ELECTRICALLY DRIVEN MEMBRANE SEPARATION PROCESSES FOR THE TREATMENT OF INDUSTRIAL EFFLUENTS

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ELECTRICALLY DRIVEN MEMBRANE SEPARATION PROCESSES FOR THE TREATMENT OF INDUSTRIAL EFFLUENTS

Final Report to the
Water Research Commission

by

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EXECUTIVE SUMMARY

ELECTRICALLY DRIVEN MEMBRANE SEPARATION PROCESSES FOR THE TREATMENT OF INDUSTRIAL EFFLUENTS

Electrically driven membrane separation processes such as electrodialysis (ED) and its variants - electrodialysis reversal (EDR); electo-electrodialysis (EED); and bipolar electrodialysis (BED) are technologies that are suitable for the reclamation of water and chemicals from industrial effluents. The conventional ED and EDR processes are applied successfully in overseas countries for the desalination of brackish waters for potable use. The EDR process is applied in South Africa at Tutuka Power Station for the treatment of cooling tower blowdown for water recovery and effluent volume reduction. Conventional ED is successfully applied in Japan for treatment of nickel rinse water in the electroplating industry for nickel and water recovery from electroplating rinse waters. Conventional ED has the potential to be applied for the treatment of chromium, cadmium, copper and zinc electroplating rinse waters for water and chemical recovery. Electro-electrodialysis can be used for the recovery of chromium from spent chromium plating baths and rinse waters in the electroplating industry.

Bipolar electrodialysis is applied in the USA for acid recovery (HNO_3 and HF) from spent pickling acid produced in the steel manufacturing process. Bipolar electrodialysis technology has the potential to be applied for:

(a) Regeneration of waste ion-exchange regenerant;
(b) Acid recovery from spent battery acid;
(c) Acid and caustic soda recovery from sodium sulphate and sodium nitrate effluents;
(d) Purification of acids and bases;
(e) Organic acid (acetic; citric and amino) recovery from industrial effluents.

This technology appears to have a tremendous potential for the recovery/recycling of valuable chemicals present in industrial effluents, for pollution prevention and resource recovery.

It has been identified that a need exists in South Africa to evaluate ED and its variants for the treatment of industrial effluents for the recovery of water and chemicals. The annual water consumption in the electroplating industry in South Africa, for example, is approximately 9×10^6 m^3, of which approximately 80 percent is discharged as effluent. In an attempt to meet receiving water standards, the industry resorts to dilution of their effluents with consequent wastage of scarce water resources. Ideally this water should be recycled to decrease water intake by the industry. Recycling of recovered toxic metals (Ni, Cr, Cd, Cu, Zn), used in the electroplating process, to the plating baths will reduce sludge volumes and water pollution dramatically.

Ion-exchange is a commonly used unit process in water and wastewater treatment. The technology is straightforward and economical, with the exception of the regeneration step.

Regeneration chemicals (caustic soda and acids) are expensive. The waste metal salts produced constitute a pollution hazard. Recovery of caustic soda and acid from this waste with BED, for reuse in the regeneration process, will reduce water pollution significantly. Expensive regeneration chemicals will also be saved in the process.

Spent pickling acids (HNO_3 and HF), produced in the steel manufacturing process, are neutralised with lime prior to disposal to evaporation ponds. The neutralised effluent, containing toxic inorganic and organic compounds, is a pollution hazard because it can pollute ground water sources. Bipolar electrodialysis technology has the ability to recover acid from the spent acid for reuse in process. Almost no effluent is produced because all the streams generated during the BED process can be reused.

Sodium sulphate, sodium nitrate and sodium acetate effluents are produced by various industries in South Africa. These effluents have the potential to pollute the water environment if not safely disposed of. Bipolar electrodialysis technology has the ability to convert these salts into valuable caustic soda and acid. Pollution will thus be prevented and chemicals can be recovered for reuse with BED technology.

Implementation of ED technology in the South African water industry will lead to water savings, chemical recovery, effluent volume reduction and pollution prevention. Electrodialysis technology will be able to recover water and plating chemicals effectively from electroplating rinse water. However, little information is available in the literature regarding:

(a) the fouling potential of electroplating effluents for ED membranes;
(b) membrane cleaning methods;
(c) BED feed water pretreatment requirements;
(d) ED operating conditions;
(e) ease of operation of the ED process for the electroplater; and
(f) the economics of the process.

It will be possible to recover acids and bases from wastewaters for reuse in the ion-exchange process with BED technology. However, little information is available regarding:

(a) the fouling potential of waste regenerant for the membranes;
(b) membrane cleaning methods;
(c) BED feed water pretreatment requirements; and
(d) the economics of the process.

It was recently demonstrated through laboratory studies in a BED unit that nitric acid could be effectively recovered from spent pickling acid produced by a stainless steel manufacturer. Nitric acid recovery of approximately 80 percent could be obtained. The recovery of hydrofluoric acid, however, was low (approximately 40%). It is claimed that hydrofluoric acid recovery of approximately 80 percent is possible with BED. This matter, however, needs further investigation. It is also claimed that the dialysate produced in the diffusion dialysis process for treatment of spent pickling acid, can be effectively treated with BED for the recovery of bound acid. Little information exists regarding the treatment of diffusion dialysis dialysate with BED for the recovery of bound acid from the dialysate. This matter also needs further investigation.

Acids and bases may be recovered from sodium sulphate, sodium nitrate and sodium acetate effluent with BED. Little information, however, is available in South Africa regarding the use of BED for the above applications. Experience in BED technology for acid and base recovery from sodium sulphate, sodium nitrate, sodium acetate and other effluents will lead to the successful application of BED technology for pollution control and resource recovery.

Implementation of ED technology into the South African water industry will lead to substantial water savings and pollution prevention. It will be possible to recover more than 80 percent of the rinse water in the electroplating process with ED. It will also be possible to recover more than 80 percent of plating metals such as nickel, chromium, cadmium, copper and zinc. Consequently sludge volumes will be reduced dramatically and toxic metals and sludge will be kept out of the water environment. Short ED plant payback periods (< 3 years) may possibly inspire electroplaters to use the ED process for electroplating effluent treatment in South Africa.

It may be possible to recover more than 80 percent of the nitric and hydrofluoric acid in spent pickling acid effluent with a combination of BED and diffusion dialysis. Water pollution caused by these hazardous acids will therefore be reduced dramatically. The demonstration of short BED plant payback periods (approximately 3 years) may motivate industry to apply this technology for resource recovery and pollution prevention.

It may also be possible to recover acid and caustic soda economically from sodium sulphate, sodium nitrate, sodium acetate and other process effluents. Acid and caustic recovery will lead to pollution prevention and savings in chemical costs for industry.

Implementation of ED technology and its variants into the market place will lead to better pollution control, water savings, resource recovery and effluent volume reduction. Wastes will therefore be minimised.

The main objectives of this investigation were to:

(a) Evaluate ED for treatment of nickel and chromium rinse waters for metal and water recovery;

(b) Evaluate EED for treatment of chromium drag-out for chromium recovery;

(c) Evaluate BED for the regeneration of waste ion-exchange regenerant;

(d) Evaluate BED for acid recovery from spent pickling acid effluent;

(e) Evaluate BED for acid and caustic soda recovery from sodium sulphate, sodium nitrate and sodium acetate effluents;

(f) Determine the economics of the processes.

Nickel drag-out can be cost-effectively treated with ED for nickel and water recovery in the electroplating industry. Plant payback period of approximately 2 years is possible. Pilot studies on nickel drag-out showed that nickel in the ED feed could be concentrated from 3,5 g/ℓ to approximately 28 g/ℓ in the ED brine. Nickel recovery rates varied between 0,83 and 1,0 kg Ni/m^2.d. Full-scale ED nickel/water recovery plant data showed that a nickel concentration level of approximately 50 g/ℓ could be reached in the ED brine. Approximately 97 percent of the drag-out can be recovered for reuse. Therefore, ED can be effectively applied as a metal/water recovery technology in the electroplating industry.

Chromium can be recovered from chromium rinse water with ED. Chromium in the ED feed could be concentrated from 1 300 mg/ℓ to 6 900 mg/ℓ in the brine. Brine volume comprised approximately 20 percent of the treated feed water volume. Therefore, effluent volume can be significantly decreased for subsequent further treatment of the ED brine for chromium removal with conventional precipitation technology. The chromium concentration level of the ED product is high (approximately 400 mg/ℓ). Ion-exchange treatment will be required to reduce the chromium level in the ED product to low concentration levels (< 0.1 mg/ℓ). Electrical energy consumption for chromium recovery/removal was high (3,1 to 8,7 kWh/kg Cr). Chromium recovery rate varied between 0,12 and 0,26 kg Cr/m^2.d.

It appears that it should be possible to use the EED process effectively for chromium recovery from chromium drag-out for reuse in the plating bath. Chromium could be concentrated from 48 g/ℓ (CrO_3) to 240 g/ℓ (CrO_3) in the EED product. This concentration level is of sufficient strength for direct reuse in the plating bath. Electrical energy consumption, however, was high (38 kWh/kg Cr). Membrane life time and the economics of the process are unknown. However, it appears that this process will be too expensive for the electroplater to use. Further work will be required to evaluate this process properly for treatment of chromium drag-out.

The bipolar electrodialysis process appears to function effectively for treatment of spent pickling acid effluent for acid recovery for reuse in the pickling process. A nitric acid concentration level between approximately 2,0 and 2,5 mol/ℓ could be obtained with ease. Hydrofluoric acid recovery, however, was poor when the nitrate concentration level in the feed water was high. However, the hydrofluoric acid concentration level in the acid product increased dramatically when most of the nitrate was removed from the feed. A hydrofluoric acid concentration level of approximately 2,5 mol/ℓ could be obtained towards the end of a run. Almost no effluent will be produced when BED is used for treatment of spent pickling acid effluent. All the chemicals produced in the process (acids and bases) can be reused in the process itself or in the pickling process. Consequently, the BED process should be the ideal solution to solve the spent pickling acid effluent problem experienced by stainless steel manufacturers. A combination of the diffusion dialysis and BED processes will function more effectively than BED alone for treatment of spent pickling acid effluent. This, however, will depend on the quality of bound or complexed acids present in the spent pickling acid effluent. It appears that there is a significant amount of bound acid present in spent pickling acid effluent.

Membrane fouling can lead to the failure of membrane separation process for effluent treatment. The fouling potential of the effluent for the BED membranes should therefore be determined through long-term laboratory or pilot studies. This will ensure that proper process design criteria will be developed for treatment of the spent pickling acid effluent. Preliminary results have shown that the capital cost for a 1 750 ℓ/h BED plant for treatment of spent pickling acid will amount to approximately R14,8 million. The annual membrane cost will amount to approximately R2,7 million. Preliminary results have shown that the capital cost for a combination of the diffusion dialysis and BED processes for a 1 750 ℓ/h plant will amount to approximately R11,5 million. (R2,3 million for diffusion dialysis and

R9,2 million for BED). Operating expenses for the diffusion dialysis process will amount to R1,3 million for membrane replacement (annual cost), approximately R35 000 for spare parts for pumps and approximately 14 kW electrical energy will be used in the process. Operating expenses for BED will amount to approximately R1,4 million for membrane replacement (annual cost) and approximately 1 290 kW electrical energy will be consumed in the process.

Preliminary tests showed that it would be possible to convert sodium nitrate effluent effectively into nitric acid and caustic soda with the BED process. Acid and caustic soda concentration levels of approximately 2 mol/ℓ could be obtained with ease when sodium nitrate solution (approximately 10%) was treated with BED. Electrical energy consumption for acid production was determined at approximately 2 000 kWh/ton acid. Electrical energy consumption for caustic soda production was determined at approximately 3 000 kWh/ton caustic soda. The capital cost for a BED plant to treat 3 600 kg per day sodium nitrate solution (10 to 15%) is estimated at R1,6 million. This cost excludes membranes, at an estimated cost of R72 000/set, with one year life time and any pretreatment or site specific cost. The expected DC power consumption would be 27kW.

Preliminary tests showed that it would be possible to convert sodium sulphate effluent effectively into acid caustic soda with BED. Acid and caustic soda concentration levels of approximately 2 mol/ℓ could be obtained with ease when sodium sulphate solutions (approximately 10 and 20%) were treated with BED. Electrical energy consumption for acid production varied between approximately 3 800 and 4 600 kWh/ton acid. The electrical energy consumption for base production varied between approximately 3 500 and 6 500 kWh/ton caustic soda. Current efficiency was lower than expected and this matter warrants further investigation.

All the major contract objectives have been achieved in this study. It was shown that:

(a) Electrodialysis can be applied cost effectively for nickel and water recovery from electroplating drag-out;

(b) Electrodialysis can be applied for chromium and water recovery from chrome bearing effluents;

(c) Electo-electrodialysis can be applied effectively for chromium recovery from chromium drag-out for reuse;

(d) Bipolar electrodialysis can be applied for regeneration of waste ion-exchange regenerant;

(e) Bipolar electrodialysis can be applied cost effectively for acid recovery from spent pickling acid effluent; and

(f) Bipolar electrodialysis can be effectively applied for acid and caustic soda recovery from sodium nitrate, sodium sulphate and sodium acetate effluents.

This report offers the following to potential users of ED technology for treatment of industrial effluents:

(a) It presents the basics of electrically driven membrane separation processes for effluent treatment;

(b) It presents process design criteria for treatment of nickel and chrome bearing effluents with ED and EED;

(c) It presents process design criteria for treatment of spent pickling acid; sodium nitrate; sodium sulphate and sodium acetate effluents with BED;

(d) It shows the economics of ED and BED for treatment of industrial effluents.

The following actions will be taken as a result of this study:

(a) Results of the investigation will be published in *Water SA*:

(b) A talk regarding treatment of industrial effluents with ED will be presented at a major conference in South Africa;

(c) A consultancy service regarding treatment of industrial effluents with electrically driven membrane processes will be rendered to the South African water industry.

The following recommendations can be made as a result of this study:

(a) Demonstrate ED technology to industry through pilot studies for nickel and water recovery from electroplating drag-out;

(b) Demonstrate BED technology to industry through pilot studies for acid and caustic soda recovery from spent acid;

(c) Demonstrate BED technology to industry through pilot studies for acid and caustic soda recovery from spent sodium nitrate, sodium sulphate and sodium acetate effluents;

(d) Exploit ED and its variants further for treatment of industrial effluents in South Africa for water and chemical recovery and effluent volume reduction.

TABLE OF CONTENTS

Page

—oOo—

LIST OF TABLES

Page

LIST OF FIGURES

Page

Page

Page

1 INTRODUCTION

Electrically driven membrane separation processes such as electrodialysis (ED) and its variants - electrodialysis reversal (EDR); electro-osmotic pumping ED (EOP.ED); electro-electrodialysis (EED); and bipolar electrodialysis (BED) are technologies that are suitable for the reclamation of water and chemicals from industrial effluents. The conventional ED and EDR processes are applied successfully in overseas countries for the desalination of brackish waters for potable use[1]. The EDR process is applied in South Africa at Tutuka Power Station for the treatment of cooling tower blowdown for water recovery and effluent volume reduction[2]. Conventional ED is successfully applied in Japan for treatment of nickel rinse water in the electroplating industry for nickel and water recovery from electroplating rinse waters[3]. Conventional ED has the potential to be applied for the treatment of chromium, cadmium, copper and zinc electroplating rinse waters for water and chemical recovery[4]. It was recently demonstrated that EOP.ED could be applied successfully for the recovery of chemicals and water from non-scaling industrial effluents[5]. Electro-electrodialysis can be used for the recovery of chromium from spent chromium plating baths and rinse waters in the electroplating industry[6].

Bipolar electrodialysis is applied in the USA for acid recovery (HNO_3 and HF) from spent pickling acid produced in the steel manufacturing process[7]. Bipolar electrodialysis technology has the potential to be applied for[8]:

(a) Regeneration of waste ion-exchange regenerant;
(b) Acid recovery from spent battery acid;
(c) Acid and caustic soda recovery from sodium sulphate and sodium nitrate effluents;
(d) Purification of acids and bases;
(e) Organic acid (acetic; citric and amino) recovery from industrial effluents.

This technology appears to have a tremendous potential for the recovery/recycling of valuable chemicals in industrial effluents for pollution prevention and resource recovery.

It has been identified that a need exists in South Africa to evaluate ED and its variants for the treatment of industrial effluents for water and chemical recovery for reuse purposes. The annual water consumption in the electroplating industry, for example, in South Africa is approximately 9 x 10^6 cubic metre[9] of which approximately 80 percent is discharged as effluent. In an attempt to prevent water pollution, the industry resorts to dilution of their effluents with consequent wastage of scarce water resources. Ideally this water should be recycled to decrease water intake by the industry. Recycling of recovered toxic metals (Ni, Cr, Cd, Cu, Zn) that are used in the electroplating process back to the plating baths will reduce sludge volumes and water pollution dramatically.

Ion-exchange is a common process step in water and wastewater treatment. The technology is straightforward and economical with the exception of the regeneration step. Regeneration chemicals (caustic soda and acids) are expensive. The waste regenerant (metal salts) is a pollution hazard. Recovery of caustic soda and acid from the waste regenerant with BED for reuse in the regeneration process will reduce water pollution significantly. Expensive regeneration chemicals will also be saved in the process.

Spent pickling acids (HNO_3 and HF) that are produced in the steel manufacturing process are neutralised with lime prior to disposal to evaporation ponds. The neutralised effluent is a pollution hazard because it can pollute ground water sources. Bipolar electrodialysis technology has the ability to recover acid from the spent acid for reuse in the process. Almost no effluent is produced in the process because all the streams generated during the BED process can be reused in the process.

Sodium sulphate, sodium nitrate and sodium acetate effluents are produced by various industries in South Africa. These effluents have the potential to pollute the water environment if not safely disposed of. Bipolar electrodialysis technology has the ability to convert these salts into valuable caustic soda and acid. Pollution will thus be prevented and chemicals can be recovered for reuse with BED technology.

Implementation of ED technology in the South African water industry will lead to water savings, chemical recovery, effluent volume reduction and pollution prevention. Electrodialysis technology will be able to recover water and plating chemicals effectively from electroplating rinse water. However, little information is available in the literature regarding[3,10]: (a) The fouling potential of electroplating effluents for ED membranes; (b) Membrane cleaning methods; (c) Feed water pretreatment requirements; (d) ED operational conditions; (e) Ease of operation of the ED process for the electroplater; (f) Economics of the process, etc.

It will be possible to recover acid and base from waste regenerant for reuse in the ion-exchange process with BED technology. However, little information is available regarding[11]: (a) The fouling potential of waste regenerant for the membranes; (b) Membrane cleaning methods; (c) BED feed water pretreatment requirements; (d) The economics of the process, etc.

It was recently demonstrated through laboratory studies in a BED unit that nitric acid could be effectively recovered from spent pickling acid produced by a stainless steel manufacturer[12]. Nitric acid recovery of approximately 80 percent could be obtained. The recovery of hydrofluoric acid, however, was low (approximately <40%). It is claimed that hydrofluoric acid recovery of approximately 80 percent is possible with BED[13]. This matter, however, needs further investigation. It is also claimed that the dialysate produced in the diffusion dialysis process for treatment of spent pickling acid, can be effectively treated with BED for the recovery of bound acid[13]. Little information exists regarding the treatment of diffusion dialysis dialysate with BED for the recovery of bound acid from the dialysate. This matter also needs further investigation.

Acid and base can be recovered from sodium sulphate, sodium nitrate and sodium acetate effluent with BED[8]. Little information, however, is available in South Africa regarding the use of BED for the above applications. Experience in BED technology for acid and base recovery from sodium sulphate, sodium nitrate, sodium acetate and other effluents will lead to the successful application of BED technology for pollution control and resource recovery.

Implementation of ED technology into the South African water industry will lead to substantial water savings and pollution prevention. It will be possible to recover more than 80 percent of the rinse water in the electroplating process with ED[3]. It will also be possible to recover more than 80 percent of plating metals such as nickel, chromium, cadmium, copper, zinc, etc. Consequently, sludge volumes will be reduced dramatically and toxic metals and sludge will be kept out of the water environment. Short ED plant payback periods[14] (< 3 years) may inspire electroplaters to use the ED process for electroplating effluent treatment in South Africa.

It may be possible to recover more than 80 percent nitric and hydrofluoric acid in spent pickling acid effluent with a combination of BED and diffusion dialysis[13]. Water pollution caused by these hazardous acids will therefore be reduced dramatically. The demonstration of short BED plant payback periods (approximately 3 years) may motivate industry to apply this technology for resource recovery and pollution prevention.

It may also be possible to recover acid and caustic soda economically from sodium sulphate, sodium nitrate, sodium acetate and other process effluents. Acid and caustic recovery will lead to pollution prevention and savings in chemical costs for industry.

Implementation of ED technology and its varients into the market place will lead to better pollution control, water savings, resource recovery, effluent volume reduction, etc. Wastes will therefore be minimised.

The objectives of this investigation were therefore to : -

(a) Evaluate ED for treatment of nickel and chromium rinse waters for metal and water recovery;

(b) Evaluate EED for treatment of chromium drag-out for chromium recovery;

(c) Evaluate BED for the regeneration of waste ion-exchange regenerant;

(d) Evaluate BED for acid recovery from spent pickling acid effluent;

(e) Evaluate BED for acid and caustic soda recovery from sodium sulphate, sodium nitrate and sodium acetate effluents; and

(f) Determination of the economics of the processes.

2 PRINCIPLES OF OPERATION

The principles of operation of the ED process will first be considered. An ion-exchange membrane is a kind of membrane in the form of a sheet while an ion-exchange resin is in granular form. The phenomenon of 'ion-exchange' is the permeation of ions in the case of an ion-exchange membrane while it is an adsorptive exchange of ions in the case of an ion-exchange resin (Figure 1.a and 1.b). Because of this different phenomenon, an ion-exchange membrane does not require regeneration but can be continuously used for a long period. The mechanism of operation of an ion-exchange membrane under the influence of an electrical potential is shown in Figure 2. The cation-exchange membrane is charged negatively and is permeable to cations such as Na^+, Ca^{2+}, while it is non-

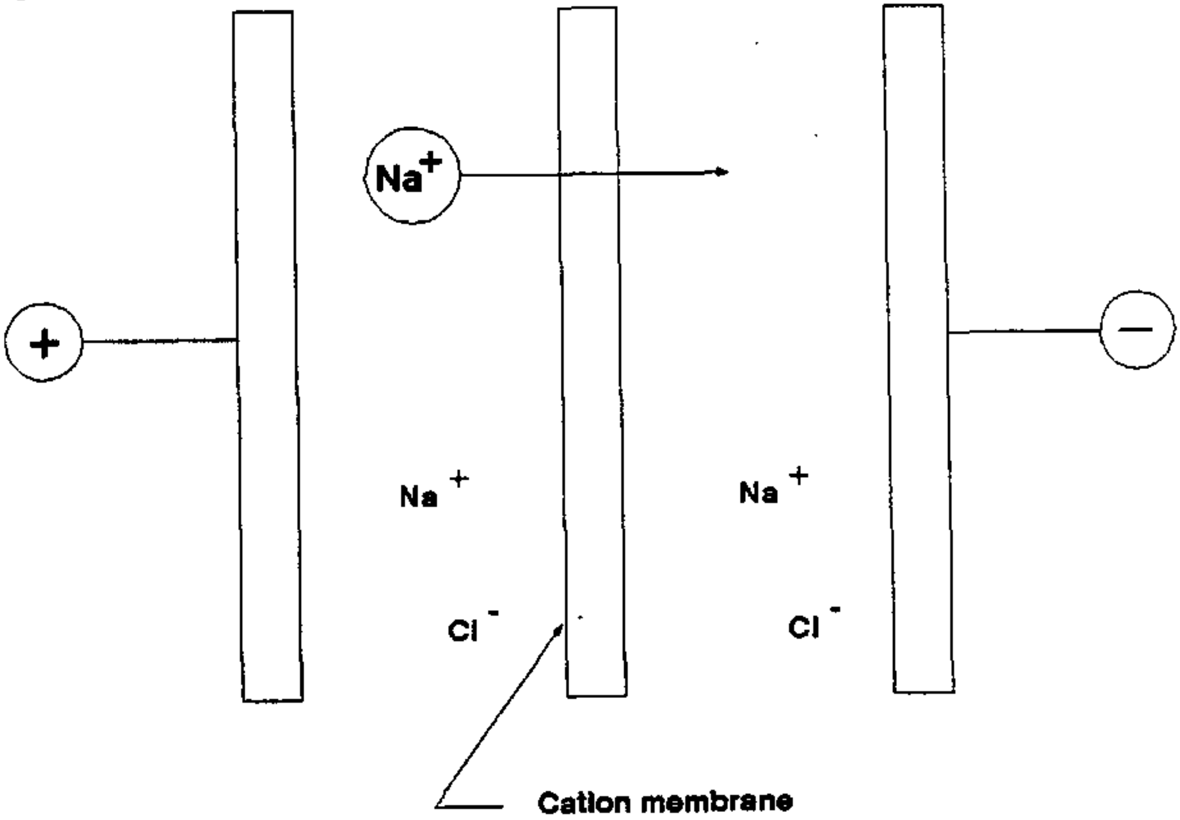


Figure 1.a : Ion-exchange membrane permeation

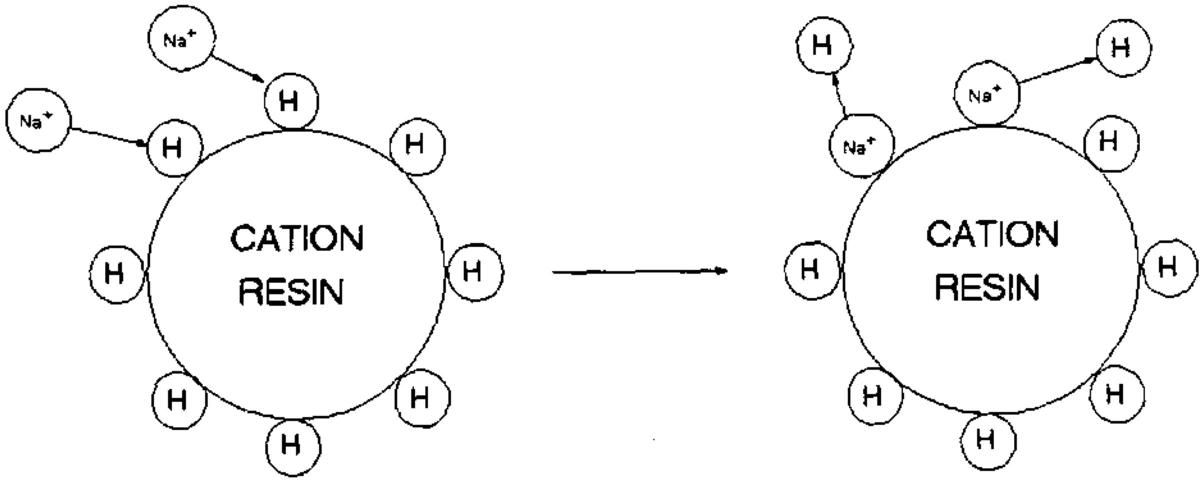
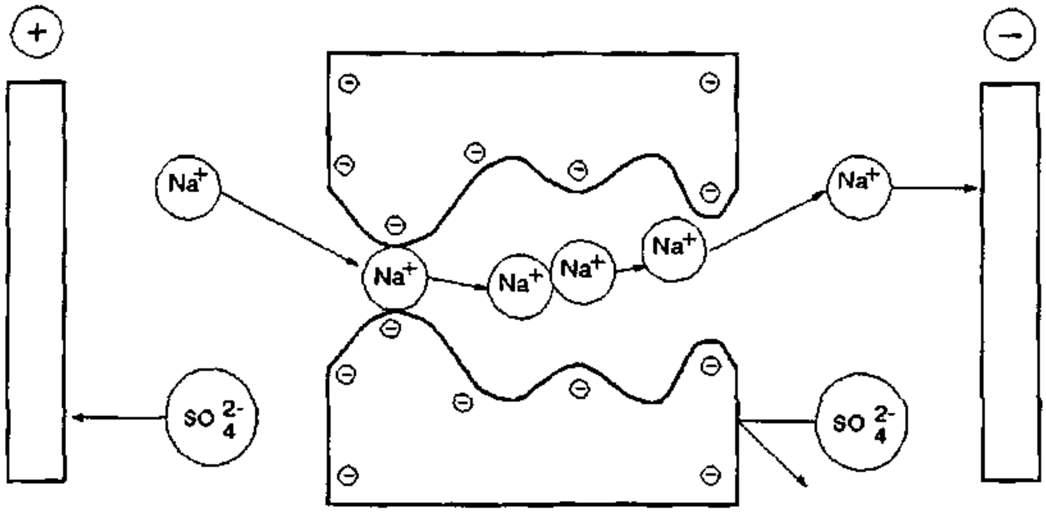


Figure 1.b : Adsorptive exchange in the case of an ion-exchange resin.



Cation membrane

Figure 2 : Ionic permselectivity of ion-exchange membranes

permeable to ions such as Cl^-, SO_4^{2-}, etc. This permselectivity encountered in ion-exchange membranes forms the basis of the ED/EDR process. Anion-exchange membranes are charged positive and behave oppositely.

2.1 The Standard ED Process

In the ED process water flows between alternately placed cation and anion-permeable membranes (Figure 3) which are built into a so-called ED stack. Direct current (DC) provides the motive force for ion migration through the membranes and the ions are removed or concentrated in the alternate water passage by means of permselective membranes.

The standard ED process often requires the addition of acid and/or polyphosphate to the brine stream to inhibit the precipitation of sparingly soluble salts (such as $CaCO_3$ and $CaSO_4$) in the stack. To maintain performance, the membrane stack needs to be cleaned periodically to remove scale and other surface fouling matter. This is done in two ways by cleaning in place (CIP), and stack disassembly.

Special cleaning solutions (dilute acids or alkaline brine) are circulated through the membrane stack for in-place cleaning, but at regular intervals the stacks need to be disassembled and mechanically cleaned to remove scale and other surface fouling matter. Regular stack disassembly is a time-consuming operation and is a disadvantage of the standard ED process.

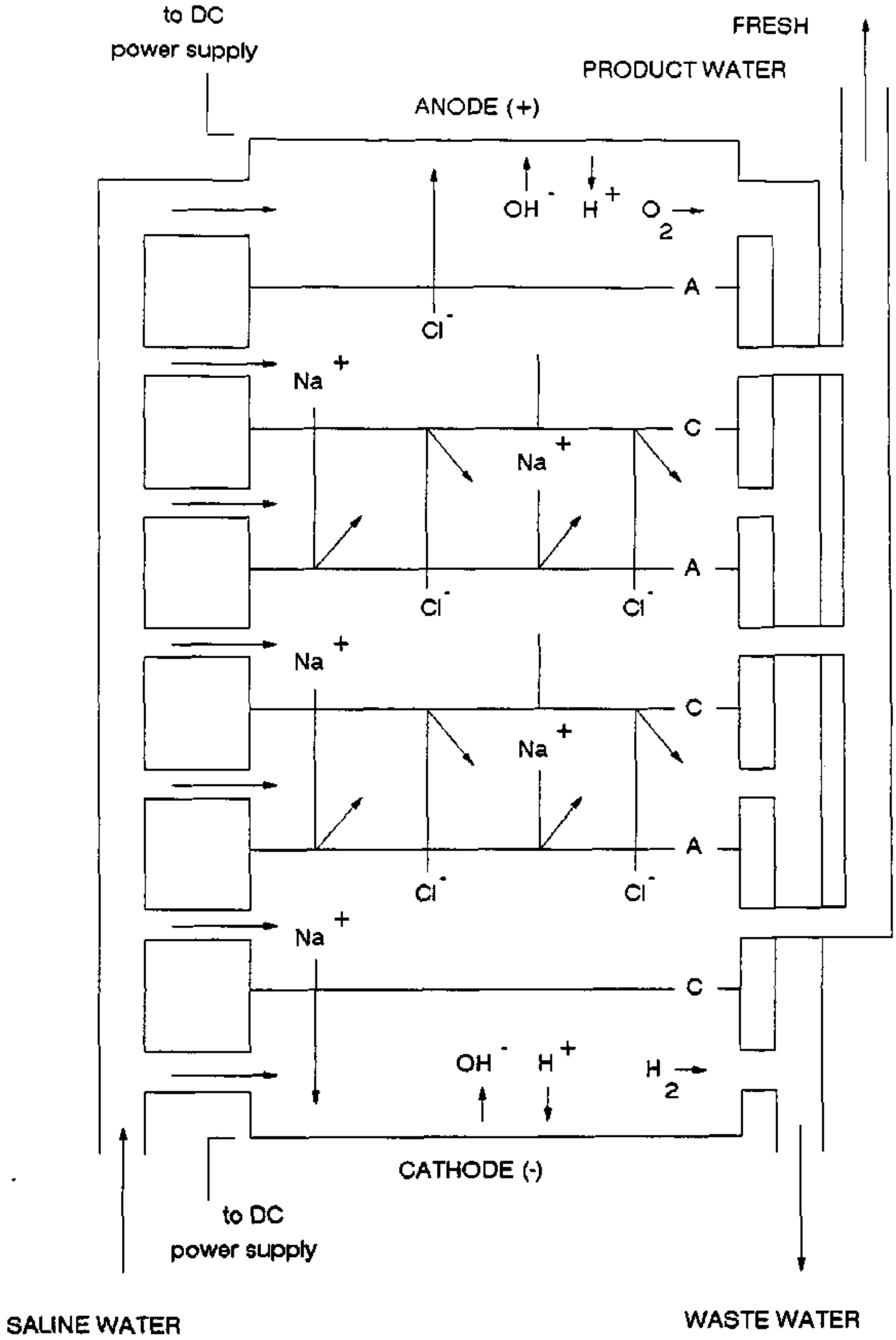


Figure 3 : The ED process. A = anion-permeable membrane; C = cation-permeable membrane

2.2 The EDR Process

The EDR process operates on the same basic principles as the standard ED process. In the EDR process, the polarity of the electrodes is automatically reversed periodically (about three to four times per hour) and, by means of motor operated valves, the 'fresh product water' and 'wastewater' outlets from the membrane stack are interchanged. The ions are thus transferred in opposite directions across the membranes. This is shown in Figure 4. This aids in breaking up and flushing out scale, slime and other deposits from the cells. The product water emerging from the previous brine cells is usually discharged to waste for a period of one to two minutes until the desired water quality is restored.

The automatic cleaning action of the EDR process usually eliminates the need to dose acid and/or polyphosphate, and scale formation in the electrode compartments is minimised due to the continuous change from basic to acidic conditions. Essentially, therefore, three methods of removing scale and other surface-fouling matters are used in the EDR process viz., cleaning-in-place; stack disassembly as used in standard ED; and reversal of flow and polarity in the stacks. The polarity reversal system greatly extends the intervals between the rather time-consuming task of stack disassembly and reassembly, with an overall reduction in maintenance time.

The capability of EDR to control scale precipitation more effectively than standard ED is a major advantage of this process, especially for applications requiring high water recoveries. However, the more complicated operation and maintenance requirements of EDR equipment necessitates more labour and a greater skill level than reverse osmosis and may be a disadvantage of the process.

