

ELECTROCHEMICAL TREATMENT FOR THE REMOVAL OF SULPHATES FROM ACID MINE DRAINAGE

**Report to the
WATER RESEARCH COMMISSION**

by

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EXECUTIVE SUMMARY

1. INTRODUCTION

Continuing assessment of pollution in the Olifants River and its associated geohydrological systems require the close monitoring of (amongst other pollutants) sulphate released as a consequence of coal mining operations in the Mpumalanga power belt. Total volumes of effluent are presented in Appendix 1

The eventual treatment of sulphate, to acceptably low concentrations specified by the legislator, is expected to be enforced in the very near future. This tendency is experienced globally and is also reflected in the requirements enforced by the International Standards Organisation (ISO). [Appendix 1]

The search for an economical treatment procedure to remove sulphate from effluent is a global problem and receives prominent attention in international scientific literature. A vast amount of research is directed towards the improvement of existing processes and the development of new processes. This research is conducted mainly in the chemical and the biological fields.

The chemical research field involves typically the absorption, or complex formation or ion exchange properties of certain specially designed chemical compounds to immobilise and concentrate the sulphate anion. The biological research field concentrates on the chemical reduction of sulphate by *sulphate reducing* bacteria. In both cases the processes are technically feasible and the main aim in current research is centred round the techno-economical refinement of these processes.

The electrochemical treatment of effluent combines very modern technology and traditional technology through various engineering disciplines. The basis of the process is a versatile electrochemical reactor able to dissolve a large range of different, highly reactive chemical species. The treatment of effluents is always aimed at removing either chemical and/or physical contaminants (pollutants) from water. The reactive species generated by the ECODOSE system and the pollutant(s) in any effluent can now be interacted, using contacting equipment (namely chemical engineering unit processes) to effect de-pollution.

The electrochemical removal of sulphate involves the reaction of sulphate in an effluent, at specific chemical conditions, to form an insoluble complex. The insoluble complex

precipitates under particular chemical conditions and can thus be concentrated and separated from the effluent. The detail of this specific electrochemical process (EC) is patented and the principle is also investigated for application in various other effluent treatment processes.

The project depends heavily on the personnel infrastructure from the Anglo coalmines. In this respect it is necessary to emphasize the reciprocation between the research team and Anglocoal regarding training and education of existing personnel. Individuals benefited from extended training, education and participation in the project regards affirmative action initiatives is highlighted in Appendix 9

2. OBJECTIVES (AIMS) OF THE PROJECT

The objective of this project is to assess and demonstrate the ability of the electrochemical process as a process for the removal of sulphate and phosphate pollutants from typical effluents.

The main aim for this research project is therefore to determine the technical and commercial potential of this 'new' technology for the removal of sulphate and phosphate from mining and sewerage effluents respectively.

The objective will be attained by investigating the performance of a newly designed electrochemical (EC) reactor after treatment of various effluents containing, respectively, sulphate and/or phosphate pollutants. [Refer to the WRC Proposal K5/940 28 Jan 1999 paragraph 5, Appended as Appendix 2].

Note:

During the first weeks of experiments it became clear that Phase 1 of the project would require more time for completion than was budgeted for. The Technical Committee decided to finalise the experiments on sulphate at the mine location before attempting any experiments on sewerage.

3. PROJECT PLANNING AND EXECUTION

The investigation was planned to proceed in two phases the first of which was directed at the design and construction of a reactor configuration, including the associated peripheral equipment. Experiments on the removal of sulphate from Acid Mine Drainage (AMD) would demonstrate the performance of the reactor for final assessment.

The second phase was envisaged to use the same reactor design and configuration (a Continuously Stirred Tank Reactor (CSTR)) for performance testing on **phosphate removal from sewerage plants**.

It is important at this stage to realise that the **technical performance** of the EC reactor would determine the ultimate success of the project. For this purpose a satisfactory **mass balance** during operation would be required for both phases of the project. **A detailed cost structure** on this mass balance can only be finalised in a subsequent detailed project directed at determining the commercialisation potential of the process.

4. SHORT DESCRIPTION OF THE ELECTROCHEMICAL PROCESS, PERFORMANCE, EXPERIMENTAL RESULTS AND FINAL RECOMMENDATIONS [for a more detailed description refer to the Progress Report at the Navigation Colliery Meeting dated June 2000]

4.1 Introduction and process description.

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 WRC, ESKOM, and ANGLOCOAL.

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.

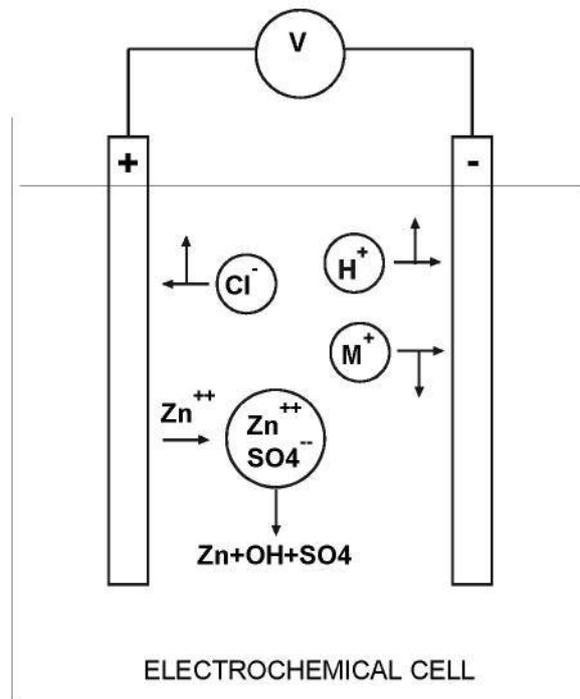


Diagram 1 (Electrochemical Cell)

The steps in the overall reaction can be described as follows: (Refer to Diagram 1)

- Zn^{2+} cations are released at the anode (+).
- Electrobalance requires the release of two electrons at the cathode (-) which dissociates two hydrogen cations H^+ .
- The two H^+ cations combine to form hydrogen gas H_2 that escapes at the cathode.
- The nett result of the anodic and cathodic reaction at low pH is the increase of OH^- anions (increase in pH) resulting after the escape of the hydrogen gas.
- The final reaction is the precipitation of the dissolved products such as Zn^{2+} , OH^- and SO_4 to form the insoluble zinc complex $(Zn)_4(OH)_6SO_4$ at pH-values of ca pH=6.6-7.0

This specific process goal is therefore to balance the incoming ions (Zn^{2+} , + OH^-) on the one hand with the electrons (=coulombic electric charge) on the other hand. By controlling the pH-value of the solution and in the presence of the correct amounts of Zn^{2+} , OH^- and dissolved sulfate (SO_4)²⁻ an insoluble zinc complex will form and precipitate. This precipitate is now easily separable from the supernatant liquid by various solid/liquid separation techniques.

An experimental protocol was designed and a process analysis schedule developed. The experimental analyses supplied sufficient results to compile an electrochemical simulation program for the EC process based on the law of Faraday. Faraday's law predicts a linear relationship between electrochemical dissolution and electrical charge and is formulated as follows:

$$m = V I T / Z F \text{ where}$$

m - mass of electrode dissolved (g)

V - Volt (electromotive force - volt)

I - electrical current (amp)

T - time (seconds)

Z - valence

F - Faraday constant ca 96000 coul/mol/s

Further detail on the process description and theory is presented in the full report §2.2, p18.

4.2 Technical performance of the demonstration plant.

This particular phase of the project entailed the initial design and field testing of a nominal 1 megaliter demonstration plant on various effluents at an ANGLOCOAL coal mining plant.

- The actual hydraulic capacity of the plant (1 megaliter) is directly proportional to the level of contaminants in the effluent. Thus more pollutants to be removed, electrochemically, would require higher electrical input and this relationship is linear following the Faraday law.
- The process uses zinc (as a sacrificial catalyst electrode) to complex and remove up to 60% of the sulfate contained a typical AMD effluent depending on the feed quality and its ionic speciation. Simultaneously the effluent is neutralised, the base metals are precipitated while the organic content and alkalinity (scaling tendency) are reduced. More sulphate can be removed if less calcium and magnesium are present [Refer to WMB Assessment Report Appendix 3]. It could thus also be advantageous to neutralise with EC-neutralisation rather than lime.
- The anodic dissolution of metals in the effluent greatly enhances the clarification by gravitational settling, filtration and/or other standard solid/liquid separation techniques. This is due to the known action of dissolved ions as coagulants and

flocculants especially trivalent iron and aluminium. .[Refer to (Cerisier publication Wisa)]

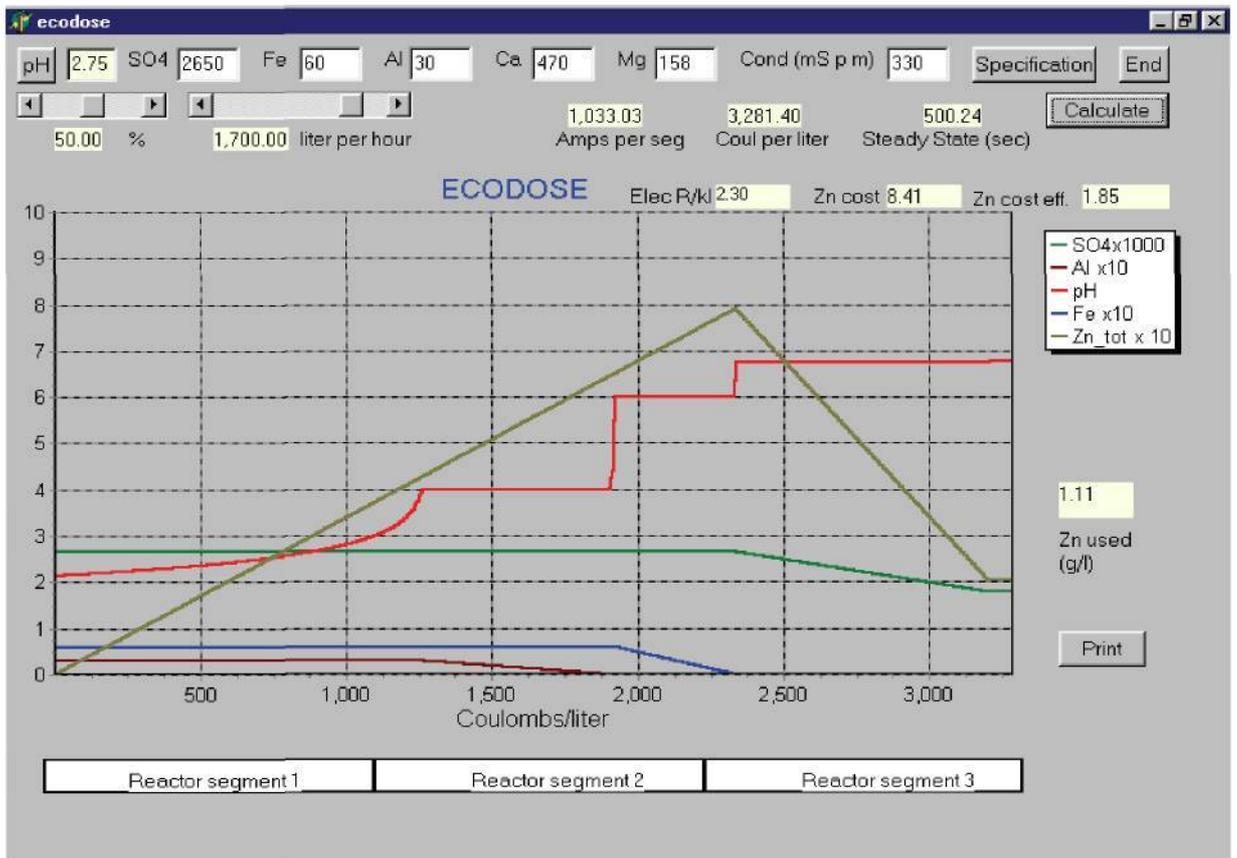
- The final disposable waste is contained in a thick sludge (in the worst case) or a moist to dry filter cake at best, depending on the efficiency of solid/liquid separation. . Settling velocities in excess of 1 meter/sec were reported by WMB and is good to superior.[Refer to Appendix(3) WMB]
- To be economically viable this final waste will have to be recycled to the supplier of the initial catalyst (zinc electrode), for recovery of the zinc content. [Refer to the standard formula for compensation of waste zinc compounds used by the London Metal Exchange Appendix 4 (Dr. N. Vegter, Kumba Resources.)]
- Lower capacity equipment (to save cost) following the current electrochemical reactor can handle only 2000 liter/hr. This imposes a serious limitation on the demonstrative performance and capacity of the EC-reactor with its maximum hydraulic treatment capacity capability at 0.1 megaliter/day (ca.4000 liter/hr) for a typical mine water with 2800 ppm SO₄ load.
- **A theoretical computer model** presenting the dynamic performance of the system from start to equilibrium is included and simulates the real experiments very closely. A very accurate response prediction can be made for the process of any known effluent with a known input analysis. [Refer mathematical model from Appendix 5].
- It is evident from all experiments that previous neutralisation by liming of any effluent had the following very important effects:
- The residual iron species in the form of both Fe(2+) and Fe(3+) must be removed rapidly after neutralisation and precipitation to prevent the iron hydroxide to hydrolyse and convert to the metal sulfate and sulfuric acid again. **This implies that liming is rapidly nullified if the solid/liquid separation is not done within hours after equilibrium is reached.**
- Effluent that was previously limed contains both Ca and Mg up to saturation levels. When treating these solutions with the Ecodose process the sulfate anion can only be removed to a certain level. This is due to the fact that the alkali metals (Ca , Mg) compete with the Zinc for the sulfate anion to stay in solution and can thus only be precipitated at a very high pH value which is not conducive to the formation of the insoluble Zinc complex. It would therefore be advantageous to use the Ecodose process for both neutralisation and sulfate removal or at least in a calculated optimised combination.This also applies for

elements such as Na, K, which also immobilises a mineral equivalent of acidic sulphate.[Refer to WMB Assessment –Appendix(3) §(1.3.2.)p3

A continuous run over a period of two weeks established the process reliability and operability when monitored and controlled by operators on shift at the mines [Refer to Report on Continuous Operation and Operation Manuals appended as Appendix 8]

4.3 Summarized attainments of the aims as stated in the original Proposal for Project K5/948 [Appendix 2]

- The symmetrical reactor proved to perform as predicted by theory. Adaptations to the geometry of this reactor type to improve retention time and kinetics were successful.
- Optimal sulphate removal can be attained by theoretical modelling as well as experimentally.
- Recycling of zinc was investigated and is possible; - recycling to the zinc primary industry is the worst case for economical recovery [Appendix 4]
- Factors such as reliability, simplicity, operability and projected economics are presented and referred to in this Executive Summary. Typical graphical presentation is contained in GRAPH 1 reflecting various input variables and the predicted reactor response for various input values of electrical charge in coulomb/liter (This is already calculated for the envisaged continuous flow reactor) [Refer to Appendix 5 (new sloped reactor design)]
- A continuous run over a period of two weeks established the process reliability and operability when monitored and controlled by operators on shift at the mines [Refer to Report on Continuous Operation and Operation Manuals appended as Appendix 8]



Graph 1.
 Various technical relationships versus electrical charge input.
 [Derived from experimental results and theoretical principals]

4.4 Results from project experiments.

A tabulated summary of the results of two experiments in this program is presented in Table 1 [the full experimental results are contained in Appendix 7 of this report.]

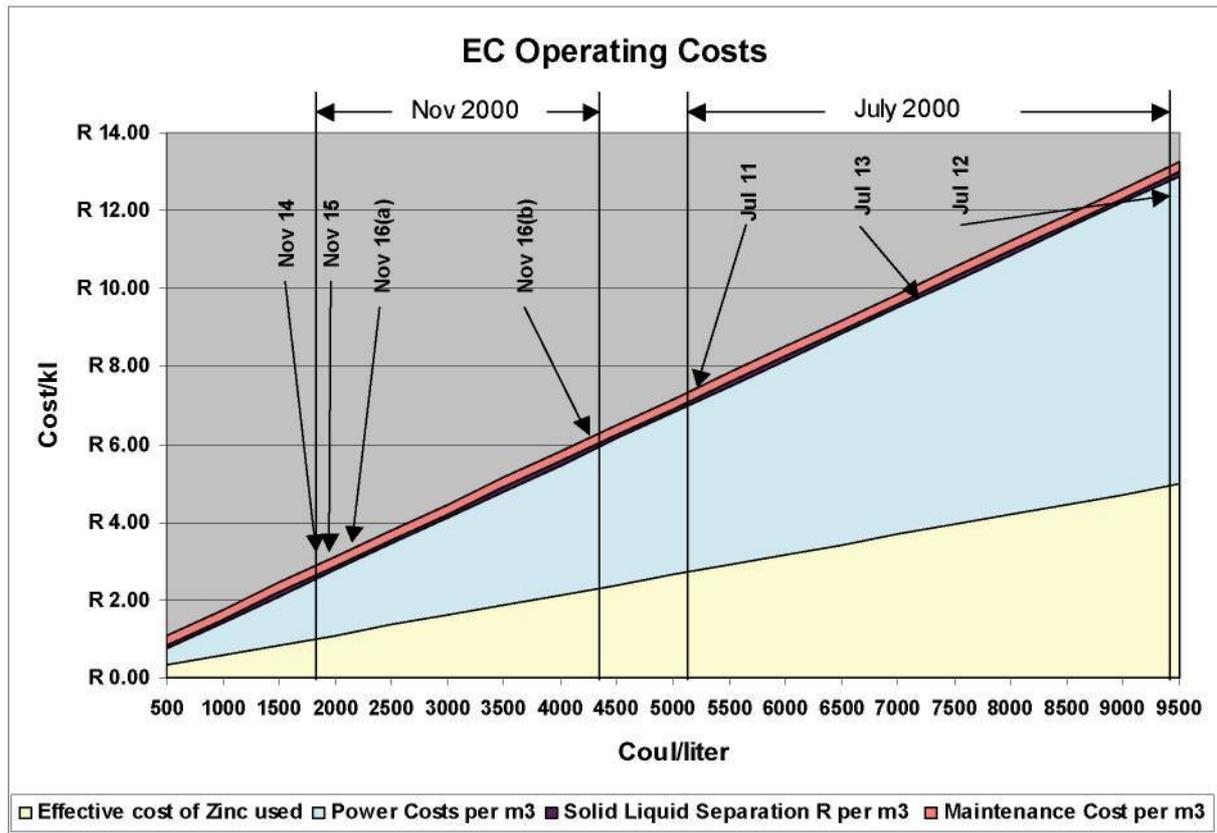
TABLE 1. Typical experimental results on Schoongezicht and Toe Seep effluents.

PROCESS VARIABLE	SCHOONGEZICHT 11/07/2000 PERFORMANCE LEVEL	TOE SEEP MIX(1) 16/11/2000 PERFORMANCE LEVEL	NOTES
FLOW RATE (2)	320 liter/hr	320-340 liter/hr	
% SULFATE REMOVED	3700 - 1600 = 56%	3464 - 1200 = .65%	
FEED TO PRODUCT pH CHANGE	2.73 - 6.58	2.73 - 5.58	
ENERGY CONSUMPTION kW	6.0 kW (metered)(3) 5.18 kW (calculated)	kW meter not operational 7.41 kW (calculated)	
Zn CONSUMPTION (4)			
BASE METALS % REDUCTION	90 - 100%	90 - 100%	
REDUCTION OF ALKALINITY (SCALE FORMATION)	+ 90%	3.31 - <0.1 mgCO ₃ /liter =+90%	
SPECIFIC ENERGY CONSUMPTION ON FLOW RATE	16.18 kWh/m ³	21.79 kWh/m ³	Calculated as follows from Table 1 [5.18 kWh /0.32.liter/hr]
SPECIFIC SULFATE REMOVAL ON ENERGY INPUT	0,672/16,18=0,0415 [kgSO ₄ /kWh]	0.104[kgSO ₄ /kWh]	Calculated as follows from Table 1 320(3700-1600)/1000/16.18 [kgSO ₄ /m ³ /kWh/ m ³]

Legend.

- i. This mixed effluent consisted of roughly 10% Toe Seep and 90% Schoongezicht
- ii. The flow rate of the feed to the system was restricted to 2000liter/hr on cost considerations pertaining to the down stream equipment.
- iii. The installed kW-meter was faulty during all the experimental runs

4.5 Graphical summary of full experimental results



Graph 2

Cost (Opex) versus electrical charge input (to remove 1000mg/l SO₄)
 [Calculated from experimental results in Appendices 7a and 7b]

Notes to Graph 2

- There is a consistent improvement in zinc/sulphate ratio as well as the projected (calculated) Opex during the course of this project which was also emphasised by the independent assessor. (WMB)
- The electrical cost can be halved by doubling the area of the electrodes.

5. PLANNED FUTURE RESEARCH AND RECOMMENDATIONS

5.1 PHASE 1: Sulphate removal

- The current project will be extended to include experiments using the full capacity of the EC reactor with suitable (temporary?) facilities for the down stream disposal of the waste and product streams.
- Detailed and more accurate evaluation of the zinc consumption can also be effected on these larger scale experiment. A complete and accurate mass balance would have to be undertaken for variable input concentrations of effluent as well as variable flowrate.
- The presence and effects (especially on sulfate removal) of the alkali metals such as Calcium and Magnesium can also be properly evaluated with these extended experiments supported by detailed laboratory experiments.
- A follow-up research program is also planned to assess the response of the Ecodose system using a continuous flow reactor. This would enable the determination of the exact percentage zinc recovery as well as the purity to which the final zinc precipitate could be recycled. The better purity has substantial cost implications on the monetary value of recycled zinc and thus on the operating cost of effluent treatment.
- The continuous flow reactor enables sampling over the length of the reactor. Because the precipitates of Aluminium, iron and zinc (in this order) takes place as a function of pH, it would be possible to separate the aluminium and iron from the final zinc precipitation. This would yield a higher value recycled zinc precipitate.

5.2 PHASE 2: Sewerage treatment by electrochemistry and research into various reactor types

This phase of research is planned after completion of the current research on the removal of sulphate. It would be especially be important to maintain the unsymmetrical reactor option in this research phase.

5.3 Theoretical investigation still to be undertaken:

From the outset it proved difficult to determine the exact Zn/SO₄ mass ratio. This was due to the very complex chemistry involved in the formation of the hydroxy-sulphate. This complexity results in the zinhydroxysulphate to precipitate containing a large variation of

zinc to sulphate ratio's in the precipitate. The discussion of some possibilities are addressed in the Progress Report appended as Appendix 6.

6. ACKNOWLEDGEMENTS

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1. INTRODUCTORY PROCESS BACKGROUND AND DESCRIPTION

1.1 Development history

The electrochemical (EC) treatment of effluents combines very modern technology and traditional technology through various engineering disciplines. The basis of the process is a versatile electrochemical (EC) reactor able to anodically dissolve a large range of different, highly reactive chemical species, usually from suitable metal electrodes. The treatment of effluents is always aimed at removing either chemical and/or physical contaminants (pollutants) from water. The reactive species generated by this treatment system, and the pollutant(s) in any effluent can now be interacted, using contacting equipment (namely chemical engineering unit processes) to effect de-pollution.

It is evident that by imaginative combination of the chemical species generated and the various pollutants to be removed a large (virtually unending) potential exists.

The application of EC water treatment is not new but dates from the turn of the century when a plant in London treated sewerage using iron electrodes and a little seawater to disinfect. This operation (plant) was soon discontinued due to the large build-up of sludge that could not be carted away by horses!

