Technical Article

Efficiency of Bauxsol™ in Permeable Reactive Barriers to Treat Acid Rock Drainage

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Abstract. Permeable reactive barriers (PRBs) and flow-through reaction cells are fairly new passive treatment alternatives to conventional lime treatment of acidic rock drainage (ARD). They are ideal for the treatment of flowing ARD and are particularly useful when contaminants are likely to persist for several years. This paper describes column tests performed to simulate a PRB constructed using Bauxsol™, a chemically and physically treated bauxite refinery residue, as a reactive material. This experimentation shows promising results for the Bauxsol™ PRB method in neutralizing pH and removing metals from acidic mine effluents.

Key words: Acid rock drainage; Bauxsol™; permeable reactive barriers

Introduction

Mining activities generate a large amount of solid waste and when the deposits containing sulphidic ore, reactions with water and air can lead to chemical and microbial oxidation of sulphides. This commonly results in the generation of acid rock drainage (ARD), with high concentrations of sulphate and metals and a pH below 4. Similar processes operate where sulphides are exposed by natural processes, or in road cuts, or other engineering operations. Poor quality ARD water can be transported by both surface runoff and groundwater flow and can be harmful to both terrestrial and aquatic ecosystems. ARD from abandoned mines, tailings impoundments, and waste rock piles is a global environmental and economic problem with estimated treatment costs of tens of billions of dollars (Benner, Blowes et al. 1999). In Canada alone, there are about 12,000 ha of mine tailings that contain acid-generating material (Itzkovitch and Feasby 1993).

Active treatments, such as pump and treat techniques, are widely used in an attempt to control ARD but their operational costs are very high and they produce huge volumes of potentially hazardous unstable sludge that creates a disposal problem. Moreover, because ARD generation can persist for many years, costs can continue to accumulate long after a mining operation or other revenue generating activities have ceased and budgeting for operational closure becomes almost impossible. Hence, the popularity of passive treatments has increased rapidly, because they are typically more cost-effective than conventional treatments (Bienvenu 2003; Walton-Day 2003) and because they require minimal maintenance.

One of the passive techniques involves permeable reactive barriers (PRBs), which consist of a reactive material placed below the surface in the plume path of the contaminated groundwater or positioned to treat surface water without impeding the flow. Effluent passes through the PRB in response to the natural gradient and treated water emerges, as shown in Figure 1.

Considerable research has been carried out on PRBs, with different materials (zero-valent iron, organic material, clinoptilolite, etc.) being used to treat a large variety of contaminants (AMD, chromium, arsenic, petroleum, ammonium, e.g. Shokes and Mõller 1999; Blowes et al. 2000; Su and Puls 2001; Ahn JS et al. 2002; Park et al. 2002).

Sustainable development promotes the use of one waste to treat another waste. Virotec International developed Bauxsol™ by treating red mud (a residue from alumina production) with seawater, or other magnesium- and calcium-rich brines, or magnesium and calcium chloride salts, or some combination of these materials, to transform it into a near-neutral material that can be used to treat AMD (McConchie et al. 2003). Several studies have demonstrated that red
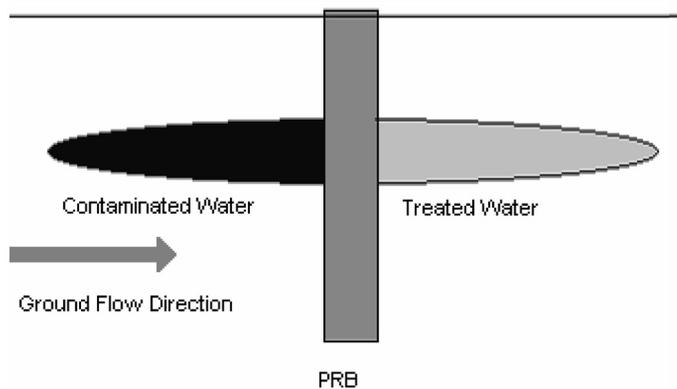
Figure 1. Principle of a permeable reactive barrier (Park et al. 2002)

mud can fix metals and increase the pH of effluents (Lopez et al. 1996; Lamontagne 2001; Doye and Duchesne 2002), but also showed that this residue is not permeable enough to be used directly for a PRB; there can also be problems with an initial caustic discharge at start-up.

