EVALUATION OF NEUTRALIZATION POTENTIAL DETERMINATIONS FOR METAL MINE WASTE AND A PROPOSED ALTERNATIVE

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Abstract: Standard acid-base accounting (standard ABA), modified ABA, and B.C. Research initial static tests tended to overestimate the neutralization potential (NP) present as calcium carbonate and magnesium carbonate, with the extent of overestimation depending on the minerals present in the 10 metal-mine wastes examined. For 6 of the 10 samples the static test NP values were within about 10 kg/mt CaCO₃ of the calculated mineralogic NP. These samples were composed largely of quartz and sheet silicates (mica, chlorite, kaolinite, montmorillonite). The excess acid neutralization measured for these samples was apparently due to the presence of some (less than 10%) calcium feldspar in the samples. For the standard ABA and modified ABA methods, the NP overestimation was higher (13 to 47 kg/mt CaCO₃) for samples containing larger amounts of calcium feldspar, pyroxene, olivine, or iron carbonate minerals. The extent of overestimation for the B.C. Research initial NP was typically slightly higher than the standard ABA and modified ABA and was greatest for samples containing iron carbonate. The maximum overestimations by the standard ABA, modified ABA, and B.C. Research initial test NP values were 33, 31, and 49 kg/mt CaCO₃, respectively. A newly proposed method of NP determination, NP available above pH 6, was more accurate than these three methods. Six of the 10 NP values determined by this method were approximately equal to the mineralogic NP values. For the remaining 4 samples, this NP was within 3 kg/mt CaCO₃ of the mineralogic NP.

Additional Key Words: acid mine drainage, prediction, static tests, mine waste characterization.

Introduction

The quality of mine waste drainage is the net result of dissolution of the minerals present in the mine waste. Acid is produced as the result of oxidation of iron sulfide minerals such as pyrite and pyrrhotite.

\[
\text{FeS}(s) + (3/2)\text{H}_2\text{O} + (9/4)\text{O}_2(g) = \text{FeOOH}(s) + 2\text{H}^+(aq) + \text{SO}_4^{2-}(aq) \quad (1)
\]

\[
\text{FeS}_2(s) + (5/2)\text{H}_2\text{O} + (15/4)\text{O}_2(g) = \text{FeOOH}(s) + 4\text{H}^+(aq) + 2\text{SO}_4^{2-}(aq) \quad (2)
\]

The most effective minerals for neutralizing (consuming, buffering) acid are those containing calcium carbonate and magnesium carbonate, examples of which are calcite, magnesite, dolomite, and ankerite (CaCO₃, MgCO₃, CaMg(CO₃)₂, and CaFe(CO₃)₂, respectively). Reactions 3 and 5 are dominant above approximately pH 6.3, while reactions 4 and 6 are dominant below this pH. The rate of magnesium carbonate dissolution is reported to be slower than that of calcium carbonate (Rauch and White 1977). Iron carbonates will provide no net neutralization of acid.

\[
\text{CaCO}_3(s) + \text{H}^+(aq) = \text{HCO}_3^-(aq) + \text{Ca}^{2+}(aq) \quad (3)
\]

\[
\text{CaCO}_3(s) + 2\text{H}^+(aq) = \text{H}_2\text{CO}_3(aq) + \text{Ca}^{2+}(aq) \quad (4)
\]

\[
\text{MgCO}_3(s) + \text{H}^+(aq) = \text{HCO}_3^-(aq) + \text{Mg}^{2+}(aq) \quad (5)
\]

\[
\text{MgCO}_3(s) + 2\text{H}^+(aq) = \text{H}_2\text{CO}_3(aq) + \text{Mg}^{2+}(aq) \quad (6)
\]
Dissolution of minerals such as anorthite (reaction 7, Busenberg and Clemency 1976) and forsterite (reaction 8, Hem 1970) can also neutralize acid, but their dissolution rate (and associated rate of acid neutralization) is slow in the neutral pH range. These minerals dissolve more rapidly as pH decreases and, therefore, provide more acid neutralization under acidic conditions.

\[
\text{CaAl}_2\text{Si}_2\text{O}_8(\text{s}) + 2\text{H}^+(\text{aq}) + \text{H}_2\text{O} = \text{Ca}^{2+}(\text{aq}) + \text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4(\text{s})
\]  
(7)

\[
\text{Mg}_2\text{SiO}_4(\text{s}) + 4\text{H}^+(\text{aq}) = 2\text{Mg}^{2+}(\text{aq}) + \text{H}_4\text{SiO}_4(\text{aq})
\]  
(8)

