# Treatment of iron(II)-rich acid mine water with limestone and oxygen

G. B. Mohajane, J. P. Maree and N. Panichev

## ABSTRACT

The main components of acid mine water are free acid, sulphate, and $Fe^{2+}$. Limestone is the most cost-effective alkali that can be used for neutralization. The purpose of this investigation was to identify conditions where $Fe^{2+}$ is removed with limestone and simultaneously oxidized with oxygen to $Fe^{3+}$, in a polyvinyl chloride pipe under pressure. Gypsum scaling is prevented by passing rubber balls through the pipe of the so-called Oxygen-Pipe-Neutralization (OPeN) process pilot plant. Two synthetic waters were treated: (A) acid mine water containing 123 mg L$^{-1}$ $Fe^{2+}$ representing gold mine water, and (B) acid mine water containing 6,032 mg L$^{-1}$ $Fe^{2+}$ representing coal mine water. Batch studies were carried out in a pipe reactor and showed that the rate of $Fe^{2+}$ oxidation depended on the $Fe^{2+}$ concentration, oxygen pressure, amount of recycled sludge, limestone dosage and the mixing rate. Continuous studies in an OPeN process pilot plant resulted in 100% removal of total acidity from synthetic coal mine water and a 98% removal from synthetic gold mine water. $Fe^{2+}$ was removed completely as precipitated $Fe(OH)_3$ from both synthetic coal and gold mine water at around pH 7 at 200 and 100 kPa oxygen pressure, respectively.

Key words | $Fe^{2+}$-oxidation, limestone, neutralization of acid mine water, OPeN process pilot plant, pipe reactor, pressure

G. B. Mohajane (corresponding author)
J. P. Maree
Department of Environmental,
Water and Earth Sciences,
Tshwane University of Technology,
Private Bag X680,
Pretoria 0001,
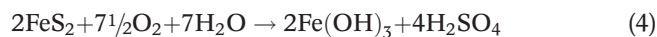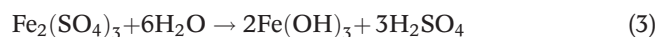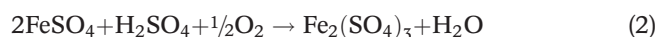South Africa
E-mail: boitumelogbmohajane@gmail.com

N. Panichev
Department of Chemistry,
Tshwane University of Technology,
Private Bag X680,
Pretoria 0001,
South Africa

## INTRODUCTION

Many gold mines on the Witwatersrand have been worked out, and pumping of water to the surface has been stopped. Mine water in the Western Basin started to decant in 2002 and is expected to begin decanting in 2014 in the Central Basin and in 2016 in the Eastern Basin (Department of Environmental Affairs & Tourism 2008).

Acid mine water forms when pyrite ($FeS_2$) that occurs in gold-carrying strata is oxidized when in contact with atmospheric oxygen and water and $Fe^{2+}$-oxidizing micro-organisms (Equations (1)–(4)). This results in high acidity and high sulphate concentrations and the leaching of metals such as $Fe^{2+}$. Dissolved metals at low pH pose a danger to aquatic life and water users if this acid water is allowed to enter water courses (Maree & Du Plessis 1994).

The oxidation of pyrite when exposed to atmospheric oxygen and water proceeds according to the following reaction equations (Costello 2003):

$$2FeS_2 + 7O_2 + 2H_2O \rightarrow 2FeSO_4 + 2H_2SO_4 \qquad (1)$$

$$2FeSO_4 + H_2SO_4 + \tfrac{1}{2}O_2 \rightarrow Fe_2(SO_4)_3 + H_2O \qquad (2)$$

$$Fe_2(SO_4)_3 + 6H_2O \rightarrow 2Fe(OH)_3 + 3H_2SO_4 \qquad (3)$$

$$2FeS_2 + 7\tfrac{1}{2}O_2 + 7H_2O \rightarrow 2Fe(OH)_3 + 4H_2SO_4 \qquad (4)$$

The main components of acid mine water are free acid, $Fe^{2+}$, $Fe^{3+}$, and low concentrations of other metals present in the rock such as $Al^{3+}$, $Mn^{2+}$, $Ca^{2+}$, and $Mg^{2+}$, in addition to $SO_4^{2-}$, as a result of sulphide oxidation. Water in the Western and Central Basins typically contains 400 mg L$^{-1}$ $Fe^{2+}$, 1,200 mg L$^{-1}$ total acidity (as $CaCO_3$), and 3,500 mg L$^{-1}$ $SO_4^{2-}$ with pH 2.8. Water from the Eastern Basin is partially neutralized when it decants due to contact with dolomite rock, and typically contains 100 mg L$^{-1}$ $Fe^{2+}$, 300 mg L$^{-1}$ total alkalinity (as $CaCO_3$), and 1,200 mg L$^{-1}$ $SO_4^2$ and is around pH 5.5 (Department of Water Affairs 2012).

Limestone has been used for neutralization of acid mine water because it is cheap compared to other alkalis, reacts rapidly with free acid and is safe to handle, and the pH cannot be increased to above 8 (Maree & Du Plessis 1993). Previous studies have been conducted on acid mine water neutralization and $Fe^{2+}$ oxidation using limestone and air/oxygen. Examples are the aerated limestone powder reactor (Volpicelli *et al.* 1982); stationary aerated limestone grit reactor (Glover *et al.* 1965); rotating drum (Mihok *et al.* 1968, 1970); and the three-stage limestone neutralization process (Maree *et al.* 1998).

