Environmental Behaviour of Sulphate-Reducing Passive Bioreactor Mixture

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Abstract
Acid mine drainage (AMD) passive treatment systems are probably the most adapted solution to reclaim closed mines because of their low investment and maintenance costs. In this study, a sulphate-reducing passive bioreactor (SRPB) was used to treat a typical AMD from an abandoned hard rock mine. Results showed good neutralization (pH close to 6 at the effluent) and good removal for Al, Cd, Cr, Ni, Pb, Zn (more than 90%). However, SRPB efficiency was time limited. SRPB mixtures storage after dismantling and their eventual environmental behaviour are scarcely discussed in the literature. In this article, SRPB mixture stability, after one year of AMD treatment in a column test, was investigated using four different tests. First, sequential extraction procedure (SEP) was performed to fractionate metal precipitates. Then, weathering cells with drying-wetting cycles were realized at different pH. The third test simulated underwater SRPB mixture storage, without water movement (in batch conditions). Finally, the mixture was stored in a water-saturated column with a continuous water flow at near neutral pH. Results from each test are presented and analysed in this article with an emphasis on the long term environmental stability of the mixture for the different storage conditions.

Key Words: Acid mine drainage, passive treatment, sulphate-reducing passive bioreactor, metal stability.

Introduction
Several approaches are available to treat mine drainage in order to meet environmental standards. The most appropriate treatment technology is no universal but site-dependent because of differences in flow and quality of each AMD stream (Aubertin et al., 2002). For mines in operation, active treatment is the most common approach. However, in the case of mines at the end of their operational period, operators tend to move towards the use of passive treatment (Johnson and Halberg, 2005). In principle, passive treatment systems (including sulphate-reducing passive bioreactor, SRPB) are energy efficient, use natural or waste materials and involve low investment costs compared to active plants (Neculita et al., 2007). They are based on natural processes, either chemical or biological or both, without continuous reagent addition.

The SRPB relies on anaerobic bacteria, including sulphate-reducing bacteria (SRB), which degrade a carbon source (from organic waste materials) and lead to reduction of sulphates into sulphides. Metals could then precipitate as low-soluble sulphide minerals. However, several other mechanisms of metal removal also occur in SRPB, such as sorption, carbonate and oxihydroxides precipitation, etc. (Neculita et al., 2007). In the case of iron-dominated AMD, SRPB performance is usually limited (Neculita, 2008; Potvin, 2009; Genty, 2011). When SRPB efficiency does not meet regulatory criteria on water discharge anymore, the replacement of the reactive mixture and its storage are required; storage should prevent metal remobilisation. However, SRPB mixtures contain metals removed under different stable or unstable phases, making its safe storage challenging. To our knowledge, there are only very few recent studies on long term environmental behaviour of spent reactive mixtures after SRPB dismantling.

This article focuses on metal speciation (fractionation) in a SRPB mixture and its relative stability under different storage conditions. The samples of SRPB mixture used in the present study were collected from a laboratory column study, which is briefly described in the section titled preliminary results.

Preliminary Results

These results were summarized from Genty (2011) and are presented to better understand the origin and the characteristics of the mixture tested for its environmental behaviour.

SRPB mixture

The mixture composition (%, dry weight) used in the SRPB column to treat iron-dominated AMD (see Table 1) is given in Table 2. This mixture contained organic waste (chicken manure and vegetable compost), cellulosic waste (maple sawdust and wood chips), a SRB inoculum (river sediments), a neutralizing agent (fine calcite), an inert structural agent (sand), and a nitrogen source (urea). The relative proportion of different types of materials previously was selected to insure appropriate hydraulic parameters and long-term efficiency of SRPB (Cocos, 2002; Neculita, 2008; Potvin, 2009).

Table 1. AMD composition (mg/L, except pH)

Elements	AMD
Al	7
Cd	0.5
Cr	1
Fe	4000
Mg	10
Mn	33
Ni	2
Pb	0.5
SO_4^{2-}	9000
Zn	40
pH	3

Table 2. SRPB mixture composition

SRPB mixture	Proportion %
Celullosic wastes	
Maple chips	5
Sawdust	10
Organic wastes	
Chicken manure	5
Compost	10
Inoculum	
Sediment	8
Inert structural agent	
Sand	10
Nutriment (Nitrogen)	
Urea	2
Neutralizing agent	
Calcite fine	50

AMD treatment with SRPB column

Iron-dominated AMD was treated for one year in duplicate Plexiglas columns (14 cm diameter and 70 cm height). Noteworthy, the AMD had very high concentrations of iron (approximately 4000 mg/L) and sulphate (approximately 9000 mg/L) (see Table 1). Column was fed under upward continuous flow using a peristaltic pump to insure a hydraulic retention time (HRT) between 5 and 7 days. The pH, redox potential (Eh), sulphate, acidity, alkalinity and metal concentrations were monitored weekly during the experiment. A statistical analysis indicated that the treatment results were repeatable (Genty et al., 2011). In this study, unless mentioned differently, only average values of all parameters are used.

