Technical Article

A Bauxsol™-based Permeable Reactive Barrier for the Treatment of Acid Rock Drainage

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Abstract. Permeable reactive barriers (PRBs) have generally been used to treat low flow and/or low contaminant loads of acid rock drainage (ARD). Bauxsol™, a product made from seawater-neutralized red mud (a by-product of alumina refining) buffers pH at 8.8 and has been shown to remove >99% of heavy metals loadings at >1000 meq/kg, which would make it an ideal medium for PRBs. Unfortunately, Bauxsol™ is very fine-grained (>90% of the material <10 µm) and therefore, possesses a very low hydraulic conductivity. Consequently, sand/Bauxsol™ mixtures were trialed to determine hydraulic conductivity and ARD treatment capacities. Column tests indicated that the sand/Bauxsol™ mixtures maintain a higher hydraulic conductivity when used to treat ARD than when used with tap water. A 75:25 sand:Bauxsol™ filter with a 130 mm thick layer of reactive media had a hydraulic conductivity of 3.06×10^{-5} m/s and except for Al, treated a highly contaminated ARD to ANZECC (2000) drinking water guidelines. A field trial of a 1 m^3 PRB (70:30 sand:Bauxsol™ mixture) with a hydraulic conductivity of 9.8×10^{-5} m/s treated about 45,000 L of highly contaminated ARD to the ANZECC (2000) drinking water standards, and about 27,000 L of this water had heavy metal loadings reduced to the ANZECC (2000) Protection of Aquatic Ecosystem guideline of >90% species protection.

The metal binding preference of Cu>Pb>Zn>Mn displayed by the PRB is consistent with the pKa of hydration values and it appears that MOH^+ formation dominates the removal of these metals. However, other removal processes appear to apply for Fe, Al, and Cd. Overall metal removal efficiencies ranged from 91.22% for Mn to >99.99% for Cu. Analysis of dried spent Bauxsol™ indicates that bound metals are not readily leachable, allowing the spent media to be disposed safely in a landfill.

Key Words: Acid rock drainage; Bauxsol™; New South Wales, Australia; permeable reactive barrier; treatment

Introduction

Acid rock drainage (ARD) results from the oxidization of pyrite (FeS_2) and other sulphide minerals in the presence of water to form ferric oxy-hydroxides and sulphuric acid (Appelo and Postma 1994; Evangelou 1995). ARD is common wherever waste rock, ore and/or mine tailings are stored and affects most Cu, Pb, Zn, Ni, Mo, As, Au, Ag, and coal beneficiation operations. ARD composition is directly linked to host rock geology and water chemistry, which combine to dictate toxicity. The combination of low pH and a potentially complex suite of metals can also promote synergistic toxic effects (Kelly 1999).

In recent years, the difficulties of treating ARD (and other) contaminated groundwater has led to greater focus on the development of permeable reactive barriers (PRBs). These passive treatment systems reduce or (potentially) eliminate on-going treatment costs and are designed to act as conduits for contaminated groundwater flow (U.S. EPA 1998). Contaminants can be contained (immobilized) and/or transformed (into non-toxic forms) within a PRB by adsorption, absorption, precipitation, redox, or biological processes (Puls 1998) and represent a novel progression from inefficient groundwater pump and treat systems (National Academy of Sciences 1994). Remediation of ARD with PRBs generally relies on raising pH, and/or chemically- or biologically-induced sulfide precipitation (see Naftz et al. 2002). Relying on a single process limits the suite of metals that can be effectively removed, so multi-stage PRBs are commonly employed for ARD remediation.

Studies of raw and neutralised red mud from alumina refining have found many potential applications for this high volume resource (e.g. Apak 1995; Summers et al. 1996; Ward and Summers 1993; Zouboulis and Kydros 1993). Of particular interest to this study is the high acid neutralising (2.6 to 7 moles/kg) and metal loading capacity (>1000 meq/kg) of seawater-neutralised red muds, which were first recognised in 1992 and led to the development of Bauxsol™ technology and its use in treating ARD (Clark 2000; McConchie et al. 1998, 1999, 2000). Bauxsol™ is a manufactured dry red solid comprising a complex mixture of minerals that includes: abundant hematite,

boehmite, gibbsite, sodalite, quartz, cancrinite, brucite, calcite, diaspore, ferrihydrite, gypsum, hydrocalumite, hydrotalcite, p-aluminohydrocalcite, portlandite, minor aragonite, and a few low-solubility trace minerals (Clark 2000; McConchie et al. 1999, 2000). The exact composition and geochemical character of Bauxsol™ depends on the bauxite feed to the refinery, the operating conditions, and the efficiency of the caustic recovery systems. In addition, the manufacturing of Bauxsol™ from the alumina refinery's caustic red mud can be manipulated because the concentration and Ca:Mg ratio used for alkalinity precipitation can be altered, which in turn changes the mineral composition by favouring either Ca or Mg end members. Bauxsol™ has been applied successfully to standing water bodies by direct spray (slurry) addition. Laboratory-scale column tests have suggested that ARD could be treated as it passes through Bauxsol™, but the hydraulic conductivity is very low because >90% of Bauxsol™ is <10 μm.

This study assessed the performance capabilities of Bauxsol™ as a reactive medium within a PRB to treat ARD. First, we determined, on a laboratory-scale, the hydraulic conductivity and treatment efficiency of Bauxsol™/sand mixtures subjected to ARD, followed by emplacement of a chosen Bauxsol™ / sand mixture within a 1 m³ PRB to further assess treatment efficiency and capacity on a pilot-scale.

