

Acid mine drainage treated electrolytically for recovery of hydrogen, iron(II) oxidation and sulphur production

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ABSTRACT

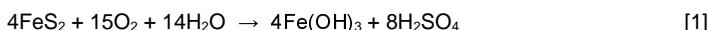
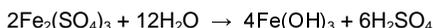
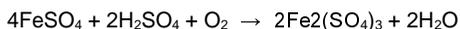
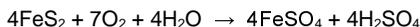
Sulphate rich waters such as acid mine drainage (AMD) contribute directly to the mineralisation and degradation of receiving waters, which pose a serious environmental threat. Several sulphate removal technologies are in place, amongst which the biological sulphate removal technology. For the treatment of these effluents, expensive organic material (e.g. ethanol or sugar) is used as the energy source. The use of hydrogen as an energy source presents a cheaper alternative for sulphate removal. Hydrogen can be generated at the cathode in an electrolytic cell by treating AMD electrolytically. While generating hydrogen electrolytically, other benefits arised, i.e. the oxidation of iron(II) to iron(III) at the anode and the conversion of hydrogen sulphide gas to elemental sulphur.

Stainless Steel (type 304) plate has been used effectively as electrode material in AMD as electrolyte for generating hydrogen in a cost effective way and at the same time oxidising iron(II) to iron(III). When relatively large quantities of hydrogen is needed for the sulphate reducing bacteria (SRB), nickel (Ni) can be used as electrode material in a KOH (3% mass) solution as electrolyte.

The reason for iron(II) to be oxidised to iron(III) is that it forms acid downstream when passing through the process unchanged. Toxicity due to increased levels of sulphide and un-ionised hydrogen sulphide will not only lead to diminished process performance of the SRB but will also become a health and safety hazard.

1. INTRODUCTION

During industrial effluent treatment, it is often found that pH is the single most important parameter, as low pH waters (below 5.5) can be toxic to plant and fish life. Industrial effluents (acid mine drainage) rich in sulphate, acid and metals are produced when pyrite is oxidised due to exposure to the atmosphere, e.g. in the coal mining industry. Barnes¹ indicated that acid is produced biologically when pyrites in coal waste are oxidised, according to the following reactions:



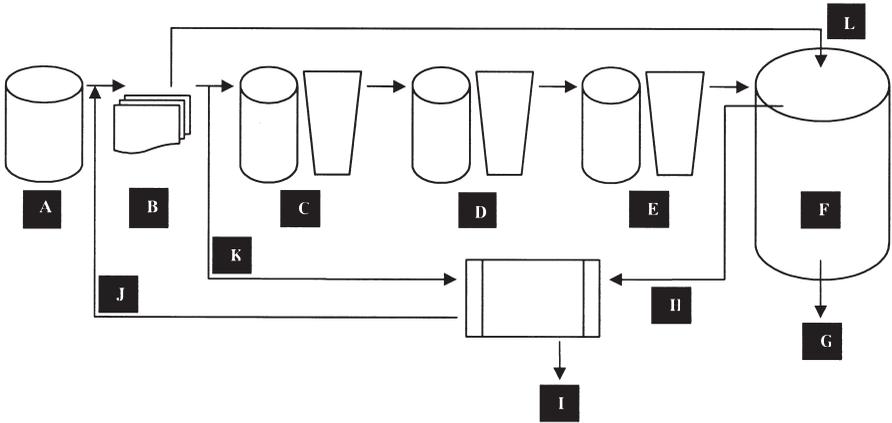
The acid water is formed as a result of bacterial oxidation of pyrites exposed to oxygen and water after or during the mining process. These acid mine waters dissolve high concentrations of metals and can have pH values as low as 1.6. Therefore, it requires treatment prior to discharge into public watercourses.

Assessments of pollution in the Olifants River and its associated surface and geo-hydrological drainage systems, monitored continuously since 1990, identified sulphate, amongst other pollutants, as a consequence of coal mining. Pressure from the legislator is mounting to demand from polluters to enforce the National Water Act to treat acid mine drainage and in particular to reduce sulphate concentrations to a level acceptable to water users. This tendency is experienced globally and is likely to be reflected in a commitment for continuous improvement that companies with ISO 14001 certification will be required to make.

These low pH effluents, rich in sulphate and metals can be treated with the *Integrated Limestone/Lime Process* which was developed by the CSIR. During this treatment, the effluent can be fully neutralised and sulphates can be reduced to the saturation level of gypsum, i.e. 1 200 mg/ℓ. Prior to this process, the iron(II) content in the water should be oxidised to iron(III) before neutralisation of the acid water with limestone. Oxidation will otherwise occur downstream of the neutralisation plant with the formation of acid. Oxidation of the iron(II) also influences the neutralisation rate of AMD greatly, as a Fe(OH)₃ coating is formed onto the limestone particles and prevents its dissolution. Magnesium can also be fully removed from the effluent. To further remove sulphates in the effluent to levels lower than 200 mg/ℓ, the Biological Sulphate Removal Process, also developed by CSIR, can be utilised.

