Gold Mine Arsenic and Antimony Removed Through Passive Treatment Using AMD Iron Oxides From Coal Mines

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Abstract
The remediation properties of two iron oxides were tested on As and Sb contaminated water from a gold mine in Waiuta, New Zealand. The iron oxides tested include sludge from an active AMD treatment plant (Stockton Mine) and a precipitate of goethite from AMD at an abandoned mine (Blackball Mine). Three passive treatment systems were operated on site, treating water containing 2-4 mg/L As and 0.0039 mg/L Sb: one with Stockton precipitate and two with Blackball precipitate at loading ratios of 78, 47, and 47 g precipitate per L water, respectively. Residence times in the systems were varied from 7 min to 6 d. Arsenic concentrations were lowered to 0.5 mg/L at the shortest residence times (7 min) and below 0.05 mg/L for residence times above 5 hr for the Blackball precipitate. The Stockton precipitate lowered As concentrations to below 0.12 mg/L at residence times above 5 hr, until maximum adsorption capacity was approached. This work suggests that a full-scale system containing either of the Fe oxides can be successful at the Waiuta Gold Mine site. These results also show that waste material from coal mine AMD can be used as a treatment medium for gold mine sites.

Key Words: adsorption, AMD sludge, small scale systems, New Zealand, vertical flow system

Introduction
Many workers have documented the removal of As from mine water by adsorption onto various iron compounds including ferric hydroxide (Dousova *et al.* 2005; Küchler *et al.* 2005), zerovalent iron (Wildeman *et al.* 2006), sulphate-ferrihydrite (Jia and Demopoulos 2005), red mud produced during the extraction of aluminum from bauxite (Altundogan *et al.* 2000, 2002), and natural red earth (Vithanage *et al.* 2007). Some of these have used passive treatment techniques to adsorb As from mine water onto iron compounds (Küchler *et al.* 2005; Wildeman *et al.* 2006).

In New Zealand, work by Rait *et al.* (2010) documents the use of iron oxyhydroxide precipitates from acid mine drainage (AMD) to remove As through adsorption. Laboratory experiments were used to determine the kinetics of adsorption onto two different AMD precipitates, one from the abandoned Blackball Coal Mine, where precipitate forms at low pH (2.9) at the adit, and one from the active Stockton Coal Mine, where precipitate forms at neutral pH from a limestone dosing treatment system. Our objective in the current study was to apply these results in a field setting by constructing and operating small-scale field trials using AMD precipitates for As adsorption at the historic Waiuta Gold Mine, near Reefton, South Island, New Zealand.

Previous Results
The work by Rait et al. (2010) found that the precipitate from the Stockton Coal Mine neutralisation treatment contained Fe_2O_3 at a concentration of 13 wt% and was composed primarily of Fe and Al oxyhydroxy sulphate minerals, whereas the precipitate from the Blackball Mine contained 74 wt% Fe_2O_3 and was composed primarily of goethite and ferrihydrite. The laboratory experiments showed that As adsorption for both precipitates is rapid over the first 5 hr reaching equilibrium after 24 hr and that adsorption capacity is up to 12 mg As/g (Stockton material) and 74 mg As/g (Blackball material).

Blackball precipitate consistently lowered As concentrations lower than the Stockton material, presumably due to the higher Fe content.

Site Background

The site used in this study is an historic processing mill and gold recovery plant that processed ore from the underground Waiuta Gold Mine from 1938 to 1951 (Latham 1992). A roasting process released As from arsenopyrite and resulted in an accumulation of arsenolite and scorodite on the ground around the site containing concentrations of As up to 400,000 mg/kg (Haffert 2009). Low-pH runoff leaves the site and flows through a wetland with dissolved As up to 100 mg/L (Rait *et al.* 2010), and pore water concentrations up to 334 mg/L As (Haffert 2009). The water flows through a waste rock dump containing iron carbonates and emerges with a neutral chemistry containing As at about 2 mg/L. Haffert and Craw (2008a; 2008b) hypothesize that the low-pH water dissolves the siderite in the rocks, the released carbonates react to neutralize the low pH water, and once the pH is raised, the liberated iron from the siderite precipitates directly to a hydrated iron hydroxide which scavenges As out of the solution through adsorption.

