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Technical Article

Chemical and Biological Oxidation of Iron in Acid Mine Water

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Abstract. Prior to limestone neutralization of acid water, ferrous iron needs to be oxidized to prevent downstream oxidation and the formation of acid. This study assessed the effect of various parameters on the biological and chemical rate of iron oxidation, both chemically and biologically. In batch experiments, it was found that although the use of support media had no effect on the chemical iron oxidation rate, it was important when iron was oxidised biologically. Under continuous flow conditions, the highest oxidation rate occurred when the initial Fe (II) concentration was between 4.5 to 4.8 g/L, geotextile was used as the support medium, and when nutrients were added to the reactor. The optimal iron oxidation rate was achieved at a hydraulic retention time of 8 h. The chemical iron oxidation rate depends on the concentration of suspended $Fe(OH)_3$ and $CaSO_4$, which act as catalysts. The biological iron oxidation rate was dependent on the bacterial growth, which was influenced by several parameters (support media, nutrients, CO_2, and oxygen).

Key words: acid mine water; biological iron oxidation; chemical iron oxidation; iron (II); iron oxidizing bacteria; oxidation rate

Introduction

A practical method of neutralizing acid mine drainage (AMD) with limestone has been developed and is being commercially applied in South Africa (Maree et al. 1992). Neutralization of AMD with limestone requires that ferrous iron, Fe(II), in the water should first be oxidized to Fe(III); otherwise, the oxidation and hydrolysis will occur downstream of the neutralization plant, producing acidity (Maree et al. 1997). Iron can be oxidized to Fe(III) chemically and biologically.

Biological oxidation is catalysed by iron-oxidizing bacteria, such as *Thiobacillus ferrooxidans,* a microorganism that lives in acidic conditions (Nemati and Webb 1996). The aim of this study was to improve Fe(II) oxidation rates by determining the effect of support media, the surface area of the support medium, the number of iterations, initial Fe(II) concentration, nutrients, CO_2, pH, temperature, air flow/concentration, and hydraulic retention time (HRT) on the rate of Fe(II) oxidation.

Materials and Methods

Batch studies were conducted using a synthetic feed solution containing: 4 000 mg/L Fe(II), 40 mg/L P, 20 mg/L Mg, 30 mg/L N, 8 900 mg/L SO_4 and 9 200 mg/L acidity (as $CaCO_3$). Phosphorus and nitrogen were added in the feed water as nutrients for bacterial growth when operating biological Fe oxidation batch studies. Limestone from Springs, South Africa was used for neutralization.

During the continuous studies, AMD from the Toe Seep Dam at the Navigation mine site (South Africa, Witbank) was used as feed water. The Fe (II) concentration was 4.5-5 g/L and the pH was 2.0. Hydroponic nutrients (Kompel Chemicult products) were added to both the synthetic Fe (II) solution and the coal discard leachate.

Figure 1 shows the beaker reactors and stirring mechanisms that were used for the chemical Fe oxidation studies. The solutions and support media in the beaker reactors were stirred continuously and aerated at a flow rate of 3L/min with compressed air through diffusers (porosity no. 2, 210 x 8mm (OD)).

Figure 2 shows the rectangular reactor that was used for the biological Fe (II) oxidation studies. The geotextile sheets used were supported in vertical positions by plastic frames. Compressed air was supplied through diffusers to the reactors at a flow rate of 3L/min for each diffuser.

Different support media (e.g., plastic rings, plastic pellets, coal discard, sand, anthracite, and geotextile) were tested to study the possible increase in the Fe (II) oxidation rate. The plastic rings were cut from pipes of approximately 5 mm diameter. The coal discard (particle size 4 mm) was a coal of inferior quality, obtained from Navigation Mine, and the plastic pellets were made of polyethylene. The sand that was used as a support medium was normal building sand. The anthracite coal had a particle size of 2 mm. Geotextile is a fabric made of synthetic material used in road construction and maintenance. The support media were added into the reactor vessel with the stirring mechanisms. The geotextile was mounted on a perspex plate.

