Acid mine water neutralisation with ammonium hydroxide and desalination with barium hydroxide

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ABSTRACT

In South Africa, acid mine drainage is polluting increasingly scarce ground- and surface water. The ammonium-barium (NB) process described in this paper consists of neutralisation and metal removal with NH\(_4\)OH, sulphate removal with Ba(OH), and Ca removal with CO\(_2\). Laboratory studies showed that metals are removed to low levels. This includes Fe(II), the predominant metal in mine water. It is first oxidised to Fe(III), whereafter it precipitates as Fe(OH). Sulphate is removed to low concentrations as BaSO\(_4\). During CO\(_2\) dosing, CaCO\(_3\) is precipitated to its saturation level. The simulation predictions followed the same pattern as the experimental results obtained. This study showed that NH\(_4\)OH can be used for treatment of acid mine drainage rich in sulphates and NH\(_4\)OH can be recycled in the process. Hydrated lime treatment resulted in removal of the remaining ammonia using a rotary evaporator.

Keywords: acid mine water, ammonium hydroxide, barium hydroxide, sulphate removal

INTRODUCTION

Acidic mine waters are continuously discharged from certain mines to the environment, with little treatment. Acid mine water contains high levels of SO\(_4\) in addition to Fe, Al, Mn and other metals. Coal mining and fertiliser manufacturing are examples of industrial operations that give rise to severe acid pollution (Maree et al., 2004). Clean water is essential for agriculture, domestic and industrial use, and increases in population have led to an increase in the water demand. South Africa (SA) is an arid country, which has exacerbated the problem. It has been predicted that the country’s freshwater resources will be fully utilised within the next 20 to 30 years if the current growth in water demand and use (or abuse) is not altered (Van Niekerk and Maree, 2001). In the Western Basin of the Witwatersrand, Gauteng Province, mine water started to décant in 2002. In the Eastern Basin, a single pump station at Grootvlei Mine pumped out between 75 and 108 Mℓ/day of mine water. The pH can be as low as 2 (Jiménex et al., 2009) and poses a problem because the majority of natural life is adapted to survive at around pH 7. About 540 Mℓ/day of acid mine water is produced in the Gauteng region alone (Hlabela, 2009).

AMD is formed when pyrite in contact with atmospheric oxygen becomes oxidised to soluble iron and sulphuric acid, frequently catalysed by sulphur-oxidising bacteria (Jennings et al., 2008).

\[
2\text{FeS}_2 + 7O_2 + 2H_2O \rightarrow 2\text{Fe}^{2+} + 4H^+ + 4\text{SO}_4^{2-}
\]

Mine-water treatment requires pre-treatment for neutralisation and metal removal, followed by desalination for removal of dissolved salts. The integrated limestone and lime process was developed for neutralisation and partial SO\(_4\) removal from AMD (Maree, 2003). Limestone and lime are used to increase the pH and, together with aeration, Fe(II) is oxidised and precipitates as Fe(OH). Limestone is used for initial AMD treatment as it is less costly than lime. It is moreover safe to handle and its dissolution occurs at pH below 7, obviating the need for pH control. In the second stage, lime is introduced to precipitate the remaining metals such as Mn and Al. Unfortunately, its successful application is limited as it only lowers SO\(_4\) concentration to around 1 200 mg/l (INAP, 2000).

Other treatment techniques have been developed that utilise limestone, which can neutralise acid but does not raise the pH sufficiently to remove metals (Ziemkiewicz et al., 1997). Several other processes can be considered for sulphate removal, e.g., biological sulphate removal, SAVMIN (by ettringite formation), and membrane processes. Barium sulphate is highly insoluble which makes Ba dosing suitable for removal of SO\(_4\) as BaCO\(_3\) can be used for SO\(_4\) removal according to the following reaction:

\[
\text{BaCO}_3 + \text{CaSO}_4 \rightarrow \text{BaSO}_4 + \text{CaCO}_3
\]

