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Adsorption of arsenic by iron rich precipitates from two coal mine drainage sites on the West Coast of New Zealand

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Adsorption of arsenic by iron rich precipitates from two coal mine drainage sites on the West Coast of New Zealand

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Dissolved As can be strongly adsorbed to fine grained Fe(III) minerals such as hydroxides, oxyhydroxides and hydroxysulphates. Therefore precipitates that form during neutralisation or treatment of acid mine drainage have potential to be useful for treatment of As-contaminated water because acid mine drainage is often Fe rich. We tested the adsorption properties of Fe(III) rich precipitates from two West Coast coal mines with As-contaminated water from an historic gold ore processing site near Reefton. Precipitates were collected from distinctly different settings, an active acid mine drainage treatment plant at Stockton mine and the neutralisation/oxidation zone of acid mine drainage discharge at the abandoned Blackball Coal Mine. The two mine sites produce precipitates with different compositions and mineralogy. Arsenic adsorption onto precipitates from each site was determined in batch and column tests under laboratory conditions. Batch experiments indicate As adsorption occurs rapidly during the first 5 h and reaches equilibrium after 24 h. At equilibrium, and for a dosing ratio of 50 g of precipitate per litre of water, As concentrations decreased from 99 mg/L to 0.0080 mg/L with precipitates from Stockton and to 0.0017 mg/L with precipitates from Blackball. Arsenic adsorption capacity is up to 12 mg/g on precipitates from Stockton sludge and 74 mg/g on precipitates from Blackball. The Blackball precipitate adsorbs more As than precipitates from Stockton which is probably due to the higher Fe oxide content but pH and surface structure could also play a role. The column experiment confirmed that adsorption of As from a continuous waste stream onto these precipitates is possible, and that passive remediation using this waste product mixed with gravel to enhance permeability could be a viable approach at As-contaminated mine sites.

Keywords: arsenic; AMD sludge; AMD precipitate; iron hydroxide; adsorption; acid mine drainage (AMD); gold mines; coal mines

Introduction

Poor discharge water quality is one the largest environmental issues associated with mining, and a substantial amount of research and technical development has been completed or is underway to address this issue (Younger et al. 2002). Acid mine drainage (AMD) is the most common contributor to poor water quality and occurs when oxygenated surface water reacts with pyrite (or other sulphide minerals) in mine waste to form sulphuric acid (Singer & Stumm 1970; Caruccio et al. 1981; Nordstrom & Alpers 1999). These acid waters are commonly accompanied by elevated concentrations of dissolved metals often including Fe(III) and/or Fe(II). When AMD is oxidised and neutralised downstream from mines, iron-rich precipitates form and these commonly include minerals such as jarosite, ferrihydrite, goethite, schwertmannite or others (Nordstrom & Alpers 1999). These minerals can often contain substantial concentrations of other trace elements and cause disruption to the aquatic ecosystem (Winterborne et al. 2000). Low pH and Fe-rich precipitates are common water quality impacts downstream of mines but mine drainage chemistry is diverse and includes neutral discharges with elevated concentrations of trace elements or acid mine drainages where the Lewis acidity from dissolved Al is the most problematic water quality issue. Arsenic in particular is a common trace element that can be extremely elevated in neutral mine waters, and removal of dissolved arsenic is a major scientific and technological challenge (Dousova et al. 2005; Mohan & Pittman 2007).

Arsenic extraction from mine waters is commonly achieved by oxidation of As(III) to As(V) and co-precipitation of ferric arsenate with iron hydroxide ($FeAsO_4 \cdot Fe(OH)_3$) in a high-density sludge process in active treatment systems (Lawrence & Higgs 1999; Leist et al. 2000). 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), ferrihydrite (Jia & Demopoulos 2005), goethite (Fendorf et al. 1997), red mud produced during the extraction of aluminium from bauxite (Altundogan et al. 2000, 2002), and natural red earth (Vithanage et al. 2007). Treatment of As-contaminated mine water through adsorption and co-precipitation in a water treatment plant is reliable and appropriate at active mine sites where power is available and personnel are on site to operate the plant. However, active

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treatment is usually prohibitively expensive at abandoned mine sites that could continue to discharge As-contaminated water for many years post closure. Development of low cost passive treatment systems to remove As from mine water through adsorption onto iron compounds is an active research area (Küchler et al. 2005; Wildeman et al. 2006).

Our research examines the use of Fe(III) rich precipitates that are waste products from coal mines to remove As from neutral mine drainage. We focus on adsorption of As from extremely enriched water at the Waiuta Gold Mine site onto Fe(III) rich precipitates from Stockton Coal Mine drainage treatment plant and the abandoned Blackball Coal Mine. This study was completed in a laboratory setting but uses materials that formed in field environments and is preliminary work for design and installation of passive As treatment system. The use of waste products that are readily available, locally sourced and low-cost is important to this study because there is limited funding available for treatment of contaminated water at abandoned mines in New Zealand.

This study includes batch and column experiments to determine arsenic adsorption onto the Fe(III) rich precipitates. The batch experiments determined the kinetic rate constant and the maximum adsorption capacity. The column experiments were to determine if the results from the batch experiments can be used to effectively predict long-term adsorption characteristics of Fe(III) precipitates. These experiments were used to determine the difference in As removal over time between the Stockton and Blackball precipitates and the effect of mass of Fe(III) precipitates on As removal over time. The column experiments were designed to simulate a passive treatment system in which As-contaminated water can be passed through a leaching bed containing an Fe(III) rich precipitates from a coal mine site.

Geological background

The mines of interest in this study occur in the West Coast region of the South Island of New Zealand (Fig. 1). The basement rocks are commonly Palaeozoic meta-greywackes which are cut by numerous gold-bearing quartz vein systems, many of which have been mined historically. One of these is the Globe Mine located near Reefton (Fig. 1). Arsenic in waters from the historical Globe Mine is largely adsorbed by Fe(III) rich precipitates formed by pyrite oxidation on the mine site, and some additional As adsorption occurs onto particulate Fe(III) rich precipitates transported in streams from the historic Alborns Coal Mine immediately upstream (Craw et al. 2004; Hewlett et al. 2005).

In contrast to typical West Coast gold mines like Globe, the Waiuta mine (Fig. 1) had ore with high arsenopyrite content and little pyrite (Christie & Brathwaite 2003). The historic Prohibition Roasting Plant site, at Waiuta mine, has high levels of As in mine waste, including solids with As up to 40 wt% and high dissolved As (up to 70 mg/L) in associated waters (Haffert & Craw 2008b). The lack of

pyrite associated with ore from Waiuta mine compared to other mines means that Fe(III) rich precipitates are less abundant and this is one reason for the exceptionally high dissolved As concentrations. We use water collected from the Prohibition site in our experiments.

The meta-greywacke basement in the West Coast region is overlain by varying thicknesses (up to 4 km) of Cretaceous-Cenozoic sedimentary rocks, including some thick non-marine sequences containing coal. Remnants of these sediments are preserved locally in basins, on high plateaus, and in fault controlled inliers, after late Cenozoic uplift and erosion associated with the nearby Australian–Pacific collisional plate boundary. Coal mines have been active at various times over the past 150 years, and many are still operating. The largest active mine is the Stockton opencast mine, and abandoned historic underground mines including the Blackball mine (Fig. 1) are widespread throughout the area.

Fe(III) rich precipitates from Stockton and Blackball

Many of the coal mines on the West Coast of the South Island of New Zealand were developed in fluvial sediments deposited in a marginal marine setting and closely overlain by marine sediment (Barry et al. 1994). Consequently, the coal and associated rocks contain abundant pyrite (Flores & Sykes 1996), which contributes to AMD at these mine sites (Pope et al. 2010a, b). For this study, we selected Fe(III) precipitates from two mine sites, Stockton and Blackball, to use as sorbent for As adsorption experiments. The Fe mineralogy of mine drainage precipitates is variable (Nordstrom & Alpers 1999) and minerals such as ferrihydrite or schwertmannite are meta-stable recrystallising to more stable minerals such as goethite with time (Cornell & Schwertmann, 1996).

Mining in the Stockton area has been underway for about 100 yr and continues currently. Sediments at Stockton contain pyrite in various forms (Weisener & Weber 2010) and AMD is present at Stockton. Fe(III) rich precipitates from Stockton form during limestone ($CaCO_3$) neutralisation of acid mine drainage that is rich in Fe, Al and trace elements. The limestone raises the pH of a stream from < 3 to near 7 over a few tens of metres (Davies et al. 2009). Modelling of mine drainage chemistry in the neutralisation zone indicates that precipitates at Stockton include schwertmannite ($Fe_8O_8(SO_4)OH_6$) and Boehmite (AlOOH) (Pope 2006; Davies 2009). The Fe(III) precipitate collected at Stockton also includes unreacted limestone, suspended sediment such as clay minerals and probably small quantities of other neutralisation reaction products such as gypsum.

