Permanganate Passivation of Sulfide Rock – Field Trial Results

Presentation at 11th Annual British Columbia ML/ARD Workshop
December 2, 2004; Vancouver, BC

Dirk van Zyl, Glenn Miller and Tim Tsukamoto
University of Nevada, Reno

dvanzyl@mines.unr.edu; gcmiller@unr.nevada.edu; timothyt@unr.edu
Introduction to Permanganate Passivation

- Technology developed by DuPont; patent donated to UNR in 1999
- A methodology to “permanently coat” sulfides with manganese oxide
- Apply permanganate, magnesium oxide at pH>12 to rock containing exposed iron-sulfide minerals
- Application:
  - Can use lime and/or sodium hydroxide to adjust pH
  - “Reaction time” ~ 2 to 3 hours
- Test for adequacy in laboratory set-up:
  - Dilute hydrogen peroxide (15 ml 30 % peroxide to 85 ml DI water)
  - Observe pH change over 3 hours
Field Trials

• Pit walls:
  – Golden Sunlight mine – weathered and fresh rock surfaces

• Rubble piles:
  – Golden Sunlight mine – weathered and fresh rubble
  – Gilt Edge – weathered materials
Pit Walls
November 2000

- Weathered pit wall high up in pit
- Initial ideas:
  - “Wash” pit wall and fractures to remove sulfates; laboratory rinsing tests show about 3 pore volumes required to do this
  - Cover the bench with clay except for front part (near face to be passivated) and irrigate solutions onto front end of bench and into the fractures until solution flows out of face
November 2000 (2)

- Approach did not work; solutions flowed downward into fractures and did not exit on face
- Applied solution directly using water truck
- Three sections:
  - No treatment
  - Control – pH and MgO
  - Permanganate
Monitoring

- Set up pit wall monitoring stations – tygon tubing siliconed to pit wall
  - Stations 1 to 4 on permanganate passivated wall
  - Stations 5 to 7 on control
  - Stations 8 to 10 no treatment
- Monitored during summer and fall of 2001
Results

• Completely inconclusive
• pH values, sulfates, metals were all variable between the sites and treatments
• Potential causes:
  – Windblown materials onto pit wall containing sulfides
  – Ongoing surface weathering of surface exposing fresh sulfides
  – Combinations of these
MSE Trials

• Series of tests to compare different treatments:
  – Ecobond™ of MT²
  – Furfuryl alcohol resin sealant (FARS)
  – MgO technology UNR
  – Permanganate passivation

• Technologies applied October to December 2001

MSE Trial Results

- Samples were taken in July, September and November 2002
- Final pH values:
  - Background, pH=3.4
  - Permanganate, pH=3.4
- For permanganate:
  - Loading reduced for all metals: Al (2.5); Cu (5.0); Fe (1.5); Mn (2.9); Ni (4.7) and Zn (5.7)
Residual Rinse
Metals Loading - Zinc

![Graph showing zinc levels in different sample ports with dates 7/22/02 and 11/4/02.](image-url)
Residual Rinse
Metals Loading - Copper

COPPER

SAMPLE PORT

GSM-2 GSM-3 GSM-4 GSM-5 FARS-1 FARS-2 FARS-3 FARS-5 MT2-2 MT2-3 MT2-4 UNR/Mg UNR/KP UNR/KP UNR/KP UNR/KP

7/22/02 11/4/02
Golden Sunlight Fresh Pitwall

- Treatment of pre-split excavated pit wall between October and December 2002
- Passivation done in sections as pit excavation proceeded
- Ultimate section of passivated pit wall was 250 feet wide by 100 feet high
Passivation Process

• Three steps:
  – MgO at pH=10 to rinse wall
  – pH=12 to raise alkalinity
  – Permanganate solution at pH>12 for 3 hours

• Monitoring done from specially marked sections on pit wall between December 2002 and July 2003

• Access became too dangerous after July 2003
Figure 6. Golden Sunlight Mine Pitwall Passivation Project. Average dissolved zinc concentration plotted vs time for the passivated plots (P), dust control liner plots (L), treatment control plots (C) and final control sample (taken off of sampling plots).
Table 9. Golden Sunlight Mine Pitwall Passivation Project. Average TDS value plotted vs time for the passivated plots (P), dust control liner plots (L), treatment control plots (C) and final control sample (taken off of sampling plots).
Overall Conclusions for Pit Wall Studies

- Passivation of fresh rock is more successful than passivation of weathered rock
- Weathered rock faces must be carefully prepared
- Sampling of pit walls causes specific problems
- Observations show that passivated fresh rock walls are visually more intact; passivation seems to improve surface integrity
Rubble Piles
Rubble Piles – Golden Sunlight

• Initial rubble piles placed in November 2000; weathered rock from initial pit wall area

• Second set of rubble piles – fresh material placed in May 2001

• Three piles in each set:
  – No treatment
  – Control: MgO and pH control
  – Permanganate
Monitoring Results