Disadvantages of these processes are the long residence times required to oxidize $Fe^{2+}$ and gypsum scaling. There is a need for a process where $Fe^{2+}$ can be oxidized rapidly in the presence of $CaCO_3$ while gypsum scaling is prevented. Sponge balls have already been used successfully to prevent gypsum scaling in heat exchangers by passing them through the pipes (Kazi 2012).

This study focused on a new process, called the OPeN (Oxygen-Pipe-Neutralization) process, where: (i) $Fe^{2+}$ is oxidized under pressure, using $O_2$; (ii) free acid is neutralized with $CaCO_3$; (iii) a pipe reactor is used for controlling pressure; and (iv) rubber balls are passed through the pipe reactor to prevent gypsum scaling on the walls (Figure 1).

## MATERIALS AND METHODS

### Feedstock

Waters were prepared to be of similar composition to that of the gold mine (Water A) and leachate from a coal mine (Water B). Water A (artificial gold mine water) contained 120 mg L$^{-1}$ $Fe^{2+}$, 500 mg L$^{-1}$ acidity, and 125 mg L$^{-1}$ $Mg^{2+}$, and was prepared by dissolving 23.84 g of $FeSO_4 \cdot 7H_2O$, 50.6 g of $MgSO_4 \cdot 7H_2O$ and 245 mL of 1 N $H_2SO_4$ in 40 L ultrapure water. All chemicals used for this preparation were of analytical grade. Water B (artificial coal mine water) contained 6,000 mg L$^{-1}$ $Fe^{2+}$, 20,000 mg L$^{-1}$ acidity, and 200 mg L$^{-1}$ $Mg^{2+}$, and was prepared by dissolving 1,192 g of $FeSO_4 \cdot 7H_2O$, 81.04 g of $MgSO_4 \cdot 7H_2O$, and 184 mL of concentrated $H_2SO_4$ in 40 L ultrapure water. The following chemicals were used: (i) limestone (81% $CaCO_3$ and 1.2% $Mg^{2+}$; Aqua Lime (Pty) Ltd, South Africa) and (ii) oxygen (99.5% purity; Afrox, South Africa).

### Real mine water

The real gold mine water was collected at Randfontein area, South Africa; the first sample was collected in a 20 L plastic bottle and closed to prevent $Fe^{2+}$ oxidation.
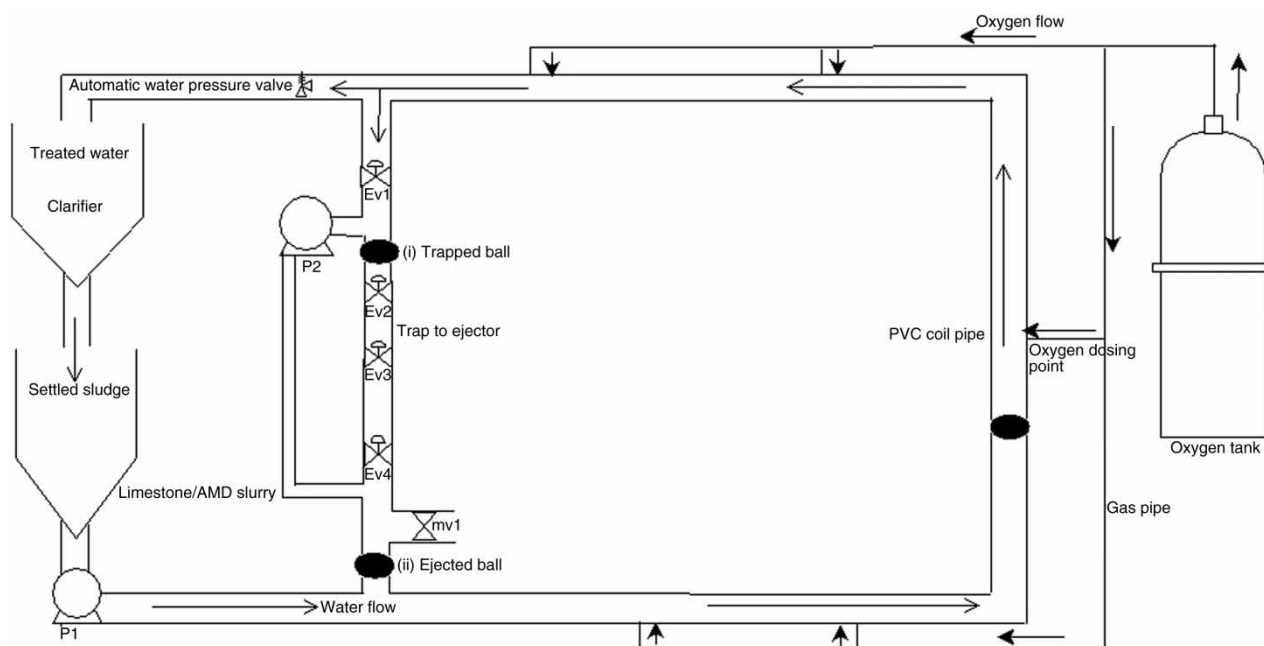


Figure 1 | Schematic diagram of the 'OPeN process' pilot plant. Pumps: P1 and P2; electronic valves: Ev1, Ev2, Ev3, and Ev4; and mechanical valves: mv1.

