



# INTEGRATED IRON(II) OXIDATION AND LIMESTONE NEUTRALISATION OF ACID MINE WATER

J. P. Maree, W. F. Strydom and M. de Beer

*Division of Water, Environment and Forestry Technology, CSIR, P.O. Box 395, Pretoria, 0001, South Africa*

## ABSTRACT

Volumetric iron(II) oxidation rates exceeding 100 g/(l.d) were achieved by dosing powdered limestone to a bio-reactor treating artificial acid mine water. Neutralisation and partial sulphate removal were achieved as well. The rate is highly dependent on the surface area exposed to the liquid (RSA) and the OH<sup>-</sup>, oxygen, CaCO<sub>3</sub>, suspended solids and iron(II) concentrations, and less dependent on specific surface area (SSA) and pressure in the pH range 5 to 6. The chemical oxidation rate (pH greater than 6) is dependent on the OH<sup>-</sup>, oxygen, and iron(II) concentrations and the reactor surface area (RSA). © 1999 Published by Elsevier Science Ltd on behalf of the IAWQ. All rights reserved

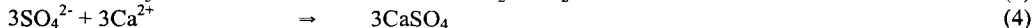
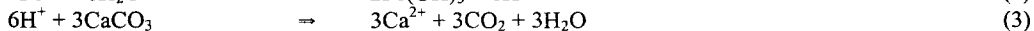
## KEYWORDS

Acid mine water; iron(II) oxidation; limestone neutralisation; reaction kinetics; sulphate removal.

## INTRODUCTION

Acid mine waters contain high concentrations of dissolved heavy metals and sulphate, and can have pH values as low as 2.5. Unless treated such waters may not be discharged into public streams. The acid water is formed as a result of bacterial oxidation when pyrites are exposed to oxygen and water after or during the mining process. Lime neutralisation is costly and often is accompanied by pH fluctuations in the case of over-dosage, malfunctioning of dosing equipment and blockages due to settling of lime particles in pipelines and valves.

Fluidised bed limestone neutralisation may be used as an alternative to lime neutralisation (Maree and du Plessis, 1994). If iron(II) is present biological pre-treatment, involving oxidation of iron(II) to iron(III), is required. Limestone particles are coated with a ferric hydroxide layer, which prevents further dissolution of limestone, at iron(II)-concentrations greater than 200 mg/l (as Fe). The objective of the research described here was to develop an integrated process to achieve iron(II) oxidation; limestone neutralisation and partial sulphate removal. Particular attention was given to the kinetics of chemical and biological iron(II) oxidation. The work is underpinned by the following chemical reactions:



## MATERIALS AND METHODS

Feedstock

A synthetic solution, similar to leachate from a waste coal dump, was used as feed water. The solution contained 4 003 mg/l Fe(II), 41 mg/l P, 23 mg/l Mg, 27 mg/l N, 8 879 mg/l SO<sub>4</sub> and 9 249 mg/l acidity (as CaCO<sub>3</sub>). Limestone from various sources and sodium hydroxide were used for neutralisation.

Table 1. Dimensions of reactor vessels

Parameter	Value			
	5.0	2.0	1.0	0.5
Beaker volume (l)	5.0	2.0	1.0	0.5
Diameter (m)	0.18	0.14	0.11	0.09
Floor area (m <sup>2</sup> )	0.025	0.014	0.009	0.006
Water height (m)	0.20	0.14	0.11	0.09
Wall area (m <sup>2</sup> )	0.11	0.06	0.04	0.02
Floor + wall area (m <sup>2</sup> )	0.14	0.07	0.05	0.03
Reactor surface area (RSA) (m <sup>2</sup> /m <sup>3</sup> )	27.3	36.8	46.2	58.1

RSA = Surface area of reactor in contact with liquid (m<sup>2</sup>) ÷ Volume of reactor (m<sup>3</sup>).

Batch studies

Slimes (coal with particle size less than 0.2 mm) was used as bacterial support medium. Batch studies (Table 1) were conducted at atmospheric and elevated pressure. The following steps were followed:

- Each new batch test was started by mixing the treated contents from the previous batch with the synthetic feed, in a ratio varying from 1:1 to 1:4, together with the appropriate alkali (limestone or sodium hydroxide). In the case of limestone an excess was applied over the amount required to ensure complete iron(II) oxidation to iron(III) and precipitation of the latter as Fe(OH)<sub>3</sub>. With NaOH additions were made as required to maintain the pH at a specific value.
- The reactor contents were aerated continuously. Filtered samples were taken regularly and analyzed for iron(II), oxygen, acidity, sulphate and pH.
- Aeration was stopped when the iron(II) was completely oxidised to iron(III), whereafter the appropriate amount of the iron(III)-containing mixture was replaced with a fresh iron(II) solution.
- Aeration was restarted and the procedure described above repeated.

