NEUTRALIZING AMENDMENTS AND RATES OF APPLICATION

Principles and Practices

Mine tailings exhibiting elevated metal concentrations and residual sulfide minerals are a significant environmental problem in the Western U.S. and around the world. Similar combined water quality and revegetation challenges are posed by sulfidic mining waste rock/overburden, coal processing wastes and anthropogenic exposure of sulfidic sediments. Acid generation caused by sulfide mineral weathering is directly responsible for creating low pH pore water conditions with concomitant signature of trace metals which can be solubilized at high concentrations by the very low pH waters. The resultant low pH cocktail of metals either inhibits or precludes establishment of stabilizing plant cover. Mobilization of metals to surface and groundwater by leaching is an ancillary environmental risk. Removal of metal-laden sulfide tailings from riparian areas is not always feasible due to multiple factors. In-place treatment can be a viable alternative. This technology has been applied worldwide to the full range of acid-forming materials cited above.

Neutralization of acid-producing mine tailings by alkaline addition has been performed in multiple locations. Appropriate lime addition and incorporation allow for permanent pH control and permanent mitigation of elevated water soluble metal levels in root-zone pore water. Total metal levels in contaminated materials remain unchanged, yet the bioavailability of trace metals to plants and aquatic resources is dramatically reduced. This in-situ treatment approach has been developed over a twenty year period with both successes and failures observed. The current treatment approach entails (A) lime addition to ameliorate acidic conditions observed currently, and (B) to provide long-term neutralization capacity to fully neutralize all future acidity caused by sulfide mineral weathering.

Successful neutralization of acid-forming mining wastes and related sulfidic materials, therefore, requires three components. First, a reproducible laboratory protocol is required for calculation of acid-base account from field soil samples. Secondly, parallel laboratory protocols are required for assessment of lime quality including calcium carbonate equivalence (CCE) (i.e. reactivity), moisture content and particle size. Thirdly, sufficient delineation of spatial variation in field lime rate is required such that appropriate amounts of neutralizing amendments are applied at the correct locations and to proper depths.

Acid-base Account Determination

Sulfidic mine tailing materials may contain two forms of acidity called active and potential acidity. Any soil or tailings material with a pH below 5.5 to 6.0 contains active acidity. The active acidity is derived from ions of hydrogen, aluminum and iron that are dissolved or adsorbed on clay surfaces (Evangelou 1995). This “active acidity” is quantified by determining the amount of alkaline material required to adjust the pH to a neutral condition. Tests used to measure active acidity include the SMP buffer lime test (Sobek et al. 1978) or whole-soil titrations.
Potential acidity is the amount of acid that may be liberated over extended periods of time due to oxidation of pyrite and other sulfide minerals contained in tailings. Potential acidity, also known as the net neutralization potential (NNP), is determined through static tests and is equal to the acid neutralization potential (ANP) minus the acid generation potential (AGP). Smith et al. (1974) and Sobek et al. (1978) found that for every 1 percent sulfur in the form of pyrite that 31.25 tons of pure limestone (CaCO₃) would be required to neutralize the potential acidity in 1,000 tons of materials (conveniently a 1 acre soil layer 6 inches deep weighs approximately 1000 tons). The quantity of limestone required to neutralize the generated acid is based on the following two equations.

\[
\text{FeS}_2 + 3.75\text{O}_2 + 3.5\text{H}_2\text{O} \rightarrow \text{Fe(OH)}_3 + 2\text{SO}_4^{2-} + 4\text{H}^+ \quad [1]
\]

\[
\text{CaCO}_3 + 2\text{H}^+ \rightarrow \text{Ca}^{2+} + \text{CO}_2\text{(g)} + \text{H}_2\text{O} \quad [2]
\]

Cravotta et al. (1990) suggested that the lime rate determined by Sobek may be insufficient because reaction [2] will only occur at low pH, and at the alkaline pH maintained in a limed soil, reaction [3] is more appropriate. Consequently, Cravotta et al. suggested that the Sobek lime rate should be doubled to 62.5 t CaCO₃ per 1,000 tons of soil.

\[
\text{CaCO}_3 + \text{H}^+ \rightarrow \text{Ca}^{2+} + \text{HCO}_3^- \quad [3]
\]

In this paper, documented examples of the efficacy of this technology are drawn from studies chiefly implemented in the western US. Similar applications of the science and technology have been completed for acid sulfate forming materials in all major metal mining regions worldwide.