Trusler et al. (1988) developed a BaCO\(_3\) method for SO\(_4\) removal by using a two-stage fluidised-bed reactor system to overcome the other problems identified by Kun (1972), i.e. long retention times and the high Ba concentrations in the treated water. BaCO\(_3\) and lime would be added to the effluent to soften the water and produce a precipitate. The disadvantage of Reaction (2) is that BaSO\(_4\) and CaCO\(_3\) co-precipitate. Maree et al. (1989) noted a problem in separating co-precipitated BaSO\(_4\) and CaCO\(_3\). However, the BaCO\(_3\) became inactive when coated with precipitated metal hydroxide, which made it unsuitable for most mine waters. Alternatively, Ba(OH), can be used in place of BaCO\(_3\), and offers the benefits of rapid reaction times and precipitation of only BaSO\(_4\).

The purpose of this investigation was to demonstrate that NH\(_4\)OH in combination with Ba(OH), and lime treatment offers an attractive solution for treatment of acid mine-water.

Received 30 May 2013; accepted in revised form 20 June 2014.

http://dx.doi.org/10.4314/wsa.v40i3.16
Available on website http://www.wrc.org.za
ISSN 0378-4738 (Print) = Water SA Vol. 40 No. 3 July 2014
ISSN 1816-7950 (On-line) = Water SA Vol. 40 No. 3 July 2014

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Identify optimum conditions for Fe(II) oxidation when
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Identify optimum conditions for removal of calcium by
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The overall objectives of the study were the following:

- Identify optimum conditions for Fe(II) oxidation when using NH₄OH as alkali
- Determine optimum conditions for removal of SO₄ when Ba(OH)₂ is added for precipitation of BaSO₄ (barite)
- Demonstrate that limestone can be used for free acid removal
- Identify optimum conditions for recovery of NH₄OH
- Identify optimum conditions for removal of calcium by introduction of CO₂
- Compare the behaviour of simulated and real acid mine water
- Compare actual measured water quality with that predicted by Visual MINTEQ software

EXPERIMENTAL

Feedstock

Mine water from the decanting site in Randfontein was used as feed water containing Fe(II) (670 mg/ℓ) and SO₄ (2 090 mg/ℓ). Simulated AMD was prepared from an aqueous mixture of FeSO₄ (Rochelle Chemicals, Pretoria) and H₂SO₄ (SMM Instruments, Johannesburg). Simulated mine-water was prepared as follows: FeSO₄.7H₂O (1.50 g) and concentrated H₂SO₄ (11.0 mL) were each dissolved together in distilled water and made up to 500 mL solution containing 600 mg/ℓ of Fe(II) and 2 063 mg/ℓ of SO₄.

Reagents

Aqueous NH₄ (SMM Instruments, Johannesburg) was used for neutralisation. Compressed air (Afrox, Pretoria) was bubbled into the reactor at a controlled flow-rate to provide the oxygen for iron oxidation. Ba(OH)₂ (Merck, SA) was used for SO₄ removal. Lime (Rochelle Chemicals, Pretoria) was used for removing the remaining NH₄ in the solution and CO₂ (Afrox, Pretoria) was used for the precipitation of Ca as CaCO₃. CaCO₃ (Rochelle Chemicals, Pretoria) was used to remove free acid in the alternative method.

Equipment

Neutralisation of acidic mine water with NH₄OH and SO₄ removal with Ba(OH)₂ was studied using arrays of stirred beakers. NH₄ stripping studies were done using a desorption column and a rotary evaporator. The desorption column was a cylinder (diameter: 223 mm; height: 2 000 mm), packed with plastic rings that served to increase the surface area, and fitted with a pump that circulated the sample. A spray nozzle on top of the column distributed the sample evenly across the cross section of the column. In this column NH₄(aq) diffuses as NH₃ gas. A rotary evaporator was used as an alternative method for removal of NH₄.

Experimental procedures

Batch studies were carried out using 5 ℓ and 500 mL stirred, glass beakers. Compressed air was passed through the solutions using sintered glass diffusers at different flow-rates. Simulated mine water and NH₄OH were mixed at Time Zero. NH₄OH was added slowly to the solution at 10 mL intervals and 10 min was allowed at each interval for equilibration. Compressed air was passed through the reaction mixture. Samples were taken at regular intervals and assayed for pH and Fe(II) concentration using redox titration.

