

# TREATMENT OF ANTIMONY AND ARSENIC WITHIN MINE WATER FROM THE DRUMLUMMON MINE, MONTANA USING TITANIUM DIOXIDE ADSORPTION MEDIA<sup>1</sup>

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**Abstract:** In recent years, Sb has received increased attention from regulatory agencies and the need for a reliable treatment technology for antimony-containing waters is necessary. Unfortunately, antimony is difficult to remove to the very low levels required. Adsorbents which have proven successful for the removal of arsenic have been disappointing when applied to Sb treatment. In the current investigation, a number of conventional media were tested at the bench-scale and in the full-scale system, including: Severn Trent E33 Bayoxide®, Severn Trent Omni-SORB™ greensands, activated carbon, and Dow ADSORBSIA™, a proprietary TiO<sub>2</sub> media. Each media was tested using pretreatment oxidation with sodium permanganate and sodium hypochlorite, and the TiO<sub>2</sub> was tested under varying pH conditions. Pre-oxidation with sodium hypochlorite followed by greensands and TiO<sub>2</sub> media was found to be the most effective and long lasting of the combinations tested. The results of the column and full-scale tests along with an evaluation of the removal mechanisms using electron microprobe analyses will be presented.

**Additional Key Words:** greensands, ADSORBSIA™, Bayoxide®, Omni-SORB™, PHREEQC modeling, electron microprobe.

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<sup>1</sup> Paper was presented at the 2011 National Meeting of the American Society of Mining and Reclamation, Bismarck, ND *Reclamation: Sciences Leading to Success* June 11 - 16, 2011. R.I. Barnhisel (Ed.) Published by ASMR, 3134 Montavesta Rd., Lexington, KY 40502.

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Proceedings America Society of Mining and Reclamation, 2011 pp 691-709

DOI: 10.21000/JASMR11010691

<http://dx.doi.org/10.21000/JASMR11010691>

## **Introduction**

### Geology

Mineralization at the Drumlummon Mine consists of hydrothermal vein deposits formed in response to emplacement of the Marysville stock and/or a series of younger intrusive centers (Walker, 1992). Gold mineralization occurred during the contact metamorphism of the host rocks and emplacement of gold bearing quartz veins during and after intrusion of the stock and associated fracturing of the Empire and Helena Formations. Free gold occurs in veins along with pyrite and chalcopyrite, which increase with depth. Pyrite occurs as minor disseminations and along thin veinlets, with minor amounts of chalcopyrite. The gangue mineralogy of veins in the Drumlummon is composed of quartz, carbonate and adularia. The Helena Formation which hosts the mineral veins consists of a 400 ft thick limestone unit that provides neutralization capacity to the area groundwater and mine waters.

### Historic Mining

Thomas Cruse located the Drumlummon claim in 1876 and in 1880 erected a 5-stamp mill at the upper end of Silver Creek. He worked shallow prospect holes for six years. By 1882 Cruse had single-handedly extended the adit 200 feet and cut the vein at a depth of 140 feet. The mine produced 6,000-7,000 tons of ore which was worked, in part, in arrastras and a little over half in the mill, with a return of \$144,539 in bullion. In February of 1883, Cruse sold the Drumlummon mine and lesser associated claims to an English syndicate for \$1,000,000 in cash and \$500,000 in shares. The English company found abundant ore reserves in the upper workings. Additional stamps were added to the mill and two amalgamating pans and a settler were put into operation. In 1885, the mill produced approximately \$80,000 each month with company profits at \$40,000 to \$50,000 each month (Goodale 1914, Goodale, 1915).

The Drumlummon was shut down in 1910 and flooded at the deeper levels when the operators lost a court case alleging they had mined onto an adjacent claim. The Drumlummon court case went on for 20 years, including 5 appeals to the Montana and US Supreme Courts by the Drumlummon operators which they ultimately lost. The successful litigant, the St. Louis Mining and Milling Company, then gained control of the Drumlummon in 1911. Between 1923 and 1929 90,995 tons were mined by leases. Another 68,662 tons is reported to have been mined

between 1946 and 1951 by the Montana Rainbow Company before that operator's mill burned down.

### RX Exploration Activities

The Drumlummon is developed down to the 1,600 foot level with 2 shafts. Substantial areas of the mine have remained flooded since 1910 and effectively have been “out of bounds” for exploration since that time. In 2007-08, RX consolidated land claims around the Drumlummon and began dewatering and underground rehabilitation. In February 2008, RX Exploration began core drilling on the 400 foot level of the Drumlummon mine under an exploration license. In April 2010, the Charley Vein system was discovered with returns as high as 3.13 ounces per ton (opt) gold and 55.6 opt silver. RX continues exploration of the area, including both unmined areas (due to historic property disputes), as well as previously mined areas with once un-economic grades of ore. As a result of the dewatering activities, the company currently generates about 300 gallons per minute of mine water containing concentrations of As and Sb which are above the permitted discharge limits set by the Montana Department of Environmental Quality (DEQ). In order to meet the relatively high flows and stringent discharge standards, an efficient and very effective treatment system had to be designed and implemented.

### Mine Water Quality and Design Considerations

A summary of the mine water quality is presented in Table 1.