## Equipment

A pipe reactor was used for laboratory studies and the OPeN process for continuous and semi-continuous studies.

### Pipe reactor for laboratory batch studies

The pipe reactor was made as follows: polyvinyl chloride (PVC) pipe, diameter 50 mm, length 1 m, capacity 1.4 L, and high pressure resistance 5 kPa. One end was closed with a PVC fitting (Plasticor, South Africa) and the other end with a valve that was used for feeding water and chemicals. An oxygen pressure regulator with a maximum pressure of 600 kPa was fitted to the feeder end. The setup was mounted on a shaker (maximum shaking rate: 250 strokes min$^{-1}$).

### OPeN system

The plant worked on the principle that sponge balls were passed, together with water and chemicals, through a coil-shaped PVC pipe (length = 8 m, diameter = 50 mm, and 5 kPa pressure) (Figure 1). In order for the balls to be recycled, the system made provision for spaces where the balls were (i) trapped before leaving the long pipe and (ii) ejected into the pipe at a point soon after the inlet point of the water. Automatically controlled valves were used to regulate the flow of the balls between the two modes. The balls were made of rubber (diameter = 45 mm). Pump P1 was used for the feed and pump P2 for the trap and eject mode. An automatic stainless-steel water-pressure valve controlled the pressure in the reactor. Oxygen was supplied from an oxygen cylinder via a pressure regulator.

## Procedure

### Kinetic studies

Studies were conducted in batch mode. One litre of synthetic mine water was introduced into the pipe reactor. Limestone (particle size, 150 μm) at a dosing mole ratio of 1:1 limestone per mole acidity was fed into the pipe reactor mounted on the shaker, followed by oxygen dosing at a pressure of 500 kPa. The shaker was operated at a rate of 150 strokes min$^{-1}$. Studies were conducted on both gold mine water (0.89 g limestone with 18–20% limestone excess) and coal mine water (22.68 g limestone with 10% limestone excess).

Fe$^{2+}$ oxidation was monitored using coal and gold mine water by keeping other parameters constant while varying one parameter of interest with samples collected at contact time intervals of 20 min and analysed for Fe$^{2+}$ (mg L$^{-1}$), acidity (mg L$^{-1}$), alkalinity (mg L$^{-1}$), and pH.

### Continuous/semi-continuous mode

A volume of 40 L of synthetic coal mine water was fed into a 60 L drum, followed by 950 g of limestone to neutralize the synthetic coal mine water. The mine water was withdrawn with pump 1 (P1) (Figure 1, above), the oxygen was dosed at four points in the PVC pipe loop at a pressure of 100 kPa, with a plant pressure of 400 kPa and flow rate of 63 L min$^{-1}$. The trap and eject was operated automatically with the modes shown in Table 1. Samples were collected and analysed for Fe$^{2+}$, acidity, alkalinity, and pH. A similar procedure was followed for synthetic gold mine water with a limestone dosage of 81.22 g.

### Experimental

The following aspects were studied:

- Types of water with different Fe$^{2+}$/acidity concentrations, mg L$^{-1}$ (100 and 6,000).
- Oxygen pressure, kPa (200, 300, 400, and 500).
- Limestone particle size, μm (45, 150, 560, and 800).
- Limestone: acidity, mole ratio (1:1, 1:2, 1:3, and 1:4).
- Sludge dosage, mg L$^{-1}$ (0, 22,490, 4,500, and 56,230 for coal mine water; 0, 774, 1,400, and 1,650, for gold mine water).
- Shaking rate, strokes min$^{-1}$ (none, 50, 150, and 250).
- Fe$^{2+}$ concentration, mg L$^{-1}$ (5,700, 1,000, 390 and 117).
- Acidity, mg L$^{-1}$ (20,000 and 500).

**Table 1** | Position of valves and pumps during various modes of operation (Figure 1)

| Controller | Mode | P1 | P2 | Ev1 | Ev2 | Ev3 | Ev4 | mv1 |
|---|---|---|---|---|---|---|---|---|
| Timer | Normal | On | On | Closed | Open | Closed | Closed | Closed |
| Timer | Trap to ejector | On | On | Open | Closed | Open | Open | Closed |
| Manual switch | Rinse trap | On | On | Open | Closed | Open | Open | Closed |

The following parameters were studied for the optimization of the 'OPeN (neutralization-pipe) system' using synthetic coal mine water:

- Flow rate, L min$^{-1}$ (50 and 63).
- Sludge concentration, mg L$^{-1}$ (1,238 and 4,950).
- Oxygen pressure, kPa (200 and 100).
- Gypsum prevention (rubber balls, diameter = 45 mm and sponge balls, diameter = 55 mm).

## Analytical methods

Sample solutions were collected and filtered (Whatman No. 1). The sample pH, alkalinity, and acidity were determined by following standard procedures (American Public Health Association (APHA) 1995). The Fe$^{2+}$ concentrations were determined by the standard permanganate titration method (Vogel 1989).

