

Iron and Sulfate Removal in Highly Contaminated Acid Mine Drainage Using Passive Multi-Step Systems

Tsiverihasina V. Rakotonimaro¹, Carmen M. Neculita¹, Bruno Bussière¹, Thomas Genty¹, Gérald J. Zagury²

¹*Research Institute on Mines and Environment (RIME), University of Quebec in Abitibi-Temiscamingue (UQAT), 445 Boul. de l'Université, Rouyn-Noranda, QC, Canada, J9X5E4*

²*RIME- Polytechnique Montréal, Department of Civil, Geological, and Mining Engineering, Polytechnique Montréal, Montreal, QC, Canada, H3C 3A7*

Abstract Remediation of high Fe and SO₄²⁻-acid mine drainage (AMD) with passive multi-step systems is less prone to clogging, but could show variable efficiency. Hence, four scenarios (MS1 to MS4) of passive multi-step treatment systems were tested. The system (MS3) composed of two pretreatment units of dispersed alkaline substrate reactors and one unit of passive biochemical reactor was found the most efficient (Fe and SO₄²⁻ removal of 99% and 77%, respectively). Clogging issues were not encountered in all reactors. Nonetheless, further studies on the treatment of highly contaminated Fe and SO₄²⁻ AMD with other dissolved metals should be undertaken.

Key words acid mine drainage, passive biochemical reactor, multi-step systems, dispersed alkaline substrate, wood ash

Introduction

Treatment of highly contaminated acid mine drainage (AMD) often involve passive multi-step systems because they are less subjected to clogging and/or passivation. Their design includes pretreatment, principal and polishing units, which can be aerobic and anaerobic, chemical, and biological. Some types may involve the combination in series of dispersed alkaline substrate (DAS – mixture of coarse (wood chips) and neutralizing materials (calcite or magnesia)) units with cascade aeration (Rötting et al. 2008) or decantation ponds (Caraballo et al. 2011; Macías et al. 2012). Passive biochemical reactors (PBRs) were combined with anoxic limestone drains (ALD) (Figueroa et al. 2007; Prasad and Henry 2009) or with peat biofilters (Clyde et al. 2016). However, a multi-step treatment has variable efficiency (in terms of Fe and SO₄²⁻ removal) depending on the water quality, and on the type and number of units composing the system. The DAS-based multi-step systems could remove up to 99.9% of Fe in AMD, at initial Fe concentrations <0.5 g/L, whereas at higher concentrations (0.5–1 g/L), the efficiency decreased to as low as 20% (Rötting et al. 2008; Caraballo et al. 2009, 2011). In addition, the SO₄²⁻ was marginally removed (Rötting et al. 2008; Caraballo et al. 2011; Macías et al. 2012). PBRs-based multi-step treatment could remove up to 99.7% of Fe and 53% of SO₄²⁻, at initial concentrations <0.5 g/L and 0.3–3 g/L, respectively (Figueroa et al. 2007; Prasad and Henry 2009). Oppositely, Fe and SO₄²⁻ removal was found around 78% and 55%, at initial Fe and SO₄²⁻ concentrations of 1.8 g/L and 4.7 g/L, respectively (Genty et al. 2016). However, AMD originating from abandoned mines and tailings can be characterized by extremely high concentrations of dissolved Fe (up to 141 g/L) and SO₄²⁻ (up to 760 g/L) (Nordstrom et al. 2000). Hence, an optimization of the performance of multi-step systems to allow treating an AMD of such quality is still

necessary.

In this context, the present study aims to evaluate the efficiency of four scenarios of laboratory PBRs-based and PBR–DAS-based multi-step systems for the treatment of AMD with initial Fe and SO₄²⁻ up to 4 g/L and 9 g/L, respectively.

Methods

Six 10.7 L columns (14 cm in diameter and 70 cm height), filled with six different mixtures were set-up (tab. 1).