Further mention of the technology's use was made in Europe, Scandinavia and in Russia. Literature on the latter only became available after 1990 and revealed high activity of research in this field. An excerpt of this literature is presented by Cerisier (1)

In 1989, after a sabbatical in the general field of Electrochemical Engineering at the Fraunhofer Gesellschaft in Germany Prof JJ Smit, with the aid of Lektratek (Pty), (Ltd) started a coherent research program at the PU for CHE. The following 7 years saw the emergence of a number of post-graduate students, research papers, research projects and a development towards an industrially acceptable reactor configuration in the generic field of effluent (and water) treatment with electrochemistry.(A list of projects and post graduate research is presented in Appendix 2.5)

A continued increase of pollution in the mining industry in general, prompted AOL to intensify research and development to curb this seemingly unbridled deterioration. Increased sulphate pollution from Acid Mine Drainage (AMD) associated with coal mining in the Mpumalanga power belt is especially disturbing and was selected as priority. The EC

removal of sulphate is novel and due to its singular attributes it was selected as one of the candidate processes to be evaluated and compared for economical removal of sulphate from effluents. The research for an economical sulphate removal process is a global quest and receives prominent attention in international scientific literature. Improvement of existing processes with simultaneous development of new processes present the only possible solution. This research is conducted mainly in the chemical and the biological fields.

The removal of sulphate to legally acceptable limits will be strongly enforced in the very near future. This tendency is experienced globally and is also reflected in current legislation in the RSA.

Since 1997 Amcoal (currently Anglo Operations Limited (AOL)) sponsored and complemented the development of an experimental pilot plant stage at the AOL (Kromdraai) mining site. This experimental test program motivated the conception of a demonstration test plant in a joint venture between AOL, Eskom and the Water Research Commission. The latter demonstration plant was designed, constructed and commissioned by Lektratek in February 2000 on a mining site at Navigation Collieries.

1.2 Electrochemical Fundamentals, Theory And Process Description.

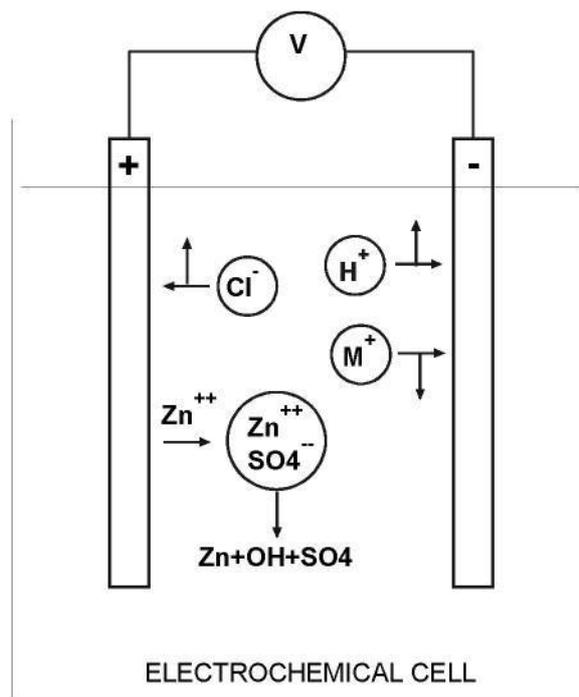


FIGURE 1

The passage of electrical current through certain substances when acting as electrodes or conductors in an electrical circuit is the basis of all electrochemistry. Consider the diagram in Figure 1.

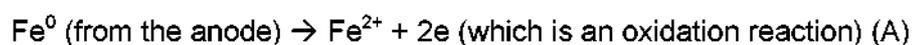
The reactor consists of a vessel (the electrochemical (EC)-reactor) containing the effluent now called an electrolyte. In this electrolyte a number of sacrificial metal electrodes are suspended in such a way that an electrical current can pass through the electrolyte from the cathode to the anode.

The passing current generates a number of reactive chemical species both at the electrodes and in the effluent. These reactive chemical species can be engineered and manipulated to convert, destroy, react with, precipitate and change some or all of the pollutants. The final products resulting from these changed pollutants can now be separated, and/or they escape from solution, and/or they even might not be polluting anymore.

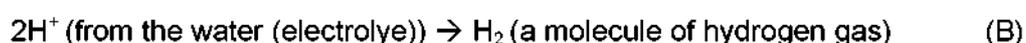
The following description gives a typical example and refers to the diagrammatic presentation of the EC-reactor attached to this documentation.

Figure 1 depicts a simple sketch of a single electrochemical cell (EC) that is provided with one pair of iron electrodes submerged in an effluent (electrolyte). When passing an electric direct current (DC) through the EC, electrons will flow from the cathode (+) through the electrolyte to the anode (-). At the electrodes the most important anodic reaction would be the dissolution of iron into ferrous ions and the cathodic reaction is the formation of two hydrogen atoms according to the following reactions:

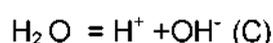
The anodic reaction is:



The cathodic reaction is:



A third reaction caused by the electrical field potential in an acidic effluent is the dissociation of water viz:



On summarising the three chemical balance equations the net equation is :

The two consequences from these two reactions are that:

- Firstly the hydrogen escapes from the effluent, leaving a hydroxyl ion (OH^-) behind which causes the pH (acidity) of the effluent to increase (change to the neutral (less acidic) side)).
- Secondly the ferrous ion (Fe^{2+}) is now unpaired and immediately upon formation, reacts with chemical species like the hydroxyl ion (OH^-), (or any other reactive anionic species) such as phosphate ion (PO_4^{3-}) or sulphate (SO_4^{2-}) to precipitate insoluble salts depending on the pH and other chemical conditions.

A typical example of such a reaction is reported in this research when Zinc electrodes interact to form an insoluble zinhydroxysulphate. These insoluble species can now be separated from the electrolyte by very well known unit processes of chemical engineering. It is obvious that when this process is continued, the effluent could be cleaned of the phosphate pollutant. The continuous removal of sulphate from effluent entails the control of acidity (pH) at a specified level within a specially designed EC reactor.

A detailed description of these reactions for the removal of sulphate can also be found in the Assessment Report by WMB appended as Appendix (1.3) to this report.

Parallel research reveals that a wide variety of pollutants can already be removed by manipulating either the electrolyte speciation, or the electrode type, or the pH or some other external factor.

Previously executed projects on electrochemistry revealed the importance of variables such as:

- Current density,
- Polarity reversal,
- Dosing of catalyst materials (the latter in the form of electrodes that are dosed or added continuously).
- Temperature effects

1.3 Operational Chemistry of the EC-reactor for the removal of sulphate.

Faraday's law predicts a linear relationship between electrochemical dissolution and/or deposition (plating) of metals. This is an exact science and concerns the variables of an electrical charge and mobile charged chemical ions. This relationship between electrical charge and mass is formulated as follows:

$$m = M I T / Z F \quad \text{where}$$

(D)

m - mass of electrode dissolved (g)

M - Molecular mass of the metal electrode (g/mol)

I - electrical current (amp)

T - time (seconds)

Z - valence

Consider the net electrochemical reaction being the sum of the balanced reactions A, B and C. It is evident that the dissolution of Fe and electrons gives rise to the production of Fe^{2+} and the hydroxyl ion $2(\text{OH})^-$. Both these two ions are very active in an acidic medium and combine to precipitate as insoluble ferrous hydroxide $\text{Fe}(\text{II})(\text{OH})_2$. Should the pH (acidity) approach a pH of higher than $\text{pH}=6$ the excess $(\text{OH})^-$ would report as an increase in the acidity (pH) of the effluent. Ferrous hydroxide only forms at $\text{pH} = 6$ where iron is precipitated as ferrous hydroxide. The same applies for most base metals where aluminium, for example, is precipitated at $\text{pH} = 4$ while zinc precipitates at ca. $\text{pH} = 7.2$.

Incidentally the latter element namely zinc was used as a catalyst to form an insoluble compound $\text{Zn}_4(\text{OH})_6(\text{SO}_4)$ that precipitated at very specific chemical and acidic conditions. The precipitate can now easily be removed from solution by various standard solid/liquid separation technologies.

It is important to realise that the EC process can simultaneously neutralise acid, precipitate base metals, radio-nuclides and clarify suspended solids by the action of dissolved trivalent metal species (such as Fe^{3+} and Al^{3+}) in solution.

1.4 The Project History, Development of this EC Project..

1.4.1 Historical development.

Contacts via the SABS Design Institute facilitated the possibility to present Emerging Technologies from South Africa at the Hannover Messe in the then Federal Republic of Germany.

This Technology Fair is a global event and attracts state of the art technology exhibitions across the globe.

Various Emerging Technologies in Water Treatment as well as Extractive Mass Transport were exhibited in 1981, 1983, 1985 and 1987. In 1989 a research assignment, accepted by Prof. Smit, was spent as a working sabbatical, jointly at the Fraunhofer Gesellschaft in Stuttgart and the German Plating Industry presented by Gramm Oberflächentechnik GmbH.

Discussions and deliberations on the electrochemical generation modification, removal and/or synthesis of pollutants and/or de-pollutants led to the development of several novel treatment procedures for specific pollutants. Among these procedures a special project was launched to re-investigate electrochemistry for specific use as a process to influence, remove, modify or re-use pollutants such as the phosphate and sulphate derivatives.

It was evident from this venture that electrochemistry could dramatically influence pollutants such as the phosphorous and all its derivatives, pH, dissolved metals, unsaturated organic material, electrical conductivity, radio active nuclides, etc. It was also clear that a novel process for anionless dosage of flocculants was possible via the electrochemical dissolution of selected sacrificial anodes. The following summary gives an indication of the various electrochemical processes researched:

1.4.2 Generation of Fe²⁺/Fe³⁺ as flocculants

The research of Fe cations in cooling water was started by an MSc-student Mr A de Villiers in 1992 at the Eskom Lethabo power station. The untimely death of Mr. De Villiers forced the project to a low at the PU for CHE. In 1993 the discussions between Prof J J Smit, Mr D Hanekom and Me SDM Cerisier resumed and a formal project was launched again. This project resulted in Me SDM Cerisier obtaining M(Eng)Chem in 1995."

The following aspects were reported in publications resulting from this research:

Chemical dosing of the trivalent metals could economically be replaced by **electrochemical (EC)** dosing.

Electrochemical dosing of the trivalent metals has a substantial number of other advantages occurring simultaneously like the **neutralisation of acidity** and the **precipitation of base metals** and radio nuclides.

A number of publications resulted namely a MEng-thesis by Me Cerisier SDM (1) and various publications and presentations at conferences Cerisier SDM (2) and Cerisier SDM (3).

- (1) *SDM Cerisier MEng: PU vir CHO 1995*
- (2) *Water SA 1996: "The electrochemical dissolution of anion free Fe³⁺ to replace the chemical dosing of Fe³⁺"*
- (3) *WISA 1996: "The Biennial Conference and Exhibition of the Water Institute of SA, Port Elizabeth, 20 - 23 May 1996."*

1.4.3 Research on phosphate removal in the fertiliser industry.

Parallel to flocculants research an EC project was investigated to neutralise and remove phosphate from two different fertiliser effluents. This project was concluded and proved to be successful although the company found another way of dealing with its effluent.

1.4.4 The removal of phosphate from sewerage plants.

Since 1993 structured research projects were undertaken on the reclamation and treatment of sewerage effluent and a gold mine sewerage was selected for evaluation of the EC plant performance. The EC treatment thus formed a major part of this research program and a MEng thesis was completed in 1997 (NT Lemmer (4)) on the evaluation of EC treatment of a sewerage plant at Western Deep Levels.

Important aspects at this stage were the following:

A **successful removal of phosphate** could be proven and a continued program is to be instituted using a slightly different EC reactor cartridge.

Substantial problems were encountered with clogging of the reactor and it subsequently was established that **Sulphate Reducing Bacteria (SRB)** were **proliferating between the electrodes**

Substantial amounts of **sulphate and phosphate** were removed from the effluent and a provisional patent (5) was prepared.

(4) *Lemmer TN, MEng thesis, PU vir CHO, 1997.*

(5) *SAPat 99/2303, Sulphate Removal.*

1.4.5 Research on the EC removal of sulphate from effluent.

In 1996 a MEng thesis was started by HJ vd Merwe that investigated the possibility of using the insolubility of certain metal salts and/or complexes to combine with sulphate in effluent rendering it insoluble and thus extractable by solid/liquid separation.

At this stage a provisional patent was prepared and the basic research configured to run at least two parallel research projects to PhD level on both the sewerage and the sulphate removal concepts mentioned.

Circumstances however forced Prof JJ Smit to retire from the PU vir CHO and only the sulphate project was pursued in cooperation with Amcoal (currently AOL) following the registry of a joint patent (6) detailing the sulphate removal process.

(6) *US Pat 09/182,230, Removal of pollutants from effluents with electrochemical treatment.*

A joint project between AOL and LEKTRATEK required the latter to design construct and commission an experimental pilot plant for operation at an AOL mine called Kromdraai. The Kromdraai results motivated a new joint project configuration in which the following parties shared, namely, AOL, Eskom, Water Research Commission and Lektratek (Pty) (Ltd).

1.4.5.1 The initial research was done at Kromdraai where an EC reactor was evaluated using zinc electrodes. This configuration proved to yield insoluble zinc hydroxysulphate at very specific chemical conditions created in the reactor. The unit was able to remove up to 70% of the sulphate [Refer to figure (2.1) Kromdraai results] contained in the run of mine effluent. The program thus far was initiated and sponsored only by Anglocoal and served as a demonstration to convince the WRC and Eskom to participate. The Kromdraai plant was assessed by an independent consultant who also subsequently designed the demonstration plant used for this project namely Envig (Weir-Envig).[Refer to Appendix (1.2)]

1.4.5.2 With the joint project it was obvious that a more accessible location had to be found. The 'new' pilot plant was thus located at the Navigation Collieries' Landau site. Several series of experiments were executed and the plant performed as theoretically predicted. [Assessed by Wates, Meiring and Barnard (WMB) reporting to Mr HC van Zyl at AOL. This report is appended as Appendix (1.3)]

1.4.6 Development on plant simulation and control

1.4.6.1 During the experimental phases the analytical results were always tested and modelled against the theoretically predicted values generated by the Faraday law. In all cases it was found that the theory is very closely simulated by the experimental results. An example of this is presented in Appendix (1.4) and is discussed in detail in (§1.3)

1.4.6.2 A theoretical computer model of the system showed that each and every variable including an operational cost estimate could accurately be simulated. It is furthermore possible to develop a completely automated process control and a comprehensive analytical protocol using the same simulation model. [For a detailed description of the model refer to Appendix (1.5)]

1.4.7 Continued research and development.

On going research is undertaken at the Vaaltriangle Technikon regarding electrochemical removal of sulphate. Mr HC vd Merwe (the Acting Head of the Department of Chemical Engineering) integrated a number of post graduate projects into their academic program. A list of students who participated is presented in Appendix (1.6)

1.4.8 Plant operation

During experimentation the infrastructure for running the pilot and demonstration plants was provided by the (AOL) mines. This included utilities, maintenance, breakdown assistance and personnel.

Regarding personnel a concerted effort was expected and delivered to enhance and improve both awareness training and empowerment tuition and training into the affirmative action initiatives of the mine and AOL in general.

For the latter purpose extended plant and procedure training sessions were given to all the student and operator participants. At Kromdraai the existing plant operators supervised the

experiments in an excellent manner. At Navigation Collieries both operators and students were trained each at their own competency levels. A list of students and operators is appended as Appendix (1.7)

A schedule for normal operation, start up and emergency shut down was thoroughly taught and it is appended in Appendix (1.8)

1.5 Project Personnel

During the course of the project at Navigation Collieries a large number of people were involved from the Mine Manager down to Site, Production and Maintenance Engineers. The full commitment of everybody was necessary to execute the project.

The project could however not do without the commitment of the supervisory and plant operating personnel and various students in training. Everybody was more than willing to do the extra training, the extra analysis and the extra bit of plant duty. A complete list of personnel would not be appropriate but the extent of their duties could be seen in these reports and the operating manuals that they had to study.

1.6 Project Objectives

The main project objectives from the mine obviously concurred with the objectives set out by the WRC Project Application which was mainly to establish the technical feasibility of sulphate removal with EC using zinc electrodes. Apart from that AOL was interested to evaluate the best available technology for sulphate removal looking and comparing existing and emerging technologies.

The removal of sulphate is certainly novel and its application a strong contender amongst the emerging technologies.

EC has a further advantage in that it can be applied and adapted much easier than any other and it is that much simpler to operate and maintain than any other novel technology.

The possibility of a synergy between itself and most of the other novel technologies could induce further research into combinations between various technologies.

In the final analysis the removal of sulphate will have to be effected to levels that will eventually be strictly controlled by (international?) laws.

2. EXPERIMENTAL DEVELOPMENT AND DEMONSTRATION.

The experimental development up to the level of a demonstration plant required the following criteria.

2.1 Laboratory Experiments for Design and Construction.

To apply EC to any effluent it is necessary to design and construct a suitable reactor. The following effluent input data is necessary:

2.1.1 Physical effluent input data:

- type of effluent,
- the quantity to be treated,
- the specific target pollutant that must be removed and
- a complete analysis of the effluent with detail concentrations of all cations and anions.

Once the effluent is properly targeted it is necessary to qualify and quantify the scientific process(es) to be used. In this phase it is necessary to define the field of available or novel technology to solve the effluent problem. This normally demands a literature study and some well defined laboratory experiments to verify literature and own interpretation or know-how. The guidelines for a Process Engineering type of project are listed as follows:

2.1.2 Science and technology available.

- Determine the branch of science,
- Evaluate the necessity and scale for laboratory verification,
- Perform a mass balance study to determine the correctness of literature and own know-how,
- Evaluate the reaction kinetic performance for dimensioning the reactors and/or containing equipment involved.
- Test design and perform experiments to extract and generat design, construction and cost datafor economic feasibility.
- Test scale up factors for sizing and design of industrial application.

2.2 Laboratory experiments

Most laboratory experiments were done by MEng students and it is contained in various publications of which the most pertinent is the project studied by HC vd Merwe (7). This project assessed the technical feasibility of using zinc sacrificial electrodes to generate the insoluble zinc complex previously mentioned. This insoluble complex could easily be separate from the remaining liquid and thus remove the sulphate anion with it.

(7) *HC vd Merwe., 1998,PU for CHE, MEng.
The removal of sulphate from effluents.*

The results in this study indicated the following technical feasibilities:

- Sulphate can be removed from acidic effluents at low pH.
- The chemical reaction is first order relative to Zn.
- The reaction is not temperature depended up to the tested 60°C.
- The anodic EC dissolution of zinc (and hydrogen) follows the Faraday law.
- In synthetic solutions containing only H₂SO₄ ca. 90% of all (SO₄)²⁻ could be removed.
- The total system behaved according to the law of Ohm when considering the inter-polar distance in the effluent as an Ohmic resistance
- Simultaneous neutralisation of the effluent is achieved.
- At the expected pH values (as pH increased) simultaneous precipitation of base metals in solution occurred.
- It was indicated that the alkaline and alkaline earth metals could not be precipitated in this way. They could therefore have an influence on the capability of zinc to precipitate (remove) sulphate.

2.3 Landau Kromdraai Experiments on a Small Pilot Plant.

[Interim Report date 29/07/1998 Appendix (2.1)]

A small pilot plant was designed constructed and commissioned in February 1998 at the Lime Dosing Site at the Kromdraai mine. This plant had a nominal flow capacity of roughly 25-30m³/day and was tested with iron, aluminium and zinc electrodes.

An "Interim Report" [Interim Report date 29/07/1998 Appendix (2.1)] was presented to Mr.B v Zyl of AOL.

The initial objective of this investigation was to prove that the acidity of 15m³ /day of effluent could be increased from pH=3 to pH = 6 with the electrical unit operating at 95% efficiency and using iron aluminium and zinc electrodes.

The Kromdraai effluent was extracted from two sources namely “Old Pit Effluent “ and “New Pit Water” of which the complete elemental analysis is reflected in TABLE 2.1

TABLE 2.1 Elemental effluent analysis.

Source	pH	SO4	Al	Fe	Mg	Mn	Ca
Main (new)	2.5	686	45	54	10	1	30
Pit (original)	3.8	1675	8	2	15	4	547

2.3.1 The results from this appended report are summarised as follows:

2.3.1.1 Both iron aluminium and zinc electrodes were effective to increase the pH. It was critically difficult to run the pilot plant for any length of time beyond one day because no automatic control equipment was installed in this test plant. The expected pH-plateau's occurred when the effluent was either electrochemically or chemically neutralised were illustrated. (Examine the plateau's at pH4 and pH6 in Figure 2.2)

2.3.1.2 The plant was eventually continuously run and controlled by the operating personnel of the Liming plant who where very quickly shown and taught the rudimentary analyses and the rectifying (controls) measures to be taken to effect controlling adjustments.. [Refer to Continuous Experiment Appendix 1.8]

2.3.1.3 It was found that the **electrochemical dissolution of iron is temperature dependent** and that some aluminium alloys tend to form an electrically isolated anodised oxide layer stopping the flow of current. This was a result that was also previously obtained during experiments on mine sewerage water.

2.3.1.4 The objective was reached with all three types of electrodes and it was also verified that SO₄ concentrate was reduced from 700 mg/l down to 200mg/l (which is ca. 80%) by using zinc electrodes at a pH=6 - 7. This experimental result is presented in FIGURE (2.1)

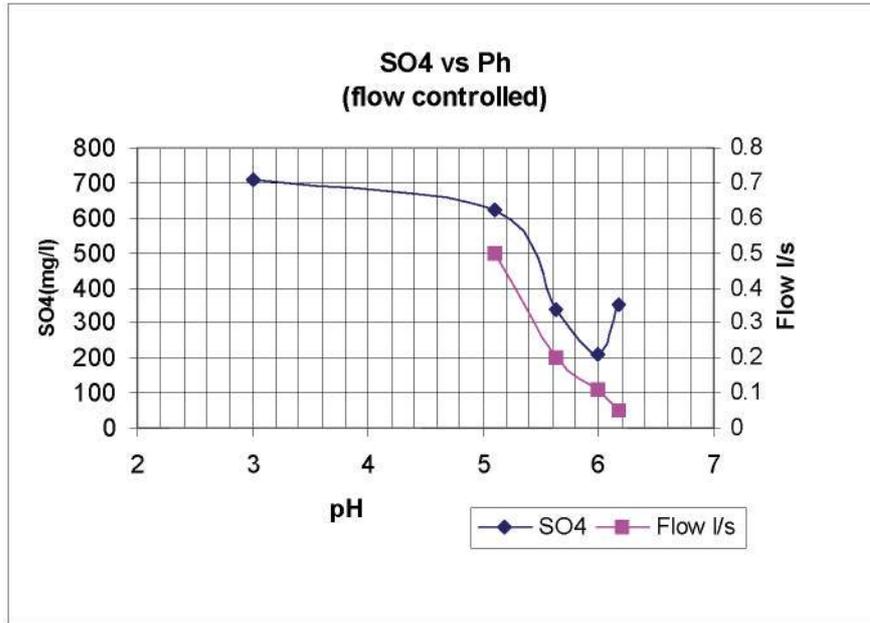


FIGURE 2.1 The removal of 80% SO₄ with zinc electrodes.