During the Biological Sulphate Removal Process, hydrogen sulphide gas is produced as a by-product that can be completely converted to elemental sulphur. Normally, in bioreactors fed with an influent containing methanol, sulphite, and sulphate, inhibition may result from high concentrations of substrates or possible intermediates and products such as acetate and sulphide. Sulphate reduction results in production of hydrogen sulphide gas (H₂S) and needs to be removed for reasons of health and safety. H₂S becomes progressively more dangerous as the level of H₂S incurs above toxic limits (70 ppm), becoming lethal at 600 ppm.

The two above-mentioned CSIR processes, combined with the electrolytic process and sulphur production process, as discussed in this paper, are illustrated in Figure 1.



A	Acid mine drainage (AMD) as effluent	pH 1.6	8 400 mg/ℓ SO ₄	310 mg/ℓ Mg	4 245 mg/ℓ Fe(II)
B	Electrolytic iron(II) oxidation	pH 1.6	8 400 mg/ℓ SO ₄	310 mg/ℓ Mg	279 mg/ℓ Fe(II)
C	Limestone neutralisation	pH 6.8	1 900 mg/ℓ SO ₄	290 mg/ℓ Mg	-
D	Gypsum crystallisation (lime treated)	pH 13.8	1 180 mg/ℓ SO ₄	0 mg/ℓ Mg	-
E	CO ₂ treatment for CaCO ₃ precipitation	pH 8.5	1 250 mg/ℓ SO ₄	0 mg/ℓ Mg	-
F	Biological Sulphate Removal				
G	Biologically treated water	pH 8.0	< 200 mg/ℓ SO ₄	-	-
H	H ₂ S gas stripped				
I	H ₂ S conversion to elemental sulphur				
J	Iron(II) rich water				
K	Iron(III) rich water				
L	Hydrogen gas				

Figure 1. Schematic diagram of combined process of all technologies, as developed by CSIR

The use of hydrogen as energy source in the biological sulphate removal technology has been shown to be successful by several researchers^{2,3} and it has been shown that sulphate reducing bacteria has the advantage over methanogenic bacteria when hydrogen is used⁴. Therefore, an alternative option to the use of ethanol or sugar as energy source is the exploitation of the AMD as source of hydrogen for bacterial proliferation. In an earlier attempt of the CSIR, hydrogen was found to be a good source of energy to sulphate reducing bacteria for sulphate removal. A removal rate of 4.42 g SO₄/ℓ.day was achieved at a reactor pH of 7.5 – 8.

Hydrogen is considered to be an ideal future energy carrier because it is a potential energy source and pollution free. The benefits of using hydrogen as energy source to the biological process are:

- Hydrogen can be produced electrolytically to be used as energy source for anaerobic bacteria in a biological sulphate removal process.
- By using hydrogen instead of sugar and ethanol as energy source to these bacteria, no residual organic material is left in the water that requires post-treatment.
- Resulted heat in the electrolytic cell can be utilised to raise the temperature to 30°C which is the optimum temperature for the anaerobic bacteria.

According to Prigent & Martin⁵, one of the most promising methods for the production of hydrogen is water electrolysis. Catalyst-activated (platinum group metal oxide) electrodes can be used for e.g. water electrolysis in the presence of an aqueous alkaline electrolyte, or more generally in any electrolysis process operated in aqueous alkaline medium. These electrodes are more particularly adopted to be used as negative electrodes (cathodes) for hydrogen release; they can also be used as positive electrodes (anodes) for oxygen release.

Various catalytic materials for use as electrolytic cell anodes have been proposed. Stainless steel (Ssteel) and nickel plated steel anodes have been most commonly commercially used. Other anode materials which exclude noble metals have been proposed, but it appears that such materials do not improve the overall anode performance in terms of overvoltage savings, material costs and operating life since such prior art anodes have not been accepted to any significant degree. One reason nickel and nickel plated steel catalytic materials have been most commonly used for the electrolysis of water is because of their relatively low costs. Ovshinsky *et al.*⁶ found that these materials are resistant to corrosion in hot concentrated caustic solutions and has one of the lowest over voltages among the non-noble metal materials for the oxygen evolution reaction.

The purpose of this investigation was to prove that hydrogen can be generated electrolytically from AMD to be utilised as an alternative energy source for sulphate reducing bacteria. The scope included (1) test work on different electrode/electrolyte combinations, and (2) other benefits that arose from the use of electrolysis to produce hydrogen, i.e. iron(II) oxidation and the conversion of hydrogen sulphide gas to elemental sulphur.

