In Situ Treatment of Acid Mine Drainage by Sulphate Reducing Bacteria [1]

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ABSTRACT

The aim of this in-situ treatment is to use flooded open pits and mine shafts as large reactors to treat AMD with sulphate reducing bacteria. In this treatment method, bacterial growth and metabolism are stimulated directly in the contaminated water body and the mine itself is used as a sedimentation basin for metal sulphide sludge formed by precipitation. In order to promote bacterial growth liquid, manure or other anaerobic sludge is added into the open pit or underground mine.

The study was conducted in the laboratory and two closed mine areas in Finland. First, a series of laboratory tests were done in order to investigate the amount of bacteria needed and the effect of environmental conditions, such as low temperature and available nutrients and organic material in the bacterial activity and treatment efficiency. A full-scale application was started in Kangasjärvi open pit. So far, clear bacterial action has been observed, but the start up of the full scale action requires a few years. The second test site was Kotalahti mine, where the results have been very promising; the pH value of mine water has increased and the metals and sulphate have been precipitated almost completely.

Additional Key Words: sulphate reduction, open pit, mine shaft, liquid pig manure

INTRODUCTION

The mining of metals and coal can produce acidic drainage water that typically contains elevated concentrations of metals and sulphate (Hedin et al., 1994). Discharges from mine sites can harmfully affect the environment in wide areas. Therefore, the treatment of acid mine drainage (AMD) is very important during the mining operations as well as after the closure. Treatment of these wastewaters has traditionally included the addition of alkaline materials to promote increase in pH and precipitation of metals as hydroxides or carbonates (Ledin and Petersen, 1996). However, chemical treatment has high operational costs and produces large quantities of bulky sludge with high concentrations of harmful substances (Gazea et al., 1996). Therefore, alternative biological treatment methods have been developed. One of these methods includes in situ treatment in an open pit or an underground mine.

The aim of the treatment is to use flooded open pits and mine shafts as large reactors to treat AMD with sulphate reducing bacteria (SRB). SRB are a diverse group of anaerobic microorganisms that can anaerobically reduce sulphate to sulphide, followed by the reaction of sulphides and metal ions to produce relatively stable metal sulphides

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(Cocos et al., 2002. Sulphate reduction also consumes hydrogen ions (H^+) (Kalin et al., 2006) and neutralises water with bicarbonate alkalinity produced by microbial metabolism (Dvorak et al., 1992). In this treatment method, bacterial growth and metabolism are stimulated directly in the contaminated water body and the mine itself is used as a sedimentation basin for metal sulphide sludge formed by precipitation. In order to promote bacterial growth liquid manure or other anaerobic sludge is added into the open pit or underground mine. In the optimal case an active anaerobic sulphate reducing population is formed to the bottom of the pit and the pit begins to function like many natural anaerobic aqueous environments (Riekkola-Vanhanen and Mustikkamäki, 1997).

MATERIALS AND METHODS

Test water

Both artificially contaminated water and natural mine water were used as a test water. The composition of artificial water was chosen in order to mimic conditions in Kangasjärvi open pit whereas natural mine water was gathered from Hammaslahti open pit (Table 1).

Table 1. Composition of artificial and Hammaslahti mine water

	pH	Zn (mg/l)	Cu (mg/l)	Fe (mg/l)	Al (mg/l)	Mn (mg/l)	Mg (mg/l)	SO_4 (mg/l)
Artificial AMD	3.7	91	2.5	20	-[a]	5.9	197	960
Hammaslahti AMD	3.4	1.5	-	5.3	5.3	2.3	39	880

[a] Not analysed

Source of bacteria

In this study, liquid pig manure was used as a source of SRB. Manure has been previously shown to be an efficient inoculum of SRB (Riekkola-Vanhanen and Mustikkamaki, 1997). The average C:N:P-ratio of the manure was 100:16:3. This is close to the optimum ratio for SRB of 100:7:1 (Cocos et al., 2002).

