



Acid-Base Accounting



David L. Fey, USGS
Billings Symposium / ASMR Annual Meeting

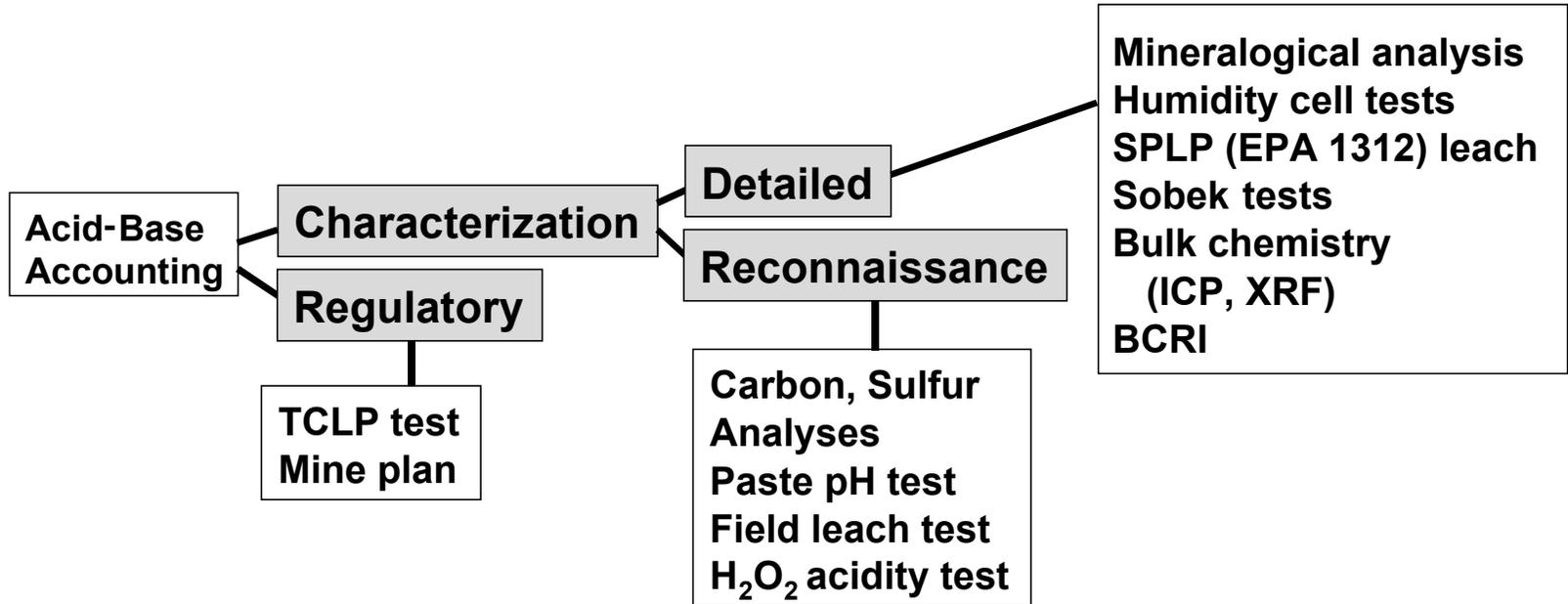
**Assessing the Toxicity Potential
of Mine-Waste Piles Workshop**

June 1, 2003

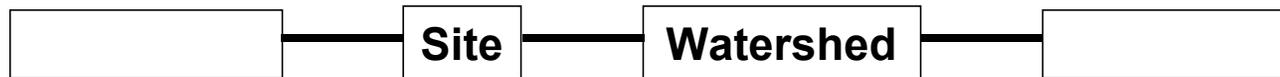
U.S. Department of the
Interior

U.S. Geological Survey

Flow Chart for Ranking and Prioritization



Scale



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.**

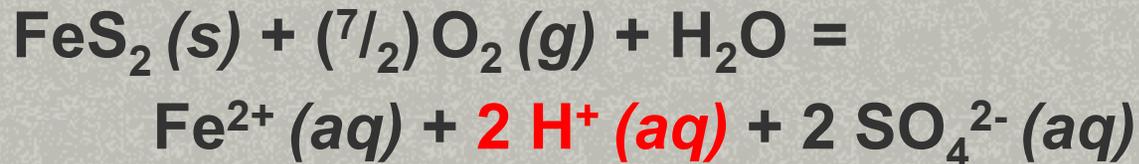


Acid-Base Accounting: What is it?