2. MATERIALS AND METHODS

2.1 FEED WATER

The following solutions were tested as electrolytic solutions for the different electrochemical systems: KOH (3% and 30% mass) and AMD as acidic effluent. The chemical composition of the AMD (originated from a Coal Mine near Witbank, Mpumalanga) is listed in Table I. The KOH was a bank reagent from Saarchem.

Table 1. Chemical composition of acid mine drainage (AMD)

Parameter	Acid feed water
pH	2.48
SO ₄ ²⁻ (mg/l)	9 150
Acidity (mg/l)	10 100
Ca (mg/l)	434
Mg (mg/l)	301
Al (mg/l)	556
Na (mg/l)	22.8

2.2 PROGRAMME FOR BATCH STUDIES IN BEAKERS AND CONTINUOUS STUDIES ON PILOT SCALE

Batch studies were conducted in the laboratory by using various types of materials as electrodes, in the form of plate. In each set-up, the electrolytic solution was recycled and monitored on a 30 minute basis for pH, conductivity, acidity and iron(II) concentration. The electric current, potential and flow rate of gas evolving from the electrodes (anode and cathode) were monitored on the same basis. The weights of the electrodes (anode and cathode) were determined before and after each experiment. The same variables as for batch studies were measured during continuous studies. Parameters that were also varied and tested in order to evaluate additional benefits that resulted from generating hydrogen electrolytically, are current density, pH, iron(II) concentration, Mn concentration and amount of sulphur produced.

2.3 EQUIPMENT AND PROCEDURE

A complete cell with plate metal as electrodes and an *Ionac MA3475* anion selective membrane (nano-filtration membrane) as diaphragm, were used for laboratory scale testing (see Figure 2). The membrane was used to separate the electrodes (anode from cathode) to ensure no contamination of the hydrogen with oxygen, generated at the cathode and anode respectively. Mild steel (Fe), zinc (Zn), nickel (Ni) and stainless steel (Ssteel) were used as electrode material. For laboratory tests, the electrodes were 1 dm² (10cmx10cm) each while for the pilot scale plant, the electrodes were scaled up by 30 times (70cmx40cm). Both the laboratory and pilot scale cell were constructed of Perspex frames that are bolted together and sealed off with rubber strips and silicon.

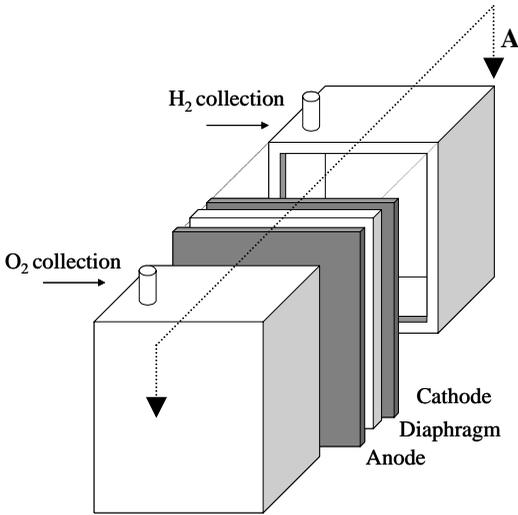
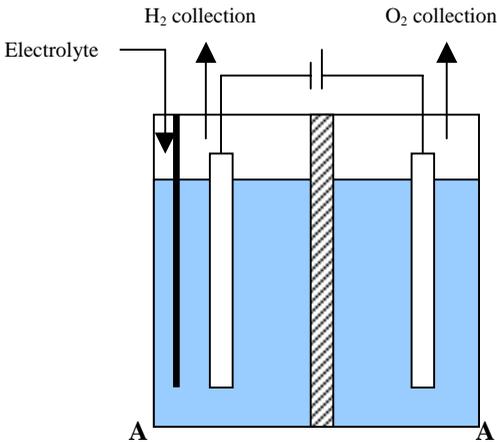


Figure 2. Illustration of electrolytic cell design for the dissociation of water



In each set-up for the laboratory studies, the electrolytic solution was 1.5 litres on both the cathode's and anode's side and was recycled through the electrolytic set-up for the duration of the experiment.

Six combinations of electrodes and electrolytes were grouped into three categories according to their expected outcome. In order to determine the electrochemical efficiency and stability of these combinations for hydrogen production, they were subjected to different analyses. Table II contains the six different electrolytic combinations that were tested.

Table II The six different electrolytic set-ups for testing

Electrode	Fe plate	Zn plate	Ni plate	Ni plate	Ni plate	SSteel plate
Electrolyte	AMD	AMD	KOH (30%)	KOH (3%)	AMD	AMD
Category	A		B		C	

A constant current was applied to the electrodes and the resulting potential between the electrodes, because of the resistance of the electrodes, was measured with 30-minute intervals between measurements. The variables listed in section 2.2 were all measured at these intervals.