Table 1 Six columns and the filling mixtures used to compose each unit of the multi-step systems

Mixture	WA50	C50	PBR#1	PBR#2	PBR#3	WA	DOL
	%v/v			% w/w			
Structural agent (sand)	-	-	10	10	20	-	-
Cellulosic wastes (wood chips and/or sawdust)	50	50	40	15	30	-	-
Organic wastes (chicken manure and/ or compost)	-	-	30	15	30	-	-
Inoculum (sediments)	-	-	-	8	15	-	-
Nutrients (urea)	-	-	-	2	3	-	-
Neutralizing agents							
Wood ash	50	-	-	-	-	100	-
Calcite	-	50	20	50	2	-	-
Dolomite	-	-	-	-	-	-	100
Total	100	100	100	100	100	100	100

WA: wood ash; DOL: dolomite

All the mixtures filling the columns (tab. 1) were fully characterized prior and/or after use, and showed effective Fe removal (>91%) for the (pre)treatment of Fe-rich AMD during previous batch testing (Genty 2012; Rakotonimaro et al. 2016). In addition, the WA mixture showed Fe and SO₄²⁻ removal >99% and 44%, respectively (Genty et al. 2012a). At the same time, the anoxic dolomitic drain (DOL) was found to have efficiency similar to calcite when used to treat moderately contaminated AMD (Genty et al. 2012b). In each column, the mixture was placed between two layers of gravel (\approx 5 cm) and fine-mesh geotextiles, at the top and bottom, prior to their covering. Thereafter, four multi-step scenarios (MS1 to MS4) were tested using the set-up reactors (tab. 2).

The first three scenarios involved diverse combinations of DAS units, DOL, and PBRs. One type among these three included 1 DAS-based pretreatment unit (WA50), whereas the two

Multi-step system	Composing units	HRT (d)	Duration (d)
MS1	WA50 + PBR#1 + DOL	$3 + 5 + 3 = 11$	70
MS2	WA50 + C50 + PBR#1	$3 + 3 + 5 = 11$	70
MS3	WA50 (1) + WA50 (2) + PBR#1 + C50	$3 + 3 + 5 + 3 = 14$	217
MS4	PBR#2 + WA + PBR#3	$5.1 + 8.9 + 5.6 = 19.6$	365

Table 2 Components of the multi-step systems, tested HRTs, and duration of the experiments

others were comprised of two pretreatment units (WA50/C50 or 2 WA50) (tab. 2). The fourth scenario was composed of two PBRs (PBR#2 and PBR#3) separated by a wood ash (WA) unit, where PBR#2 and WA were considered as the pretreatment units. All four scenarios were run for 70 to 365 d. The reactors were started at 3 d of HRT, except the PBRs and WA, which were operated at HRT \geq 5 d for total HRTs of 11 d (MS1, MS2), 14 d (MS3), and 19.6 d (MS4) (tab. 2).

Prior to starting the continuous feed of the columns with AMD, the PBRs were saturated with a Postgate B medium, which composition was prepared in distilled water with 3.5 g/L sodium lactate (or 4.67 mL lactate liquid 56.8%); 2.0 g/L $MgSO_4 \cdot 7H_2O$; 1.0 g/L NH_4Cl ; 1.27 g/L $CaSO_4 \cdot 2H_2O$; 1.0 g/L yeast extract; 0.5 g/L KH_2PO_4 ; 0.5 g/L $FeSO_4 \cdot 7H_2O$; 0.1 g/L thioglycolic acid, and 0.1 g/L ascorbic acid (Postgate 1984). Then, the columns were incubated with the medium at room temperature (four weeks for PBR#2 and #3 and 2 weeks before being acclimated for another week with diluted AMD (3:1 of DI water: AMD) for PBR#1). Finally, calibrated peristaltic pumps (Masterflex) were used to feed upward all the columns with synthetic AMD (pH 2–5, 1.8–5 g/L Fe, <0.007 g/L Al, <0.33 g/L Mn, 4–9 g/L SO_4^{2-} and <0.033 g/L of Pb, Ni, Zn), which quality is typical of effluents from hard rock mines in Canada (Zinck and Griffith 2013).

