BIOLOGICAL IRON(II) OXIDATION AS PRE-TREATMENT TO LIMESTONE NEUTRALISATION OF ACID WATER

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ABSTRACT

Iron(II) should be oxidised to iron(III) before the neutralisation of acid water with limestone, otherwise the oxidation will occur downstream of the neutralisation plant with the formation of acid (reactions 1 and 2). This study aimed at investigating the effect of surface area of the medium that supports bacterial growth on the rate of biological iron(II) oxidation. The study showed that the biological iron(II) oxidation rate is directly proportional to the square root of the medium specific surface area. © 1998 Published by Elsevier Science Ltd. All rights reserved
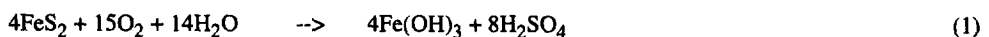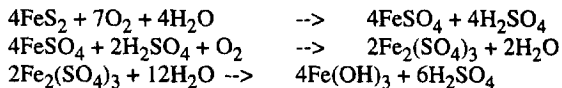
KEYWORDS

Acid mine water; iron(II) oxidation; limestone neutralisation.

INTRODUCTION

pH often is the single most important parameter to be adjusted during industrial effluent treatment. Waters with pH levels below 5.5 can be toxic to plant and fish life.

Acid mine waters contain high concentrations of dissolved heavy metals and sulphate, and can have pH values as low as 2.5. Acid is produced biologically when pyrites in the coal waste is oxidised as indicated by the following reactions (Barnes, 1968):

$$4FeS_2 + 7O_2 + 4H_2O \quad --> \quad 4FeSO_4 + 4H_2SO_4$$
$$4FeSO_4 + 2H_2SO_4 + O_2 \quad --> \quad 2Fe_2(SO_4)_3 + 2H_2O$$
$$2Fe_2(SO_4)_3 + 12H_2O --> \quad 4Fe(OH)_3 + 6H_2SO_4$$

$$4FeS_2 + 15O_2 + 14H_2O \quad --> \quad 4Fe(OH)_3 + 8H_2SO_4 \tag{1}$$

Unless treated such waters may not be discharged into public streams. The acid water is formed as a result of bacterial oxidation of pyrites exposed to oxygen and water after or during the mining process. Acid water typically is neutralised with lime and then re-used. This approach has the following disadvantages:

-       scaling of equipment by the water produced if over-saturated with respect to gypsum;
-       malfunctioning of lime dosing equipment which may result in blockages due to the settling of lime particles in pipelines and valves which in turn may result in under-dosage and acid corrosion;
-       Lime is costly.

The fluidised bed limestone neutralisation process is an alternative to lime neutralisation (Maree *et al.*, 1996). If iron(II)-containing water is treated, pre-treatment is required to oxidise iron(II) to iron(III). If influent acid water containing more than 200 mg/l iron(II), is treated directly, the limestone particles are coated with a ferric hydroxide layer which prevents further reaction between acid and limestone.

Du Preez and Maree (1994) showed that iron(II) can be oxidised to iron(III) in the presence of acidophilic iron-oxidising bacteria, such as *Ferrobacillus ferrooxidans*, and precipitated as $Fe(OH)_3$ at pH values greater than 3:

$$4Fe^{2+} + O_2 + 4H^+ \quad \longrightarrow 4Fe^{3+} + 4H_2O \qquad (2)$$

$$4Fe^{3+} + 12H_2O \quad \longrightarrow 4Fe(OH)_3 + 12H^+ \qquad (3)$$

A volumetric reaction rate of 5.5 g Fe/(l.d) was observed at an initial iron(II) concentration of 5 g/l Fe, a dissolved oxygen concentration of 8 mg/l, and a temperature of 25°C. The contact time required was 22 h. The oxidation rate did not increase significantly at higher oxygen concentrations but the rate of iron(II) oxidation is influenced by factors such as iron(II) concentration, bacterial concentration, and temperature.

The objectives of this project were to investigate the effect of surface area on the rate of biological iron(II) oxidation in an immobilised biomass system, to identify a process configuration suitable for full-scale application and to determine whether the product water is stable (no chemical precipitation occurs).