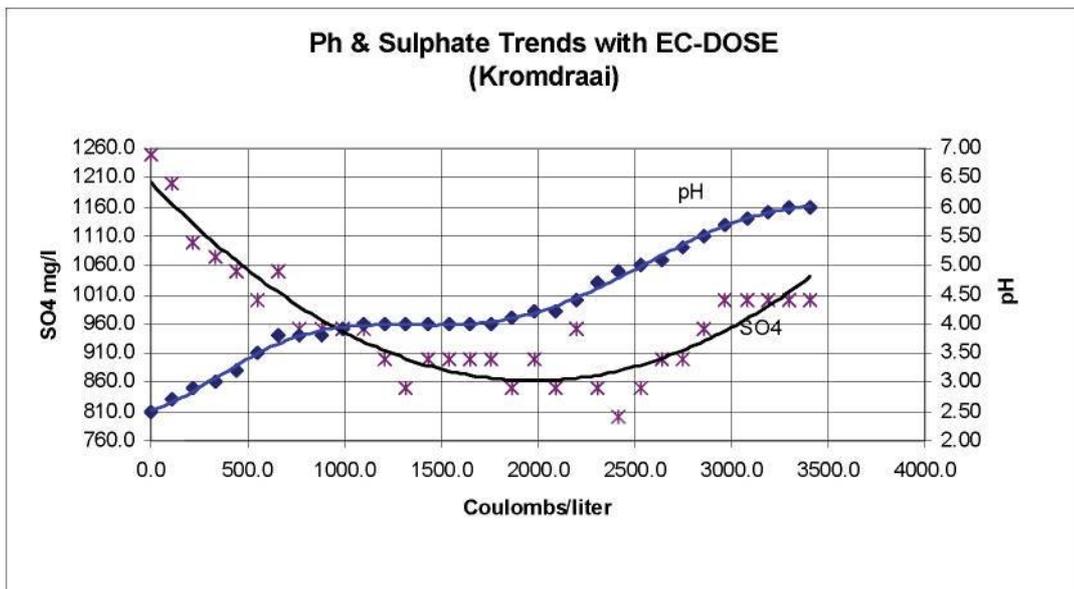


FIGURE 2.2 pH trends while dosing with Zinc electrodes

2.3.2 A preliminary direct cost estimate with these zinc consumption figures is reflected for the specific effluent treated.

Cost of Zinc electrodes consumed (@R6/kg)

R3.52 / kiloliter (no resale or re-use for zinc).

R3.10 / kiloliter (resale of reactor scrap at R2.80/kg)

R0.70 / kiloliter (85% recovery of Zinc including electroplating cost (*))

(* Refer to Appendix (2.2))

Cost of electricity: (R0.10/unit) R0.49/kiloliter

Total cost: (a) R4.01 / kiloliter (running cost basic)

(b) R1.19 / kiloliter (Zinc recovered - no value addition)

(c) R1.19/kiloliter (Zinc recovered + value addition)

2.4 Experiments at Kromdraai reported in a Final Report to AMCOAL

[Refer to Appendix (2.3): A Final Progress Report to AMCOAL. Dec 1998]

Note: The two report dates are fairly close to each other and most of the material reported are the same but more detail is provided in this report. This report also served as the motivation for a bigger demonstration plant, at Navigation Collieries, to be researched jointly by WRC, AOL, and Eskom.

2.4.1 Executive summary

2.4.1.1 Introduction

An affordable electrochemical (EC) water treatment technology, converts effluents into valuable water resources.

2.4.1.2 Description

Central to the technology is an EC-reactor able to release electrons into an aqueous effluent via two selected electrodes. The electrodes generate highly active chemical species in the aqueous medium. The electrode products are chemically exploited (engineered) to elegantly remove a host of pollutants currently stored, transported or generated in the community. Typical pollutants are, acidity, sulphate, phosphate, base metals, organic, radio nuclides, odor, and color. The final product of de-pollution from the EC-reactor in this case is a highly

compacted zinhydroxysulphate complex, precipitated with minimum possible quantity and clean water.

2.4.1.3 Status of the system.

The system consists of the EC-reactor and standard solid/liquid separation equipment. The reactor was conceptualised in 1992 and developed to handle a hydraulic flow of 1 megaliter/day. Laboratory experiments, field tests and demonstration units yielded four different pilot units treating from 50 - 200 kiloliter/day. These are currently being tested on respectively sewerage (phosphate removal) and Acid Mine Drainage (AMD).

An overview of results on removal of sulphate from AMD.

- Continuous simultaneous removal (one pass) of:
- 80%+sulphate removal from 700-200 mg/l
- Acidity – increased pH from 1.8 to 6.5
- Removed 95%+ of the base metals.
- A first order cost indication
- Capital investment - ca.10% of existing processes
- Operating cost – ca.R1.50-R2.40/kiloliter.subject to the electrochemical recovery cost of the zinc catalyst.

2.4.2 A resume of the contents of this final report to Amcoal. (Dec 1998)

The main thrust of the joint project can be summarised as follows:

- To present Amcoal with the **EC-results** obtained during an initial demonstrating test period at SACE, Landau Colliery (Kromdraai), which mainly spans the last ten months of 1998.
- To show that the new electrochemical water treatment system called (ECODOSE) can satisfactorily **treat AMD (Acid Mine Drainage) to remove sulphate and the acidity** associated with these typical mine effluents.
- To integrate the test results of the EC-reactor and those of the envisaged demonstration unit in a process for the **continuous removal of acidity and sulphate.**
- To give an appreciation of the potential of the EC-system system **in wider applications** like sewerage, gold mine effluents, organic pollution, recovery of base metals and its very promising synergy with other processes such as the synergy with the bacterial sulphate reducing (BSR) processes.

- To generate enough data to **compare between the current candidate processes** for sulphate removal

2.4.3 The candidate processes for sulphate removal.

The following existing and “new” processes are contenders:

Pressure driven Membrane Processes (RO)

This process uses an external pressure to permeate water through a semi-permeable membrane. The pressure energy requirement makes the system very expensive both from capex and opex considerations. The brine resulting from these systems poses a further (more aggravating) pollution disposal problem. Dissolved salts having low solubility can not be tolerated by these membranes.

Electrodialysis (ED)

The driving force in this case is an electric current driving charged ions across a selective membrane to accumulate in respectively a salt and a clean water compartment. The capex and opex of these systems are very expensive and suitable only for high-value metals extraction from relatively high concentrations.

Ion exchange (IX)

IX uses the ability of specially designed synthetic resins to exchange a pollutant ion for a less polluting ion. It does also not effect demineralization and again presents the disposal problem of the brine. The capex and the subsequent opex of these processes are also prohibitively high. The NIMSIX and GYPSIX processes are typical hybrid IX processes using the insolubility of calcium to effect demineralization.

2.4.4 New generation processes

In lieu of the seriousness of the pollution problems, especially the removal of sulphate and neutralization from collieries, it is not surprising that a whole range of “new” process systems are currently being developed. The following processes are being tested and/or developed.

2.4.4.1 The bacterial processes.

The bacterial process for the reduction of sulphate to sulfide and eventually to elemental sulfur seems to be the most promising of the bacterial processes. The Sulphate Reduction Bacteria (SRB) however need energy and nutrient input via from proton and electron donators. It furthermore produces elemental sulfur or insoluble sulfides that must be disposed of while low winter ambient temperature causes “hibernation” of the bacteria.

2.4.4.2 The Ethringite Process

This process was patented in Germany on the 30th June 1985

[Patent Anmelde­nummer 96108876.3]

[Veröffentlichungsnummer 0 250 626]

[Veröffentlichungstag der Anmeldung 7th Jan 1988]

The process consists of several stages which essentially takes the alkalinity of the effluent to ca. pH = 13 before dosing the effluent with an aluminate solution to effect the formation of ethringite. Ethringite is an insoluble double salt complex and consequently precipitates as a solid containing magnesium, calcium and sulphate.

Two problems associated with this process are the recovery of the Aluminum and the re-adjustment of the pH to acceptable discharge levels. Seen in total it is an elegant system but it is highly "process-intensive" using a large number of solid/liquid separation processes.

Forced recovery of the aluminium to offset the process cost could however render the system prohibitively expensive

Purely from a technical viewpoint the system has the advantageous ability of removing sulphate, calcium and magnesium to very low levels.

It could therefore be sensible to take advantage on a synergism existing between this process and the EC-reactor.

2.5 Recommendations, Conclusions and Motivations from the Kromdraai Experiments.

The experiments at Kromdraai motivated the investigation of a suitably designed EC-reactor with its associated peripheral equipment and controls. It was at this stage that a project application was launched to the Water Research Commission resulting in WRC and Eskom to participate in the extended project research. Accordingly the following two aspects were investigated and assessed:

- The objectives as set out in the **WRC application K5/940** [Appended as Appendix (2.6)].
- The capital investment and the operational cost of the system which were largely the **objectives of AOL** which could be summarised as follows:

- Design and evaluate a more powerful EC-reactor (capable of dosing at least 3000 Coul/sec).
- Equip the new reactor with its own completely integrated pre- and post treatment unit operations to simulate a full-scale plant.
- Make provision for the plant to be tested on the widest variety of effluents on the test site.
- Task an independent consultant to assess and design the plant. (**Envig** was tasked to assess and design such an integrated plant while **Lektratek** constructed, commissioned and operated the plant. The detailed **Envig Design Report** is appended as Appendix (3.2) [The Envig Design Report.]
- A detailed **Experimental Operation Report** on the experimental assessment by **Lektratek** is reflected and appended in Appendix (2.4).
- Determine and evaluate the adaptability, operability and sustainability of the plant in the mining environment with special reference to personnel, safety and affirmative action requirements.

A concise discussion of the experimental work at Navigation Collieries is undertaken in Chapter 3 of this report while the detail is presented in Appendix (3.1) [First Penultimate Progress Report on Electrochemical Sulphate Removal.]

2.5.1 Research at Kromdraai

As a first step in research at Kromdraai neutralization was to be affected by electrochemical dosing with ferric electrodes. This dosing technique move the pH from 2.5 to 3.8 in several attempts[figure (2.3)]

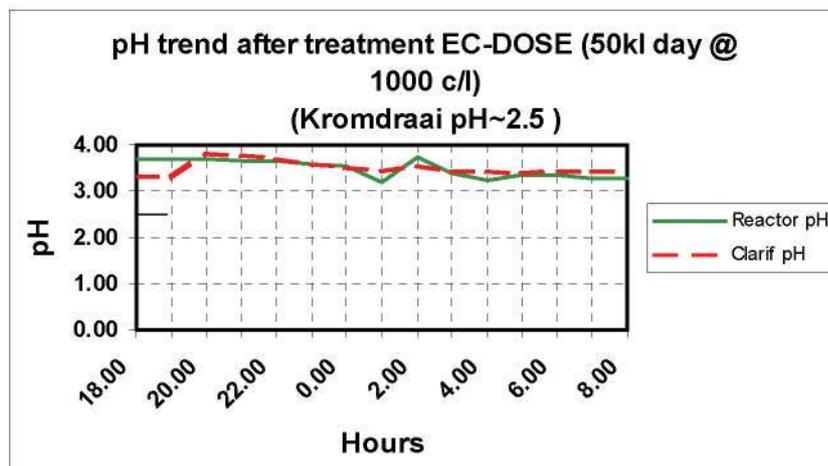


FIGURE 2.3

Neutralization of AMD was subsequently also effected by **chemical neutralization** using lime from the liming plant. The comparative result of this experiment is shown in FIGURE 2.4

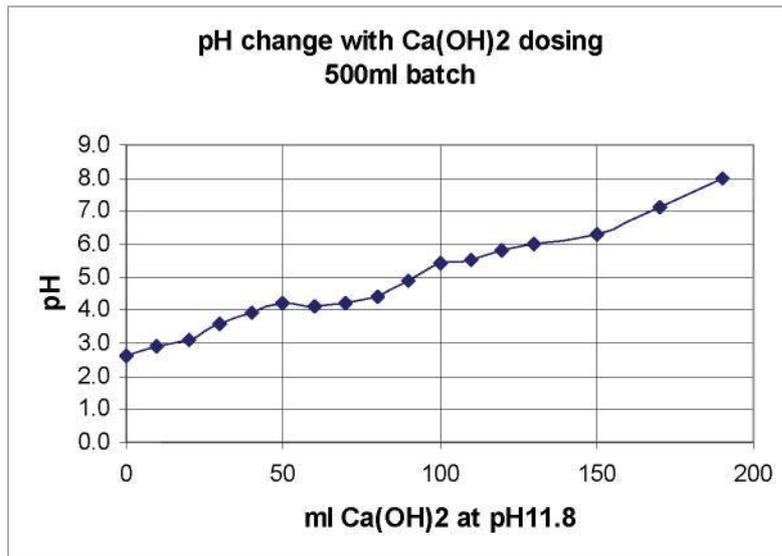


FIGURE 2.4

This EC neutralizing effect was confirmed with a continuous flow experiment as well as with another source of AMD.[TABLE 2.1]. This was also expected but it must be stated that the pH could not be driven far enough.

During the continuous experiments it was apparent that an optimum pH (**thus an optimum charge dosage**) must exist where the sulphate removal is a maximum. This was investigated by starting with an extremely low effluent flow rate and gradually increasing the flow rate while taking samples and analyzing for pH and sulphate in each sample. Through the duration of this experiment the dosing condition was constant at 500 coulomb/sec. The results of this experiment are presented in Figure 2.1. From this figure it is apparent that this optimum is at ca. pH=6. Therefore a 3000coul/liter reactor was required.

The 500coulomb/liter experimental reactor was intermittently operated and supervised by the existing personnel at the Liming Plant for a period of ten weeks (13th.May 1998 to 30th. June 1998.)

Positive identification of the precipitate was effected by X-ray diffraction indicating that the precipitate contained large amounts of zinhydroxysulphate. This was also confirmed in the dissertation (6) by vd Merwe when treating analytically pure sulphate solutions.

A further confirming elemental analysis by ESKOM enabled the composition of a mass balance. This analysis revealed that two distinct precipitates were collected. The first one was virtually pure stoichiometric zinhydroxysulphate whilst the other was a compound that consisted of the same elements but it contained a much higher concentration of sulphate.

This implies that two different species may exist and that they are probably precipitated under slightly different chemical conditions.

A special analysis is envisaged to determine the chemical species and the exact electrochemical set of conditions dictating the formation of these species.

2.5.2 CONCLUSIONS AND RECOMMENDATIONS

From the experimental and demonstration results it is apparent that the system has merit and should be investigated further. The analysis of cost is favourable especially considering the very high potential of zinc recovery either by electrowinning or by direct resale to the supplier. Refer to paragraph 2.3.2.

It is important to recognize that zinc can be considered as a catalyst in the process and it is not at all uncommon to recover the catalyst from catalytic processes.

The EC-reactor, uncommon to most normal effluent treatment processes, removes several pollutants simultaneously. Normal treatment systems (processes) can only remove one pollutant and therefore require a series of unit processes to treat effluent effectively. The dosing of electrons in stead of chemicals enhances the sustainability, operability and controllability of sulphate/acidity removal as an environmental treatment process

2.6 Publications by post graduate students Appendix (2.5)

3. EXPERIMENTS AND PLANT RESPONSE AT NAVIGATION COLLIERIES.

During the initial experiments, several key questions had to be answered. These questions presented themselves very early in the project and had to be answered from the results obtained during experimentation.

3.1 Key questions to be investigated:

- Can the sulphate anion be removed by EC treatment with zinc electrodes?
- Can this insoluble zinc product be separated from the reaction mixture?
- Can this insoluble zinc product be recovered and/or recycled and/or disposed of?
- What is the reaction rate (size of the reactor) between zinc and sulphate?
- What is the Zn/SO₄ consumption ratio for the removal of 1kg sulphate?
- Is the plant cost effective and operable in the mining environment

The answers to the first three questions were largely obtained with laboratory scale investigations and at the Kromdraai test plant. The last three questions however were assessed on the larger scale demonstration plant at Navigation Collieries.

This plant was commissioned and experimentally evaluated by **Lektratek** while an independent assessment and report were executed by **WMB**. **[Refer to appendix (1.3) WMB Assessment Report]**

It was shown that the sulphate anion could be generated in the EC-reactor and that it could be predictably precipitated and separated from the effluent. Recovery as a value added product and/or recycle to the primary industry were technically feasible and a value addition recovery is possible which has promising cost benefits.

[Refer to Appendix (2.2) Recycling Price for Zinc Product Khumba Resources]

The reaction rate between zinc and sulphate was quantified in an MEng thesis by HC vd Merwe and this determined the size of the Continuously Stirred Tank Reactor (CSTR) which was used through out this experimental phase. *[Literature citation (.)]*

3.2 The plant design. [Refer to Appendix (3.2) for detailed design by Envig]

The EC reactor was designed at a nominal capacity of 1 megaliter/day but the budget for the downstream peripheral unit processes allowed a capacity constraint of only 2000 liter/hour (ca. 48000liter/day).

The peripheral unit processes associated with the EC reactor took care of the two streams exiting the EC reactor. These units consisted of:

A specifically designed solid/liquid separator (an inclined plate settling unit) to separate the underflow sludge (the precipitated zinc complex) from the clarified overflow.

A sludge pump to transfer sludge from the separator into drummed storage for subsequent disposal and investigations.

A storage tank to finally condition and release the clarified overflow via an automatically controlled pressure filtration system to an existing disposal facility.

3.3 The objectives for the project.

The experimental part of the project at the Navigation Collieries site was directed at:

Commissioning the integrated demonstration plant and get all systems to operate as designed.

Determining the **technical and economic feasibility** of sulphate removal by electrochemical zinc addition.

Compile an operations manual for the plant with complete education and tuition to all personnel on **starting, operating, controlling and shutting down** the plant under normal as well as emergency conditions.

It was strongly emphasised that the plant should be operator friendly and that it should **enhance the awareness and empowerment** of previously disadvantaged technical plant personnel.

The plant was to be an **educational tool and a technical example** of the design, evaluation, and assessment of emerging technology in the mining industry.

[Refer Appendix (1.6 &1.7) for Affirmative Action Initiatives.]

[Refer Appendix (1.8) Operating manual and procedure]

3.4 The experimental program at Navigation Collieries.

All experiments indicated that sulphate removal is technically feasible but that an integrated larger scale experimental set up was called for. The newly designed demonstration plant fulfilled this need and the following experimental program was scheduled on the plant.

NOTES TO THE FOLLOWING EXPERIMENTAL RESULTS.

NOTE 1.

During this (and the following test periods) the procedure and operation of the plant was assessed by an independent assessor Dr A van Niekerk of Wates, Meiring and Barnard (WMB). Refer in this context to the Assessment Report by WMB appended in Appendix (1.3). The following aspects are emphasised from this report and the Progress Report by Lektratek appended as Appendix (2.4)

NOTE 2.

All results were collected and analysed both on-site and by Eskom. The results for especially sulphate concentration were collated and correlated with zinc consumption and Faraday's law. A computer model to predict and simulate the experimental results was developed and a computer disc with a sample calculation is included with this script. These results are reported in three reports to the WRC namely:

1. First Progress Report (Project K5/940 dated March 2001)
2. Second Progress Report (project K5/940 dated Jan 2002)
3. Final Report for Electrochemical Removal of Sulphate From Effluents in the Mining Industry (Project K5/940 dated May 2002)

NOTE 3.

A concise resume of these reports will be presented here and reference will be made to the relevant reports above and their contents. Only a discussion of the most important results as well as final conclusions and recommendations of the progress reports will be repeated here.

NOTE 4.

The experimental program was divided in three sections namely:

- Commissioning and qualification for the new plant
- Determination of plant performance regarding zinc consumption and cost of operation.
- Dependability during a continuous run.

3.5 Commissioning and qualification experiments.

(5 July 2000 - 6 July 2000)[Refer to Appendix (3.3)]

These experiments were executed to qualify all equipment, to test the control instruments and to ascertain constant flow of the correct effluent to the experimental plant. Four different effluents were available namely

- Schoongezicht (SC)
- Jacuzzi (Jac)
- Fire Hazard (FH)
- Toe Seep or Blaauwkrantz (TS)

The first (SC) and the fourth (TS) were selected for treatment because they represented the two extremes on the mining site. A test program Table (3.1) was designed to start the plant and qualify all unit processes.

TABLE (3.1). Preparation, commission and assessment experiments.

DATE	ACTIVITY (ACHIEVEMENT) ON-SITE
5/5/00	INVENTORY OF ELECTRICAL AND MECHANICAL EQUIPMENT
8/5/00	EXP FH1 DRY AND WET RUN + TEST RUN ON FH EFFLUENT.
11//5/00	TEST FUNCTIONAL INTEGRITY OF CONTROLS AND POWER.
12/5/00	TEST WITH FH TEST PLANT OPERATING SET VALUES
19/5/00	TEST pH + FLOW BALANCE FOR pH CONTROL.
8/6/00	EXP FH2 COMPARE INPUT/OUTPUT ELEMENTAL ANALYSIS
20/6/00	EXP FH2 (=EXP FH3) REPEAT + MIX IN 10% SC EFFLUENT.
5/7/00	EXP SCT1PREP FOR TEST WEEK ON SC + FH EFLUENT MIX

DATE	ACTIVITY (ACHIEVEMENT) ON-SITE
6/7/00	EXP SCT1 PROFILING pH & SULPHATE VS TIME
10/7/00	EXP SCT2 REPEAT - ATTAIN BALANCE + OPTIMUM SULPHATE
11/7/00	EXP SCT3 REPEAT TO CONFIRM SC2 INTERPRETATION.
12/7/00	EXP SCT4 PERFORMED BY LANDAU PERSONNEL ALONE
13/7/00	EXP SCT5 REPEAT EXP SC5 FOR START-UP TRAINING
13/11/00	EXP SCA1.PREPARE FOR ASSESSMENT BY WMB 13-16/11/00
14/11/00	EXP SCA2 IN/OUT EQUILIBRATE & RUN @ "BEST" SETTINGS
15/11/00	EXP SCA3 REPEAT AND CONFIRM SCA2
16/11/00	EXP TSA1 IN/OUT EQUILIBRATE & RUN @ BEST EXP (TS+SC) A1 IN/OUT EQUILIBRATE ,RUN AND EVALUATE.

Legend:

EXP – Experiment on (effluent type) (number)

EXP (TS+SC)A – Experiment on Toe Seep and Schoongezicht effluents mixed for assessment

FHT - Fire Hydrant effluent for own Test purposes.

SCA – Schoongezicht effluent for assessment purposes

SCT - Schoongezicht effluent for own test purposes.

TSA – Toe Seep effluent for assessment purposes.

3.5.1 The following operational and analytical aspects were confirmed:

- The plant performed as predicted and an equilibrium was reached within 2 hours with the input pH = 3,94. At this stage the output effluent showed a consistent pH = 6,6 which is expected to be close to the anticipated optimum target pH = 6,8.
- During these experiments it was evident that the determination of sulphate concentration after treatment had to be effected on site. If a proper field test kit is not available, immediate separation (filtration) of the precipitate from the sample and a subsequent (later) analysis was found to yield satisfactory results.
- With the design constraint (refer § 3.2.1) the EC reactor operated on the lower 30% of its performance capability. This created a control problem because the current generator capacity could only be adjusted in discrete steps. The system was controlled at the lowest setting (25%) of the current generator. A stable operation at the equilibrium point could be maintained.

- It was also evident that the inclined plate clarifier was operating at its design capacity. A decision was made by the mine personnel to discard the final overflow from the clarifier directly to the existing effluent drainage system.
- Starting and operating the plant was always under control and could effectively be communicated to and executed by supervisory personnel on shift.

