikokan coal mine</td>
<td>Northwestern Ontario</td>
<td>ABA</td>
<td>Yehneys et al. (2009)</td>
</tr>
<tr>
<td>Waterberg coal mine</td>
<td>Limpopo Province, South Africa</td>
<td>ABA</td>
<td>Bester and Vermeulen (2010)</td>
</tr>
<tr>
<td>Copper mine</td>
<td>South Africa</td>
<td>ABA and NAG</td>
<td>Hesketh et al. (2010b)</td>
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<tr>
<td>Brunner, Paparoa, Morley Coal and Gore Lignite Measures</td>
<td>West Coast and Southland, New Zealand</td>
<td>ABA, NAG and Paste pH</td>
<td>Pope et al. (2010)</td>
</tr>
</tbody>
</table>

CONCLUSION

There are many static tests for characterizing the potential acid-forming prediction in mining sites. The commonly applied static tests yield information about the acid-forming generation and acid neutralization of samples. In recent years many techniques have been developed but deciding which are the most appropriate for any given number or type of samples requires taking into consideration many factors, including the geochemical and mineralogical characterization of the samples collected from the sites. Although many techniques have been developed, no single technique is ideal or likely to be accurate, but rather each technique needs to be used together with others to obtain a more reliable estimate of the acid generating potential of a sample. The KNAG test could be applied to evaluate the rate of the oxidation reaction of AMD with a shorter time, as compared with leached column tests.

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REFERENCES


