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Task 6.9.2
Treatment of Sulphate Rich Effluents with the Combined Electrolytic/Biological Process

by

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Table of Contents

List of Figures

Part 1

Part 2

List of Tables

PART 1

PART 2

Glossary of Abbreviations, Symbols, Terms & Definitions

AMD - Acid Mine Drainage
E - potential (V)
EC - EcoDose Process
F - Faraday constant (96 000 coulomb/mole/sec)
Fe - Iron
h - hour
I - electrical current (A)
m - mass of electrode (g)
Ni - Nickel
η - charge transfer resistance
ppm - parts per million
sec - second
Ssteel - Stainless steel
SRB - Sulphate Reducing Bacteria
V - electromotive force (V)
Z - valence
Zn - Zinc

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Part 1

An Electrolytic Process for the Production of Hydrogen by means of Water Electrolysis

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 have been developed, amongst which the biological sulphate removal process. For the treatment of AMD, 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 and pre-treatment of the effluent (AMD that is rich in iron(II)) is also achieved via iron(II) oxidation. By using hydrogen instead of organic energy sources, no residual organic material is left behind that would require post-treatment. Stainless steel (type 304) plate can be used effectively as electrode in AMD as electrolyte for generating hydrogen in a cost effective way and at the same time oxidising Fe(II) to Fe(III). When relatively large quantities of hydrogen are needed, nickel (Ni) can be used as electrode material in a KOH (3% mass) solution as electrolyte can be used for electrochemical generation of hydrogen.

1. Introduction

1.1 Background

Industrial effluents rich in sulphate, acid and metals are produced when sulphuric acid is used as a raw material, and when pyrite (associated with coal deposits) is oxidized due to exposure to the atmosphere, e.g. in the mining industry. Acid mine waters contain high concentrations of dissolved metals and sulphate, and can have pH values as low as 1,6. Acidic industrial effluents require treatment prior to discharge into public water sources. 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 on the regulator 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.

Hydrogen is considered to be an ideal future energy source because it is a potential energy source and pollution free. This prompted the adaptation of the existing EcoDose Process to a process that is based on the exact same principles, but focussed on hydrogen generation. The benefits of using hydrogen as energy source to the biological process are:

1. Hydrogen can be produced electrolytically for use as energy for biological sulphate removal. By using hydrogen instead of sugar and ethanol, no residual organic material is left in the water that requires post-treatment.
2. Resistive heat is produced which will raise the temperature to 30°C, which is the optimum temperature for the biological process.
3. The combined process, EcoDose / Biological sulphate removal has the following benefits and synergies:

Sulphate reducing bacteria (SRB)	EcoDose Process (EC)
The SRB needs hydrogen	The EC produces hydrogen
The SRB needs reduction	The EC process produces Fe-reduction
The SRB needs heat energy	The EC produces resistive heat

One of the most promising methods for production of hydrogen is water electrolysis. The electrolysis of water is also called the dissociation of water and is characterised by the following two equations. These equations are also illustrated in Figure 1.1:

Reduction of water (Cathode): $4H_2O + 4e^- \rightarrow H_2 + 2OH^-$ [1]

Oxidation of water (Anode): $2H_2O \rightarrow H^+ + O_2 + 4e^-$ [2]

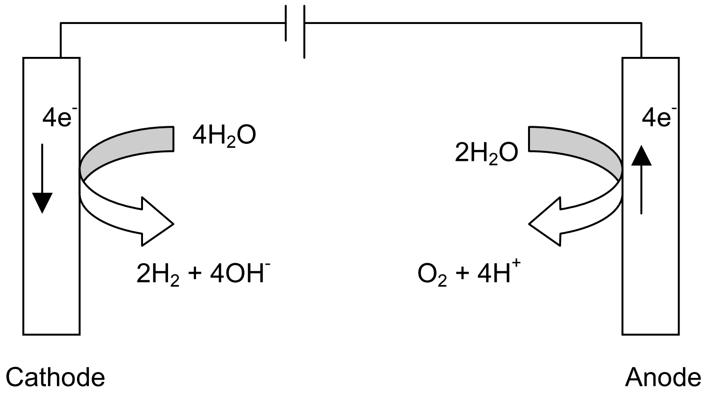

Figure 1.1: Illustration of the dissociation of water

Catalytically activated 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 adapted to be used as negative electrodes (cathodes) for hydrogen release; they can also be used as positive electrodes (anodes) for oxygen release (Prigent & Martin, 1982).

In an electrolysis apparatus, a medium (electrolyte) is electrolytically decomposed by applying a supply voltage between an anode and a cathode. If water is used as the medium, hydrogen and oxygen are thereby produced. For the use of an electrolysis apparatus as a hydrogen generator in the industrial sector, it is necessary for its production capacity to be designed to meet the basic hydrogen requirement (Hu, 2000).

Various catalytic materials for use as electrolytic cell anodes have been proposed. Nickel (Ni) 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. Another reason is 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 (Ovshinsky *et al.,* 1985).

The cost of water electrolysis is equal to the energy cost and cost of investment. The energy cost (operating cost) consists mainly of the energy consumption. The investment cost consists of the electrode material, electrode area, reactor reticulation and hardware to transfer fluids. To keep cost to a minimum, the cell voltage should be reduced to a minimum. This can be done by increasing the electrode area. The cell potential (E_{cell}) is a function of the cell resistance (R) and the charge transfer resistance (η) which is illustrated in Equation 3:

$$E_{cell} = (E_{anode} - E_{cathode}) + \eta_{anode} + \eta_{cathode} + RI \qquad [3]$$

The cell resistance depends on:

- The electrolyte
- The temperature (a higher temperature will produce a lower cell potential)
  log(1/delta V) = 1/T
- The distance between the electrodes should be a minimum for the ions not to travel to far (implies minimum electrical resistance). The charge transfer resistance "η" should also be low for cost reduction (that is the reason why Pt is such a popular choice as electrode → low η). The charge transfer resistance is determined by:
  - The electrode material (electrode property)
  - The preparation procedure (electrode property)
  - The current density (process parameter)

1.2 Generic scope of investigation

The EcoDose-system is an electrochemical treatment process designed to treat various effluents contaminated with diverse pollutants at different levels of contamination. The project was funded and executed jointly by the WRC, Eskom and Anglo Coal.

The EcoDose effluent treatment process doses an electrical current via suitable electrodes, through an electrolyte which is constituted by the effluent. These metal electrodes release electrode products, such as electrons, cations and hydroxyl anions in the particular effluent. These electrode products can be selected and engineered to precipitate contaminants from the effluents, neutralise the effluent and render the effluent less obnoxious. Essentially an electrical current (electrons = coulombic charge) is thus used as a reagent to complex, precipitate, demineralise, neutralise or manipulate an effluent quality to more acceptable, less polluting qualities.

Hydrogen was found to be one of the by-products of the EcoDose Process. The EcoDose Process was therefore altered to a process with the main focus on the generation of hydrogen cheaper than purchasing it in bulk from industry. This new process will be a process where the electrodes are not consumed during the process, i.e. the electrodes do not take part in the process in order to save on running costs.

1.3 Research protocol

- The theory as set out in the introduction requires the balancing of a flow of electrons (electricity) with a flow of H^+ (in the effluent).
- It is indicated that it is possible to produce hydrogen gas economically from such an electrochemical arrangement.
- The route that was investigated to produce hydrogen was in a separate reactor and dosing it to the SRB in the Biological reactor.

The purpose of this investigation is to prove that hydrogen is a valid economic alternate energy source for sulphate reducing bacteria. The scope will include (1) test work on different electrode/electrolyte combinations in order to determine the electrolytic stability and efficiency of these combinations and to study the specific electrode reactions and (2) the possibility of other benefits that arise from the use of electrolysis to produce hydrogen. All these elements will be factored together and an optimum combination for the economically viable production of hydrogen will be proposed. All these elements will be factored together and an optimum combination of electrode/electrolyte for the most economical way of producing hydrogen will be proposed.

1.4 Guidelines for investigation.

The following aspects will indicate the initial, very basic guidelines for the research project.

- The production and dosing of hydrogen gas outside the SRB reactor might have the advantage of not using sacrificial electrodes which might not be necessary in this case.
- The generation of only hydrogen gas with no deleterious (other) effluents will thus have to be considered
- The cheapest non-replaceable electrodes and effluents will reduce running costs of the electrolytic production of hydrogen to a minimum.

2 Materials and Methods

2.1 Feed Water

The following solutions were tested as electrolyte(s) for the different electrochemical systems: KOH (3% and 30% mass), acid mine drainage (AMD) and hydrated lime ($Ca(OH)_2$). The chemical composition of the AMD (originating from a Coal Mine near Witbank, Mpumalanga) and hydrated lime are listed in Tables 2.1.(1) and 2.1.(2) respectively. The KOH was a shelf reagent from Saarchem.