## RESULTS AND DISCUSSION

### Water quality

#### Synthetic mine water

Tables 2 and 3 show the chemical composition of gold and coal mine water before and after treatment. It was noted that Fe$^{2+}$ and acidity were removed for both gold and coal mine waters and the pH was raised to almost 7 due to Reactions (1) and (2). The treated water had a low total acidity due to the removal of H$^+$, Fe$^{2+}$, and Fe$^{3+}$ (Reaction (5)):

$$Acidity \left(mg\,L^{-1}\right) = [H^+] + 2[Fe^{2+}] + 3[Fe^{3+}] + 2[CO_2]$$
$$+ [HCO_3] - [OH^-] \qquad (5)$$

**Table 2** | Chemical composition of synthetic gold mine water before and after neutralization with CaCO$_3$. (Experimental conditions: pressure in the system = 400 kPa, oxygen pressure = 100 kPa, flow rate = 63 L min$^{-1}$, 18% excess limestone, limestone dosage = 36 g L$^{-1}$, sludge dosage = 0 mg L$^{-1}$, ball material = rubber, volume neutralized = 40 L, and residence time of Fe$^{2+}$ = 20 min)

| Parameter | Feed water | Treated water |
|---|---|---|
| Temperature (°C) | 23 | 48 |
| [Fe$^{2+}$] (mg L$^{-1}$) | 123 | 5.6 |
| Acidity (mg L$^{-1}$) | 600 | 12.5 |
| Alkalinity (mg L$^{-1}$) | 0 | 35 |
| pH | 2.5 | 6.5 |

**Table 3** | Chemical composition of synthetic coal mine water before and after neutralization with CaCO$_3$. (Experimental conditions: pressure in the system = 400 kPa, oxygen pressure = 200 kPa, flow rate = 63 L min$^{-1}$, 1% excess limestone, limestone dosage = 950 g L$^{-1}$, sludge dosage = 0 mg L$^{-1}$, ball material = rubber and volume neutralized = 40 L, and residence time of Fe$^{2+}$ = 120 min)

| Parameter | Feed water | Treated water |
|---|---|---|
| Temperature (°C) | 23 | 48 |
| [Fe$^{2+}$] (mg L$^{-1}$) | 6,032 | 55.9 |
| Acidity (mg L$^{-1}$) | 19,000 | 50 |
| Alkalinity (mg L$^{-1}$) | 0 | 30 |
| pH | 1.5 | 6.9 |

Alkalinity (mg L$^{-1}$) was low due to the release of CO$_2$ (Reaction (6)):

$$2Fe^{2+} + \tfrac{1}{2}O_2 + 2CaCO_3 + 3H_2O$$
$$\rightarrow 2Fe(OH)_3 + 2Ca^{2+} + 2CO_2 \qquad (6)$$
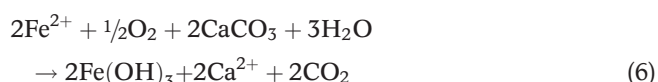
In the case of coal mine water, the total acidity was decreased from 19,000 to 50 mg L$^{-1}$ and Fe$^{2+}$ from 6,032 to 56 mg L$^{-1}$ when limestone and oxygen were dosed. In the case of gold mine water, the acidity decreased from 600 to 12.5 mg L$^{-1}$ and Fe$^{2+}$ from 123 to 5.6 mg L$^{-1}$. The pH was raised to near 7 for both mine waters. The alkalinities of 30 and 35 mg L$^{-1}$, respectively, were obtained from gold and coal mine water due to formation of bicarbonate.

#### Real mine water

Table 4 shows the chemical composition of real gold mine water before and after treatment. The total acidity was decreased from 1,125 to 197 mg L$^{-1}$ and Fe$^{2+}$ from 625 to 66 mg L$^{-1}$ when limestone and oxygen were dosed. The pH was raised to 6.5, and alkalinity was 30 mg L$^{-1}$ after treatment.

**Table 4** | Treatment of real gold mine water before and after neutralization with CaCO$_3$ in pipe reactor. (Experimental conditions: pressure = 400 kPa, 18% excess limestone, limestone dosage = 2.7 g L$^{-1}$, sludge dosage = 10,000 mg L$^{-1}$, volume neutralized = 1 L, and residence time of Fe$^{2+}$ = 60 min)

| Parameter | Feed water | Treated water |
|---|---|---|
| Temperature (°C) | 23 | 23 |
| [Fe$^{2+}$] (mg L$^{-1}$) | 625 | 66 |
| Acidity (mg L$^{-1}$) | 1,125 | 197 |
| Alkalinity (mg L$^{-1}$) | 50 | 30 |
| pH | 5.9 | 6.5 |

## Kinetic studies

Tables 4 and 5 show the effect of various parameters on the rate of $Fe^{2+}$ oxidation for both coal and gold mine waters, respectively. Figure 2 shows the rate of $Fe^{2+}$ removal in the presence of various $O_2$ partial pressures, 22.7 g $L^{-1}$ $CaCO_3$, 0 mg $L^{-1}$ sludge, with a limestone particle size of <150 μm, and shaking at 150 strokes $min^{-1}$. The reaction rate for each experiment was determined from the slope of $Fe^{2+}$ versus time graphs. The reaction order for each parameter was determined from log (reaction rate) versus log (concentration) for the various experiments listed in Tables 4 and 5 for mine waters A and B, respectively. For comparison purposes, the experiments had been conducted at 100 kPa using air and oxygen (see supplementary material, Figure S1, available online at http://www.iwaponline.com/wst/070/178.pdf).

