EXECUTIVE SUMMARY

1. Background

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. Currently, acid water is neutralized with lime before it is re-used (e.g. for coal washing in the coal mining industry) or discharged into public streams. The following disadvantages can be linked to lime neutralization:

Scaling of equipment by the unstable water produced.

Malfunctioning of lime dosing equipment. Settling of lime particles in pipelines and valves often causes blockages, which may result in under-dosage and acid corrosion.

Lime is costly. The cost of slaked lime (HDS process), unslaked lime (HDS process), unslaked lime (modified HDS process) and limestone amounts to R4.93/m^3, R3.36/m^3, R2.48/m^3 and R1.57/m^3 respectively for the treatment of water with an acidity of 10 g/ℓ (as $CaCO_3$).

Neutralization is generally the first step in treating acid mine water (gold, operational and abandoned coal mines). In Gauteng a volume of 240 Mℓ/d of acid mine water from gold mining requires treatment. At an acidity of 3 g/ℓ (as $CaCO_3$), a lime (CaO) price of R360 and a purity of 93 % the neutralization cost would amount to R57 million/a. It is therefore essential that the most suitable and cost-effective technology should be identified or developed.

The aim of this project (see Objectives) is to identify the most cost effective neutralization process which meets the following criteria for water with a specific chemical composition:

1. Treated water which is neutral and stable with respect to gypsum crystallisation.
2. Sludge with a high solids content.
3. Minimum alkali cost.
4. Minimum capital cost of plant and
5. Confidence in the selected process.

Legislation requires that sludge from neutralization plants be discharged into lined ponds to prevent metal leachate from polluting underground water. If leachate studies could show that sludge is stable with respect to leachate of metals, as long as it is not contacted with acid water, such information could be used to assist in formulating a strategy for sludge disposal in a less costly way (e.g. to use open cast or underground voids for discard of sludge) than in costly lined ponds.

Sludge disposal in lined ponds is costly due to the following:

Large masses of sludge is produced. An estimated amount of 20 t/d of sludge is produced from 1 Mℓ/d of discard leachate when neutralized with lime or limestone. Plastic lining of sludge pond. Sludge produced from acid mine water is classified as a class 3 waste due to its metal content and must be discharged into a lined pond.

Other, more cost effective methods of sludge discharge, such as worked out open cast or underground voids, may be used for this purpose. This approach would be in line with the accepted backfill approach in the gold, nickel and copper mining industry where waste rock is returned to underground. With the proposed approach, ferric hydroxide ($Fe(OH)_3$), which is stable, would be returned to its origin, and not pyrites (FeS_2), which could be oxidized to generate acid. Acid water in underground voids can be pumped to the surface and treated in an integrated plant. The amount of sludge produced from the integrated process will amount only to 5% the volume of dischard leachate with an acidity of 15 g/ℓ (as $CaCO_3$). Benefits of this approach are:

Cost reduction as costly sludge disposal ponds are not required.
Reduced seepage to underground water. Settled sludge has a low permeability and will reduce the rate of seepage to underground water.
Neutralization capacity is created in terms of underground acid water. Sludge contains unused alkali (e.g. 10% to 30 % of the lime used for neutralization in the HDS process is not utilized for neutralization) which can be used to neutralize underground acid water.
Aesthetic benefits. No waste from water treatment needs to be stored at the surface.

2. Objectives

Against this background the following aims were set for the project:

1. Biological iron(II) oxidation. Determine the conditions required for rapid iron(II) oxidation under acidic conditions within a residence time of one hour.

2. Integrated neutralization process. Obtain design criteria for the treatment of low acidity water (2 000 mg/ℓ acidity (as $CaCO_3$) and 300 mg/ℓ iron(II) (as Fe)) with the integrated neutralization and iron(II) oxidation process.

3. High density sludge (HDS) process. Optimize the process flow diagram of the HDS process to meet the following criteria for different water qualities:

   - produce sludge with a high solids content (greater than 25% for water containing 10 g/ℓ acidity (as CaCO3))

   - produce sludge with a rapid settling rate

   - achieve maximum lime utilization (greater than 95%).

4. Leachate studies. Determine the stability of mine water sludge (neutralized with lime and limestone) with respect to re-dissolution and metal leachate as a function of pH, for the following wastes:

   - Sludge produced during treatment of acid mine water with lime or limestone.

   - Coal discard (rich in FeS_2) to confirm that discard leachate is the main source of acid generation of the various wastes produced during coal mining.