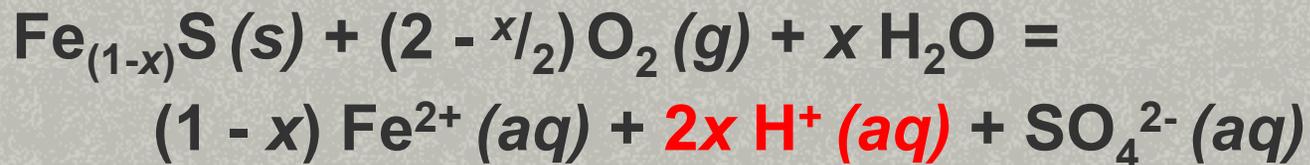
- Acid-Base Accounting (ABA) is the balance between the acid-production and acid-consumption properties of a mine-waste material.
- Minerals in waste material (mostly sulfides; mostly pyrite) react with water and oxygen to produce sulfuric acid.
- This acid is itself detrimental to water quality.
- Acid leaches metals from material and introduces them into environment.

Some Acid Producing Reactions

pyrite



pyrrhotite



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_3AsS_4)
- Marcasite (FeS_2)
- Arsenopyrite (FeAsS)
- Tennantite ($\text{Cu}_{12}\text{As}_4\text{S}_{13}$)
- Orpiment (AsS)

Acid Neutralization Reactions

above pH 6.4



below pH 6.4



Or



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: $NNP = NP - AP$

And

Neutralization Potential Ratio: $NPR = NP/AP$

The unit of measurement is kg CaCO₃ per ton,
or equivalently

parts per thousand CaCO₃

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:
 - $100 \text{ g CaCO}_3/\text{mole CaCO}_3 : 32\text{g S} / \text{mole S}$
 - or in standard AP units
 - $31.25 \text{ ‰ CaCO}_3 \text{ per } \% \text{ S}$ (‰ 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 CaCO_3 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).
- $(9.5 * 31.25 * 3 = 891 \text{ parts per thousand } \text{CaCO}_3)$

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.

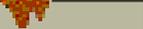


British Columbia Research Initial Test (BCRI)