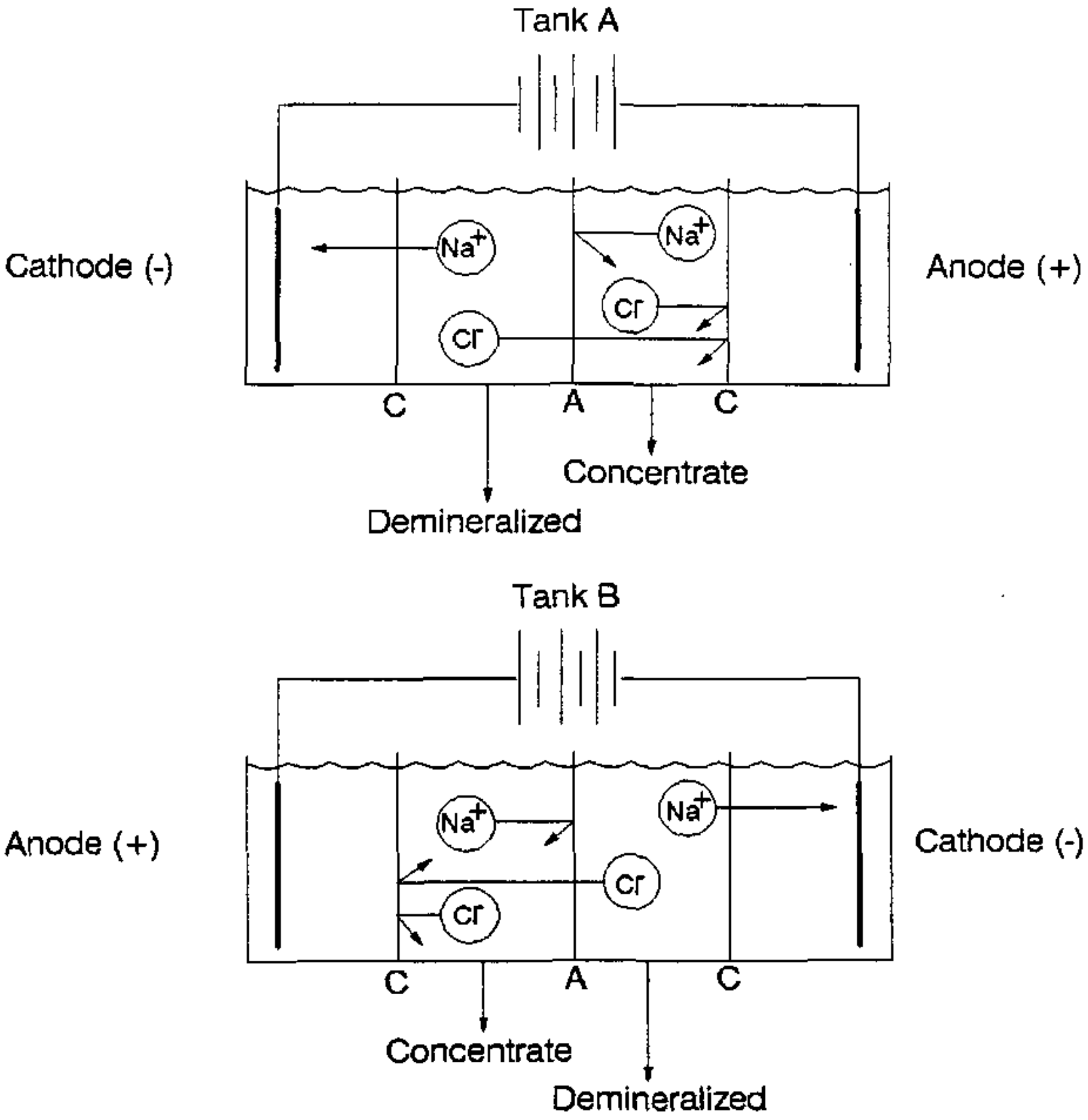


Figure 4 : Controlling of film and scale formation in an EDR stack

2.3 The Bipolar Electrodialysis Process

The bipolar ED process uses ion-exchange membranes to separate and concentrate the acid and base constituents from a salt stream. The key element in this electrodialytic process is the bipolar membrane, so-called because it is composed of two distinctive layers which are selective to ions of opposite charges. An expanded view of this membrane and its operation is shown in Figure 5. Under the influence of an applied current, water diffuses into the membrane interface where it dissociates to hydrogen and hydroxyl ions. The H^+ and OH^- ions are then transported across the cation and anion selective layers respectively to chambers on either side of the bipolar membrane. Acidification/basification of these chambers is the overall result.

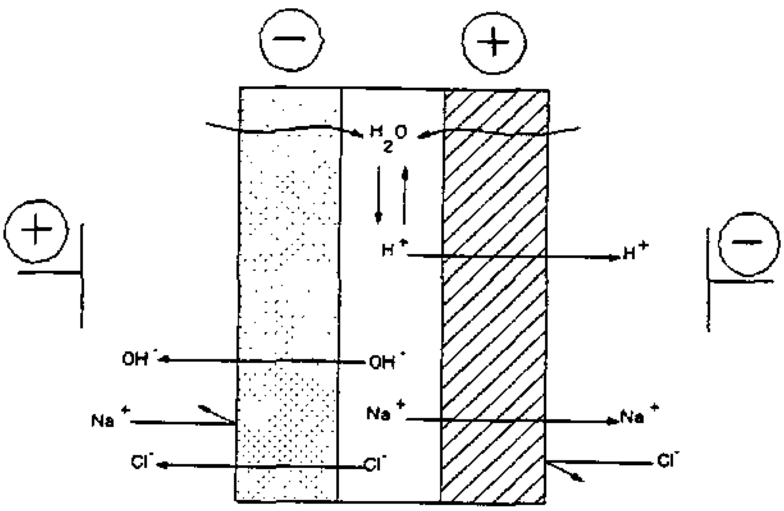


Figure 5: Operation of bipolar membrane

To achieve net production of acid and base, monopolar (i.e. cation and anion-exchange) membranes are used in conjunction with the bipolar membrane. A schematic of a generalised three compartment cell unit is shown in Figure 6. The salt (i.e. sodium sulphate) is fed to a chamber between the cation and anion-selective membranes. The cations (Na^+) and anions (SO_4^{2-}) move across the monopolar membranes and combine with the hydroxide and hydrogen ions, as shown, to form acid and base. In a commercial operation up to 200 of such cell units are assembled between a single set of electrodes to form a compact water splitting stack. Feed to the acid, base and salt chamber is achieved via internal manifolds built into the stack. If only one of the components (NaOH) needs to be obtained in a pure form the cell can be simplified to a two compartment unit as shown in Figure 7. Only the bipolar and cation membranes are used here. The acid product from such a cell using sodium sulphate feed would be a mixture of sulphuric acid and the unconverted salt.

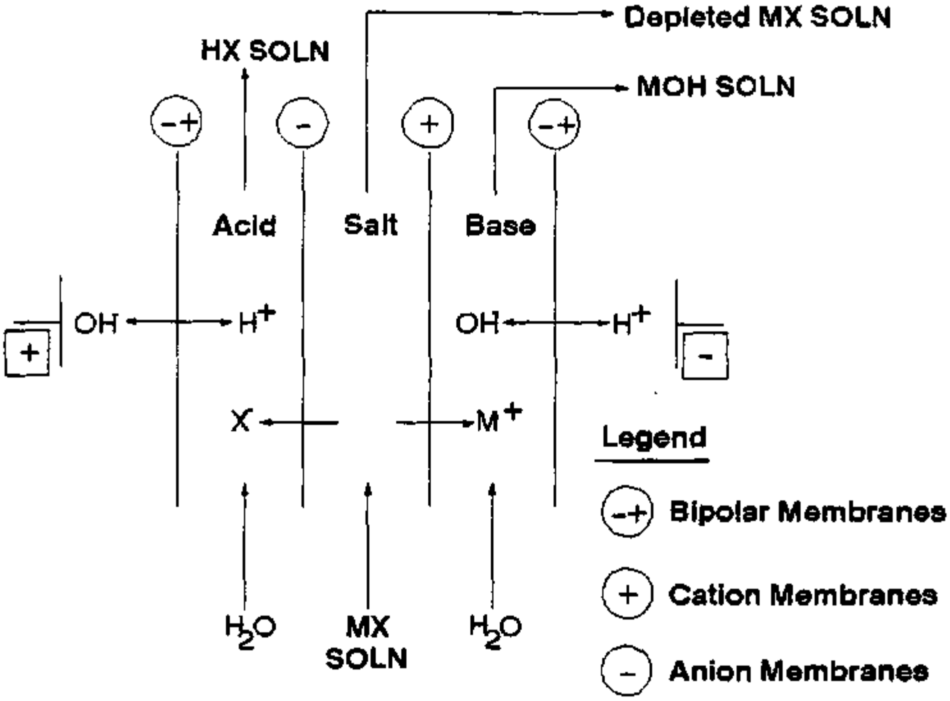


Figure 6 : Three compartment bipolar ED cell for conversion of salt into acid and base.

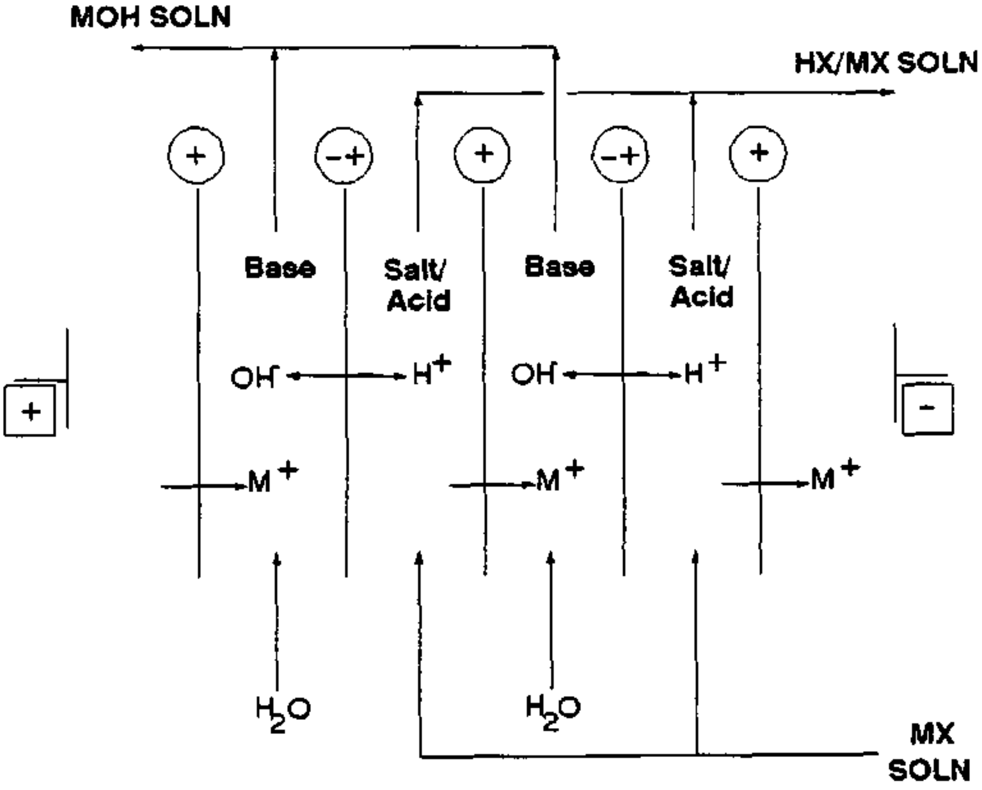


Figure 7 : Two compartment bipolar ED cell for conversion of salt into base.

3 EXPERIMENTAL

3.1 Treatment of Nickel Drag-out

The ED pilot plant that was used for the study is shown in Figure 8. Nickel drag-out (30 ℓ) and brine (5 ℓ) were circulated through the ED stack (75 cell pairs Selemion AMV and CMV membranes; 204 cm^2 membrane area) at a flow rate of 900 ℓ/h. A 30 litre sodium sulphate solution (10 g/ℓ) was used as electrode rinse water. Constant voltage (58 volt) was applied across the electrodes and the ED run was terminated after approximately 70 minutes of operation. The feed water was replaced with fresh feed (30 ℓ) and six more runs were conducted. The electrical conductivity of the ED product and brine was measured as a function of time. The pH of the ED feed, brine and electrode rinse was kept between 2 and 3 by addition of sulphuric acid.

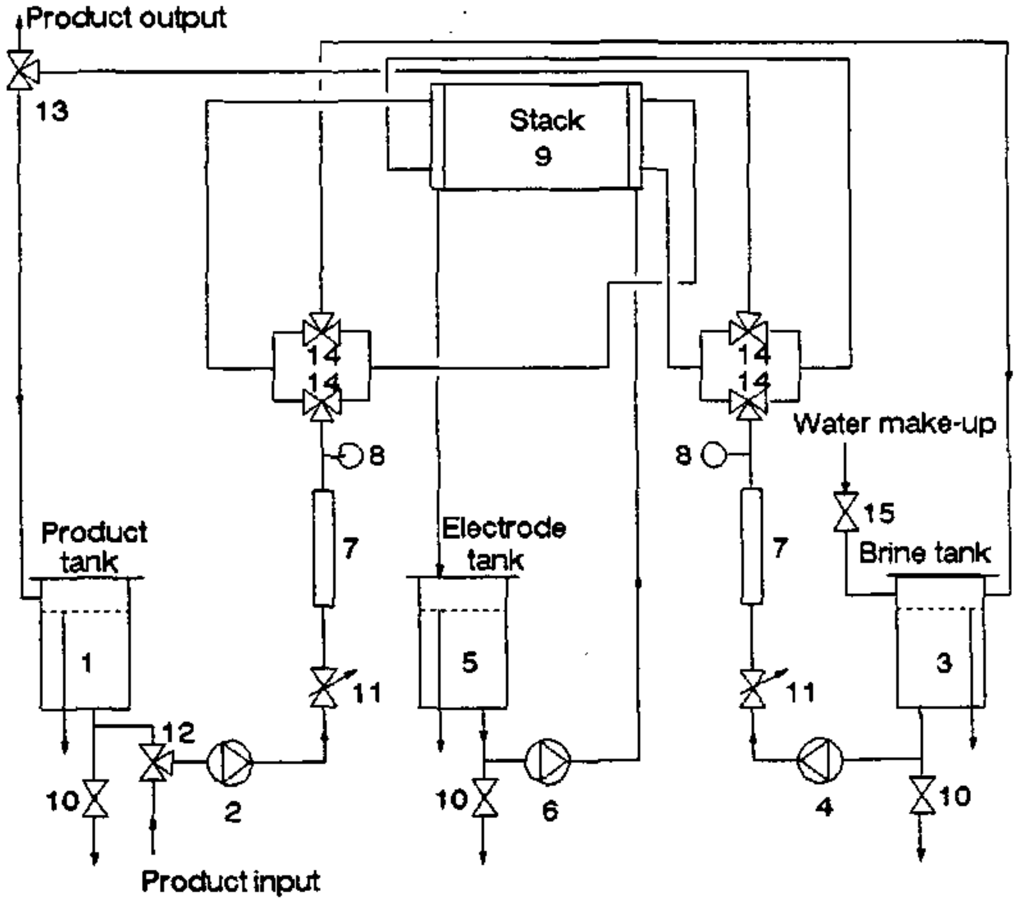


Figure 8 : Electrodialysis pilot plant

The chemical composition of the ED feed, product and brine was determined with automated methods. Current efficiency, nickel recovery and electrical energy consumption were calculated for the different runs.

3.2 Treatment of Chromium Rinse Water with Electrodialysis

The laboratory scale ED unit that was used for the study is shown in Figure 9.

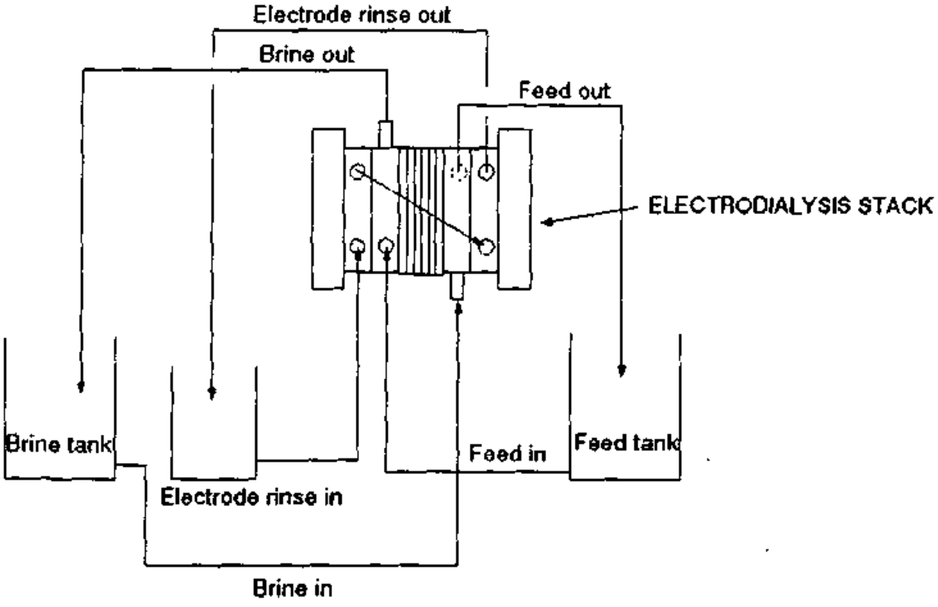


Figure 9 : Laboratory scale ED unit

The membrane stack contained 19 cell pairs Morgane ARA (anionic) and Nafion (cationic) membranes with an effective membrane area of 69 cm². Feed (5 litre; approximately 1 000 mg/ℓ $Cr^{(VI)}$) was circulated through the membrane stack at a flow rate of 1,68 ℓ/min (4,11 cm/s) and brine at a flow rate of 1,26 ℓ/min. An approximately 10 000 mg/ℓ sodium sulphate solution was used as electrode rinse solution. Electrodialysis was conducted at constant voltage of 24 volt across the stack. Feed was replaced with fresh feed after the first run without replacing the brine. Four batch runs were conducted.

3.3 Treatment of Chromium Drag-Out with Electro-Electrodialysis

A schematic diagram of the EED cell that was used for the treatment of chromium drag-out is shown in Figure 10. Chromium drag-out (20 ℓ) and tap water (2 ℓ) were circulated at a flow rate of 920 mℓ/min through the membrane stack. Morgane ARA and Ionac MA-3475 anion-exchange membranes were used with a membrane area of 72,25 cm². A current density of 80 mA/cm² membrane area was applied and the chromium concentration in the feed and product was determined as a function of time. A stainless steel cathode and a platinised titanium anode were used.

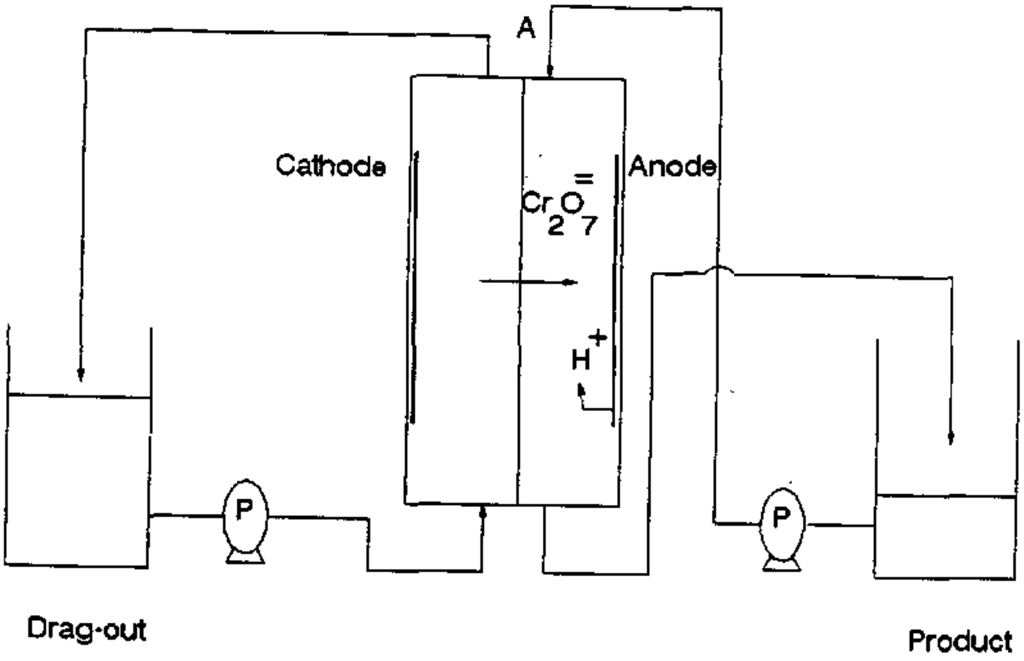


Figure 10 : Experimental set-up for treatment of chromium rinse water with EED

3.4 Treatment of Spent Pickling Acid Effluent with Bipolar Electrodialysis

Spent pickling acid (approximately 23 litre) was neutralised with potassium hydroxide (approximately 7,6 kg) until the pH of the effluent remained constant at approximately 10,5. The precipitated metal hydroxides (Fe, Cr and Ni) were separated from the water in a cross-flow microfiltration unit and the potassium salts of the acids (HNO_3 and HF) were used as feed water to a laboratory size BED stack.

The experimental set-up that was used is shown in Figure 11. The potassium salts of a spent acid sample obtained from a stainless steel manufacturer were electrodialysed in the batch mode of operation.

The laboratory BED stack contained eight cell pairs containing approximately 817 cm^2 active membrane area. The initial feed volume was 60 litre. Acid and base volumes were 20 litre each. The initial acid (HNO_3) and base (KOH) concentration levels in the acid and base tanks were approximately 0,1 mol/ℓ (acid and base made up in deionised water).

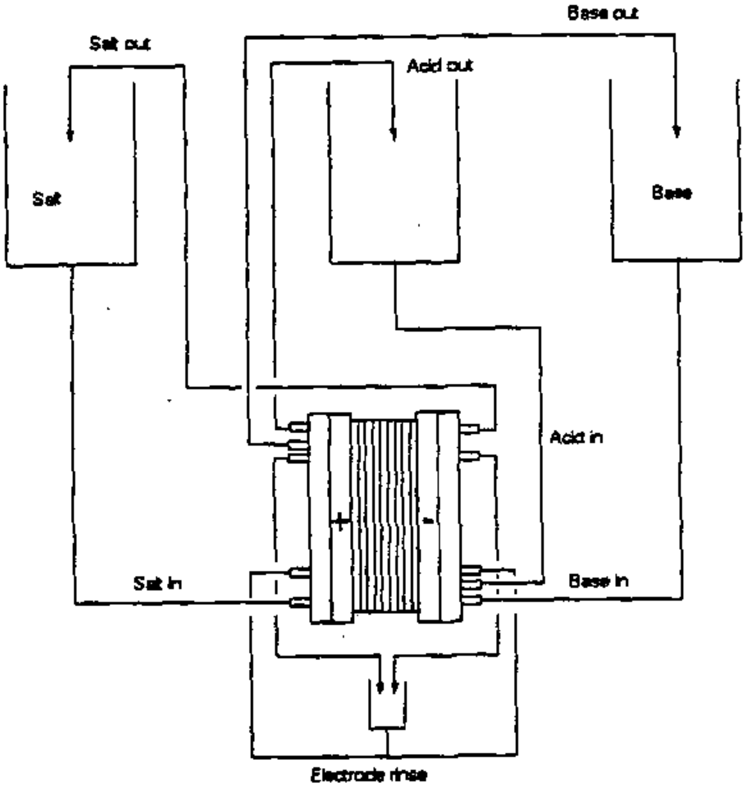


Figure 11 : Simplified diagram of experimental set-up of BED unit.

The potential difference across the electrodes was set at approximately 28 volt at the beginning of the run. The electrode rinse (10% KOH) was passed through the stack at a flow rate of approximately 1,5 litre/min.

The base and acid were batched when their concentration levels reached approximately 1,9 and 2,5 mol/ℓ, respectively. Two litre acid and base solution were left in the tanks after batching and the tanks were filled up to 20 litre with deionised water before the start of the next batch run. Batched feed was used as make-up for the base product.

The potential across the electrodes and the electric current was measured as a function of time during the tests. The electrical conductivity of the feed solution and the concentration levels of the acid and base products were measured after certain time intervals. Current efficiency was calculated from Faraday's law. The electrical energy consumption was calculated from voltage, current and time data. The nitrate, fluoride, potassium, chromium, iron and nickel concentration levels in the initial feed, during and at the end of the batch runs, were measured. The concentration levels of chromium, nickel and iron in the acid and base products were determined as well as the acid and base concentration levels. The chemical composition of the spent pickling acid was also determined.

The concentration of nitric acid was determined by titration with a standard 0,5 mol/ℓ potassium hydroxide/methanol solution with bromophenol blue as indicator. The total acid concentration was determined with phenolphthalein as indicator. The hydrofluoric acid concentration was calculated as the difference between the total acid concentration and the nitric acid concentration.

3.5 Treatment of Sodium Nitrate Effluent with Bipolar Electrodialysis

Two sodium nitrate samples were electrodialysed in the BED stack shown in Figure 11 (817 cm^2 active membrane area). The pH of the first sodium nitrate sample (60 ℓ) was reduced to a pH of approximately 2 (17 mℓ 55% HNO_3; run 1) and that of the second sample (run 2) with 10 mℓ 5% HNO_3 to approximately the same pH prior to electrodialysis. Nitric acid (33 mℓ, 55%) was added to the feed water after 1 500 minutes of operation to reduce the pH of the feed water which had increased to approximately 10,99.

Feed solution ($NaNO_3$, 60 ℓ) was circulated through the salt loop while acid (20 ℓ 0,5 mol/ℓ HNO_3 and 20 ℓ 0,5 mol/ℓ NaOH) were circulated through the acid and base loops, respectively. The flow rates of the feed, acid and base streams were 3 ℓ/min. The electrode rinse (3 ℓ) consisted of a 10 percent sodium hydroxide solution which was circulated at a flow rate of 1,5 ℓ/min through the electrode compartments.

A potential difference of 27 volt was applied across the stack. The acid and base were batched when their concentration levels reached approximately 2 mol/ℓ . Two litre acid and base solution were left in the tanks after batching and the tanks were filled up to 20 litre with water before the start of the next run. The volume increase in the product tanks was measured as a function of time.

The potential across the electrodes and the electric current were measured as a function of time. The electrical conductivity of the feed solution as well as the concentration levels of the acid and base products were also measured after certain time intervals. Acid and base condentration levels were determined by titration with standard caustic soda and sulphuric acid solutions with phenolphthalein indicator, respectively. Sodium and nitrate analysis were conducted on the feed at regular time intervals. Impurities in the acid (Na) and base streams (NO_3) were also determined. The chemical composition of the feed water was determined before the run was started.

Current efficiency was calculated from Faraday's laws. The electrical energy consumption was determined from voltage, current and time data.

3.6 Treatment of Sodium Sulphate Effluent with Bipolar Electrodialysis

Two sodium sulphate samples were electrodialysed in the BED stack shown in Figure 11 (8 cell pairs, 817 cm^2 active membrane area). The first sodium sulphate batch (approximately 10% Na_2SO_4) was prepared by adding 6 kg sodium sulphate (anhydrous) to 60 litre tap water. The second batch was prepared from 48 litre 12 percent Na_2SO_4 to which enough Na_2SO_4 was added (2,4 kg Na_2SO_4 in 12 litre tap water) to give a 20 percent solution. The pH of the second feed water batch was adjusted to a pH of 2,8 (110 g 98% H_2SO_4 to 60 litre feed water).

The same operational procedure was followed as described under 3.5. Sodium and sulphate analysis were conducted on the feed at regular time intervals. Impurities in the acid (Na) and base (SO_4) streams were also determined. The chemical composition of the feed was determined before the run was started.

3.7 Treatment of Sodium Acetate Effluent with Bipolar Electrodialysis

A two compartment cation cell arrangement was used for the study (Figure 7). This cell arrangement is appropriate for converting salts of weak acids into a mixed acid/salt stream and a relatively pure base stream.

One sodium acetate sample was electrodialysed in the BED stack (active membrane area 545 cm^2) shown in Figure 11 (Note: only two loops nl. salt/acid and base were used). The sodium acetate batch (approximately 14 percent (H_3COONa) was prepared by adding 6 kg acetic acid to 60 litre tap water. The acid was neutralised with the stoichiometric amount (4 kg) caustic soda (97%) to produce the sodium salt of the acid.

The feed water was filtered after neutralisation to remove suspended solids formed during the process.

The same operational procedure as described under 3.5 was followed. The base product was picked up in deionised water.

A constant current of 14 ampere was applied for the first 1 500 minutes of operation. A potential difference of 27 volt was applied across the membrane stack from 1 500 to 2 460 minutes of operation. The base was batched when its concentration level reached approximately 2 mol/ℓ. Two litre base solution was left in the tank after batching and the tank was filled up to 20 litre with deionised water before the start of the next run. Sodium analysis was conducted on the feed at regular time intervals.

4 RESULTS AND DISCUSSION

4.1 Treatment of Nickel Drag-out with ED

The chemical composition of both the ED feed and product for seven batch runs is shown in Tables 1 to 7. The nickel concentration levels in the ED brine as a function of time for the seven batch runs are shown in Figures 12 to 18. The chemical composition of the ED brine at the beginning of each run is shown in Table 8. The chemical composition of the ED brine after seven batch runs is shown in Table 9. Current efficiency, electrical energy consumption and nickel removal are shown in Table 10.

Feed nickel concentrations varied between 1 690 and 3 700 mg/ℓ (Tables 1 to 7). The nickel concentration levels in the ED product water varied between 190 and 1 100 mg/ℓ. Nickel removals varied between 66,7 and 88,8 percent for the different batches. Therefore, a considerable amount of nickel can be recovered from the feed for reuse. Nickel removal was higher when the nickel feed water concentration level was lower (Tables 5 to 7). The same phenomenon was observed for the sulphate.

Table 1 : Chemical composition of ED feed and product (run 1)

Constituents (mg/ℓ)	Feed beginning	Feed end	Removals (%)
COD	1 550	900	41,94
Ammonia (N)	39,4	0,4	98,98
Nitrate (N)	0,9	0	100,00
Nickel	3 400	830	75,59
Iron	9,5	3,2	66,32
Sodium	870	68,4	92,14
Potassium	12,9	0,63	95,12
Calcium	109	18,2	83,30
Magnesium	55,6	16,46	70,40
Sulphate Total	7 520,76	2 005,32	73,34
Chloride	1 386	99	82,86
TDS	18 599	5 673	69,50
Conductivity (mS/m)	1 179	318	73,03
pH	2,81	2,61	

Table 2 : Chemical composition of ED feed and product (run 2)

Constituents (mg/ℓ)	Feed beginning	Feed end	Removals (%)
COD	1 690	488	71,12
Ammonia (N)	36,3	2,9	92,01
Nitrate (N)	0,6	0	100,00
Nickel	3 300	1 100	66,67
Iron	13,5	4,4	67,41
Sodium	859	75,1	91,26
Potassium	10,1	0,61	93,96
Calcium	87	16,8	80,69
Magnesium	54,9	21,8	60,29
Sulphate Total	7 713	2 626	65,95
Chloride	1 386	78	94,37
TDS	18 515	7 047	61,94
Conductivity (mS/m)	1 217	384	68,45
pH	2,85	2,88	

Table 3 : Chemical composition of ED feed and product (run 3)

Constituents (mg/ℓ)	Feed beginning	Feed end	Removals (%)
COD	1 510	890	41,06
Ammonia (N)	34,41	2,31	93,29
Nitrate (N)	0,29	0,11	62,07
Nickel	3 070	720	76,55
Iron	9,4	3,6	61,70
Sodium	770	86	88,83
Potassium	8,8	0,89	89,89
Calcium	80,2	16,3	79,68
Magnesium	49,9	15,5	68,94
Sulphate Total	7 213	1 864	74,16
Chloride	1 208	104	91,39
TDS	17 916	5 964	66,71
Conductivity (mS/m)	1 187	412	65,29
pH	2,74	2,66	

Table 4 : Chemical composition of ED feed and product (run 4)

Constituents (mg/ℓ)	Feed beginning	Feed end	Removals (%)
COD	1 630	930	42,94
Ammonia (N)	38,59	5,11	86,76
Nitrate (N)	0,98	0,41	58,16
Nickel	3 460	1 000	71,10
Iron	10,4	3,5	66,35
Sodium	866	121	86,03
Potassium	9,6	0,86	91.04
Calcium	827	16,7	79,81
Magnesium	52,3	16,9	67,69
Sulphate Total	7 635	2 417	68,34
Chloride	1 433	139	90,30
TDS	18 565	6 403	65,51
Conductivity (mS/m)	1 272	422	66,82
pH	2,80	2,85	

Table 5 : Chemical composition of ED feed and product (run 5)

Constituents (mg/ℓ)	Feed beginning	Feed end	Removals (%)
COD	1 070	640	40,19
Ammonia (N)	19,19	0,51	97,34
Nitrate (N)	0,66	0,07	89,39
Nickel	1 910	242	87,33
Iron	11,2	2,4	78,57
Sodium	427	36,7	91,41
Potassium	6,39	0,37	94,13
Calcium	65,6	8,5	87,04
Magnesium	32,1	6,7	79,13
Sulphate Total	4 327	532	87,71
Chloride	734	99	86,51
TDS	10 084	2 584	74,38
Conductivity (mS/m)	960	161	83,23
pH	2,18	2,87	

Table 6 : Chemical composition of ED feed and product (run 6)

Constituents (mg/ℓ)	Feed beginning	Feed end	Removals (%)
COD	1 050	660	37,14
Ammonia (N)	20,41	1,68	91,77
Nitrate (N)	0,96	0,05	94,79
Nickel	1 690	190	88,76
Iron	12,8	2,5	80,47
Sodium	406	43,3	89,33
Potassium	5,4	0,65	87,96
Calcium	64,2	8,2	87,23
Magnesium	32,2	6,1	81,06
Sulphate Total	5 778	413	92,85
Chloride	508	107	78,94
TDS	9 655	2 103	78,22
Conductivity (mS/m)	960	153	84,06
pH	2,20	2,82	

Table 7 : Chemical composition of ED feed and product (run 7)

Constituents (mg/ℓ)	Feed beginning	Feed end	Removals (%)
COD	1 030	720	30,10
Ammonia (N)	19,5	4,29	78,00
Nitrate (N)	0,87	0,08	90,8
Nickel	1 740	209	87,99
Iron	11,9	3,0	74,79
Sodium	397	63	84,13
Potassium	5,3	0,74	86,04
Calcium	61,4	7,8	87,30
Magnesium	31,4	6,1	80,57
Sulphate Total	4 303	312	92,75
Chloride	510	237	53,53
TDS	9 457	2 068	78,13
Conductivity (mS/m)	984	163	83,43
pH	2,17	2,77	

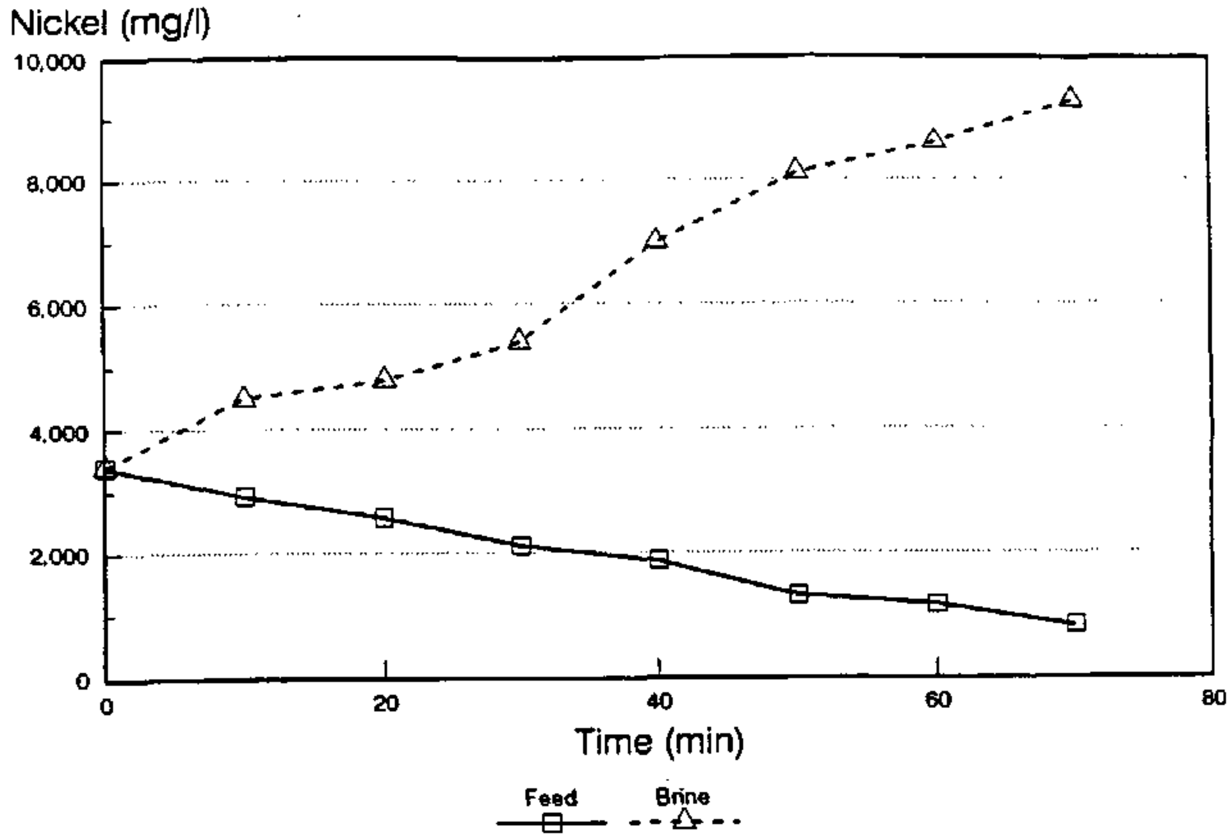


Figure 12 : Nickel concentration as a function of time during ED of nickel drag-out (Run 1).

