

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

MD Maila¹, JP Maree² and LM Cele¹

¹Department of Chemistry, Tshwane University of Technology, Private Bag X680, Pretoria, 0001, South Africa

²Department of Environmental, Water and Earth Sciences, Tshwane University of Technology, Private Bag X680, Pretoria, 0001, South Africa

ABSTRACT

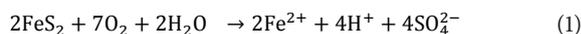
In South Africa, acid mine drainage is polluting increasingly scarce ground- and surface water. The ammonium-barium (NB) process described in this paper consists of neutralisation and metal removal with NH_4OH , sulphate removal with $\text{Ba}(\text{OH})_2$ and Ca removal with CO_2 . Laboratory studies 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 $\text{Fe}(\text{OH})_3$. 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_4OH can be used for treatment of acid mine drainage rich in sulphates and NH_4OH 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 decant 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 (Jiménez et al., 2009) and poses a problem because the majority of natural life is adapted to survive at around pH 7. About 540 Mℓ/d of acid mine water is produced in the Gauteng region alone (Hlabela, 2009).

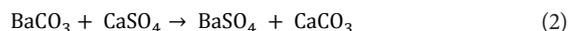
AMD is formed when pyrite in contact with atmospheric oxygen becomes oxidised to soluble iron and sulphuric acid, frequently catalysed by sulphur-oxidising bacteria (Jennings et al., 2008).



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 $\text{Fe}(\text{OH})_3$. 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 .

BaCO_3 can be used for SO_4 removal according to the following reaction:



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, $\text{Ba}(\text{OH})_2$ 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_4OH in combination with $\text{Ba}(\text{OH})_2$ and lime treatment offers an attractive solution for treatment of acid mine-water

* To whom all correspondence should be addressed.

☎ +27 12 382 6315; fax: +27 86 642 5592 ;

e-mail: mavis.dineo@gmail.com

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

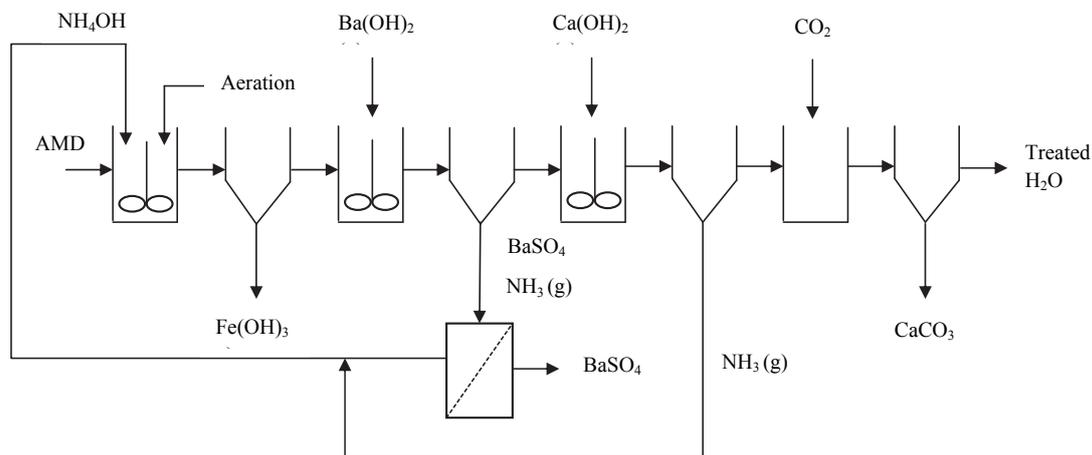


Figure 1
Process flow-diagram of integrated $\text{NH}_4\text{OH}/\text{Ba}(\text{OH})_2/\text{lime}$ process for acid mine water treatment

rich in Fe(II). In this approach, Fe(II) is oxidised and precipitated in the presence of added NH_4OH as $\text{Fe}(\text{OH})_3$, allowing the precipitated $\text{Fe}(\text{OH})_3$ to be separated. In the following stage, SO_4 is precipitated with $\text{Ba}(\text{OH})_2$, as BaSO_4 , and separated as a sludge. NH_3 is partially stripped off because of the increased pH when $\text{Ba}(\text{OH})_2$ is dosed. Next, lime is added to increase the pH to above 12.4, to allow stripping off of the remaining NH_3 . Calcium is recovered as CaCO_3 by introducing CO_2 into the solution.

