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# Biological manganese removal from mine drainage in a fixed bed bioreactor at pilot scale

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## Abstract

*The closed underground fluorspar Burg mine (Rio Tinto France) produces a near-neutral mine drainage (pH 6.3) with high concentrations of iron and manganese (14 mg.L<sup>-1</sup> and 12 mg.L<sup>-1</sup> respectively). Average flow rate is 27 m<sup>3</sup>.h<sup>-1</sup>. A passive water treatment is being developed by BRGM, the French geosurvey to replace the current lime treatment by a more environmentally friendly, economical and lower sludge producing technology. Different set-up and operating conditions were investigated at laboratory-scale and are still currently being optimised at pilot scale. The pilot consists of a 1 m<sup>3</sup> settling tank, in which iron (Fe<sup>2+</sup>) is oxidised and iron hydroxides are settled, followed by an up-flow 1 m<sup>3</sup> fixed-bed bioreactor filled with a mixture of limestone and pyrolusite (MnO<sub>2</sub>) and supplied with air, in which manganese precipitates. The fixed-bed was inoculated with sludges coming from two passive mine drainage treatment plants in which some manganese removal occurs. Residence time ranged from 50 h to 20 h. Results are promising: maximum removal rates were 99% for both iron and manganese. Iron and manganese concentrations were decreased under the 1 mg.L<sup>-1</sup> standard. Iron removal rate in the settling tank varied from 80 µg.L<sup>-1</sup>.h<sup>-1</sup> to 160 µg.L<sup>-1</sup>.h<sup>-1</sup>. Manganese removal rate in the bioreactor ranged from 130 µ.L<sup>-1</sup>.h<sup>-1</sup> to 350 µ.L<sup>-1</sup>.h<sup>-1</sup>. Surprisingly, up to 38% of the manganese was removed in the settling tank at low residence time. Residence time and aeration rate are still being optimised and clogging is being assessed. Currently, the pilot has been operating for 6 months and will continue to operate for another 6 months.*

**Keywords:** mine drainage, passive water treatment, iron, manganese, bioreactor

## 1 Introduction

Manganese and iron are major contaminants of large range of mine drainages (USEPA, 2014). High concentrations of manganese can cause toxicity in aquatic and terrestrial ecosystems (Howe et al. 2004). In humans, manganese can be a toxic substance when present in excessive concentrations in air, water and food (US DHHS, 2012). In France, the quality standard for manganese in waters used for human consumption is 50 µg.L<sup>-1</sup>.

The removal of manganese from mine drainage has been extensively studied for years. Neculita and Rosa (2018) recently produced an excellent review on manganese in mine drainage and the means to treat it. The most widespread passive manganese treatments for mine drainage, such as oxic rock filters (Tan et al. 2010) or the patented pyrolusite process (Vail and Riley, 2000), use microorganisms to improve manganese oxidation rate without increasing pH up to 10. Many different microorganisms can remove manganese from water by oxidising it as a precipitate through a wide variety of pathways (Barboza et al. 2016).

The closed Burg mine (France) produces a circumneutral mine drainage with relatively high concentrations of iron and manganese. A passive treatment is currently being tested to replace lime treatment. The

objective of this study is to evaluate and optimise the size and the footprint of this passive treatment process through an on-site pilot plant experiment.