The underground Blackball mine operated from 1939 until it was abandoned in the mid 1960s. Recovery of coal was poor due to weak roof conditions, which required that the top of the coal seam be left behind to reduce infiltration of water. Approximately 3000 cubic metres of water was
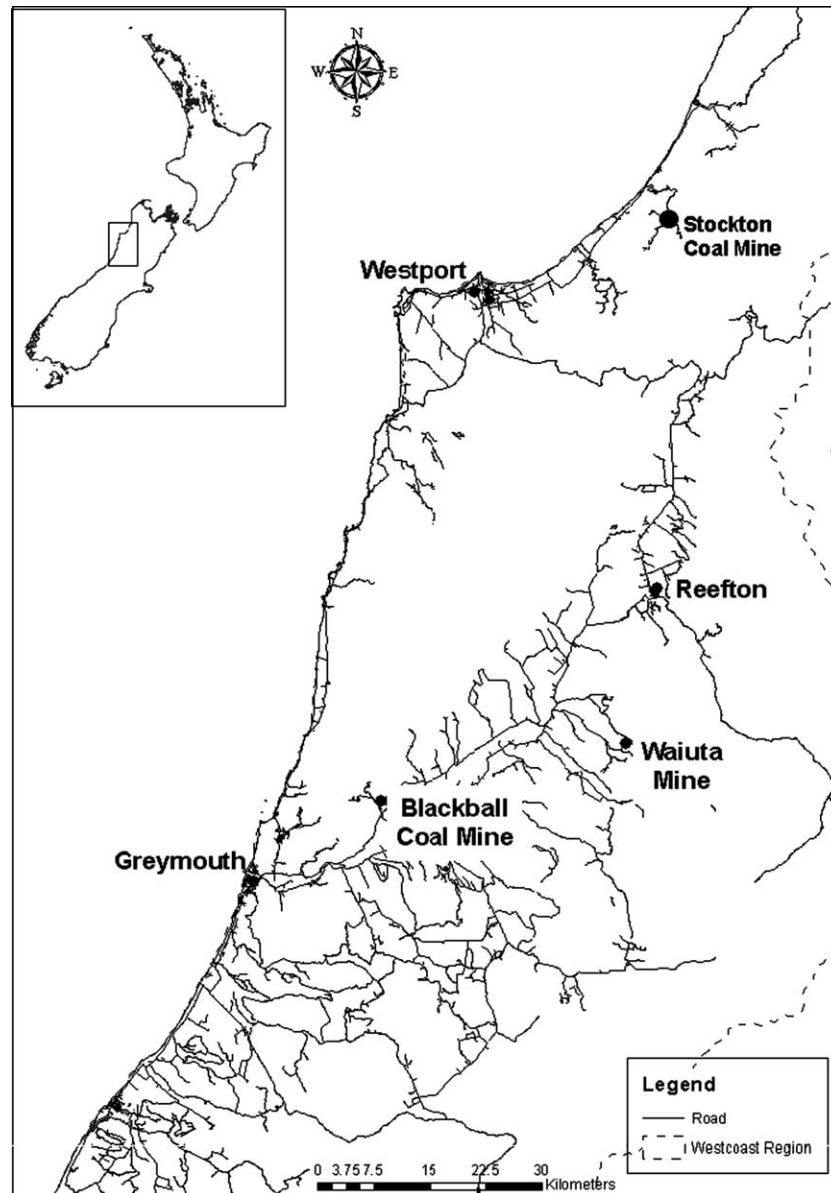
Fig. 1 Location of AMD sites and As-contaminated water site. The active Stockton mine, northwest of Westport, is producing abundant AMD, currently controlled by addition of finely ground limestone to the main discharge stream containing AMD. The underground Blackball mine, northwest of Greymouth, currently discharges AMD with high concentrations of Fe and Al depositing thick orange-red precipitate on a terrace. Waiuta is the site of the former Prohibition Mill processing site which currently discharges As-contaminated water.

removed from the mine during each shift and the water was noted as being highly corrosive due to the presence of sulphuric acid (Gage 1952). The coal from the Blackball mine had a high sulphur content, and since much of the coal remained as roof rock, was likely a contributing source of the acidic water. Regionally, the overlying Brunner Coal Measures are also known to be pyritic and locally permeable. Currently, AMD with high concentrations of Fe and Al discharges from one of the lower mine portals with flow rates between 36 and 101 L/s (Trumm & Gordon 2004). The AMD flows out onto a terrace approximately 12 m wide and 25 m long, 3 m above an adjacent stream. During high flow,

the entire terrace is inundated with AMD which flows off the terrace in three waterfalls into the stream that increases pH of the mine drainage though buffering and dilution. A thick deposit of orange-red precipitate accumulates on the terrace. Little is known about the mineralogy of the precipitates that form at Blackball and no modelling of the precipitate zone has been conducted.

In this study we have completed preliminary characterisation of the Stockton and Blackball precipitates by X-ray Diffraction (XRD) and X-ray fluorescence (XRF). The objective of this laboratory study is to examine the practicality of using these substrates for As sorption in passive

systems. Follow up work examines the mineralogy, variability and additional adsorption characteristics of the most promising of the two substrates used in these experiments.

Methods

Sampling

The water used in the As adsorption experiments was collected from the Prohibition Roasting Plant site of the abandoned Waiuta Gold Mine (Fig. 1). The water was collected from a wetland area downstream of the foundations of the processing plant. A field pH measurement was made using a WTW Multiline P4 and a sample collected for laboratory analysis. The water used for laboratory experiments was not filtered or preserved because our objective was to treat the As-contaminated water with as many of the field characteristics of the water in place. Field characteristics include all other dissolved trace elements, other dissolved and particulate components, and possibly microbial communities. Other studies have completed detailed field characterisations of this water (Haffert & Craw 2005, 2008a, b, 2009).

Precipitate from the Blackball mine site was collected into several large containers and transported to the laboratory. Sludge from the water treatment plant at Stockton mine was supplied by Solid Energy New Zealand. In a similar manner to the water sampling strategy, precipitates were collected in a manner to preserve field characteristics, so the precipitates were not rinsed or otherwise pre-treated.

Analytical methods

The bulk chemistry of the Fe(III) rich precipitates from Stockton and Blackball was determined by X-ray fluorescence using the powder briquette X-ray spectrometry method in a Siemens SRS3000 XRF. Minerals were identified by powder X-ray diffraction using a Phillips PW1729 X-ray diffractometer with a Cu anode. Samples were oven-dried at 110°C and hand crushed using mortar and pestle. The samples were prepared as unoriented powder mounts and scanned over the range of 5–80° 2 theta at a scan speed of 0.02°/min. Phase identification was carried out using EVA search/match programme and manual search match from data bases.

Water analyses were completed for dissolved Al, As, Ca, Fe, Mg, Mn, Ni, K, Na, Zn by inductively coupled plasma mass spectrometry using American Public Health Association (APHA) method 3125-B, pH by APHA method 4500, total alkalinity by APHA method 2320-B, chloride by APHA method 4110 Cl$^-$ E, nitrite-N and nitrate-N by APHA method 4500-NO$_3^-$ I, dissolved reactive phosphorus by APHA method 4500-P E, and sulphate by APHA method 4110-B (APHA 2005). Samples for dissolved metal analyses were nitric preserved and filtered in the laboratory through an acetate 0.45 µm membrane (APHA Method 3030B).

Batch experiments

Two batch experiments were conducted to determine the As adsorption characteristics of the Fe(III) rich precipitates from Stockton and Blackball. These batch experiments consisted of mixing dried precipitate material with As-contaminated water in small vials and measuring the amount of As removed from the water.

In the first experiment (Batch Experiment 1), the kinetic rate constant for As adsorption was determined by keeping the ratio of precipitate to As-contaminated water constant but varying the contact time. Eight samples of each precipitate were prepared by mixing 0.4 g of dried precipitate with 40 ml of As-contaminated water in 50 ml polyethylene vials (10 g/L ratio). Each vial was mechanically shaken for a predetermined time, after which the vial was removed from the shaker, put in a centrifuge for 5 min and water-decanted and filtered through a 0.45 µm filter for analysis. The total contact time for the precipitate and As-contaminated water ranged from 1.3 to 120.5 h. Two duplicates were run for the Stockton precipitate and one duplicate was run for the Blackball precipitate. The initial contaminated water and the supernatants from the batch experiment were analysed for dissolved As, Fe, Mn, Al, Ni and Zn. For selected As-contaminated water and vials the pH was measured by a WTW Multiline P4 probe.

In the second batch experiment (Batch Experiment 2), the ratio of precipitate to As-contaminated water was varied. This was designed to determine the maximum adsorption capacity of the precipitates (mg As adsorbed/g precipitate). The contact time for this experiment was 48 h because results from Batch Experiment 1 indicated that after this contact time, no additional adsorption occurs. Five samples of the Stockton precipitate were prepared by mixing dried precipitate to As-contaminated water at ratios of 1, 5, 10, 25 and 50 g/L in 50 ml polyethylene vials. Six ratios were prepared for the Blackball precipitate (1, 2.5, 5, 10, 25 and 50 g/L). Each vial was shaken for 48.7 hours and the water extracted and filtered in a similar manner to the first experiment. Two duplicates were prepared, shaken and analysed for the Stockton precipitate and one duplicate was run for the Blackball precipitate. The initial contaminated water and the supernatant were analysed for dissolved As. For selected As-contaminated water and vials the pH was measured by a WTW Multiline P4 probe.