The waste rock dump serves as a natural passive treatment system, reducing the As concentration from 100 mg/L down to 2 mg/L. Our goal in this work was to trial a passive treatment system at the base of the rock dump to treat the residual 2 mg/L As. New Zealand regulatory guidelines for environmental impacts are risk based and are site specific. Screening level guideline values for protection of the aquatic ecosystem which can trigger further investigation have been developed for some parameters. The guideline value for As for protection of 95% of aquatic species is 0.013 mg/L, for protection of 90% of aquatic species is 0.042, and for protection of 80% of aquatic species is 0.14 mg/L (ANZECC 2000). The guideline value for Sb for protection of the aquatic ecosystem is undetermined. The New Zealand drinking water standards for As are 0.01 mg/L and for Sb are 0.02 mg/L (Ministry of Health 2008).

Methods

Three small-scale treatment systems were constructed at the base of the large waste rock pile at the Waiuta Gold Mine site. Water emerges from the rock pile at a flow rate of about 2 L/s with As concentrations ranging from 2 to 4 mg/L and Sb concentrations ranging from 0.0021 to 0.0042 mg/L (Table 1). The treatment systems were constructed using 1000 L plastic tubs filled with gravel/AMD precipitate mixtures. The gravel was greywacke grade 6 road sealing chip (2-5 mm dia). The AMD precipitate was excavated from the field setting and placed into perforated containers to drain as much water as possible prior to mixing with the gravel. The precipitates were otherwise unprocessed. All of the precipitate was very fine grained and unconsolidated. No provisions were made to enhance water flow through the systems, except that the precipitate was mixed thoroughly with the gravel using a shovel.

Water flowed from a header dam through alkathene and PVC piping and gate valves into the base of each tub, flowed upward through each unit and out the top through PVC and alkathene piping (Figure 1). Upward flow was used to prevent plugging of the perforated PVC piping with AMD precipitate and to prevent loss of AMD precipitate out of each system. The systems only treated a portion of the total flow of the stream. One tub contained 32.5 kg of Stockton material and had a capacity of 417 L of water (a loading ratio of 78 g precipitate/L water). The second and third tubs each contained 22.5 kg of Blackball material and had a capacity of 484 L of water (a loading ratio of 47 g precipitate/L water).

The systems operated for a period of nine months. Flow rates were varied to determine As and Sb removal for different residence times. Blackball-2 was used to test As removal at very short residence times (< 1 hr), at the start of the experiment during the first month, and later at month eight, whereas the other two systems operated at longer residence times. Inlet and outlet samples were collected weekly from each tub or more often for the very short residence time experiment. Antimony was analysed for only the system containing the Blackball material.

Table 1. Waiuta mine water chemistry used in the field trials.

Parameter	Units	Result	Parameter	Units	Result
Dissolved Sodium	mg/L	2.4	Dissolved Reactive Phosphorus	mg/L	0.36
Dissolved Potassium	mg/L	0.90	pH	pH Units	7.4
Dissolved Calcium	mg/L	13	Dissolved Aluminium	mg/L	0.15
Dissolved Magnesium	mg/L	14	Dissolved Arsenic	mg/L	2.3
Sulphate	g/m^3	24	Dissolved Antimony	mg/L	0.0039
Total Alkalinity	mg/L as $CaCO_2$	62	Dissolved Iron	mg/L	0.36
Chloride	mg/L	4.3	Dissolved Manganese	mg/L	0.013
Nitrite-N	mg/L	0.0028	Dissolved Nickel	mg/L	0.0032
Nitrate-N	mg/L	0.25	Dissolved Zinc	mg/L	0.036

Figure 1. Passive treatment systems at the Waiuta Gold Mine.