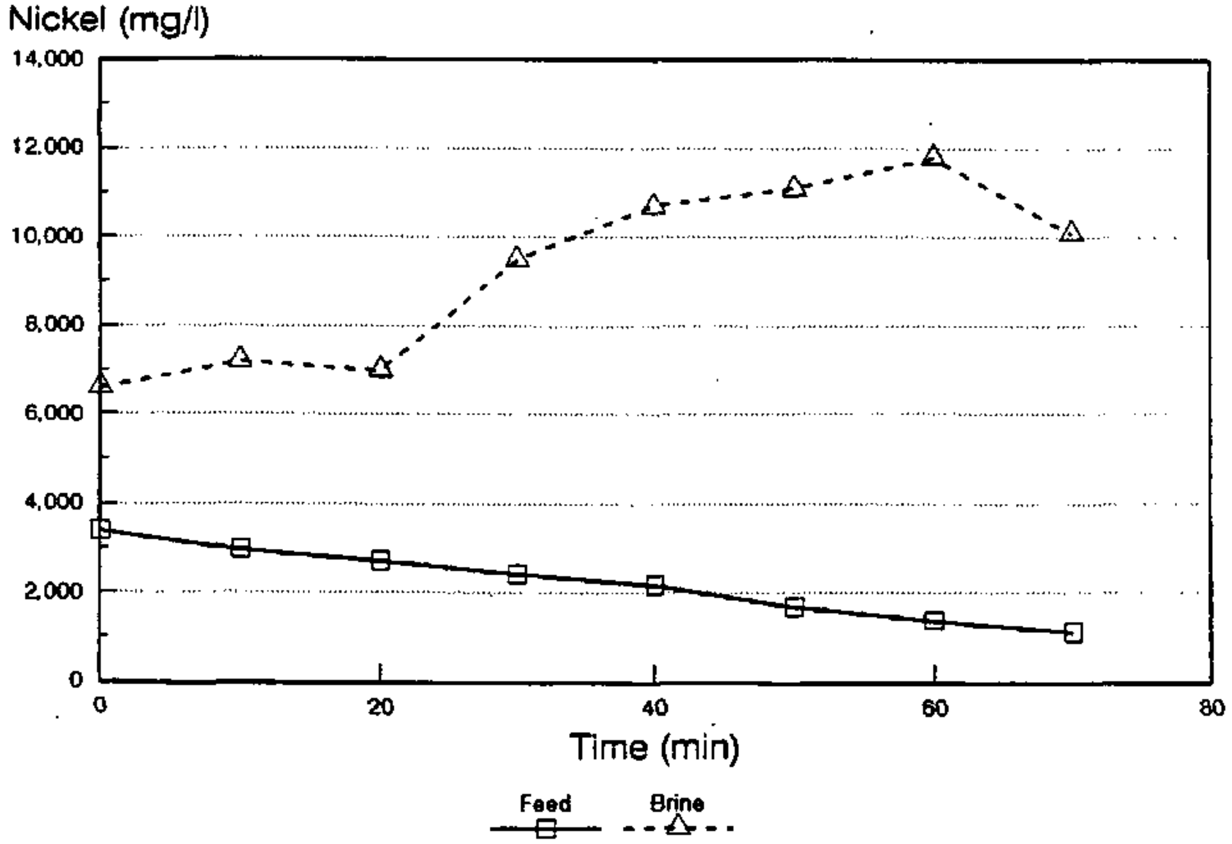


Figure 13: Nickel concentration as a function of time during ED of nickel drag-out (Run 2)

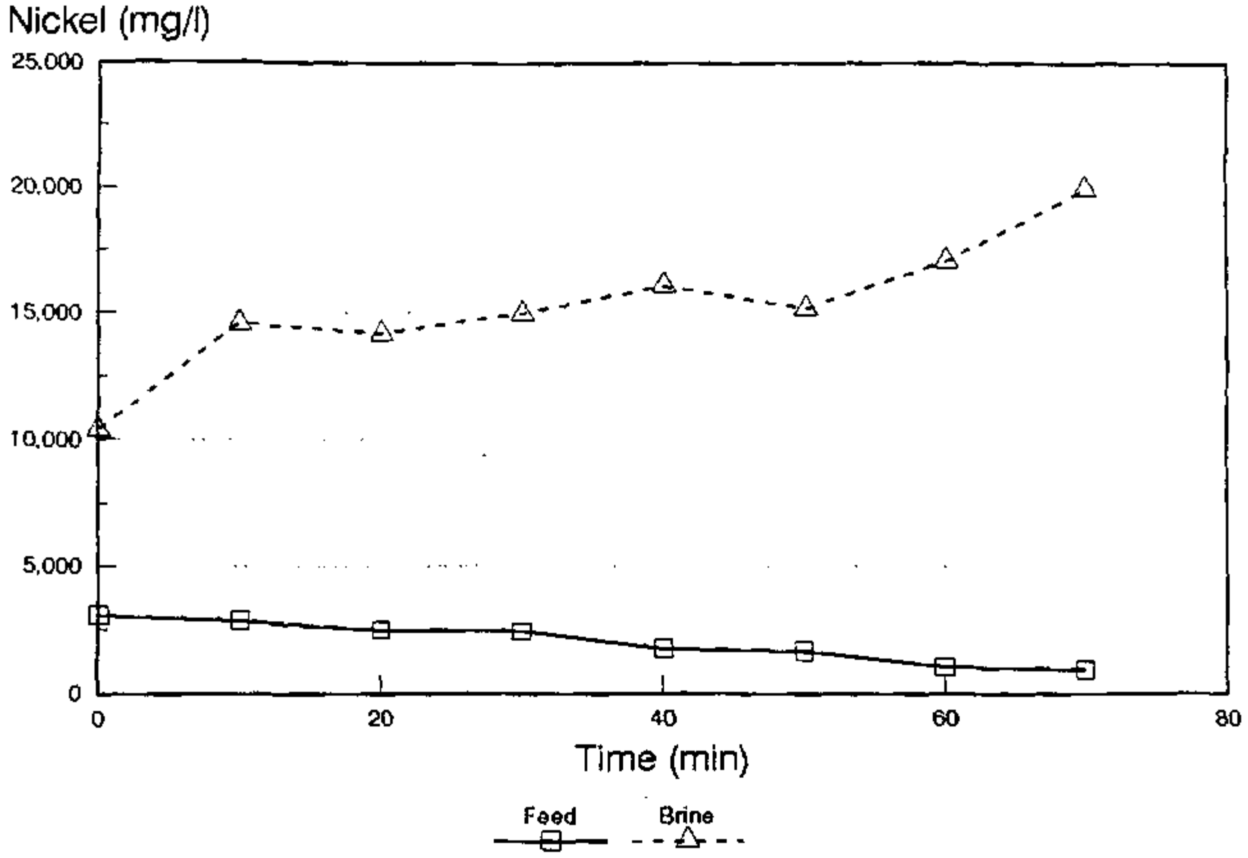


Figure 14 : Nickel concentration as a function of time during ED of nickel drag-out (Run 3)

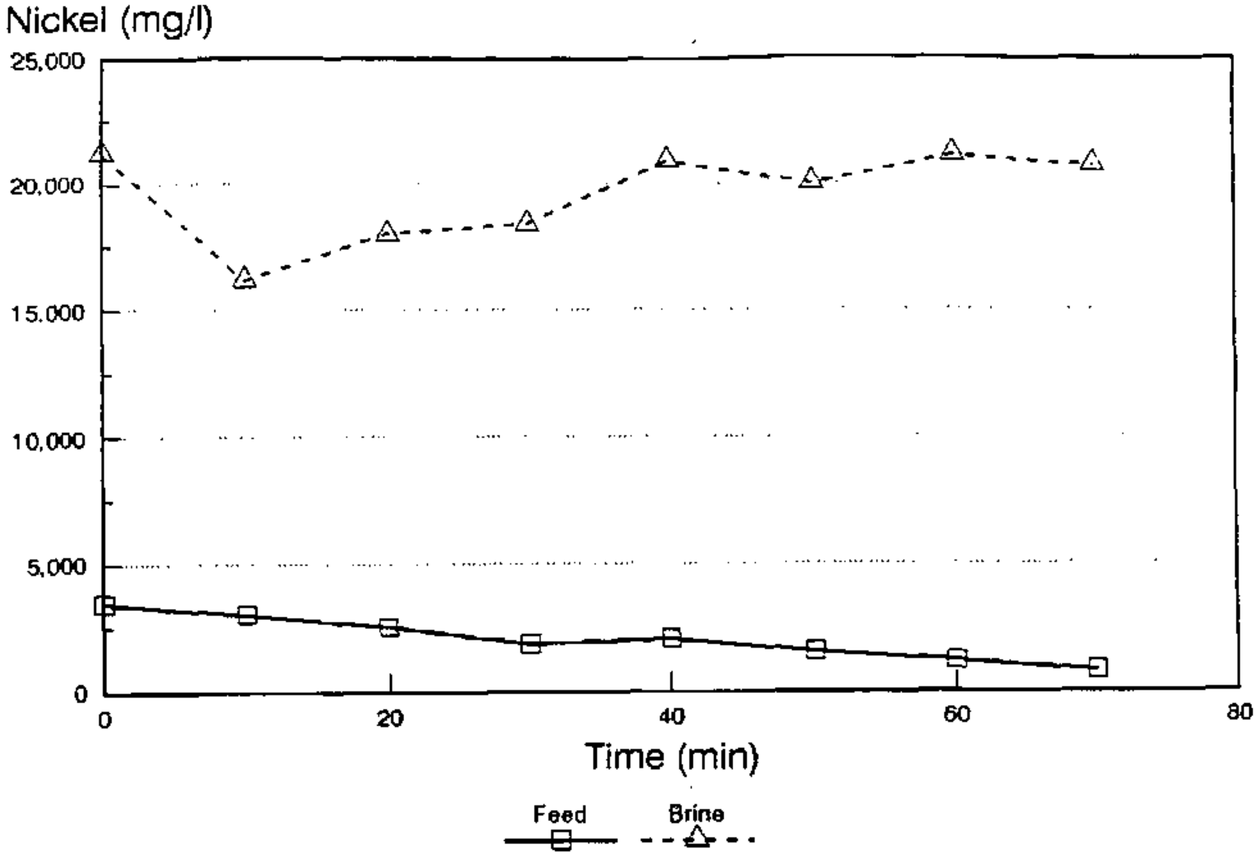


Figure 15 : Nickel concentration as a function of time during ED of nickel drag-out (Run 4)

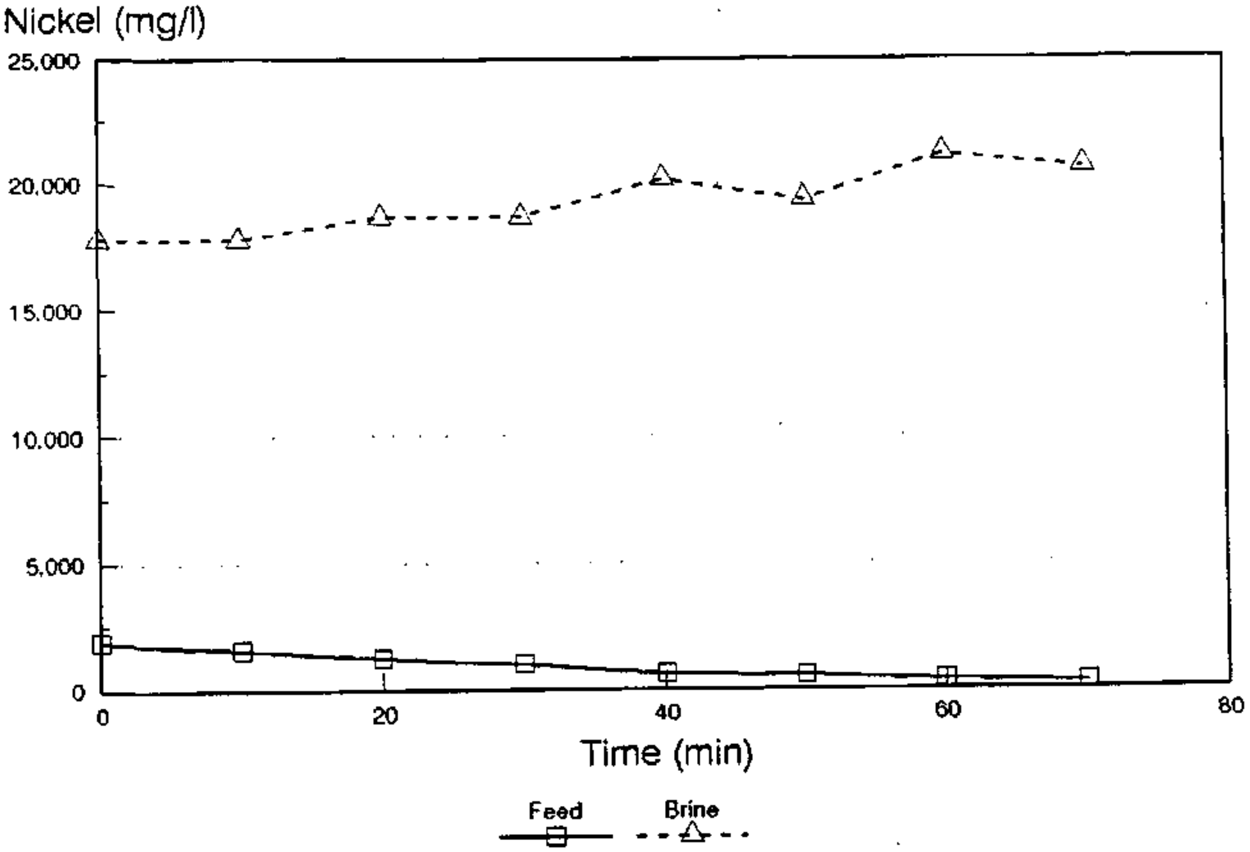


Figure 16: Nickel concentration as a function of time during ED of nickel drag-out (Run 5)

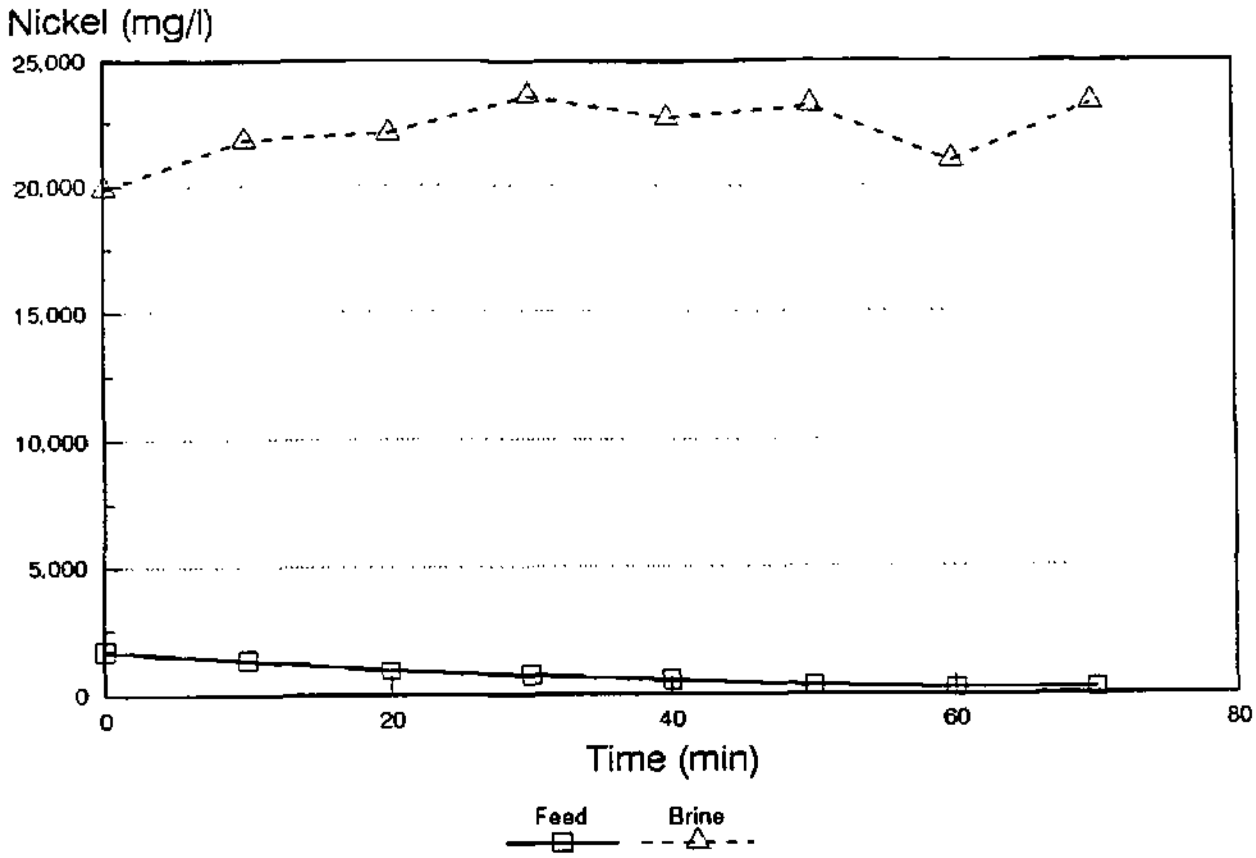


Figure 17: Nickel concentration as a function of time during ED of nickel drag-out (Run 6)

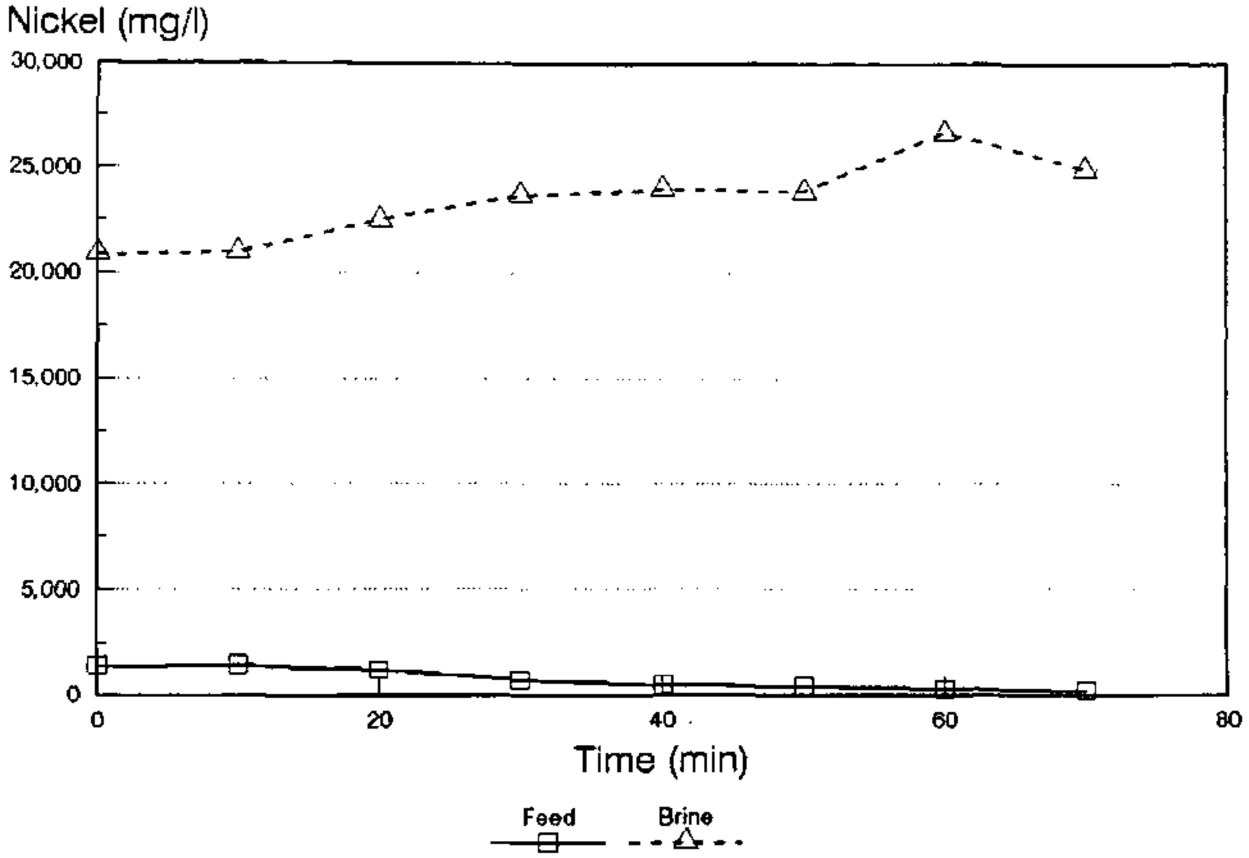


Figure 18: Nickel concentration as a function of time during ED of nickel drag-out (Run 7)

Table 8 : Chemical composition of ED brine in the beginning and end of each run

Constituents (mg/ℓ)	Batch 1		Batch 2		Batch 3		Batch 4	
	Feed	Brine	Feed	Brine	Feed	Brine	Feed	Brine
COD	1 550	2 920	2 000	3 130	2 900	4 510	4 490	5 430
Nickel	3 530	9 800	10 000	13 100	13 900	20 900	20 500	26 200
Calcium	109	578	342	960	637	719	748	835
Sulphate	7 521	27 376	19 518	36 180	35 233	16 141	48 626	61 237
Conductivity (mS/m)	1 179	4 120	3 240	5 340	5 180	6 490	6 460	7 560
pH	2,81	1,76	2,1	1,64	1,72	1,53	1,65	1,47

Table 8 : Chemical composition of ED brine in the beginning and end of each run (continued)

Constituents (mg/ℓ)	Batch 5		Batch 6		Batch 7	
	Feed	Brine	Feed	Brine	Feed	Brine
COD	4 700	5 270	5 120	5 800	5 530	6 020
Nickel	21 100	22 800	23 700	26 000	26 100	28 400
Calcium	920	908	684	1 430	702	1 025
Sulphate	39 695	40 135	40 402	40 489	40 608	16 223
Conductivity (mS/m)	7 370	8 020	8 060	8 610	8 880	9 250
pH	1,17	0,98	1,07	0,87	0,97	0,79

Table 9 : Chemical composition of ED brine after seven batch runs

Constituents	Concentration (mg/ℓ)
COD(N)	6 020
Ammonia (N)	281,6
Nitrate (N)	5,1
Nickel	28 400
Iron	108
Sodium	6 610
Potassium	87
Calcium	1 025
Magnesium	390
Sulphate Total	16 224
Chloride	7 471
TDS	>50 000
Conductivity (mS/m)	9 250
pH	0,79

Table 10 : Current efficiency, electrical energy consumption and nickel removal

Feed Batch No	CE_{Ni} (1) (%)	EC (2) (kWh/m³)	EC (3) (kWh/kg Ni)	Nickel Recovery Rate (4) (kg Ni/m².h)	Nickel Removal
1	33,4	6,03	2,11	0,0443 (1,06)	75,59
2	23,7	6,51	2,98	0,0344 (0,83)	66,67
3	23,68	7,67	2,98	0,0403 (0,97)	76,55
4	22,45	8,37	3,15	0,0423 (1,01)	71,10
5	18,71	6,66	3,77	0,0282 (0,68)	87,33
6	14,94	7,49	4,73	0,0254 (0,61)	88,76
7	11,06	8,04	6,38	0,0257 (0,61)	87,95

(1) Current efficiencies calculated as a function of nickel removed
(2) Electrical energy consumption per cubic metre of product water
(3) Electrical consumption per kg of Nickel removed from feed water
(4) ( ) : kg Ni/m².d

The COD in the ED feed varied between 1 030 and 1 690 mg/ℓ (Tabels 1 to 7). COD removals varied between 30,1 and 71,1 percent. Therefore, organic additives added to the drag-out will be poorly recovered by ED.

The iron concentration level in the ED feed (Tables 1 to 7) varied between 9,4 and 13,5 mg/ℓ. Iron at this concentration level can foul ED membranes. Therefore, it will be necessary to clean the ED membranes regularly with acid to prevent membrane fouling.

Nickel concentration level in the ED brine increases as a function of time and batch run number (Figures 12 to 18). However, it appears that there has been little increase in the nickel concentration level in the ED brine from run 4 to run 7. This can be ascribed to the large concentration gradient between the ED feed and the ED brine. However, it appears that it will be possible to obtain a nickel concentration level of approximately 26 g/ℓ in the ED brine (Figure 18) (Note: The variation in nickel concentration level in the ED brine (Figures 12 to 18) can be ascribed to inaccurate analysis due to large dilutions used for analysis).

The data in Tables 8 and 9 shows that nickel can be concentrated from 3 530 mg/ℓ (first batch) to 28 400 mg/ℓ in the last batch. It should also be noted that a considerable concentration of calcium took place from the first to the last run. Excessive concentration levels of calcium in the ED brine can cause scaling of the membranes in the concentrate compartments. High concentration levels of iron, sodium, magnesium and ammonia-nitrogen in the brine may affect the plating process adverseley (see Table 9). This matter warrents further investigation.

Current efficiency decreases with increasing batch run number (33,4 to 11,1%) and electrical energy consumption increases (2,11 to 6,38 kWh/kg Ni) (Table 10). This may indicate that membrane fouling has been experienced. This matter, however, needs further investigation. Nickel recovery rate varied between 0,83 to 1,01 kg Ni/m^2.d for the first four batch runs and then decreased to between 0,61 and 0,68 kg Ni/m^2.d for the last three runs. Higher nickel recovery rates were obtained at higher nickel feed water concentration levels (first four runs, Table 10).

Nickel recovery rates of 0,92 kg Ni/m^2.d (feed concentration 2 to 3 g/ℓ Ni) and 1,47 kg Ni/m^2.d (feed concentration 3 to 5 g/ℓ Ni) have been reported in the literature[12]. Nickel recovery rates obtained (Table 10) in this study are in this order.

Water recovery of approximately 80 percent was obtained with ED. Therefore, brine only comprises a relatively small percentage of the initial feed volume.

4.2 Treatment of Chromium Rinse Water with ED

Electrical conductivity of the ED feed and brine as a function of time for four feed batches is shown in Figure 19. Chromium concentration levels in the ED feed and brine and chromium removals are shown in Table 11 and Figure 20. Current efficiency, electrical energy consumption and chromium recovery rate are shown in Table 12.

The electrical conductivity of the ED brine increased significantly during the first three batch runs (Figure 19). However, increase in electrical conductivity during the fourth batch run was not very significant. This shows that the limit in brine concentration has been reached.

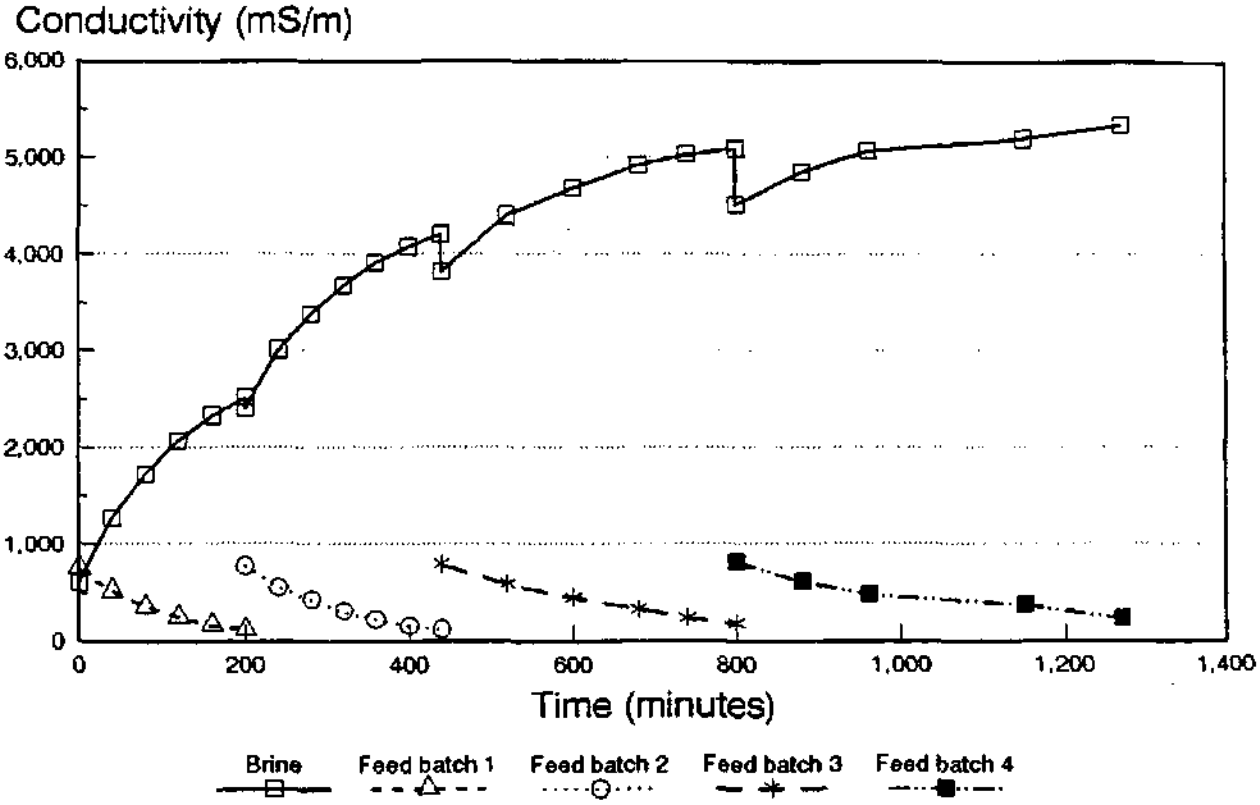


Figure 19 : Electrical conductivity of ED feed and brine as a function of time during ED of chromium drag-out (24 volt)

The feed chromium concentration levels for the four batch runs varied between 1 280 and 1 360 mg/ℓ (Table 11). Chromium was reduced to between 350 and 460 mg/ℓ in the ED product. Chromium removals varied between 66,2 and 73,6 percent. Therefore, a significant amount of chromium remained in the ED product. A final brine chromium concentration level of 6 900 mg/ℓ could be obtained. This means that chromium could be concentrated approximately 5,3 times. Therefore, a significant reduction in effluent volume, can be obtained with ED concentration of chromium effluent.

Table 11 : Chromium concentration levels in the ED feed and brine and chromium removals (24 volt)

Run	Cr Feed beginning (mg/ℓ)	Cr Feed end (mg/ℓ)	Cr Brine (mg/ℓ)	Chromium removal (%)
6	1 300	350	2 920	73,08
7	1 290	240	6 600	73,64
8	1 360	460	6 500	66,18
9	1 280	430	6 900	66,41

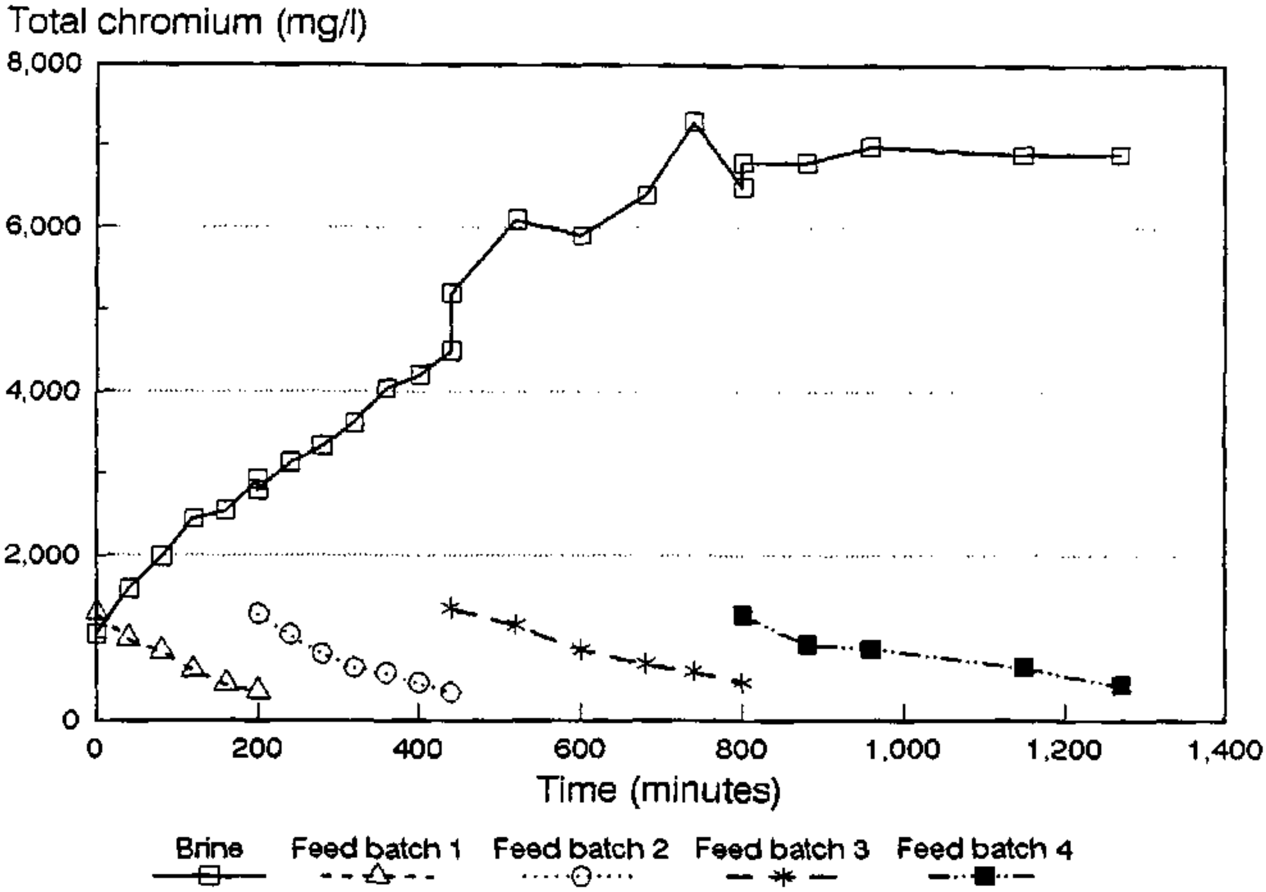


Figure 20 : Chromium concentration levels in the ED feed and brine as a function time during electrodialysis of chromium drag-out (24 V)

The ED feed and brine chromium concentration levels are also shown in Figure 20. Figure 20 clearly shows shows that very little chromium concentration is possible after three batch runs.

Table 12 : Current efficiencies, electrical energy consumptions and chromium recovery rates during ED of chromium drag-out (24 V)

Run	Current efficiency (%)	Electrical energy consumption		Recovery rate (kg Cr/m².h)
		(kWh/m³ H_2O)	(kWh/kg Cr)	
1		2,951	3,050	0,011 (0,26)
2	86,24	4,369	4,534	0,009 (0,22)
3	55,14	6,665	7,086	0,006 (0,14)
4	44,84	7,581	8,713	0,005 (0,12)

( ) : kg Cr/m².d

Current efficiency decreased (from 86,2 to 44,8%) with increasing run number (Table 12). The reduction in current efficiency can be ascribed to increasing back diffusion of chromium from the brine as the brine becomes more concentrated. Electrical energy consumption increased from 3,1 to 8,7 kWh/kg Cr removed for the four batch runs. Chromium recovery rate varied between 0,26 and 0,12 kg Cr/m².d.

Membrane fouling was experienced during ED treatment of the chromium effluent. However, it seems that it should be possible to control membrane fouling with acid cleaning. Brine volume comprised approximately 20 percent of the effluent treated. Therefore, effluent volume can be considerably reduced with ED treatment.

4.3 Treatment of Chromium Drag-out with Electro-Electrodialysis

The experimental results showing chromium concentration levels as a function of time during EED of chromium drag-out are summarised in Table 13 and Figures 21 and 22 (Morgane ARA membrane). Chromium could be concentrated from 48,1 to 240,4 g/ℓ (as CrO_3) (Table 13 and Figure 22). Current efficiency and electrical energy consumption were determined at 58,7 percent and 38,3 kWh/kg CrO_3, respectively. The electrical conductivity versus time graph (Figure 21) indicates that electrical conductivity can be used as a measure to determine chromium concentration levels in the EED product.

Table 13: Chromium oxide concentration as a function of time during EED treatment of chromium rinse water (Morgane ARA membranes)

Time (h)	Current (A)	Volt (V)	Feed			Feed		
			Cr^{6+} (g/ℓ)	CrO_3 (g/ℓ)	Conduct (mS/m)	Cr^{6+} (g/ℓ)	CrO_3 (g/ℓ)	Conduct (mS/m)
0	5,78	78	25	48,08	12 460	0	0,00	22,4
10		20,35	25	48,08	10 990	10	19,23	7 220
20		17,37	25	48,08	10 140	20	38,46	10 480
30		18,25	23,25	44,71	9 940	12,5	24,04	9 960
40		16,08	22,5	43,27	10 010	17,5	33,65	12 890
50		14,25	21,25	40,87	9 460	25	48,08	16 200
60		13,89	20	38,46	9 050	32,5	62,50	19 400
70		13,16	18,75	36,06	8 670	40	76,92	22 500
80		12,5	21,1	40,58	8 360	57,5	110,58	25 800
90		14,25	20,1	38,65	8 110	60,21	115,79	29 200
100		12,58	20	38,46	7 680	67,5	129,81	31 200
110		11,09	16,25	31,25	7 660	72	138,46	37 500
120		10,47	18,75	36,06	7 450	82,5	158,65	40 000
130		9,28	16,25	31,25	7 120	80	153,85	44 500
140		8,35	13,75	26,44	6 750	87,5	168,27	46 600
150		8,5	11,25	21,63	6 530	92,5	177,88	49 300
160		8,21	15	28,85	6 400	100	192,31	50 800
170		7,36	15	28,85	5 970	97,5	187,50	51 400
180		7,48	12,5	24,04	5 660	115	221,15	52 900
190		6,64	15	28,85	5 290	125	240,38	52 700

Current density 80 mA/cm²;
Feed volume 20 litre;
Product volume : 2 litre.

