ASSESSING THE TOXICITY OF MINE WASTE PILES: CHEMICAL CRITERIA

TOM WILDEMAN
Colorado School of Mines
Flow Chart for Ranking and Prioritization

- Chemical Assessment
  - Regulatory
    - Characterization
      - Detailed
        - Reconnaissance
          - Scale
            - Microscopic
            - Site
            - Watershed
              - Regional

- Paste pH
- Modified TCLP
- USGS FLT Test
- CDMG Test
  - pH
  - Conductivity
  - Acidity
  - Alkalinity
OUR GOAL

• PROVIDE TOXICITY ASSESSMENT & RANKING OF MINE-WASTE PILES
  – PHYSICAL & CHEMICAL ASSESSMENT
  – SIMPLE ASSESSMENT TESTS

CHEMICAL CRITERIA BUILD ON THE WORK BY THE USGS & CDMG, ESP. THE LEACHING TESTS THEY DEVELOPED
BACKGROUND

• **USGS WORK**
  – How To Sample A Waste-Rock Pile
  – USGS Field Leach Test

• **CSM WORK (WILDEMAN & RANVILLE)**
  – Search For Good Materials (Animas River)
  – Russell Gulch and North Clear Creek Studies

• **CDMG WORK (JIM HERRON)**
  – CDMG Leach Test (Animas River)
  – Waste-Pile Assessment (Virginia Canyon)
SUMMARY OF STUDIES

• Upper Animas River (CDMG)
  – 50 sulfidic waste piles
• Upper Animas River (CSM)
  – 28 sulfidic & carbonate waste piles
• USGS Studies
  – Approx. 300-400 samples in at least 10 studies
• Virginia Canyon (CDMG)
  – 29 stream sediments from sulfidic wastes
• Russell Gulch (CSM)
  – 27 sulfidic waste piles
• THE DECISION TREE HAS BEEN DEVELOPED PRIMARILY FROM INVESTIGATION OF WASTE PILES FROM SULFIDE ORE MINING, PRIMARILY IN THE WESTERN U.S.

• HOWEVER, OVER 300 WASTE PILES AND 30 SEDIMENTS HAVE BEEN ASSESSED DURING THE DEVELOPMENT.

• EVEN THOUGH THE TESTS ARE COMPARABLE TO REGULATORY TESTS, THIS IS STILL CONSIDERED A RECONNAISSANCE TOOL.

• APPLICATION IS TO MINE-WASTE PILES & NOT TO ACIDIC SOILS.
Concerning the tests and observations within the criteria, only the paste pH test can be used as an either/or criterion for determining toxicity. For the other tests, ratings will have to be developed for which the aggregate score will determine the degree of hazard of a waste-rock pile.
SCIENTIFIC BACKGROUND & HIGHLIGHTS

• VIRGINIA CANYON STUDY
  – SIMILARITY OF WATER CHEMISTRY DURING RUNOFF & STORM EVENTS
  – WHICH LEACHATE TESTS COMPARE BEST WITH THE WATER.
  – COMPARISON OF LEACHATE TESTS WITH WATER FROM SEDIMENTS (pH < 5)

• UPPER ANIMAS RIVER STUDY
  – THE ELEMENT CONCENTRATION PATTERN GRAPH (ECPG)
  – RESULTS FROM SEDIMENTS WITH pH > 5.
UNKNOWN MINE NEAR
GLORY HOLE, CENTRAL CITY
USGS SAMPLING PROTOCOL

DIVIDE DUMP INTO AT LEAST 30 CELLS OF EQUAL AREA

COLLECT SURFACE SAMPLE (15 cm) OF AT LEAST 100 g FROM EACH CELL

COMBINE SUB-SAMPLES INTO A COMPOSITE

DRY SIEVE COMPOSITE TO < 2 mm FOR AT LEAST 1 kg OF FINAL COMPOSITE SAMPLE
NANCY DOING RANDOM SAMPLING
USGS FLT LEACHATE TEST

• Determines the potential for metal and acid release from mine waste when exposed to natural waters
• Extraction Ratio 20:1 on a mass basis (Same as EPA 1311 and EPA 1312)
• 50 g < 2 mm (< 10 mesh) sediment sample is brought to 1 L using deionized water
• Hand shaken for 5 minutes; allowed to settle for 10 minutes
• Leachate is filtered for ICP-AES analysis
CDMG LEACHATE TEST

• Determines the potential for metal release from soils when exposed to natural waters

• Volume basis with low water / sediment

• 300 ml of deionized water was added to 150 ml of whole sediment sample

• Stirred for 15 seconds; allowed to settle for 90 minutes

• Leachate prepared for ICP-AES analysis
CSM MODIFIED TCLP TEST

- Modification of Method 1311 developed by the EPA
- Determines the mobility of metals in the presence of acidic waters
  - Extraction fluid of 5.7 ml concentrated acetic acid, 64.3 ml 1 M NaOH and ~930 ml deionized water (pH=4.93)
  - 40 ml of the extraction fluid was added to 2.0 g < 80 mesh sediment sample
  - Solution agitated end over end for 18 hours
BIG QUESTION ON TCLP

Should a pH of 5 or 3 be used???