The discharge standards for As and Sb are 0.003 mg/L and 0.006 mg/L, respectively. Arsenic concentrations within the mine water have been mostly in the 0.010-0.020 mg/L range, although an occasional spike to 0.030 mg/L is observed. Antimony has ranged mostly in the 0.020 to 0.030 mg/L range with occasional spikes to 0.040 mg/L. The very low standards for As and Sb limited the technologies that could be applied, and given that ion exchange and reverse osmosis were cost prohibitive, it was decided to pursue an adsorption-based system. Initially, before significant drawdown of the water level within the mine, concentrations of Fe, Sb, and Mn were very low or below the analytical reporting limit. Therefore, it was decided to pilot an iron-based adsorption media, Bayoxide®, that has been used successfully in the past to treat arsenic down to very low levels. Due to the initially low iron and manganese concentrations, fouling of the adsorption media by iron and manganese phases was not expected to be an issue. Given the track record of the media, the apparent lack of competing ions and potential media foulants

within the water, and the need to provide immediate treatment to maintain the mine development schedule, it was decided to implement a full-scale system. However, as the pumping lowered the level of the mine water, the chemistry of the influent to the system changed, particularly with respect to Fe and Mn. Although Mn and Fe are not important from a regulatory standpoint, the impact to the surfaces of the media was found to be important. Concentrations of Mn increased from <0.005 mg/L in 2008 to around 1 mg/L with occasional spikes up to 2 mg/L by 2010. Iron increased from 0.006 mg/L up to as high as 0.030 mg/L, with a typical concentration of about 0.015 mg/L.

**Table 1. Mine Water Quality, 2008-2010**

Parameter	Range	DEQ Permit Limits <sup>1</sup>
pH (su)	7.0 – 8.0 (3) <sup>2</sup>	-
Alkalinity (mg/L)	200 – 300 (3)	-
Sulfate (mg/L)	3-5 (3)	-
Sulfide (mg/L)	<1 (3)	-
Arsenic (mg/L)	0.010 – 0.030 (23)	0.003
Antimony (mg/L)	0.020 – 0.040 (23)	0.006
Cadmium (mg/L)	<0.0001 (3)	0.005
Calcium (mg/L)	60 – 100 (3)	-
Copper (mg/L)	0.002 – 0.003 (3)	1.3
Iron (mg/L)	0.006 – 0.03 (23)	-
Lead (mg/L)	<0.0005 (3)	0.015
Magnesium (mg/L)	20 – 30 (3)	-
Manganese (mg/L)	<5 – 2000 (23)	-
Mercury (mg/L)	<0.00010 (3)	0.002
Zinc (mg/L)	0.010 – 0.047 (3)	2

1 Human Health

2. Parenthetic values are the number of analyses included for the range.

## **Bayoxide® Full-Scale Trial**

### **Objectives**

The objectives of the full-scale trial were to treat arsenic to below the discharge limit of 0.003 mg/L and to determine the required replacement frequency of the Bayoxide® media. The full-scale trial was designed based on 2008 data, which indicated that only arsenic was above the DEQ discharge criteria. In addition, it was anticipated that the media would not be subject to fouling as both Fe and Mn concentrations were low. As previously, discussed, conditions changed over the course of operations. The chemical changes included not only increases in Fe and Mn concentrations, but also increases in the organic C concentrations and overall lower redox. In addition, as the inlet to the pump was lowered deeper into the mine (due to lowering the water level), particulate loads to the system increased. The bag filters used to remove the particulates then became overloaded which allowed suspended particles to reach the lead adsorption vessel. One or more of the system changes resulted in lower than expected media life and the addition of new tasks as follows:

- System diagnostics to determine the cause or causes of the low media life.
- Determine the best solution to the problem and recommend changes to the system.

### **System Design and Operation**

With input from the vendor, CDM designed a system consisting of two circuits, each with a lead and lag vessel to prevent breakthrough (see Fig. 1).

The vessels were installed within the mine workings in order to prevent the freezing issues that would occur for an outside installation (see Fig. 2). The system worked well initially, but after only one month of operation breakthrough occurred. The manufacturer of the media predicted a 6 month media life. The reason for the much less than expected media life was believed to have been caused by biofouling, buildup of particulates within the vessels and/or inactivation of the media by chemical precipitates.