Tables 2 and 3 show that the rate of iron(II) oxidation is influenced by various parameters such as pressure, limestone dosage, limestone particle size, and iron(II)

concentration. Figure 2 shows that increasing the pressure of oxygen in the closed pipe reactor resulted in an increase in the rate of $Fe^{2+}$ oxidation. This supports the ideal gas law:

$$PV = nRT \tag{7}$$

(where $P$ = pressure of the gas (kPa), $V$ = volume of the oxygen gas (L), $T$ = temperature of the gas (K), $R$ = gas constant, 0.0083 J $K^{-1}$ $mol^{-1}$, and $n$ = moles oxygen). This implied that the pressure created in the reactor by oxygen was directly proportional to the concentration of oxygen introduced into the reactor:

$$C = n/V \tag{8}$$

(where $C$ = concentration of oxygen (M), $n$ = moles of oxygen, and $V$ = the volume occupied by oxygen (i.e. 0.4 L as the reactor is 1.4 L and volume of acid mine water fed is 1 L)). When sludge is absent from the reactor the

**Table 5** | Effect of various parameters on the rate of $Fe^{2+}$ oxidation for synthetic coal mine water

| Parameter | $Fe^{2+}$ oxidation rate (mg $L^{-1}$ $min^{-1}$) | Reaction order, $n$ | [$Fe^{2+}$] (mg $L^{-1}$) | Shaking rate ($min^{-1}$) | Limestone (mg) | Oxygen pressure (kPa) | Sludge added (mg $L^{-1}$) | Particle size (μm) |
|---|---|---|---|---|---|---|---|---|
| Oxygen pressure | 26.0 | | 5,700 | 150 | 22,680 | 200 | 0 | 150 |
| | 37.0 | | 5,700 | 150 | 22,680 | 300 | 0 | 150 |
| | 49.0 | 0.88 | 5,700 | 150 | 22,680 | 400 | 0 | 150 |
| | 58.6 | | 5,700 | 150 | 22,680 | 500 | 0 | 150 |
| $CaCO_3$ | 40 | 0.30 | 5,700 | 150 | 22,680 | 500 | 0 | 150 |
| | 50 | | 5,700 | 150 | 45,360 | 500 | 0 | 150 |
| | 50 | | 5,700 | 150 | 68,040 | 500 | 0 | 150 |
| | 60 | | 5,700 | 150 | 90,750 | 500 | 0 | 150 |
| $Fe^{2+}$ concentration | 1.0 | 0.90 | 117 | 0 | 22,680 | 500 | 0 | 150 |
| | 4 | | 390 | 150 | 22,680 | 500 | 0 | 150 |
| | 11 | | 1,000 | 150 | 22,680 | 500 | 0 | 150 |
| | 50 | | 5,700 | 150 | 22,680 | 500 | 0 | 150 |
| Sludge concentration | 24 | 0.03 | 5,700 | 150 | 22,680 | 500 | 0 | 150 |
| | 24 | | 5,700 | 150 | 22,680 | 500 | 22,490 | 150 |
| | 40 | | 5,700 | 150 | 22,680 | 500 | 45,000 | 150 |
| | 67 | | 5,700 | 150 | 22,680 | 500 | 57,490 | 150 |
| Shaking rate | 22 | | 5,700 | 0 | 22,680 | 500 | 0 | 150 |
| | 22 | 0.03 | 5,700 | 150 | 22,680 | 500 | 0 | 150 |
| | 28 | | 5,700 | 250 | 22,680 | 500 | 0 | 150 |
| | 32 | | 5,700 | 150 | 22,680 | 500 | 0 | 150 |
| Particle size | 22 | | 5,700 | 150 | 22,680 | 500 | 0 | 800 |
| | 22 | | 5,700 | 150 | 22,680 | 500 | 0 | 560 |
| | 29 | −0.3 | 5,700 | 150 | 22,680 | 500 | 0 | 150 |
| | 45 | | 5,700 | 150 | 22,680 | 500 | 0 | 45 |
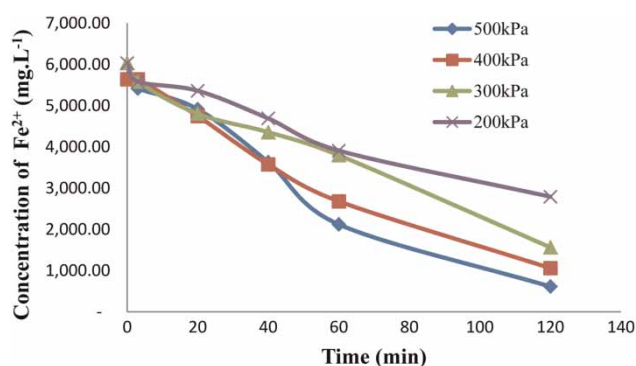
**Figure 2** | Effect of oxygen pressure on the rate of $Fe^{2+}$ oxidation in coal mine water using the pipe reactor. (Experimental conditions: temp $= 23\,°C$, $Fe^{2+} = 5,640$ mg $L^{-1}$, limestone $= 22.7$ g $L^{-1}$, sludge $= 0$ mg $L^{-1}$, shaking rate $= 150$ strokes $min^{-1}$, and limestone particle size $= 150\,\mu m$).

simplified mathematical expression is as follows: $P$ (oxygen) $\infty$ $C$ (oxygen) where $k =$ the constant

$$P_{O2} = kC_{O2} \qquad (9)$$

This leads to Henry's law which predicts the amount of gas dissolved in the acid mine water to oxidize the $Fe^{2+}$

(Ebbing & Gammon 1999):

$$P = k_H X \qquad (10)$$

where $P =$ partial pressure above the liquid (acid mine water) (kPa), $X =$ mole fraction of the gas in the water during oxidation of $Fe^{2+}$, and $k_H =$ pressure (kPa) divided by the concentration at 298 K.