Analytical methods

The redox potential was measured with a platinum electrode using a Pt/H_2 electrode as reference. pH was measured using pH meter (pHM240 pH/Ion meter). Metal analyses were made with inductively coupled plasma atomic emission spectroscopy (ICP-AES) and sulphate was analysed with ion chromatography (IC).

Batch tests

The first series of laboratory scale batch tests were run for 4 weeks in 250 ml Erlenmyer flasks. The bottom of the flasks was filled with glass beads. Artificial or natural mine water was added to the flasks and purged with nitrogen. Eight series of tests were run for both waters in order to evaluate the separate effects of bacterial source, nutrients and organic carbon on the sulphate reduction. The experimental conditions were as follows:

(1) Tests with bacterial source: For the four tests, liquid pig manure of 6.4 % (v/v), 13 % (v/v), 26 % (v/v), or 51 % (v/v) was added.

(2) Tests with bacterial source and nitrogen or phosphorus addition: 13 % (v/v) of liquid pig manure was added to the flasks and supplemented with 0.4 % (w/v) of $(NH_4)_2SO_4$ or $K_2HPO_4 \bullet 3H_2O$.

(3) Tests with bacterial source and organic carbon addition: 13 % (v/v) of liquid pig manure was added to the flask and supplemented with 0.4 % (w/v) ethanol.

(4) Blank tests: Tests were carried out without bacterial source, nutrients and ethanol.

Flasks were sealed and placed in an anaerobic container. Samples were taken at the beginning and end of the experiment for analysis of pH, redox potential, and to determine dissolved metal and sulphate concentrations.

Cylinder tests

A second series of tests were run in Plexiglas cylinders which imitate the conditions in open pits. Cylinders were narrow (diameter 5 cm) and 1.5 meter high. Cylinders were filled with AMD from Hammaslahti mine (Table 1). Based on the batch tests results, 6.4 % (v/v) of pig manure was added to three cylinders. One of the cylinders contained less bacterial source (0.2 % (v/v) of pig manure) to see whether sulphate reduction will start in these conditions. One of the cylinders that contained higher amount of manure was kept at 4ºC whereas other cylinders were in room temperature (22±2ºC). The effect of higher pH on sulphate reduction capacity was studied in one of the columns by adding of 0.3 % (v/v) of NaOH prior to manure addition. Tests were run continuously for 164 days. At the end of the experiment samples were taken from the bottom of each cylinder for microbial analysis.

Full-scale tests in flooded open pits and mine shafts

The first test site was Kangasjärvi open pit, which is located in the middle of the Finland. It is 55 m deep and its water volume is 260 000 m^3. Mine was closed in 1985 and is now filled with water. The zinc and sulphate concentrations of the AMD are elevated and water pH is very low (below 4.0). A full-scale in-situ treatment experiment was started in Kangasjärvi in the summer 2005 when 460 m^3 of liquid pig manure was brought to the open pit. Amount of the added manure was calculated based on the sulphate concentration of the mine water.

The second test site was Kotalahti mine, where Outokumpu Oy started to examine the applicability of SRB in the treatment of acid mine drainage in 1996. At that time, silage press-juice and liquid pig manure were added to the mine shaft to create optimal growth conditions for SRB. Kotalahti mine is nearly 800 meters deep and the total water volume is almost 3.5 million m^3. The nickel and sulphate concentrations are elevated, and water pH is close to neutral (6.5).

RESULTS

A series of laboratory tests were conducted in order to investigate the amount of bacteria source needed for the successful treatment and the effect of environmental conditions, such as low temperature and available nutrients and organic material in the bacterial activity and treatment efficiency. Treatment method was then tested in full-scale in two closed mine sites in Finland.

Batch tests

The neutralisation capacity of liquid pig manure was determined with pH measurement. The pH increased approximately 4 units from 3.7 or 3.4 to 7.0 in inoculated flasks, indicating that microbial metabolism is responsible for alkalinity production. Redox potential was used to determine if preferable sulphate-reducing conditions of -100 Pt/H_2 mV (-300 mV Ag/AgCl) (Prasad et al., 1999) were reached. At the end of the experiment, the redox potential varied between -41 mV and -566 mV in all the flasks showing that favourable reducing conditions existed.