- **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)**

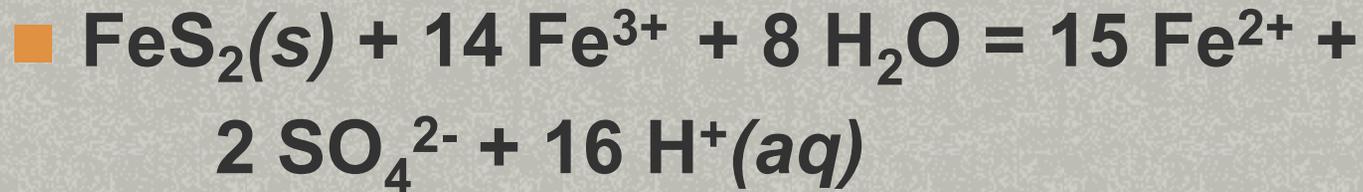
Effect of siderite



and



but



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**



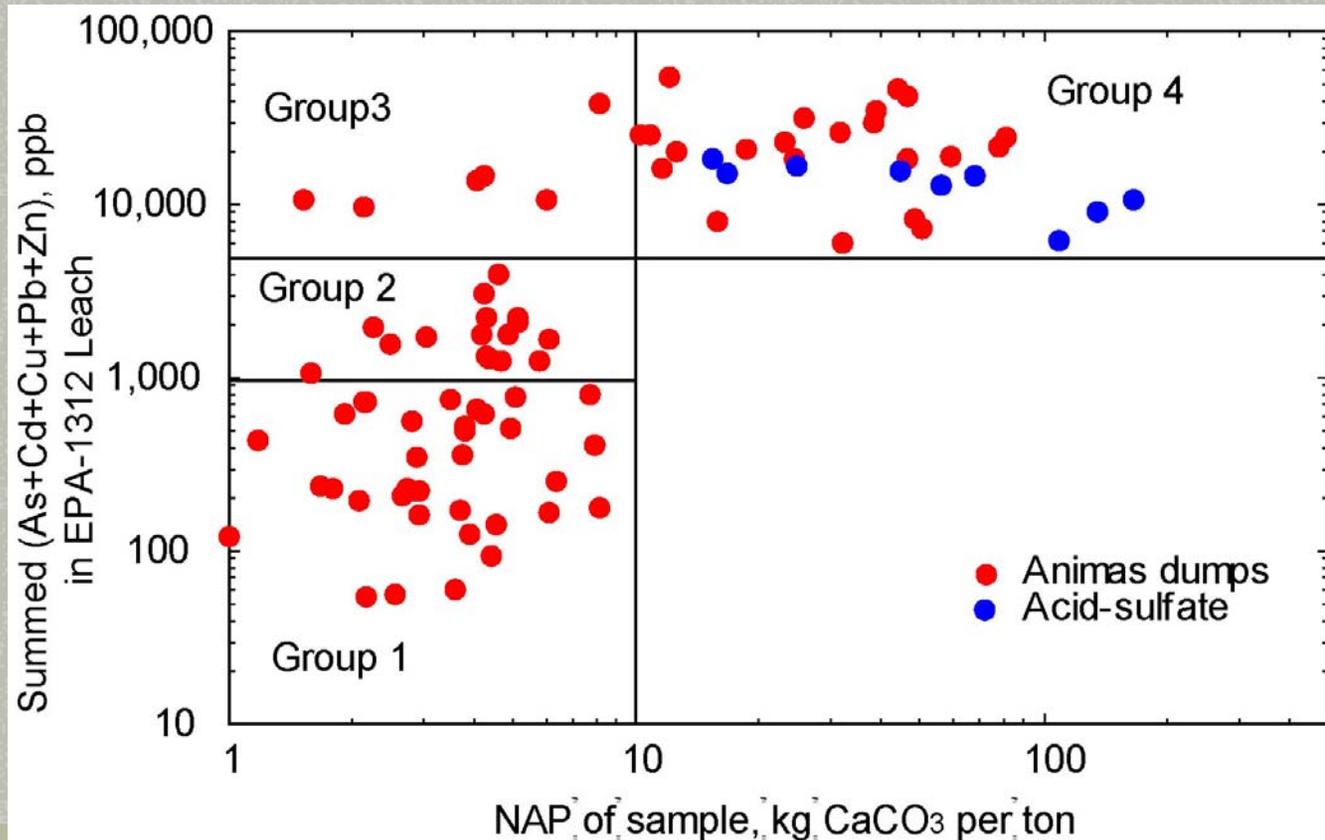
What does it mean?