Water quality results

SRPB successfully increased the pH from 2.8 in AMD to 6.5 at the exit of the column, while a relatively high acidity (1500 mg/L $CaCO_3$) characterized the effluent, apparently due to the high iron concentrations (see Figure 1). In addition, the Eh decreased from 555 mV to approximately 23 mV in the SRPB effluent. Optimal redox conditions for sulphates reduction (-100 mV approximately, Neculita et al., 2008) were not reached in these reactors.

Efficient metal removal was found for Al, Cd, Cr, Ni, Pb, and Zn (71%-99%) (see Figure 2); the final concentrations met Canadian regulation criteria on water discharge. However, Fe and Mn removal were less efficient, with values of 30% and of 21%, respectively. A high Fe/Mn ratio and the thermodynamic advantage of Fe could partially explain the dissolution of Mn precipitates, which probably formed after the start-up of SRPB (Edwards et al., 2009).

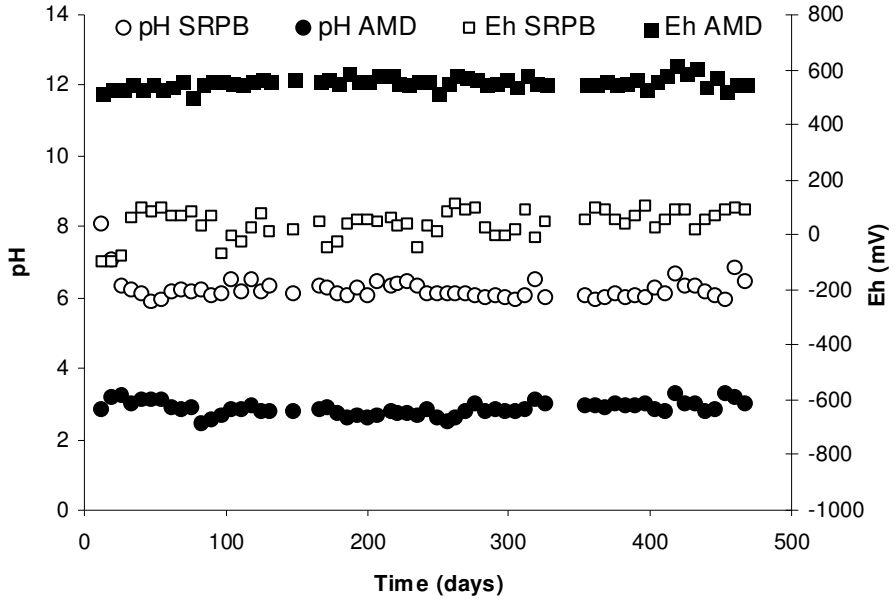

Figure 1. pH and Eh (mV) before and after SRPB treatment

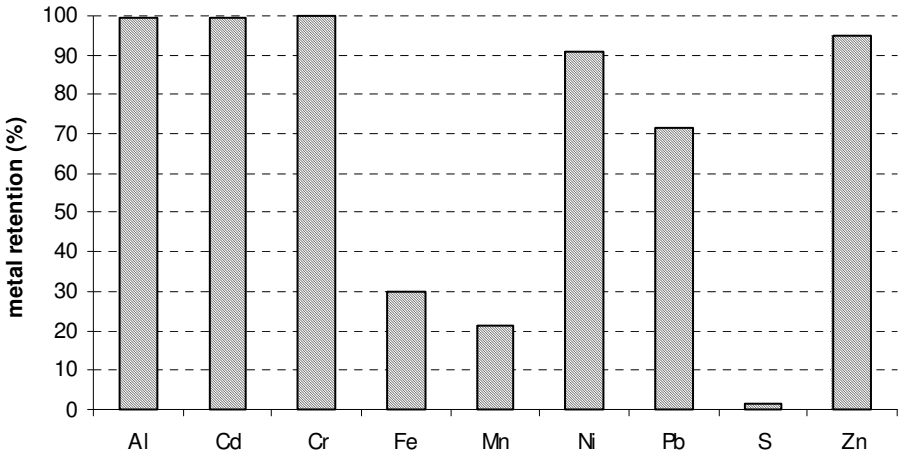

Figure 2. Metal retention in SRPB (% on average)

At the end of tests, after one year of treatment, the long-term stability of SRPB mixture, which contained metal precipitates under different forms precipitates, was investigated in order to find the appropriate storage conditions.