The overall objectives of the study were the following:

- Identify optimum conditions for Fe(II) oxidation when using NH_4OH as alkali
- Determine optimum conditions for removal of SO_4 when $\text{Ba}(\text{OH})_2$ is added for precipitation of BaSO_4 (barite)
- Demonstrate that limestone can be used for free acid removal
- Identify optimum conditions for recovery of NH_4OH
- Identify optimum conditions for removal of calcium by introduction of CO_2
- 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 SO_4 (2 090 mg/l). Simulated AMD was prepared from an aqueous mixture of FeSO_4 (Rochelle Chemicals, Pretoria) and H_2SO_4 (SMM Instruments, Johannesburg). Simulated mine-water was prepared as follows: $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ (1.50 g) and concentrated H_2SO_4 (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 SO_4 .

Reagents

Aqueous NH_3 (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. $\text{Ba}(\text{OH})_2$ (Merck, SA) was used for SO_4 removal. Lime (Rochelle Chemicals, Pretoria) was used for removing the remaining NH_3 in the solution and CO_2 (Afrox, Pretoria) was used for the precipitation of Ca as CaCO_3 . CaCO_3 (Rochelle Chemicals, Pretoria) was used to remove free acid in the alternative method.

Equipment

Neutralisation of acidic mine water with NH_4OH and SO_4 removal with $\text{Ba}(\text{OH})_2$ was studied using arrays of stirred beakers. NH_3 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 $\text{NH}_3(\text{aq})$ diffuses as NH_3 gas. A rotary evaporator was used as an alternative method for removal of NH_3 .

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 NH_4OH were mixed at Time Zero. NH_4OH 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.

SO_4 was removed as precipitated BaSO_4 by addition of $\text{Ba}(\text{OH})_2$. NH_3 was removed in 2 stages: $\text{Ba}(\text{OH})_2$ 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 NH_3 as NH_3 gas. The remaining sample was taken at intervals and assayed for pH and NH_3 concentration. NH_3 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 NH_3 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 NH₄OH 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)

ANALYTICAL

Water samples were collected at various stages, filtered (Whatman 0.45 µm filter paper) and assayed for Fe(II), pH, NH₃, Ca, SO₄ and alkalinity concentrations using standard procedures (APHA, 2012; Vogel, 1989). NH₃ analyses were done using BÜCHI Distillation Unit B-324. Metals were assayed using atomic absorption spectroscopy.

Fe(II) concentrations were determined by adding filtered sample (10 ml), 1N H₂SO₄ (10 ml) and Zimmerman-Reinhard reagent (10 ml) to an Erlenmeyer flask (100 ml) and titrating the solution with 0.1 N KMnO₄ until pale pink (Vogel, 1989). NH₃ was determined by distillation, where 100 ml of sample was placed in a distillation flask and adjusted to pH 12.4 with addition of Ba(OH)₂·8H₂O. Indicator boric acid solution was used as absorbent for the NH₃ distillate (APHA, 2012). Calcium was determined as total hardness because magnesium was not present. Filtered sample (5 ml), water (45 ml), dilute NH₄ and Eriochrome Black T indicator were added to an

Erlenmeyer flask (100 ml). The solution was titrated with 0.02 M EDTA to colour change (APHA, 2012). SO₄ was determined by adding filtered sample (2 ml) and conditioning reagent (2 ml) to a volumetric flask (50 ml) made up to volume with distilled water. A 20 ml aliquot of the solution was mixed with 0.15 g of BaCl₂ in the cuvette and the turbidity was measured using a turbidity meter (Vogel, 1989).

Alkalinity was determined by titration of sample (5 ml) to pH 4.3 using 0.1 N HCl (APHA, 2012). Ca, Ni, Co, Zn, K and Mn were assayed using atomic absorption spectrophotometry (APHA, 2012).