## 2 Methodology

### 2.1 Mine site and mine water description

The Burg mine was an underground mine located in the southwest of France and operated since 1954 for fluorspar ( $\text{CaF}_2$ ) extraction by Sogerem, a company which is today part of Rio Tinto group. The extracted ore contained massive fluorspar with 95% calcium fluoride. The Burg Mine geological substratum is formed of Albigeois's shale, a complex system of shale, sandstone, and quartzite with low permeability. The fluorspar production ceased in 2006 after fifty years of activity, for economical reasons after the other near-by two main fluorspar open pit mines owned by Sogerem ceased operations due to the exhaustion of the orebody. Mine drainage first appeared fifteen months after dewater stopped. The mine drainage was initially slightly acidic and contained high levels of iron, manganese and fluorine. Since 2007, water has been treated with a lime process. The water quality objectives are to decrease fluorine concentration below  $15 \text{ mg.L}^{-1}$  and iron and manganese concentrations below  $1 \text{ mg.L}^{-1}$ . The concentrations of contaminants present in the mine water have decreased significantly over time. Currently the major contaminants in Burg mine water are iron and manganese, whereas fluorine concentration has decreased below the water quality objective and thus no longer requires treatment (Table 1). The surface area available on site to implement a passive treatment plant is limited. The treatment must therefore be optimised to minimise the footprint of the plant. Burg mine water alkalinity is  $240 \text{ mg.L}^{-1}$  calcium carbonate ( $\text{CaCO}_3$ ). Sulphate concentration ranges from  $200 \text{ mg.L}^{-1}$  to  $300 \text{ mg.L}^{-1}$ , and the average water flow rate is  $27 \text{ m}^3.\text{h}^{-1}$ .

Table 1 Main characteristics of Burg mine water; (average values of 38 analysis over a 6-month period in 2018)

Parameter	Units	Burg mine water
pH		6.33
Dissolved oxygen	$\text{mg.L}^{-1}$	2.70
Temperature	$^{\circ}\text{C}$	16.2
Conductivity	$\mu\text{S.cm}^{-1}$	581
Dissolved Fe	$\text{mg.L}^{-1}$	13.5
Dissolved Mn	$\text{mg.L}^{-1}$	11.6
Dissolved F	$\text{mg.L}^{-1}$	7.6

### 2.2 Experimental set-up

The pilot plant consists of an aeration tank, a settling tank for removal of iron and a fixed-bed bioreactor for the removal of manganese (Figure 1). The pilot plant was fed by a GA10 diaphragm pump (MILTON ROY) that enables flow rates from 0 to  $18 \text{ L.h}^{-1}$ .