Several static tests have been developed to estimate quickly and inexpensively if a mine waste will produce acidic drainage (Ferguson and Erickson 1987). The results are commonly used as a first-cut screening in the process of mine waste characterization. Standard acid-base accounting (standard ABA, Sobek et al. 1978), modified acid-base accounting (Lawrence 1990), and B.C. Research initial tests (Duncan and Bruynesteyn 1979) determine the maximum potentials for acid production (acid production potential or APP) and acid neutralization (neutralization potential or NP). The APP is based on sulfur analysis, and the NP is determined by the amount of acid neutralized when the sample is in contact with a solution in the approximate pH range of 1 to 3.5. Whether or not a mine waste will produce acidic drainage is determined by the difference (net NP) or ratio (NP/APP) of these values. Additional information on static testing is presented in Lapakko (1992a).

Technology for determination of sulfur species present in the solid phase is adequate to determine the maximum potential of a mine waste to produce acid. However, Lutwick (1986) contended that static tests overestimate NP available to maintain an environmentally acceptable drainage pH, owing to acid neutralization by host rock components under the strongly acidic conditions created in the NP determination. Lapakko and Antonson (1991) reported that the pH of drainage from a sample of Duluth Complex rock decreased below 6.0 after an NP depletion of only 0.5 kg/mt CaCO₃, considerably less than the 11 kg/mt CaCO₃ neutralization potential determined by standard ABA (Sobek et al. 1978). Apparently dissolution of plagioclase, pyroxenes, and olivine present in the host rock neutralized acid at low pH in the NP "digestion" but, during dissolution simulating that in the environment, the rate of acid neutralization was too slow to maintain drainage pH above 6.0. For similar reasons standard ABA (Sobek et al. 1978) overestimated the NP present as calcium carbonate and magnesium carbonate, or mineralogic NP, in 10 gold mine tailings (Lapakko 1992b). Inadequate quantification of ferrous iron acidity during the titration step may have further contributed to the overestimation of NP for a sample containing a large amount of siderite (FeCO₃). The modified ABA (Lawrence 1990) was reasonably accurate in quantifying the mineralogic NP of these samples.

Errors in NP measurement may result in the erroneous classification of acid-producing waste as non-acid producing, thereby creating an unexpected environmental liability. In such cases, the method of NP determination proposed in the present study may provide a more accurate mine waste assessment. Given the increased use of these tests for metal mine waste characterization and the potential magnitude of mine waste financial liabilities, this accuracy must be considered.

Objectives

The objective of this study was to assess the accuracy of NP measurements by standard ABA, modified ABA, and B.C. Research initial static tests. An alternative method for determining NP was also proposed, and its accuracy was evaluated.
Methods

Materials

Four waste rock samples, identified as RK1 to RK4, and six tailing samples, identified as TL1 to TL6, were collected for testing. The mine waste samples were split into different subsamples for subsequent chemical and mineralogical analyses, as well as static testing. The splitting procedure (ASTM E877-82) was tested by determining the sulfur (ASTM E395 using a Dietert furnace) and carbon dioxide contents (ASTM E350-89C) of three sample splits, to ensure uniformity of the samples generated. The standard deviations for the sulfur and carbon dioxide determinations on the triplicate splits ranged from 0 to 6.8% of the mean value, except for the carbon dioxide content of sample TL4 (17%, Table 1).

Table 1. Sulfur, carbon dioxide, and mineral content (wt %) and mineralogic NP (kg/mt CaCO₃).

