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Int. J. Miner. Process. 62 (2001) 309–320

INTERNATIONAL JOURNAL OF
**MINERAL
PROCESSING**

www.elsevier.nl/locate/ijminpro

Bacterial ferrous iron oxidation of acid mine drainage as pre-treatment for subsequent metal recovery

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Received 15 August 1999; accepted 17 July 2000

Abstract

Mining activities at Falu copper mine in Sweden started around the year 1080 AD and continued until 1993. During all these centuries, the acid mine drainage has caused low pH values and high metal levels in the nearby Falu river and its surroundings. This work is part of a plan to achieve a long-term solution to this environmental problem, where the aim is to treat the mine water overflow in such a way that a neutral pH and an essentially metal free aqueous effluent is obtained. The idea is to first oxidise the ferrous iron with bacteria, in order to be able to make a selective ferric iron precipitation at a pH of around 3. One possible process option is to use the precipitated ferric hydroxide for the production of red pigment. Thereafter, zinc will be recovered in such a way that it will be suitable for recycling. In this paper, only the initial stage of bacterial ferrous iron oxidation is discussed.

The ferrous iron oxidation was initially studied in laboratory scale using batch cultures of mesophilic (35°C), moderate thermophilic (45°C) and extreme thermophilic (65°C) microorganisms. The ferrous iron oxidation kinetics was determined with two different concentrations of ferrous iron. The moderate thermophilic culture did not grow well on ferrous iron only. Since the mesophilic and extreme thermophilic microorganisms showed approximately the same oxidation kinetics, the mesophilic bacteria was selected for further studies in pilot scale, due to their lower operating temperature which reduces the heating cost.

A pilot plant was erected at the mine site with three 500 l reactors in series with a treatment capacity of up to approximately 500 l h⁻¹. The reactors were filled with plastic bodies in order to support the formation of a permanent biofilm to avoid bacterial washout. The pilot plant has been operating continuously for several months and the influence of flow rate, ferrous concentration,

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pH and temperature was investigated. The feasibility for a biological ferrous iron oxidation step was successfully demonstrated. With a ferrous concentration of 3.5 g l^{-1} , 35°C , pH 1.8 and a flow rate of 330 l h^{-1} a ferrous iron oxidation rate of $750 \text{ mg l}^{-1} \text{ h}^{-1}$ was achieved. The results obtained will be used to calculate the capital and operating cost for a full scale plant, capable of treating 25 m^3 of acid mine drainage per hour.

Before the final decision, regarding the ferrous iron oxidation step is made, alternative processes such as hydrogen peroxide and ozone oxidation will be evaluated. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: biooxidation; AMD; suspended biofilm carrier; pilot plant

1. Introduction

From records, it is believed that mining at Falu copper mine in Sweden started around 1080 AD, but by modern ^{14}C dating and palynology there are indications that mining might have started as early as 400–800 AD (Eriksson and Qvarfort, 1996). The mining of copper has been of great importance for the Swedish State and copper from the mine in Falun became the basis for the expanding Swedish power from the 14th to the 17th century. After intensive mining for hundreds of years, the “roof” of the mine collapsed in 1687 and a great depression was created, 400 m wide and 150 m deep. Mining continued until 1993 when the mine was finally closed. After closure, the mine started to be filled up with water. Due to the great cultural values at the old mine site, it has been decided that the mine should be preserved for future generations and the mine water is therefore held constant at a certain level in the mine. The flow of mine water will be $25 \text{ m}^3 \text{ h}^{-1}$ with a pH of 2.5 and the average temperature will be 13°C . The expected chemical analysis of the mine water is shown in Table 1.

