EVALUATION OF ACID GENERATING ROCK AND ACID CONSUMING ROCK MIXING TO PREVENT ACID ROCK DRAINAGE

Stephen J. Day

Abstract: Mixing acid generating and acid consuming rocks is an attractive and potentially low cost alternative for in situ prevention of acid generation in waste rock piles at some mine sites. In addition to the practicalities of day-to-day management of mixed waste rock piles, the success of the mixing will probably depend on the proportion of acid-consuming material, the availability of the acid consuming minerals, and the intimacy of mixing. A 5-yr column study for the Cinola Gold project, an epithermal gold deposit located in a cool, moist maritime area of northwestern British Columbia, Canada, was initiated in 1988 to evaluate limestone requirements to prevent acid and metal release from waste rock stockpiles. Limestone content in five columns varied from zero (control, net neutralization potential = -58 kg/mt CaCO₃) to 6.6% (NNP = 7 kg/mt CaCO₃). Four of the columns generated acid. The column containing the highest concentration of limestone did not release acid, although residues in the upper part of the column were acidic and sulfate concentrations in leachate were gradually increasing. It was concluded that (1) the actual quantity of limestone required to prevent acid drainage in perpetuity would probably be at least twice that determined by conventional acid-base accounting, (2) limestone availability was not reduced by ferric hydroxide coatings, (3) the time required for marginally acid generating rock to release acidity increased exponentially as the quantity of limestone increased, and (4) the time required for zinc release to begin increasing was linearly proportional to the neutralization potential. Limestone addition was therefore highly effective in delaying acid release but was less effective in delaying zinc release.

Additional Key Words: acid rock drainage, waste rock, alkaline addition.

Introduction

Many potentially economic mineral deposits contain high concentrations of iron sulfides and therefore waste rock, mine workings and tailings associated with such deposits are prone to acid generation. However, a significant number of deposits also have associated acid consuming minerals in the mineralization or nearby host and country rocks. In some situations, the possibility of mixing acid generating and acid consuming rocks is an attractive and potentially low cost alternative for in situ prevention of acid generation. When correctly engineered, mixing (or blending) may yield a long term waste management solution without the long term liability and maintenance of artificial structures such as dry covers, artificially flooded impoundments, or water treatment plants.

This paper presents results for a 5-yr column leaching study conducted on marginally acid-generating materials. The study was initiated by City Resources (Canada) Inc. to evaluate the inhibition of acid generation by adding limestone to stockpiles of potentially acid-generating rock at the proposed Cinola Gold Project in northwestern British Columbia (BC). The limestone is not naturally available at the site but is found on an island off BC.

General Background

A number of uncertainties remain regarding design of mixed rock waste piles. Although some of these uncertainties relate to the practicalities of day-to-day management of such piles under operating conditions, a more
fundamental issue relates to the amount of neutralizing material required to effectively consume acid produced by oxidation of iron sulfides.

The commonly used acid-base accounting procedure represented one of the first attempts to determine an acid producing-consuming balance in heterogeneous materials (Sobek et al. 1978). The theory was based on the assumption that neutralizing minerals (represented by calcium carbonate) are consumed completely to release carbon dioxide (gaseous or dissolved). In reality, the initial phases of acid generation occur under approximately pH-neutral conditions and carbonates neutralize acid incompletely, forming the bicarbonate ion (\( \text{HCO}_3^- \)). In natural rock mixtures, other considerations arise, such as the heterogeneous distribution of sulfide and carbonate minerals, the slow dissolution of carbonate minerals in the absence of acid, and the coating of carbonate grains by precipitated hydroxides. In recognition of these uncertainties, regulators in some jurisdictions (for example, California and British Columbia) require that blended rock mixtures at metal mines contain at least three times as much neutralizing material as acid generating material (both expressed in equivalent concentration units of calcium carbonate). Some support for these requirements can be found in the data from coal mines in the eastern United States which indicate that the ratio of neutralization potential to potential acidity in waste rock should be at least 2.4 to ensure acid is not released (Cravotta et al., 1990).

One of the difficulties in determining acceptable mixing ratios is that results from laboratory and field tests tend to be inconclusive. The success of a mixing approach is shown by the lack of acid generation. The problem is that most tests are not continued to a definitive end point which indicates that acid will not be produced. Ferguson and Morin (1991) showed that the time for acid to be produced increases exponentially as the ratio of neutralization potential (NP) to maximum potential acidity approaches 1. Any experiment designed to address marginal acid generating conditions must operate for an extended period (often several years) to demonstrate conclusively that acid will not be produced.