Table 2.I.(1): Chemical composition of acid mine drainage (AMD)

Parameter	AMD
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
Fe(II) (mg/ℓ)	4 580

Table 2.I.(2): Chemical composition of powder lime ($Ca(OH)_2$)

Bulk density (kg/m^3)	Available $Ca(OH)_2$ (min %)	Available CaO (min %)	Total CaO (min%)	MgO (max%)	Al_2O_3 + Fe_2O_3 (max %)	SiO_2 (max %)	Acid insolubles (max %)
560	94	71	72	1	0,3	0,5	1

Particle size: Fine powder, 100% passing 90 micron

2.2 Programme for Batch Studies in Beakers and Continuous Studies on Pilot Scale

Batch studies were conducted in the laboratory by using various combinations of electrodes (plate or mesh) with electrolytic solutions in order to determine the most economically viable combination for generating hydrogen as energy source to the SRB in the Biological Sulphate Removal Process. In each electrolytic laboratory configuration, the electrolytic solution was recycled and monitored on an hourly basis for pH, conductivity, acidity and Fe(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.

2.3 Equipment and Procedure

A complete cell with plate/mesh metal as electrodes and an *Ionac MA3475* anion selective membrane (nano-filtration membrane) as diaphragm, was used for laboratory scale testing (see Figure 2.3.(1) and Figure 2.3(2)). A diaphragm was used to separate the electrodes (anodes from cathodes) 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 dm^2 (10 cm x 10 cm) each while for the pilot scale plant (see Figure 2.3.(3)), the electrodes were scaled up by 30 times (70 cm x 40 cm). The cells (laboratory and pilot scale) were constructed of Perspex frames that are bolted together and sealed off with rubber strips and silicon.

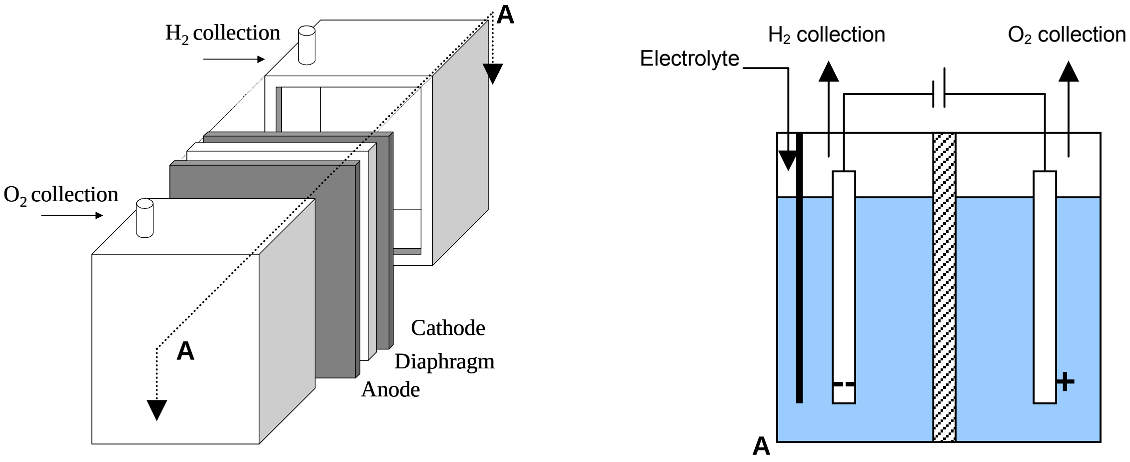

Figure 2.3.(1): ***Illustration of electrolytic cell design for the dissociation of water***

Figure 2.3.(2): ***Electrolytic cell for dissociation of water on laboratory scale (electrodes on sides and membrane in centre)***

Figure 2.3.(3): The electrochemical cell and power supply unit built on pilot plant scale for 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.

Ten combinations of electrodes and electrolytes were grouped into four 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 2.3 contains the ten different electrolytic combinations that were tested.

Table 2.3: The ten different electrolytic set-ups for testing

Electrode	**Fe**	**Zn**	**Ni**	**Ni**	**Ni**	**Fe**	**Ni**	**Ni**	**Ni**	**Ssteel**
Electrolyte	AMD	AMD	KOH (30%)	KOH (3%)	30% KOH + AMD	Lime +AMD	Lime +AMD	AMD	AMD	AMD
Category	A		B		C			D		

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 on an hourly basis 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 Ten Different Systems

The volt-amperometric results for the ten hydrogen production systems, as tested, are listed in Table 3.1. In certain configurations, an acidic and an alkaline solution were used as electrolyte. In these cases, the acid was at the cathode's side of the cell set-up with the alkali at the anode's side.

Table 3.1: Volt-amperometric results of hydrogen production versus electrode consumption

Electrolytic Combination	**Category**	**$pH_{cathode}$**	**pH_{anode}**	**Current (ampere)**	**Potential (volt)**	**H_2 prod ($\ell.hr^{-1}$)**	**O_2 prod ($\ell.hr^{-1}$)**	**Electrode Consumption ($g.\ell^{-1}H_2$ prod)**	**Membrane**
Fe+AMD	A	3,26	3,26	5	32	2,15	×	2,43	None
Zn+AMD	A	3.13	3,13	5	38	2,33	×	3,53	None
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	2,80	✓	0,00	Anionic
Ni+KOH(30%)/AMD	C	2,73 to 12,63	13,98	5	4,3	4,00	✓	0,00	Anionic
Fe+Lime /AMD	C	2,64 to 3,12	12,00 to 9,70	5	22	0,30	x	137,07	Anionic
Ni+Lime /AMD	C	2,95 to 5,77	12,61 to 6,93	5	17,2	1,10	x	0,38	Anionic
Ni-mesh +AMD	D	3,15	3,15	5	28	2,00	×	0,00	None
Ni-plate+AMD	D	3,49	3,49	5	6	4,00	×	0,00	None
Ssteel+AMD	D	2,45	2,45	1	3,7	0,72	×	0,00	None

In category A, hydrogen was produced at the cathode while the anode started to dissolve due to the anodic reaction. Because no oxygen was produced, no membrane was needed. The main reactions are given by:

Anode: $Fe/Zn \rightarrow Fe^{2+}/Zn^{2+} + 2e^{-}$ [1]

Cathode: $2H_2O + 2e^{-} \rightarrow H_2 + 2OH^{-}$ [2]

Although hydrogen was generated at a fairly high rate at the cathode by using Fe/Zn electrodes, the potential became increasingly high, because of the decreasing surface area that resulted in a much higher resistance. It has been found experimentally that for every gram of hydrogen produced, 12,66 gram of Fe or 17,02 gram of Zn is needed. The costly effect of the destructive 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. To avoid oxygen contamination of the hydrogen, an anionic selective membrane was used as diaphragm. The reactions at the anode and cathode can be given as:

Anode: $2OH^- \rightarrow H_2O + ½O_2 + 2e^-$ [3]

Cathode: $2H_2O + 2e^- \rightarrow H_2 + 2OH^-$ [4]

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

It has been found that AMD can be neutralised while producing hydrogen electrolytically. This has been demonstrated by using AMD at the cathode and an alkali (KOH/Lime) at the anode as electrolyte(s). In category C, the AMD at the cathode's side was fully neutralized by the KOH/Lime at the anode's side. Hydrogen was generated at the cathode while oxygen was generated at the anode. Therefore, an anionic selective membrane was used to separate the two gases from each other. Because of the AMD at one side of the membrane and an alkali at the other side, the neutralization of the AMD took place directly onto the membrane that immediately got blinded after starting the experiment and caused the membrane to block. These blockages resulted in high voltages of which the costly impact can be seen in section 3.3.

From the volt-amperometric results in category D, high volumes of hydrogen can be generated, using AMD as electrolytic medium. Because of the low pH of the AMD, no oxygen was generated below a specific current density. For optimal biological sulphate removal, the oxygen level should be kept to a minimum as anaerobic sludge is used. Initially, the current density was kept at 1 $A.dm^{-2}$ as higher voltages (higher current density, constant cell resistance) will enable a higher production rate of hydrogen but could also initiate the production of unwanted oxygen. Tests have shown that no oxygen will be generated at a current density lower than 0,5 $A.dm^{-2}$. Much smaller amounts of hydrogen were generated this way. It is, however, possible to increase the H_2 production rate. This is currently under investigation.

3.2 Extent of iron(II) oxidation

One of the main benefits that arises from the use of electrolysis in order to generate hydrogen economically, is 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, Fe(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:

Anode $2Fe^{2+} \rightarrow 2Fe^{3+} + 2e^-$ [5]

Cathode $2H_3O^+ + 2e^- \rightarrow 2H_2 + H_2O$ [6]

Figure 3.2.(1) illustrates the relevant reactions at the anode and cathode. The oxidation of Fe(II) to Fe(III) can be proved by the transparent, ocher coloured AMD that was transformed to a dark brown solution. Precipitates forming from these solutions, onto the anode, were analysed by means of Mössbauer spectroscopy. Signatures of β-FeOOH (akaganeite) are quite distinct in these spectra and appears to have evolved partially to α-FeOOH (goethite).