2.4 ANALYTICAL

Samples were collected every 30 minutes for analysis. A Hewlett Packard power supply unit (0 - 60 V, 0 - 15 A) was linked to the cell set-up. A conductivity meter (WTW - LF318) was used for measuring conductivity while the power supply unit digitally displayed the electric current and cell potential. Schlumberger flow meters were used for measuring the amount of hydrogen and oxygen gas, generated at the cathodes and anodes respectively.

3. RESULTS AND DISCUSSION

3.1 ELECTROCHEMICAL PROPERTIES OF SIX DIFFERENT SYSTEMS

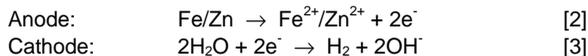
The volt-ampereometric results for the six hydrogen production systems, as tested, are listed in Table III. The amount of hydrogen gas generated was determined on a pure basis (>99%), based on gas chromatographic results from the SABS where the gas samples were analysed for hydrogen purity.

Table III Volt-ampereometric results of hydrogen production versus electrode consumption

Electrolytic Combination	Category	pH _{cathode}	pH _{anode}	Current (ampere)	Potential (volt)	H ₂ prod (ℓ.hr ⁻¹)	O ₂ prod (ℓ.hr ⁻¹)	Electrode Consumption (g.ℓ ⁻¹ H ₂ prod)	Membrane
Fe+AMD	A	3.26	3.26	5	32	2.15	√	2.43	Anionic
Zn+AMD	A	3.13	3.13	5	38	2.33	√	3.53	Anionic
* Ni+30%KOH	B	13.78	13.83	5	3.8	2.43	√	0.00	Anionic
* Ni+3%KOH	B	13.49	13.53	5	6	2.50	√	0.00	Anionic
Ni-plate+AMD	C	3.49	3.49	5	6	4.00	√	0.00	Anionic
Ssteel+AMD	C	2.44	2.45	2	4.3	1.68	√	0.00	Anionic
Ssteel+AMD	C	2.45	2.45	1	3.7	0.72	√	0.00	Anionic

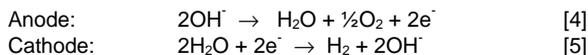
* KOH concentration not yet optimised for maximum hydrogen production

In category A, hydrogen was produced at the cathode while the anode started to dissolve due to the anodic reaction. The main reactions are given by:



Although hydrogen was generated at a fairly high rate at the cathode by using Fe/Zn electrodes, the potential became increasingly high due to the decreasing surface area that resulted in a much higher resistance and electrode inhibition by electrode products. For every litre of hydrogen produced, 1.13 gram of Fe or 1.52 gram of Zn is needed. The costly effect of the sacrificial nature of Fe/Zn in AMD will be presented in section 3.4.

In category B, hydrogen was generated at the cathode while oxygen was generated at the anode. Not only was hydrogen produced at a higher rate and at an almost ten times smaller potential, but the electrodes were totally unaffected by the KOH used as electrolyte. The amount of gas production can be increased by increasing the current density. This will, however result in an increase in production cost as the voltage will also increase. The reactions at the anode and cathode can be given as:



After 72 hours of running the set-up continuously, the diaphragm developed micro-holes as a result of the caustic nature of the KOH (30%). This phenomenon however abated when a more diluted solution of KOH (3%) was used.

From the volt-amperometric results in category C, fairly high volumes of hydrogen can be generated, using AMD as electrolytic medium. The electrodes (Ni and Stainless Steel) and membrane were totally unaffected by the AMD that was used as electrolytic medium. It has been proved that the higher the current density, the higher is the amount of gas that is generated electrolytically. This also results in an increase in production cost as a result of higher voltages. The membrane was unaffected by the AMD.

3.2 EXTENT OF IRON(II) OXIDATION

One of the main benefits that resulted from the use of electrolysis in order to generate hydrogen economically, was the oxidation of iron(II) at the anode in using stainless steel as electrode material in AMD as electrolytic medium. This means that, while producing hydrogen, iron(II) oxidation as a pre-treatment stage to AMD can be applied. The half-cell reactions for the stainless steel/AMD cell are illustrated by:

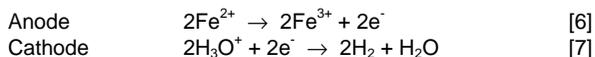


Figure 3 illustrates the relevant reactions at the anode and cathode. The oxidation of iron(II) to Fe(III) can be proved by the transparent, ocher coloured AMD that was transformed to a dark brown solution. Precipitates that formed from these solutions, onto the anode, were analysed by means of Mössbauer spectroscopy. Signatures of β -FeOOH (akaganeite) were quite distinct in these spectra and appears to have evolved partially to α -FeOOH (goethite).