**Cinola Project Background**

The Cinola Gold Deposit is located on the Queen Charlotte Islands off the north BC coast. The deposit is classified as epithermal Carlin-type by Champigny and Sinclair (1982) owing to the small (<0.5 µm) particle size of gold, age of about 14 million years, presence of argillic alteration, association with faults and felsic intrusions, and porosity of the host rock. Disseminated, fine-grained (<25 µm) sulfide minerals (primarily pyrite, with lesser marcasite) occur throughout the mineralization and host rocks, generally in concentrations of a few percent. In contrast, calcite occurs sporadically, and in one important unit, the Skonun Sediments, is almost completely absent. Acid-base accounting indicated that the Skonun Sediments are potentially acid generating. Laboratory and field kinetic tests confirmed that acid would be produced.

The region hosting the deposit experiences seasonal weather patterns typical of coastal western Canada, that is, most precipitation occurs as rain during October to March. Annual precipitation ranges from 1,700 to 2,200 mm. Average monthly temperatures are never less than 0° C. As a result of the high precipitation rate, the potential for mobilization of acid weathering products from waste rock dumps composed of Skonun Sediments is high. Waste rock management was therefore planned to address perpetual prevention of acid generation. It was proposed that the potentially acid generating Skonun Sediments be stockpiled during operation and then backfilled and submerged in the open pit during mine decommissioning. To prevent extensive oxidation and the release of acid rock drainage from the stockpiles prior to submergence, it was proposed that limestone be added to the stockpiles in a controlled fashion. A column leach study was designed to evaluate such factors as limestone requirement, availability of limestone for reaction, and the effect of intimate mixing and layering of acid consuming and acid generating rock.
Experiment Design

Five columns were designed:

Column 1: Waste rock only (control test).
Column 2: Approximately 6.6% limestone intimately mixed with waste rock (theoretically sufficient to neutralize maximum potential acidity).
Column 3: Approximately 3.2% limestone mixed with waste rock capped with 1 cm of column 2 mixture (50% of maximum potential acidity). The cap was intended to investigate one dump design option.
Column 4: Approximately 0.84% limestone mixed with waste rock capped with 1 cm of column 2 mixture (acid neutralized for 10 weeks at a rate predicted from humidity cells).
Column 5: Approximately 1.2% limestone as five 1-cm thick layers of column 2 material alternating with four 10-cm layers of column 4 material to evaluate the effects of layering.

Materials and Methods

Test Materials

Waste rock for the columns was derived from composited reverse circulation drill cuttings from various subgroups of the Skonun Sediments. The composites were designed to approximate the expected composition of waste rock piles. Limestone for the experiments was obtained from Texada Island, the proposed source of limestone if the deposit were developed. The limestone was dried and crushed to a diameter of 0.6 mm or smaller. Limestone and waste rock were mixed on plastic sheets before placement in the columns.

Test Material Characteristics

The waste rock contained approximately 2.1% total sulfur and had a neutralization potential of 8 kg/mt CaCO₃. Net neutralization potential (NNP) was approximately -58 kg/mt CaCO₃. The limestone contained some sulfur (0.22%), and based on the neutralization potential of 932 kg/mt CaCO₃ had a high purity. The dominant carbonate mineral in the limestone was calcite. Dolomite was expected to be a minor component. The surface area of particles was estimated using size fraction analysis and assuming that particles were perfectly spherical. Waste rock and limestone had surface areas of 5.4 and 30.9 m²/kg, respectively. These values are gross approximations but show that the reactive surface area of the limestone was about five times that of the waste rock. The limestone was deliberately crushed finer than the waste rock to yield a greater reactive surface area.

Acid-base accounts (ABA) for the four columns containing limestone (2 through 5) were determined using mass-weighting. Values for each parameter were determined using the formula

\[ P_{\text{weighted}} = \frac{P_{\text{int}} \cdot M_{\text{int}} + P_{\text{rock}} \cdot M_{\text{rock}}}{M_{\text{int}} + M_{\text{rock}}} \]  

where \( P \) is the parameter (e.g., neutralization potential, NP; maximum potential acidity, MPA), and \( M_{\text{int}} \) and \( M_{\text{rock}} \) are the masses of limestone and waste rock in the column. Values for each column are summarized in table 1. Neutralization potential ratio (NPR) was determined as equal to \( \frac{NP_{\text{weighted}}}{MPA_{\text{weighted}}} \). Since the quantity of limestone was relatively small, the MPA of the columns varied over a small range (62 to 65 kg/mt CaCO₃). Only column 2 was considered potentially acid consuming from conventional interpretation of ABA. The remaining columns had NNP<0 and NPR<1, implying a potential for net acid generation.