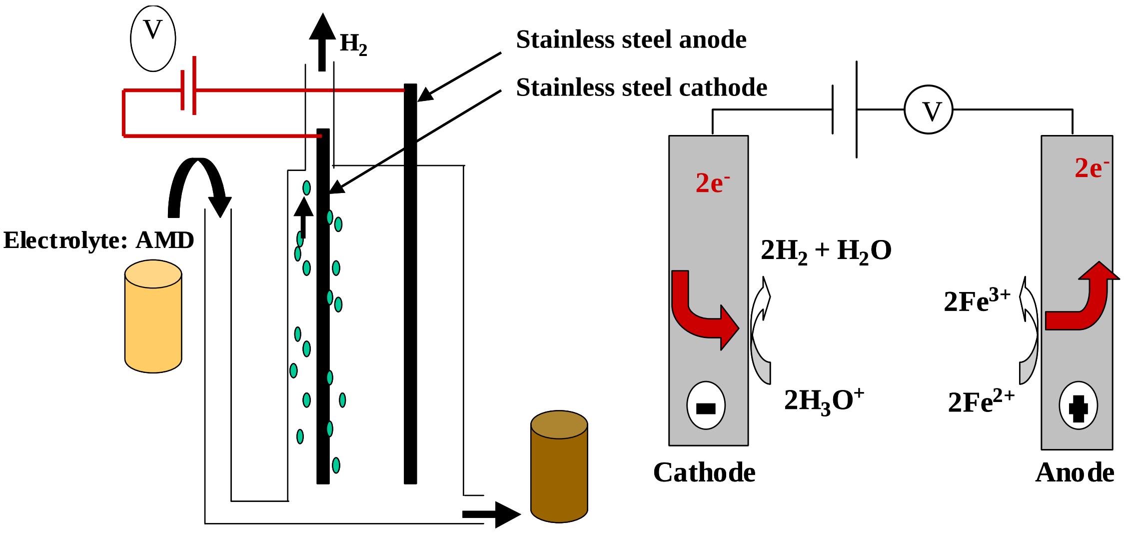

Figure 3.2.(1): ***Illustration of electrolytic set-up: stainless steel electrodes in AMD***

The oxidation of iron(II) is illustrated in Figure 3.2.(2) over a period of 65 hours. A tabulated profile of the pH, current input and voltage during the 65 hours are listed in Table 3.2.(2)

Table 3.2.(1) ***pH, current input and voltage during 65 hours continuous running (stainless steel in AMD)***

Time (hrs)	Fe(II) (mg/l)	pH	Current (A)	Potential (V)
0	4245	3.1	1.00	3.48
3	3965	2.97	1.04	4.44
15	2513	2.88	1.02	4.34
18	1955	2.65	1.00	4.50
19	1899	2.79	1.01	4.48
20	1843	2.83	1.06	4.54
21	1676	2.85	1.07	4,33
22	1620	2.86	1.00	4.36
41	614	2.83	1.04	4.57
45	335	2.82	1.05	4.45
65	279	2.79	1.00	4.44

In the CSIR's integrated limestone/lime process for neutralisation and partial sulphate removal[6], calcium carbonate is used to precipitate iron and sulphates. Due to the fact that iron(II) stays in solution up to a pH 7, it is beneficial to convert iron(II) to iron(III), which will precipitate at pH 3. Iron(II) also readily coats the carbonate particles which slows down the neutralisation reaction significantly. Calcium carbonate can raise 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 oxidized iron(II) incurs a cost benefit.

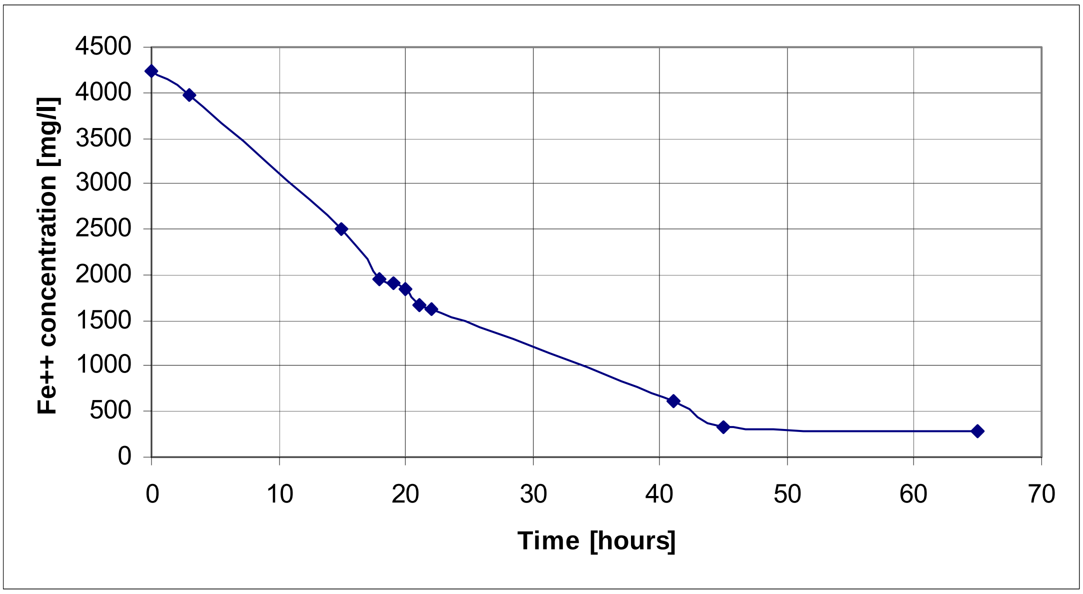

Figure 3.2.(2): Iron(II) oxidation of AMD using stainless steel electrodes

An increase in acidity (8 400 mg/ℓ to 11 200 mg/ℓ) resulted with decreasing iron(II)-concentration (4 245 mg/ℓ to 279 mg/ℓ), which is illustrated in Table 3.2.(2). The pH remained fairly constant during this period of time.

Table 3.2.(2): Electrolyte characteristics (stainless steel in AMD)

Time (hours)	pH	Fe(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 neutralising effect of SSteel, Ni- or Ni-plated electrodes on AMD as electrolyte is listed in Tables 1.8 and 1.10 in Appendix A.

3.3 Cost analysis

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. This can be expressed by the following equation and is listed in Table VI:

$$\text{Production cost} = \frac{\text{V x I x Electricity cost}}{\left[\dfrac{\text{P x Vol x M}}{\text{R x T}}\right]} \qquad [7]$$

with V the potential (volt), I the electric current (ampere) and [(PxVolxM)/(RxT)], the Ideal Gas Law. No mass lost occurred in the stainless steel (Ssteel) electrodes after they were used, proving that the electrodes are resistant to corrosion. With the AMD as electrolyte, the iron serves as a reducing agent and therefore limited amount of oxygen was produced. Test, performed by the SABS on the gas that was generated, showed that it contains 87% hydrogen, 2,9% oxygen and 9,3% nitrogen when the electrolytic set-up was running at a current density of 1 A.dm^{-2}. By reducing the current density to 0,5 A.dm^{-2}, only hydrogen was generated and no oxygen.

Table 3.3: Electrolytic hydrogen production cost

Electrode / Electrolyte	**H_2 production cost (R/kg)**	**Percentage of H_2 cost (Ssteel plate as 100)**	**Advantage**	**Disadvantage**
H_2 bought commercially	25,00	261	No production cost	More expensive
Fe plate / AMD	138,84	1 448	No O_2 produced	Electrode corroded
Zn plate / AMD	151,94	1 584	No O_2 produced	Electrode corroded
Ni plate / KOH (30%)	14,57	152	Low cost	Membrane compromised
Ni plate / KOH (3%)	10,03	105	Membrane not compromised	O_2 produced
Ni plate / KOH (30%) + AMD	684,08	7 133	AMD neutralised	Membrane blinded
Fe plate / Lime + AMD	145,86	1 521	AMD neutralised	Membrane blinded
Ni plate / Lime + AMD	130,60	1 362	AMD neutralised	Membrane blinded
Ni mesh / AMD	13,99	146	Fe(II) oxidised	Fe(III) must be present
Ni plate / AMD	22,39	233	Fe(II) oxidised	Fe(III) must be present
Ssteel plate / AMD	9,59	100	Fe(II) oxidised	Fe(III) must be present

From the cost analysis, as listed in Table 3.3, it can be noted that Fe(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 Fe(II) and 9 150 mg/ℓ SO_4^{-2} (see Table 2.1.(1)) would only be able to deliver 0,08 moles/ℓ of hydrogen which is only enough bacterial energy to reduce 2 000 mg/ℓ SO_4^{-2}. The combination of nickel (Ni) electrodes in an electrolytic medium of KOH (3%) will therefore be the most economically viable way of producing hydrogen electrolytically.

4 Conclusions and Recommendations

1. Hydrogen can be produced electrolytically cheaper than buying it in bulk commercially. The purity of this hydrogen will be of such standard that it can be used as energy source to sulphate reducing bacteria in a biological sulphate removal process.
2. AMD can be effectively neutralised by means of lime or KOH (30%). One big disadvantage of neutralising the AMD with lime or KOH is that the membrane is easily blinded by the precipitate that forms during neutralisation. In order to solve this problem, the lime on the anode's side should be first go into a settling tank to allow solids to settle out before recycled back into the cell. The recycle rate of the AMD on the cathode's side should be increased to avoid crystallisation at the surface of the membrane.
3. Fe and Zn dissolved at a too high rate during the electrolytic process which made them not economically viable as electrodes for the production of hydrogen.
4. The use of stainless steel electrodes in AMD as electrolytic medium, not only produces the most cost-effective hydrogen (three times cheaper than buying from industry), but also oxidises Fe(II) to Fe(III). This reaction is beneficial to the down stream processes as Fe(II) precipitates at a lower pH than Fe(III).
5. If higher volumes of hydrogen is needed, it can be generated 40% cheaper than buying it from industry, making use of nickel electrodes in an electrolytic medium of KOH (3%). This set-up however incurs the cost of membranes as oxygen is also produced.
6. The most synergetic and optimum solution to maximise H_2-production would probably be a combination between two or three or more combinations as mentioned above.