Since 1987, the mine water has been pumped to a nearby sewage treatment plant where the iron content in the mine water has been used as flocculant at the chemical precipitation stage. The sewage treatment plant has, however, not been working according to design and it has therefore not been possible to treat all mine water produced, causing the water level in the mine to increase. The high amount of metal hydroxides in the sludge causes problems during dewatering. Therefore, can the sludge not be used for other purposes and has to be deposited in a landfill. Another problem at the sewage treatment plant is that the quality of the water produced is not good enough, therefore it has been decided that a biological cleaning stage should be installed at the plant. The high metal content in the mine water is not compatible with a biological treatment step. Therefore, alternative methods for treatment of the mine water have been sought after and bacterial oxidation of ferrous iron was one of the pre-treatment options examined, before the final metal removal or recovery. After iron oxidation has been performed, ferric iron will be precipitated. One possible use of the iron hydroxide precipitate could be for the production of red pigment, which for a long time has been produced in a plant situated close to the mine site. Eventually, the zinc content in the mine water will be recovered, before the remaining metal ions are completely removed by precipitation.

The biological oxidation of ferrous sulphate by acidophilic iron and sulphur oxidising bacteria has been studied extensively and recent reviews exist (Jensen and Webb, 1995;

Table 1

Predicted long term chemical analysis of water from Falu mine (in mg l^{-1})

Fe^{2+}	6700
Fe^{3+}	300
Zn	2200
Mg	3000
Na	800
Ca	400
Al	300
Mn	200
Cu	8
Pb	3
Co	1.2
Cd	1
Sr	0.9
Ni	0.4
Cr	0.25
Li	0.1
B	0.1
As	< 0.5
Ba	< 0.1
Mo	< 0.1
SO_4^{2-}	35000
S	10000
Cl^-	40
Si	35
P	4

Nemati et al., 1998). The most studied species is the mesophilic bacterium *Thiobacillus ferrooxidans*, which has been studied in the temperature range 1–45°C. A number of studies has also been performed for the treatment of acid mine drainage, ranging in size from laboratory scale up to full scale treatment. A rotating biological contactor (RBC) was developed for continuous flow experiments with working volumes up to 4.6 m^3 (Olem and Unz, 1977, 1980). During operation a biofilm is produced on the rotating discs, thereby, a high number of bacteria was maintained in the unit. Real acid mine drainage from a number of mines was studied with influent levels of ferrous iron in the range 32–356 mg l^{-1} . It was concluded that the bacterial oxidation activity could be maintained even at temperatures as low as 0.4°C but with a reduced oxidation rate. The oxidation efficiency was not pH dependent in the pH range from 2.2 to 5.5. The effect of operation parameters on ferrous oxidation in a rotating biological contactor has also been studied with synthetic solutions in a laboratory scale set up (Nakamura et al., 1986). Full-scale treatment plants at Yanahara mine exist in Japan, treating 72 $\text{m}^3 \text{h}^{-1}$ of acid mine drainage containing 2100 mg l^{-1} ferrous iron. Another full scale plant in Japan is located at the Matsuo mine, where bacterial oxidation is used for the treatment of mine water from a closed sulphur-pyrite mine at a flow of 1200 $\text{m}^3 \text{h}^{-1}$ (Imaizumi, 1986). In this plant, diatomite acts as bacterial cell carrier, which is recovered after oxidation and recirculated to the oxidation step.

By oxidising ferrous iron to the ferric form, it is possible to selectively precipitate iron from solution, since ferric iron precipitates at a much lower pH than ferrous iron. Another advantage is that when ferric iron is precipitated, usually at a pH of 2–3, calcium carbonate, which is a much cheaper reagent than calcium hydroxide can be used.

The aim of the research study initiated by StoraEnso Environment, is to find a long-term solution to the acid mine drainage problem, by producing a pH neutral and metal free effluent. In the present work, the initial stage with bacterial oxidation of ferrous iron was studied. The alternative methods of ozone and hydrogen peroxide oxidation will also be evaluated before the final decision of process layout is made. After the iron oxidation step, the ferric iron will be precipitated as hydroxide. One possibility is to use this ferric hydroxide for production of red pigment at a plant located at the mine site. Thereafter, the idea is to recover zinc by ion exchange or by precipitation in such a way that it can be recycled back for metal production. Finally, the remaining heavy metal ions in the mine water will be precipitated so that a metal free and pH neutral effluent is produced.