Column experiment

Based on the results of Batch Experiment 1 and 2, a column leaching experiment was conducted to determine the long-term effectiveness of As removal from a continuous waste stream by the Stockton and Blackball Fe(III) rich

precipitates. In the experiment, water contaminated with As was passed continuously through columns packed with sand-precipitate mixtures and the removal of As from the water by the columns over time was monitored.

The column experiment was carried out using polyvinyl chloride (PVC) columns with an 80 mm internal diameter and 750 mm height, and a volume of 3.77 L (Fig. 2). Each column contained 2.3 L of treatment media, consisting of 4 kg of washed river sand (< 2mm) and various amounts of dried precipitate (Table 1). The void volume in each column was 1.5 L. Column 1 contained Stockton precipitate,

columns 2 and 3 contained Blackball precipitate, and column 4 was a control containing only sand. Columns 1 and 3 contained equal masses of precipitate and column 2 contained Blackball precipitate at 1/5 the mass of precipitate in columns 1 and 3. The sand and precipitate was mixed by hand until evenly distributed. The river sand used in the column experiment was obtained from a local garden centre. The sand consisted of fine to medium quartz-rich greywacke from the Torlesse Supergroup of New Zealand which is a zeolite facies metamorphosed sandstone and mudstone turbidite sequence (MacKinnon 1983).
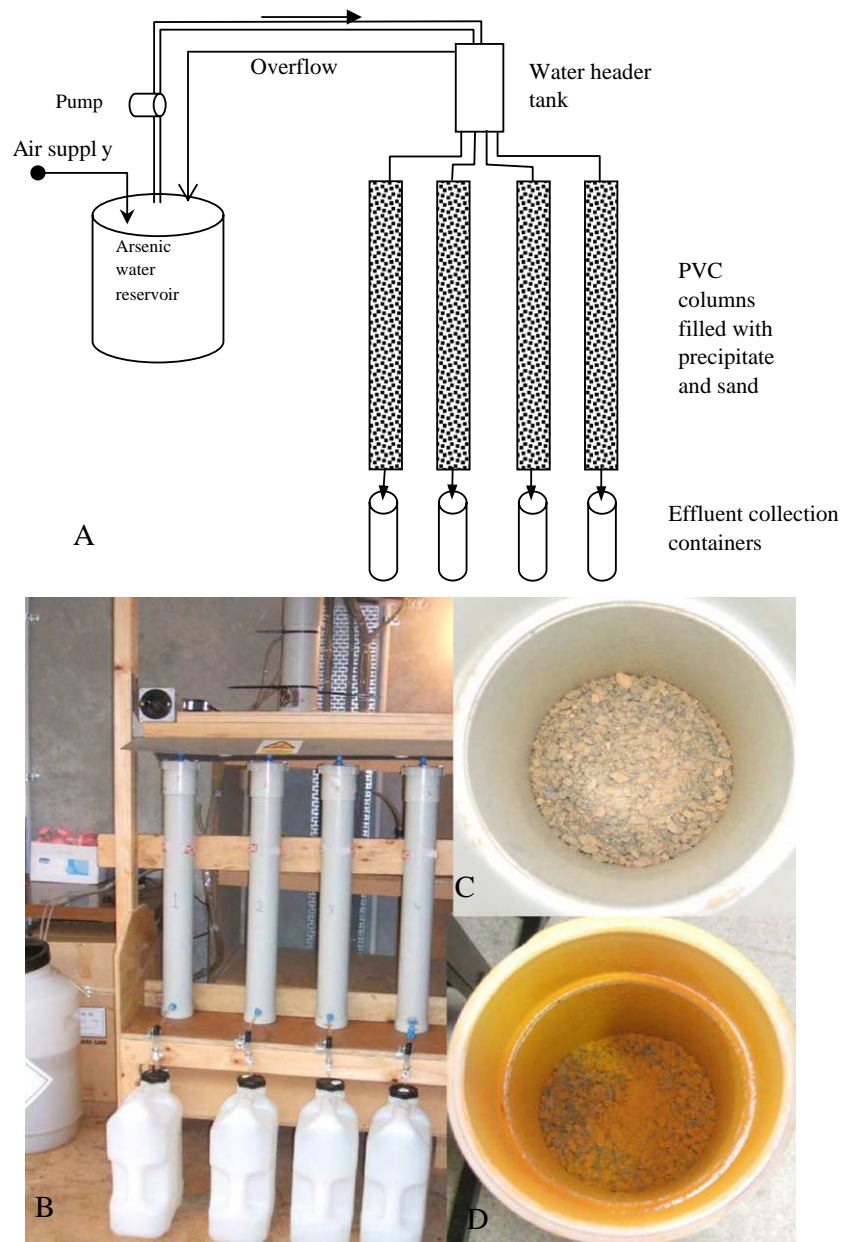

Fig. 2 Column experimental setup. **(A)** Schematic of setup. **(B)** Actual setup. In the experiment, water contaminated with As was passed continuously through columns packed with sand-precipitate mixtures and the removal of As from the water by the columns over time was monitored. **(C)** Stockton precipitate mixed with sand. **(D)** Blackball precipitate mixed with sand.

Table 1 Composition and operating parameters for columns in column leaching experiment

	Column 1	Column 2	Column 3	Column 4
Total volume	3.77 L	3.77 L	3.77 L	3.77 L
Sand weight	3992 g	3998 g	3999 g	4082 g
Precipitate source	Stockton	Blackball	Blackball	None
Precipitate weight	73 g	15 g	73 g	None
Volume precipitate + sand	2.3 L	2.3 L	2.3 L	2.3 L
Void volume	1.5 L	1.5 L	1.5 L	1.5 L
Average water flow rate	1.8 L/d	1.8 L/d	1.8 L/d	1.8 L/d
Water residence time	20 h	20 h	20 h	20 h
Precipitate dose amount	48.7 g/L	10 g/L	48.7 g/L	

The results from columns 1 and 3 are used to compare As adsorption characteristics between Stockton and Blackball precipitates. The results from columns 2 and 3 are used to compare different dosing amounts of Blackball precipitate on As adsorption characteristics. The precipitate dose amount is the amount of precipitate in contact with each L of water over the residence time of 20 h.

Arsenic-contaminated water was contained in a large reservoir that was aerated by bubbling air into the water to maintain the majority of arsenic remains oxidised as As(V). Aeration of the As-contaminated water was incorporated into the experiment because treatment sites at the Waiuta mine site were likely to be downstream of the wetland where the As-contaminated water was collected. The water collected from the lower wetland at Waiuta exhibits arsenic speciation that indicates the bulk of the of As is oxidised (As(V) > 97.5%) As(III) < 2.5%; Haffert et al. in press). Water flow through each column was kept at an average of 1.8 L/day yielding a contact residence time with the precipitate, based on a pore volume of 1.5 L, of 0.833 days (20 h) over 10 days. The influent water was analysed for dissolved As daily and dissolved Al, Fe, and Mn on days 0, 4, and 10. The effluent from each column was analysed for dissolved As daily. The influent was also monitored daily and the effluent monitored on one occasion for pH, conductivity, temperature, total dissolved solids, salinity and dissolved oxygen using a WTW Multiline P4 probe.

To determine if the As adsorbed onto Stockton and Blackball Fe(III) rich precipitates was stable under environmental conditions, standardised leaching tests were conducted at the end of the column experiment. The precipitates were tested using the toxicity characteristic leaching procedure (TCLP; US Environmental Protection Agency test method 1311; Environmental Protection Agency [EPA] 1995) and the synthetic precipitation leaching procedure (SPLP; US Environmental Protection Agency test method 1312; EPA 1995). The TCLP method involved the addition of an extraction buffer to the solids to produce an extract for

analysis. If the initial pH of the sample was acidic or neutral, the extraction buffer used was sodium acetate (pH 4.93); if the initial pH of the sample was basic, the extraction buffer used was acetic acid (pH 2.88). The extract was separated from the solids by filtering through a glass fibre filter paper with a pore size of 0.6 to 0.8 μm. The SPLP procedure is similar to the TCLP procedure except the extraction fluid used was a liquid with a pH of 4.20, made of sulphuric/nitric acid in reagent water. The leachate from both tests was analysed for total As (APHA Method 3125B; APHA 2005).

Results

Precipitates from Stockton and Blackball mines

The results of XRF analyses show that the Stockton precipitate contains significant quantities of Al, Si, Fe and Ca. Fe content comprises 13 wt% Fe_2O_3 equivalent (Table 2). The XRD diffractogram for the Stockton sludge contains sharp peaks and a broad diffuse background (Fig. 3A). The sharp peaks correlate with quartz, calcite and an unknown mineral while the broad background occurs in the zone where poorly crystalline Fe and Al oxy-hydroxy-sulphate minerals produce a diffuse response (Carlson & Schwertmann 1981). There is poor correlation between the diffractogram and minerals that are expected in an AMD neutralising environment (Nordstrom & Alpers 1999).