During formulation of liming protocols for the Silver Bow Creek NPL Site (Streambank Tailings and Revegetation Treatability Study-STARS), Schafer and Associates and MSU (1989) developed a lime rate (LR) equation that incorporated both the active and potential acidity, accounted for different forms of sulfur, ignored the contribution of alkalinity from the measured ANP, and added a factor of safety [4].

\[
\text{LR} = 1.25 \times \{31.25 \times \text{(nitric acid plus residual S)} + 23.44 \times \text{(HCl S)} + \text{SMP Buffer}\} \quad [4]
\]

The coefficient of 23.44 for the hot HCl extractable fraction of sulfur was intended to account for acidity generated by the mineral jarosite (KFe₅(SO₄)₂(OH)₆). The reason that the ANP was not used in the STARS lime rate equation is that tests on many low pH samples yielded very high ANP values. Usually carbonate minerals that typically account for ANP are absent at low pH. The high ANP values in the acidic samples were attributed to dissolution of feldspar minerals. It was felt that any buffering that feldspars could provide would be ineffective at a higher pH.

Concerns have been raised about the adequacy of lime rates used in the Clark Fork basin, and about the longevity of such treatments. The Sobek method for determining potential acidity, and the implicit relationship between pyritic sulfur and lime requirement has been used throughout the world to assess the risk of acid generation of mining waste. Despite suggestions by Cravotta et al. (1990) that lime rate for a mine
waste containing 1 percent pyritic sulfur should be 62.5 t CaCO_3 / 1,000 tons of soil, most reclamation scientists finds the 31.25 coefficient adequate to achieve lasting pH control (Skousen et al. 2002).

Two methods can be used to assess the adequacy of the STARS lime rate, comparison of carbonate consumption to acid production and measurement of residual alkalinity in amended samples. Morin and Hutt (1997) report the results of numerous laboratory humidity cell tests in which the carbonate consumption (estimated from dissolved calcium and magnesium contained in column leachate) was compared to pyrite oxidation. If equations [1] and [2] are occurring as assumed in the Sobek method, then the ratio of calcium to sulfate in solution should be 1:1 (on a molar basis). If equation [3] is predominant, then the ratio will be 2:1. In humidity cells that had a neutral to alkaline pH, the calcium to sulfate ratio varied from 1:1 to 1.5:1, with most cells close to 1:1, indicating that the Sobek method is accurate. Morin and Hutt (1997) also described results of several large scale (20 ton) 5-year column tests in which limestone was added to several acid generating waste rock mixtures. While the columns remained alkaline, the ratio of calcium to sulfate in column drainage was closer to 2.0. Based on the variable ratio of calcium to sulfate in kinetic tests described in the literature, there is no basis upon which to conclude whether the 31.25 or the 62.5 coefficient is correct (Skousen et al 2002).

The second means used to determine the adequacy of the lime rate used in the Clark Fork basin is evaluation of the residual carbonate remaining in soil after addition of the prescribed amount of alkaline amendments. In the STARS research study, the lime requirement was precisely measured in each plot, and the lime rate increased by a 25 percent factor of safety. The STARS plots were re-sampled in 1996, 8 years after amendment addition to determine their residual net neutralization potential. Samples were collected at 0-5 and 5-15 cm, the depth at which agricultural tillage was employed. The NNP values showed that when enough amendments were added to boost the NNP to +2 t/1,000 t or higher, that adequate pH control was maintained.