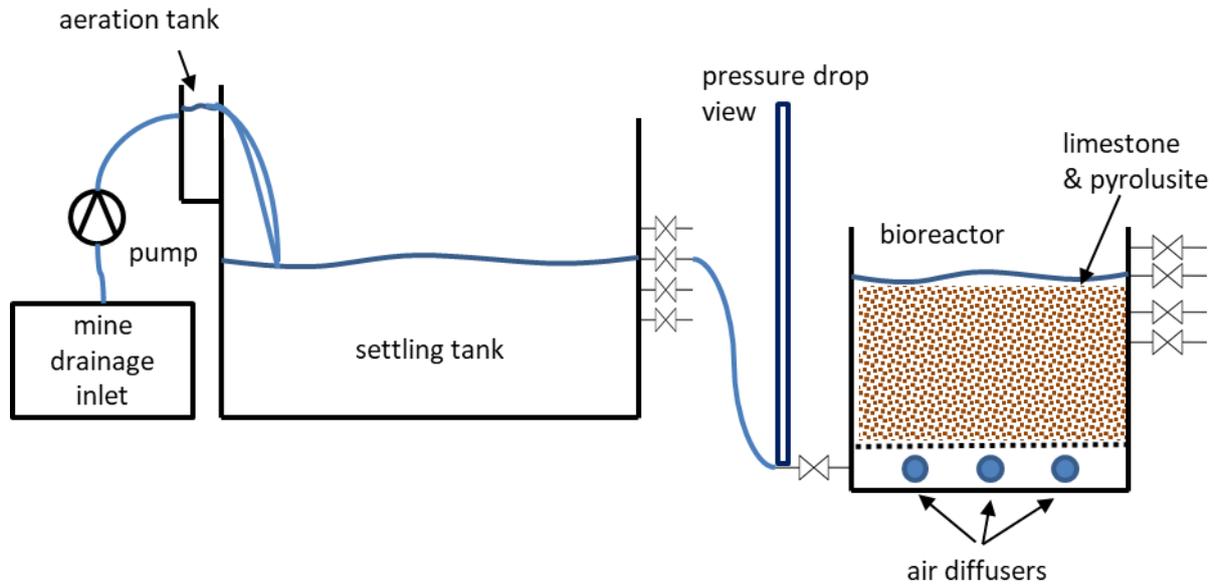


Figure 1 Sketch diagram of the pilot plant

The aeration tank was a 7 L tank with a V-notch weir placed 0.5 m above the settling tank. The settling tank was made from a 2 m<sup>3</sup> polyethylene water transport tank (1.54 m × 2.23 m). Four outlets were created to modify the tank's volume: 750, 900, 1050 or 1200 L. The settling tank was raised 0.8 m above the bioreactor to feed it by gravity.

The fixed-bed bioreactor was made from a 1 m<sup>3</sup> PVC Intermediate Bulk Containers (1.0 m × 1.2 m). The design of this bioreactor enables four water volumes: 230, 280, 330, and 400 L. The bioreactor was filled with a mix of 91% (m/m) limestone gravel (Milhau Company) and 9% pyrolusite (MnO<sub>2</sub>) sand (Water Concept Company). A small biological inoculum coming from two passive mine drainage treatment plants in which some manganese removal occurs was also added. The particles size of the limestone was 20-40 mm and it was composed of 44% calcium carbonate and 48% dolomite (CaMg(CO<sub>3</sub>)<sub>2</sub>). The particles size of the pyrolusite was 0.3-0.8 mm and it contained 80% of pyrolusite.

Aeration was provided by three EPDM cylindrical air diffusers of 0.75 m placed below the limestone and three air pumps. Three rotameters were used to control the airflow rate. A grid with a mesh of 2 cm × 2 cm was set up between the air diffusers and the fixed-bed to prevent clogging of the aeration system and channelling in the bed. A transparent graduated tube was installed between the tank and the bioreactor to read the water height and therefore the pressure drop.

### 2.3 Investigated conditions

This paper presents the results after 147 days of pilot operation, which covers the period from July to December 2018. During this period, the water volume of the settling tank was set to 1050 L and the bioreactor was set to 350 L. The total airflow rate in the bioreactor was about 1 L.min<sup>-1</sup>.

Three operating conditions were investigated. Condition 1 lasts from day 1 to day 27 with a water flow rate of 7 L.h<sup>-1</sup>. On day 27, the aeration tank was removed and water flow rate was maintained at 7 L.h<sup>-1</sup> until day 76 for condition 2. From day 76 to day 103, water flow rate was 11 L.h<sup>-1</sup>, but on day 103 the water pump broke down and it was decided to change the water flow rate. The results of this period are not significant because it did not last long enough. During condition 3, from day 105 to day 147, water flow rate was 17 L.h<sup>-1</sup>. On day 155, the pilot plant froze due to the cold weather. At 7 L.h<sup>-1</sup>, water residence time is 150 h in the settling tank and 50 h in the bioreactor. At 17 L.h<sup>-1</sup>, water residence time is 60 h in the settling tank and 20 h in the bioreactor. Residence times were calculated taking into account the porosity of the limestone in the fixed-bed bioreactor. A picture of the pilot plant is presented in Figure 2.