5. References

1. Prigent, M. & Martin, L. *Activated nickel-containing electrode and its use particularly for water electrolysis.* US Patent 4,363,707: Appl. 18 June 1980: Acc. 14 December 1982

2. Hu, W. *Electrocatalytic properties of new electrocatalysts for hydrogen evolution in alkaline water electrolysis.* International Journal of Hydrogen Energy, Vol. 25, 2000. pp. 111-118.

3. Ovshinsky, S.R., Sapru, K. and Liang, G. *Energy conversion devices*. US Patent 4,537,674: Appl. 19 July 1982: Acc. 27 August 1985.

Appendix 1

Table 1.1: Volt-Amperometric results for the hydrogen production system with Fe as electrode and AMD as electrolyte

Electrode - Fe plate (100 cm^2)
Electrolyte - AMD with flow rate 1,54 ℓ/min

Time (min)	0	15	30	45	60	90	120
Current (Ampére,A)	5,0	5,0	5,0	5,0	5,0	5,0	5,0
Voltage (Volt,V)	8,9	9,3	9,5	10,2	13,9	30	32
pH: *C* *A*	2,76 2,76	3,18 2,74	3,60 2,80	3,98 2,81	4,08 2,87	4,11 2,96	4,00 3,04
Temperature (°C) *C* *A*	22,9 22,9	28,7 29,0	30,9 31,1	32,1 31,5	33,3 33,4	35,5 40,0	42,3 45,2
Conductivity (mS/cm) *C* *A*	11,97 11,97	9,91 11,51	8,90 11,60	8,34 11,45	7,84 11,33	7,42 11,20	6,73 11,04
Weight (g)	Initial Cathode: 109,580 Final Cathode: 109,414 Cathode weight loss: 0,166 Initial Anode: 131,480 Final Anode: 121,208 Anode weight loss: 10,272						
H_2 volume (ℓ)	Volume H_2 generated: 4,3						

C: Cathode
A: Anode

Table 1.2: Volt-Amperometric results for the hydrogen production system with Zn as electrode and AMD as electrolyte

Electrode - Zn plate (100 cm^2)
Electrolyte - AMD with flow rate 1,54 ℓ/min

Time (min)	0	15	30	45	60	90
Current (Ampére,A)	5,0	5,0	5,0	5,0	5,0	5,0
Voltage (Volt,V)	4,1	4,9	6,0	9,5	19,7	62,0
pH: *C*	2,76	2,93	3,03	3,08	3,33	3,81
A	2,76	2,88	2,91	3,03	3,53	3,48
Temperature (°C) *C*	21,9	26,1	27,4	28,8	31,6	40,4
A	21,9	26,2	26,9	28,7	33,4	57,0
Conductivity (mS/cm) *C*	11,96	10,14	9,69	9,16	8,14	6,81
A	11,96	10,59	11,30	11,57	11,62	10,80
Weight (g)	Initial Cathode: 141,516 Final Cathode: 141,262 Cathode weight loss: 0,254 Initial Anode: 141,637 Final Anode: 129,550 Anode weight loss: 12,087					
H_2 volume (ℓ)	Volume H_2 generated: 3,5					

C: Cathode
A: Anode

Table 1.3: Volt-Amperometric results for the hydrogen production system with Ni as electrode and KOH (30%) as electrolyte

Electrode - Ni plate (100 cm^2)
Electrolyte - 30% KOH with flow rate 1,54 ℓ/min

Time (min)	0	15	30	45	60	90	120	150	180
Current (Ampére,A)	5,0	5,0	5,0	5,0	5,0	5,0	5,0	5,0	5,0
Voltage (Volt,V)	6,0	5,0	4,8	4,7	4,5	4,0	3,9	3,8	3,8
pH: *C*	14,38	14,10	13,72	13,50	13,60	13,44	13,71	13,77	13,82
A	14,38	14,03	13,73	13,64	13,37	13,62	13,91	13,83	13,93
Temperature (°C) *C*	25,0	28,0	31,0	32,0	33,0	34,0	34,7	35,5	36,0
A	25,0	27,0	30,0	31,5	32,0	33,5	34,3	34,5	34,7
Conductivity (mS/cm) *C*	325	325	326	324	325	324	326	325	324
A	325	324	325	324	324	325	324	326	325
Weight (g)	No weight loss								
H_2 volume (ℓ)	Volume H_2 generated: 7,3								

C: Cathode
A: Anode

Table 1.4: Volt-Amperometric results for the hydrogen production system with Ni as electrode and KOH (3%) as electrolyte

Electrode - Ni plate (100 cm^2)
Electrolyte - 3% KOH with flow rate 1,54 ℓ/min

Time (min)	0	30	60	90	120	150	180	210
Current (Ampére,A)	5,0	5,0	5,0	5,0	5,0	5,0	5,0	5,0
Voltage (Volt,V)	4,0	5,0	5,0	5,0	6,0	5,5	5,5	5,5
pH: *C* *A*	13,57 13,55	13,36 13,55	13,49 13,50	13,53 13,50	13,54 13,57	13,49 13,46	13,47 13,56	13,44 13,56
Temperature (°C) *C* *A*	n/a							
Conductivity (mS/cm) *C* *A*	116,8 117,9	114,7 127,2	112,4 126,6	116,3 128,0	112,9 122,8	96,8 103,4	97,3 101,1	101,2 124,6
Weight (g)	No weight loss							
H_2 volume (ℓ)	Volume H_2 generated: 9,8							

C: Cathode
A: Anode

Table 1.5: Volt-Amperometric results and chemical composition for the hydrogen production system with Ni as electrode and KOH (30%) and AMD as electrolytes at the anode and cathode respectively

Electrode -	Ni plate (100 cm^2)						
Electrolyte -	30% KOH and AMD as electrolytes at the anode and cathode respectively with flow rate 1,54 ℓ/min						
Time (min)	0	30	60	90	120	150	180
Current (Ampére,A)	5,0	5,0	5,0	5,0	5,0	5,0	5,0
Voltage (Volt,V)	6,0	6,0	4,6	4,3	4,1	4,1	4,2
pH: *C*	2,73	6,54	7,88	11,64	12,30	12,58	12,63
A	14,08	14,07	14,03	14,11	14,00	13,77	13,83
Temperature (°C) *C*	24,0	29,8	33,0	34,0	34,2	34,5	34,5
A	26,6	29,3	32,7	33,3	33,8	34,1	34,1
Conductivity (mS/cm) *C*	12,63	10,72	10,91	16,40	19,60	21,50	23,00
A	325	325	324	325	325	325	326
Weight (g)	Initial Cathode: 140,049 Final Cathode: 141,029 Cathode weight loss: -0,980 Initial Anode: 141,085 Final Anode: 141,122 Anode weight loss: -0,037						
H$_2$ volume (ℓ)	Volume H$_2$ generated: 6,4						

Chemical composition of treated water before and after treatment

	Before treatment		After treatment	
	Anode: 30% KOH	Cathode: AMD	Anode: 30% KOH	Cathode: AMD
Alkalinity (mg/ℓ)	> 4 000	- 9 400	> 4 000	> 4 000
SO$_4^{2-}$ (mg/ℓ)	1 600	19 000	9 500	15 500
Ca (mg/ℓ)	2,53	423	4,53	140
K (mg/ℓ)	6 710	10,7	4 600	256
Fe^{2+} (mg/ℓ)	< 26	< 26	< 26	4 747
Fe$_{Total}$ (mg/ℓ)	-	3 220	-	2 790

C: Cathode
A: Anode

Table 1.6: Volt-Amperometric results for the hydrogen production system with Fe as electrode and lime (14 mg/ℓ) and AMD as electrolytes at the anode and cathode respectively

Electrode -	Fe plate (100 cm^2)	
Electrolyte -	Lime and AMD as electrolytes at the anode and cathode respectively with flow rate 1.54 ℓ/min	
Time (min)	0	60
Current (Ampére,A)	5,0	5,0
Voltage (Volt,V)	10	22
pH: *C*	2,64	3,12
A	12,00	9,7
Conductivity (mS/cm) *C*	9,84	8,95
A	9,45	3,82
Weight (g)	Initial Cathode: 141,081	
	Final Cathode: 131,480	
	Cathode weight loss: 9,601	
	Initial Anode: 141,101	
	Final Anode: 109,580	
	Anode weight loss: 31,521	
H_2 volume (ℓ)	Volume H_2 generated: 0,3	

Chemical composition of treated water before and after treatment

	Before treatment		After treatment	
	Anode: Lime	Cathode: AMD	Anode: Lime	Cathode: AMD
SO_4^{2-} (mg/ℓ)	-	9 600	-	9 400

