NEUTRALIZATION OF ACID MINE WATER AND SLUDGE DISPOSAL

Report to the
WATER RESEARCH COMMISSION

by

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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+}/(l.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/m^3, R2.79/m^3, R1.37/m^3 and R1.95/m^3 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 dassified 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.

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"Underground neutralization of mine water with limestone".

The Steering Committee responsible for this project consisted of the following persons:

MEMBER	AFFILIATION
Mr H M du Plessis	Water Research Commission
Mr G N Steenveld	Water Research Commission
Ms M de Beer	CSIR
Mr N C Swiegelaar	Department of Water Affairs and Forestry
Mr W H Peek	Department of Water Affairs and Forestry

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1.1 SOURCE OF ACID MINE WATER

Acid mine waters contain high concentrations of dissolved heavy metals and sulphate, and can have pH values as low as 2.5. In South Africa emphasis is placed the removal of sulphate from such effluents due to salinisation of surface water (low dilution effect when discharged into public streams due to small rivers in South Africa compared to North America and Europe). In the USA emphasis is placed the removal of heavy metals due to its toxicity. Acid is produced biologically when pyrites in the coal waste is oxidized as indicated by the following reactions (Barnes, 1968):

$$4FeS_2 + 7O_2 + 4H_2O \quad --> \quad 4FeSO_4 + 4H_2SO_4$$

$$4FeSO_4 + 2H_2SO_4 + O_2 \quad --> \quad 2Fe_2(SO_4)_3 + 2H_2O$$

$$2Fe_2(SO_4)_3 + 12H_2O \quad --> \quad 4Fe(OH)_3 + 6H_2SO_4$$

$$4FeS_2 + 15O_2 + 14H_2O --> \quad 4Fe(OH)_3 + 8H_2SO_4 \qquad (1)$$

Unless treated such waters may not be discharged into public streams.

1.2 QUANTITY AND QUALITY OF MINE WATER

In Gauteng about 240 Ml/d of acid mine water from gold mining requires treatment. Mine water discharged from coal mines in the Upper Olifants River Catchment currently amounts to approximately 44 Ml/d during an average hydrological year (van Zyl *et al.*, 2000) (Table 1.1). It is expected that this figure will increase to an estimated 131 Ml/d by 2020. The quality of mine water is generally poor with a sulphate concentration between 800 and 3 000 mg/l. It is not acceptable to discharge such poor quality mine water into high quality surface water. The current background sulphate load of water in the Upper Olifants River Catchment is estimated at 28,4 t/d (as SO_4) (947 Ml/d @ 30 mg/l SO_4), which is small compared to the estimated 102,9 t/d sulphate load associated with excess mine water (2 337 mg/l SO_4 @ 44 Ml/d). The above-mentioned figures show that a relatively small volume of excess mine water is responsible for a major contribution of salinity. Excess mine water in the Olifants River Catchment currently amounts, volume wise, to only 4,6% of the total water usage, but contributes 78,4% of the sulphate load.

Table 1.1 : Comparison between water volumes and sulphate load of fresh water usage and excess mine water discharges in the Upper Olifants River Catchment

Parameter	Fresh water	Mine Water	Total	Fresh water	Mine water
	Ml/d	Ml/d	Ml/d	%	%
Volume (Ml/d)	947	44,0	991	95,6	4,4
Sulphate concentration (mg/l)	30	2337			
Sulphate load (t/d)	28,4	102,9	131,3	21,6	78,4

1.3 PROBLEMS ASSOCIATED WITH ACID MINE WATER

Acid mine water is associated with the following problems:

- Acidification and salinisation of surface water due to the presence of acid and high concentrations of sulphate and metal pollution.
- Corrosion to and scaling of equipment. When the pH is below 5.5, water can be toxic to plant and fish life and corrosive to pipelines and equipment. When acid water is neutralized with lime and often over-saturated with respect to gypsum. This practice results in the scaling of equipment by the unstable water produced, malfunctioning of dosing equipment and settling of particles in pipelines and valves. The latter often causes blockages which may result in under-dosage, which in turn leads to acid corrosion.
- High treatment cost. Lime is generally used for neutralization of acid mine water. Should limestone be used for the neutralization of acid water the cost could be reduced significantly as shown in Table 1.2. Desalinisation of neutralized mine water is not applied yet due to high treatment cost. A number of alternative desalinisation treatment technologies were considered when treated mine water must meet more stringent quality requirements for industrial reuse, discharge to a public stream, drinking or power station cooling water (van Zyl *et al.*, 2000). Table 1.3 shows the cost associated with various treatment processes including Aqua K, Barium, Biological sulphate removal, EDR, Electrolytic, GYPCIX, RO or Savmin.

- Sludge disposal. Legislation requires that sludge from neutralization plants be discharged into lined ponds to prevent metal leachate from polluting ground water. Construction of lined ponds are costly. The volume of sludge to be disposed also influences the cost and processes that produce sludge with a high solids content would be preferred.

Table 1.2 : Price comparison of neutralization alkalies (2001 cost figures; 1 US$ = S A R9)

Cost	Sodium hydroxide	Hydrated lime	Unhydrated lime	Lime-stone
Cost (R/t)	2000	500	480	110
Cost (c/kl)†	320	74	53.8	22

† Treatment cost for the neutralization of water with an acid content of 2 g/l as $CaCO_3$. Total utilization and 100% purity are assumed.

Table 1.3 : Capital and running cost of various treatment processes (treatment module of 15 Ml /d).

Treatment Process	SO_4 level in treated water	Capital cost (R million / (Ml/d))	Running cost (R/m³)
Limestone neutralization (incl. iron(II) oxidation)	2 500	0,50	0,59
Lime neutralization (pH 8)	1 500	0,53	1,36
Limestone/lime treatment (pH 11) & gypsum crystallisation	1 100	0,88	1,02
Lime treatment (pH 11.5) & gypsum crystallization	1 100	0,57	1,61
Advanced sulphate removal (including neutralization pre-treatment	200	4,0 to 10,0	2,0 to 5,0

1.4 TREATMENT OF ACID MINE WATER

Acid water required treatment for both neutralization and desalinisation. Neutralization is required as pre-treatment to desalinisation. Various processes are developed for desalinisation and includes the following: Biological sulphate removal, SAVMIN, Aqua-K, Reverse Osmosis, Electro dialysis. This investigation only deals with neutralization and only with desalinisation that is associated with gypsum crystallization.

Currently, acid water is neutralized with lime and then re-used. 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 about 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 be identified or developed.

Passive treatment is also evaluated for treatment of acid and sulphate-rich mining effluents. This method would be suitable to treat water with low acid concentrations (less than 300 mg/l $CaCO_3$).

1.5 ALTERNATIVE SOLUTIONS AS PROPOSED IN THIS INVESTIGATION

1.5.1 Limestone Neutralization

In contrast to lime treatment, limestone is relatively cheap and readily available, process control is simplified (no pH-control is required as limestone dissolution essentially occurs at pH-values below 7), and material wastage through overdosage is minimized. Also limestone is non-hazardous and easy to store. Raw material can be stockpiled in the open as $CaCO_3$ is not readily soluble in neutral water.

Notwithstanding these advantages, limestone neutralization has had limited application as a result of low neutralization rates compared to other alkalies and the phenomenon of surface scaling, which inhibits the reaction rate (Maree and du Plessis, 1993). The CSIR has overcome these limitations by developing a fluidized-bed process (Maree and Clayton, 1992), which ensures a high effective limestone concentration in the reactor and counters scale formation by particle attrition.

Despite this developments, the following areas still need to be solved:

- Iron(II) need to be oxidized to iron(III) upstream of the neutralization stage or simultaneously.
- Sludge of high density need to be produced to minimize sludge volumes.

- Sludge disposal criteria need to be relaxed.

1.5.2 Sludge Disposal

Legislation requires that sludge from neutralization plants be discharged into lined ponds to prevent metal leachate from polluting ground water as it is classified as a class 3 waste. If leachate studies would show that sludge is stable with respect to leachate of metals, as long as it is not acidified, 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 rather than in costly lined ponds if the pH is kept neutral where metals will not redissolve).

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

- Large mass of sludge. 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 therefore be discharged into a lined pond.

Other, more cost effective methods of sludge discharge, such as worked out open casts 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 surface and treated. The amount of sludge produced from the integrated process will amount only to 5% of the volume of discard leachate with an acidity of 15 g/l (as $CaCO_3$). Benefits of this approach are:

- Cost reduction. Costly sludge disposal ponds are not required.
- Reduced seepage to ground water when pond is lined. Settled sludge has a low permeability and will reduce the rate of seepage to underground water.
- Neutralization capacity is created in terms of acid ground 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.

1.6 AIMS

The overall aim underlying research conducted as part of this and complementary projects, is to identify the most suitable 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 crystallization.
2. Sludge with a high solids content.
3. Minimum alkali cost.
4. Minimum capital cost of plant and
5. Confidence in the selected process.

The specific aims set for this project were: (The chapter(s) in Report where a specific aim is addressed in brackets):

1. Biological iron(II) oxidation. Determine the conditions required for rapid iron(II) oxidation under acidic conditions within a residence time of one hour (Chapters 3 & 4).
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 (Chapters 5 & 6).
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 $CaCO_3$)
    - produce sludge with a rapid settling rate
    - achieve maximum lime utilization (greater than 95%) (Chapter 7).

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.
    - Slimes (fine waste coal).
    - 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 (Chapter 8).

All of the above aims were addressed through laboratory studies. Full-scale application of the findings are discussed in Chapter 9, while overall conclusions are reported in Chapter 10 and recommendations for further research and follow-on studies are made in Chapter 11.

The various aspects of the investigation were investigated individually and reported on in separate chapters. Chapters were written largely in a format and style suitable for publication.

CHAPTER 2 : LITERATURE SURVEY

2.1 INTRODUCTION

Lime and limestone is generally used for the treatment of acid water. Lime has been used in the past as the main neutralization agent but might be replaced with limestone as progress is made with technology development.

2.2 LIME TREATMENT PROCESSES

The conventional lime treatment process was first applied for neutralization of acid mine water. The next development was the High Density Sludge Process which offers the benefit of sludge with a higher density that is produced. Limestone is currently evaluated as an alternative to lime due to cost advantages.

2.2.1 Conventional Treatment with Lime

The flow diagram of the conventional process is shown in Figure 2.1. The main disadvantage of this process is that sludge with a low density is produced.

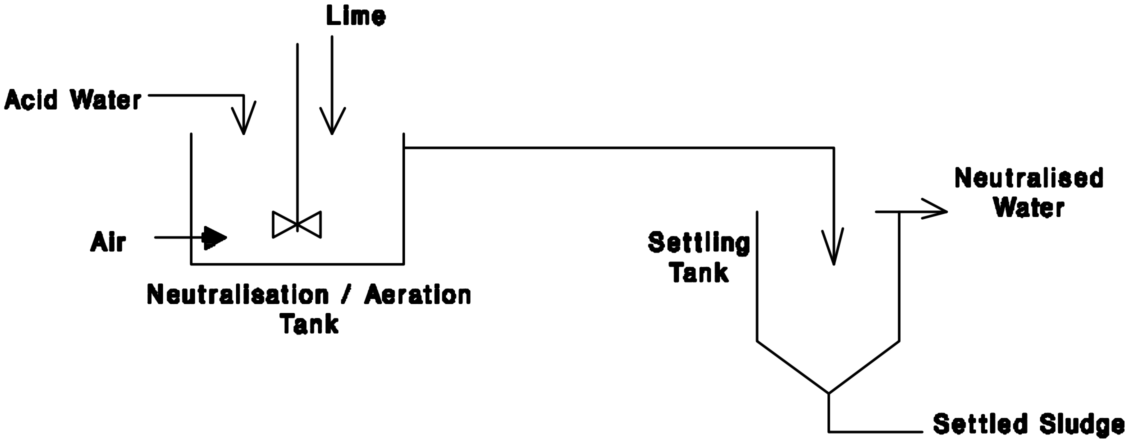


Figure 2.1 : The conventional process for acid water neutralization.

2.2.2 High Density Sludge (HDS) Process

The HDS process (Figure 2.2), which is a modification of the conventional lime treatment process and aimed at producing a higher density sludge, consists of the following stages:

- pH correction/sludge conditioning stage
- aeration/neutralization stage, and
- solid/liquid separation stage.

The pH correction stage consists of a tank for the preparation of a lime solution and a sludge conditioning tank which receives recycled settled sludge from the clarifier underflow and the lime solution. The lime dosage in the pH correction stage is such that the pH of the final treated water is pH 8.

The conditioned sludge from the pH correction stage overflows into the aeration tank. This tank serves as mixer to keep the solids in suspension, to mix the conditioned sludge with the acid mine water entering the tank and for aeration. In this tank ferrous iron is also oxidized to ferric iron.

The neutralized and oxidized effluent overflows to the clarifier where sludge is separated from the liquid. A poly-electrolyte can be dosed to the clarifier to promote flocculation.

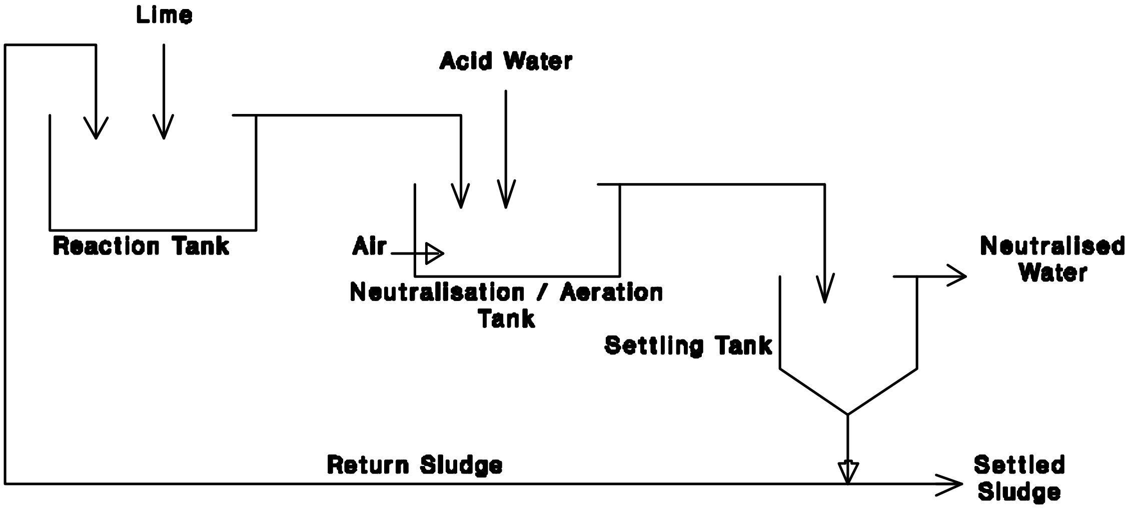


Figure 2.2 : The High Density Sludge process for acid water neutralization.

The HDS Process has the following advantages over the conventional process (Osuchowski, 1992):

- A sludge with a density 10 times higher than that of the conventional process is produced. As a result less demanding sludge drying facilities are required. The capital costs associated with the construction of sludge ponds (including pumping and piping facilities) vary between R1/m^3 and R3/m^3 of sludge handling (2001 cost figures).
- The sludge settles faster, therefore, a smaller clarifier is required. The saving on the clarifier is approximately 38%.

2.3 LIMESTONE TREATMENT SYSTEMS

Various limestone treatment systems have been investigated (Hill and Wilmoth,, 1971).

2.3.1 **Aerated Limestone Powder Reactor**

Volpicelli *et al*. (1982) showed that effluent from a sugar plant containing sulphuric acid can be neutralized with powdered limestone. Two backmix reactors were used to perform the operation in order to reduce the required residence time. The first reactor is working at pH 4 under steady state conditions as the dissolution rate of limestone is fast at that low pH. The dissolution rate is very slow as the system approaches neutrality. A single backmix reactor would require a high residence time. Disadvantages associated with this system are that a long residence time is required unless powder is dosed, and that dosages, higher than stoichiometrically required, are necessary.

Limestone powder was found to react rapidly with free acid, ferric and aluminium salts in AMD, but not in the ferrous containing AMD (Glover *et al*, 1965). Ferrous containing AMD can only be treated if aeration is also applied as it has the effect that iron(II) is slowly oxidized (Figure 2.3).

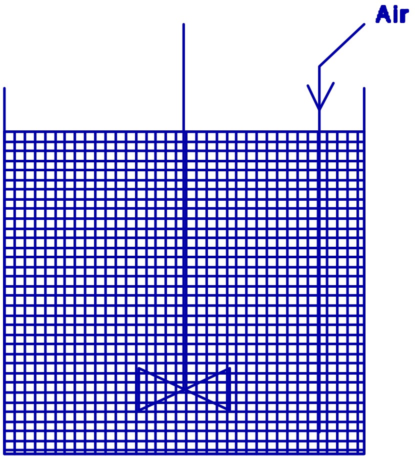


Figure 2.3 : Aerated powder limestone reactor.

2.3.2 **Stationary Limestone Grit Reactor**

Stationary limestone beds can be operated by vertical fluid flow (Figure 2.4) or horizontal fluid flow (Figure 2.5). These approaches have the advantage that an excessive amount of limestone is in contact with the acid water. Losses of limestone particles can still be recovered by a screening or sedimentation device downstream of the limestone bed.

A disadvantage of this approach is that the vertical reactor and the channel blocks due to the formation of reaction products such as gypsum or ferric hydroxide on the limestone particles.

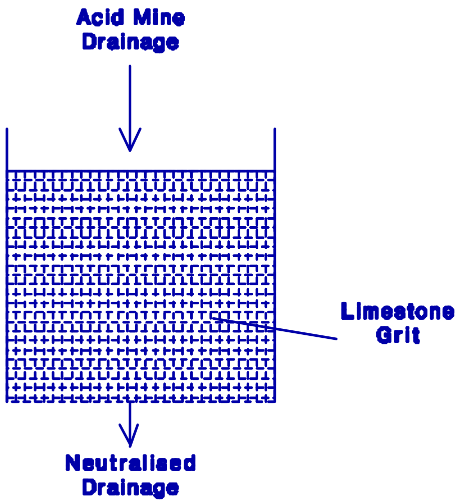


Figure 2.4 : Stationary limestone grit reactor with vertical fluid flow.

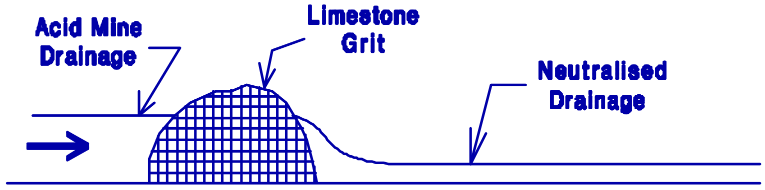


Figure 2.5 : Stationary limestone grit reactor with horizontal fluid flow.

2.3.3 Stationary Aerated Limestone Grit Reactor

The purpose of stationary aerated grit reactors (Figure 2.6) is to treat ferrous containing acid water. The reactivity of the limestone bed in these aerated stationary beds fell appreciably after one or two per cent of the limestone has been consumed under continuous flow conditions, but it was possible to restore the activity by upflow fluid expansion of the beds (Figure 2.7). However, after seven per cent of the limestone had been consumed, a hard, dark-coloured scale formed on the limestone particles and the activity could no longer be restored by upflow expansion (Glover *et al*, 1965).

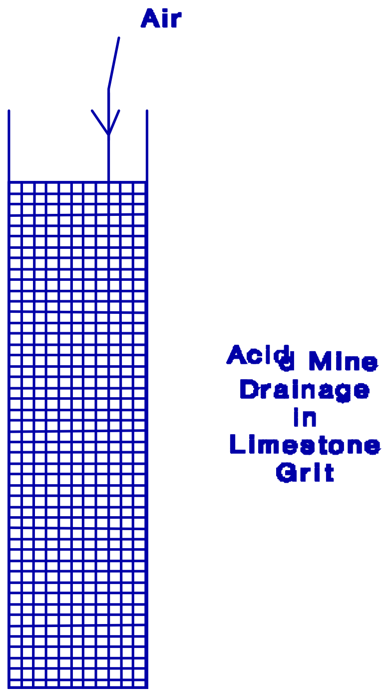


Figure 2.6 : Stationary aerated limestone grit reactor.

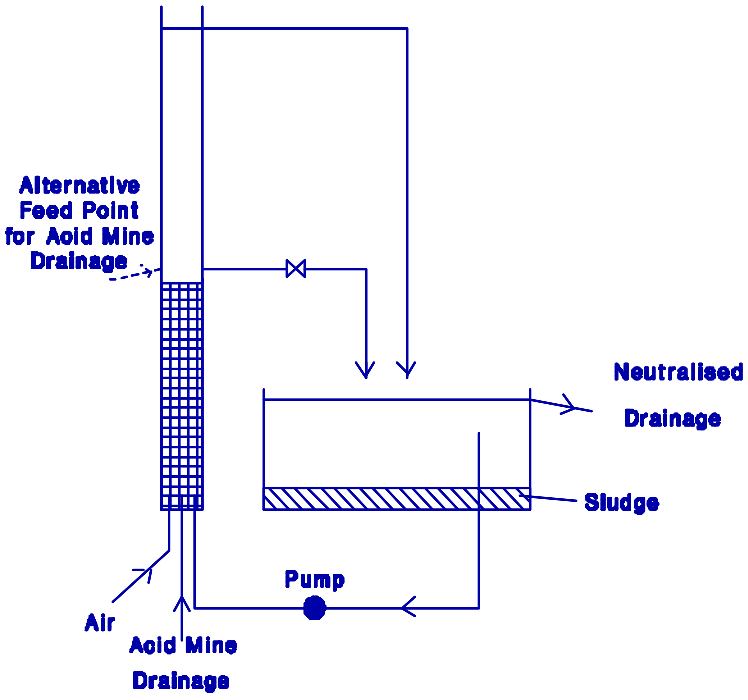


Figure 2.7 : Stationary aerated limestone grit reactor with intermittent wash by upflow expansion.

2.3.4 Rotating Drum

The U S Bureau of Mines investigated the use of the tube mill for limestone neutralization (Deul and Mihok, 1967; Mihok, *et al.*, 1968; Mihok, 1970). In this process, 3 inch pieces of limestone were fed, together with acid mine water, to a rotating tube mill. The drum had a diameter of 1 m, a length of 8 m, and was rotated at a speed of 25 rpm. The rotation has the effect that the limestone is milled to a powder of less than 400 mesh. Acid water was fed to the drum at a rate of 2,3 Ml/d. The retention time of the water in the tube is calculated to be 0,25 min (2300 kl/d ÷ (24 h/d x 60 min/h x p x $(0,5\ m)^2$ x 8 m). The chemical composition of the water that was treated is shown in Table 2.1. A schematic diagram of a rotating drum reactor is shown in Figure 2.8.

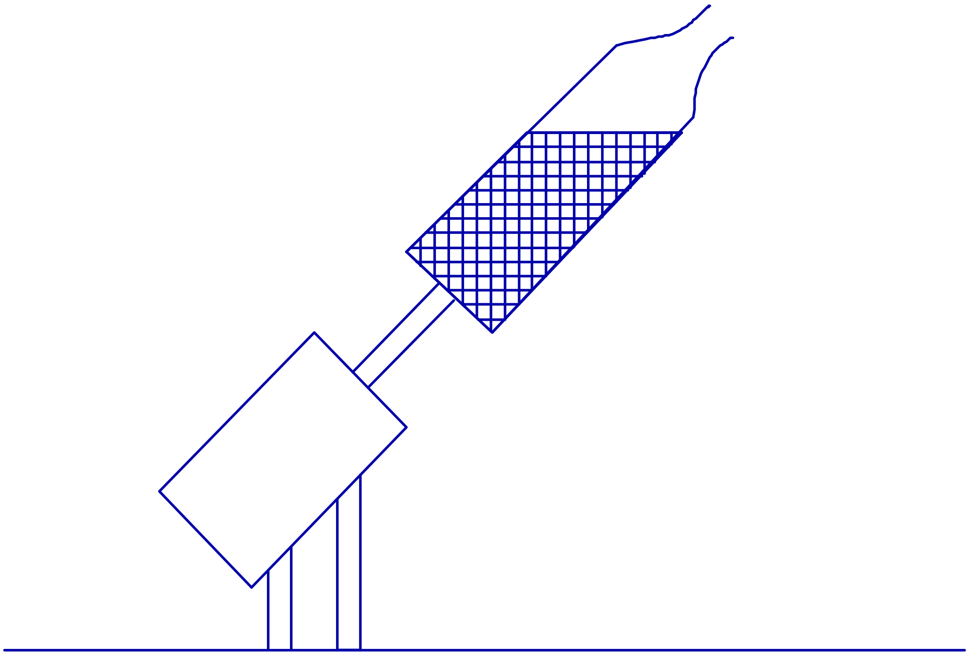


Figure 2.8 : Schematic diagram of a rotating drum reactor.

The pH of the water after treatment was 7,4. The process is not yet implemented. One disadvantage of the process is high losses of limestone (about 40%).

At the Rochester and Pittsburgh Coal Co.'s Lucerne 3A mine (Coal Age, 1969), acid mine water containing iron was continuously treated in a revolving drum charged with limestone chips. The treated water was fully neutralized and all iron was removed. A drawback of the above systems is that $CaCO_3$ is used inefficiently - a large portion being washed out with the treated effluent stream.

Table 2.1 : Chemical quality of acid water fed to the rotating drum.

Parameter	Concentration (mg/l)
Acidity	1700
Iron(II)	36
Iron(III)	324
pH	2,8

2.3.5 Limestone Lime Treatment

Wilmoth (1974) compared in parallel studies the cost advantage associated with the use of limestone-lime treatment versus lime in a completely mixed reactor. As limestone is not effective for the treatment of iron(II)-rich effluents, he proposed a two-stage process where limestone is used in the first stage and lime in the second stage. First, the AMD is treated with limestone to a pH of 4,0 to 4,5 to take advantage of the pH range when limestone is most effective. The water then passes through a second reactor where lime is applied to raise the pH range to the desired level. Benefits associated with this approach are the following:

- Iron(II) can be removed.
- Sludge of high density is produced which is characteristic of the limestone process.
- Cost is reduced by 25%.

Although this two-stage process is more cost effective than the conventional lime neutralization process, it was not adopted in general by the mining industry because it is more complex (two stages instead of one).

2.3.6 Fluidized-bed Neutralization Process

The CSIR has developed, with financial support from the WRC, a fluidized-bed neutralization process which uses limestone or dolomite as the neutralizing agent (Maree, *et al.*, 1992; du Plessis and Maree, 1994; Maree and du Plessis, 1994; Maree, *et al.,* 1996a; Maree, *et al*., 1996b.). In this process crushed limestone (particle size less than 4 mm) is dosed to a column type reactor. The particles are kept in suspension by controlling the up-flow velocity by means of a recycle pump. In case of the fluidized limestone process, no accurate control of the dosage is required. This is because limestone only dissolves as long as the water is under-saturated with respect to $CaCO_3$. This usually occurs at a pH below 7.

By replacing lime with limestone, the following benefits can be achieved:

- Direct savings on the purchase cost of neutralization media.
- Simplified process control. No pH-control is required as limestone and dolomite dissolution occurs mainly at pH-values below 7. Since the flow rate of underground mine water may vary by a factor of 10 (Pulles *et al.*, 1994), lime/soda ash systems can only function well if its dosing rates are adjusted accordingly.
- Minimization of material wastage which would occur as a result of over-dosage (due to pH-solubility relationship referred to above).
- Elimination of hazardous chemical usage for neutralization (limestone/dolomite is easy and safe to handle).
- Simple bulk chemical storage facilities (the raw materials are not readily soluble in neutral water).
- Utilization of equipment at existing lime neutralization plants is possible.

A limitation of the fluidized-bed process is that acid water rich in iron(II) can not be treated directly. Iron(II) pass through the fluidized-bed reactor. When aeration is applied to remove iron(II) it as ferric hydroxide, the limestone particles become coated with a layer of gypsum and ferric hydroxide which prevent dissolution of the limestone particles.

A three-stage neutralization process consisting of biological iron(II) oxidation, limestone neutralization in a fluidized-bed reactor and gypsum crystallisation was evaluated for treatment of discard leachate (Maree, 1994; Maree 1995). Laboratory studies at CSIR and on-site pilot plant studies at Navigation Section of Landau Colliery over the period January 1995 to March 1997 showed that:

- Complete neutralization of discard leachate (10 g/l acid (as $CaCO_3$) and 4 000 mg/l iron(II) (as Fe)) can be achieved in a limestone neutralization fluidized-bed reactor, provided that iron(II) is oxidized beforehand.
- Iron(II) can be oxidized biologically to iron(III) at low pH-values (required as pre-treatment to limestone neutralization). The rate of iron(II) oxidation is related to the surface area of the support medium. With plastic medium (specific surface area of 200 m^2/m^3 a residence time of 18 h is required for water containing 4 g/l iron(II) (as Fe).
- Sulphate can be reduced from 18 000 mg/l (as SO_4) to less than 2 500 mg/l by gypsum crystallization in a contact reactor (when 300 mg/l magnesium (as Mg) is present). With a fluidized-bed contactor, a residence time of 2 h is required.

A disadvantage of the three-stage process is that the capital cost turned out to be unacceptably high as a result of the long residence time of 18 h required for iron(II) oxidation.

2.3.7 Integrated Limestone Neutralization Process

To overcome the disadvantages associated with the long residence time required for iron(II) oxidation under acidic conditions, the CSIR developed the integrated iron(II) oxidation and limestone neutralization process.

The integrated neutralization process consists of the following stages:

- *Neutralization stage.* Discard leachate is treated in a sludge reactor where powder limestone (<200 µm) is dosed (slightly in excess of stoichiometrical requirements) and aeration is applied to achieve the following:

  - Complete neutralization due to limestone dissolution.
  - Iron(II) oxidation within a reaction time of 2 h when the plant is operated in sequential batch mode and less than 5 h under continuous conditions. This is due to the relatively high pH (greater than 5) obtained after addition of powder limestone to Toe dam water and the resulting high suspended solids concentration (from reaction products such as gypsum and ferric hydroxide).
  - Gypsum crystallisation to an over-saturation index less than 1.1. The rate of gypsum crystallization is rapid due to initial high over-saturation level (600%) and high gypsum crystal concentration in suspension.

- *Clarifier.* A clarifier is required from which sludge is returned to the neutralization reactor to maintain a minimum concentration of suspended solids.

Benefits of the integrated neutralization process are:

- A single-stage system is needed for removal of iron(II), acidity and gypsum.
- Sludge of high solids content (50%) is produced.
- Limestone is the most cost-effective alkali.
- It is flexible as both lime or limestone can be used in the same reactor.
- Pilot plant studies showed that discard leachate can be treated effectively in the integrated process when limestone is used as alkali (Maree, *et al.*, 1998). It was found that:

1. The integrated iron(II) oxidation and limestone neutralization process can be used for the removal

of acidity, iron(II), iron(III) and aluminium (less than 2 mg/l (as Al) and sulphate to a level of 2 500 mg/l (as SO_4). All reactions take place simultaneously. For water containing 3 g/l iron(II) (as Fe), a reaction time of 2 h is required when operated in sequencing batch mode and 5 h when operated on a continuous basis.