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 NH₄OH. 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 NH₄OH. During NH₄OH 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 NH₄OH 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 ($K_{sp} = 2.64 \times 10^{-39}$). NH₄OH 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

Parameter	Chemical composition				
	Feed	Treated			
		NH ₄ OH	Ba(OH) ₂	Ca(OH) ₂	CO ₂
Dosage (mmol)	-	73	14.4	15.0	-
NH ₃ /Acidity (mol/mol)		1.2			
Ba dosage/SO ₄ removed (mol/mol)			0.96		
Water quality (mmol where applicable)					
pH	1.9	9.9	10.6	12.6	6.5
Acidity (mmol CaCO ₃)	2 1.5	N/A	N/A	N/A	N/A
Fe(II)	10.74	0.15	0.148	0.146	0.143
SO ₄	21.49	18.6	3.66	3.63	3.57
NH ₃	N/A	60	25	5	0.48

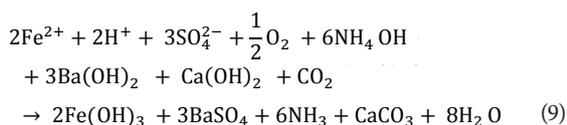
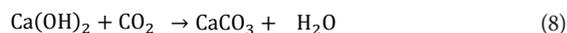
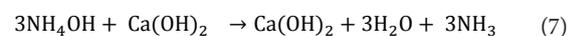
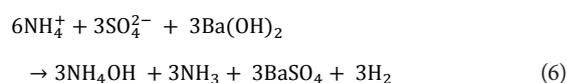
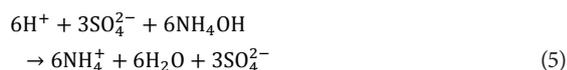
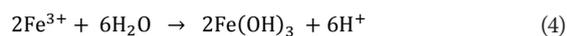
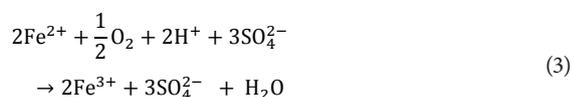
N/A: not assayed

Parameter	Chemical composition			
	Feed	Treated		
		NH ₄ OH	Ba(OH) ₂	CO ₂
Dosage (mmol)	-	73.0	14.4	N/A
NH ₃ /acidity (mol/mol)		1.2		
Ba dosage/SO ₄ removed (mol/mol)			0.83	
Water quality (mmol where applicable)				
pH	3.8	9.6	11.2	6.8
Acidity (mmol CaCO ₃)	8.50	N/A	N/A	N/A
Fe	12.0	0.016	0.002	< DL
Mn	1.16	0.036	< DL	<DL
Co	0.34	0.0043	<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
SO ₄	23.1	21.6	4.97	N/A
NH ₃	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

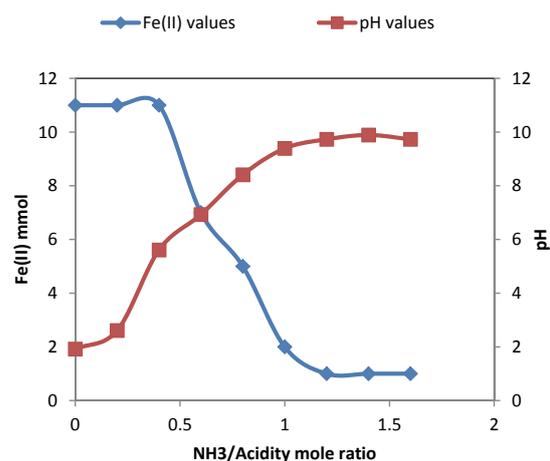


Figure 2

Effect of NH₃/acidity on the rate of Fe(II) removal by oxidation and precipitation (600 mg/l Fe(II), 2 150 mg/l acidity, 25°C)

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 NH₃ 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.

The optimum NH₃/acidity mol ratio was 1.2, because at that mol ratio the pH of the solution was above 9 and the Fe(II) concentration was <10 mg/l. Figure 3 shows the effect of aeration rate on the oxidation rate of Fe(II). It was noted that the higher the flow-rate of aeration the faster the oxidation rate, although the effect was marginal. Due to the high solubility of (NH₄)₂SO₄ (74.4 g/100 ml), co-precipitation of sulphates and metal hydroxides was avoided.