Materials and Methods

Operational Speciation

Samples were collected at middle of the SRPB columns (35 cm from the top). Metal fractionation was evaluated using a 5-step sequential extraction procedure (SEP, Zagury et al., 1997). The five fractions described below were extracted from 1 g of wet solid sample:

- Fraction 1: Soluble and exchangeable metals (extracted with 8 mL $MgCl_2$ 0.5 M, pH 7, 1 h at room temperature)
- Fraction 2: Carbonate bound (leached by 8 mL NaOAc 1 M buffered with HOAc, pH 5, 5 h at room temperature)
- Fraction 3: Reducible or bound to Fe–Mn oxides (extracted with 20 mL NH_2OH-HCl 0.04 M in 25% (v/v) HOAc, 6 h at 96°C)
- Fraction 4: Oxidisable or bound to organic matter (released by 3 mL HNO_3, 5 mL H_2O_2 30% at pH 2, 2 h at 85°C, then 3 mL H_2O_2 30% pH 2, 3 h at 85°C, and 5 mL NH_4OAc 3.2 M in 20% (v/v) HNO3, 0.5 h at room temperature). Then, the solution was diluted to 20 mL.
- Fraction 5: Residual metal fraction (dissolved by acid attack with HNO_3, HF, and HCl).

Weathering cells

Dry SRPB mixture (67g) was packed in three weathering cells (see Figure 3) as per Plante (2010). Metal leaching from SRPB mixture was simulated at different pH values (7.1, 2.6 and 0.8 on average) using deionised water and sulphuric acid (0.02N and 0.1N). Every day 50 mL were added to the cells for one week, whereas the last addition was carried out after another one week. Noteworthy, the solid dried partially or totally under ambient conditions between each two leaching. The leachate from each weathering cell was collected and analyzed for pH and metal concentrations.

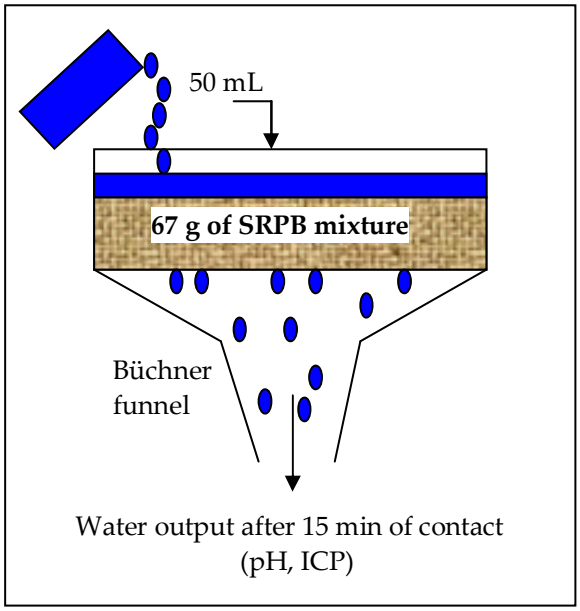

Figure 3. Weathering cell (modified from Plante, 2010)

Batch storage test

Dry SRPB mixture (200 g) was packed in a 500 mL beaker, to which 250 mL of deionised water was added. The pH and metal concentrations of the supernatant were measured after 1, 2, 4, 7, 14, and 21 days of contact.

Column storage test

Column test was performed to simulate mixture storage under water with a low flow rate. Dry SRPB mixture (863 g) was packed in a 4,14L Plexiglas column (14 cm diameter and 26.9 cm length) provided at the bottom side with a perforated plate and a geotextile (see Figure 4). The sample thickness was approximately 7.5 cm and the volume of 3.16 L. To prevent particle floating, 2 cm of sand were added at the top of the column. Up-flow movement of water in the mixture was simulated using deionised water (pH of 7; 18 MΩ.cm) and a peristaltic pump at a rate of 0.6 mL/min for the first 50 days and at a rate of 0.4 mL/min for the next 50 days.