2. The rate equation for iron(II) oxidation over the pH range 5 to 6 is influenced by iron(II), oxygen, hydroxide and suspended solids concentrations, reactor surface area, mixing intensity and temperature.
3. Sludge with a solids content of more than 50% can be produced with the integrated process.

2.3.8 Biological Iron(II) Oxidation

Both limestone and lime neutralization of acid water is influenced by the ratio of iron(II) to iron(III). If acid feed water containing more than 200 mg/l iron(II) is treated in the fluidized bed limestone neutralization process, the limestone particles are coated with a ferric hydroxide layer which prevents further reaction between acid and limestone, (Maree *et al.*, 1996).

Du Preez and Maree (1994) showed that iron(II) can be oxidized to iron(III) in the presence of acidophilic iron-oxidizing bacteria, such as *Ferrobacillus ferrooxidans*, and precipitated as $Fe(OH)_3$ at pH values greater than 3:

$$2Fe^{2+} + \tfrac{1}{2}O_2 + 2H^+ \quad \Rightarrow \quad 2Fe^{3+} + 2H_2O \tag{1}$$

$$2Fe^{3+} + 6H_2O \quad \Rightarrow \quad 2Fe(OH)_3 + 6H^+ \tag{2}$$

Maree, *et al*. (1998) showed that:

1. The relationship between rate of iron(II) oxidation and specific surface area is given by the equation:

$$-d[Fe^{2+}]/dt \quad = 0.21 \times S^{\frac{1}{2}}$$

Where S - Surface area

2. Iron(II) (2 g/l) can be oxidized effectively under continuous conditions in a plastic medium filter at an iron(II) oxidation rate of 2 g Fe/(l.d).
3. Ferric hydroxide precipitates slowly on the plastic medium as a result of the solubility of ferric

hydroxide that is exceeded during iron(II) oxidation under acidic conditions.

During lime neutralization in the HDS process, the optimum process configuration is determined by the chemical composition of the feed water, in particular the ratio of iron(II) to iron(III).

Should the rate of iron(II) oxidation be reduced to less than 1 h, it will benefit both limestone and lime neutralization. In the case of limestone, coarse particles can be used and not only fine particles as the case is with the integrated process. In the case of lime neutralization, the preferred modified HDS process can be used which has a better lime utilization efficiency.

2.3.9 Limestone Properties and its Selection

Limestone is composed primarily of calcium carbonate or combinations of calcium and magnesium carbonate with varying amounts of impurities, the most common of which are silica and alumina (Boynton, 1966). Since limestone does not have a constant chemical composition, it is important to know what characteristics are necessary for a good neutralizing agent. Most limestones are rated by the producer with regard to their calcium carbonate or calcium carbonate equivalent content. The higher the $CaCO_3$ content, the greater the alkalinity available and the fewer the impurities. In comparing pure lime and limestone, it should be noted that when both are compared on the same basis, such as $CaCO_3$ equivalent, 1 kg of lime has 1,35 times the alkalinity of 1 kg of limestone.

Several investigators have reported that limestone that contains magnesium carbonate in appreciable quantities reacts very slowly (Jacobs, 1947; Hoak *et al.*, 1945; Ford, 1970). Hoak *et al.* (1945) reported that dolomitic limestone's rate of reaction was approximately inversely proportional to the quantity of magnesium carbonate it contained (above about 2%). Ford (1970) conducted studies with 14 limestones of various compositions by treating both artificial and actual mine drainage and found that in general the neutralizing efficiency of a stone increased with higher percentages of $CaCO_3$ and lower percentages of $MgCO_3$, thus, the calcites, $CaCO_3$, were more effective than dolomites or magnesites. Empirically he established that the efficiency of a limestone can be predicted by the following equation:

Efficiency (%) = CaO + (SA x D)

where: CaO = CaO (as $CaCO_3$) (%)
SA = Surface area (m^2/g)
D = Density (g/ml)

A good limestone should have a high neutralizing rate, fast settling sludge, small volume of sludge, and a sludge with a high solids content. The following factors should thus be considered in the selection of a limestone:

- high calcium carbonate content,
- low magnesium content,
- low amount of impurities and
- large surface area, i.e. smallest particle size.

After a preliminary screening of the proposed stones by their chemical analysis, a simple laboratory test is recommended. Twice the stoichiometric amount of limestone of the size to be used is added to a sample of AMD. The sample is mixed by introducing air. The pH is recorded for 5 h. A pH-time plot is used to evaluate the limestone.

In addition to the reaction rate, the characteristics of the sludge should also be considered. Three characteristics of the sludge are important, i.e., settling rate, sludge volume and sludge solids content. To perform these tests, a sample of the unsettled neutralized AMD is placed in a 1 000 ml graduated cylinder and the depth of the sludge blanket determined periodically for 2 to 12 h. This data is then plotted. The final reading is considered the sludge volume, usually expressed as a percent of the total sample. The supernatant water should then be drained off.

The sludge is then dried and the percentage of solids is calculated.

In addition to the chemical properties of the limestone, the geological history of the stone and its crystal structure play some role in its neutralization ability. Crystal structure has some bearing on the surface area of the stone particle. Several investigators have shown that the reaction rate is a function of the size of the particle (Jacobs, 1947; Hoak *et al.*, 1945; Ford, 1970). The limit on the fineness of the stone is an economic one. Cost of grinding increases at an accelerating rate as the particle size decreases. The cheapest small particle size material in mining areas is 'rock dust' of which 60 to 70%

passes a 200 mesh. To obtain a smaller size may not be economically viable.

2.4 SLUDGE

Leachate studies need to be carried out to determine the stability of sludge with respect to dissolution of metal as a function of pH. The sludge produced during neutralization of acid mine water has the following characteristics:

- Low water permeability, once settled.
- No potential for acid generation. Acid can only be generated from iron or sulphur compounds that are at a reduced oxidation state, such as FeS_2. In FeS_2 the oxidation state of Fe is “+2", compared to its maximum state of “+3", while the oxidation state of S is “-1", compared to its maximum state of “+6". Sludge produced during lime or limestone neutralization contains no FeS_2, only $Fe(OH)_3$ and $CaSO_4.2H_2O$. In the latter case, both Fe and S are at their highest oxidation states, namely “+3" and “+6" respectively.
- No iron leachate results if the sludge is contacted with rain water as iron(III) only dissolves at pH values below 3.

It can thus be argued that there is no merit in discharging sludge produced during neutralization of acid mine water to plastic lined dumps, while the coal discard, which is present in large tonnages and rich in FeS_2, is discharged directly on to the soil.

CHAPTER 3 : CHEMICAL AND BIOLOGICAL OXIDATION OF IRON IN ACID MINE WATER

3.1 INTRODUCTION

A practical method of neutralizing acid mine drainage (AMD) with limestone has been developed and is being commercially applied in South Africa (Maree *et al.* 1992). Neutralization of AMD with limestone requires that ferrous iron, Fe(II), in the water should first be oxidized to Fe(III); otherwise, the oxidation and hydrolysis will occur downstream of the neutralization plant, producing acidity (Maree *et al.* 1998). Iron can be oxidized to Fe(III) chemically and biologically.

Biological oxidation is catalyzed by iron-oxidizing bacteria, such as *Thiobacillus ferrooxidans,* a microorganism that lives in acidic conditions (Nemati and Webb 1996). The aim of this study was to improve Fe(II) oxidation rates by determining the effect of support media, the surface area of the support medium, the number of iterations, initial Fe(II) concentration, nutrients, CO_2, pH, temperature, air flow/concentration, and hydraulic retention time (HRT) on the rate of Fe(II) oxidation.

3.2 MATERIALS AND METHODS

Batch studies were conducted using a synthetic feed solution containing: 4 000 mg/l Fe(II), 40 mg/l P, 20 mg/l Mg, 30 mg/l N, 8 900 mg/l SO_4 and 9 200 mg/l acidity (as $CaCO_3$). Phosphorus and nitrogen were added in the feed water as nutrients for bacterial growth when operating biological Fe oxidation batch studies. Limestone from Springs, South Africa was used for neutralization.

During the continuous studies, AMD from the Toe Seep Dam at the Navigation mine site (South Africa, Witbank) was used as feed water. The Fe (II) concentration was 4.5-5 g/l and the pH was 2.0. Hydroponic nutrients (Kompel Chemicult products) were added to both the synthetic Fe (II) solution and the coal discard leachate.

Figure 3.1 shows the beaker reactors and stirring mechanisms that were used for the chemical Fe oxidation studies. The solutions and support media in the beaker reactors were stirred continuously and aerated at a flow rate of 3l/min with compressed air through diffusers (porosity no. 2, 210 x 8mm (OD)).

Figure 3.2 shows the rectangular reactor that was used for the biological Fe (II) oxidation studies. The geotextile sheets used were supported in vertical positions by plastic frames. Compressed air was supplied through diffusers to the reactors at a flow rate of 3l/min for each diffuser.

Different support media (e.g., plastic rings, plastic pellets, coal discard, sand, anthracite, and geotextile) were tested to study the possible increase in the Fe (II) oxidation rate. The plastic rings were cut from pipes of approximately 5 mm diameter. The coal discard (particle size 4 mm) was a coal of inferior quality, obtained from Navigation Mine, and the plastic pellets were made of polyethylene. The sand that was used as a support medium was normal building sand. The anthracite coal had a particle size of 2 mm. Geotextile is a fabric made of synthetic material used in road construction and maintenance. The support media were added into the reactor vessel with the stirring mechanisms. The geotextile was mounted on a perspex plate.

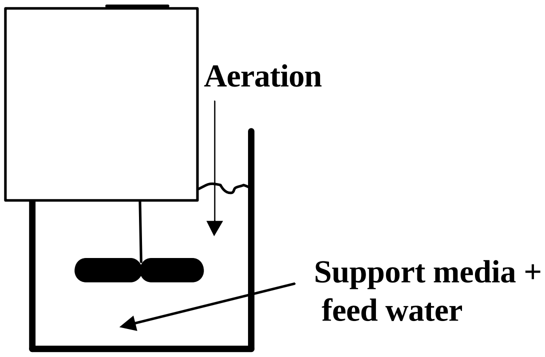


Figure 3.1 : Set -up for chemical iron oxidation studies

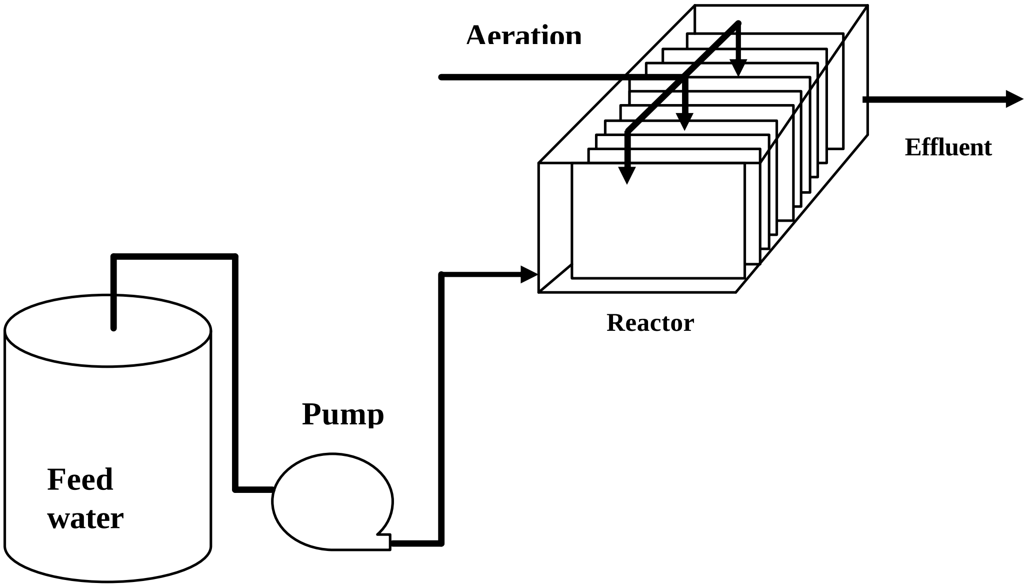


Figure 3.2 : Schematic flow diagram for biological iron oxidation studies

3.2.1 Experimental Procedure

(a) Biological Iron Oxidation

The various reactors were inoculated by adding 5% (vol/vol) AMD from the Navigation Mine to the water in the reactor vessels. Then*:*

- The reactor contents were aerated continuously until the Fe (II) was completely oxidized.
- Aeration was then stopped and the appropriate amount of the Fe(III) containing mixture was replaced with a fresh Fe(II) solution.
- Aeration was restarted and the procedure was repeated.
- Each run was started by mixing treated water from the previous run with feedstock in the ratio 1:1 or 1:4.
- Samples were taken at 30 minutes intervals, filtered and analyzed for Fe(II) concentration and pH.

(b) Chemical iron oxidation

During the chemical studies, the same procedure was followed as in the biological studies. However, 7.8 g/l $CaCO_3$ was added at the start of each experiment to raise the pH to 6.5 and precipitate $Fe(OH)_3$ and $CaSO_4$. The effects of support media concentration (0, 50, and 100 g/l pellets) and increased iterations (1-6) on the chemical oxidation rate were assessed while holding the temperature, pH, air flow, and initial Fe(II) concentration constant at T = 29 ºC, pH = 6.5, AF = 3 l/min, and Fe(II) = 2 g/l Fe(II), respectively.

3.2.2 Analytical Procedures

Samples (20 ml) were taken at 30 min intervals and filtered through Whatman No 1 filter paper. The Fe(II) determinations were carried out as described by Vogel (1989). A 691 Metrohm meter was use to measure pH. The surface areas of the support media were measured using a BET surface area analyzer (Micromeritics FlowSorb II 2300). Iron oxidation rates were measured at the beginning of the tests for several different initial concentrations of reactants by calculating the initial slope of the curve of iron (II) concentration versus time.

3.3 RESULTS AND DISCUSSION

Figure 3.3 shows the experimental results after 6 iterations. When the initial slope was calculated for the graphs in Figure 3.3, the oxidation rates were 48.9, 44.0, and 50.2 g Fe/(l·d) (d = experimental time in days) using 100, 50, and 0 g/l pellets, respectively. These results showed that the pellets had no significant effect on the Fe oxidation rates.

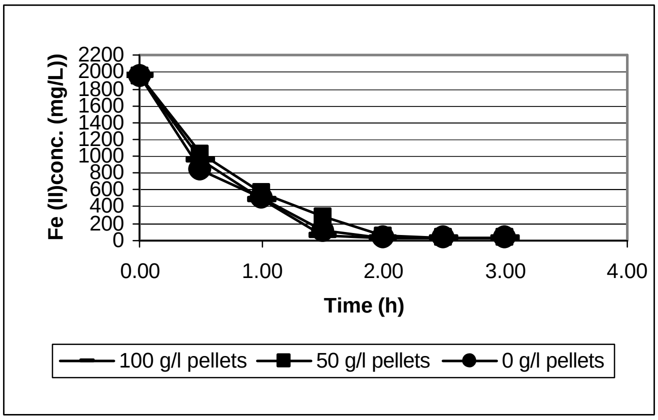


Figure 3.3 : Effect of pellets concentration on the iron oxidation rate

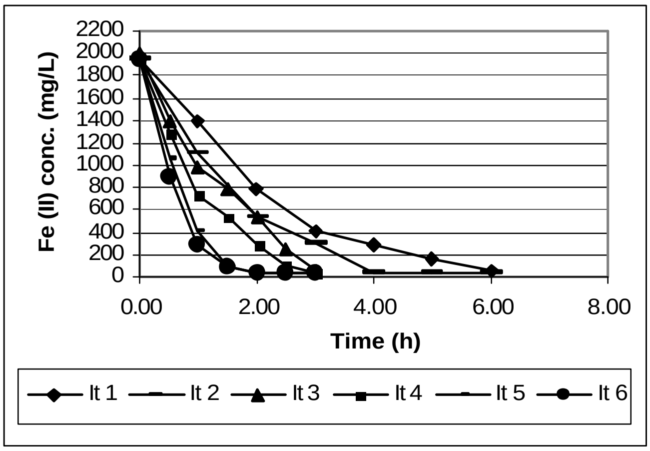


Figure 3.4 : Effect of the number of iterations on the iron oxidation rate

Figure 3.4 shows the effect of number of iterations when no support media was used. With one iteration, the reaction time was 6 h; when the iterations increased (2, 3, 4, 5, and 6 iterations), the reaction time decreased (from 4, to 3, to 2.5, to 1.5, and 1.5 h, respectively). As the number of iterations increased, the reaction rates increased from 14.1 to 17.1, 24.6, 29.5, 36.9, and 40.2 g Fe/(l·d), respectively. This increase in oxidation rate can be ascribed to the increase in $CaCO_3$

concentration in the reactor and to the suspended solids ($Fe(OH)_3$) and $CaSO_4$) formed, both of which act as catalysts for the reaction (Maree *et al*. 1997).

The effect of support media (sand, plastic rings, plastic pellets, coal discard, anthracite, and geotextile), number of iterations (1-10), geotextile surface area, initial Fe(II) concentration (2 to 20 g/l), nutrients (2 ml/l hydroponic nutrient), CO_2, pH (1.7, 2.0, and temperature (25 to 30 ºC) on the biological iron oxidation were assessed (Table 1 to 4). Temperature, pH, AF, and the initial Fe (II) concentration were kept constant at T= 29 ºC, pH = 2.0, AF = 3 l/min, and Fe (II) conc. = 2 g/l respectively, unless otherwise stated.

Table 3.1 shows the effect of support media on the rate of iron oxidation. It can be noted that the geotextile was the best support medium, due presumably to the nature of the textile, which accelerated bacterial adsorption and biofilm formation (a complex, multicellular structure formed when microorganisms attach or colonize to a surface, Nemati and Webb 1999). Due to the porosity of the geotextile, air can penetrate easily into the fibers and, due to its texture, the geotextile provides a large surface area for the bacteria to adhere onto.

Table 3.1 : Effect of the support medium on the rate of iron oxidation

Support media	Reaction rate g Fe/(l·d)
Control	1.3
Rings	4.1
Pellets	4.7
Coal discard	7.0
Sand	7.7
Anthracite	9.0
Geotextile	18.1

Table 3.2 shows the effect of surface area (using the BET surface analyzer) on the rate of iron oxidation relative to the number of iterations, when AMD was used as the feed water and geotextile was used as a support medium. The iron oxidation rate increased with the number of iterations, while the surface area of the geotextile decreased due to the biofilm formation.

Table 3.3 shows the effect of the initial Fe (II) concentration on the rate of iron oxidation, using artificial Fe (II)-rich water and geotextile as the support medium. When 2 g/l Fe (II) was used, the oxidation rate was 5.4 g Fe/(l·d). Further increases in Fe (II) concentration from 4 to 12 g/l increased the oxidation rates from 9.5 to 27.6 g Fe/(l·d) respectively. Silvermann and Lundgren (1959) reported that the growth of iron-oxidizing bacteria and its ability to oxidize ferrous iron is significantly influenced by the concentration of ferrous iron. Similar observations were reported by Kelly and Jones (1978).

Table 3.2 : Change in surface area of the geotextile and iron oxidation rate with respect to the number of iterations

Iteration	Fe(II) oxidation Rate (g Fe/(l·d))	Surface area (m^2/g)
1	2.7	2.5
2	3.62	2.3
3	5.89	1.7
4	6.08	1.2
5	7.96	0.9
6	8.38	0.8
7	8.78	0.7
8	9.23	0.6
9	10.03	0.4
10	10.62	0.3

Table 3.3 : Effect of Fe(II) concentration on the iron oxidation rate

Initial Fe(II) concentration	Fe(II) oxidation rate (g.Fe/(l.d))
2	5.4
4	9.5
8	17.2
12	27.6
16	26.1
20	22.5

Initial Fe(II) concentrations of 12 and 16 g/l gave almost similar results, 27.6 g Fe/(l·d) and 26.1 g Fe/(l·d), respectively. However, higher initial Fe(II) concentrations (20 g/l) inhibited the growth of iron-oxidizing bacteria, resulting in a decreased oxidation rate (22.5 g Fe/(l·d)).

3.3.1 Nutrients, CO_2, Air flow, pH and Temperature

Providing nutrients necessary for the growth of bacterial cells (Brock and Madigan 1991) increased the biological Fe oxidation rate (Table 3.4). The reaction rate was also faster when CO_2 was bubbled through the reactor vessel than when no CO_2 was added. These results support the findings of Nemati and Webb (1998) that iron-oxidizing bacteria need CO_2 as a carbon source for growth. Holuigue *et al.* (1987) and Barron (1990) demonstrated that the availability of CO_2 is important for achieving optimal growth rates and maximum cell yields. Our results also showed that when more air was supplied, the oxidation rate increased, due presumably to the increased respiration rate of the iron-oxidizing bacteria. When more air was supplied, the respiration rate of the biomass increased, resulting in faster iron oxidation rates.

The optimum oxidation rate was achieved when the pH was 2.0 and when the temperature was

29 ºC.

Table 3.4 : Effect of different parameters on the iron oxidation rate

Variables	Value	Fe (II) oxidation rate (g Fe/(l·d)
Nutrients	0 ml/l	5.7
	2 ml/l	8.4
CO_2	0%	4.0
	3%	6.1
Air flow	3 ml/l	10.0
	5.6 ml/l	10.6
	8.9 ml/l	13.9
pH	1.7	15.4
	2.0	20.8
	2.3	11.4
Temperature	25 ºC	6.7
	26 ºC	8.3
	27 ºC	12.1
	29 ºC	15.8
	30 ºC	14.7

3.3.2 Continuous Studies

Further studies were carried out to determine process performance under continuous conditions using AMD as feed water. The results (Table 3.5) show that when support media was used, the highest oxidation rate was 11.02 g Fe/(l·d); when no support media was used, the highest oxidation rate was 8.30 g Fe/(l·d). It can be concluded that support media are important for the bacteria to adhere onto. It can also be seen that the optimum HRT for the continuous study was obtained at 8 h when geotextile was used as a support medium and when nutrients were added. Furthermore, when nutrients were added, the highest oxidation rate was 12.10 g Fe/(l·d); when no nutrients were added, the oxidation rate was slightly lower at 11.02 g Fe/(l·d) (Table 3.6).

3.3.3 Kinetic Studies

The data in Table 3.6 show the effect of various factors on the kinetics of biological iron oxidation. The slopes of the graphs log R versus log (value of variable) show that the rate of iron oxidation is of order 1, 1, and 0.5 with respect to Fe^{2+}, support media, and O_2 concentration, respectively. These findings suggest that the rate equation for biological iron oxidation should be modified (Maree *et al.* 1998) for suspensions to:

$$-d[Fe^{2+}]/dt = k[Fe^{2+}]^{1\cdot}[SM]^{1\cdot}[O_2]^{0.5} \qquad (5)$$

where $-d[Fe^{2+}]/dt$ = rate of iron oxidation; k = reaction rate constant; $[Fe^{2+}]$ = ferrous iron concentration; SM= reactor surface area; and O_2 = oxygen concentration.

Table 3.5 : Effect of the support media and nutrients on the iron oxidation rate

Feed rate (l/d)	**HRT (h)**	**Fe (II) oxidation rate(g Fe/(l·d)**		
		No support media	Brown geotextile	Nutrients (2ml/l) & Geotextile
15	24.0	4.20	4.20	4.08
20	18.0	6.01	6.37	6.48
25	14.4	7.12	7.33	7.45
30	12.0	7.60	8.66	8.60
40	9.0	8.34	10.98	12.02
45	8.0	8.30	11.02	12.10
50	7.2	5.02	8.46	11.03
55	6.5	4.56	7.37	9.40
65	5.5	3.25	6.35	7.82

Other experimental parameters: Fe(II) concentration of the coal discard leachate varied from 4.5 to 4.8 g/l, pH = 2.0, temperature = 29 ^{0}C and air flow = 3 l/min

Table 3.6 : Effect of various factors on the kinetics of biological iron oxidation

Variable	Conc.	Rate (g Fe/(l·d))	Log C*	Log R*	Rxn order
Fe (II) (g/l)	2	5.4	0.30	0.73	1
	4	9.5	0.60	0.98	
	8	17.2	0.90	1.24	
	12	27.6	1.08	1.44	
	16	26.1	1.20	1.42	
Support media (m^2/m^3)	5	4.1	0.70	0.61	1
	10	7.2	1.00	0.86	
	19	10.2	1.28	1.01	
O_2(in air) (mg/l)	0.05	7.8	-1.301	0.89	0.5
	0.5	9.5	-0.30	0.98	
	1.0	13.5	0	1.14	

*C = Fe (II) concentration;
Type of support media = geotextile;
*R = Iron oxidation rate;
pH = 2.0; temperature = 29 ^{0}C

3.3.4 Conclusions

The chemical iron oxidation rate, conducted with an initial pH of 6.5, was increased by: the addition of $CaCO_3$, increasing the number of iterations, and increasing the level of suspended $Fe(OH)_3$ and $CaSO_4$, which acted as catalysts in the reactor vessel. The addition of support medium did not have a significant effect.

The biological iron oxidation rate was increased by: the addition of support media, an increase in support media concentration, an increase in Fe (II) concentration, an increase in the number of iterations, the addition of nutrients, the addition of CO_2, and increased air flow. Optimum iron oxidation rates were obtained at: pH = 2, temperature = 29°C, HRT = 8 h, Fe(II) concentration = 16 g/l, and when geotextile was used as support media.

CHAPTER 4 : BIOLOGICAL IRON(II) OXIDATION AS PRETREATMENT TO LIMESTONE NEUTRALIZATION

4.1 INTRODUCTION

Laboratory and pilot plant studies showed that the limestone neutralization process is significantly impaired by the presence of iron(II) (Maree and du Plessis, 1993; Van Tonder and Schutte, 1997). Laboratory and pilot plant studies (Maree *et al.*, 1997) further showed that limestone neutralization takes place effectively (at acceptable reaction rates and limestone utilization levels), if biological pre-oxidation (at low pH) of iron(II) to iron(III) is implemented (Equation 1). It was further found that the biological iron(II) oxidation rate is related to the surface area available for bacterial growth (Maree *et al.*,1998a).

$$Fe^{2+} + \frac{1}{4}O_2 + H^+ \ ? \ Fe^{3+} + \frac{1}{2}H_2O \qquad (1)$$

Nemati and Webb (1996) showed that biological iron(II) oxidation rates of up to 822 g Fe/(l.d) could be attained with polyurethane foam as biomass support medium (at a temperature of 30 °C, feed and effluent iron(II) concentrations of 5 g/l and 3 g/l, respectively). It was further found that high iron(II) concentrations (20 g/l) gave lower oxidation rates, indicating an inhibitory effect on the growth and activity of *Thiobacillus ferrooxidans* at these concentrations. Nemati and Webb (1997) further investigated the effect of reaction temperature on the biological iron(II) oxidation rate and found a significantly higher oxidation rate at 30 °C (maximum of 31.7 g Fe/(l.d)) compared to that at 20 °C (maximum of 21.5 g Fe/(l.d)). The performance of the system was also considerably less stable for the latter temperature. These studies evaluated biological iron(II) oxidation in the presence of relatively high iron(II) concentrations. However, beaker studies (van Tonder, 1997) indicated that the iron(II) concentration needs to be less than 100 mg/l for 80% limestone utilization. To facilitate effective limestone neutralization, biological iron(II) oxidation at low iron(II) concentrations therefore needs to be optimized.

The aims of this investigation were to:

- Determine the effect of various parameters on biological iron(II) oxidation kinetics, including the oxygen transfer, iron(II) concentration, support medium surface area, type of support medium, and flow regime;

- Identify the most cost-effective support medium and reactor configuration. Such a configuration needs to provide a consistent low effluent iron(II) concentration, which is a requirement for effective limestone neutralization.

4.2 MATERIALS AND METHODS

4.2.1 Feed Solution

Artificial mine water was used as feed. The solution was prepared by dissolving the following ingredients (concentrations in g/l given in brackets) in tap water: $FeSO_4.7H_2O$ (15.04), KH_2PO_4 (0.18), $MgSO_4.7H_2O$ (0.23), $(NH_4)_2SO_4$ (0.23) and H_2SO_4 (2.04).

4.2.2 Reactor Configurations

Two different reactor configurations were used in the investigation:

- Reciprocating disc-pack reactor (Figure 4.1): PVC medium (Table 4.2, medium A or B) was reciprocated up and down, into and out of the reaction solution using a pneumatic cylinder. The reactor volume was 5.0 l.
- Submersed packed-column reactors (Figure 4.2): Reaction solution was recycled through a silica sand/gravel bed (Table 4.2, media C to G). Air was introduced at the bottom of the packing. Different systems (column and recycle sump) were used with volumes of 1.8, 2.5 and 3.0 l. Oxygen for oxidation was supplied by bubbling air or pure oxygen through the submersed packing.

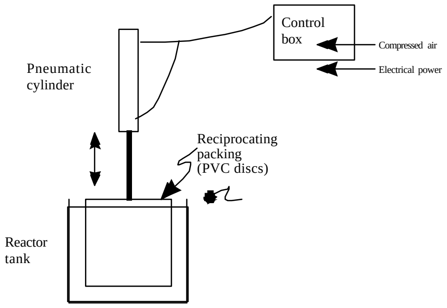


Figure 4.1 : Reciprocating disc-pack reactor

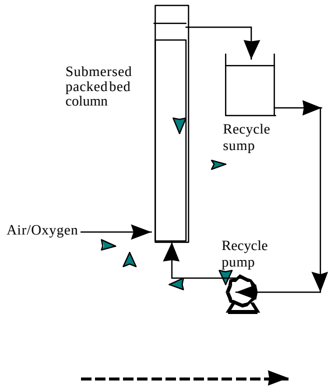


Figure 4.2 : Submersed packed-column reactor

4.2.3 Media

The media used were PVC discs and various grades of silica sand (Table 4.2). The sand media’s specific surface areas were estimated by a salt solution retention method: The amount of salt solution retained on a known amount of medium (subsequent to submersion of the medium in the salt solution and allowing it to drain freely) is proportional to the surface area of the medium. Salt retention was measured by the change in the conductivity of a known amount of distilled water, when the medium with the drained medium was submersed in the distilled water. A calibration curve was developed for a medium with known surface area, and used to calculate the surface area of the irregular sand medium from salt retention readings.

4.2.4 Operation Procudure

Reactors were operated both in batch and continuous mode. For batch tests the reactor (with packing) was filled with an iron(II) stock solution. Time measurement commenced with the initiation of recycling and aeration. The reactor content (i.e. reaction solution) was analyzed at periodic intervals (e.g. 2 or 4 hourly) for iron(II) concentration. The ambient air and reaction solution temperatures were monitored. The experimental run was terminated when the reaction solution iron(II) concentration was below 30 mg/l. For bacterial acclimatisation, at least five runs (repetitions) were required before the iron(II) oxidation rate stabilised at a maximum value. Only the packed-column reactor was operated continuously and the feed water was introduced to the reactor system on the suction side of the recycle pump (dotted arrows in Figure 4.2). The treated effluent overflowed from the recycle sump.