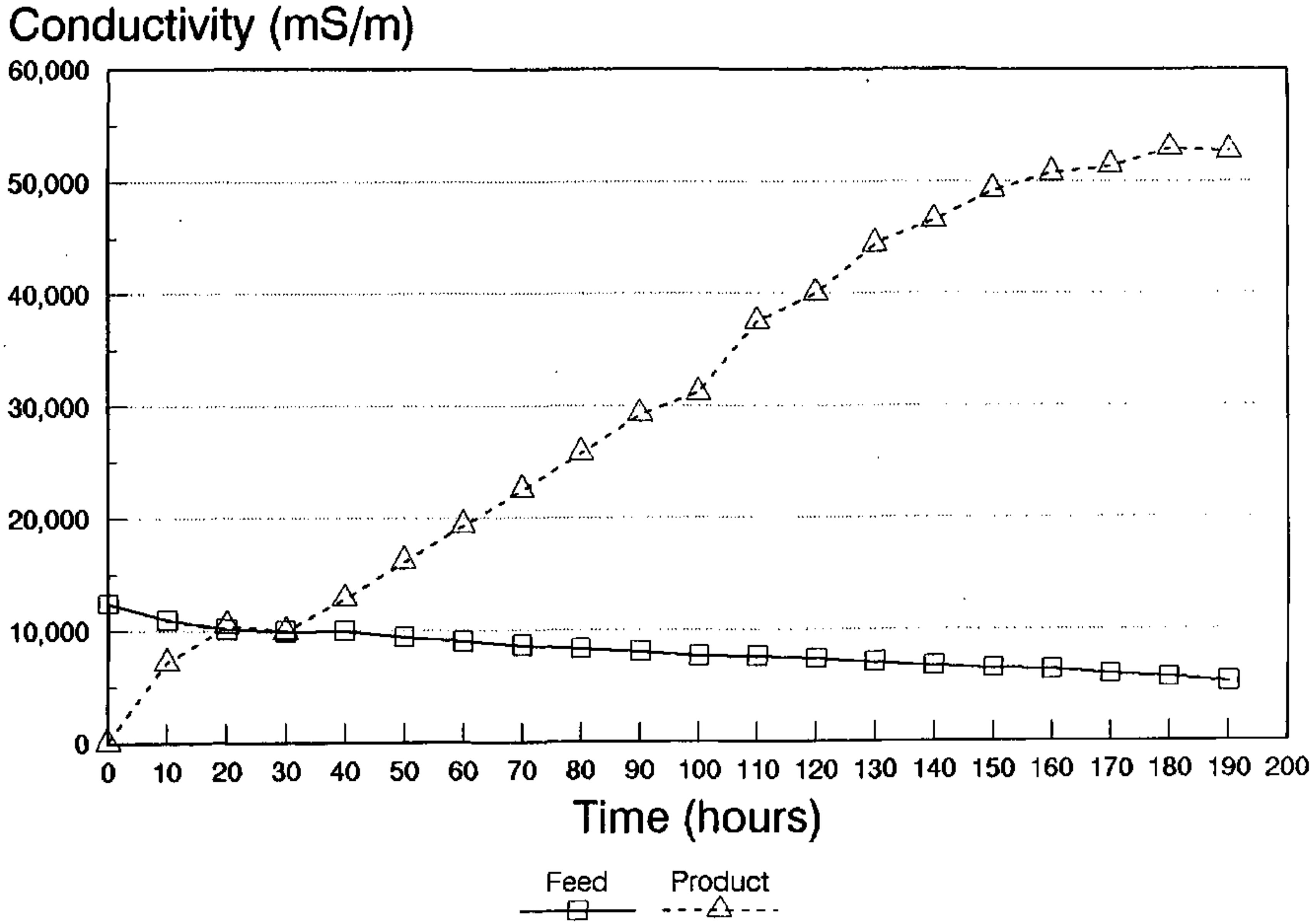


Figure 21 : Electrical conductivity as a function of time during EED treatment of chromium rinse water (Morgane ARA membrane)

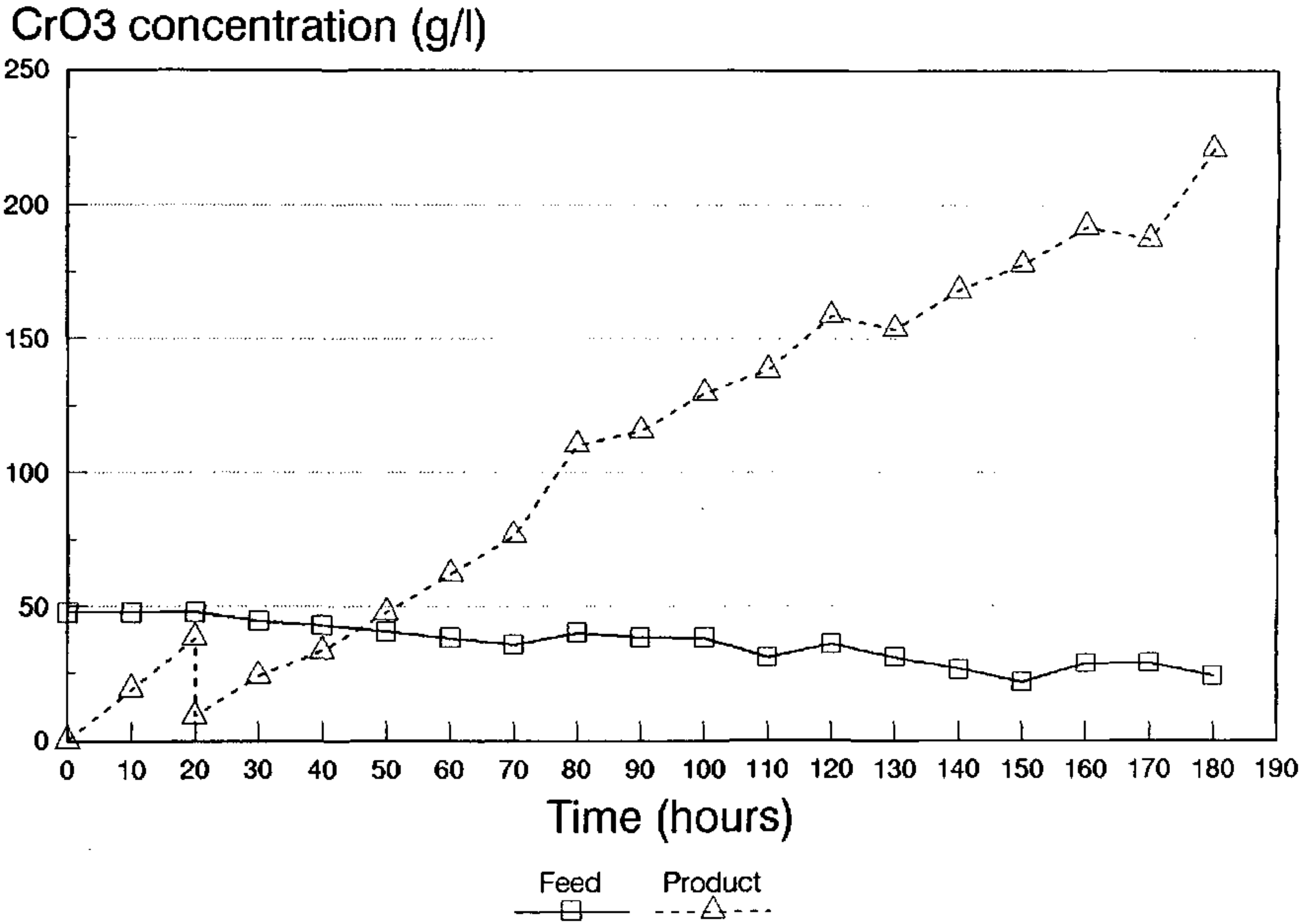


Figure 22 : Chromium oxide concentration as a function of time during EED treatment of chromium rinse water (Morgane ARA membrane)

The same results using Ionac MA 3475 membrane are shown in Table 14 and Figures 23 and 24. Chromium could only be concentrated from 43 g/ℓ (as CrO_3) to 158,7 g/ℓ . Current efficiency was 58,5 percent and electrical energy consumption 50,92 kWh/kg CrO_3. Therefore, it appears that better results can be obtained with the Morgane ARA membrane.

Table 14 : Chromium oxide concentration as a function of time during EED treatment of chromium rinse water (Ionac MA 3475 membrane)

Time (h)	Current (A)	Volt (V)	Feed			Feed		
			Cr^{6+} (g/ℓ)	CrO_3 (g/ℓ)	Conduct (mS/m)	Cr^{6+} (g/ℓ)	CrO_3 (g/ℓ)	Conduct (mS/m)
0	7,23	120	22,5	43,27	11 650	0	0,00	21,5
5		37,6	21,25	40,87	11 560	43,8	8,42	4 690
15		12,5	20,63	39,67	10 680	13,13	25,25	10 740
25		9,55	20	38,46	10 120	24,38	46,88	16 660
35		10	16,88	32,46	9 400	31,88	61,31	21 200
45		9	16,25	31,25	9 000	52,5	100,96	27 300
55		7,23	17,5	33,65	8 810	57,5	110,58	26 000
65		10	17,5	33,65	7 980	75	144,23	33 000
75		9,5	18,75	36,06	7 400	82,5	158,65	30 400
85		9,5	17,5	33,65	7 210	82,5	158,65	30 600

The results indicate that it should be possible to use EED effectively for chromium recovery from chromium drag-out in the plating process for chromium reuse. The chromium concentration level (240 g/ℓ CrO_3) is of sufficient strength to be put back into the plating bath for reuse. Electrical energy consumption, however, is high. Membrane life time is also an unknown factor. Consequently, further work will be required to evaluate this process properly for chromium recovery from chromium drag-out. Initial results, however, appears interesting although the process may be too expensive to apply successfully in practice.

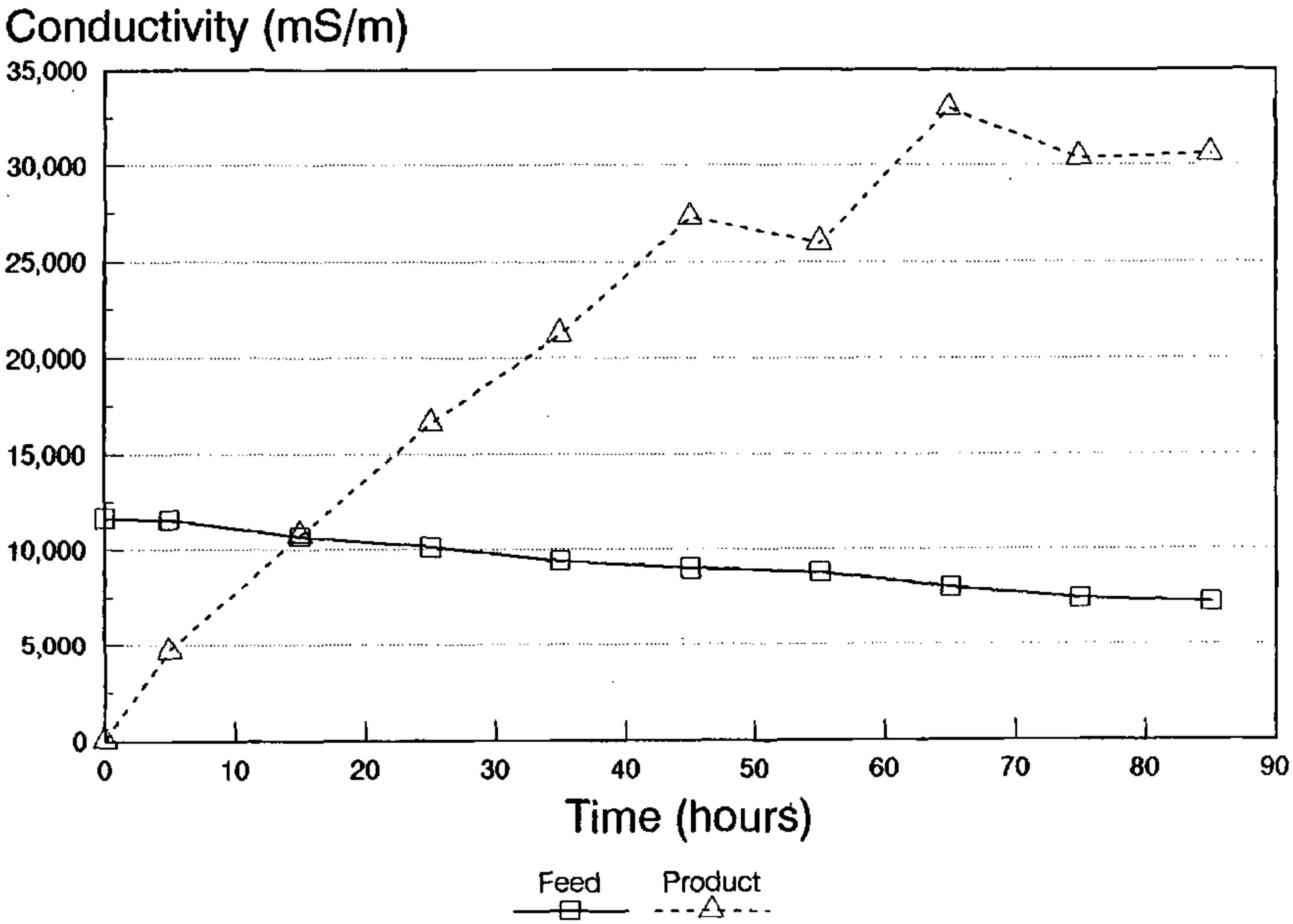


Figure 23 : Electrical conductivity as a function of time during EED of chromium rinse water (Ionac MA 3475 membrane)

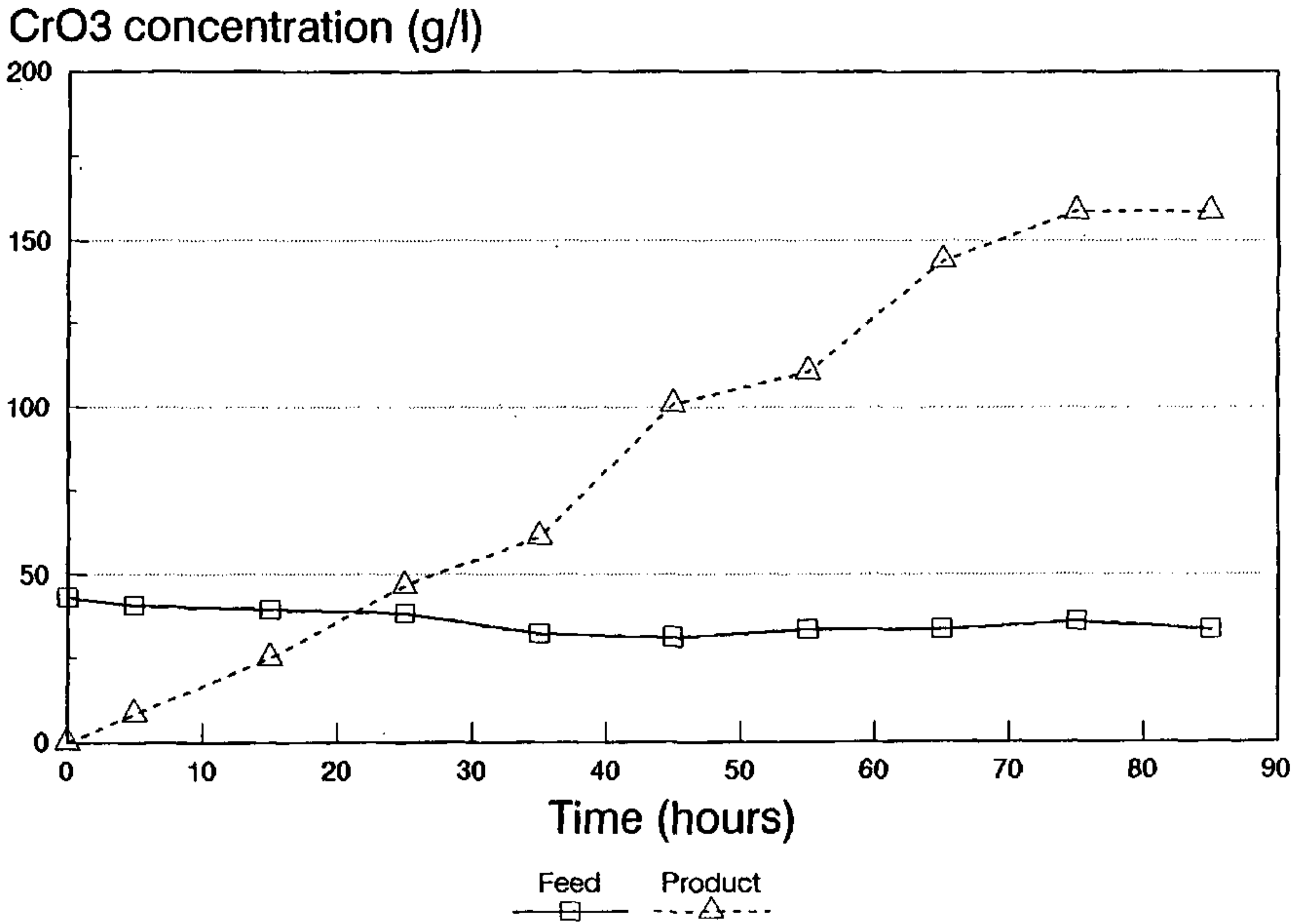


Figure 24 : Chromium oxide concentration as a function of time during EED treatment of chromium rinse water (Ionac MA 3475 membrane)

4.4 Treatment of Waste Ion-exchange Regenerant with Bipolar Electrodialysis

Manufacturers literature indicates that BED can be used to recover caustic soda and acid from waste ion-exchange regenerant (NaCl) for reuse in the ion-exchange process. This process, however, is considered to be uneconomical for treatment of waste ion-exchange regenerant according to Bar[14]. This process will therefore not be further considered for treatment of waste ion-exchange regenerant.

4.5 Treatment of Spent Pickling Acid with Bipolar Electrodialysis

The chemical composition of the spent pickling acid effluent before neutralisation with lime was determined and the results are shown in Table 15. The nitric acid and hydrofluoric acid concentration levels (free) were 149,9 and 23,8 g/ℓ, respectively. It is interesting to note that a significant amount of bound acids (both HNO_3 and HF) are present in the sample. The iron concentration level is very high in this case (49,7 g/ℓ). It is interesting to note that the nickel concentration level in the effluent is also high (6 700 mg/ℓ).

The experimental data obtained during BED of the two feed water batches is shown in Tables 16 and 17. The data for the two batch runs are also graphically shown in Figures 25 to 34. Current efficiencies for acid and base for the two feed water batches are shown in Figures 35 and 36 respectively. The potassium, nitrate-nitrogen, fluoride, iron, chromium and nickel concentration levels in the two feed water batches as a function of time during electrodialysis are shown in Tables 18 and 19. The electrical energy consumption for acid and base production and the composition of the acid and base products are shown in Tables 20, 21 and 22.

Table 15 : Chemical composition of spent pickling acid effluent

Constituents	Concentration*
Sodium	87
Potassium	3
Calcium	79
Magnesium	15
Nitrate N	39 150
Sulphate	7 686
Fluoride	61 200
Chromium	4 900
Iron	49 699
Nickel	6 700
Total Acid (g/ℓ)	173,74
Nitric Acid (g/ℓ)	149,94
Hydrofluoric Acid (g/ℓ)	23,8

*Concentrations in mg/ℓ unless otherwise stated.

Table 16 : Summary of experimental results during first batch run with new anion-exchange membranes (60 litre feed, 20 litre acid and base each)

Time (Cum min)	Time	Current (A)	Voltage (V)	HNO$_3$ (mol/ℓ)	TA (mol/ℓ)	HF (mol/ℓ)	KOH (mol/ℓ)	Feed (mS/m)	Feed pH	Feed °C	Acid Volume (ℓ)	Acid CE (%)	Base Volume (ℓ)	Base CE (%)
0	8:00 8.30	11,98 14,62	27,07 26,68	0,55	0,55	0	0,62	19 000	0,07	31,00	20		20	
60	9:00 9:30	15,44 16,25	26,52 25,79	0,725	0,725	0	0,80	19 400	7,42	31,00				
120	10:00 10:30	16,25 16,25	25,07 24,75	0,775	0,80	0,025	0,97	20 400	7,33	34,70				
180	11:00 11:30	16,25 16,25	24,32 24,21	0,90	0,95	0,05	1,15	20 700	7,20	35,00				
240	12:00 12:30	16,25 16,25	23,90 23,72	1,025	1,075	0,05	1,38	20 400	7,06	34,60				
300	13:00 13:30	16,25 16,25	23,63 23,49	1,10	1,175	0,075	1,54	20 700	6,99	34,70				
360	14,00 14,30	16,25 16,25	23,51 23,40	1,25	1,275	0,025	1,74	21 000	6,84	34,80				
420	15:00	16,25	23,23	1,30	1,35	0,05	1,94	20 900	6,81	35,10	20,96	49,13	20,558	83,11
						BATCH 1 KOH							20,558	82,62

Table 16 : (CONTINUED)

Time (Cum min)	Time	Current (A)	Voltage (V)	HNO_3 (mol/ℓ)	TA (mol/ℓ)	HF (mol/ℓ)	KOH (mol/ℓ)	Feed (mS/m)	Feed pH	Feed °C	Acid Volume (ℓ)	Acid CE (%)	Base Volume (ℓ)	Base CE (%)
420	7:15 7:45	12,88 13,81	24,45 24,14	1,30	1,35	0,05	0,77	20 900	6,81	35,10	20,96		20	
480	8:15 8:45	14,80 15,60	23.81 23,69	1,40	1,475	0,075	0,93	21 100	6,75	32,60				
540	9:15 9:45	15,99 16,16	23,56 23,50	1,575	1,675	0,100	1,17	21,600	6,79	34,80				
600	10:15 10:45	16,25 16,25	23,40 23,26	1,60	1,75	0,075	1,31	21 500	6,57	35,80				
660	11:15 11:45	16,25 16,25	23,18 22,97	1,725	1,775	0,05	1,57	21 000	6,57	33,80				
720	12:15 12:45	16,26 16,25	22,99 22,98	1,75	1,875	0,12	1,74	21 300	6,62	35,80				
780	13:15	16,25	22,90	1,875	1,975	0,10	2,05	21 300	6,64	35,00			20,465	94,54
							BATCH 2 KOH						20,465	94,54
780	13:30 14:00	12,89 13,96	23,62 23,45	1,875	1,975	0,10	0,58	21 300	6,64	35,00			20	
840	14:30 15:00	14,38 14,73	23,30 23,18	1,925	2,00	0,075	0,79	21 100	6,67	34,60				
900	15:30 16:00	14,86 15,08	23,10 23,08	1,975	2,10	0,125	0,97	21 100	6,70	35,00				
960	16:30 17:00	15,31 15,38	23,30 23,00	2,075	2,175	0,10	1,18	21 200	6,57	35,10	23,04	9,51		
1 020	17:30	15,42	22,98	2,10	2,25	0,15	1,38	21 000	6,82	34,87				
1 170	20:00	15,95	22, 94	2,15	2,425	0,275	1,84	21 000	7,20	35,50	23,52	18,86	20,372	88,28
				BATCH 1 HNO_3			BATCH 3 KOH				23,52	49,65	20,372	88,28

Table 16 : (CONTINUED)

Time (Cum min)	Time	Current (A)	Voltage (V)	HNO_3 (mol/ℓ)	TA (mol/ℓ)	HF (mol/ℓ)	KOH (mol/ℓ)	Feed (mS/m)	Feed pH	Feed °C	Acid Volume (ℓ)	Acid CE (%)	Base Volume (ℓ)	Base CE (%)
1 170	8:00 8:30	9,81 10,54	24,39 24,32	0,8	0,4	0,10	0,5	21 000	7,2	35,52	20		20	
1 230	9:00 9:30	11,41 12,47	24,19 23,94	0,375	0,45	0,075	0,68	21 500	6,42	33,30				
1 290	10:00 10:30	12,70 13,26	23,71 23,58	0,475	0,65	0,175	0,82	21 900	6,43	34,00				
1 350	11:00 11:30	13,46 13,75	23,50 23,36	*0.65*	*0.825*	*0.175*	*0.99*	21 600	6,86	33,50				
1 410	12:00 12:30	14,08 14,32	23,30 23,24	0,75	1,05	0,30	1,18	21 500	7,28	33,30				
1 470	13:00 13:30	14,35 16,52	23,24 23,17	0,90	1,175	0,275	1,35	21 700	7,17	34,60	21,04	68,01	20,372	90,97
1 530	14:00 14:30	14,71 14,88	23,14 23,10	1,00	1,3	0,300	1,55	21 600	7,31	34,80				
1 590	15:00 15:30	14,83 14,92	23,10 23,05	1,125	1,425	0,300	1,74	21 500	7,05	33,50				
1 650	16:00	16,25	23,94	1,225	1,625	0,400	1,92	21 100	6,81	33,40	21,68	56,96	20,744	92,11
							BATCH 4 KOH						20,744	92,06
1 650	16:15	13,27	25,11	1,225	1,625	0,400	0,63	21 100	6,81	33,4			20	
1 710	16:45 17:15 7:00 7:30	14,38 15,01 12,00 12,65	24,70 24,56 25,40 25,11	1,275	1,75	0,485	0,79	21,400	6,35	3,00				
1 770	8:00 8:30	13,85 14,60	24,85 24,86	1,375	1,80	0,425	0,97	20 900		29,80				
1 830	9:00 9:30	15,33 15,95	24,23 24,62											
1 890	10:00 10:30	16,15 16,24	24,24 24,19											
19 50	11:00 11:30	16,35 16,32	24,11 24,00											

Table 16 : (CONTINUED)

Time (Cum min)	Time	Current (A)	Voltage (V)	HNO_3 (mol/ℓ)	TA (mol/ℓ)	HF (mol/ℓ)	KOH (mol/ℓ)	Feed (mS/m)	Feed pH	Feed °C	Acid Volume (ℓ)	Acid CE (%)	Base Volume (ℓ)	Base CE (%)
2 010	12:00 12:30	15,87 16,17	23,59 23,85	1,75	2,35	0.60	1,73	21 800	3,13	34,70				
2 070	13:00	16,13	23,86	1,85	2,45	0,60	1,92	21 600	2,14	34,50	22,96	49,73	20,558	63,94
							BATCH 5 KOH						20,558	79,83
2 070	14:00 14:30	13,45 14,59	25,19 24,98	1,85	2,45	0,60	0,62	21 600	2,14	34,50			20	
2 130	15:00 15:30	14,85 15,19	24,85 24,75	1,90	2,55	0,65	0,77	21 100	2,29	34,40				
2 190	16:00	15,50	24,70	2,15	2,75	0,60	0,94	20 700	2,28	33,40				
			BATCH 2 HNO_3								23,91	74,99		
2 190	08:00 08:30	10,36 11,42	26,24 25,75	0,35	0,5	0,15	0,94	20 900	2,28	33,40	20			
2 250	09:00 09:30	12,40 14,57	25,55 25,18	0,50	0,7	0,20	1,11	20 100	1,82	31,30				
2 310	10:00 10:30	14,28 14,74	25,02 24,94	0,55	0,925	0,375	1,32	21 000	2,02	34,50				
2 370	11:00 11:30	14,79 15,02	24,71 24,60	0,575	1,175	0,60	1,50	20 800	1,92	35,10				
2 430	12:00 12:30	15,37 15,42	24,64 24,76	0,80	1,425	0,625	1,70	20 600	2,53	36,20				
2 490	13:00	15,59	24,70	0,85	1,625	0,775	1,85	20 300	2,29	35,60	21,52	54,19	20,465	83,88
							BATCH 6 KOH						20,465	83,88

Table 16 : (CONTINUED)

Time (Cum min)	Time	Current (A)	Voltage (V)	HNO_3 (mol/ℓ)	TA (mol/ℓ)	HF (mol/ℓ)	KOH (mol/ℓ)	Feed (mS/m)	Feed pH	Feed °C	Acid Volume (ℓ)	Acid CE (%)	Base Volume (ℓ)	Base CE (%)-
2 490	7:30 8:00	10,20 11,00	26,23 25,89	0,85	1,625	0,775	0,6	20 300	2,29	35,60			20	
2 550	8:30 9:00	12,15 13,18	25,58 25,30	0,975	1,825	0,85	0,76	19 200	2,16	30,40				
2 610	9:30 10:00	13,90 14,66	25,25 24,94	0,95	2,00	1,05	0,98	20 000	2,25	32,30				
2 670	10:30 11:00	15,03 15,13	24,80 24,79											
2 730	11:30 12:00	15,16 15,28	24,77 24,75											
2 790	12:30 13:00	15,41 15,36	24,70 24,56	1,25	2,70	1,45	1,54	18 800		35,20				
2 850	13:30 14:00	15,09 15,00	24,62 24,64	1,3	2,825	1,525	1,73	17 600		32,40	23,44	48,42	20,558	93,67
2 910	14:30	14,88	24,66	1,325	2,975	1,65	1,84	17 200		33,80				
							BATCH 7 KOH						20,558	87,17
2 910	14:30 15:00	12,74 12,86	25,24 25,33	1,325	2,825	1,45	0,62	17 200		33,80			20,00	
2 970	15:30 16:00	12,98 13,12	25,33 25,30	1,55	3,125	1,575	0,77	15 900	29,70					
3 030	16:30	13,14	25,29	1,50	3,325	1,825	0,92	9 590	2,05	28,10				
3 090	8:15 8:45	13,40 14,45	25,13 25,00	1,575	3,575	2,00	1,11	14 700	2,27	30,80				
3 150	9:15 9:45	14,95 15,15	24,83 24,77	1,570	3,55	1,95	1,30	14 600		34,80				
3 210	10:15 10:45	15,44 15,46	24,75 24,71	1,575	3,75	2,175	1,47	14 200		35,10				
3 270	11:15 11:45													
3 330														
				BATCH 3 HNO_3			BATCH 8 KOH				26,80	121,9	20,744	86,80

Table 17 : Summary of experimental data during second batch run with new anion-exchange membranes (60 ℓ feed, 20 litre acid and base each)

Time (Cum min)	Time	Current (A)	Voltage (V)	HNO$_3$ (mol/ℓ)	TA (mol/ℓ)	HF (mol/ℓ)	KOH (mol/ℓ)	Feed (mS/m)	Feed pH	Feed °C	Acid Volume (ℓ)	Acid CE (%)	Base Volume (ℓ)	Base CE (%)
0	7:30 8:00	10,98 12,30	25,61 25,46	0,7	0,7	0	0,68	20 500	10,12	35,00	20		20	
60	8:30 9:00	12,98 13,78	24,98 24,87	0,825	0,85	0,025	0,82	20 300	7,33	33,10				
120	9:30 10:00	14,40 14,79	24,75 24,64	0,875	0,95	0,075	1,01	20 800	7,10	35,30				
180	10:30 11:00	14,95 15,50	25,54 24,42											
240	11:30 12:00	15,80 16,08	24,30 24,26	1,125	1,525	0,10	1,43	20 500	6,83	34,70	20,64	55,44	20,186	91,80
300	12:30 13:00	16,19 16,25	24,45 24,34	1,20	1,3	0,10	1,59	20 800	6,75	34,30				
360	13:30 14:00	16:24 16:25	24,11 24,13	1,275	1,45	0,175	1,78	20 700	6,76	35,10				
420 14:30	14:30	16,24	23,94	1,400	1,5	0,10	1,84	20 600	6,67	34,80	21,04	43,13	20,372	59,40
Batch 1 KOH													20,372	76,83
420	14:30 15:00	13,50 14,06	24,81 24,49	1,400	1,5	0,10	0,63	20 600	6,67	34,80			20	
480	15:30 16:00	14,56 15,00	24,34 24,24	1,50	1,55	0,05	0,83	20 400	6,68	33,70			20	
540	16:30 17:00	15,34 15,44	24,17 24,15	1,575	1,675	0,10	1,06	20 700	6,61	35,50				
600	17:30 7:00 7:30	15,62 13,26 14,08	24,06 24,92 24,62	1,625 1,625	1,7 1,7	0,075 0,075	1,22 1,22	20 600 20 600	6,57 6,57	34,70 34,70	21,60	42,54	20,093	90,07
600	8:00 8:30	15,16 15,80	24,25 24,14	1,725	1,80	0,075	1,37	21 900	7,25	33,20				
720	9:00 9:30	16,14 16,25	24,07 23,99	1,795	1,85	0,075	1,58	22 800	6,95	34,70				
780	10:00 10:30	16,21 16,25	24,00 23,96	1,85	1,975	0,125	1,98	22 600	6,48	34,10				

Table 17 : (CONTINUED)

Time (Cum min)	Time	Current (A)	Voltage (V)	HNO_3 (mol/ℓ)	TA (mol/ℓ)	HF (mol/ℓ)	KOH (mol/ℓ)	Feed (mS/m)	Feed pH	Feed °C	Acid Volume (ℓ)	Acid CE (%)	Base Volume (ℓ)	Base CE (%)
840	11:00	16,25	23,86	1,90	2,075	0,175	1,96	22 500	6,80	35,50	22,08	36,29	20,56	84,94
							BATCH 2 KOH						20,56	86,01
840	11:00 11:30	13,20 13,70	24,90 24,75	1,90	2,075	0,175	0,59	22 500	6,80	35,50			20	
900	12:00	14,25	24,60											
960	14:00	25,40	24,15											
1 020	15:00 15:30	15,45 15:60	24,10 24,04	2,20	2,40	0,20	1,45	22 200	4,95	35,50				
1 080	16:00 16:30	15,60 15,66	24,00 23,94	2,275	2,5	0,225	1,52	21 900	4,68	35,30	22,88	50,52	20,372	98,51
1 110	7:15	12,61	25,15											
1 140	7:45 8:15	14,32 15,13	24,51 24,18	2,325	2,525	0,200	1,665	20 600	4,36	30,60				
1 200	8:45 9:15	15,38 15,54	23,91 23,85	2,325	2.55	0,225	1,83	21 000	4,24	34,50				
1 260	9:45	15,56	23,73	2,40	2,575	0,175	2,04	20 200	2,81	34,80	23,12	30,93	20,65	98,76
							BATCH 3 KOH						20,65	97,40
1 260	9:45 10:15	12,80 13,60	24,90 24,60	2,40	2,575	0,175	0,69	20 200	2,87	34,80			20	
1 320	10:45 11:15	13,68 14,00	24,23 23,96	2,475	2,65	0,175	0,85	20 500	2,77	34,70				
1 380	11:45 12:15	14,24 14,52	24,03 24,03	2,475	2,675	0,200	1,04	20 500	2,58	34,80				
1 440	12:45	14,67	23,94	2,575	2,825	0,250	1,20	20 500	2,12	34,30	23,52	40,80	20,093	82,95
				BATCH 1 HNO_3							23,52	48,68		

Table 17 : (CONTINUED)

Time (Cum min)	Time	Current (A)	Voltage (V)	HNO_3 (mol/ℓ)	TA (mol/ℓ)	HF (mol/ℓ)	KOH (mol/ℓ)	Feed (mS/m)	Feed pH	Feed °C	Acid Volume (ℓ)	Acid CE (%)	Base Volume (ℓ)	Base CE (%)
1 440	12:45 13:15	13,29 13,56	24,98 0,80	0,925	0,125	1,20	20 500	2,12	34,30	20				
1 500	13:45 14:15	13,62 13,86	24,13 24,03	0,90	0,95	0,05	1,38	20 600	1,92	34,70				
1 560	14:45 15:15	14,14 14,47	23,96 23,98	1,025	1,15	0,125	1,51	21 900	3,68	35,90				
1 620	15:45 16:15	14,56 14,81	23,89 23,97	1,10	1,275	0,175	1,67	22 200	2,17	34,20				
1 680	16:45 17:15	14,82 15,06	23,90 23,93	1,225	1,425	0,20	1,86	22 900		35,20	20,64	55,18	20,372	81,41
1 740	7:15 7:45	12,60 13,28	24,96 24,00	1,35	1,55	0,2	2,01	22 900	1,94	30,80				
							BATCH 4 KOH						20,372	80,39
1 740	7:45	11,40	25,00	1,35	1,55	0,2	0,72	22 900	1,94	30,80			20	
1 800	8:15 9:45	13,12 13,48	24,49 24,32	1,475	1,675	0,2	0,825	23 000	1,81	32,20				
1 860	9:45 10:15	13,75 13,91	24,22 24,15	1,50	1,75	0,25	1,00	23 400	2,30	34,00				
1 980	11.45 12:15	14,66 14,73	24,05 24,02	1,60	1,95	0,35	1,29	23 400	1,91	34,30				
2 040	12:45 13:15	14,81 14,96	24,00 24,10	1,70	2,025	0,325	1,46	23 700	2,01	35,60	21,26	40,49	20,186	73,42
2 100	13:45 14:15	15,07 14,99	24,01 23,88	1,775	2,15	0,365	1,67	23 500	1,85	35,70				
2 160	14:45	15,10	23,93	1,80	2,2	0,40	1,82	23 500	1,82	35,80	21,52	28,57	20,186	81,10
							BATCH 5 KOH							

Table 17 : (CONTINUED)