Aluminium, zinc, iron, manganese and sulphate concentrations were reduced during the experiment. However, sulphate reduction and metal precipitation capacities varied largely between different test conditions. Best metal and sulphate reduction for Hammaslahti mine water was measured in the flask containing 6.4 % (v/v) of pig manure and best reductions for artificial mine water were achieved in the flask containing 51 % (v/v) pig manure. Hammaslahti water contains small amount of naturally occurring SRB, whereas artificial mine water did not contain carbon source or SRB and therefore, a higher amount of pig manure was needed. Addition of nutrients and organic carbon source did not improve the sulphate reduction capacity. This indicates that pig manure contained enough nutrients and organic material to promote bacterial growth.

Batch tests indicated the conditions in which sulphate was reduced and metals precipitated most effectively. By plotting the redox values and metal and sulphate reductions in the same graph (Fig. 1), it can be seen that efficient removal of metals and sulphate as metal sulphides requires highly reducing conditions i.e. redox potential must be less than −100 mV Pt/H_2.

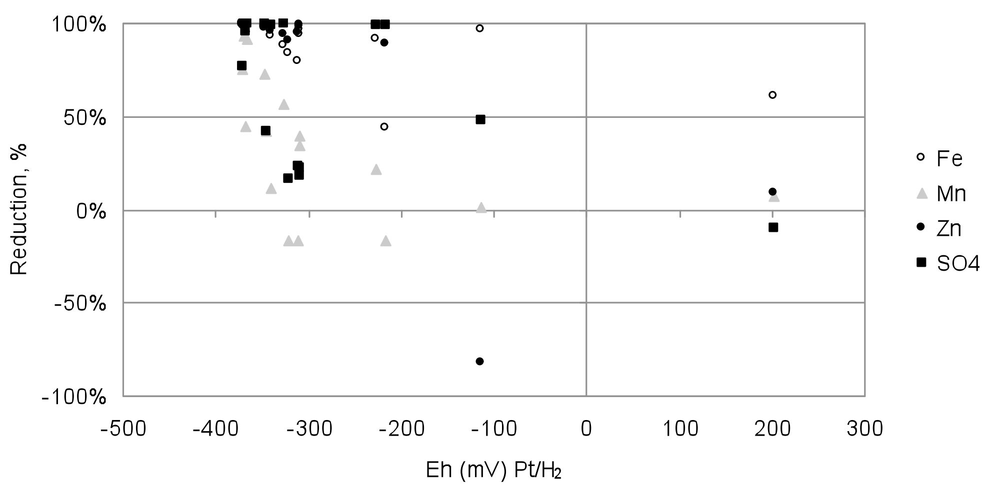

Figure 1. Metal and sulphate reduction vs. redox potential.

Cylinder tests

Redox potential fluctuated throughout the experiment, varying from 65 to -465 mV Pt/H_2 and the conditions for the sulphate reduction were not favourable. However, results indicated that the addition of pig manure decreased the redox potential, metal and sulphate concentrations and increased the pH. No sulphate reduction and metal precipitation was recorded in cylinder containing 0.2 % (v/v) pig manure indicating that the added amount was not large enough to promote sulphate reduction. Moreover, addition of NaOH did not increase the sulphate reduction capacity. Sulphate reduction was significantly slower in the cylinder kept in 4ºC and metal and sulphate concentrations fluctuated significantly. The amounts of SRB varied from $8x10^1$-$1x10^4$ SRB/ml being lowest in the cold cylinder and in the cylinder with 0.2 % (v/v) of pig manure and highest in the cylinder with 6.4 % (v/v) pig manure and no added NaOH.

It can be concluded that liquid pig manure contains enough nutrients and organic carbon to promote bacterial growth and was a very good source of sulphate reducing bacteria. Based on these results it was decided to start a full scale demonstration experiment in Kangasjärvi open pit and continue the ongoing experiment in Kotalahti mine.