Site Description

The study site is located at the Mt Carrington silver and gold mine, near the community of Drake, in northern New South Wales, Australia (Figure 1). The mineralisation of the Drake area occurred through late Permian to early Triassic hydrothermal volcanics with many base metal veins and stockworks (Scheiber and Basden 1998). Two main stages of mineralization have been identified: the first, rich in Au and Zn; the latter, chalcopyrite ($CuFeS_2$)-dominant with chalcocite (Cu_2S) (Clark et al. 2000; Houston 1993) The veining of the area is generally rich in sulphur-containing minerals such as: sphalerite (ZnS), pyrite (FeS_2), chalcopyrite ($CuFeS_2$), and galena (PbS), in addition to quartz, electrum, gold, and hematite. Various sediment and water surveys of the site have indicated high levels of TCLP leachable Cd (up to 18.32 mg/kg), Cu (up to 263.9 mg/kg), Pb (up to 11.42 mg/kg) and Zn (up to 162.84 mg/kg) and similarly poor water throughout the site with high concentrations of dissolved metals, which concentrate during the dry season (Cd – up to 1.7 mg/L; Cu – up to >200 mg/L; Pb – up to 0.12 mg/L; Zn – up to 175 mg/L) (Clark et al 2001; Collins 1994; Maddocks 2000).
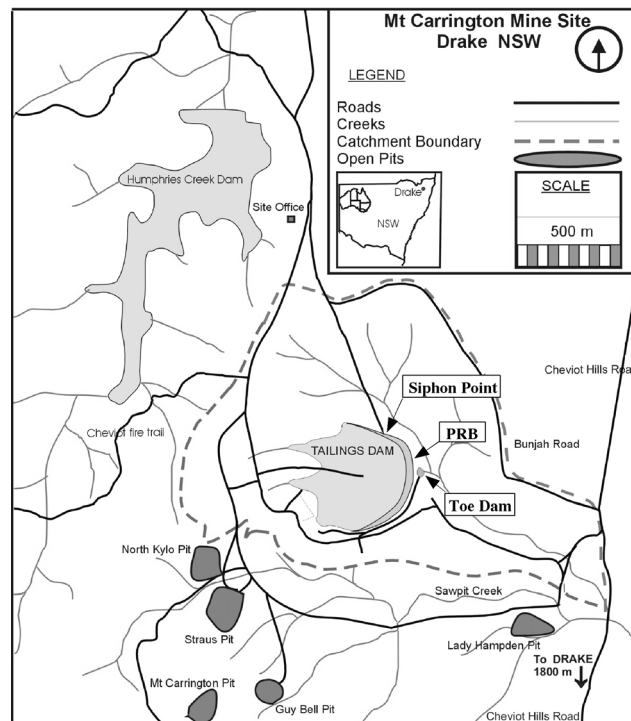

Figure 1. Location and details of the Mt. Carrington mine and PRB Site (modified from Maddocks 2000)

Small-scale mining in the Drake area commenced around 1886, with the discovery of rich gold and other mineral deposits in the area (Dept. of Mineral Resources 1999). However, it was not until 1974-76 that large-scale commercial mining took place (Terill 1992); mining recommenced in 1988 and ceased in 1990. During this time, an extension of the tailings dam wall commenced, but was not completed. This resulted in a large quantity of waste and low-grade ore rock being dumped on the lower side of the dam wall as containment material. This exposed rock, rich in sulphide minerals (pyrite, chalcopyrite, chalcocite and sphalerite) is the main source of ARD at the mine (Lin et al. 2002).

Methods

Stage 1: Laboratory trials

Hydraulic conductivity tests

Three bottom-feed constant-head permeameters were constructed to establish hydraulic conductivity of a range of Bauxsol™ and sand mixtures; the sand used was a well-sorted medium sand (determined by shaking sieve analysis [>70% between 0.5 and 1.2 mm]). The proportions of Bauxsol™ in the mixture tested ranged from 15-50% (by weight). All laboratory tests used Bauxsol™ <500 μm and field trials used a sieved Bauxsol™ <1 mm; both were mixed with (the above) well-sorted, medium sand. Columns were filled by pouring the sand/Bauxsol™

mixture into the permeameter and gently tapping the sides to promote settling (but were not actively compacted). Each hydraulic conductivity test was conducted in triplicate with freshly packed material, with laboratory tap water and ARD water from the test site. Conductivity constants (k) were calculated from the average of the three replicates using equation (1):

$$k = Q\,L\,/\,h\,A \qquad (1)$$

where: Q = the water volume discharged (m^3/sec), L = the length of the test sample (m), h = hydraulic head (m), and A = the cross section area of the sample (m^2).

The pH and EC (electrical conductivity) were measured during the ARD column trials, and samples required for analysis were collected from the discharge points once the pH was within ANZECC (2000) limits for drinking water or aquatic ecosystem discharge (6.5<pH<8.5).

Treatment Efficiency and Capacity

For the column tests, treatment efficiency was determined by calculating total metal concentration reduction from the inflow to the outflow once the pH reached 8.45, whereas the field trial efficiency was determined by calculating the total metal mass reduction (derived from the concentration data) from the inflow to the outflow whilst outflow pH and metal concentrations were within ANZECC (2000) guidelines. Treatment capacity was calculated from the total mass of Bauxsol™ within the PRB divided by the volume of water treated to within ANZECC (2000) guidelines for drinking water and/or protection of aquatic ecosystems.

Field Trial

PRB Construction

A 2 m wide, 0.7 m high, and 0.7 m thick (1 m^3) PRB was emplaced within and keyed into the walls and base of the tailings dam drain (Figure 2). The reactive medium comprised 70% well-sorted medium sand and 30% Bauxsol™ and was contained within a wooden frame lined with a geotextile that was rated at a 20 μm pore size. Sand was placed both up and downstream of the barrier to provide mass against the pooled water; 25 mm of crushed basalt was laid over the sand on the downstream side to prevent sand erosion from rainfall or overtopping. Two sampling pipes were placed against the downstream face of the barrier, 0.2 m above the base of the barrier.

ARD was created by siphoning tailings dam water onto an area of actively oxidising sulfidic rocks. This water
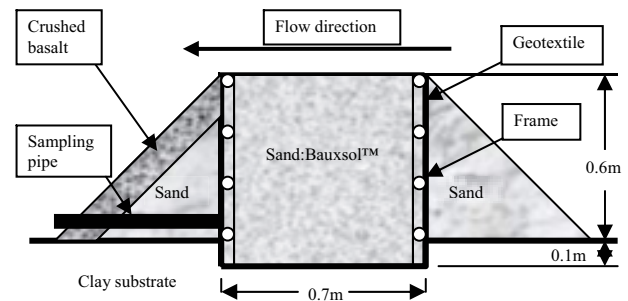

Figure 2. Cross-section of the PRB

then flowed into the tailings dam wall interception drain system. The siphon was approximately 230 m upstream of the PRB (Figure 1) to provide sufficient time for dissolution of acidity and metals from rocks and the drainage system, and was closed during rainfall events.

Sampling and Analysis

The ARD used in the laboratory trials was sampled from the tailings dam wall runoff interception dam (Toe Dam, Figure 1) after a rain event and compared with a second sample after 5 weeks without rain. Three standards and one blank were run prior to analyses of all samples, with each sample subjected to 3-5 replicates, which gave intersample variation of <5%. ARD samples were tested for pH and EC and diluted by 50% (due to high Al and Cu levels), then analysed for Al, Cu, Fe, Mn, Ag, Au, Cd, Cr, Hg, Ni, Pb, Se, Zn, K, Na, Mg, Ca, and As using an Elan 6000 ICP-MS, and cross-checked by ICP-OES for Cu and Se. Due to possible interferences, additional analyses were conducted for Cd, Cu, Pb, Se and Zn, using graphite furnace atomic adsorption (AA) spectroscopy with Zeeman background correction using 5 replicates with an intersample variation of <5%.

These data allowed the streamlining of subsequent sample preparation and analyses to testing only for the suite of metals found to exceed the ANZECC (2000) water quality guidelines (Al, Cu, Fe, Mn, Cd, Pb and Zn), in addition to Ca, Mg, K and Na. Drinking water guidelines presented in this paper are the most stringent values for either health or aesthetics.