SO₄ was removed as precipitated BaSO₄ by addition of Ba(OH)₂. NH₄ was removed in 2 stages: Ba(OH)₂ was used in the first stage for partial removal and in the second stage lime was added into the solution, fed into the column by a pump and recycled under room temperature for 3 h. Compressed air removed NH₃ as NH₃ gas. The remaining sample was taken at intervals and assayed for pH and NH₄ concentration. NH₃ gas was not adsorbed to any surface; hence further experiments to investigate adsorption to an acidic solution are planned.

The previous method needs hydrated lime to remove the remaining NH₄ from the solution. The costs can be minimised.
by addition of limestone in the first stage of the process. In this experiment, CaCO₃ was added to remove free acid so that NH₃OH only removes metal hydroxides. In this process, addition of hydrated lime for NH₃ removal was eliminated.

**Experimental programme**

The effects of the following parameters on the Fe (II) oxidation were determined:
- Air flow-rates (3.1, 5, 5.6, 7.9 ℓ/min)
- NH₃/acidity (mol ratios of 0.2, 0.4, 0.6, 0.8, 1.0, 1.2, 1.4, 1.6)
- Temperature (25, 35, 45, 65°C)

Batch studies were carried out to demonstrate the removal of SO₄ in the solution with addition of Ba(OH)₂ by varying the SO₄ removed/Ba dosed mol ratio (mol/mol: 0.5, 1, 1.5).

The effects of the following parameters on the NH₃ stripping were determined:
- Air bubbled through to the desorption column (119, 145, 168 ℓ/min)
- Amount of packing material in the desorption column (empty, half-full and fully-packed)
- Temperature in the rotary evaporator for removal of NH₃ as a gas in the solution (25, 35, 45, 55°C)

**RESULTS AND DISCUSSION**

**Water quality**

*Comparison between real and simulated acid mine water*

Tables 1 and 2 show the chemical compositions of the water after various treatment stages for simulated and real acid mine water, respectively. Fe(II) concentrations were lowered to <10 mg/ℓ in both cases, after addition of NH₃OH. SO₄ concentrations after Ba(OH)₂ addition were < 400 mg/ℓ. In real acid mine-water, the initial pH was 4.2 and less free acid was present. Ba(OH)₂ was added to raise the pH to 11.9. This made addition of lime unnecessary for removal of NH₃.

**Chemical reactions for simulated acid mine water**

In the ammonium-barium (NB) process, a variation of the MBO (magnesium barium oxide) process (Bologo et al., 2011), Mg(OH)₂ was replaced with NH₃OH. During NH₃OH treatment, acid and the metals assayed for were reduced to below the maximum permissible limit according to the general standard. The lowering of the metals in the case of NH₃OH treatment was mainly due to the oxidation of Fe²⁺ to Fe³⁺ (Reaction (3)) and precipitation as Fe(OH)₃ (Reaction (4)). This was owing to the low solubility-product for Fe(OH)₃ (Ksp = 2.64 x 10⁻³⁹). NH₃OH neutralises the acid produced and forms NH₄⁺ ions (Reaction (5)). NH₃ concentration was lowered from 1 020 mg/ℓ to 425 mg/ℓ by dosing Ba(OH)₂, 8H₂O (Reaction (6)) and simultaneously lowering SO₄ concentration from 1 786 mg/ℓ to 350 mg/ℓ (Reaction (6)). Lime was added to lower the remaining NH₃ concentration to 8.5 mg/ℓ by stripping using rotary evaporator.