The AMD and treated water quality were monitored by a weekly sampling and analysis of the physicochemical parameters, including the pH, redox potential (ORP), alkalinity, acidity, and concentrations of total iron (Fe_t), SO_4^{2-} and total metal. Measured hydraulic parameters included the k_{sat} and porosity (n). Water pH was measured with an electrode Orion 3 Star Thermo (GENEQ Inc.). The ORP was determined with a potentiometer (Sension1 POR HACH 51939-00) coupled with an internal Pt/Ag/AgCl electrode. Alkalinity and acidity were determined by titration with a Metrohm Binkmann, 716 DMS Trinitro titrator (APHA 2012). Concentrations of Fe_t and SO_4^{2-} were analyzed on filtered samples (0.45 μm), within 1–2 h after collection, with a DR/890 HACH colorimeter (Method 8008 – 1, 10 phenanthroline, Method 8146 – 1, 10 phenanthroline, and Method 8051 – barium chloride powder pillows for Fe_t and SO_4^{2-} , respectively). Total metal concentrations of filtered (0.45 μm) and acidified (with 2% (v/v) of nitric acid) samples were analyzed by ICP-AES. Removal of metals r (%) was calculated with the following equation: $r = [(C_{in} - C_{out})/C_{in}] \cdot 100$; where C_{in} and C_{out} are input and output concentrations (mg/L).

Sulfate reducing bacteria (SRB) counting in effluents from PBRs was performed by using

the most probable number (MPN) method (Cochran 1950; ASTM 1990). After 21 d of incubation at 30°C and under anaerobic conditions, the SRB growth was either indicated by the presence of black FeS precipitate. When this last was not obvious, a test with FeCl_3/HCl and p-aminodimethylaniline dihydrochloride/HCl was performed (Postgate 1984; ASTM 1990). The k_{sat} was evaluated by using the falling head method (ASTM 1995). Porosity was calculated as the ratio between void volumes, which considers the specific gravity (G_s), and total volume of the reactive mixture.

Results and discussion

In general, multi-step treatment with two pretreatment units gave better performance compared to one unit. Nonetheless, all systems allowed pH increase from 2–4.1 to 4.4–8.1 (fig. 1). The low ORP values showed that reducing conditions were maintained in all reactors (fig. 1). Better acidity removal was observed in MS3 (89%) and entailed a higher removal of Fe (99%) and SO_4^{2-} (61%) all along the testing (217 d), at input Fe and SO_4^{2-} concentrations <2.5 g/L and <5 g/L, respectively (fig. 2). On the contrary, MS1 showed the lowest efficiency