- 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



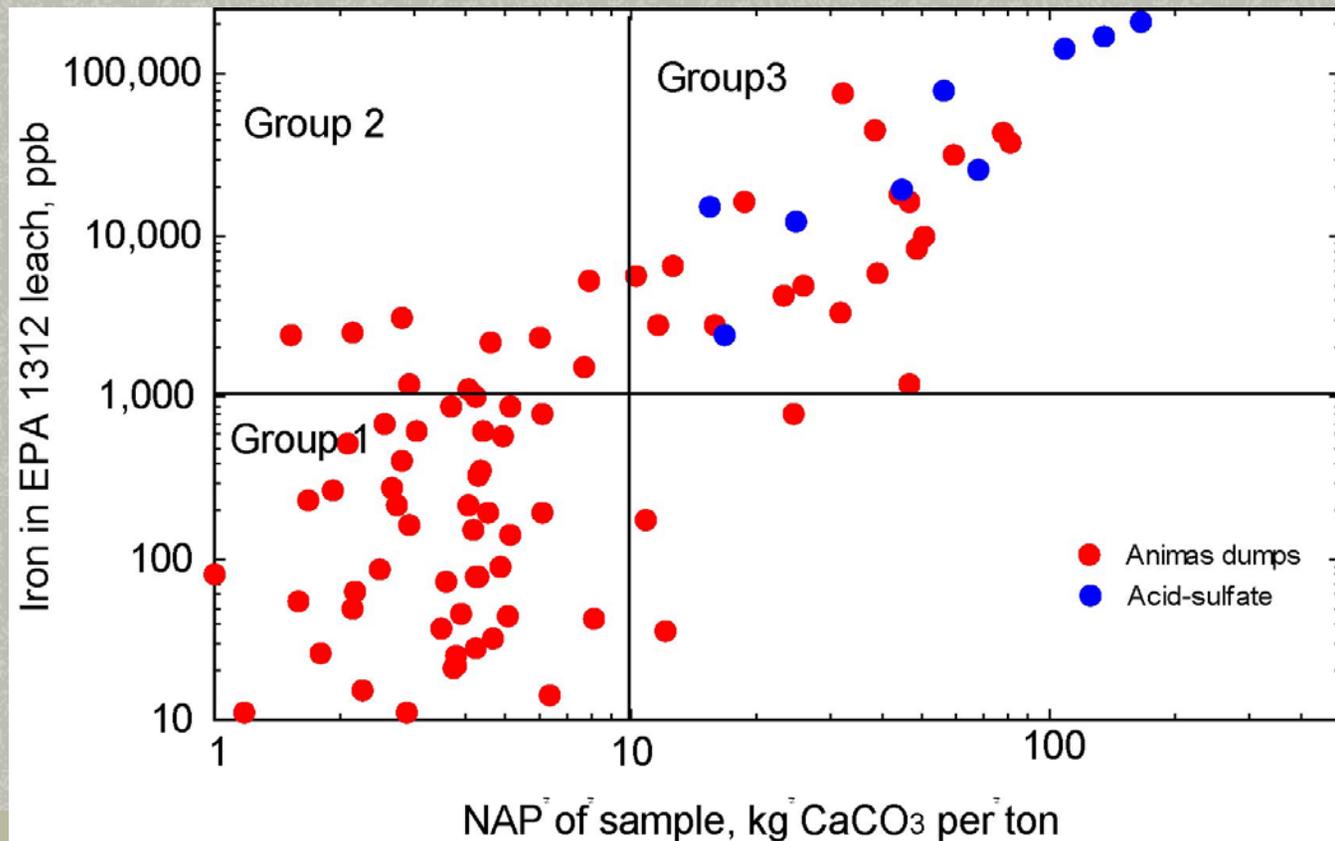
***Chemical* potential of mine waste to be an environmental concern**

- 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 CaCO_3 , 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 CaCO₃/ton) and <1,000 μg/L SDE
- Group 2, which has low acidity and moderate SDE (between 1,000 and 5,000 μg/L)
- Group 3, which has low acidity and high SDE (>5,000 μg/L)
- Group 4, which has high acidity (>10 kg CaCO₃/ton) and high SDE (>5,000 μg/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