This paper describes the behaviour of PRBs that use Bauxsol[TM] as a reactive material. To simulate PRBs, several mixtures were leached in Plexiglas columns with acid effluent from the Doyon Mine in Val d'Or, Canada. The experiments described in this paper are a continuation of previous work (Lapointe et al. 2005) when tests were carried out in columns filled with different mixes of Bauxsol[TM] and river sand. During those tests, there were clogging problems that reduced the lixiviation capacity of the columns. Those problems were caused by the high iron concentration of the mine effluent used (around 2500-3000 mg/L) when the rapid increase in the pH caused the precipitation of large volumes of iron and aluminium oxyhydroxides that blocked the columns (Figure 2).

The objectives of the experiments described in this paper were to test the effectiveness of Bauxsol[TM] for treating ARD and to prevent clogging of the columns. First, a reactive mixture with more interstitial space was used to accommodate the iron and aluminium oxyhydroxides precipitates. Second, we pretreated the effluents with a mixture of alkaline materials (Bauxsol[TM], lime, magnesium oxide) to precipitate some of the iron and aluminium before introducing the effluents into the column.

Virotec International provided the pellets of Bauxsol[TM], which have a high porosity and permeability (Figure 3), a compressive strength of about 8.2 MPa, a high slake durability and a very low solubility in an acidic environment (Lin et al. 2002). The particle size was determined by sieving between 3.8 and 2000 µm (Figure 4). The alkalinity of Bauxsol[TM], 0.3 $CaCO_3$ eq/g,

was determined by potentiometric titration, using ASTM method D1067-02. The composition of Bauxsol[TM] before pelletisation averages about 32.3% iron oxides and oxyhydroxides, 18.2% hydrated alumina, 17.5% sodalite, 7.1% quartz, 6.6% cancrinite, 5% TiO_2, 4.6% Ca(Al) hydroxides and hydroxycarbonates, 3.9% Mg(Al) hydroxides and hydroxycarbonates, 2.3% calcium carbonates (and others 2.5%) (Lapointe et al. 2005).

The acidic effluent, used for the lixiviation of our columns, provided by the Doyon mine in Quebec, has a strong orange color and a light sulphurous odour; Table 1 presents its principal chemical characteristics.

Methods

Experiments were performed in five 130 cm high, 7.5 cm diameter Plexiglas columns with 10 sampling ports each (Figure 5). Material was packed about 100 cm high between two layers of industrial quartz to avoid dispersion. The effluent was pumped in at the bottom of the column by a multi-speed pump. Ten
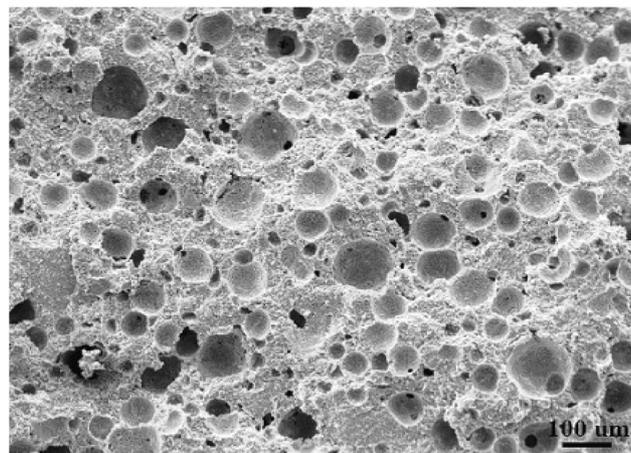
Figure 3. SEM picture of a Bauxsol[TM] pellet (McConchie 2003)
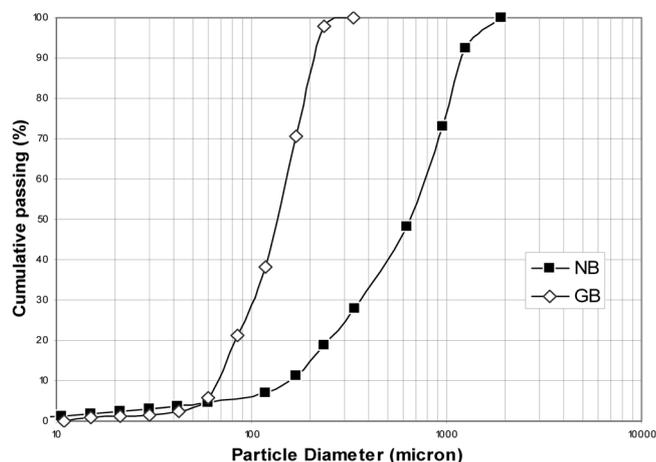
Figure 4: Particle size distribution of the raw (NB) and ground (GB) Bauxsol[TM] pellets used