The recycle sump contents (i.e. effluent) was analyzed at periodic intervals (e.g. 4 hourly) for iron(II) concentration. The ambient air and reaction solution temperatures were monitored.

4.2.5 Analyses

Iron(II) was determined by titration with potassium permanganate (Vogel, 1989).

4.3 RESULTS AND DISCUSSION

4.3.1 Kinetics

The effect of various parameters on the rate of iron(II) oxidation was determined in batch runs using the reciprocating disc-pack reactor. Maree *et al.* (1998b) showed that the rate equation proposed by Stumm and Lee (1961) in the absence of micro-organisms for clear solutions, should be adapted to include a surface-related term for solid suspensions, to take the form:

$$-\frac{d[Fe(II)]}{dt} = k[Fe(II)]^{a}[OH^{-}]^{b}[O_2]^{b}\ A^{d} \qquad (2)$$

Where, [Fe(II)] = iron(II) concentration, [OH-] = hydroxide concentration, $[O_2]$ = oxygen concentration/partial pressure, A = suspended solids surface area, and a, b, c & d = reaction order constants. The biological iron(II) oxidation kinetics in the disc-pack reactor was analyzed according to a rate equation of similar form:

$$-\frac{d[Fe(II)]}{dt} = k[Fe(II)]^{a} R_{f}^{\ b} A^{c} \qquad (3)$$

Where, R_f denotes the reciprocating frequency (in cycles per minute), [Fe(II)] denotes the iron(II) concentration (in mg/l), A denotes the disc-pack surface area (m^2) and a, b & c denotes reaction order constants. The reciprocating frequency gives a measure of the oxygenation intensity.

The reaction order constants were calculated from the slope of the log(rate) against log(variable) regression line, when one variable was varied between a number of batch runs (Table 4.1).

Table 4.1 : Effect of various parameters on the kinetics of iron(II) oxidation (feed iron(II) concentration = 3 g/l , pH = 2 and temperature = 25 °C)

Parameter	Value	Rate g Fe/(l.d)	log(value)	log(rate)	Reaction order constant
Iron(II) concentration, mg/l	1.0	16.69	0.00	1.22	a = 0.41 (0.5)
	3.0	27.05	0.30	1.43	
	5.0	38.40	0.48	1.58	
	9.0	39.31	0.70	1.59	
	2.50	49.97	0.40	1.70	
Reciprocating frequency (R_f), cycles/min	1.67	42.09	0.22	1.62	b = 0.43 (0.5)
	0.83	31.27	- 0.08	1.50	
Surface area (A), m^2	2.54	49.86	0.40	1.70	c = 1.13 (1.0)
	1.90	38.10	0.28	1.58	
	1.27	26.54	0.10	1.42	
	0.64	10.46	- 0.20	1.02	

4.3.2 Support Media

Table 4.2 shows the reaction rates obtained for the various media. From these results it is noted that lower iron(II) oxidation rates were obtained with the finer particulate media (C, E and F), than with the coarser media (D and G) notwithstanding the large surface areas of the fine media. The low reaction rates obtained with the finer media are ascribed to poor liquid distribution in these media. The small openings between the particles were rapidly blocked by biofilm and precipitate, causing channelling of the water through the bed.

The relative high reaction rates that were obtained for media A and B was the result of optimum mixing, contact and flow distribution that was obtained by using the reciprocating PVC disc-pack set-up.

Table 4.2 : Iron(II) oxidation rate with various support media (1 USD = S.A. R6; initial iron(II) concentration = 3 g/l ; temperature = 25 °C; pH = 2)

	Description	**Specific surface area, m^2/m^3**	**Medium cost, R/m^3**	**Column upflow velocity¶, m/h**	**Iron(II) oxidation rate, g Fe/(l medium.d)**
A	2 mm spaced PVC discs (1 mm thick)	630	5000	Disc-pack	23
B	12 mm spaced corrugated PVC (0.1mm thick)	373	560	Disc-pack	10.5
C	Silica filtersand: 0.6 mm mean particle size	17300	800	9.6	7.1
D	Silica filtersand: 6 mm silica particle size	2100	850	17.7	15.0
E	Low grade silica sand: particle size < 2 mm	12500	80	10.6	7.4
F	Low grade silica sand: particle size: 2.8 to 3.35 mm	7900	100	4.9	8.5
G	Low grade silica sand: particle size: 4.75 to 6.35 mm	1200	100	10.6	9.4

Note: Media A and B were evaluated in the disc-pack unit, while the sand media were evaluated in the submersed-column unit. The upflow velocity is based on the recycle flow rate and empty column cross-sectional area.

4.3.3 Upflow Velocity

Figure 4.3 shows the iron(II) removal rate for medium G at various upflow velocities and oxygen concentrations. The iron(II) oxidation rate increased from 9.0 to 12.8 g Fe/(l medium.d) between runs 9 and 10 (Figure 4.3) when the upflow velocity was increased from 10.6 to 21.5 m/h. The oxidation rate therefore increased by a factor of 1.4 for an increase of the upflow velocity by a factor of 2, which constitutes a relative gain of 70%.

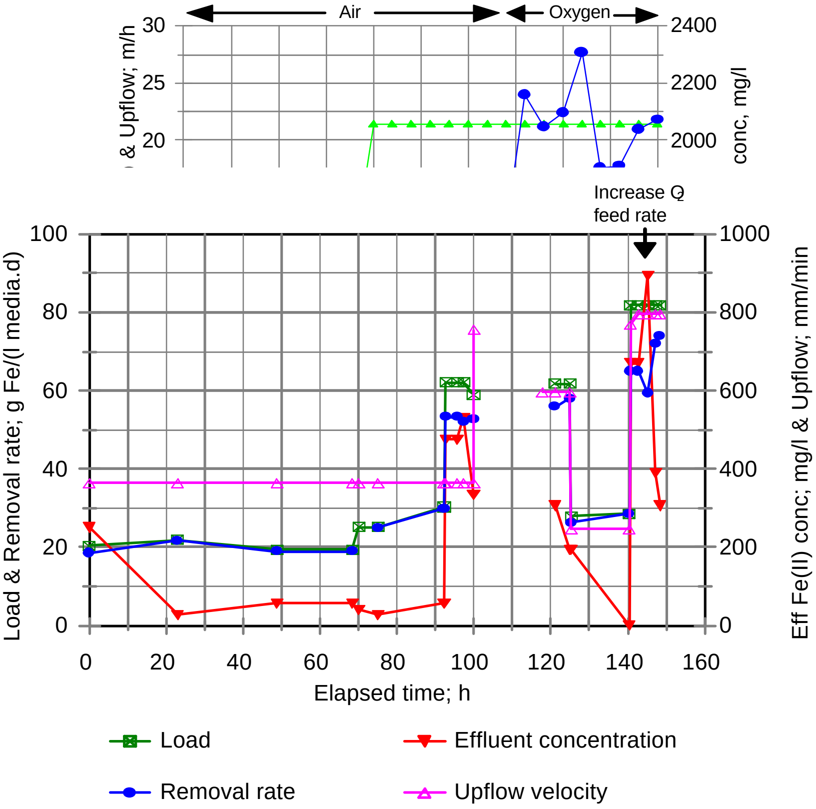


Figure 4.3 : Effect of upflow velocity and oxygen concentration for medium G at 24 °C (initial iron(II) concentration = 3 g/l ; pH = 2)

4.3.4 Effect of Oxygen Concentration

Figure 4.3 further shows that the iron(II) oxidation rate increased from 12.8 to 21.7 g Fe/(l medium.d) when the oxygen concentration of the gas bubbled through the medium in the submersed packed-column reactor increased from 21 to 100%(v/v). According to Henry's law the saturation concentration of oxygen in solution is proportional to the oxygen concentration in the gas phase. The rate of oxygen mass transfer is further proportional to the difference between the solution oxygen concentration and the saturation concentration of oxygen in solution. The results obtained therefore indicate that the dissolved oxygen concentration in the reaction solution increased as a result of the change from air to pure oxygen. Oxygen transfer is therefore not rate limiting.

4.3.5 Continuous Operation

The performance of the submersed packed column with medium G is shown in Figure 4.4. In Figure 4.4 it was noted that:

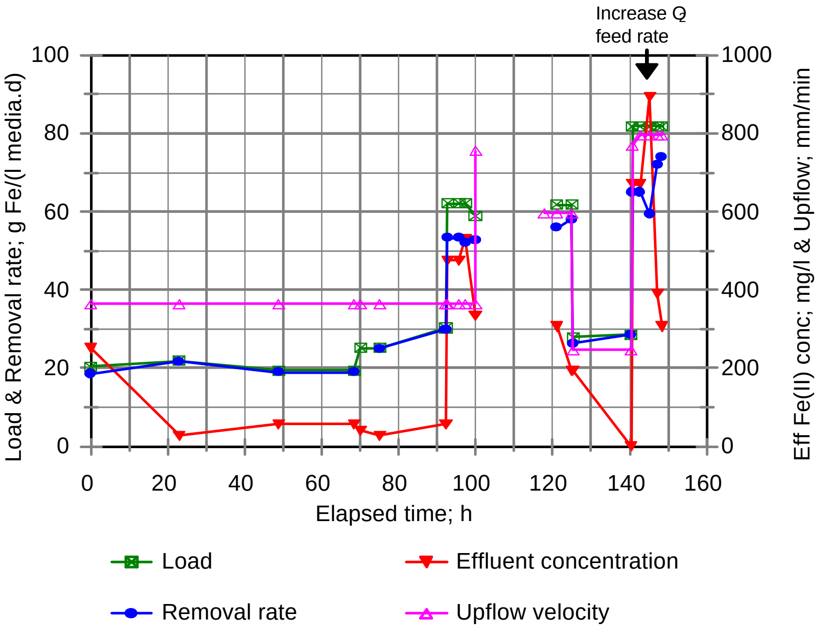


Figure 4.4 : Iron(II) oxidation in a submersed packed-bed column reactor under continuous operation (medium G; feed iron(II) concentration = 3 g/l ; temperature = 24 °C; pure oxygen and pH = 2)

At low loading rates of 20 g Fe/(l.d) most of the iron(II) was oxidized giving effluent concentrations of less than 60 mg/l iron(II). At 92 hours of operation the loading rate was increased to 62 g Fe/(l.d), which resulted in the removal rate increasing to 53 g Fe/(l.d). To improve performance even further, the upflow velocity was increased to 45 m/h (at 120 hours of operation) with concomittant increase in removal rate to 58 g Fe/(l.d). At 143 hours of operation the oxygen feed rate was increased from 100 to 300 g O_2/d, with a concomitant increase of iron(II) removal to 74 g Fe/(l.d) and effluent iron(II) concentration of 300 mg/l.

This rate is significantly lower than that obtained by Nemati and Webb (1996) of 822 g Fe/(l.d) at an effluent iron(II) concentration of 3000 mg/l with polyurethane medium (at 30 °C). However, if the concentration effect is taken in account according to Equation 2, and the temperature effect is accounted for (Nemati and Webb, 1997), the adapted rate for the sand medium would be 295 g Fe/(l.d) $\{74.(3000/300)^{0.5}(1.26)\}$. The Arrhenius equation was used for temperature adaption and the activation energy was estimated from the maximum rates obtained by Nemati and Webb at temperatures of 20 and 30 °C.

4.3.6 General

Factors that need to be taken into account in addition to rate considerations in the evaluation of various biological iron(II) oxidation options as pre-treatment prior to limestone neutralization of acid mine drainage, include the medium cost, reactor cost and the effluent iron(II) concentration. If the media in Table 4.2 are compared on a rate per cost basis, then media A, B, D and G give values of 4.6; 18.8; 17.6 and 94 g Fe/(R.d). Medium G (silica sand with particle size of 4.75 to 6.35 mm) is therefore the most cost-effective. To obtain both high oxidation rates as well as low effluent iron(II) concentrations, a plug-flow type of system would be needed: for example, two or three submersed packed-column reactors can be linked in series.

4.4 CONCLUSIONS

1. The kinetics of biological iron(II) oxidation was determined in a reciprocating disc-pack reactor to follow the rate equation.
2. A relative gain of 70% in oxygenation rate was obtained by increasing the flow velocity through the medium.
3. The reaction rate was improved by using pure oxygen rather than air. However, the oxygenation is not rate limiting.
4. Silica sand medium (particle size of 4.75 to 6.35 mm, medium G) proved to be the most cost-effective giving a rate per cost value of 94 g Fe/(R.d).
5. A biological iron(II) oxidation rate of 74 g/(l medium.d) and effluent iron(II) concentration of 300 mg/l has been attained in a continuously operated submersed packed-column reactor (at a feed iron(II) concentration of 3000 mg/l and 24 °C). An effluent iron(II) concentration of below 60 mg/l can be attained at a loading rate of 20 g/(l medium.d) under the same conditions. The medium used was silica sand (particle size of 4.75 to 6.35 mm). The low cost of the medium and relatively high oxidation rates at low effluent iron(II) concentration, would facilitate cost-effective pre-treatment of acid mine drainage for limestone neutralization.

CHAPTER 5 : INTEGRATED PROCESS FOR LIMESTONE NEUTRALIZATION OF ACIDIC EFFLUENT AND METAL AND PARTIAL SULPHATE REMOVAL

5.1 INTRODUCTION

For treatment of iron(II)-rich water, a multiple-stage limestone neutralization system is required. The expected capital cost of such a system is unacceptably high as a result of the long residence time required for iron(II) oxidation. The integrated iron(II) oxidation and limestone neutralization process was developed to overcome these disadvantages.

An integrated neutralization process consists of a neutralization reactor and a clarifier. Discard leachate is treated in an aerated sludge reactor into which powder limestone (<200 µm) is dosed to a level slightly in excess of stoichiometrical requirements. Iron(II) oxidation is achieved within 2 h when the plant is operated in sequential batch mode and within 5 h under continuous conditions. Gypsum crystallises to an over-saturation index less than 1.1. The clarifier is required to return sludge to the neutralization reactor to maintain a minimum concentration of suspended solids.

The objectives of this investigation were to determine the quality of treated water and sludge solids content when discard leachate is neutralized with the integrated iron(II) oxidation and limestone neutralization process to determine the economic feasibility of the process and to obtain design criteria for full-scale implementation.

5.2 MATERIALS AND METHODS

5.2.1 Feedstock

A synthetic solution, similar to leachate from a waste coal dump, was used as feed water. The solution contained 4 000 mg/l Fe(II), 40 mg/l P, 20 mg/l Mg, 30 mg/l N, 8 900 mg/l SO_4 and 9 200 mg/l acidity (as $CaCO_3$). Limestone from Rustenburg and sodium hydroxide were used for neutralization.

5.2.2 Batch Studies in Beakers

Batch studies were conducted in 0.5, 1.0, 2.0 and 5.0 l beakers at atmospheric pressure to determine the rate of iron(II) oxidation and neutralization. The specific surface areas of the beakers were 58.1, 46.2, 36.8 and 27.3 m^2/m^3 respectively. The following steps were followed:

Each batch test was started by mixing the treated contents from the previous batch with the synthetic feed, in a ratio varying from 1:1 to 1:4. An excess amount of $CaCO_3$ (up to 40%) was applied over the amount required to ensure complete iron(II) oxidation to iron(III) and precipitation of the latter as $Fe(OH)_3$. NaOH additions were made as required to maintain the pH at a specific value when the influence of pH was determined.

The reactor contents was aerated continuously. Filtered samples were taken regularly and analyzed for iron(II), oxygen, acidity, sulphate and pH.

Aeration was stopped when the iron(II) was completely oxidized to iron(III), whereafter the appropriate Amount of the iron(III)-containing mixture was replaced with a fresh iron(II) solution.

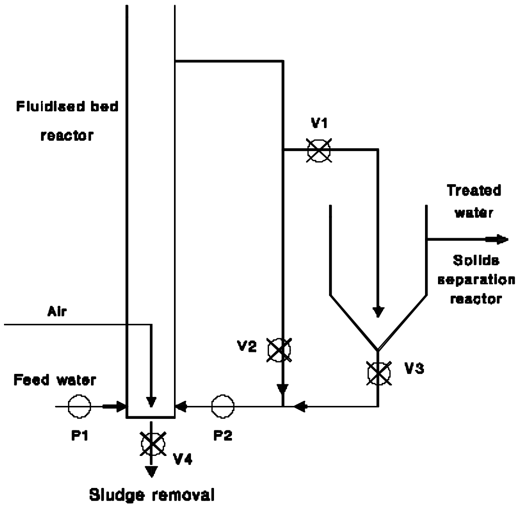
Aeration was restarted and the procedure described above repeated.

5.2.3 Batch and Continuous Studies on Pilot Scale

A pilot plant (Figure 5.1 and Table 5.1) consisting of a fluidized-bed reactor and a sludge separator was used for batch and continuous studies. During batch studies water was recycled through a fluidized-bed consisting of slimes/limestone/gypsum and during continuous studies through both the fluidized-bed reactor and the sludge separator. The purpose of the sludge separator during continuous operation was to prevent wash-out of support medium in an uncontrolled manner. Compressed air was used for iron(II) oxidation.

5.2.4 Analytical

Samples were collected regularly and filtered through Whatman No 1 filter paper. Sulphate, acidity and pH determinations were carried out manually according to procedures described in Standard Methods (APHA, 1985), and iron(II) as described in Vogel (1989). Calcium was analyzed using atomic absorption spectrophotometry. Acidity was determined by titrating the solution to pH 8.3 using NaOH.



P1 - Feed pump; P2 - Recycle pump; V1, V2, V3 & V4 - Valves

Figure 5.1 : Schematic diagram of integrated iron(II) oxidation/limestone neutralization pilot plant.

Table 5.1 : Dimensions of pilot plant.

Parameter	Value	
	Fluidized-bed	Solids separation
Feed rate (l/h)	24	
Recycle (l/h)	200	
Diameter (m)	0.20	0.53
Water height (m)	4.99	0.35
Specific surface area (m^2/m^3)	20.2	-
Upflow velocity (m/h)	6.37	0.91
Residence time (h)	6.53	3.22

5.3 RESULTS AND DISCUSSION

5.3.1 Water Quality

Limestone can be used in the integrated process for treatment of acid water. Table 5.2 shows the results when synthetic discard leachate was treated with limestone. The water was neutralized effectively and sulphate was reduced from 8 342 to 1 969 mg/l (as SO_4).

5.3.2 Kinetics

Stumm and Lee (1961) determined the following relationship between the iron(II) oxidation rate and pH in the absence of micro-organisms for clear solutions (Equation 1).

$$-d[Fe(II)]/dt = k[Fe(II)][OH^-]^2P_{O2} \qquad (1)$$

where

$-d[Fe(II)]/dt$ - rate of iron(II) oxidation;
k - reaction rate constant;
[Fe(II)] - iron(II) concentration (moles/l);
$[OH^-]$ - hydroxide concentration (moles/l);
P_{O2} - partial pressure of oxygen (mm Hg).

Table 5.2 : Chemical composition of feed and treated water (in mg/l where applicable) when synthetic discard leachate was treated with limestone

	Feed (Synthetic discard leachate)	Treated (Limestone)
pH	1.8	6.6
Acidity (as $CaCO_3$)	7 300	100
Sulphate	8 342	1 969
Ortho phosphate (as P)	2.9	0.0
Chloride	27	30
Iron(II)	2 500	56
Total iron	2 500	56
Aluminium	6.8	7.3
Manganese	15.7	21.8
Magnesium	35	45
Calcium	40	682
Sodium	25.2	29.5

It appears that iron(II) oxidation occurs either at pH levels less than 4 when catalyzed by bacterial activity, or at pH values greater than 6 through chemical oxidation. Maree *et al.* (1987) showed that the rate of chemical iron(II) oxidation is also catalyzed by suspended solids. The result is that the lower limit of the pH range where the rate of chemical oxidation is fast enough for practical application is reduced from 6.5 to 5.0. The integrated iron(II) oxidation and limestone neutralization process is based on this finding as limestone can raise the pH of iron(II)-rich water to between 5 and 6. Volumetric iron(II) oxidation rates exceeding 100 g/(l.d) were achieved when artificial acid mine water was treated with powdered limestone and pure oxygen in a sludge contact reactor. Neutralization and partial sulphate removal were achieved as well.

The relative importance of various factors in terms of their influence on the rate of iron(II) oxidation was determined by a series of controlled tests in which the dependence of the rate on one variable at a time was determined. In the pH range 5 to 6, which is of importance from the point of view of limestone neutralization, the iron(II) oxidation rate was assumed to have the following functional form:

$$-d[Fe^{2+}]/dt = k.[Fe^{2+}]^{n1}.[O_2]^{n2}.[OH^-]^{n3}.[RSA]^{n4}.[SS]^{n5}.M^{n6} \qquad (2)$$

where

$-d[Fe^{2+}]/dt$ or R = rate of iron(II) oxidation

k = reaction rate constant

$[Fe^{2+}]$ = iron(II) concentration (moles/l)

$[O_2]$ = oxygen concentration (moles/l)

$[OH^-]$ = hydroxide concentration moles/l)

RSA = reactor surface area (m^2/m^3)

[SS] = suspended solids concentration (g/l)

M = mixing intensity (rpm)

By varying the value of only one parameter in a series of experiments, say $[Fe^{2+}]$, equation 2 can be written as:

$$-\partial[Fe^{2+}]/\partial t = K.[Fe^{2+}]^{n1} \quad \text{or} \quad \log(-\partial[Fe^{2+}]/\partial t) = \log K + n_1 \log [Fe^{2+}] \qquad (3)$$

where $K = k.[O_2]^{n2}.[OH]^{n3}.[RSA]^{n4}.[SS]^{n5}.M^{n6}$

Table 5.3 : Effect of various factors on the kinetics of iron(II) oxidation

Exp No	Variable	Value	Rate g Fe/(l.d)	Log C	Log R	Reaction order
1.	pH (no bacteria)	4.50	22.56	-9.50	1.35	1.33
		5.00	90.22	-9.00	1.95	
		5.25	229.20	-8.75	2.36	
		5.50	462.44	-8.50	2.67	
2.	pH (with bacteria)	4.50	18.40	-9.50	1.26	1.41
		5.00	93.48	-9.00	1.97	
		5.25	233.24	-8.75	2.37	
		5.50	454.39	-8.50	2.66	
3.	Fe(II) (g/l)	0.30	21.72	-0.52	1.34	0.42
		1.00	41.24	0.00	1.62	
		3.00	82.04	0.48	1.91	
		10.00	88.46	1.00	1.95	
4.	SS (g/l)	0.00	30.36		1.48	0.37
		4.70	42.93	0.67	1.63	
		12.00	53.15	1.08	1.73	
		49.30	66.07	1.69	1.82	
		75.20	129.25	1.88	2.11	
		152.00	155.75	2.18	2.19	
		328.10	136.34	2.52	2.13	
5.	O_2 (air) (mg/l)	0.10	18.16	-1.00	1.26	0.51
		0.50	30.41	-0.30	1.48	
		2.00	92.79	0.30	1.97	
		5.00	113.93	0.70	2.06	
6.	Stirring (rpm)	20	50.83	1.30	1.71	0.43
		150	120.25	2.18	2.08	
7.	Stirring (pure O_2) (rpm)	50	80.09	1.70	1.90	0.41
		150	136.92	2.18	2.14	
		300	163.73	2.48	2.21	
8.	RSA (m^2/m^3)	58.12	100.18	1.76	2.00	1.25
		46.13	94.06	1.66	1.97	
		36.61	84.64	1.56	1.93	
		26.98	37.57	1.43	1.57	
9.	Temperature (^{0}C)			1/T		E (kcal/mole)
		5.0	13.56	0.00265	1.13	21.55
		11.0	26.99	0.00261	1.43	
		18.7	48.77	0.00256	1.69	
		25.0	81.94	0.00252	1.91	
		37.0	128.64	0.00244	2.11	
		45.0	147.30	0.00240	2.17	

Typical values for various parameters: Iron(II) = 2.8 to 4.7 g/l; $CaCO_3$ = 10 g/l; pH = 4.8 to 6.0; O_2 = 1 to 24 mg/l; SS = 94 to 291 g/l; Temperature = 23 to 28 ^{0} C; Bacteria only present in Experiments 1 and 2; Stirring rate = 150 rpm; Reactor volume = 0.5 to 4 l.

The contribution, n_1, of iron(II), to the overall reaction rate was determined from the slope of the graph obtained by plotting log R versus log [Fe^{2+}]. From pH, log R was plotted against log[OH^-] ([OH^-] = $10^{pH - 14}$). The data in Table 5.3 show that the rate of iron(II) oxidation is of order 0.42 (≈ 0.5), 1.41 (≈ 2), 0.51 (≈ 0.5), 0.37 (≈ 0.5) and 0.43 (≈ 0.5) in respect of Fe^{2+}, OH^-, O_2 and SS concentrations, and mixing intensity (M), respectively. The findings suggest that the rate equation as proposed by Stumm and Lee (1961) for clear solutions, should be modified for suspensions to:

$-d[Fe^{2+}]/dt = k.[Fe^{2+}]^{½}.[OH^-]^{1.5}.[O_2]^{½}.[SS]^{½}.M^{½}$(4)

Other conclusions to be drawn from Table 5.3 include the following:

- The rate of iron(II) oxidation in suspensions with high concentrations of suspended solids in the pH range 4.5 to 5.5 is dominated by chemical oxidation. This was concluded from studies where experiments were carried out on sterilized and unsterilized suspensions respectively (Table 5.3, Experiments 1 and 2). This finding contradicts that reported by Maree *et al.* (1997). In the previous study chemical iron(II) oxidation was studied by using a clear solution (the only solids present was that which precipitated from solution during iron(II) oxidation and neutralization) and was compared with biological iron(II) oxidation where solids were present from the start of the experiment (medium to support bacterial growth). The slower oxidation rates determined for chemical iron(II) oxidation at pH values between 5 and 5.5 should be ascribed to lower suspended solids concentrations and not to the absence of bacterial activity.
- In a previous investigation Maree *et al.* (1997) determined that the rate of iron(II) oxidation in the pH range 4.5 to 6 is influenced by the reactor surface area (RSA). It was pointed out that this behaviour is in line with the behaviour of iron(II) oxidation in the pH range 2 to 3 where the rate is directly proportional to the square root of the medium specific surface area (Maree *et al.*, 1998). The current investigation, however, shows that chemical iron(II) oxidation in the pH range 4.5 to 6 is not influenced by the medium specific surface area (RSA), but by the mixing intensity, M. In the previous investigation the values of RSA and M were varied simultaneously. This happened as beakers of different sizes were used to provide different RSA values (see Table 5.3, Experiment 8 for the relationship between RSA and beaker volume). Unfortunately, the mixing intensity decreases when larger beakers are used if the stirring rate is not adjusted accordingly (Table 5.3, Experiments 6 and 7). The iron(II) oxidation rate increases with increased mixing intensity.

The Arrhenius equation $\log k = \log A - E/(2.303RT)$ can be used to estimate the value of the reaction rate k at other temperatures. The amounts E, R and log A have the values 21.55 kcal/mole (activation energy), 13.70 (a constant) and 1.987 cal $mole^{-1}$ $degree^{-1}$ (gas constant) respectively (Table 5.3, Exp 9). A linear relationship was obtained over the range 5 to 25 ^{0}C. It is expected that the linear relationship will fail at higher temperatures as optimum reaction rates are often achieved at 37 ^{0}C.

5.3.3 Design Criteria Continuous Operation

(a) Oxygen versus air

The iron(II) oxidation rate increases with increased oxygen concentrations (Table 5.4). For a specific oxygen concentration (0.2 mg/l) similar reaction rates are measured for pure oxygen and air (between 44.9 and 65.8 g Fe/(l.d)). Although high iron(II) oxidation rates can be achieved by dosing pure oxygen, air is a more suitable oxidant for full-scale application due to safety reasons.

Table 5.4 : Effect of oxygen concentration on the rate of iron(II) oxidation.

Parameter	Oxygen concentration (mg/l O_2)						
	0.11	0.20	0.20 air	0.20	0.27	5.7	10
Iron(II) oxidation rate (g Fe/(l.d)	22.8	44.9	59.0	65.8	86.4	183	163
Reaction time (h)	>>4	2.25	2.00	>1.75	1.75	1.0	0.75
Order	0.37						

Note: Data collected during batch operation of pilot plant.

Conditions: pH = 5.9; Suspended solids in recycle stream = 240 to 360 g/l;
Initial iron(II)-concentration = 3.2 to 6.3 g/l; Initial acidity = 8.8 to 12.0 g/l (as $CaCO_3$);
Temperature = 15.0 to 20.0 ^{0}C.

(b) ***Suspended solids concentration***

The optimum suspended solids concentration for iron(II) oxidation in the fluidized-bed reactor of the integrated iron(II) oxidation and limestone neutralization process is 190 g/l (Table 5.5). The decrease in the iron(II) oxidation rate for suspended solid concentrations greater than 190 g/l can possibly be ascribed to decreased oxygen transfer. It is expected that the optimum level of 190 g/l can be increased when pure oxygen is used and/or when the mixing intensity is increased. The reaction order with respect to suspended solids (over the range 0 to 190 g/l) is 0.50.

Table 5.5 : Effect of suspended solids on the rate of iron(II) oxidation.

Parameter	**Suspended solids (g/l)**					
	41.1	91.2	95.6	190	277	462
Iron(II) oxidation rate (g Fe/(l.d)	28.7	38.6	47.7	61.9	42.3	32.3
Order	0.50					

Note: Data collected during batch operation of pilot plant.

Conditions: pH of feed = 5.0;

Excess alkali dosage = 41 %;

Initial sulphate concentration = 5.7 to 12.2 g/l; Initial iron(II)-concentration = 2.4 to 5.6 g/l;

Initial acidity = 4.2 to 9.2 g/l (as $CaCO_3$); Temperature = 14.5 to 17.5 ^{0}C.

(c) Upflow velocity

Upflow velocity has no influence on the rate of iron(II) oxidation in the range 5 to 45 m/h.

(d) Residence time and mode of operation

A shorter reaction time is required during batch operation than in continuous operation. For the removal of 4 g/l iron(II) (as Fe) reaction times of 2.0 and 4.5 h are required for continuous and batch operations respectively (Figure 5.2). The shorter reaction time required during batch operations can be explained by the iron(II) oxidation rate equation:

$$-d[Fe^{2+}]/dt = k.[Fe^{2+}]^{½}.[OH^-]^{1.5}.[O_2]^{½}.[SS]^{½}.M^{½} (5)$$

The values for O_2 and SS are the same for batch and continuous operations. The oxygen level is controlled at a specific concentration of say 2 mg/l (as O_2) while the SS concentration is kept at a high concentration of say 150 g/l. During continuous operation sludge would be withdrawn continuously to maintain a specific level. During batch operation the suspended solids will increase during the course of each batch operation. The increase would, however, be small compared to the initial concentrations. The values of Fe^{2+} and OH^- during batch operation are, except for the values at the end of the batch experiment, higher than those measured during continuous operation. As the order of the latter parameters are greater than 0, the reaction rate increases with increased values for the parameters mentioned.