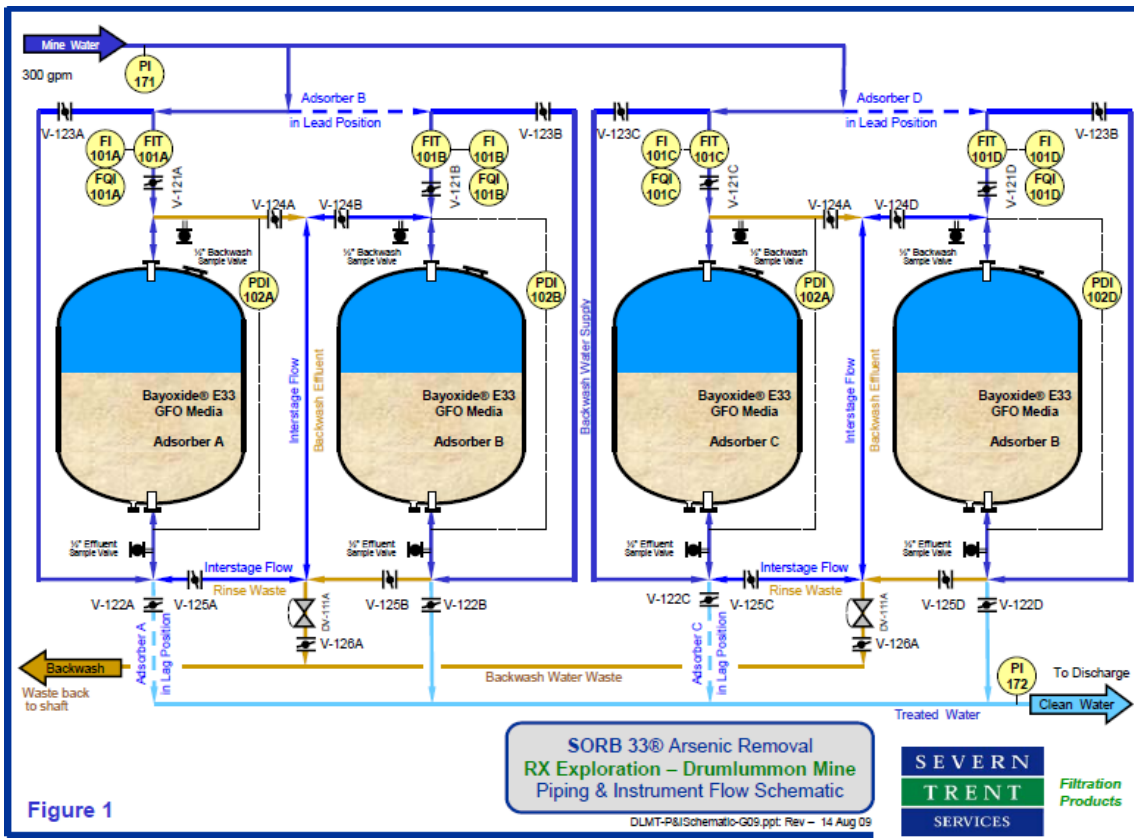


Figure 1 – Schematic of the initial treatment system for the Drumlummon Mine water.



Figure 2 – Completed installation.

## System Diagnostics

The spent media was evaluated using a number of techniques, including the following:

- Elemental analysis of the media
- Geochemical modeling of the media porewater using PHREEQC
- Electron Microprobe (EMP) analysis of the media
- Leaching/Regeneration Testing

The elemental analysis was performed by x-ray fluorescence (XRF) and was limited mostly to the transition metals.

The EMP allowed the media grains to be viewed at magnifications up to 300,000 times and to perform an analysis on a single grain or part of a grain (such as a coating).

## Elemental Analysis

X-ray fluorescence analyses were performed on December 4, 2009 on a sample collected from the lead Bayoxide® vessel. Of the metals analyzed, only Mn was found to be building up within the media, with a concentration of 8,549 mg/kg after one month of operation. The As concentration was only 191 mg/kg, which should have been well below the adsorption site saturation according to the manufacturer.

## Geochemical Modeling

Geochemical modeling was performed using the USGS program PHREEQC (Parkhurst and Appelo, 1999). The results indicated that the mine waters were at saturation or supersaturated with respect to both Ca and Mn carbonates (see Table 2). The mine waters were also supercharged with CO<sub>2</sub> (partial pressures were over an order of magnitude higher than atmospheric levels of 10<sup>-3.5</sup> atm), which when degassed at the surface, would result in an increase in the pH and precipitation of carbonate minerals.

Table 2. PHREEQC Modeling Results.

Date	Calcite SI <sup>1</sup>	Rhodochrosite SI	Carbon Dioxide pp <sup>2</sup>
2/12/2008	0.71	1.27	10 <sup>-2.54</sup>
8/26/2008	0.21	0.83	10 <sup>-2.03</sup>
11/06/2008	0.48	1.04	10 <sup>-2.24</sup>
12/16/2009	-0.12	0.52	10 <sup>-1.76</sup>

1. SI = Saturation Index (SI = 0±0.5 indicates saturation, SI>0.5 indicates supersaturation, and SI<0.5 indicates undersaturation of the phase)
2. pp = Partial pressure in atmospheres

### EMP Analysis Results

Analysis of the media showed that significant non-media grains were present within the vessels (mostly quartz) and that the media and non-media grains were coated with either a manganese oxide or carbonate phase (see Fig. 3). Tiny grains of iron sulfide, on the order of 2 µm in diameter were also identified but this phase was not found coating any of the grains.

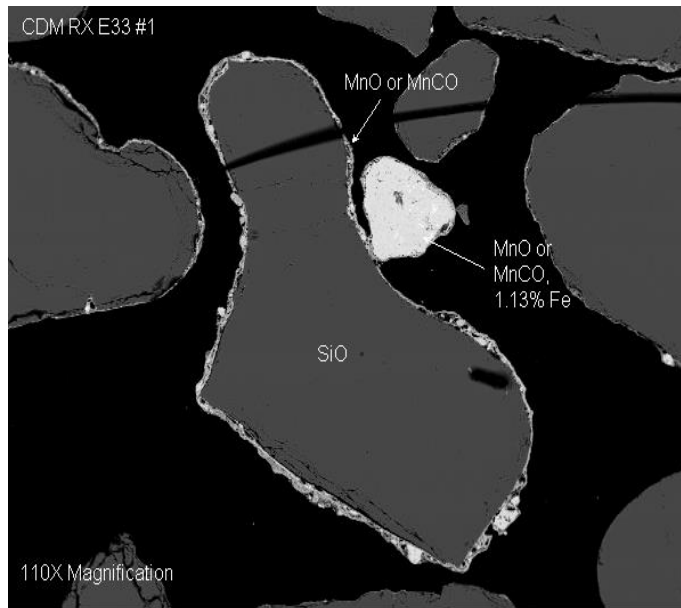


Figure 3 – Quartz grain coated with manganese oxide.