Test Procedures

Test materials were placed in 15-cm diameter plastic columns to a thickness of 0.5 m. Column tops were covered with a plastic plate to minimize evaporation. Holes in the plate allowed humidified air and de-ionized water (at a rate of 0.4 to 0.5 mL/min) to be continuously introduced into the column. The top plate was rotated daily so
Table 1. Acid-Base Accounting - Test Materials and Residues.

<table>
<thead>
<tr>
<th>Position in column</th>
<th>S, %</th>
<th>Sulfate, S, %</th>
<th>Sulfide, S, %</th>
<th>MPA kg/m³</th>
<th>NP</th>
<th>NNP kg/m³</th>
<th>Paste pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>Column 1, Control</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pre-test Bulk</td>
<td>2.10</td>
<td>NA</td>
<td>NA</td>
<td>66</td>
<td>8</td>
<td>-58</td>
<td>.12</td>
</tr>
<tr>
<td>Residue Top</td>
<td>.53</td>
<td>.09</td>
<td>.44</td>
<td>17</td>
<td>-2</td>
<td>-19</td>
<td>.00</td>
</tr>
<tr>
<td>Residue Middle</td>
<td>.55</td>
<td>.10</td>
<td>.45</td>
<td>17</td>
<td>-2</td>
<td>-19</td>
<td>.00</td>
</tr>
<tr>
<td>Column 2, 6.6% Limestone</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pre-test Bulk</td>
<td>1.98</td>
<td>NA</td>
<td>NA</td>
<td>62</td>
<td>69</td>
<td>7</td>
<td>1.11</td>
</tr>
<tr>
<td>Residue Oxidized</td>
<td>1.12</td>
<td>.05</td>
<td>1.07</td>
<td>35</td>
<td>3</td>
<td>-33</td>
<td>.07</td>
</tr>
<tr>
<td>Residue Non-oxidized</td>
<td>1.72</td>
<td>&lt;0.01</td>
<td>1.71</td>
<td>54</td>
<td>57</td>
<td>2</td>
<td>1.05</td>
</tr>
<tr>
<td>Column 3, 3.2% Limestone</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pre-test Bulk</td>
<td>2.05</td>
<td>NA</td>
<td>NA</td>
<td>65</td>
<td>38</td>
<td>-27</td>
<td>.58</td>
</tr>
<tr>
<td>Post-test Top</td>
<td>.85</td>
<td>.05</td>
<td>.80</td>
<td>27</td>
<td>0</td>
<td>-26</td>
<td>.01</td>
</tr>
<tr>
<td>Post-test Middle</td>
<td>.77</td>
<td>.11</td>
<td>.66</td>
<td>24</td>
<td>-2</td>
<td>-26</td>
<td>.00</td>
</tr>
<tr>
<td>Column 4, 0.84% Limestone</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pre-test Bulk</td>
<td>2.08</td>
<td>NA</td>
<td>NA</td>
<td>66</td>
<td>16</td>
<td>-50</td>
<td>.24</td>
</tr>
<tr>
<td>Post-test Bulk</td>
<td>.65</td>
<td>.11</td>
<td>.59</td>
<td>20</td>
<td>-2</td>
<td>-22</td>
<td>.00</td>
</tr>
<tr>
<td>Column 5, 1.2% Limestone in layers</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pre-test Bulk</td>
<td>2.08</td>
<td>NA</td>
<td>NA</td>
<td>66</td>
<td>19</td>
<td>-46</td>
<td>.29</td>
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<tr>
<td>Post-test Bulk</td>
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<td>.12</td>
<td>.56</td>
<td>21</td>
<td>-2</td>
<td>-23</td>
<td>.00</td>
</tr>
</tbody>
</table>

NA - Not analyzed.