Time (Cum min)	Time	Current (A)	Voltage (V)	HNO_3 (mol/ℓ)	TA (mol/ℓ)	HF (mol/ℓ)	KOH (mol/ℓ)	Feed (mS/m)	Feed pH	Feed °C	Acid Volume (ℓ)	Acid CE (%)	Base Volume (ℓ)	Base CE (%)
2 160	14:45	12,64	25,57	1,80	2,2	0,40	0,60	25 900	1,85	34,90			20	
2 220	15:15 15:45	13,65 14,09	25,35 25,25	1,875	2,3	0,425	0,79	25 900	1,85	34,90	21,76	34,72		
2 250	16:15 7:15	14,38 12,06	25,14 25,68											
2 280	7:45 8:15	13,12 14,19	25,47 25,23	1,95	2,45	0,50	0,96	25 400	2,01	32,10				
2 340	8:45 9:15	14,68 15,03	25,17 25,06	2,025	2,525	0,50	1,15	26 000	2,16	35,00	22,00		20,186	
2 400	9:45 10:15	15,23 15,39	24,89 24,23	2,075	2,6	0,525	1,34	25 400	2,22	34,70				
2 460	10:45 11:15	15,40 15,50	24,93 24,87	2,175	2,775	0,60	1,48	24 900	6,41	34,50				
2 520	11:45 12:15	15,60 15,64	24,81 24,79	2,2	2,875	0,675	1,66	24 600	6,39	35,20				
2 580	12:45 13:15	15,61 15,81	24,88 24,69	2,375	3,00	0,625	1,81	23 500	6,36	34,60				
2 640	13:45	15,74	24,72	2,40	3,1	0,70	2,03	24 000	6,36	34,80	22,72	43,39	20,465	79,71
				BATCH 2 HNO_3			BATCH 6 KOH				22,72	62,90	20,465	83,95
2 640	13:45 14:15	11,50 11,66	25,83 25,70	0,85	1,05	0,20	0,65	24 000	6,36	34,80	20		20	
2 700	14:45 15:15	12,38 13,04	25,53 25,35	0,80	1,15	0,35	0,77	22 900	6,37	33,90				
2 760	15:45	13,20	25,30	0,85	1,35	0,50	0,99	23 100		34,40				
2 790	16:15 7:15	13,60 9,60	25,20 24,21											

Table 17 : (CONTINUED)

Time (Cum min)	Time	Current (A)	Voltage (V)	HNO_3 *(mol/ℓ)*	TA *(mol/ℓ)*	HF *(mol/ℓ)*	KOH *(mol/ℓ)*	Feed *(mS/m)*	Feed *pH*	Feed °C	Acid Volume (ℓ)	Acid CE (%)	Base Volume (ℓ)	Base CE (%)
2 820	7:45 8:15	10,78 11,98	25,85 25,46	0,975	1,625	0,65	1,03	19 200		24,80				
2 880	8:45 9:15	13,13 13,80	25,22 25,60	1,125	1,80	0,675	1,19	22 000		33,70				
2 940	9:45 10:15	14,09 14,34	25,04 24,98	1,225	2,05	0,825	1,39	21 700		34,90	21,04	47,20	20,093	80,21
3 000	10:45 11:15	14,55 14,74	24,96 24,92	1,25	2,30	1,05	1,54	21 300		34,70				
3 060	11:45 12:15	14,81 14,91	24,91 24,90	1,325	2,55	1,225	1,66	20 400		34,20				
3 120	12:45 13:15	14,91 14,92	24,88 24,88	1,375	2,70	1,325	1,81	19 600		35,40				
3 180	13:45	15,00	24,88	1,45	2,975	1,50	1,97	18 400		34,10	22,88	34,47	20,56	58,56
							BATCH 7 KOH						20,56	76,10
3 180	13:45 14:15	12,51 12,63	25,54 25,45	1,45	2,925	1,50	0,70	18 400		34,10			20	
3 240	14:45 15:15	13,10 13,50	25,32 25,23	1,575	3,15	1,575	0,78	17 700		35,20				
3 300	15:45 16:15	13,63 13,61	25,13 25,21	1,60	3,40	1,80	0,93	16 800		35,70				
3 360	7:00 7:30 8:00	10,55 11,19 12,48	25,84 25,71 25,40	1,60	3,45	1,85	1,02	13 600		26,00				
3 420	8:30 9:00	13,39 13,77	25,20 25,08	1,625	3,6	1,975	1,17	14 400		34,00				
3 480	9:30 10:00	13,96 13,83	25,07 25,07	1,70	3,925	2,225	1,33	13 100		35,60				
3 540	10:30 11:00	13,80 13,53	25,09 25,16	1,70	4,05	2,35	1,48	11 210		35,80				
3 600	11:30	13,31	25,22	1,725	4,25	2,525	1,53	8 630	2,15	35,20	24,16	30,96	20,47	63,09
			BATCH 3 HNO_3			BATCH 8 KOH								

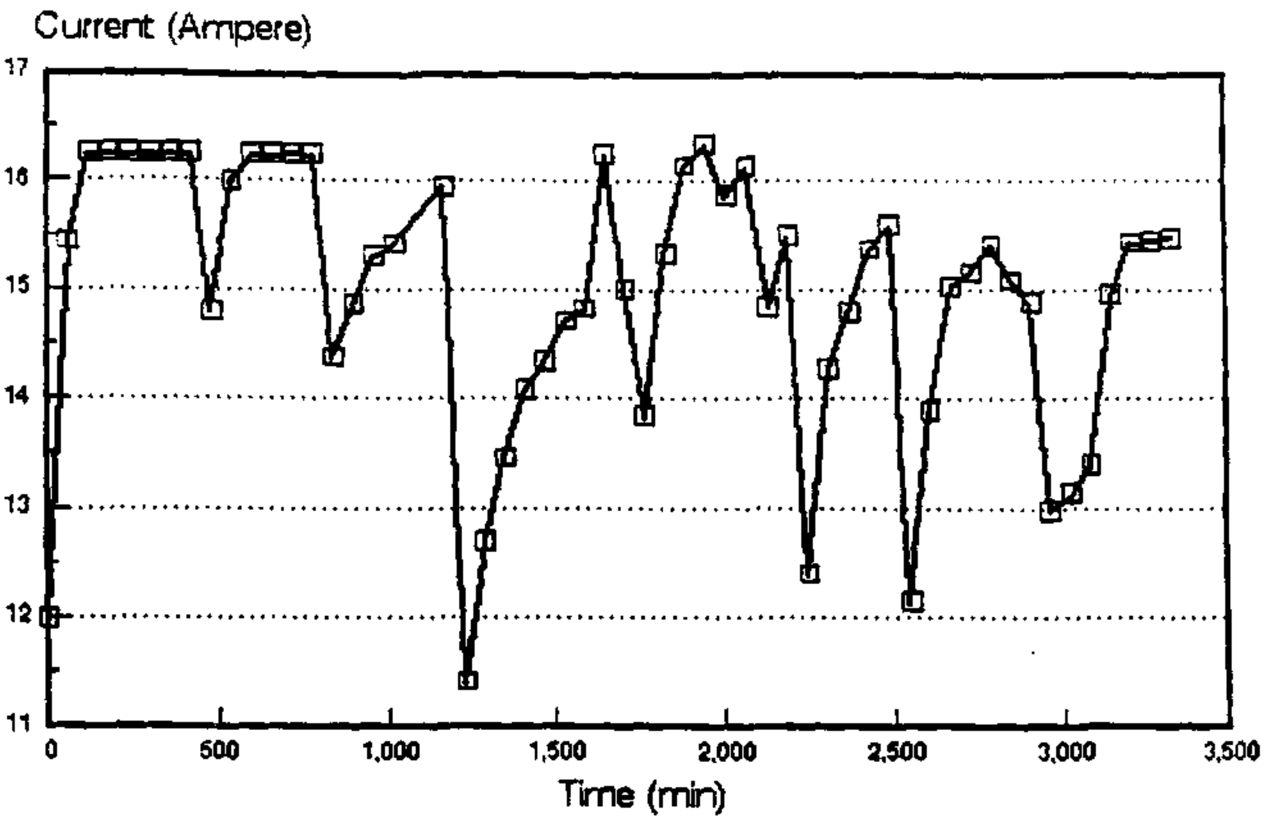


Figure 25 : Electrical current as a function of time during BED treatment of neutralised spent pickling acid effluent (1st batch).

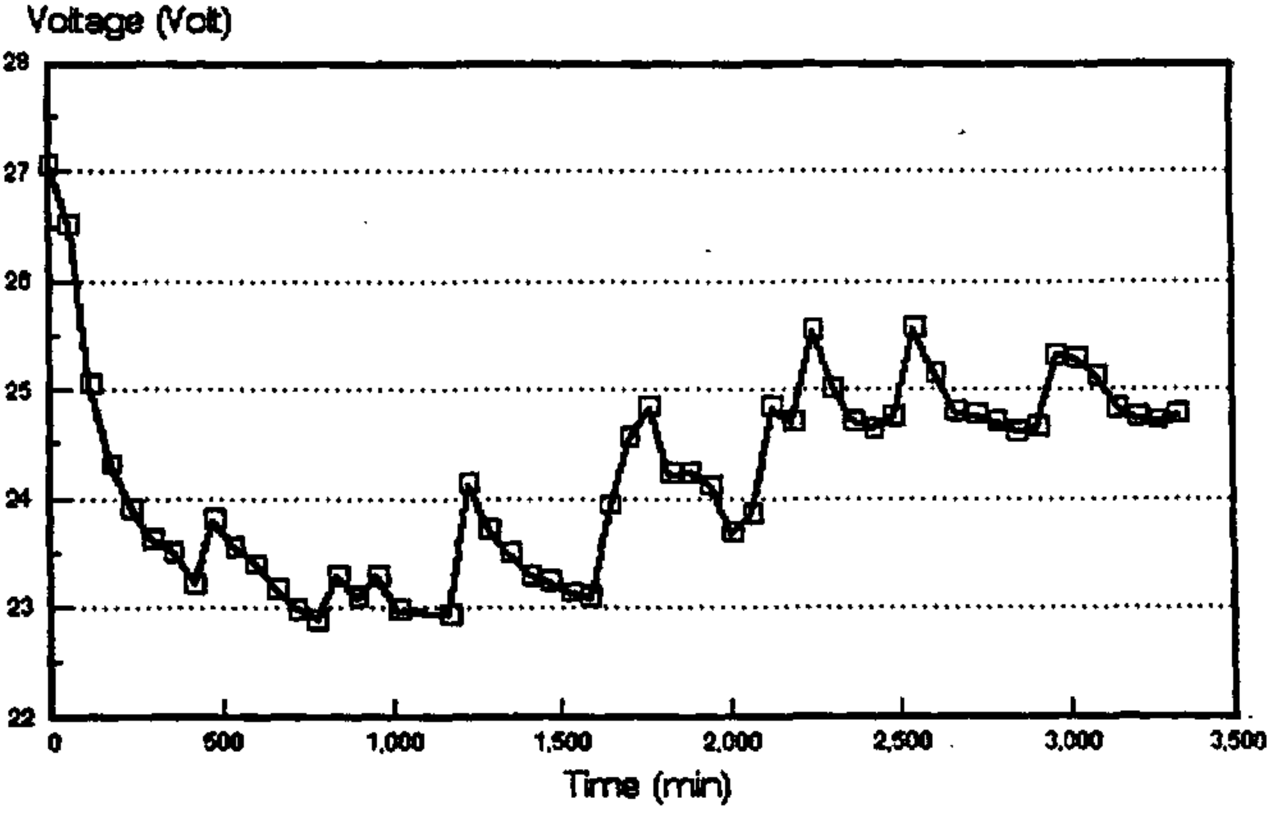


Figure 26 : Voltage as a function of time during BED treatment of neutralised spent pickling acid effluent (1st batch).

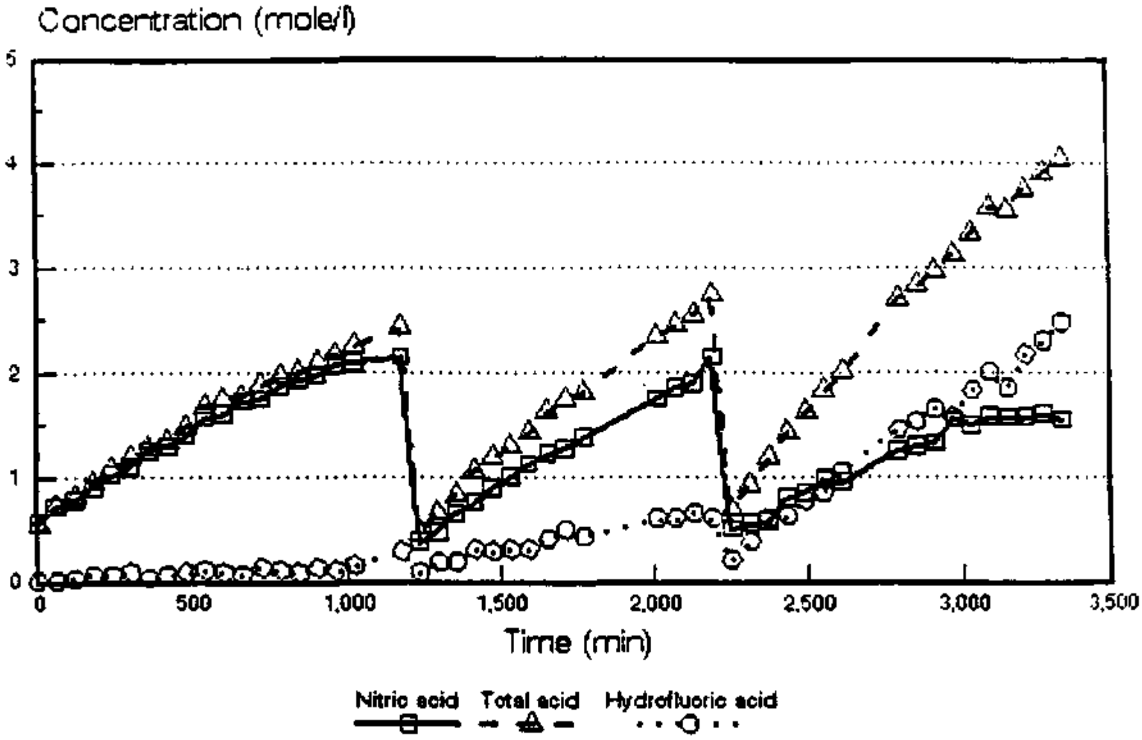


Figure 27 : Acid concentration (HNO_3, total acid and HF) as a BED treatment of neutralised spent pickling acid effluent (1st batch)

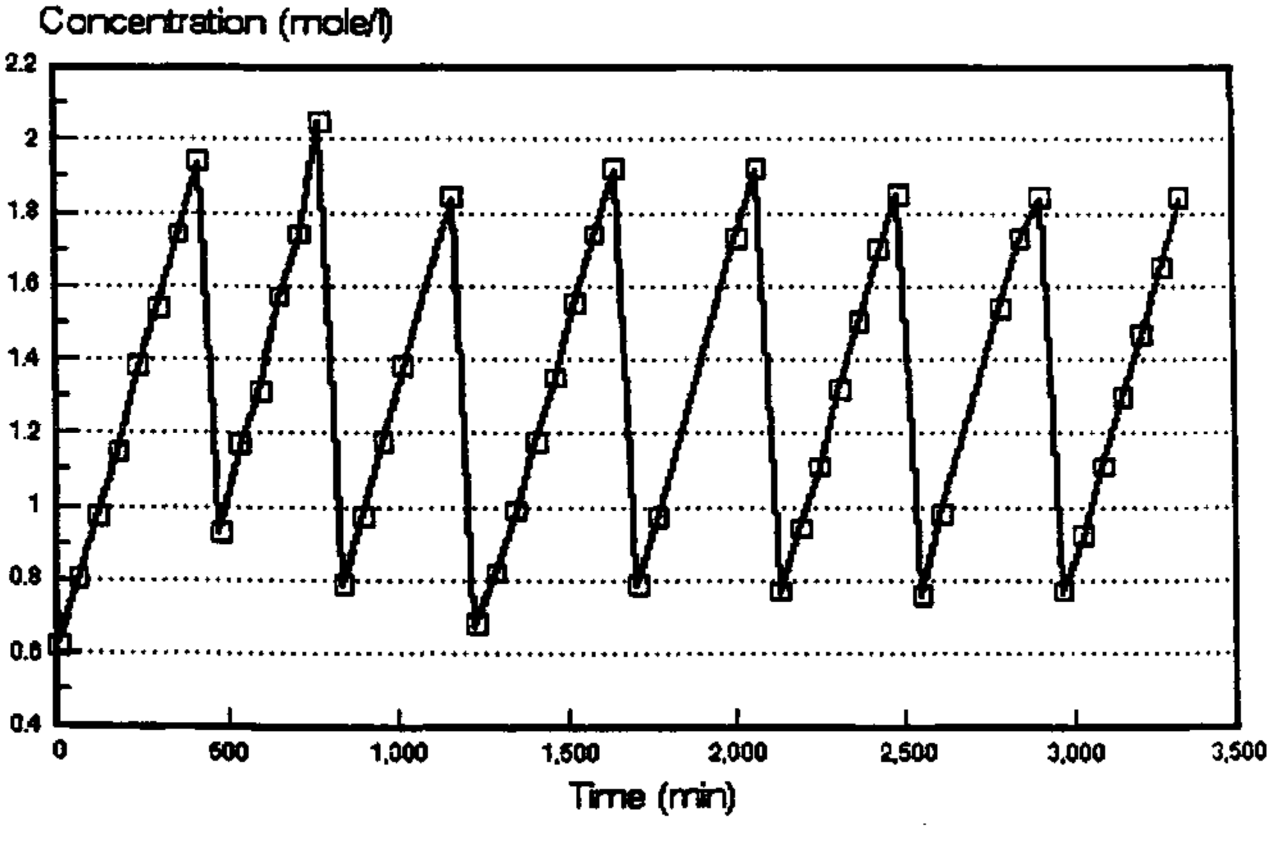


Figure 28 : Potassium hydroxide concentration as a function of time during BED treatment of neutralised spent pickling acid effluent (1st batch).

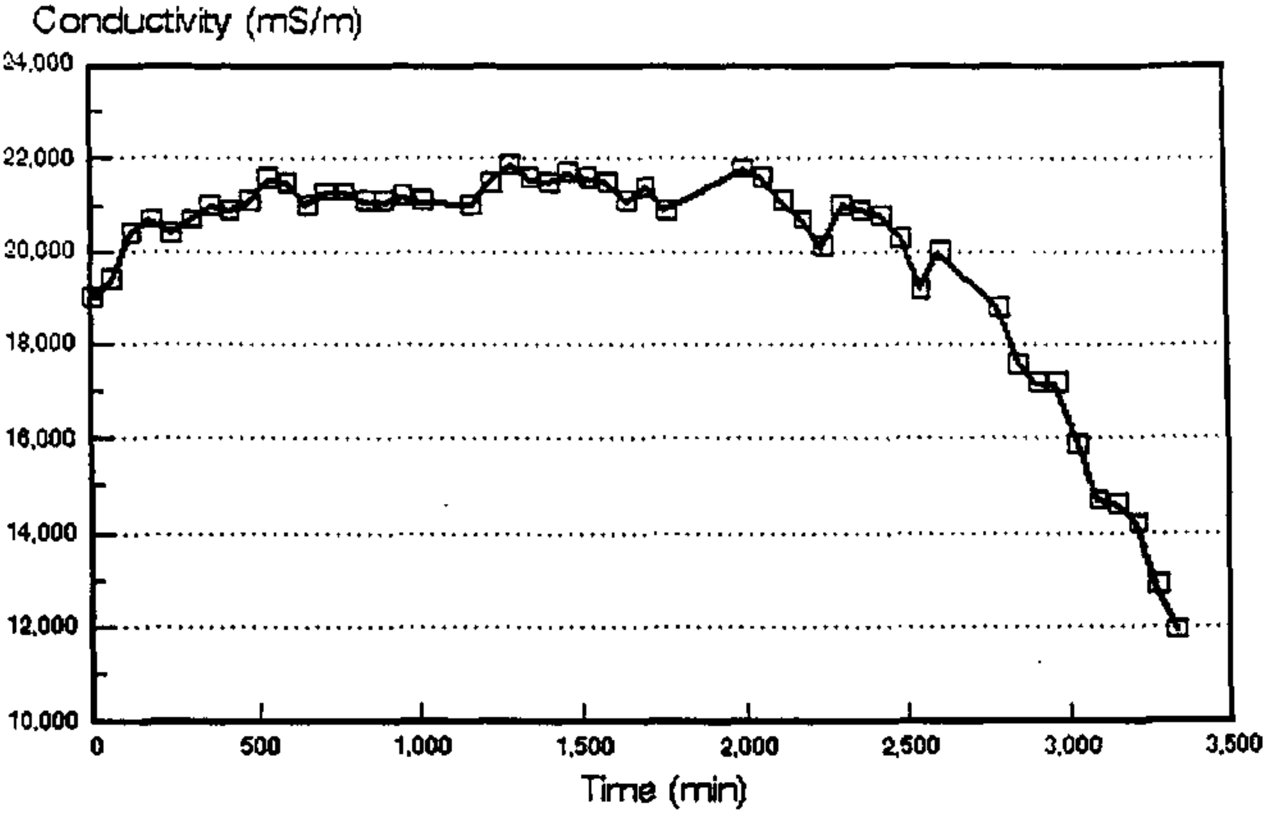


Figure 29 : Feed water conductivity as a function of time during BED treatment of neutralised spent pickling acid effluent (1st batch)

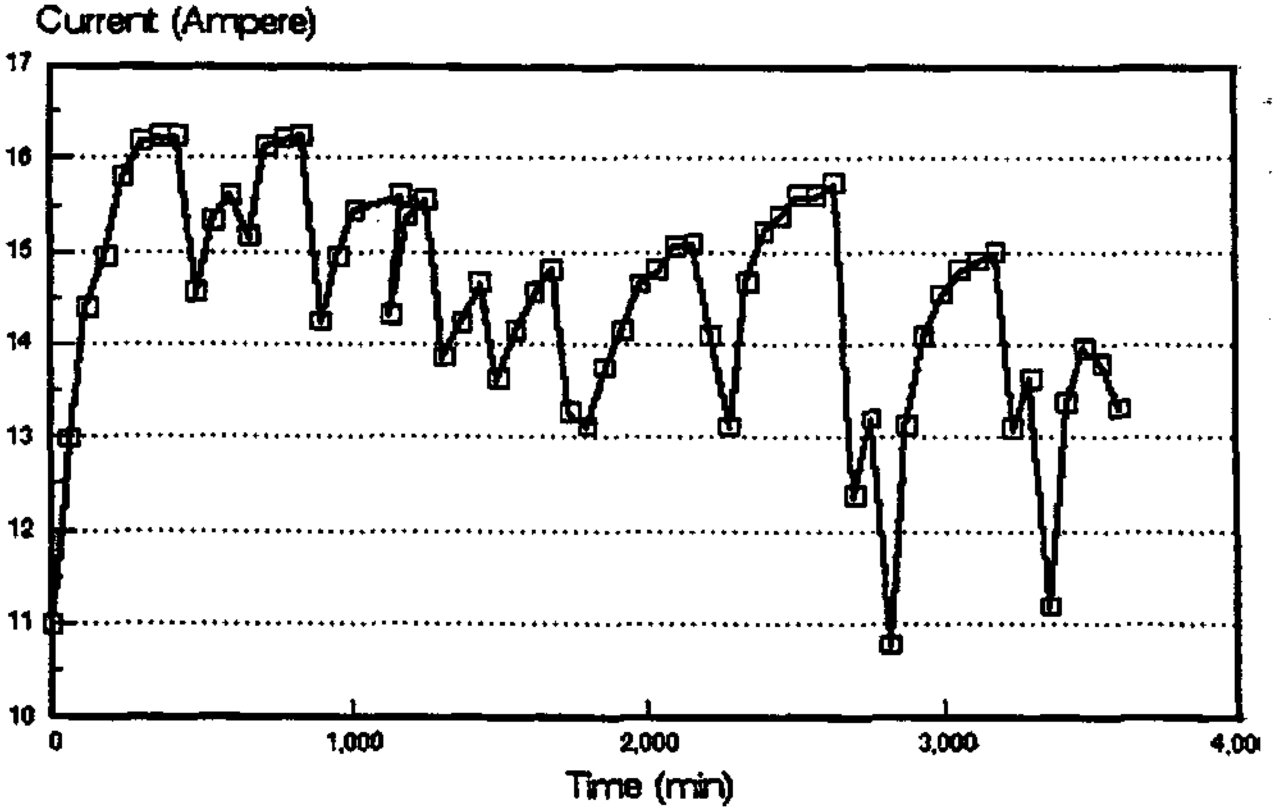


Figure 30 : Electrical current as a function of time during BED treatment of neutralised spent pickling acid effluent (2nd batch).

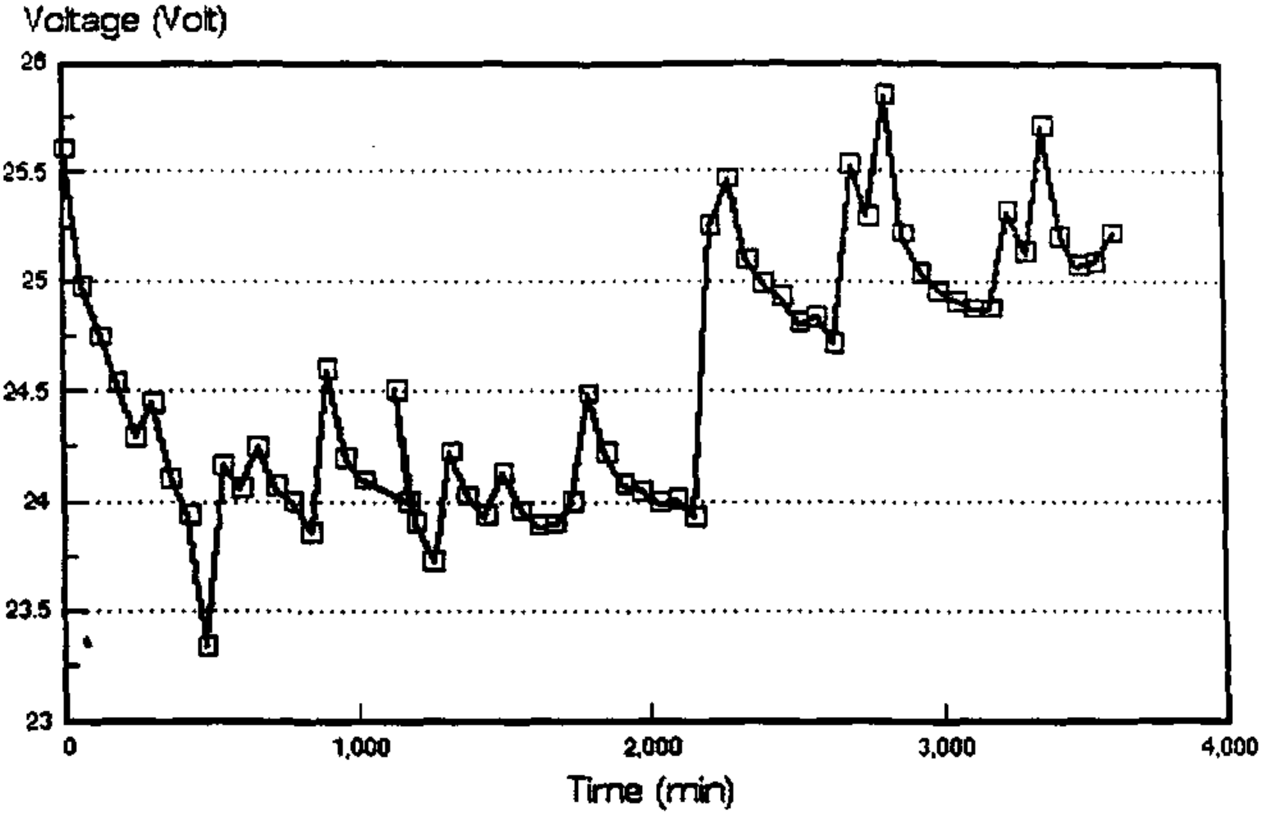


Figure 31 : Voltage as a function of time during BED treatment of neutralised spent pickling acid effluent (2nd batch)

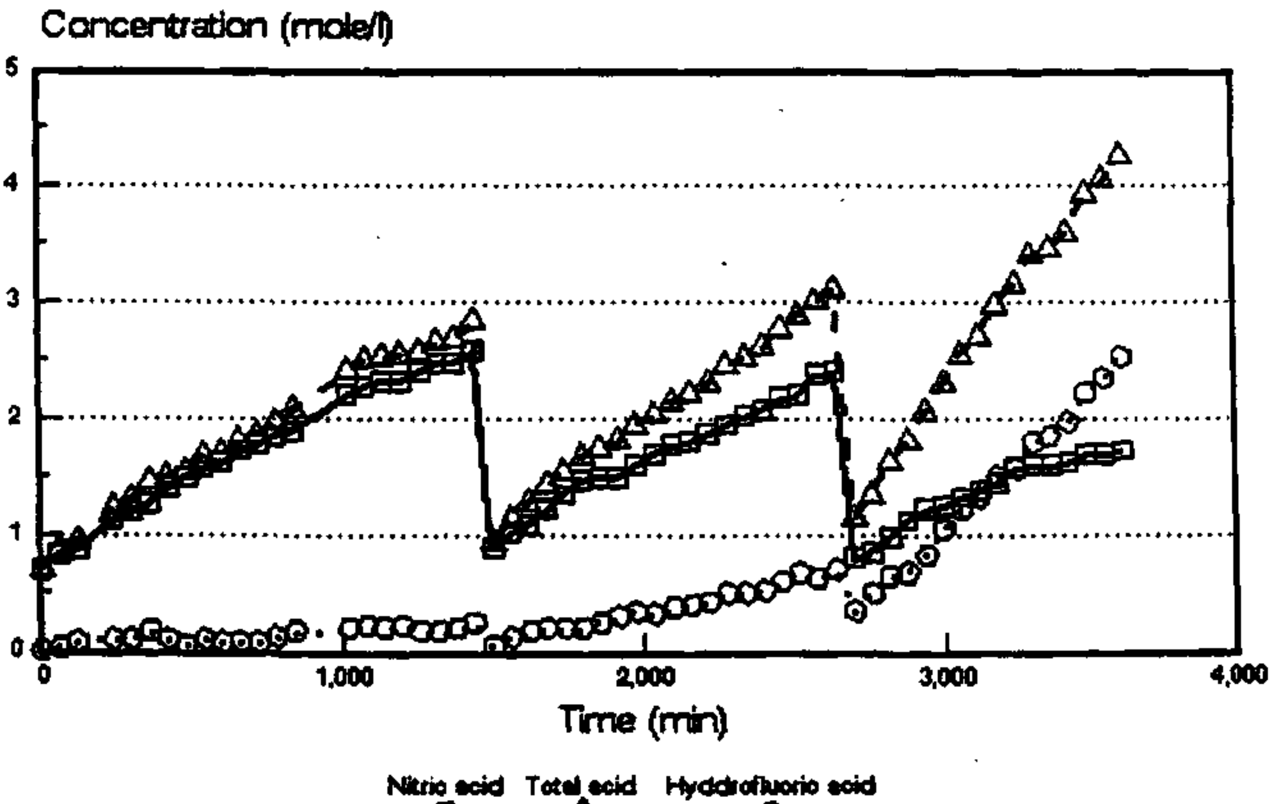


Figure 32 : Acid concentration (HNO_3, total acid and HF) as a function of time during BED treatment of neutralised spent pickling acid effluent (2nd batch).

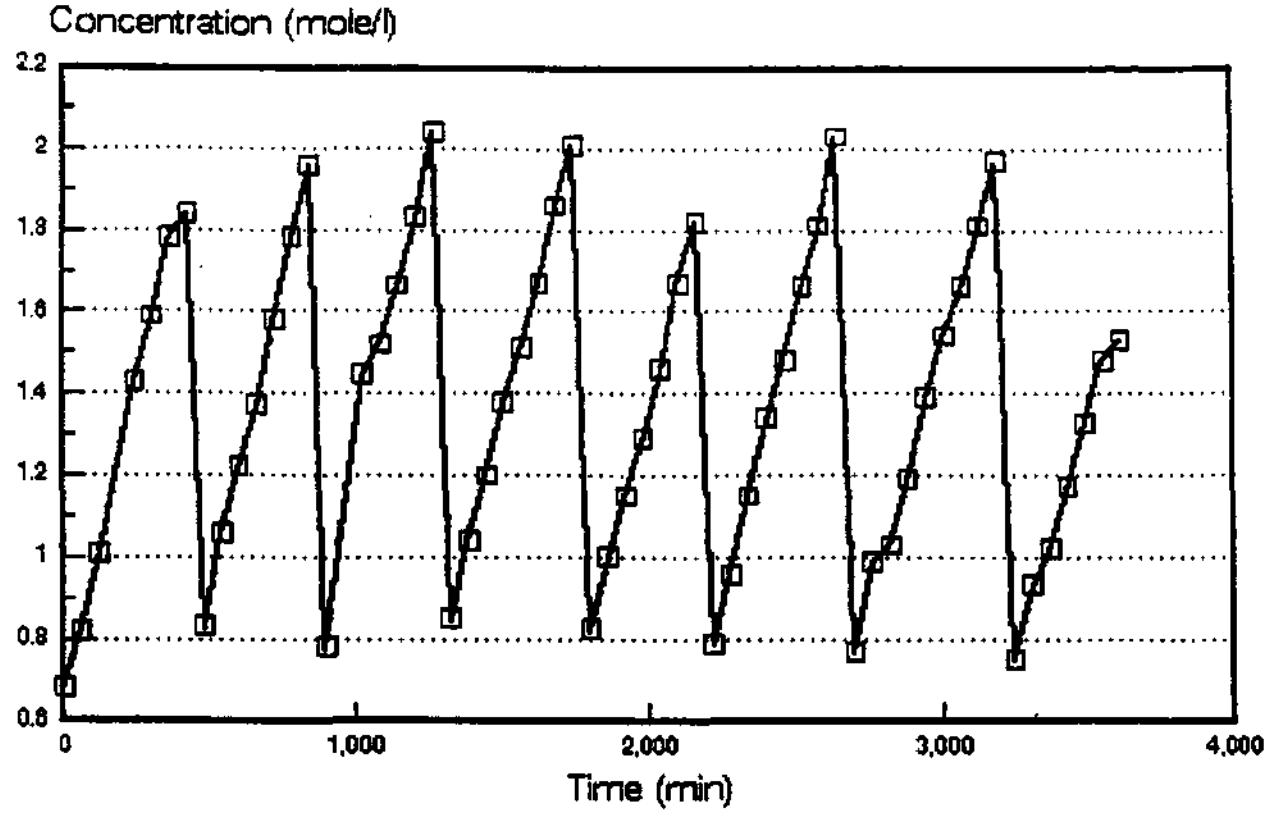


Figure 33 : Potassium hydroxide concentration as a function of time during BED treatment of neutralised spent pickling acid effluent (2nd batch).