### Leaching/Regeneration Testing

Regeneration of a sample of the media was tested initially using sodium hypochlorite (to oxidize sulfides present and to kill any bacteria that may have been responsible for biofouling). Addition of the sodium hypochlorite resulted in significant gas generation, suggesting that organic matter was present that was being oxidized to CO<sub>2</sub> and water, and/or that sulfides were present that were being oxidized to SO<sub>2</sub>. Treatment of the media with HCl acid resulted in vigorous gas generation which had a H<sub>2</sub>S odor, suggesting the presence of sulfides and possibly carbonates within the spent media. However, neither sodium hypochlorite or HCl acid was found to be effective in regenerating the media, suggesting that oxide phases were also likely to have been present.

A more aggressive technique was performed using the methodology of Chen and Wang (2009), which consisted of the following steps:

- Bleach – To oxidize sulfides
- pH 2 Oxalic Acid – To dissolve Manganese (6 empty bed volumes [EBVs])
- pH 12 Caustic – To remove arsenic (5 EBVs)
- pH 2.5 HCl – To neutralize media surfaces (15 EBVs)
- H<sub>2</sub>O Rinse

Analyses of the leachate was performed following each step. The results are presented in Table 3.

**Table 3. Leaching/Regeneration Test Results.**

Solution	As (mg/L)	Fe (mg/L)	Mn (mg/L)
Oxalic	0.096	677	172
Caustic	18.8	239	3.45
HCl	1.77	59.5	0.42

The results indicated that the media could be regenerated with caustic, but only after removing the Mn with oxalic acid. The results also showed that the Mn identified during the

EMP analysis was likely  $\text{MnO}_2$  and not  $\text{MnCO}_3$ . The acid should have dissolved any divalent  $\text{MnCO}_3$  present, but it proved to be entirely ineffective. Oxalic acid dissolves Mn (and Fe) by reducing the ion to the more soluble +2 oxidation state ( $\text{Mn}^{+2}$ ). The fact that oxalic was so effective is a strong indication that the Mn was present as an oxidized phase ( $\text{Mn}^{+3}$  and/or  $\text{Mn}^{+4}$  oxide).

### **Column Study for Antimony Treatment**

Just as the mysteries of the arsenic treatment were being solved, Sb emerged as a parameter of concern. Apparently, the deeper levels of the mine contained higher antimony concentrations than were anticipated based on the initial, near surface, samples collected in 2008. The Bayoxide®, even when it was working for As, proved to be ineffective for treatment of Sb.

#### **System Conceptual Design**

Based on the findings from the As loading study, a new conceptual design was developed which included the following elements (starting at the upgradient end of the system):

- Bag Filters – to remove the particulates
- Sodium Hypochlorite addition – To oxidize the sulfide, Fe, a small fraction of the Mn, and to prevent biological activity
- Omni-SORB™ Greensand Filter – To oxidize and remove the Mn and Fe
- pH Adjustment – To optimize adsorption capacity of Sb and As (optional)
- ADSORBSIA™ Titanium Oxide Media – To remove the As and Sb

The design included filtration to address the particulate accumulation identified during the electron microprobe analysis. The sodium hypochlorite addition acted as a disinfectant to inhibit biological growth that may take place within the media. According to several studies (Fiella et al., 2002; Nakamaru et al., 2006, etc.), lowering the pH of the influent can enhance adsorption of Sb. However, some studies have shown that the benefits of pH adjustment are not worth the cost (Najm et al., 2010). Therefore, pH adjustment was viewed as an optional component of the system. The greensands would perform the function of removing the Fe and Mn from the system before coming in contact with the more expensive media. The Omni-SORB™ is a patented material manufactured by Severn Trent that has reactive surfaces capable of oxidizing Mn and Fe which can be regenerated using an oxidant such as hypochlorite. The adsorptive media is a

titanium oxide product called ADSORBSIA™ As500 which is manufactured by Dow. Literature from the vendor indicated that the material could be successfully applied for Sb removal. The new system was tested at the bench-scale in order to test the design elements and to optimize system performance.