Analytical

Samples were collected regularly 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). Calcium was analyzed using atomic absorption spectrophotometry. Acidity was determined by titrating the solution to pH 8.3 using 0.1 N NaOH.

## RESULTS AND DISCUSSION

Oxidation reactions

Figure 1 illustrates the results obtained when an iron(II) solution is oxidised with air in the presence of bacteria, slimes and limestone. Neutralisation and iron(II) oxidation started immediately after  $\text{CaCO}_3$  addition. Iron(II), acidity and sulphate concentrations (in  $\text{g/l}$ ) declined within 75 min from 3.7 to 0.1 (as Fe), 3.45 to 0.15 (as  $\text{CaCO}_3$ ) and 5.4 to 2.0 (as  $\text{SO}_4$ ), respectively. The pH gradually increased from 5.2 to 7.1. The pH increased to above 7 only after complete removal of iron(II) had been achieved. Calcium varied between 0.5 and 0.8  $\text{g/l}$  (as Ca), which is ascribed to the effects of simultaneous  $\text{CaCO}_3$  dissolution and gypsum crystallisation. The rate of gypsum crystallisation depends on the surface area of gypsum crystals in suspension, which only formed after  $\text{CaCO}_3$  had been added.

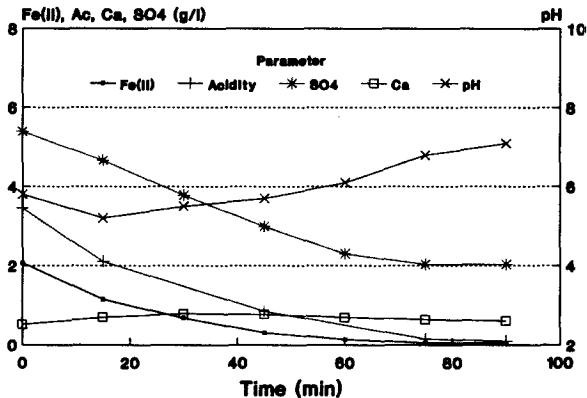


Figure 1. Temporal removal of iron(II), acidity and sulphate during neutralisation of acid water with 10 g/l powder Savanna fine limestone (100 g/l slimes, 100 kPa, 500 ml beaker).

Kinetics

Complete neutralisation of iron(II)-rich water was achieved only after completion of iron(II) oxidation (Figure 1). At pH values less than 5.1 biological iron(II) oxidation is the preferred option to use with limestone. For example, the chemical and biological iron(II) oxidation rates at pH 5.05 are 2.72 and 28.11 g Fe/(l.d) respectively (Figure 2). At pH values greater than 6 chemical iron(II) oxidation rates exceed the biological rates (Experiments 1.3 and 4.5). Lime is needed to raise the pH of iron(II)-rich water to this level. In the pH range 5.1 to 6.0 both biological and chemical iron(II) oxidation occur if microorganisms are present. This pH range can be achieved with limestone.

The relative importance of various factors in terms of their influence on the rate of iron(II) oxidation was determined by a series of controlled tests in which the dependence of the rate on one variable at a time was determined. This was done at pH 6, where chemical oxidation rates exceed biological oxidation rates, and the pH range 5 to 6, where both biological and chemical iron(II) oxidation occur. The contribution of only the three most dominant variables ( $\text{OH}^-$ ,  $\text{Fe}^{2+}$ , and reactor surface area) was studied at pH 6 to confirm consistency with reported findings. In the pH range 5 to 6, which is of greater importance from the point of view of limestone neutralisation, an extended number of variables were included. For this purpose the iron(II) oxidation rate was assumed to have the following functional form:

$$-d[\text{Fe}^{2+}]/dt = k \cdot [\text{Fe}^{2+}]^{n1} \cdot [\text{O}_2]^{n2} \cdot [\text{OH}^-]^{n3} \cdot [\text{RSA}]^{n4} \cdot [\text{CaCO}_3]^{n5} \cdot \text{SSA}^{n6} \cdot [\text{SS}]^{n7} \quad (5)$$

where  $-d[\text{Fe}^{2+}]/dt$  = rate of iron(II) oxidation  
 $k$  = reaction rate constant  
 $[\text{Fe}^{2+}]$  = iron(II) concentration (moles/l)

[O <sub>2</sub> ]	=	oxygen concentration (moles/ℓ)
[OH]	=	hydroxide concentration (moles/ℓ)
RSA	=	reactor surface area (m <sup>2</sup> /m <sup>3</sup> )
[CaCO <sub>3</sub> ]	=	CaCO <sub>3</sub> solids concentration (moles/ℓ)
SSA	=	CaCO <sub>3</sub> specific surface area (m <sup>2</sup> /m <sup>3</sup> )
[SS]	=	Suspended solids concentration (g/ℓ)

The results of the tests are given in Table 2.