C: Cathode
A: Anode

Table 1.7: Volt-Amperometric results and chemical composition for the hydrogen production system with Ni as electrode and lime (14 mg/ℓ) and AMD as electrolytes at the anode and cathode respectively

Electrode - Ni plate (100 cm^2)
Electrolyte - Lime (14 g/ℓ) and AMD as electrolytes at the anode and cathode respectively with flow rate 1.54 ℓ/min

Time (min)	0	15	30	45	60
Current (Ampére,A)	5,0	5,0	5,0	5,0	5,0
Voltage (Volt,V)	6,8	8,5	9,9	11,9	17,2
pH: *C*	2,95	4,19	4,22	4,72	5,77
A	12,61	11,50	7,01	7,00	6,93
Temperature (^{o}C)					
C	23,2	27,0	28,0	30,4	30,8
A	24,0	26,7	27,3	28,5	30,9
Conductivity (mS/cm)					
C	11,0	10,28	9,94	9,29	8,76
A	9,47	5,13	5,12	4,91	4,90
Weight (g)	Initial Cathode: 141,029 Final Cathode: 141,012 Cathode weight loss: 0,017 Initial Anode: 141,122 Final Anode: 140,724 Anode weight loss: 0,398				
H_2 volume (ℓ)	Volume H_2 generated: 1,1				

Chemical composition of treated water before and after treatment

	Before treatment		After treatment	
	Anode: Lime	Cathode: AMD	Anode: Lime	Cathode: AMD
Alkalinity (mg/ℓ)	95% pure $Ca(OH)_2$	- 9 400	- 5 600	280
SO_4^{2-} (mg/ℓ)		19 000	9 200	5 600
Ca (mg/ℓ)		423	2 060	551
K (mg/ℓ)		10,7		
Fe^{2+} (mg/ℓ)		< 26	3 853	< 26
Fe_{Total} (mg/ℓ)		3 220	700	2 640

C: Cathode
A: Anode

Table 1.8: Volt-Amperometric results and chemical composition for the hydrogen production system with Ni (mesh) as electrode and AMD as electrolyte

Electrode - Ni mesh (100 cm^2)
Electrolyte - AMD with flow rate 1,54 ℓ/min

Time (min)	0	30	60	90	120	150	180	210
Current (Ampére,A)	5,0	5,0	5,0	3,5	3,0	2,5	2,0	4,0
Voltage (Volt,V)	23	28	28	28	28	28	28	28
pH: *C*	2,80	2,63	2,62	3,00	3,17	3,64	3,72	3,42
A	2,80	2,80	2,81	3,05	3,10	3,65	3,58	3,66
Conductivity (mS/cm) *C*	13,33	12,4	9,79	10,37	9,10	8,84	8,45	7,53
A	13,50	13,0	10,40	11,00	10,50	11,00	11,42	12,40
Acidity (mg/ℓ) C	12 100	12 200	13 000	14 100	11 500	14 200	15 800	16 500
A	10 600	10 040	9 000	8 700	8 400	7 100	6 400	6 600
Fe(II) (mg/ℓ) C	3 965	3 407	3 854	3 463	3 630	3 658	3 643	3295
A	4 133	4 356	4 468	5 641	5 920	6 981	6 981	7763
Weight (g)	No weight loss							
H_2 volume (ℓ)	Volume H_2 generated: 7,90							

C: Cathode
A: Anode

Table 1.9: Volt-Amperometric results and chemical composition for the hydrogen production system with Ni (plate) as electrode and AMD as electrolyte

Electrode - Ni plate (100 cm^2) Electrolyte - AMD with flow rate 1,54 ℓ/min								
Time (min)	0	30	60	90	120	150	180	210
Current (Ampére,A)	5,0	5,0	5,0	5,0	5,0	5,0	5,0	5,0
Voltage (Volt,V)	6	6	6	6	6	6	6	6
pH: *C* *A*	3,26 3,23	3,25 3,29	3,45 3,42	3,42 3,65	3,61 3,65	3,47 3,51	3,55 3,65	3,58 3,65
Conductivity (mS/cm) *C* *A*	24,00 23,80	19,80 20,20	13,60 13,10	13,00 9,98	11,42 12,14	8,49 9,20	7,98 8,01	8,45 9,90
Acidity (mg/ℓ) C A	n/a							
Fe(II) (mg/ℓ) C A	4 412 4 468	3 742 3 798	1 676 1 508	2 066 1 564	1 452 1 508	1 508 1 452	1 508 1 508	1 229 1 229
Weight (g)	No weight loss							
H_2 volume (ℓ)	Volume H_2 generated: 14,00							

C: Cathode
A: Anode

Table 1.10: Volt-Amperometric results and chemical composition for the hydrogen production system with Ssteel as electrode and AMD as electrolyte

Electrode - Ssteel plate (100 cm^2)
Electrolyte - AMD with flow rate 1.54 ℓ/min

Time (min)	0	15	60	180	300	480	660
Current (Ampére,A)	1,0	1,0	1,0	1,0	1,0	1,0	1,0
Voltage (Volt,V)	1,76	3,48	4,34	4,31	4,11	4,21	2,90
pH:	2,48	2,49	2,36	2,09	2,13	2,74	2,90
Fe(II) (mg/ℓ)	4 580	3 351	2 569	1 955	1 620	614	279
Acidity (mg/ℓ)	7 200	10 100	9 300	8 100	n/a	n/a	n/a
Conductivity (mS/cm)	10,22	11,03	10,07	10,65	10,89	10,77	11,01
Weight (g)	No weight loss						
H_2 volume (ℓ)	Volume H_2 generated: 0,72						

C: Cathode
A: Anode

Part 2

The Utilisation of the Electrolytic Generation of Hydrogen Gas as the Energy Source for the Biological Sulphate Reduction

Part 1 of 2

1. Introduction

When treating a wastewater, such as AMD, which contains no electron donor and carbon source, an appropriate electron donor has to be added, to obtain sulphate reduction. The selection of the electron donor is determined by

1. The costs of the added electron donor per unit reduced sulphate
2. The rest pollution of the added agent, which should be low and/or easily degradable

In order to achieve these set criteria, it can be advised that simple organic compounds, such as ethanol (De Smul *et al.,* 1997, Greben *et al*., 2000a, 2000b) or methanol (Weyma, 2000), are used. Alternatively the use of synthesis gas can be considered. Other options are the use of a combination of H_2 (energy source) and CO_2 (carbon source) or the use of CO on its own.

Hydrogen gas is a clean and sustainable fuel, which can be considered an important alternative energy resource for the future. Specific microorganisms, such as the SRB can use hydrogen as the energy source and CO_2 as the electron donor for the reduction of sulphate, which serves as the electron acceptor. Several researchers (Badziong *et al.,* (1979), Du Preez *et al.,* 1992 and van Houten, 1996) have shown the use of hydrogen in the biological sulphate removal technology.

A fierce competition exists between the methanogenic bacteria (MB) and the SRB in an anaerobic reactor. The acetogenic bacteria (AB) degrade organic material, such as glucose and volatile fatty acids into acetate and hydrogen, which then form the substrate for the MB and the SRB. However, the SRB have the advantage over MB, when H_2 is used as the energy source and when an oversupply of sulphate is present (Visser, 1995, Oude Elferink, 1998). Therefore, an alternative option to the conventional use of e.g. ethanol or sugar as the energy source could be provided in the form of hydrogen gas in combination with CO_2 and/or acetate for the carbon requirements.

In an anaerobic digester, high molecular-weight substances, such as polysaccharides, proteins and fats are converted to H_2 and CO_2 as the precursors of the conversion to CH_4 by the methanogens. Any H_2 produced in a primary fermentative process is immediately consumed by methanogens, homoacetogens, or SRB (in environments containing significant levels of sulphate (Brock, 1997). In general, the H_2 consuming bacteria live of the H_2 producing bacteria, which is considered a synthrophic relationship (synthrophy = eating together). It has been shown that the syntrophic bacteria tend to form flocs, pellets or other types of aggregates, containing one or more H_2 consuming organisms, such that both organisms, the H_2 producer and the H_2 consumer are in close association for effective H_2 transfer (Brock, 1997).

As indicated, hydrogen gas can be used as the energy source for the SRB, however in order to obtain sulphate reduction a carbon source is needed. When producer gas is not available, the alternative can be the use of H_2 combined with CO_2 gas. The study of Schutte & Maree (1989) reports on the autotrophic sulphate reduction using hydrogen. They operated both under batch and under continuous conditions, using the same upflow packed bed reactor for both experimental conditions. The results of that study showed that good sulphate removal (91%) was obtained at a hydraulic retention time (HRT) of 2,4 days. The need of the SRB for CO_2 was illustrated in this study by omitting the CO_2. When the CO_2 flow to the reactor was stopped, the sulphate reduction stopped, when, however, the CO_2 gas flow was restored, the sulphate removal efficiency was back to the same level as before the CO_2 omission.