### Column Study Design

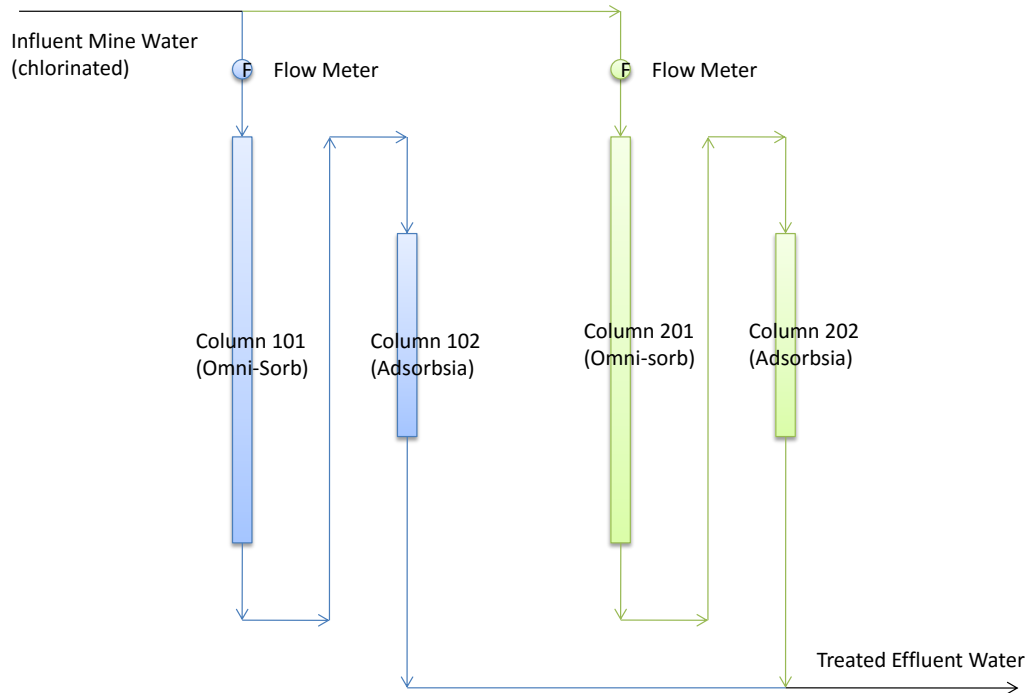
A bench-scale test column apparatus was constructed using translucent 2" PVC. The test unit was set up with two parallel test systems in order to operate two simultaneous test runs under different operating conditions. Each setup consisted of a lead and a lag column. The lead column was 60" in length and the lag column 24" in length. Each lead column was filled with 36" of Omni-SORB™ media from Severn Trent Services. This is a specialty catalytic greensand type media designed to oxidize Fe and Mn and then filter it from the water. This type of media requires the addition of sodium hypochlorite but does not require periodic regeneration using potassium permanganate. There are other competing brands of similar media available.

Each lag column was filled with 12" of adsorption media. Each train of columns was outfitted with a flowmeter and each column was equipped with pressure gauges and a valve manifold. Additionally, a common back-wash flowmeter and valving was included so that any single column could be backwashed individually, as necessary. Figure 4 depicts the test column configuration.

Each set of columns included a dedicated metering pump and injection point prior to the ADSORBSIA™ media. A dilute solution of H<sub>2</sub>SO<sub>4</sub> was metered into each set of columns (after greensand filtration) in order to lower the pH. Water in the first set of columns was lowered to approximately 6.5 su, and water in the second set of columns was lowered to approximately 5.5 su. The pH was manually monitored and adjusted as necessary.

Water was passed through each series of columns at a rate of approximately 600 mL/min; this resulted in a hydraulic loading rate of 6.8 gpm/ft<sup>2</sup> (277 L/m<sup>2</sup>), comparable to the full scale system at a maximum continuous flow of 300 gpm (1136 L/min.). This flow was monitored periodically, and the throttling valves were adjusted as necessary to maintain it. When system flows could no longer be maintained, or pressure drop through any individual vessel reached approximately 15 psi, the given vessel was backwashed until 40% bed expansion was achieved.

**Figure 4 – Block Flow Diagram**



The pH values were monitored periodically and the metering pump rates adjusted accordingly in an attempt to maintain a steady pH adjustment; however in reality it was quite difficult to maintain.

The following data were collected from the test columns periodically:

- Analytical Data: samples for dissolved metals were collected throughout the testing. Dissolved constituents analyzed included As, Sb, Fe, and Mn. Sample locations were (a) raw feed, (b) chlorinated feed, (c) vessel 101 effluent, (d) vessel 102 effluent, (e) vessel 201 effluent, and (f) vessel 202 effluent.
- Column flowrates
- Column pH values
- Chlorine testing (as part of the full scale operations)

### Column Study Results – Omni-SORB™

The pre-removal of Fe and Mn was shown during the Bayoxide® full-scale trial to be important to the proper functioning of the adsorption media. The raw data are presented in Table 4 and in Fig. 5a, 5b, 5c & 5d. The removal of Fe was largely achieved using sodium hypochlorite alone, although additional removal occurred within the Omni-SORB™ media. Manganese was largely unaffected by the hypochlorite addition. Removal within the Omni-SORB™ media was effective at times, with removals of over 99% of the Mn. However, due to plugging issues within the small-diameter columns used, efficiency decreased to the point where Mn passed through the media with little or no attenuation. The results also show that some As and Sb is removed within the Omni-SORB™, but not enough to meet discharge standards.

### Column Study Results – ADSORBSIA™

The results of the column testing are shown in Table 5 and Figures 5a, 5b, 5c & 5d.