Once PRB saturation was achieved (when water flowed from both downstream sampling pipes), two 60 mL samples were taken twice daily from both outflow sampling pipes of the barrier and from the inflow pool. These samples were analysed as indicated above, except that outflow samples were not diluted.

At the completion of the field trial, the PRB was divided into three areas: inflow, middle, and outflow; core samples were taken from the centre of each area.

The cores were divided into four equal vertical zones, dried at 70°C for 24 hours and analysed by a slightly modified version of Australia's Environmental Protection Authority (EPA) Toxicity Characteristic Leaching Procedure (TCLP): Australian Standard (AS) 4439.3 (1999) to determine the extent of metals leached from the spent Bauxsol™ under simulated natural conditions. This test requires tumbling a 2 g sample diluted in 40 mL of acidic solution (pH 2.88) for 18 hours, followed by centrifuging, filtration, digestion and analysis. AS 4439.3 avoids drying the sample drying the sample could promote volatilisation or breakdown of organic contaminants, and/or the stabilisation of labile minerals. Samples were drained and dried because a) ARD was still flowing through the PRB when core samples were taken and; b) spent PRB material is easier to transport and dispose of when dry. Furthermore, the heavy metals investigated in this study and all minerals contained within Bauxsol™ are neither volatile nor thermally unstable at 70°C; consequently, core samples were dried to a constant weight prior to step 1 of the TCLP process.

In addition, to quantify the fraction of trapped metals able to be actively extracted, dried and crushed samples of unused sand/Bauxsol™ and spent core samples were digested in hot aqua-regia (3:1 mixture of concentrated nitric and hydrochloric acid) for one hour. Metal loads of unused media were subtracted from spent media values. These data were then compared to the calculated metal removals from known inflow and outflow metal concentrations and flow rate during the entire sampling PRB period. Both TCLP and digest samples were analysed by ICP-MS for the metals in the ARD, with the addition of As, B, Cr and Mo.

Results

Stage 1: Laboratory trials

Hydraulic conductivity tests

The results of the hydraulic conductivity tests for the range of sand:Bauxsol™ ratios for the ARD and tap water are presented in Figure 3. The 60% Bauxsol™ with tap water and both ARD and tap water with 50% Bauxsol™ were below the optimum working range ($<10^{-5}$m/s) for a constant head permeameter (Fair and Loadwick 2001) and have been omitted. Hydraulic conductivity values for individual columns increased by up 20% during ARD treatment and the variance between individual columns was up to 35%.

Figure 3 shows that sand:Bauxsol™ mixes have higher hydraulic conductivities when treating ARD
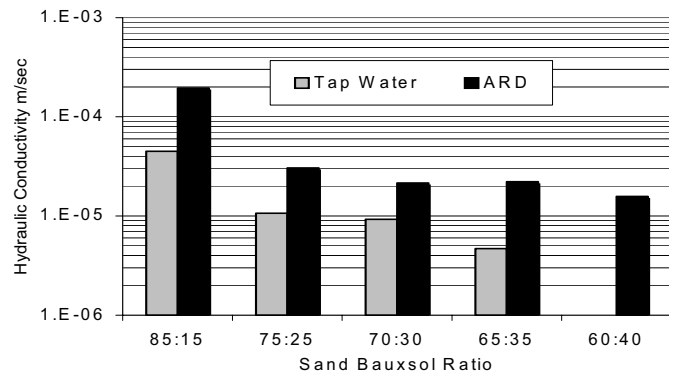

Figure 3. Results of hydraulic conductivity lab trials

than when treating tap water. The outflow from test columns subjected to tap water were observed to remain red, indicative of solution/mobilisation of Bauxsol™, whereas only the first few minutes of outflow was red in the ARD trials.

Results for ARD water from the column tests taken at pH 8.45 of a 75:25 sand:Bauxsol™ ratio are presented in Table 1. Table 1 shows that water quality for the column tests meets all guidelines for ANZECC (2000) drinking waters except for Al; aquatic ecosystem guidelines were not met for Al, Cu, or EC. Ca, K, and to a lesser extent, Mg concentrations increased through the column, whereas Na was virtually unchanged. The hydraulic conductivity (k) for this column was 3.06×10^{-5} m/sec, which gives a calculated water velocity of 4.84×10^{-5} m/s and a residence time of 45 minutes within the active part of the column (130 mm of sand:Bauxsol™).

Based on column test data (Table 1) and the hydraulic conductivity values (Figure 3), a 70:30 sand:Bauxsol™ blend would be used for field trials, which would increase the treatment capacity of and residence time in the PRB, without substantially diminishing the flow rate. However, Bauxsol™ <1 mm was used for field trials because <500μm sieved material was unavailable. Consequently, although this mixture possessed a higher Bauxsol™ content than that analysed in Table 1, permeability was raised to 9.8×10^{-5}m/sec.

Stage 2: PRB field trial

Application of equation 1 to the PRB dimensions gives a maximum flow rate of 6.05 L/min and an average residence time of 2 hr and 20 min; these values were closely reflected in the field trial with a maximum flow rate of ≈6 L/min, demonstrating that experimental hydraulic conductivity test results carried over to field trials. The tailings dam siphon was set at 6 L/min, but provided a flow at the PRB of 4 L/min, indicating a loss of water between the two

Table 1. Column test performance data of a 75:25 sand: Bauxsol™ mix (all metal concentrations in mg/L)

| Parameter | Inflow | Outflow | Removal (%) | ANZECC Guidelines | | | |
				Drinking water	Pass/ fail	Aquatic ecosystems	Pass/fail
Al	20144	366	98.183	200	Fail	27-150	Fail
Cd	2144	0.4	99.981	2	Pass	0.06-0.8	Pass 90%
Cu	31258	12.3	99.961	1000	Pass	1-2.5	Fail
Fe	493	2.6	99.473	300	Pass	No set limit	Pass
Mn	7653	81	98.942	100	Pass	1200-3600	Pass 99%
Pb	133	1	99.248	10	Pass	1-9.4	Pass 99%
Zn	52464	7.8	99.985	3000	Pass	2.4-31	Pass 95%
Ca	24716	88626	-258.5	No set limit	Pass	No set limit	Pass
Mg	188415	192800	-1.028	No set limit	Pass	No set limit	Pass
Na	5274	5275	-	No set limit	Pass	No set limit	Pass
K	3480	5140	-47.701	No set limit	Pass	No set limit	Pass
pH	3.00	8.45	-	6.5-8.5	Pass	6.5-9.0	Pass
EC	3.03 mS	4.13 mS	-	No set limit	Pass	1.5mS	Fail

Table 2. Flow rate, pH, EC and metal concentrations (μg/L) for ARD inflow

	Flow rate	pH	EC (ms)	Al	Cd	Cu	Fe	Mn	Pb	Zn
Maximum	19.2L/min	3.98	2.77	41651	765	27414	4437	9057	63	28109
Minimum	1L/min	3.45	1.64	7079	172	4471	357	2262	4	7029
Average	4.9L/min	3.72	2.12	28073	554	17318	2109	6497	38	20157

flow measuring points. Rainfall events occurred the first night (Day 1-2) and again on Day 4, and, although the siphon was closed during both rainfall events, bypass flow (overtopping) of the barrier occurred. A lag time of >6 hr existed between siphon adjustment and a change in flow at the barrier.