Figure 2. Reactive mixture after clogging

Table 1. Characteristics of the acidic effluent used during experiments

pH	≈ 2
Acidity	16 500 meq/CaCO$_3$
Conductivity	198 mSiemens
Fe	8560 mg/L
Cu	31.2 mg/L
Ni	5.1 mg/L
Zn	5.3 mg/L
Pb	1.1 mg/L
SO$_4^{2-}$	46 211 mg/L
F$^-$	123 mg/L

sampling ports were installed on each column at distances of 2, 7, 13, 18, 24, 32, 42, 56, 71, and 87 cm above the base and sealed to the column wall; a glass syringe was inserted to each port to allow sampling. A total of 80 L of effluent was leached through each column over a three month period.

Mine waste effluents from the Doyon Mine in Val d'Or were used to simulate contaminated groundwater flow. These effluents have a pH of 2.1 and contain high concentrations of heavy metals. We chose these effluents in order to test a "worst case scenario" for the clean up of contaminated plumes at mine sites. The Doyon mine spends a considerable amount of money every year for the neutralisation of these effluents and this will continue for at least another 30 to 40 years (i.e. well beyond the expected mine life).

Five columns were tested, each containing Bauxsol^{TM} and an additional material in various proportions. The additional materials used were crushed granitic stone (3/4 in. mean size) (C1), wood chips (C2), chopped straw (C3), synthetic sponge (C4) and quartz (C5). Their quantities and volume ratios are shown in Table 2. The role of these additional materials was to ensure a homogeneous matrix and avoid blockage or development of preferential flow paths of simulated contaminated groundwater flow. Furthermore, they increased the void volume available for the precipitation of iron and aluminium oxyhydroxides, which previously caused clogging of the columns (Lapointe et al 2005). Layers of sand were placed above and below the reactive medium in the columns to ensure good flow distribution.