Schutte & Maree (1989) explained the dependence of SRB on CO_2 because in an anaerobic environment, synthrophic bacteria can utilize carbon dioxide, forming intermediates such as lactate, ethanol and other carbon sources, which can be utilized by the SRBb. The investigations of Van Houten (1996) confirmed this finding, showing that the hydrogen utilizing SRB (HSRB) are not autotrophic, thus that they do not assimilate CO_2 but that they are dependent on other anaerobes to produce acetate, which they need for their additional carbon requirements.

Acetate is formed by the homoacetogens, a group of obligate anaerobes, which utilize CO_2 as a terminal electron acceptor, producing acetate as the sole product of anaerobic respiration. Electrons for the reduction of CO_2 to acetate can be derived from H_2, a variety of C_1 compounds, sugars, organic acids, alcohols, amino acids and certain nitrogen bases. Many homoacetogens can also reduce NO_3^- and $S_2O_3^{2-}$. However, CO_2 reduction is probably the major reduction of ecological significance (Brock *et al.,* 1997). Due to the low affinity of the homoacetogens, it is possible that under H_2 limitation insufficient amounts of acetate become available for the HSRB, which may result in predominance of the hydrogen utilizing methanogenic bacteria (HMB). It can also be assumed that under CO_2 limiting conditions, no acetate is being produced, thus limiting or stopping the SRB respiration (Hulshoff-Pol, 1998).

Van Houten, (1996) reported the use of a gas mixture of H_2 and CO_2 (80% : 20%), resulting in a volumetric sulphate reduction rate of 30 g $SO_4/(\ell.d)$ this sulphate reduction rate was achieved within ten days of operation at 30 °C using a gas-lift reactor, which provided good mass transfer rates, with pumice as carrier material for the SRB. When examining the structure of the biomass, he found that the *desulfovibrio* sp. And the *acetobacterium* sp. Were the most abundant microorganisms present. This confirms the assumption that the H_2, provided in the reactor, was both consumed by the SRB and the homoacetogens, which formed biofilms on the pumice particles.

2. Aim

The aim of this part of the study was to investigate whether the electrolytically produced hydrogen can be used as the energy source for the biological sulphate reduction technology.

3. Coaltech Project

The Coaltech project in which to achieve the aim was a two year project. During the first year, the main aim was to investigate whether hydrogen could be produced electrolytically. It was envisaged that this way of producing hydrogen would be more cost effective than producing it by the conventional method. After achieving this objective, the aim of the second part of the study focussed on the use of hydrogen as the energy source for the biological sulphate reduction. If it can be proven that the electrolytical method of producing hydrogen is more cost effective than buying ethanol as the energy source for the biological sulphate removal technology, it will result in a cheaper acid mine water treatment. A costing study is included in the EcoDose part of this report.

3.1 The EcoDose Process

The EcoDose Process (EC) is an innovative process for the production of hydrogen gas in an economic viable way by means of water electrolysis. The produced hydrogen will be used as the energy source for the biological reactor used for the treatment of sulphate rich effluents. By using hydrogen as the energy source no residual organic material is left in the treated water, which is in most instances is the case when using ethanol or sugar.

Nickel mesh can be used effectively as electrode material in a strong alkali medium (30% KOH) for generating hydrogen in a cost effective way. A membrane is needed between the two electrodes as oxygen is generated at the anode's side in the electrolytic set-up.

3.1.1 Experimental

Hydrogen was produced continuously and bubbled through the anaerobic biological reactor with the aim to function as the energy source for the sulphate reducing bacteria. The experimental set up is given in Figure 3.1.1. Samples were taken before the hydrogen was bubbled through the reactor and after the hydrogen production was stopped. The samples were analysed for the sulphate and sulphide concentration, as sulphide is the product of the biological sulphate removal process (reaction 1). Also the reactor pH was monitored regularly, as the optimum pH for the biological sulphidogenic reactor is about pH=7.5.

$$4H_2 + SO^{2-}_4 \rightarrow HS^- + 4H_2O \qquad (1)$$

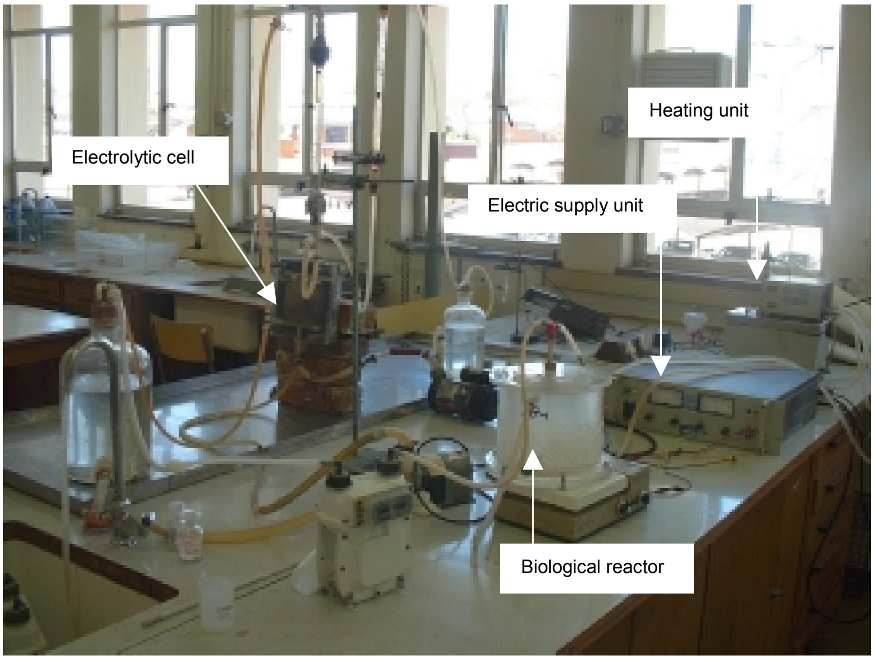

Figure 3.1.1: Laboratory set-up

3.1.2 Results

The results of the hydrogen utilisation are given in Table 3.1.2.

Table 3.1.2: The SO_4 and S_2- concentration before and after hydrogen utilisation

DATE	2/7	4/7	12/7	18/7	22/7	23/7
SO_4 start	1250	2400	1650	2100	1950	2000
SO_4 final	800	1750	1450	1950	1650	2150
S_2- start	48	164	21	10	4	20
S_2- final	52	212	4	36	20	52

The results in Table 3.1.2 indicated that in most cases the sulphate concentration was reduced in the bioreactor and that the sulphide concentration increased. However, on 23/7, the SO_4 concentration increased, rather than decreased. This result may be because the membrane between the cells deteriorated. When the gas analyses were carried out at the South African Bureau of Standards (SABS), it was established that the hydrogen (89%) was contaminated with 2,9% oxygen and 9,3% nitrogen.

The oxygen, with which the hydrogen was contaminated, might have been the cause for the increase rather than the decrease of sulphate in the reactor on 23/7. The sulphide present in the reactor was most likely oxidised to sulphur. When more oxygen is available the sulphur can be oxidised to sulphur dioxide and to sulphate.

Part 2 of 2

Hydrogen as Electron Donor in the Biological Reduction using a Column Reactor

The second part of the study concentrated on the use of hydrogen as the energy source applying a column reactor to obtain a good gas/liquid interface for the solubility of gas. The purpose of this part of the study was to investigate whether biological sulphate reduction was obtainable using a mixture of hydrogen and CO_2 gas.

1. Background

This research deals with studies treating artificial AMD, using immobilised hydrogen-consuming SRB. In principle, hydrogen utilisation by the sulphate-reducing bacteria, is similar to that of aerobic forms of hydrogen oxidizers, although the carriers in electron transport and the hydrogenase enzymes differ. It is indicated that sulphate reduction is coupled to ATP (an energy containing compound called Adenosine Triphosphate) formation by a PMF (Proton motive force) derived from electron transport. Sulphate is therefore reduced in a stepwise fashion to H_2S by intracellular enzymes, necessitating transport of sulphate from the external environment by active transport, involving ATP expenditure. Inside the cell, sulphate is reduced to sulphite and H_2S by a collection of enzymes (ATP sulfurylase and adenoxine phosphosulphate (APS) reductase). Sulphide is then formed by the action of sulphite reductase, during which action sufficient energy is released for the formation of two to three ATP moles per mole of sulphite reduced. Hydrogen then serves as the electron donor for the reduction of sulphite by the action of an electron transport chain. This requires the presence of hydrogenase enzymes, which are Ni-containing (Daniel R. Caldwell, 1995). This information should be kept in mind when developing an efficient system for the use of hydrogen as electron source for the biological reduction of sulphate. Studies by van Houten (1996) demonstrated the optimisation of biological sulphate reduction process using a gas-lift reactor, fed with hydrogen and carbon dioxide as energy and carbon source respectively. Attention was paid to biofilm formation, sulphide toxicity, the sulphate conversion rate, optimisation and gas liquid mass transfer limitations. It was shown that:

- The SRB formed stable biofilms on pumice particles.
- High free H_2S concentrations caused reversible inhibition rather than acute toxicity.

- If H_2S concentrations were kept below 450 mg/ℓ at a pH of 7,0, a maximum sulphate conversion rate of 30 g SO_4^{2-} /ℓ-d could be achieved.
- The gas to liquid hydrogen mass transfer capacity of the reactor determined the maximum sulphate conversion rate.
- A gas mixture of hydrogen and carbon dioxide (80% : 20%) was used to cultivate the hydrogen consuming SRB

2. Aim

The objectives of part 2 of the study were:

To show that hydrogen gas can be used by SRB, utilizing a tall column reactor, to optimise the gas to liquid hydrogen mass transfer and that using geotextile as the immobilisation material would prevent washout of the biomass.