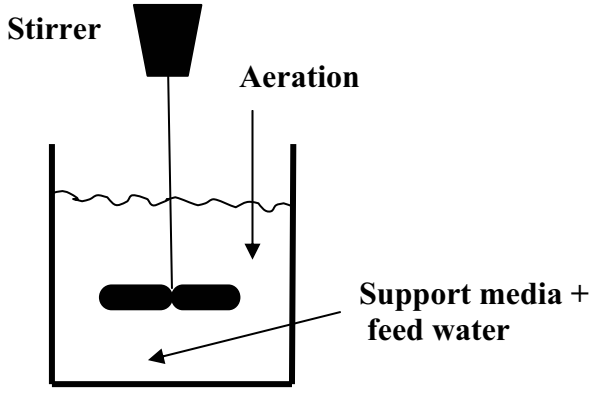

Figure 1. Set -up for chemical iron oxidation studies

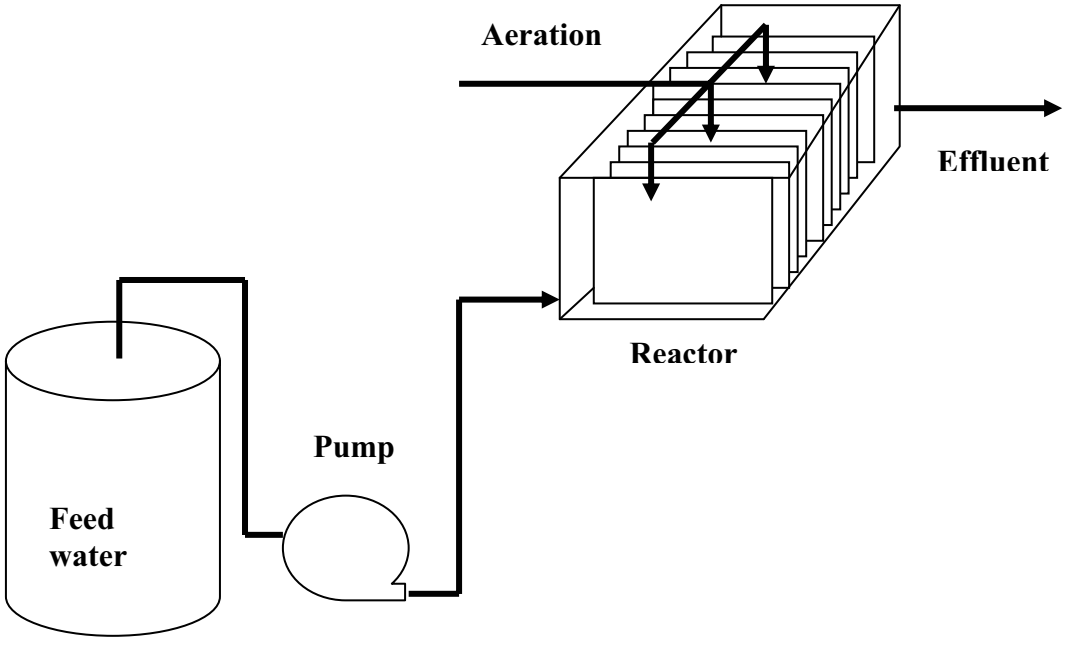

Figure 2. Schematic flow diagram for biological iron oxidation studies

Experimental Procedure

Biological Iron Oxidation

The various reactors were inoculated by adding 5% (vol/vol) AMD from the Navigation Mine to the water in the reactor vessels. Then*:*

- The reactor contents were aerated continuously until the Fe (II) was completely oxidised.
- Aeration was then stopped and the appropriate amount of the Fe (III) containing mixture was replaced with a fresh Fe(II) solution.
- Aeration was restarted and the procedure was repeated.
- Each run was started by mixing treated water from the previous run with feedstock in the ratio 1:1 or 1:4.
- Samples were taken at 30 minutes intervals, filtered and analysed for Fe(II) concentration and pH.

Chemical Iron Oxidation

During the chemical studies, the same procedure was followed as in the biological studies. However, 7.8 g/L $CaCO_3$ was added at the start of each experiment to raise the pH to 6.5 and precipitate $Fe(OH)_3$ and $CaSO_4$. The effects of support media concentration (0, 50, and 100 g/L pellets) and increased iterations (1-6) on the chemical oxidation rate were assessed while holding the temperature, pH, air flow, and initial Fe(II) concentration constant at T = 29º C, pH = 6.5, AF = 3 L/min, and Fe(II) = 2 g/L Fe(II), respectively.