Table 5 – Antimony Column Testing – ADSORBSIA™ Results

Elapsed Time	Mine Shaft			102 ADSORBSIA™			202 ADSORBSIA™		
	Sb	As	pH	Sb	As	pH	Sb	As	pH
0.00	0.024	0.016	7.4	<0.003	<0.001	-	<0.003	<0.001	-
3.00	0.023	0.012	7.4	<0.003	<0.001	2.2	<0.003	<0.001	2.5
5.74	0.032	0.016	7.4	0.001	<0.001	6.2	<0.003	<0.001	5.9
7.74	0.030	0.017		0.001	<0.001	6.0	<0.003	<0.001	3.8
11.74	0.030	0.016	7.5	0.002	<0.001	6.5	0.002	<0.001	6.2
14.74	0.024	0.013	7.8	0.003	<0.001	-	0.003	<0.001	-
18.74	0.024	0.013	7.8	<b>0.008</b>	<0.001	-	<b>0.007</b>	<0.001	-
21.74	0.034	0.015	7.7	<b>0.008</b>	<0.001	7.5	<b>0.033</b>	0.012	2.5
24.74	0.032	0.015	7.5	0.006	<0.001	7.5	<0.003	0.001	2.3
28.74	0.033	0.013	7.4	0.006	<0.001	-	0.001	0.001	-
32.74	0.029	0.012	7.5	<b>0.010</b>	<0.001	7.4	0.003	<0.001	6.2
35.74	0.028	0.012	7.4	0.002	0.001	3	0.001	0.001	2.7
39.74	0.024	0.012	7.5	0.006	<0.001	6.5	<b>0.009</b>	<0.001	7
42.74	0.021	0.010	7.4	0.005	<0.001	6	0.002	<0.001	2.6
45.74	0.020	0.010	7.9	0.005	<0.001	7.2	0.004	<0.001	2.1
49.74	0.024	0.014	8	0.003	<0.001	6.7	0.004	<0.001	6.6
51.74	0.024	0.010	8.1	0.004	<0.001	7.2	0.001	0.001	3.1
53.74	0.034	0.012	8.2	0.004	<0.001	7.2	0.004	<0.001	7.1
60.74	0.031	0.008	8	<b>0.030</b>	<b>0.007</b>	8.1	<b>0.014</b>	<0.001	7.2
67.74	0.034	0.011	8	<b>0.014</b>	0.001	8	0.005	<b>0.004</b>	2.4

Note: Bold indicates that the value was above the DEQ discharge criteria

Table 4 – Antimony Column Testing – Chlorination/Omni-SORB™ Results

Elapsed Time	Mine Shaft				Sodium Hypochlorite				101 (Omni-SORB™)				201 (Omni-SORB™)			
	Sb	As	Fe	Mn	Sb	As	Fe	Mn	Sb	As	Fe	Mn	Sb	As	Fe	Mn
0.00	0.024	0.016	0.016	0.912	0.024	0.016	0.004	0.902	0.016	ND	0.003	0.020	0.023	0.015	0.016	0.837
3.00	0.023	0.012	0.016	0.858	0.023	0.011	0.012	0.862	0.023	0.008	0.002	0.830	0.023	0.009	0.001	0.832
5.74	0.032	0.016	0.010	0.860	0.032	0.016	0.005	0.880	0.032	0.013	0.004	0.899	0.032	0.014	0.014	0.881
7.74	0.030	0.017	0.009	0.903	0.030	0.016	0.007	0.879	0.030	0.015	0.005	0.902	0.030	0.015	0.009	0.88
11.74	0.030	0.016	0.006	0.866	0.030	0.016	0.004	0.872	0.030	0.015	0.005	0.868	0.029	0.015	0.008	0.851
14.74	0.024	0.013	0.006	0.849	0.024	0.013	0.003	0.828	0.024	0.014	0.003	0.036	0.024	0.013	0.004	0.191
18.74	0.024	0.013	0.016	0.853	0.024	0.012	0.005	0.837	0.026	0.013	0.001	0.019	0.026	0.012	0.016	0.012
21.74	0.034	0.015	0.017	0.846	0.033	0.014	0.004	0.812	0.033	0.012	0.003	0.723	0.033	0.013	0.004	0.679
24.74	0.032	0.015	0.011	0.868	0.032	0.014	0.004	0.846	0.034	0.015	0.003	0.025	0.032	0.014	0.003	0.002
28.74	0.033	0.013	0.012	0.809	0.033	0.013	0.011	0.78	0.034	0.012	0.002	0.025	0.033	0.012	0.011	0.005
32.74	0.029	0.012	0.01	0.867	0.029	0.012	0.003	0.825	0.028	0.011	0.002	0.02	0.029	0.012	0.002	0.02
35.74	0.028	0.012	0.009	0.859	0.029	0.012	0.003	0.839	0.032	0.01	0.001	0.03	0.029	0.01	0.005	0.025
39.74	0.024	0.012	0.016	0.846	0.024	0.012	0.005	0.794	0.021	0.011	0.002	0.022	0.021	0.011	0.002	0.003
42.74	0.021	0.010	0.031	0.833	0.021	0.01	0.022	0.777	0.021	0.011	0.001	0.031	0.021	0.011	0.002	0.006
45.74	0.02	0.010	0.011	0.832	0.02	0.01	0.003	0.795	0.018	0.01	0.005	0.028	0.019	0.009	0.002	0.005
49.74	0.024	0.014	0.019	0.874	0.025	0.014	0.007	0.825	0.021	0.014	0.002	0.025	0.02	0.014	0.002	0.026
51.74	0.024	0.01	0.017	0.822	0.025	0.011	0.003	0.81	0.019	0.011	0.008	0.035	0.018	0.012	0.003	0.03
53.74	0.034	0.012	0.011	0.87	0.034	0.012	0.005	0.866	0.021	0.011	0.002	0.237	0.024	0.012	0.002	0.509
60.74	0.031	0.008	0.03	0.881	0.031	0.008	0.006	0.877	0.03	0.007	0.004	0.755	0.03	0.007	0.003	0.815
67.74	0.034	0.011	0.022	0.882	0.034	0.011	0.003	0.842	0.033	0.011	0.002	0.757	0.034	0.011	0.003	0.749

Arsenic was effectively treated to below the discharge limit of 0.003 mg/L until the end of the testing when breakthrough occurred. Antimony was removed most of the time, but had occasional spikes in concentrations which exceeded the discharge criteria. The Sb spikes often corresponded with periods in which the Omni-SORB™ pre-treatment columns were experiencing plugging, and Mn in particular was passing through to the ADSORBSIA™ columns.