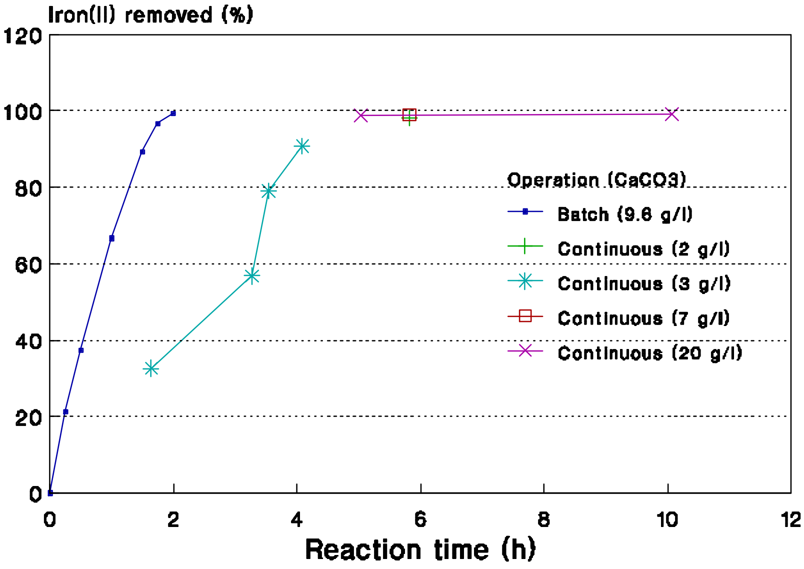


Figure 5.2 : Comparison between batch and continuous operation during iron(II) oxidation.

Note: Data collected during batch operation of pilot plant.

Conditions: pH of feed = 2.4; Excess alkali dosage = 2 to 20 %; Initial sulphate concentration = 6.2 to 8.3 g/l; Initial iron(II)-concentration = 2.4 to 4.2 g/l; Initial acidity = 6.88.7 g/l (as $CaCO_3$); Oxygen = 0.2 mg/l O_2; Suspended solids = 200 to 400 g/l; Temperature = 15 to 22 ^{0}C.

5.3.4 Sequential Batch Mode Operation

Sequential batch mode operation versus continuous operation of the integrated iron(II) oxidation and limestone neutralization process offers the benefits of a faster reaction rate and better lime utilization. The reaction rate is faster due to a greater driving force as a result of high iron(II) concentration in solution, except for the final period of the reaction. Limestone utilization is better as unused limestone can be contacted with acid feed water while final treated water can be contacted with fresh limestone for maximum neutralization.

Figure 5.3 shows the behaviour of the most important parameters for a typical batch operation. It is noted that iron(II) was removed during consecutive batch operations in less than 2 h at an average rate of 35 g Fe/(l.d). The experimental conditions were as follows: Temperature = 24 ^{0}C and suspended solids = 250 g/l. The pH was raised from 5.3 to 6.1 or higher while acidity was reduced from 5.6 g/l (as $CaCO_3$) to 0.3. Sulphate was reduced from 6.6 to 2.2 g/l (as SO_4) due to gypsum crystallization.

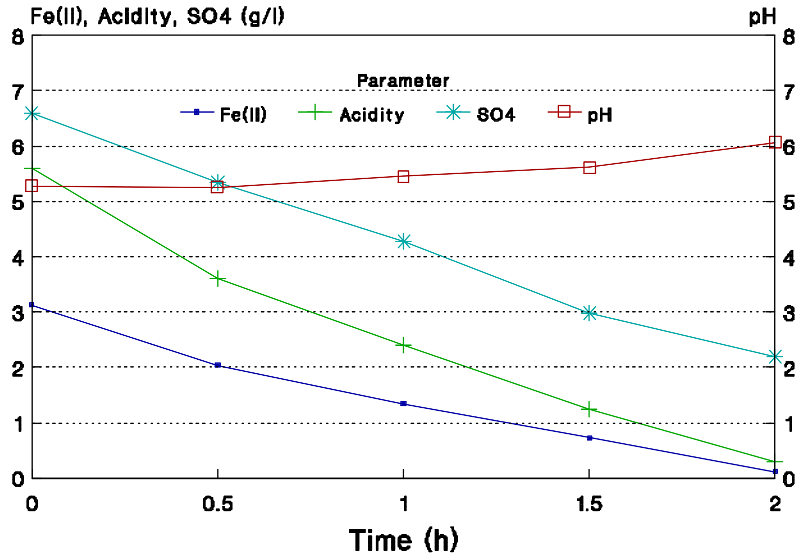


Figure 5.3 : Behaviour of various parameters during batch operation of the integrated iron(II) oxidation and limestone neutralization process

5.3.5 Sludge Characteristics

(a) Settling rate and solids content

Table 5.6 shows the suspended solids content of the sludge in the fluidized-bed reactor at different dilutions (1, 2, 5, 10 and 20 times) before and after settling, as well as the settling rate at each dilution. The settling rate increases from 0.07 to 2 m/h as the dilution factor increases from 1 to 20. A low sludge settling rate (0.07 m/h) would therefore be expected in the fluidized-bed reactor where the sludge solids content is high (200 to 300 g/l) and a high sludge settling rate (2 m/h) in the sludge separation stage where the solids content is low (less than 10 g/l). The sludge concentration can be controlled by withdrawing sludge from the bottom of the fluidized-bed reactor, where the solids content would be at a maximum. One of the major benefits of the integrated iron(II) oxidation and limestone neutralization process is that sludge with a high solids content is produced (up to 550 g/l). This compares well with the typical 200 g/l solids content that can be achieved with the High Density Sludge process.

Table 5.6 : Suspended solids content of the sludge at different dilutions (1, 2, 5, 10 and 20 times) before and after settling, as well as the settling rate at each dilution (Exp 11.1)

Parameter	Dilution				
	1x	2x	5x	10x	20x
Suspended solids before settling (g/l)	619	595	165	59	16
Settling rate (m/h)	0.07	0.10	0.37	0.88	2.00

(b) Utilization of excess $CaCO_3$ in the waste sludge

Waste sludge withdrawn from the bottom of the fluidized-bed reactor can contain between 0 and 30% $CaCO_3$ (m/m dry basis), depending on the limestone excess that is applied. If the sludge contains a significant amount of $CaCO_3$, it might be cost-effective to contact the waste sludge with acid feed water prior to discharge in order to achieve maximum utilization of the $CaCO_3$. Table 5.7 shows that 70.8% of the $CaCO_3$ content of the waste sludge that was dosed to discard leachate was utilized for neutralization of acid. The amount of acidity removed was 4.83 g/l (as $CaCO_3$) as a result of $CaCO_3$ dissolution from the waste sludge and 4.75 g/l (as $CaCO_3$) as a result of acidity removed from the discard leachate.

Table 5.7 : Partial neutralization of discard leachate with $CaCO_3$-rich waste sludge.

Parameter	Feed	Treated
$CaCO_3$-rich waste sludge:		
Dosage (ml/l)	50.00	
Suspended solids (g/l)	44.02	36.62
$CaCO_3$-content (%)	13.77	4.83
$CaCO_3$-content (g/l)	6.06	1.77
$CaCO_3$-utilized (g/l)		4.29
$CaCO_3$-utilized (%)		70.82
Water composition:		
Acidity (g/l $CaCO_3$)	7.75	3.00
Acidity removed (g/l $CaCO_3$)		4.75
pH	2.28	6.06
Iron(II) (g/l Fe)	3.02	1.59
Sulphate (g/l SO_4)	8.27	4.84

5.3.6 Economic Feasibility

The cost figures for the treatment of 1 Ml/d of discard leachate with an acidity of 10 g/l (as $CaCO_3$) are as follows:

- The estimated alkali cost to treat discard leachate with an acidity of 10 g/l (as $CaCO_3$) is R5.15/m^3, R2.79/m^3, R1.37/m^3 and R1.95/m^3 for slaked lime, unslaked lime, limestone (milled on-site) and limestone (purchased) respectively. The corresponding cost ratios with respect to unslaked lime are 1.84, 1.00, 0.49 and 0.70. The alkali cost per ton (purity and alkali utilization are shown in brackets) was based on delivery prices (1999) of R500 (90%, 80%), R360 (90%, 80%), R99.84 (85%, 85%) and R140 (85%, 85%) respectively. The electricity cost for milling of limestone was calculated to be R9.84/t (30 kW/h x R0.20/kW / 0.61 t/h).

- The capital cost for 1 Ml/d plant remains the same at R1.87 million when the alkali is purchased and when limestone is milled on-site.

5.4 CONCLUSIONS

The following conclusions were reached:

1. The integrated iron(II) oxidation and limestone neutralization process can be used for the removal of acidity, iron(II), iron(III), aluminium (to less than 2 mg/l (as Al) and sulphate (to a level of 2 500 mg/l (as SO_4)). All reactions take place simultaneously. For water containing 3 g/l iron(II) (as Fe), a reaction time of 2 h is required when operated in sequencing batch mode and 5 h when operated on a continuous basis.
2. Sludge with a solids content of more than 50 % can be produced with the integrated process.
3. The estimated alkali cost to treat discard leachate with an acidity of 10 g/l (as $CaCO_3$) is R5.15/m^3, R2.79/m^3, R1.37/m^3 and R1.95/m^3 for slaked lime, unslaked lime, limestone (milled on-site) and limestone (purchased) respectively.
4. The estimated capital cost for a 1 Ml/d plant remains the same at R1.87 million when the alkali is purchased and when limestone is milled on-site.

CHAPTER 6 : DESIGN OF FULL-SCALE LIMESTONE NEUTRALIZATION PLANT

6.1 INTRODUCTION

The design of a full-scale iron(II) oxidation / limestone neutralization system for a typical acid mine drainage is discussed in this Chapter. The design basis used is as follows:

Flow rate:	1.2 Ml/d

Acid water composition:

HCO_3^- acidity:	4000 mg/l as $CaCO_3$
Iron(II) concentration:	1000 mg Fe/l
Sulphate concentration:	5000 mg SO_4/l

The following process design aspects are dealt with:

- Process description
- Plant configuration
- Control philosophy
- Process flow diagram with design calculations
- Equipment list
- Capital cost of the plant
- Running cost of the plant

6.2 PROCESS DESCRIPTION

6.2.1 Limestone Neutralization

The acid feed water is contacted with limestone particles in a fluidized-bed reactor. The limestone dissolves and neutralizes the acid by the following reaction:

$$CaCO_3 + 2H^+(aq) \text{ ? } Ca^{2+}(aq) + H_2O + CO_2$$

As a result of this reaction the following side-reactions occurs:

When iron(III) is present, it precipitates due to the high pH level:

$$2Fe^{3+}(aq) + 3CaCO_3 + 3H_2O \rightarrow 2Fe(OH)_3(s) + 3Ca^{2+}(aq) + 3CO_2$$

When acid associated sulphate is present at concentrations above 2000 mg/l it precipitates as gypsum due to the increased calcium concentration in the water:

$$Ca^{2+}(aq) + SO_4^{2-}(aq) + 2H_2O \rightarrow CaSO_4.2H_2O(s)$$

6.2.2 Iron(II) Oxidation

The presence of iron(II) in the acid feed water, does however cause a highly persistent scale to form on the limestone particles, which impairs limestone dissolution. To overcome this problem, iron(II) oxidation is needed as pre-treatment to limestone neutralization, for waters that contains more than 100 mg Fe(II)/l.

The iron(II) oxidation reaction takes the following form at low pH:

$$4Fe^{2+} + O_2 + 4H^+ \rightarrow 4Fe^{3+} + 2H_2O$$

The biological iron(II) oxidation reaction is dependent on surface area for bacterial support.

6.3 PLANT CONFIGURATION

A biologically aerated filter (BAF) set-up is used for iron(II) oxidation (Figure 6.1). A low-cost medium is used to provide a large surface for bacterial support. The filter is operated submersed. Air or oxygen is bubbled through from the bottom.

A fluidized-bed reactor with a cone at the top has been developed by the CSIR for limestone neutralization (Figure 6.2). Water/slurry is recycled upward through the reactor column to effect fluidisation. The top-cone acts as particle separator, preventing loss of limestone to the effluent.

The fluidized-bed configuration has the following benefits:

- A limestone concentration of up to 500 g/l can be attained, which provides a large surface area, and therefore a high reaction rate.
- The fluidisation action causes attrition between particles that helps to prevent or minimize scaling.

6.4 CONTROL PHILOSOPHY

6.4.1 Iron(II) Oxidation

The level in the transfer sump subsequent to the iron(II) oxidation reactor needs to be controlled by level measurement and changing the feed pump rate to the limestone neutralization column.

Backwash / air scouring of the iron(II) oxidation bed will be performed manually using an arrangement of valves.

6.4.2 Limestone Neutralization

Limestone feed to the neutralization reactor can be controlled in two ways, dependent on the characteristics of the limestone:

1. For powder limestone, the limestone is slurried to a specified consistency (using load cells and level control in the slurry system) and fed to the reactor proportionally to the feed water. The feed water flow rate are measured and used as control input. The daily manual acidity analysis of the feed water is used additionally to fine tune the controller (i.e. adapt the controller constant).
2. For particulate limestone, the weight of the limestone bed in the first reactor column is monitored by load cell and used to control the feed of limestone.

6.5 PROCESS FLOW DIAGRAM AND COSTING

The process flow diagram is given in Figure 6.3, which is supported by design calculations in Table 6.1. Table 6.2 gives the equipment list for this plant (1999 cost figures). The capital and running costs for this plant are given in Tables 6.3 and 6.4 respectively (1999 cost figures).

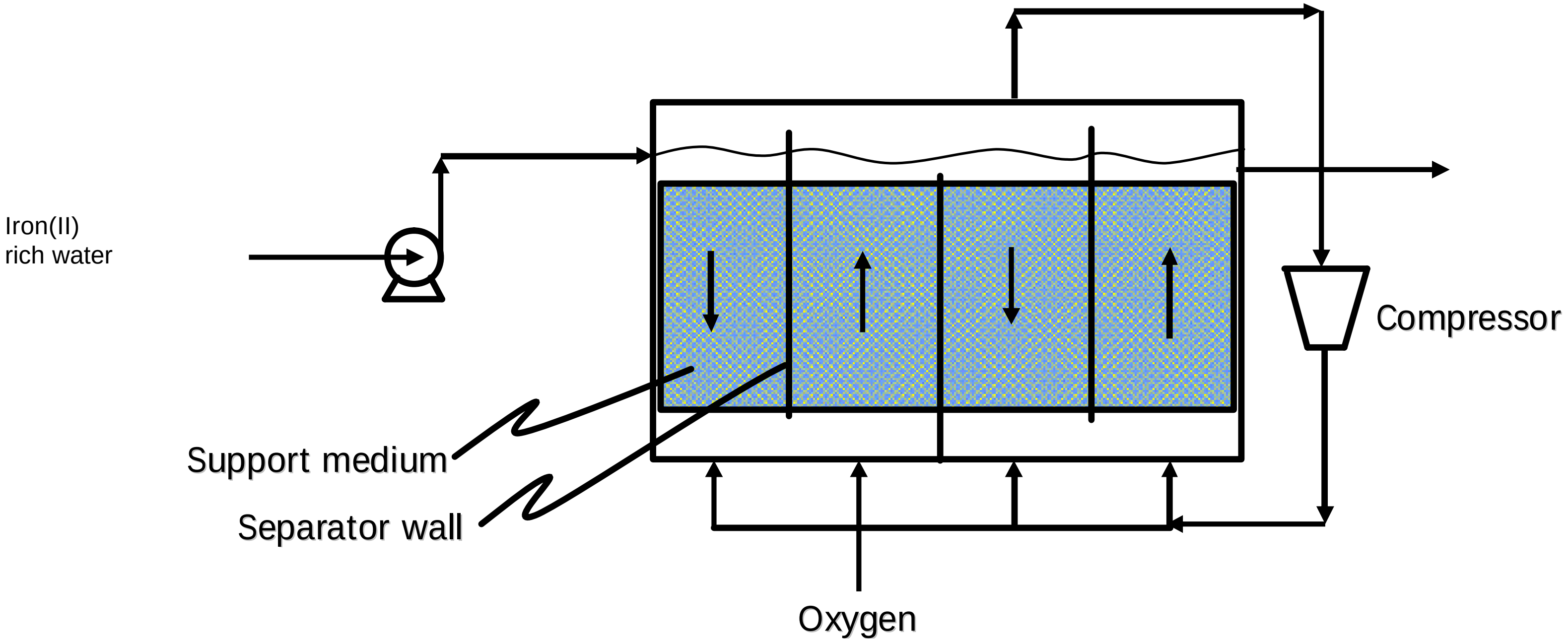


Figure 6.1 : Iron(II) oxidation reactor.

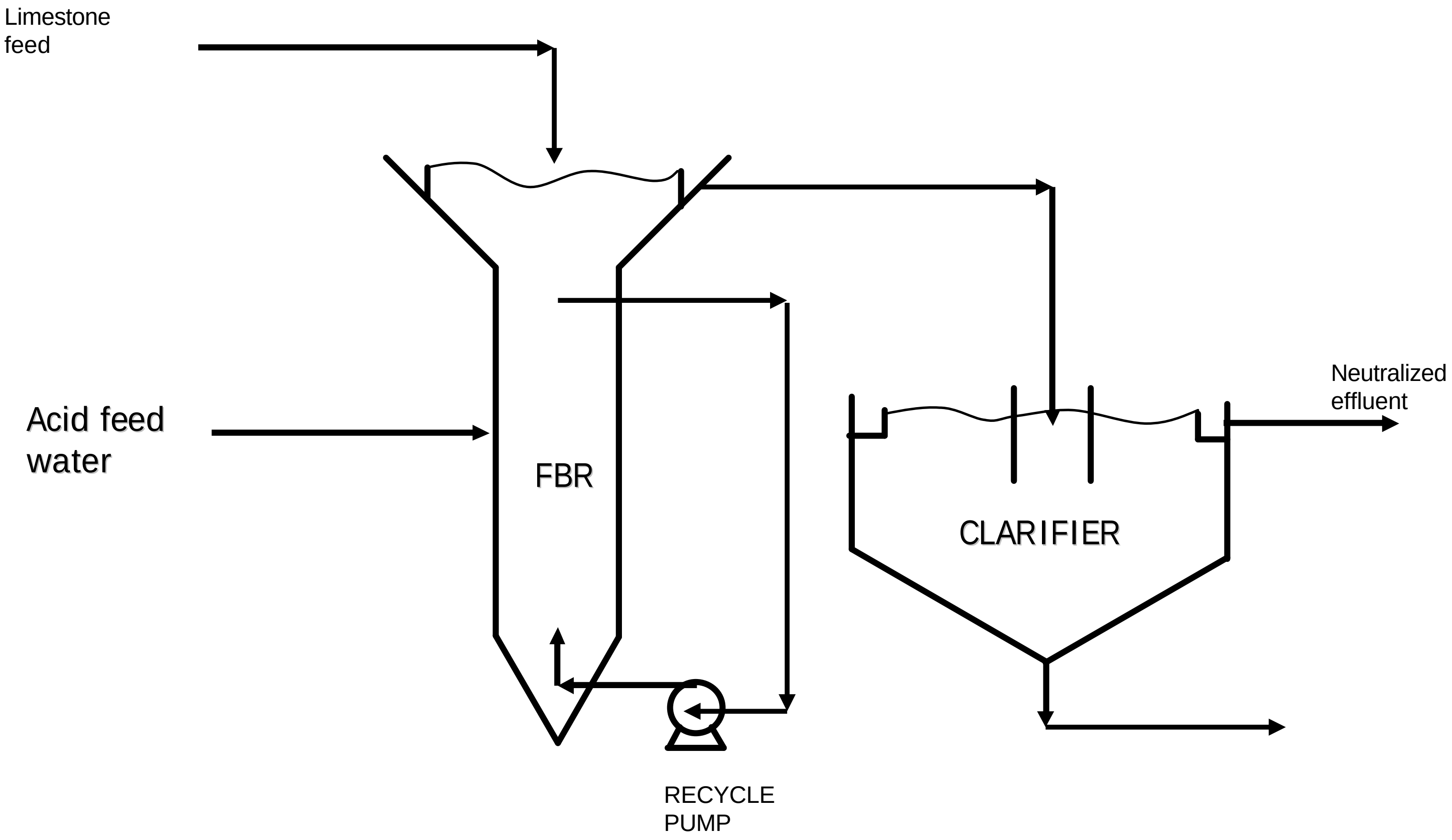


Figure 6.2 : Fluidized-bed limestone neutralization reactor

TABLE 6.1. DESIGN CALCULATIONS for LIMESTONE NEUTRALISATION of TYPICAL ACID MINE WATER at 1.2 Ml/d

DESIGN BASIS:

Parameter	*Value*	*Units*	
Leachate flow rate	50	kl/h	1.2 Ml/d
Iron(II) conc.	1.000	g/l	
Acidity	4.000	g/l	
Sulphate conc.	5.000	g/l	

IRON OXIDATION REACTOR (IOR) & EQUIPMENT:

Parameter	*Value*	*Units*	
Reactor:			
Pilot run reaction rate/air	11.25	g Fe/(liter reactor.d)	
Pilot run reaction rate/O2	22.5	g Fe/(liter reactor.d)	
Reactor volume	106.7	m^3	
Safety factor	20	%	
Design volume	128	m^3	
Dimensions:			
Height of bed	4.0	m	
Clear board	0.5	m	
Reactor height	4.5	m	
Area of bed	32.0	m^2	
Area per cell	4.0	m^2	
Number of cells	8		
Reactor length	11.2	m	
Reactor width	2.9	m	
Actual reactor volume	144.0	m^3	
Bed: packing material	179.2	tons	R 44 800 (@R250/t)

Equipment:

Parameter	*Delivery Value*	*Units*	
Aeration compressor/blower:	238.7	Nkl/h	
oxidation requirement	7.2	kg O2/h	
transfer efficiency	10.0	%	
Feed pump	50	kl/h	
8 Recycle pump(s):	60.0	kl/h	
upflow velocity/bed	15	m/h	Normal operation
Level-control system			
Transfer pump	50	kl/h	
Nutrient feed tank	0.45	m^3	
inventory	7.0	days	
Nutrient tank stirrer			
Nutrient feed pump	2.7	l/h	
nitrogen requirement	20	g N/h	
$(NH_4)_2SO_4$	94	g/h	
phosphorus requirement	4	g P/h	

TABLE 6.1 (continue). DESIGN CALCULATIONS

LIMESTONE NEUTRALISATION REACTOR SYSTEM (LNR) & EQUIPMENT

Reactor:

	Delivery						
Parameter	*Value*	*Units*					
Column 1:	16.7	m^3					
reaction time	20	min					
height to dia ratio	5.5						
diameter	1.6	m					
height	8.6	m					
specified upflow velocity	200	m/h					
recycle rate/pump	386	kl/h					
back-up fluidisation pump	386	kl/h					
Column 2:	25.0	m^3					
reaction time	30	min					
height to dia ratio	3.5						
diameter	2.1	m					
height	7.3	m					
specified upflow velocity	40	m/h					
recycle rate/pump	137	kl/h					
Loadcell system							
Limestone feed	0.25	t/h					
limestone utilisation eff.	80.0	%					
Limestone silo / dump	30	m^3					
inventory	7.0	days					
diameter	5	m					
height	1.5	m					
Slurry system	0.25	t/h					
Limestone slurry consistency	10%						
Limestone density	2700	kg/m^3					
Slurry density	1067	kg/m^3					
Slurry feed rate	2.3	m^3/h					
Make-up water flow rate	2.3	m^3/h					
MOL slurry buffer tank							
inventory	0.20	days					
volume	11.2	m^3					
			Amounts		Solids density		Mass frac
Ferric hydroxide	1913	mg/l	95.7	kg/h	3400	kg/m^3	0.30
Gypsum	4479	mg/l	224.0	kg/h	2320	kg/m^3	0.70
Total:			319.6	kg/h	2564	kg/m^3	
Slurry consistency	0.64%						
Slurry density	1004	kg/m^3					
Slurry flow rate	52.4	m^3/h					
Effluent sump:	4.4	m^3					
hydraulic retention time	5	min					
height	1.7	m					
diameter	1.8	m					
Effluent return pump	52.4	m^3/h					

TABLE 6.2. EQUIPMENT SIZING for LIMESTONE NEUTRALISATION of TYPICAL ACID MINE WATER at 1.2 Ml/d

REACTOR TANKS

Item description	Item type	Throughflow m^3/h	HRT h	Inventory days	SLR m/h	Volume m^3	Area m^2	Height m	Diameter m	Length m	Width m	H/D
Feed sump		50.0	0.08			4.2		1.7	1.8			1.0
Iron(II) oxidation reactor	square cells	50.0	2.56			144.0						
per cell (8 cells)		6.3				18.0	4.0	4.5		2.8	1.4	
packing material	silica gravel					128.0						
nutrient feed tank				7.0		0.45		2.3	0.5			4.6
Transfer sump		50.0	0.08			4.2		1.7	1.8			1.0
Limestone neutralisation col 1	fluidised bed	50.0	0.33			16.7		8.6	1.6			5.5
Limestone neutralisation col 2	fluidised bed	50.0	0.50			25.0		7.3	2.1			3.5
Limestone hopper				7.0		30.0						
Limestone MOL tank	cylindrical, fb			0.2		11.2		1.6	3.0			0.5
Effluent sump		52.4	0.08			4.4		1.7	1.8			0.9

FLUID TRANSPORT EQUIPMENT

Item description	Item type	Flow m^3/h	Gas Nm^3/h	Solids/O_2 kg/h	Fluid/slurry characteristics				
					Solids type	Solids %	Density kg/m3	Viscosity kg/(m.s)	Viscosity cP
FeOX feed pump		50.0			none				
Aeration blower/compressor	acid resist.		238.7						
FeOX recycle pump(s): 8 pumps	centrifugal	60			none				
Column 1 feed pump	centrifugal	50			none				
Column 1 recycle pump + back-up	centrifugal	386			LS, $Fe(OH)_3$ slurry	1.00%	1004		
Column 2 recycle pump + back-up	centrifugal	137			LS, $Fe(OH)_3$ slurry	0.64%	1004		
LS slurry system				250					
Limestone MOL feed pump	centrifugal	2.3		250	Limestone slurry	10.00%	1067		
Effluent to tailings pump	centrifugal	52			LS, $Fe(OH)_3$ slurry	0.64%	1004		

SPECIALISED EQUIPMENT

Item description	Item type	Inventory days	Capacity kg		
Loadcell control instrumentation			25000		

TABLE 6.3. CAPITAL COST for LIMESTONE NEUTRALISATION of TYPICAL ACID MINE WATER at 1.2 Ml/d

REACTOR TANKS			
Item description	**Item type**	**Cost R**	**Power kW**
Feed sump		15 000	
Iron(II) oxidation reactor	square cells	172 800	
per cell (8 cells)			
packing material	silica gravel	44 800	
nutrient feed tank		2 000	
Transfer sump		15 000	
Limestone neutralisation col 1	fluidised bed	41 667	
Limestone neutralisation col 2	fluidised bed	62 500	
Limestone hopper		100 000	
Limestone MOL tank	cylindrical, fb	16 867	
Effluent sump		15 000	
FLUID TRANSPORT EQUIPMENT			
Item description	**Item type**	**Cost R**	**Power kW**
FeOX feed pump		34 000	10
Aeration blower/compressor	acid resist.	50 000	50
Oxygen evaporator		10 000	0
FeOX recycle pump(s): 8 pumps	centrifugal	240 000	80
Column 1 feed pump	centrifugal	34 000	10
Column 1 recycle pump + back-up	centrifugal	150 000	75
Column 2 recycle pump + back-up	centrifugal	100 000	20
LS screw feeder / slurry system		50 000	5
Limestone MOL feed pump	centrifugal	20 000	1
Effluent to tailings pump	centrifugal	34 000	10
SPECIALISED EQUIPMENT			
Item description	**Item type**	**Cost R**	**Power kW**
Oxygen tank	pressure vessel	20 000	
Loadcell control instrumentation		30 000	
BASIC EQUIPMENT COST		**1 257 633**	**261**
Piping & valves	20%	251 527	
Electrical & Instrumentation	10%	125 763	
Civils	10%	125 763	
TOTAL INSTALLATION COST (CAPEX)		**1 760 687**	

TABLE 6.4. OPERATING COST for LIMESTONE NEUTRALISATION of TYPICAL ACID MINE WATER at 1.2 Ml/d

Chemical cost:		**R/month**		
Limestone (R/month):		27 000		
Limestone cost (R/t)	150			
Actual limestone requirement (t/d)	6.0			
Total chemical cost (R/month)		**27 000**		
Other running expenses:		**R/month**		
Electrical (kW)	161	23 184	(@ R0.2/kWh)	
Maintenance (10% of EQUIP/a)	10	10 480		
Operating labour (3 operators @R4000/month)	4000	12 000		
Sub-total		**45 664**		
TOTAL OPERATING COST (R/month)		**72 664**		
R/m^3		2.02		

CHAPTER 7 : LIME NEUTRALIZATION WITH THE MODIFIED HDS PROCESS

7.1 INTRODUCTION

7.1.1 Background

Acid mine drainage (AMD) emanates from active and abandoned mining operations. Pyrite (FeS_2) is found in waste rock of mines. When pyrite is exposed to oxygen and water during or after mining operations, it is oxidized, resulting in high concentrations iron in acid water (Equation 1). This poses serious pollution problems.

$$FeS_2 + 3.5O_2 + H_2O \longrightarrow Fe^{2+} + 2SO_4^{2-} + 2H^+ \qquad (1)$$

(a) Comparing the HDS process with the conventional liming process

The conventional and High Density Sludge (HDS) processes are to date the most suitable technologies for the treatment of acid water. The flow diagram of the conventional process (Figure 7.1) explains this neutralization process. The main disadvantage of this process is that sludge with a low density is produced, resulting in large volumes of sludge that have to be disposed of.