Effluent fed into column C5 was pretreated to remove some of the iron; the effluent was treated in a large container until the pH had increased to about 4.5 and then it was pumped into the column. The treating mix contained magnesium oxide (MgO), Bauxsol^{TM} powder, and hydrated lime (Ca(OH)$_2$). The mix had an alkalinity of 0.9 CaCO$_3$ eq and 10 g could treat 1 L
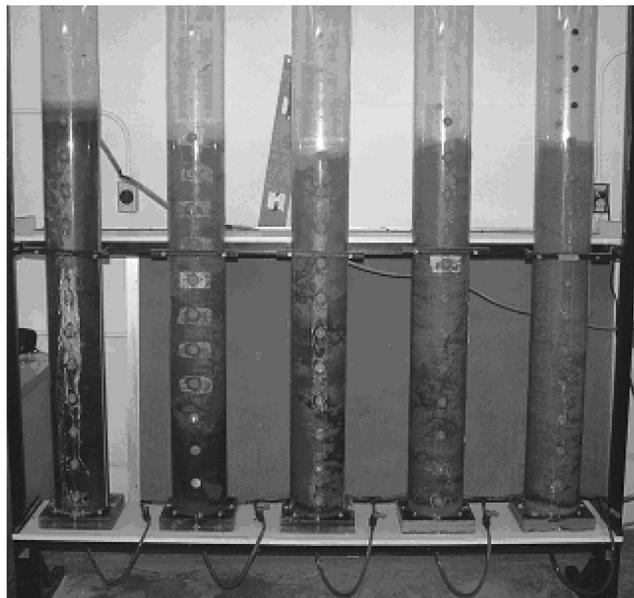
Figure 5. Set up of experimental columns

Table 2. Composition of columns

Columns packing	Bauxsol^{TM} (kg)	Proportions (v/v) (Bauxsol^{TM} / packing material)
C1-Crushed stone	4.32	1:3
C2-Wood chips	4.89	1:3
C3-Chopped straw	4.35	1:3
C4-Sponge	4.45	1:3
C5-Quartz	3.34	1:4

of the acidic effluent, which should require an alkalinity of 1.65 CaCO$_3$ equivalents (from Table 1) but less added alkalinity is required because some acidity is stored as hydroxysulfate minerals and by adsorption in the solid residues; hence, a lower alkalinity is required than theoretically expected. Proportions of each component are shown in Table 3. The objective of the pre-treatment was to investigate the role of a PRB as a final polishing step before the effluent is released into the environment.

The five columns were leached twice a week at a flow rate between 10 and 20 mL/min for three hours. Leaching tests were discontinuous in order to better represent likely field conditions. The pH and Fe, Zn, Ni, Cu, and Pb concentrations in the outgoing leachate were determined weekly for the first month, then every 15-20 days for the next three months, using a Perkin Elmer 3110 atomic absorption spectrophotometer. The mineralogy and composition of the reactive material in

Table 3. Composition of the pre-treatment solution

Component	% (volume)	Weight ratio
MgO	50	5
Bauxsol^{TM}	35	5
Ca(OH)$_2$	15	1

the columns were characterized before and after leaching by X-ray diffraction with a Siemens D5000 diffractometer using Cu radiation (40kV/30ma), SEM using a JEOL 840-with an EDS Tracor-Northern detector, and neutron activation using a Slowpoke reactor to irradiate the sample and two GEM-20180P co-axial detectors, with a resolution between 1.8 keV and 1332 keV.

Results and Discussion

Metal Removal

Columns C1, C2, C3, and C4

The evolution of metal concentrations and pH in outgoing leachate from columns C1, C2, C3, and C4 is shown in Figure 6. Table 4 presents the average metal removal efficiency for each column.