Pretest results were calculated from mass-weighted averages of limestone and waste rock components that the introduced water contacted different surface locations. In addition to the direct weekly measurement of conductivity and pH, leachates in the collection vessel were analyzed for sulfate (by a gravimetric method), alkalinity/acidity (by titration with sulphuric acid and sodium hydroxide, respectively), and dissolved (<0.45 µm) metals, which included iron, copper, zinc, arsenic, lead, and the major alkali and alkali earth metals. Metal concentrations were determined by several methods including atomic absorption, flameless atomic absorption and inductively coupled argon plasma (mass spectroscopy). After completion of the tests, the columns were dismantled and examined. Samples of the residues were collected for chemical analysis (acid-base accounting, carbonate and sulphur species) and preparation of polished thin sections for identification of secondary minerals.

Results

Leachate Chemistry

Leachate from all four columns containing some limestone was initially pH neutral (fig. 1). Column 1 (control) generated leachate with pH 3 for about 11 weeks. The pH then dropped to near 2. The pH of leachate from this column then steadily increased to greater than 3. Column 4 (low limestone concentration) and column 5 (layered limestone) both generated acidic leachate at week 33. For both columns, pH dropped to between 2 and 3 very rapidly, without intermediate plateaus. Column 3 (intermediate limestone concentration) generated acidic leachate after about 4 yr of operation. The transition to low pH conditions was not quite as rapid as for columns 4 and 5. The column containing the highest concentration of limestone (column 2) generated pH-neutral water throughout the 5-yr experiment.

Sulfate concentrations in the leachate from each of columns 1, 3, 4, and 5 followed similar trends (fig. 1). Sulfate loadings show the same trends because the water percolation rate was relatively constant. All columns
Figure 1. Trends in pH, sulfate, and zinc concentrations in leachates.
showed initially decreasing sulfate concentrations. Concentrations then increased several weeks before pH dropped to between 2 and 3, and peak sulfate release occurred several weeks after the pH dropped.

The observations can be summarized and correlated as follows:

- The time elapsed from a noticeable increase in sulfate concentration to the production of a low pH leachate increased with the proportion of limestone. For columns 4 and 5, 12 weeks elapsed. For column 3, 100 weeks elapsed. Although column 2 did not generate acidic leachate, the time elapsed would be expected to be greater than 180 weeks.

- The time elapsed from release of acidic leachate to peak sulfate concentration was between 9 and 21 weeks for all tests, including the control column.

- The intensity of the sulfate concentration peak decreased with increasing limestone concentration.

- The sulfate concentration peak became less well-defined with increasing limestone concentration, and

- The sulfate decay curve slopes appear to be similar on semilogarithmic graphs, indicating half lives (i.e. time taken to reach half the maximum sulfate concentration) of 5 (control) to 22 weeks.

Sulfate concentrations from column 2 were increasing when the test was terminated. Characteristics of the curve were similar to those of the other tests. Sulfate concentrations had not reached a level that might be expected prior to the onset of fully acidic conditions.

Trends in leachate alkalinity and calcium concentrations were very similar reflecting the dissolution of calcium carbonate. Calcium determinations were most useful for monitoring leaching of limestone because determinations were made regardless of pH. Alkalinity in leachate from column 3 began to increase about 20 weeks after sulfate concentrations increased and peaked at 110 mg/L CaCO$_3$ just before pH dropped. Calcium concentrations also increased during this period, and peaked at about the same time as sulfate concentrations. Once pH decreased, alkalinity also decreased very rapidly and could not, by definition, be measured once pH dropped to less than 4.5. Alkalinity in leachate from column 2 began increasing about 30 weeks after sulfate concentrations began increasing. Calcium also began increasing.

Dissolved iron was the most significant heavy metal in the column leachates. Sulfate and iron concentrations showed similar trends, although iron varied over a wider range. At low pH (less than 2.9), iron and sulfate concentrations (in mg/L) were comparable. At near neutral pH, iron concentrations were commonly less than the detection limit of 0.03 mg/L. Zinc concentrations (fig. 1) showed similar trends to sulfate. Zinc concentrations began increasing as sulfate increased, long before pH decreased. Peak zinc concentrations tended to precede peak sulfate concentrations by a few weeks.

**Characteristics of Column Residues**

Column residues were of two types: Columns 1, 3, 4, and 5 (acid generators) contained visibly oxidized (orange-colored) rock. Column 2 residue was vertically zoned. The upper one third of the column contained oxidized material similar to that in the acid-generating columns. These residues also yielded low paste (de-ionized water) pH. Residue from the lower portion of this column were relatively unweathered (grey-colored), reacted strongly with dilute HCl (indicating readily available NP), and was pH neutral.