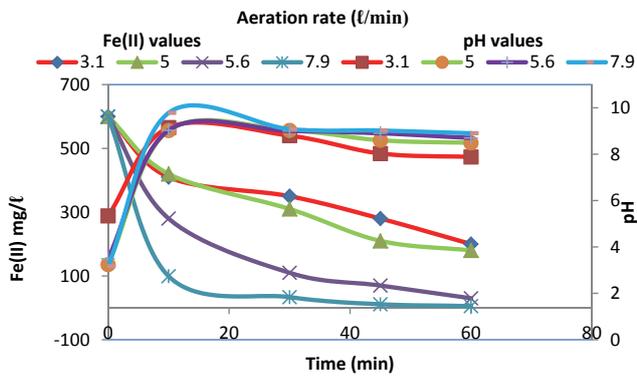


Figure 3
Effect of aeration-rate (l/min) on the rate of Fe(II) oxidation (600 mg/l Fe(II), 2 150 mg/l acidity; 876 mg/l NH₃, 25°C)

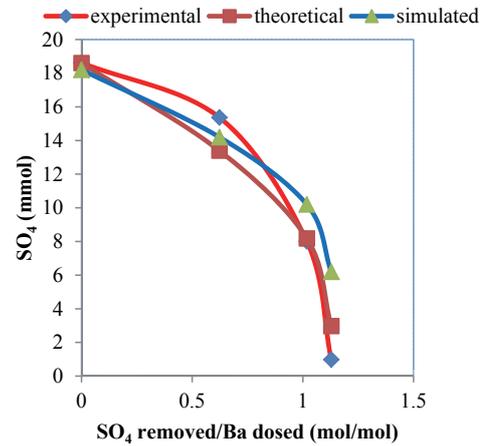


Figure 5
Comparison on the effect of Ba/SO₄ mol ratio dosed, on SO₄ (25°C)

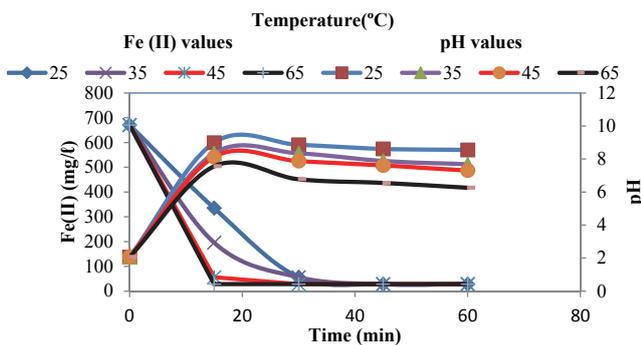


Figure 4
Effect of temperature on the rate of Fe(II) oxidation (600 mg/l Fe (II), 2 150 mg/l acidity, 876 mg/l NH₃)

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 NH₃ 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 SO₄ removal instead of lime because of the low solubility product of barite ($K_{sp} = 1.08 \times 10^{-10}$) compared to gypsum ($K_{sp} = 4.93 \times 10^{-5}$). Figure 5 shows experimental, theoretical and simulated results for optimum Ba/SO₄ mol ratio dosed. The pattern for the removal of SO₄ was similar.

Ammonia removal using hydrated lime

The rate of NH₃ 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, NH₃ 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 NH₃ gas being stripped out.

Figure 7 shows the effect of amounts of column packing material on NH₃ removal. It was noted that the stripping of NH₃ with a fully packed column proceeded at the fastest rate.

The effect of temperature on NH₃ stripping using a rotary evaporator was determined. Figure 8 showed that, as expected, the higher the temperature the more NH₃ becomes stripped out

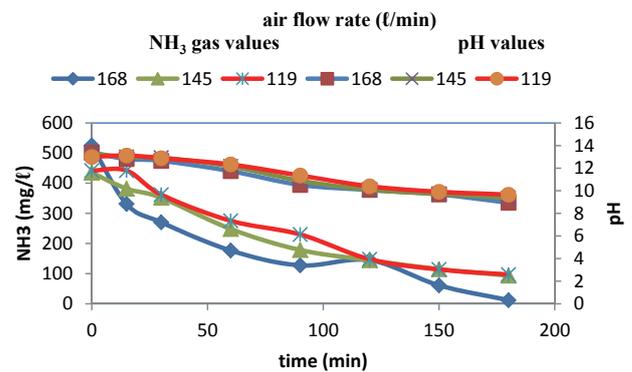


Figure 6
Effect of airflow rate (l/min) for NH₃ removal (fully packed material, 500 mg/l NH₃, 25°C)