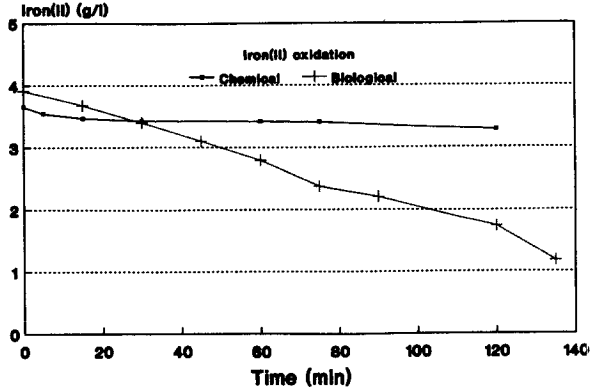


Figure 2. Chemical and biological/chemical iron(II) oxidation rates at pH 5.05.

#### Chemical iron(II) oxidation (pH 6 and higher)

The data in Table 2 (Experiments 1.1 to 3.4) were used to show that the rate of chemical iron(II) oxidation (pH >6) is of order 1.94 ( $\approx 2$ ), 0.80 ( $\approx 1$ ) and 1.68 ( $\approx 2$ ) in respect of OH<sup>-</sup>, Fe<sup>2+</sup> and RSA respectively. This agrees with the finding of Stumm and Lee (1961), who proposed the following rate equation for chemical iron(II) oxidation:

$$-d[\text{Fe}^{2+}]/dt = k \cdot [\text{Fe}^{2+}] \cdot [\text{OH}^-]^2 \cdot P_{\text{O}_2} \quad (6)$$

where  $P_{\text{O}_2}$  = partial pressure of oxygen (kPa).

The current findings suggest that this be modified to:

$$-d[\text{Fe}^{2+}]/dt = k \cdot [\text{Fe}^{2+}] \cdot [\text{OH}^-]^2 \cdot P_{\text{O}_2} \cdot \text{RSA}^2 \quad (7)$$

#### Biological/chemical iron(II) oxidation (pH range 5 to 6)

The biological/chemical iron(II) oxidation rate (in the pH range 5 to 6 with bacteria present) was derived in a similar way (Equation 8 and Table 2, Experiments 4.1 to 12.6). The rate was found to be order 1.26 ( $\approx 1$ ), 0.30 ( $\approx 0.5$ ), 0.48 ( $\approx 0.5$ ), 0.75 ( $\approx 1$ ), 0.38 ( $\approx 0.5$ ) and 1.01 ( $\approx 1$ ) in respect of OH<sup>-</sup>, Fe<sup>2+</sup>, CaCO<sub>3</sub>(s), O<sub>2</sub>, SS and RSA respectively.

$$-d[\text{Fe}^{2+}]/dt = k \cdot [\text{Fe}^{2+}]^{0.5} \cdot [\text{OH}^-] \cdot [\text{O}_2] \cdot \text{RSA} \cdot [\text{CaCO}_3(\text{s})]^{0.5} \cdot [\text{SS}]^{0.5} \quad (8)$$

The rate proved almost independent of: SSA (specific surface area of CaCO<sub>3</sub> solids) and pressure.

Other observations to be drawn from Table 2 include the following:

- The reaction rate is of order 1 with respect to  $O_2$  over the range 1 to 2 mg/l. The relationship between oxygen concentration and reaction rate at higher concentrations need to be investigated further.
- Reactor surface area (RSA) plays a significant role in iron(II) oxidation. Maree *et al.* (1997) determined that, at pH 2.5, the rate of biological/chemical iron(II) oxidation is directly proportional to the square root of the surface area of the reactor. This study showed that the biological oxidation rate is directly proportional to the surface area of the reactor in the pH range 5 to 6 and to the square of the surface area at levels above pH 6 (chemical oxidation).
- The biological and chemical iron(II) oxidation rates are first and second order with respect to hydroxide concentration respectively.