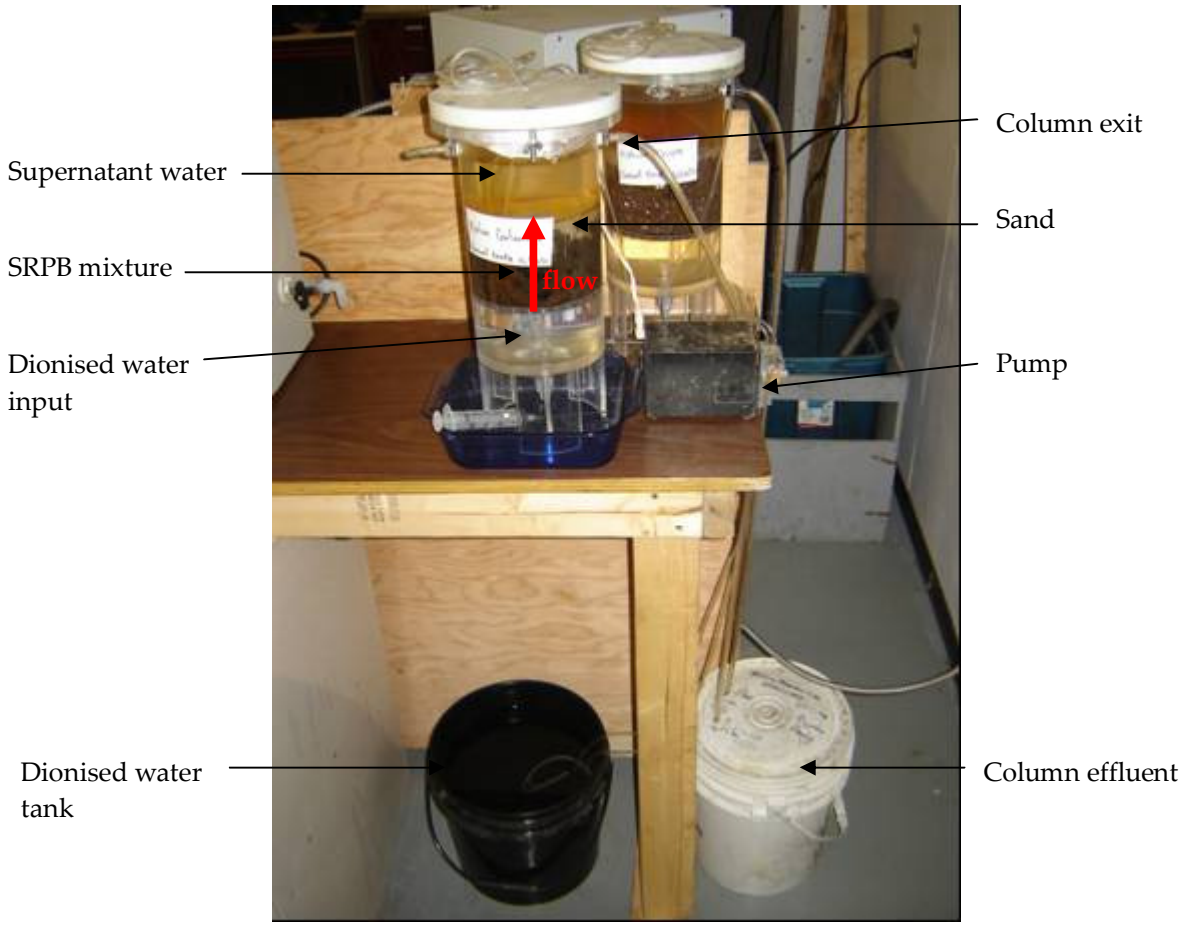

Figure 4. Column storage set-up

Supernatant quality was evaluated based on parameters such as pH, Eh, conductivity, metal content, acidity and alkalinity that were measured every week for a period of 100 days.

To evaluate metal release during the storage under oxidizing conditions, digestion of SRPB mixture using a mixture of acids (HNO_3, HF, and HCl) was carried out before and after column storage test followed by the determination of metal concentrations on filtered samples (0.45 µm filter).