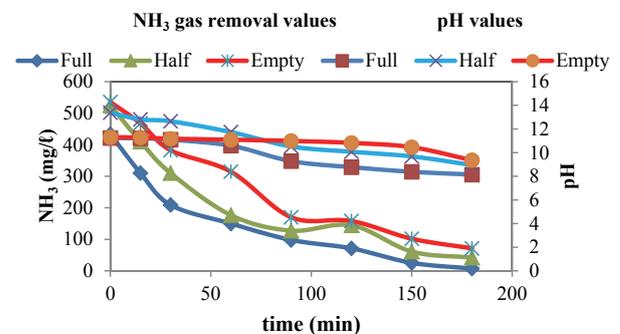


Figure 7
Effect of amount of packing material on NH₃ removal (510 mg/l NH₃, 168 l/min air flow rate, 25°C)

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 CaCO₃, it is expected that no addition of lime will be required after Ba dosing for NH₃ removal. Table 3 shows the chemical composition of simulated AMD after adding limestone in the first stage,

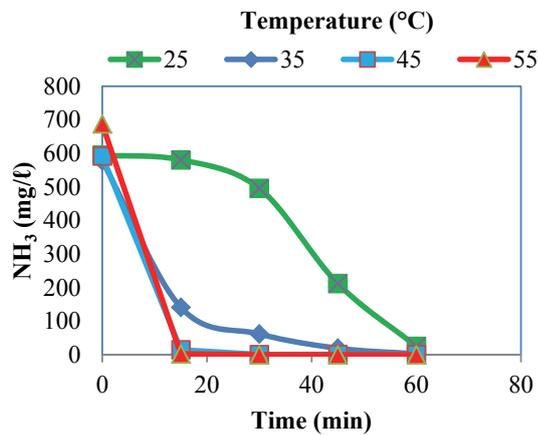


Figure 8

Effect of temperature on the rate of NH_3 gas removal in the solution using rotary evaporator (600 mg/l NH_3)

followed by various treatment stages. Limestone was added to pH 5.5 to remove the acid. The addition of NH_4OH 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 $\text{Ba}(\text{OH})_2$ 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.

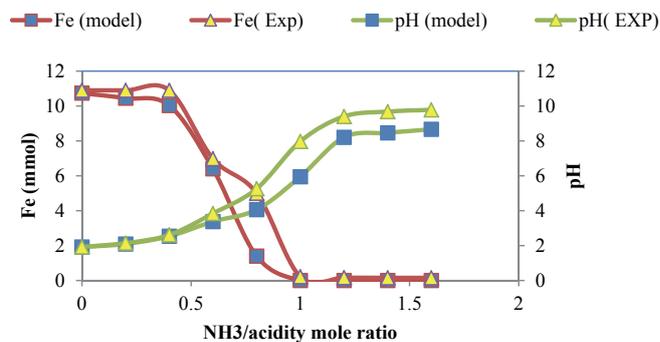
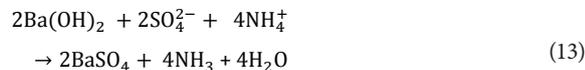
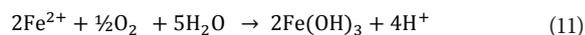
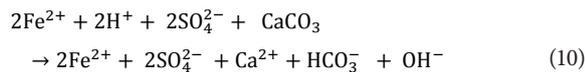
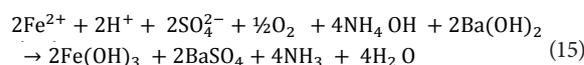


Figure 9

Comparison of the effect of NH_4OH /acidity on the rate of oxidation (600 mg/l $\text{Fe}(\text{II})$, 2 149 mg/l acidity, 876 mg/l NH_3 , 25°C)



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 $\text{Fe}(\text{II})$ oxidation to occur at a NH_3 /acidity mol ratio of unity. Experimentally, the optimum $\text{Fe}(\text{II})$ oxidation was found to occur at a mol ratio of 1.2.

CONCLUSIONS

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

Parameter	Chemical composition				
	Feed	Treated			
		CaCO_3	NH_4OH	$\text{Ba}(\text{OH})_2$	CO_2
Dosage (mmol)	-	-	73.7	14.4	-
NH_3 /acidity (mol/mol)			1.2		
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
$\text{Fe}(\text{II})$	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 NH_4OH instead of $\text{Ca}(\text{OH})_2$, gypsum scaling can be avoided in the full-scale process.
- NH_4OH precipitated Fe as the hydroxide in the simulated and real mine-water.
- $\text{Ba}(\text{OH})_2$ precipitated SO_4 in the mine water as BaSO_4 which resulted in partial NH_3 removal on account of the raised pH, and the NH_4^+ compound did not precipitate because of the solubility of NH_4SO_4 .
- Hydrated lime treatment resulted in removal of the remaining NH_3 by using a rotary evaporator.
- In the treated mine-water, CO_2 treatment precipitated Ca as CaCO_3 .
- The method was able to remove metal in real and simulated acid mine-water.
- Addition of CaCO_3 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 SO_4 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.