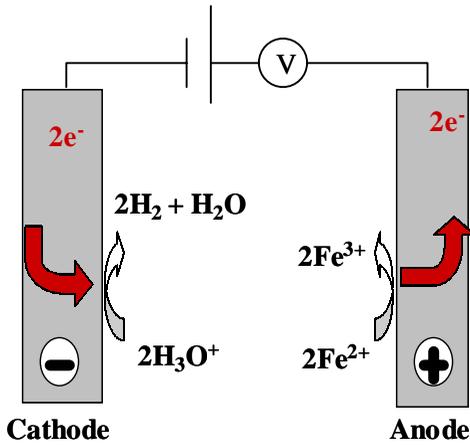
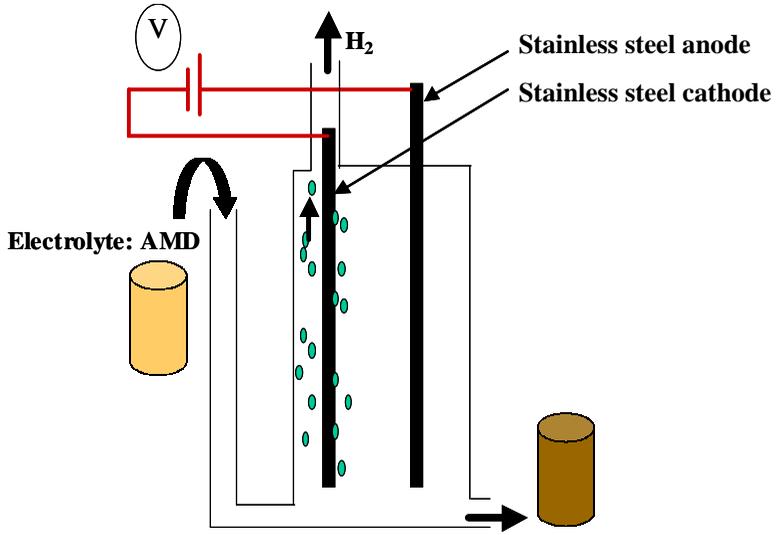


Figure 3. Illustration of electrolytic set-up: stainless steel electrodes in AMD

The oxidation of iron(II) is illustrated in Figure 4 over a period of 55 minutes.

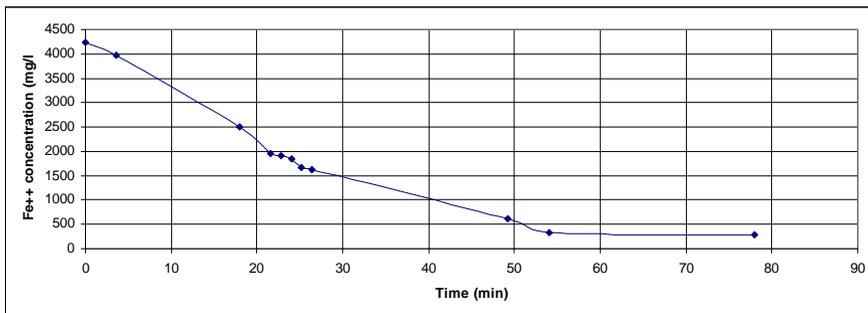


Figure 4. Iron(II) oxidation of AMD using stainless steel electrodes

In the CSIR’s integrated limestone/lime process for neutralisation and partial sulphate removal⁷, calcium carbonate is used to precipitate iron and sulphates. Due to the fact that iron(II) stays in solution up to a pH of 7, it is beneficial to convert iron(II) to iron(III), which will precipitate at pH 3. As stated earlier, iron(II) also readily coats the carbonate particles which slows down the neutralisation reaction significantly. Calcium carbonate can lift the pH of the solution to around 6 after which calcium oxide is dosed to increase the pH to above 10. As calcium carbonate is much cheaper than calcium oxide, the decreased amount of oxide needed with regards to the oxidised iron(II) incurs a cost benefit. From Figure 4 it is clear that the iron(II) in the water can be oxidised by 50% in 18 minutes’ time while it will be fully oxidised after 53 minutes.

An increase in acidity (8 400 mg/ℓ to 11 200 mg/ℓ) resulted from oxidation of the iron(II) (4 245 mg/ℓ iron(II) to 279 mg/ℓ iron(II)). During oxidation, the pH also dropped from 3.10 to 2.65. This drop in pH and increase in acidity can be ascribed to the higher oxidation state of the iron ion (iron(II) to iron(III)). These results are illustrated in Table IV.

