Antimony Removal From Mine Water Using Adsorbent Media

June 6, 2013
Drumulummon Mine

History

• Underground gold and silver mine dating to the 1870s
• Mine reaches a depth of 1,600 ft bgs
• Following closure in the early 1900’s, the deeper workings flooded (daylight at the 400 level)

Current Operations

• In 2007 RX Exploration (owner/operator) began further exploration of the property.
• Dewatering the workings (300 gpm) to allow further exploration of the existing workings, and to support subsequent mining
Initial Water Treatment

• DEQ issued a temporary discharge permit. Based on the initial analyses of mine water, arsenic was the only constituent above discharge limits

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Historic Value</th>
<th>Discharge Limit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Arsenic</td>
<td>0.018 mg/L</td>
<td>0.003 mg/L</td>
</tr>
</tbody>
</table>

• CDM Smith installed arsenic treatment system underground, in the old hoist room. Treatment consisted of arsenic adsorption onto iron-based media (Bayoxide SORB 33®) prior to discharge

• Initial operation of the treatment system worked well
Water Treatment, Continued

• As treatment continued, adsorption media life was significantly shorter than predicted, requiring media change-out. Troubleshooting was performed.

• As dewatering continued and the water level in the mine receded, water quality changed significantly. Suspended solids, iron, manganese, arsenic, and pH increased. Antimony concentrations increased from non-detect to above the discharge limits.
EMP Results

Manganese oxides coating the media

Manganese concentrations exiting the final adsorption vessels were much less than influent concentrations, indicating manganese precipitation within the media beds.
## Mine Water Quality

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Historic Values</th>
<th>Post Dewatering Values</th>
<th>Discharge Limit</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>7.2-7.7</td>
<td>7.9-8.5</td>
<td>NA</td>
</tr>
<tr>
<td>Alkalinity</td>
<td>200-300 mg/L</td>
<td>300 mg/L</td>
<td>NA</td>
</tr>
<tr>
<td>TDS</td>
<td>300 mg/L</td>
<td>300 mg/L</td>
<td>NA</td>
</tr>
<tr>
<td>Antimony</td>
<td>ND</td>
<td>20-40 mg/L</td>
<td>0.006 mg/L</td>
</tr>
<tr>
<td>Arsenic</td>
<td>0.018 mg/L</td>
<td>20-30 mg/L</td>
<td>0.003 mg/L</td>
</tr>
<tr>
<td>Iron</td>
<td>ND</td>
<td>0.5 mg/L</td>
<td></td>
</tr>
<tr>
<td>Manganese</td>
<td>&lt;1 mg/L</td>
<td>1-2 mg/L</td>
<td>NA</td>
</tr>
</tbody>
</table>
Conventional Antimony Treatment Options

- EPA BATs
  - Coagulation and Filtration
    - Iron or aluminum coagulant
    - Requires pH control (4.5 to 5.5)
    - Generates sludge
    - Competing oxidation states (oxidized arsenic, reduced antimony are optimum for adsorption)
  - RO
    - Generates continuous brine stream requiring disposal
- Approaches are effective for both antimony and arsenic removal, but neither was practical at the Mine
Antimony Removal

- Goal: identify an alternative means to achieve arsenic and antimony removal in a single process
- Arsenic removal chemistry well understood, but antimony removal mechanisms are not nearly as well known
- Titanium Dioxide media was identified as a possible adsorbent media that could achieve treatment objectives
- Iron and Manganese were identified as likely foulants and would require removal
- The approach would require testing
Column Test Design

Influent Mine Water (chlorinated)

Backwash Waste

Backwash Tubing connected to any of the 4 Columns as Necessary

Column 101 (Greensand)

No pH Adjustment ~7.5

Column 102 (TiO2)

Flow Meter

pH Adjustment to 5.5

Acid

Flow Meter

Column 201 (Greensand)

Column 202 (TiO2)

Flow Meter

Treated Effluent Water

Backwash Waste

Flow Meter

Connected to any of the 4 Columns as Necessary

Influent Mine Water

Flow Meter
Effect of Manganese and Influent Antimony at Existing pH

![Graph showing the effect of manganese and influent antimony at existing pH. The graph includes concentrations in milligrams per liter (mg/L) plotted against bed volumes. The x-axis represents bed volumes, while the y-axis represents concentration (mg/L). The graph has three lines: one for Antimony (Eff), one for Shaft Antimony (Raw), and one for Manganese. The concentration ranges from 0.005 to 0.035 mg/L, and the bed volumes range from 0 to 70,000.]
Effect of Manganese and Influent Antimony with pH Adjustment to 5.5 su

![Graph showing the effect of manganese and influent antimony with pH adjustment to 5.5 su. The graph includes lines for manganese, antimony (raw), and antimony (eff) concentrations over bed volumes.]
Column Testing Results

• Antimony removal was achieved under both test conditions
• Effluent arsenic concentrations were all were below detection
• Operating issues (poor chlorine and pH control) created some uncertainty in the test data
• Recommended optimum pH (~5.5 s.u.) was not necessary to obtain removal. Raw water and pH-adjusted water performed similarly for extended runtimes.
• Media is readily fouled from manganese
Treatment System Modifications

- Install modified greensand media (Omni-SORB<sup>TM</sup>) to remove iron and manganese prior to the adsorption vessels.
- Addition of bleach upstream to disinfect the influent, maintain continuous regeneration the greensand media, and increase ORP (oxidize arsenic to As(V))
- Install TiO2 adsorption media (Adsorbsia/Metsorb) for removal of arsenic and antimony
Operational Issues and Experience

• Titanium Dioxide Media – not dense and therefore backwashing is ineffective. Effective pretreatment is very important.

• Breakdown of media in the presence of chlorine. Concentrations over 3 mg/L caused rapid breakdown of media. Concentrations ~1 mg/L allowed for extended operation of media. At Drumlummon, most media change-outs were due to media breakdown prior, not breakthrough.

• Recommended optimum pH (~5.5 s.u.) was not necessary to obtain removal. pH adjustment may improve adsorption capacity for arsenic and antimony, but is not required. Not cost effective or worth hassle to include pH control equipment at Drumlummon Mine.
Operational Issues and Experience

- Greensand media reduced Mn to 0.015 mg/L and Fe to 0.05 mg/L
- TiO2 media capacity is greater than 1 mg Sb/gram media, based on full scale operation
- Upstream removal of particulates, iron, and manganese is critical to the performance of the media. Pretreatment is more cost effective than frequent media replacement
- Vendors can’t effectively model antimony removal
- Pros – simple, flexible, low capital cost
- Cons – operating costs highly dependent on WQ
Conclusions

• Titanium Dioxide media is an effective approach for removing both antimony and arsenic. With increasing regulatory presence, treatment using adsorption may be a cost effective approach in many applications.

• Bench/Pilot Testing is highly recommended for any new application.
Questions