2. Material and methods

2.1. Microbial cultures

Microorganisms of three different temperature ranges were used. The mesophilic bacteria were maintained at 35°C and contained species like *T. ferrooxidans*, *Leptospirillum ferrooxidans* and *Thiobacillus thiooxidans*. The moderate thermophiles, operating at 45°C, were also a mixed culture containing non-identified ferrous oxidising bacteria and the sulphur oxidiser *Thiobacillus caldus*. The extreme thermophilic microorganisms were a culture of *Sulfolobus metallicus* and was maintained at 65°C. The bacteria were maintained at pH 1.6 on a medium containing sulphur and ferrous iron and before the start of the experiments, the bacteria were sub-cultured for three to five times on ferrous iron only.

2.2. Laboratory scale experiments

The laboratory scale experiments were performed in 1-l glass vessels equipped with small propeller stirrers. Air enriched with 1% CO₂ was bubbled through the solution. The reaction vessels were immersed into a water bath, where the temperature was maintained at the desired oxidation temperature within $\pm 1^\circ\text{C}$ by an immersion heater. Nutrients in all experiments were the iron free 9 K minerals salt medium (Silverman and Lundgren, 1959).

Synthetic acid mine drainage solutions containing ferrous sulphate and zinc sulphate were prepared from chemicals from KEBO Lab AB of purum quality. The pH of the solutions was adjusted to 1.6 with the addition of sulphuric acid. The oxidation of ferrous iron was followed by titration with ceric sulphate with 1,10 phenontraline as

end-point indicator. Total iron concentration was analysed by Atomic Absorption Spectroscopy.

2.3. Pilot scale experiments

The pilot scale experiments were performed at the mine site. A schematic flowchart of the biooxidation process is seen in Fig. 1. Mine water was pumped to a 10 m³ holding tank from which the water was pumped at the desired flow rate through a heat exchanger, where the temperature was raised from 10–12°C to 35°C. The pH in the solution leaving the heat exchanger was adjusted to 1.6 with addition of sulphuric acid, before being fed into the bottom of the first oxidation tank. The oxidation unit consisted of three 500 l tanks in series, where the overflow from one tank was fed into the bottom of the next tank in the series. A suspended biofilm carrier filled the first two oxidation tanks to 50% and the third tank to 40%. The biofilm carrier, Natrix™ (supplied by ANOX AB, Lund, Sweden) was made of high-density polyethylene and was designed to provide a large surface area for bacterial attachment. Air, enriched with 1% CO₂, was added in the bottom of the tanks through a rubber membrane. During the first 90 days, the air flow rate was maintained at 280 l min⁻¹ and was thereafter increased to approximately 600 l min⁻¹. The airflow caused the biofilm carriers to move in the tank, and thereby also served the purpose of mixing. A fluid nutrient solution (Nutriol™ from HydroCare, Landskrona, Sweden) was added at a rate of 360 ml h⁻¹. The fluid nutrient solution with a density of 1.27 kg l⁻¹ contained 22% total nitrogen in the form of urea, ammonia and nitrate and 2.5% phosphorus as phosphate.

During the 4-month period, the pilot plant was in operation, the ferrous iron content in the mine water varied irregularly in the range 0.75–4.4 g l⁻¹, and the pH was between 1.5 and 3.1. The redox potential varied between 340 and 430 mV, depending on the ferrous iron concentration in the water that was pumped from the mine.