3. Materials and Methods

3.1 Column Reactor

This reactor is a tall column reactor in which the feed is pumped from the top and the gas is pumped into the recycle of the reactor (Figure 3.4). Inside the reactor two pipes, covered with biomass are hanging from the top to the bottom, to provide a large surface area for the biomass to form a biofilm.

Reactor specifications:	Total volume:	200 ℓ	Active volume:	175 ℓ
	Length thick pipe:	6 m	Length thin pipe:	5 m
	Thick pipe radius:	10 cm	Thin pipe radius:	2,5 cm

3.2 Feed water

The reactor feed water comprised a synthetic sulphate rich water, consisting of 50 mg H_3PO_4/ℓ, 100 mg $(NH_4)SO_4$/ℓ, 2 mg $FeSO_4$/ℓ, 1 mℓ Hydroponic nutrients/ℓ and 1,9 g $MgSO_4$/ℓ. The hydroponic nutrients (2 g/ℓ concentration) consisted of the following: Macro elements: 5% N; 2,7% P; 13% K; 7% Ca; 2,2% Mg; 7,5% S and the Micro-elements are: 0,15% Fe; 0,024% Mn; 0,024% B; 0,005% Zn; 0,002% Cu; 0,001% Mo.

3.3 Biomass

Sulphate Reducing Bacteria mixture (SRB), obtained from the CSIRosure demo plant, Navigation Mine, Witbank, South Africa.

3.4 Experimental

The gas mixture (80% H_2: 20% CO_2) was pumped into the recycle stream of the reactor (Figure 3.4) into the liquid medium, comprising the feed water. The pumping of the gas mixture caused gas bubbles to form, which could effectively mix with the liquid medium.

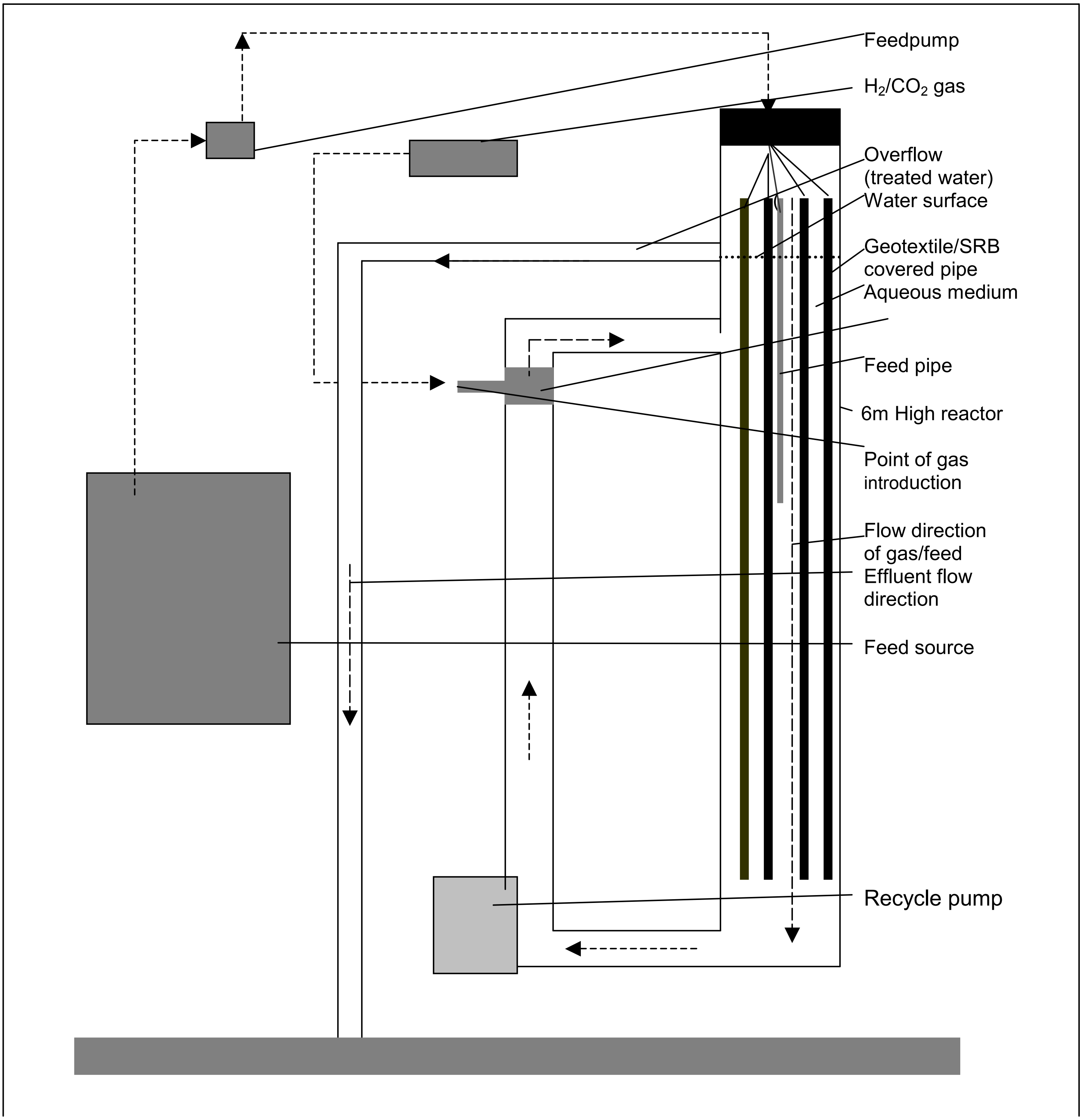

Figure 3.4: The Column Reactor

3.5 Analytical

The sulphate, sulphide, alkalinity, COD, and pH were manually determined according to the analytical procedures as described in Standard Methods (APHA, 1985). The analyses were all carried out on filtered samples, except for the feed COD and the sulphide samples. The alkalinity of the samples was determined by titrating with 0.1N NaOH to a pH of 9.0. The COD samples were pre-treated with a few drops of H_2SO_4 and N_2 gas to correct for the COD value caused by the sulphide concentration.

4. Results and Discussion

The sulphate removed and sulphide produced and the reactor pH results are given in Figures 4(1) and 4(2).

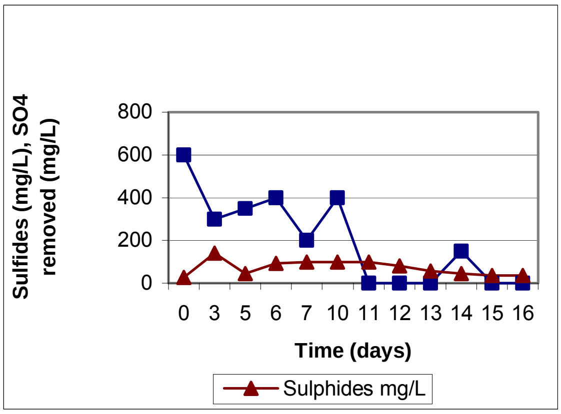

Figure 4(1): Sulphide concentration and Sulphate (mg/ℓ removed) operating column reactor.

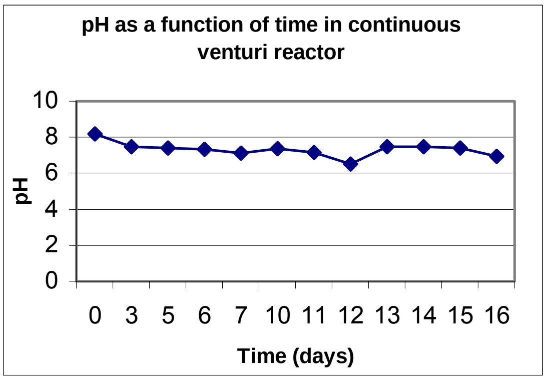

Figure 4(2): pH values as a function of time operating the column reactor.

4.1 Sulphate removal

The sulphate removal is demonstrated in Figure 4(1). It is shown that after the first day, 600 mg/ℓ sulphate was removed in the reactor. On day 14, although the sulphate was removed, no sulphide was produced. This could be ascribed to the formation of sulphur, which could be observed in the reactor. Initially, the alkalinity (mg/ℓ $CaCO_3$) was high (2000 mg/ℓ) and the pH was relatively constant between seven and eight. This was due to the fact that the pH was adjusted with $NaHCO_3$, during the first 10 days. The sulphide concentration was also high (Figure 4(1)) at first, which could be ascribed to the initial sulphate removal in the reactor. However, the pH decreased to a level of 6.5 on day 12. On this day, it was also evident that the alkalinity decreased, as well as the sulphide concentration, and that no sulphate was removed. This showed that the system was not functioning optimally. When no activity in the reactor could be observed, it was decided to stop the reactor.

Pase 2: Operating The Column Reactor.