Figure 2 Picture of the pilot plant on site

## 2.4 Analytical Methods

Samples were taken and measurements made at the inlet and at the outlet of the settling tank and in the outlet of the fixed-bed bioreactor. During the first two months, measurements were taken every day and samples were taken every two days. After two months measurements and samples were taken every two weeks. pH, redox, and dissolved oxygen were measured using a WTW Multi 3620 with Sen Tix 940, Sen Tix ORP-T900 and FDO925 probes respectively. For each sampling point, two water samples were taken. The first one was immediately filtered using 0.45  $\mu\text{m}$  filters for analysis of dissolved iron and manganese. The second one was not filtered for analysis of total Fe and Mn. All samples were acidified at pH 2 with nitric acid ( $\text{HNO}_3$ ) 67%. Iron concentrations were measured by UV-visible spectrophotometry using FerroVer HACH PERMACHEM REAGENTS containing 10-phenanthroline. Manganese concentrations were measured using HACH PERMACHEM REAGENTS containing Ascorbic Acid. Flow rates were checked using a graduated container and a stopwatch.

## 3 Results

Water in the settling tank and in the bioreactor was always saturated with dissolved oxygen. The aeration tank was not necessary to ensure proper oxygenation. Average dissolved oxygen level in the settling tank was 7.94  $\text{mg}\cdot\text{L}^{-1}$  during condition 1 and 7.80  $\text{mg}\cdot\text{L}^{-1}$  during condition 2.

While the water temperature at the inlet was steady at  $16.2\pm 0.1^\circ\text{C}$ , temperature in the settling tank and in the bioreactor decreased significantly over time. Average temperature in the settling tank was  $25.4^\circ\text{C}$  during condition 1 and  $9.8^\circ\text{C}$  during condition 3. There were very little temperature differences between the settling tank and the bioreactor.

No differences in water level between the upstream and downstream of the fixed-bed bioreactor were observed. The absence of pressure drop in the bioreactor shows that there was very little clogging after 157 days of operation.

The effluent pH increased from 6.33 at inlet to 6.92 in the settling tank during the 3 tested conditions as shown in Figure 3. In the limestone bioreactor, average pH was 7.87 during condition 1, 7.79 during condition 2 and 7.23 during condition 3. The effluent pH increase in the settling tank can be explained by the naturally high alkalinity of the water and the degassing of CO<sub>2</sub> during the aeration (Kirby & Cravotta 2005) according to equation (1).



Increase of pH between the settling tank and the bioreactor is obviously due to the limestone filling. The decrease of pH in the bioreactor over time can be explained by the armoring of limestone by manganese-oxide and the decrease of water retention time between condition 1 and 3.