3. Findings

The following findings were made during the investigation:

Biological iron(II) oxidation

Iron(II) should be oxidized to iron(III) before the neutralization of acid water with limestone, otherwise the oxidation will occur downstream of the neutralization plant with the formation of acid. This study aimed at investigating the kinetics of biological iron(II) oxidation in a plate reactor and to identify the suitability of a plate reactor for biological iron(II) oxidation. The study showed that the highest achievable rate was 120 g $Fe^{2+}/(\ell.d)$ (O_2-flow= 70 mℓ/min; T = 20.5°C; surface area = 847 m^2/m^3). The kinetics of the biological iron(II) oxidation in a plate reactor can be described as: $d[Fe^{2+}]/dt = k.[Fe^{2+}]^{0.5}.[RSA]^{1}.[O_2]^{0.5}$

Biological iron(II) oxidation to achieve low iron(II) concentrations is needed as pre-treatment to enable effective limestone neutralization. The effect of various parameters on biological iron(II) oxidation was investigated, including oxygen transfer, iron(II) concentration, support medium surface area, type of support medium, reactor configurations and flow regime. The study showed that the kinetics of biological iron(II) oxidation follow the rate equation:

$$-\frac{d[Fe(II)]}{dt} = k[Fe(II)]^{0.5} R_f^{0.5} A^{1.0}$$

where, R_f = reciprocating frequency (oxygenation), and

A = support medium surface area.

By treating acid water with a pH of 2 and an iron(II) concentration of 3000 mg/ℓ, an oxidation rate of 74 g Fe/(ℓ medium.d) and effluent iron(II) concentration of 300 mg/ℓ was attained in a continuously operated submersed packed-column reactor (at 24 °C). The medium used was silica sand (particle size of 4.75 to 6.35 mm) at a cost of R100/t. At a loading rate of 20 g Fe/(ℓ medium.d) the iron(II) is removed to less than 60 mg/ℓ in the effluent.

Integrated neutralization process.

A novel process is described for the neutralization of acid streams produced during coal mining and processing. The leachate from a waste coal dump was neutralized with limestone for the removal of iron, aluminium and sulphate. Specific aspects studied were the process configuration, the rates of iron(II) oxidation, limestone neutralization and gypsum crystallization, the chemical composition of the effluents before and after treatment, the efficiency of limestone

utilization and the sludge solids content.

The study showed that the acid content was reduced from 12 000 to 300 mg/ℓ (as $CaCO_3$), sulphate from 15 000 to 2 600 mg/ℓ (as SO_4), iron from 5 000 to 10 mg/ℓ (as Fe), aluminium from 100 to 5 mg/ℓ (as Al) while the pH increased from 2.2 to 7.0. Reaction times of 2.0 and 4.5 h are required under continuous and batch operations respectively for the removal of 4 g/ℓ iron(II) (as Fe). The iron(II) oxidation rate equation is a function of the iron(II), hydroxide, oxygen and suspended solids concentrations. The optimum suspended solids concentration for iron(II) oxidation in a fluidized-bed reactor is 190 g/ℓ. Upflow velocity has no influence on the rate of iron(II) oxidation in the range 5 to 45 m/h. Sludge with a high solids content of 55% is produced. This compares well with the typical 20% solids content that can be achieved with the High Density Sludge process in the case of lime neutralization. Neutralization cost of acid water can be reduced significantly with the integrated iron(II) oxidation and limestone neutralization process as limestone instead of lime is used and sludge with a high solids content is produced. The alkali cost to treat discard leachate with an acidity of 10 g/ℓ (as $CaCO_3$) amounts to R5.15/m³, R2.79/m³, R1.37/m³ and R1.95/m³ for slaked lime, unslaked lime, limestone when milled on-site and purchased limestone respectively. The expected capital cost for a 1 Mℓ/d integrated iron(II) oxidation and neutralization plant is R1.87 million when the alkali is purchased and R1.95 million when limestone is milled on-site.

Design criteria are provided for application on full-scale.

High density sludge (HDS) process.

Acid mine drainage (AMD) poses serious pollution problems if discharged untreated into public streams. Up to date, the conventional and High Density Sludge (HDS) processes are used to neutralized AMD. The conventional neutralization process produces sludge with low sludge solids content. Although the HDS process produces sludge with high sludge solids content, one of the disadvantages is the difficulty to control the process, especially where there is fluctuation in flow rates and acid concentrations. It is thus priority to improve the existing HDS process. Less pH fluctuation occurred during the operation of the Modified HDS process due to better pH control. The pH fluctuated between pH 7.47 and 7.59. Existing lime neutralization plants can be adapted with minor changes to accommodate the modified HDS process.