The Arrhenius equation

$$\log k = \log A - \frac{E}{2.303R} \times \frac{1}{T} \quad (9)$$

where E	(activation energy)	=	14.31 kcal/mole
	log A (a constant)	=	12.43
	R (gas constant)	=	1.987 cal mole <sup>-1</sup> degree <sup>-1</sup>

can be used to express the reaction rate constant, k, as a function of temperature (Equation 9 and Table 2, Exp 12). The terms  $E/2.303R$  and  $\log A$  were calculated from the slope and intercept of the graph  $\log k$  against  $1/T$  (T - Temperature in °K). A linear relationship was obtained over the range 5 to 25°C. It is expected that the linear relationship will fail at higher temperatures as optimum reaction rates are often achieved at 37°C.

Table 2. Effect of various factors on iron(II) oxidation rate. [Solid concentrations are given in g/l, reactor surface area (RSA) in  $\text{m}^2/\text{m}^3$ , specific surface area in  $\text{m}^2/\text{g}$ , dissolved oxygen in mg/l, hydroxide concentration in moles/l and temperature in  $^{\circ}\text{C}$ ]

Exp No	Results				Experimental conditions				
	Variable	Value	Rate g Fe/( $\ell$ .d)	Reaction order *1	CaCO <sub>3</sub>	pH	OH <sup>-</sup> x10 <sup>-9</sup>	RSA	Temp
Chemical iron(II) oxidation:									
1.1	pH	5.0	2.72	1.94	*4	5.0	1.0	58	14
1.2		5.5	62.9			5.5	3.2		
1.3		6.0	236.9			6.0	10.0		
2.1	Fe <sup>2+</sup>	0.3	48.2	0.80	*4	6.0	10.0	46	25
2.2		1.0	102.2						
2.3		3.0	217.3						
2.4		10.0	836.4						
3.1	RSA	58.11	455.2	1.68	*4	6.0	10.0	58	25
3.2		46.13	348.3					46	
3.3		36.77	233.6					37	
3.4		27.32	130.4					27	
Biological/chemical iron(II) oxidation:									
4.1	pH	5.0	28.11	1.26	*4	5.0	1.0	58	14
4.2		5.3	125.5			5.3	2.0		
4.3		5.5	138.4			5.5	3.2		
4.4		5.7	234.0			5.7	5.0		
4.5		6.0	234.0*2			6.0	10.0		
5.1	Fe <sup>2+</sup>	0.3	34.7	0.30	10	6.5	7.9	46	25
5.2		1.0	46.7			5.8			
5.3		3.0	82.1			5.5			
5.4		10.0	90.9			5.2			
6.1	RSA	58.11	113.6	1.01	10	5.5	3.2	58	25
6.2		46.13	83.3					46	
6.3		36.77	78.1					37	
6.4		27.32	50.5					27	
7.1	CaCO <sub>3</sub> conc	10	31.9	0.48	10	5.6	4.0	58	12
7.2		15	39.5		15				
7.3		20	47.6		20				
7.4		40	66.2		40				
7.5		80	86.1		80				
8.1	CaCO <sub>3</sub> SSA	7.92	98.7	0.12*3	10	5.4	2.5	46	25
8.2		7.68	88.5						
8.3		2.81	79.1						
8.4		2.20	96.2						
8.5		1.93	83.0						
8.6		1.57	68.6						

Exp No	Results				Experimental conditions				
	Variable	Value	Rate g Fe/(ℓ.d)	Reaction order *1	CaCO <sub>3</sub>	pH	OH <sup>-</sup> x10 <sup>-9</sup>	RSA	Temp
9.1	SS	11.4	46.38	0.53	10	5.5	3.2	46	25
9.2		10.7	48.51						
9.3		15.7	62.51						
9.4		33.9	79.53						
9.5		53.6	109.1						
9.6		116.8	172.8						
10.1	O <sub>2</sub>	0.1	9.75	0.75	10	5.6	4.0	46	26
10.2		0.5	42.6						
10.3		2.0	91.2						
10.4		5.0	103.7*5						
11.1	Pres- sure	0	60.9		10	5.4	2.5	58	13
11.2		100	51.4						
11.3		200	53.1						
11.4		300	56.6						
		Ave	55.5						
12.1	Temp	6	16.2		10	5.7	5.0	46	6
12.2		12	27.0						12
12.3		17	48.7						17
12.4		25	81.9						25
12.5		37	131.0*6						37
12.6		45	141.5*6						45

Other experimental conditions (unless indicated otherwise): O<sub>2</sub> (from air) > 2 mg/l (Experiments 1 to 8 and 11 to 12), O<sub>2</sub> (from pure O<sub>2</sub>) = 18 mg/l (Exp 9), Pressure = 0 kPa, Initial iron(II) concentration = 3 g/l, CaCO<sub>3</sub> concentration = 10 g/l, SSA of CaCO<sub>3</sub> = 100 m<sup>2</sup>/g, Suspended solids (SS) concentration = 0.5 to 4.0 g/l (Expts 1.1 - 3.4) (due to Fe(OH)<sub>3</sub>), Suspended solids (SS) concentration = 37 g/l (Expts 4.1 - 12.6), SSA of CaCO<sub>3</sub> = 100 m<sup>2</sup>/g