Tables 5 and 6 show that the higher the limestone/ acidity dosage ratio, the faster the $Fe^{2+}$ oxidation rate. At a ratio of 4:1 it was faster than at a ratio of 1:1. This was due to the high alkalinity in solution due to the higher limestone dosage (Ebbing & Gammon 1999). In the case of limestone particle size, the oxidation rate increased with smaller particle size. With a particle size of 45 $\mu m$ the rate was faster than with a particle size of 800 $\mu m$. This was due to 45 $\mu m$ particles of limestone presenting a higher surface area for the reaction to take place than with the 800, 560, 250, and 150 $\mu m$ limestone particle sizes (Ebbing & Gammon 1999).

Increased sludge contents resulted in faster iron(II)-oxidation rates. At sludge contents of 22,490 and 4,500 mg $L^{-1}$

**Table 6** | Effect of various parameters on the rate of $Fe^{2+}$ oxidation for synthetic gold mine water

| Parameter | $Fe^{2+}$ oxidation rate (mg $L^{-1}$ $min^{-1}$) | Reaction order, $n$ | [$Fe^{2+}$] (mg $L^{-1}$) | Shaking rate ($min^{-1}$) | Limestone (mg) | Oxygen pressure (kPa) | Sludge added (mg $L^{-1}$) | Particle size ($\mu m$) |
|---|---|---|---|---|---|---|---|---|
| Oxygen pressure | 1.1 | | 117 | 150 | 890 | 200 | 0 | 150 |
| | 1.2 | | 117 | 150 | 890 | 300 | 0 | 150 |
| | 1.5 | 0.60 | 117 | 150 | 890 | 400 | 0 | 150 |
| | 1.8 | | 117 | 150 | 890 | 500 | 0 | 150 |
| $CaCO_3$ | 1.8 | 0.10 | 117 | 150 | 890 | 400 | 0 | 150 |
| | 1.8 | | 117 | 150 | 1,780 | 400 | 0 | 150 |
| | 1.9 | | 117 | 150 | 2,670 | 400 | 0 | 150 |
| | 2.0 | | 117 | 150 | 3,560 | 400 | 0 | 150 |
| $Fe^{2+}$ concentration | 1.4 | 0.90 | 117 | 0 | 890 | 400 | 0 | 150 |
| | 3.7 | | 390 | 150 | 890 | 400 | 0 | 150 |
| | 10.6 | | 1,000 | 150 | 890 | 400 | 0 | 150 |
| | 50.0 | | 5,700 | 150 | 890 | 400 | 0 | 150 |
| Sludge concentration | 1.2 | 0.03 | 117 | 150 | 890 | 400 | 0 | 150 |
| | 1.9 | | 117 | 150 | 890 | 400 | 774 | 150 |
| | 2.0 | | 117 | 150 | 890 | 400 | 1,400 | 150 |
| | 2.0 | | 117 | 150 | 890 | 400 | 1,650 | 150 |
| Shaking rate | 1.1 | | 117 | 0 | 890 | 400 | 0 | 150 |
| | 1.1 | 0.01 | 117 | 50 | 890 | 400 | 0 | 150 |
| | 1.3 | | 117 | 150 | 890 | 400 | 0 | 150 |
| | 1.4 | | 117 | 250 | 890 | 400 | 0 | 150 |
| Particle size | 0.9 | | 117 | 150 | 890 | 400 | 0 | 800 |
| | 1.1 | | 117 | 150 | 890 | 400 | 0 | 560 |
| | 1.5 | −0.2 | 117 | 150 | 890 | 400 | 0 | 150 |
| | 1.5 | | 117 | 150 | 890 | 400 | 0 | 45 |

(Table 5), the rate of oxidation was faster than when no sludge was added. In the case of gold mine water (Table 6), when no sludge was added the oxidation rate was slower than when 774, 1,400 and 1,650 mg L$^{-1}$ sludge were added.

The rate of iron(II) oxidation also increased with increased iron(II) concentrations. Tables 5 and 6 show that a concentration of 5,700 mg L$^{-1}$ Fe$^{2+}$ gave a faster oxidation rate when compared with 1,000, 390, and 117 mg L$^{-1}$ Fe$^{2+}$ concentrations.

The rate of Fe$^{2+}$ oxidation depended on the concentration of Fe$^{2+}$ and the concentration of oxygen with the following first-order rate equation according to Stumm & Lee (1961):

$$- \partial[Fe^{2+}]/\partial t = k[Fe^{2+}][O_2] \tag{11}$$

where [ ] = concentration, $t$ = time, $\partial$ = partial rate of change, (−) = reactants consumed, and $k$ = reaction constant.

But further investigations of the Fe$^{2+}$ revealed that the rate of Fe$^{2+}$ oxidation also depended on the amount of suspended solids, i.e. gypsum and ferric hydroxide sludge, and their surface areas (Maree *et al.* 1997). The rate of Fe$^{2+}$ oxidation was investigated and it was found that the mixing rate and the surface area of the reactor, also played a role (Maree *et al.* 2004).