Water analysis

Standard methods were used for the analyses of all parameters. The pH was determined with an Orion Triode sensor coupled with a Benchtop pH/ISE Meter Orion model 920 (relative precision +/- 0.01 pH) and Eh (values were corrected relative to the standard hydrogen electrode) was measured by a Pt/Ag/AgCl

sensor link to a Benchtop pH/ISE Meter Orion 920 (relative precision +/- 0.1 mV). Ionic conductivity was measured with an OAKION Con 6 Accor series. Alkalinity was determined by titration on non-filtered sample with sulphuric acid 0.02N (relative precision of 1 mg $CaCO_3$/L) and acidity by titration with sodium hydroxide 0.1N (precision of 1 mg $CaCO_3$/L) (APHA, 1995). Filtered samples used to quantify metal content were acidified with 2% volume with concentrated nitric acid before analysis with a Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES) using a Perkin Elmer OPTIMA 3100 RL (relative precision of 5%).

Results and Interpretations

Metal fractionation

The SEP allowed the separation of metals present in mobile forms, such as soluble and exchangeable (fraction 1), possible to mobilize forms, such as the carbonates-bound (fraction 2), the reducible or bound to Fe–Mn oxides (fraction 3), the oxidisable or bound to organic matter (fraction 4) and stable forms, such as the residual part (fraction 5). Results of metal fractionation are summarized in Figure 5.

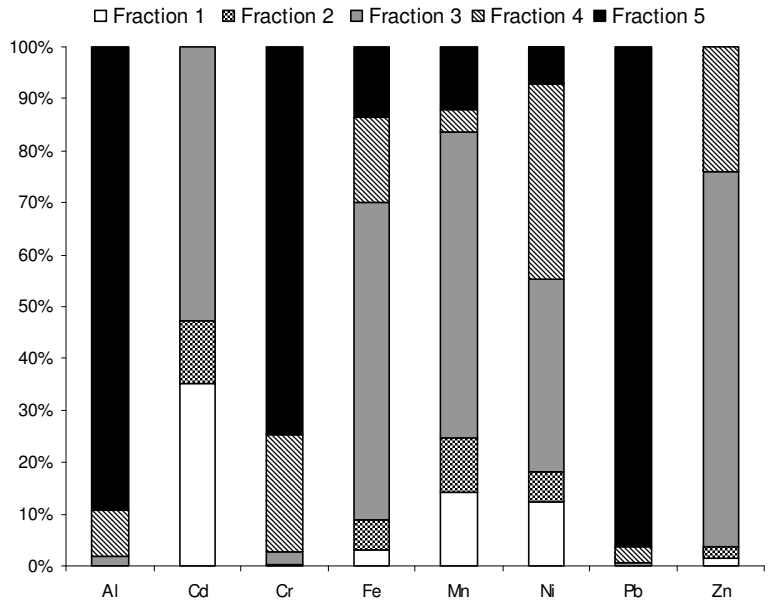

Figure 5. Metal fractionation in SRPB mixture

Among metals, Cr, Al and Pb were mainly present under the most stable forms with residual fraction of 75%, 89%, and 96%, respectively. This is an indication about a possible lower leaching of these metals during long-term storage of spent SRPB mixture. The other important forms of Al, Cr and Pb were the oxidisable or bound to organic matter fraction and the reducible or bound to Fe-Mn oxides-hydroxides (between 1% and 23%), whereas the fractions bound to carbonate or soluble and exchangeable were negligible.

On the contrary, a non-negligible part of Cd (35%), Mn (14%) and Ni (12%) was in soluble and exchangeable forms. In addition, Cd, Fe, Mn, Ni and Zn could be potentially mobilized under different pH-Eh conditions. In general, Cd, Fe, Mn, Ni and Zn showed similar behavior, with the main proportion in the reducible or bound to Fe-Mn oxides-hydroxides fraction (between 37% and 70%). This is an indication about these metals being relatively stable under oxidizing conditions, even at low pH. The second highest fraction of Cd, Fe, Mn, Ni and Zn was the oxidisable or bound to organic matter (with

values ranging from 5% for Mn to 37% for Ni), whereas the carbonate-bound (fraction 2) and residual (fraction 5) fractions were the lowest (varied between 0% for Cd and 13% for Fe).
Based on these results, storage of spend reactive mixture should be performed with precaution in non-acidic (pH close to 7) and strong oxidising conditions to avoid metal resolubilization (especially for Cd, Fe, Mn, Ni and Zn).