MATERIAL AND METHODS

Feed water

Leachate from a waste coal dump was used as feedstock. The water contained 10 g/l acid (as $CaCO_3$) and 3 g/l iron(II) (as Fe). The leachate contained 2.5 g/l iron(II) (as Fe), 11 g/l acid (as $CaCO_3$) and 15 g/l sulphate (as SO_4).

Table 1. Physical details of ponds used to study iron(II) oxidation

Reactor	Dia (m)	Depth (m)	Surface area (m^2)	Volume (m^3)
Temporary pond	2.76	0.5	10.3	3.0
Aeration pond	17.3	1.0	398	300

Pilot plant

Ponds and fixed-bed systems were used to study iron(II) oxidation (Table 1). The ponds were lined with plastic. The aeration pond was used to determine the oxidation rate of iron(II) for a system with a low specific surface area as well as for storage of feed water. The surface area of the floor and walls was

calculated. Plastic media were used in the fixed-bed systems to obtain a high surface area. Two types of media were used. The surface area per unit volume in the two cases was 112 (Type A) and 233 (Type C) m^2/m^3 respectively.

Batch studies

Iron(II) oxidation. The feedstock, without inoculation, was aerated by introducing compressed air through diffusers to stimulate iron oxidation bacteria naturally present in the water.

Each run was started by mixing treated water from the previous run with feedstock in the ratio 1:1 or 1:4. The reactor contents were aerated continuously until the iron(II) was completely oxidised to iron(III). After the appropriate amount of iron(III) solution was replaced with a fresh iron(II) solution aeration was restarted.

The ambient temperature during the study varied between 19 and 24°C and the dissolved oxygen concentration between 2 and 8 mg/l.

Continuous studies

During continuous studies iron(II)-rich water was passed through a 9 m^3 reactor, packed with plastic medium B (surface area 142 m^2/m^3) (Figure 1). Compressed air was used for aeration.
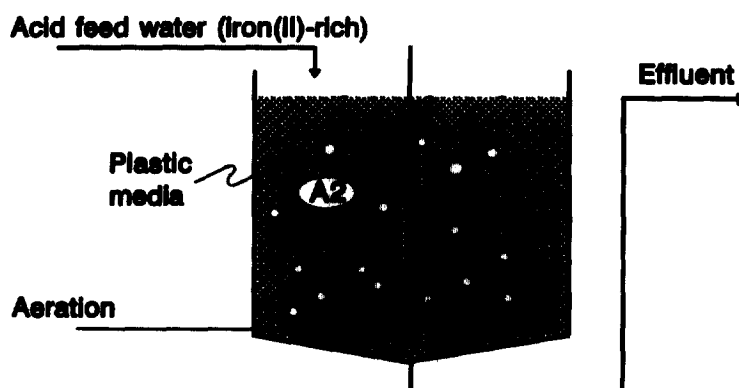

Figure 1. Flow diagram of iron(II)-oxidation reactor.

Analytical

Samples were collected at eight hourly intervals and filtered through Whatman No 1 filter paper. Sulphate, acidity and pH determinations were carried out manually according to procedures described in Standard Methods (APHA, 1985), and iron(II) as described in Vogel (1989). Iron(III), aluminium, manganese, calcium, magnesium and sodium were analysed using atomic absorption spectrophotometry. Total phosphate, ortho phosphate, ammonia, nitrate and chloride were analysed using automated techniques.