**TABLE 1**

| Parameter                      | Chemical composition          | Feed | Treated |
|--------------------------------|--------------------------------|------|--------|
| Dosage (mmol)                  | NH₃OH  | Ba(OH)₂ | Ca(OH)₂ | CO₃⁻ |
| NH₃/acidity (mol/mol)          | 1.2    | 73      | 14.4    | 15.0 |
| Ba dosage/SO₄ removed (mol/mol)|        | 0.96    |         |      |
| Water quality (mmol where applicable) | pH | 1.9 | 9.9 | 10.6 | 12.6 | 6.5   |
|                                | Acidity (mmol CaCO₃) | 2.15 | N/A    | N/A   | N/A   |
|                                | Fe(II)     | 10.74 | 0.15   | 0.148 | 0.146 | 0.143 |
|                                | SO₄        | 21.49 | 18.6   | 3.66  | 3.63  | 3.57  |
|                                | NH₃        | N/A   | 60     | 25    | 5     | 0.48  |

N/A: not assayed
Calcium was recovered by dosing CO₂ (Reaction (8)). NH₃ was partially stripped from the solution as NH₃ gas after addition of Ba(OH)₂ (pH 10.6), as NH₃ becomes sufficiently volatile only at pH > 12.4; hence the need for lime addition to increase the pH. Excess Ba(OH)₂ was not added to increase the pH because excess Ba in the treated water must be avoided on account of its toxicity to humans and animals.

$$2\text{Fe}^{2+} + \frac{1}{2}\text{O}_2 + 2\text{H}^+ + 3\text{SO}_4^{2-} \rightarrow 2\text{Fe}^{3+} + 3\text{SO}_4^{2-} + \text{H}_2\text{O}$$  (3)

$$2\text{Fe}^{3+} + 6\text{H}_2\text{O} \rightarrow 2\text{Fe(OH)}_3 + 6\text{H}^+$$  (4)

$$6\text{H}^+ + 3\text{SO}_4^{2-} + 6\text{NH}_4\text{OH} \rightarrow 6\text{NH}_4^+ + 6\text{H}_2\text{O} + 3\text{SO}_4^{2-}$$  (5)

$$6\text{NH}_4^+ + 3\text{SO}_4^{2-} + 3\text{Ba(OH)}_2 \cdot \rightarrow 3\text{NH}_4\text{OH} + 3\text{NH}_3 + 3\text{BaSO}_4 + 3\text{H}_2$$  (6)

$$3\text{NH}_4\text{OH} + \text{Ca(OH)}_2 \rightarrow \text{Ca(OH)}_2 + 3\text{H}_2\text{O} + 3\text{NH}_3$$  (7)

$$\text{Ca(OH)}_2 + \text{CO}_2 \rightarrow \text{CaCO}_3 + \text{H}_2\text{O}$$  (8)

$$2\text{Fe}^{2+} + 2\text{H}^+ + 3\text{SO}_4^{2-} + \frac{1}{2}\text{O}_2 + 6\text{NH}_4\text{OH} + 3\text{Ba(OH)}_2 + \frac{1}{2}\text{Ca(OH)}_2 + \text{CO}_2 \rightarrow 2\text{Fe(OH)}_3 + 3\text{BaSO}_4 + 6\text{NH}_3 + 3\text{CaCO}_3 + 8\text{H}_2\text{O}$$  (9)

### Table 2

| Parameter                         | Feed | NH₄OH | Ba(OH)₂ | CO₂ |
|----------------------------------|------|-------|---------|-----|
| Dosage (mmol)                    | -    | 73.0  | 14.4    | N/A |
| NH₄/acidity (mol/mol)            | 1.2  |       |         |     |
| Ba dosage/SO₄ removed (mol/mol)  | 0.83 |       |         |     |

### Water quality (mmol where applicable)

| Parameter     | Feed | Treated | Treated | Treated |
|---------------|------|---------|---------|---------|
| pH            | 3.8  | 9.6     | 11.2    | 6.8     |
| Acidity (mmol CaCO₃) | 8.50 | N/A     | N/A     | N/A     |
| Fe            | 12.0 | 0.016   | 0.002   | < DL    |
| Mn            | 1.16 | 0.036   | < DL    | < DL    |
| Mg            | 13.3 | 16.83   | 5.54    | < DL    |
| Ca            | 10.5 | 10.0    | 5.5     | < DL    |
| Zn            | 0.0017 | < DL | < DL | < DL |
| Ni            | 0.017 | < DL | < DL | < DL |
| Cl            | 20.57 | 15.796 | 15.4    | 7.90    |
| K             | 0.11 | 0.053   | 0.095   | < DL    |
| SO₄           | 23.1 | 21.6    | 4.97    | N/A     |
| NH₃           | N/A  | 51.94   | 0.47    | N/A     |