All samples taken upstream of the PRB (inflow) had their lowest metal concentrations during the rainfall events (corresponding with the highest pH, 3.98). The highest metal concentrations were within 24 hours after attaining the minimum flow rate (corresponding with the lowest pH, 3.45). The ranges of values shown for the ARD during sampling are given in Table 2. The decrease in metal concentrations and increase in pH coincides with the rainfall events. Results of all samples taken from the PRB for metal concentrations are presented in Figures 4a and 4b.

Comparison of data from Figures 4a and b shows that all metal concentrations from Days 2 –10 fall within ANZECC (2000) drinking water guidelines ($\approx$ 47,250 L), whereas aquatic ecosystem guidelines (>90%) were met from Days 2 (pm) – 6 ($\approx$ 27,720 L), with Zn limiting further treatment success. Figures 4a and b also show that the PRB rapidly removed all metals at maximum efficiency through Day 4, followed by a steady increase in metal concentrations for Mn, Zn, Pb, and to a lesser extent, Cu, over the remaining 6 days. The data indicates there is a metal loading capacity order of Cu>Pb>Zn>Mn. Conversely, Al, Fe and Cd removal was maintained for the duration of sampling. Results for Ca, Mg, Na, and K are given in Figures 5a and 5b.

Figures 5a and 5b show only minor changes in Mg and Na concentrations through the PRB for the trial, although there appears to be some minor leaching of Na from the PRB material for the first couple of days. Conversely, outflow of Ca concentrations were consistently higher and K was consistently lower than inflow. Maximum K removal coincided with minimum Mn and other metal values (Day 4). When compared with ANZECC (2000) guidelines for aquatic ecosystems, data from Figures 5a and 5b fail to reach accepted values for EC in any samples.

Spent PRB Analyses

Metal Trapping Capacity, Digest Results, and TCLP

Calculated values for total metal loadings trapped, metal removal efficiency and proportion of trapped metals able to be leached by a hot acid digest are given in Table 3, which indicates that the PRB possessed a heavy metal trapping capacity of >90% for all metals, with an average overall efficiency (for the metals investigated) of 98.75%. The metal removal efficiency order is Cu>Al>Cd>Fe>Zn>Pb>Mn, with 25-98% of metals removed able to be leached via hot acid digest. Given the weight of Bauxsol™ within the barrier (1.1 T/m^3 x 0.3 m^3 = 330 kg), the mass loading (metal trapped/weight of Bauxsol™) is >1%. Furthermore, because 47,250 L of ARD were treated to drinking water guidelines, the treatment efficiency of Bauxsol™ within the PRB was 7 g/L. Metal loading increases recorded for each area of the PRB are presented in Figure 6. Figure 6 shows that metal loading increased in all areas of the PRB for all

metals. Zn and Mn display increased loading with barrier penetration. Conversely, Cu and to a lesser extent, Al, Cd, and Pb, display decreasing values with PRB penetration. Surprisingly, Cr appears to be more leachable in the spent Bauxsol, even though no Cr was detected in the ARD.

Results of the modified TCLP analyses (Table 4) shows that all dried samples met the guidelines for disposal as a solid waste, with only Cd preventing the spent barrier material from being classified as inert (EPA limit: 0.1 ppm).
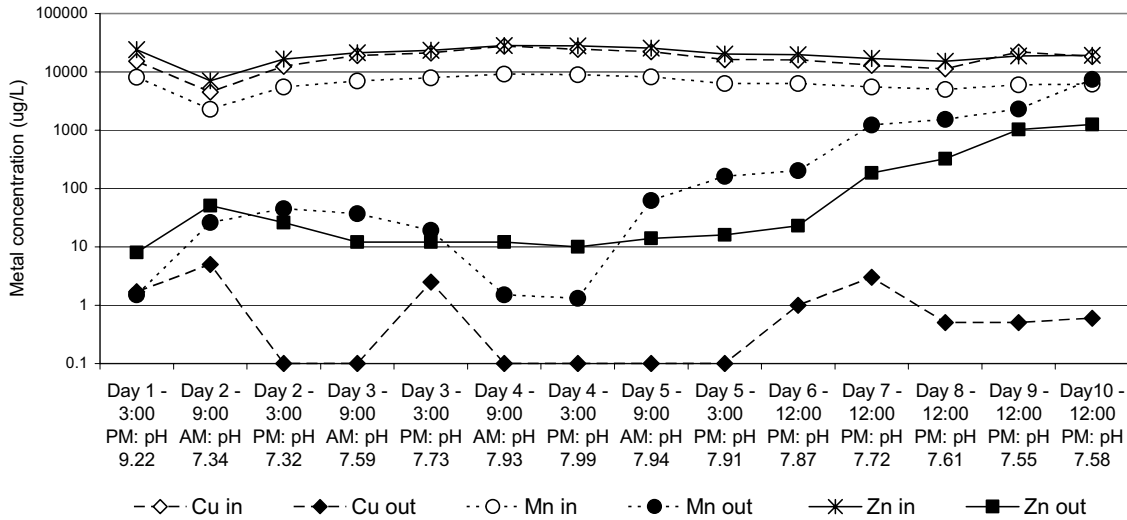

Figure 4a. Cu, Mn, and Zn concentrations for the entire sampling period; values of 0.1 µg/L (ppb) were assigned to analytical results below the working limits of the ICP-MS and/or graphite furnace AA