Table IV Electrolyte characteristics (stainless steel in AMD)

Time (hours)	pH	Iron(II) (mg/ℓ)	Acidity (mg/ℓ)
0	3.10	4 245	8 400
3	2.97	3 965	8 800
15	2.88	2 513	8 100
18	2.65	1 955	9 700
19	2.79	1 899	10 200
20	2.83	1 843	11 700
21	2.85	1 676	11 200
22	2.86	1 620	11 000
41	2.83	614	11 000
45	2.82	335	11 200
65	2.79	279	11 200

The effect of various other parameters on the rate of oxidation, as illustrated in Figures 5 to 8, have been tested.

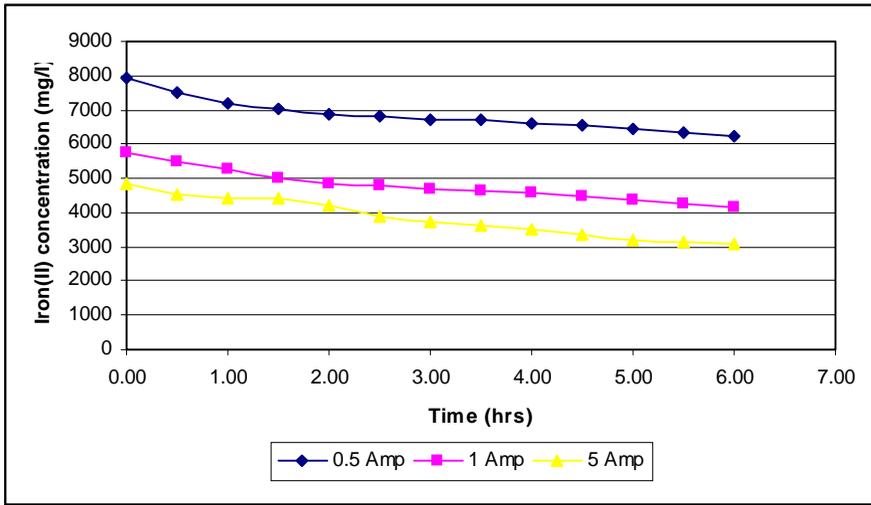


Figure 5. Effect of current density on the rate of iron(II) oxidation

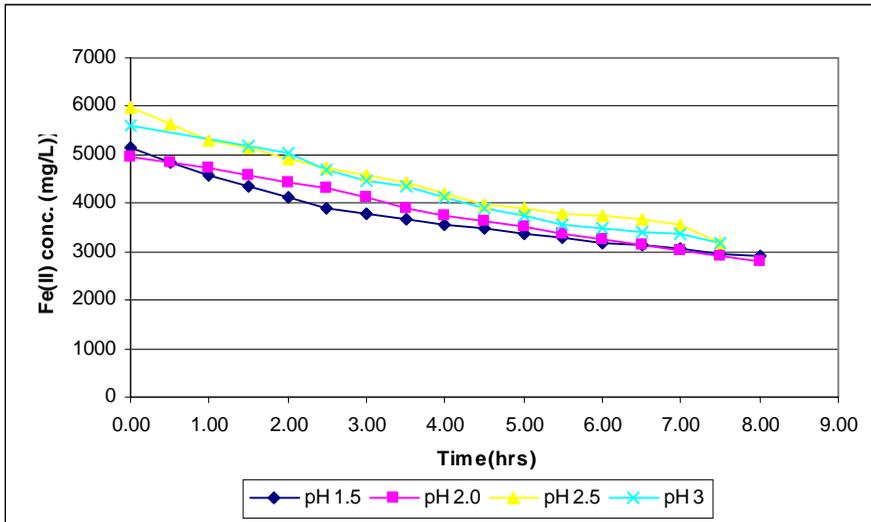


Figure 6. Effect of pH on the rate of iron(II) oxidation

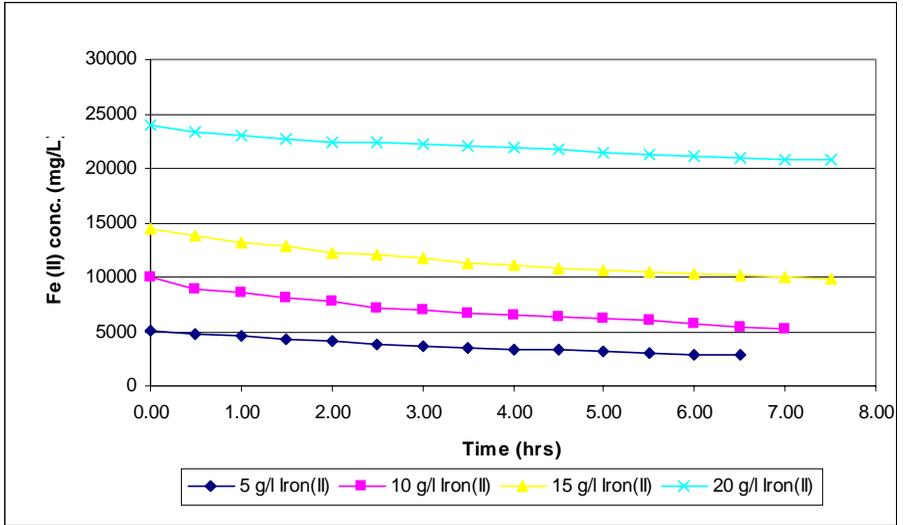


Figure 7. Effect of initial iron(II) concentration on the rate of iron(II) oxidation