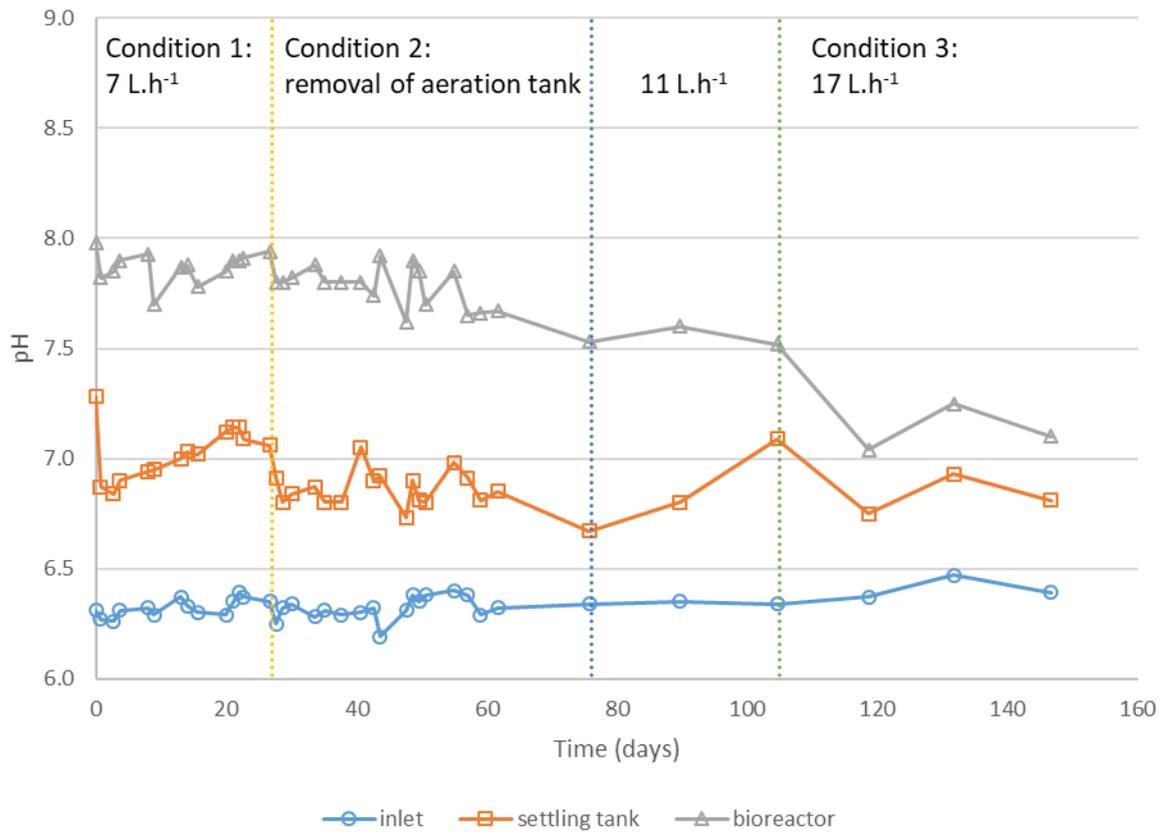


Figure 3 pH in the pilot plant

Figure 4 shows that the removal of the aeration tank did not affect iron concentration in the settling tank. However, it is apparent that at 17 L.h<sup>-1</sup> iron concentration increases in the settling tank up to 7 mg.L<sup>-1</sup>. This result suggests that the residence time is no longer sufficient to remove all dissolved iron. During the entire pilot operation, iron concentration in the bioreactor remained very low.