Evaluations of the permanence of phytostabilization at six different locations within the Clark Fork River Basin were conducted by a team of researchers from RRU (Munshower et al. 2003). These high metal, low pH sites varied in age of treatment from 6 to 19 years. Materials at sites were treated with neutralizing amendments to raise pH to a target level of 7.0. Acid base potential of samples from these six sites ranged from +1 t/1000 t to +123 t/1000 t, indicated neutral to basic conditions persist multiple years (to nearly two decades) after lime treatment.

**Lime Quality**

A variety of candidate neutralizing amendments are available for consideration as mine waste treatment amendments. Amendments may include ground limestone (CaCO_3), burnt lime (CaO), hydrated lime (Ca(OH)₂) and industrial waste products such as cement kiln dust, sugar beet precipitated calcium carbonate, flue gas desulfurization sludge, and others. The applicability of each amendment is subject to chemical analysis of calcium carbonate equivalence (CCE), moisture content and particle size. Reactivity of applied amendments is highly correlated with particle size and solubility (Table 1). Additionally, lime amendments must not contain phytotoxic constituents that limit plant
growth. Phytotoxicity effects of industrial waste products can be determined by greenhouse bioassay testing, but not by chemical analysis alone. Pure alkaline products such as ground limestone, calcium oxide and calcium hydroxide do not require independent greenhouse evaluation prior to field use but should be certified or labeled by their state of origin or use.
Table 1. Calcium carbonate equivalence (CCE) and solubility of common neutralizing amendments

<table>
<thead>
<tr>
<th>Compound</th>
<th>Chemical Formula</th>
<th>CCE</th>
<th>Solubility in Water (g L⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Calcium oxide</td>
<td>CaO</td>
<td>179%</td>
<td>0.131</td>
</tr>
<tr>
<td>Calcium hydroxide</td>
<td>Ca(OH)₂</td>
<td>136%</td>
<td>0.185</td>
</tr>
<tr>
<td>Magnesite*</td>
<td>Mg CO₃</td>
<td>119%</td>
<td>0.011</td>
</tr>
<tr>
<td>Dolomite</td>
<td>CaMg(CO₃)₂</td>
<td>109%</td>
<td>0.032</td>
</tr>
<tr>
<td>Calcium carbonate</td>
<td>CaCO₃</td>
<td>100%</td>
<td>0.0014</td>
</tr>
</tbody>
</table>

* High Mg lime materials may increase EC due to higher solubility of Mg sulfates.

While single amendment additions of alkalinity sources can be applied, research has shown that mixtures of limestone with either calcium oxide or hydroxide perform better in long-term control of water soluble metal levels. Laboratory and field experimentation have identified methodologies to attain maximum precipitation of contaminants in acidic-metalliferous wastes using alkaline amendments (RRU 1993, Schafer & Assoc. and RRU 1989 and RRU 1997). The pH of acidic-metalliferous waste must be raised into a range of 10-12 in order to attain maximum precipitation of contaminants such as Zn, Cu, Mn, and Pb. When only limestone (CaCO₃) was used, which will raise the soil pH to a maximum of approximately 8.6, precipitation of contaminants of concern was comparatively less. Raising the waste pH into a range of 10-12 maximized precipitation of contaminants which did not resolubilize when the pH was allowed to regress back down to a level <8.5. A pH <8.5 is necessary if plant growth is desired in the lime-amended mine waste. Bulk pH will naturally fall from the 10-12 range to <8.5 as oxides and hydroxides of calcium undergo carbonation with water and atmospheric CO₂. Therefore, a portion of the alkaline amendment must be composed of oxides and/or hydroxides of calcium in order to initially drive the waste pH into the 10-12 range. In areas with existing desirable vegetation that should be preserved, only calcium carbonate should be used as an amendment since calcium oxide/hydroxide will burn adjacent vegetation. Calcium oxide (CaO) should also be used sparingly in dry climatic conditions since it requires addition of water to form calcium hydroxide (Ca(OH)₂). Conversely, calcium oxide can be used to facilitate drying of saturated mine waste due to water consumption caused by ‘slaking’ and creation of calcium hydroxide.