<table>
<thead>
<tr>
<th></th>
<th>RK-1</th>
<th>RK-2</th>
<th>RK-3</th>
<th>RK-4</th>
<th>TL-1</th>
<th>TL-2</th>
<th>TL-3</th>
<th>TL-4</th>
<th>TL-5</th>
<th>TL-6</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sulfur</td>
<td>0.46</td>
<td>0.64</td>
<td>1.63</td>
<td>2.91</td>
<td>0.96</td>
<td>1.49</td>
<td>2.19</td>
<td>2.30</td>
<td>5.05</td>
<td>5.81</td>
</tr>
<tr>
<td>SD²</td>
<td>0.012</td>
<td>0.006</td>
<td>0.111</td>
<td>0.055</td>
<td>0.040</td>
<td>0.012</td>
<td>0.025</td>
<td>0.071</td>
<td>0.308</td>
<td>0.379</td>
</tr>
<tr>
<td>CO₂</td>
<td>0.11</td>
<td>0.03</td>
<td>1.41</td>
<td>1.42</td>
<td>0.87</td>
<td>0.80</td>
<td>0.46</td>
<td>0.25</td>
<td>0.65</td>
<td>2.01</td>
</tr>
<tr>
<td>SD</td>
<td>0.006</td>
<td>0.015</td>
<td>0.095</td>
<td>0.045</td>
<td>0.031</td>
<td>0.047</td>
<td>0.104</td>
<td>0.038</td>
<td>0.023</td>
<td>0.078</td>
</tr>
<tr>
<td>Quartz</td>
<td>24</td>
<td>-</td>
<td>41</td>
<td>34</td>
<td>38</td>
<td>53</td>
<td>42</td>
<td>45</td>
<td>21</td>
<td>12</td>
</tr>
<tr>
<td>Feldspar</td>
<td>24</td>
<td>54</td>
<td>29</td>
<td>29</td>
<td>39</td>
<td>30</td>
<td>12</td>
<td>13</td>
<td>52</td>
<td>5</td>
</tr>
<tr>
<td>Mica</td>
<td>6</td>
<td>4</td>
<td>12</td>
<td>4</td>
<td>14</td>
<td>10</td>
<td>10</td>
<td>30</td>
<td>10</td>
<td>2</td>
</tr>
<tr>
<td>Calcite</td>
<td>?</td>
<td>.1</td>
<td>.5</td>
<td>-</td>
<td>1.5</td>
<td>.7</td>
<td>.2</td>
<td>.6</td>
<td>-</td>
<td>4.6</td>
</tr>
<tr>
<td>Dolomite</td>
<td>?</td>
<td>-</td>
<td>-</td>
<td>3.0</td>
<td>.4</td>
<td>.8</td>
<td>-</td>
<td>-</td>
<td>1.10</td>
<td>-</td>
</tr>
<tr>
<td>Ankerite</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>1.9</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Siderite</td>
<td>.3</td>
<td>-</td>
<td>3.2</td>
<td>-</td>
<td>-</td>
<td>.2</td>
<td>8.3</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Rhodochrosite</td>
<td>-</td>
<td>-</td>
<td>?</td>
<td>&lt;1</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Magnesite</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>.23</td>
<td>-</td>
</tr>
</tbody>
</table>

Mineral NP | 0 | 1 | 5 | 32 | 19 | 16 | 19 | 5 | 12 | 46 |
Error Int.³ | 0-2.9 | 0-2.3 | 1.9-9.7 | 28-37 | 17-23 | 13-21 | 8.1-33 | 3.7-6.6 | 9.8-17 | 35-52 |

? indicates probably present but not positively identified by XRD.
- indicates mineral not present.
1 Trace amounts of copper carbonates were noted in TL-2.
2 SD standard deviation.
3 Error bar for mineralogic NP.

Silica and major metal components were extracted using borate fusion and analyzed using direct current plasma. The carbon dioxide content of the samples was used to determine the total carbonate mineral content. The carbonate minerals present were identified by X-ray diffraction (XRD, Phillips), and checked by scanning electron microscopy (Amray model 1200B) and energy dispersive spectroscopy (Noran Instruments model 2010). For some samples, optical microscopy (standard Zeiss petrographic microscope) was used for additional verification. Heavy mineral concentrates were separated using a Haultain Superpanner (Infrasizers Ltd.) and analyzed by XRD. These results were used to ascertain the presence of small amounts of siderite. The relative amounts of carbonate minerals present were determined by interpretation of the major peak heights based on the analyst's twenty years of experience. The potential error in the carbonate mineral determination was estimated as 20%; additional work is planned to further assess the potential error. XRD was also used to determine the amounts of other major minerals present in the samples and a potential 20% error is assumed for the values discussed.
**Static Test Procedures**