This investigation compared the HDS and modified HDS process configurations with beaker studies and an laboratory pilot plant scale. Results from the continuous laboratory pilot scale

studies confirmed findings from the laboratory beaker studies. The Modified HDS process gave better lime utilization, higher sludge solids concentrations, and faster settling rates.

The more $CaCO_3$ added during the beaker studies, the less lime was used; the higher the sludge solids content; and the faster the settling rates.

Water with high sulphate concentrations is less suitable for treatment with the HDS or Modified HDS processes due to gypsum scaling.

Leachate studies

Coal discard, fines and high density sludge (HDS-sludge) are generated during coal mining. Both, discard and HDS-sludge can be classified as hazardous wastes which require special disposal criteria. Discard dumps need to be designed in such a way that contact between discard, water and air is minimized to ensure minimum acid formation. For the disposal of hazardous HDS-sludge, legislation requires that it be discharged into lined ponds, which is costly, to prevent metal leachate from polluting groundwater. The purpose of this study was to investigate the benefits associated with co-disposal of HDS-sludge and coal discard. It is argued that there is little environmental benefit in disposal of HDS-sludge in lined ponds compared to the co-disposal of HDS-sludge with coal discard. Co-disposal of High Density sludge (HDS-sludge) with coal discard would offer the following benefits: cost reduction as costly sludge disposal ponds are not required and neutralization capacity is created as HDS-sludge usually contains unused alkali. Permission for such co-disposal, however, is dependant on an Environmental Impact Assessment as required by DWAF.

The purpose of this investigation was to:

- Demonstrate that co-disposal of HDS-sludge and coal discard offers an effective alternative to disposal of HDS-sludge in lined landfills.
- Compare the efficiency of HDS with other methods for the control of pyrite oxidation in coal discard.
- Determine the potential toxicity of leachate from the untreated and treated coal discard.

It was found that:

1.   HDS-sludge from Brugspruit liming plant contains 50 g/kg alkali (as CaCO3) which can be

used for the neutralization of coal discard,

2. The rate of pyrite oxidation and metal leachate are reduced significantly when HDS-sludge is co-disposed with coal discard, compared with that of coal discard on its own.

3. Acid generation from coal discard can also be controlled with methods such as addition of activated sludge (to create reducing conditions) or submersion (to eliminate oxygen ingress).

Full-scale application

A $CaCO_3$ handling and dosing has been developed and demonstrated on full-scale that: (i) powdered calcium carbonate in a dump can be slurried to a constant density and applied for treatment of acid water; (ii) Acid water, rich in iron(II) can be treated with calcium carbonate for neutralization, complete removal of metals (iron(II), iron(III) and aluminium) and partial sulphate removal (to saturation level).

4. Recommendations for further research

It is recommended that further work be done in order to provide an integrated solution to treat water to the level suitable for discharge into public streams and for drinking water. This would entail the following :

Evaluate the calcium carbonate/lime/gypsum crystallization process for partial sulphate removal to less than 1 100 mg/ℓ. In this process sulphate is reduced to less than 1 100 mg/ℓ through gypsum crystallization by raising the pH with lime to 12. Increased sulphate removal is achieved as magnesium and sulphate associated with magnesium is removed. Due to the high calcium concentration in solution at pH 12, sulphate is removed to lower levels due tot the solubility product of calcium and sulphate ions.

Evaluate the biological sulphate removal process for the reduction of sulphate to levels less than 500 mg/ℓ using coal gas as energy source. It has been demonstrated on pilot-scale (400 m^3/d) that sulphate can be removed to less than 200 mg/ℓ provided that sufficient energy source is dosed. Ethanol was used as energy source. Ethanol, unfortunately has the following disadvantages:

- Costly. At a dosage of 0.8 g/ℓ and a price of R3 750/ton the ethanol cost amount to R3/m^3.
- An aerobic stage is required for removal of residual organic material as a portion of the ethanol is converted to acetate and is not utilized for sulphate reduction.

Develop a spreadsheet based model to identify the most cost-effective combination of

processes for a specific application. Sulphate for instance can be removed at the lowest cost with limestone (14 c/kg SO_4 for chemical cost, but only to a level of 2 500 mg/ℓ), or at a higher cost with lime (41 c/kg SO_4 for chemical cost, to a level of 1 100 mg/ℓ) or to low levels with the biological process (R1.50/kg SO_4, to a level less than 500 mg/ℓ). Such a model will determine the chemical composition of the treated water, size and cost of the various capital items, total capital and running cost. As input the model will require the flow rate of the various feed water streams and their chemical compositions.

Estimate the total volume and chemical composition of mining effluents (coal, gold and platinum) that need to be treated.