XRF data indicate that the Blackball precipitate is Fe rich (74 wt% Fe_2O_3) with minor concentrations of Si (1.10 wt% SiO_2) and all other major oxides below 1 wt% (Table 2). The XRD spectra for the Blackball precipitate contains peaks that correlate with goethite (Bayliss 1986) and six line ferrihydrite (Carlson & Schwertmann 1981; Fig. 3B). Peak intensities and shapes indicate that these minerals are poorly crystalline and it is likely that goethite

Table 2 Major oxides from XRF analyses of precipitate used in batch and column experiments

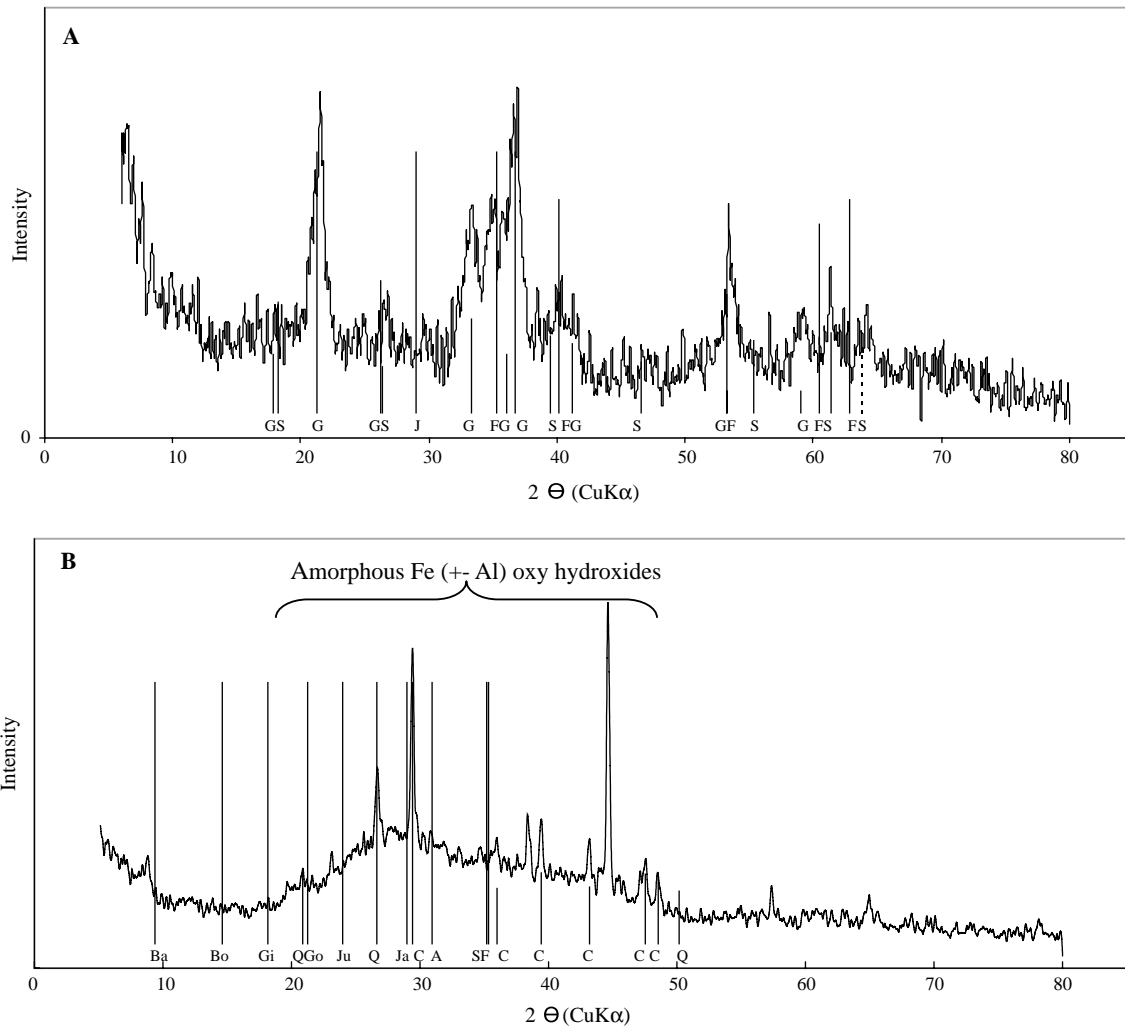|	Stockton precipitate (wt%)	Blackball precipitate (wt%)
SiO_2	17.57	1.10
Al_2O_3	29.75	0.21
Fe_2O_3	13.41	74.12
CaO	11.18	0.02
MgO	0.88	0.02
K_2O	0.86	0.01
Na_2O	0.18	0.12
MnO	0.03	0.02
TiO_2	0.26	<0.01
SO_3	3.00	0.02
P_2O_5	0.12	0.03
LOI	22.45	23.56
SUM	99.69	99.23

LOI, loss on ignition.

Fig. 3 XRD spectra. **(A)** Blackball precipitate with ideal peak locations for goethite (G) ferrihydrite (F) and schwertmannite (S) and the most intense peak for jarosite (J). **(B)** Stockton sludge with peak locations shown for identified minerals, calcite (C), quartz (Q). Most intense peak locations are also shown for common minerals that form during AMD neutralisation, basaluminite (Ba), Boehmite (Bo), gibbsite (Gi), jurbanite (Ju), jarosite (Ja), alunite (A) schwertmannite (S) and ferrihydrite (F).

recrystallised from ferrihydrite (Cornell & Schwertmann 1996).

Batch experiments

The water used in Batch Experiment 1 and 2 contained 61 and 99 mg/L As, respectively (Table 3). The pH was uniform for the selected vials with Blackball experiments pH ranging from 3.5 and 4.0 and Stockton experiments pH ranging between 6.5 and 6.7. In Batch Experiment 1 As concentrations in the As-contaminated water after contact with the precipitates from Stockton and Blackball was less for all contact times investigated (1.3 to 120.5 h) and As removal increased as with contact time (Table 4). As is rapidly removed in the first 5 h reaching equilibrium after about 48 h (Fig. 4). In the first 5 h, 94.75% and 99.92% of As was

adsorbed onto the Stockton precipitate and Blackball precipitate, respectively. At 24 h of contact time, 98.46% and 99.97% of As was adsorbed onto the Stockton precipitate and Blackball precipitate, respectively.

In Batch Experiment 2 the ratios of Stockton and Blackball precipitate was 1 to 50 g/L) and As concentrations decreased in the As-contaminated water after contact with the precipitates (Table 6). As the precipitate to As-contaminated water increases the removal of As also increases. At 1 and 5 g/L water, the Stockton precipitate decreased As concentrations by 21.18% and 60.61%, respectively. At both 25 and 50 g/L water, the Stockton precipitate decreased the As concentration by 99.90%. In comparison, for 1 and 2.5 g/L water, the Blackball precipitate decreased As concentrations by 74.75% and 99.79% respectively. At both 25 and 50 g/L water the Blackball

Table 3 Results of laboratory-analyses of As-bearing water from Prohibition Mine processing site used in batch and column experiments

	Units	Field sample	Laboratory sample
pH	pH units	4.1	3.9
Cations			
Dissolved Sodium	mg/L	4.2	3.7
Dissolved Potassium	mg/L	1.5	1.5
Dissolved Calcium	mg/L	15	15
Dissolved Magnesium	mg/L	3.6	3.2
Anions			
Sulphate	mg/L	15	15
Total Alkalinity	mg/L as $CaCO_2$	<1.0	<1.0
Chloride	mg/L	4.3	4.4
Traces			
Dissolved Aluminium	mg/L	0.5	0.44
Dissolved Arsenic	mg/L	62	61
Dissolved Iron	mg/L	0.53	0.38
Dissolved Manganese	mg/L	0.11	0.11
Dissolved Nickel	mg/L	0.013	0.013
Dissolved Zinc	mg/L	0.41	0.41
Nitrite-N	mg/L	0.0037	<0.0020
Nitrate-N	mg/L	0.0041	0.46
Nitrate-N+ Nitrite-N	mg/L	0.0078	0.46
Dissolved Reactive Phosphorus	mg/L	21	19

Analytical methods are described in the Methods section.

precipitate reduced the As concentration by >99.99%. Arsenic concentrations were reduced to below 0.01 mg/L for both precipitates at 50 g/L water.

Column experiment

The column experiment was designed to determine the effectiveness of As removal from a continuous waste stream by Stockton and Blackball precipitates over a period of 10 days. The amount of precipitate included in the columns and the residence time of water in the columns were determined from the batch experiments. The results of Batch Experiment 1 indicate that little As adsorption occurs after 24 h of contact time, therefore, a residence time of 20 h was selected for the column experiment. At a ratio of 50 g/L, the results of Batch Experiment 2 indicate that the Stockton precipitate can remove 99.90% of As from the water and the Backball precipitate can remove >99.99% of As from the water. Therefore, the ratio of precipitate for columns 1 and 3 was

Table 4 Results from first batch experiment

Stockton precipitate		Blackball precipitate	
Contact time (h)	Dissolved As (mg/L)	Contact time (h)	Dissolved As (mg/L)
initial	61	initial	61
1.7	15	1.3	0.12
3.5	7.6	3.3	0.067
5.5	3.2	5.5	0.048
8.3	2.4	8.3	0.039
24.6	0.94	24.7	0.021
48.6	0.57	48.8	0.016
68.4	0.77	68.4	0.017
120.6	0.39	120.5	0.015

Ratio of precipitate to As-contaminated water was kept constant at 10 g/L and contact time varied from 1.3 to 120.6 h to determine the adsorption amount of As onto each precipitate. The amount of adsorption is rapid over the first 5 h.