#### Notes:

- \*1 - Calculated from slope of graph log Rate versus log (Value of variable).
- \*2 - Reaction rate for pH 6 (Exp 4.5) not included during calculation of the reaction order.
- \*3 - Only reaction rates from natural CaCO<sub>3</sub> samples (Experiments 8.2 to 8.6) included in calculation of the reaction order.
- \*4 - pH controlled with NaOH.
- \*5 - Reaction rate for 5 mg/l O<sub>2</sub> (Exp 10.4) not included in calculation of the reaction order. Reaction rate is influenced by low O<sub>2</sub> concentrations only.
- \*6 - Reaction rates for 37 and 45 °C (Experiments 12.5 to 12.6) not included in calculation of the activation energy.

#### General discussion

The rate of iron(II) oxidation, as reported in literature and confirmed in this investigation, depends on the OH<sup>-</sup>, O<sub>2</sub> and Fe<sup>2+</sup>-concentrations. This investigation shows that surface area also plays a significant role. The walls of the reactor, packed media, solid reactants or reaction products all contribute to surface area. The values of RSA and SA (surface area of suspended solids) (Equation 10) were typically 58 m<sup>2</sup>/m<sup>3</sup> (0.5 l reactor) and 1 732 000 m<sup>2</sup>/m<sup>3</sup> (at 37 g/ℓ suspended solids x 46.8 m<sup>2</sup>/g) respectively.

The two types of surface area contribute in different ways to the kinetics of iron(II) oxidation. It is assumed that SA acts as support medium for bacterial growth while RSA has a catalytic effect on the iron(II) oxidation rate.

### CONCLUSIONS

The following conclusions are drawn from the study:

Chemical iron(II) oxidation is slow at the pH values resulting from the neutralisation of iron(II)-rich water with limestone (5 to 6). By combining limestone neutralisation with biological/chemical iron(II) oxidation, acceptable reaction rates are obtained in that pH range, provided that a suitable reactor is used (large surface area). With a surface area of  $58 \text{ m}^2/\text{m}^3$ , iron(II) can be oxidised at rates exceeding  $100 \text{ g Fe}/(\text{l.d})$ .

Neutralisation and partial sulphate removal are achieved simultaneously. Iron(II), acidity and sulphate concentrations (in g/l) decreased within 75 min from 3.7 to 0.1 (as Fe), 3.45 to 0.15 (as  $\text{CaCO}_3$ ) and 5.4 to 2.0 (as  $\text{SO}_4$ ) respectively. The pH increased from 5.2 to 7.1.

The chemical iron(II) oxidation ( $\text{pH} > 6$ ) rate was found to be of order 1.94 ( $\approx 2$ ), 0.80 ( $\approx 1$ ) and 1.68 ( $\approx 2$ ) in respect of  $\text{OH}^-$ ,  $\text{Fe}^{2+}$  and RSA respectively.

The biological/chemical iron(II) oxidation rate in the pH range 5 to 6 was found to be of order 1.26 ( $\approx 1$ ), 0.30 ( $\approx 0.5$ ), 0.48 ( $\approx 0.5$ ), 0.75 ( $\approx 1$ ), 0.38 ( $\approx 0.5$ ) and 1.01 ( $\approx 1$ ) in respect of  $\text{OH}^-$ ,  $\text{Fe}^{2+}$ ,  $\text{CaCO}_3(\text{s})$ ,  $\text{O}_2$ , SS and RSA respectively.

### REFERENCES

- APHA (1985). *Standard methods for the Examination of Water and Wastewater Treatment*. Twelfth Edition, American Public Health Association, New York.
- Maree, J. P. and du Plessis, P. (1994). *Neutralisation of acidic effluents with limestone*, WRC Report No 355/1/94.
- Maree, J. P., Dingemans, D. R. W., van Tonder, G. J. and Mtimkulu, S. (1997). *Biological iron(II) oxidation as pre-treatment to limestone neutralisation of acid water* (in press).
- Vogel, A. I. (1989). *Textbook of quantitative chemical analysis*. Fifth edition, John Wiley and Sons, New York, 368.
- Stumm, W. and Lee, G. F. (1961). Oxygenation of ferrous iron. *Industrial and Engineering Chemistry*, 53(2), 143 - 146.