RESULTS AND DISCUSSION

Iron(II) can be oxidised to iron(III) at low pH values provided iron oxidising bacteria are present. The oxidation rate is influenced by bacterial numbers, which can be increased by providing more surface area per unit volume to support bacterial growth, and by available nutrients.
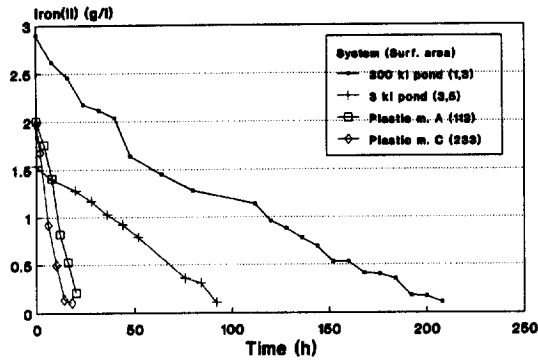
Figure 2. Iron(II) concentration as a function of time (batch studies) during aeration of systems with various specific surface areas (in m^2/m^3).
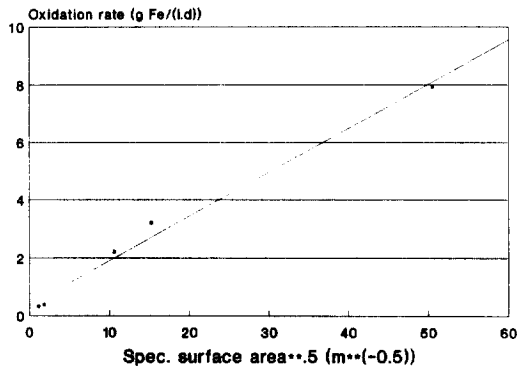

Figure 3. Relationship between rate of iron(II) oxidation and specific surface area.

Table 2. Relationship between rate of iron(II) oxidation in a packed-bed reactor and specific surface area of the medium

System	Specific surface area (m^2/m^3)	Initial Fe(II) conc. (g/ℓ Fe)	HRT (h)	Iron(II) oxidation rate[*] (g Fe/(ℓ.d))
Pond A (300 m^3)	1.33	2.90	218.1	0.32
Pond B (3 m^3)	3.45	1.55	99.2	0.38
Medium A	112	2.00	21.7	2.21
Medium C	233	2.00	15.0	3.20

Effect of surface area

In open ponds the rate of iron(II) oxidation is slow (Figure 2 and Table 2, Ponds A and B). This can be ascribed to the low specific surface area (ratio of surface area of walls and bottom to the volume of water). The rate of iron(II) oxidation increased from 0.32 to 0.38 g Fe/(l.d) when the specific surface area increased from 1.33 to 3.45 m^2/m^3 for ponds with a volume of 300 and 3 m^3, respectively. In systems with a high surface area (e.g. plastic media) the iron(II) oxidation rate is high. For mediums A and C the iron(II) oxidation rates were 2.21 and 3.2 g Fe/(l.d), respectively (Figure 2 and Table 2).

The retention time required for complete iron(II) oxidation decreased as the specific surface area increased (Figure 2 and Table 2). The relationship between rate of iron(II) oxidation and specific surface area can be described by the following equation (Figure 3):

$$-d[Fe^{2+}]/dt = 0.21 \times S^{1/2}$$

where: $d[Fe^{2+}]/dt$ -   oxidation rate of iron(II)
           k   -   reaction rate constant
           S   -   specific surface area.

Evaluation of iron(II) oxidation system for full-scale application

Medium B (142 m^2/m^3) was used to determine the performance of the immobilisation media under continuous conditions. This medium was chosen to reduce the probability of clogging as a result of chemical precipitation.
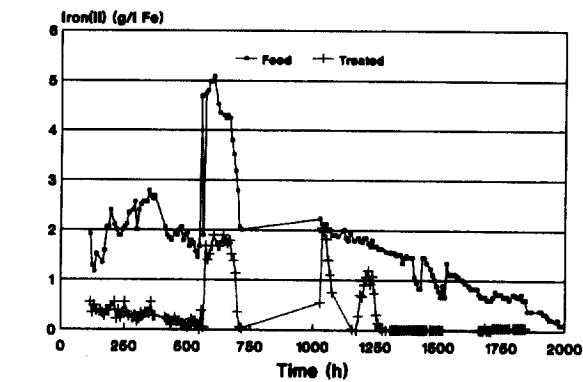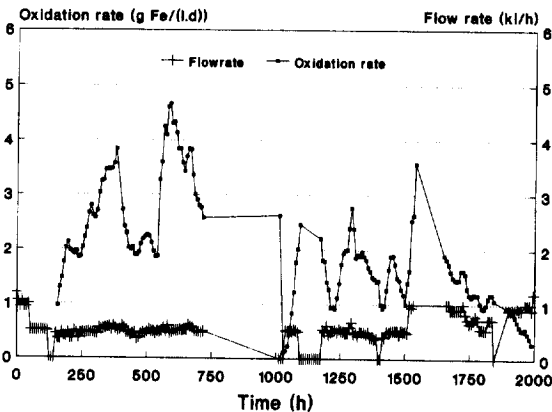