50 g/L water. Batch experiments also indicate that Blackball precipitate is five times more effective at As adsorption than the Stockton precipitate, therefore column 2 was set up with Blackball precipitate at 1/5 the ratio of columns 1 and 3, at 10 g/L water.

The input water had As concentrations from 34 to 49 mg/L with an average of 42 mg/L due to the need to recharge the input water reservoir during the experiment (Table 5). Samples from the input water were taken and analysed at the same time as the effluent water. The input water had a pH of 3.6 and this remained constant on passing through columns with Blackball precipitate (column 2 and 3) but increased to pH 6 after passing through Stockton precipitate (column 1), probably because of the unreacted limestone content of this precipitate material.

Arsenic was removed from the inlet water by each column containing Stockton or Blackball precipitate. Concentrations of As decreased from 47 mg/L to below 0.1 mg/L in the first 24 h for all columns except the control column that did not contain precipitate (Table 5). In column 1, As concentrations decreased by 99.9% to 0.0078 mg/L in the effluent after 48 h but removal was less effective over the next 8 days with effluent As concentration at 21 mg/L (a decrease of 43%) at the end of the experiment (t = 238 h). In column 2, As concentration decreased by 99.9% to 0.0001 mg/L in the effluent after 24 h but removal was less effective over the next eight days with effluent As concentration at 17 mg/L (a reduction of 54%) by the end of the experiment. In column 3, As concentrations decreased by 99.9% to 0.0023 mg/L after 48 h and effective removal continued even at the end of the experiment with effluent As concentration at 0.04 mg/L. Effluent As concentrations from column 4 (no precipitate) remained reasonably constant and similar to the input water As concentrations.
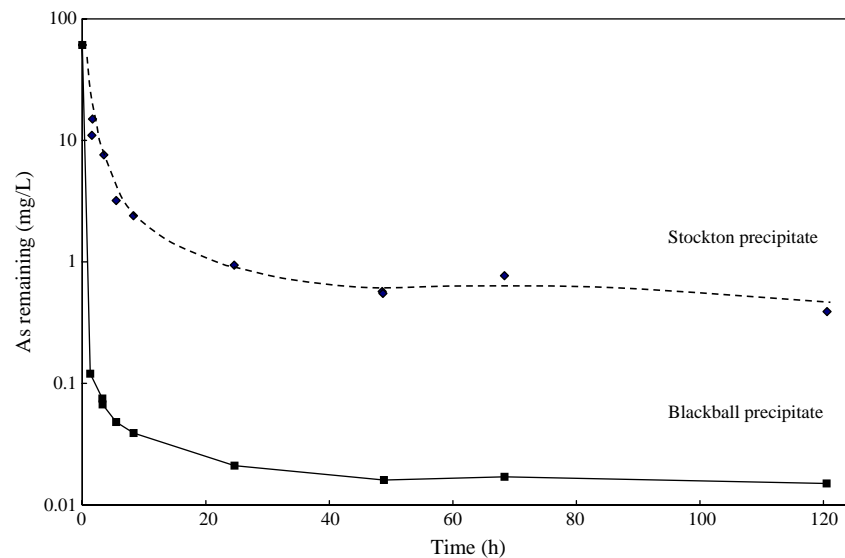
Fig. 4 Results for Batch Experiment 1. The contact time varied but the ratio of precipitate to As-contaminated water was kept constant at 10 g/L. Initial As concentration was 61 mg/L. The results showed that Blackball precipitate reduced As concentrations in the water greater than Stockton precipitate. Blackball precipitate was more effective at As adsorption than Stockton precipitate because Blackball precipitate contained substantially more Fe oxides (74% Fe_2O_3 vs 13% Fe_2O_3; Table 2).

Leachate results

SPLP tests on the sand plus precipitate were carried out for all four columns. Stockton precipitate from column 1 leached 0.420 mg/L As compared to Blackball precipitate from column 3 that leached 0.18 mg/L As. Blackball precipitate from column 2 leached less than column 3, at 0.150 mg/L As. The control column leached 0.002 mg/L As. SPLP tests were considered to be more representative of the disposal method for the media than an acidic environment that is reflected in TCLP. Leachate of Blackball precipitate from only column 3 was analysed for total As, by the TCLP procedure with a low result of <0.021 mg/L.

Table 5 Results from second batch experiment

	Arsenic remaining (mg/L)	
AMD precipitate to As water (g/L)	Stockton precipitate	Blackball precipitate
1	67	25
2.5	no data	0.21
5	39	0.07
10	0.57	0.016
25	0.087	0.0051
50	0.008	0.0017

The ratio of precipitate to As-contaminated water varied from 1 to 50 g/L and contact time remained constant at 48.7 h. The results from the first batch experiment suggested equilibrium is reached at 48 h, therefore this experiment determined the maximum adsorption capacity of precipitate (mg As adsorbed/g precipitate). Starting As concentration was 99 mg/L.

Discussion

Batch experiments

Batch Experiment 1 showed that Blackball precipitate lowered As concentrations in water more than Stockton precipitate (Fig. 4). In the first 4 h, Blackball precipitate decreased As concentrations by three orders of magnitude, nearly two orders of magnitude lower than the Stockton precipitate. At 5 and 8 h, water treated with the Blackball precipitate showed further decline in As levels to approximately 60 times lower than water treated by Stockton precipitate. In Batch Experiment 1 As concentrations were relatively steady after about 24 h for both precipitates suggesting that equilibrium had been reached. At the ratio of precipitate to As-contaminated water used in Batch Experiment 1 (10 g/L), the Stockton precipitate removed 6.01 mg As/g precipitate (98% of available As) after 24 h of contact time. In comparison, the Blackball precipitate removed 6.09 mg As/g precipitate (99% of available As) after 24 h.

Batch Experiment 2 results indicated a decline in As concentrations with increasing ratio of precipitates to As-contaminated water (Fig. 5). At 1 g/L, the Stockton precipitate lowered the As concentration from 99 mg/L to 67 mg/L whereas the Blackball precipitate decreased As concentration to 25 mg/L. If the precipitate to As-contaminated water ratio is increased to 10 g/L, the Stockton precipitate decreased the concentration by two orders of magnitude, while the Blackball precipitate lowered the As concentrations by three orders of magnitude. At 50 g/g arsenic concentrations were reduced by four orders of

Table 6 Analyses of As water from column experiments

Duration of experiment (h)	Influent As (mg/L)	Effluent As (mg/L)			
		Column 1 (Stockton precipitate 50g/L)	Column 2 (Blackball precipitate 10g/L)	Column 3 (Blackball precipitate 50g/L)	Column 4 (Blank—No precipitate)
2	49	0.054	0.015	0.19	38
24	47	0.011	0.001	0.0049	43
48	41	0.0078	0.0051	0.0023	45
72	41	0.49	0.06	0.002	44
96	40	1.1	0.045	0.0022	44
121	37	2	1.3	0.0023	40
144	34	2.5	2.6	0.0027	40
168	37	11	10	0.002	38
191	36	14	13	0.0046	33
216	35	18	16	0.0063	39
238	37	21	17	0.04	42

Removal of As from water over time was similar for columns 1 and 2. Arsenic removal was best in column 3 although treatment effectiveness decreased near the end of the experiment. Column captions show the precipitate dose in mg for each litre of water in 20 h period. Detection limit for arsenic was 0.00020 mg/L. Water with high arsenic concentrations were diluted for analysis.

magnitude by Stockton precipitate and nearly five orders of magnitude by Blackball precipitate. The Stockton precipitate removed between 2.0 and 12 mg of As/g precipitate, and the Blackball precipitate removed between 2.0 and 74 mg of As/g precipitate. The experiment was limited by the amount of precipitate in the vials and the concentration of the contaminated water, whereby As became totally depleted at high precipitate loading.

Column experiment

Arsenic concentrations in effluent from column 1 (50g Stockton precipitate/L water) and column 2 (10g Blackball precipitate/L of water) have similar trends over the experimental period (Fig. 6), lowering As concentrations by 3.5

Fig. 5 Results for Batch Experiment 2. The ratio of precipitate to As-contaminated water varied but the contact time was kept constant at 48.7 h. For all ratios of precipitate to water (1 to 50 g precipitate/L water), As concentrations were less in the water after contact with the precipitate. The data show a decrease in As concentrations with increasing ratio of g of precipitate to volume of As-contaminated water.

and 4.5 orders of magnitude, respectively, in the first 24 h. Arsenic concentrations increase in the effluent after 48 and 24 h for column 1 and column 2 respectively, indicating adsorption capacity has been reached for both precipitates. After 144 h, both precipitates show similar increasing trends in effluent As concentrations (Fig. 6). These results indicate that the Blackball precipitate is five times more effective at As adsorption than the Stockton precipitate. These results also suggest that available adsorption sites are filled within 10 days for Stockton and Blackball precipitates at ratios of 50 and 10 g/L of As-contaminated water, respectively.

In column 3 (50 g Blackball precipitate/L water), the effluent As concentrations decreased by four orders of magnitude within 24 h and remain reasonably constant from 48 to 168 h, then increase by one order of magnitude to 0.04 mg/L, indicating decrease in As adsorption with time. These results confirm batch results showing that the adsorption capacity of Blackball precipitate is better than Stockton precipitate.