Analytical Procedures

Samples (20 mL) were taken at 30 min intervals and filtered through Whatman No 1 filter paper. The Fe(II) determinations were carried as described by Vogel (1989). A 691 Metrohm meter was use to measure pH. The surface areas of the support media were measured using a BET surface area analyser

(Micromeritics FlowSorb II 2300). Iron oxidation rates were measured at the beginning of the tests for several different initial concentrations of reactants by calculating the initial slope of the curve of iron (II) concentration versus time.

Results and Discussion

Figure 3 shows the experimental results after 6 iterations. When the initial slope was calculated for the graphs in Figure 3, the oxidation rates were 48.9, 44.0, and 50.2 g Fe/(L·d) (d = experimental time in days) using 100, 50, and 0 g/L pellets, respectively. These results showed that the pellets had no significant effect on the Fe oxidation rates.

Figure 4 shows the effect of number of iterations when no support media was used. With one iteration, the reaction time was 6 h; when the iterations increased (2, 3, 4, 5, and 6 iterations), the reaction time decreased (from 4, to 3, to 2.5, to 1.5, and 1.5 h, respectively). As the number of iterations increased, the reaction rates increased from 14.1 to 17.1, 24.6, 29.5, 36.9, and 40.2 g Fe/(L·d), respectively. This increase in oxidation rate can be ascribed to the increase in $CaCO_3$ concentration in the reactor and to the suspended solids ($Fe(OH)_3$) and $CaSO_4$) formed, both of which act as catalysts for the reaction (Maree et al. 1999).

The effect of support media (sand, plastic rings, plastic pellets, coal discard, anthracite, and geotextile), number of iterations (1-10), geotextile surface area, initial Fe(II) concentration (2 to 20 g/L), nutrients (2 mL/L hydroponic nutrient), CO_2, pH (1.7, 2.0, and temperature (25 to 30 ºC) on the biological iron oxidation were assessed (Table 1 to 4). Temperature, pH, AF, and the initial Fe (II) concentration were kept constant at T= 29 ºC, pH = 2.0, AF = 3 L/min, and Fe (II) conc. = 2 g/L respectively, unless otherwise stated.

Table 1 shows the effect of support media on the rate of iron oxidation. It can be noted that the geotextile was the best support media, due presumably to the nature of the textile, which accelerated bacterial adsorption and biofilm formation (a complex, multicellular structure formed when microorganisms attach or colonize to a surface, Nemati and Webb 1999). Due to the porosity of the geotextile, air can penetrate easily into the fibers and, due to its texture, the geotextile provides a large surface area for the bacteria to adhere onto.

Table 2 shows the effect of surface area (using the BET surface analyser) on the rate of iron oxidation relative to the number of iterations, when AMD was used as the feed water and geotextile was used as a support media. The iron oxidation rate increased with

