Passive biochemical treatment of ferriferous mine drainage: Lorraine mine site, Northern Quebec, Canada

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Abstract

The Lorraine mine site is located in the Temiscamingue region of the Quebec's province, Canada. The mine operated only for four years (1964-1968) for the extraction of Au, Ag, Cu, and Ni, but left behind around 600 000 t of tailings, disposed in a pond area of about 15.5 ha. The unsaturated zone of the tailings, located partially below the water table, has been exposed to the atmosphere for about 30 years, entailing sulfides oxidation and the generation of highly contaminated ferriferous (iron-rich) acid mine drainage (AMD).

In 1998 Quebec's Ministry of Energy and Natural Resources initiated a rehabilitation program of the mine site to limit the AMD generation and environmental damages. The restoration plan mainly consisted of prevention measures of the further weathering of tailings using a multi-layer solid cover (cover with capillary barrier effects), as well as four passive treatment units, for the AMD flowing from the underneath of cover, using one limestone and three dolomite drains.

Reclamation strategy proved effective, but the iron-rich AMD in the tailings pores is only progressively leached out over time. Hence, total Fe concentrations decreased from about 11 g/L, before the construction of the preventive cover, to around 2.5 g/L in 2015, while the pH increased from < 3 to 5-6 within only 12 years. However, in 2011 the replacement of one clogged dolomite drain by a three-unit passive biochemical treatment system (train) was necessary. The new train consisted of two biochemical reactors (filled with mixtures of limestone, poultry manure, compost, wood waste, and sand), separated by a wood ash unit. In addition, in 2012 some design changes, entailed by the very slow flow through the three-unit passive treatment system, were required.

Yearly monitoring, during the warm seasons, was implemented and proved the efficiency of passive biochemical treatment system. Results showed that the pH increased from 5 to 6, and Fe and sulfate removal exceeds 70 % and 57% (from average initial concentrations of about 1.85 g/L and 4.7 g/L), respectively. Few more years would still be necessary for the complete leaching out and passive treatment of the ferriferous AMD.

Key words: Iron-rich AMD, dolomite drains, passive biochemical treatment, three-unit system

Introduction

Mine drainage is the most common water-related problem to mining activities worldwide (Nordstrom et al., 2015). Environmental impacts of acid mine drainage (AMD), characterized by low pH (-3.6 < pH < 6) and high concentrations of dissolved metals/metalloids and sulfate, are well documented (Neuman et al., 2014). Several active/passive, physicochemical, and biochemical technologies are available for AMD treatment (USEPA, 2014).

Passive treatment is preferred on closed, abandoned or partially rehabilitated mine sites because of the use of low cost natural / residual materials, as well as of the satisfactory performance (Neculita et al., 2007; USEPA, 2014). Research and field experience showed that passive treatment systems give better performance when used as complement to mine drainage prevention measures, and / or with slightly contaminated waters (USEPA, 2014). However, AMD on several mine sites is often highly contaminated with metal/metalloids, such as Fe, Zn, As etc. (Ayora et al., 2013; Genty et al., 2012a, 2012b; Giloteaux et al., 2013). Hence, a combination of two or more units of passive treatment (multi-step systems or trains) has been developed (Ayora et al., 2013; Genty, 2012). To limit coating/passivation (loss of reactivity) and clogging (loss of permeability) caused by secondary minerals (e.g., gypsum, metal oxides-hydroxides) precipitated during the treatment, innovative approach using reactive mixtures, composed of coarse and highly porous material (wood chips), and fine grain size neutralizing agents (e.g., calcite, magnesia), i.e. dispersed alkaline substrate, have also been developed (Macías et al., 2012; Ayora et al., 2013).

Despite the satisfactory performance of the multi-step treatment systems on some mine sites (e.g., Iberian Belt Pyrite, Spain), additional knowledge is required on their long-term efficiency and the stability of metal-rich produced sludge (Macías et al., 2012). Ongoing laboratory and at field-pilot scale research shows promising results on the performance of this last approach for the remediation of iron-rich AMD on several closed and abandoned mine sites in Quebec, Canada and worldwide (Rakotonimaro et al., 2015).