The input water for the experiments had pH of 3.6 and this remained unchanged as the water passed through the columns with Blackball precipitate (column 2 and 3), but increased to pH 6 for column 1 as the Stockton precipitate contains unreacted lime which neutralised the acid water. Column 4 containing only sand also neutralised the water as the greywacke sand generally contains some minor carbonate. Arsenic concentrations in water through column 4 were similar to the influent concentrations indicating little As adsorption onto the sand.

Mass balance of the input and effluent water for the columns shows that over the 10 days of the experiment column 1, column 2 and column 3 removed 529 mg, 491 mg and 581 mg of As, respectively. This represents 7.2, 32.7 and 8.0 mg/g precipitate, respectively. Normalising this to the Fe content in the precipitate, this equates to 54.13, 44.49 and
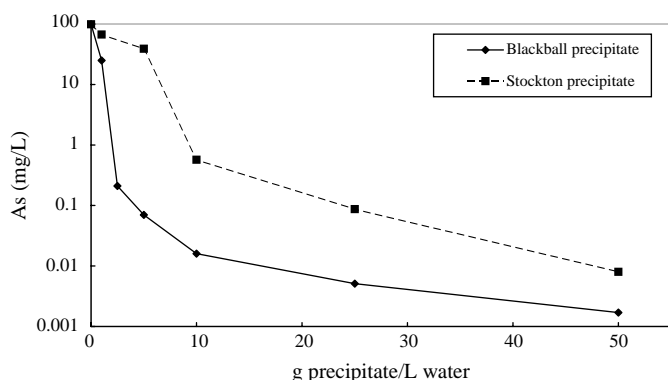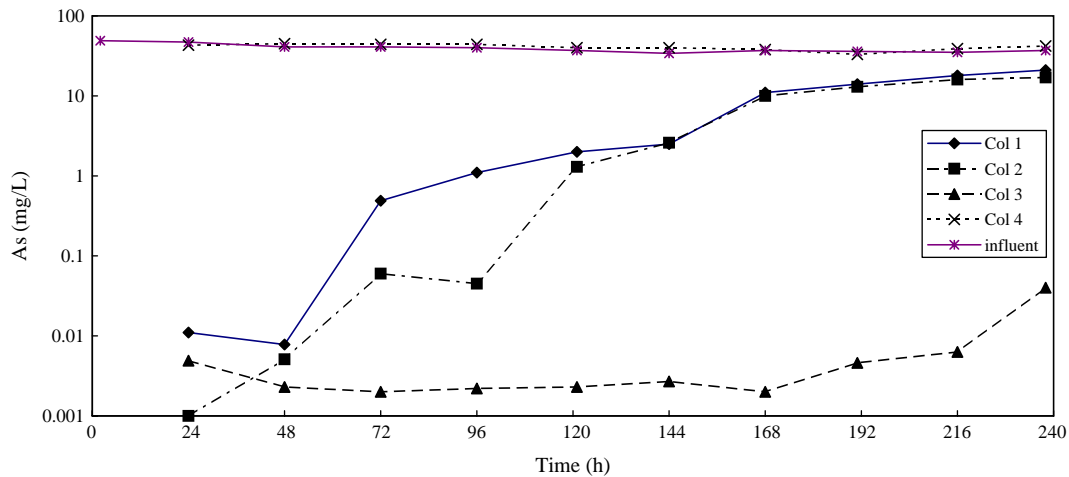
Fig. 6 Arsenic removal in column experiment with initial As concentration of 42 mg/L. Arsenic concentrations in effluent from column 1 and column 2 exhibited similar trends over the experimental period. As concentrations decreased initially but started to increase in the effluent after 48 and 24 h indicating reduced adsorption capacity of both precipitates. These results show that the Blackball precipitate is five times more effective at As adsorption than the Stockton precipitate likely because the Blackball precipitate contains about five times more Fe oxides than Stockton precipitate.

10.79 mg/g, respectively. Since breakthrough of As adsorption occurred in columns 1 and 2 at 10 days, indicating that available adsorption sites had been filled, these results suggest a maximum adsorption capacity of about 7 and 33 mg/g for Stockton and Blackball precipitates respectively. In addition, when the As adsorption capacity is normalised to the Fe content, both precipitates remove about the same amount of As for each g of Fe in the precipitate. Based on the observed capacity of Blackball precipitate compared to Stockton precipitate it is likely that if the experiment had continued the breakthrough of As from column 3 would not have occurred until about 40 days.

There are several factors that could contribute to different adsorption characteristics between Stockton and Blackball precipitates. Sorption characteristics of different Fe(III) minerals that can precipitate in mine drainage environments are specific to each mineral. For example, goethite has a higher sorption capacity for some cations than ferrihydrite (Webster et al. 1998). In addition, the adsorption characteristics of other components in the precipitates such as Al-oxyhydroxide minerals are unknown. The reaction pH in these experiments was not controlled, instead reactions were permitted to equilibrate between precipitates and As-contaminated water. Arsenic adsorption to idealised ferrihydrite indicates that As(V) is strongly partitioned into adsorbed species throughout the pH range 4 to 10 and As III is likely to favour adsorbed species though not as strongly as As(V) (Dzombak & Morell 1990). It is likely that As(V) is substantially more abundant than As(III) in our study (Haffert et al. in press) and therefore, while pH is an important variable between the two sets of experiments this is unlikely to cause major changes to As adsorption partitioning assuming the precipitates used in

these experiments behave similarly to ideal materials. As partitions strongly onto Fe(III) mineral surfaces throughout the pH range of these experiments (3.6–6) however, these precipitates are complex field samples rather than idealised minerals. In general the As removal properties in each experiment are proportional to the total Fe content of the precipitates as indicated by XRF analyses. Our experiments best reflect the conditions that might be expected should these precipitates be incorporated into large scale field trials.

Bacteria are also an important factor influencing arsenic adsorption and remobilisation in arsenic rich systems (Lloyd & Oremland 2006; Babechuk et al. 2009; Langley et al. 2009). However this topic is this is beyond the scope of this study.

Adsorption kinetics

By plotting and analysing the As adsorption over time, the rate constant can be determined for the Stockton and Blackball precipitates. The rate constant is a coefficient that is specific to each adsorption media and quantifies the speed of adsorption of As. Adsorption under non-equilibrium conditions can be described by pseudo-second-order Lagergren kinetics (Eq. 1; Singh & Pant 2006; Liu 2008)

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \qquad (1)$$

where q_t and q_e is the amount of As adsorbed/mass of absorbent (mg/g) at time t (in min) and at equilibrium respectively, and k_2 is the second order sorption rate constant specific to each precipitate (min^{-1}). Equilibrium was reached in the first batch experiment at about 24 h of

contact time. This model demonstrates that adsorption is dependent on the surface adsorption site availability rather than the concentration of As in the water (Liu 2008).

After integration and rearranging Eq. 1, the constant k_2 is determined by a plot of t/q vs t (Eq. 2; Singh & Pant 2006; Liu 2008).

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \qquad (2)$$

The pseudo-second-order rate equation derived from the Lagergren kinetics model (Eq. 2; Singh & Pant 2006) is only valid if a plot of t/q vs t is a straight line, with the slope and intercept in the plot giving the values of q_e and k_2. Both Stockton and Blackball precipitates plot with correlation coefficients above 0.99, indicating the pseudo-second-order is a good fit for the data (Fig. 7A, B). The calculated q_e values for Stockton and Blackball precipitates are 6.079 mg/g and 6.098 mg/g, respectively. The kinetic rate constants, k_2 are 7.35×10^{-3} and 9.27×10^{-1} min^{-1} for Stockton and Blackball precipitate, respectively. This indicates Blackball precipitate adsorbs As more rapidly than Stockton precipitate.

Adsorption isotherm

The adsorption capacity of the Stockton and Blackball precipitates (mg As per g precipitate) can be determined by plotting an adsorption isotherm for each and this shows the relationship between As concentration in the water at equilibrium and the amount of As adsorbed onto the precipitate data from Batch Experiment 2 can be used to plot adsorption isotherms. During this experiment, the ratio of precipitate to water varied and different amounts of As were adsorbed onto precipitate, generating different equilibrium concentrations of As in the water. Adsorption isotherm plots were prepared for each precipitate, where q_e is the amount of As adsorbed in mg/g and C_e is the equilibrium concentration of As in the water in mg/L (Fig. 8A, B). The data in these plots exhibit L-curves (Essington 2004), implying that at low surface coverage, the adsorbate (As) has high affinity for the solid surface but at higher coverage the surface sites are saturated.