- Water quality samples were taken on a regular basis from May 2001 to August 2003 for the weathered rock and August 2001 to August 2003 for the fresh rock.
Fresh Rock

Date | pH
--- | ---
1/9/2001 | 4
4/19/2001 | 2
7/28/2001 | 6
11/5/2001 | 8
2/13/2002 | 10
5/24/2002 | 12
9/11/2002 | 14
12/10/2002 | 0
3/20/2003 | 2
6/28/2003 | 4
10/6/2003 | 6
1/14/2004 | 8

Legend:
- No Treatment
- Control
- Passivated
Weathered Rock

Copper (mg/l) vs. Date

- No Treatment
- Control
- Passivated

Date:
- 1/9/2001
- 4/19/2001
- 7/28/2001
- 11/5/2001
- 2/13/2002
- 5/24/2002
- 9/1/2002
- 12/10/2002
- 3/20/2003
- 6/28/2003
- 10/6/2003
- 1/14/2004

Copper (mg/l)
- 0
- 5
- 10
- 15
- 20
- 25
- 30
- 35
Discussion of Results

• Weathered rock:
  – pH about the same for all treatments
  – TDS for passivated rock somewhat lower up to the end
  – Cu for passivated rock lower

• Fresh rock:
  – pH higher for passivated rock
  – TDS lower for passivated rock
  – Cu lower for passivated rock

• Weathering products interfere with passivation unless they can be “washed” off – consistent with laboratory tests
Gilt Edge Waste Rock

- Part of EPA Multi-Cell Treatability study:
  - Lime (the presumptive remedy; about 35 lb/ton)
  - KEECO
  - Envirobond™ of MT²
  - Permanganate
  - ViroMine™ of Virotec International from the Bauxsol™ Technology (this technology was added later)

- 12 specially prepared lined cells with drains; each containing about 140 yd³
- Field installation September to November 2000
Application and Monitoring

- Mix lime and MgO with rock using a backhoe
- Place in one foot thick lifts
- Spray permanganate solution over the whole area
- Sample and analyze effluent from drain pipe
- Add water to top of cells if not enough precipitation for samples
Gilt Edge TDS

<table>
<thead>
<tr>
<th>Date</th>
<th>UNR Cell 3</th>
<th>UNR Cell 8</th>
<th>Control</th>
<th>PR</th>
</tr>
</thead>
<tbody>
<tr>
<td>1/9/2001</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4/19/2001</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>7/28/2001</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>11/5/2001</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2/13/2002</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5/24/2002</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>9/1/2002</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>12/10/2002</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3/20/2003</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>6/28/2003</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>10/6/2003</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Gilt Edge Dissolved Zinc

<table>
<thead>
<tr>
<th>Date</th>
<th>Zn (mg/l)</th>
<th>UNR Cell 3</th>
<th>UNR Cell 8</th>
<th>Control</th>
<th>PR</th>
</tr>
</thead>
<tbody>
<tr>
<td>1/9/2001</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4/19/2001</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>7/28/2001</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>11/5/2001</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2/13/2002</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5/24/2002</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>9/1/2002</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>12/10/2002</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3/20/2003</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>6/28/2003</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>10/6/2003</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Results to Date

- Samples taken between March 2001 and summer 2004 (newer data not available)
- A 2002 report by MSE summarizes the results for all the treatments and concluded that the permanganate treatment resulted in (note % reduction is with respect to one control cell):
  - pH that will meet South Dakota ambient water quality criteria
  - 88.5 percent reduction in TDS
  - 99.8 percent reduction in dissolved As
  - 99.9 percent reduction in dissolved Cd
  - 99.8 percent reduction in dissolved Cu
  - 99.7 percent reduction in dissolved Zn
Overall Outcomes of Passivation Field Trials

- Scaling up from laboratory tests on small samples (10 g samples) to the field is not trivial
- Optimum application method of passivation solution for field applications is still under investigation
- More difficult to passivate weathered materials
- Fresh pit wall surfaces at Golden Sunlight resulted in good passivation; long-term monitoring not available
- Passivation of fresh rock pile at Golden Sunlight was more successful than weathered rock pile
- Passivation of weathered rock piles at Gilt Edge worked well, providing consistent data for three years
Next Steps

• Larger field trials; or full scale application
• Field application methods of technology: spray, tumble, immersion?
• Better understanding of the mechanisms, both chemical and physical
• Understanding the potential long-term success of passivation; effects of physical and chemical weathering, reduced conditions, vegetation, etc.
Acknowledgements

- Placer Dome for sponsoring the work at Golden Sunlight, especially the help of Rory Tibbals
- EPA and MSE for funding the Golden Sunlight Pitwall and Gilt Edge field trials
- Lynn McCloskey of MSE for copies of Golden Sunlight data and photos
- Vaughn Moncrieff who helped with the Gilt Edge study and is presently completing a thesis on the work
Questions?