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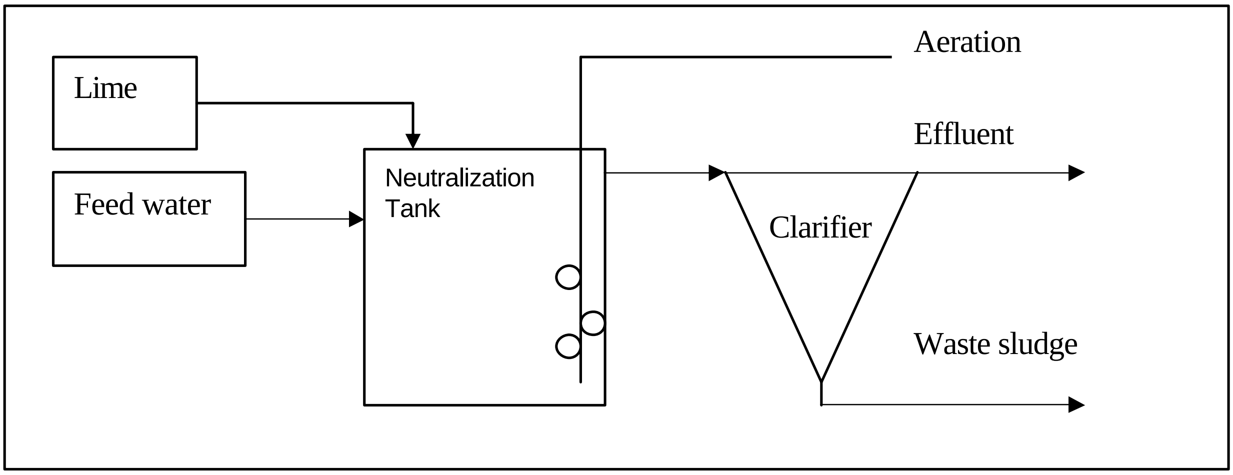


Figure 7.1 : The conventional treatment of acid mine water

The main advantage of the HDS process (Figure 7.2) over the conventional lime treatment process is (Osuchowski, 1992):

- high density sludge produced – up to 10 times higher than the conventional process.
- less sludge drying facilities and disposal volume requirements, and
- the sludge settles faster, requiring smaller clarifiers
- cost saving implications

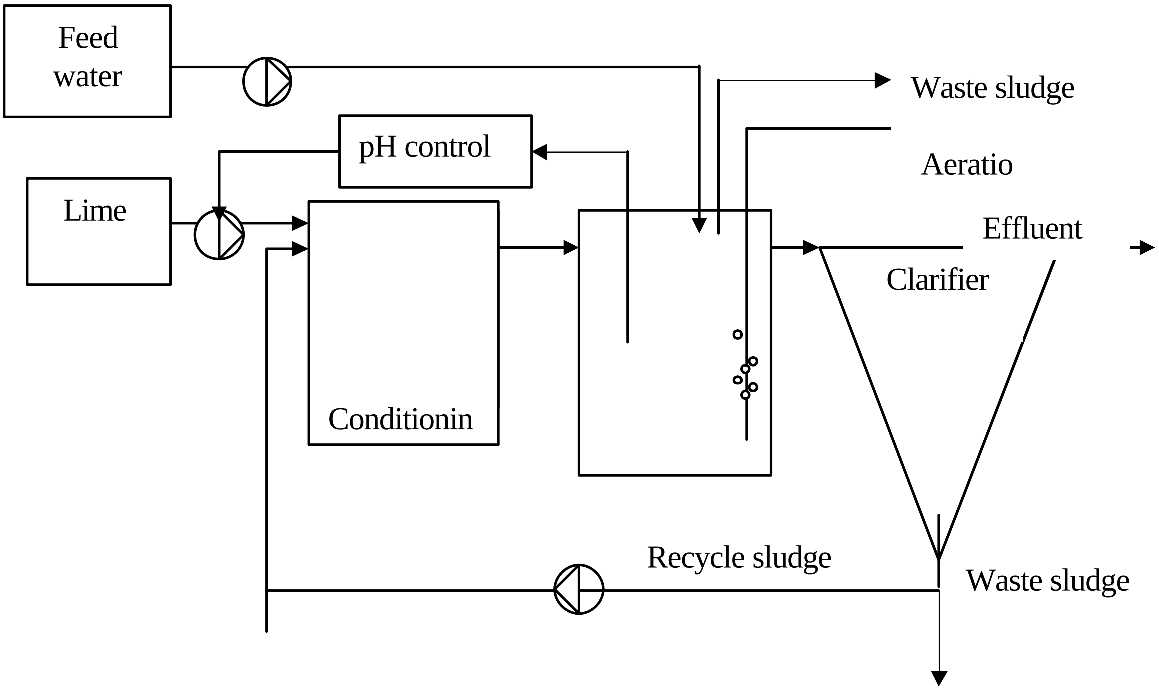


Figure 7.2 : The HDS process for treatment of acid mine water.

(b) The HDS process

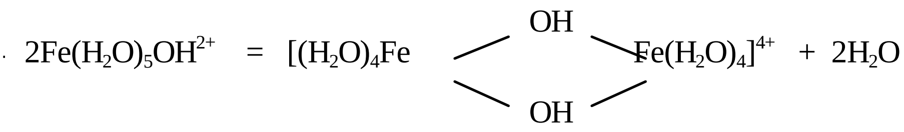
The HDS process is still the preferred method for neutralization of AMD due to the wide application of the process and extensive process knowledge available. Where the HDS process has been installed, industry is reluctant to consider alternatives, due to the capital already employed. One of the disadvantages of the HDS process is the difficulty to control the process, especially where there is fluctuations in flow rates and acid concentrations. The clarifier is the most costly item of a water neutralization plant. It is therefore important to use a process that produces sludge with high solids contents and high settling rates resulting in a smaller clarifier and lower disposal volume requirements.

It became thus priority to improve the existing HDS process in order to obtain sludge with higher densities, better lime utilization, faster settling rates as well as easier operation.

(c) *Ferric hydroxide precipitation and polymerization*

When acid mine drainage is neutralized, iron hydroxide sludge precipitates. When iron precipitates rapidly, very small particles are formed which separates slowly from water. The produced ferric hydroxide thus remains high in water content, does not separate easily and makes handling and disposal costly (Diz *et al.*, 1999).

The High Density Sludge (HDS) process results in the formation of polymeric hydrolysis species. The hydrolyzed species of iron (monomers) can be considered to form a dimer by a condensation process (Stumm and Morgan, 1970) as follows:



$$2Fe(H_2O)_5OH^{2+} = [(H_2O)_4Fe \begin{matrix} OH \\ \\ OH \end{matrix} Fe(H_2O)_4]^{4+} + 2H_2O$$

The dimer may undergo additional hydrolytic reactions. This would provide additional additional hydroxo groups that could form more bridges. Under conditions of oversaturation of the ferric hydroxide, this olation (formation of Fe-OH-Fe bonds) and oxolation (formation of Fe-O-Fe bonds) reactions forms colloidal hydroxo polymers. These polymeric complexes precipitates and result in high-density sludges.

Knight and Silva (1974) observed colour changes from the characteristic yellow of the low molecular weight species $FeOH^{2+}$ and $Fe_2(OH)_2^{4+}$, through orange to the deep red-brown of high molecular weight iron hydroxide polymers.

(d) *Sludge recycle to precipitation ratios*

According to Kostenbader (1970) the ratio of solids recirculated within the system to the solids precipitated from AMD by the neutralization reaction had an effect on the solids concentrations of settled sludges. The optimum range was 25:1 to 30:1 with the production of near-maximum sludge densities, minimum area requirements for sludge settling and thickening. They found that the optimum ratio was the same for both ferrous (Fe(II)) and ferric (Fe(III)) waters.

(e) Settling rates

Experiments, conducted by Diz *et al*. on AMD to investigate the behaviour of ferric iron solutions after bicarbonate addition, concluded that the time needed for iron precipitation is a function of pH and iron and sulphate concentrations. Increasing sulphate concentrations increased the time from neutralization to the detection of iron precipitation. The time decreased with increasing iron concentrations. The rate of iron precipitation in AMD is a function of the particle size. The faster the iron precipitation, the smaller the particles that forms and the larger the clarifiers needed to effectively separate the solids from the water. Precipitation times depend on the Fe(III) concentration; higher Fe(III) concentrations decrease precipitation time.

7.1.2 Purpose of Investigation

The aim of this investigation was to compare the HDS and the Modified HDS neutralization processes and identify the neutralization process that meets the following criteria for water with a specific chemical composition:

- treated water that is neutral and stable with respect to gypsum crystallisation.
- sludge with a high solids content.
- minimum alkali cost.
- minimum capital cost of plant and
- confidence in the selected process.

The HDS and modified HDS processes were studied in order to meet the following criteria for different water qualities:

- produce sludge with high suspended solids contents (greater than 25%)
- produce sludge with fast settling rates (>1 m/h)
- achieve maximum lime utilization (better than 95%)
- simple, easy to operate process

The influence of the oxidation state of iron, limestone addition, contact time as well as a high sulphate concentration on the performance of the processes was investigated.

SECTION 1 : LIME NEUTRALIZATION WITH HDS, MODIFIED HDS AND NEUTRAL PROCESSES DURING LABORATORY BEAKER STUDIES

7.2 INTRODUCTION

The purpose of this study was to determine the difference between the HDS, modified HDS and neutral processes as far as lime utilization, sludge solids content, settling rates and simplicity of operation are concerned. The influence of the oxidation state of iron, limestone addition, contact time and high sulphate concentration on the performance of the processes were investigated.

7.3 MATERIALS AND METHODS

7.3.1 Experimental

(a) Beaker Studies

Synthetic iron-rich acid mine water, simulating various acid mine drainage (AMD) compositions was neutralized with lime to pH 7 on a batch basis during the beaker studies. A total of 33 beaker studies, 16 repetitions each, were done.

The chemical compositions of the different waters that were prepared for this investigation were as follows:

- Ferrous sulphate 1000 mg/l (as Fe)
- Ferric sulphate 1000 mg/l (as Fe)
- $FeSO_4$ 500 mg/l (as Fe) + $Fe_2(SO_4)_3$ 500 mg/l (as Fe)
- $FeSO_4$ 500 mg/l (as Fe) + $Fe_2(SO_4)_3$ 500 mg/l (as Fe) + H_2SO_4 10 000 mg/l Acidity (as $CaCO_3$) (over-saturated with respect to gypsum after neutralization).

Throughout this section Ferrous sulphate will be referred to as Fe(II), Ferric sulphate as Fe(III), the Ferric- and Ferro sulphate mix as Fe(II)(III) and the Ferric- and Ferro sulphate mix with added acidity as Fe(II)(III)Ac.

- **Table 7.1 : Summary of variables investigated during beaker studies**

Beaker study number	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31	32	33
Process configuration:																																	
HDS	✓	✓	✓							✓	✓	✓				✓	✓	✓	✓	✓	✓							✓	✓	✓			
Mod HDS				✓	✓	✓							✓	✓	✓							✓	✓	✓	✓	✓	✓				✓	✓	✓
Neutral							✓	✓	✓																								
Water Type:																																	
Fe(II)										✓	✓	✓	✓	✓	✓																		
Fe(III)	✓	✓	✓	✓	✓	✓																											
Fe(II)(III)							✓	✓	✓							✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓						
Fe(II)(III)Ac																												✓	✓	✓	✓	✓	✓
$CaCO_3$ added																			✓	✓	✓				✓	✓	✓						
Contact Time:																																	
5 minutes	✓			✓			✓			✓			✓			✓						✓						✓			✓		
10 minutes		✓			✓			✓			✓			✓			✓		✓	✓	✓		✓		✓	✓	✓		✓			✓	
20 minutes			✓			✓			✓			✓			✓			✓						✓						✓			✓

The other process conditions varied as follows (summarised in Table 7.1):

- neutralizing processes:
  - HDS process
  - Mod HDS process
  - Neutral HDS process
- conditioning pH value (acid, neutral and alkali)
- conditioning residence time (5, 10, and 30 min)
- $CaCO_3$ addition (0.2, 0.5 and 2 g/l)

Limestone of different concentrations namely 0.2 g/l, 0.5 g/l and 2 g/l were added to 6 of the beakers. In the Modified HDS process the limestone was added together with the acid water to the sludge from the previous repetition. In the HDS process the limestone was added to the acid water and mixed for 10 minutes prior to adding to the conditioned sludge. This was done to allow sufficient dissolution of the $CaCO_3$ in the acid water.

The following parameters were monitored to evaluate the effect of the various conditions on the different processes:

- sludge solids content,
- sludge settling rate and
- lime utilization efficiency

(i) High Density Sludge Process

The following procedure was used during the batch tests to simulate the HDS process:

1. 1 1000 ml iron-rich acid was neutralized with lime to a level between 7.0 and 8.0.
2. The sludge was allowed to settle in a measuring cylinder for 60 minutes.
3. The top 650 ml water (or water with sludge, if the sludge volume was more than 350 ml) was discarded.
4. 50 ml of the remaining sludge/slurry was used for determination of suspended solids.
5. The remaining 300 ml sludge was transferred into a 1000 ml beaker and lime (the equivalent of 700 ml neutralized acid water) was added.
6. The sludge was conditioned for either 5, 10 or 20 minutes while being stirred.
7. The pH was measured in each beaker and 700 ml of an iron-rich acid water added.
8. After allowing for aeration time, which in each case would be the same as the conditioning time, the pH was determined.
9. The contents of each beaker were emptied into a measuring cylinder and the sludge settled for 60 minutes, while the settling rates were monitored.
10. Steps 3 to 9 were repeated 16 times for each beaker.

(ii) Modified High Density Sludge Process

The following procedure was used during the batch tests to simulate the Modified HDS process:

1. 1 000 ml iron-rich acid was neutralized with lime to a level between 7.0 and 8.0.
2. The sludge was allowed to settle in a measuring cylinder for 60 minutes.
3. The top 650 ml water (or water with sludge, if the sludge volume was more than 350 ml) was discarded.
4. 50 ml of the remaining sludge/slurry was used for determination of suspended solids.
5. The remaining 300 ml sludge was transferred into a 1000 ml beaker and 700 ml iron-rich acid water added
6. This slurry was aerated for either 5, 10 or 20 minutes while being stirred.
7. The pH was measured in each beaker and lime added to neutralized the acid.
8. After additional stirring, which in each case would be the same as the aeration time, the pH was determined.
9. The contents of each beaker were emptied into a measuring cylinder and the sludge settled for 60 minutes, while the settling rates were monitored.

10. Steps 3 to 9 were repeated 16 times for each beaker.

(iii) Neutral HDS Process

The following procedure was used during the batch tests to simulate the Neutral “HDS” process:

1. 1 000 ml iron-rich acid was neutralized with lime to a level between 7.0 and 8.0.
2. The sludge was allowed to settle in a measuring cylinder for 60 minutes.
3. The top 650 ml water (or water with sludge, if the sludge volume was more than 350 ml) was discarded.
4. 50 ml were used for determination of suspended solids.
5. The remaining 300 ml sludge was transferred into a 1 000 ml beaker and 700 ml iron rich acid water together with lime (the equivalent of 700 ml neutralized acid water), was added.
6. This slurry was aerated for either 5, 10 or 20 minutes while being stirred.
7. The pH was measured in each beaker.
8. The contents of each beaker were emptied into a measuring cylinder and the sludge settled for 60 minutes, while the settling rates were monitored.
9. Steps 3 to 8 were repeated 16 times for each beaker.

7.3.2 Analytical

pH were measured with either a Mettler Toledo 320 or an Orion 710A pH-meter. Settling rates were manually observed and suspended solids determined according to Standard Methods on every third sample.

7.4 RESULTS AND DISCUSSION

The average of the results for repetitions 7 – 16, and in some cases repetitions 10 – 16, of each experiment are presented below.

7.4.1 Contact Time

(a) Lime utilization

Shorter conditioning times appeared to result in better lime utilization (lower lime (as $CaCO_3$)/Ac ratio (as $CaCO_3$)) when Fe(III), Fe(II) and Fe(II)(III) waters were neutralized using the HDS, Modified HDS or Neutral HDS processes (Table7.2). When acid was added to the Fe(II)(III) mix prior to neutralization, the results were indecisive. Ratios below 1.0 (above 100%) can be ascribed to either incomplete oxidation, average pH values being low (<7.0) or CaO impurities in the $Ca(OH)_2$ chemical.

The lime utilization efficiency, indicated by lime dosage/acidity removed ratio, (expressed as % between brackets), as a function of contact time for various processes (and feed water compositions) is as follows:

HDS process (Table 7.2)

· Fe(III)	Lime/Ac ratio increased from 1.01 (99%) for 5 min to 1.04 (96%) for 20 min conditioning time (Exp.1-3)
· Fe(II)	Lime/Ac ratio increased from 0.80 for 5 min to 1.04 (96%) for 20 min (Exp. 10-12)
· Fe(II)(III)	Lime/Ac ratio increased from 0.89 for 5 min to 1.05 (95%) for 20 min (Exp. 16-18)
· Fe(II)(III)Ac	There was no significant change with ratios of 1.0 (100%) for 5min and 0.97 for both 10 and 20 minutes conditioning time (Exp. 28-30)

Modified HDS process (Table 7.3)

· Fe(III)	increased from 0.93 for 5 min to 1.02 (98%) for 20 min conditioning time (Exp. 4-6)
· Fe(II)	increased from 0.89 for 5 min to 1.04 (96%) for 20 min (Exp. 13-15)
· Fe(II)(III)	increased from 0.89 for 5 min to 1.01 (99%) for 20 min (Exp. 22-24)
· Fe(II)(III)Ac	There was no significant change in the Lime/Ac ratio: 1.0 for 5 min, 0.98 for 10 min and 1.0 (100%) for 20 minutes conditioning time (Exp. 31-33).

Neutral HDS process (Table 7.3):

There was no significant difference in the Lime/Ac ratio where the Neutral process was used.

- Fe(II)(III) 1.03 (97%) for 5 minutes contact time and 1.04 (96%) for both 10 and 20 minutes (Exp. 7-9)

(b) Settling rates

HDS process:

Best settling rates were achieved with shortest conditioning times, but little difference with the Fe(III) and Fe(II)(III) water (Table 7.2).

- Fe(III) Settling Rate of 0.32 m/h for 5 minutes compared to 0.30 m/h for 20 minutes (Exp. 1-3)
- Fe(II) 1.15 m/h for 5 minutes and 0.90 m/h for 20 minutes (Exp. 10-12)
- Fe(II)(III) 0.30 m/h for 5 minutes and 0.27 m/h for 20 minutes (Exp. 16-18)
- Fe(II)(III)Ac 0.74 m/h for 5 minutes and 0.57 m/h for 20 minutes (Exp. 28-30)

Mod HDS process:

In all experiments done the Modified HDS process gave the best settling rates when the shortest conditioning or contact time was applied (Table 7.3) i.e.

- Fe(III) Settling Rate of 0.69 m/h for 5 minutes compared to 0.4 m/h for 20 minutes (Exp. 4-6)
- Fe(II) 0.83 m/h for 5 minutes and 0.58 m/h for 20 minutes (Exp. 13-15)
- Fe(II)(III) 0.51 m/h for 5 minutes and 0.38 m/h for 20 minutes (Exp. 22-24)
- Fe(II)(III)Ac 0.53 m/h for 5 minutes and 0.45 m/h for 20 minutes (Exp. 31-33)

Neutral HDS process:

Contact time had no effect on the settling rates of Fe(II)(III) water when it was neutralized with the neutral process (0.24 m/h) (Exp. 7-9, Table3).

7.4.2 Process Configuration

(a) Lime utilization

The Modified HDS process (results in bold), when compared to the HDS process and Neutral process (Fe(II(III) water), gave better lime utilization when Fe(III), Fe(II) and Fe(II)(III) waters were neutralized. The largest difference between the Mod HDS and HDS processes occur mainly at 5 minutes conditioning times. The lime utilization is expressed as a ratio with percentage between brackets.

- Fe(III) The Lime/Ac ratio were **0.93** (**107%**); 1.01 (99%) (Exp 4 and 1, Table 7.4) for 5 minutes conditioning times. Both values are lower than expected due to average pH below 7. The ratios for 10 minutes conditioning times (Exp. 5 and 2) where the average pH values were 7.17 and 7.19 respectively were **1.0** (**100%**); 1.03 (97%).
- Fe(II) The Lime/Ac ratio is **0.89**; 0.80 for 5 min conditioning time (Exp 13 and 10, Table 7.4) and **1.04** (**96%**);1.04 (96%) for 20 minutes conditioning time (Exp. 15 and 12).
- Fe(II)(III) The Lime/Ac ratio is **1.01** (**99%**); 1.05 (95%) with 1.04 (96%) for the Neutral process (Exp.24, 18 and 9, Table 7.5).
- Fe(II)(III)Ac The lime utilization is very much the same (Table 7.6):
- **1.0** (**100%**); 1.0 (100%) for 5 minutes (Exp. 31 and 28)
- **0.98** (**102%**); 0.97 (103%) for 10 minutes (Exp. 32 and 29) and slightly in favour of the HDS process **1.0** (**100%**); 0.97 (103%) for 20 minute conditioning times (Exp. 33 and 30).

(b) Sludge solids contents

The only instance where the HDS process yielded better sludge solids contents than the Mod HDS process is where Fe(II) water was neutralized.

- Fe(III) Mod HDS process yields best sludge solids content irrespective of conditioning times (Exp. 1-6, Table 7.4) i.e.
  - 5 min 1.79% for Mod HDS process compared to 0.99% for HDS process
  - 20 min 1.49% for mod HDS process compared to 1.04% for HDS process
- Fe(II) HDS process yields best sludge solids content irrespective of conditioning times (Exp. 10-15, Table 4) i.e.
  - 5 min 3.34% for HDS process compared to 3.08% for Mod HDS process
  - 20 min 2.89% for HDS process compared to 1.60% for Mod HDS process
- Fe(II)(III) Mod HDS process yields best sludge solids content irrespective of conditioning times (Table 7.5) i.e.
  - 5 min 1.44% (Mod HDS), 1.08% (Neutral) and 0.95% (HDS process)
  - 20 min 1.57% for Mod HDS process compared to 0.99% for the Neutral and 1.1% for the HDS process

- Fe(II)(III)Ac Mod HDS process yields best sludge solids contents for 5 and 10 minute conditioning times (Table 7.6) i.e.
  - 5 min 14.66% (Mod HDS process) compared to 14.32% (HDS process)
  - 10 min 13.64% (Mod HDS) compared to 13.35% for the HDS process

(c) Settling rates

The best settling rates were obtained with the Mod HDS process when Fe(III) and Fe(II)(III) water were used (Tables 7.4, 7.5 and 7.6). The HDS process had slightly better settling rates than the Neutral process when Fe(II)(III) water was neutralized. The differences between the settling rates of the Mod HDS and HDS processes where 5 minutes contact time was allowed were up to twice that of the 20 minute contact times and very much the same for the 10 minute contact time. When Fe(II) water was neutralized the difference between the HDS and Mod HDS process settling rates was the same. The settling rates (**Mod HDS** process in bold, and the Neutral process between brackets) for the different waters are given as:

- Fe(III) 5 minutes contact time **0.69 m/h**; 0.32m/h and 20 minutes **0.40 m/h**; 0.30 m/h (Exp. 1-6, Table 7.4)
- Fe(II) **0.83 m/h**; 1.15 m/h and **0.58 m/h**; 0.90m/h (Exp. 10-15, Table 7.4)
- Fe(II)(III) **0.51 m/h**; 0.30 m/h; (0.23 m/h) and **0.38 m/h**; 0.27m/h; (0.24m/h) (Table 7.5)
- Fe(II)(III)Ac **0.53 m/h**; 0.74 m/h and **0.45 m/h**; 0.57 m/h for 20 minutes contact time (Table 7.6)

7.4.3 Iron Content

(a) Lime utilization

The lime utilization, irrespective of the neutralization process followed, was always the best with the Fe(II) water and the worst with the Fe(III) water. The Fe(II)(III) water's lime utilization was in-between. The Lime/Ac ratios for the Mod HDS (values in bold) and HDS process were as follows (Tables 7.7 and 7.8):

5 minutes contact time

- Fe(II) **0.89**; 0.80 (Exp. 13, Table 7.8 and Exp. 10, Table 7.7)
- Fe(III) **0.93**; 1.01 (Exp. 4, Table 7.8 and Exp. 1, Table 7.7)
- Fe(II)(III) **0.89**; 0.89 (Exp. 22, Table 7.8 and Exp. 16, Table 7.7)

10 minutes contact time

- Fe(II) **0.95**; 0.98 (Exp. 14, Table 7.8 and Exp. 11, Table 7.7)
- Fe(III) **1.00**; 1.03 (Exp. 5, Table 7.8 and Exp. 2, Table 7.7)
- Fe(II)(III) **0.89**; 0.95 (Exp. 23, Table 7.8 and Exp. 17, Table 7.7)

20 minutes contact time

- Fe(II) **1.04**; 1.04 (Exp. 15, Table 7.8 and Exp. 12, Table 7.7)
- Fe(III) **1.02**; 1.04 (Exp. 6, Table 7.8 and Exp. 3, Table 7.7)
- Fe(II)(III) **1.01**; 1.05 (Exp. 24, Table 7.8 and Exp. 18, Table 7.7)

The values below 1 can be ascribed to the iron oxidation not being completed in the 5-minute period. A contact time of more than 10 minutes is recommended where Fe(II) water needs to be neutralized.

(b) Sludge solids contents

The highest average (repetition 7 to 16) sludge solids content (3.34%) was obtained with Fe(II) water during neutralization with the HDS process and 5 minutes conditioning time (Exp 10, Table 7.7). The highest sludge solids content (5.56%) during neutralization with the HDS process was obtained during repetition 13 with 5 minutes conditioning time (Exp 10). The highest sludge solids content (5.67%) during neutralization with the Mod HDS process was obtained during repetition 16 with 5 minutes conditioning time (Exp 13). The sludge solids content for both processes had an increasing trend as repetition proceeded (Figure 7.4).

(c) Settling rates

Fe(II) water combined with the HDS process gave fastest settling rates (1.15 m/h), with the Fe(III) and Fe(II)(III) water nearly the same (0.32 m/h and 0.30m/h respectively). When Fe(II) water was neutralized with the Mod HDS process, higher settling rates (0.83 m/h) were achieved than with Fe(II)(III) (0.51 m/h) or Fe(III) (0.69 m/h) water. Values given are for 5-minute contact times.

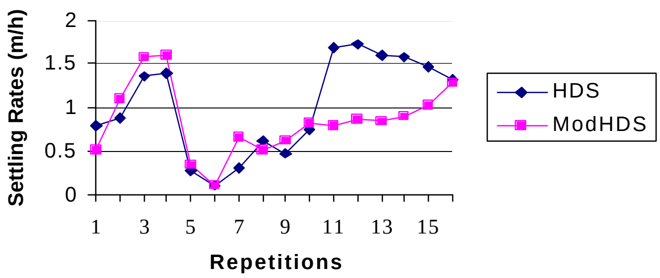


Figure 7.3 : HD er of repetitions.

Settling rates for experiments 10 and 13, expressed as a function of the number of repetitions, are given in Figure 7.3.

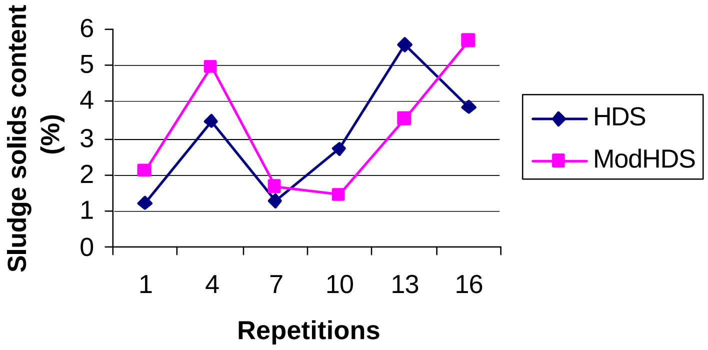


Figure 7.4 : HDS vs Mod HDS treatment of AMD: Sludge solids concentration as a function of number of repetitions

The sludge solids content expressed as a function of the number of repetitions are shown in Figure 7.4.

7.4.4 Calcium Carbonate Addition

Increasing amounts of $CaCO_3$ were added to Fe(II)(III) water prior to being neutralized with the HDS or Mod HDS processes. The Mod HDS process yielded better lime utilization, higher sludge solids content as well as faster settling rates. Both neutralization processes used less lime, had higher sludge solids contents and faster settling rates with increasing limestone concentrations. The results are summarized in Table 7.9.

The limestone decreased the amount of lime needed to neutralized the acid water.

7.4.5 Acidity

Acid mine water consists seldom of stoichiometric quantities of iron and acidity. Iron precipitates with carbonate with resulting formation of free acid. The addition of sulphuric acid to the iron water was to simulate acid mine waters.

High sludge solids contents of nearly 15 % were measured when sulphuric acid was added to the iron water prior to neutralization. Where the acidity was the stoichiometric quantity of the iron, it is assumed that the sludge consisted of $Fe(OH)_3$. The resulting higher sludge concentrations can be ascribed to the formation of gypsum together with iron hydroxide.

7.4.6 pH

The pH of the conditioning stage during the HDS process was between 11.5 and 12.0 for contact times of 10 and 20 minutes. The pH of the slurry, after acid water was added to the sludge, during the modified HDS process was between 2.4 and 2.5 for Fe(III) and Fe(II)(III) water, 4.3 for Fe(II) water and between 1.5 and 1.7 for Fe(II)(III)Ac water. The electrode response time made it impossible to obtain reliable readings for the experiments where the contact times were 5 minutes.

7.5 CONCLUSIONS

Shorter conditioning times resulted in

- better lime utilization irrespective of water type
- faster settling rates with Fe(II) water for both HDS and Mod HDS treatments

The Modified HDS process, compared to the HDS process, gave for all waters except Fe(II)

- better lime utilization
- higher sludge solids concentrations
- faster settling rates

Fe(II) water showed

- better lime utilization irrespective of neutralization process
- fastest settling rates with HDS process

The more $CaCO_3$ added the

- Less lime was used
- Higher the sludge solids content
- Faster the settling rates
- Free acid in water caused higher sludge solids content due to gypsum in sludge.