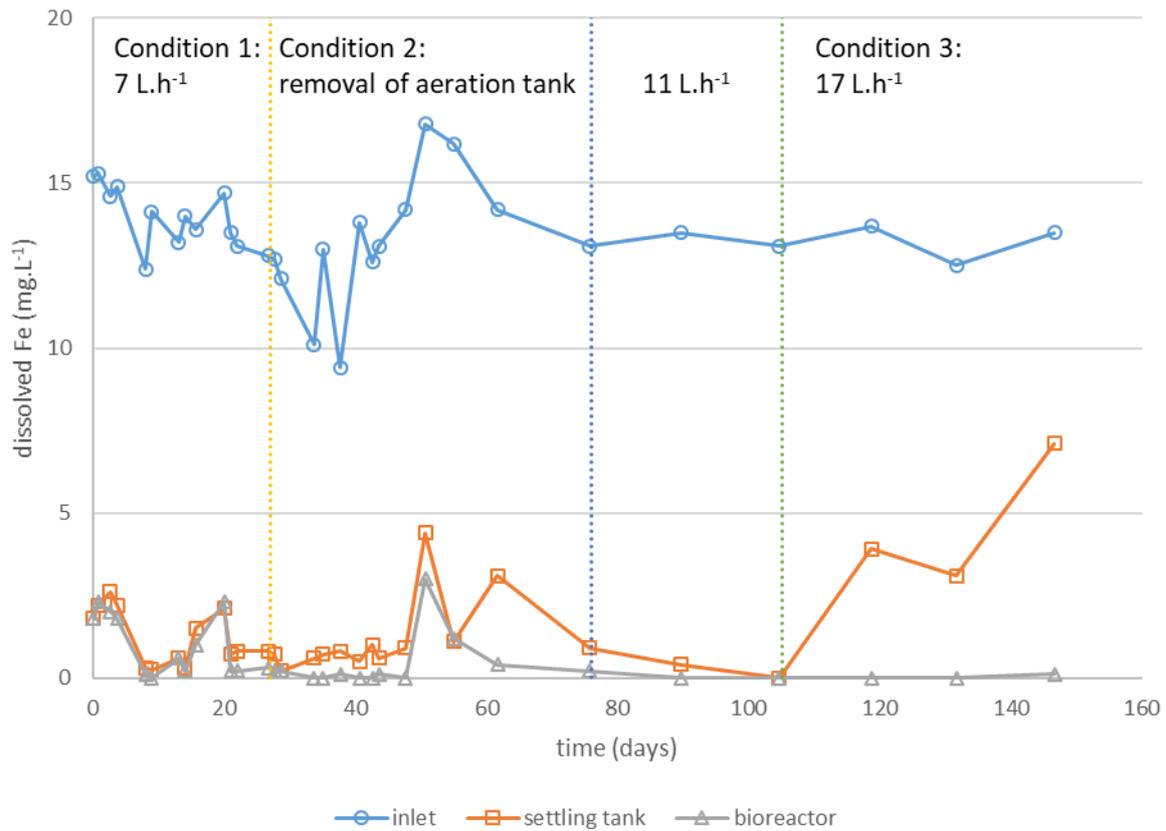


Figure 4 Dissolved iron levels in the pilot plant

During conditions 1 and 2, manganese concentration decreases from 12 mg.L<sup>-1</sup> at the inlet to 7 mg.L<sup>-1</sup> in the settling tank and to 0 mg.L<sup>-1</sup> in the bioreactor (Figure 5). The removal of the aeration tank did not affect manganese concentration. However, during condition 3 at a water flow rate of 17 L.h<sup>-1</sup>, manganese concentration increased to 10 mg.L<sup>-1</sup> in the settling tank and to 2 mg.L<sup>-1</sup> in the bioreactor.