a.   Iron(II) in feed and treated waters

Figure 4. Oxidation of iron(II) under continuous conditions in a plastic medium filter (medium B, surface area of 142 m^2/m^3).

Figures 4a and b show the results when iron(II)-rich water was passed through a 9 m^3 reactor, filled with medium B.

The results show the following.

Iron content in feed water

The iron concentration in the feed water (leachate from waste coal dump) to the plastic medium filter varied between 1 and 5 g/l during the period 0 to 800 h. The iron concentration was about 2 g/l during period 0 to 600 h. Thereafter iron(II) concentrations increased from 2 to 5 g/l as a result of heavy rain. The plant was stopped during the period between 800 and 1 000 hours and the reactor contents drained. After 1 000 hours, feed water was stored in a 300 m^3 pond (no aeration was applied to water in the storage pond) from where it was fed to the filter (9 m^3). The iron(II) concentration dropped gradually from 2 to 0.5 g/l while stored in the pond over the period 1 000 to 2 000 h as a result of natural air diffusion.

Flow rate

The flow rate was maintained at 0.5 m^3/h for the period 0 to 1 550 h, except for the periods that the plant was stopped. From 1 550 h the flow rate was increased to 1.0 m^3/h.

Iron oxidation rate

Over the period 200 to 550 h, the iron(II) concentration gradually declined from 2 g/l to between 0.1 and 0.4 g/l. The corresponding oxidation rate over this period varied between 2 and 4 g Fe/(l.d).

Over the period 550 h to 700 h, the iron(II) concentration increased in both the feed and treated water. The iron(II) concentration in the feed water increased from 2 to values as high as 5 g/l and in the treated water from 0.2 to 2 g/l. The corresponding iron oxidation rates varied from 2 to 4.7 g Fe/(l.d).

When the plant was started up again at 1 036 h, a period of 3 days was required to restore good iron removal. This can be ascribed to drying out of the biomass following drainage of the water in the reactor during the period 800 to 1000 h.

From 1268 h the iron(II) concentration in the treated water was consistently less than 0.01 g/l. During this period an oxidation rate of less than 2 g Fe/(l.d) was required to remove the relatively low iron(II) concentration of 2 g/l in the feed water. The feed rate during this period was 0.5 m^3/h until 1 500 h and 1.0 m^3/h thereafter.

With the plastic media an oxidation rate of up to 5 g Fe/(l.d) can be achieved, which is similar to that achieved with batch systems.

Stability of water during iron(II) oxidation

A ferric hydroxide precipitate formed on the plastic medium over time. This is due to the high concentrations of iron(II) and iron(III) in the feedstock and the low solubility of ferric hydroxide. After oxidation of iron(II) to iron(III) the solubility of ferric hydroxide is exceeded and precipitates from solution. It is speculated that this compound can be removed by dissolving it with sulphuric, hydrochloric or nitric acid should it be required. The acid used for cleaning the plastic medium can be passed on to the downstream fluidised-bed reactor for neutralisation with limestone.

CONCLUSIONS

1. The relationship between rate of iron(II) oxidation and specific surface area is given by the equation:

$$-d[Fe^{2+}]/dt \quad = 0.21 \times S^{1/2}$$

2. Iron(II) (2 g/l) can be oxidised effectively under continuous conditions in a plastic medium filter at an iron(II) oxidation rate of 2 g Fe/(l.d).

3. Ferric hydroxide precipitates slowly on the plastic medium as a result of the solubility of ferric hydroxide that is exceeded during iron(II) oxidation under acidic conditions.

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