Table 7.2 : Results of beaker studies where the influence of contact times were compared. Different oxidation stages of iron water were neutralized with the HDS process

Exp no.	1	2	3	10	11	12	16	17	18	28	29	30
Process	HDS			HDS			HDS			HDS		
Water type: Fe(III)	Fe(III)	Fe(III)	Fe(III)				Fe(III)	Fe(III)	Fe(III)	Fe(III)	Fe(III)	Fe(III)
Fe (II)				Fe(II)	Fe(II)	Fe(II)	Fe(II)	Fe(II)	Fe(II)	Fe(II)	Fe(II)	Fe(II)
Ac (H_2SO_4 10g/l as $CaCO_3$										Ac	Ac	Ac
$CaCO_3$ added)												
Volume recycled sludge (ml/l)	300	300	300	300	300	300	300	300	300	300	300	300
Sludge conditioning time	5	10	20	5	10	20	5	10	20	5	10	20
Results (average repetitions 7-16):												
Lime dosage (g/l $Ca(OH)_2$)	1.57	1.6	1.61	1.06	1.31	1.38	1.33	1.42	1.58	8.67	8.71	8.76
Lime ratio: Lime/Ac (mol/mol)	1.01	1.03	1.04	0.80	0.98	1.04	0.89	0.95	1.05	1.0	0.97	0.97
Solids content (%)	0.99	0.84	1.04	3.34	3.27	2.89	0.95	1.04	1.31	14.32	13.35	14.97
Settling rate (m/h)	0.32	0.24	0.30	1.15	1.21	0.90	0.30	0.30	0.27	0.74	0.71	0.57
pH of conditioned sludge	-	11.55	11.96	-	11.55	11.88	-	11.52	11.83	-	11.64	12.01
pH of treated water	6.98	7.19	7.05	7.22	6.85	7.46	7.39	7.19	7.51	8.02	7.03	7.65

Table 7.3 : Results of beaker studies where the influence of contact times were compared. Different oxidation stages of iron water were neutralized with the Modified HDS or Neutral processes

Exp no.	4	5	6	13	14	15	22	23	24	31	32	33	7	8	9
Process	Modified HDS			Modified HDS			Modified HDS			Modified HDS			Neutral		
Water type: Fe(III)	Fe(III)	Fe(III)	Fe(III)				Fe(III)	Fe(III)	Fe(III)	Fe(III)	Fe(III)	Fe(III)	Fe(III)	Fe(III)	Fe(III)
Fe(II)				Fe(II)	Fe(II)	Fe(II)	Fe(II)	Fe(II)	Fe(II)	Fe(II)	Fe(II)	Fe(II)	Fe(II)	Fe(II)	Fe(II)
Ac (H_2SO_4 10g/l as $CaCO_3$)										Ac	Ac	Ac			
$CaCO_3$ added															
Volume recycled sludge (ml/l)	300	300	300	300	300	300	300	300	300	300	300	300	300	300	300
Sludge conditioning time	5	10	20	5	10	20	5	10	20	5	10	20	5	10	20
Results (average repetitions 7-16):															
Lime dosage (g/l $Ca(OH)_2$)	1.44	1.55	1.59	1.16	1.17	1.38	1.34	1.34	1.52	8.79	8.89	9.05	1.54	1.56	1.56
Lime ratio: Lime/Ac (mol/mol)	0.93	1.00	1.02	0.89	0.95	1.04	0.89	0.89	1.01	1.00	0.98	1.00	1.03	1.04	1.04
Solids content (%)	1.79	1.27	1.49	3.08	2.42	1.60	1.44	2.21	1.57	14.6	13.6	14.3	1.08	1.21	0.99
Settling rate (m/h)	0.69	0.43	0.40	0.83	0.65	0.58	0.51	0.48	0.38	0.53	0.51	0.45	0.23	0.24	0.24
pH of conditioned sludge	-	2.5	2.42	-	4.32	4.31	-	2.51	2.45	-	1.56	1.71	-	-	-
pH of treated water	6.74	7.17	6.94	6.87	7.44	7.43	7.06	7.1	7.31	7.89	7.19	7.35	7.32	7.21	7.18

Table 7.4 : Results of beaker studies where the influence of the HDS and Modified HDS neutralization processes on Fe(II) and Fe(III) water were compared

Exp no.	**1**	**4**	**2**	**5**	**3**	**6**	**10**	**13**	**11**	**14**	**12**	**15**
Process	HDS	ModHDS	HDS	ModHDS	HDS	ModHDS	HDS	ModHDS	HDS	ModHDS	HDS	ModHDS
Water type:	Fe(III)	Fe(III)	Fe(III)	Fe(III)	Fe(III)	Fe(III)	Fe(II)	Fe(II)	Fe(II)	Fe(II)	Fe(II)	Fe(II)
Volume recycled	300	300	300	300	300	300	300	300	300	300	300	300
Sludge	5	5	10	10	20	20	5	5	10	10	20	20
Results (average)												
Lime dosage (g/l)	1.57	1.44	1.6	1.55	1.61	1.59	1.06	1.16	1.31	1.17	1.38	1.38
Lime ratio:	1.01	0.93	1.03	1.00	1.04	1.02	0.80	0.89	0.98	0.95	1.04	1.04
Solids content	0.99	1.79	0.84	1.27	1.04	1.49	3.34	3.08	3.27	2.42	2.89	1.60
Settling rate	0.32	0.69	0.24	0.43	0.30	0.40	1.15	0.83	1.21	0.65	0.90	0.58
pH of conditioned	-	-	11.55	2.5	11.96	2.42	-	-	11.55	4.32	11.88	4.31
pH of treated water	6.98	6.74	7.19	7.17	7.05	6.94	7.22	6.87	6.85	7.44	7.46	7.43

Table 7.5 : Results of beaker studies where the influence of the HDS and Modified HDS neutral neutralization processes on Fe(II) and (III) water were compared

Exp no.	7	16	22	8	17	23	9	18	24
Process	N	HDS	ModHDS	N	HDS	ModHDS	N	HDS	ModHDS
Water type: Fe(III)	Fe(III)	Fe(III)	Fe(III)	Fe(III)	Fe(III)	Fe(III)	Fe(III)	Fe(III)	Fe(III)
Fe(II)	Fe(II)	Fe(II)	Fe(II)	Fe(II)	Fe(II)	Fe(II)	Fe(II)	Fe(II)	Fe(II)
Ac (H_2SO_4 10g/l as $CaCO_3$)									
$CaCO_3$ added)									
Volume recycled sludge (ml/l)	300	300	300	300	300	300	300	300	300
Sludge conditioning time	5	5	5	10	10	10	20	20	20
Results (average repetitions 7-									
Lime dosage (g/l $Ca(OH)_2$)	1.54	1.33	1.34	1.56	1.42	1.34	1.56	1.58	1.52
Lime ratio: Lime/Ac (mol/mol)	1.03	0.89	0.89	1.04	0.95	0.89	1.04	1.05	1.01
Solids content (%)	1.08	0.95	1.44	1.21	1.04	2.21	0.99	1.31	1.57
Settling rate (m/h)	0.23	0.30	0.51	0.24	0.30	0.48	0.24	0.27	0.38
pH of conditioned sludge	-	-	-	-	11.52	2.51	-	11.83	2.45
pH of treated water	7.32	7.39	7.06	7.21	7.19	7.1	7.18	7.51	7.31

Table 7.6 : Results of beaker studies where the influence of the HDS and Modified HDS neutralization processes on Fe(II)(III)Ac water were compared

Exp no.	28	31	29	32	30	33
Process	HDS	ModHDS	HDS	ModHDS	HDS	ModHDS
Water type: Fe(III)	Fe(III)	Fe(III)	Fe(III)	Fe(III)	Fe(III)	Fe(III)
Fe(II)	Fe(II)	Fe(II)	Fe(II)	Fe(II)	Fe(II)	Fe(II)
Ac(H_2SO_4 10g/l as $CaCO_3$)	Ac	Ac	Ac	Ac	Ac	Ac
$CaCO_3$ added	-	-	-	-	-	-
Volume recycled sludge (ml/l)	300	300	300	300	300	300
Sludge conditioning time	5	5	10	10	20	20
Results (average repetitions 7-16):						
Lime dosage (g/l $Ca(OH)_2$)	8.67	8.79	8.71	8.89	8.76	9.05
Lime ratio: Lime/Ac (mol/mol)	1.00	1.00	1.00	0.98	0.97	1.00
Solids content (%)	14.32	14.66	13.35	13.64	14.97	14.36
Settling rate (m/h)	0.74	0.53	0.71	0.51	0.57	0.45
pH of conditioned sludge	-	-	11.64	1.56	12.01	1.71
pH of treated water	8.02	7.89	7.03	7.19	7.65	7.35

Table 7.7 : Results of beaker studies where the influence of the iron oxidation stages of the feed waters were compared when neutralized with the HDS process

Exp no.	**1**	**10**	**16**	**2**	**11**	**17**	**3**	**12**	**18**
Process	HDS	HDS	HDS	HDS	HDS	HDS	HDS	HDS	HDS
Water type: Fe(III)	Fe(III)		Fe(III)	Fe(III)		Fe(III)	Fe(III)		Fe(III)
Fe(II)		Fe(II)	Fe(II)		Fe(II)	Fe(II)		Fe(II)	Fe(II)
Ac (H_2SO_4 10g/l as $CaCO_3$)									
$CaCO_3$ added									
Volume recycled sludge (ml/l)	300	300	300	300	300	300	300	300	300
Sludge conditioning time	5	5	5	10	10	10	20	20	20
Results (average repetitions 7-16):									
Lime dosage (g/l $Ca(OH)_2$)	1.57	1.06	1.33	1.6	1.31	1.42	1.61	1.38	1.58
Lime ratio: Lime/Ac (mol/mol)	1.01	0.80	0.89	1.03	0.98	0.95	1.04	1.04	1.05
Solids content (%)	0.99	3.34	0.95	0.84	3.27	1.04	1.04	2.89	1.31
Settling rate (m/h)	0.32	1.15	0.28	0.24	1.21	0.3	0.3	0.9	0.27
pH of conditioned sludge	-	-	-	11.55	11.55	11.52	11.96	11.88	11.83
pH of treated water	6.98	7.22	7.39	7.19	6.85	7.19	7.05	7.46	7.51

Table 7.8 : Results of beaker studies where the influence of the oxidation stages of the feed waters were compared when neutralized with the Modified HDS process

Exp no.	4	13	22	5	14	23	6	15	24
Process	ModHD	ModHDS	ModHD	ModHD	ModHD	ModHD	ModHD	ModHD	ModHD
Water type: Fe(III)	Fe(III)		Fe(III)	Fe(III)		Fe(III)	Fe(III)		Fe(III)
Fe(II)		Fe(II)	Fe(II)		Fe(II)	Fe(II)		Fe(II)	Fe(II)
Ac (H_2SO_4 10g/l as $CaCO_3$)									
$CaCO_3$ added)									
Volume recycled sludge (ml/l)	300	300	300	300	300	300	300	300	300
Sludge conditioning time	5	5	5	10	10	10	20	20	20
Results (average repetitions 7-16):									
Lime dosage (g/l $Ca(OH)_2$)	1.44	1.16	1.34	1.55	1.17	1.34	1.59	1.38	1.52
Lime ratio: Lime/Ac (mol/mol)	0.93	0.87	0.89	1.00	0.95	0.89	1.02	1.04	1.01
Solids content (%)	1.79	3.08	1.44	1.27	2.42	2.21	1.49	1.60	1.57
Settling rate (m/h)	0.69	0.83	0.51	0.43	0.65	0.48	0.4	0.58	0.38
pH of conditioned sludge	-	-	-	2.5	4.32	2.51	2.42	4.31	2.45
pH of treated water	6.74	6.87	7.06	7.17	7.44	7.1	6.94	7.43	7.31

Table 7.9 : Results of beaker studies where the influence of limestone addition on the different parameters were compared when feed waters were neutralized with the HDS or Modified HDS processes

Exp no.	17	19	20	21	23	25	26	27
Process	HDS	HDS	HDS	HDS	ModHDS	ModHDS	ModHDS	ModHDS
Water type: Fe(III)	Fe(III)	Fe(III)	Fe(III)	Fe(III)	Fe(III)	Fe(III)	Fe(III)	Fe(III)
Fe(II)	Fe(II)	Fe(II)	Fe(II)	Fe(II)	Fe(II)	Fe(II)	Fe(II)	Fe(II)
Ac(H_2SO_4 10g/l as $CaCO_3$)								
$CaCO_3$ added (g/l)	0	0.2	0.5	2	0	0.2	0.5	2
$CaCO_3$ added (as $Ca(OH)_2$)	0	0.148	0.37	1.48	0	0.148	0.37	1.48
Volume recycled sludge (ml/l)	300	300	300	300	300	300	300	300
Sludge conditioning time	10	10	10	10	10	10	10	10
Results (average repetitions 7-16):								
Lime dosage (g/l $Ca(OH)_2$)	1.42	1.42	1.18	0.87	1.34	1.29	1.03	0.48
Total: lime + limestone added	1.42	1.568	1.55	2.35	1.34	1.438	1.4	1.96
Lime ratio: Lime/Ac (mol/mol)	0.95	0.94	0.79	0.58	0.88	0.86	0.69	0.32
Ratio: Lime+Limestone/Ac (mol/mol)	0.95	1.05	1.03	1.57	0.88	0.96	0.93	1.31
Solids content (%)	1.04	1.01	2.34	6.94	2.21	3.06	3.01	5.8
Settling rate (m/h)	0.3	0.22	0.46	0.77	0.48	0.71	0.8	0.82
pH of conditioned sludge	11.52	12.56	12.43	11.76	2.51	2.73	3.59	6.12
pH of treated water	7.19	7.04	7.05	7.07	7.1	7.14	7.35	7.26

SECTION II : LIME NEUTRALIZATION WITH HDS AND MODIFIED HDS PROCESSES DURING CONTINUOUS OPERATION WITH LABORATORY-SCALE PLANTS

7.6 INTRODUCTION

Two 24 l/h laboratory scale pilot plants were operated continuously at the CSIR to confirm the findings collected with the beaker studies.

The purpose of this investigation was to compare the Modified HDS process with the HDS process to determine whether there could be lime savings, and changes in sludge densities and settling rates.

The High Density Sludge (HDS) and the Modified High Density Sludge (Mod HDS) processes were compared in parallel during neutralizing experiments. The plants were run continuously to determine whether findings from the beaker studies would be confirmed.

7.7 MATERIALS AND METHODS

7.7.1 Feedstock

Iron-rich acidic waters were prepared to simulate acid mine drainage (AMD) compositions. Table 10 gives the chemical compositions of the different feed waters.

Table 7.10 : Chemical compositions of feed waters used in continuous studies.

Parameter	Water		
	A	B	C
$FeSO_4$ (mg/l as Fe)	200		200
$Fe_2(SO_4)_2$ (mg/l as Fe)		200	
H_2SO_4 (mg/l as SO_4)	1500	1500	2500
Acidity (mg/l as $CaCO_3$)	1500	1500	2500

The artificial AMD were neutralized with 10% suspension of industrial lime.

7.7.2 Equipment

Figure 7.5 shows the experimental units as captured during operation.

Figure 7.5 : HDS and Modified HDS laboratory-scale plants in operation.

The conditioning tanks, one for the HDS process and one for the Modified HDS process, had a capacity of 4 litres. The conditioning tanks overflowed into aeration tanks with volumes of 10 litres.

The conditioning tanks as well as the aeration tanks were stirred (between 180 and 220 rpm) with paddle stirrers to keep the suspended solids in solution. After a few days of operation, the stirrer in the conditioning tank of the HDS process was replaced with a bigger paddle to enable sufficient mixing.

Compressed air and two diffusers in each aeration tank were used.

The aeration tanks overflowed into clarifiers of 20-liter capacity, with sidewalls tapered at 60° and top diameter of 44 cm.

Watson-Marlow pumps with variable speed settings were used to control the feed rates.

Metrohm 691 pH meters, with automatic temperature compensation, connected to the pumps feeding the lime solution, were used to control the pH at 7.5.

A Lightnin stirrer was used in each of the lime slurry tanks, one for each process, to keep the lime in suspension.

7.7.3 Procedure

(a) Operation

Two laboratory scale pilot plants were run in parallel, one on the High Density Sludge (HDS) process and the other on the Modified HDS process. Figures 7.6 and 7.7 shows the HDS and Modified HDS process configurations. The plants were run continuously, 5 days per week, for up to 7 weeks in order to achieve steady state.

The average of the results obtained during the last 4k litres of feed water that were neutralized by the processes are discussed unless stated otherwise. In all instances, this covered more or less 2 weeks of operation time. This period was chosen because the initial sludge build-up was completed and a steady state developed. Between 4 and 5 weeks were necessary for sludge build-up. Because the HDS and modified HDS processes ran in parallel, the conditions were the same throughout the experiments and comparison between the processes can be done on an equal basis.

(b) The HDS process

The HDS process is best explained by way of a diagram (Figure 7.6).

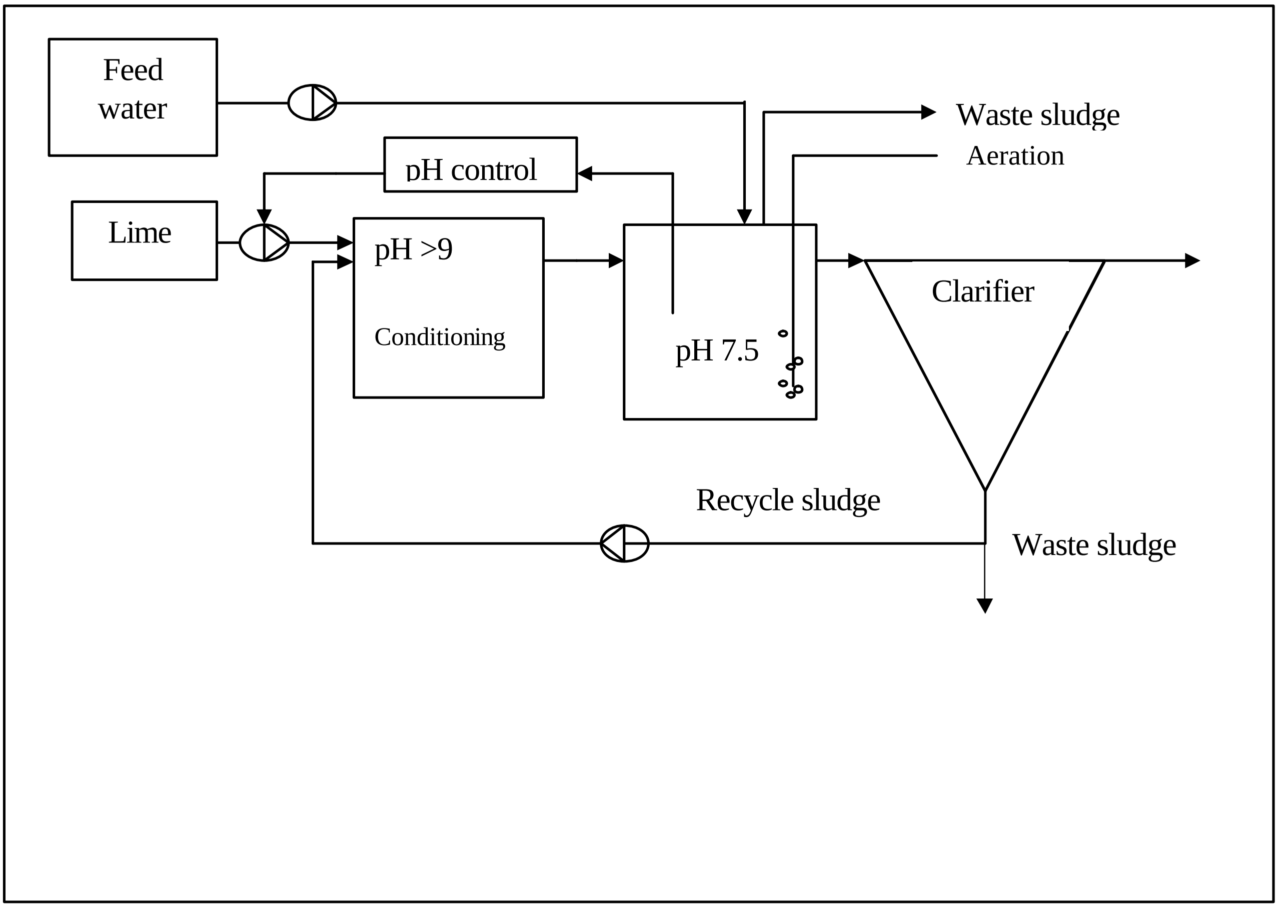


Figure 7.6 : Diagram of HDS laboratory scale plant

The HDS process consists of three stages:

- Sludge conditioning stage
- Aeration stage
- Solid/liquid separation phase

The conditioning stage consists of a tank for the preparation of a lime solution and a sludge-conditioning tank. The conditioning tank receives recycled settled sludge from the clarifier underflow and the lime solution. The lime dosage into the conditioning tank is such that a pH of 7.5 is maintained in the aeration stage.

The sludge from the conditioning tank overflows into the aeration tank. This tank serves as mixer to keep the solids in suspension, to mix the conditioned sludge with the acid mine water entering the tank and for aeration to enable ferrous iron oxidation to ferric iron.

The neutralized and oxidized slurry overflows to the clarifier where sludge is separated from the liquid. The effluent overflows and the settled sludge is recycled to the conditioning tank.

(c) The modified HDS process

The Modified HDS process (Figure 7.7) consists of three stages:

- Mixing/conditioning stage
- Aeration/neutralization stage
- Solid/liquid separation phase

The mixing or conditioning stage consists of a sludge-conditioning tank that receives recycled settled sludge from the clarifier underflow and the feed water. The sludge from the conditioning tank overflows into the aeration tank.

The aeration stage consists of an aeration tank and a tank for the preparation of a lime solution. The lime dosage into the aeration tank is controlled to maintain a pH of 7.5. The tank serves as mixer to keep the solids in suspension. Sufficient aeration oxidizes ferrous iron to ferric iron.
The neutralized and oxidized slurry overflows to the clarifier where sludge is separated from the liquid. The effluent overflows and the settled sludge is recycled to the conditioning/mixing tank.

(d) Maintenance

The following maintenance procedures were followed:
pH electrodes: The pH electrodes were thoroughly cleaned when the plants were stopped, topped up with KCL solution and rested over the weekend. This procedure ensured quality pH control during the experiments.

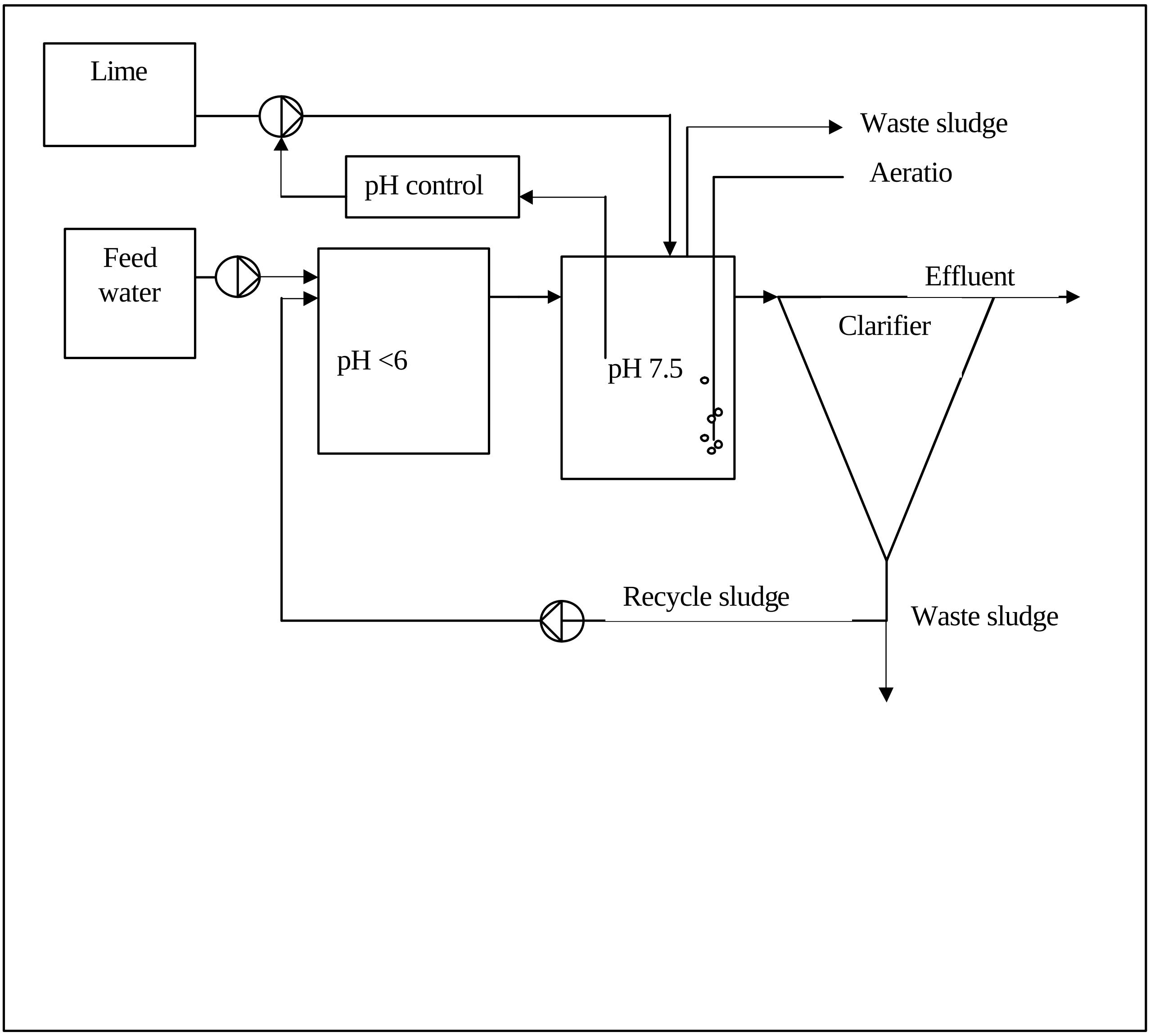


Figure 7.7 : Diagram of Modified HDS laboratory scale plant

- Pumps and stirrers: The plants were run 24 hours per day, 5 days per week. All moving parts, except the recirculation pumps, were stopped during weekends. The lack of supervision over weekends, heavy thunderstorms sometimes causing power failures, and the pH electrodes maintenance, made this the better option.
- Lime feeding: Lime feeding pipes were thoroughly backwashed once a week. Lime blockages occurred from time to time despite all known precautions taken. pH control results in the flow through the lime dosing pumps being stopped if the pH rise above 7,5. The lime suspension then settles in the tubes. Depending on the time lapse before the pH drop low enough to activate the pumps again, blockages can occur.

7.7.4 Experimental Programme

The following parameters were varied:

- Process configuration (HDS and Mod HDS)
- Water quality (Water A – Fe^{2+}, 1500mg/l Ac; Water B – Fe^{3+}, 1 500mg/l Ac; Water C – Fe^{2+}, 2 500mg/l Ac)
- Sludge age: Sludge age varied between 3,5 and 12,7 days. The sludge concentration was a function of the sludge production and sludge withdrawal. The sludge withdrawal was on purpose through regular withdrawal or through sampling.
- Feed flow rates: Feed water was pumped into the reactor at fixed rates varying between 22 and 38 l/h. Initial feed rates were in the upper range (more than 30 l/h) to aid sludge build-up and lowered to between 22 and 25 l/h during the last 2 weeks of each experiment.
- HRT (hydraulic retention times): Retention times varied between 23 and 41 minutes over the whole range of the experiments, but between 34 and 38 minutes during the last 2 weeks (steady state) of each experiment.
- Recirculation: The sludge were recycled from the bottom of the clarifiers to the conditioning tanks at an initial rate of between 24 and 33 l/h, and decreased to between 5 and 10 l/h during the last 2 weeks of each experiment.
- Sludge recycled to precipitated ratios: The ratio of the sludge solids recirculated to the sludge solids precipitated were >30:1, except for the first 3 days of operation. Ratios during the last 2 weeks of operation were above 70:1 due to the inability to decrease recirculation rates any further.

Polyelectrolite addition: No polyelectrolyte was dosed during any of the experiments. During operation at mines this is often done to enhance sludge settling during the separation phase.

7.7.5 Analytical

(a) Sampling

Samples were taken from the feed, effluents, aeration tanks and underflows and analyzed for iron content, acidity or alkalinity, sulphate, pH and suspended solids. Settling rates of samples taken from the aeration tanks were manually observed.

The settled sludge concentrations were calculated from the suspended solids in the aeration tank and the settled volume after 24 hours.

7.8 RESULTS AND DISCUSSION

7.8.1 Starting of Experiments

Figures 7.8 and 7.9 and Table 7.11 show the change in key parameters (sludge solids content and settling rates) over the start-up period until steady state conditions were achieved. Results for feed water A (200mg/l Fe(II)) while treated with the HDS configuration are represented.

Figure 7.10 shows the sludge age for the corresponding period and was calculated as follows:
Sludge age (d) =sludge in reactor (g)/sludge in feed water after neutralization (g/d).

The sludge settling rates remained constant at between 0,5 and 1.0 m/h. The settled sludge concentration increased from 1 to 15% over time. The increase in sludge solids concentration can be ascribed to the formation of polymeric iron species. The colour changes as described by Knight and Silva were observed during the experiments. The settled sludge concentration represents the sludge solids content after 24 hours settling time.

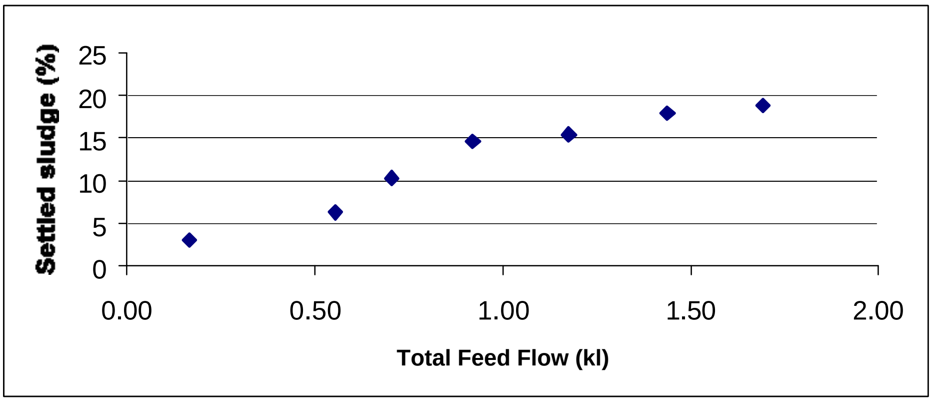


Figure 7.8 : The settled sludge concentration as a function of the total feed flow through the HDS plant (feedwater A)

Figure 7.9 shows the change in settling rates as the total flow through the system increased. The trendline indicates an initial decrease in settling rates where after the rates increased to 1 m/h. Figure 10 shows the initial increase in sludge age as the total feed flow through the HDS system increased

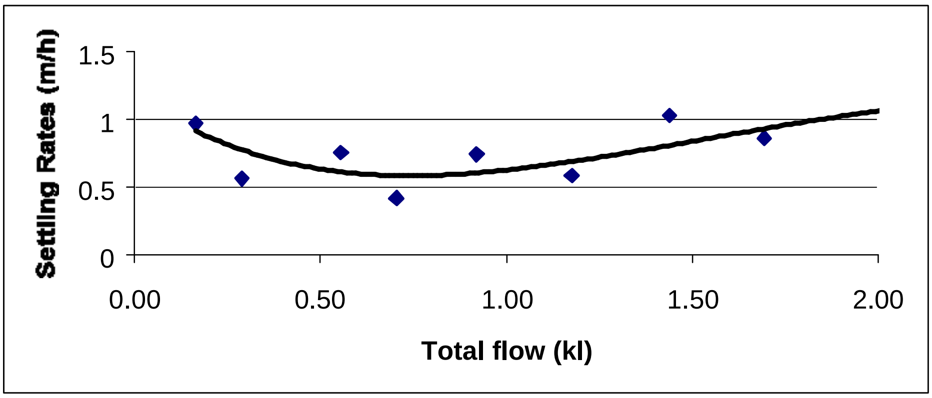


Figure 7.9 : Settling rates as a function of total feed flow through the HDS system (feed water A)

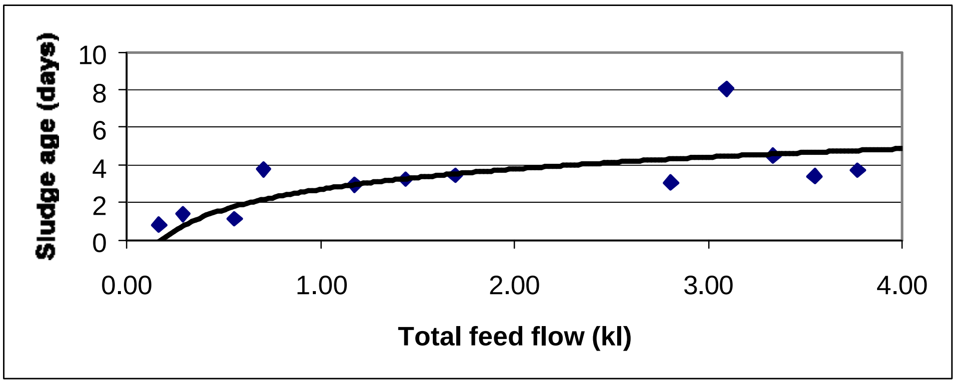


Figure 7.10 : Sludge age as a function of total feed flow through the HDS system (feed water A)

7.8.2 Sludge Age

The sludge age in the aeration tank increased as the total flow through the system increased. At steady state the same amount of sludge were wasted as the build-up for that period. Average sludge ages for the different process configurations and feed water is at steady state, were as follow:

Feed water A: HDS process 7.5 days and Mod HDS process 6 days
Feed water B: HDS process12.7 and Mod HDS process 3.5 days

7.8.3 Process Configuration

Table 11 compares the performance of the HDS and Mod HDS processes for feed water A (Fe(II)

200 mg/l) and B (Fe(III) 200 mg/l). The results are average readings of the last 4 kl of feed that was treated. This represents the steady state conditions that were achieved.