The research cited above found maximum precipitation of contaminants was attained when the amendment was composed of 60% carbonates and 40% oxides + hydroxides (weight basis). Increasing the oxide + hydroxide content to more than 40% did not increase contaminant precipitation, but could increase the period of time required to attain a pH <8.5 by carbonation reactions. Prolonged periods of amended waste recarbonation could be a problem in areas that must be seeded since recarbonation may require 4-12 months of time. Consequently, site revegetation may be delayed as the oxide and hydroxide content of the amendment exceeds 40%. If the amended waste is
not intended for use in a plant root zone, such as the deeper portion of a repository, the time required for recarbonation is not important. Table 2 shows the suggested alkaline amendment analytical methods.

Table 2. Desired physicochemical characteristics for the alkaline amendment.

<table>
<thead>
<tr>
<th>Property</th>
<th>Recommended Characteristic</th>
<th>Analytical Method¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample Preparation</td>
<td>Disaggregate, Do Not Crush</td>
<td>Mortar and Rubber Tipped Pestle</td>
</tr>
<tr>
<td>Calcium Carbonate Equivalence (CCE)</td>
<td>&gt; 90 %</td>
<td>AOAC 1975 or ASA 1965 (method 91-4.2)</td>
</tr>
<tr>
<td>Water Content, weight basis</td>
<td>&lt; 10 %</td>
<td>ASA 1965 (method 7-2.2)</td>
</tr>
<tr>
<td>Particle Size Distribution, weight basis</td>
<td>&gt;90 % passes 60 mesh sieve</td>
<td>Wet Sieve³</td>
</tr>
<tr>
<td>Composition as a % of the CCE</td>
<td>30-60 % OXide+Hydroxide of Ca and 40-70% CaCO₃</td>
<td>LOI Test, ASTM C25-90, Section 21² . N atmosphere recommended.</td>
</tr>
<tr>
<td>pH</td>
<td>&gt; 10</td>
<td>ASA 1965 (method 62-1.3.2.1)</td>
</tr>
<tr>
<td>Total As, Cd, Mn, Cu, Zn, Pb, and others</td>
<td>As&lt; 30 mg/kg Cu&lt;100 mg/kg</td>
<td>Test Methods for Evaluating Solid Waste, 1986. Method 3050 (HNO₃ and H₂O₂ digestion.</td>
</tr>
<tr>
<td></td>
<td>Cd&lt; 4 mg/kg Zn&lt;250 mg/kg</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Mn&lt; 200 mg/kg Pb&lt;100 mg/kg</td>
<td></td>
</tr>
<tr>
<td>Sodium Adsorption Ratio (SAR)</td>
<td>Na/((Ca+Mg)/2)²&lt;10</td>
<td>USSLS 1969 (method 20b)</td>
</tr>
<tr>
<td>Water Extractable Al</td>
<td>&lt;1 mg/L</td>
<td>ASA 1965 (method 62-1.3.2.1)</td>
</tr>
<tr>
<td>Electrical Conductivity</td>
<td>No criterion</td>
<td>ASA 1965 (method 62-1.3.2.1)</td>
</tr>
<tr>
<td>Dry Bulk Density, pounds/ ft³</td>
<td>Required for field application</td>
<td></td>
</tr>
<tr>
<td>Greenhouse Plant Growth Tests</td>
<td>May be required if alkaline amendment will be used in the plant root zone.</td>
<td></td>
</tr>
</tbody>
</table>

¹/ Associated method citations are located in Literature Cited.
²/ For composition, report the % CaCO₃ content based on the LOI test. Estimate the % CaO and/or Ca(OH₂) content from the following equations:
   • If the material is known to contain a mixture of oxide and hydroxides, then % Ca(O + OH₂) = (% CCE - % CaCO₃)
   • If the material is known to contain only CaO, report the CCE emanates from CaO.
   • If the material is known to contain only Ca(OH₂), report the CCE emanates from Ca(OH₂).
³/ Pass the dried-disaggregated sample through a 60 mesh sieve. Report this result. That portion failing to pass a 60 mesh sieve should be wet sieved. For this step, samples should be shaken in deionized water for 8 hours and then washed through the 60 mesh sieve. Report the total percent of the sample mass, dry plus wet sieve that passed a 60 mesh sieve.
Water content in neutralizing amendments should be quantified to adjust field application rates. Water in the amendment serves to increase the actual field lime application rate on a weight basis and may lead to application difficulty due to clumping and/or freezing. Alkaline amendments having significant water content should be avoided due to difficulty in applying and incorporating them into the waste material. The physical state of the alkaline amendment upon delivery must be such that 60 mesh particles remain unattached to each other as opposed to a cemented, consolidated or caked mass.

