Flow Chart for Ranking and Prioritization

- **Acid-Base Accounting**
  - TCLP test
  - Mine plan

- **Characterization**
  - Regulatory

- **Detailed**
  - Carbon, Sulfur Analyses
  - Paste pH test
  - Field leach test
  - $\text{H}_2\text{O}_2$ acidity test

- **Reconnaissance**
  - Mineralogical analysis
  - Humidity cell tests
  - SPLP (EPA 1312) leach
  - Sobek tests
  - Bulk chemistry (ICP, XRF)
  - BCRI

- **Scale**
  - Site
  - Watershed
Acid-Base Accounting (ABA)

- Who Cares?
- What is it?
- How does one do it?
- What does it mean?
Who Cares?

- Anyone concerned about the environmental effect from mines
- Those responsible for storing overburden, waste rock, and other mine-waste materials
- Underestimation of the Acid-Production or overestimation of Neutralization Potential can lead to incorrect decisions regarding treatment or storage.
A typical mine site in the San Juan mountains. Steep slopes, ready transport of waste downhill.
Acid-Base Accounting: What is it?

- Acid-Base Accounting (ABA) is the balance between the acid-production and acid-consumption properties of a mine-waste material.

- Minerals in waste material (mostly sulfides; mostly pyrite) react with water and oxygen to produce sulfuric acid.

- This acid is itself detrimental to water quality.

- Acid leaches metals from material and introduces them into environment.
Some Acid Producing Reactions

**pyrite**

\[
\text{FeS}_2(s) + \left(\frac{7}{2}\right) \text{O}_2(g) + \text{H}_2\text{O} =
\]
\[
\text{Fe}^{2+}(aq) + 2 \text{H}^+(aq) + 2 \text{SO}_4^{2-}(aq)
\]

**pyrrhotite**

\[
\text{Fe}_{(1-x)}\text{S}(s) + (2 - \frac{x}{2}) \text{O}_2(g) + x \text{H}_2\text{O} =
\]
\[
(1 - x) \text{Fe}^{2+}(aq) + 2x \text{H}^+(aq) + \text{SO}_4^{2-}(aq)
\]

where \(x\) ranges between 0.000 and 0.125
Another typical mine site in the San Juan mountains. Steep slopes, ready transport of waste downhill. Draining adit to left.
Some acid-generating sulfides

- Pyrite (FeS$_2$)
- Pyrrhotite (Fe$_{1-x}$S)
- Enargite (Cu$_3$AsS$_4$)
- Marcasite (FeS$_2$)
- Arsenopyrite (FeAsS)
- Tennantite (Cu$_{12}$As$_4$S$_{13}$)
- Orpiment (AsS)
Acid Neutralization Reactions

above pH 6.4
\[ \text{CaCO}_3(s) + \text{H}^+(aq) = \text{HCO}_3^-(aq) + \text{Ca}^{2+}(aq) \]

below pH 6.4
\[ \text{CaCO}_3(s) + 2\text{H}^+(aq) = \text{H}_2\text{CO}_3(aq) + \text{Ca}^{2+}(aq) \]
Or
\[ \text{CaCO}_3(s) + \text{H}_2\text{SO}_4 = \text{CaSO}_4(s) + \text{CO}_2(g) + \text{H}_2\text{O} \]

Other mineral dissolution reactions (chlorite, biotite, other silicates) produce less neutralization and have lower solubilities at moderate pH.
How does one do it?

- many approaches and methods developed
- acid-producing potential
- neutralization potential of mine-waste material
- early work was applied to coal mining

Each modification or new method has been developed to address various shortcomings, with the aim to make the end-result estimation as accurate as possible.
Acid and Neutralization Potential

The aim of these tests is to produce an AP value (Acid Production Potential) and/or an NP value (Neutralization Potential).

Net Neutralization Potential: \( \text{NNP} = \text{NP} - \text{AP} \)

And

Neutralization Potential Ratio: \( \text{NPR} = \text{NP}/\text{AP} \)

The unit of measurement is \( \text{kg CaCO}_3 \text{ per ton} \), or equivalently

\( \text{parts per thousand CaCO}_3 \)
Acidic leachate transports metals into headwaters of high mountain stream in San Juan mountains
NNP and NPR
interpretation is not simple

- If the NNP is greater than 20 kg/ton CaCO$_3$, it is generally accepted that the material is non-acid producing.
- If the NNP is less than –20 kg/ton CaCO$_3$, it is generally accepted that the material is acid producing.
- NNP values between –20 and 20 kg/ton CaCO$_3$ are in the gray range of uncertainty. Kinetic tests may be needed.
- If the NPR value is < 1, the material is considered acid producing.
- If the NPR value is > 3, the material is considered non-acid producing (California and Nevada).
- If the NPR value is > 4, the material is considered non-acid producing (British Columbia).
**Methods**

- **Sobek method (Standard ABA method)**
  - Assumption: oxidation of pyrite by oxygen

- The earliest and still much-used method estimates the acid potential based on the sulfur content
- Each mole of sulfur produces two moles of acid neutralized by one mole of calcium carbonate
- The mole ratio of sulfur to calcium carbonate is therefore 1:1. The weight ratio is then:
  - $100 \text{ g } \text{CaCO}_3 / \text{mole } \text{CaCO}_3 : 32\text{ g } \text{S} / \text{mole } \text{S}$
  - Or in standard AP units
    - $31.25 \% \text{ CaCO}_3 \text{ per } \% \text{ S}$ (%o is same as kg/ton)
Upper limit to pyrite sulfur

- If the material contains ~ 9.5% sulfide sulfur (assuming pyrite), the rest of the material would have to be CaCO₃ to meet the 3:1 criterion.
- This provides an upper boundary for sulfide content (that is, if sulfide sulfur is > 9%, no test is needed: it’s acid producing).