Table 7.11 : Comparative parameter values during steady state for each of the process configurations

Parameter	Feed water (Fe^{2+})		Feed water (Fe^{3+})	
	HDS	Mod HDS	HDS	Mod HDS
Settled Sludge Solids (%)	42.8	30.9	10.6	23.2
Settling Rate (m/h)	0.81	0.81	0.63	0.83
Lime Utilization (%)	76	78	87	96

(a) Lime utilization

Lime utilization is better for the Modified HDS process than for the HDS.

- Fe(II)-rich water (feed water A) 1.28 (78%) vs 1.32 (76%)
- Fe(III)-rich water (feed water B) 1.04 (96%) vs 1.15 (87%)
- Fe(II) and high SO_4 (feed water C) 1.15 (87%) vs 1.22 (82%)

(b) Settling rates

- Fe(II)- and Fe(III)-rich water (feed water A and B): Average settling rates between 0.63 and 0.83 m/h were observed for both processes (HDS and Modified HDS) and water types (Fe(II) and Fe(III)). Settling rates (up to 1.2 m/h) were, however, observed with the HDS as well as the Modified HDS processes when Fe(II) rich water were treated. When Fe(III)-rich water were treated with the Modified HDS process, settling rates of 0.96 m/h were recorded during the latter part of the experiment.

- Fe(II) and high SO_4 (feed water C): Average settling rates of 0.77 m/h were recorded with the Modified HDS process and 0.55 m/h with the HDS process.

(c) Sludge solids concentration

Average sludge solid concentrations for feed water A and B at different sampling points are given in Table 12. The settled sludge solids concentrations after 24 hours of settling were allowed are used for discussion. 99% of the maximum settling was reached within 3 hours.

- Fe(II)-rich water (feed water A): Average sludge solids concentrations were higher for the HDS process (42.8%) than for the Modified HDS process (30.9%)
- Fe(III)-rich water (feed water B): Results were the opposite of those for Fe(II) water. Average sludge solids concentrations were 23.2% for the Modified HDS process and 10.6% for the HDS process.
- Fe(II) and high SO_4 (feed water C): Average settled sludge solids concentrations were 34.6% for the HDS process and 7.5% for the modified HDS process.

Table 7.12 : Summary of suspended solids results obtained with Fe(II) water (Feed water A) and Fe(III) water (feed water B)

Sampling Point	Sludge Solids Content (%)			
	Feed water A (FeII)		Feed water B (FeIII)	
	HDS	Modified HDS	HDS	Modified HDS
Sludge after settling	42.8	30.9	10.6	23.2
Aeration tank	9.1	6.1	2.1	4.1
Underflow	25.0	16.5	7.8	15.6
Effluent	<0.01	<0.01	<0.01	<0.03

7.8.4 Gypsum Scaling

Blockages occurred while feeding water C (2500mg/l as SO_4). Gypsum scale caused blockages that made continuous operation impossible. It was cleaned out as often as possible. This experiment was abandoned after 5 weeks since the sludge being lost during cleaning operations became so much that no sludge build-up pattern could be established.

7.9 CONCLUSIONS

1. The HDS process is most suitable for the treatment of Fe(II)-rich water
2. The Modified HDS process is most suitable for Fe(III)-rich water
3. Water high in sulphates is less suitable for the HDS and the Modified HDS processes due to gypsum scaling in the recycle pipelines
4. Results obtained from continuous operations confirm findings from beaker studies

CHAPTER 8 : CONTROL OF ACID GENERATION IN COAL DISCARD DUMPS USING LIMING PLANT SLUDGE

8.1 BACKGROUND

Coal discard, fines and high density sludge (produced during acid water neutralization with lime (HDS-sludge)) are generated during coal mining. Coal discard and fines are sometimes disposed together. Coal discard is used as a wall for the waste dump while the fines are deposited in the centre. The **fines** are generally of good quality with a future value, while **discard** is responsible for environmental pollution due to its pyrite content. The pyrite present in the discard when exposed to atmosphere, is oxidized producing sulphuric acid (Equation 1). The acidic water is collected and neutralized with lime to produce **HDS-sludge** which is rich in gypsum and metal hydroxides. For the disposal of discard, current practices dictate that discard dumps should be designed in such a way that the contact between discard, water and air is minimised to ensure minimum acid formation. Surface runoff of (rain water and process water) is maximised to minimise seepage. Air contact is minimised by compacting the coal discard. Upon mine closure, rehabilitation of the discard dump by e.g. placing a clay capping over the site is required to ensure minimum further acid formation. For the disposal of HDS-sludge (if classified as a hazardous waste), legislation requires that it be discharged into lined ponds to eliminate the possibility of acid water induced metal leaching to groundwater. However, sludge disposal in lined landfills is costly.

$$4FeS_2 + 15O_2 + 14H_2O \Rightarrow \quad 4Fe(OH)_3 + 8H_2SO_4 \qquad (1)$$

The aim of this investigation was to investigate the benefits associated with the co-disposal of HDS-sludge and coal discard. The following arguments indicate that there is little environmental benefit in disposal of HDS-sludge in lined ponds (when the impact of HDS-sludge is compared with that of the coal discard dump):

- The amount of HDS-sludge generated is insignificant compared to discard. For a coal mining operation with a throughput of 20 000 t/d of raw coal, typically 6 000 t/d of discard is generated compared to only 10 t/d or less of HDS-sludge (dry basis).
- The metals in HDS-sludge are in the oxidized form and cannot generate acid, as is the case with discard during pyrite oxidation (Equation 1).
- HDS-lined ponds are usually adjacent to discard dumps.

Co-disposal of HDS-sludge with coal discard on surface or direct discharge into worked out open cast or underground voids could be more cost effective. This approach would be in line with the backfill approach applied sometimes (although not in line with current legislation) in the mining industry where waste rock is returned to underground. Co-disposal would offer the following benefits: cost reduction as costly sludge disposal ponds are not required and the creation of neutralization capacity, as HDS-sludge contains 5% to 30% unused alkali, depending on the efficiency of the plant. Other researchers also reported that less metals are leached out from metal-rich waste when in contact with alkali-wastes. Hölström *et al*. (1999) found from their humidity cell tests that a high pH in tailings prevent the leaching of heavy metals. This is due to the low solubility of metals at higher pH values. Pritts *et al*. (1999) found during evaluation studies on the stabilization of hazardous wastes, with a byproduct from Clean Coal Technology, a decrease in toxicity of the wastes. Toxicity Characteristic Leaching Procedure (TCLP) tests were used. They ascribed it to cementitious reactions that occurred in the wastes that contained lime, $CaSO_4/CaSO_3$ and fly ash. They mixed the byproduct and hazardous wastes in the ratio of 1:10 and higher.

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. It is hypothesised that the unused alkali in the HDS-sludge will raise the pH of the coal discard to levels above 7 where the solubility of metals is low. This depends on the coal quality which is highly variable and site specific.
- Compare the efficiency of HDS-sludge and activated sewage sludge co-disposal with coal discard, and submersion of the coal discard for minimizing acid formation from coal discard.
- Determination of the potential toxicity of leachate from the untreated and treated coal discard.

8.2 MATERIAL AND METHODS

8.2.1 Materials

The HDS-sludge used in this study was obtained from the Brugspruit liming plant near Witbank and consisted mainly of iron- and aluminium hydroxide, gypsum and water (Table 8.1). A representative sample of HDS-sludge was fused with sodium peroxide, dissolved in dilute acid and analyzed with ICP-AES spectroscopy.

Table 8.1 : Chemical composition of HDS-sludge.

Parameter	Concentration (mg/kg)	Parameter	Concentration (mg/kg)
Zinc	400	Sodium	3 000
Silica	7 000	Potassium	200
Manganese	1 000	Magnesium	3 000
Iron	40 000	Sulphur	4 000
Chromium	60	Hydroxide	58 719
Aluminium	9 000	Sulphate	96 000
Calcium	40 000	Water	144 444
Solids	406 379	Other metals	Below detection limit

Coal discard was obtained from a colliery near Witbank. It was sieved and the less than 20 mm fraction was used for column leaching studies. Activated sewage sludge from the Daspoort sewage works in Pretoria was used.

8.2.2 Column Leaching Studies

Column leaching studies were carried out to determine the rate of acid generation from pyrite-rich coal discard. The following procedure was followed:

- PVC columns (180 mm diameter and 1.2 m heigh) were filled with solid waste material (30 kg). The columns were packed with various combinations of coal discard and HDS-sludge or activated sewage (AS) sludge (Table 8.2). The different coal discard and HDS or AS sludge combinations were thoroughly mixed before filling the columns.
- Tap water (10 - 12 litres) was added (day 1) and drained (day 3) in weekly cycles for a period of 22 weeks. During the rest of the period (day 4 to day 7), the content of the columns was exposed to air. Two columns (W9 and W11) were operated as a “submersed system” meaning that these columns were not drained after the addition of water to a level above the packed height. The water was topped up as samples were extracted from the bottom on a weekly basis. Sampling and analyses of all columns were carried out weekly.
- A coal discard sample was taken at the beginning of the project for analyses of the nett neutralization potential of the discard using the modified acid-base accounting procedure of Lawrence (1990). The acid potential (AP) was based on the pyrite content of the coal (expressed as %S x 31.25 = kg CaCO3 equivalent/ton). The neutralization potential (NP) (as kg CaCO3 equivalent/ton) was determined by digesting the sample in a standard HCl-solution for 24 h and back titrating with a standard NaOH solution. The nett neutralization potential (NNP) is the difference between NP and AP.

8.2.3 Beaker Tests for Evaluating the Stability of HDS

Beaker tests were carried out to determine the stability of the HDS-sludge as a function of pH. HDS-sludge (50 g/l) samples were stirred at 80 rpms for a period of 24 hours in a range of HCl solutions (0 mg/l, 300 mg/l, 2200 and 101 850 mg/l (as $CaCO_3$)). The leachate was analyzed for iron, aluminium, manganese, zinc, cadmium, chromium, lead and nickel, acidity, sulphate and pH.

8.2.4 Waste Classification Studies

The EPA's TCLP (Toxicity Characteristic Leaching Procedure) method (no 1311) was used for characterising of the HDS-sludge and the coal discard (EPA, 1992). Prescribed solutions containing acetic acid was used. The solid (waste) to extractant ratio was 1:20 by weight. A minimum sample of 100 g was agitated in a rotating apparatus for 20 h. In this method 100 ml acidic solution (e.g. acetic acid) was contacted with 20 g of solids in a closed container for a 24 h period. The filtrate was analyzed for iron, aluminium, manganese, zinc, cadmium, chromium, lead and nickel.

8.2.5 Analytical

Leachate samples from the column leaching studies were filtered through Whatman No 1 filter paper. Sulphate, acidity and pH determinations were carried out manually according to procedures described in Standard Methods (APHA, 1989). Metals (e.g. iron, aluminium and manganese) were analyzed using atomic absorption spectroscopy and ICP spectroscopy. A standard spectrophotometric method were used for Cr(VI) analyses.

8.3 RESULTS AND DISCUSSION

Table 8.2 shows the load of various parameters that is leached out from coal discard/HDS during various treatment options. The various studies are divided into three groups for discussion purposes.

Group 1.	Leachate from coal discard (control) - Column W6
Group 2.	Comparison between coal discard (control) and HDS-sludge - Columns W6 and W7 respectively
Group 3.	Comparison between coal discard (control) (W6) and various control/inhibition options, namely HDS-sludge (W3), Activated sludge (W10), Submersed discard (W9), Submersed activated sludge/discard (W11).

8.3.1 Control of Acid Generation from Coal Discard with HDS-Sludge

(a) Coal discard (control)

The initial nett neutralization potential (NNP) of the coal discard was 56 g (as $CaCO_3$)/kg discard) with a neutralization potential:acid potential (NP:AP) ratio of 2:1. Coal discard with a NP:AP ratio of 4 and higher is considered to be alkaline discard (Price *et al.*, 1997). This indicates that the specific coal discard will be acid generating as evident by the low leachate pH values (Table 8.2, W6). Figure 8.1 shows the acid and iron load leached out from coal discard (control) due to the oxidation of pyrite (equation 1). Iron analyses is shown for a period of 12 weeks and acidity for 22 weeks.

Figure 8.1 shows that acidity and iron leach out at constant rates over time, namely 1 120 mg acid (as $CaCO_3$)/(kg.week) and 326 mg Fe/(kg.week) respectively (calculated from the slopes of accumulated acidity/iron versus time). The measured ratio of iron to acidity of 0.24 corresponds reasonably with the expected ratio of 0.28 calculated from equation 1. Factors like the presence of pyrite compounds other than FeS_2 could explain the difference.

The acid potential (AP) of the coal discard used is 56 g acid (as $CaCO_3$)/(kg discard). Under laboratory conditions, where the leachate rate is high compared to field conditions, a minimum period of 50 weeks (56 g acid (as $CaCO_3$)/kg discard ÷ 1.12 g acid (as $CaCO_3$)/(kg.week)) is estimated for complete leaching of the oxidation products of pyrite. This indicates that only a small portion of the pyrite content of the discard can be leached in a short period of time. The aim, therefore, in the management of discard dumps, is to reduce the rate of pyrite oxidation to the minimum. Complete or enhanced leaching of pyrite will result in unacceptably high neutralization and sludge disposal cost.

The other metals analyzed (Zn, Al and Mn) leached out at much lower rates than iron and do not leach at a constant rate with time. The leachate rates of Zn, Al and Mn are at least an order of magnitude less than that of the iron due to lower concentrations in the discard (Table 8.2, Column W6).

Table 8.2 : Effect of HDS-sludge and other treatment options (submersed and activated sludge) on the specific weekly load of environmental parameters in the leachate from coal discard

Parameters	**Column media specifications**					
Column no.	W7	W6	W3	W10	W9	W11
	Controls		Comparison between HDS and other treatment options			
Column description	HDS-sludge	Discard	Discard/ HDS-sludge	Discard/ AS Sludge	Discard submersed	Discard/ AS Sludge submersed
Experimental conditions						
Discard	N	Y	Y	Y	Y	Y
HDS-sludge (dewatered)	Y	N	Y	N	N	N
Activated sludge (AS)	N	N	N	Y	N	Y
Ph	7	7	7	7	7	7
Water	Tap	Tap	Tap	Tap	Tap	Tap
Cycle (days)	7	7	7	7	7	7
Submersed	N	N	N	N	Y	Y
Drain	Y	Y	Y	Y	N	N
Mass HDS-sludge (kg)	30	0	10	0	0	0
Mass discard (kg)	0	30	20	20	30	20
Mass activated sludge (kg)	0	0	0	10	0	10
Volume in (l)	12	12	12	12	12	12
Experimental results						
Leachate rates at selected contact times						
Acidity (mg acid (as $CaCO_3$)/kg discard.week, for all except W7), (mg acid (as $CaCO_3$)/kg HDS.week, for W7)						
Week (initial)	36	1516	65	482	275	48
Week (4)	52	1277	131	139	175	52
Week (8)	37	1319	78	93	91	38
Week (12)	29	1245	41	72	48	38
Average (weeks 0, 4, 8 & 12)	38.5	1339	79	197	147	44
Average (weeks 0 - 22)	33	1120	56	130	127	44
Total iron (mg Fe/kg discard.week, for all except W7), (mg Fe/kg HDS.week, for W7)						
Week (initial)	0.021	314	0.03	0.84	65	0.07
Week (4)	0.02	370	0.01	0.02	61	0.05
Week (8)	0.01	295	0.01	0.74	24	0.03
Week (12)	0.008	307	0.01	0.11	10	0.09
Average	0.015	321.5	0.02	0.43	40	0.06
Aluminium (mg Al/kg discard.week, for all except W7), (mg Al/kg HDS.week, for W7)						
Week (initial)	1.0	18.1	1.4	0.26	4.5	0.08
Week (4)	0.5	5.0	0.4	0.04	1.3	0.01
Week (8)	0.4	4.2	0.7	0.34	0.45	0.05
Week (12)	0.5	3.5	0.5	0.08	0.15	0.03
Average	0.6	7.7	0.8	0.18	1.6	0.04
Manganese (mg Mn/kg discard.week, for all except W7), (mg Mn/kg HDS.week, for W7)						

Parameters	**Column media specifications**					
Column no.	W7	W6	W3	W10	W9	W11
	Controls		Comparison between HDS and other treatment options			
Column description	HDS-sludge	Discard	Discard/ HDS-sludge	Discard/ AS Sludge	Discard submersed	Discard/ AS Sludge submersed
Week (initial)	4.1	15.2	41	0.09	3.0	0.50
Week (4)	2.3	2.7	16	0.02	2.5	0.00
Week (8)	0.02	1.9	7	0.01	1.3	0.00
Week (12)	0.01	1.0	3	0.01	1.0	0.00
Average	1.61	5.2	17	0.03	1.95	0.13
Zinc (mg Zn/kg discard.week, for all except W7), (mg Zn/kg HDS.week, for W7)						
Week (initial)	0.039	7.8	0.23	0.08	1.0	0.01
Week (4)	0.01	2.7	0.05	0.00	0.8	0.01
Week (8)	0.01	3.0	0.04	0.00	0.6	0.01
Week (12)	0.015	0.6	0.06	0.00	0.1	0.01
Average	0.02	3.53	0.10	0.02	0.6	0.01
Ph						
Week (initial)	6.6	2.6	6.0	6.7	2.6	6.3
Week (4)	6.7	2.5	6.5	7.3	2.8	6.9
Week (8)	7.1	2.4	6.9	8.1	2.9	7.2
Week (12)	7.0	2.2	7.1	8.0	2.6	7.1
Average	6.85	2.43	6.6	7.5	2.7	6.9
COD concentration (mg/l O_2)						
Week (initial)				2760.0		550.0
Week (4)				98.0		260.0
Week (8)				80.0		109.0
Week (12)				33.0		63.0

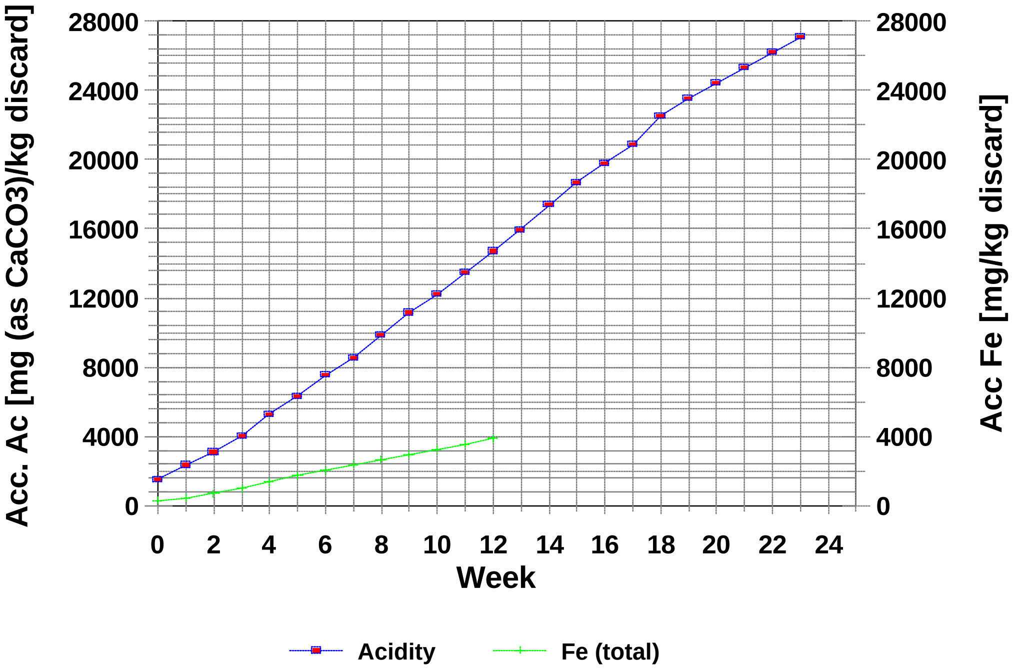


Figure 8.1 : Leachate of acid and iron from coal discard (control) - W6.

(b) HDS-sludge

Table 8.3 shows the results obtained from the dissolution of HDS-sludge in a range of acidic solutions. It shows that:

- The metals in HDS-sludge dissolves only in acidic medium and not at pH values above 6.
- Calcium and magnesium salts would dissolve over the whole pH range (0 to 6), as indicated by the dissolution of sulphate to between 1 600 and 2 400 mg/l .
- HDS-sludge contains 50 g/kg alkali (as $CaCO_3$)/kg sludge. This was determined experimentally and is also confirmed by the observation that 2.4 g acid (as $CaCO_3$) is needed to reduce the pH of 50 g HDS-sludge to less than 7 (2.4 g/50 g = 48 g alkali (as $CaCO_3$)/kg HDS-sludge).

(c) Comparison between coal discard (control) and HDS-sludge

Figure 8.2 and Table 8.2, Columns W6 and W7, compares the leachate rate of various parameters from coal discard and HDS-sludge.

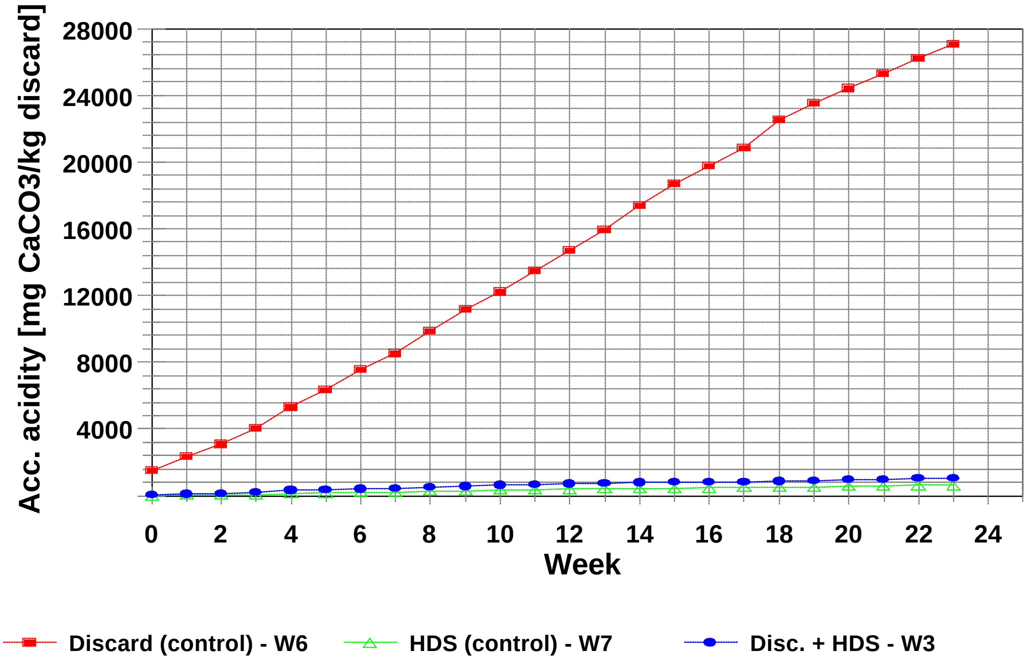


Figure 8.2 : Comparison of the acid leached from coal discard and HDS-sludge.

Acid and metals are leached at a much slower rate from HDS-sludge, than from coal discard, as noted below:

Acidity. From the slope of the graphs, it is calculated that 1120 mg acid (as CaCO$_3$)/(kg discard.week) and 39 mg acid (as CaCO$_3$)/(kg sludge.week) is leached from coal discard and HDS-sludge respectively (Figure 8.2). The almost zero acid leachate from HDS-sludge shows that it is stable with regard to acid formation when contacted with water and air over time. This is due to the iron being in the hydroxide form (Fe(OH)$_3$) in the HDS-sludge and not in the sulphide form (FeS$_2$), as is the case with the coal discard.

Alkalinity. Small amounts of alkalinity is leached from the HDS-sludge. The sludge contains mainly CaCO$_3$ as alkali (50 g CaCO$_3$ (as CaCO$_3$)/kg sludge) and no free lime. The solubility of CaCO$_3$ is very low in neutral water.

Iron and Zinc. Insignificant amounts of total iron and zinc are leached from HDS- sludge. Although HDS-sludge contained 40 000 mg total Fe/kg sludge, iron in the leachate decreased from a low 0.021 mg Fe/(kg sludge.week) during the initial week to 0.008 mg/(kg sludge.week) during week 12. This is totally different from the constant high iron content in leachate from coal discard (321 mg Fe/(kg discard.week)). Similarly, of the 400 mg Zn/kg sludge content, the initial and 12th weeks leached 0.039 and 0.015 mg Zn/(kg sludge.week) respectively. This is significantly less than the 7.8 and 0.6 mg Zn/(kg discard.week) respectively for these two weeks in the case of coal discard.

Aluminium. In the case of aluminium (HDS-sludge contains 9000 mg Al/kg sludge) the leached aluminium during the initial week and week 12 were 1.0 and 0.5 mg Al/(kg sludge.week) respectively. This is less than that leached from coal discard (18.1 and 3.5 mg Al/(kg discard.week) in the initial and 12th weeks respectively).

Manganese. In the case of manganese (HDS-sludge contains 1000 mg Mn/kg sludge) the leached manganese during the initial week and week 12 were 4.1 and 0.01 mg Mn/(kg sludge.week) respectively. This is less than that leached from coal discard (15.2 and 1.0 mg Mn/(kg discard.week) in the initial and 12th weeks respectively).

Table 8.3 : Dissolution of HDS-sludge (50 g) as a function of acid concentration (24 h contact period)

Parameter	Concentration			
Acid dosage (ml/l 100 % HCl)	0	0.5	5	200
Acidity added (mg/l $CaCO_3$)	0	300	2200	101850
Acidity determined (mg/l $CaCO_3$)	250	300	2400	110000
pH	6.6	6.5	3.9	0.1
Sulphate (mg/l SO_4)	1695	1768	2011	2421
Iron (mg/l Fe)	0.03	0.03	0.03	1340
Aluminium (mg/l Al)	0.1	0.1	34.1	350
Manganese (mg/l Mn)	0.03	0.03	17.9	96
Zinc (mg/l Zn)	0.03	0.03	3.7	14.0
Cadmium (mg/l Cd)	0.005	0.006	0.010	0.020
Chromium (mg/l Cr)	0.07	0.06	0.15	
Lead (mg/l Pb)	0.24	0.29	0.54	1.33
Nickel (mg/l Ni)	0.12	0.13	2.22	

8.3.2 Comparison between HDS and Other Treatment Options

(a) Acid generation

Figure 8.3 and Table 8.2 show the effect of various control methods on the leachate quality from coal discard. All the methods investigated show that the nett acid generation (oxidation rate minus neutralization rate) can be reduced effectively as indicated by the acid generation rates for the corresponding treatment methods (Table 8.4).

This result proves that HDS-sludge, as well as activated sewage sludge, can be used effectively to control acid generation caused by pyrite oxidation, and can be explained by the following mechanisms:

HDS-sludge. The pH of discard leachate amounts to between 2.2 and 2.6 (W6 - control), while when mixed with HDS-sludge (W3), the pH is raised to between 6.0 (initial week) and 7.1 (week 12). The effectiveness of HDS-sludge can be ascribed to the free alkali present in the sludge which neutralized any acid produced as a result of FeS_2 oxidation, or reduces the rate of pyrite oxidation due to the increased pH. The HDS-sludge has a moisture content of 70 % and a free alkali-content of 50 g (as $CaCO_3$)/kg HDS-sludge. The discard contains 56 g (as $CaCO_3$)/kg acid. Thus, by mixing discard and HDS-sludge in the ratio 1:1, an excess alkali is available to neutralized the acid that might be generated in the long term from the coal discard.

Table 8.4 : Acid generation rates for the various treatment options.

Option (Column no.)	**Rate in mg acid(as $CaCO_3$)/ (kg discard.week)**
Coal discard only (Control) (W6)	1120
Coal discard/Activated sludge (W10)	130
Discard submersed (W9)	127
Coal discard/HDS-sludge (W3)	56
Coal discard/Activated sludge submersed (W11)	44

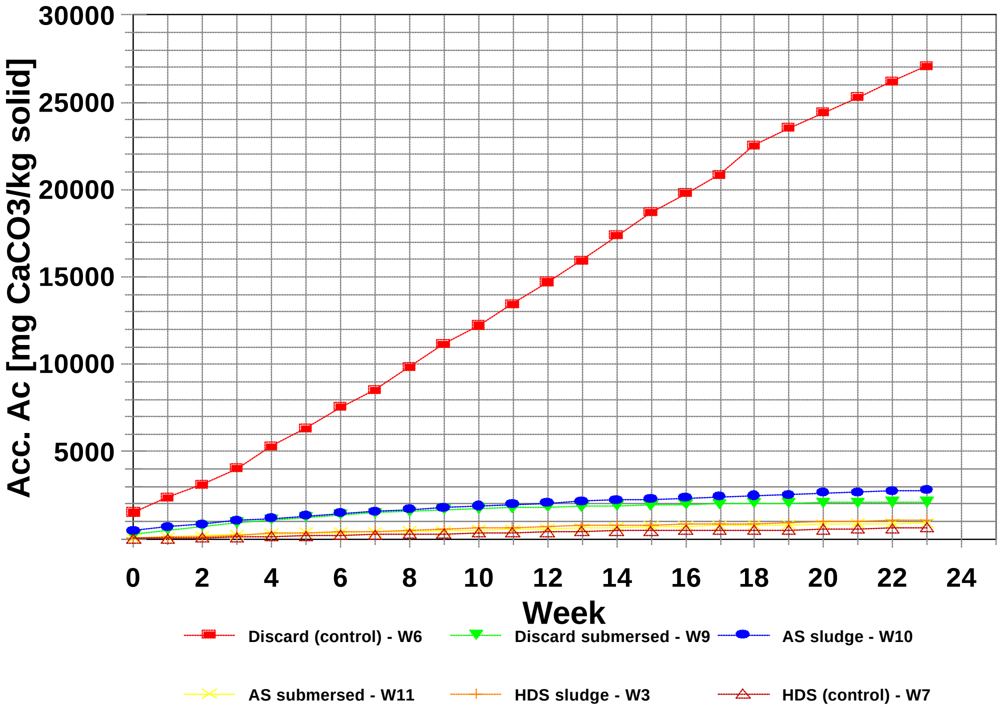


Figure 8.3 : Effect of various control methods on the acid generated by coal discard.