Figure 4b. Cd, Fe, Al, and Pb concentrations for the entire sampling period; values of 0.1 µg/L (ppb) were assigned to analytical results below the working limits of the ICP-MS and/or graphite furnace AA
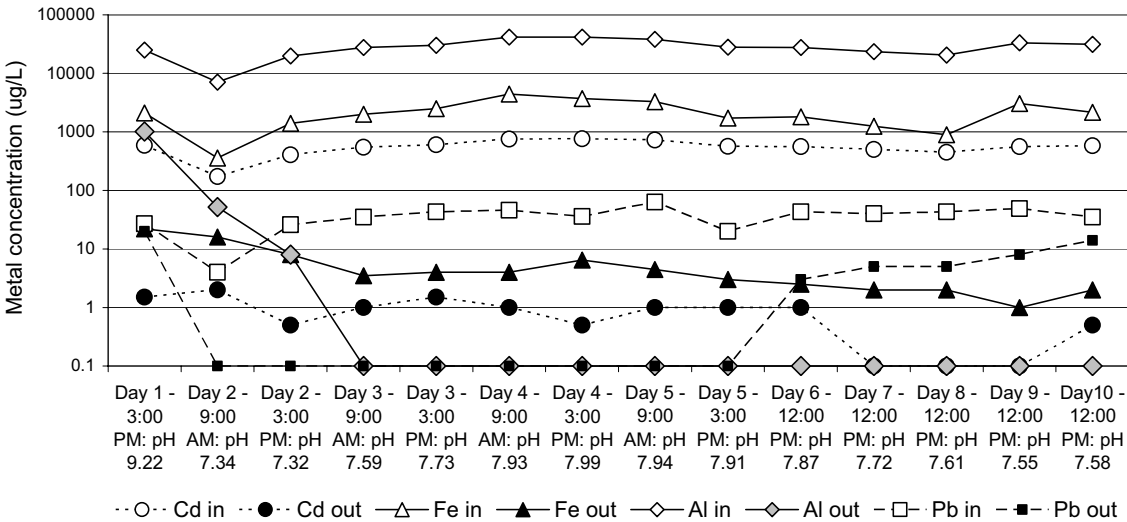
Table 3. Metal trapping capacity and percentage of loaded metal able to be removed via digestion

Metal	Inflow Total (g)	Outflow (g)	Trapped (g)	Removal efficiency	Digestible
Al	1245.32	1.73	1243.59	99.86%	97.46%
Cd	25.18	0.04	25.14	99.84%	66.03%
Cu	782.39	0.05	782.34	>99.99%	60.90%
Fe	86.96	0.26	86.70	99.70%	NA*
Mn	341.78	30.00	311.78	91.22%	25.53%
Pb	1.74	0.15	1.59	91.38%	94.34%
Zn	901.22	10.01	891.21	98.89%	49.46%
Total	3384.59	42.24	**3342.35**	**Average 98.75%**	**Average 35.95%**

*Fe has been omitted as it is a major component of Bauxsol™ and a minor contaminant within the ARD, creating statistical difficulty in accurately determining values.
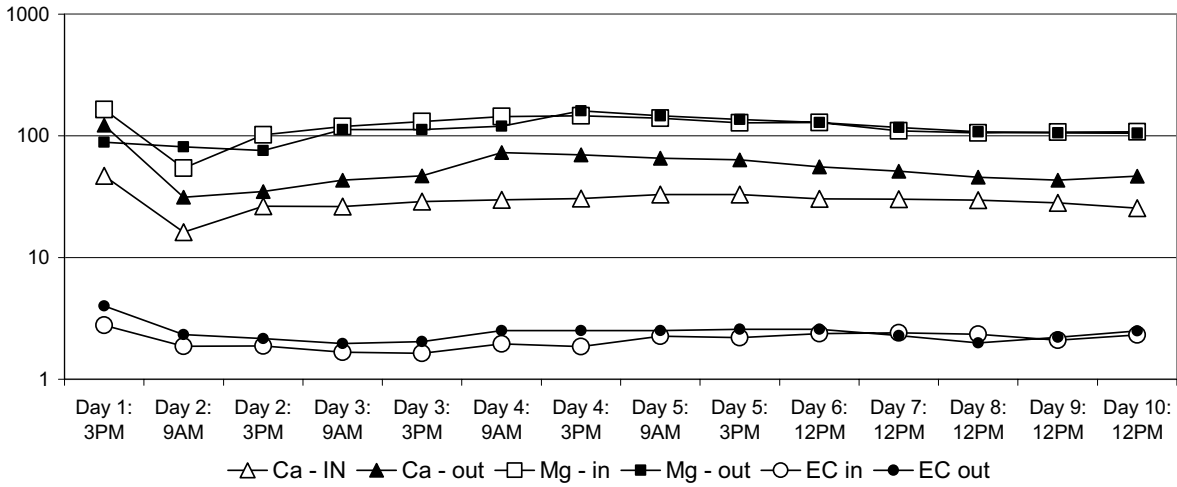
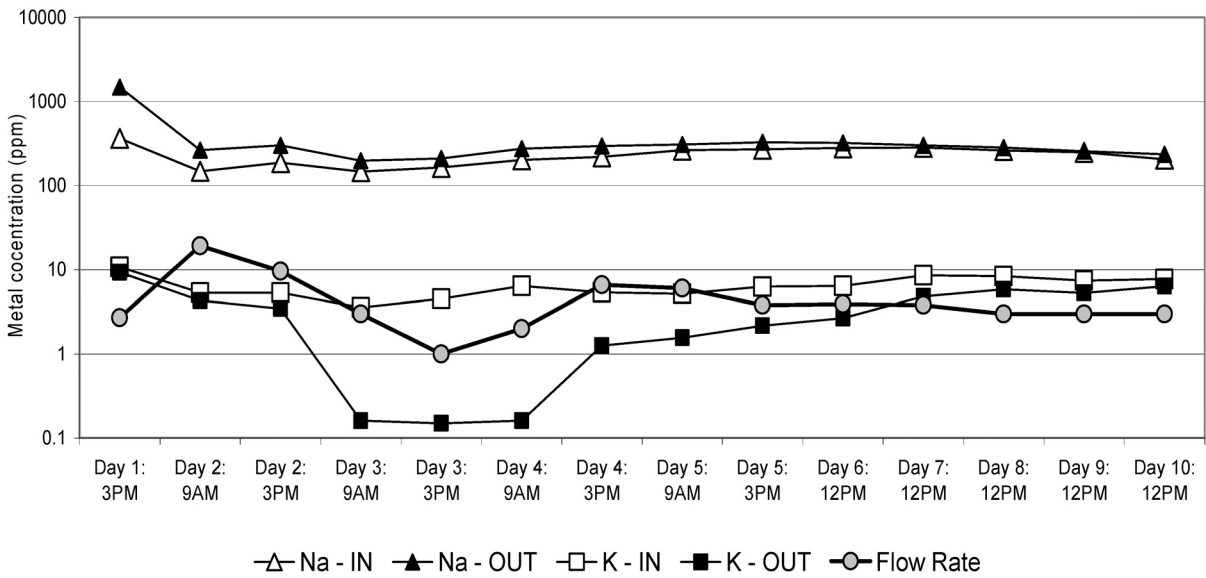**Figure 5a.** Ca and Mg concentrations (mg/L) and EC (mS) for the entire sampling period