Results and Discussion

Arsenic

The two systems with Blackball precipitate consistently lowered As concentrations to below 0.05 mg/L (> 98% removal) over the duration of the experiment (Figure 2). Concentrations of As in the outlet from Blackball-1 ranged from 0.0067 to 0.05 mg/L; in the outlet from Blackball-2, As concentrations ranged from 0.0103 to 0.035 mg/L. The system with the Stockton precipitate initially lowered As concentrations to below 0.05 mg/L (> 98% removal) but then at five months of operation, removal efficiency declined,

suggesting the precipitate was reaching adsorption capacity. Initial As outlet concentrations were 0.016 mg/L, rising to 0.28 mg/L at the end of the experiment.

Arsenic was removed to lower levels at the longer residence times for both precipitates (Figure 3). Although there is substantial scatter in the data for the Blackball precipitate, concentrations were consistently lowered to below 0.05 mg/L at all residence times above 5 hr. The high As concentrations at 20 hr residence time in the outlet from the system containing Stockton precipitate occurred at eight months when maximum adsorption capacity was approached and treatment effectiveness dropped. Overall better performance by the Blackball precipitate is likely due to the higher Fe content.

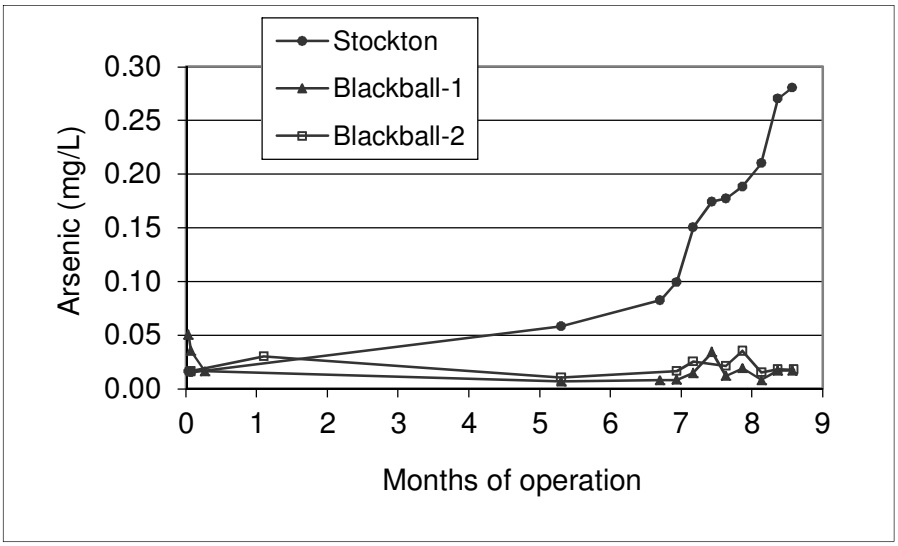

Figure 2. Arsenic concentrations in outlets from field trials over nine months of operation.