3.6 Experimental Results And Plant Performance.

(10 July - 13 July 2000)(13 Nov - 16 Nov 2000)

The Technical Committee decided to evaluate the performance of the EC plant on only one effluent called the Schoongezicht (SC) effluent. A typical elemental analysis of this effluent is shown in Appendix (3.3) and the typical EC treatment procedure and results are presented in the same Appendix

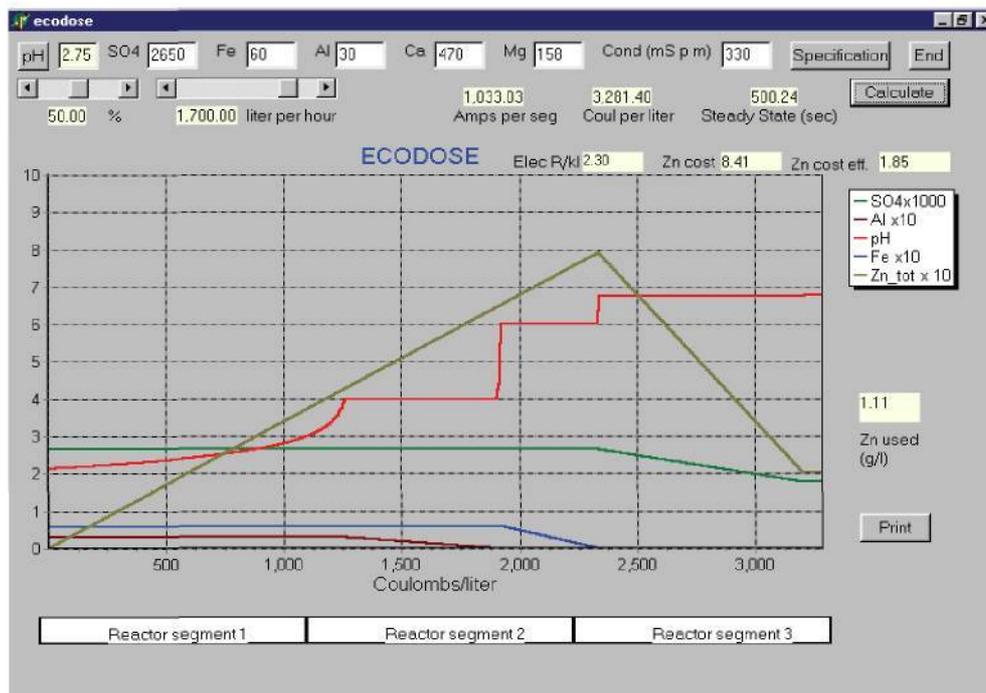


FIGURE 3.1

An example of the **simulation program result** is presented graphically on Figure (3.1) giving an indication of how the different variables change with electrical dosage of coulomb (electrical current/time).

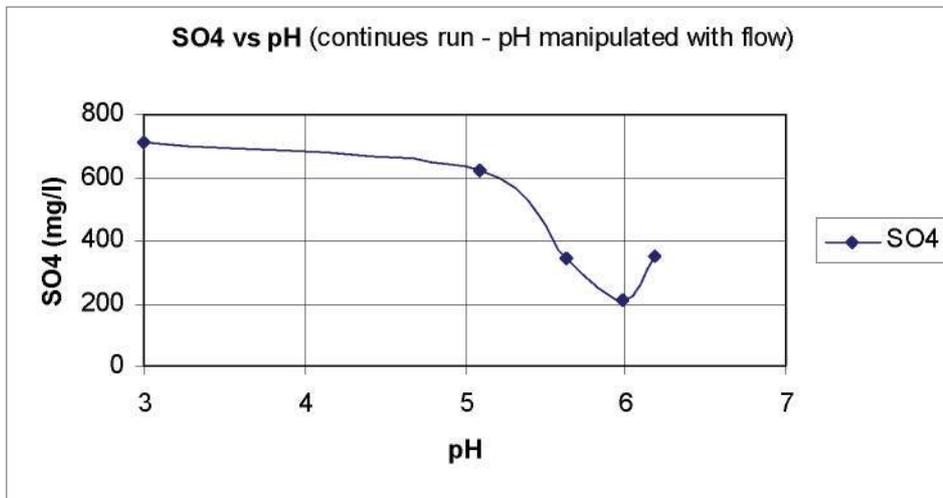


FIGURE 3.2

The **experimental relationship** between sulphate/pH and time is shown for EC treatment. [FIG 3.2].

These two figures depict the experimental and theoretical relation between sulphate/pH with electrical charge or dosage.

This relationship is extremely important because it stresses the fact the formation of the zinc complex is (amongst others) dependent on the pH (acidity), the zinc/sulphate ratio, the chemical speciation and the electrical dosage.

It was clear at an early stage that the ultimate consumption (and possible recovery of zinc) would eventually determine the technical and economic feasibility of the EC process

The data for the experimental results is representative of all the responses during three sets of experiments conducted in May, July and November 2000. Comparing the experimental results of the three periods the following critical variables were identified.

3.6.1 The zinc/sulphate ratio

The zinc consumption is the most crucial variable in this process. It determines the power consumption, the sulphate removal and the operational expenditure. Zinc consumption was estimated through four possible means:

Calculate the theoretical zinc/sulphate ratio from the stoichiometrical formula obtained from XRD analysis.

Weighing the electrodes before and after experiments

Analyse the process streams and determine a mass balance.

Calculate the zinc consumption via the Law of Faraday.

This ratio decreased steadily as experimental optima were attained. This is evident from the calculations presented in a previous report. (WRC First Progress Report. Project K5/940, §4, p14, March, 2001). Graph 1 p18 (Zinc/sulphate ratio vs. dates) shows this tendency clearly. The following three tabulations reported previously verify this adamantly. It is repeated for clarity and to strengthen the argument:[TABLE (3.2)(3.3)(3.4)]

TABLE 3.2. TABULATION OF Zn/SO₄ RATIO AND PERFORMANCE VARIABLES FOR SC AND TS EFFLUENT TREATMENT CALCULATED FROM THE FARADAY LAW.

[Refer to Appendix 3 nov 2000] [first progress report march 2001]

EXP DATE	Zn/SO ₄ THEORY +XRD	Zn/SO ₄ EXP	pH OUT TIME	SO ₄ REMOVED ppm	SO ₄ IN ppm
14/11/2000	2.7	0.61	6.48 13h58	1000 37.7%	2650
15/11/2000	2.7	0.66	6.71 13h25	1403 52.8%	2653
16/11/2000	2.7	0.70	3.83 10h16	6404 41.2%	15550
16/11/2000	2.7	1.47	5.58 14h26	>2800 >70%	>4000

TABLE 3.3: Zn/SO₄ RATIOS FROM RECLAIMED SLUDGE (ANALYSES BY ESKOM TSI)

(Refer to Appendix 3)

DATE	ZINC (mg)	SO ₄ (mg)	MASS RATIO [Zn/SO ₄]
14/11/00 TSI No 200247807	555531	191044	2.907
14/11/00 (S1) TSI No 200250857	239700	121500	1.973
14/11/00 AGED SLUDGE TSI No 200247895	494712	268290	1.844 (#) TSI No 200247894

TABLE 3.4: COMPARISON OF ALL THE METHODS TO DETERMINE THE ZINC CONSUMPTION

	SPECIFIC Zn CONSUMPTION IN (m/m)[Zn/SO ₄]			
THEORY STOICHIOMETRY	2.7/1.35 (REFER TO p... FOR THE RATIONALE)			
WEIGHING	WEIGHING IS INACCURATE WITH THE CURRENT MASSMETER			
ESKOM ANALYSES	2.907	1.907	1,844	
FARADAY	(0.6) (0.66) (0.70) (1.47) ----	FROM EXPERIMENTS ON 14-16/11/2000		
	(1.73) (3.53) (2.50) -----	FROM EXPERIMENTS ON 11-13/7/2000		

3.6.1.1 This tabulated theoretical and experimental detail suggest the following deductions:

- The stoichiometry of $Zn_4(OH)_6(SO_4)$ predicts a $[Zn/SO_4] = 2.7$ as reflected in (Table 3.2). This stoichiometrical formula was determined by XRD at the Eskom TSI laboratories.
- The experimental results analysed by Eskom on recovered sludge samples shows different (LOWER) values. (Table 3.3)
- Analyses obtained from the supernatant effluent after treatment indicate even LOWER values.
- Literature (1) as quoted below, suggests inorganic polyionic complex formation for the base metal hydroxysulphates with $[Zn/SO_4]$ ratios of 1.35 down to 0,66.

(1) Chemistry of the Elements p 1404 & 132.

Authors: Greenwood & Earnshaw.

- Considering KNOWN AND STABLE CHEMICAL SPECIES the minimum value that the zinc/sulphate could attain is determined by $Zn(OH)_2$ or ZnO . These would yield ratios of respectively 0.8 and 0.65. The latter two ratios are more in line with what was consistently obtained in the complete series of experiments.
- The best ratio could not be attained in this series of experiments due to the following pronounced influence of acidity.

3.6.2 pH Influence On Sulphate Removal.

From Fig 3.2 it can be seen that a maximum sulphate removal presents itself between pH = 4 and pH = 6. The maximum removal is obviously present over a large (very sensitive) pH range and an optimum must be established taking into account dosage, chemical speciation

and retention time in the reactor. It is for this reason that pH is used to control the steady state (equilibrated) operation of the currently used Continuously Stirred Tank Reactor (CSTR). The reactor characteristics are very good for initial experiments when the relationship between process variables is established. This type of reactor is however not ideal to investigate process reaction kinetics or to produce commercially. The main disadvantages are:

- Slow response (long residence time) for step changes in the feed.
- Difficult and slow feedback control response due to long residence time
- At pH = 6-7 in the reactor the pH correction with a strong acid (low pH feed) is very rapid and the controller tends to oscillate.
- The principle of control is to balance the alkalinity created by the electrical current with the flow rate of acidic effluent into the reactor.

3.7 Necessity For A New Continuous Flow Reactor (CFR)

The CFR is ideally suited for electrochemical processes because electrodes can be staggered and the current densities varied to suit the reactions. This configuration will have the following advantages:

- Extremely stable and high integrity of control.
- By-products such as the base metal hydroxides can be separated at any position along the flow path. This would enable the recovery of a higher value (purer) zinhydroxysulphate for recycle.
- Different metal electrodes could be utilised to get the benefit of cheaper iron electrodes for the neutralisation mode and zinc is then used only for the sulphate extraction mode

A new CFR was designed and can be engineered to replace the current CSTR while using the same basic structure at Navigation Collieries

3.8 Continuous operation.

Continuous operation, minimum supervision and simple operating procedures are prerequisites for any service plant. It was required to run the EC-reactor for a non-stop period of 12 days. Only casual supervision was effected once a shift. The operators were taught and instructed to shut down the plant if anything seems abnormal.

The full period was completed without a single stoppage and consistent results were obtained from the pre-set control equipment as well as the final analyses profiles.

A report on all observations is presented in Appendix (1.8)

This proves the EC plant's simplicity, operability and dependability.

3.9 Other attributes of the EC System.

During the extensive experimentation that was undertaken with EC in various environments and conditions the following, usable (?) peculiarities came to the fore.

3.9.1 Synergism with bacteria

Experiments at a sewerage plant resulted in a massive proliferation of bacteria in winter. Upon investigation it turned out to be mainly Sulphate Reducing Bacteria (SRB).

Further analysis revealed that the sulphate was indeed lower after treatment. It was obvious that the conditions created between the electrodes were conducive to the bacterial proliferation.

These conditions were the resistive heat generation between the electrodes (higher, more acceptable temperature) and an abundant nutrient supply in the form of easily accessible hydrogen gas.

Excess nutrients - also from chemical reduction products of hydrogen gas - were obviously also available.

A joint project together with Coal 2020 is investigating this.

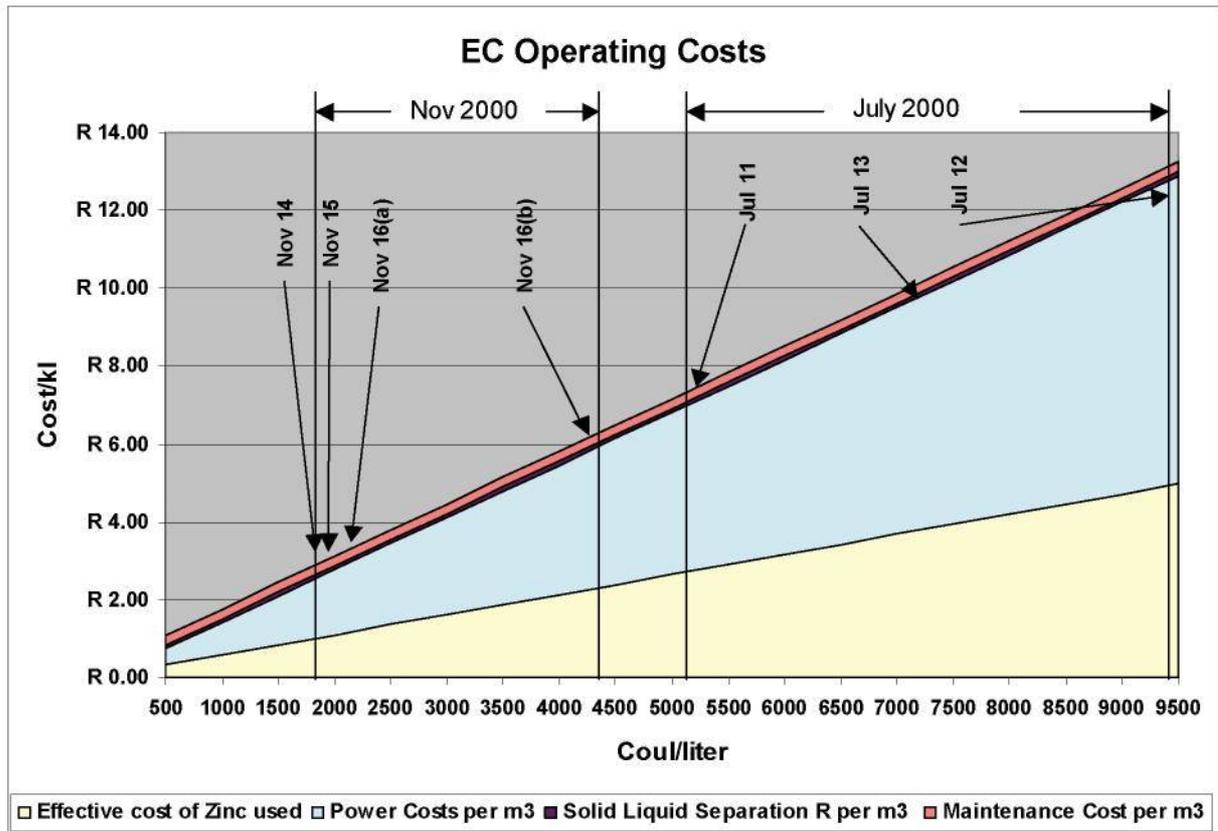
3.9.2 Synthesis of in situ chemical reactants

In this case several reactants can be generated to obtain various chemical effects. A typical example is the anionless production of the trivalent cations for flocculation namely Al(III) and Fe(III). The elegance of this technology when considering the transport of only metal instead of liquid soluble salt as well as the prevention of ingress of anions such as chloride and sulphate into the ecosystem is dramatic.

3.10 Computer model and cost estimation.

3.10.1 Graphical summary of full experimental results

From results of trial runs at Navigation (Appendix 3.3) it is possible to estimate the operating costs as shown in graph 3.1. This is also confirmed by the computer simulation as discussed in paragraph 3.6



GRAPH 3.3

Cost (Opex) versus electrical charge input (to remove 1000mg/l SO₄)

[Calculated from experimental results in Appendices 3.3]

3.10.1.1 Notes to Graph 2

- There is a consistent improvement in zinc/sulphate ratio as well as the projected (calculated) Opex during the course of this project which was also emphasised by the independent assessor. (WMB)
- The electrical cost can be halved by doubling the area of the electrodes.

3.10.2 Cost Estimation

- From the above graph it is possible to estimate the operating costs at approx R5/kl for a sulphate loading of 1000mg/l .
- The capital outlay can be extrapolated from the cost of building the existing plant and comes to approx R 2.5M per MI/day

[See appendix 1.3 (WMB report) for an independent estimation of costs]

4. Appendices

The appendices are a selection of separate Word and Excel document files.

- Appendix 1 Mine decant volumes
- Appendix 2 Research objectives
- Appendix 3 Evaluation report by WMB on the EcoDose process
- Appendix 4 Zinc cost estimation
- Appendix 5 Mathematical model
- Appendix 6 Interim Progress Report to Steering Committee
- Appendix 7a Results July 2000
- Appendix 7b Results November 2000
- Appendix 8 Assessment report on continuous operation of EC reactor
- Appendix 9 Affirmative cooperation and participation in the EC project

Extract from the IMF Report to the WRC (To be published in 2002)

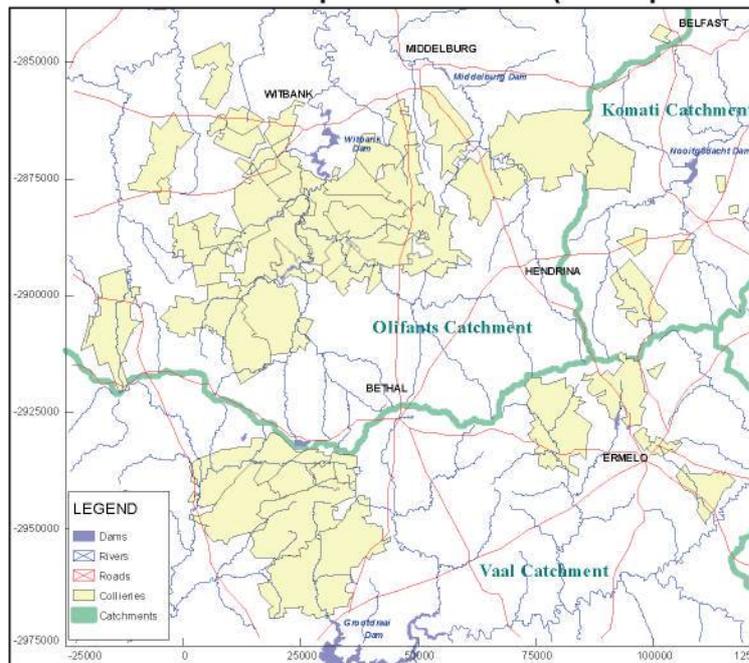


Figure 1. Distribution of mine lease areas in Mpumalanga.

The total volume of water expected to eventually decant from the mines is difficult to anticipate. This can, at best, be estimated from current information if we are looking at a time frame some 40 years down the line. Through the application of existing methodologies the potential decanting volumes have been calculated for each of the mines that submitted information for evaluation. This constitutes an estimated 95% (by surface area) of all the collieries present in the Mpumalanga Coalfield. The predicted decanting volumes are graphed in Figure 2.

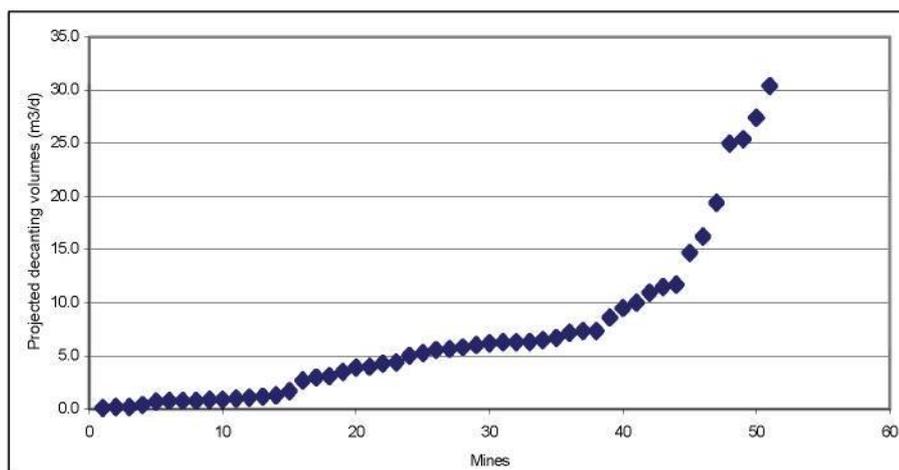


Figure 2. Projected flux from each of the existing collieries during future decanting (each dot represents a mine, sorted from the lowest to the highest value).

The volumes are related to the size of the mine but also to the mining method applied. The mines with the anticipated high volumes are the modern high-extraction mega-mines. In this respect, it should be stressed that the actual decanting quantity in the above graph is meaningless without also considering the circumstances at the mine itself. These values are merely issued as a range of values for mines to examine their relative position to the whole ensemble of collieries.

In total, about 360 ML/d will decant from all the mines together. On a catchment basis, the breakdown is:

Wilge/Klip	Olifants	Klein Olifants	Vaal	Komati
(ML/d)	(ML/d)	(ML/d)	(ML/d)	(ML/d)
23	170	45	120	2

For illustrating the significance of these volumes, the total volume to decant from these mines is in the same order as the annual natural run-off into the Witbank Dam.

The aforementioned information demonstrates that intermine flow can and must be managed. It is essential that mines start planning their water management in conjunction with adjacent collieries. Two levels of planning are suggested:

- The local level where neighbouring mines plan together.
- The regional level where corporate head offices and the government get together. At this level policy matters and regional planning matters should receive attention. The prime question that needs to be addressed should be how to minimise and manage the problem on a catchment-specific basis.

WRC Proposal K5/940 28 Jan 1999 paragraph 5

5. RESEARCH OBJECTIVES.

The main thrust of this research is to commercialise and transfer a new technology to remove sulphates and phosphates from effluents at the Lethabo Power Station:

PHASE I

- The **determination of an existing symmetrical reactor's** optimal phosphate removal performance regarding system variables such as flow rate, concentration, retention times, geometry and kinetic performance.
- The **determination of an existing symmetrical reactor's** optimal sulphate removal performance regarding system variables such as flow rate, concentration, retention times, geometry and kinetic performance.
- The **recycling and re-use of electrodes** used in the electrochemical processes.
- Identification and testing of the **solid-liquid separation** processes required for maximising water recovery and water quality improvement.
- Demonstrate the simplicity, operability, reliability and capital and operating cost effectiveness.
- Environmental sustainability

PHASE II

- The design, development and qualification of an **'improved' unsymmetrical reactor**, able to handle scrap metal of various kinds for the treatment of various effluents.

Note: The concept of **symmetrical/unsymmetrical** reactors distinguishes between the two cases where a reactor has a fixed (geometrical) form, which stays the same during operation, as opposed to an unsymmetrical reactor where internal variables such as the geometry, packing density etc. change continuously.