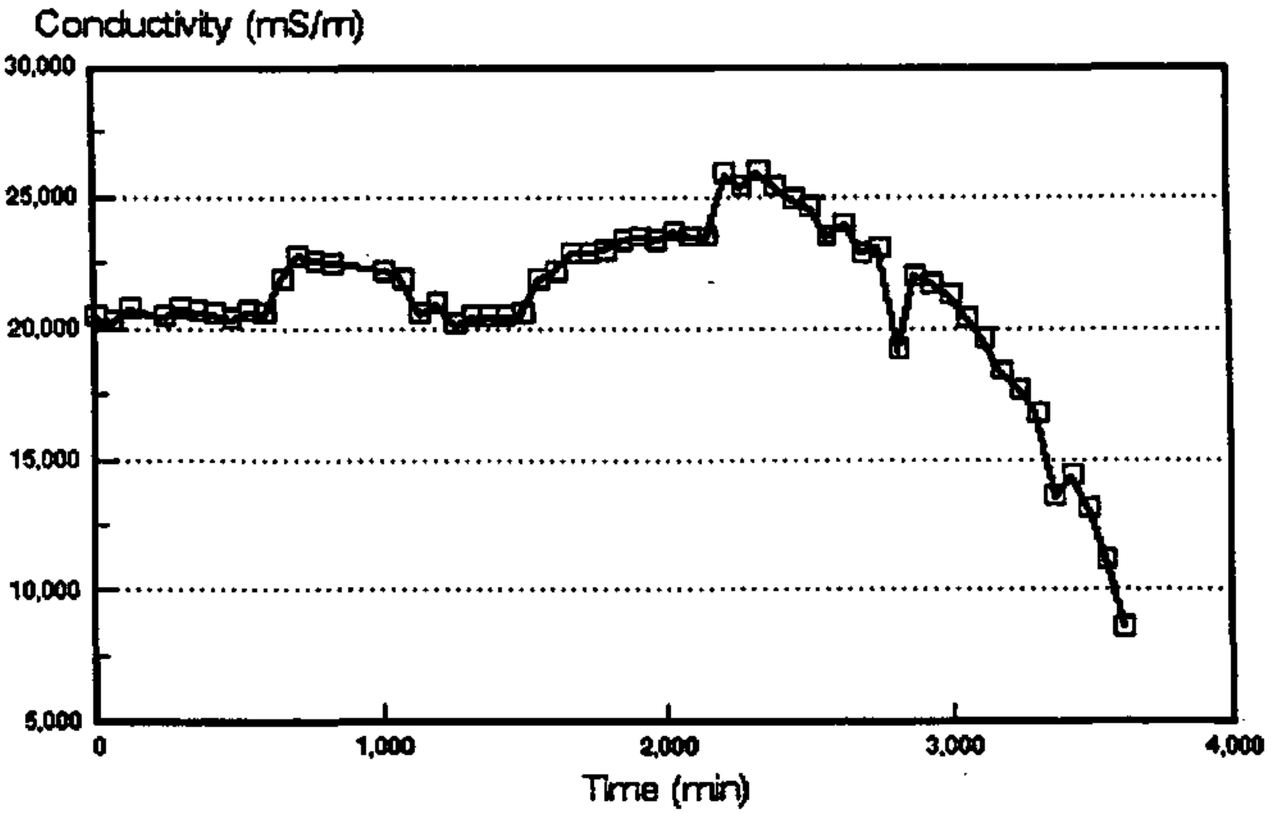


Figure 34 : Feed water conductivity as a function of time during BED treatment of neutralised spent pickling acid effluent (2nd batch)

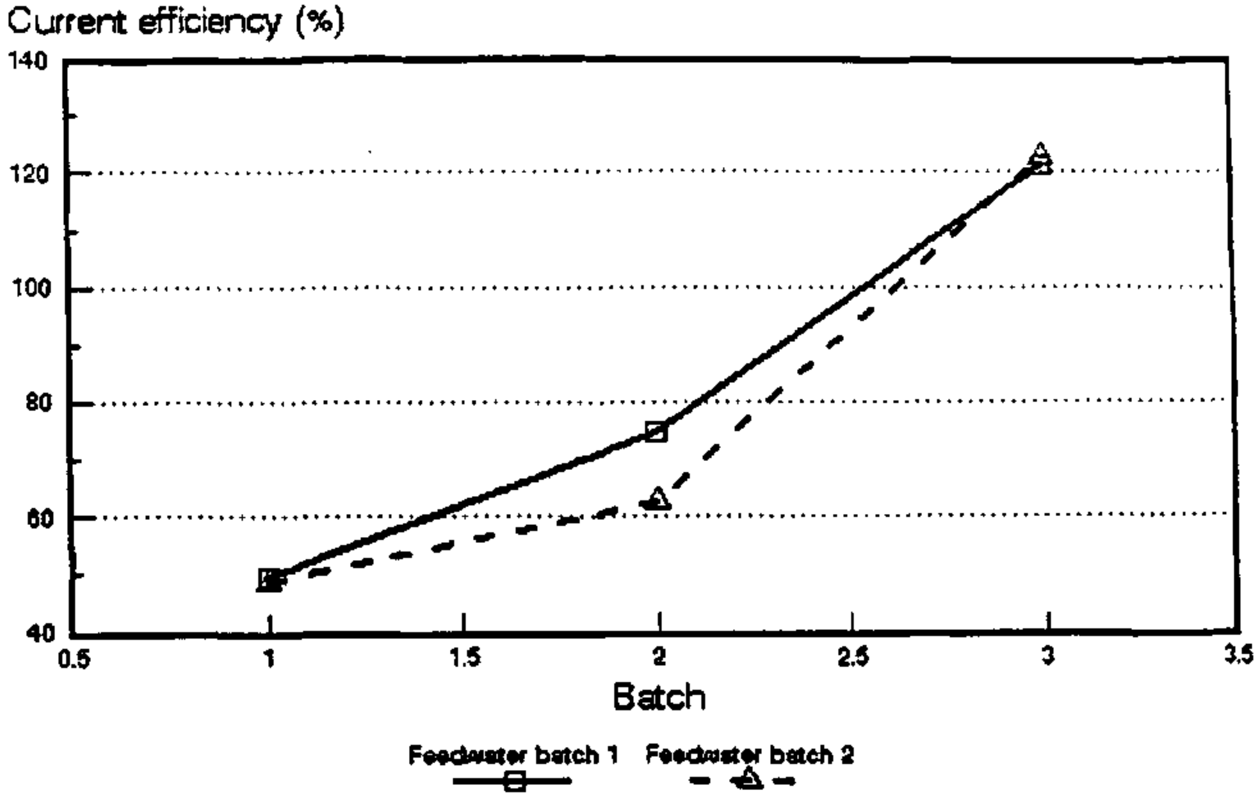


Figure 35 : Current efficiency of acid product for the two feed water batches for different acid batches.

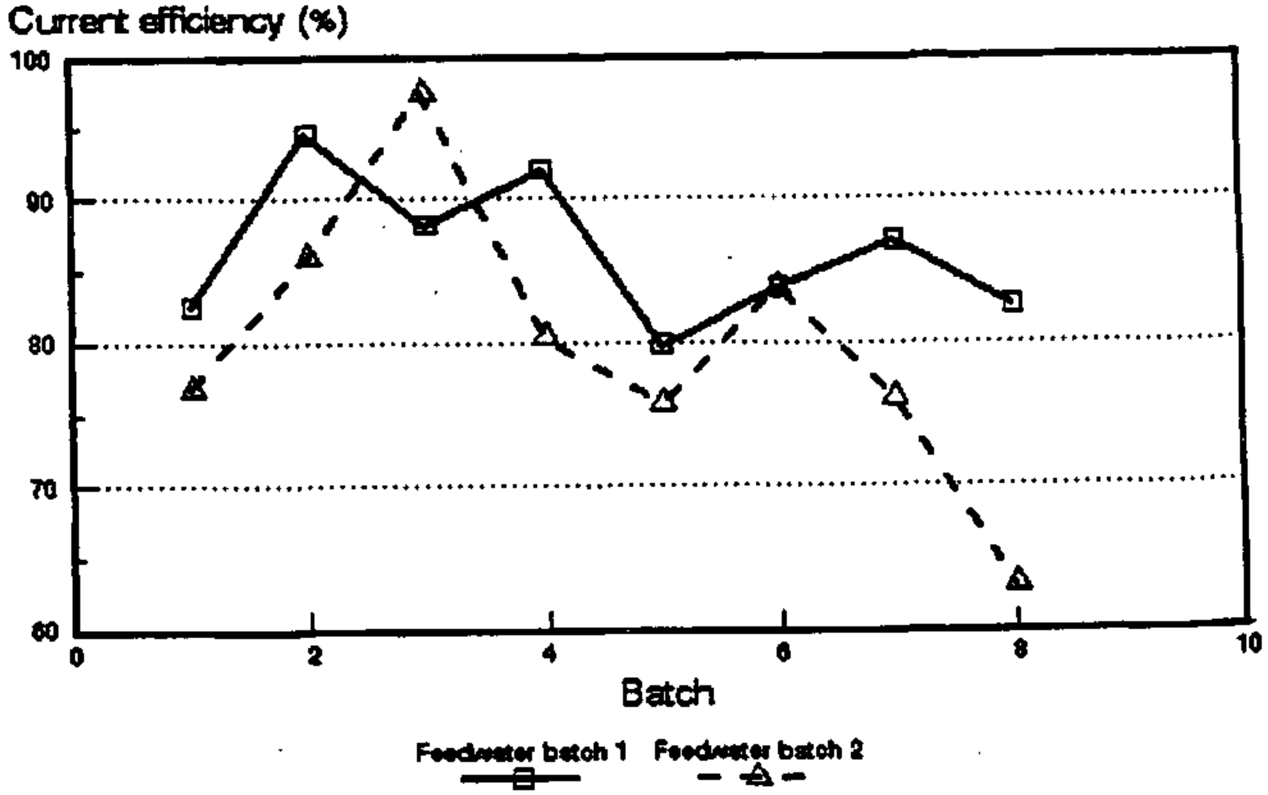


Figure 36 : Current efficiency of base product for the two feed water batches for different base batches.

Table 18 : Concentration levels of potassium, nitrate-nitrogen, fluoride, iron, chromium and nickel in the feed water as a function of time in the first feed water batch

Time (min)	K^+ (mg/ℓ)	N-NO_3 (mg/ℓ)	F^- (mg/ℓ)	Fe (mg/ℓ)	Cr (mg/ℓ)	Ni (mg/ℓ)
0	159 280	35 100	63 200	1,9	2,2	1,82
240	139,820	33 400	68 000			
420	140 360	20 748	74 800			
660	143 700	20 250	78 400			
960	131 890	20 724	65 200			
1 230	123 600	21 114	84 400			
1 470	125 040	6 940	77 600			
1 710	120 900	5 930	79 999			
2 070	119 390	8 900	95 600			
2 310	110 000	6 570	77 600			
2 490	103 640	5 540	87 200			
2 850	92 500	3 593	102 000			
3 030	71 160	811	54 000			
3 330	50 500	436	55 500			

Note: Feed volume 60 ℓ; Volume remaining at end of batch was 16 ℓ .

Table 19 : Concentration levels of potassium, nitrate-nitrogen, fluoride, iron, chromium and nickel in the feed water as a function of time in the second feed water batch

Time (min)	K^+ (mg/ℓ)	N-NO_3 (mg/ℓ)	F^- (mg/ℓ)	Fe (mg/ℓ)	Cr (mg/ℓ)	Ni (mg/ℓ)
0	161 700	37 490	75 500	2,7	2,2	1,4
600	152 200	22 091	80 400			
1 140	168 800	19 076	59 600			
1 680	149 400	12 651	69 999			
2 760	113 500	10 890	70 399			
3 360	59 700	4 820	57 999			
3 600	29 100	1 680	76 799			

Note : Feed volume 60 ℓ; Volume remaining at end of batch was 12 ℓ.

Table 20 : Electrical energy consumption for acid production and composition of the acid product in the different batches.

Acid	**Feed Water Batch 1**			**Feed Water Batch 2**		
	Batch 1	**Batch 2**	**Batch 3**	**Batch 1**	**Batch 2**	**Batch 3**
Energy consumption (kWh/kg acid)	2,78	1,99	1,96	2,87	2,51	2,10
Nitric acid (mol/ℓ)	2,15	2,15	1,55	2,575	2,40	1,725
Hydrofluoric acid (mol/ℓ)	0,275	0,60	2,475	0,25	0,70	2,525
Chromium (mg/ℓ)	0,29	0,13	0,11	0,44	0,41	0,46
Iron (mg/ℓ)	0,57	1,15	1,10	0,47	0,24	0,34
Nickel (mg/ℓ)	0,20	0,11	0,11	0,12	0,12	0,17

Table 21 : Electrical energy consumption for base production and composition of the base product in the different batches (1st batch run).

Batch	1	2	3	4	5	6	7	8
Energy consumption (kWh/kg KOH)	1,78	1,48	1,44	1,54	1,73	1,76	1,72	1,71
KOH (mol/ℓ)	1,94	2,05	1,84	1,92	1,92	1,85	1,84	1,84
Chromium (mg/ℓ)	0,86	0,81	0,75		0,34			0,30
Iron (mg/ℓ)	0,90	0,94	0,68		0,43			0,42
Nickel (mg/ℓ)	0,47	0,50	0,47		0,31			0,30

Table 22 : Electrical energy consumption for base production and composition of the base product in the different batches (2nd batch run).

Batch	1	2	3	4	5	6	7	8
Energy consumption (kWh/kg KOH)	1,92	1,67	1,49	1,80	1,91	1,82	2,00	2,34
KOH (mol/ℓ)	1,84	1,96	2,04	2,01	1,82	2,03	1,97	1,53
Chromium (mg/ℓ)	0,40	0,39	0,39		0,52			0,56
Iron (mg/ℓ)	0,50	0,51	0,45		0,43			0,39
Nickel (mg/ℓ)	0,44	0,44	0,46		0,54			0,55

Nitric acid concentration levels between 2 and 2,5 mol/ℓ were obtained (Figures 27 and 32). It is interesting to note that the hydrofluoric acid concentration level has increased dramatically during the third acid batch when most of the nitrate has been removed. The hydrofluoric acid concentration level in the third batch was approximately 2,5 mol/ℓ . Consequently, it appears that hydrofluoric acid can be effectively recovered with BED technology. It is also interesting to note that a total acid concentration of approximately 4 mol/ℓ has been obtained in the third acid batch.

The potassium hydroxide was again batched when the concentration level reached approximately 2 mol/ℓ (Figures 28 and 33). Acid current efficiency varied between approximately 48 and 122% (Figure 35) for the different acid batches. Base current efficiency varied initially between approximately 63 and 95% and decreased towards the end of the run (Figure 36). Acid and base current efficiencies were higher in the beginning of the run than later in the same batch (Table 16 and 17).

The potassium in the first and second feed water batches were reduced by approximately 68 and 82%, respectively (Tables 18 and 19). The nitrate-nitrogen concentration levels were reduced by approximately 99 and 94%, respectively. The fluoride concentration level was reduced only by approximately 12% and no apparent reduction, respectively. However, the feed volume was reduced from 60 litre to 16 litre from the beginning to the end of the first feed batch run and from 60 litre to 12 litre at the end of the second feed batch run. The temperature of the feed water was maintained at approximately 37 °C with a heater during the runs. Consequently, evpaoration took place which resulted in a significant reduction in the feed water volume. Approximately 99% nitrate-nitrogen and 77% fluoride could be recovered with BED (Tables 18 and 19).

The acid and base products had a satisfactory purity (Tables 20 to 22). The chromium, iron and nickel concentration levels were less than 1 mg/ℓ . The electrical energy consumption for acid production varied between approximately 1,96 and 2,87 kWh/kg acid (Table 20). The electrical energy consumption for acid production varied between approximately 1,96 and 2,87 kWh/kg acid (Table 20). The electrical energy consumption for base production varied between approximately 1,4 and 2,3 kWh/kg base (Tables 21 and 22).

The following material balance was derived from the results shown in Tables 15 and 16. The results are shown in Table 23.

Less nitric acid and hydrofluoric acid could be recovered than was present in the feed. The total nitric and hydrofluoric acid concentration levels shown in Table 23 may not be very accurate due to the high dilution levels (1 000 x and more) that have been necessary for the analysis. However, it appears that a significant amount of nitric acid and hydrofluoric acid can be recovered.

Table 23 : Material balance for BED derived from experimental results.

Feed Water	60 ℓ (1 750 ℓ/h)	
Total HNO_3	176,2 g/ℓ	308,4 kg/h
Free HNO_3	149,9 g/ℓ	263,3 kg/h
Total HF	64,4 g/ℓ	112,7 kg/h
Free HF	23,8 g/ℓ	41,7 kg/h
Acid Product	68,23 ℓ (1 990,04 ℓ/h)	
HNO_3	121,8 g/ℓ	242,2 kg/h
HF	23,6 g/ℓ	47,0 kg/h
Base Product	148,46 ℓ (4 330,1 ℓ/h)	
KOH	106,4 g/ℓ	460,7 kg/h
Sludge	450 kg/h at approximately 35% solids.	

Note: Approximately 578 kg/h base required for neutralization.

It appears that not enough potassium hydroxide will be produced for neutralisation of the spent acids. Consequently, it will be necessary to purchase additional potassium hydroxide for this purpose.

The following flow diagram is suggested for treatment of the spent pickling acid effluent produced at the stainless steel manufacturer (Figure 37). The process is similar to a process used at the Washington Steel Plant in the USA. However, diffusion dialysis may be used in a first step to recover the free acids before BED if it can be demonstrated that a combination of diffusion dialysis and BED is more economic than BED alone.

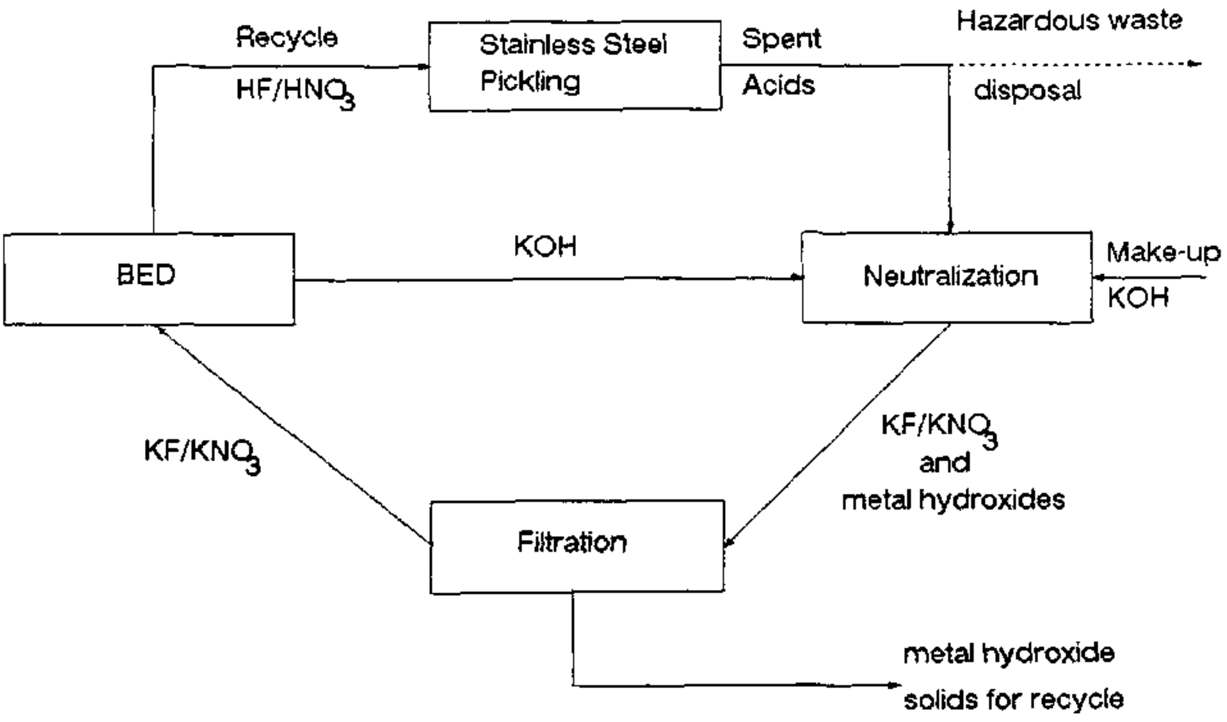


Figure 37: Proposed flow diagram for treatment of spent pickling acid effluent produced by the stainless steel manufacturer.

4.6 Treatment of Sodium Nitrate Effluent with Bipolar Electrodialysis

The chemical composition of the sodium nitrate feed (run 1) before and after bipolar electrodialysis is shown in Table 24.

The sodium, nitrate-nitrogen and electrical conductivity of the solution is high. Approximately 90 percent of the sodium nitrate was converted into caustic soda and acid.

The pH of the feed was lowered with nitric acid to a pH of approximately 2 prior to electrodialysis to improve process performance.

The sodium and nitrate-nitrogen levels in the BED feed as a function of time are shown in Table 25 for the two runs that were conducted.

Approximately 88 percent sodium and 91 percent nitrate-nitrogen were converted into acid and base (run 1). Approximately 86 percent sodium and nitrate-nitrogen were converted into acid and base at the end of run 2.

Table 24: Chemical composition of sodium nitrate effluent before and after electrodialysis (run 1)

Constituents*	Feed before pH adjust	Feed after pH adjust	Feed at end of run
COD	73	43	53
Nitrate as N	18 810	21 510	1 885
Alkalinity as $CaCO_3$	13 000		112,5
Total sulphate	1,7	3,3	24,8
Potassium	13,8	36,5	2,15
Sodium	26 700	25 100	2 900
Magnesium	2,09	2,78	1,57
Calcium	1	1	2,77
TDS	135 116	133 780	12 016
Chloride	139	40	29
Fluoride	1		
Conductivity (mS/m)	10 020	10 630	1 430
pH	8,19	1,92	10,44

*Values in mg/ℓ unless stated otherwise.

Table 25: Sodium and nitrate nitrogen concentration levels in the feed solution as a function of time during BED treatment of a 10% sodium nitrate solution (runs 1 and 2).

Time (minutes)	Sodium (mg/ℓ)	Nitrate (mg/ℓ as N)
0	25 100	21 510
240	26 200	19 800
480	22 600	15 410
720	21 400	16 830
960	21 300	11 800
1 200	18 170	12 610
1 440	15 670	11 560
1 680	11 600	9 658
1 920	8 160	6 931
2 160	5 590	4 495
2 400	3 530	3 673
2 640	4 670	2 558
2 760	2 900	1 885
Run 2		
0	23 000	14 700
1 020	10 700	7 362
1 960	3 300	2 126

The electrical conductivity of the feed as a function of time during BED treatment of the effluent for the two runs is shown in Figures 38 and 39. The initial conductivity of the first sample (run 1) was higher than that of the second sample. Conductivity removals of between approximately 80 to 88% were obtained.

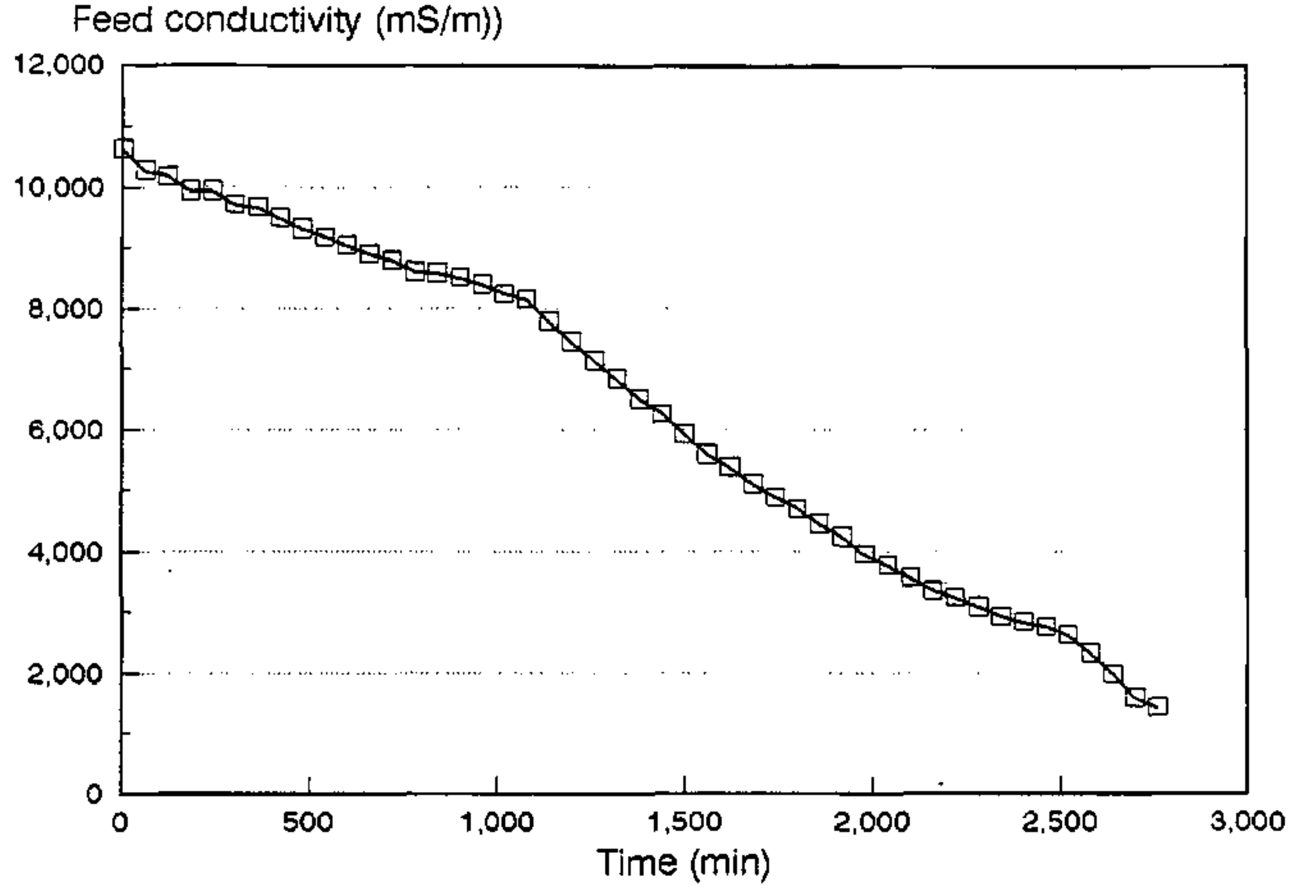


Figure 38: Feed conductivity as a function of time during BED treatment of the sodium nitrate solution (run 1).

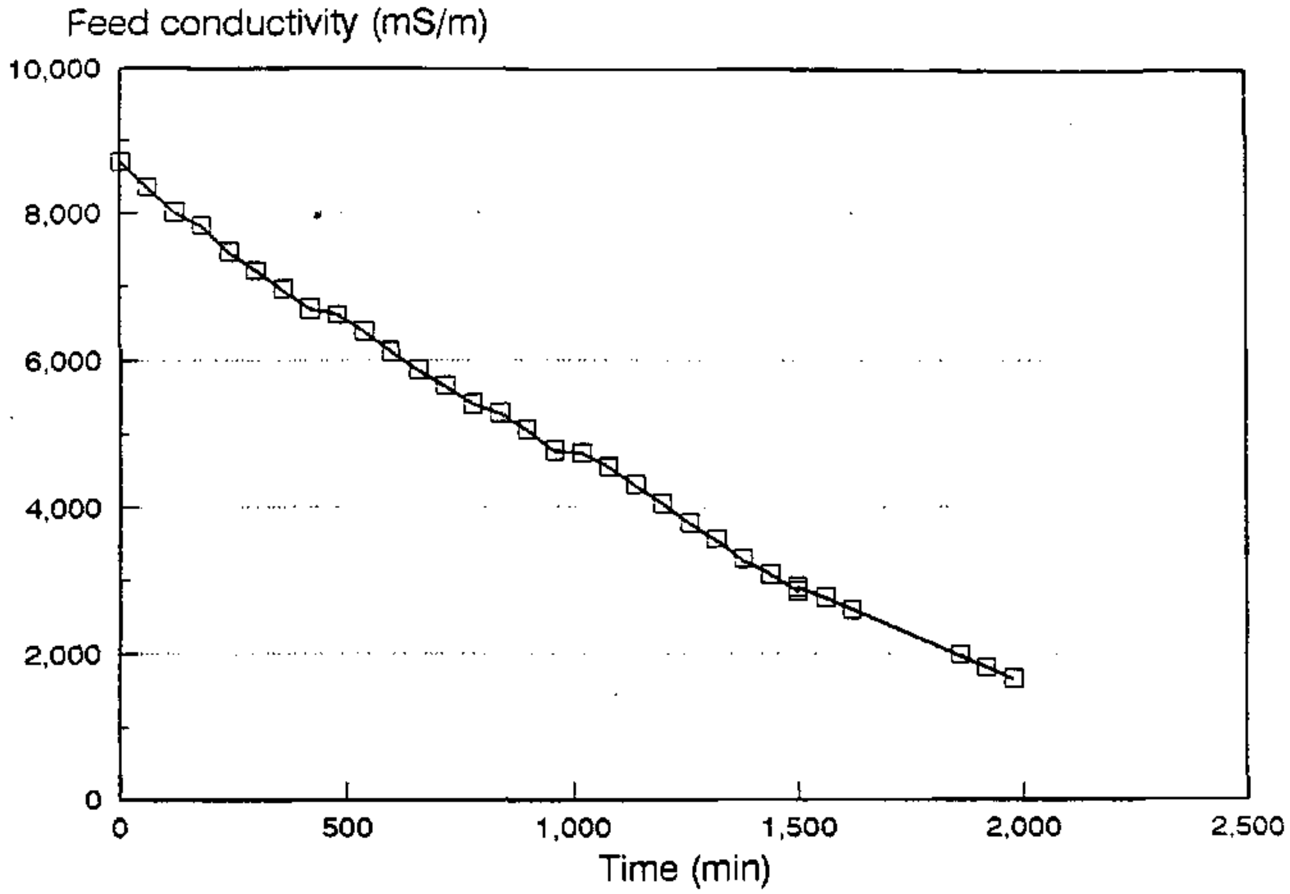


Figure 39 : Feed conductivity as a function of time during BED treatment of the sodium nitrate solution (run 2).

The electric current as a function of time during BED treatment of the two effluent samples is shown in Figures 40 and 41. The electrical current usually decreases after batching and when the salinity in the feed becomes depleted of ions. This is typical of a batch operation at constant voltage.

The pH of the feed during BED treatment is shown in Figures 42 and 43. The pH of the feed (lowered pH) remained at approximately 2 during run 1 and increased sharply towards the end of the run (Figure 42). The pH of the feed during run 2, however, remained approximately constant for a short period and then increased sharply to pH of about 9. It then decreased to a pH of approximately 3,5 and increased to a pH of approximately 11. The feed pH was then acidified with nitric acid in an attempt to improve process performance.

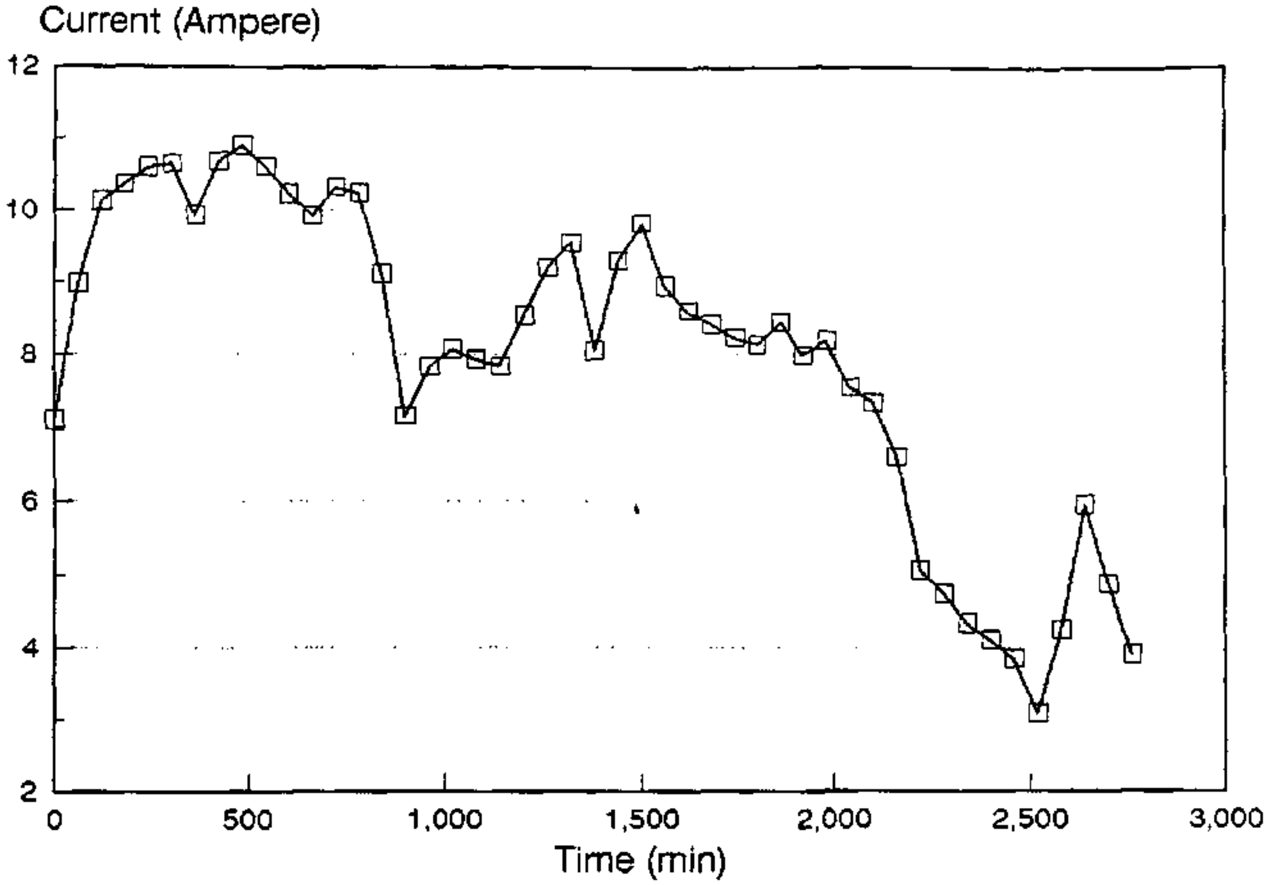


Figure 40 : Electrical current as a function of time during BED treatment of the sodium nitrate solution (run 1).

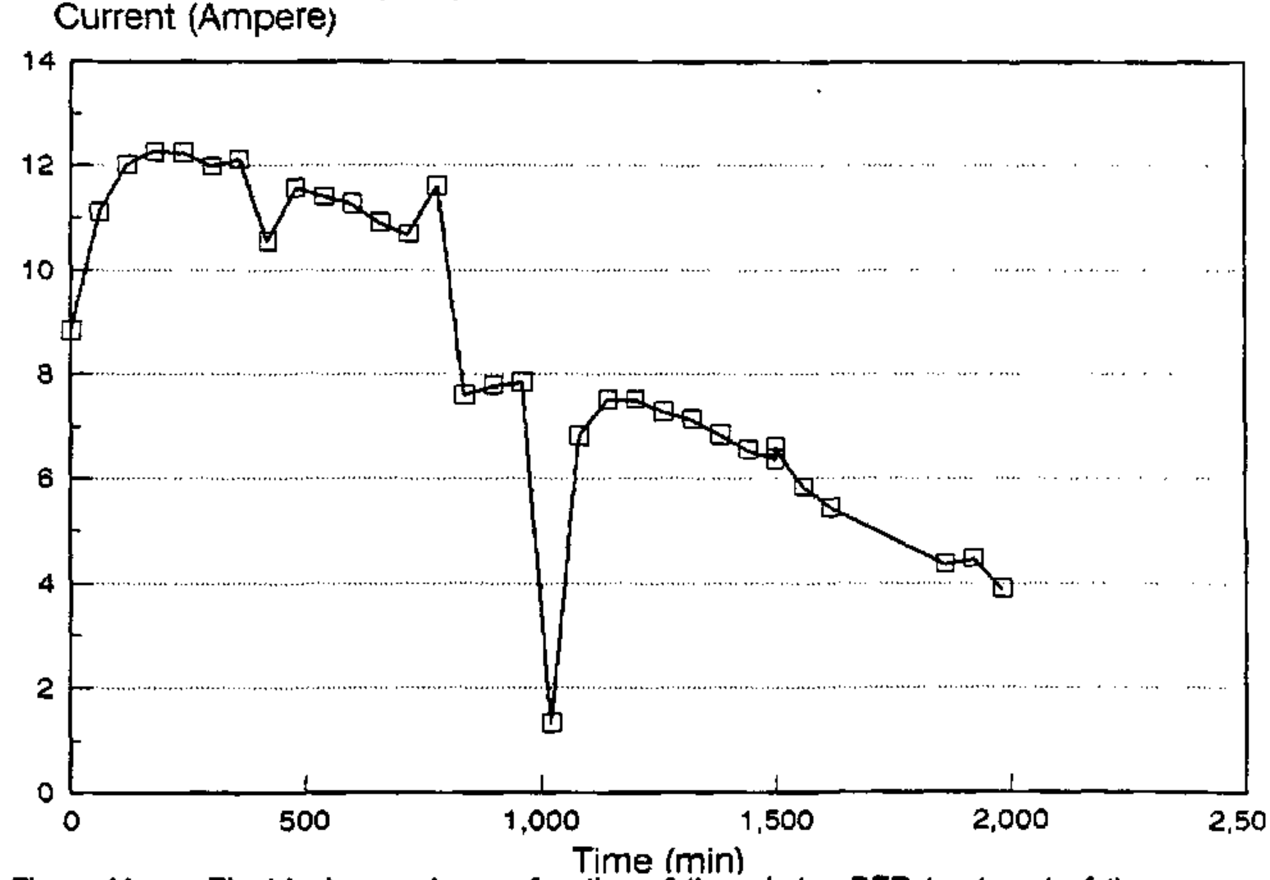


Figure 41 : Electrical current as a function of time during BED treatment of the sodium nitrate solution (run 2)

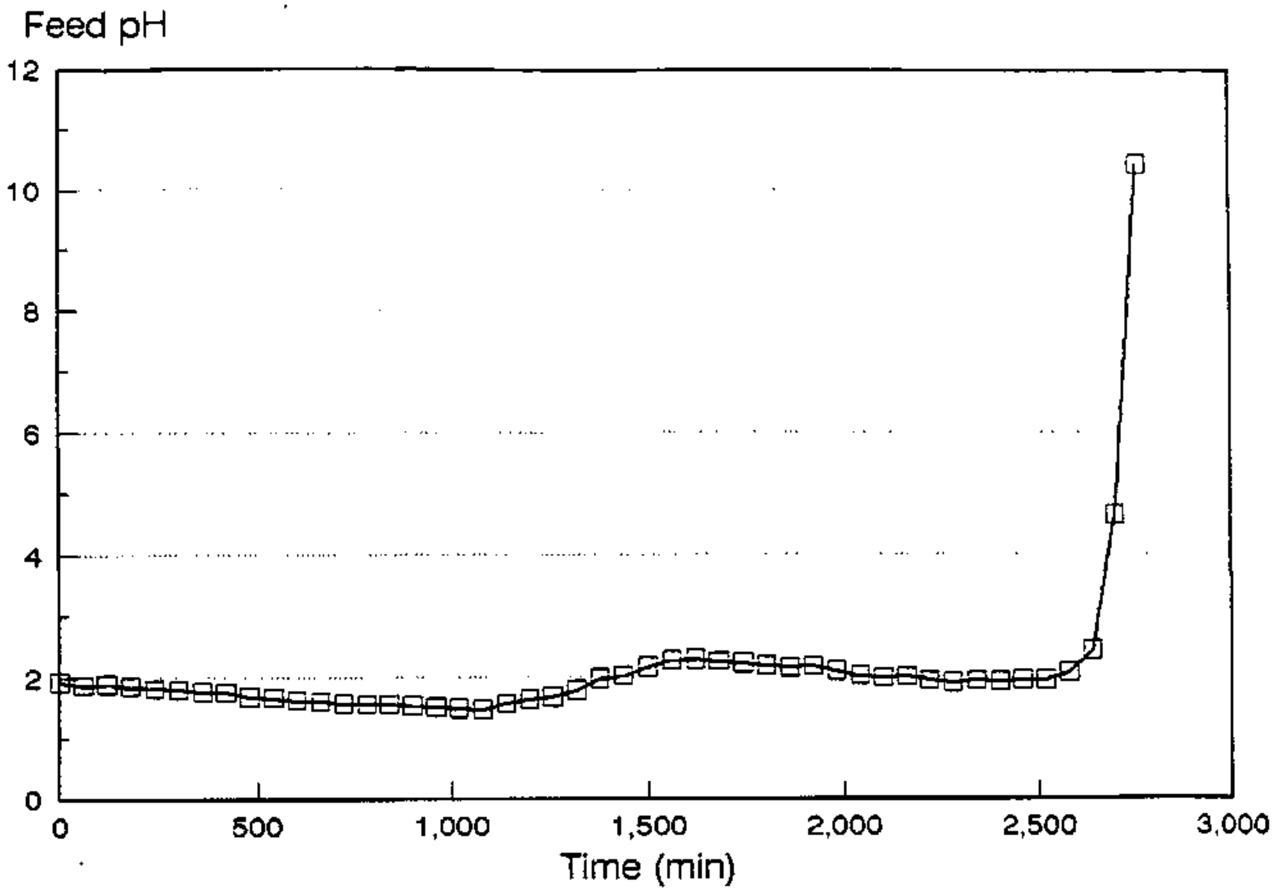


Figure 42 : Feed water pH as a function of time during BED treatment of the sodium nitrate solution (run 1).