Activated sludge (AS). Table 8.4 shows that activated sludge treatment is also effective, although not as effective as HDS treatment (130 versus 56 mg acid(as $CaCO_3$)/(kg discard.week)). The effectiveness of activated sewage sludge can be ascribed to reducing conditions generated by organic material.

Submersed discard. The effectiveness of submersion of discard (discard kept under water) can be ascribed to the limitation of oxygen availability for pyrite oxidation.

Submersed and activated sludge. This method is the most effective due to the combined effect of reducing conditions created by the activated sewage sludge and limited oxygen availability.

(b) Sulphate behaviour

Figure 8.4 shows the behaviour of sulphate when discard or HDS is combined with other solids and contacted with water. It is noted that:

- Coal discard only. Accumulated sulphate increased with time mainly due to the oxidation of pyrite (1318 mg (as SO_4)/(kg discard.week)). The dissolution of gypsum that has accumulated on the discard during the coal washing process does not contribute significantly to the sulphate load.
- HDS-sludge (control) and coal discard (2 parts) combined with HDS-sludge (1 part). Accumulated sulphate increases with time due to dissolution of excess gypsum in the water which is under-saturated with respect to gypsum (gypsum under-saturated water was used in this investigation). The sulphate dissolution rate amounted to 918 mg (as SO_4)/(kg sludge.week) in the case of HDS-sludge only and to 1127 mg (as SO_4)/(kg discard.week) in the case of coal discard combined with HDS. Excess gypsum is present in HDS-sludge due to crystallisation of gypsum. Precipitated gypsum dissolves quickly in water that is under-saturated with respect to gypsum until the saturation level is reached. Should HDS-sludge be contacted with water that is saturated with gypsum (as the case will be in the coal processing industry), no further gypsum dissolution is likely to occur.
- Coal discard (2 parts) combined with activated sludge (1 part) and submersed coal discard. Little increase in sulphate (Figure 8.4) and acidity (Figure 8.3) was observed. This confirmed that:
    - Discard is not responsible for release of sulphate due to the presence of precipitated gypsum.
    - Only limited pyrite oxidation occurred due to reducing conditions created by activated sludge and elimination of oxygen in the case of submersion.

- Coal discard combined with activated sludge and when it is submersed. No increase in sulphate concentration (as well as in the acidity) was observed, which indicated that the combination is effective for inhibition of pyrite oxidation.

A disadvantage associated with the use of activated sludge for the control of pyrite oxidation is the release of organic material. During the first week 2 760 mg COD/l leached out into the water when coal discard is contacted with activated sludge. This amount decreased rapidly to 98 mg COD/l after 4 weeks. In the case of activated sludge combined with submersion, the COD of leachate amounted to 550 mg COD/l during the initial week.

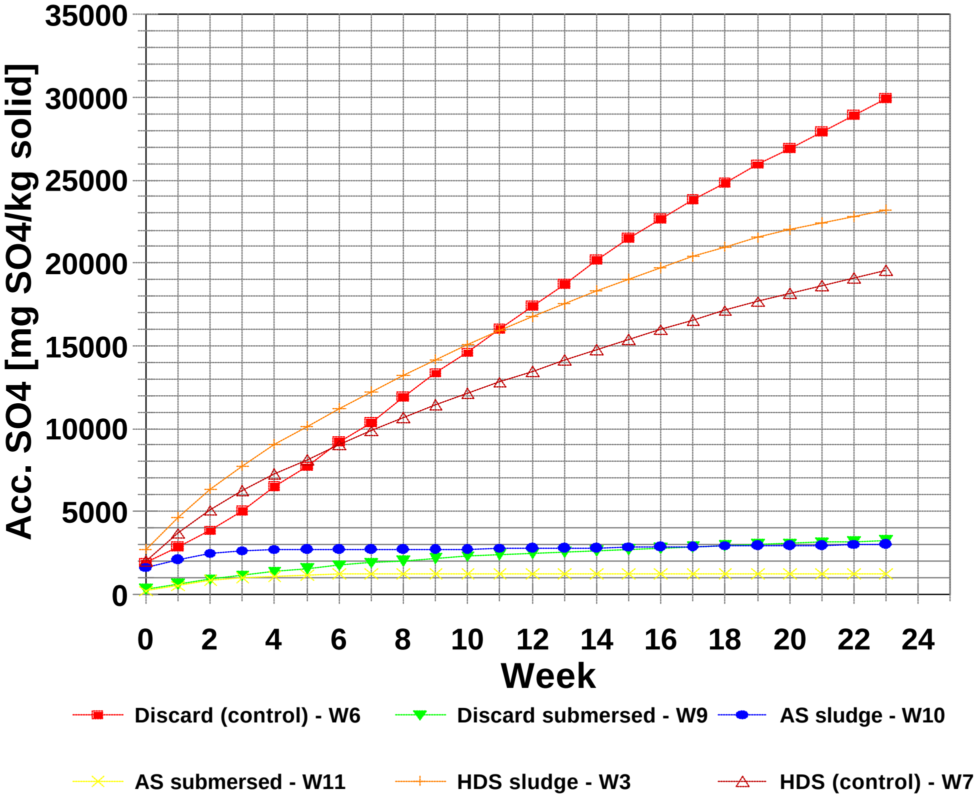


Figure 8.4 : Effect of various control methods on sulphate generated by coal discard.

8.3.3 Waste Classification of HDS-Sludge and Coal Discard

DWAF requires that wastes that need to be landfilled be characterised by using the EPA's TCLP (Toxicity Characteristic Leaching Procedure) method to determine the Estimated Environmental Concentration (EEC) of toxic components. Landfill wastes is characterised into four Risk Hazard Ratings (RHR) categories (1 - extreme hazard, 2 - high hazard, 3 - moderate hazard and 4 - low hazardous), which is a function of chemical content, chemical load and disposal area (DWAF, 1998a). The criteria for the landfill is determined by the RHR of the waste, e.g. RHR 1 to 4 can be disposed into a H:H type landfill, RHR 3 to 4 in H:h type landfill and non-hazardous wastes to G:B$^+$ and G:B$^-$ type landfills (DWAF, 1998b).

Table 8.5 compares:

- The hazardous rating (RHR) of HDS-sludge with that of coal discard when disposed separately (Columns B and C).
- The effect of area of the disposal facility on the hazardous rating (RHR) of HDS-sludge (Columns B and D).
- The hazardous rating (RHR) of HDS-sludge with that of coal discard when co-disposed on the current coal discard site (Columns C and D).

It is noted that:

- HDS-sludge from Brugspruit liming plant can be classified as a hazardous waste. This is due to the fact that Zn, Mn, Co, Cd and Ni do not delist when measured against the set guidelines (Table 8.5, Columns B2 versus A2). Disposal in a H:H type landfill is therefore required. Final classification lies with DWAF.
- The hazardous rating (RHR) of HDS-sludge is improved when disposed on an increased area (Columns B2 and D2). When HDS-sludge is disposed in a large area, only two elements are not delisted (Mn and Cd) (Column D2), compared to seven elements when disposed in a small area (Zn, Mn, Fe, Al, Co, Cd and Ni) (Column B2). This means that HDS-sludge almost delists when disposed on the same site as the coal discard. Cadmium is a borderline case (e.g. EEC value of 5 that would have delisted at an EEC value of less than 3.1) and manganese is a more serious problem in coal discard with an EEC value of 66710 (Column C1) opposed to 3613 (Column D1) for the HDS-sludge (Table 8.5).

Table 8.5 : Comparison of HDS-sludge and coal discard waste classification.

Para-meter	**Guideline**		**HDS disposed in lined pond**		**Coal discard**		**HDS disposed on large area**	
Column No	A		B		C		D	
Size (Ha)			0.37		21.37		21.37	
Load (t/month)			997		180000		997	
	ARL (ppb)	RHR	EEC (ppb)	RHR	EEC (ppb)	RHR	EEC (ppb)	RHR
Column No	A1	A2	B1	B2	C1	C2	D1	D2
Zn	700	2	20264	2	77829	2	347	D

Para-meter	Guideline		HDS disposed in lined pond		Coal discard		HDS disposed on large area	
Column No	A		B		C		D	
Size (Ha)			0.37		21.37		21.37	
Load (t/month)			997		180000		997	
Mn	300	2	210974	2	66710	2	3613	2
Fe	9000	3	25840	3	24460	3	442	D
Cr(III)	4700	3	1978	D	3336	D	34	D
Al(III)	10000	3	230279	3	11118	3	3943	D
Co	6900	2	13190	2	3336	D	226	D
Cu	100	2	96	D	667	2	2	D
As	430	2	180	D	556	2	3	D
Cd	31	1	294	1	556	1	5	1
Ni	1140	2	16487	2	3336	2	282	D

ARL (Acceptable Risk limit) - Minimum requirement that need to be met by EEC values for delisting
EEC (Estimated Environmental Concentration) - (Metal concentration in TCLP extract of HDS or coal discard (g/kg) x waste load (kg/month) ÷ size of site (ha)) x 0.66
RHR - Risk Hazard Rating
D - Delist to a general waste

8.3.4 Practical Considerations

The following arguments, developed from this study, can be raised why permission should be considered (by DWAF) for co-disposal of HDS-sludge with coal discard as a possible alternative to disposal of HDS-sludge in lined ponds (depending on the outcome of similar and EIA studies as may be required by DWAF):

- DS-sludge, when co-disposed with coal discard, will not contribute to increased toxicity of the waste, in fact it will reduce the leachate of toxic metals from the coal discard as long as the pH stays higher than 7. Excess alkali in the HDS-sludge will buffer the pH of the discard to levels above 7, where the solubility of metals is low. Over dosages of HDS-sludge should be applied when co-disposed with coal discard (recommended ratio for alkali:acid potential is 4:1) to prevent acidic conditions due to pyrite oxidation. This will prevent additional metal leachate from the HDS-sludge. Due to limited quantities of HDS-sludge compared to coal discard, co-disposal should be limited to a small section of the coal discard dump in order to meet the above-mentioned alkali:acid potential requirements. This will result in an excess of alkali, compared to the nett acid potential of the discard, and will prevent free acid conditions in the long term due to pyrite oxidation.

  If the above criteria are not met, acid conditions in the coal discard dump could cause metals in the HDS-sludge to re-dissolve in the long term. This will contribute to the metal load in the leachate from the coal discard dump. However, the nett effect on the metal load in the leachate will be insignificant (Table 8.6). It is calculated from TCLP extracts that the metal contribution from HDS-sludge, compared with that from coal discard, amounts to e.g. only 0.004 % for iron, and 0.5% for manganese.

The co-disposal of HDS-sludge and coal discard, is an effective way for disposing HDS-sludge, and could be integrated with the current approach where coal waste dumps need to be rehabilitated after mine closure. The proposed co-disposal will prevent or reduce acid formation in coal discard significantly for the period that it is exposed to atmosphere (water and air). When rehabilitation is completed, such atmospheric contact would be eliminated almost completely, and the potential for acid formation and HDS-sludge re-dissolution reduced even further.

Table 8.6 : Contribution of HDS-sludge to metal load in the leachate of coal discard during co-disposal (as measured in TCLP extracts)

Parameter	**Coal discard only**		**HDS-sludge**		**Metal load ratio (HDS-sludge: Discard) (%)**
	Concentration (mg/kg)	Load (kg/d)	Concentration (mg/kg)	Load (kg/d)	
Coal discard		20000000			
HDS-sludge				10000	
Zinc	7.8	156	11.3	0.113	0.072
Manganese	12	240	117	1.17	0.488
Iron	200	4000	14	0.14	0.004
Chromium	1	20	1.1	0.011	0.055
Aluminium	40	800	128	1.28	0.160
Cobalt	3.8	76	7.3	0.073	0.096
Nickel	4.6	92	9.2	0.092	0.100

- The quantity of HDS-sludge produced at a colliery, compared to coal discard, is insignificant. For a mining operation of 20 000 t/d of raw coal, typically 6 000 t/d of coal discard is produced compared to less than 10 t/d of HDS-sludge (when 100 % dry or 33 t/d when containing 70 % water).

The alternative to co-disposal of HDS-sludge with coal discard in a specific section of the discard dump is separate disposal. The justification for separate HDS-disposal in lined ponds, when it is adjacent to the coal discard dump, should be reconsidered. This is supported by the low quantities of HDS-sludge compared to coal discard and the almost zero leachate rate of metals from HDS-sludge, provided that contact with acidic water is avoided.

8.4 CONCLUSIONS

The following conclusions are made from the investigation:

1. HDS-sludge from Brugspruit liming plant contains 50 g/kg alkali (as CaCO3) which can be used for the neutralization of coal discard. Coal discard can have a nett neutralization potential of 56 g/kg (as CaCO3).
2. The rate of pyrite oxidation and metal leachate production are reduced significantly when HDS-sludge is co-disposed with coal discard. The acid generation rate of coal discard on its own was 1120 mg acid (as $CaCO_3$)/(kg discard.week), as opposed to 39 mg acid (as $CaCO_3$)/(kg sludge.week) for coal discard combined with HDS-sludge.
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 introduction). A disadvantage associated with activated sludge, however, is the leachate of organic material and metals. Submersion is difficult to apply practically, and continuous wetting and drying conditions can only aggravate the situation.
4. The hazardous rating (RHR) of HDS-sludge is improved when disposed on an increased area (e.g. co-disposed with coal discard instead of separate disposal). HDS-sludge almost delists when disposed on the same site as the coal discard. When HDS-sludge is disposed on only a section of the discard dump, excess alkali, compared to the nett acid potential of the discard will prevent free acid conditions due to pyrite oxidation, which will reduce the possibility of metal leachate in the long term from both the HDS-sludge and the discard.

CHAPTER 9 : LIMESTONE HANDLING AND DOSING SYSTEM FOR FULL-SCALE APPLICATION

9.1 INTRODUCTION

Coal discard, that contains pyrites, is produced as a waste during coal mining. When coal discard is exposed to oxygen and water in the presence of iron oxidizing bacteria, acid leachate is produced which contains high concentrations of acid, sulphate and metals due to oxidation of pyrites (Reaction 9.1).

$$2FeS_2 + 71/2O_2 + H_2O \ ? \qquad Fe_2(SO_4)_3 + H_2SO_4 \qquad (9.1)$$

Since 1996 extensive research and development work has been carried out at the Navigation Section of Landau Colliery near Witbank in order to address the following problems associated with the leachate from raw coal and coal discard: High cost of neutralization; High maintenance cost in the coal processing plant and the lime neutralization plant due to acid corrosion and scaling of equipment; and Desalinisation of effluent that is discharged into public streams.

Water is used in the coal processing plant to separate coal from waste, to grade the coal into different particle size fractions, and for dust suppression. Water leaving the coal processing plant contains slimes which are settled in a thickener. This slurry is pumped to the slimes dump and coarse coal discard is transported on a belt conveyor to a discard dump. The slimes (fine coal) are disposed of in the centre of the waste dump and the coarse discard disposed of around the perimeter to contain the slimes. Decanted water is returned via the penstock to the coal processing plant. Some of this water seeps through the discard dump and, together with rainwater, is collected in cut-off trenches at the base of the dump. The seepage is stored in a toe dam. A portion of the toe dam water is combined with the penstock water and other slightly polluted water prior to treatment in a primary liming plant.

In this operation, 20 000 ton per day (t/d) of raw coal is mined to produce 15 500 t/d of final product, 3 000 t/d of coal discard and 1 500 t/d of slimes (fine coal). The dump has an area of 72.5 ha (25.6 ha under slimes and 46.9 ha under discard) and a height of 12 m. It is estimated that the dump contains 2.4 million tons of slimes and 4.3 million tons of discard, with the latter containing 2% pyrites (as S). The discard is responsible for most of the pollution. A number of studies have been conducted at this site since 1996 to characterize the nature and extent of pollution. The key findings are summarized below:

- Acid leachate. Chemical leaching studies showed that 0.33 g acid (as $CaCO_3$) is leached from each kilogram of coal.
- Pyrites oxidation. The rate of biological oxidation of pyrites under laboratory conditions was determined as 148 mg acid (as $CaCO_3$)/(kg.d).
- Modelling of the water network showed that 24.1 t/d of sulphate enters the water network. Of this 7.3 t/d originates from the feed water, 5.8 t/d from the raw coal and 11 t/d from the coal discard. An equal amount of sulphate leaves the system through gypsum precipitation (11 t/d through neutralization of the toe seep water, 0.2 t/d in the primary neutralization plant, 4.5 t/d in the coal processing plant and 3.2 t/d in the penstock) or with the seepage (5.1 t/d). A portion of the sulphate that crystallizes out in the coal processing plant is in the form of scale on equipment such as spirals, sieves and pipelines, as well as on magnetite used in the separation process.
- Magnetite behaviour. Electron microscope studies have shown the presence of needle-like gypsum crystals surrounding the magnetite particles. These crystals interfere with the recovery of magnetite at the magnetic separators.
- Relationship between the pH of the water and the alkali content in the ore. Acid water is produced at mines having raw coal with a low alkali content. Other mines also produce high sulphate concentrations due to pyrites oxidation, but the water is neutral as there is sufficient alkali present in the raw coal to neutralize the acid produced from pyrites.
- Gypsum Over-Saturation Index (OSI – values shown in brackets). The OSI is the most important parameter used as an indication of the likelihood of gypsum scaling. The water in the coal processing plant (1.47), the thickener overflow (1.23) and the neutralization plant (1.07) are over-saturated with respect to gypsum, with the return water from the penstock being the least over-saturated (0.99). The latter can be attributed to the high rate of gypsum crystallization associated with the contact of over-saturated feed with the high surface area afforded by the fine particles.
- The cost of neutralization could be reduced from R0.57/m^3 (1 US$ = SA R8.50, August 2001) to R0.16/m^3 by replacing unslaked lime (acidity = 1000 mg/l, utilization efficiency = 60%, purity = 90%, price = R550/t) with powdered $CaCO_3$ (acidity = 1000 mg/l, utilization efficiency = 90%, purity = 75%, price = R110/t).
- Waste stream separation and treatment. A modelling exercise showed that the capital cost associated with the neutralization and gypsum crystallization of 40 m^3/h discard leachate with an acidity of 11.5 g/l, could be reduced from R10.3 million to R3.0 million by treating streams with high pollution loads separately from streams with low pollution loads. The total volume of the less polluted streams is 3 Ml/d. Only slightly lower gypsum removal is achieved during separate treatment, i.e. 8.9 t/d versus 9.5 t/d for of combined treatment.
- A modelling exercise showed that 30% of the over-saturated fraction in the primary neutralization plant and 60% in the coal processing plant, crystallizes out as gypsum.

- A flow of 210 m^3/h needs to be treated for the removal of sulphate to 350 mg/l in order to obtain an OSI value of 0.98 (less than 1) in the coal processing plant. The capital cost of a biological sulphate removal plant with this capacity is estimated at R11.6 million (R2.3 million/(Ml/d)) and the running cost at R2.54/m^3 (1.00 US $ = R8.50, August 2001).

As a result of these investigations and observations, an integrated process was proposed for the treatment of coal discard leachate, consisting of the following stages (Figures 9.1 and 9.2):

- $CaCO_3$ handling and dosing system
- $CaCO_3$-neutralization stage which includes iron oxidation, precipitation and neutralization
- The treatment approach offers the following benefit: The cheapest alkali, a by-product from the paper industry, is used for neutralization of the acid and for the removal of the bulk of the sulphate concentration through gypsum crystallization.

The purpose of this chapter is to address the following:

- The performance of the full-scale calcium carbonate handling and dosing system.
- Pilot plant evaluation of calcium carbonate neutralization for the treatment of acid leachate.

9.2 MATERIALS AND METHODS

9.2.1 Feedstock

Powdered calcium carbonate, a by-product from the paper industry, was used for neutralization of acid water. It contained 25% moisture and 10% impurities (dry mass) which was mainly silica. Coal discard leachate or a synthetic solution of similar chemical composition was used as feed water for the $CaCO_3$ neutralization stage.

9.2.2 Equipment

The three stages of the integrated process were studied separately. The *$CaCO_3$ - handling and dosing system* (Figures 9.1 and 9.2) was evaluated on the first full-scale plant of its kind. It has a capacity of 23 t/d $CaCO_3$. The plant consists of the following:

A sloped concrete slab onto which the $CaCO_3$ powder is dumped and stored. The $CaCO_3$ powder is slurried with a water jet and collected in a slurry tank through gravity flow.

- Ball valve in the slurry tank to maintain the water level at a specific height.
- $CaCO_3$- recycle slurry pump that withdraws slurried $CaCO_3$ of higher density from the slurry tank or clear water through a water jet onto the $CaCO_3$ dump to maintain a constant $CaCO_3$ concentration. The slurried $CaCO_3$ is returned by gravity via the sloped concrete slab back to the slurry tank. The $CaCO_3$ concentration is controlled by the load cells underneath the slurry tank which activate/stop the recycle pump at preset low/high values.
- Transfer pump, feeding slurried $CaCO_3$ to the neutralization reactor.

Figure 9.1 Limestone handling and dosing system.

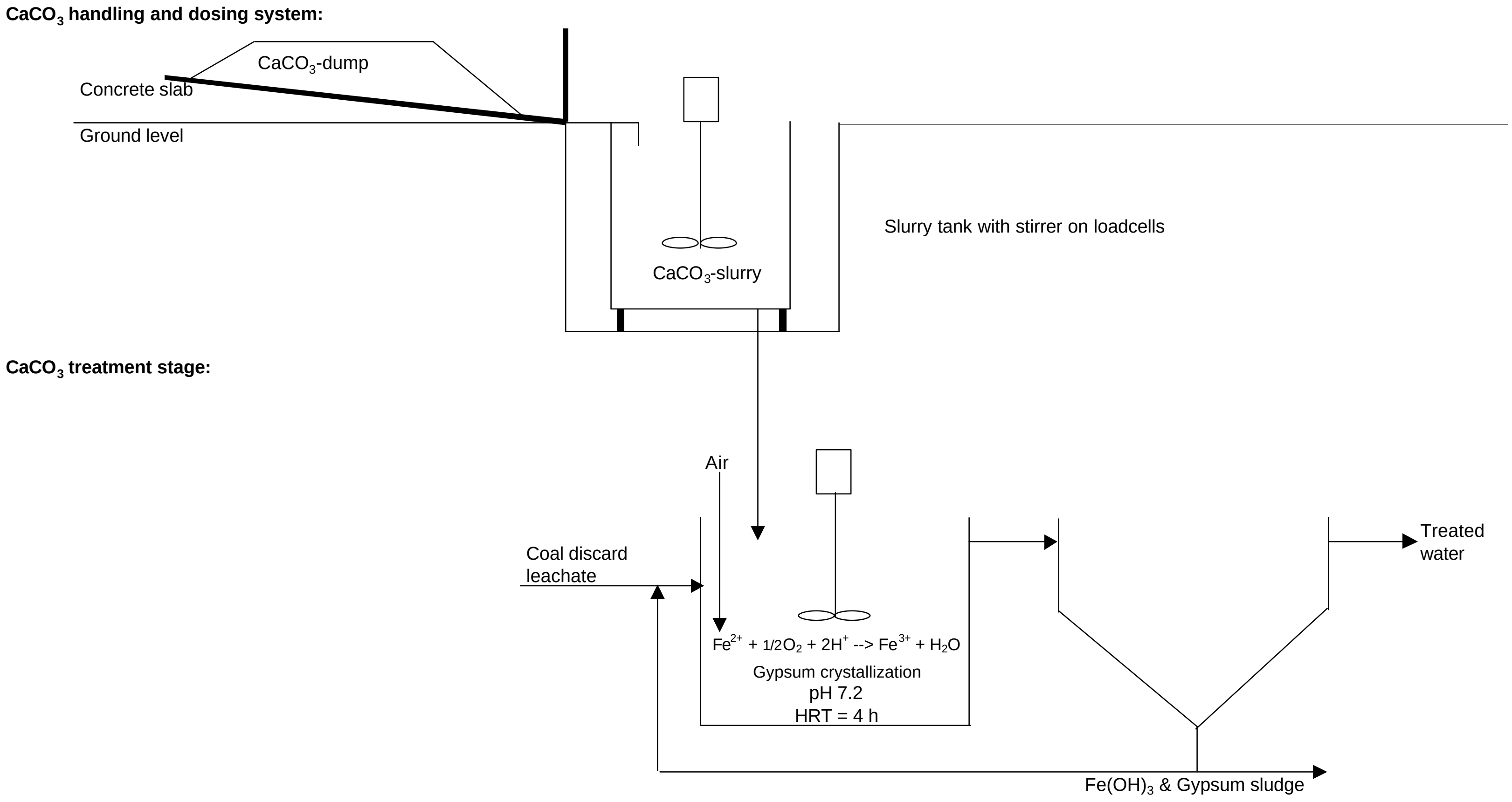


Figure 9.2. **Process flow diagram for the treatment of coal discard leachate**.

The *$CaCO_3$ neutralization stage* consisted of a fluidized-bed reactor and a sludge separator (Table 9.1). Compressed air was used for iron(II) oxidation.

Table 9.1 : Dimensions of $CaCO_3$ neutralization pilot plant.

Parameter	Value	
	Fluidized-bed	Solids separation
Feed rate (l/h)	24	
Recycle rate (l/h)	200	
Diameter (m)	0.20	0.53
Water height (m)	4.99	0.35
Specific surface area (m^2/m^3)	20.2	-
Up-flow velocity (m/h)	6.37	0.91
Residence time (h)	6.53	3.22

9.2.3 Experimental

The performance of the various stages ($CaCO_3$ neutralization, sulphate reduction and H_2S-stripping) was evaluated by determining the chemical composition of the feed and treated water during continuous operation.

9.2.4 Analytical

Samples were collected regularly and filtered through Whatman No 1 filter paper. Sulphate, sulphide, alkalinity, calcium, iron(II), mixed liquor suspended solids (MLSS), volatile suspended solids (VSS), acidity and pH determinations were carried out manually according to procedures described in Standard Methods (APHA, 1985). Calcium was analyzed using atomic absorption spectrophotometry. Acidity was determined by titrating the solution to pH 8.3 using NaOH. The COD samples were pre-treated with a few drops of H_2SO_4 and N_2 to strip off H_2S gas.

9.3 RESULTS AND DISCUSSION

9.3.1 $CaCO_3$ Handling and Dosing System

Acidic water was neutralized effectively when powdered $CaCO_3$ was used. The pH was raised from 2.9 to 6.5, acidity was reduced from 650 to 50 mg/l and iron(II) from 110 to less than 28 mg/l when 20% excess $CaCO_3$ was dosed. Initially problems were experienced with blocked feed and recycle pipelines as a result of grit and stone in the $CaCO_3$. The recycle pipeline problem was solved by installation of a sieve in the slurry tank opposite to the inlet of the recycle pipe. Grit and stones were prevented from entering the feed line by installation of a grit separator. This unit consists of a pipe (diameter = 450 mm, length = 1.2 m) positioned vertically in the reactor with its upper end above the water level. The inlet of the feed pipe was moved from the bottom of the slurry tank to inside this pipe at a level of 800 mm below water level. This arrangement ensured that the up-flow velocity in the unit was high enough (20 m/h) to keep the fine $CaCO_3$ particles in suspension but low enough to allow settlement of all unwanted larger particles (coal, sand, grit and stones) before reaching the inlet of the feed line.

9.3.2 $CaCO_3$ Neutralization of Coal Discard Leachate

Limestone can be used in the integrated process for treatment of acid water. Table 9.2 shows the results obtained when synthetic discard leachate was treated with limestone. The water was neutralized effectively and sulphate was reduced from 8 342 to 1 969 mg/l (as SO_4). It was possible to achieve complete iron(II) oxidation by using only $CaCO_3$ as the neutralization agent. This differs from the standard approach where the pH is raised to 7.2 with lime where the rate of iron(II) oxidation is fast. By using $CaCO_3$, the pH of the water remains at 6 while iron(II) is oxidized.

Table 9.2 : Chemical composition of feed (synthetic discard leachate) and $CaCO_3$ treated water

Parameter	Feed	Treated
pH	1.8	6.6
Acidity (mg/l $CacO_3$)	7 300	100
Sulphate (mg/l SO_4)	8 342	1 969
Ortho phosphate (mg/l P)	2.9	0.0
Chloride (mg/l Cl)	27	30
Iron(II) (mg/l Fe)	2 500	<56
Total iron (mg/l Fe)	2 500	<56

In this investigation it was determined that the rate of iron(II) oxidation is not only influenced by the iron(II) , hydroxide and oxygen concentrations as suggested by Stumm and Lee (1961), but also by the suspended solids concentration as suggested by Maree *et al.* (1998). In order to achieve complete iron(II) oxidation sufficient reaction time was allowed for gypsum crystallization to reach its saturation level (2 h). Aeration and sludge recirculated were applied to maintain a suspended solids concentration at 50 g/l.

9.4 CONCLUSIONS

The following conclusions followed from the investigation:

- Powdered calcium carbonate in a dump can be slurried to a constant density and applied in the treatment of acid water.
- 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).

CHAPTER 10: CONCLUSIONS

The following findings were made during the investigation:

10.1. 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+}/(l.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/(1 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 (1 USD = S.A. R6). 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.

10.2 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 crystallisation, 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/m^3, R2.79/m^3, R1.37/m^3 and R1.95/m^3 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 R1.87 million when limestone is milled on-site.

Design criteria were provided for full-scale application.

10.3 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 neutralize 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 and fluctuation could be contained between pH 7.47 and 7.59 for most of the time. 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 on 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.

Waters high in sulphates are less suitable for treatment with the HDS or Modified HDS processes due to gypsum scaling.

10.4 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 minimised 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 investigation was to investigate the benefits associated with co-disposal of HDS-sludge and coal discard. It is argued that there is little environmental benefit to 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 and to 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 $CaCO_3$) 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 and (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).

10.5 Full-scale Application

A $CaCO_3$ handling and dosing has been developed and demonstrated at 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).

CHAPTER 11: RECOMMENDATIONS

11.1 RECOMMENDATIONS

It has been demonstrated in this investigation that limestone neutralization can be implemented on full-scale and will achieve the following:

- Neutralization of strong or weak acidic solutions using limestone or powder calcium carbonate in the most cost-effective way.
- Removal of metals such as iron(II), iron(III) and aluminium. Metals such as zinc and manganese are not removed during limestone neutralization.
- Partial sulphate removal through gypsum crystallization to the saturation level of gypsum. Sulphate can be removed to between 1 500 and 2 500 mg/l (as SO_4) through gypsum crystallization, depending on the sodium and magnesium concentrations in solution. This value is higher than the 200 to 500 mg/l that is required for discharge into public streams, or to be suitable for drinking water.

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.

CHAPTER 12: REFERENCES

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