Several significant textural features were noted in polished thin sections. In residues from nonacidic columns, abundant fresh pyrite and marcasite grains were observed. These grains showed some in situ replacement by limonite along grain boundaries. By contrast, alteration of pyrite grains varied from negligible to complete in acidic material,
and in situ replacement of sulfide grains by limonite was common. Replacement had taken place along grain edges and along internal fractures and crystal boundaries. In both nonacidic and acidic material, limestone particles appeared fairly fresh and did not have significant limonite rinds. In summary, pseudomorphic (one-for-one replacement) of iron sulfide grains by limonite (primarily goethite, FeOOH) appeared to be common. Coating of limestone grains by transported limonite was not observed.

Acid-base accounting results for residues are summarized in table 1. Reproducibility of duplicate analyses was excellent and confirmed that differences in chemistry between column zones and experiments were significant. Columns 4 (0.8% Limestone) concentration) and 5 (layered) yielded very similar results for total sulfur and sulfate. Total sulfur concentrations decreased by about 1.3% over the 2-yr of weathering. All reactive neutralizing material was consumed, as shown by negative neutralization potentials. Column 1 (control) had slightly lower sulfur concentrations after 5-yr of leaching and similarly contained no detectable NP (the negative NP shown in table 1 indicates the presence of soluble acidity). Column 3 yielded slightly greater sulfur concentrations and no NP. Rock from the top part of column 2 (6.6% Limestone) contained higher concentrations of sulfur than any of the other well-oxidized material, and contained a small amount of NP. The deeper, less oxidized material contained about 0.3% less sulfur than at the start of the experiment. NP decreased by 12 kg/mt CaCO₃.

**Discussion**

**Leachate Chemistry**

Column leachate chemistries followed a series of stages. Initially, sulfate concentrations were elevated but then decreased rapidly as weathering products accumulated during sample storage were flushed from the columns. During stable pH neutral conditions, the dominant ions in solution were calcium and sulfate. The molar ratio of sulfate to calcium under these conditions was between 0.5 and 1 (fig. 2) which is consistent with general chemical theory for acid generation and neutralization. The usual reaction used to express overall acid generation at pH>3 is

\[
\text{FeS}_2 + 15/4\text{O}_2 + 7/2\text{H}_2\text{O} \rightarrow 2\text{SO}_4^{2-} + \text{Fe(OH)}_3 + 4\text{H}^+,
\]

Under strongly acidic conditions, the acidity will be neutralized by CaCO₃:

\[
\text{CaCO}_3 + 2\text{H}^+ \rightarrow \text{Ca}^{2+} + \text{H}_2\text{CO}_3^-.
\]

Under mildly acidic to mildly alkaline conditions, the reaction will be, as follows:
CaCO$_3$ + H$^+$ $\rightarrow$ Ca$^{2+}$ + HCO$_3^-$, \hspace{1cm} (4)

Under acidic conditions, the molar ratio of sulfate to calcium should be equal to or greater than 1, whereas under less acidic conditions the ratio will be less than 1 owing to the formation of bicarbonate (Cravotta et al. 1990). Several months prior to generation of acidic leachate, this ratio steadily increased and gradually approached 1 (Columns 2 and 3, fig. 2). Once acidic leachate was produced, the ratio passed 1.

**Consumption of Alkaline Minerals**

Acid-base accounting results for columns generating acid leachate (1, 3, 4, 5) indicated that no neutralization potential remained in the residues. Petrographic observations support the conclusion that all limestone was available for buffering of acidic leachate. Very few limestone fragments were observed in the residues from acidic columns. In the oxidized part of column 2 (highest limestone concentration), remaining limestone fragments were corroded and did not have a thick coating of transported limonite.

The lack of limonite rinds on limestone fragments is consistent with the low iron concentrations in leachate prior to generation of acid and the observed in situ one-for-one replacement of pyrite by limonite (goethite). During overall pH neutral conditions, iron probably remained at the source of oxidation as goethite and was not transported to limestone grains. This result is only observed when limestone and acid generating rock are relatively well mixed. If very acidic conditions are generated in isolated spots, allowing iron to move away from the oxidation site, the resulting iron would precipitate and cement limestone grains. This shows that the availability of calcareous material would probably decrease as the mixture becomes more heterogeneous and may explain the result observed for the layered column. For this column, the higher limestone concentration in the layers did not appear to be available, perhaps owing to cementing once the material above the individual layers became acidic.