Methods

Study site

The Lorraine mine site is located in the Témiscamingue region of the Quebec's province, Canada (fig. 1). The mine operated only for four years (1964-1968) for the extraction of Au, Ag, Cu, and Ni, but left behind around 600 000 t of tailings, disposed in a pond area of about 15.5 ha. The unsaturated zone of the tailings, located partially below the water table, has been exposed to the atmosphere for about 30 years, entailing sulfides oxidation and the generation of highly contaminated ferriferous/iron-rich AMD.

In 1998 Quebec's Ministry of Energy and Natural Resources initiated a rehabilitation program of the mine site to limit the AMD generation and environmental damages. The restoration plan mainly consisted of prevention measures of the further weathering of tailings using a multi-layer solid cover (cover with capillary barrier effects), as well as four passive treatment units, for the AMD flowing from the underneath of cover, using one limestone and three dolomite drains.

Figure 1 *Lorraine site localisation (Source: St Arnault et al., 2005).*

Reclamation strategy proved effective (Dagenais et al., 2005), but the iron-rich AMD in the tailings pores is only progressively leached out over time. Hence, total Fe concentrations decreased from about 11 g/L, before the construction of the preventive cover, to around 2.5 g/L in 2015, while the pH increased from < 3 to 5-6 within only 12 years (table 1).

The efficiency of one of the three dolomitic drains deteriorated over time due to the built-up of iron precipitates, which clogged the pore spaces, and limited the flow through (Potvin, 2009).

***Table 1** Average composition of iron-rich AMD between 2011 and 2015.*

pH	Alkalinity	Acidity	Al	Ca	Fe	Mg	Mn	Ni	Pb	S_{total}	Zn
	mg/L of $CaCO_3$		mg/L								
5.8	74	2670	0.50	377	1814	30	6.6	0.62	0.19	1583	0.25

Hence, in 2011 the replacement of this clogged dolomite drain by a three-unit passive biochemical treatment system (train) was necessary (Genty, 2012).

Design of the passive biochemical treatment system

The 3-unit treatment system built on Lorraine mine site (figs. 2 and 3) is composed of two sulfate-reducing passive biofilters (SRPB), separated by a wood ash unit. The system was constructed and operated since August of 2011 to treat the iron-rich AMD, for a design flow rate of 5 l/min. The hydraulic retention time within the three treatment units is of 11 days, and the total volume of 120 m^3.

The aim of the first biofilter (SRPB1 - mixture # 4; see table 2 for composition and component proportions) is to decrease the Eh, neutralize free acidity and partially remove metals. The effluent then feeds a wood ash unit to decrease iron concentrations by sorption and precipitation. Finally, the effluent is polished in the second biofilter (SRPB2 - mixture # 1), which also removes the residual metals.

In 2012 some design changes, entailed by the very slow flow through the treatment system, were required. The changes included the mixing of each part of the system, addition of coarse rock between each two units, and removal of the top soil to allow gas evolving (from organic material decomposition).

***Table 2** Components and proportions of reactive mixture composition (Genty, 2012).*

Components (% dry weight)	Mixture # 1	Mixture # 4
Wood chips	36	18
Manure	17	10
Compost	24	12
Sand	21	10
Calcite	2	50