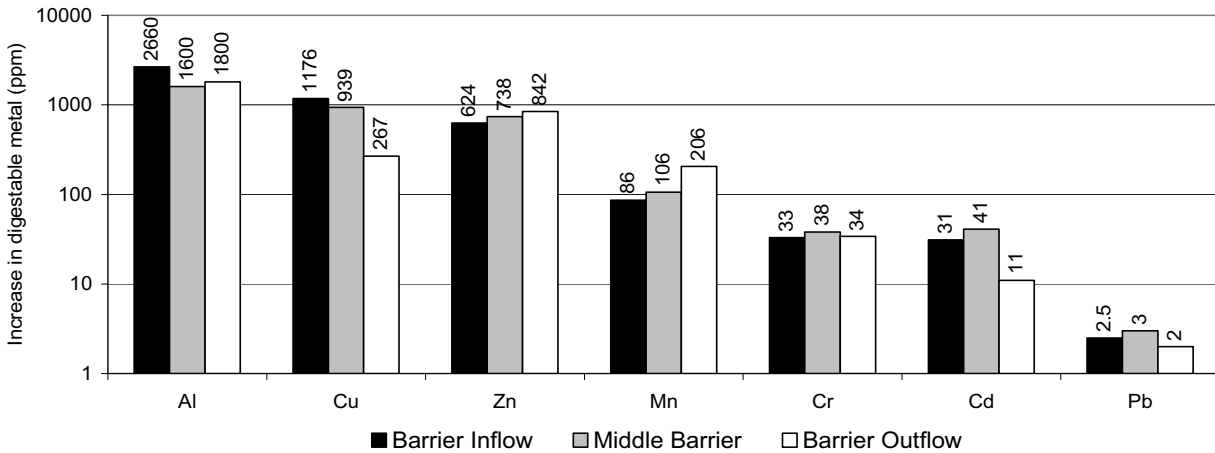**Figure 5b.** Na and K concentrations (mg/L) and flow rate (L/min) for the entire sampling period

Figure 6. Metal loading increases for the three zones of the PRB

Table 4. Results of the modified TCLP procedure compared with the EPA (1999) guidelines for non-liquid waste disposal; Mo and As were not detected in any samples and Cr was only detected in one sample (at 0.01 ppm), so these elements have been omitted.

Metal	Unused Sand / Bauxsol	Barrier Inflow	Middle Barrier	Barrier Outflow	Limit for solid waste	Pass / Fail	Limit for inert waste	Pass / Fail
Al	5.26	67.04	13.77	7.64	No set limit	Pass	No set limit	Pass
Cd	<0.001	0.45	0.72	0.15	1	Pass	0.1	Fail
Cu	0.7	14.75	11.65	2.13	No set limit	Pass	No set limit	Pass
Fe	0.11	5.56	1.04	0.26	No set limit	Pass	No set limit	Pass
Mn	0.03	1.71	2.02	3.73	No set limit	Pass	No set limit	Pass
Pb	<0.001	0.05	0.02	<0.001	5	Pass	05	Pass
Zn	0.1	18.63	20.84	25.08	No set limit	Pass	No set limit	Pass
Ni	0.007	0.038	0.036	0.076	2	Pass	0.2	Pass
B	0.15	0.39	0.35	0.34	No set limit	Pass	No set limit	Pass

Discussion

Hydraulic Conductivity

Mobilisation of fines during laboratory hydraulic conductivity trials may be a result of the low Ca content of the tap water promoting stripping of Ca ions from the Bauxsol™, promoting floc collapse and mobilization of Bauxsol™ fines as new solubility equilibria are established. Consequently, the mobilisation of fines from floc collapse contributes to clogging of pore space pathways and decreased hydraulic conductivity. However, it appears that in the ARD tests, divalent Ca is displaced by ion exchange, as indicated by the elevated Ca concentrations in the column test outflow (Table 1) and PRB field trial effluent waters (Figure 5). Because ARD has high concentrations of divalent and trivalent metals, the Ca can be replaced by these contaminant metals, maintaining the flocculated nature of the Bauxsol™. Consequently, for the ARD, the loss of fines is only observed during the initial wetting stage. The net result of this replacement behaviour is that pore structure remains open and the hydraulic conductivity high. The maintenance of hydraulic conductivity demonstrated by the PRB in the field trial further supports the creation of an open and highly permeable system during ARD treatment.

It is generally accepted that pore spaces will fill during the treatment of ARD in a $CaCO_3$ PRB because metals (especially Al and Fe) and gypsum are precipitated from solution as the pH rises (Eary 1999; Morrison et al. 2002). Where $CaCO_3$ is used to treat ARD by replacement (e.g., anoxic limestone drains), the gypsum precipitated has a lower specific gravity than the calcite (2.3 g/cm^3 for gypsum; 2.7-2.9 g/cm^3 for calcite) (Deer et al. 1985). Consequently, the precipitated gypsum occupies a greater volume than the calcite that it replaces, increasing mineral content volume and narrowing pore spaces within a calcite barrier as treatment continues. However, the

majority of minerals involved in acid neutralisation in Bauxsol™ all have similar specific gravities to gypsum ($\approx$2.1 g/cm^3) (Deer et al. 1985), except for minor quantities of calcite (Clark 2000; McConchie et al. 1999); consequently, there is little or no volume change experienced during the acid neutralisation and precipitation reactions. Hence, pore spaces remain open. Furthermore, as overall metal removal processes are not dominated by amphoteric metal-hydroxide (e.g. $Zn(OH)_2$) precipitation but potentially by crystal growth, as suggested by Clark (2000) and McConchie et al. (2001, 2002), higher density minerals should be created, which would occupy lower volumes for the quantity of metals removed, thereby preserving pore space and hydraulic conductivity. New mineral precipitation and mineral growth supports the greater occlusion of metals from TCLP leaching and acid digestion results (Tables 3 and 4, Figure 6). This hypothesis is significant because, if correct, it indicates that higher Bauxsol™ loadings can be applied within a PRB treating ARD without substantial loss of permeability.

The maintenance of pH >7 at the end of sampling indicates the presence of residual acid neutralisation capacity (ANC). This may have also affected digestion and TCLP results by decreasing the amount of metal remobilisation possible. This would be a favourable property of a spent PRB material because it indicates a resistance to heavy metal remobilisation under acidic conditions.

Water Quality and Metal Removal Processes

ANZECC water quality guidelines for aquatic ecosystems are among the most stringent in the world, which makes it difficult to achieve the highest level of protection in many industrial situations. There is a desire to achieve the minimum trigger values because at those values, no further assessment of the waters is required. However, the trigger values are determined at an alkalinity of 30 mg/L $CaCO_3$

equivalent, while residual alkalinities in treated ARD waters using Bauxsol™ may exceed 60 mg/L $CaCO_3$ equivalent (Clark et al. 2004). Alkalinity strongly influences toxicity (and hence trigger values) for Cd, Cr, Cu, Pb, Ni, and Zn (ANZECC 2000). The performance of the PRB demonstrated that minimum trigger values for aquatic ecosystems were achieved for all metals (except Zn) over certain periods and it appears that Zn removal limited further overall treatment success, despite an average Zn removal for the entire sampling period of 98.89%. This lower-than-desired removal of Zn may be due to a combination of extremely high inflow concentrations and/or competition with other metals for potential removal sites.