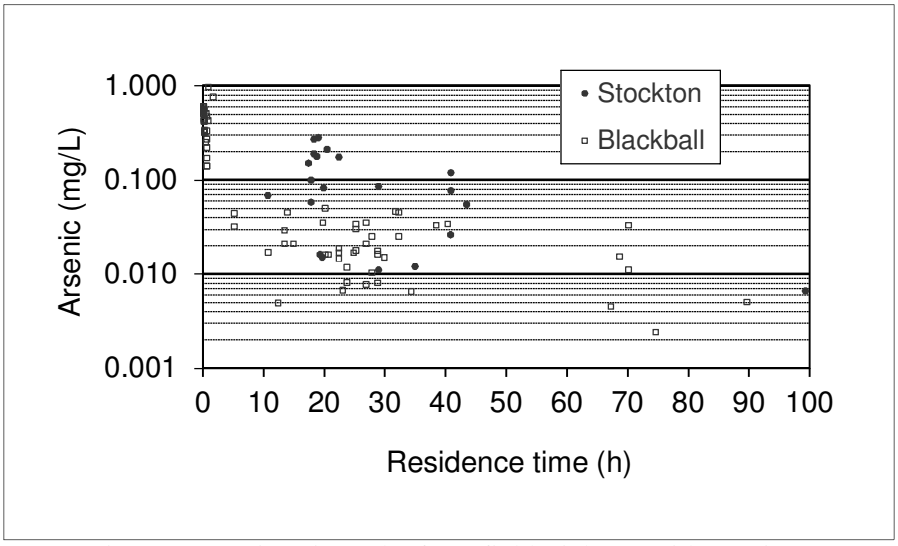

Figure 3. Arsenic concentrations in outlet from field trials at residence times up to 100 hr.

For residence times less than 1 hr, As removal by the Blackball precipitate shows a good logarithmic trend, suggesting that removal rates at these short residences times are somewhat predictable (Figure 4). However, after eight months of operation at low flow rates, the high flow rate experiment was repeated resulting in a much higher As concentrations in the effluent and a much greater scatter in the data. This suggests that maximum adsorption capacity was being approached for the Blackball precipitate.

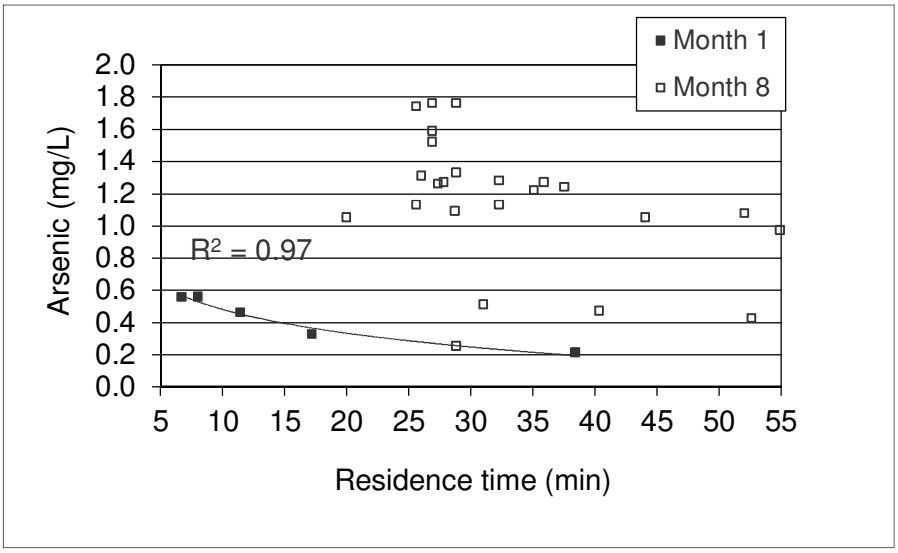

Figure 4. Arsenic concentrations in outlet from treatment system containing Blackball precipitate at residence times less than 1 hr.

At the end of the experiment, the Stockton material had treated 92,500 L of water, and although treatment efficiency had declined, was still removing up to 84% of the As in the inlet water through adsorption onto iron oxyhydroxide precipitates. The Blackball material had treated 1,430,000 L of water at the end of the experiment and the removal efficiency had dropped to 2%. At the time the experiment was terminated, the Stockton material had adsorbed 5.08 mg As/g precipitate and the Blackball material had adsorbed 27.32 mg As/g precipitate. Rait *et al.* (2010) showed that a Freundlich Isotherm model adequately describes the adsorption behaviour for both precipitates. Using the As concentrations in the inlet water, the model predicts a maximum adsorption capacity of 7.6 mg As/g precipitate (Stockton) and 36.22 mg As/g precipitate (Blackball). Potential reasons for the difference between predicted and measured adsorption capacity are overestimation of the volume of precipitate in the systems, uncertainty of flow rates and hence removal rates between site visits, and uncertainty of water chemistry between site visits. Additionally, the Stockton precipitate had not yet reached capacity as it was still removing up to 84% of the inlet As concentration.