At the beginning of the test, Bauxsol™ demonstrated a strong alkalinity for 15-20 days, until the material reached equilibrium. The amount of Bauxsol™ in columns C1, C3, and C4 was similar and presented a similar efficiency in removing metals. Column C2, which had comparable quantities of Bauxsol™, presented a higher removal rate than the three others because it was filled with crushed Bauxsol™. This suggests that not all the Bauxsol™ in the other columns had time to react due to the coarser particle size and/or the partial isolation of metal ions from Bauxsol™ particle surfaces by precipitated iron hydroxides. Hence, as a result of the particle size, columns C1, C3, and C4 may have been overdriven with respect to flow rates. If the flow rate through the columns had been reduced but continued for a longer time during each leaching test, both the output pH and the metal removal efficiency would probably have been much higher.
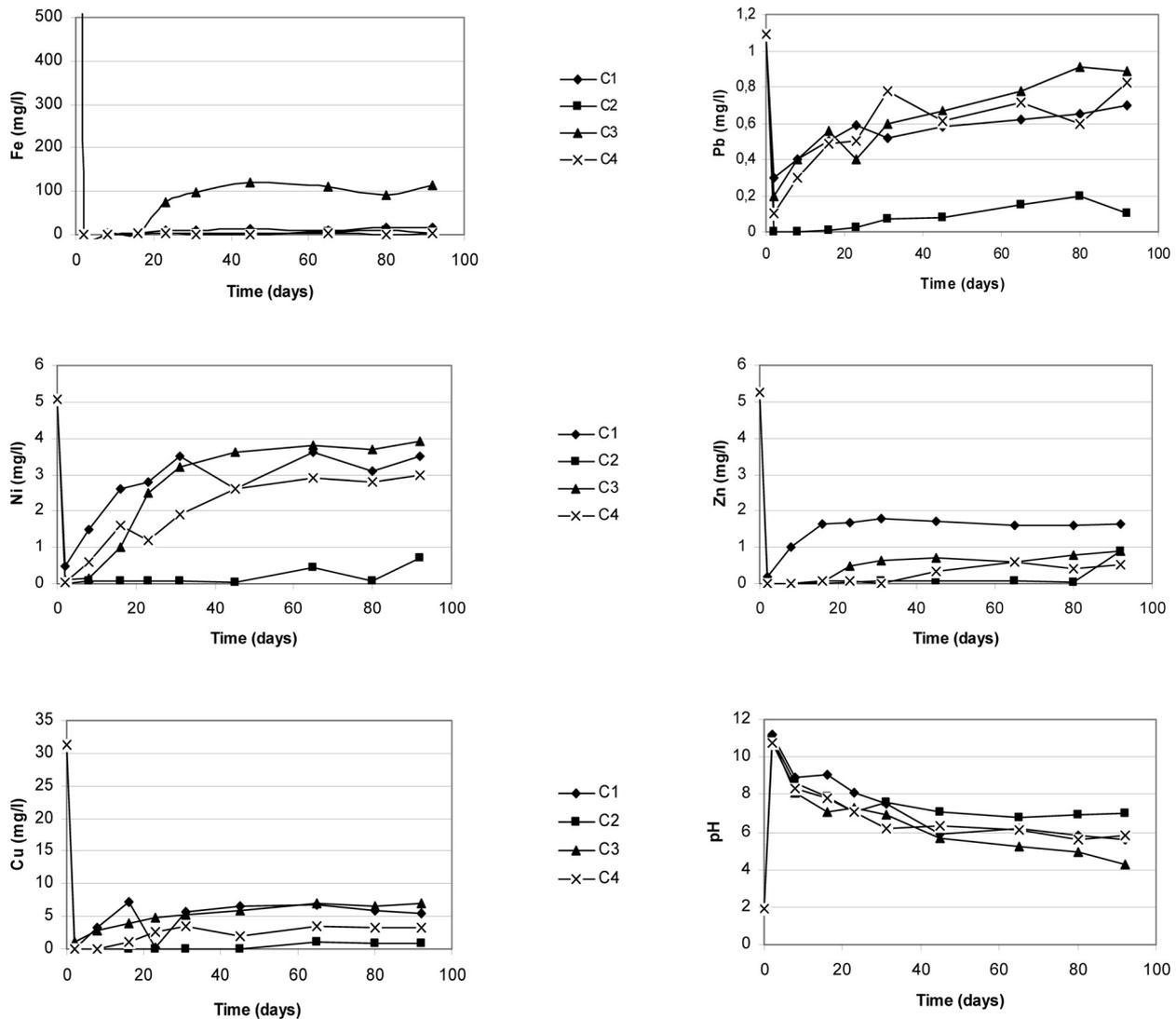
Figure 6. Evolution of pH and Fe, Cu, Pb, Zn, Ni concentrations in the leachates of columns C1, C2, C3, and C4 over 90 days