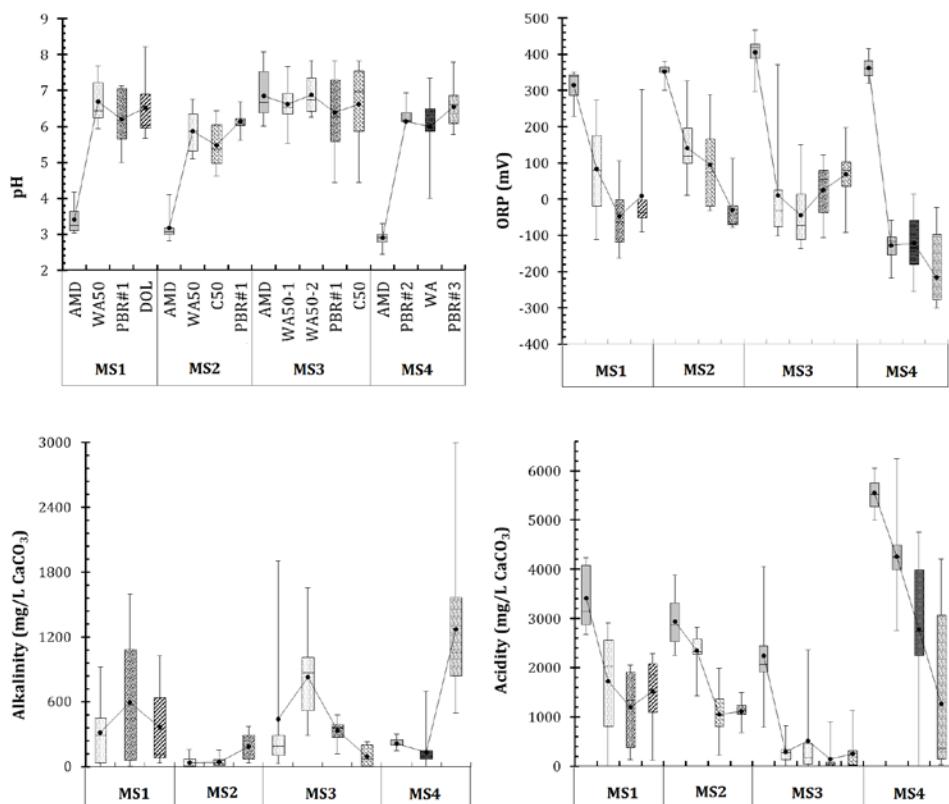


Figure 1 Physicochemical evolution of effluents in the columns during laboratory multi-step treatment of AMD (minimum, 25% percentile, median, 75% percentile, mean, maximum) AMD, WA50, PBR#1, PBR#2, PBR#3, DOL, C50, WA

(acid, Fe and SO_4^{2-} removal of 51, 53 and 29%, respectively) (tab. 3). Over time (after 139 d), the effectiveness of MS4 decreased to half fold, probably due to WA unit saturation as well as a decrease of alkalinity (down to 73%). Hence, Fe and SO_4^{2-} removal dropped, respectively from 99% to 45% and from 49% to 13%. Moreover, only half of the acidity was neutralized (45%).

The performance of a multi-step treatment appears to be dependent on the effectiveness of the pretreatment units as well as on the initial Fe and SO_4^{2-} concentrations. Higher efficiency was found with two WA50 pretreatment units in MS3 (removal of up to 96% of Fe; load of 427 g Fe/m³/d and 58% of SO_4^{2-}). Subsequently, the following PBR#1 could treat 4–73 g Fe/m³/d. At the same time, a possible oxidation of sulfur/sulfide from the PBR#1 could have

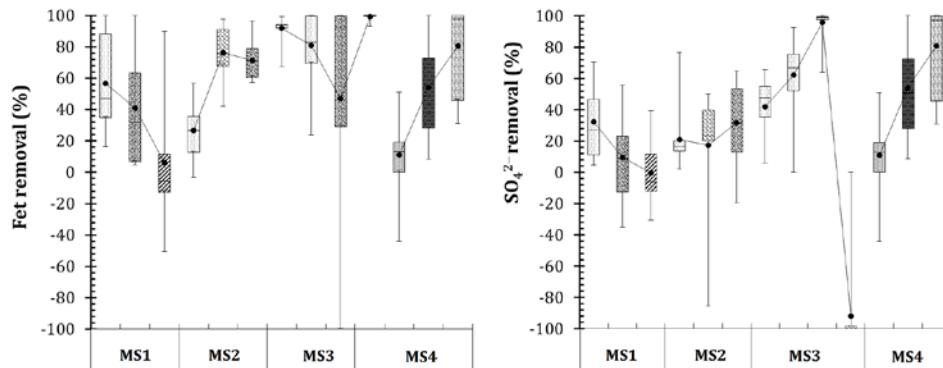


Figure 2 Relative removal of Fe and SO_4^{2-} (minimum, 25% percentile, median, 75% percentile, maximum, mean) during multi-step treatment of AMD

Table 3 Efficiency of the different multi-step systems

	MS1	MS2	MS3	MS4
pH	5-8.21	4.73-6.68	4.44-8.09	5.78-7.79
ORP (mV)	-18	-29	81	-65-101
Fe _t removal (%)*	53	76	99	31-100
SO_4^{2-} removal (%)**	29	61	65	-16-83
Acid removal (%)	51	78	89	-27-100
Alkalinity (mg CaCO ₃ /L)	26-1597	3-630	7-1905	500-3000

*Input concentrations in MS1, MS2, and MS3: 2.5±0.4 g/L and 4±0.4 g/L in MS4

** Input concentrations in MS1, MS2, and MS3: 5±0.6 g/L and 9±1.2 g/L in MS4

increased SO_4^{2-} concentration in the last unit (i.e. C50) of the system (fig. 2).