Adjustment of pH was not consistent due to the plugging of the Omni-SORB columns. The acid for the pH adjustment was added downstream of the Omni-SORB™ columns, which had variable flow rates due to plugging. Therefore, the acid dosing was inconsistent. Initial pH values, at times, decreased to as low as 2, which introduced some variability within the data. Figure 5c shows that pH spikes often corresponded with antimony spikes. In general, pH adjustment to lower values did tend to improve the removal efficiency for Sb.

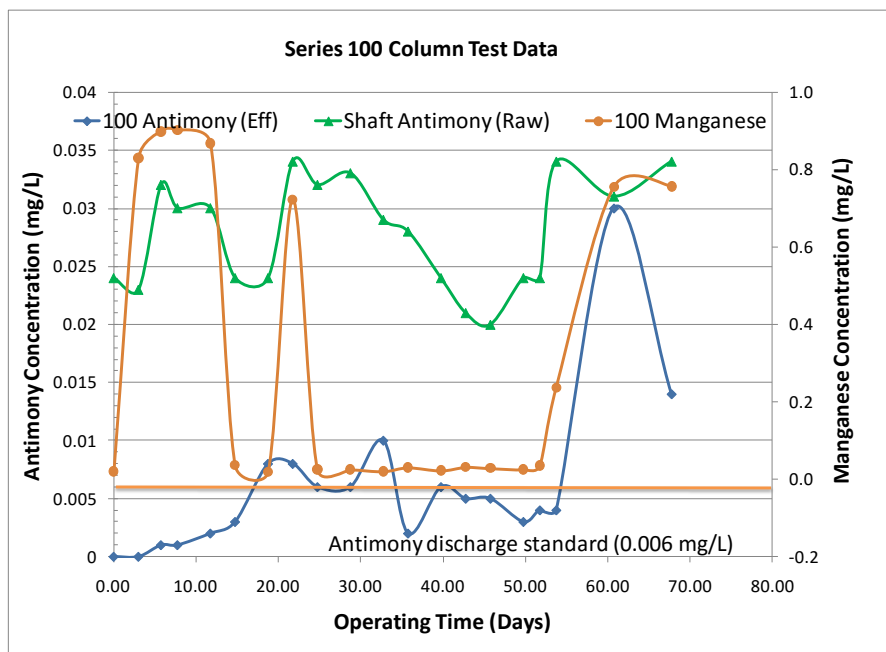


Figure 5a – Series 100 Omni-SORB™

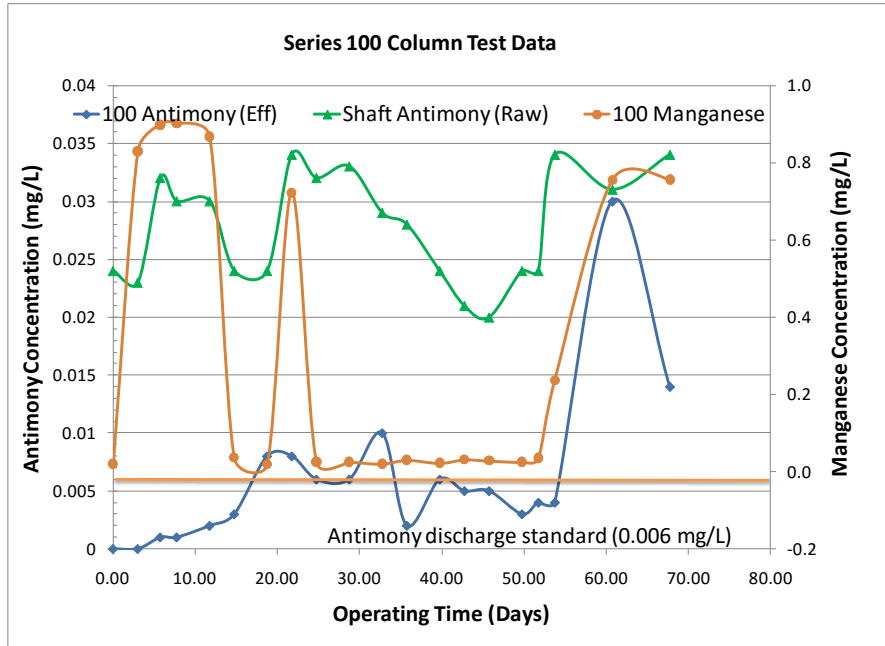


Figure 5b – Series 100 ADSORBSIA™

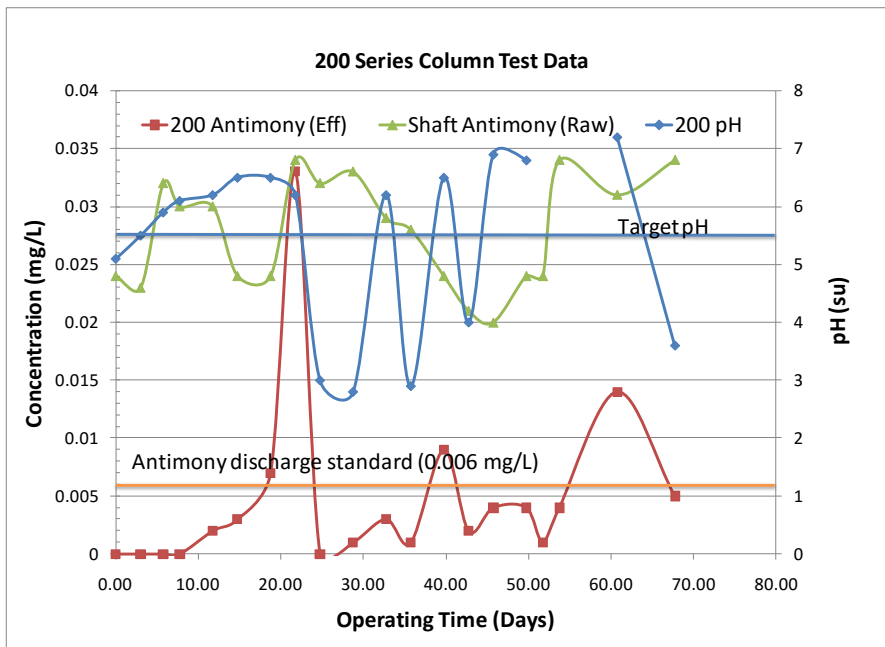


Figure 5c – Series 200 Omni-SORB™



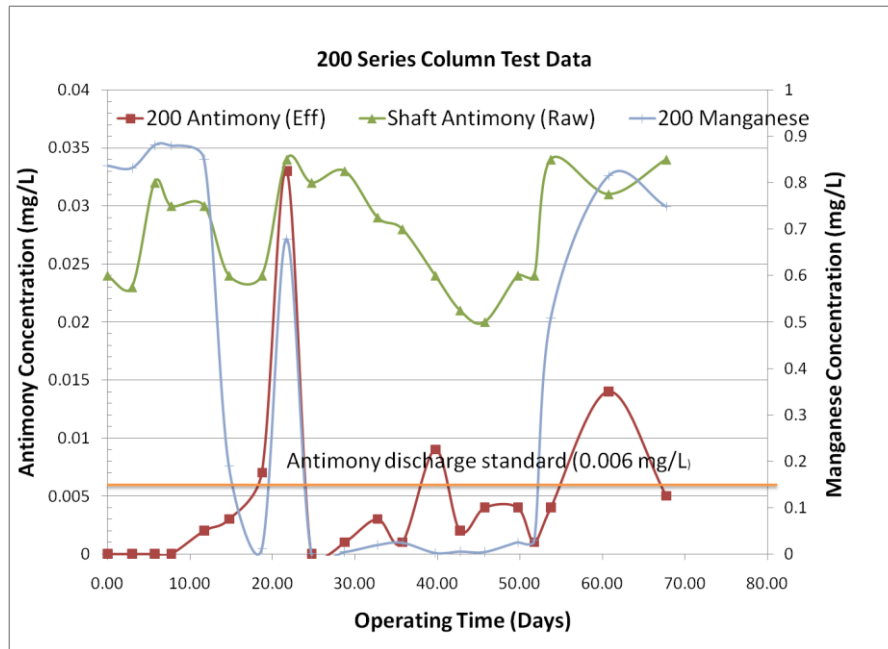


Figure 5d –Series 200 ADSORBSIA™

### Media Life

Testing with no pH adjustment resulted in approximately 12,400 BVs (bed volumes) treated before breakthrough occurred. Adjustment of the pH of the influent water to 6.5 resulted in approximately 22,000 BVs treated until the effluent concentrations exceeded the discharge limit. Adjustment to a pH of 5.5 resulted in 23,500 BVs treated. However, for both pH-adjusted tests, after the initial spike in effluent Sb, concentrations decreased to below the limit and continued for 25,000 BVs when the test was discontinued. All of these data were generated with the presence of Mn, and so it is impossible to determine to what extent the media was passivated by manganese versus Sb and As. The performance of the media with proper Mn removal will likely be greater than experienced during the testing, however given all of the uncertainty, these treated bed volumes can only be considered estimates. Decreasing the pH showed an increase in media capacity as compared to the neutral pH test, but due to the number of variables involved during the test, accurately determining the benefit of pH adjustment cannot be determined from the test data.