The two most commonly used isotherm models are the Langmuir and Freundlich Isotherms (Stumm & Morgan 1996; Essington 2004). The simplest model is the Langmuir
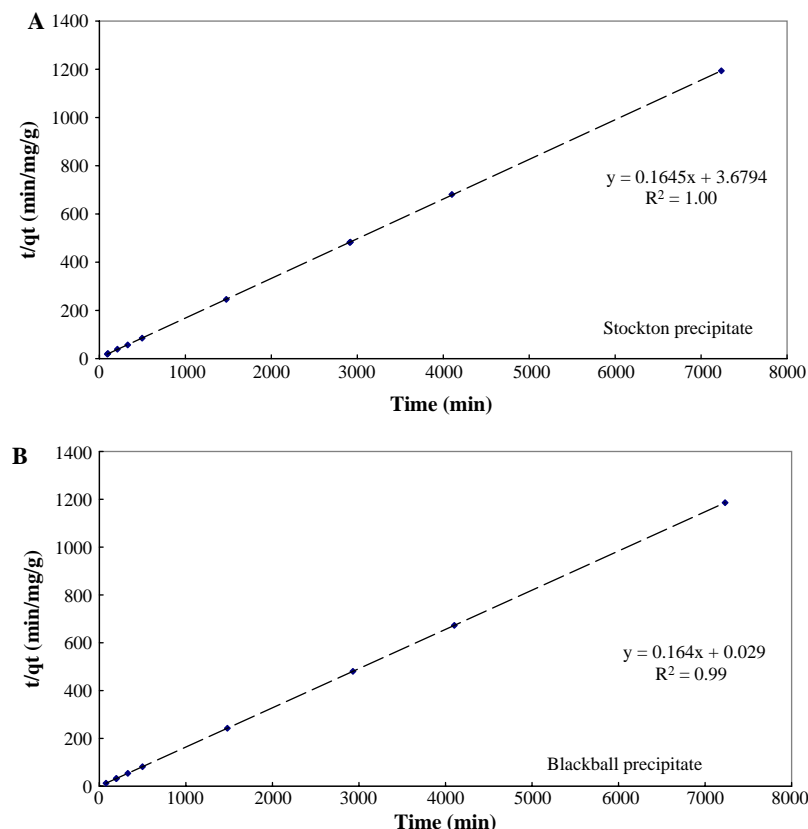

Fig. 7 The pseudo-second-order rate equation derived from the Lagergren kinetics model (Eq. 2; Singh & Pant 2006) is only valid if a plot of t/q vs t is a straight line, with the slope and intercept in the plot giving the values of q_e and k_2. **(A)** The Stockton precipitate plots with correlation coefficients above 0.99. The calculated q_e and k_2 for Stockton precipitate are 6.079 mg/g and 7.35x10^{-3} min^{-1}, respectively. **(B)** The Blackball precipitate plot with correlation coefficients above 0.99. The calculated q_e and k_2 for Blackball precipitate are 6.098 mg/kg and 9.27x10^{-1} min^{-1}, respectively. q_t, amount of As adsorbed per mass of absorbent at time t (in min); q_e (mg/kg) amount of As adsorbed per mass of absorbent at equilibrium; k_2, second order sorption rate constant specific to each precipitate (1/min).
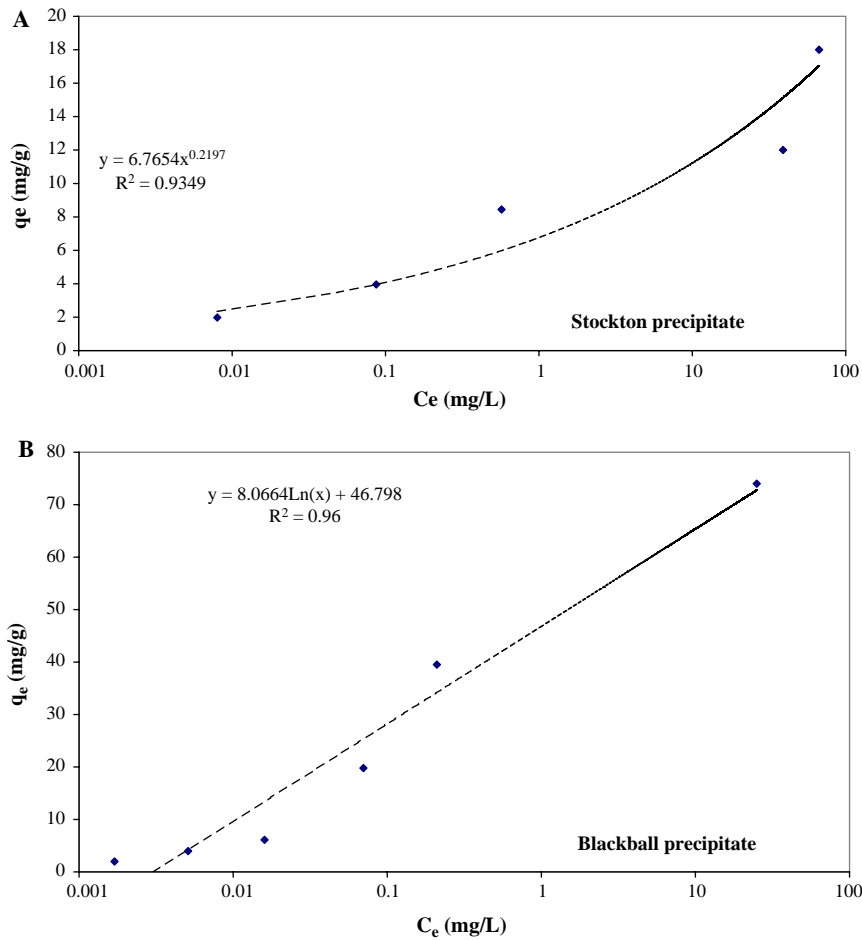
Fig. 8 Data from Batch Experiment 2 using precipitate were used to plot adsorption isotherms, q_e versus C_e. The data in these plots exhibit L-curves (Essington 2004), implying that at low surface coverage on the precipitate, the adsorbate (As) has high affinity for the solid surface but at higher coverage the affinity for the surface decreases. **(A)** Stockton precipitate. **(B)** Blackball precipitate. C_e, equilibrium solute concentration (mg/L); q_e, amount of As adsorbed at equilibrium (mg/g).

Isotherm, in which the adsorption sites on the surface of the solid become occupied by adsorbate from the solution at a rate defined as the Langmuir adsorption constant which differs for each mineral and increases with an increase in the binding energy of adsorption (Stumm & Morgan 1996). The Langmuir model assumes monolayer sorption onto a homogeneous surface with a finite number of identical sites (Kundu & Gupta 2007). The Langmuir equation used for As adsorption (Essington 2004; Kundu & Gupta 2007; Guo et al. 2007a, b) is

$$q_e = \frac{bK_L C_e}{(1 + K_L C_e)} \qquad (3)$$

where b is the Langmuir constant related to total concentration of available sites or the adsorption capacity (mg/g), C_e is the equilibrium solute concentration (mg/L), q_e is the amount of As adsorbed at equilibrium (mg/g), and K_L is a measure of the intensity of the adsorption isotherm (Essington 2004). The slope and intercept of the linear plot

of $1/q_e$ versus $1/C_e$ gives the values of the Langmuir constants b and K_L (Fig. 9A, B). A double log plot of the Langmuir isotherm should have an initial straight line with slope of 1 (Stumm & Morgan 1996; Essington 2004). If the slope is less than 1, then the ratio of dissolved As to adsorbed As is better described by a Freundlich isotherm. For the Stockton and Blackball precipitates the initial slopes are not unity therefore the Langmuir isotherm is not applicable to describe the adsorption to these complex precipitates.

The Freundlich isotherm applies to heterogeneous solids (Stumm & Morgan 1996; Essington 2004; Eq. 4). The linear expression of the Freundlich isotherm is shown in Equation 5 below (Stumm & Morgan 1996; Essington 2004),