Even when exposed to higher acidity as well as Fe and SO_4^{2-} concentrations, the first pre-treatment unit in MS4 (i.e. PBR#2) showed a steady acidity and Fe removal (23% and 12% or equivalent to 13 g Fe/m³ substrate/d, respectively) all along the testing. In addition, the produced alkalinity was also maintained (around 214 mg/L as CaCO₃; fig. 1). However, this alkalinity was not sufficient enough to allow SRB to thrive. Accordingly, the SRB counts did not exceed 200 cells/100 mL, which may explain the negligible SO_4^{2-} removal. Nevertheless, the following WA unit presented a better efficiency (Fe removal of 40%, and 32% of SO_4^{2-}) during the first 125 d and subsequently the last unit (PBR#3) could remove 98% of Fe and 33% of SO_4^{2-} (fig. 2).

Additionally, all the tested multi-step systems could decrease up to 98% of Al, Ni, Pb and Zn concentrations. These metals were removed early in the pre-treatment units (>72%). The most significant Zn removal (94%) in PBR#1 during MS2 was possibly promoted by its adsorption onto Fe and Al (oxy) hydroxides. Up to 99.4% of Mn was also removed during the first phase of the pretreatment unit(s) in MS1 to MS3 because of the high pH value (>8). On the contrary, higher Mn removal (83%) was found in the last unit of MS4 before day 132, when Fe concentration was lowered before WA saturation (Fe/Mn ratio <1).

Little change of the overall k_{sat} in all reactors (from the initial value 7.7×10^{-3} – 1.4×10^{-2} cm/s to an order of 10^{-4} – 10^{-3} cm/s) suggested that clogging issues and short circuiting did not occur during the experiments. Hence, mixtures with $k_{\text{sat}} > 10^{-3}$ cm/s are recommended for an efficient multi-step treatment composed of DAS and PBR units.

Conclusions

Amongst the four tested multi-step treatment systems, MS3, composed of two pretreatment units (WA50) and one PBR, was the most efficient in Fe and SO_4^{2-} removal from highly contaminated AMD. MS4 (consisting of two PBRs separated by a WA unit) showed a higher efficiency (Fe and SO_4^{2-} removal of 99% and 50%, respectively) before WA saturation (i.e. during the first 132 d). A PBR-based pretreatment unit could be an efficient Fe-pretreatment (even at a low load; around 13 g/m³/d) at initial Fe concentrations up to 2.5 g/L, providing that enough alkalinity can ensure acid neutralization and microbial activity. Even though clogging was not observed during testing and the k_{sat} was relatively stable (10^{-3} – 10^{-4} cm/s) in all multi-step systems, the use of mixture with $k_{\text{sat}} > 10^{-3}$ cm/s is recommended when using DAS and PBR units. Further studies on passive multi-step treatment of AMD with high Fe, SO_4^{2-} and other dissolved metals need to be carried out.

Acknowledgements

The authors thank the NSERC (Natural Sciences and Engineering Research Council of Canada), the MERN (Ministère de l'Énergie et des Ressources Naturelles – Québec's Ministry of Energy and Natural Resources), and the industrial partners of the RIME UQAT-Polytechnique Montreal, including Agnico Eagle, Canadian Malartic Mine, Iamgold, Raglan Mine-Glencore, and Rio Tinto. The authors want also to thank Marc Paquin, Mélanie Bélanger, Patrick Bernèche, Joël Beauregard and Alain Perreault for

technical assistance during the laboratory experiments.