The static tests were conducted by consulting firms involved in mine waste characterization. For the standard acid-base accounting (Sobek et al. 1978) determination of neutralization potential (NP), samples were crushed to minus 60 mesh (diameter less than 0.25 mm). Approximately 0.5 g of sample was placed onto a piece of aluminum foil, and one or two drops of 1:3 hydrochloric acid (HCl) was added to the sample. Based on the extent of "fizzing" in this test, a volume and concentration of HCl were selected and added to 2 g of minus 60 mesh mine waste in a flask. The mixture of acid and mine waste was then boiled until the reaction ceased, as indicated by the termination of the production of bubbles. Distilled water was added to attain a total volume of 125 mL, and the contents of the flask were boiled for 1 min and then cooled to room temperature. The mixture was then titrated to pH 7.0 with sodium hydroxide to determine the amount of acid (as CaCO₃) neutralized by the sample. The NP (acid neutralization per unit mass rock) was expressed in units of metric tons CaCO₃ per 1000 metric ton mine waste or, equivalently, kilograms of CaCO₃ per metric ton of mine waste (kg/mt CaCO₃).

For the modified acid-base accounting (Lawrence 1990) determination of neutralization potential, the fizz test was also used to determine the volume and strength of HCl addition to a 2-g sample (minus 60 mesh). The acid-mine waste mixture was digested for 24 h at room temperature, at which time pH was measured. If pH was not in the range of 1.5 to 2.0, the digestion was rerun with an acid addition adjusted, based on the observed pH, until the pH range of 1.5 to 2.0 was attained. After the pH criterion was met, the amount of acid neutralized by the rock was determined by titrating the acid-mine waste mixture with NaOH until a pH of 8.3 was maintained for at least 30 seconds. The NP was then expressed in kilograms of CaCO₃ per metric ton.

The B.C. Research initial test (Duncan and Bruynesteyn 1979) uses different terminology and different units of quantification. The terminology and units were translated to be consistent with those of the standard ABA method for ease of presentation in this paper. The NP was determined by titrating, with 1.0 N sulfuric acid, a stirred mixture of 10 g mine waste (70% minus 325 mesh or, equivalently, 70% of the particles having diameter less than 0.044 mm) and 100 mL distilled water. The titration was continued until pH 3.5 was reached and less than 0.1 mL of acid was added over a period of 4 h. Type 45 AR Chemtrix pH controllers with Cole Parmer electrodes were used for the titration.

The proposed alternative method of NP determination was the same as the B.C. Research initial test, except a titration endpoint of 6.0 was used in the present study rather than 3.5. pH 6 was selected since it is a commonly applied water quality standard. Therefore, the neutralization potential available above this pH represents the amount of acid that a mine waste could neutralize while maintaining drainage pH in a range that meets water quality standards. The test is referred to as the NP available above pH 6, or NP(pH6). Other pH values could also be used, depending on the drainage pH required at a specific site, and an endpoint pH of 5 was also examined in the present study.

**Determination of Neutralization Potential Accuracy**

Assessment of the accuracy of NP values is complicated by the fact that mineral dissolution, and the attendant acid neutralization, is a function of solution pH. To assess the accuracy of the static test NP values, the NP available to maintain a pH above 6.0 was calculated based on sample mineralogy. The mineralologic calculation assumed that the calcium carbonate and magnesium carbonate present in the mine waste samples, and only these minerals, would dissolve to maintain a drainage pH of least 6.0; that is,

\[
\text{Mineralogic NP} = 10 \times (\% \text{CaCO}_3) + 11.9 \times (\% \text{MgCO}_3). \quad (9)
\]

This approach assesses the accuracy of the various methods in determining the mineral content available to maintain a drainage pH of 6. It does not address how much of this neutralization is available nor the rate at which the neutralizing minerals will dissolve.
Error bars for the mineralogic NP values were established by different methods, all of which accounted for error contributed by splitting and determination of total carbon dioxide content. For most of the samples (RK1, RK2, RK4, TL1, TL2, TL4, TL5, TL6) the upper error bar was determined by assigning the maximum potential carbonate content, as indicated by carbon dioxide determination, to neutralizing minerals. The lower error bar for these samples (minimum amount of carbonate occurring with calcium and magnesium) was calculated as the minimum total carbonate content minus the maximum possible carbonate occurring with iron. For all of these samples except TL6, the maximum iron carbonate content was calculated based on the presence of less than 0.5% siderite (i.e. not detected) in the heavy mineral fractions. For TL6 a maximum iron carbonate content of 0.5% in the entire sample was used. For samples containing substantial siderite, RK3 and TL3, a potential 50% error in calcium carbonate and magnesium carbonate analysis was used.