**INDEPENDENT ASSESSMENT BY WMB
EVALUATION OF THE ECODOSE PROCESS**

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 - 1.1 Process Description
 - 1.2 Auxiliary Reactions
 - 1.3 Process Constraints
 - 1.3.1 Competing reactions
 - 1.3.2 Partial sulphate removal
 - 1.4 Electrical Power Requirements

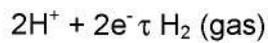
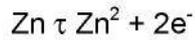
- 2. PROCESS EVALUATION
 - 2.1 Start-up of Process
 - 2.2 Process Loading
 - 2.3 Process Conditions
 - 2.3.1 Pre-treatment
 - 2.3.2 Electrical power addition
 - 2.3.3 Temperature
 - 2.3.4 Toxicity/inhibition
 - 2.4 Process Control
 - 2.5 Process Performance
 - 2.6 Residue Generation
 - 2.7 By-product Generation

COALTECH 2020 EVALUATION OF THE ECODOSE PROCESS

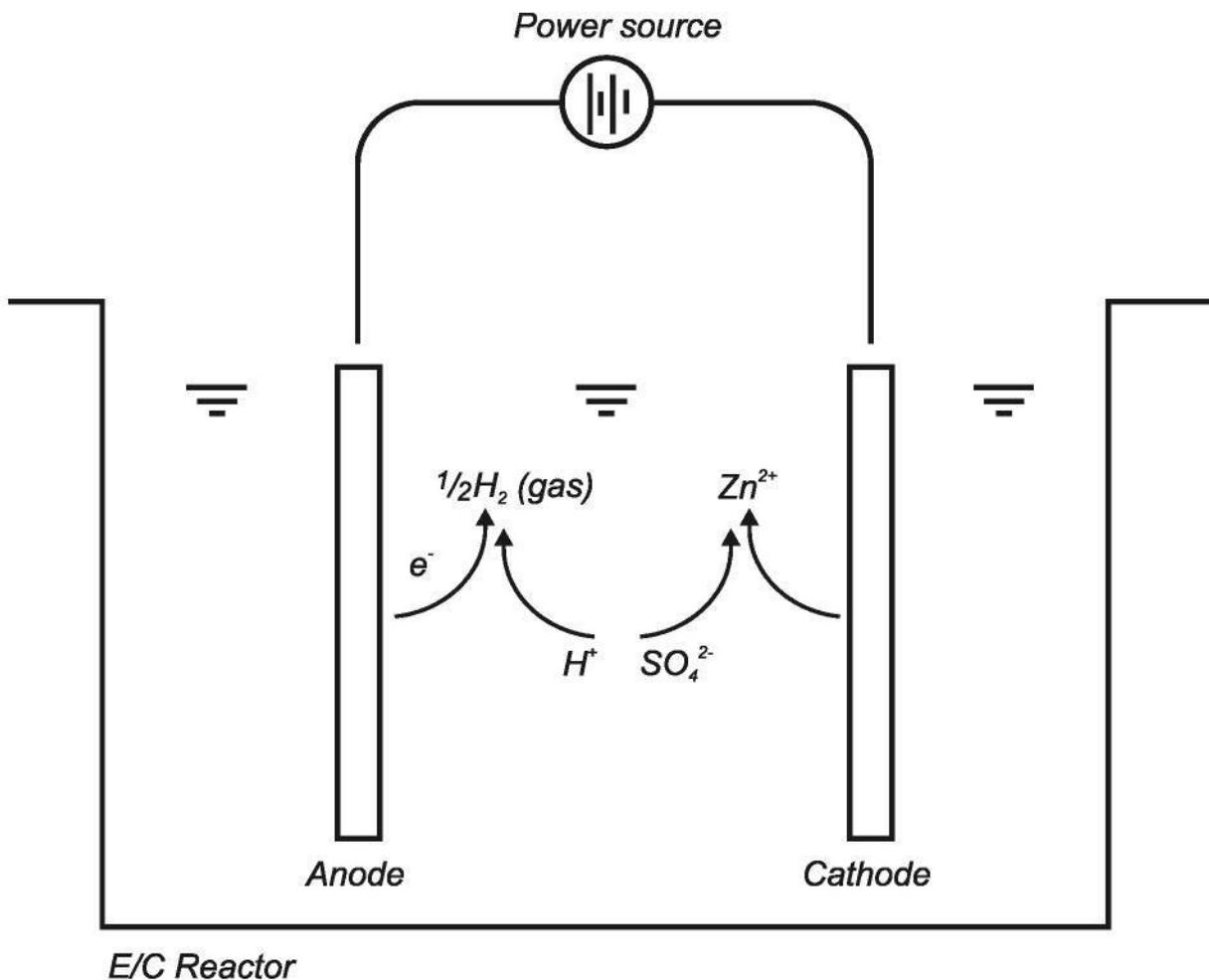
1. PROCESS FUNDAMENTALS

1.1 Process Description

EcoDose is an electrochemical process which utilise the following two (2) coupled reactions:



These two (2) coupled reactions take place at the cathode electrode and anode electrode respectively, as shown below:



At the optimum process conditions of temperature and pH, the liberated zinc forms an insoluble zinc – hydroxy –sulphate precipitate. Two alternative, but not mutually exclusive precipitate compositions have been postulated:

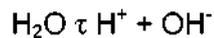
- $Zn_4(OH)_6SO_4$ with the following mass ratio:
 $Zn : SO_4$
 $2.7 : 1(kg/kg)$
- $Zn_2(OH)_2SO_4$ polymers with the following mass ratio:
 $Zn : SO_4$
 $1.36 : 1(kg/kg)$

The amount of zinc required to drive the sulphate precipitation reactions can therefore vary, depending on the chemical precipitate composition.

The nett E/C treatment effect on the chemistry on an acid mine water is progressive neutralisation and removal of some sulphate.

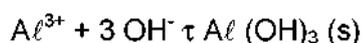
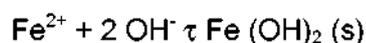
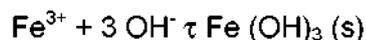
1.2 Auxiliary Reactions

The electrochemical treatment progressively removes the free hydrogen ion (H^+) and shifts the pH of the water. As more H^+ is effectively removed, dissociation of water takes place:



The relative abundance of OH^- increases, reflected in an increased pH.

Acid mine waters typically contain dissolved metals species, specifically aluminium, iron and manganese. As the mine water pH increases, some of these metals will start to precipitate as metal hydroxides:



These metal hydroxides have different pH thresholds, above which the metal will start to precipitate. These pH thresholds are typically as follows:

- for ferrous iron, Fe^{2+} @ 6.5 – 7.0
- for ferric iron, Fe^{3+} @ 3.5 – 4.0
- for aluminium, Al^{3+} @ 4.5 – 5.0

The manganese metal (Mn^{2+}) will typically not precipitate at the relatively low pH at which the electrochemical reaction takes place. The threshold pH for manganese hydroxide precipitation is typically > 8.

The nett effect of the metal hydroxide precipitation is that the OH^- generated in the dissociation of water is effectively consumed. The process pH will therefore not increase above certain thresholds, until the metal hydroxides are precipitated. The plateau-effect of a temporary stable pH as the electrochemical reaction proceeds has been well documented by a number of batch studies.

1.3 Process Constraints

1.3.1 Competing reactions

The optimum pH for the formation of zinc-hydroxy-sulphates appears to be in the range 6.2 to 6.8. This implies that the bulk of the mine water acidity has to be satisfied, before the optimum process pH is achieved. There may be an imbalance in the process requirements for:

- *acidity neutralisation*
- *sulphate precipitation*

The typical situation, if any significant metal concentrations are present in the acid mine water, is that an excess of Zn^{2+} (in terms of SO_4 precipitation requirements) could be released into the water. The excess Zn would precipitate as either:

- *zinc-hydroxy-sulphates*
- *zinc hydroxide*

The nett effect of the excess Zn^{2+} is that a relatively large amount of zinc is consumed in the process of sulphate removal.

1.3.2 Partial sulphate removal

The electrochemical process also has a constraint in terms of the fraction of sulphate, which can practically be removed. The sulphate ion in mine water is typically present in the hydrogen sulphate (HSO_4^-) and in the sulphate form (SO_4^{2-}). The hydrogen sulphate and the sulphate anions are associated with different counter cations. In acid mine water, these counter cations may typically be H^+ , Al^{3+} , Fe^{3+} , Fe^{2+} , Ca^{2+} , Mg^{2+} , Na^+ etc. The process development work done to date indicated that only the HSO_4^-/SO_4^{2-} associated with free acidity (H^+) and mineral acidity (Al^{3+} , Fe^{3+} etc) will be removed by the E/C process. The HSO_4^-/SO_4^{2-} associated with counter-cations such as Ca^{2+} , Mg^{2+} , Na^+ etc will not be removed by the E/C process.

The E/C process is therefore only applicable to acid mine water and will not be effective in neutral or pre-limed mine waters.

1.4 Electrical Power Requirements

The electrochemical reaction is driven by electrical power, as quantified in terms of Faraday's Law:

$$M = (Z.I.t)/F$$

Where

$$M = \text{mass of metal (zinc) released over a time (gm)}$$

$$Z = \text{equivalent mass of metal}$$

$$= (\text{gram/mole}) / \text{valence}$$

$$I = \text{electrical current (Amps)}$$

$$t = \text{time (secs.)}$$

$$F = \text{number of charges per equivalent mass} = 96\ 500$$

In the case of a zinc electrode, the mass of zinc released by a current of 1000 A flowing for 1 second is as follows:

$$M = (65.4/2)(1000)(1)(96\ 500)$$

$$= 0.336 \text{ gram of zinc}$$

The relationship between electrical charge and electrical current:

$$C = I \cdot t$$

Coulomb = Ampere x Secs

The electrical power consumption in the electrochemical reactor:

$$\begin{aligned} \text{Power (W)} &= V \cdot I = I^2 R \\ \text{Energy (J)} &= V \cdot I \cdot T = I^2 R \cdot t \\ \text{Where } V &= \text{voltage across electrodes (volt)} \\ I &= \text{current flow (ampere)} \\ R &= \text{electrical resistance (ohm)} \end{aligned}$$

The electrical power input to an E/C reactor is typically expressed in terms of Coulomb/ℓ (or m³) of mine water treated.

The power input, into the E/C reactor also has the effect of heating the water, due to the energy dissipation. For example, in a perfect E/C reactor with no side-reactions and operating at an electrical current of 1000 Ampere/L with a voltage differential of 6 12, the temperature increase would be as follows:

$$\begin{aligned} \text{Power} &= V I \\ &= 12 \text{ V} \times 1000 \text{ A} = 12\,000 \text{ W} \\ \text{Energy} &= VIt, \text{ for one second} \\ &= 12\,000 \text{ J} = 12 \text{ kJ/sec} \end{aligned}$$

At a mine water feed rate of 0.5 ℓ/sec, the temperature increase:

$$\begin{aligned} \Delta T &= E / (Sh \times Q) \\ \text{Where } \Delta T &= \text{temperature increase (}^\circ\text{C)} \\ E &= \text{energy input (kJ)} \\ Sh &= \text{specific heat of water} \\ &= 4.22 \text{ kJ/kg/}^\circ\text{K} \\ Q &= \text{flow rate (kg/sec)} \\ &= 0.5 \text{ kg/sec} \\ \text{Thus } \Delta T &= 12 \text{ kJ} / (4.22 \times 0.5) \\ &= 5.7 \text{ }^\circ\text{C} \end{aligned}$$

The following table gives an indication of the potential temperature increase, associated with different energy inputs:

Electrical dose (Coulomb/ℓ)	Electrical voltage		
	4V	8V	12V
1 000	0.9	1.9	2.8
2 000	1.9	3.8	5.7
3 000	2.8	5.7	8.5
4 000	3.8	7.6	11.4
5 000	4.7	9.5	14.2
10 000	9.5	18.9	28.4

The temperature increase can therefore, be conveniently manipulated by the voltage at which the E/C reactor operates.

2 process evaluation

The EcoDose process was evaluated on the basis of pilot plant operations and results at Navigation Colliery. The pilot plant configuration is shown in **Figure 2** and incorporates the following features:

- *Mine water feed tank.*
- *Mine water feed pump.*
- *Mine water feed flow meter.*
- *Electrochemical reactor with three parallel compartments.*
- *Electrical power supply*
- *Lamella clarifier with desludging pump*
- *Treated mine water filter.*

The pilot plant power supply had a maximum capacity of 45 kW and provided a reverse polarity electrical current. The electrical current was supplied in cycles, which lasted 16 secs. The power supply could be operated for 25 % (4 secs out of 16 secs), 50 % (8 secs out of 16 secs), 75 % (12 secs out of 16 secs), or 100 % (16 secs out of 16 secs) of the maximum installed capacity. The polarity could be reversed at a selected frequency. The polarity reversal is important to prevent the passivation of the zinc electrodes.

The downstream clarification/filtration processes dictated the pilot plant hydraulic capacity of 48 m³/day. The electrochemical reactor could be operated at a much higher flow rate.

2.1 Start-up of Process

The E/C process could be started up very rapidly. The normal start-up procedure is to first operate in a batch mode, before switching to a continuous flow mode. The batch operation was continued until the optimum pH for zinc-hydroxy-sulphate is reached, before switching to the continuous flow mode of operation.

The process could be started up within 1 to 2 hours.

2.2 Process Loading

The EcoDose Process was operated successfully in July 2000 and November 2000 on two (2) types of mine water:

- *Acidic Schoongezicht mine water*
- *A blend of Schoongezicht mine water(90 %) and Toe Seepage (10 %)*

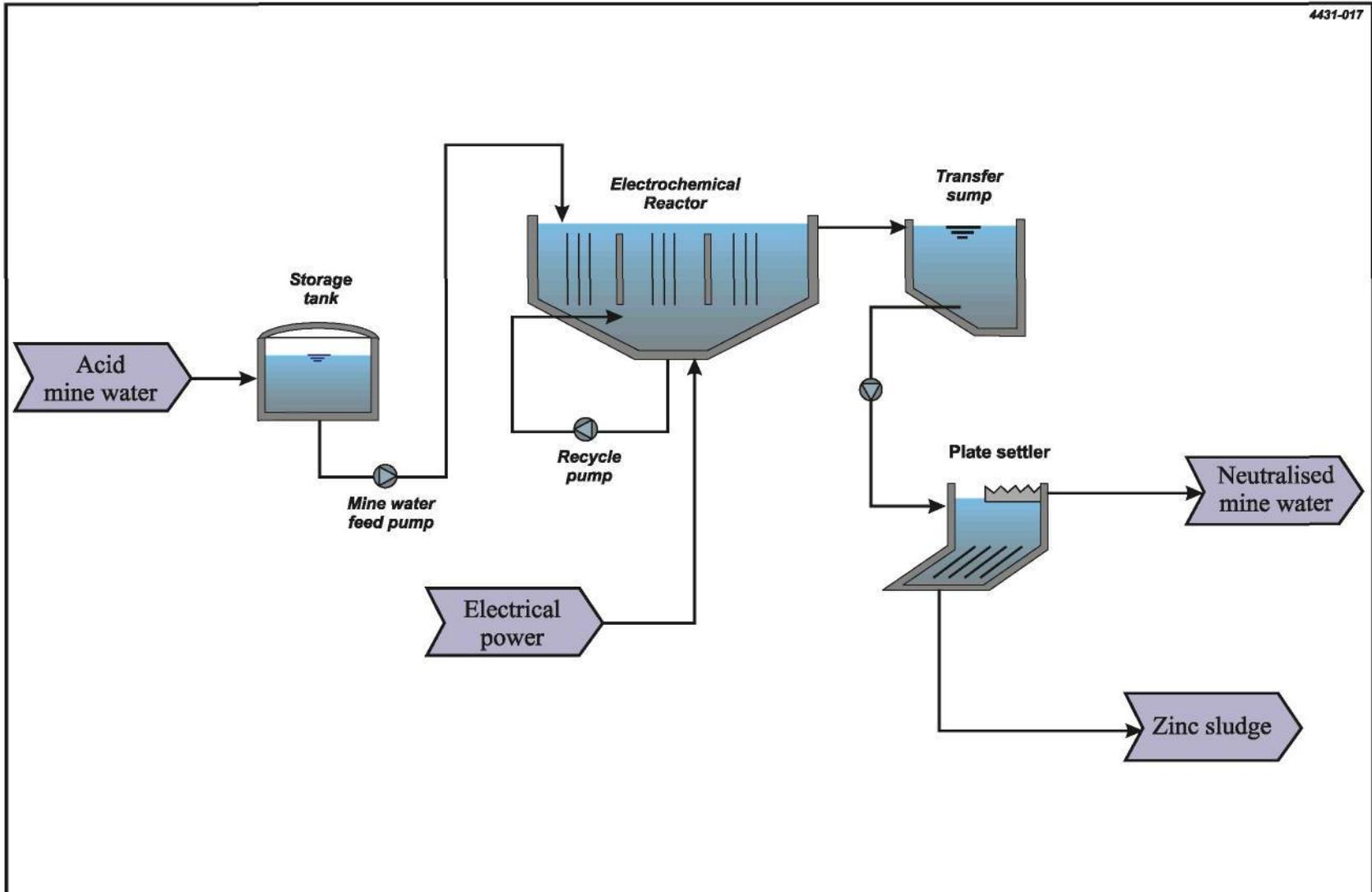


Figure 2 : Electro-Chemical Ecodose Process - Pilot Plant Flow Diagram

The reactor was regularly operated at the maximum feed capacity of 48 m³/day. The feed water sulphate concentration was typically in the range of 2 400 to 2 600 mg/ℓ for Schoongezicht mine water and in the range 3 400 to 3 600 mg/ℓ for the Schoongezicht/Toe Seepage blend water.

2.3 Process Conditions

2.3.1 Pre-treatment

The acid Mine water did not receive any form of pre-treatment.

2.3.2 Electrical Power Addition

The power input was dictated by the voltage across the electrodes, the electrical current and the fraction of time that the power was on. The electrical current was determined by the conductivity of the mine water between the electrode plates.

The charge input to the process can be expressed in terms of Coulombs per unit volume of mine water treated. The electrical charge input was varied between 2 000 to 10 000 Coulombs/ℓ for the different experiments. The electrical charge input can be related to the influent sulphate concentration, although the relationship differed for different experiments. This is illustrated below:

< Pilot Test on 14 November 2000

The acid Mine water feed was on average 42 m³/day with a feed SO₄ concentration of 2600 mg/ℓ. The E/C reactor was operated at a pH = 6.4 to 6.6.

The electrical charge dose fluctuated between 1800 and 2200 Coulomb/ℓ. The sulphate was removed down to a concentration of 1 600 to 1 700 mg/ℓ. The calculated ratio of Zn/SO₄ was only 0.63.

< Pilot Test on 16 November 2000

The acid Mine water feed rate was 8.1 m³/day with a feed SO₄ concentration of 3 800 to 4 000 mg/ℓ. The E/C reactor was operated at a pH = 5.4 to 5.6.

The electrical charge dose was relatively constant at 10 000 Coulomb/ℓ. The sulphate was removed down to a concentration of 1 200 to 1 600 mg/ℓ. The calculated Zn/SO₄ ratio was 1.4 to 1.6.

The electrical charge input has to be modified to pace the feed mine water flow and sulphate load. The Zn/SO₄ ratio differs for various mine water and operating conditions (specifically the reactor pH). This latter factor makes the prediction of the electrical charge dose requirements difficult.

2.3.3 Temperature

The process was not sensitive to the feed mine water temperature. The reactor temperature did increase, depending on the electrical power input to the process. This is again demonstrated by comparing two (2) different pilot plant tests.

< Pilot Test on 14 November 2000

The average energy input to the process was 5.85 kW, which equated to 12.1 kJ/ℓ treated. The feed mine water temperature was 25 °C and the reactor temperature operated at steady state was 29 °C.

< Pilot Test on 16 November 2000

The average energy input to the steady state process was 9.9 kW, which equated to 106 kJ/ℓ treated. The feed water temperature was 25 °C and the reactor temperature during the last part of the test was as high as 49 °C.

The E/C reaction could therefore increase the mine water temperature, depending on the energy input.

2.3.4 Toxicity/inhibition

To form of toxicity or inhibition was recorded in any of the pilot plant tests.

The only malfunction was recorded during a pilot test performed on a highly polluted mine water (Toe Seepage). The Toe Seepage conductivity was so high (> 1 200 mS/m), that the electrical control system interpreted the high electrical currents as a short circuit and the plant was automatically shut down.

2.4 Process Control

The E/C process control is based on the synchronisation of two aspects:

- *The feed mine water flow and the associated sulphate load.*
- *The electrical charge dose as dictated by the electrical current.*

It is also known that the zinc-hydroxy-sulphate precipitation is optimised at a pH in the range 6.4 to 6.8. The process control is designed to achieve the target optimum pH.

The process control strategy is therefore typically based on the following approach:

- *Select an average mine water feed flow rate and associated sulphate load.*
- *Calculate the electrical charge requirements to achieve the optimum sulphate removal.*
- *Set the potential differential between the electrodes*
- *The electrical current (and by implication the electrical charge dose, Coulomb/h) will stabilise at a certain level, mainly dictated by the reactor liquor conductivity and temperature.*
- *The Mine water feed rate is controlled from a feedback signal originated by the reactor pH meter, to maintain the target optimum pH level.*

The use of process control instrumentation in the E/C reactor must also be approached with caution. The electrical fields set up in the E/C reactor will interfere with most process instrumentation, such as pH meters. The pH meter must therefore be installed on an isolated re-circulating side-stream.

2.5 Process Performance

The E/C process ability to neutralise mine water and precipitate sulphate is well proven. The process can, however, only remove the fraction of the total sulphate associated with free and mineral acidity.

The ionic composition of a typical mine water used in the pilot plant testing is reflected below in terms of the major ionic species:

Table 2.5 (a) High calcium/magnesium mine water composition

Cations			Anions		
Species	mg/ℓ	mequi/ℓ	Species	mg/ℓ	mequi/ℓ
Calcium	470	23.5	Sulphate	2550	53.1
Magnesium	158	13.0	Chloride	103	2.9
Sodium	38	1.7	Bicarbonate	0	0
Iron -II	33	1.2			
Iron -III	200	10.8			
Aluminium	31	3.4			
Manganese	28	1.0			
Hydrogen	pH = 2.75	1.8			
Total		56.4			56.0

The ionic composition is also shown graphically in **Figure 2.5 (a)** below:

The fraction of sulphate, which can be removed electrochemically, is associated with the free acidity (H^+) and mineral acidity (Fe-II, Fe -III, Al). The manganese will typically not precipitate under the E/C reactor operating conditions, and is excluded from the estimate of the fraction of sulphate, which could be precipitated. The estimated fraction of sulphate, which could precipitate, is therefore:

$$\begin{aligned} SO_4 \text{ removal fraction} &= (1.2 + 10.8 + 3.4 + 1.8)/56.4 \\ &= 30.5 \% \end{aligned}$$

By contrast, if the acid mine water contains a relatively low calcium/magnesium content, a much higher sulphate fraction may be removed electrochemically. The ionic composition of a low calcium/magnesium mine water is reflected below:

Table 2.5 (b) Low calcium/magnesium mine water composition

Cations			Anions		
Species	mg/ℓ	mequi/ℓ	Species	mg/ℓ	mequi/ℓ
Calcium	65	3.2	Sulphate	1 150	24.0
Magnesium	35	2.9	Chloride	15	0.4
Sodium	12	0.5	Bicarbonate	0	0.0
Iron -II	33	1.2			
Iron -III	200	10.8			
Aluminium	31	3.4			
Manganese	28	1.0			
Hydrogen	pH = 2.7	2.0			
Total		25.0			24.4

The ionic species composition is shown in **Figure 2.5 (b)**.

The fraction of sulphate, which can be precipitated from this low calcium/magnesium water is:

$$\begin{aligned} \text{SO}_4 \text{ removal fraction} &= (1.2 + 10.8 + 3.4 + 2.0)/25.0 \\ &= 69 \% \end{aligned}$$

The performance of the E/C process is therefore very dependant on the ionic species composition of the feed Mine water.

The fraction of sulphate removed in the pilot plant tests are summarised below:

Date	Sulphate Concentration		Sulphate Removal (%)
	Feed (mg/ℓ)	Product (mg/ℓ)	
11 July 2000	3 700	2 000	46
13 July 2000	2 650	1 650	38
14 November 2000	2 650	1 650	38
15 November 2000	2 650	1 850	30
16 November 2000	3 460	1 200	65

The percentage sulphate removal is therefore quite variable, depending on the feed water composition.

2.6 Residue Generation

The E/C process generates a well-flocculated zinc-hydroxy-sulphate and metal hydroxide sludge. The composition of the sludge is dependant on two aspects:

- *The metal composition of the feed acid mine water, specifically in terms of the iron and aluminium concentrations.*
- *The zinc : sulphate ratio in the zinc-hydroxy-sulphate precipitate.*

The typical metal composition of the E/C treatment process sludge is reflected below in the sample/analysis done on the 14 November 2000:

Zinc	=	256 g/kg solids
Iron	=	82 g/kg solids
Aluminium	=	33 g/kg solids
Manganese	=	1.4 g/kg solids

The E/C sludge composition can also be calculated on the basis of a theoretical model, based on the chemical composition of the feed mine water. The sludge production calculation is based on the following mine water composition.

Table 2.6

Cations			Anions		
Species	mg/l	mequi/l	Species	mg/l	mequi/l
Calcium	470	23.5	Sulphate	2550	53.1
Magnesium	158	13.0	Chloride	103	2.9
Sodium	38	1.7	Bicarbonate	0	0
Iron -II	33	1.2			
Iron -III	200	10.8			
Aluminium	31	3.4			
Manganese	28	1.0			
Hydrogen	pH = 2.75	1.8			
Total		56.4			56.0

Assuming that all the iron and aluminium is precipitated and that the sulphate is precipitated as a $Zn_4(OH)_6SO_4$ precipitate, the sludge composition is as follows:

-	$Fe(OH)_2$	=	53 mg/L	(1.3%)
-	$Fe(OH)_3$	=	383 mg/L	(9.0%)
-	$Al(OH)_3$	=	89 mg/L	(2.1%)
-	$Zn_4(OH)_6SO_4$	=	<u>3723 mg/L</u>	(87.6%)
			<u>4247 mg/L</u>	

The sludge flocculates well and also settles readily in conventional gravity solids separation devices. Sludge settling rates of 1.2 – 1.3 m/hour has been reported.