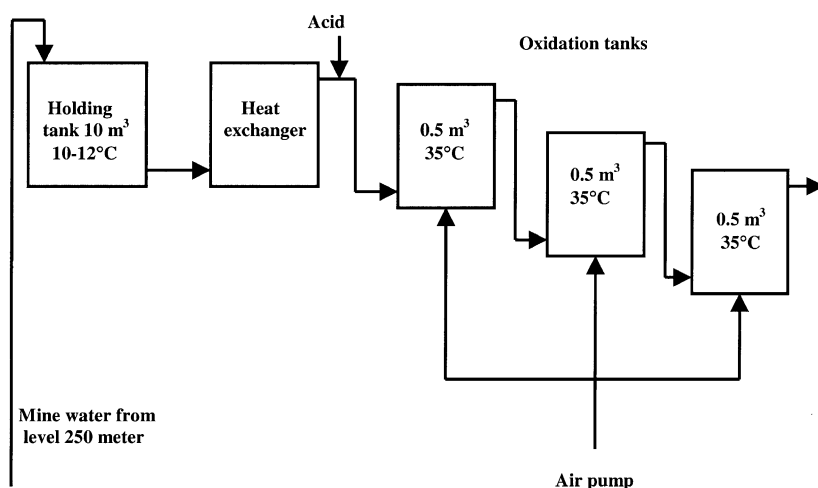


Fig. 1. Principal layout of the biooxidation plant at Falu mine.

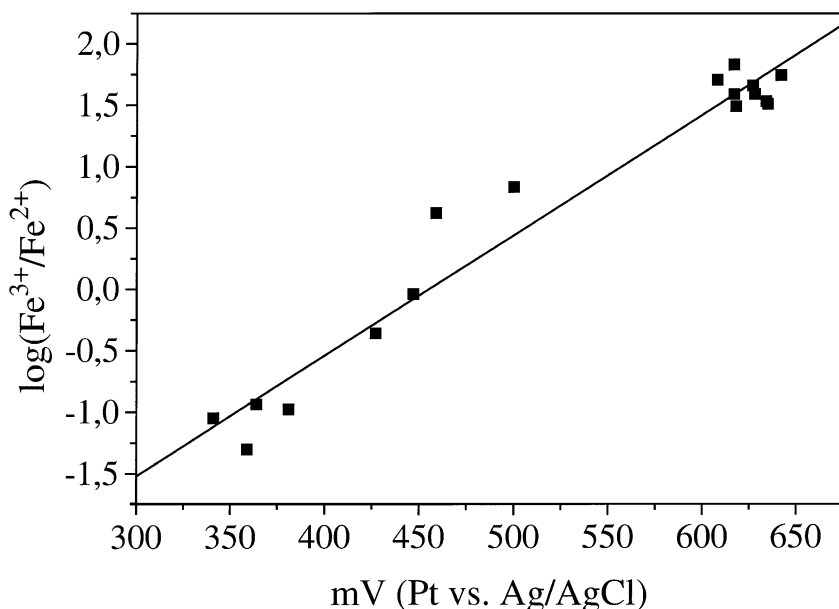


Fig. 2. Redox electrode calibration curve.

The ferrous iron oxidation was followed by measurements of the redox potential with a platinum electrode with an Ag/AgCl reference electrode. Calibration of the redox electrode was made with both synthetic solutions and with oxidised mine water, where the ferrous to ferric ratio was determined by titration. The calibration curve was made with a total iron concentration in the range of 2–4 g l⁻¹ and is shown in Fig. 2.

3. Results and discussions

3.1. Laboratory scale experiments

The initial laboratory scale experiments were performed in order to compare the temperature dependence of the ferrous iron oxidation kinetics. The experiments were performed at 35°C, 45°C and 65°C with the addition of different microorganisms. Three experiments were done at each temperature. Two experiments were performed with 10% inoculum, one with an initial concentration of 2 g l⁻¹ ferrous iron and one with 17 g l⁻¹. An additional experiment with 25% inoculum and 17 g l⁻¹ of ferrous iron was also performed in order to determine the dependence on the initial number of bacteria on the oxidation kinetics. In all experiments, the pH was controlled to 1.6 and the zinc content in the solutions was 4 g l⁻¹.

The oxidation of ferrous iron is acid consuming according to the following reaction.



Due to the hydrolysis of ferric iron, acid is also produced according to reactions (2) and (3).



At higher pH values, ferric iron is further hydrolysed and precipitates from solution as $\text{Fe}(\text{OH})_3$. The hydrolysis of ferric iron is also temperature dependent and at 65°C, in contrast to oxidation at lower temperatures, it was found that some of the ferric iron precipitated. Since the precipitation appeared already at pH 1.6, it was most probably in the form of ammonium jarosite, $\text{NH}_4\text{Fe}_3(\text{SO}_4)_2(\text{OH})_6$. In all experiments pH control was not needed, indicating that the consumption and production of acid is in balance at pH 1.6.