The sequence of metal loading limits displayed by the PRB (Cu>Pb>Zn>Mn) follows the increasing pKa of hydration values from Aylward and Findlay (1994) and suggests metal removal processes (for these metals) are controlled by the equilibrium formation of the hydrous metal species (MOH^+). This removal mechanism is further supported by the slight reduction of metal removal after Day 4 seen in Figures 4a and 4b, which coincides with a decrease in the acid neutralising capacity of the PRB. As pH falls, metals such as Mn and Zn fall below their optimum removal conditions and consequently progress through the barrier (Figure 6), indicating that Mn and Zn have more specific adsorption preferences.

The ongoing removal of Al, Fe, and Cd for the duration of sampling may also be partly attributed to maintenance of pH above the pKa of hydration for these species, although the loading preference and capacity orders are not entirely consistent with pKa of hydration values. This inconsistency suggests that metal removal processes other than formation of MOH^+ and removal to the Bauxsol™ surfaces are occurring, which may include direct absorption and/or co-precipitation (Clark 2000).

The incremental metal removal and increased loadings of Mn and Zn with increased PRB penetration suggest that chromatography theory may apply as an overall model for solid/water interactions, i.e. solutes are removed from the liquid to solid phase by a number of theoretical plates: the greater the number of plates, the more efficient the system. However, removal processes in chromatography analyses are intended to be reversible, whereas data presented in Tables 3 and 4 and Figure 6 indicate a very strong partitioning of metals from the mobile to solid phase, highly resistant to remobilisation, even for the most weakly bound metals. Furthermore, it is difficult to apply a single theory or defining mechanism for Bauxsol™ because it is composed of a complex suite of minerals (which possess different metal removal processes and capacities) and consequently, metal removal processes are not consistent or uniform. Furthermore, within complex mineral systems, there are no distinct borders between adsorption, precipitation and co-precipitation reactions (Allard et al 1986). However, if pKa values are a controlling factor, it is expected that the progression and accumulation of Zn and Mn in the downstream area of the PRB would soon be followed by Pb and Cu.

The higher levels of Cr extracted from spent Bauxsol™ than unused Bauxsol™ (Figure 6) further suggests that Cr is contained in minerals that are only subject to acid attack under low buffering conditions, i.e., when the vast majority of the Bauxsol™ acid neutralising capacity is consumed.

Direct addition of Bauxsol™ to standing water bodies has been shown to achieve a maximum treatment over several weeks or even months (Clark 2000; Virotec 2000). However, data from this study indicates that the removal of metals and adjustment of pH are achieved more rapidly by passing ARD through a permeable Bauxsol™ media, although an increased residence time may be necessary to promote a more complete removal of Mn, Pb, and Zn.

Salts and EC

The near-constant concentrations of Na and Mg through the column tests (Table 1) and PRB (Figure 5) indicates that these metals are conservative within the system: i.e. they are not involved in metal removal processes and are not effectively trapped by the system. However, there appears to be some release of Na from the Bauxsol™ (Figure 5a), which diminishes with time, suggesting that some residual Na is present from the Bauxsol™ manufacturing process and can be readily overcome by rinsing the Bauxsol™ prior to use.

Conversely, the increase in Ca in the discharge waters during sampling indicates that Ca is actively liberated from Bauxsol™ during metal removal and/or acid neutralizing processes. Clark (2000) and McConchie et al. (1999, 2000) suggest that much of the acid neutralising capacity of Bauxsol™ extends from complex Ca and Mg alumino-hydroxycarbonates. In addition, the increased Ca in outflow samples may also contribute to the minor increase in EC shown for most of the sampling regime (Figure 5a). However, K concentrations were reduced over the period of the sampling, especially when the maximum removal of metals occurred on Day 4 (Figures 4a and b). This maximum removal most likely indicates an interaction between K, sulphate, and Al to form

alunite, which is a documented control on Al concentrations in ARD waters (Eary 1999). Although Fe is present in the ARD and there is the possibility that jarosite may also potentially play a role in the removal of K, it is more commonly ferrihydrite that controls Fe concentrations in ARD at low pH, and little K would be removed (Eary 1999). Consequently, K concentrations are more likely controlled by alunite precipitation than jarosite formation.

Influent Parameters and PRB Design

The loss of flow from the siphon to the PRB is attributed to infiltration into the drain sediments/substrate, and is a consequence of poor drainage system design and choice of drain-lining materials. The decrease in metal concentrations coinciding with the rainfall events indicates dilution of the ARD (Figure 4). However, maintenance of low pH during the rainfall events suggests that there may also be a flushing of acidity from the surfaces of rocks undergoing sulphide oxidation. These fluctuations in flow, pH, and metal concentrations highlight the fact that PRB designers (particularly for above-ground PRBs or permeable treatment dams) consider all flow and contaminant loading variations to insure adequate treatment. This can be achieved by increasing either the thickness, or the Bauxsol™ content of the lower section of the PRB profile. This would in effect give an increased residence time or variable permeability to the PRB and allow maintenance of treatment throughout contaminant concentration and flow fluctuations. If these design principles were reapplied to the field trial, it is highly likely that Mn removal could have been maintained for a much longer period, and that the increased residence time would have reduced Zn concentrations, possibly achieving the ANZECC (2000) trigger values.

Summary and Conclusions

During this study, over 45,000 L of poor quality ARD was treated to ANZECC (2000) drinking water guidelines by a 1 m^3 above-ground PRB containing 30% Bauxsol™ with a grain size <1 mm and 70% medium, well-sorted sand. The water treatment quality was improved by increased ARD residence time. Treatment efficiency of the reactive media within the PRB was approximately 7 g Bauxsol™/L, indicating that Bauxsol™ is well-suited as a PRB medium to treat ARD.

Bauxsol™ blended with well-sorted medium sand maintained a high hydraulic conductivity during ARD treatment, suggesting that acid neutralising dissolution is commensurate with the formation of new Al and Fe

minerals. Consequently, these data indicate that a Bauxsol™ PRB is able to avoid clogging, which is a common problem associated with many other PRBs, particularly those solely reliant on carbonates or hydroxides for acid neutralisation.

Metal removal processes within the barrier appear to be controlled by the formation of MOH$^+$, particularly for Mn, Zn, Pb, and Cu, although the data suggests that other mechanisms may also be active in the removal of Al, Fe and Cd. Because of the complex nature of Bauxsol™ mineralogy and their potential metal removal processes, the metal removal efficiency ranged from >99.99% for Cu to 91.22% for Mn, with a removal order of Cu>Al>Cd>Fe>Zn>Pb>Mn. A modified TCLP analysis of the spent Bauxsol™ material indicates that metals are retained in forms that resist leaching. Furthermore, acid digest data indicate that only 25-98% of the metals removed are able to be acid-mobilised. However, residual acid neutralising components of the spent Bauxsol™ may be a contributing factor to limited metal remobilisation; therefore, further investigation is required to determine long term disposal stability of the spent material.