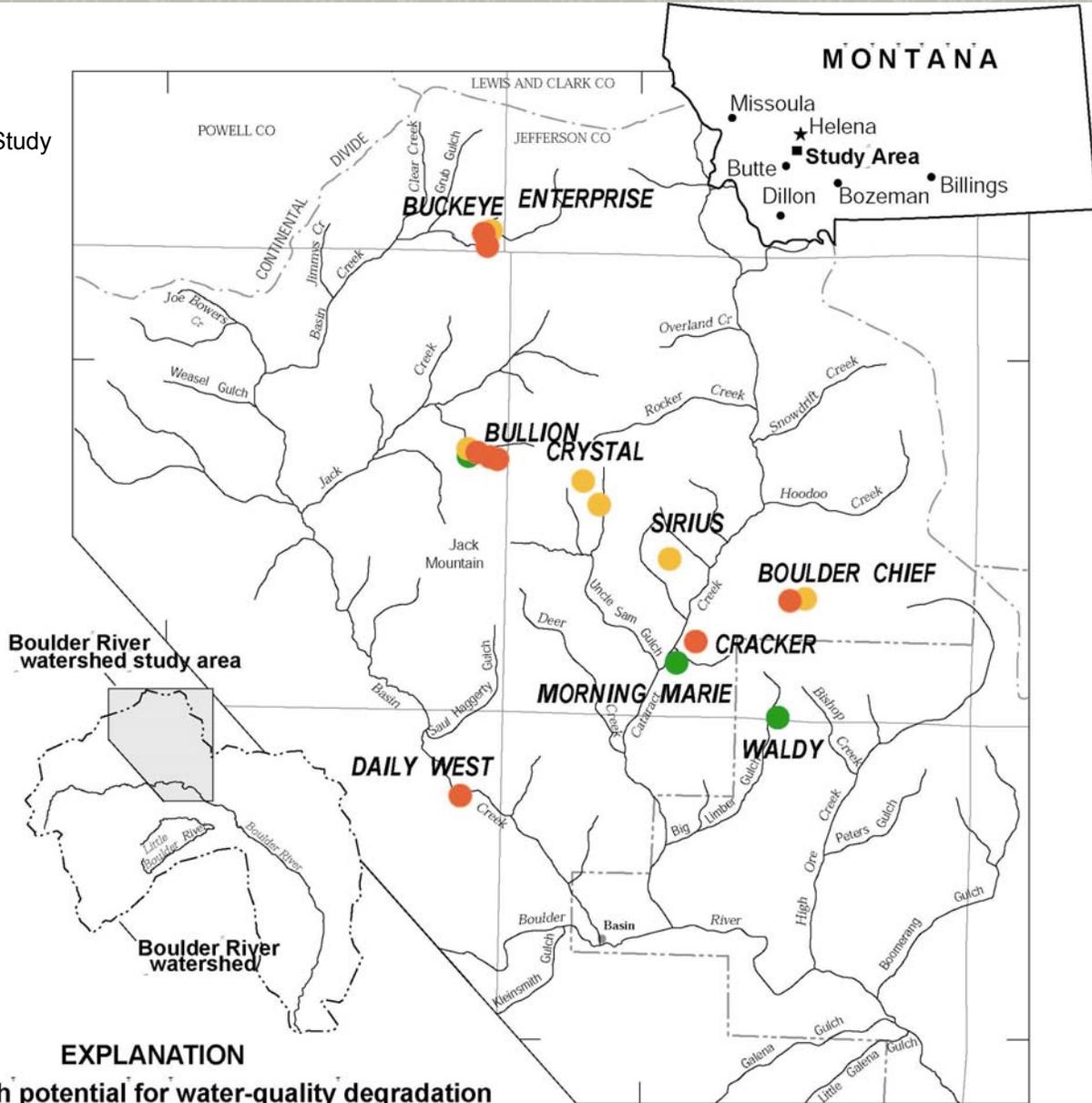
Aspects of the leachate chemistry groups

- **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

Map of Boulder Study area



EXPLANATION

- High potential for water-quality degradation
- Intermediate potential for water-quality degradation
- Low potential for water-quality degradation