The ferrous iron oxidation experiments were started with a culture that had just completely oxidised a solution containing 10 g l⁻¹ ferrous iron in the 9 K medium, therefore, the lag phase for all types of bacteria was short.

The oxidation kinetics was followed by titration of ferrous iron. The decrease in ferrous concentration with time was linear and the results on the oxidation kinetics are shown in Table 2. From the data, it can be seen that the moderate thermophilic bacteria at 45°C were less efficient in oxidising the ferrous iron. As mentioned earlier, the stock cultures were grown on ferrous iron and elemental sulphur and before the experiments were started the bacteria were sub-cultured on ferrous iron for three to five times. It was found that for each sub-culture of the moderate thermophilic culture, the time needed to oxidise the 10 g l⁻¹ ferrous iron solution was longer. It is therefore concluded that these bacteria need sulphur or sulphides in order to grow and oxidise ferrous iron efficiently. This was not observed for the other types of microorganisms.

The mesophilic culture at 35°C and the extreme thermophilic culture at 65°C produced similar rates of ferrous oxidation, as can be seen in Table 2. The rate of oxidation increased by three times at 35°C and by five times at 65°C with the increase in ferrous iron concentration from 2 to 17 g l⁻¹. For the extreme thermophilic culture, it was found that the dependence of the amount of inoculum on the oxidation rate was minor, while the rate for the mesophilic culture was increased by 61%.

During bioleaching of sulphide minerals in stirred tank reactors, cooling is needed due to the exothermic sulphide oxidation reactions. This is not the case for oxidation of ferrous iron, where the heat released during oxidation not is sufficient to maintain the

Table 2
Rate of ferrous iron oxidation in batch experiments

Temperature °C	Rate (mg l ⁻¹ h ⁻¹)		
	Fe ²⁺ = 2 g l ⁻¹ 10% inoculum	Fe ²⁺ = 17 g l ⁻¹ 10% inoculum	Fe ²⁺ = 17 g l ⁻¹ 25% inoculum
35	64	178	286
45	(24)	(95)	(83)
65	45	230	261

desired temperature. Therefore, it was decided to carry on the investigation with continuous experiments in pilot scale using the mesophilic culture, since that reduces the heating costs. A short retention time is also necessary in order to reduce the plant size and thereby the cost. It was finally decided that the pilot plant should be operated as a suspended carrier process, in order to avoid bacterial washout from the tanks.

3.2. Pilot scale experiments

During construction of the pilot plant, inoculum was sent to the mine site so that a sufficient amount of inoculum could be built up by the personnel at site. At start up, the first tank in the pilot plant was inoculated with 50 l of bacterial solution. The volume was then gradually increased in batch mode operation until all tanks in the pilot plant were filled and the bacteria had attached to the suspended carrier. Continuous feeding was then initiated at a rate of 120 l h^{-1} .

In Figs. 3 and 4, the variation of ferrous iron concentration in the feed and the redox potential in the third oxidation tank during the campaign are shown. In Fig. 4, the mine water flow rate to the oxidation plant is also shown as an inset. As can be seen in the figures, the redox potential was maintained rather stable initially at a level of approximately 475 mV, whereas at the same time the ferrous content in the feed was gradually increasing from 2 to 4.4 g l^{-1} . After 25 days, there was a sudden decrease in ferrous concentration down to 0.75 g l^{-1} , resulting in a sharp increase in redox potential up to 650 mV. By comparing the two figures, it can be seen that the redox potential responded quickly to changes in flow rate and ferrous content. An increase in flow rate resulted in a decrease in the redox potential, which in a few days again reached levels around 650