References

Allard B, Hakansson K and Karlsson S (1986) The importance of sorption phenomena in relation to trace element speciation and mobility. In: Landner L (Ed), Lecture Notes in Earth Sciences; Speciation of Metals in Water, Sediment and Soil Systems, Springer-Verlag

ANZECC (2000) Australian Water Quality Guidelines for Fresh and Marine Waters. Australia and New Zealand Environment and Conservation Council, Canberra, Australia

Apak R (1995) Sorptive removal of Cesium-137 and Sr-90 from water by unconventional sorbents, 1: usage of bauxite wastes (red muds). J of Nuclear Science and Technology 32: 1008-1017

Appelo CAJ, Postma D (1994) Geochemistry, Groundwater and Pollution. AA Balkema, Rotterdam

Aylward GH, Findlay T (1994) SI Chemical Data. John Wiley and Sons, Hong Kong

Clark MW (2000) Geochemical Cycling of Heavy Metals in Brisbane River Estuary Dredge Sediments During Sub-aerial Disposal, and the Consolidation at

the Port of Brisbane Authority's Fisherman Islands Reclamation Paddocks. PhD Thesis, Southern Cross Univ, NSW

Clark MW, Walsh SJ, Smith J (2001) The distribution of trace-heavy metals in an abandoned mining area; a case study of Strauss Pit, the Drake mining area, Australia: implications for the environmental management of mine sites. Environ Geology and Water Science 40: 655-663

Clark MW, McConchie D, Caldicott W, Davies-McConchie F, Castro J (2004) Bauxsol™ technology to treat acid and metals; applications in the coal industry. In: Barnhisel RI (ed), Proc, 21st Annual National Conf American Soc of Mining Reclamation, Morgantown, West Virginia, pp 293-321

Collins M (1994) A Study of Heavy Metal Leachate in the Plumbago Creek Catchment, Northeastern NSW. Honours Thesis, Southern Cross Univ, NSW

Deer WA, Howie RA, Zussman J (1985) An Introduction to the Rock Forming Minerals. Longman, Hong Kong

Dept of Mineral Resources (1999) 200 Years of Mining – Gold Minfact, 81 pp

Eary LE (1999) Geochemical and equilibrium trends in mine pit lakes. Applied Geochem 14: 963-988

Environmental Protection Authority (1999) Assessment, Classification and Management of Liquid and Non-liquid Wastes. Environmental Protection Authority, Sydney

Evangelou VP (1995) Pyrite Oxidation and its Control. CRC Press

Fair EJ, Loadwick F (2001) Geomechanics, Study Book 1. Faculty of Engineering and Surveying, Univ of Southern Queensland

Houston MJ (1993) The geology and mineralisation of the Drake mine area, northern NSW, Australia. Proc, New England Oregon Conf (NEO '93), Dept of Geology and Geophysics, Univ of New England, Armidale

Kelly MG (1999) Effects of heavy metals on the aquatic biota. In: Plumlee GS, Logsdon MT (eds), The environmental geochemistry of mineral deposits, part A: processes, techniques and health issues, Reviews in Economic Geology 6A, pp363-371

Lin C, Maddocks G, Bateman E, Clark M, McConchie D (2002) Acidity and major acidic cations in surface soils of a sulfidic mine site, Australia: implications for mine site rehabilitation. Environ Sciences 10 (3): 165-173

Maddocks G (2000) Soluble and Readily Extractable Copper, Cadmium, Lead and Zinc Concentrations in the Surface Soil Horizon of Sawpit Gully, Drake, NSW, Australia. Integrated Project, Southern Cross Univ, NSW

McConchie D, Clark MW, Hanahan C (1998) The use of seawater neutralised red mud from bauxite refineries to control acid mine drainage and heavy metal leachate. Geological Soc of Australia Abstracts, No 49, Townsville, p 298

McConchie D, Clark M, Hanahan C, Fawkes R (1999) The use of seawater neutralised bauxite refinery residues (red mud) in environmental remediation programs. Proc, Global Symp on Recycling, Waste Treatment and Clean Technology, San Sebastian, Spain, Vol 1, pp 391-400

McConchie D, Clark MW, Fawkes R, Hanahan C, Davies-McConchie F (2000) The use of seawater-neutralised bauxite refinery residues in the management of acid sulphate soils, sulphidic mine tailings and acid mine drainage. Proc, 3rd Queensland Environment Conf, Brisbane, Australia, pp 201-208

Morrison SJ, Naftz DL, Davis JA and Fuller CC 2002. Introduction to groundwater remediation of metals, radionuclide and nutrients with permeable reactive barriers. Handbook of Groundwater Remediation Using Permeable Reactive Barriers; Applications to Radionuclides, Trace Metals and Nutrients, Academic Press

Naftz DL, Morrison SJ, Davis JA, Fuller CC (Eds) (2002) Handbook of Groundwater Remediation Using Permeable Reactive Barriers; Applications to Radionuclides, Trace Metals and Nutrients. Academic Press

National Academy of Sciences (1994) Alternatives for groundwater cleanup. National Acad of Science, Committee on Groundwater Cleanup Alternatives, Washington, D.C., National Academy Press

Puls RW (1998) Permeable reactive barrier research at the National Risk Management Research Laboratory, U.S. Environmental Protection Agency. Evaluation of Demonstrated Emerging Technologies for the Treatment of Contaminated and Groundwater (Phase III): Special Session; Treatment Walls and Permeable Reactive Barriers. North Atlantic Treaty Organisation/Committee on the Challenges of Modern Society

Scheiber E (1998) Geology of New South Wales – Synthesis. In: Basden H (ed), Vol 2 Geological evolution. Dept of Mineral Resources

Summers RN, Guise NR, Smirk DD, Summers KJ (1996) Bauxite residue (red mud) improves pasture

growth on sandy soils in western Australia. Australian J of Soil Research 34: 569-581

Terill J (1992) Notes for field visit – Drake Mining Area, NSW. CRA Exploration Pty Ltd

U.S. EPA (United States Environmental Protection Agency) (1998) Permeable Reactive Barrier Technologies for Contaminant Remediation. EPA/600/R-98/125, Washington, DC

Virotec (2000) Bauxsol Studies: Mount Carrington Tailings Dam Treatment. Virotec International, Australia

Ward SC, Summers RN (1993) Modifying sandy soils with the fine residue from bauxite refining to retain phosphorus and increase plant yield. Fertiliser Research 36: 151-156

Zouboulis AI, Kydros KA (1993) Use of red mud for toxic metals removal – the case of nickel. J of Chemical Technology and Biotechnology 58: 95-101