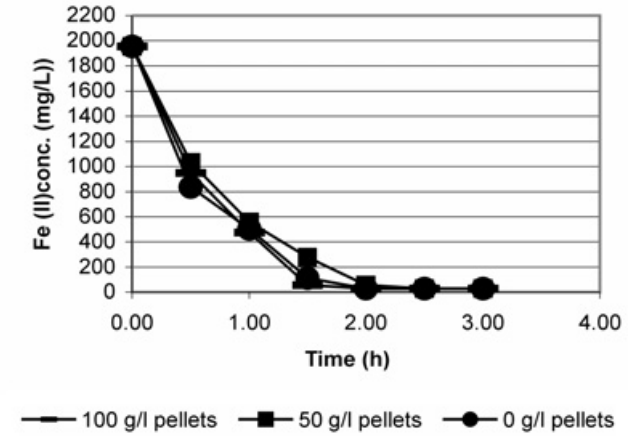

Figure 3. Effect of pellets concentration on the iron oxidation rate

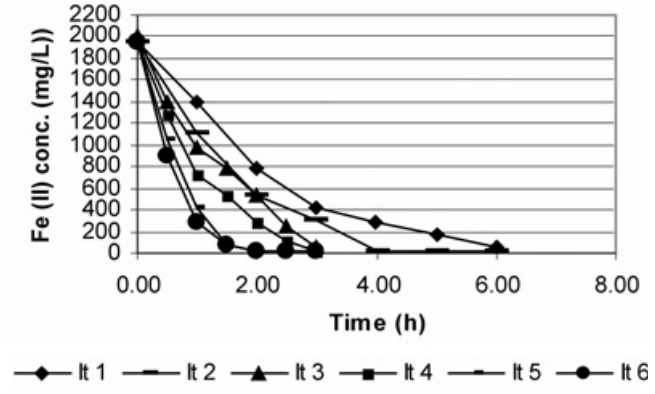

Figure 4. Effect of the number of iterations on the iron oxidation rate

Table 1. Effect of the support medium on the rate of iron oxidation

Support media	Reaction rate g Fe/(L·d)
Control	1.3
Rings	4.1
Pellets	4.7
Coal discard	7.0
Sand	7.7
Anthracite	9.0
Geotextile	18.1

the number of iterations, while the surface area of the geotextile decreased due to the biofilm formation.

Table 3 shows the effect of the initial Fe (II) concentration on the rate of iron oxidation, using artificial Fe (II)-rich water and geotextile as the support medium. When 2 g/L Fe (II) was used, the oxidation rate was 5.4 g Fe/(L·d). Further increases in Fe (II) concentration from 4 to 12 g/L increased the oxidation rates from 9.5 to 27.6 g Fe/(L·d) respectively. Silvermann and Lundgren (1959) reported that the growth of iron-oxidizing bacteria and its ability to oxidize ferrous iron is significantly influenced by the concentration of ferrous iron. Similar observations were reported by Kelly and Jones (1978).

Table 2. Change in geotextile surface area and iron oxidation rate with respect to the number of iterations

Iteration	Fe(II) oxidation Rate (g Fe/(L·d))	Surface area (m^2/g)
1	2.7	2.5
2	3.62	2.3
3	5.89	1.7
4	6.08	1.2
5	7.96	0.9
6	8.38	0.8
7	8.78	0.7
8	9.23	0.6
9	10.03	0.4
10	10.62	0.3

Table 3. Effect of Fe (II) concentration on the iron oxidation rate

Initial Fe (II) concentration (g/L)	Fe (II) oxidation rate (g Fe/(L·d))
2	5.4
4	9.5
8	17.2
12	27.6
16	26.1
20	22.5

Initial Fe(II) concentrations of 12 and 16 g/L gave almost similar results, 27.6 g Fe/(L·d) and 26.1 gFe/(L·d), respectively. However, higher initial Fe (II) concentrations (20 g/L) inhibited the growth of iron-oxidizing bacteria, resulting in a decreased oxidation rate (22.5 g Fe/(L·d)).

Nutrients, CO_2, Air flow, pH and Temperature

Providing nutrients necessary for the growth of bacterial cells (Brock and Madigan 1991) increased the biological Fe oxidation rate (Table 4). The reaction rate was also faster when CO_2 was bubbled through the reactor vessel than when no CO_2 was added. These results support the findings of Nemati and Webb (1998) that iron-oxidizing bacteria need CO_2 as a carbon source for growth. Holuigue et al. (1987) and Barron (1990) demonstrated that the availability of CO_2 is important for achieving optimal growth rates and maximum cell yields. Our results also showed that when more air was supplied, the oxidation rate increased, due presumably to the increased respiration rate of the iron-oxidising bacteria. When more air was supplied, the respiration rate of the biomass increased, resulting in faster iron oxidation rates. The optimum oxidation rate was achieved when the pH was 2.0 and when the temperature was 29 ºC.

Continuous Studies

Further studies were carried out to determine process performance under continuous conditions using AMD as feed water. The results (Table 5) show that when support media was used, the highest oxidation rate was 11.02 g Fe/(L·d); when no support media was used, the highest oxidation rate was 8.30 g Fe/(L·d). It can be concluded that support media are important for the bacteria to adhere onto. It can also be seen that the optimum HRT for the continuous study was obtained at 8 h when geotextile was used as a support media and when nutrients were added. Furthermore, when nutrients were added, the highest oxidation rate was 12.10 g Fe/(L·d); when no nutrients were added, the oxidation rate was slightly lower at 11.02 g Fe/(L·d) (Table 6).