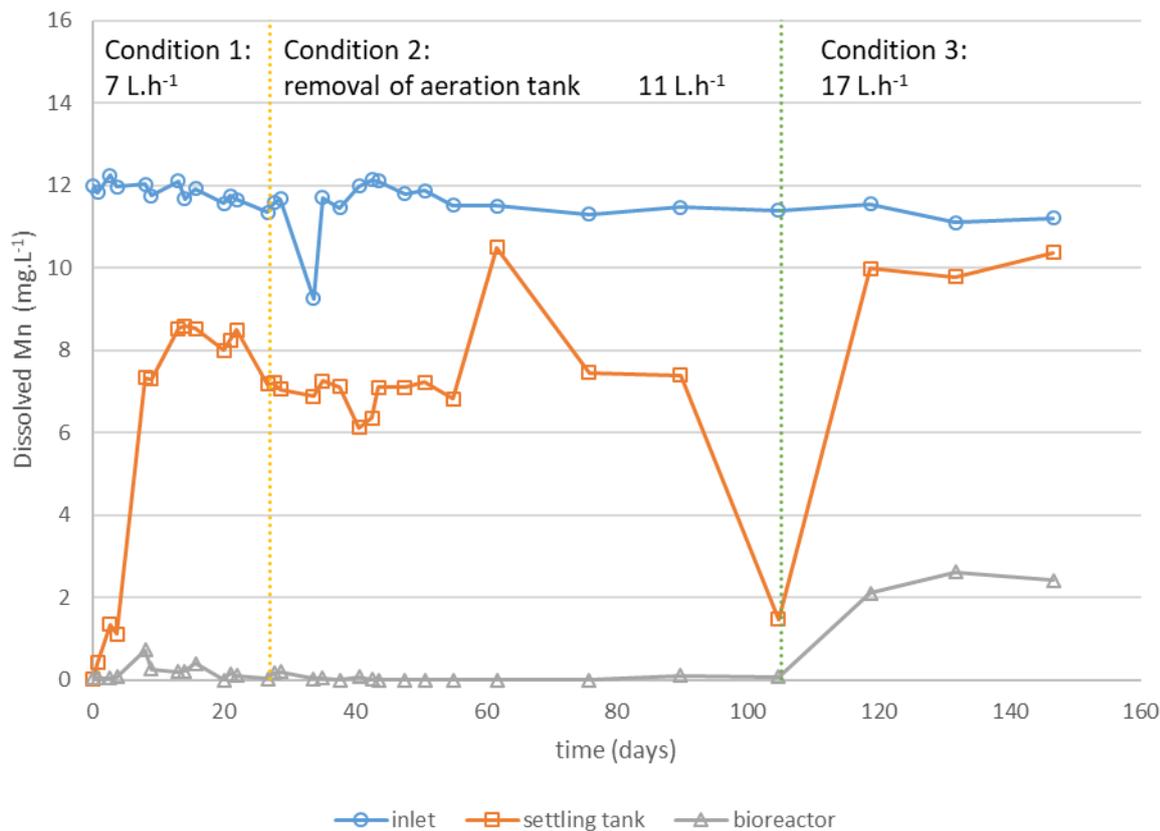


Figure 5 Dissolved manganese levels in the pilot plant

Table 2 summarises the average dissolved iron and manganese removal measured in the pilot plant. The results of conditions 1 and 2 are closely matched. As expected based on the kinetics measured at laboratory scale (data not shown), residence time in the settling tank was sufficient to remove most of the iron (90%). However, the significant manganese removal in the settling tank (38%) was surprising. The complete removal of manganese in the bioreactor indicates that the residence time was longer than necessary. These results suggest that the bioreactor performances are better than expected or it can be due to the significant and unexpected removal of manganese in the settling tank. During condition 3, iron removal decreased to 65% in the settling tank, but iron was still fully removed in the bioreactor. Manganese removal in the settling tank decreased significantly to 11%, however, did not reach 0%. In the bioreactor, manganese removal decreased to 76%, which means that the residence time was no longer sufficient to treat the remaining iron and the manganese.

Table 2 Average dissolved iron and manganese removal in the settling tank and the bioreactor during the pilot experiment

Parameter	Units	Condition 1	Condition 2	Condition 3
Fe removal in settling tank	%	93	90	65
Mn removal in settling tank	%	38	38	11
Fe removal in bioreactor	%	-	-	100
Mn removal in bioreactor	%	97	100	76

## 4 Discussion

Iron and manganese removal rates in the pilot were calculated for each condition and they are presented in Table 3. The iron removal rate increased from 85 to 135  $\mu\text{g}\cdot\text{L}^{-1}\cdot\text{h}^{-1}$  between conditions 1 and 3 because iron oxidation rate follows first order kinetics with respect to  $\text{Fe}^{2+}$  concentration (Morgan and Lahav, 2007). During condition 3, iron removal rate was much more important in the bioreactor than in the settling tank because pH was higher and because limestone retained iron oxides solid phases, which promote the quick heterogeneous oxidation of iron (Sapsford et al. 2007). In this context of limited surface area, the use of a settling pond to treat iron should be carefully considered, although this solution is very traditional, easy to implement and to maintain.

Manganese oxidation can occur at a pH of 6 to 9 (Sikora et al. 2000), but the reaction must be catalysed by manganese oxide precipitates via heterogeneous oxidation (Stumm and Morgan, 2012), and/or by microorganisms (Bender et al. 1994). The settling tank does not contain solids with large surface area to fix microorganism or manganese oxides. However, although manganese removal speed in the settling tank was low (30  $\mu\text{g}\cdot\text{L}^{-1}\cdot\text{h}^{-1}$ ), it remained significant since it allowed the removal of 38% of manganese in condition 1 and 2. It is possible that a population of planktonic microorganisms established in the pond and a biofilm may have covered the tank surface. Microbiological sampling and analysis will be conducted to investigate this hypothesis. In any case, these results show that the treatment of iron and manganese in the same pond is possible if the residence time is long enough.