## Conclusions

Based on the initial full-scale and column results, the following conclusions can be drawn:

- Upstream removal of particulates, Fe, and Mn are critical to the performance of the media
- Bayoxide®, while effective for As removal, it was not appropriate for Sb at this site.
- Dow ADSORBSIA™ As500 (TiO<sub>2</sub> media) is effective at removing both Sb and As, but the media capacity could not be quantified due to fluctuating operating conditions.
- Manganese must be removed prior to the adsorption media. The test data showed that effluent Mn concentrations from the adsorption media beds was quite low even when the upstream Omni-SORB™ media was not performing properly and allowing high Mn concentrations to enter the adsorption beds. This indicates that Mn is being removed by the adsorption media and is occupying valuable adsorption sites needed for As and Sb removal. Also from the plotted data, whenever Mn concentrations in the water exiting the Omni-SORB™ columns spiked, this was quickly followed by a sharp increase in Sb concentrations in the effluent water. These trends show the proper Mn removal is critical for proper treatment for As and Sb.
- Causes for the upsets in the Omni-SORB™ media beds could not be verified, but likely have to do with operation of the chlorine addition system on the full scale plant. Operating trends of both parallel Omni-SORB™ columns mirrored each other closely indicating that it was not an individual upset condition in either of the beds. Operation of the chlorine addition system is therefore critical to proper Sb and As treatment.
- pH adjustment resulted in an efficiency increase of approximately 77%.
- Media life (pH adjusted) is on the order of two months based on the column studies, but can probably be extended by optimizing the reagent dosing and backwash procedures at full-scale.

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