Antimony

Antimony concentrations were also lowered through adsorption by the Blackball precipitate. Outlet concentrations over the first eight months at residence times greater than 5 hr were all below detection limits (<0.00020 mg/L), indicating removal rates of greater than 91% to greater than 96%.

During the high flow experiment conducted at month 1 and month 8, where As removal rates were determined at low residence times by the Blackball precipitate, the outlet water was also analysed for Sb. Similar to As, there is a good logarithmic trend, suggesting removal of Sb is predicable as these short residence times (Figure 5). After eight months of operation, however, when the high flow rate experiment was repeated, removal rates dropped as maximum adsorption capacity was approached.

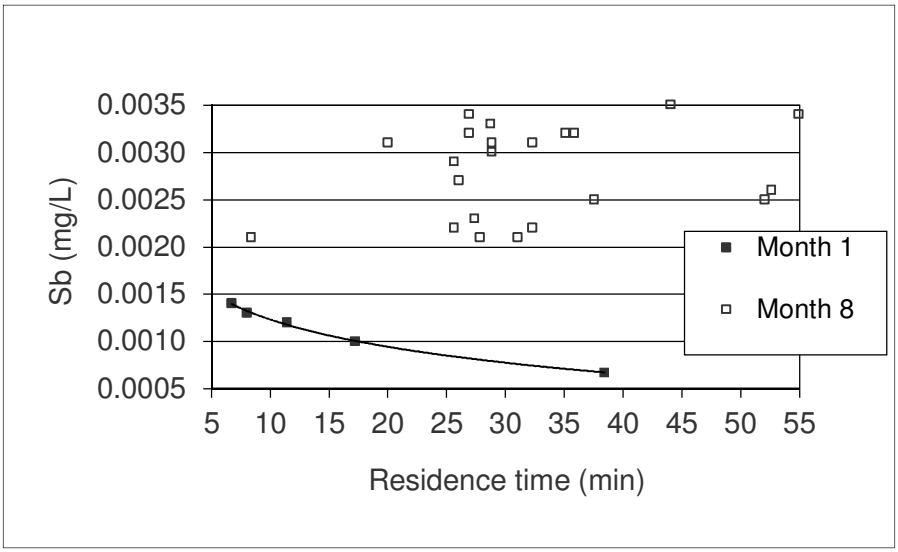

Figure 5. Antimony concentrations in outlet from treatment system containing Blackball precipitate at residence times less than 1 hr.

Other Constituents

Twice during the experiment an extended suite of dissolved metals and other parameters were analysed to determine changes in water chemistry by the treatment systems. The system containing the Blackball precipitate removed Fe, Al, Zn, Cu, Li, Rb, Mg, Mn, Ba, sulphate, and dissolved reactive phosphorous and exported K. The system with Stockton precipitate removed Fe, Zn, Li, Mg, Mn, sulphate, and dissolved reactive phosphorous and exported Al, Cu, Rb, Ba, and K. Because of the importance of Fe in treatment effectiveness, Fe was analysed on eight occasions. All samples showed significantly lower concentrations of dissolved Fe in the outlet from the systems compared to the inlet concentrations, with removal rates up to 94%.

Conclusions

Results confirm that the both the Blackball precipitate and the Stockton precipitate are effective at As and Sb adsorption and can be used in a passive treatment system to remove As and Sb from gold mine drainage. Blackball precipitate can adsorb more As than Stockton precipitate likely due to a higher Fe content. The use of AMD precipitate is practical if there is a nearby, abundant source to the remediation area.

Acknowledgements

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