The composition of the sludge is very important from a zinc recovery point of view. It is desirable to limit other contaminants, such as the other metal hydroxides, in the sludge. This will reduce the amount of low value constituents, which must be thickened, dewatered, dried and transported to a zinc refinery.

The observed zinc : sulphate mass ratio of the sludge varied substantially, as reflected below:

Date	Zn : SO_4 mass ratio in sludge
11 July 2000	1.73
12 July 2000	3.53
13 July 2000	2.50
14 November 2000	0.61
15 November 2000	0.66
16 (a) November 2000	0.70
16 (b) November 2000	1.47

The Zn : SO₄ mass ratio was substantially lower during the November 2000 pilot testing campaign, compared to the July 2000 pilot testing campaign. The lower zinc requirement is encouraging, but the mechanism to consistently achieve this, was not established.

Note that the theoretical minimum zinc : sulphate mass ratio, assuming a ZnSO₄ precipitate, is 0.72.

Earlier observations also indicated that the zinc-hydroxy-sulphate might not be stable during prolonged sludge storage. It is therefore essential to rapidly dewater and dry the sludge for further zinc recovery.

2.7 By-product Generation

A potentially valuable by-product is generated in the form of hydrogen gas, H₂. The amount of hydrogen gas formed is directly proportional to the electrical charge dose. For every 1 000 A flowing for 1 second, the mass of H₂ released is calculated as follows:

$$\begin{aligned} M &= \left(\frac{1}{2}\right) (1000)(1) / 96500 \\ &= 10.4 \text{ mg, H}_2 \end{aligned}$$

Appendix 4

A formula that could be used to estimate the price of oxide materials

is the following:

If the LME zinc metal price is below US\$1000/t:

oxide price per ton = (LME US\$/t x %Zn in material x 0.83) - (175 - (1000 - LME US\$/t) X 0.075)

If the LME zinc metal price is above US\$1000/t:

oxide price per ton = (LME US\$/t x %Zn in material x 0.83) - (175 + (LME US\$/t - 1000) X 0.15)

Depending on the presence of deleterious elements in the material penalties could be charged by the refinery. These formulas are not cast in concrete, terms are periodically renegotiated and they depend on market conditions.

Regards

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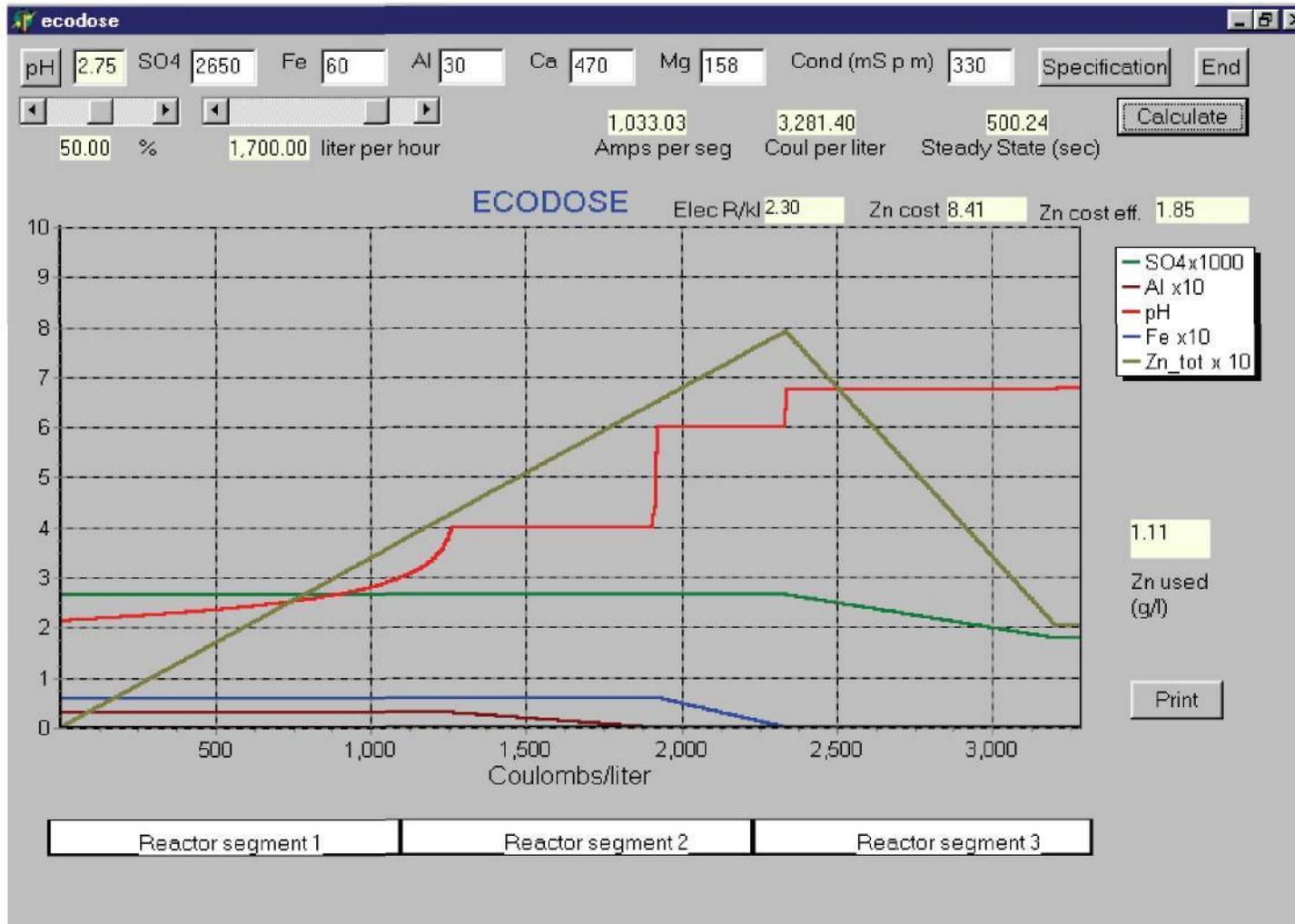
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Results From Mathematical Model



INTERIM PROGRESS REPORT TO STEERING COMMITTEE

WRC PROJECT K5/940

PROJECT TITLE: ELECTROCHEMICAL TREATMENT PROCESS.

Project leader: HC v Zyl (AOL)

Reporter: Prof JJ Smit (Lektretrek)

Date: March 2001

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1. SUMMARY

This is a concise progress report on the **results** regarding the design, operation and performance of **only the sulfate removal plant** at Landau using mainly the goals and rationale developed in:

- the **Envig Assessment an Evaluation Report (EAERK)** of a similar plant at Kromdraai and,
- the **Comments by Prof Smit (CPS)** on the EAERK Report, and,
- the contents reported in the **WRC Progress Report (WRC Project K5/940)** dated 30 June 1999.

The demonstration EC reactor and its associated plant at Landau were tested since May 2000. Three different effluents as well as mixtures of the latter were subjected to treatment between July 2000 and February 2001.

Typical results from in situ and Eskom TSI chemical analyses of the pre- and post treated effluents with the EC-system revealed the following positive treatment results:

- From **30 - 57% of sulfate is removed** depending on the Ca and Mg liming levels. No liming is expected to improve sulfate removal.

Refer [EXP SCT3 11/7/00] (para 3.2.2)

- **All the base metals precipitate simultaneously** with sulfate removal to levels of less than 1 mg/liter

Refer [EXP SCA2 14/11/00] (para 3.2.3)

- **Alkalinity is simultaneously improved** to 20 mg/liter in the product as opposed to zero mg/liter in the feed and could greatly improve the scaling properties of these typical effluents.

Refer [EXP SCA2 14/11/01] (para 3.2.3)

- The effluent is also **simultaneously neutralised** from a pH = 2.7 to a pH = 6.4 or higher.

Refer [EXP SCA3 15/11/01] (para 3.2.3)

- The **zinc consumption is substantially lower** than theoretically expected from the suggested stoichiometry obtained by XRD analysis. (para 4.1.1 and Table 3)

The following aspects will have to be pursued by further investigation and/or processing:

- Determine the **exact zinc consumption** for various effluents.
- **Optimise the reactor flow dynamics and reaction kinetics** to prevent reagent bypass.
- **Optimise the speciation of effluents** by mixing to attain an effluent most suitable to treat with this process.
- Investigate the initial **separate precipitation of iron at pH = 2.5 – 3** as Fe(III) by bacteriological oxidation thus improving recovered zinc quality and the credit on zinc recycle.
- Investigate the subsequent **separate precipitation of aluminium at pH=5** followed by zinhydroxysulfate precipitation at its higher pH.
- The latter two would imply a **lower total zinc consumption, a cheaper process and a purer zinhydroxysulfate recycle for resale.**
- Investigate **larger reductions of sulfate** by **not liming** and/or by **mixing effluents** before EC treatment
- **Reduce the zinc loss** in the final outlet by ultimate pH adjustment.

NOTE: A possible flow diagram for these process additions is presented in paragraph 5

Taking into account only the chemical results from the July and November 2000 test runs and costing the EC-reactor yields the Capex [~R1.5M/megaliter/day]and Opex [~R3/m³ , referred to a zinc recovery of 65%]. These calculations are presented on Graphs 1 and 2 and in APPENDIX 5.

These graphs also illustrate the progressive improvement of the effectiveness of the Zinc consumption as it is reflected by the all important Zinc/Sulfate removal ratio.

2. INTRODUCTION:

2.1 Adaptation of the previous project goals, operation and phases of execution

- The technical committee decided to focus initial investigation on the newly designed sophisticated demonstration plant to evaluate only the **removal of sulfate** from Acid Mine Drainage (AMD). The response of this particular symmetrical reactor plant for the depollution of sewerage (particularly phosphate reduction) will therefore to follow at a later date.

- Two independent parties assisted. One with the capacity design of the total plant and one with the final operational assessment of the plant. The two parties were respectively:
 - **ENVIG** and
 - **WATES, MEIRING and BARNARD (WMB)**

NOTE: [The Kromdraai assessment report by Envig and our comments are contained in (APPENDIX 1A)]

[An assessment report (WMB) on plant performance during experiments is expected in due course.]

- The plant is designed as a symmetrically configured Electrochemical (EC) plate reactor with a 45 kW power source configured in eight different discrete energy output settings. Each of these delivering ca. 12.5% of the 45 kW (Thus 45kW=100% duty cycle).
- The plant was successfully commissioned using rough zinc (Zn) electrodes obtained from Zincor as unrolled cathode plates which were subsequently replaced by rolled zinc plates.
- Three different effluents were treated in the plant to produce product water and sludge for discard. It was established that the zinc could be recovered for resale.
- Analytical results of the input and output (product water and sludge) were obtained by both portable on-site field test kits and by the accredited Chemical Analysis Facility of the TSI (ESKOM). All experimental results referred to in this report are tabulated in the appendices. Only elemental analyses were asked for on all the samples. Various XRD analyses confirmed the precipitated zinc complex to be $Zn_4(OH)_6SO_4$.
- The Landau personnel did the daily preparations of the plant. Lektratek (Pty) (Ltd) managed the experiments, sampled and analysed the process variables.
- **The Technical Committee** and the designers (**Envig and Lektratek**) decided to restrict the **hydraulic capacity** (unpolluted) of the down-stream equipment to a maximum of 2000 liter/hour (~48kl / day). This was a cost saving consideration but it restricted the plant capacity to a factor of ca. 10-20 times lower than that of the EC reactor which is designed for a nominal (unpolluted) capacity of 1000m³/day (~42kl / hr)

2.2 Summarised Experimental Program

TABLE 1. Preparation, commission and assessment experiments.

DATE	ACTIVITY (ACHIEVEMENT) ON-SITE
5/5/00	INVENTORY OF ELECTRICAL AND MECHANICAL EQUIPMENT
8/5/00	EXP FH1 DRY AND WET RUN + TEST RUN ON FH EFFLUENT.
11//5/00	TEST FUNCTIONAL INTEGRITY OF CONTROLS AND POWER.
12/5/00	TEST WITH FH TEST PLANT OPERATING SET VALUES
19/5/00	TEST pH + FLOW BALANCE FOR pH CONTROL.
8/6/00	EXP FH2 COMPARE INPUT/OUTPUT ELEMENTAL ANALYSIS
20/6/00	EXP FH2 (=EXP FH3) REPEAT + MIX IN 10% SC EFFLUENT.
5/7/00	EXP SCT1PREP FOR TEST WEEK ON SC + FH EFLUENT MIX
6/7/00	EXP SCT1 PROFILING pH & SULFATE VS TIME
10/7/00	EXP SCT2 REPEAT - ATTAIN BALANCE + OPTIMUM SULFATE
11/7/00	EXP SCT3 REPEAT TO CONFIRM SC2 INTERPRETATION.
12/7/00	EXP SCT4 PERFORMED BY LANDAU PERSONNEL ALONE
13/7/00	EXP SCT5 REPEAT EXP SC5 FOR START-UP TRAINING
13/11/00	EXP SCA1.PREPARE FOR ASSESSMENT BY WMB 13-16/11/00
14/11/00	EXP SCA2 IN/OUT EQUILIBRATE & RUN @ "BEST" SETTINGS
15/11/00	EXP SCA3 REPEAT AND CONFIRM SCA2
16/11/00	EXP TSA1 IN/OUT EQUILIBRATE & RUN @ BEST EXP (TS+SC) A1 IN/OUT EQUILIBRATE ,RUN AND EVALUATE.

Legend:

EXP – Experiment on (effluent type) (number)

EXP (TS+SC)A – Experiment on Toe Seep (TS) and Schoongezicht (SC) effluents mixed for assessment (A).

FHT - Fire Hydrant (FH) effluent for own Test (T) purposes.

SCA – Schoongezicht effluent for assessment (A) purposes

SCT - Schoongezicht effluent for own test (T) purposes.

TSA – Toe Seep effluent for assessment (A) purposes.

3. DISCUSSION OF RESULTS

3.1 Exploratory experiments on the FH effluent. (5/5/00 - 20/06/00)

The results of the first seven (7) experiments dated 5/5/00 - 20/06/00 are of concern here. These experiments were of an exploratory nature to verify the design parameters, the equipment integrity and the control logistics. No analyses were taken during these runs. The following **qualitative information** was gained from these experiments:

- The electrical noise generated by the different variable speed drives rendered the **data logger unusable**. Although this phenomenon could technically be rectified by shielding it would involve design time and considerable cost. It was decided to make do without the elegance of automatic data logging.
- All the unit processes functioned satisfactorily although **an inaccurate pH meter after the reactor** could not be rectified. The difference however was negligible at the pH values where optimum sulfate removal occurred.
- Treatment of the limed effluent (FH) clearly exhibited a lower sulfate removal potential. This is ascribed to the presence of higher calcium and magnesium concentrations due to previous lime dosing. It is thus suggest that **competition exist between the Zinc (wanting the SO₄ to precipitate) and the Ca/Mg (wanting the SO₄ in solution)**. This interpretation was later confirmed when using SC effluent that which was with Ca, Mg whereby only 20% of the sulfate could be removed. (refer to the experiment on 12 Jul 2000).
- From the FH series of experiments it was also quantitatively evident that the EC system on its lowest electrical setting provided substantially more electricity to balance the incoming pH. Due to its high pH it was not possible to attain an equilibrated operational point as the equilibrium pH was overshoot most of the time. By lowering the pH (blending and mixing) it is however treatable.
- A full load of plates could not be accommodated in the reactor due to the very high electrical conductivity of the effluents. The current controller would not switch on because it interpreted the high currents as a short circuit.

3.2 Experiments with the SC effluent.

The detailed results from this series of experiments are presented in APPENDIX 2 and APPENDIX 3 and were executed from 5/7/00 – 13/7/00 and from 13/11/00 – 16/11/00 respectively.

The **goals** with these experiments were:

- To verify the approximate process variables for optimal extraction of sulfate from these effluents.
- To determine values for the process variables at steady state operation of the plant.
- To do elemental analyses during the steady state and compute mass balances across the EC reactor.
- To verify from these the specific consumption of Zinc, electricity and other variables for an ultimate Capex and Opex profile.
- To establish the plant performance on 25, 50, 75 and 100% of its electrical duty cycle.

DISCUSSION:

- The plant and its associated equipment operated according to the design criteria.
- The capacity of the down stream equipment was designed for a lower capacity and operational instability occurred at feed flow rates higher than 2000 liter /hour.

3.2.1 EXPERIMENTAL RESULTS. (5/7/00-10/7/00)

[Refer to EXP SCT1 – EXP SCT2 and appended results]

These experiments were executed during (5/7/00-10/7/00) and prepared the plant and personnel for a test series of three days using Schoongezicht effluent (SC) with various parameter settings. These results are summarised, interpreted **and presented as follows:**

DISCUSSION:

- The first experiments on 5 and 6 July 2000 verified the condition of the EC reactor and the peripheral equipment.
The design criteria and process parameters were evaluated against performance. It was found to conform to the original design specifications.
- The first test runs were executed with the purpose of determining the adaptability and ranges within which the plant and the control equipment could operate.

- Successful test runs were undertaken in July 2000 indicating clearly that:
- Sulfate can be removed from Schoongezicht effluent
- The maximum and minimum ranges are attainable by the control instruments.
- The downstream unit processes are satisfactory although lacking capacity when compared to the EC reactor.
- Further experiments were undertaken and the previous exploratory results were confirmed.

3.2.2 Experimental results.(11/7/00-13/7/00) [refer to exp sct3 - exp sct5.]

These three experiments on three consecutive days were conducted as qualifying experiments to determine plant performance, operability and the level of personnel competency in operating the plant. Detailed sampling was done and presented to TSI ESKOM for elemental and other analyses. These analyses were to enable the determination of a mass balance over the reactor, the kinetic dependence of the reaction on residence time at various plant capacities and with as many effluents as possible.

Discussion:

From previous experiments some process variables were fixed (like the electrical duty cycle) to achieve an optimum by manipulating the flow rate to the reactor. The following represent an extract and the calculation obtained from a series of typical dated experiments (refer to Appendix 2)

1. **56% sulfate could be removed** calculated from the data reported on 11 July 2000.
2. The pH was neutralised from 2.73 to 6.55 whilst both the **alkalinity** and the base metal concentrations were **improved by 90%+**.
3. The zinc/sulfate consumption ratio was calculated both by weight determination of the zinc electrodes (before and after **all experiments were completed**), and from the Law of Faraday.
4. These calculations were performed on the data sheets presented in **Appendix 2** and are tabulated as follows:

TABLE 2 COMPARISON OF THE (Zn/SO₄) RATIO (THEORY AND EXPERIMENT) FOR SC EFFLUENT.[Appendix 2]

EXPERIMENT	Zn/SO ₄ RATIO THEORY	Zn/SO ₄ RATIO EXPERIMENTAL
11/7/2000	2.7	1.73
12/7/2000	2.7	3.53
13/7/2000	2.7	2.50

3.2.3 EXPERIMENTAL RESULTS. (13/11/00 – 16/11/00)

[Refer to EXP SCA1 – EXP SCA3.]

The detailed results from this series of experiments are presented in APPENDIX 3 and were executed from 13/11/00 – 16/11/00.

With this series of experiments special attention was given to correct analyses and the determination of an operational optimum for maximum sulfate removal from solution.

In order to achieve this aim a mixing pump was introduced into the reactor itself to improve contact time between the zinc plates and the effluent as well as to convert the reactor to a continuously stirred tank reactor (CSTR). This yielded a vast improvement on the Zn/Sulfate ratio as will be shown graphically on Graph 2 where the Zinc cost (for Zinc consumption (ratios of Zinc/Sulfate)) is shown.

This series of experiments are similar to the previous set and aimed at the following:

- To clarify the **sulfate analyses discrepancy** between the HACH Field Test kit and the sophisticated equipment used in an accredited laboratory.
- To **demonstrate the sulfate removal capacity** at electrical duty cycles of 25, 50, 75 and 100%
- To determine and demonstrate the performance of the EC reactor on **extremely heavily polluted effluent** like the Toe Seep effluent.
- To have the **process independently assessed** and determine its adaptability to commercial scale.

These results are presented in APPENDIX 3 (13-16 Nov 2000).

Discussion:

This test series yielded similar results to the previous series in July 2000 except for a substantial improvement in the removal capacity of Zinc for sulfate. The percentage improvement in the sulfate removal, the pH increase, the base metal and alkalinity concentration decrease is in the same order and summarised in the following table using Appendix 3. (This result can also be seen on Graph 2 showing the improvement in Zinc consumption since 5th July 2000.)

TABLE 3. TABULATION OF Zn/SO4 RATIO AND PERFORMANCE VARIABLES FOR SC AND TS EFFLUENT TREATMENT CALCULATED FROM THE FARADAY LAW.

[Refer to Appendix 3]

EXPERIMENT	Zn/SO4 STOICHIOMETRY	ZN/SO4 EXPERIMENT	pH IN	pH OUT TIME	SO4 REMOVED ppm	SO4 IN ppm
14/11/2000	2.7	0.61	2.75	6.48 13h58	1000 37.7%	2650
15/11/2000	2.7	0.66	2.68	6.71 13h25	1403 52.8%	2653
16/11/2000	2.7	0.70	2.8	3.83 10h16	6404 41.2%	15550
16/11/2000	2.7	1.47	2.78	5.58 14h26	>2800 >70%	>4000

4. SUMMARY OF FINDINGS.

This section is aimed at clarification of the progressive calculation and determination of the Zinc/Sulfate mass ratio which in turn determines the economics of the process as described by Graph 2 on page 19.

4.1 Zinc consumption

The zinc consumption is the most crucial variable in this process. It determines the power consumption, the sulfate removal and the operational cost. Zinc consumption was estimated through four possible means:

- Calculate the theoretical zinc/sulfate ratio from the **stoichiometric formula** obtained from XRD analysis.
- **Weighing** the electrodes before and after experiments
- **Analyse** the process streams and determine a mass balance

- **Calculate** the zinc consumption via the Law of Faraday. (Refer to Appendix 4 for a theoretical sample calculation.)

4.1.1 Stoichiometric calculation for Zinc consumption

As a first approach the ratio of Zinc/Sulfate ratio could be calculated with a formula (obtained by X-Ray Diffraction (XRD)) to be that which is reflected in the formula $(Zn)_4(OH)_6(SO_4)$ namely:

$$[4 \text{ moles Zn}/1 \text{ mole Sulfate}] = [(4 \times 65) \text{g Zn}/96 \text{g Sulfate}]$$

This yields a mass ratio of $Zn/SO_4 = 2.708$

There is however mention (Chemistry of the Elements by Greenwood and Earnshaw p 1404 and 132) that the metaloxyhydroxides (like zinc) form isopolyanions (a type of inorganic polymer) with the formula

$[Zn_2(OH)_2]^{2-}$. This would then yield a mass ratio of;

$$Zn/SO_4 = 1.35$$

This implies only 50% of the previously calculated ratio and thus a potential reduction in operating cost.

4.1.2 Electrode weighing for the Zinc consumption

An ordinary mass meter with an accuracy of ca. +/- 5% (+/- 4.5 kg) at full scale deflection (=100kg) was used to determine the mass of each electrode pack before and after a series of three to five days of experiments. This gave a mass difference of about 5 - 10 kg/day on a total electrode charge of ca. 80kg. A typical Zinc consumption is recorded as (80.5kg - 62.0kg) = 9.5kg (+/- 4.5 kg) Zinc used for the experiments performed over 3 days (11/7/01 - to- 13/7/00). The calculation is presented in Appendix 2.

4.1.3 Chemical analyses for Zinc consumption

The process streams were sampled and analysed by ESKOM TSI and only sulfate was analysed with a field test kit as a control. Serious problems occurred with **ageing of samples** due to the hydrolysis of iron. This hydrolysis released acid that subsequently re-

dissolved the precipitated zinc complex. Some ratios are shown in the following tabulation. The variation in the Zinc/Sulfate ratio is obvious.