N/A: not assayed
<DL: below detection limit

(Reaction (7)). Calcium was recovered by dosing CO₂ (Reaction (8)). NH₃ was partially stripped from the solution as NH₃ gas after addition of Ba(OH)₂ (pH 10.6), as NH₃ becomes sufficiently volatile only at pH > 12.4; hence the need for lime addition to increase the pH. Excess Ba(OH)₂ was not added to increase the pH because excess Ba in the treated water must be avoided on account of its toxicity to humans and animals.

Fe(II)-oxidation in the presence of NH₄OH for neutralisation

The rate at which Fe(II) is oxidised depends on variable parameters, including pH, concentration of dissolved O₂ and temperature (Werner and Lee, 1961). Figure 2 shows that the presence of NH₄OH in the acidic solution affects the oxidation of Fe(II). The mol ratio of NH₄ to acidity was determined to establish how much NH₃ was required to remove the free acid so as to remove Fe by raising the pH.

![Figure 2](http://dx.doi.org/10.4314/wsa.v40i3.16)

**Figure 2**

Effect of NH₄/acidity on the rate of Fe(II) removal by oxidation and precipitation (600 mg/l Fe(II), 2150 mg/l acidity, 25°C)
Figure 4 shows the effects of temperature and the graphs showed, as expected, that an increment in temperature resulted in slightly faster Fe(II) oxidation. A problem was that the pH dropped due to NH$_3$ stripping. Therefore, for optimum Fe(II) oxidation, it was carried out at room temperature.

Sulphate and partial ammonia removal using barium hydroxide

Ba(OH)$_2$ was used for SO$_4$ removal instead of lime because of the low solubility product of barite (K$_{sp}$ = 1.08 x 10$^{-10}$) compared to gypsum (K$_{sp}$ = 4.93 x 10$^{-5}$). Figure 5 shows experimental, theoretical and simulated results for optimum Ba/SO$_4$ mol ratio dosed. The pattern for the removal of SO$_4$ was similar.

Ammonia removal using hydrated lime

The rate of NH$_3$ desorption depends on the temperature, the height of the packed column and air flow rate (Orvos et al., 2010). Figure 6 shows the effect of air flow rate. It was noted that at the air flow rate of 168 ℓ/min, NH$_3$ concentration was reduced from 525 mg/ℓ to 11.9 mg/ℓ and the pH was lowered from 13.4 to 9.0 due to NH$_3$ gas being stripped out.

Figure 7 shows the effect of amounts of column packing material on NH$_3$ removal. It was noted that the stripping of NH$_3$ with a fully packed column proceeded at the fastest rate.

The effect of temperature on NH$_3$ stripping using a rotary evaporator was determined. Figure 8 showed that, as expected, the higher the temperature the more NH$_3$ becomes stripped out of the solution. The optimum temperature was 45°C and further increases in temperature, resulted in insignificant effects.

Removal of free acid using limestone

Should the acid in mine-water first be neutralised with CaCO$_3$, it is expected that no addition of lime will be required after Ba dosing for NH$_3$ removal. Table 3 shows the chemical composition of simulated AMD after adding limestone in the first stage,
followed by various treatment stages. Limestone was added to pH 5.5 to remove the acid. The addition of NH$_4$OH resulted in the removal of metals as hydroxides and increases the pH to 10.5, which was higher than that when limestone was omitted. Limestone was essential because addition of Ba(OH)$_2$ was sufficient to allow all of the NH$_3$ to be removed from the solution. The chemical reactions below show how limestone addition assisted in the elimination of hydrated lime for NH$_3$ removal.