Results

Sample Composition

Chemical and mineralogical analyses indicated the samples displayed a fair degree of compositional diversity. The carbon dioxide content of the 10 mine waste samples ranged from less than 0.1% to 4.1%. The reported calcium carbonate and magnesium carbonate mineral content of the samples ranged from trace amounts to a maximum of 4.6%. Siderite was also present in measurable amounts in four of the samples (table 1). Quartz, feldspar, and mica were the major host rock minerals in all samples except TL-6, in which pyroxene was dominant.

Accuracy of Standard Static Tests

There was good agreement among the NP values determined by the three standard tests for samples RK1, RK4, TL1, and TL2. For samples RK3, TL4, and TL5 the B.C. Research initial test values were roughly 10 to 15 kg/mt CaCO3 higher than the standard ABA and modified ABA values. The variation among the three methods was greatest for samples RK2, TL3, and TL6, with no consistent trend in the relative magnitudes of the three values (table 2). For all samples except TL3 and TL6, there was good agreement between NP values determined by the standard ABA and modified ABA methods.

Table 2. Neutralization potential, kg/mt CaCO3.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Standard ABA</th>
<th>Mod ABA</th>
<th>B.C. Research</th>
<th>Mineralogic NP</th>
<th>Available above pH6</th>
</tr>
</thead>
<tbody>
<tr>
<td>RK1</td>
<td>12</td>
<td>9.6</td>
<td>7.7</td>
<td>0</td>
<td>(0-2.9)</td>
</tr>
<tr>
<td>RK2</td>
<td>35</td>
<td>33</td>
<td>11</td>
<td>1</td>
<td>(0-2.3)</td>
</tr>
<tr>
<td>RK3</td>
<td>15</td>
<td>14</td>
<td>25</td>
<td>5</td>
<td>(1.9-9.7)</td>
</tr>
<tr>
<td>RK4</td>
<td>28</td>
<td>28</td>
<td>33</td>
<td>32</td>
<td>(28-37)</td>
</tr>
<tr>
<td>TL1</td>
<td>27</td>
<td>27</td>
<td>30</td>
<td>19</td>
<td>(17-23)</td>
</tr>
<tr>
<td>TL2</td>
<td>18</td>
<td>20</td>
<td>25</td>
<td>16</td>
<td>(13-21)</td>
</tr>
<tr>
<td>TL3</td>
<td>46</td>
<td>61</td>
<td>82</td>
<td>19</td>
<td>(8.1-33)</td>
</tr>
<tr>
<td>TL4</td>
<td>3.8</td>
<td>2.9</td>
<td>15</td>
<td>5</td>
<td>(3.7-6.6)</td>
</tr>
<tr>
<td>TL5</td>
<td>7.5</td>
<td>3.2</td>
<td>20</td>
<td>12</td>
<td>(9.8-17)</td>
</tr>
<tr>
<td>TL6</td>
<td>99</td>
<td>72</td>
<td>58</td>
<td>46</td>
<td>(35-52)</td>
</tr>
</tbody>
</table>

1 Error bar in parenthesis.

The agreement between the static test NP values and the mineralogic NP was determined based on comparison with the error bars for the mineralogic NP. Samples within or below the error bars were assigned a value of zero, which indicated no error. It was assumed that NP values below the error bar were the result of acidic sulfide oxidation on the sample surface which were not accounted for by the mineralogic NP. The error for
the remaining values was calculated as the difference between the reported NP and the upper mineralogic error bar (table 3).