TABLE 4: Zn/SO₄ RATIOS FROM SLUDGE ANALYSES BY ESKOM TSI

(Refer to Appendix 3)

DATE	ZINC (mg)	SO ₄ (mg)	MASS RATIO [Zn/SO ₄]
14/11/00 TSI No 200247807	555531	191044	2.907
14/11/00 (S1) TSI No 200250857	239700	121500	1.973
14/11/00 AGED SLUDGE TSI No 200247895	494712	268290	1.844 (#) TSI No 200247894

(#) The is the supernatant of a sample after extended ageing (weeks) at pH=6, Sulfate=1720 ppm, Zn=35.5 ppm. It had an initial value of sulfate=2650 ppm. (refer to Eskom analysis 200247894).

4.1.4 Calculation of the Zinc consumption. (using Faraday)

The zinc consumption can be accurately calculated from electrical current measurements by using the Law of Faraday. These calculations were performed on some of the experiments and the following results were calculated and compared from the experimental results in Tables 2 and 3.

TABLE 5. COMPARISON OF ALL METHODS FOR DETERMINING ZINC CONSUMPTION

	SPECIFIC Zn CONSUMPTION IN (m/m)[Zn/SO ₄]			
THEORY STOICHIOMETRY	2.7/1.35 (REFER TO para 4.1.1 FOR THE RATIONALE)			
WEIGHING	WEIGHING IS INACCURATE WITH THE CURRENT MASSMETER			
ESKOM ANALYSES	2.907	1.907	1.844	
FARADAY(#)	(0.6) (0.66)	(0.70) (1.47)	---- FROM EXPERIMENTS ON 14-16/11/2000	
	(1.73) (3.53)	(2.50)	-----FROM EXPERIMENTS ON 11-13/7/2000	

(#) refer to Appendix 4C for calculations

(#) Compare Graph 2 to see the progressive improvement over the period of experimentation.

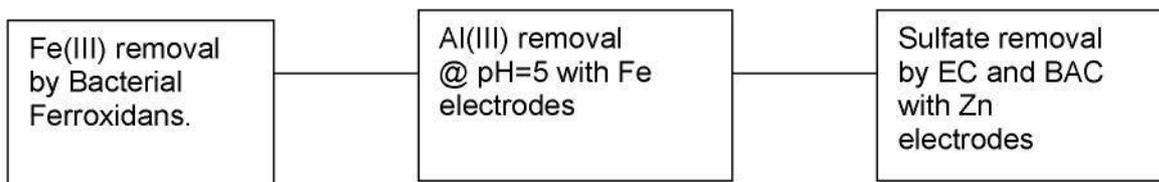
5. FURTHER TESTING AND RESEARCH

5.1 Evaluate pilot scale Zinc consumption both on pilot site and in laboratory experiments using the most accurate

- reductive polarographic,
- chemical speciation and
- **chemical reaction kinetic determinations.**

5.2 Evaluate the combination of ELECTROCHEMICAL (EC) and BACTERIAL (BAC) sulfate removal to establish synergism :

- With regards to nutrients,
- Growth and sustenance and,
- Energy effects on both the Ferroxidans and the Sulfate Reducing Bacteria (SRB) previously mentioned in this report. This synergy could be illustrated in the following suggested flow sheet for such a combined process:



5.3 Evaluate the flow dynamics of the reactor and adapt that to the reaction kinetics. It is obvious from the latest experiments that a channel reactor in stead of a Continuously Stirred Tank Reactor (CSTR) would be the better reactor model for this application.

6. RECOMMENDATIONS

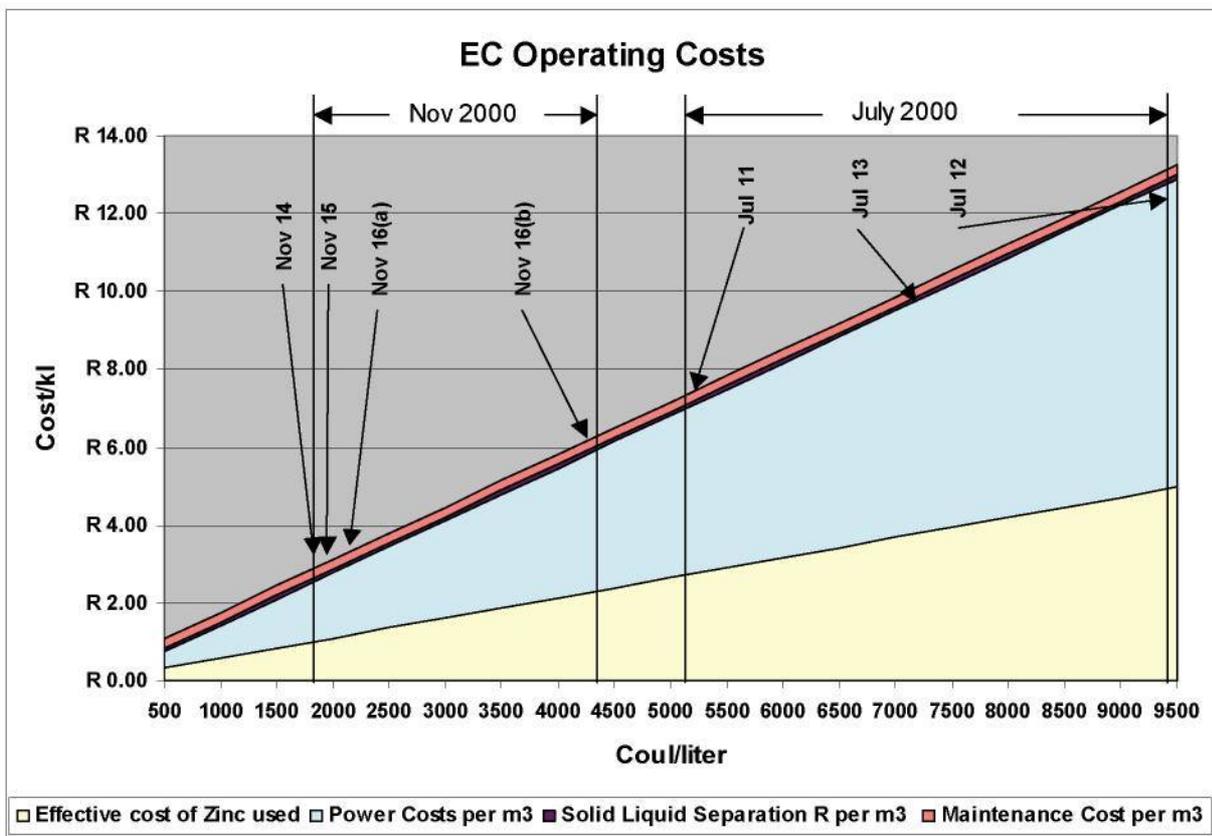
It is recommended that the research on sulfate removal continue along the suggested lines mentioned in the previous paragraph.

The process shows merit in comparison with other sulfate removal systems. The main advantages are embodied in simplicity, operability, adaptability to different effluents and conditions and a flexible versatility in the pollutants that can be simultaneously extracted or rectified.

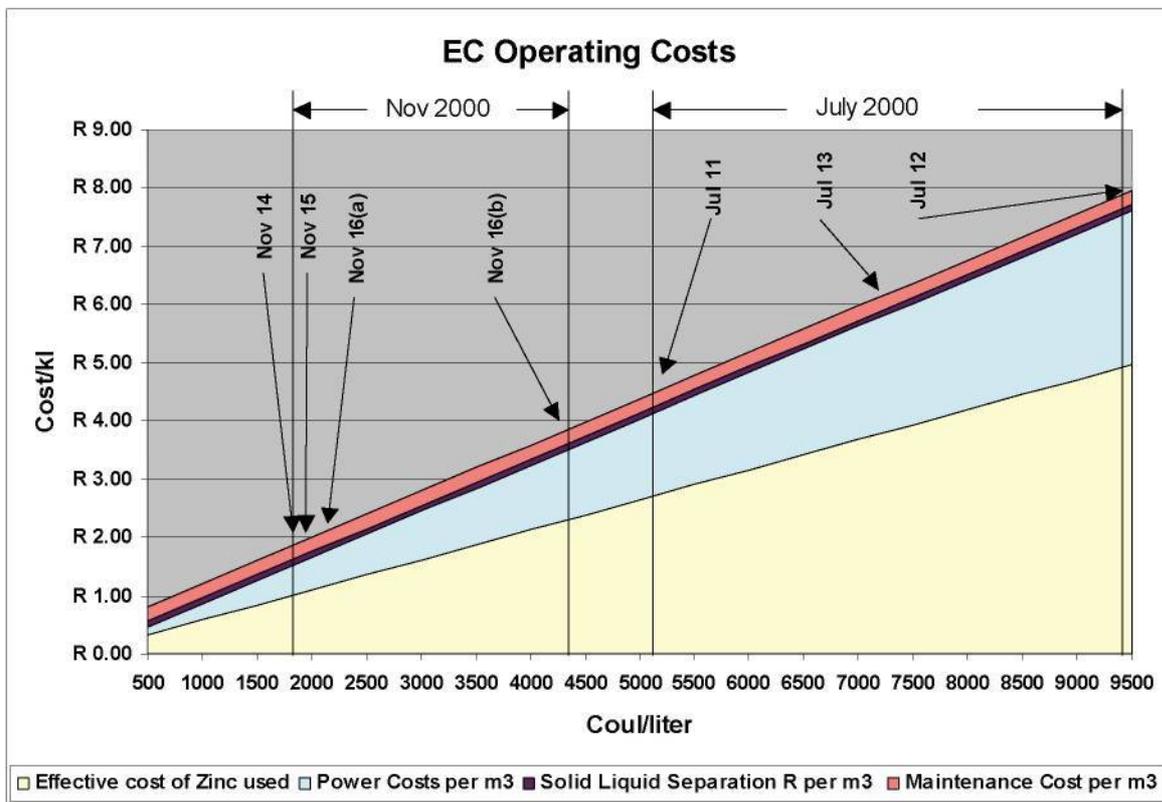
7. OPEX AND CAPEX CALCULATIONS

7.1 Operational Costs

The following graphs illustrate the running cost as obtained from the results during the tests at Navigation (Appendix 2 and 3). All the primary cost items were taken into account and include maintenance, sludge handling, etc as calculated in Appendix 5. Zinc is seen as a catalyst and the cost of recovering and recycling is reflected in the calculations. The standard sulfate removal for the calculations was 1000 mg/l SO₄. The input of electrical charge in Coulomb/liter (and all other relevant cost items) are expected to increase/decrease linearly with a sulfate load and/or sulfate removal between 500 to 4000mg/l SO₄



Graph 1: Results from experiments



Graph 2: Power Costs extrapolated for increased cell area

Graph 1 is the summary of the results from experiments SCT3-5 and SCA1-3.

In Graph 2 the cost of power used was recalculated for a three times increase in cell area that will decrease the cell voltage (and power) by a factor of three. And consequently also the electrical power consumption.

7.2 Capital Cost

The capital cost of a typical 300kl per day plant was calculated from the known costs of the current installation at Navigation. The standard average sulfate removal from all the experiments was calculated as 1000 mg/l SO₄. (see Appendix 5).

A first cost estimate is R1.5 M for a 1MI/day installation.

From the latter figure the cost was normalised and extrapolated for a plant with a capacity of 1 MI/day at 1000mg/l sulfate removal.

Again this cost is expected to increase linearly with an increasing removal capacity up to about 4000mg/l SO₄.

8. APPENDICES

The appendices are a selection of separate document files.

- Appendix1A_Envig_report_May1999.doc
- Appendix1B_WRC_REPORT_K4.doc
- Appendix2_Results_Jul2000.xls
- Appendix3_Results_Nov2000.xls
- Appendix4_fundamentals.doc
- Appendix5_Opex-Capex.xls

APPENDIX 7a

NOTES

A 1mg/l SO4 vra 2.7mg/l Zn (as molverhouding= 1:4)

mg/l SO4	molmassa	mmol/l SO4	4:1	mmol/l Zn	molmassa	mg/l Zn
1000	96	10.41666667	4	41.66667	65	2708.333

B 1000 Coul/l doseer 336.78 mg/l Zn

Coul/l	Coul/lading	ladings/l	Zn valen2	mmol/l Zn	molmassa	mg/l
1000	96500	0.010362694	0.005181	5.181347	65	336.7876

C

Coul	Amp*sec	mg Zn
1000	1000	336.788

JULY 10

EC TEST RUN ON SCHOONIE WATER- DATE 10/07/2000
BASIC DATA SHEET FOR RAW DATA WORK-UP

Assessor: Dr A v Niekerk
Operators: JJ Smit, P Rousseau
Flow settings P1: 20% x 2000l/hr = 400l/hr
Electrical settings: : 25% duty cycle @ 50% capacity
KWhr reading: Start: 15.5 End : 18.5 (KWhr)
Feed temperature: 18 C
Start-up at 12h47 Stop at 16h19 Date: 10/07/00

Time	pH(in)	pH reactor	Remarks
12h47	2.93		EC=670 mikroS/cm (Flow= 20%)
13h17	2.84	3.23	Current 250,300,350 (Amp)
13h48	2.82	5.55	
13h49		5.61	Current 575,670, 670 (Amp)
13h51		5.75	
13h52		5.82	
13h54		5.9	
13h56		5.9	White specs in precipitate
13h58		5.87	
14h43		3.51	Increase EC to 50% duty cycle
14h59		4.61	
15h07		5	
15h12		5.75	
15h19		6.08	
15h22			M1 sample taken
15h26		6.24	
15h35		6.3 (#)	(#) Control pH = 6.53, EC=556
15h40		6.41	Reactor temp 33.4 C M2 sample
15h47		6.44	No schoonie water - try batch
15h53		6.59	
16h11		6.59	M3 sample taken
16h19		6.71	Experiment aborted -No Schoonie water

NOTES:

1. Four samples taken including an initial sample of the feed
2. Sludge settling sample was provided
3. Reactor sludge sample was also provided.
4. All samples were marked with date time and pH
5. Raw data is attached as a photocopy.

NOTE :

The experimental data of the 12 July 2000 is provided by S Finger and Hvd Merwe

JULY 11

EC TEST RUN ON SCHOONIE WATER DATE:11/07/2000

Assessor

Operation: J Smit, S Finger, H vd Merwe.

Flow settings P1 Batch +20 %x2000l/hr

Electrical settings: Batch + 50%xduty cycle

80.5

KW/hr readings: Start :18.5 KW/hr Stop: 24.5KW/hr

Mass of zinc plates: 23,29,28.5 kg (total=80.5 kg)

Feed Temperature: 13C

Start-up at Stop at Date

Time	pH (in)	pH reactor	SO4(in)	SO4(out)	Flow(l/s)	Coul/l	Remarks comments and changes in operation
10h40	2.73	3.26	3700				Batch operation Current (300, 300, 300)
10h45	2.73	3.35			0.111	4050	Batch operation
10h51	2.73	3.51			0.111	4050	E = 50% F=20%x2000l/hr
10h53	2.73	3.85			0.111	4050	
10h55	2.73	4.26			0.111	4050	
10h59	2.73	3.5			0.111	4050	
11h02	2.73	4.47			0.111	4050	
11h05	2.73	4.74			0.111	4050	
11h06	2.73	4.84			0.111	6300	
11h07	2.73	4.9			0.111	6300	Current (450, 500, 450)
11h09	2.73	5.01		2500(M1)	0.111	6300	Sample M1 for sulfate
11h12	2.73	5.27			0.111	6300	
11h18	2.73	5.52			0.111	6300	
11h21	2.73	5.67			0.111	6300	
11h23	2.73	5.73			0.111	6300	
11h29	2.73	5.89			0.111	6300	
11h34	2.73	5.97			0.111	6300	
11h37	2.73	6.02		2450(M2)	0.111	6300	
11h43	2.73	6.09			0.111	6300	Sample S1 for TRI analysis-- 11h45
11h52	2.73	6.15		2350(M3)	0.111	6300	
12h01	2.73	6.23			0.111	8100	
12h06	2.73	6.26		2350(M4)	0.111	8100	
12h19	2.73	6.32			0.111	8100	
12h29	2.73	6.4		2200(M5)	0.111	8100	Current (550,600,650)12h34
12h37	2.73	6.42			0.111	8100	
12h45	2.73	6.44		2100(M6)	0.100	9000	Flow down to 18%x2000l/hr
12h57	2.73	6.45			0.100	9000	
13h25	2.73	6.49			0.100	9000	Temperature 35C
13h30	2.73	6.51		2050(M7)	0.100	8750	KW/hr reading = 22.7KW/hr
14h00	2.73	6.53			0.100	8750	Current (500,600,650) Flow=16%
14h07	2.58	6.54		2050(M8)	0.100	8750	T=38C
14h18	2.58	6.6		2000(M9)	0.100	8750	F=0 @ 14h24 (= Batch)
14h34	2.58	6.7			0.100	8750	M10 sample was aborted 14h24
14h44	2.58	6.63			0.090	9722	F=16%
14h48	2.58	6.58			0.090	9722	E=75%, T=45.6C
14h53	2.58	6.55		1600(M11)	0.090	9722	
14h59	2.58	6.58			0.090	9722	Stopped - reactor contents too hot(60C)

NOTES

- A. Time * Current =Coulombs
- B. Coul = mass Zn dissolved
- C. 1000 Coulombs = 336.788mg Zn

1. Sludge settling sample 30minutes 480,60 minutes 390

Time(min)	Curr (A)	E-ratio	Coul	g Zn
25	900	0.5	675000	227.33
47	1400	0.5	1974000	664.82
90	1800	0.5	4860000	1636.79
95	1750	0.5	4987500	1679.73
			gm Zn =	4208.67
			Kg Zn =	4.21

2. Electrode mass 1(23,29,28.5)

3. Samples for complete analysis by TRI

S1 @ 11h45 @ pH=6.09

S2 @ 12h45 @ pH=6.44

S3 @ 13h27 @ pH=6.45

S4 @ 14h30 @ pH=6.60

S5 @ 14h57 @ pH=6.55

Comparison between results from math Model and actual readings			Ratio Zn:SO4
Avg SO4 removed	1700 (3700-2000)		
Measured Coulomb/l	8750		
Calculated mgZn/l	2947 using Faraday		1.73
Old rule 1000mg/l SO4 use	2708 mgZn/l	2708 mgZn/l	2.70

- A. Time * Current =Coulombs
- B. Coul = mass Zn dissolved
- C. 1000 Coulombs = 336.788 mg Zn

Time(min)	Curr (A)	E-ratio	Coul	g Zn
55	450	0.5	742500	250.07
10	750	0.5	225000	75.78
10	1100	0.5	330000	111.14
15	1350	0.5	607500	204.60
90	1650	0.5	4455000	1500.39
			gm Zn =	2141.97
			Kg Zn =	2.14

Comparison between results from math Model and actual readings			
Avg SO4 removed	1000 (2700-1700)		Ratio Zn:SO4
Measured Coulomb/l	10485		
Calculated mgZn/l	3531 using Faraday		3.53
Old rule 1000mg/l SO4 use	2708 mgZn/l	2708 mgZn/l	2.70

JULY 14

EC TEST RUN ON SCHOONIE WATER DATE:13/07/2000

Assessor Dr. A v Niekerk

Operation: J Smit, S Finger, H Els.

Flow settings P1 20 %x2000l/hr

62

Electrical settings: 50%xduty cycle

KW/hr readings: Start : KW/hr Stop: KW/hr #

Feed Temperature: C

Mass of Zn-electrodes at end of run: 15,25,22 (total mass=62kg)

Start-up at Stop at Date

Time	pH (in)	pH reactor	SO4(in)	SO4(out)	Flow(l/s)	Coul/l	Remarks comments and changes in operation
10h30					0.111	4500	
	2.84	6.43	2650	2650	0.111	4500	F=20%, E=50%, T=29.7C, SO4 (in) =2650
11h22		6.43			0.111	7425	
11h30					0.111	7425	
ss							
11h04				1650	0.111	7425	
11h55		6.51		1650	0.111	7425	
12h19		6.51			0.111	7425	T=33.4
12h50	2.66	6.5			0.111	7425	
13h15		6.5			0.111	7425	T=33.6
13h30		6.49			0.111	7425	
14h30		6.5			0.111	7425	T=33.9

Plant was started by S Finger alone and brought to a steady state before 11h22

NOTES

1. Me. Susan Finger started the plant alone and brought it to a successful steady state
2. Me. Finger's report on the first part of this run will be included.
3. Sludge settling 340 ml after 30 minutes.
4. EC-Reactor amps (500,600,550) @ 13V
5. Weight of electrodes after shut down.

- | |
|----------------------------------|
| A. Time * Current = Coulombs |
| B. Coul = mass Zn dissolved |
| C. 1000 Coulombs = 336.788 mg Zn |

Time(min)	Curr (A)	E-ratio	A*sec	g Zn
50	1000	0.5	1500000	505.18
183	1650	0.5	9058500	3050.79
			gm Zn =	3555.98
			Kg Zn =	3.56

Kg used in total test 80.5 - 62= kg 18.5
Kg calculated 4.21+2.14+3.56 = kg 9.91

Comparison between results from math Model and actual readings			
Avg SO4 removed	1000	(2650-1650)	Ratio Zn:SO4
Measured Coulomb/l	7425		
Calculated mgZn/l	2501	Using Faraday	2.50
Old rule 1000mg/l SO4 use	2708 mgZn/l	2708 mgZn/l	2.70

APPENDIX 7b

NOTES

A 1mg/l SO4 vra 2.7mg/l Zn (as molverhouding= 1:4)

mg/l SO4	molmassa	mmol/l SO4	4:1	mmol/l Zn	molmassa	mg/l Zn
1000	96	10.41666667	4	41.66667	65	2708.333

B 1000 Coul/l doseer 336.78 mg/l Zn

Coul/l	Coul/lading	ladings/l	Zn valen2	mmol/l Zn	molmassa	mg/l
1000	96500	0.010362694	0.005181	5.181347	65	336.7876

RESULTS OF EXPERIMENTS ON ECODOZE AT LANDAU

DATE: 13 NOVEMBER 2000

ATTENDANTS : JJ Smit, G Kruger, C Smit, S Finger, Melda, Ananias.

PREPARATION FOR THE EXPERIMENTAL PROCEDURE

Electrode Mass: 33.5, 31.0, 28,0 kg

Plant preparation from 06h00

Start up and testing hydraulics 15h40

Testing flow rate and power settings.

14 NOV 2000 LANDAU EXPERIMENTS ON ECODOZE

DATE: 14 NOVEMBER 2000

ATTENDANTS: JJ SMIT, G KRUGER, C. SMIT

EXPERIMENTAL SETTINGS

Flow rate : 25 % of 2000l/hr

Electrical current duty cycle : 25% on lower transformer tap

Effluent: Schoongezicht water

Temperature of input effluent: T=25C

Energy consumption: $11.7V \times (750+650+600)A =$

TIME	pH(in)	pH(out)	SO4(in)	SO4(out)	Flow(l/s)	Coul/l	REMARKS
8h50	2.75		2650	2650	0.006	90000	E=25%, F=25%, EC(in)=1016
					0.006	90000	Operate in batch mode
9h05	2.75	6.6			0.006	90000	Power trip due to earth leakage
10h15				1800	0.278	1800	Continuous mode from 10h00
11h15				1600	0.278	1800	Adjust F=50%, T=34C
11h40		6.96			0.278	1800	
11h50		6.83			0.389	1286	F=70%
11h59		6.89			0.444	1125	F=80%
12h10		6.85			0.444	1125	
12h30		6.69			0.444	2250	F=80%, E=50%
12h38		6.69			0.472	2118	F=85%
12h45		6.66			0.500	2000	F=90%
12h50		6.65		1750	0.500	2000	F=90%
12h53		6.61			0.500	2000	T49
1257		6.59			0.500	2000	
1404		6.57			0.500	2000	
1314		6.56			0.500	2000	
1321		6.49		1700	0.556	1800	F100,E50,T29.
1321					0.556	1800	DRUM 1 sampled for sludge 2
1321		6.43		1650	0.556	1800	
1340		6.38			0.556	1800	
1355		6.48		1700	0.556	1800	
1358		6.48			0.556	1800	S1+S2 Special Escom samples
1405		6.48		1650	0.556	1800	
1445		6.35			0.556	1800	NO RESULTS RECEIVED

15h00 = Experiment concluded to prepare the next

- 2 What was envisaged for these drums
- 4 For all sludge analyses we need a ratio of Zn/SO4

- A. Time * Current = Coulombs
- B. Coul = mass Zn dissolved
- C. 1000 Coulombs = 336.79 mg Zn

Time(min)	Curr (A)	E-ratio	Coul	g Zn
220	2000	0.25	6600000	2222.80
150	2000	0.5	9000000	3031.09
			gm Zn =	5253.89
			Kg Zn =	5.25

Comparison between results from math Model and actual readings

Avg SO4 removed	1000 (2600-1600)	Ratio Zn:SO4	
Measured Coulomb/l	1800		
Calculated mgZn/l	606 using Faraday		0.61
Old rule 1000mg/l SO4 use 2708 mgZn/l	2708 mgZn/l		2.70

ESKOM – 14 NOVEMBER

TIME WHEN SAMPLE WAS TAKE 1
13H20-13H30?