5.1 Biomass

During phase two of operating the column reactor, it was decided to start with another micro organisms stock. For this reason fresh anaerobic sludge was collected from Daspoort, the sewage farm west of Pretoria. When the fresh biomass was added to the reactor, the reactor was operated in batch mode for the first four weeks. When the results showed that sulphate reduction could be obtained, the reactor was operated in continuous mode, at a Hydraulic retention Time (HRT) of 48 h. The results obtained during phase two, operating in the continuous mode (from day 31 onwards) of the column reactor, are shown in Figures 5.1(1) – 5.2.

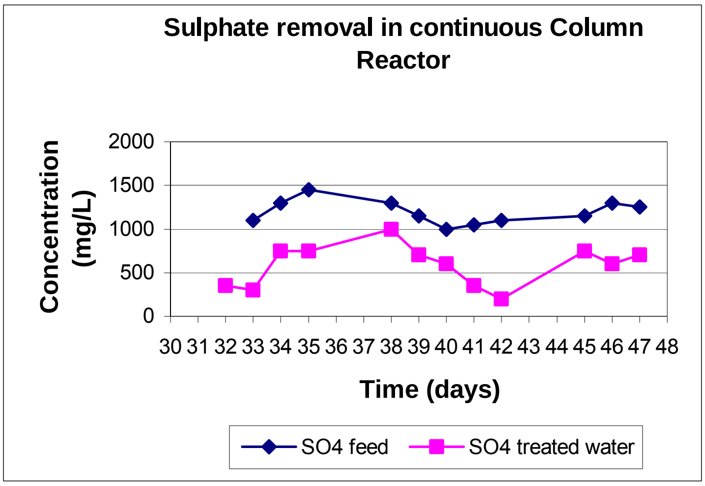

Figure 5.1(1): The SO_4 concentration in the column reactor

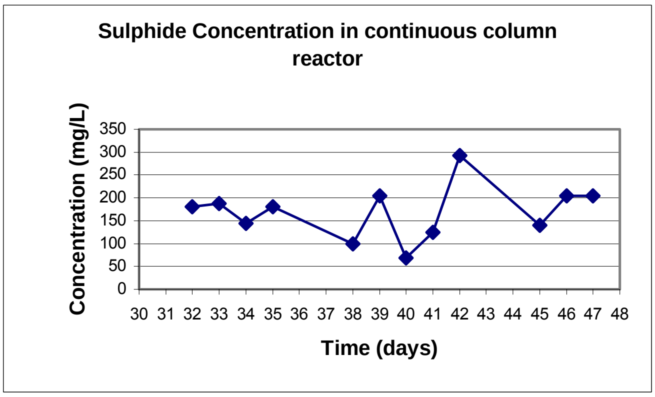

Figure 5.1(2): The Sulphide concentration operating the column reactor

5.2 Sulphate removal

It can be observed from Fig. 5.1.(1) that good SO_4 removal could be observed on day 33, where after it deteriorated slightly till day 38. After day 38, the SO_4 reduction improved again, till day 42. Generally, the sulphate reduction was continuous, as was the sulphide production (Fig.5.1.(2)). It can be seen from Fig. 5.1.(2) that when the sulphate reduction was the highest (day 42), the highest sulphide concentration (300 mg/ℓ) was observed.

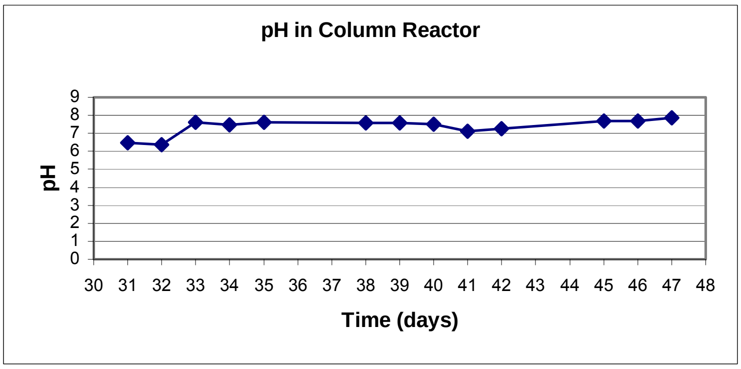

Figure 5.2: The pH values in the continuous operating column reactor.

The graph in Fig. 5.2 shows that the pH in the column reactor was maintained at the favourable reactor pH of seven < pH < eight. Initially the pH was corrected by adding a solution of $NaHCO_3$, but once the sulphate reduction started, the reactor pH could be maintained at these values. The increased pH in the reactor was due to the fact that both alkalinity and sulphide are formed.

6. Conclusions and recommendations

It has been proven in the laboratories of the Sulphate and Neutralisation Group of the Water Programme, Environmentek, CSIR, that hydrogen can be produced electrolytically. When this produced hydrogen was used for the biological sulphate removal technology, no consistent biological sulphate removal could be observed. The reason for this might be three fold:

1. The hydrogen produced gets contaminated with oxygen, which is not favourable for the SRB, as they are anaerobes.
2. When Fe rich mine water was used as the electrolyte, the system got blocked with iron deposits. Due to the blockage, iron rich water entered the biological reactor.
3. The used biomass population did not contain hydrogen-consuming SRB.

When the researchers of the SO_4/Neutralisation group investigated whether the use of bottled hydrogen as the energy source would provide biological sulphate reduction, the results showed that hydrogen can be used as the energy source (Figs 5.1.(1) and 5.1.(2)).

This finding confirmed, that the biomass used in the laboratories of the CSIR, which had adapted to the frequently used energy sources were no hydrogen utilising SRB. It became furthermore evident from the literature that the homoacetogens produce acetate from the available H_2 and CO_2 gases. The hydrogen utilising SRB (HSRB) make use of the formed acetate as the carbon source. The to ethanol adapted microorganisms in the CSIR laboratories are no acetate consumers. When the research was conducted with a fresh batch of microorganisms, it was found that biological sulphate reduction could be observed with hydrogen and CO_2 gas as the energy source.

The next step in this research project will focus on the use of the electrolytically generated hydrogen gas, combined with CO_2, generated elsewhere in the neutralisation and sulphate removal process, as the energy and carbon sources for the biological sulphate reduction, using the new strain of biomass. This strain is now adapted to hydrogen as the energy source.

7. References

APHA (1985). Standard Methods for the Examination of Water and Wastewater 16th Edition, Washington DC.

Badziong, W., Ditter, B and Thauer, R.K.(1979). Acetate and carbon dioxide assimilation by desulfovibrio vulgaris (Marburg), growing on hydrogen and sulphate as sole energy source. Arch. Microbiol.123: 301-305.

Brock (1997). Madigan, M,T., Martinko, J.M. and Parker, J. (1997) Brock: Biology of Microorganisms. Eigth Ed. Prentice-Hall, Inc.

Caldwell, Daniel R. (1995). Microbial Physiology & Metabolism. Wm. C. Brown Publishers.

De Smul, Dries, J A; Goethals, L; Gootaerd, H; and Verstraete, W. (1998). High rate biological treatment of sulfate-rich waste water in an acetate-fed EGSB reactor. Biodegradation, 9:103-111

Du Preez, L.A., Odendaal, J.P., Maree, J.P., and Ponsonby. (1992). Biological removal of sulphate from industrial effluents using producer gas as energy source. Environ.Technol. 13: 875-882.

Greben, H.A.; Maree, J.P.; Singmin, Y.; and Mnqanqeni, S. (2000). Biological sulphate removal from acid mine effluent using ethanol as carbon and energy source. Water Science and technology, 42(3-4): 339-344

Van Houten, Renze T. (1996). Biological sulphate reduction with synthesis gas. Ph.D. thesis, Wageningen Agricultural University, Wageningen, The Netherlands.

Hulshoff-Pol, L.W, Lens, P.N.L, Stams, A.J.M and Lettinga,G (1998). Anaerobic treatment of sulphate-rich wastewaters. Biodegradation, Volume 9: 3-4: 213-224

Schutte, C.E and Maree, J.P. (1989) Autotrophic sulphate reduction using hydrogen as the energy source. Proc. of the 2nd Anaerobic Digestion Symposium, University of the Orange Free State, Bloemfontein.

Tuttle, J.H.; Dugan, P.R.; Macmillan, C.B.; and Randles, C.I. (1969). Microbial dissimilatory sulfur cycle in Acid Mine water. J. Bacteriol., 97: 594

Lettinga, G; Rebac, S; Parshina, S; Nozhevnikova, A; Van Lier, J.B.; Stams, A.J.M. (1999). High rate Anaerobic treatment of wastewater at low temperatures. Applied and Environmental microbiology, 65(4): 1696-1702

Oude Elferink, S.J.W.H., Visser, A., Hulshoff Pol, L.W. and Stams, A.J.M. (1994). Sulphate reduction in methanogenic bioreactors. Fems Microb. Rev. 15:119-136.

Visser, A. (1995) The anaerobic treatment of sulphate containing wastewater. PhD Thesis, Wageningen Agricultural University, Wageningen, The Netherlands.

Weijma, J; Stams, A.J.M.; Hulshoff Poll, L.W.; Lettinga, G. (2000). Thermophilic sulfate reduction and methanogenesis with methanol in a high rate anaerobic reactor. Biotechnol Bioeng 67: 354-363