Table 4. Average metal removal efficiency of the columns (%)

	C1	C2	C3	C4	C5
Fe	99.9	99.9	98.8	99.9	99
Cu	37	95	32	53	99
Zn	68	96	87	94	99
Ni	37	95	52	53	99
Pb	44	91	35	38	99

A comparable study of a PRB constructed (Munro et al. 2004) using very fine-grained Bauxsol™ (>90% of the material <10 μm) showed a similar efficiency to trap metals to that of C2. It also appears that MOH^+ (M is a metal cation), which largely depends on the pH, dominates the removal of Cu, Pb, Zn, and Mn. Thus, the key to treating ARD with a Bauxsol™-based PRB is to get the pH between 7.5 and 8.5. Bauxsol™ can take more than 48 hours to provide its full potential of alkalinity (McConchie et al. 1996); there are three ways to achieve this: a smaller particle size, more reactive material, or a lower flow rate.

Column C5 and pre-treatment

The pre-treatment caused a rapid pH increase to 4.5, but the general process was delayed by the decantation time (around 1.5 hours). The supernatant was easily recovered and pumped into the column for leaching. The pre-treatment was very efficient in removing metals (85 to 90% for Fe, 70-75% for Zn, 72-75% fir Ni, 93-97% for Cu, and 45-50% for Pb). Overall, the combination of the pre-treatment and the C5 column treatment removed more than 99% of each metal, and the final pH was between 6.5 and 7.5.

This procedure is similar to pump-and-treat techniques widely used in the mining sector, but it could be more economical. First, because effluents from the pre-treatment procedure have lower quality requirements than effluents treated by conventional methods, pre-treatment requires less neutralizing material. Second, the use of Bauxsol™ powder reduces the amount of limestone (or other sources of alkalinity) required to treat the effluent compared to conventional treatment and pre-treatment produces much less solid waste, which reduces costs. Finally, to get the same metal removal efficiency using hydrated lime alone, the pH would usually need to be raised to 7.5 - 8.0 for copper, almost 9 for zinc and nickel, and about 10 for manganese (Eary 1999), and at pH values above 9 there is a significant risk of releasing previously immobile arsenic and other oxyanions. The data from this study show that Bauxsol™ increased the metal binding capacities of conventional limestone treatment and lowered the pH at which metals such as Cd, Cu, Mn, Ni and Zn were precipitated by 1 - 1.5 pH units thereby allowing the final treated effluent pH to be kept to about 8.5 or a bit less. Consequently, a Bauxsol™ based PRB could provide a cost effective polishing step for mine effluents.

Material Characterisation

To get a better idea of the geochemical reactions occurring during the experiments, comparative neutron activation data for fresh (unreacted) Bauxsol™ (NB) and ARD-reacted Bauxsol™ are shown in Figure 7. The material from these tests came from Column C1. The outer crust (mainly formed by precipitation) on the ARD-reacted Bauxsol™ pellets (CB) and the inner core (mainly reflecting absorption processes) of the ARD-reacted Bauxsol™ pellets (LB) were characterized separately.

Iron concentrations were very high in our ARD test water, and iron was found in both CB and LB. However, considering that there was no crust before leaching, the contribution of iron from the effluent is much higher in CB (precipitation) than in LB (absorption). Thus, as a result of the rapid increase in the pH, iron mainly precipitated outside the pellet.

The As, Ni, and Cr concentrations in the LB (absorption) are much higher than in the NB. Consequently, metal retention occurred principally inside the pellets. These metals were also present, albeit in lower concentrations, in CB. This might be explained by the sample preparation for the neutron activation tests, because it was impossible to get only the crust of the pellets, thus the samples were probably slightly contaminated by material from LB. There may also have been some co-precipitation of these elements with the iron oxy-hydroxides that precipitated to form the crust.