ANALYTICAL RESULT FROM ESKOM

Received from Ananias Molefe on 27 November 2000

Note difference from previous results dated 24 November 2000

14/11/2000 SAMPLES

	FEED	PR1(F)	PR1(UF)	PR2(F)	PR2(UF)	REF
EC	3750	3020	3105	3300	3350	3
PH	2.75	6.47	6.48	6.36	6.33	
ALK (CO3)	<0.1	21	23	18	20.4	2
Ca	470	482	488	448	457	
Mg	158	141	144	151	153	
Na	37.5	42.7	37.1	37.8	38.2	
Zn	0.79	70	66	220	227	1
Cl	103	120	686	117	429	4
SO4	2550	1690	2368	1751	2458	
Al	30.7	1.21	1.31	1.20	1.28	
Mn	27.9	23.4	26.6	33.6	35.6	
Fe	66.7	0.004	0	0	0.05	
TDS	3745	2870	3110	3135	3150	5

- 1 Zinc concentration is not consistent with the pH
- 2 Alkalinity of the feed is lower than the product water?
- 3 There is a discrepancy between TDS, Ec, and pH
- 4 The Cl- could not increase from feed to product
- 5 Refer to (3)

Analysis of sludge sample

	MG/KG	SLUDGE
ZINC (AS ZN)		255531
ALUMINIUM (AS AL)		33282
IRON (AS FE)		81941
MANGANESE (AS MN)		1378

SULFATE 3

- 1 What was the time this sample was taken
- 3 Were these special samples analysed

15 NOVEMBER

15 NOVEMBER 2000 LANDAU EXPERIMENTS ON ECODOZE

SCHOONGEZICHT EFFLUENT @ E=50%

ATTENDANTS: JJ SMIT, H vd MERWE, C. SMIT

EXPERIMENTAL SETTINGS

Flow rate : 100 % of 2000l/hr

Electrical current duty cycle :50% on lower transformer tap

Effluent: Schoongezicht Effluent

Temperature of input effluent: T=25C

Energy consumption: $11.7V \times (750+650+600)A = 23.4kW$

TIME	pH(in)	pH(out)	SO4(in)	SO4(out)	Flow(l/s)	Coul/l	REMARKS
9h00	2.68		2653	2450	0.556	1800	Batch start E=50, F=100, T=25
10h45	2.68	6.03		2150	0.556	1800	
11h00	2.68	6.16		2000	0.556	1800	
11h02	2.68	6.27		2150	0.556	1800	
11h05	2.68	6.27			0.556	1800	
11h57	2.68	6.45		1650	0.556	1800	T=27
	2.68	6.35		1650	0.556	1800	T=28
12h40	2.68	6.35			0.556	1800	V1=11.58, V2=11.71, V3=11.43
	2.68	6.35			0.556	1755	A1=650, A2=600, A3=700
12h40	2.68	6.35			0.556	1755	T=28
12h44	2.68	6.35			0.556	1755	DRUM 2 SAMPLE FOR SLUDGE
12h50	2.68	6.34		1650	0.556	1755	
							E=25% and adjust flow for balance???
13h00	2.68	6.61		1650	0.250	1950	F=45%
13h25	2.68	6.71		1250/1400	0.272	1791	F=49%
13H49	2.68	6.38		1850	0.278	1755	F=50
14H00	2.68	6.23			0.306	1595	F=55
14H20	2.68	6.23			0.278	1755	F=50
14H48	2.68	6.5		2000	0.222	2194	F=40
16H18	2.68	6.44			0.250	1950	F=41
16H39	2.68	6.44		2000	0.250	1950	F=45
16H42	2.68	6.46			0.253	1929	F=45.5
16H40	2.68	6.46			0.256	1908	F=46
16H45	2.68	6.45			0.256	1908	F=46, T=29
16H56	2.68	6.42			0.258	1891	F=46.4
17H40	2.68	6.5		1850	0.258	1891	F=46.4

<p>A. Time *Current =Coulombs B. Coul = mass Zn dissolved C. 1000 Coulombs = 336.788 mg Zn</p>
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Sample taken for ESKOM
 Sample taken for ESKOM

Time(min)	Curr (A)	E-ratio	Coul	g Zn
240	1950	0.5	14040000	4728.50
240	1950	0.25	7020000	2364.25
40	1950	0.25	1170000	394.04
				gm Zn = 7486.80
				Kg Zn = 7.49

Comparison between results from math Model and actual readings		
Avg SO4 removed	1000 (2600-1600)	Ratio Zn:SO4
Measured Coulomb/l	1950	
Calculated mgZn/l	657 using Faraday	0.66
Old rule 1000mg/l SO4 use	2708 mgZn/l	2.70

ESKOM – 15 NOVEMBER

ANALYTICAL RESULT FROM ESKOM for 15/11/2000
 Received from Ananias Molefe on 27 November 2000

	FEED	PROD(F)		PROD(UF)		
		12H40	12H40	15H05	15H05	
EC	3580	3130	3170	3180	3220	1
PH	2.7	6.38	6.38	6.48	6.41	
ALKCO3)	<0.1	15.7	16.0	16.8	13.5	
Ca	411	406	408	421	419	
Mg	151	147	150	150	149	
Na	39.6	38.7	42	40.1	39.2	
Zn	1.95	241	245	231	231	2
Cl	107	204	107	118	112	
SO4	2653	1780	2419	1744	2510	
Al	20	1.36	1.40	1.41	1.39	
Mn	17.6	21.5	22.9	31.7	33.1	
Fe	86.7	0.01	0.06	0.21	0.11	
TDS	3600	3090	3030	2730	3150	3

- 1 Discrepancy between TDS, pH and EC
- 2 Zn could not be so high at these pH-values.
- 3 REFER 1

16 NOVEMBER

16 NOVEMBER 2000 LANDAU EXPERIMENTS ON ECODOZE

TOE SEEP EFFLUENT @ E=50%

ATTENDANTS: JJ SMIT, H vd MERWE, C. SMIT

EXPERIMENTAL SETTINGS

Flow rate :F= 20 % of 2000l/hr

Electrical current duty cycle :50% on lower transformer tap

Effluent: Toe Seep Effluent

Temperature of input effluent: T=25C

Energy consumption: $11.7V \times (1200+1300+1200)A=43.29kW$

EC=2100 mS/cm

pH[in]=2.8

TIME	pH(in)	pH(out)}	SO4(in)	SO4(out)	Flow(l/s)	Coul/l	SO4(out)	REMARKS
8h30	2.8		15550		0.139	13320	22000	E=50%, F=25%
8h45	2.8	4			0.139	13320		
9h52	2.8	4.08			0.139	13320		
10h08	2.8	3.8			0.139	13320		T=31C
10h16	2.8	3.83		9145	0.139	13320	19000	T=35C

Abort experiment - connector cables overheated

10h25 Eskom sample taken for record ????

- A. Time * Current = Coulombs
- B. Coul = mass Zn dissolved
- C. 1000 Coulombs = 336.788 mg Zn

Eskom results

Time(min)	Curr (A)	E-ratio	Coul	g Zn
120	3700	0.5	13320000	4486.02
			gm Zn =	4486.02
			Kg Zn =	4.49

Comparison between results from math Model and actual readings

Avg SO4 removed	6400 (15550-9145)	Ratio Zn:SO4
Measured Coulomb/l	13320	
Calculated mgZn/l	4486 using Faraday	0.70
Old rule 1000mg/l SO4 use 2708 mgZn/l	2708 mgZn/l	2.70

ESKOM – 16 NOVEMBER

	FEED	PR(F)	PR(UF)	
EC	11800	10610	10820	4
PH	2.69	3.59	3.53	
ALK (CO3)	<0.1	<0.1	,0.1	1
Ca	452	455	464	
Mg	146	296	326	2
Na	33.1	34.5	34.4	
Zn	13.2	1274	1294	
Cl	2228	1965	2102	3
SO4	15553	9145	9145	
Al	361	224	234	
Mn	261	237	238	
Fe	4487	3519	3633	
TDS	12570	11010	11130	4

- 1 Not consistent with previous analyses
- 2 Can not increase after treatment
- 3 Inconsistent with previous analyses
- 4 REFER to 1

16 NOVEMBER

16 NOVEMBER 2000 LANDAU EXPERIMENTS ON ECODOZE

MIXED 10% TOE SEEP + SCHOONGESICHT EFFLUENT @ E=25%

ATTENDANTS: JJ SMIT, H vd MERWE, C. SMIT

EXPERIMENTAL SETTINGS

Flow rate :F=46.4% of 2000l/hr

Electrical current duty cycle :50% on lower transformer tap

Effluent: 10% Toe Seep + 90% Schoonie Effluent

Temperature of input effluent: T=25C

Energy consumption:11.7V x (500+700+500)A =

EC=1460 mS/cm

pH(in)=2.78

TIME	pH(in)	pH(out)	SO4(in)	SO4(out)	Flow(l/s)	Coul/l	REMARKS
11h08	2.78		>4000		0.011	76500	Operate in batch mode
11h38	2.78	3.15			0.011	76500	FINE yellow ferric precipitate Fe3+
11h45	2.78	3.55			0.011	76500	T=33
11h50	2.78	4.20-4.26			0.011	76500	Small black particles precipitate
11h58	2.78	4.26			0.011	76500	Small white particles precipitate
	2.78				0.011	85500	A=(600,650,650)
12h02	2.78	4.47			0.011	85500	
12h15	2.78	4.97	3800	3000	0.011	85500	
					0.011	85500	
12h21	2.78	5.19		2500	0.094	10059	Flow opened to F=17%
12h34	2.78	5.42			0.094	10059	
12h50	2.78	5.49		2000	0.083	11400	F=15%
13h08	2.78	5.59		3100	0.094	10059	F17%
13h12	2.78	5.57		1650	0.094	10059	F17%
13h17	2.7	5.56			0.094	10059	2.7
13h30	2.7	5.56	4000	3300	0.094	10059	2.7
					0.094	10059	
13h42	2.7	5.51			0.094	10059	T=49C
14h15	2.72	5.54	3800		0.094	10059	2.72
	2.7			1600	0.094	10059	2.7
14h26	2.7	5.58		1200	0.094	10059	2

- A. Time * Current = Coulombs
- B. Coul = mass Zn dissolved
- C. 1000 Coulombs = 336.788 mg Zn

LEGEND

- 1 First ESKOM sample taken
- 2 Second ESKOM sample taken

Time (min)	Curr (A)	E-ratio	Coul	g Zn
60	1800	0.5	3240000	1091.19
60	1900	0.5	3420000	1151.81
80	1900	0.5	4560000	1535.75
				gm Zn = 3778.76
				Kg Zn = 3.78

Assumed values

Kg used in total test	kg	5.1
Kg calculated 3.78+7.49+5.25 =	kg	16.25

Comparison between results from math Model and actual readings		
Avg SO4 removed	2400 (4000-1600)	Ratio Zn:SO4
Measured Coulomb/l	10485	
Calculated mgZn/l	3531 using Faraday	1.47
Old rule 1000mg/l SO4 use	2708 mgZn/l	2.70

ESKOM – 16 NOVEMBER

ANALYTICAL RESULT FROM ESKOM

Received from Ananias Molefe on 27 November 2000

Note difference from results dated 27 November 2000

16/11/2000 SAMPLES

	FEED	PR(F)	PR(UF)	PR(F)	PR(UF)	
		12H38	12H38	14H50	14H50	
EC	4700	4680	4750	4060	4070	
PH	4.96	4.03	5.08	4.2	5.2	1
ALK (CO3)	3.31	<0.1	3.72	<0.1	5.16	2
Ca	469	452	467	461	487	
Mg	168	158	165	153	159	
Na	37.4	36.8	36.7	36.7	36.7	
Zn	576	510	558	399	456	3
Cl	107	121	107	109	108	4
SO4	3464	3391	3420	2588	2884	5
Al	3.76	1.52	2.85	1.53	1.87	
Mn	89.7	85.8	92.1	75.7	74.8	
Fe	459	491	483	246	213	6
TDS	4690	4610	4700	4000	4120	7

LEGEND

1	First ESKOM sample taken
2	Second ESKOM sample taken
1	There is probably no effluent at Landau with such a high pH
2	Not consistent with the previous Toe Seep Analysis
3	Very high and not consistent with the previous Toe Seep analysis
4	Inconsistent
5	Inconsistent analyses or reporting
]	pH - values are about all the same - no difference in [Fe]
7	Inconsistent analyses or reporting i.r.o. pH-value

Assessment report on the continuous operation of the EC Reactor

Execution dates: 28 May 2001 to 8 June 2001 (inclusive)

Executed by: JJ Smit and C Smit

Executive Summary:

The reactor operated for 264 hours with only three thirty minute stoppages caused by shift operators switching off the power due to low level feed water indication. In every one of these cases the EC reactor could be switched on within half an hour by restoring the flow and rinsing out the accumulated precipitate. Very important effects were noted to occur when the pH-value is pushed to its limit for this effluent. These effects are summarized in the Conclusions of this report.

1. Background

After the experiments performed in April 2001 it was felt that a continuous run of the plant should be undertaken to establish the following aspects:

1.1 Assessment aspects:

- The continuous operational reliability of the EC reactor.
- The maintenance and supervision requirements of the reactor under continuous operation conditions.
- The ease of selecting and maintaining a set point or an operational equilibrium in a continuous mode.

The continuous experiment was therefore designed to be operate and assessed on the following operational guidelines:

1.2 Operational guidelines:

- The current generator will be operated on a 25% electrical duty cycle while the flow of effluent will be automatically controlled at ca. 25% of the pump capacity.

- The constant header tank will be used to provide a constant head to the automatic feed pump while the product water will be discharged to waste via the second storage tank.

Under these conditions the following operational settings were attained:

1.3 Operational settings:

- Operational current (refer to paragraph) 500A to 700A.
- Operational voltage 12V
- Flow rate (refer to paragraph) 500 to 700liter/hr
- Acidity decrease (pH increase) 3.10 to >7.

2. Tabulated daily recorded readings:

A log sheet was to be filled out daily by the assessment team as well as the shift operators. The original log sheets are appended as Appendix 1 and had to contain the following instrument readings directly from the reactor. It was thus not necessary for the operators to enter into the control room. These with our own readings, measurements and recordings will be tabulated followed by an events discussion.

Instrument readings to be logged:

INSTRUMENT	INSTRUCTION
pH-meter No1	Read & record only
pH-meter No2	Read & record only
Flow meter	Read & record & if zero turn off current generator.

NOTES:

- (a) The instruction message contains only two actions with one "if" message and only one alternative. The required decision level is thus of the lowest order. This decision level could be lowered by installing a temperature sensor turning the power off at a selected elevated temperature.
- (b) A restricted number of random samples will be analysed in situ with the field test kit for sulfate. This kit however developed an electronic failure during the course of the experiment.

- (c) Approximately 20 randomly taken samples were presented to Eskom for analysis. [Refer to the attached Sampling Schedule]

Table 1: [Day 1 = 28 May 2001]

DAY	TIME	pH in	pH out	Flow	Remarks
1	14h20	3,15	7,59	0,12	E=25%,F=25%,3x800A
	20h20	3,13	8,13	0,125	FEA constant
	24h00	3,14	7,79	0,10	FEA constant
2	08h30	3,17	7,87	000	Dry! Stop due to no effluent
	08h55				Start again. FEA Constant
	10h15	3,16	7,25	0,204	Plant in equilibrium
	11h45	3,17	7,37	0,204	Changed pH- meter
3	14h20	3,14	7,58	0,147	
	08h30	3,15	7,56	0,145	Feed pump bearing noisy
	10h20	3,18	7,51	0,148	Feed & Mix pump burnt out
4	12h37	3,20	7,28	0,148	Feed gravitate through
	18h25	3,20	7,37	0,144	
	20h50	3,19	7,73	0,145	
5	10h30	3,21	7,85	0,140	
	16h14	2,83	7,85	0,14	Dry! Filled effluent tank
6	17h10	3,19	7,12	0,148	
7	10h46	3,24	7,66	0,148	
8	02h00	3,23	7,44	0,159	
	10h15	3,26	7,25	0,154	
	11h10	3,26	6,42	0,145	
	14h35	3,25	7,01	0,176	
	15h36	3,24	7,09	0,176	
9	02h30	3,25	7,06	0,013	Dry! Restart
	10h45	3,28	8,45	0,182	Rinse mix pump failed.
	11h45	3,28	8,61	0,226	
	11h22	3,26	7,21	0,119	
10	15h50	3,26	7,34	0,109	
	09h00	3,26	7,22	0,051	
	10h45	3,29	6,30	0,131	
	12h00	3,30	7,08	0,142	
	13h40	3,27	7,19	0,125	
11	15h35	3,27	7,31	0,131	
	08h30	3,29	7,76	0,131	Plant normal
12	10h56	3,26	7,67	0,134	Plant shut down & end exp

4. Events during testing

Day 1: Monday 28/5/01:

- 1.1 Starting the plant took ca. 1 hour before current was turned on.
- 1.2 Tests showed that the controlled feed pump could constantly provide 500liter/hr at 25% flow setting. The full static head of the 10000liter tank however increased flow to 700liter/hour using the same controller settings. The static head alone gave a 500litre/hour.

Day 2: Tuesday 29/5/01:

2.1 Early morning (8h30) the operator turned the reactor off because of no flow. It is expected that at 700liter/hour the 10 00 liter tank ran dry. $[700\text{liter/hr}] \times [18\text{hrs}] = 12600\text{liter}$. At 11h45 the plant was running normal again after rinsing the excess sludge.

Note: An unusually thick white sludge formed which could be $\text{Mg}(\text{OH})_2$ at the specific chemical conditions of high pH and elevated temperature. The submerged mixing pump and feed pumps were damaged probably due to high temperatures reach when the reactor ran dry. The system was adapted to function without both these pumps.

Day 3: Wednesday 30/5/01:

The plant operated normally for 24 hours but the effluent level in the feed tank was then very low. Consequently the operators were requested to just fill the header tank once per shift. Over the weekend this arrangement proved to be unsatisfactory and a constant overflow was used to maintain the header tank level.

Day4: Thursday 31/5/01:

The plant operated normally for 24 hours.

Day 5: Friday 1/6/01

A faulty pH-meter was changed to read the pH of the product stream.

The plant ran dry again due to a new operator closing the regulating overflow valve of the feed effluent. Corrective action was taken and the system operated for the next four days without any problem. A daily rinse of precipitate accumulating in the reactor had to be flushed out daily

Day 6: Saturday 2/6/01:

Normal operation

Day 7: Sunday 3/6/01

Normal operation

Day 8: Monday 4/6/01

Normal operation.

Day 9: Tuesday 5/6/01

Normal operation

Day 10: Wednesday: 6/6/01

Normal operation

Day 11: Thursday: 7/6/01

Normal operation

Day 12: Friday: 8/6/01

Plant operating normally until stopped at 10h56

5. Conclusions

The experiment conclusively demonstrated the ease, simplicity and reliability of the EC reactor. In all cases of an interruption the cause was singularly due to peripheral equipment and/or conditions. The reactor is at the very least as reliable as any typical utility equipment such as pumps, welding equipment and/or electrical machinery.

During ca. 20 months of experimentation the EC reactor never broke down and was only subject to overheating due to loose cable connections. Once corrected the unit was fully available during all of this period.

Two valuable lessons were learnt during these experiments. Firstly that future reactors should be fitted with complete drainage systems to waste. Secondly, a reliable temperature sensor should be used in the reactor to stop the reactor should a certain temperature be reached.

APPENDIX 9

AFFIRMATIVE COOPERATION AND PARTICIPATION IN THE EC - PROJECT

The project required the input of various assistants in the disciplines of chemical analysis, engineering plant supervision and plant operators. These participant skills were supplied from the Amcoal mines' infrastructure.

1. The following assistance in the various disciplines was provided:

1.1 Me Finger and Me. Melba (Technikon Environmental Trainees):

Topics of involvement:

- Start up, stable operation and plant shut down of the EC Plant.
- Routine sampling and analysis of plant effluent streams.
- Special hourly analyses of sulphate during test runs.
- Recording of all plant variables such as electrical conductivity, pH and supervising and setting of the automatic control set points.
- Control of the Electrochemical Cell current duty cycle.
- Assist with the weighing and assembly of electrodes and sludge.

1.2 Plant operational assistance: (Regular plant operators on shift)

Topics of involvement:

- Three operators were engaged to supervise the plant over a period of two (2) weeks for 24 hours/day at ca. 2 hourly intervals.
- Responsibility was to maintain, control and adjust effluent flow to the plant as well as to take emergency shut down steps in case of any abnormal function.

1.3 Chemical Engineering students involved in sulphate removal projects at the Vaal Triangle Technikon.

Students involved:

- Mr. SA Tsienyane (B Tech student)
- Mr. MD Chuene (B Tech student)

Supervisors:

Mr HC vd Merwe (a/HOD Chem. Eng.- Vaal Triangle Technikon)

Prof JJ Smit (Consultant and External Examiner)

NOTE: Project titles and reports are available.

2. Training and Education:

With all trainees the requirements of the mine was effective as far as safety and health is concerned Training varied from rudimentary awareness training on plant site for everybody to post secondary school tuition of the Technikon students. In all cases where direct plant exposure was necessary the following training and tuition were compulsory:

3. Awareness Training:

- 3.1 Awareness training of mine operators.
- 3.2 Extended on the job training of operators on newly developed, first world first world technologies.
- 3.3 Job enhancement and enrichment for operating personnel at existing plants. [Both at Kromdraai and Landau where operators on shift were integrated to supervise the EC plant , take samples and do adjustment or take corrective action.]
- 3.4 Networking and capacity building between various companies and institutions (Eskom, Anglocoal, WRC and the Technikon for example) to introduce newly developed technology .{Mention the participation, on the analytical chemistry, of Ananias Molefe from Eskom side]
- 3.5. All of the above should also be referenced to the concepts of black empowerment and capacity building.

4. Empowerment and capacity building:

Several graduates were introduced to the novelty of the electrochemical treatment of effluents against the background of the necessity for effluent treatment in general. The requirements for sustainable processes and sustainability of resources were emphasised.

In cases where direct involvement on the plant was required the awareness tuition was enforced with detailed instructive and explanatory training on the plant such as:

- 4.1. All tuition was complemented by detailed instructions manuals of the procedures for starting, running and stopping the plant during normal and planned situations.

- 4.2. Detailed description of possible emergency and contingency situations were described and strategies to normalise or prevent such situations were discussed.
- Process description and on site demonstration served the purpose of empowering the student and to integrate plant knowledge with his own educational capacity.