Table 3. Difference between static test NP and mineralogic NP, kg/mt CaCO₃. The method of calculation is presented in the preceding paragraph.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Standard ABA</th>
<th>Mod. ABA</th>
<th>B.C. Research</th>
<th>Available above pH6</th>
</tr>
</thead>
<tbody>
<tr>
<td>RK1</td>
<td>+9.1</td>
<td>+6.7</td>
<td>+4.8</td>
<td>+0.1</td>
</tr>
<tr>
<td>RK2</td>
<td>+33</td>
<td>+31</td>
<td>+8.7</td>
<td>+0.5</td>
</tr>
<tr>
<td>RK3</td>
<td>+5.3</td>
<td>+4.3</td>
<td>+15</td>
<td>0</td>
</tr>
<tr>
<td>RK4</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>TL1</td>
<td>+4</td>
<td>+4.0</td>
<td>+7</td>
<td>1</td>
</tr>
<tr>
<td>TL2</td>
<td>0</td>
<td>0</td>
<td>+4</td>
<td>0</td>
</tr>
<tr>
<td>TL3</td>
<td>+13</td>
<td>+28</td>
<td>+49</td>
<td>0</td>
</tr>
<tr>
<td>TL4</td>
<td>0</td>
<td>0</td>
<td>+8.4</td>
<td>0</td>
</tr>
<tr>
<td>TL5</td>
<td>0</td>
<td>0</td>
<td>+8.0</td>
<td>0</td>
</tr>
<tr>
<td>TL6</td>
<td>+47</td>
<td>+20</td>
<td>+6</td>
<td>3</td>
</tr>
</tbody>
</table>

The standard ABA and modified ABA NP values were within the mineralogic NP error bars for samples RK4, TL2, TL4, and TL5 (table 3). The major rock-forming minerals in these samples were quartz, feldspar, and mica, although sample RK4 did contain a substantial amount of clay. Examination of the sample chemistry suggests that the feldspar was largely potassium feldspar. The NP values for these two tests were 4 to 10 kg/mt CaCO₃ above the upper mineralogic NP error bar for of samples RK1, RK3, and TL1. Once again the major rock forming minerals present in these samples were quartz, feldspar, and mica, with substantial chlorite and clay also present in sample RK1. The major difference between these samples and the samples mentioned above is that the feldspar is largely calcium feldspar.

The standard ABA and modified ABA NP values were least accurate for samples RK2, TL3, and TL6, exceeding the upper mineralogic NP error bar by 13 to 47 kg/mt CaCO₃. Samples RK2 and TL6 both contained pyroxene (18% and 55%, respectively), and sample RK2 also contained 11% olivine. No other samples contained these minerals. In addition, sample RK2 had the highest feldspar content, most of which was calcium feldspar, of the samples.

As was the case for the standard ABA and modified ABA NP values, the accuracy of the B.C. Research initial test NP for sample RK4 was good. However, on samples TL2, TL4, and TL5 (samples for which the standard ABA and modified ABA NP values were within the mineralogic NP error bars), the B.C. Research initial test NP values were about 4 to 9 kg/mt CaCO₃ higher than the upper mineralogic NP error bar (table 3). The B.C. Research initial NP error was also in this range for samples RK1, RK2, TL1, and TL6. Thus, the accuracy for samples RK1 and TL1 was similar to that for the standard ABA and modified tests, while the B.C. Research initial values were more accurate for samples RK2 and TL6.

The accuracy of the B.C. Research initial NP test was poor for samples RK3 and TL3, exceeding the upper mineralogic NP error bars by 15 and 49 kg/mt CaCO₃, respectively. These samples had iron carbonate contents of 3.2 and 8.7 wt %, respectively. Thus, the B.C. Research initial NP was less accurate than the standard ABA and modified ABA NP tests for samples with elevated iron carbonate contents.

Neutralization Potential Available Above pH 6

With the exception of samples TL3 and TL4, the NP available above pH 6 was lower than that determined by the three commonly applied static tests (table 2). The NP available above pH 6.0 was in good agreement with
the mineralogic NP (table 2). Six of these values were within the mineralogic NP error bars and the remaining four values were within 3 kg/mt CaCO$_3$ of the upper mineralogic NP error bar.

Discussion

The standard ABA and modified ABA NP values were in fairly good agreement, and the B.C. Research Initial NP was slightly higher than these values for most samples. The agreement of the NP values with the mineralogic NP was dependent on both the test and the sample composition. The NP values for the standard ABA and modified ABA were within the mineralogic NP error bars for samples RK4, TL2, TL4, and TL5. The B.C. Research initial NP was typically slightly higher than these values for these samples, with only one value (RK4) within the mineralogic NP error bars. These samples were comprised largely of quartz, feldspar (mostly potassium feldspar), and mica. The presence of these minerals apparently has little effect on the accuracy of the standard ABA and modified ABA NP determination. The smaller particle size used in the B. C. Research initial NP determination may have contributed to the slightly elevated NP values for TL2, TL4, and TL5. The tailings were crushed to minus-300 mesh, as opposed to being run "as received" in the standard ABA and modified ABA NP determinations. The minus-300 mesh fraction comprised roughly 50% of each of the "as received" samples.