Only those alkaline amendment materials having a particle diameter sufficient to pass a 60 mesh sieve (0.25 mm) are considered reactive with the active and potentially acid materials in amended mine waste. Oversize material may be present, but must not be considered as part of the active neutralizing amendment. A wet sieving procedure should be used to assess the particle size distribution but the material may only be disaggregated, not crushed, during sample preparation. The wet sieving procedure may serve to solubilize oversize particles of CaO and Ca(OH)₂ which is acceptable. Alkaline amendments having a high percentage of over-size material should be avoided. Smaller particles therefore are considered more reactive owing to the surfaces exposed for chemical reactions to occur (Table 2.3).

Table 3. Lime amendment particle size and ranking for relative effectiveness.

<table>
<thead>
<tr>
<th>Sieve Number (mesh)</th>
<th>Particle Size (µm)*</th>
<th>Relative Effectiveness (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaCO₃</td>
<td>Ca(OH)₂</td>
<td>CaO</td>
</tr>
<tr>
<td>&gt; 8</td>
<td>&gt; 2380</td>
<td>0</td>
</tr>
<tr>
<td>8 - 20</td>
<td>840-2380</td>
<td>0</td>
</tr>
<tr>
<td>20 - 60</td>
<td>250-840</td>
<td>50</td>
</tr>
<tr>
<td>&lt; 60</td>
<td>&lt; 250</td>
<td>100</td>
</tr>
</tbody>
</table>

The key finding of Table 3 is that coarse calcium carbonate (> 840 µm, 0.84 mm) is considered not to contribute to the neutralization of a site. Over the passage of decades or centuries, this may not be true, but in the short term coarse CaCO₃ should not be counted towards neutralization.

Rock content also plays a role in selection of lime application rates. By definition (using the USDA soil classification system) a rock is any soil particle greater than 2 mm. Rocks are typically not acid forming materials and no lime amendment is required for the rock portion of the treated soil profile. An exception occurs when mine waste rock is present that may be acid-forming. Typically, fluvially deposited mine tailings are smaller than 2mm while stream system alluvial rock is chemically non-reactive and larger than 2mm. By example, if a field lime rate for a 1-acre treatment area is 40 tons CaCO₃/2000 tons (i.e. 1 acre tilled 12 inches deep) across an area with 20% content in the 0-12 inch
soil profile, the lime rate should be reduced by 20% to account for rock. That is, the adjusted field application rate is 32 tons CaCO_3/acre-12 inch depth. In hard rock overburden materials, in which the entire soil/rock mass may be acid forming, no adjustment to field lime rate are required.

Assurance must be provided that alkaline amendment used for project work shall not contain enriched levels of metals or salts that could be a detriment to plant growth or water resources. For example, enriched levels of Cu, Zn, Pb and Mn in the alkaline amendment may exacerbate the problem at the field site since acidic-metalliferous wastes already contain high levels of these metals. Similarly, alkaline amendments that have a high sodium adsorption ratio (SAR) are not desirable since the excess sodium can negatively impact plant growth and may leach into water resources. High concentrations of Cl, NO_3 or other anions in the alkaline amendment are not acceptable since they may be a detriment to plant growth and can leach into water resources.