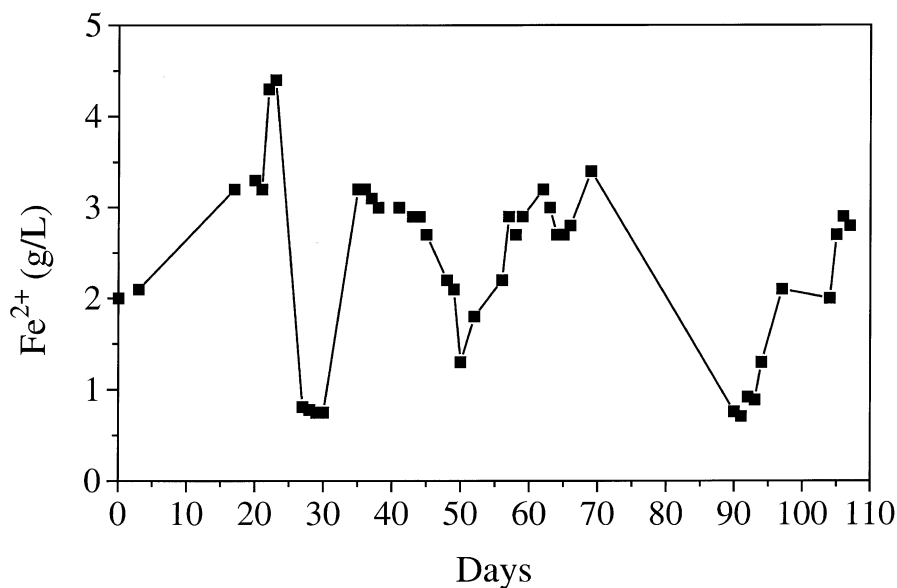


Fig. 3. Variation in ferrous iron content during the pilot campaign.

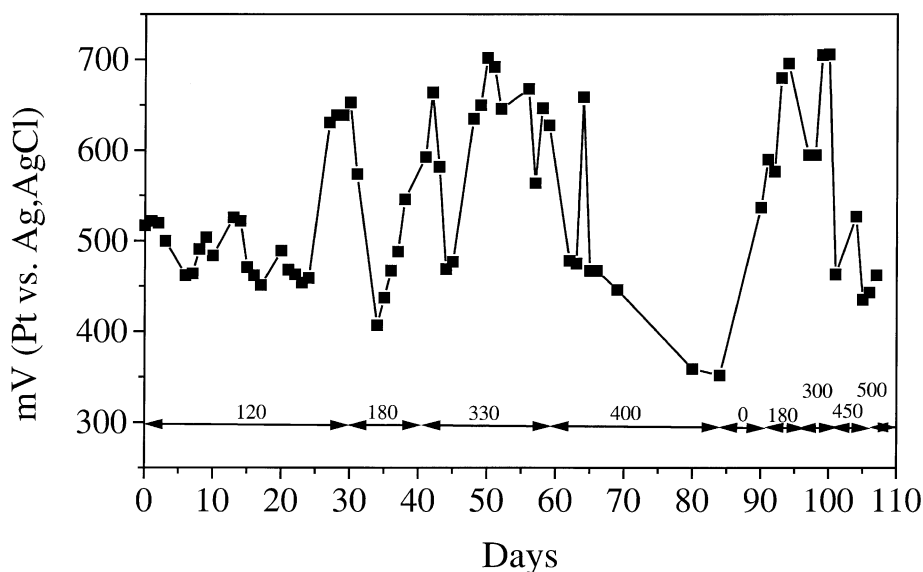


Fig. 4. The redox potential measured in the third tank during the continuous run.

mV. The pilot plant operated very efficient during the period from day 30 until day 67 when the acid in the storage tank was emptied. The fact that the storage tank for acid was empty was not observed for more than a week, and feeding of the pilot plant continued for more than a week at a rate of 400 l h^{-1} , which resulted in almost a complete loss of oxidation. However, when the pH in the oxidation tanks was restored and the flow of fresh mine water to the reactors was stopped, with internal circulation within the oxidation tanks, the oxidation of ferrous iron started quickly again. It should be mentioned that after 110 days, a number of mechanical problems associated with pumps and air supply appeared. Despite this, the activity of the bacteria and the ferrous iron oxidation rates were quickly restored.