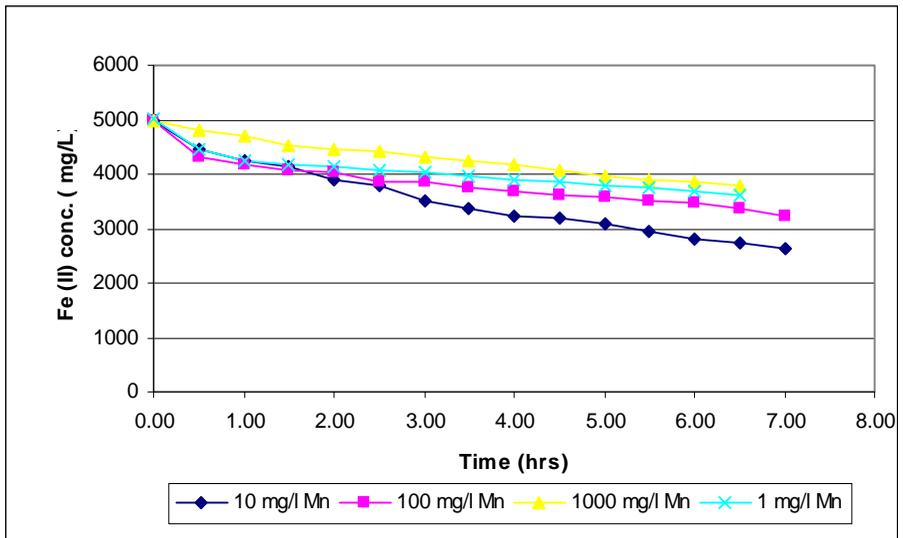


Figure 8. Effect of Mn concentration on the rate of iron(II) oxidation

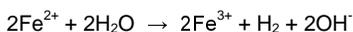
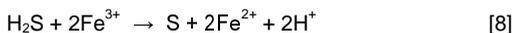
From Figures 5 to 7, it is clear that the current density, pH and initial Iron(II) concentration had no effect on the rate of oxidation. The Mn concentration in the AMD as electrolytic

solution, however reached an optimum at 10 g/l of Mn, resulting in the highest oxidation rate for iron(II).

3.3 CONVERSION OF HYDROGEN SULPHIDE TO ELEMENTAL SULPHUR

The presence of sulphide, produced as a waste product after the Biological Sulphate Removal Process, may affect the sulphate reducing bacteria (SRB) in several ways. Because of its detrimental characteristics, it is forbidden to drain sulphide containing effluents to sewer pipes or surface waters. Since a number of physicochemical methods require large investment and operational costs, e.g. high temperatures, high pressures or special chemicals, the continuing search for more economical methods has led to partly investigating this issue of purifying H₂S.

The oxidation of the iron(II)-rich effluent (AMD) as a pre-treatment stage prior to limestone/lime neutralisation, produced an iron(III)-rich water that can be reduced back to iron(II) by contacting it with the waste product, H₂S of the biologically stage, as illustrated by reactions 8 and 9. The result of reactions 6 and 7, combined with reaction 8, proves the production of sulphur from H₂S gas and illustrated in reaction 9.



A major advantage of this new process is that a potentially valuable end-product is produced without large cost implications. No additional energy, e.g. pressure or temperature, needs to be applied. The produced iron(II)-rich water can now be recycled back to the oxidation stage for re-use in the production of hydrogen. During an experiment, it has been found that at a specific pH of 2.5, the maximum amount of sulphur can be produced from the H₂S gas, and is illustrated in Photo 1. Table V contains the values for the amount of sulphur, produced per litre of iron(III)-rich water, when contacted with the stripped H₂S gas.