Weathering cells

The concentrations of Fe and S in collected leachates are showed in Figure 6, while Table 3 presents the other parameters. Firstly, iron concentrations decreased in the beginning (between the first and the second leaching) probably due to leaching of the soluble and exchangeable fraction. Similar behavior was found whatever the pH of the leaching solution (7, 2.6 or 0.8). Secondly, the lower is the pH of leaching solution the higher is the metal concentration in the leachate. The concentrations of Fe averaged values of 0.14 mg/L, 3.28 mg/L and 24.9 mg/L when initial pH was 7, 2.6 and 0.8, respectively. These results translate in a 250 times higher Fe concentration at pH 0.8 relative to pH 7. Moreover, The SRPB mixture could partially neutralize the acidity of the leaching solution by the residual calcite in its composition (increased of pH from 2.6 to 3.6 and from 0.8 to 2.5 on average). However, the contact time between the mixture and the leaching solution was not long enough to allow the total neutralization of acidity.

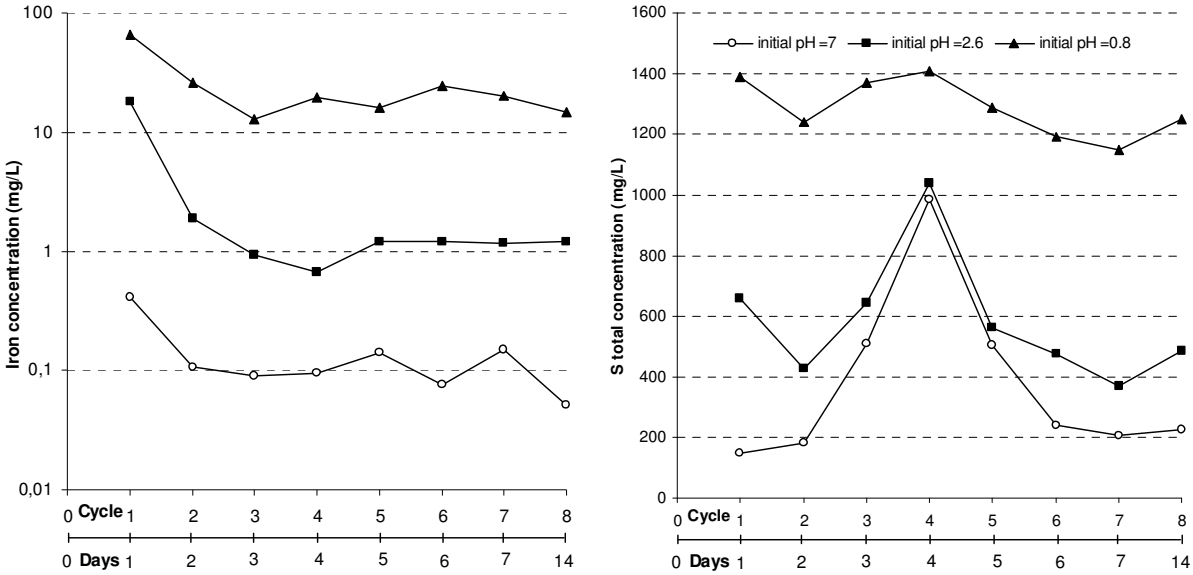

Figure 6. Fe and S concentrations (mg/L) in water of each leachate

Table 3. Average pH and metal concentration (mg/L) after leaching

Initial pH	Final pH	Al	Cd	Cr	Fe	Mn	Ni	Pb	S total	Zn
7.0	7.0	0.008	0.004	0.003	0.14	0.38	0.11	0.013	374.9	0.12
2.6	3.6	0.10	0.06	0.002	3.28	1.67	0.8	0.013	583.3	3.3
0.8	2.5	1.45	0.37	0.01	24.9	5.2	4.8	0.05	1286.3	27.2

In addition, metal concentrations at initial pH of 7 were relatively low, whereas S concentrations (representative of sulphate concentration) were high. Sulphate could result from the oxidation of unstable sulphides between each two leachings. This test clearly shows that SRPB mixture should not be in contact with acidic solution if one wants to avoid metals leaching from the mixture.