The overall reaction for coal mine water was first order (Table 5):

$$-\partial[Fe^{2+}]/\partial t = k[Fe^{2+}]^{0.90}[P_{O2}]^{0.88}[CaCO_3]^{0.3}[SS]^{0.03}[SR]^{0.03} \tag{12}$$

The overall reaction for gold mine water was also first order (Table 6):

$$-\partial[Fe^{2+}]/\partial t = k[Fe^{2+}]^{0.90}[P_{O2}]^{0.60}[CaCO_3]^{0.1}[SS]^{0.01}[SR]^{0.01} \tag{13}$$

The negative partial order indicated that the particle size did not influence the reaction. $P_{O2}$ = oxygen pressure above the acid mine water, [CaCO$_3$] = limestone concentration (i.e. OH$^-$ ions), [SS] = suspended gypsum and ferric hydroxide sludge, [O$_2$] = concentration of pure oxygen, [SR] = shaking rate (in a form of mixing rate), and [Fe$^{2+}$] = concentration of Fe$^{2+}$.

## Optimization of OPeN process pilot-plant operational parameters

Figures 3–5 show the effects of various parameters during optimization of the OPeN process plant. For comparison
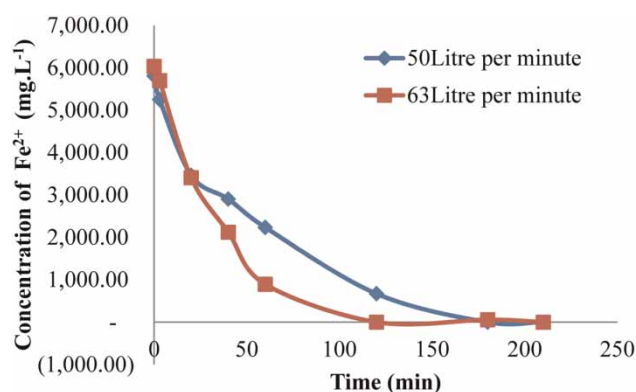
**Figure 3** │ Optimization of flow rate on the rate of Fe$^{2+}$ oxidation in coal mine water in the OPeN process. (Experimental conditions: temp = 23–50 °C, limestone (% CaCO$_3$) = 81.2%, limestone = 1,192 g with 18% excess, volume = 40 L, 99.5% oxygen, oxygen pressure = 200 kPa, and sludge = 0 mg L$^{-1}$.)
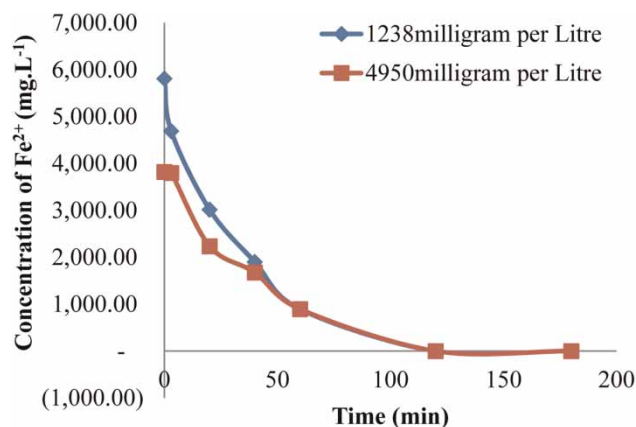
**Figure 4** │ Optimization of sludge content on the rate of Fe$^{2+}$ oxidation in coal mine water in the OPeN process. (Experimental conditions: temp = 23–50 °C, limestone (% CaCO$_3$) = 81.2%, limestone = 1,192 g with 18% excess, volume = 40 L, 99.5% oxygen, oxygen pressure = 200 kPa, and flow rate = 63 L min$^{-1}$.)
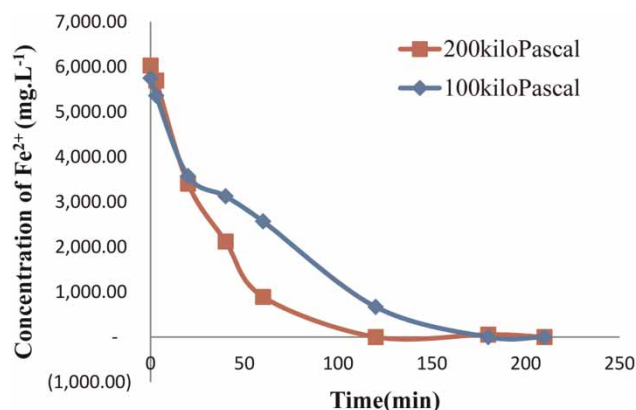
**Figure 5** │ Optimization of oxygen pressure on the rate of Fe$^{2+}$ oxidation in coal mine water in the OPeN process. (Experimental conditions: temp = 23–50 °C, limestone (% CaCO$_3$) = 81.2%, limestone = 1,192 g with 18% excess, volume = 4 L, 99.5% oxygen, flow rate = 63 L min$^{-1}$, and sludge = 0 mg L$^{-1}$.)

purposes the influence of different parameters on the rate of $Fe^{2+}$ oxidation, such as pressure, flow rate, and amount of sludge added, was studied.

## Flow rate

Figure 3 shows that the faster the flow rate the faster the oxidation rate of $Fe^{2+}$ owing to the higher oxygen pressure and also to the balls moving faster and preventing gypsum build-up in the pipe.