REFERENCES

- APHA (2012) *Standard Methods for the Examination of Water and Wastewater* (22nd edn.). American Public Health Assoc, New York.
- BOLOGO V, MAREE JP and CARLSSON F (2012) Application of magnesium hydroxide and barium hydroxide for the removal of metals and sulphate from mine water (MBO). *Water SA* **38** (1) 23–28.
- HLABELA P (2009) The integrated barium carbonate process for sulphate removal from acid mine water. Ph.D. thesis, North West University.
- INAP (INTERNATIONAL NETWORK FOR ACID PREVENTION) (2003) Treatment of sulphates in mine effluents. URL: http://www.inap.com.au/public_downloads/Research_Projects/Treatment_of_sulphate_in_Mine_effluents_LoraxReport.pdf (Accessed 12 April 2012).

- JENNINGS SR, NEUMAN DR and BLICKER PS (2008) *Acid Mine Drainage and Effects on Fish Health and Ecology: A Review*. Reclamation Research Group Publication, Bozeman, MT.
- JIMÉNEZ A, AROBA J, DE LA TORRE ML, ANDUJAR JM and GRANDE JA (2009) Model of behaviour of conductivity versus pH in acid mine drainage water, based on fuzzy logic and data mining techniques. *J. Hydroinf.* **11** (2) 147–153.
- KUN LE (1972) A report on the reduction of the sulphate content of acid mine drainage by precipitation with barium carbonate. Internal report, Anglo American Research Laboratories, Project D/3/W/1.
- MAREE JP (2003) Integral Chemical/Biological Process, Republic of South Africa (Patent No. 2003/1362), Australia (Patent No. 2001279996), Canada (Patent No. 2, 418, 472) United States of America (Patent No. 6,863,819), China (Patent 018162053), Great Britain (Patent No. 1,313,668), France (Patent No. 1,313,668), German (Patent No. 1,313,668).
- MAREE JP, BOSMAN DJ and JENKINS GR (1989) Chemical removal of sulphate, calcium and heavy metals from mining and power station effluents. *Proc. 1st Biennial Conf. of the Water Inst. of Southern Africa*, 29–30 March 1989, Cape Town.
- MAREE JP, DE BEER M, STRYDOM WF, CHRISTIE ADM and WAANDERS FB (2004) Neutralizing Coal Mine effluent with limestone to decrease metals and sulphate concentrations. *Mine Water Environ.* **23** 81–86.
- MINTEQ Visual (2000) URL: http://www2.lwr.kth.se/English/OurSoftware/vminteq/Visual%20MINTEQ_tutorial.pdf (Accessed 24 November 2011).
- ORVOS M, BALALZ T and BOTH KF (2010) Waste water treatment with ammonia recovery system. *J. Civ. Environ. Eng.* **2** (2) 113–117.
- TRUSLER GE, EDWARDS RI, BROUCKAERT CJ and BUCKLEY CA (1988) The chemical removal of sulphates. *Proc. 5th National Meeting of the South african Institution of Chemical Engineers*, (15–16 August 1988) Pretoria. W3-0–W3-11.
- VAN NIEKERK AM and MAREE JP (2001) *Coaltech 2010 Colloquium*, 2 March 2001, Witbank Civic Theatre, Witbank.
- SVEHLA G (2011) *Vogel's Quantitative Inorganic Analysis* (7th edn.). John Wiley and Sons, New York. 368 pp.
- VOLMAN R (1984) The use of barium sulphide to remove sulphate from industrial effluents. M.Sc. thesis (Chem. Eng.), University of Stellenbosch.
- WERNER S and LEE GF (1961) Oxygenation of ferrous iron. *Ind. Eng. Chem.* **53** (2) 143–146.
- ZIEMKIEWICZ PF, SKOUSEN JG, BRANT DL, STERNER PL and LOVETT RJ (1997) Acid mine drainage treatment with armored limestone in an open limestone channel. *J. Environ. Qual.* **26** 560–569.