Batch storage test

Figure 7 shows the evolution of pH and metal concentrations in supernatant during the bath storage of SRPB mixture. The pH was relatively stable at values around 6.3. However, some metals were soluble such as Fe, Mn, Ni, Pb, Zn, as well as sulphate (quantified as S in ICP analysis). The concentrations of Ni and Zn were relatively stable, with values of approximately 0.1 and 0.063 mg/L, respectively (see Table 4), whereas Mn was remobilized and its concentration reached 4 mg/L. The dissolution of a large part of soluble and exchangeable fraction of Mn that was extracted from the solid matrix could account for these relatively high concentrations of Mn. However, Fe and sulphate concentrations (as S) reached quickly high values of 127 mg/L and 438 mg/L, respectively. Overall, batch storage of SRPB mixture seems inappropriate as option, given the fact that Fe concentration exceeded Canadian regulation criteria for mine water effluent (3 mg/L).

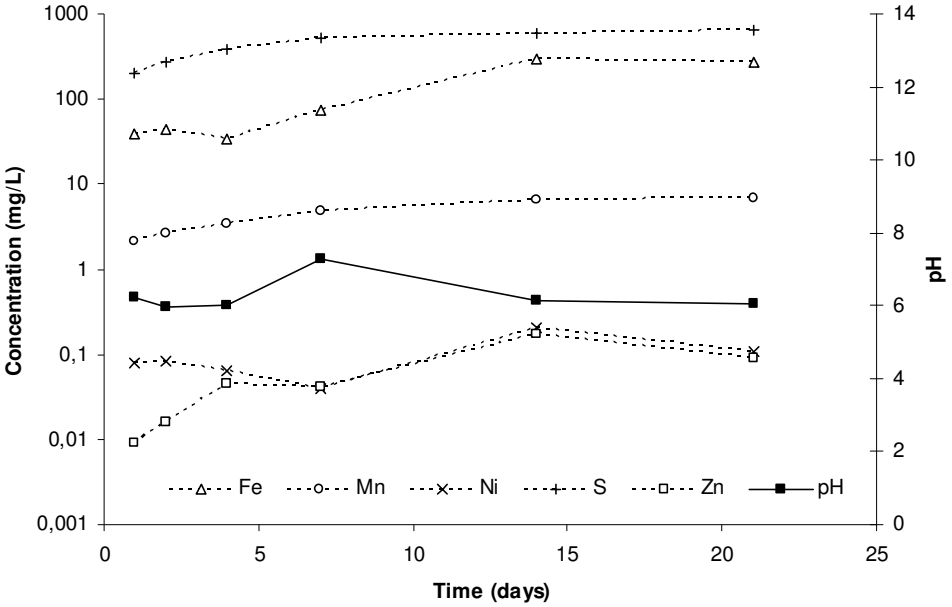

Figure 7. pH and metal concentration (mg/L) evolution during batch storage

Table 4. Average pH and metal concentration (mg/L) during batch storage

pH	Al	Cd	Cr	Fe	Mn	Ni	Pb	S total	Zn
6.3	0	0	0	127	4	0.10	0	438	0.063

Column storage test

The pH of column effluent remained relatively stable at 7.2 throughout the experiment (see Figure 8). Redox potential (Figure 8) maintained values around 535 mV, except for the first 50 days when Eh reached values as high as 588 mV and the last 50 days when Eh values decreased to approximately 437 mV. The difference between these two periods was mainly due to the decrease of the flow rate after 50 days from 0.6 mL/min to 0.4 mL/min that allowed increasing the contact time between water and SRPB mixture and, consequently, decreasing the redox potential. The conductivity evolution (Figure 8) which is related to the water ion content decreased during the first 40 days probably due to the leaching of dissolved organic matter and soluble and exchangeable metals. Then, conductivity values stabilized at approximately 229 µS/cm.