- \( (9.5 \times 31.25 \times 3 = 891 \text{ parts per thousand } \text{CaCO}_3) \)
Neutralization Potential by reaction with acid and back-titrating

- The NP in the Sobek test is determined by reacting the sample with HCl, and back-titrating with NaOH.
- The strength and amount of HCl to use is estimated with a “fizz test.”
- Introduces a large uncertainty in the final NP calculated.
- With a stronger amount of initial acid, the solution reacts at a lower pH and involves phases that would not react at the more realistic pH of the real situation.
- Therefore, the simple Sobek test tends to overestimate the NP of a material, and this affects the AP/NP ratio. The presence of siderite (iron carbonate) can greatly affect the laboratory determination of NP.
**Modified Sobek Method**

- This method is similar to the Sobek method, but bases the AP on *sulfide* sulfur rather than *total* sulfur.
- Using total-sulfur analyses can lead to error if non-acid producing sulfates such as gypsum and barite are present.
- Also, the NP test uses an ambient temperature digestion at pH 1.5 to 2.0 (less acidic than standard method), and a titration endpoint of 8.3 instead of 7.0.
- This method can miss acidity produced by sulfates, such as copiapite. Mineralogical knowledge of the material is an important adjunct to the chemical tests.
British Columbia Research Initial Test (BCRI)

- AP based on total S content. NP is determined by titrating a stirred mixture of mine waste and water with strong sulfuric acid to a pH of 3.5.
NP (pH6)

- Developed by Lapakko, is similar to the BCRI test
- 1.0 N sulfuric acid is used as titrant
- The endpoint is pH 6
- This test is designed to give the “effective NP,” or the calcium carbonate equivalent NP available at pH 6.
Concerns with traditional approaches

- Presence of sulfide minerals other than pyrite
- Presence of acid-producing minerals that aren’t sulfides
- Presence of carbonate minerals that don’t produce alkalinity
- Presence of non-carbonate minerals that can buffer acidity (e.g., chlorite, biotite)
Effect of siderite

- FeCO₃ + H₂SO₄ = Fe²⁺ + H₂CO₃ + SO₄²⁻
  and
- 4Fe²⁺ + O₂ + 4H⁺(aq) = 4Fe³⁺ + 2 H₂O
  but
- FeS₂(s) + 14 Fe³⁺ + 8 H₂O = 15 Fe²⁺ + 2 SO₄²⁻ + 16 H⁺(aq)
Hydrogen Peroxide-based Tests

- A hydrogen peroxide digestion of waste material produces acid by oxidizing sample pyrite.
- The resulting acid may be partially or wholly consumed by available neutralizing material.
- The filtered solution is titrated to pH 7 with NaOH to measure how much acidity is left.
- Provides an empirical measure of NNP that doesn’t rely on assumptions about mineralogical residence.
- It does not, however, provide the individual AP and NP values, and so a NPR is not calculable.
Field method of water analysis that has nothing to do with this talk
What does it mean?

- Two case histories using Peroxide NAP method of Lapakko and Lawrence (1993)
- 1) Animas River, southwest Colorado
- 2) Boulder River, Jefferson County, Montana
- Watershed scale studies
- Polymetallic vein deposits
- Volcanic and plutonic terrane
- Approximately 120 samples of mine waste analyzed for NAP and EPA-1312 leach
Water-soluble salts in mine waste
Plot of net acid production (NAP) vs. summed metals in EPA-1312 leach
Chemical potential of mine waste to be an environmental concern

- Plot the sum of (As+Cd+Cu+Pb+Zn) in ppb vs. the NAP as measured from peroxide test
- Can break up the data points into 4 different Groups, separated by NAP and metal concentration values
- Note that above 10 kg/ton CaCO₃, all samples from this study released more than 5,000 ppb summed metals (Group 4)
- Note that some samples with low acidity can still release high summed metals (Group 3); this is often zinc
Group score for acidity and summed dissolved elements (SDE)

- Group 1, which has low acidity (<10 kg CaCO$_3$/ton) and <1,000 $\mu$g/L SDE
- Group 2, which has low acidity and moderate SDE (between 1,000 and 5,000 $\mu$g/L)
- Group 3, which has low acidity and high SDE (>5,000 $\mu$g/L)
- Group 4, which has high acidity (>10 kg CaCO$_3$/ton) and high SDE (>5,000 $\mu$g/L)
Plot of net acid production (NAP) vs. Iron in EPA-1312 leach
Group score for acidity and dissolved iron

- Iron plotted separately, or would dominate the plot
- Iron a problem either as a toxic component or as reactant in acid-producing reactions
- Group 1, which has low acidity (<10 kg CaCO₃/ton) and dissolved iron less than 1,000 µg/L
- Group 2, which has low acidity (<10 kg CaCO₃/ton) and dissolved iron greater than 1,000 µg/L
- Group 3, which has high acidity (>10 kg CaCO₃/ton) and dissolved iron greater than 1,000 µg/L
Aspects of the leachate chemistry groups

- NAP > 10 kg/ton produce metal-rich leachates
- NAP < 10 kg/ton can produce either metal-poor or metal-rich leachates
- Near-neutral pH or near-zero acidity leachate can contain high zinc concentrations
The size of the waste pile also influences the ranking

- for size <500 tons, Group 1
- for size between 500 and 2,500 tons, Group 2
- for size >2,500 tons, Group 3
- (this size ranking only for this study)

- Add the Group scores from summed dissolved metals, dissolved iron, and size for range of 3 to 10. Rank of 3 means low, rank of 10 means very high potential for environmental effect

- Should still account for other site factors, such as draining adits, proximity to ground or surface water, water flowing across dumps, and others