References

- APHA (American Public Health Association) (2012) Alkalinity titration, standard methods for the examination of water and wastewater, 22nd ed. Greenberg A (Eds), Washington DC, USA
- ASTM (American Society for Testing and Materials) (1995) Standard test method for permeability of granular soils. Annual book of ASTM Standards.08. D 2434 – 68, Philadelphia, PA, USA
- ASTM (American Society for Testing and Materials) (1990) Standard methods for sulphate reducing bacteria in water and water-formed deposit. In: Annual book of ASTM Standards, vol. 04.08. Section D 4412–84, Washington, DC, pp. 533–535.
- Caraballo MA., Rötting TS., Macías F, Nieto JM, Ayora C (2009) Field multi-step limestone and MgO passive system to treat acid mine drainage with high metal concentrations. *Appl Geochem* 24: 2301–2311
- Caraballo MA, Macías F, Rötting TS, Nieto JM, Ayora C (2011) Long term remediation of highly polluted acid mine drainage: A sustainable approach to restore the environmental quality of the Odiel river basin. *Environ Pollut* 159: 3613–3619
- Cochran, WG (1950) Estimation of bacterial densities by means of the most probable number. *Biometrics* 6, 105–116
- Clyde EJ, Champagne P, Jamieson HE, Gorman C, Sourial J (2016) The use of passive treatment for the mitigation of acid mine drainage at the Williams Brothers Mine (California): Pilot-scale study. *J Clean Prod* 130: 116–125
- Figueredo L, Miller A, Zaluski M, Bless D (2007) Evaluation of a two-stage passive treatment approach for mining influenced waters. In: Proc. of the American Society of Mining and Reclamation (ASMR). June 2–7, Lexington, KY, USA. pp. 238–247
- Genty T, Bussière B, Paradie M, Neculita CM (2016) Passive biochemical treatment of ferriferous mine drainage: Lorraine mine site, Northern Quebec, Canada. In: Proc. of the International Mine Water Association (MWA). July 11–15, Leipzig, Germany
- Genty T, Bussière B, Potvin R, Benzaazoua M, Zagury GJ (2012a) Capacity of wood ash filters to remove iron from acid mine drainage: Assessment of retention mechanism, *Mine Water Environ.* 31 (4): 273–286
- Genty T, Bussière B, Potvin R, Benzaazoua M, Zagury GJ (2012b) Dissolution of calcitic marble and dolomitic rock in high iron concentrated acid mine drainage: Application to anoxic limestone drains, *Environ Earth Sci* 66: 2387–2401
- Genty, T (2012) Comportement hydro-bio-géo-chimique de systèmes passifs de traitement du drainage minier acide fortement contaminé en fer. PhD dissertation. Applied Sciences, UQAT, Rouyn-Noranda, QC, Canada, 270p
- Macías F, Caraballo MA, Rötting TS, Pérez-López R, Nieto JM, Ayora C (2012) From highly polluted Zn-rich acid mine drainage to non-metallic waters: Implementation of a multi-step alkaline passive treatment system to remediate metal pollution. *Sci Tot Environ* 433: 323–330
- Nordstrom DK, Alpers CN, Ptacek CJ, Blowes DW (2000) Negative pH and extremely acidic mine waters from Iron Mountain, California. *Environ Sci Technol* 34: 254–258
- Postgate JR (1984) The sulfate-reducing bacteria. 2nd ed. Cambridge University Press: Cambridge
- Prasad D, Henry JG (2009) Removal of sulphates, acidity and iron form from acid mine drainage in a bench scale biochemical system. *Environ Technol* 30 (2): 151–160
- Rakotonimaro TV, Neculita CM, Bussière B, Zagury GJ (2016) Effectiveness of various dispersed alkaline substrates for the pretreatment of ferriferous acid mine drainage. *Appl Geochem* 73: 13–23
- Rötting TS, Caraballo MA, Serrano JA, Ayora C, Carrera J (2008) Field application of calcite Dispersed Alkaline Substrate (calcite-DAS) for passive treatment of acid mine drainage with high Al and metal concentrations. *Appl Geochem* 23: 1660–1674
- Zinck J, Griffith W (2013) Review of acidic drainage treatment and sludge management operations, MEND Report 3.43.1. CANMET-MMSL, 101p