***Figure 2** Passive treatment system on Lorraine mine site, Quebec, Canada.*

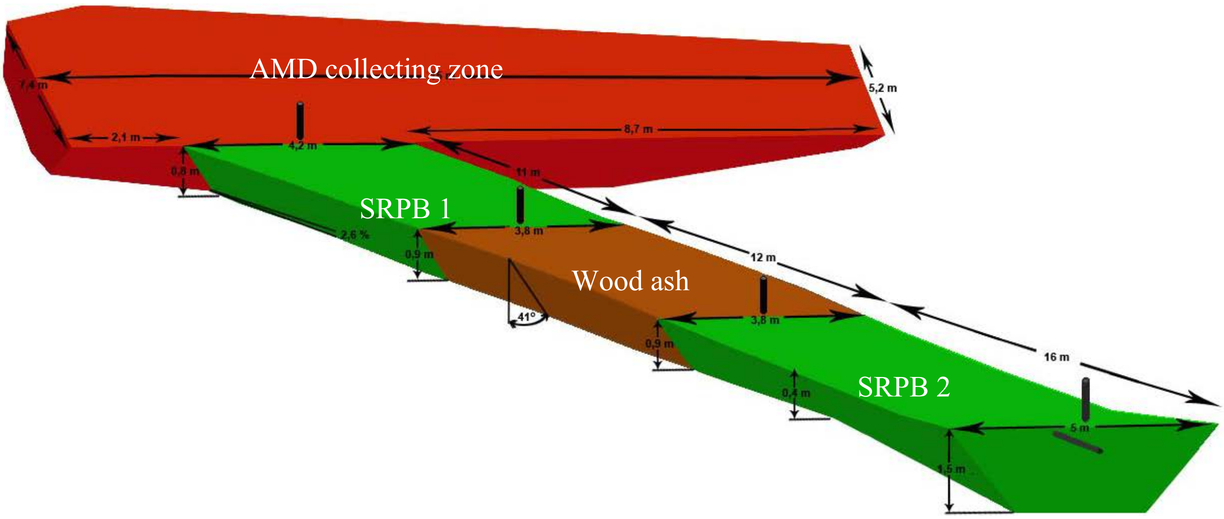

***Figure 3** Model of the passive treatment system constructed on the Lorraine mine site, Quebec, Canada.*

Water sampling and analysis

Water sampling is systematically performed every year, during the warm seasons (usually from May to October). To do so, four piezometers are installed to sample the AMD feed and each treatment unit (fig. 2). Some parameters, such as pH and Eh, are analyzed on site, while preserved samples are transported back to laboratory for other analysis. The pH of sample was determined with an Orion Triode sensor coupled with a Benchtop pH/ISE Meter Orion model 920 (relative precision +/- 0.01 pH) and the Eh (redox potential, 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). The alkalinity was obtained by titration on non-filtered sample with sulphuric acid 0.02N (relative precision of 1 mg $CaCO_3$/L) and the acidity by titration on non-filtered sample with sodium hydroxide 0.1N (precision of 1 mg $CaCO_3$/L) (APHA, 2012). Filtered samples (with a 0.45 µm filter) used to quantify metal content were acidified with 2% volume with nitric acid (70%) before analysis. The technique used to evaluate metals concentration was the Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES) using a Perkin Elmer OPTIMA 3100 RL (relative precision of 5%).

Results

Global performance of the passive system

The pH at the exit of the treatment system is in the range 5.8-7 (table 3). However, net acidity (acidity-alkalinity) is high (up to 1010 mg/L of $CaCO_3$) mainly due to the high iron concentration (390 mg/L). Hence, despite a high treatment efficiency (66%) in Fe removal, final concentrations exceed the discharge allowed limits of the Quebec's Directive 019 (table 3). The performance in Mn removal is marginal, with residual concentrations of about 5 mg/L. The presence of high concentrations of iron, which inhibits Mn removal, are partially responsible for this limited efficiency (Neculita et al., 2011). The sulfur concentration is around 610 mg/L (approximately 2070 mg/L of sulfates), which translated in a decrease of 55% of the AMD concentration. In August 2015 the average concentrations of Ni, (<0.004 mg/L), Pb (<0.07 mg/L), and Zn (0.055 mg/L) meet the Directive 019 requirements.

Table 3 *Composition of AMD vs. treated effluent during a 4-year monitoring period (2011-2015).*

Sampling point/others	pH	As	Cu	Fe	Ni	Pb	Zn
				mg/L			
AMD	4.3-6.9	<0.06	<0.003	1799	0.62	0.19	0.26
Treated effluent	5.8-7	<0.01	<0.003	411	0.06	0.03	0.07
Worst values*	5.8	0.18	0.19	1120	0.56	0.094	0.34
Values in August 2015*	6	<0.01	<0.01	389	<0.004	<0.07	0.055
Quebec discharge regulation	6-9	0.2	0.3	3	0.5	0.2	0.5
Compliance with regulation	Yes	Yes	Yes	No	Yes	Yes	Yes