Overall, 38 metals were analyzed, and most of these had a similar pattern to that for As, Ni and Cr, except for Ca and Zn. As expected, the concentration of Ca in CB or LB was lower than in NB because reactions between carbonate or hydroxycarbonate minerals in the Bauxsol™ and acid in the ARD water released some calcium that could be leached out. The concentration of Zn was similar in NB, CB, and LB, indicating that most Zn precipitated with the newly formed outer crust and was not absorbed inside the pellets.

The XRD pattern of NB shows boehmite (AlOOH), aluminite ($Al_2(SO_4)(OH)_4 \cdot 7(H_2O)$), calcite ($CaCO_3$), quartz ($SiO_2$), gypsum ($CaSO_4$), and hematite ($Fe_2O_3$). On the CB, XRD mainly shows hematite (Fe_2O_3) and gypsum ($CaSO_4$), confirming that iron reacted on the outside of the pellets. Finally, the XRD analysis of LB
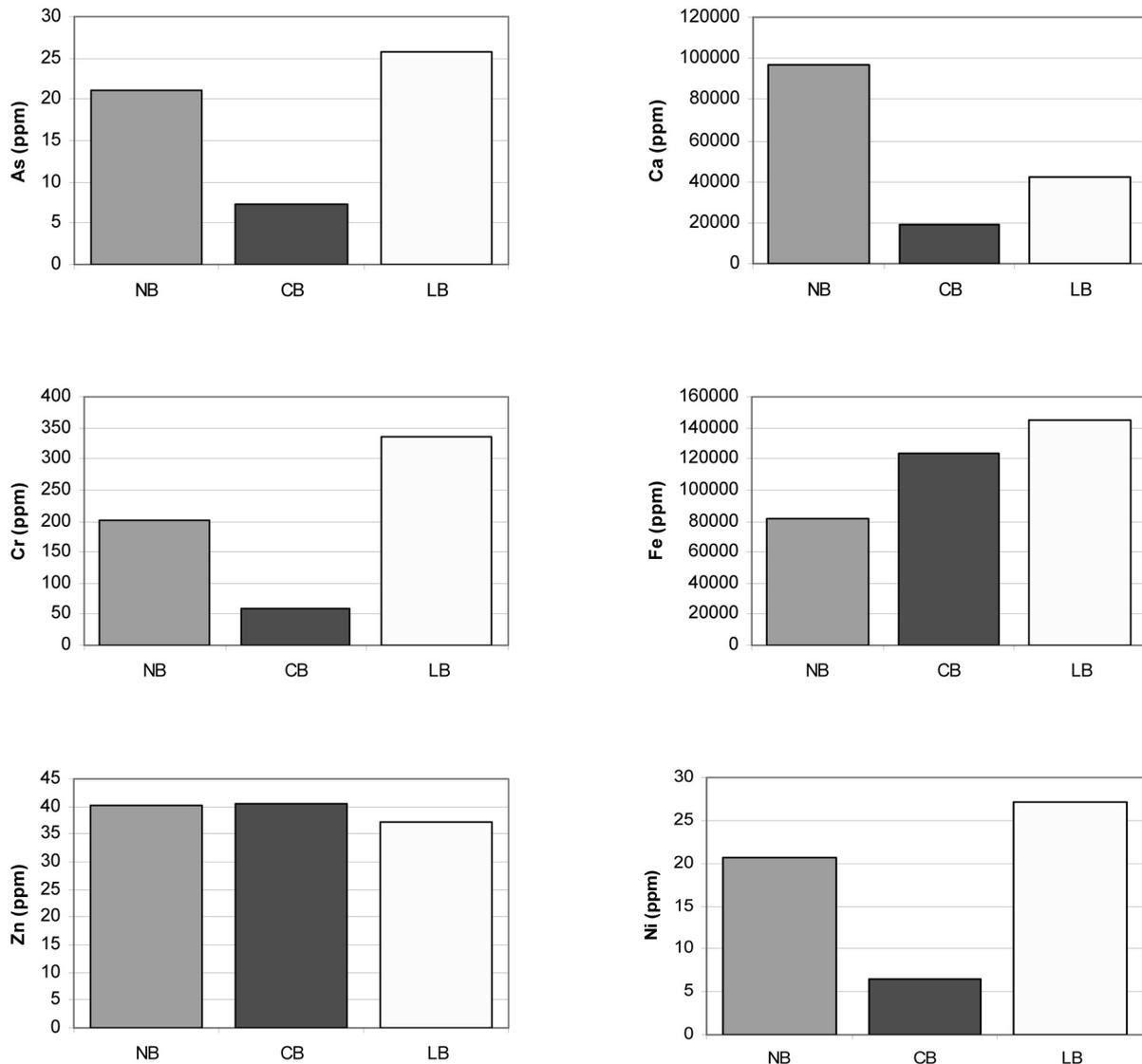
Figure 7. Concentrations of As, Ca, Cr, Fe, Ni and Zn for Bauxsol^{TM} (NB), crust formed on leached Bauxsol^{TM} pellets (CB), and the inner core of leached Bauxsol^{TM} pellets (LB)