**Estimation of Alkaline Mineral Requirements**

Four of the columns were predicted to be acid generating based on mass-weighted acid-base accounts, and all four columns produced acidic leachate during the course of the experiment. Column 2 (6.6% limestone) did not yield acidic leachate during 5 yr of weathering; however, the upper part of the column was clearly acidic (as shown by low paste pH and negligible neutralization potential), and sulfate and metal concentrations were increasing at the time the experiment was terminated. This column fits the relationship (fig. 3):

\[ t_{SO_4\text{ increase begin}} = 2.9NP - 25. \] \hspace{1cm} (5)

Although based on only five points (fig. 3), the correlation coefficient \( r=0.991 \) is statistically significant with a confidence level of better than 95%.

It is expected that column 2 would have eventually produced acidic leachate. The time required to produce acidic leachate for this column can be estimated from results from the other columns. However, since the time taken for column 1 leachate to become fully acidic is not well defined, the following relationship was determined instead (fig. 3).

\[ t_{\text{max SO}_4} = 11e^{0.079NP}. \] \hspace{1cm} (6)

For column 2, the peak sulfate concentration is predicted to occur after 2,600 weeks (50 yr). Leachate pH would be expected to drop to less than 3 about 20 weeks before the peak. The visual progress of the acid generation front suggests a much shorter time frame. If the rate of migration was constant, acid release would have been expected in about 15 yr. The sulfate peak would probably have been at a much lower concentration than for the other columns and would have been poorly defined.

84
Figure 3. Relationships between beginning of sulfate increase, peak sulfate concentration and time.

<table>
<thead>
<tr>
<th>Column no. and Limestone (LS)</th>
<th>NP, kg/mt</th>
<th>Sulfate release increasing, week</th>
<th>Leachate pH&lt;7, week</th>
<th>Sulfate peak, week</th>
<th>Half sulfate peak, week</th>
<th>Sulfate released, % of total</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Control</td>
<td>8</td>
<td>1</td>
<td>1</td>
<td>20</td>
<td>25</td>
<td>62</td>
</tr>
<tr>
<td>2. 6.6% LS</td>
<td>69</td>
<td>170</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>11</td>
</tr>
<tr>
<td>3. 3.2% LS</td>
<td>38</td>
<td>100</td>
<td>200</td>
<td>219</td>
<td>241</td>
<td>50</td>
</tr>
<tr>
<td>4. 0.84% LS</td>
<td>16</td>
<td>19</td>
<td>31</td>
<td>40</td>
<td>58</td>
<td>61</td>
</tr>
<tr>
<td>5. 1.2% LS, layers</td>
<td>19</td>
<td>19</td>
<td>31</td>
<td>54</td>
<td>72</td>
<td>49</td>
</tr>
</tbody>
</table>

Columns indicated by numbers next to symbols

\[ t = 2.9NP - 25 \]

\[ t = 11\exp(0.079NP) \]
The amount of limestone required to neutralize any acid for an indefinite period cannot be estimated from the above relationships since neither converges to a limiting value. However, the molar ratio of sulfate to calcium during the pre-acid leachate phase indicates the release of calcium in proportion to sulfate. The ratio is typically 0.5 to 0.6. As the conventional acid-base account assumes a 1:1 relationship, the actual NP required to prevent acid release is double the amount in column 2 (NP=69 kg/mt CaCO₃), or 138 kg/mt CaCO₃.

Mitigation of Metal Release by Calcareous Rock Mixing

Results indicated that under fully alkaline conditions where sulfate production is fairly uniform, metal and arsenic concentrations will remain low and stable. Once sulfate production begins increasing, metal release also increases. Zinc is the first to appear (at about the same time as increasing sulphate concentrations) followed by arsenic and copper (the latter being coincident with low pH conditions). This is consistent with commonly understood relationships between pH and dissolved metal concentrations. It appears therefore that limestone addition will only delay the release of zinc according to relationships of the form of equation (5), but will delay copper release for a much longer period (equation 6).

Conclusions

The following was concluded:

1. The actual quantity of limestone required to prevent acid drainage in perpetuity would probably be at least twice that determined by conventional acid-base accounting provided that the limestone and rock are intimately mixed (not thickly layered) and zinc release is not expected;

2. The time elapsed before marginally acid generating rock released acidity increased exponentially as the quantity of limestone increased; and

3. The time elapsed before sulfate and zinc release began increasing prior to release of low pH leachate was linearly proportional to the neutralization potential.

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