Table 4. Effect of different parameters on the iron oxidation rate

Variables	Value	Fe (II) oxidation rate (g Fe/(L·d)
Nutrients	0 mL/L	5.7
	2 mL/L	8.4
CO_2	0%	4.0
	3%	6.1
Air flow	3 mL/L	10.0
	5.6 mL/L	10.6
	8.9 mL/L	13.9
pH	1.7	15.4
	2.0	20.8
	2.3	11.4
Temperature	25 ºC	6.7
	26 ºC	8.3
	27 ºC	12.1
	29 ºC	15.8
	30 ºC	14.7

Kinetic Studies

The data in Table 6 show the effect of various factors on the kinetics of biological iron oxidation. The slopes of the graphs log R versus log (value of variable) show that the rate of iron oxidation is of order 1, 1, and 0.5 with respect to Fe^{2+}, support media, and O_2 concentration, respectively. These findings suggest that the rate equation for biological iron oxidation should be modified (Maree et al. 1997) for suspensions to:

$$-d[Fe^{2+}]/dt = k[Fe^{2+}]^{1}\cdot[SM]^{1}\cdot[O_2]^{0.5} \quad (5)$$

where $-d[Fe^{2+}]/dt$ = rate of iron oxidation; k = reaction rate constant; $[Fe^{2+}]$ = ferrous iron concentration; SM= reactor surface area; and O_2 = oxygen concentration.

Conclusions

The chemical iron oxidation rate, conducted with an initial pH of 6.5, was increased by: the addition of $CaCO_3$, increasing the number of iterations, and increasing the level of suspended $Fe(OH)_3$ and $CaSO_4$, which acted as catalysts in the reactor vessel. The addition of support medium did not have a significant effect.

Table 5. Effect of the support media and nutrients on the iron oxidation rate

Feed rate (L/d)	HRT (h)	Fe (II) oxidation rate(g Fe/(L·d)		
		No support media	Brown geotextile	Nutrients (2mL/L) & geotextile
15	24.0	4.20	4.20	4.08
20	18.0	6.01	6.37	6.48
25	14.4	7.12	7.33	7.45
30	12.0	7.60	8.66	8.60
40	9.0	8.34	10.98	12.02
45	8.0	8.30	11.02	12.10
50	7.2	5.02	8.46	11.03
55	6.5	4.56	7.37	9.40
65	5.5	3.25	6.35	7.82

Other experimental parameters: Fe(II) concentration of the coal discard leachate varied from 4.5 to 4.8 g/L, pH = 2.0, temperature = 29 ^{0}C and air flow = 3 L/min

Table 6. Effect of various factors on the kinetics of biological iron oxidation

Variable	Conc.	Rate (gFe/(L·d))	Log C*	Log R*	Rxn order
Fe (II) (g/L)	2	5.4	0.30	0.73	1
	4	9.5	0.60	0.98	
	8	17.2	0.90	1.24	
	12	27.6	1.08	1.44	
	16	26.1	1.20	1.42	
Support media (m^2/m^3)	5	4.1	0.70	0.61	1
	10	7.2	1.00	0.86	
	19	10.2	1.28	1.01	
O_2(in air) (mg/L)	0.05	7.8	-	0.89	0.5
	0.5	9.5	1.301	0.98	
	1.0	13.5	-0.30	1.14	

*C = Fe (II) concentration; *R = Iron oxidation rate; type of support media = geotextile; pH = 2.0; temperature = 29 ^{0}C

The biological iron oxidation rate was increased by: the addition of support media, an increase in support media concentration, an increase in Fe (II) concentration, an increase in the number of iterations, the addition of nutrients, the addition of CO_2, and increased air flow. Optimum iron oxidation rates were obtained at: pH = 2, temperature = 29°C, HRT = 8 h, Fe(II) concentration =16 g/L, and when geotextile was used as support media.

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