The percentage of the ferrous iron that was oxidised to the ferric form was calculated with the aid of the redox electrode calibration curve and is shown in Fig. 5. As can be seen from this figure, a high degree of ferrous iron conversion was obtained at times of stable operating conditions. Based on the feed rate and the degree of ferrous conversion, the ferrous iron oxidation rate was calculated and is shown in Fig. 6. The highest rates of oxidation, $700\text{--}750 \text{ mg l}^{-1}$, were obtained during the period from day 55 to day 67 with a feed rate of 330 l h^{-1} and a ferrous content of approximately 3 g l^{-1} . It is believed that higher oxidation rates would have been obtained when the feed rate was increased to 400 l h^{-1} if pH was controlled successfully throughout the test period.

During the campaign, there were problems with the heat exchanger on two occasions, on day 44 and on day 57, resulting in decrease in temperature down to 25°C . These problems were however overcome within 1–2 days on both occasions. The decrease in temperature resulted in an immediate decrease in the ferrous iron oxidation activity.

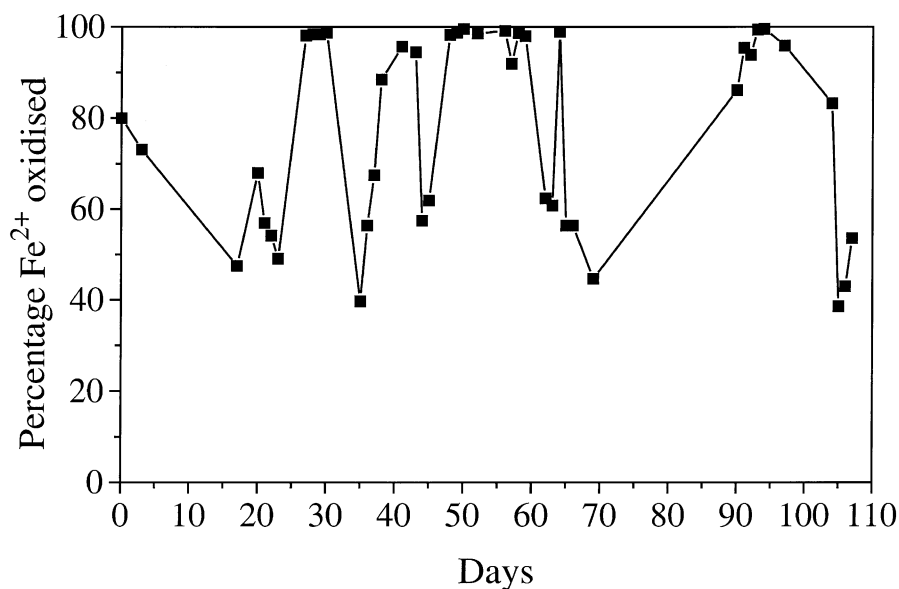


Fig. 5. Percentage of the ferrous iron oxidised during the campaign.

When the temperature control was restored, the bacteria regained the activity quickly and high redox potential was recorded. As mentioned in the introduction, it has been reported (Olem and Unz, 1980) that fast oxidation kinetics were also obtained at low