Identification of alkaline materials which have the proper neutralization characteristics is just the first step in assessing the suitability of the material to be used as an amendment. Mined/crushed CaCO_3 and industrial grades of Ca(OH)_2 and CaO have been used throughout the Anaconda Montana area and in greenhouse studies at MSU with no phytotoxic effects. However, industrial by-products such as lime kiln dust, cement kiln dust, flux bar residue and acetylene waste may provide adequate neutralization, but may have potential phytotoxic effects which must be assessed. Kelly (1997) studied industrial by-products which were effective in neutralizing acidic-metalliferous wastes. However, plant growth tests in the greenhouse with the amendments exhibited phytotoxic effects from no germination to very poor growth compared to wastes amended with traditional lime products of Ca(OH)_2 and CaCO_3 (Kelly, 1997). Later work by Mehlenbacher (2002) revealed fewer limitations, yet uncertainty related to the use of industrial waste products as a soil amendment are recurring issues. Similar issues exist when alkaline coal combustion byproducts are utilized (NRC, 2006) in coal mining environments.

**Field Lime Application**

Chemical characteristics must be accurately delineated so that lime application rates are known within +/- 10 tons CaCO_3 /1000 tons of tailings across the treated landscape. The entire depth unit to be amended must be sampled, and analyzed to determine the lime requirement. Samples must be collected at a frequency to adequately characterize the spatial and vertical extent of treatment required. Amendments must be uniformly incorporated throughout the zone to be treated. The lime requirement determined from analytical tests presumes each lime particle applied will be in contact with the soil cation exchange sites and surfaces of sulfide minerals. Since it is impossible to accomplish this goal with surficial applications of lime followed by a tillage procedure, extra lime (25 %) is applied to enhance the opportunity for contact between the lime and every soil particle surface. The amendment materials must be thoroughly mixed into the wastes to assure that sulfide-rich particles are in contact with the amendment. If the materials are not thoroughly mixed, there is potential for acidic hot spots which would diminish the effectiveness of the treatment. Furthermore, the incorporation method must
be able to amend the wastes uniformly throughout the zone to be treated. Multiple passes across the ground with deep tillage equipment may be required to achieve adequate mixing (see Issues 3 and 4 in this document). To assure that the amendment material has been successfully mixed to the proper depth, test pits should be constructed following the amendment addition as a Quality Control step. Degree of mixing can be assessed through field application of pH indicator solution (Hellige-Truog solution or equivalent) across an individual soil pit face excavated across the tilled interval to identify the pH levels in the profile.

The field application rate can be determined by multiple approaches including composite sampling, geo-statistical prediction models, and GIS controlled custom application technologies that vary local application rates to match site specific data. Field sampling can be performed to create master composite samples prior to laboratory analysis. Many sub-samples are required attain a representative lab sample. Alternately, individual samples may be collected and analyzed. Spatial variability in lime rate is commonly observed. Lime can be added in the field at a varying rate in response to the data or the data can be used to develop a statistical distribution leading to selection of a ‘master rate’ for an area such as the 90% confidence interval. Availability of analytical data and characteristics of a site should guide selection of an appropriate model for lime rate selection. The intrinsic lime requirement of tailings has been found to be spatially quite heterogeneous. Samples collected as little as 30 to 100 feet apart have widely disparate lime requirement.

Limitations associated with lime treatment of acid-forming mine waste have been observed. Problems have been encountered in excessively rocky soil in achieving adequate mixing. Lime that is not well mixed into the full depth of the profile is one issue, while another is that tillage equipment tends to create a rock pavement veneer with repeated incorporation passes over soils with >40% rock. A second limitation encountered with lime treatment relates to contamination levels. When trace metals levels are at modest levels, neutral pH achieved by alkaline addition has been adequate to allow control of phytotoxicity. However, when high levels of metals are present in the neutralized root-zone following treatment, residual phytotoxicity has caused apparent vegetation failure. No rigid criteria have been developed to address this issue, rather progressively more intensive treatments implementing additional organic matter and fertilizer addition have been employed with modest success. At the highest levels of total metals in the treated soil profile, very few plants will persist.

References


Site Selection. Reclamation Research Unit, Montana State University, Bozeman, MT.