Full-scale tests in Kangasjärvi and Kotalahti mines

Zinc, iron and oxygen concentrations of the Kangasjärvi pit water before and after the pig manure addition are shown in the Figure 2. Before the treatment bottom layer of the pit was anaerobic and zinc concentrations decreased with depth indicating that zinc was precipitated as sulphides. Iron concentrations were stable in the upper layers whereas in the bottom of the pit the iron concentration suddenly increased due to the change in redox potential. In the upper layers where the redox potential was over + 300 Pt/H_2 mV iron was precipitated as oxides, but at the bottom of the pit in more reducing conditions, iron was again dissolved.

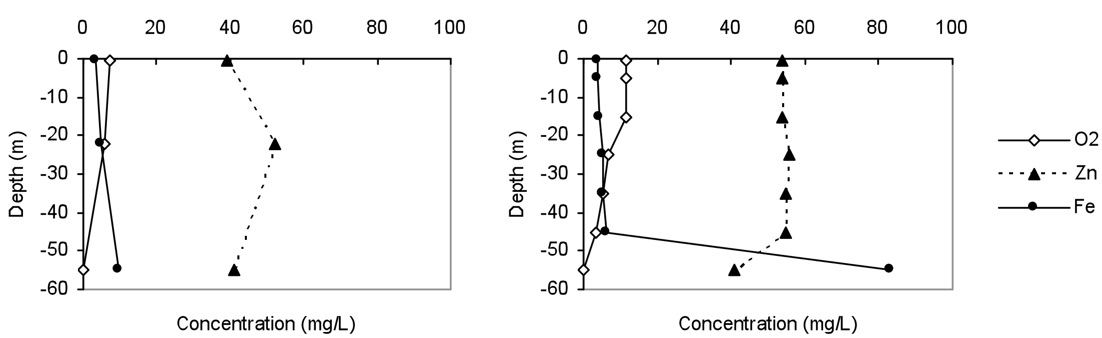

Figure 2. Concentration profiles of the Kangasjärvi open pit water before and after the pig manure addition

After the pig manure addition, concentration profiles changed slightly and zinc and iron concentrations decreased. Still, redox potential was not low enough to promote complete metal precipitation as sulphides. However, results indicated that some bacterial activity can be observed in the pit, but the start up of the full scale action requires a few years.

Silage press-juice effectively removes oxygen from the water and it was used to create optimal conditions for sulphate reducing bacteria in Kotalahti mine. The results obtained have been very promising; the pH value of mine water increased and the metals and sulphate were precipitated almost completely (Fig. 3).