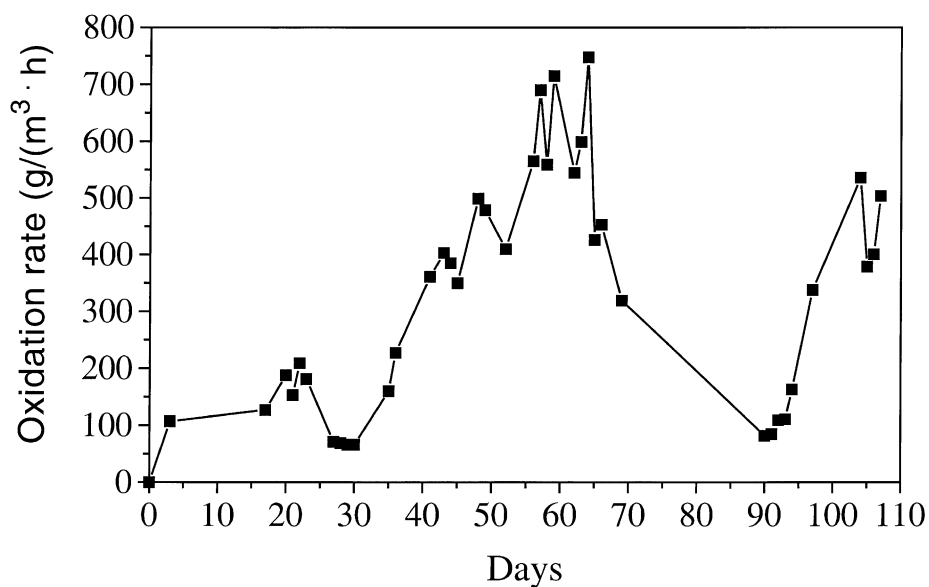


Fig. 6. Ferrous iron conversion rate during the campaign.

temperatures. It might be possible, that if the bacteria had been allowed to adapt to lower temperatures for some time, good oxidation rates would also have been obtained at 25°C or even lower temperatures.

Clogging problems in the reactor tanks and in the overflow pipes were also encountered due to precipitation, when pH control was inefficient. The composition of the precipitate was determined with X-ray diffraction, which showed that it consisted mainly of jarosite. These problems were encountered when pH in the oxidation tanks was 2 or higher.

During the pilot plant campaign, successful bacterial oxidation of mine water has been achieved under the following conditions.

Ferrous concentration	3.5 g l ⁻¹
Retention time	3.6 h
pH after oxidation	1.9
Temperature	35°C

The consumption of sulphuric acid and nutrient solution per kg of ferrous iron oxidised was 0.5 and 0.2 l, respectively. No attempt to optimise the nutrient addition has been made. The energy needed for aeration was 1 kW h per kg of iron oxidised. Based on these figures and mine water flow of 25 m³ h⁻¹ with the composition given in Table 1, the following yearly consumption can be calculated.

Sulphuric acid	734 m ³ year ⁻¹
Nutrient solution	293 m ³ year ⁻¹
Energy	1467 MW h year ⁻¹

It is probable that the energy consumption will be lower in a full scale plant, because the increased height of the oxidation tanks will increase the oxygen utilisation efficiency, due to the longer retention time of the air bubbles. Since the expected ferrous iron content in the mine water, as seen in Table 1, will be higher than that used in the pilot plant, the retention time has to be increased accordingly. The great variation in ferrous ion content in the feed should also be considered in a continuous full-scale operation. In order to achieve a complete conversion to ferric ions, it is probably necessary to have a variable retention time in the oxidation tanks with a longer retention time during periods of high ferrous content. The most convenient way to control the process is probably to vary the feed rate depending on the redox potential in the oxidation tanks.

4. Conclusions

The oxidation kinetics of ferrous iron using a mesophilic culture at 35°C and an extreme thermophilic culture at 65°C in stirred suspended-cell batch reactors gave similar results. The moderate thermophilic culture used did not grow well on ferrous iron only.

The suspended carrier process for bacterial oxidation of ferrous iron has been proven to be technically feasible. The process was easy to operate and during the pilot plant campaign, only some minor technical problems were encountered. The bacterial activity was easily restored after disturbances in control of pH and temperature. With mine water containing approximately 3.5 g l^{-1} ferrous iron, a retention time of 3.6 h is considered sufficient for complete conversion of the iron into the ferric form.

The major drawbacks for the process involving bacterial oxidation of mine water from Falu mine is the extremely high levels of ferrous iron. When the water level in the mine is held constant, the expected ferrous concentration is 6.7 g l^{-1} . The high iron content requires a longer retention time for complete oxidation of the ferrous iron. The consumption of sulphuric acid in order to control pH was also relatively high.

The alternative methods of ferrous oxidation with the use of hydrogen peroxide and ozone will be evaluated also before the final decision on oxidation process is made. Independent of which oxidation process is chosen, further work on down stream processing has to be done. Work on selective precipitation of ferric iron and the possibility to use the precipitate for production of colour pigment is under progress. Finally, methods for separation of zinc and the precipitation of other elements have to be investigated.

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