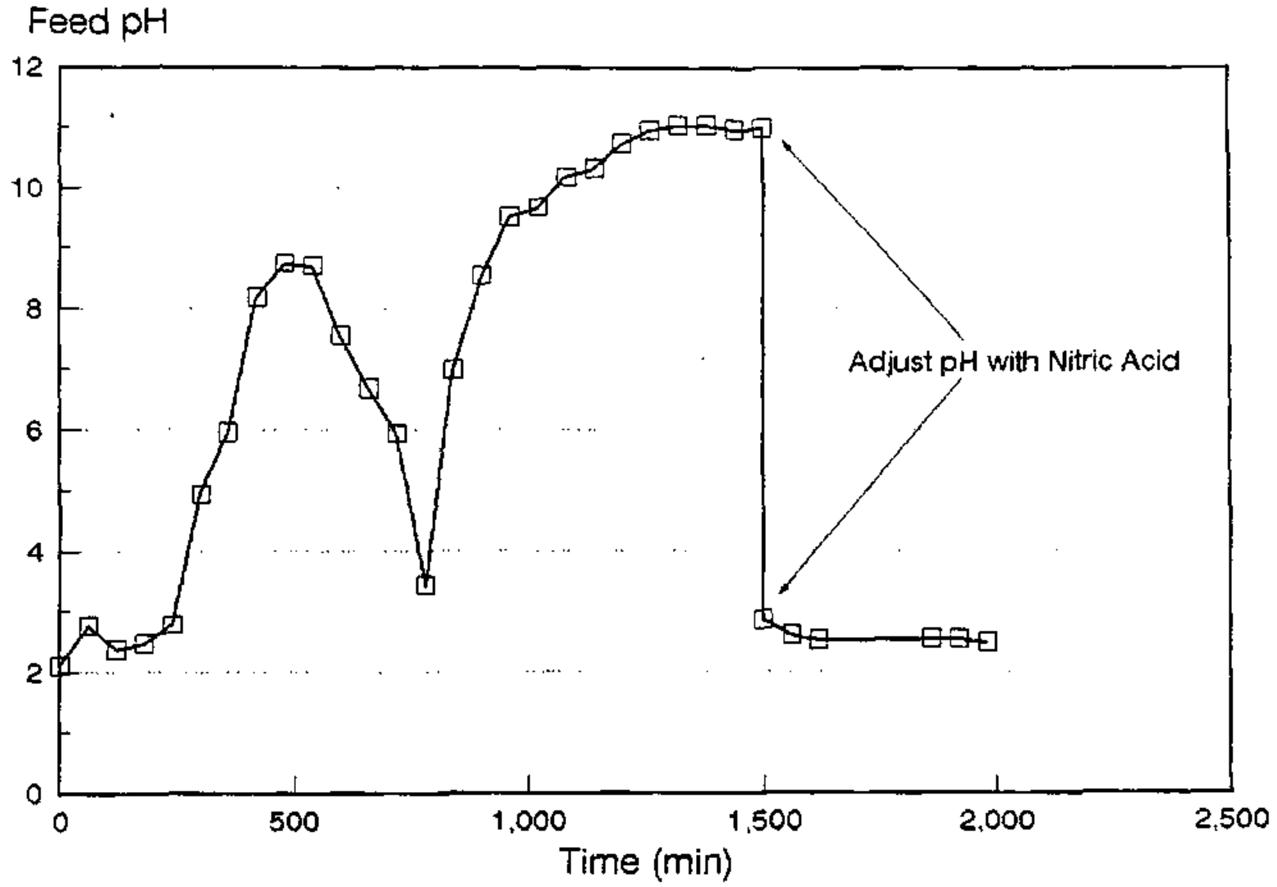


Figure 43 : Feed water pH as a function of time during BED treatment of the sodium nitrate solution (run 2).

The acid and base concentration levels in the different batches and current efficiency and electrical energy consumption are shown in Table 26.

Table 26 : Energy consumptions, current efficiencies and concentrations of acid and base batches during BED treatment (runs 1 and 2)

Parameters	Nitric acid			Sodium hydroxide		
	Run 1		Run 2	Run 1		Run 2
	Batch 1	Batch 1	Batch 1	Batch 1	Batch 2	Batch 1
Energy consumption (kWh/ton)	2 075	2 020	1 877	2 936	3 326	2 995
Current efficiency (%)	69,19	71,07	76,43	77,03	68,01	75,52
Concentration (N)	2,05	2	2	1,89	1,963	1,913

Acid and base concentration levels of approximately 2 mol/ℓ could be obtained with ease (Table 26 and Figures 44 and 45). Electrical energy consumption was determined at approximately 3 000 kWh/ton base. Current efficiency for acid production varied between 69 and 76 percent and for base production between 68 and 77 percent.

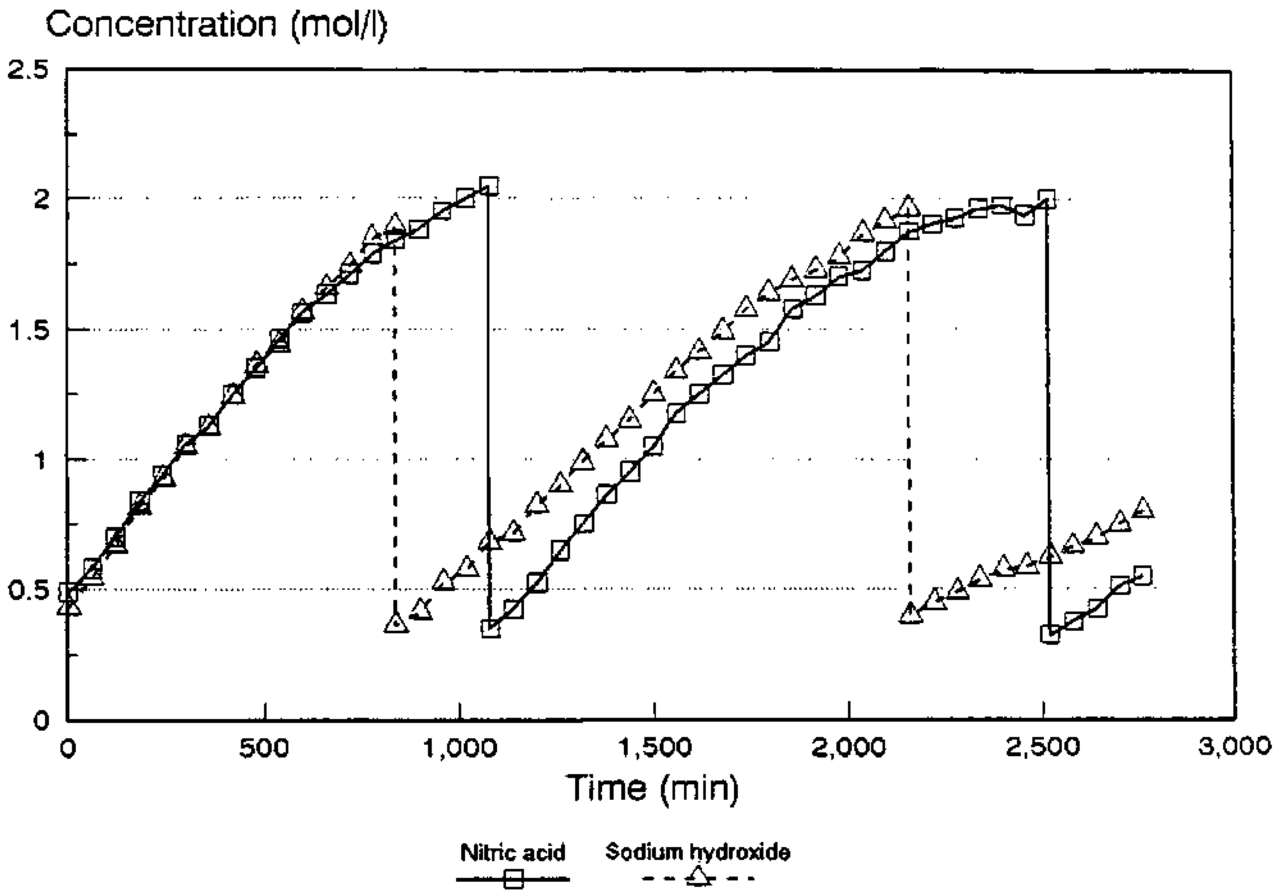


Figure 44 : Acid and base concentrations as a function of time during BED treatment of the sodium nitrate solution (run 1).

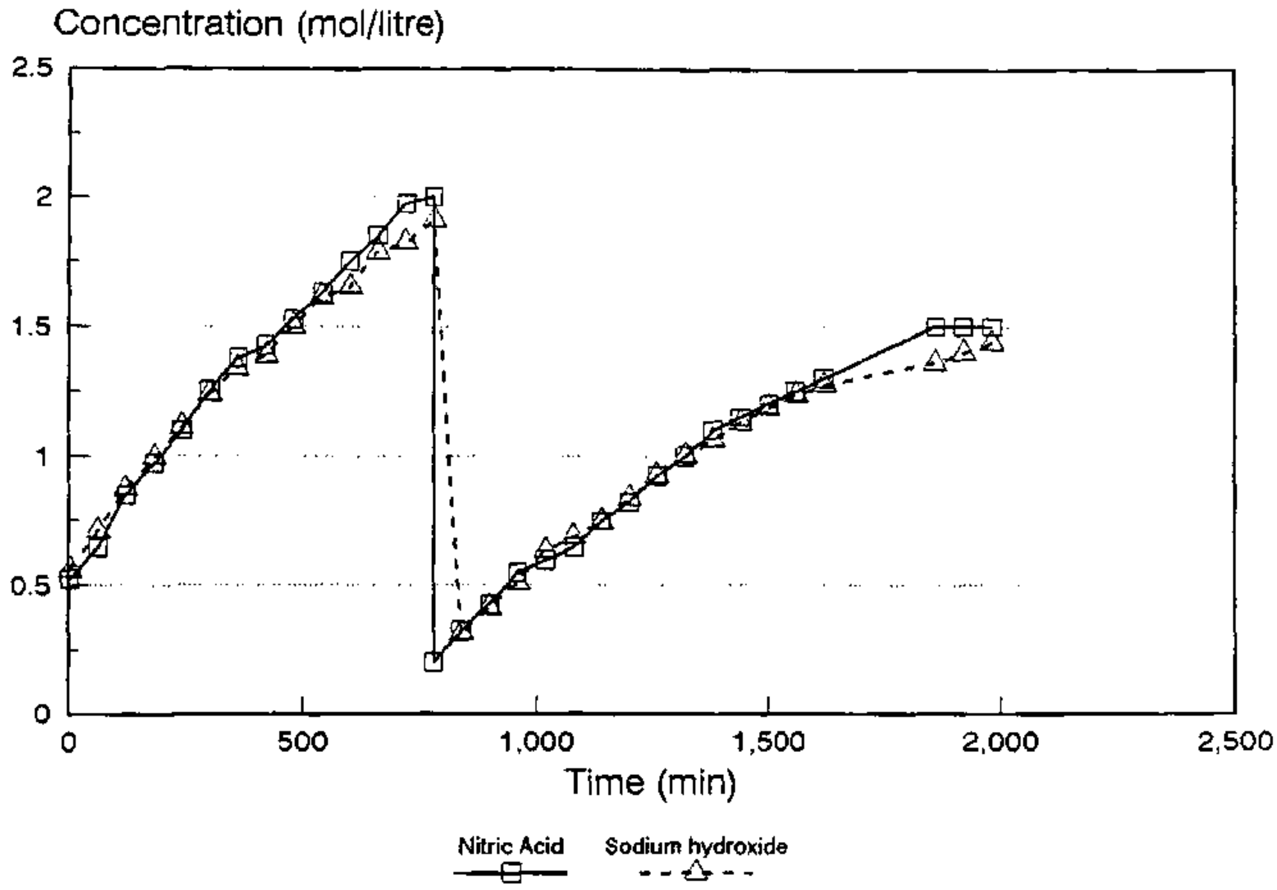


Figure 45 : Acid and base concentrations as a function of time during BED treatment of the sodium nitrate solution (run 2).

4.7 Treatment of Sodium Sulphate Effluent with Bipolar Electrodialysis

The sodium and sulphate concentration levels in the BED feed as a function of time are shown in Table 27 for the two runs that were conducted.

Approximately 95 and 92 percent sodium and sulphate were removed from the feed, respectively. The sulphate concentration during the second run was significantly higher than during the first run and 88 and 80% sodium and sulphate were removed from the BED feed at the end of the run.

The electrical conductivity of the feed as a function of time during BED treatment of the effluent for the two runs is shown in Figures 46 and 47.

Table 27 : Sodium and sulphate concentration levels in the BED feed as a function of time (runs 1 and 2).

Time (min)	Sodium (mg/ℓ)	Sulphate (mg/ℓ)
Run 1 (10% sodium sulphate)		
0	24 800	71 100
1 440	13 600	48 800
2 640	8 840	32 600
4 020	4 110	18 100
5 460	1 220	6 000
Run 2 (20% sodium sulphate)		
0	50 100	141 500
960	51 200	128 300
2 040	42 800	112 200
2 940	32 100	94 200
3 960	18 000	70 900
5 040	8 660	39 600
5 280	7 300	33 300
5 520	6 020	27 600

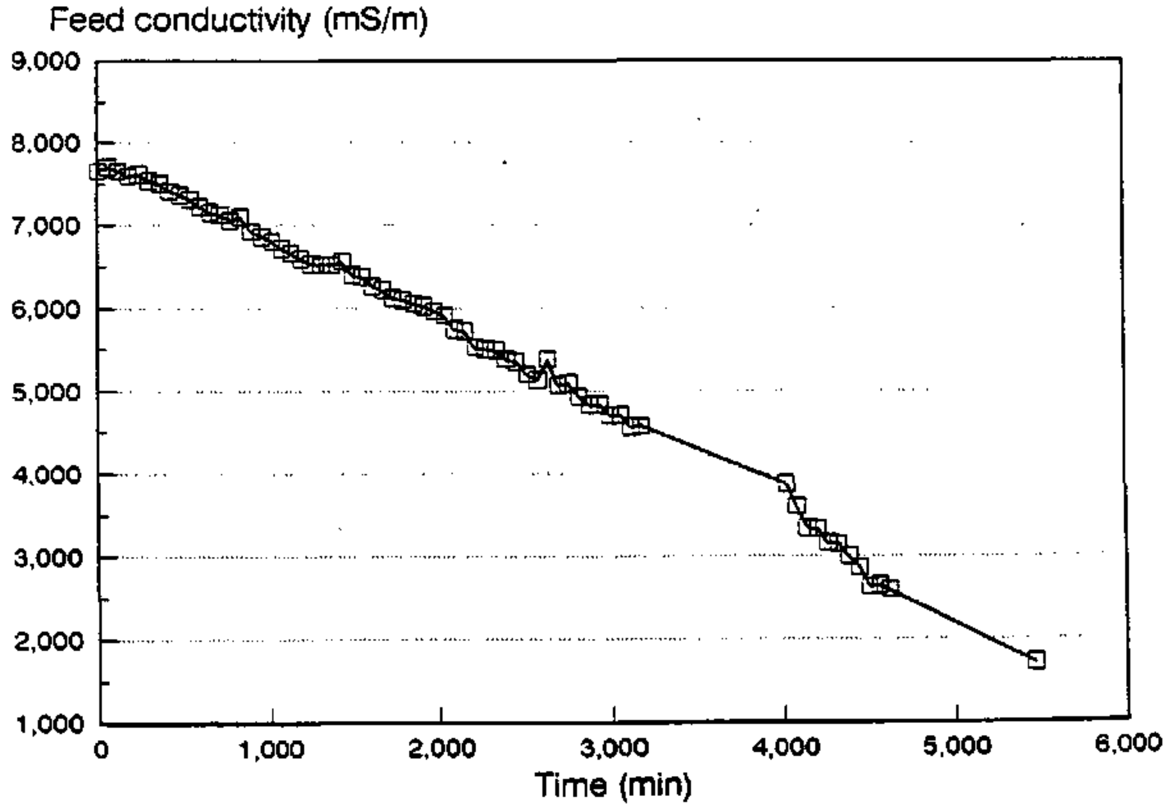


Figure 46 : Feed conductivity as a function of time (run 1)

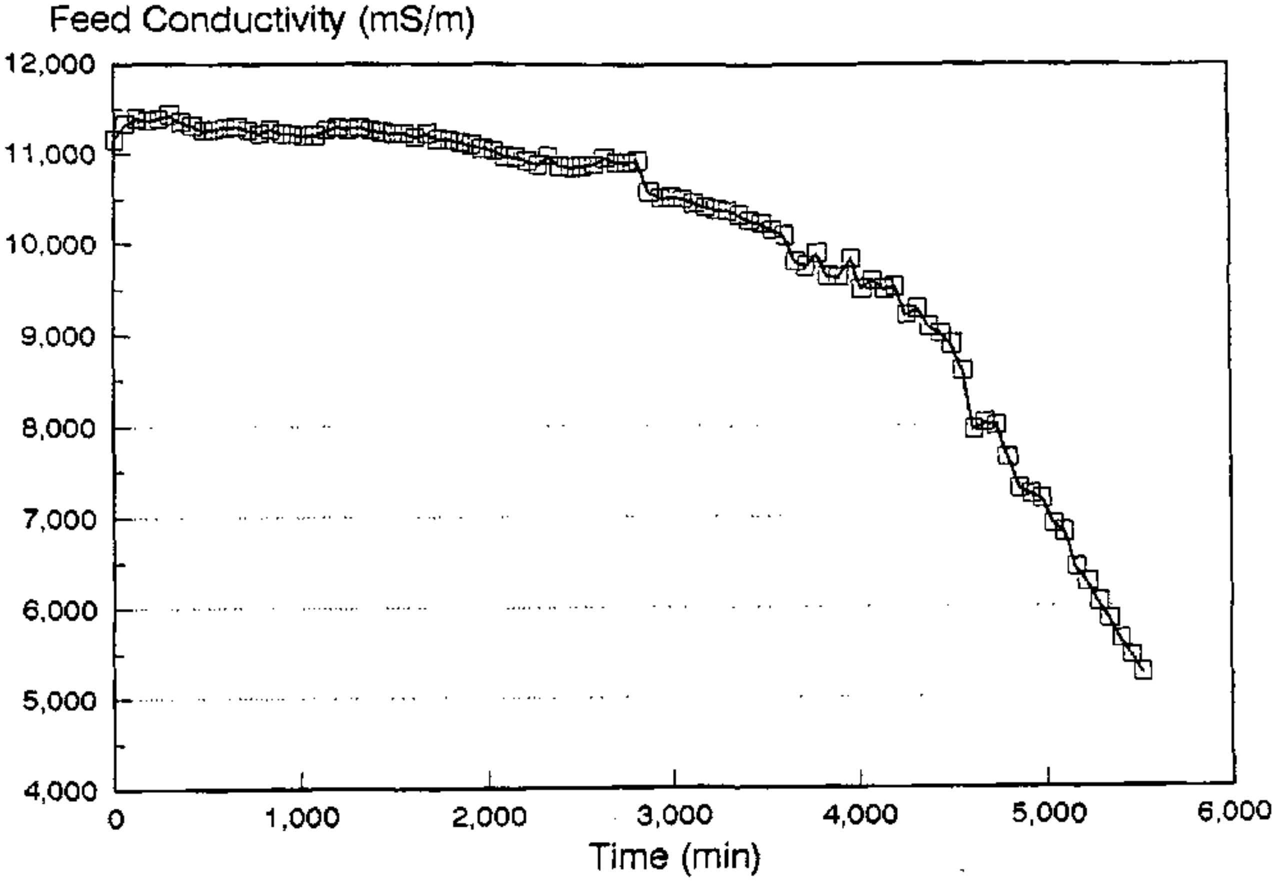


Figure 47 : Feed conductivity as a function of time (run 2)

The electrical conductivity of sample 2 (run 2) was significantly higher than that of sample 1. Conductivity decreased rapidly as a function of time when the lower conductivity sample was electrodialysed. However, conductivity initially decreased much slower when the higher conductivity sample was electrodialysed. Conductivity started to decline much faster when a significant amount of the sodium sulphate had been converted into acid and base.

The electrical current as a function of time during BED treatment of the two effluent samples is shown in Figures 48 and 49. The electrical current decreases rapidly after batching. The electrical current also decreased as a function of time when more salt was removed from the feed.

The pH of the feed during BED treatment of the effluent is shown in Figures 50 and 51.

No acid was added to sample 1 before the run. The pH of the feed declined rapidly and remained at approximately pH 1 until the end of the run. The pH of the second sample was reduced to a pH of approximately 3 before the run. The pH of the feed declined further as a function of time and remained at a pH between approximately 1 and 1,5 until the end of the run.

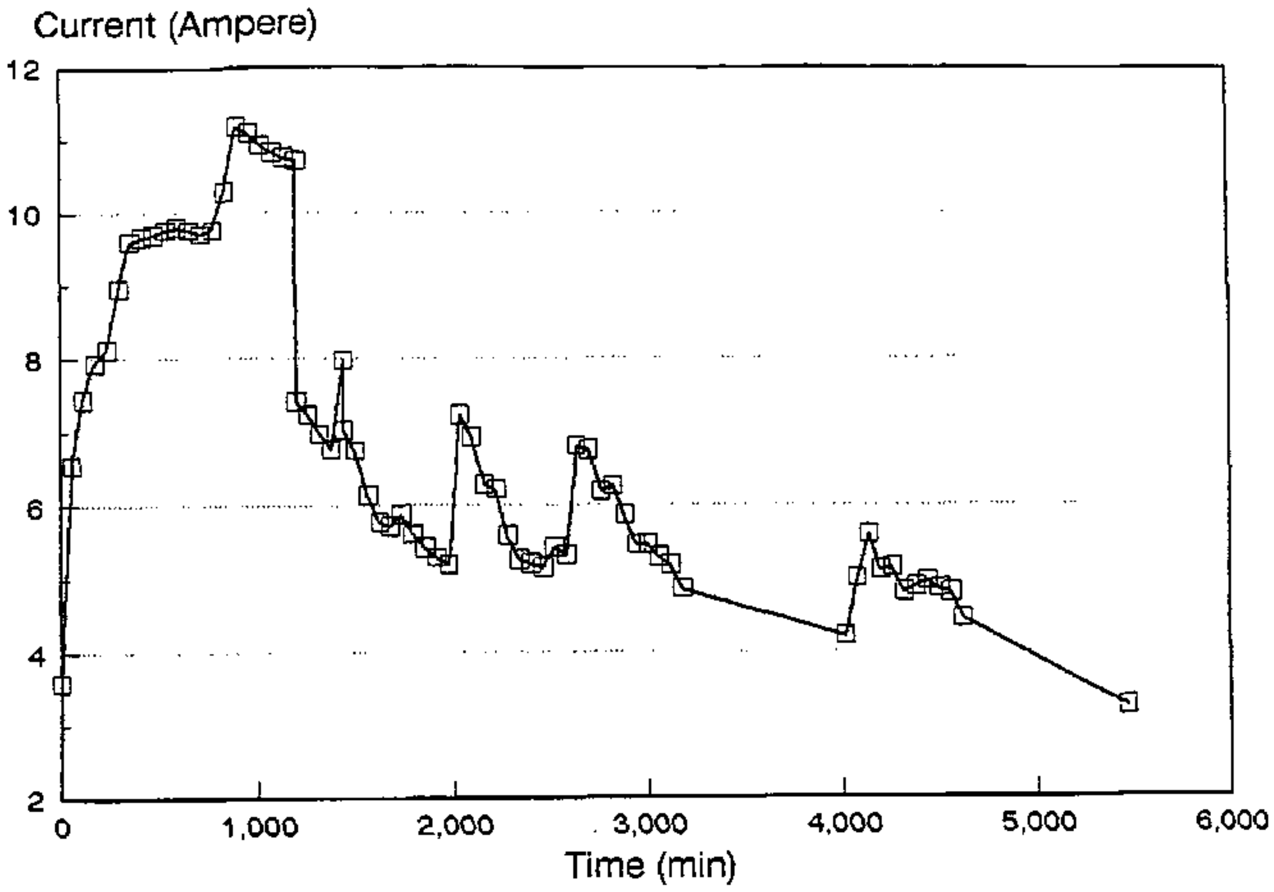


Figure 48 : Electrical current as a function of time (run 1)

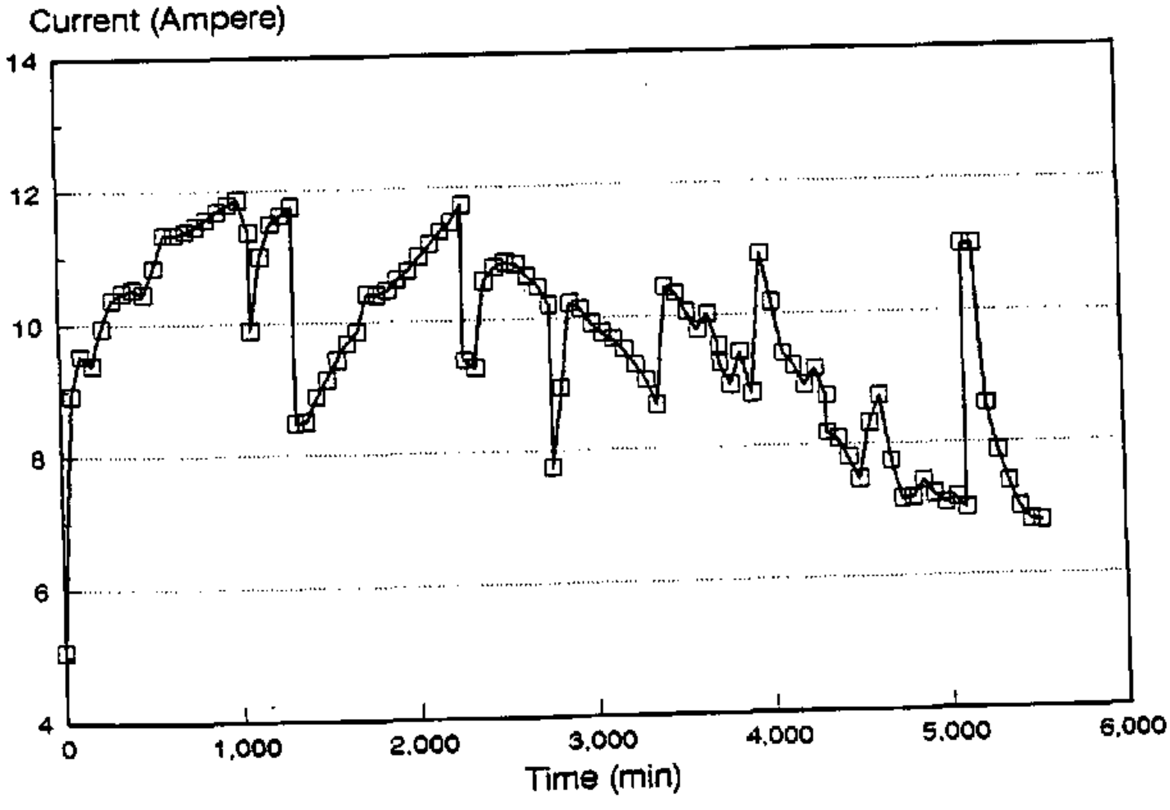


Figure 49 : Electrical current as a function of time (run 2).

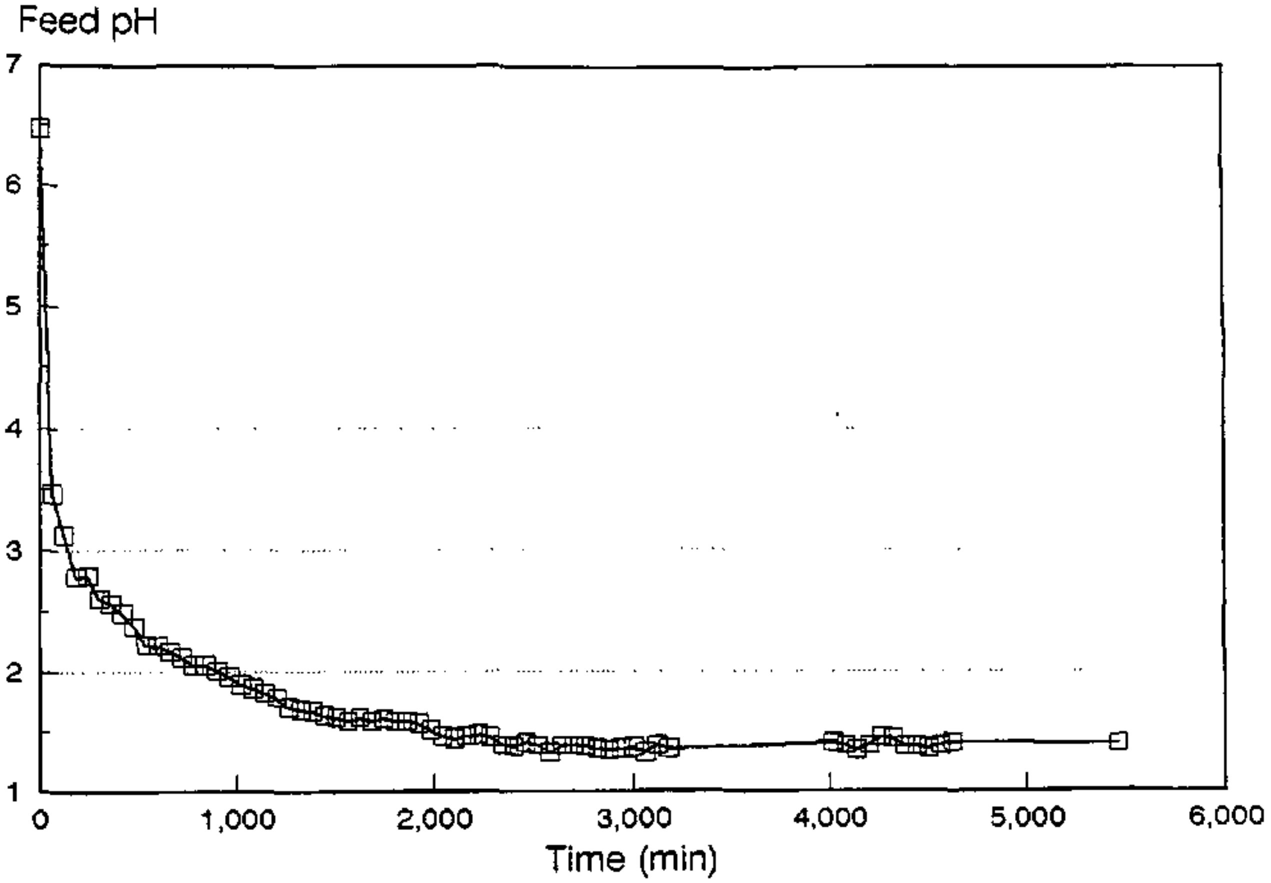


Figure 50 : **Feed pH as a function of time (run 1).**

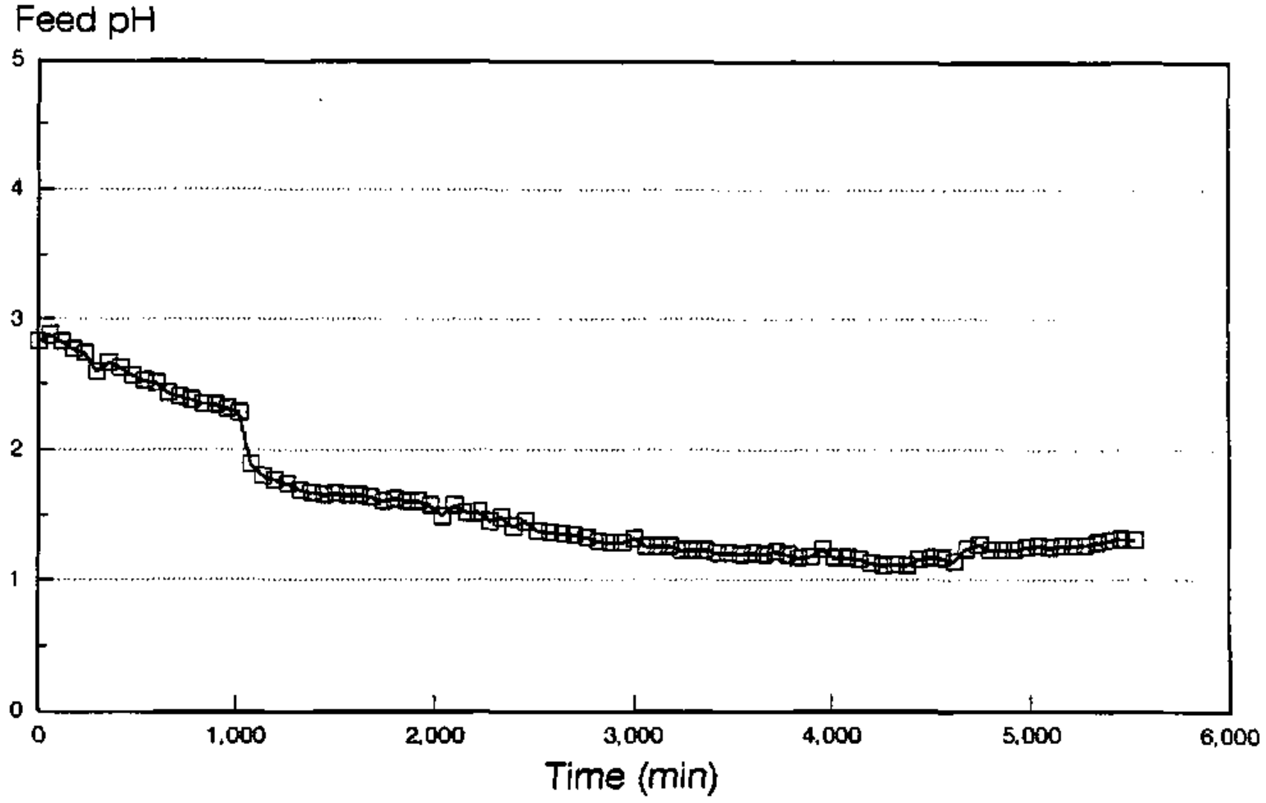


Figure 51 : **Feed pH as a function of time (run 2)**

The acid and base concentration levels in the different batches and the impurities in the batches are shown in Tables 28 and 29, respectively. The acid and base concentration levels during BED treatment are shown in Figures 52 and 53 for the two runs.

Table 28 : Chemical composition of acid product (runs 1 and 2)

	Run 1		Run 2		
	Batch 1	Batch 2	Batch 1	Batch 2	Batch 3
Concentration (N)	1,975	2,125	2,05	2,013	2
Sodium (mg/ℓ)	991	3 490	1 660	1 930	1 840

Table 29 : Chemical composition of base product (runs 1 and 2)

	Run 1		Run 2		
	Batch 1	Batch 2	Batch 1	Batch 2	Batch 3
Concentration (N)	2	1,9	1,925	1,9	1,925
Sulphate (mg/ℓ)	288,1	691,5	1 115	836	716

Acid and base concentration levels of approximately 2 mol/ℓ could be obtained with ease. It is interesting to note that it takes much longer to reach a concentration level of 2 mol/ℓ after the first batching (Figure 52). The could be ascribed to the lower feed concentration level. This was also noticed during run 2 (higher feed concentration) towards the end of the run (Figure 53).

The sodium concentration level in the acid product varied between approximately 1 and 3,5 g/ℓ (Table 28). The sulphate in the base product varied between approximately 0,3 and 1,1 g/ℓ .