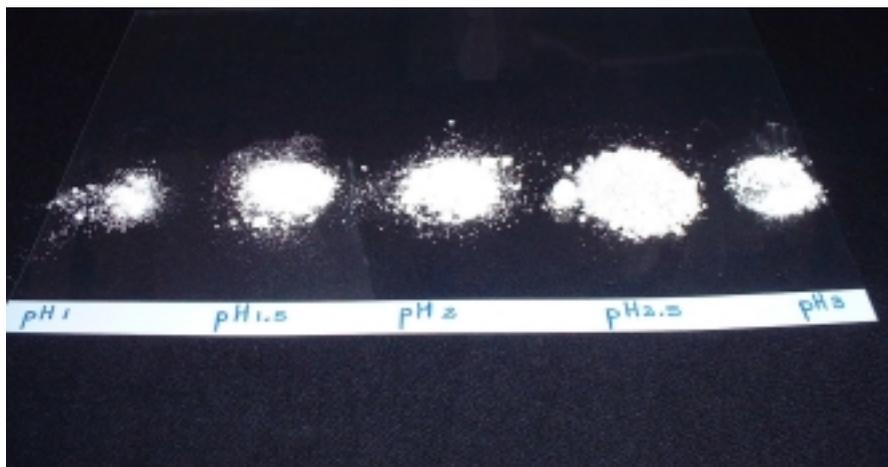


Photo 1 Effect of pH on the amount of sulphur produced when contacting iron(III)-rich water with stripped H₂S gas

Table V Amount of sulphur, produced per litre of iron(III)-rich water, when contacted with the stripped H₂S gas

pH	1.0	1.5	2.0	2.5	3.0
Mass S produced (g)	0.014	0.122	0.217	1.565	0.089

3.4 COST ANALYSIS

No mass lost occurred when stainless steel (Ssteel) electrodes were used, proving that the electrodes are resistant to corrosion. With AMD (which is a waste product) served as electrolyte, the iron content in the AMD served as a reducing agent and therefore limited amount of oxygen was produced. Stainless steel in AMD as electrolytic medium was found to be the cheapest way of generating hydrogen electrolytically and was therefore used as benchmark to calculate the cost efficiency of the other possible electrolytic set-ups. The electrolytic production cost of hydrogen is mainly influenced by the voltage in the electrolytic cell which is directly related to the resistance in the cell set-up, and the cost of electricity. The costing values are listed in Table VI.

Table VI Electrolytic hydrogen production cost

Electrode/Electrolyte	Cost of H ₂ generated (R/kg)	Percentage of H ₂ cost (Ssteel plate as 100)
H ₂ bought commercially	25.00	207
Fe plate / AMD	138.84	1 159
Zn plate / AMD	151.94	1 268
Ni plate / KOH (30%)	14.57	122
Ni plate / KOH (3%)	22.39	187
Ni plate / AMD (5Amp)	21.20	177
Ssteel plate / AMD (2Amp)	11.98	100
Ssteel plate / AMD (1Amp)	11.98	100

From the cost analysis, as listed in Table V, it can be noted that iron(II) oxidation is an excellent benefit added to the electrolytic production of hydrogen. It will however not produce enough hydrogen as energy source to the sulphate reducing bacteria to remove all the sulphates in the water that needs to be treated biologically. For example, an AMD stream containing 4 580 mg/l iron(II) and 9 150 mg/l SO₄²⁻ (see Table I) would only be able to deliver 0.08 mole/l of hydrogen which is only enough bacterial energy to reduce 2 000 mg/l SO₄²⁻. The combination of nickel (Ni) electrodes in an electrolytic medium of KOH (30%) will therefore be an economically alternative way of producing extra hydrogen electrolytically to remove sulphate concentrations higher than 2 000 mg/l.

4. CONCLUSIONS

- Hydrogen can be produced electrolytically, 52% cheaper than buying it in bulk commercially. Stainless steel electrodes in acid mine drainage as electrolytic medium were found to be the most cost effective way to generate hydrogen electrolytically. The use of a membrane has the advantage that the purity of this hydrogen will be of such a standard that it can be used as energy source to sulphate reducing bacteria in a biological sulphate removal process.
- If higher volumes of hydrogen is needed, it can be generated 42% cheaper than buying it from industry, making use of nickel electrodes in an electrolytic medium of KOH (30%).
- One major benefit in the generation of hydrogen electrolytically by means of stainless steel electrodes in AMD was the oxidation of iron(II) to iron(III). This reaction is beneficial to the downstream processes as iron(II) precipitates at a lower pH than iron(III) and will not form acid further down in the process. During neutralisation, the formation of an Fe(OH)₃ layer onto the calcium carbonate particles affects the dissolution rate of the calcium carbonate negatively which will have a direct effect on the rate of neutralisation. It is therefore vital to assure oxidation of iron(II) in AMD as pre-treatment to neutralisation of the effluent by means of limestone and lime.
- After the AMD has been treated biologically to remove the sulphates to below 200 mg/l, unwanted and toxic H₂S gas was produced as waste product. An alternative way of treating this gas economically had been developed by contacting the H₂S gas with part of the iron(III)-rich effluent, resulted from electrolytic oxidation of iron(II) as pre-treatment to neutralisation. This resulted in a low cost and uncomplicated conversion of H₂S gas to a valuable end-product, i.e. elemental sulphur.

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