Iron removal in each section of the three-unit passive treatment system

The evolution of iron concentrations over the 4-year monitoring period (2011-2015) shows little variation in the AMD feed, with concentrations toggling yearly between 1 and 3 g/L (fig. 4). This could be seen as an indication of the slow and incomplete flushing-up of the residual contamination of the pore water in the severely weathered tailings (during over 30 years of exposure to water and air) underneath the cover. Once entering the treatment system, iron removal significantly decreased, especially in the SRPB1 and the wood ash unit, sometimes to values as low as below 0.1 mg/L Fe. This high efficiency was recorded prior to 2013. After that, due to the deterioration in the performance of wood ash unit and to some surface overflow, Fe concentrations in the final treated effluent are very high.

Few more years would still be necessary for the complete leaching out and passive treatment of the ferriferous AMD.

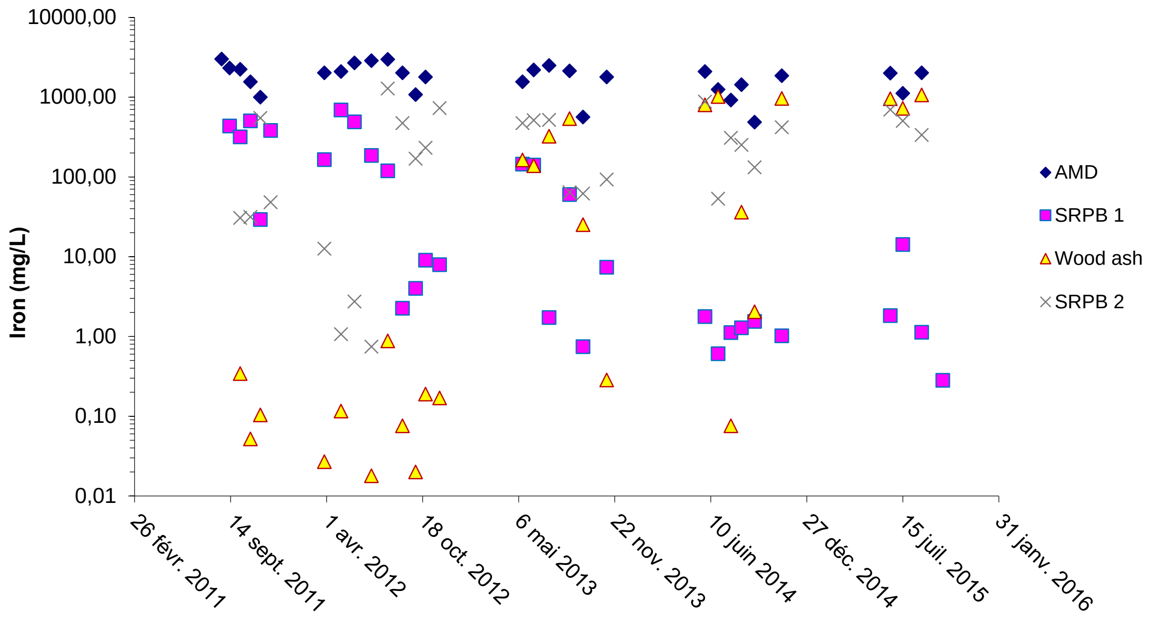

Figure 4 *Iron concentrations in each of the three-unit the passive treatment system constructed on Lorraine mine site, Quebec, Canada.*

Conclusion

The treatment of iron-rich AMD on the Lorraine mine site, Quebec, Canada is performed using a three-unit passive system, installed in 2011. The monitoring of the treatment system performed at various sampling points in the first 48 months of operation shows significant improvement of AMD quality discharged into the environment. The pH and most of the metals meet the discharge regulatory limits of Quebec's Directive 019, with the exception of iron which remains high (despite the decrease from 1800 mg/L to 390 mg/L). Ongoing research work are undertaken at RIME (Research Institute on Mines and Environment)-UQAT (University of Quebec in Abitibi-Temiscamingue) to find viable options to reduce the coating and clogging of the treatment system and improve the overall iron retention performance.

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