The manganese removal rate in the settling tank decreased from 30 to 20  $\mu\text{g}\cdot\text{L}^{-1}\cdot\text{h}^{-1}$  between conditions 1 and 3, which means that the decrease in manganese removal in the settling tank is not only a consequence of the decrease in residence time. It may also be explained by the increase of  $\text{Fe}^{2+}$  concentration in the settling tank to 5  $\text{mg}\cdot\text{L}^{-1}$ . Ferrous iron is known to limit manganese removal by reducing oxidised manganese precipitates back into soluble Mn(II) (Hedin et al. 1994, Burdige et al. 1992).

The manganese removal rate increased from 142 to 358  $\mu\text{g}\cdot\text{L}^{-1}\cdot\text{h}^{-1}$  between conditions 1 and 3. Since the bioreactor can no longer treats all manganese, this removal speed could be considered as an optimum. However, this is still much lower than the speeds reported on a similar set-up by Johnson and Younger (2005) (2500  $\mu\text{g}\cdot\text{L}^{-1}\cdot\text{h}^{-1}$ ) or by Duarte and Ladeira (2011) (30300  $\mu\text{g}\cdot\text{L}^{-1}\cdot\text{h}^{-1}$ ). In our experiment, the bioreactor also received and treated some iron during condition 3. Thus, manganese removal rate in the bioreactor may be even faster without the adverse effect of ferrous iron.

Table 3 Average iron and manganese removal rate in the settling tank and the bioreactor during the pilot experiment

Parameter	Units	Condition 1	Condition 2	Condition 3
Fe removal speed in settling tank	$\mu\text{g}\cdot\text{L}^{-1}\cdot\text{h}^{-1}$	85	82	134
Mn removal speed in settling tank	$\mu\text{g}\cdot\text{L}^{-1}\cdot\text{h}^{-1}$	30	30	20
Fe removal speed in bioreactor	$\mu\text{g}\cdot\text{L}^{-1}\cdot\text{h}^{-1}$	-	-	216
Mn removal speed in bioreactor	$\mu\text{g}\cdot\text{L}^{-1}\cdot\text{h}^{-1}$	142	146	358

## 5 Conclusion

A pilot plant composed of a settling tank and an aerated fixed-bed bioreactor filled with limestone and pyrolusite has been operated for 147 days to treat the neutral mine drainage, rich in iron and manganese, of the closed Burg mine. The removal efficiency reached 100% for both iron and manganese with a water residence time of 150 h in the settling tank and 50 h in the bioreactor. Surprisingly, up to 30% of the manganese could be removed in the settling tank. With a residence time of 60 h in the settling tank and 20 h in the bioreactor, removal rates were 100% for iron and 75% for manganese. Maximum removal rates in the bioreactor were 358  $\mu\text{g}\cdot\text{L}^{-1}\cdot\text{h}^{-1}$  for manganese and 216  $\mu\text{g}\cdot\text{L}^{-1}\cdot\text{h}^{-1}$  for iron. In the settling tank, maximum

removal rate of iron was only  $134 \mu\text{g}\cdot\text{L}^{-1}\cdot\text{h}^{-1}$ . After 147 days of operation, the fixed-bed bioreactor displayed no signs of clogging.

The pilot will continue to be operated for a few months during which several parameters will be studied. The oxygen uptake rate will be determined and the injected gas flow rate will be optimised. The water flow rate will be decreased and the volume of the bioreactor will be decreased in order to remove all iron in the settling tank and assess the optimal manganese removal speed in the bioreactor. The pressure drop in the bioreactor will continue to be monitored and the sludge from the settling tank will be characterised at the end of the pilot study. A variant of the bioreactor based on a wetland type design to oxygenate the waters with plants growing on a substrate similar to bed of the bioreactor will also be assessed in parallel.

Finally, all results will be integrated in the design of a real-scale treatment scheme.

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