\[
\begin{align*}
2\text{Fe}^{2+} + 2\text{H}^+ + 2\text{SO}_4^{2-} + \text{CaCO}_3 &\rightarrow 2\text{Fe}^{2+} + 2\text{SO}_4^{2-} + \text{Ca}^{2+} + \text{HCO}_3^- + \text{OH}^- \quad (10) \\
2\text{Fe}^{2+} + \frac{1}{2}\text{O}_2 + 5\text{H}_2\text{O} &\rightarrow 2\text{Fe(OH)}_3 + 4\text{H}^+ \quad (11) \\
4\text{NH}_4\text{OH} + 4\text{H}^+ &\rightarrow 4\text{NH}_4^+ + 4\text{H}_2\text{O} \quad (12) \\
2\text{Ba(OH)}_2 + 2\text{SO}_4^{2-} + 4\text{NH}_4^+ &\rightarrow 2\text{BaSO}_4 + 4\text{NH}_3 + 4\text{H}_2\text{O} \quad (13)
\end{align*}
\]

Comparison of the experimental results with Visual Minteq model predictions

Visual Minteq software is used to predict experimental results at equilibrium (Visual MINTEQ, 2010). Figure 9 showed that the pH predicted by the model and that established experimentally followed the same pattern. The model predicted optimum Fe(II) oxidation to occur at a NH$_3$/acidity mol ratio of unity. Experimentally, the optimum Fe(II) oxidation was found to occur at a mol ratio of 1.2.

CONCLUSIONS

It was demonstrated using the NB process at laboratory scale, that:

### TABLE 3

| Parameter | Chemical composition of feed | Chemical composition of treated water |
|-----------|------------------------------|----------------------------------------|
| Dosage (mmol) | CaCO$_3$ | NH$_4$OH | Ba(OH)$_2$ | CO$_3^-$ |
| NH$_3$/acidity (mol/mol) | | | | |
| Ba dosage/SO$_4$ removed (mol/mol) | | | | 0.85 |
| Water quality (mmol where applicable) | | | | |
| pH | 2.95 | 5.5 | 10.5 | 11.1 | 6.5 |
| Acidity (mmol CaCO$_3$) | 12.5 | N/A | N/A | N/A | N/A |
| Fe(II) | 11.63 | 9.97 | 0.13 | 0.11 | N/A |
| Ca | 12.0 | 18.35 | 17.66 | 3.21 | N/A |
| Mg | 11.0 | 11.35 | 12.11 | 1.12 | N/A |
| Mn | 0.833 | 0.721 | 0.011 | < DL | < DL |
| K | 0.241 | 0.192 | 0.026 | < DL | < DL |
| Cl | 19.18 | 18.82 | 14.2 | 13.2 | 8.20 |
| SO$_4$ | 21.4 | 21.4 | 21.1 | 4.12 | N/A |
| NH$_3$ | N/A | N/A | 60 | 0.2 | N/A |

N/A: not assayed
<DL: below detection limit
• By using NH₄OH instead of Ca(OH)₂, gypsum scaling can be avoided in the full-scale process.
• NH₄OH precipitated Fe as the hydroxide in the simulated and real mine-water.
• Ba(OH)₂ precipitated SO₄ in the mine water as BaSO₄ which in partial NH₄ removal on account of the raised pH, and the NH₄⁺ compound did not precipitate because of the solubility of NH₄SO₄.
• Hydrated lime treatment resulted in removal of the remaining NH₄ by using a rotary evaporator.
• In the treated mine-water, CO₂ treatment precipitated Ca as CaCO₃.
• The method was able to remove metal in real and simulated acid mine-water.
• Addition of CaCO₃ eliminated the need for addition of hydrated lime and limestone is cheaper than hydrated lime.
• The simulation predictions were similar to the experimental results obtained.

ACKNOWLEDGEMENTS

Thanks are due to the following organisations: the National Research Foundation, for funding TUT projects on mine-water neutralisation and SO₄ removal. Rand Water, for funding the activities of the Rand Water Chair at TUT, and Tshwane University of Technology, which provides substantial financial support for the research programme on mine-water. The inputs of the following people are acknowledged: Professor Fritz Carlsson for editing the document and Mr Luke Gwatidzo (PhD student) for assistance with the laboratory work.

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