• pH of 5 simulates most carbonate extractions
• Most waste piles are already acidic
• Primarily looking for comparisons among the three leachate tests, and not necessarily for regulatory problems.
OTHER MEASUREMENTS

- Fizz test with 10 % HCl for presence of carbonates
- pH on the CDMG leachate
- Ionic conductivity on CDMG leachate
- Acidity/ alkalinity measurement on CDMG leachate
NOW, ON TO THE RESULTS
BASE OF VIRGINIA CANYON

- pH: 3.00
- Eh: 702.1 mV
- Conductivity: 1475 $\mu$S/cm
VIRGINIA CANYON WATER

Base of Virginia Canyon Water Data

<table>
<thead>
<tr>
<th>Elements</th>
<th>Concentration (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al</td>
<td>0.01</td>
</tr>
<tr>
<td>Ca</td>
<td>0.10</td>
</tr>
<tr>
<td>Cu</td>
<td>1.00</td>
</tr>
<tr>
<td>Fe</td>
<td>10.00</td>
</tr>
<tr>
<td>Mg</td>
<td>100.00</td>
</tr>
<tr>
<td>Mn</td>
<td>1000.00</td>
</tr>
<tr>
<td>Ni</td>
<td>0.01</td>
</tr>
<tr>
<td>P</td>
<td>0.10</td>
</tr>
<tr>
<td>Pb</td>
<td>1.00</td>
</tr>
<tr>
<td>Sr</td>
<td>10.00</td>
</tr>
<tr>
<td>Zn</td>
<td>100.00</td>
</tr>
</tbody>
</table>

May H20, Aug H20, Rain Storm
OTHER POSSIBLE LEACHATE TESTS

Sediment at Base of Virginia Canyon
Selected Extraction Data

<table>
<thead>
<tr>
<th>Elements</th>
<th>Concentration (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al</td>
<td>May H2O</td>
</tr>
<tr>
<td>Ca</td>
<td>SPLP</td>
</tr>
<tr>
<td>Cu</td>
<td>FeO Digest</td>
</tr>
<tr>
<td>Fe</td>
<td>APP</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Elements</th>
<th>Al</th>
<th>Ca</th>
<th>Cu</th>
<th>Fe</th>
<th>Mg</th>
<th>Mn</th>
<th>Ni</th>
<th>P</th>
<th>Pb</th>
<th>Sr</th>
<th>Zn</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Sediment at Base of Virginia Canyon
Selected Extraction Data

Elements

Log Concentration (ppm)

Al Ca Cu Fe Mg Mn Ni P Pb Sr Zn

May H20
CDMG Test
USGS Test
TCLP
VIRGINIA CANYON JUST BELOW ROBINSON GULCH

- pH: 4.39
- Eh: 666.2 mV
- Conductivity: 831 μS/cm
Virginia Canyon Sediment Below Robinson Gulch
Selected Extraction Data
SCIENTIFIC BACKGROUND & HIGHLIGHTS

• VIRGINIA CANYON STUDY, 29 SEDIMENTS
  – SIMILARITY OF WATER CHEMISTRY DURING RUNOFF & STORM EVENTS
  – WHICH LEACHATE TESTS COMPARE BEST WITH THE WATER.
  – COMPARISON OF LEACHATE TESTS WITH WATER FROM SEDIMENTS (pH < 5)

• UPPER ANIMAS RIVER STUDY, 11 SEDIMENTS
  – THE ELEMENT CONCENTRATION PATTERN GRAPH (ECPG)
  – RESULTS FROM SEDIMENTS WITH pH > 5
ELEMENT PATTERN GRAPH

• USE A LOG SCALE FOR GOOD RELATIVE COMPARISONS

• GROUP ELEMENTS ACCORDING TO CHEMISTRY
  – Na, K, SO₄ readily soluble
  – Ca, Mg, Sr carbonate phases
  – Pb, Cu, Zn, Ni carbonate/sulfide phases
  – Fe, Mn, Al oxide phases
SCIENTIFIC BACKGROUND & HIGHLIGHTS

• VIRGINIA CANYON STUDY 29 SEDIMENTS
  – SIMILARITY OF WATER CHEMISTRY DURING RUNOFF & STORM EVENTS
  – WHICH LEACHATE TESTS COMPARE BEST WITH THE WATER.
  – COMPARISON OF LEACHATE TESTS WITH WATER FROM SEDIMENTS pH < 5

• UPPER ANIMAS RIVER STUDY 11 SEDIMENTS
  – THE ELEMENT CONCENTRATION PATTERN GRAPH (ECPG)
  – RESULTS FROM SEDIMENTS WITH pH > 5.
Concerning the tests and observations within the criteria, only the paste pH test can be used as an either/or criterion for determining toxicity. For the other tests, ratings will have to be developed for which the aggregate score will determine the degree of hazard of a waste-rock pile.
BOTH CRITERIA ARE IMPORTANT

• CHEMICAL
  – Ranks availability of contaminants

• PHYSICAL
  – Ranks ability to deliver contaminants