shows a similar pattern as for NB. Calcite was still present in LB as the second main crystalline phase, indicating that carbonates were in a form that leaches slowly. Hence, Bauxsol™ could efficiently increase the pH of effluents for a long time.

Iron Oxide Trapping Capacities

All reactive mixes efficiently avoided the clogging problem noted previously (Lapointe et al. 2005). Nevertheless, in column C1, some iron precipitate was washed out of the column with the effluent. Therefore, to be efficient, the column material must present a lot of interstitial space and fine pores in order to act like a filter and to accommodate neoformational precipitates. In addition, it must be

inert in an acidic environment and inexpensive. These findings suggest that, in large commercial applications, crushed pumice (1 – 10 mm particle size) or similar highly porous materials could be an excellent additive to maintain high void volumes. Finally, the pre-treatment used in column C5 removed 85-95% of the iron; the remaining amount of iron was not enough to block the columns.

Conclusion

An experimental method was developed in a previous study to simulate permeable reactive barriers using Bauxsol^{TM} as a reactive material. Here, five different mixes were evaluated to treat acid rock drainage. The objective was to increase pH, remove metals and

avoid the clogging of the columns previously caused by iron oxyhydroxide precipitation. The results showed that the Bauxsol™ used in the columns with the various packing materials resisted clogging over a longer period of time than the Bauxsol™ used in previous experiments. Moreover, columns C1, C3, and C4 had a similar efficiency in removing metals. Column C2 (containing a similar quantity of Bauxsol™) presented a higher removal rate than the three others since the crushed Bauxsol™ had more reactive surface area.

The results of the tests also show that PRBs using Bauxsol™ have the potential to treat acidic effluents and remove metals over a long period of time; most metals are trapped in the cores of pellets and are likely to be very difficult to remove by conventional leaching reagents (e.g. using the TCLP test). However, due to slow reaction kinetics, the ratio of reactive mixture to acidic effluent would have to be increased to attain the full potential of the treatment. Future work should consider both long-term tests and large scale in situ applications of Bauxsol™ in a PRB. Estimation of the required PRB thickness and void volume in the PRB should be also carried out in order to meet the environmental standards for mine effluents. In the future, it may be desirable to develop design criteria for both Bauxsol™ – based PRBs and for PRBs constructed using other reactive media that specify the void volume in the PRB required to accommodate the Fe and Al oxyhydroxide precipitates that could form from the effluent being treated. The same applies for the flow path length in the PRB required to provide sufficient residence time for complete reaction and the cross-sectional area of the PRB perpendicular to the flow direction required to handle the applicable flow rates.

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Erratum

On page 192 of the last issue, 24(4), there were question marks where there should have been deltas in Figure 4 of the article by Dr. Klein and Dr. Neufeld. The authors and editors apologize if this caused any confusion.