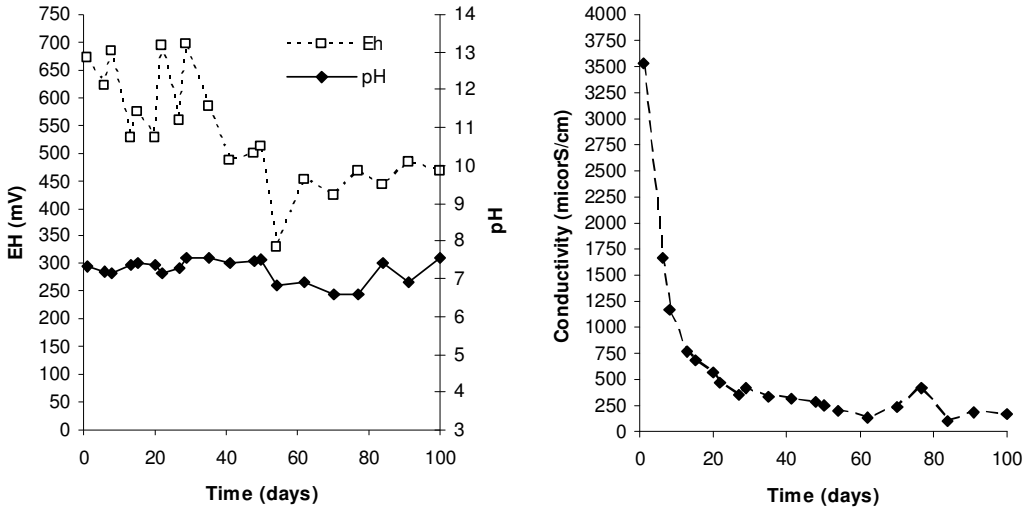

Figure 8. Eh, pH and conductivity at the exit of the storage column

Metal concentrations (Al, Cd, Cr, Fe, Ni, Pb, and Zn) in supernatant were relatively low (or under the detection limit of the method, see Table 5). The Mn concentration was higher mainly due to the fact that Mn was 14% in a soluble and exchangeable form. Moreover, Mn mineral precipitates could be easily dissolved (Edwards et al., 2009). Finally, SRPB mixture generated alkalinity due to carbonate and organic matter content at approximately 100 mg/L $CaCO_3$. Column effluent water had a positive net alkalinity (calculated as the difference between alkalinity and acidity) at 86 mg/L $CaCO_3$ and thus prevented water re-acidification due to metal precipitation. Total S (under sulphate form) at the exit of the column was of 41 mg/L probably due to dissolution of sulphides or of soluble sulphates contained in the SRPB mixture.

Table 5. Average pH, Eh (mV), conductivity (micros/cm), alkalinity (mg/L $CaCO_3$), acidity (mg/L $CaCO_3$) and metal concentration (mg/L) during column storage

pH	Eh	Acidity	Alkalinity	Al	Cd	Cr	Fe	Mn	Ni	Pb	S total	Zn
Detection limit (mg/L)				0.01	0.003		0.006	0.002	0.004	0.02	0.09	0.05
7.2	535	14	100	0.01	0	0	0.02	0.35	0.04	0	41	0.02

Metal content in SRPB mixture, before and after column storage is presented in Table 6. Metal concentrations decreased mainly for Al, Cr and Mn due to their water leaching. However, Zn concentration in SRPB mixture increased. Nevertheless, this difference could originate in some inherent quantification errors that occur during the analysis of a non-representative (or homogeneous) SRPB mixture sample.

Table 6. Metal proportion (%) in SRPB mixture

Metal % in SRPB mixture	Al	Cd	Cr	Fe	Mn	Ni	Pb	Stot	Zn
Before column storage	1.3	0	0	3.9	0.05	0.01	0	0.77	0.11
After column storage	0.82	0	0	3.5	0.04	0.01	0	0.69	0.15
Difference (before - after)	-0.5	0	0	-0.4	-0.05	0	0	-0.08	+0.04

Conclusions

The main conclusions of this study are:

- Iron, which was the most challenging metal to treat in the tested AMD, was mainly retained in SRPB mixture under sulphides and oxyhydroxides forms,
- SRPB spent mixture should be stored in a non acidic water (close to neutral pH) to prevent metal remobilization,
- Batch storage of SRPB mixture is not appropriate since iron concentration can exceed water regulation criteria,
- SRPB storage in neutral water with a natural flow was efficient and allowed respecting water regulation criteria. However, one should interpret these findings with caution, as in this case, leached metal concentration could have remained low due to the dilution caused by water flow.
- SRPB storage should be practised with a complete understanding of metal phase stability.

Acknowledgements

This research was supported by the Canada Research Chair on Restoration of Abandoned Mine Sites and the Natural Sciences and Engineering Research Council of Canada (NSERC) through the Industrial NSERC Polytechnique-UQAT Chair in Environment and Mine Wastes Management. The authors gratefully acknowledge the industrial and governmental partners of the industrial Chair for the funding of this study. Finally, thank you to V. Gozdz and J. Brousseau for the laboratory work.

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Acronyms

Eh: redox potential normalising to the standard hydrogen electrode
ICP-AES: Inductively Coupled Plasma-Atomic Emission Spectrometry
SEP: Sequential extraction procedure
SRPB: Sulphate-reducing passive bioreactor