## Recycled sludge

Figure 4 shows that the higher the amount of recycled sludge the faster the rate of $Fe^{2+}$ oxidation (Maree *et al.* 1997); it was also found that the ferric hydroxide sludge caused blockage and also increases the rate of $Fe^{2+}$ oxidation by a heterogeneous reaction as outlined by Van Beek (2010).

## Pressure

The results in Figure 5 show that an increase in oxygen pressure increased the rate of $Fe^{2+}$ oxidation, which also has an impact on the flow rate.

## Pipe blockage prevention

The rubber balls proved better than the sponge balls because they were able to move faster and were harder than the sponge balls. The sponge balls tended to adhere to the walls of the pipe, causing them to move slower or not at all, leading to blockage. If the pressure in the system was greater than the pressure due to the water flow, the balls did not move, creating a partial blockage and a resultant slow flow rate.

## CONCLUSIONS

The OPeN process for the oxidation of $Fe^{2+}$ in acid mine water was developed and tested. The results showed the following:

- A residence time of 120 min was needed to remove $Fe^{2+}$ from coal mine water and a residence time of 20 min was needed to remove $Fe^{2+}$ from gold mine water, using the OPeN process pilot plant in a continuous

mode at oxygen pressures of 200 and 100 kPa, respectively.
- The above showed that the oxygen pressure, calcium carbonate, and $Fe^{2+}$ concentrations played a role in the oxidation rate of $Fe^{2+}$ in acid mine water.
- The faster the flow rate the faster the ball movement and the $Fe^{2+}$ oxidation.
- The rubber balls prevented gypsum scaling inside the pipe under pressure better than sponge balls that moved slower and caused blockage.

## REFERENCES

APHA 1995 *Standard Methods for the Examination of Water and Wastewater*. American Public Health Association/American Water Works Association/Water Environment Federation, New York, USA.

Costello, C. 2003 *Acid Mine Drainage: Innovation Treatment Technologies*. United States Environmental Protection Agency, Washington, DC, USA.

Department of Environmental Affairs and Tourism (DEAT) 2008 Mine Water Pollution. Available from http://www.environmentalaffairs.gov (accessed 1 March 2008).

Department of Water Affairs (DWAF) 2012 *Assessment of the Water Quality and Quality of the Witwatersrand Mine Water Voids (No. 107748/6169)*. DWAF, Pretoria, South Africa.

Ebbing, D. D. & Gammon, S. D. 1999 *General Chemistry*. Houghton Mifflin Company, Boston, MA, USA.

Glover, H. G., Hunt, J. & Konyon, W. G. 1965 Process for the bacteriological oxidation of ferrous salts in acid solution. United States Patent No. 2,218,252.

Kazi, S. N. 2012 Fouling and fouling mitigation on heat exchanger surfaces. In: *Heat Exchangers – Basics Design Application* (J. Mitrovic, ed.), InTech. Available from http://www.intechopen.com/download/pdf/30778 (accessed 9 March 2012).

Maree, J. P. & Du Plessis, P. 1993 Neutralization of acid mine water calcium carbonate. *Paper presented at the Proc. IAWQ Conference on Pre-treatment of Industrial Wastewaters*, Athens.

Maree, J. P. & Du Plessis, P. 1994 Neutralization of acid mine water with calcium carbonate. *Water Science and Technology* **29** (9), 285–296.

Maree, J. P., Van Tonder, G. J., Adlem, C., Millard, P., De Beer, M. & Strydom, W. F. 1997 *Pilot Plant Studies on Limestone Neutralization and Gypsum Crystallization of Acidic Colliery Effluent*. Confidential CSIR Report. Division of Water, Environment and Forestry Technology, CSIR, Pretoria, South Africa.

Maree, J. P., Dingemans, D., Van Tonder, G. J. & Mtimkulu, S. 1998 Biological iron(II) oxidation as pre-treatment to limestone neutralization of acid water. *Water Science and Technology* **38** (4–6), 331–337.

Maree, J., Strydom, W. F., Adlem, C. J. L., De Beer, M., Van Tonder, G. J. & Van Dijk, B. J. 2004 *Neutralization of Acid Mine Water and Sludge Disposal*. Report No. 1057/1/4,

Division of Water, Environment and Forestry Technology, CSIR, Pretoria, South Africa.

Mihok, E. A., Deul, M. & Chanbertain, C. E. 1968 *The Limestone Neutralization Process*. Report No. 7191, Mine Water Research, US Department of the Interior, Bureau of Mines, Pittsburgh, PA, USA.

Mihok, E. A., Deul, M. & Chanbertain, C. E. 1970 Plant Design and Cost Estimates, (Report No. 7368). Mine Water Research, US Department of the Interior, Bureau of Mines, Pittsburgh, PA, USA.

Stumm, W. N. & Lee, G. F. 1961 Oxygenation of ferrous iron. *Industrial and Engineering Chemistry* **53**, 143–146.

Van Beek, C. G. E. M. 2010 *Cause and Prevention of Clogging of Wells Abstracting Groundwater from Unconsolidated Aquifers*. PhD Thesis, Vrije Universiteit, Amsterdam, The Netherlands.

Vogel, A. I. 1989 *Vogel's Textbook of Quantitative Inorganic Analysis*. Wiley, New York, USA.

Volpicelli, G., Caprio, V. & Santoro, L. 1982 Process for neutralizing acid waste waters by powdered limestone. *Environmental Technology Letters* **3**, 97–103.