$$q_e = K_F C_e^N \qquad (4)$$

$$\log q_e = \log K_F + N \log C_e \qquad (5)$$

where K_F and N are Freundlich constants. N indicates the heterogeneity of the solid; as it increases the heterogeneity
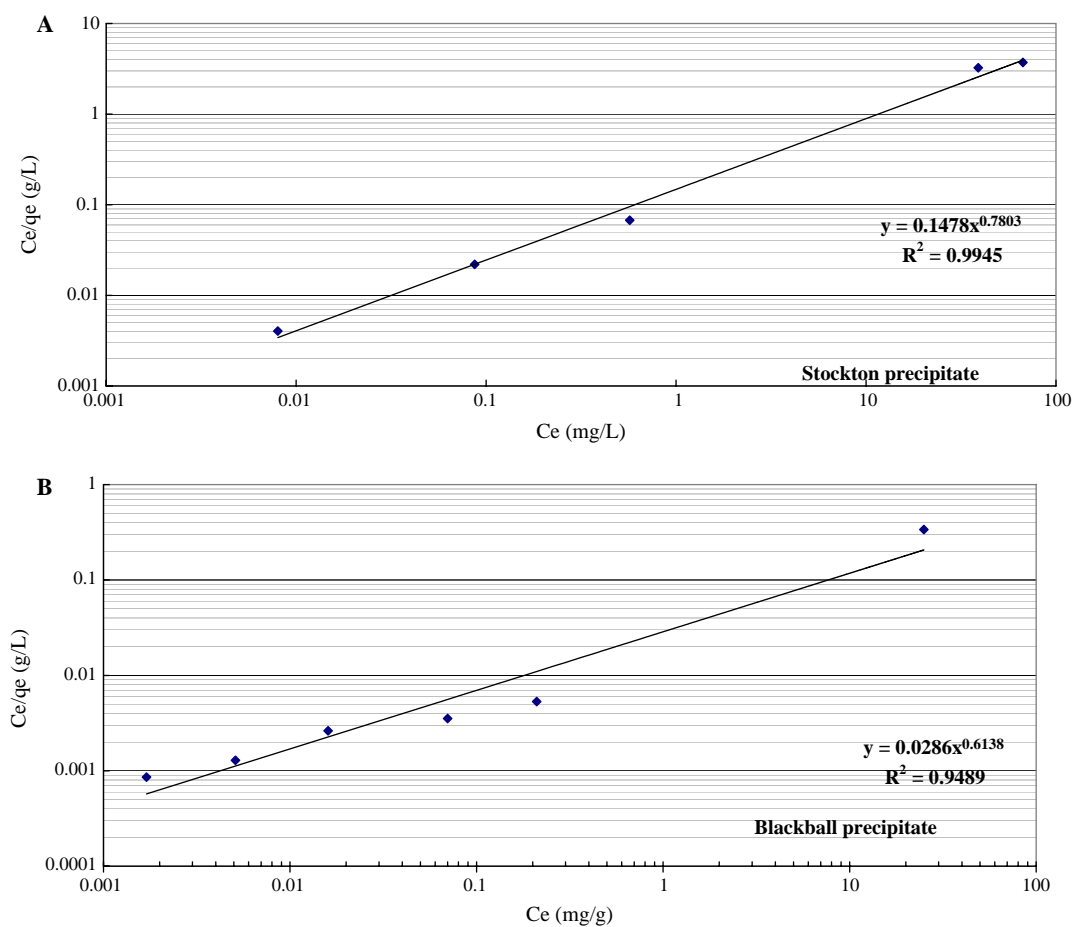
Fig. 9 Langmuir isotherm plots for **(A)** Stockton precipitate from Batch Experiment 2 and **(B)** Blackball precipitate from Batch Experiment 2. The slope and intercept of the linear plot of $1/q_e$ versus $1/C_e$ gives the values of the Langmuir constants b and K_L. Both batch experiments were run for 48 h with initial As concentrations of 67 mg/L. b, Langmuir constant related to total concentration of available sites or the adsorption capacity (mg/g); C_e, equilibrium solute concentration (mg/L); q_e, amount of As adsorbed at equilibrium (mg/g); K_L, measure of the intensity of the adsorption isotherm (Essington 2004).

decreases (Essington 2004). A plot of log q_e versus log C_e yields a straight line with the intercept as log K_F and the slope N. Data from the second batch experiment can be modelled using the Freundlich isotherm (Fig. 10A, B). For Stockton precipitate, N is 0.22 and for Blackball precipitate, N is 0.37, indicating greater heterogeneity in the Stockton precipitate. This matches well with the XRF results showing that this contains a mixture of Fe, Al, Si and Ca compounds whereas the Blackball precipitate is mostly Fe. The pH of the system may also be a factor influencing adsorption behaviour but this study did not provide adequate data to quantify this aspect. The Freundlich Isotherm adequately describes the adsorption behaviour for both precipitates as the linear regressions are 0.93 and 0.88, for the Stockton and Blackball materials, respectively.

Using this data the Freundlich Isotherm model predicts that if a final As concentration in the water of 0.01 mg/L is desired (current New Zealand drinking water standard), the amount of As that can be adsorbed onto Stockton and Blackball precipitates would be 2.46 mg/g and 5.90 mg/g, respectively.

Comparison with previous studies

In Batch Experiment 2, As was removed at 2.0 to 12 mg/g by the Stockton precipitate and 2.0 to 74 mg/g by the Blackball precipitate. The As removal using precipitates collected from field AMD sites is comparable to ferrihydrite (Grafe et al. 2002) which removed 60 mg/g and 37 mg/g at pH 3 and 6, respectively. Red mud (Altundogan et al. 2000), siderite, hematite (Guo et al. 2007a, b) and iron-coated sand (Nguyen et al. 2006) removed between 0.1 to 0.5 mg As/g material. Pedogenic Fe-Mn nodules removed up to 2 mg As/g nodule. Zerovalent iron and iron oxyhydroxide can remove up to 33 mg As/g material (Leupin & Hug 2005; Sarkar et al. 2007). The adsorption capacity of the Blackball precipitate exceeds all of these.
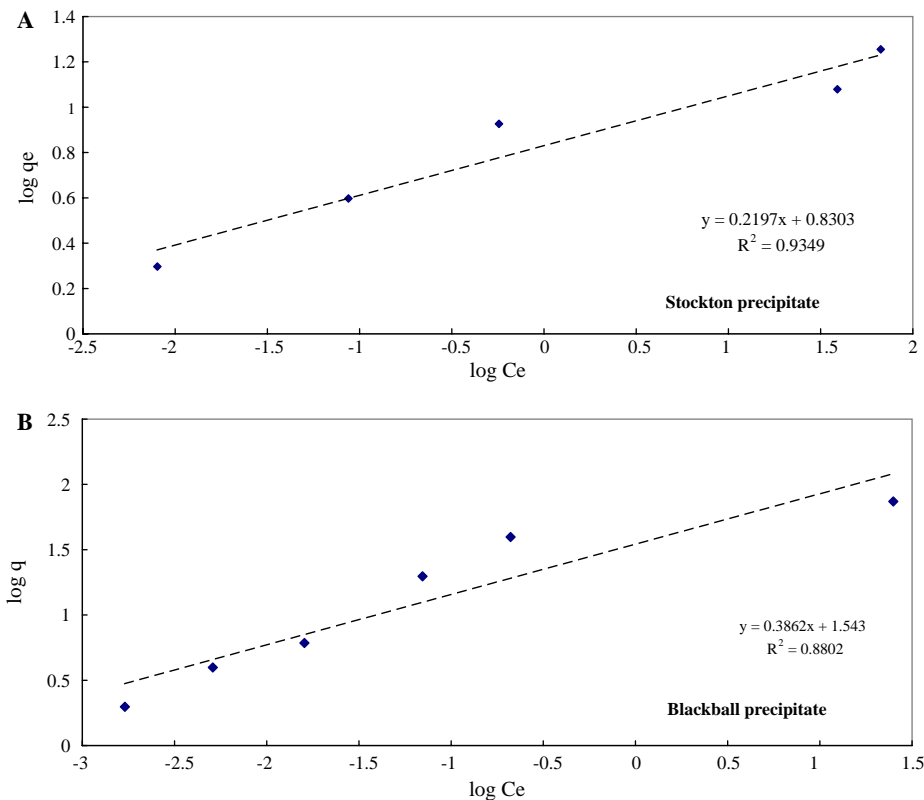
Fig. 10 Freundlich isotherm plots for **(A)** Stockton precipitate from Batch Experiment 2 and **(B),** Blackball precipitate from Batch Experiment 2. A plot of log q_e versus log C_e yields a straight line with the intercept as log K_F and the slope N. For Stockton precipitate and Blackball precipitate, N is 0.22 and 0.37, respectively. K_F, Freundlich constant; N, Freundlich constant, N is between 0 and 1 and is a measure of heterogeneity, which increases as N becomes 0 (Essington 2004).

Future work: field trials

For the next phase of this project, it is planned to conduct small-scale field trials at the Prohibition site to remove As from the water. Currently, water from the wetland where As-contaminated water was collected for this study flows through a man-made dam and emerges on the other side at a flow rate of about 2.0 L/s and As concentrations about 2.4 mg/L. The dam acts as a natural As removal system reducing concentrations from 52 to 2.4 mg/L (Haffert & Craw 2008a). Field trials will use plastic tubs (filled with sand/precipitate mixtures) PVC piping and valves. Sampling of water inflow and outflow will occur weekly. Analysis of results will provide information on the effectiveness of the treatment system and allow for later design of a full scale remediation system. A conservative approach to estimating the amount of precipitate required for treating water in the small-scale field trials can be completed using the Freundlich Isotherm results.

Summary and conclusions

Precipitates from AMD sites have potential as substrates to treat As-contaminated water by adsorption. Precipitates from an AMD water treatment system at Stockton mine

and from uncontrolled AMD discharge at Blackball mine were tested for As adsorption properties. Two batch tests and a column leaching experiment were conducted to determine the characteristics of As adsorption of each precipitate. Both Stockton and Blackball precipitate batch experimental data are a good fit to the pseudo-second-order rate equation. Batch Experiment 1 showed that As adsorption onto each precipitate occurs rapidly during the first 5 h, reaching equilibrium after 24 h, and that Blackball precipitate consistently removes more As than Stockton precipitate.

The higher adsorption capacity of Blackball compared to Stockton precipitates match XRF results that indicate Blackball precipitate contains 74 wt% Fe_2O_3 whereas Stockton precipitate contains 13 wt% Fe_2O_3. Although several other factors could influence the adsorption characteristics of the precipitates including mineralogy and pH these have not been rigorously evaluated in this study. Batch Experiment 2 showed that the adsorption capacity is up to 12 mg/g and 74 mg/g for Stockton and Blackball precipitates respectively. The adsorption capacity of Stockton precipitate is similar to that reported in the literature for other Fe compounds, but the adsorption capacity of the Blackball precipitate exceeds those reported in the literature. The column experiment confirmed that adsorption of As from a

continuous waste stream onto these precipitates is possible and that passive remediation using this waste product mixed with sand in a reaction chamber could be a viable solution to As-contaminated water.

Acknowledgements

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