For three of the remaining samples the standard ABA and modified NP values were within 10 kg/mt CaCO$_3$ of the upper mineralogic NP error bar. As with the samples for which the NP values were within the mineralogic NP error bars, quartz, feldspar, and mica were the major minerals in these samples. However, the plagioclase was more calcic and the calcic plagioclase apparently neutralized some acid in the static tests. It should be noted that one of these samples (RK-3) contained 3.2 wt % siderite, which apparently contributed little error. For the standard ABA and modified ABA methods, the overestimation was higher yet (13 to 47 kg/mt CaCO$_3$ above the upper mineralogic NP error bar) for samples containing larger amounts of calcium feldspar, pyroxene, olivine (RK2, TL6), or iron carbonate minerals (TL3).

Apparently the pyroxene, olivine, or calcium feldspar present in samples RK2 and TL6 neutralized acid under the low-pH conditions in the NP tests. Whereas dissolution of these minerals can neutralize the acid produced by low-sulfur mine wastes (Lapakko 1988, Lapakko and Antonson 1993, Morin 1993), laboratory experiments and field data indicate that their dissolution may not be capable of maintaining a drainage pH above 6.0 for mine wastes of moderate sulfur content (Lapakko and Antonson 1991, Lapakko 1994). It should be noted, however, that dissolution of these minerals, and the attendant acid neutralization, will generally increase as particle size decreases.

The large discrepancy observed for TL3 was apparently due to interference from iron carbonate. The major rock-forming minerals present in sample TL3 are similar to those present in samples in closer agreement with the mineralogic NP values. However, this sample contained ankerite and siderite which yielded a total iron carbonate content of 8.6 wt % (table 1). The iron carbonate apparently contributed to the excessive static test NP. Such interference could be eliminated by enhancing the ferrous iron oxidation by using a higher endpoint pH, hydrogen peroxide addition during the titration (as prescribed in the ASTM method), or elevating the temperature.

The B.C. Research NP values were within 9 kg/mt CaCO$_3$ for the samples lacking substantial amounts of iron carbonate. This indicates that the pyroxene and olivine present in RK2 and TL6 (and calcium feldspar in RK2) did not dissolve as extensively as in the standard ABA and modified ABA NP tests. The lower pH conditions in the latter tests apparently resulted in the more extensive dissolution of these minerals. The extent of overestimation was considerably higher for samples containing iron carbonate (RK3, TL3). A maximum error of 49 kg/mt CaCO$_3$ above the upper mineralogic NP error bar was observed for a sample containing 8.6% iron carbonate.

This overestimation is likely due to incomplete oxidation of ferrous iron released from the carbonate minerals in the B.C. Research initial test. The B.C. Research initial NP determination involves only an acid addition, as opposed to an acid addition followed by a titration with a base. Oxidation of iron released from the mine waste during the acid addition is slower under the acidic conditions of the B. C. Research initial test, as opposed to the
higher pH conditions during the base titration in the standard ABA and modified ABA tests. Consequently, the B.C. Research initial test measures the acid neutralized by iron carbonate dissolution, but not the subsequent acid generation due to the oxidation of ferrous iron and precipitation of ferric hydroxide.

The newly proposed method, the neutralization potential available above pH 6, consisted of acid titration of a mixture of a mine waste sample and distilled water down to pH 6.0. This approach is designed to conservatively determine the neutralization potential necessary to meet water quality standards which typically require pH in excess of 6. This method yielded NP values which were within the error bars for the mineralogic NP for six of the ten samples and was within 3 kg/m^2 CaCO_3 of the upper mineralogic NP error bar for the four remaining samples. For the ten samples examined, the titration was generally more conservative in determining the neutralization potential available for maintaining drainage pH above 6.0. Although the titration slightly overestimated the mineralogic NP for some samples, the magnitude of this overestimation was less than that for the standard static tests. This technique merits additional examination as a viable technique for determination of neutralization potential.

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References


Lapakko, K. A. 1994. Comparison of Duluth Complex rock dissolution in the laboratory and field. This volume. http://dx.doi.org/10.21000/JASMR94010419

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Morin, K. A. 1993. Telephone conversation with Kevin Morin, Morwijk Enterprises, Vancouver, BC.