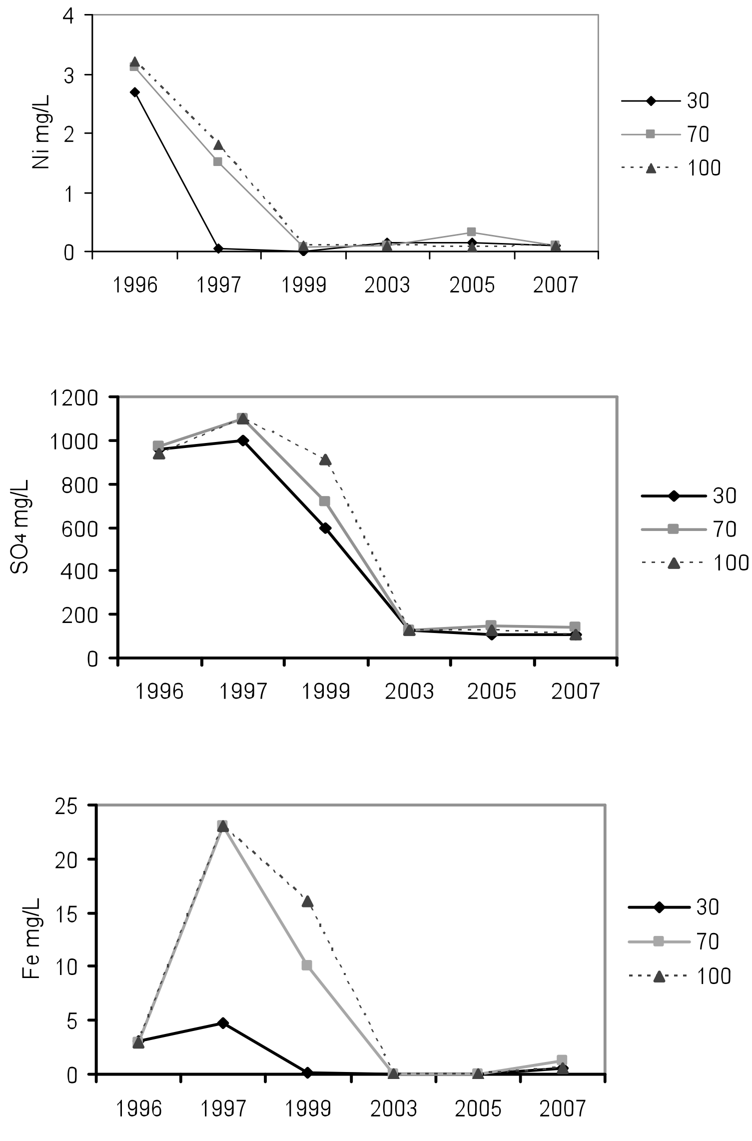

Figure 3. Nickel, iron and sulphate concentrations (mg/L) at different depths in Kotalahti mine.

Concentrations of metals and sulphate started decreasing after a couple years indicating that approximately two years was required until the sulphate reduction process starts and the sulphate concentrations started to decrease. A sharp increase in iron concentration was caused by the ferric hydroxide ($Fe(OH)_3$) dissolution. When highly reducing conditions were achieved, iron was again precipitated as ferrous sulphide (FeS_2) and soluble iron concentration started to decrease.

DISCUSSION

A series of laboratory tests indicated that liquid pig manure was a good source of SRB and contains enough nutrients and organic carbon to promote bacterial metabolism. Manure has been previously shown to be an efficient inoculum of SRB (Riekkola-Vanhanen and Mustikkamaki, 1997). The approximate C:N:P-ratio of the manure is 100:16:3, which is close to the optimal ratio of SRB, 100:7:1 (Cocos et al., 2002). Because manure has high nutrient and organic carbon content, no additional nutrients or carbon source are needed.

Batch tests indicated that adequate manure addition is 6.4 % (v/v). However, in cylinder tests sulphate reduction and metal precipitation rates were considerably slower because of the different test set-up. Oxygen concentration in cylinders was significantly higher than in flasks and optimal reducing conditions were not achieved. It can be assumed that for passive full-scale treatment system sulphate and metal reduction rates are even lower. At least two years start-up period can be expected. Also, extra attention must be paid to the adequate amount of manure addition, which must be calculated based on the sulphate concentration in the water. Moreover, nutrient and organic carbon contents in the AMD must be taken into consideration.

In flooded open pits and mine shafts optimal reducing conditions for SRB can be normally found in anaerobic layers at the bottom. However, temperature at the bottom remains constant at 4°C throughout the year slowing down the bacterial activity. Wildeman et al. (1994) found that even though temperature remained under 10 °C in the passive treatment module, sulphate and metal concentration were still decreasing. Similar results were reported by (Riekkola-Vanhanen and Mustikkamäki, 1997) concluding that sulphate reduction occurred in lower temperatures, but at a slower rate. Sahinkaya et al. 2007a reported that acetate oxidation was found to be the limiting step in ethanol fed FBR operated at 8°C and acetate was accumulating in the reactor. Because ethanol oxidation was incomplete, excess alkalinity must therefore be supplemented to keep the pH neutral. It was also concluded that the sulphate reduction rate is three times and acetate oxidation rate is four times higher at 65°C than at 8°C (Sahinkaya et al. 2007b).

Full-scale tests in two mine sites prove that in-situ treatment of AMD can be effective if certain limiting environmental factors are fulfilled. Conditions in the water must be anaerobic and highly reducing. Enough nutrients and carbon source must be present and the pit or shaft must be deep enough to prevent the temperature stratification between anaerobic and aerobic water layers.

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