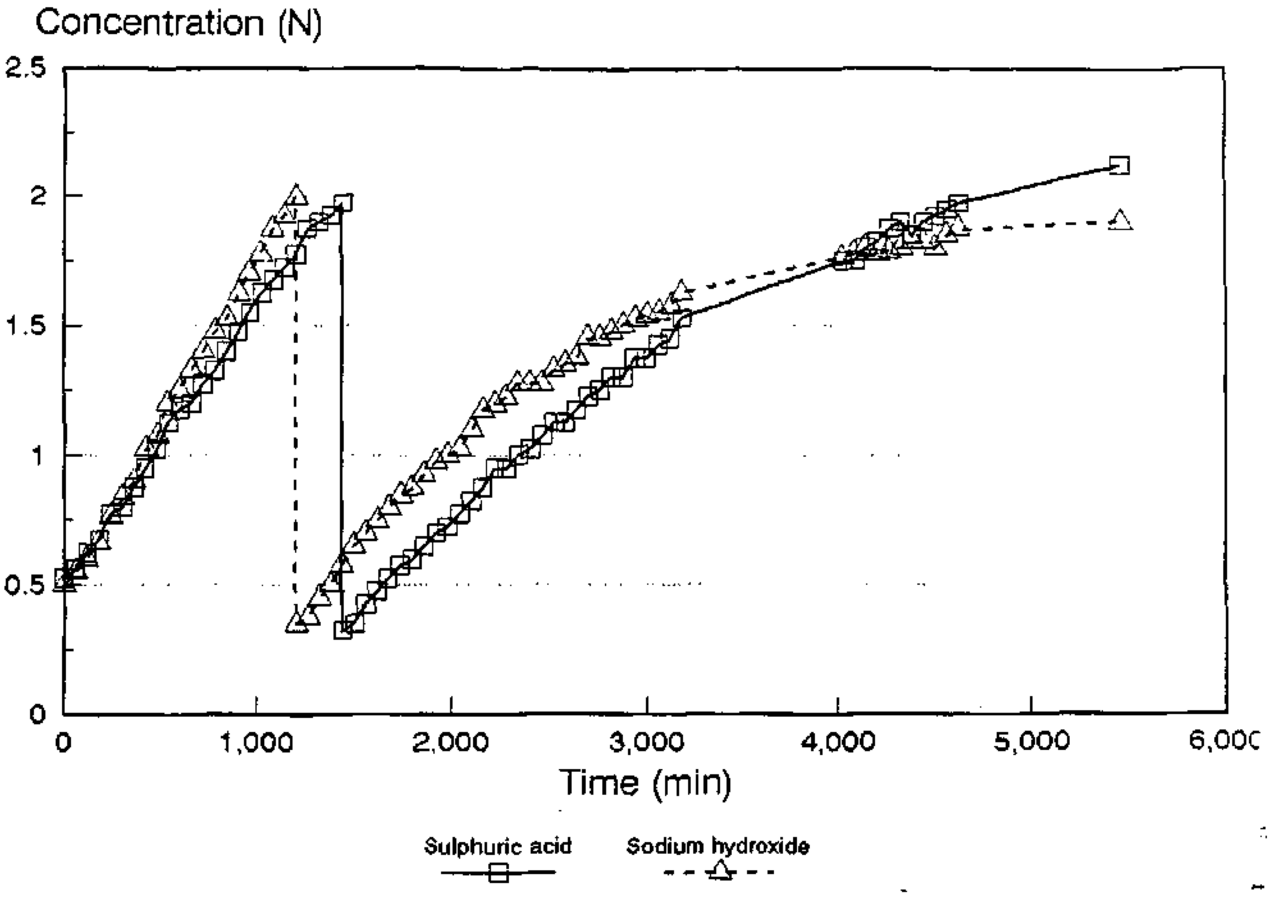


Figure 52 : Acid and base concentration as a function of time (run 1).

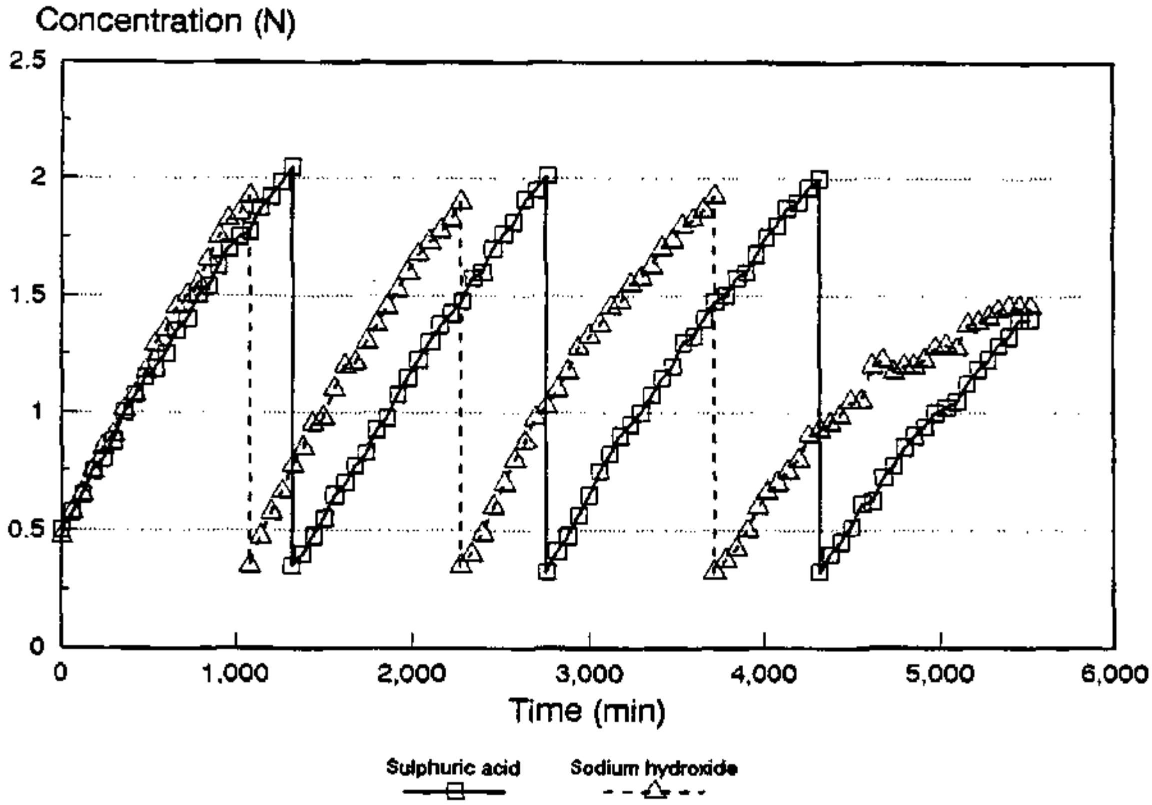


Figure 53 : Acid and base concentration as a function of time (run 2).

The current efficiency and electrical energy consumption for the different acid and base batches are shown in Tables 30 and 31.

Table 30 : Current efficiencies and energy consumption for the different acid batches (runs 1 and 2).

Acid Batches	Concentration (mol/ℓ)	Current efficiency (%)	Energy consumption (kWh/ton Acid)
Run 1			
Batch 1	1,975	49,11	3 760
Batch 2	2,125	39,91	4 620
Run 2			
Batch 1	2,05	48,92	3 771
Batch 2	2,013	43,94	4 199
Batch 3	2,000	49,94	3 694

Table 31 : Current efficiencies and energy consumption for the different base batches (runs 1 and 2).

Base Batches	Concentration (mol/ℓ)	Current efficiency (%)	Energy consumption (kWh/ton Base)
Run 1			
Batch 1	2,000	64,61	3 500
Batch 2	1,900	34,61	6 540
Run 2			
Batch 1	1,925	60,40	3 745
Batch 2	1,900	59,14	3 825
Batch 3	1,925	53,53	4 225

Current efficiency for acid production (Table 30) varied between approximately 40 and 49 percent for run 1 and between approximately 44 and 50 percent for run 2. Higher current efficiencies were expected (approximately 70%). The electrical energy consumption for acid production varied between approximately 3 800 and 4 600 kWh/ton acid (run 1) and between approximately 3 700 and 4 200 kWh/ton acid (run 2). The low current efficiencies obtained might be ascribed to membrane plugging.

Current efficiency for base production varied between approximately 36 and 65 percent (Table 31) for run 1 and between approximately 54 and 60 percent for run 2. It is interesting to note that a low current efficiency is obtained when the feed solution becomes more diluted (run 1, batch 2, Table 30). The electrical energy consumption for base production varied between approximately 3 500 and 6 500 kWh/ton base (run 1) and between approximately 3 700 and 4 200 kWh/ton base (run 2). The low current efficiencies that were obtained for base production could also be ascribed to membrane plugging. This matter, however, needs further investigation.

4.8 Treatment of Sodium Acetate Effluent with Bipolar Electrodialysis

The sodium concentration level in the BED feed as a function of time is shown in Table 32.

Approximately 95 percent sodium was removed from the feed water.

The electrical conductivity of the feed as a function of time during BED treatment of the effluent is shown in Figure 54.

The electrical conductivity of the feed water decreased steadily as a function of time. The conductivity of the feed water decreased from 7 320 to 525 mS/m after 2 460 minutes of operation.

Table 32 : Sodium concentration level in the BED feed as a function of time.

Time (min)	Sodium (mg/ℓ)
0	30 800
240	26 200
480	23 300
780	23 100
960	19 740
1 200	15 570
1 440	11 980
1 560	10 350
1 800	6 890
2 040	4 720
2 280	2 420
2 460	1 528

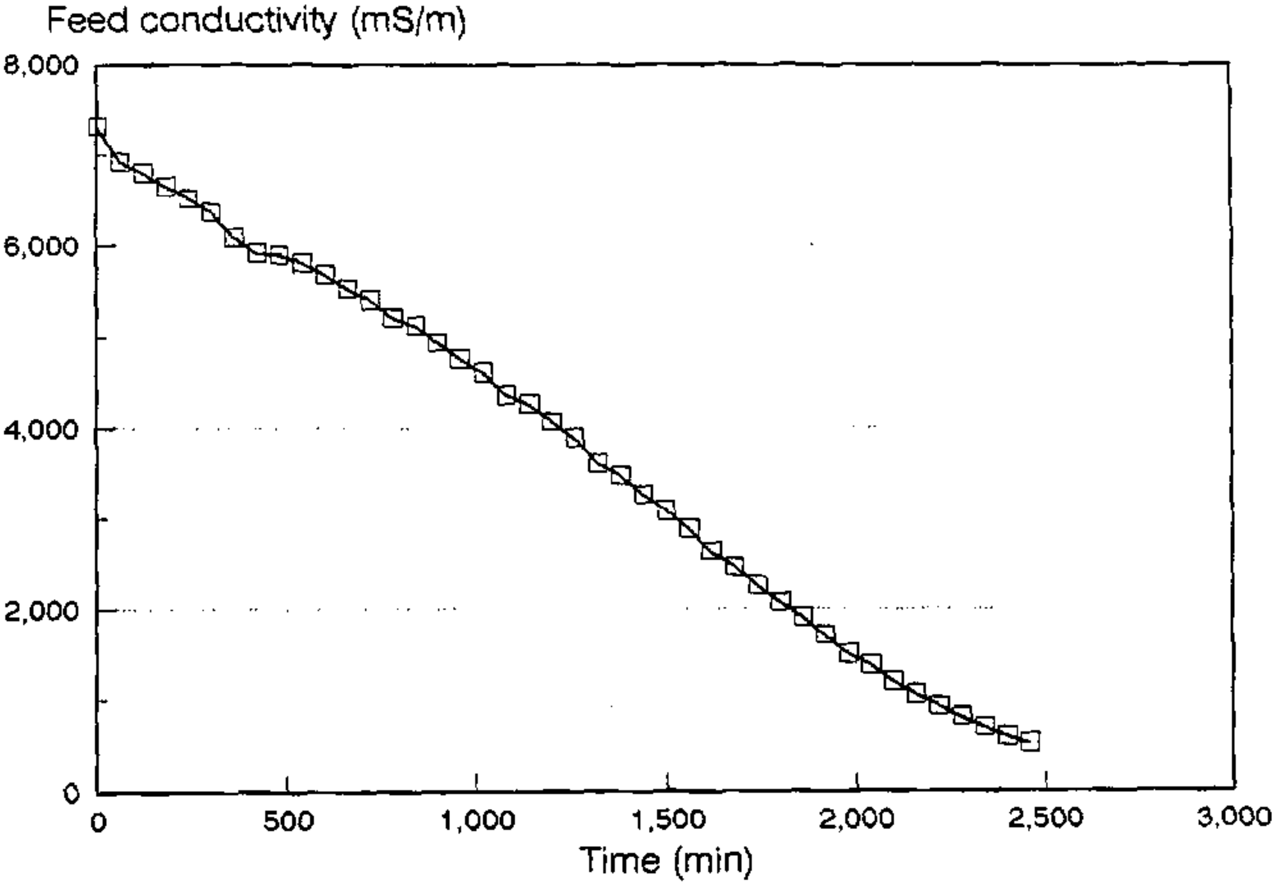


Figure 54 : Feed conductivity as a function of time.

The electrical current and voltage as a function of time during BED treatment of the effluent sample are shown in Figures 55 and 56. The electrical current was kept constant at 14 ampere for the first 1 500 minutes of the run while the voltage was allowed to vary. This was done to prevent the current from exceeding 16 ampere, which is the maximum capacity for the power pack. The voltage was kept constant, when the voltage across the stack had risen to 27 V, which is the maximum recommended voltage by the supplier. The voltage was kept constant at 27 V from 1 500 to 2 460 minutes while the current was allowed to vary.

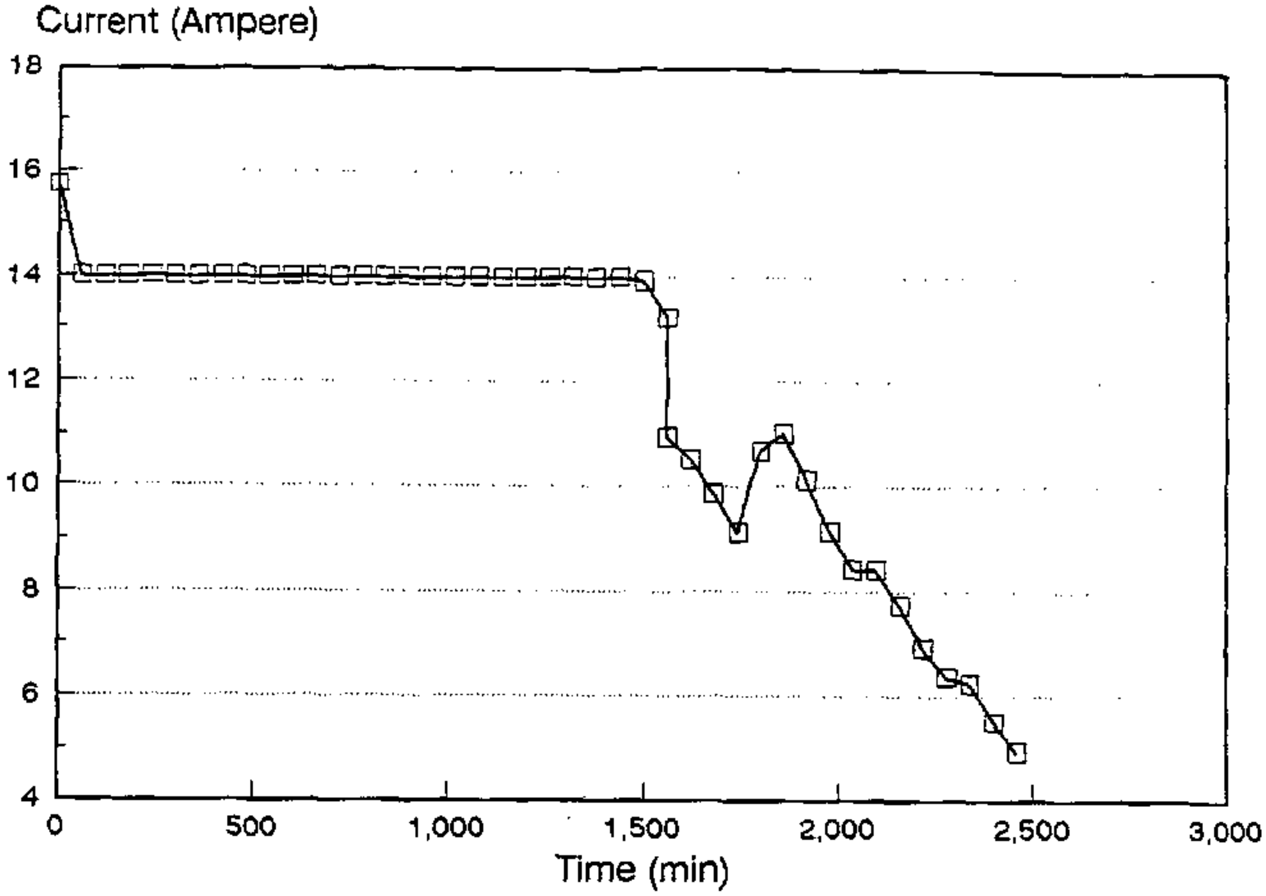


Figure 55 : Electrical current as a function of time.

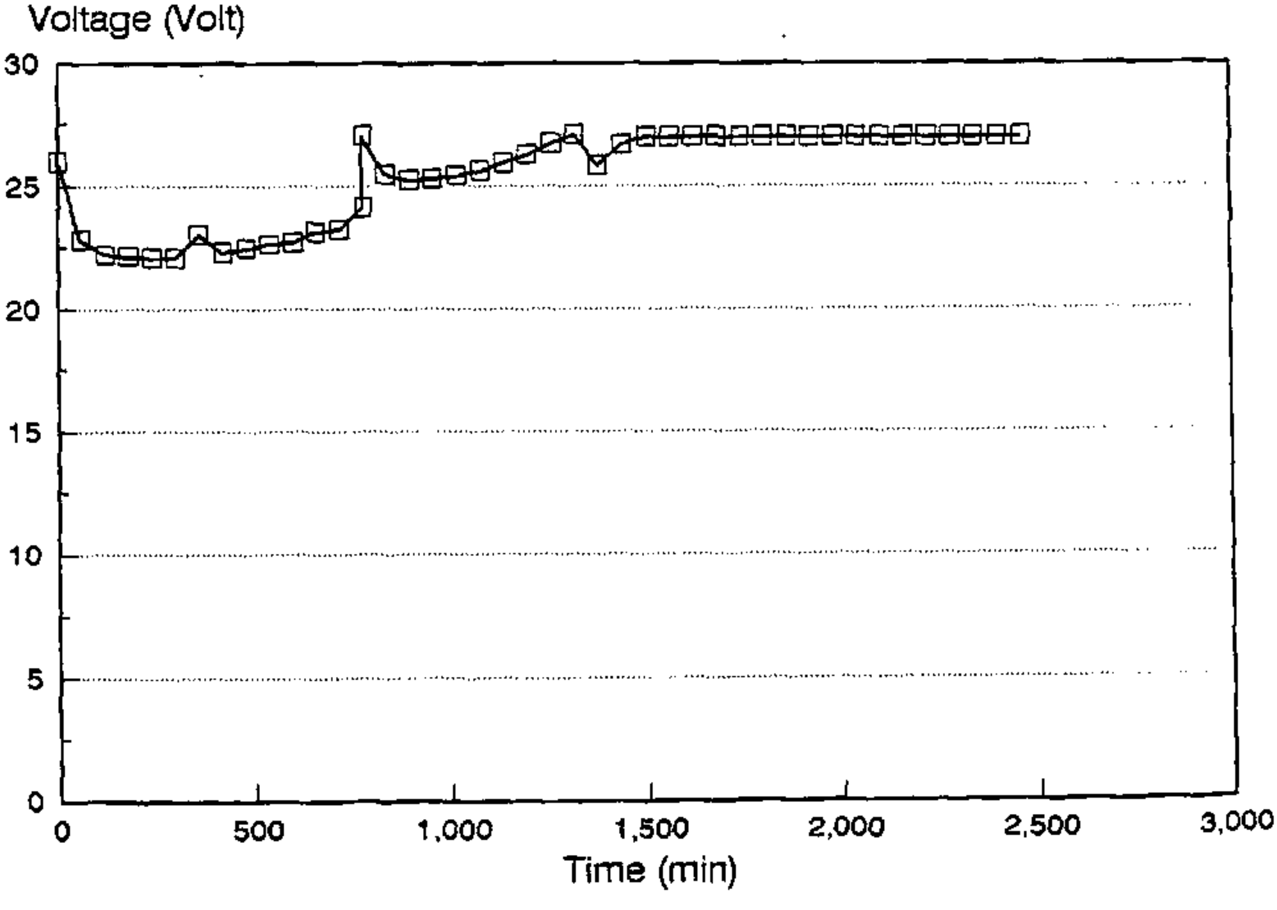


Figure 56 : Voltage as a function of time.

The pH of the feed during BED treatment of the effluent is shown in Figure 57.

The pH of the feed water was 12,49 when the run commenced. The pH of the feed decreased rapidly to 7,45 after 60 minutes of operation and then kept on decreasing at a slower rate as the acid concentration in the feed increased.

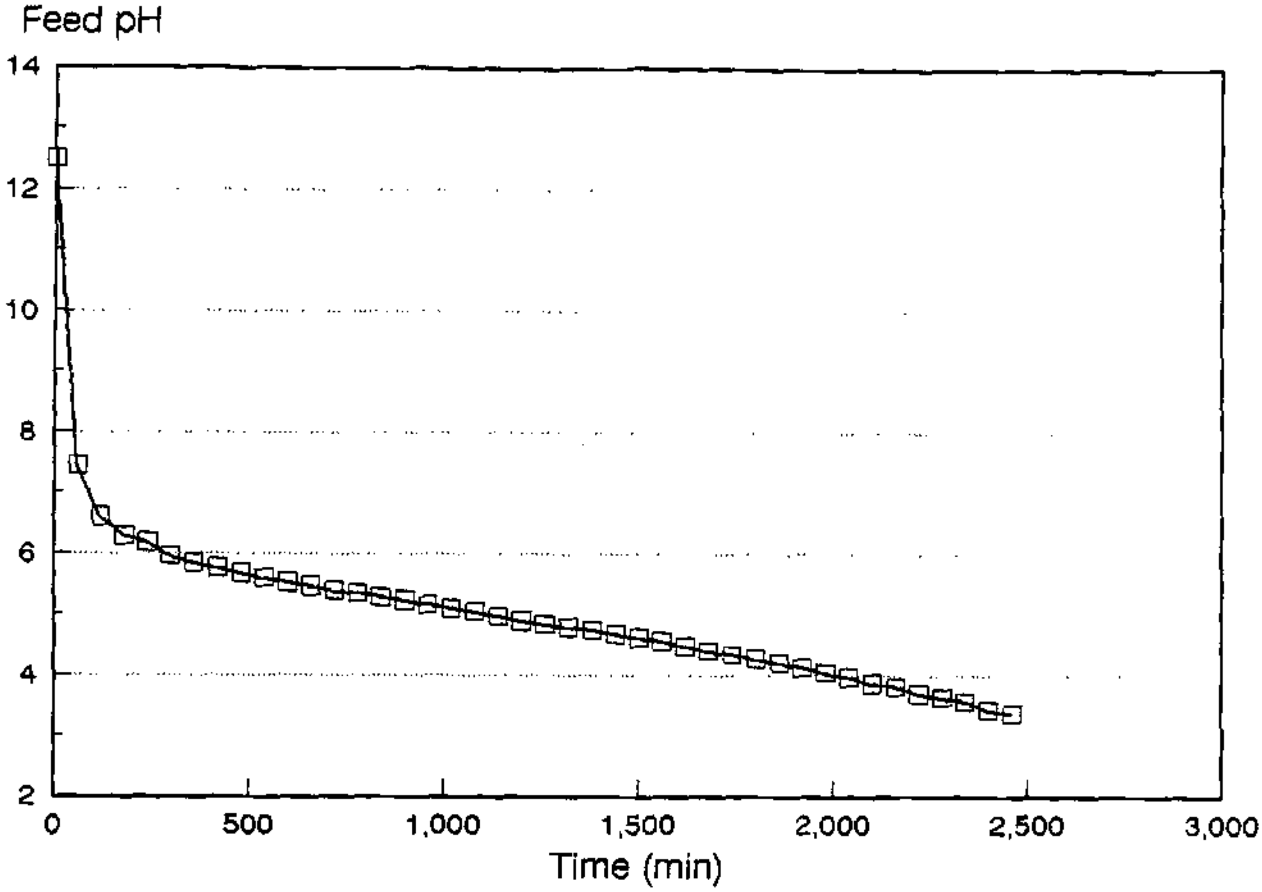


Figure 57 : Feed pH as a function of time.

The base concentration level in the different base batches are shown in Table 33. The acid and base concentration levels during BED treatment is shown in Figure 58.

Table 33 : Chemical composition of base product.

Batch	Concentration (mol/ℓ)
1	1,925
2	1,900

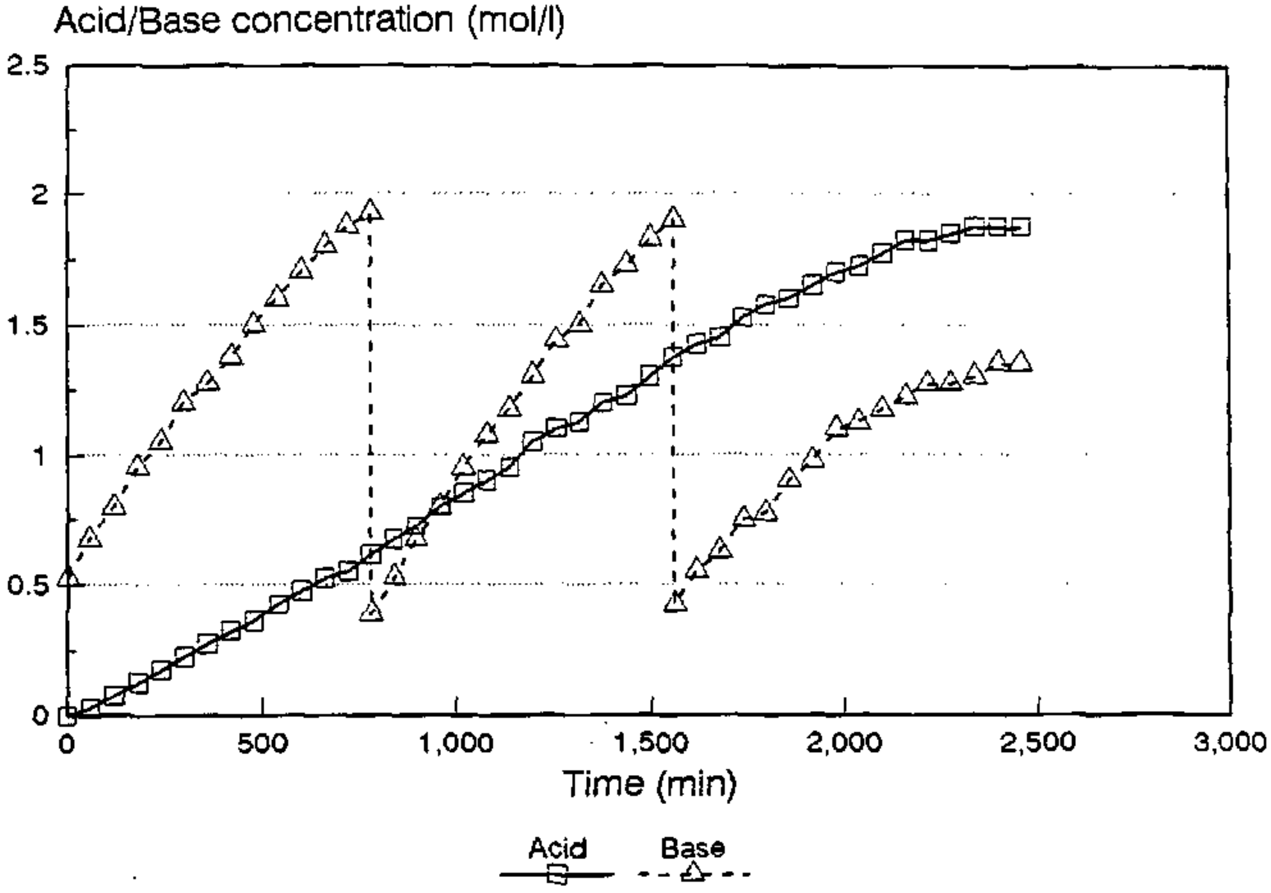


Figure 58 : Acid and base concentration as a function of time.

The acid concentration in the acid/salt loop reached a concentration of 1,875 mol/ℓ when the run was terminated. The concentration of sodium in the acid was 1 528 mg/ℓ . Base concentration levels of approximately 2 mol/ℓ could be obtained with ease. The time needed for the two base batches were the same (780 minutes) (Figure 58). The base concentration levelled off at the end of the run and was 1,350 mol/ℓ when the run was terminated.

The current efficiency and electrical energy consumption for the different acid and base batches are shown in Tables 34 and 35, respectively.

Current efficiency for acid production (Table 34) was 56,48 percent. The electrical energy consumption for acid production was 2 285 kWh/ton acid.

Table 34 : Current efficiency and energy consumption for the acid batch.

Acid Batch	Concentration (N)	Current efficiency (%)	Energy consumption (kWh/ton Acid)
Batch 1	1,875	56,48	2 285

Current efficiency for base production varied between approximately 51 and 60 percent. The electrical energy consumption for base production varied between approximately 3 100 and 3 500 kWh/ton base. The low current efficiencies and high energy consumption for base production might be ascribed to plugged membranes. The anion selective membranes have previously been used for other applications and were stained white with blisters on the membranes. This matter, however, needs further investigation.

Table 35 : Current efficiencies and energy consumption for the different base batches.

Base Batch	Concentration (N)	Current efficiency (%)	Energy consumption (kWh/ton Base)
Batch 1	1,925	56,87	3 183
Batch 2	1,90	58,81	3 430

4.9 Economics

4.9.1 Treatment of nickel drag-out with electrodialysis

The economics of the EDR process for nickel and salt recovery from electroplating rinse water is shown in Table 36[14]. Plant payback for two case studies was determined at 1,7 and 2,6 tears. Fromonot[15] has determined a 1,5 year payback period for nickel and water recovery from nickel drag-out. Therefore, it appears that it will be economical to recover nickel and water from nickel drag-out in the electroplating industry.

Table 36 : Economics of electrodialysis reversal process for nickel salt recovery from plating rinse water.

Item		North Central Plant	Eastern Seabord Plant
1	Installed Cost		
	- Equipment	50 000	100 000
	- Installation, labour and materials	1 500	1 500
	- Total	51 500	101 500
2	Annual Operating Cost (Estimated		
	- Labour, 100 hours/year @ $10/hour	1 000	1 000
	- Maintenance @ 2½% of investment	1 250	2 500
	- Raw Materials		
	Filter Cartridges	750	1 000
	Membrane Replacement[1]	3 000	6 000
	- Electricity ($0,05/kWh)	750	1 500
	- Total	6 750	12 000
3	Annual Fixed Cost		
	- Depreciation, 10% of investment	5 150	10 150
	- Tax and Insurance, 1% of investment	515	1 015
	- Total Fixed Cost	5 665	11 165
4	Total Cost of Operation	12 415	23 165
5	Annual Savings		
	- Plating Chemicals	21 000	110 000
	- Sludge Disposal Cost[2]	6 000	6 600
	- Water Treatment Chemicals	1 100	2 200
	- Water Usage	1 200	
	- Total	40 100	118 800
6	Net Savings (annual savings - (operating + fixed cost))	27 685	95 635
7	Net Savings after Tax 48% Tax Bracket	14 397	49 730
8	Average ROI (%) (Net savings after tax/total/investment	27,9	49,0
9	Cash flow form Investment (net savings after tax + depreciation)	19 547	59 880
10	Payback Period = Total Investment / Cash Flow	2,6	1,7

[1] Assuming 2 year membrane life

[2] @ 35% solids for North Central plant and @ 94% solids for Eastern Seabord plant.

4.8.2 Treatment of spent pickling acid effluent with bipolar electrodialysis and a combination of bipolar electrodialysis and diffusion dialysis.

Material balances for the BED and of a combination of the diffusion dialysis and BED processes were derived from the chemical composition of the spent pickling acid effluent shown in Table 15. The results are shown in Tables 37 and 38 respectively.

Table 37 : Material balance for BED process

Capacity : 1 750 ℓ/h (approximately)

Concentration feed
Total HNO_3 : 176,2 g/ℓ
Free HNO_3 : 149,9 g/ℓ
Total HF : 64,4 g/ℓ
Free HF : 23,7 g/ℓ
Metals : Fe : 49,7 g/ℓ
Ni : 6,7 g/ℓ
Cr : 4,9 g/ℓ

Products
3 200 kg/h of acid with :

105 kg/h HF - 3,3% (m)
304 kg/h HNO_3 - 9,5% (m)

Metal cake : approximately 450 kg/h at 35% (m)

Table 38 : Material balance for a combination of the diffusion dialysis and BED processes.

Capacity :	1 750 ℓ/h (approximately)
Concentration feed	
Free HNO_3 :	24,8 g/ℓ
Total HNO_3 :	54,6 g/ℓ
Free HF :	9,2 g/ℓ
Total HF :	49,8 g/ℓ
Metals : Fe :	49,7 g/ℓ
Ni :	6,7 g/ℓ
Cr :	4,9 g/ℓ
Products	
1 700 kg/h of acid[*] with :	
81,3 kg/h HF -	4,8% (m)
94,3 kg/h HNO_3 -	5,6% (m)
Metal cake : approximately 450 kg/h at 35% (m)	

[*] The acid will be mixed with the product acid of the diffusion dialysis process and concentrated to the required level with an evaporation process.

The economics of the BED and a combination of the diffusion dialysis and BED processes for effluent treatment are shown in Tables 39 and 40, respectively.

Table 39 : Economics of the BED process for treatment of 1 750 ℓ/h of spent pickling acid effluent

Capital Investment[1]	:	Approximately R14 872 000
Operating Expenses[2]		
Membranes[3] (annual cost)	:	R2 717 000
DC power stack (avg)	:	1 400 kW
Cooling	:	1 200 kW
KOH (make-up)	:	23,2 kg/h (100% basis)

[1] Including filtration, neutralisation, ED, BED, membranes, building, site-work, etc. Building accounts for approximately R858 000 in the above estimate. Diffusion dialysis and evaporation are not included.

[2] Labour : 2 persons / shift if filtration is not automatic

[3] Excluding freight and duty : ED and BED membranes

Note : 1 US $ - R2,86.

Table 40 : Economics of the diffusion dialysis and BED processes for treatment of 1 750 ℓ/h of spent pickling acid effluent.

Diffusion Dialysis		
Capital investment	:	approximately R3 262 955[1] (R2 303 280)[2]
Operating Expenses		
Membranes (annual cost)	:	R 1 314 779
Spare parts for pumps	:	R 34 549
Electricity	:	14 kW
Bipolar Electrodialysis		
Capital investment[3]	:	R 9 152 000
Operating Expenses[4]		
Membranes (annual)	:	R1 358 500
DC power at stack (avg)	:	700 kW
Cooling	:	590 kW
KOH (make-up)	:	14,3 kg/h (100% basis)

[1] : Based on feed liquor flow rate of 1,0 ℓ/min
[2] : Based on feed liquor flow rate of 1,5 ℓ/min
[3] : Including filtration, neutralisation, ED, BED, membranes, building, site-work, etc. Building accounts for approximately R858 000 in above estimate
[4] : Labour : 2 persons / shift if filtration is not automatic.

4.9.3 Treatment of sodium nitrate effluent with bipolar electrodialysis

Estimated cost to treat 3 600 kg per day sodium nitrate solution (10 to 15%) with BED would be as follows : -

(a) The capital investment for a plant will be approximately $ 450 000 including engineering. This would exclude membranes at an estimated cost of $ 20 000 / set with one year life and any pretreatment or site-specific cost. The expected DC power consumption would be (average) 27 kW.

The products would be 335,5 kg/d of HNO_3 at 16 wt % (100 basis) and 211,8 kg/d NaOH at 15 wt %. There will be a maximum of 2 wt % $NaNO_3$ in both acid and base products.

4.10 General Discussion

Nickel drag-out can be cost-effectively treated with ED for nickel and water recovery for reuse in the electroplating process. Plant payback period of approximately 1,5 years is possible. Membrane fouling, however, may affect process performance adversely.

Membrane fouling can be caused by additives in the plating bath. Therefore, long term pilot studies should be undertaken to evaluate membrane fouling and to develop membrane cleaning methods.

Pilot studies have indicated that a nickel concentration level of approximately 28 g/ℓ could be obtained in the ED brine when treating nickel drag-out (batch system) with a nickel concentration level of approximately 3 g/ℓ . Full-scale application, however, of an ED nickel / water recovery system (continuous system) showed that nickel concentration levels of approximately 60 g/ℓ could be obtained. The higher nickel concentration level that was obtained with the continuous ED system could be ascribed to less water transfer in the continuous ED system than was obtained with the batch ED system. Higher nickel concentration levels in the ED brine are more suitable for use in the nickel plating bath because less nickel salt make-up will be required to increase nickel concentration strength in the plating bath. A smaller volume of ED brine is also produced when the metal concentration level is higher.

It should be possible to treat chromium rinse water (approximately 1 300 mg/ℓ Cr^{6+}) effectively with ED for effluent volume reduction and pollution control. The ED product water, however, contains relatively high concentration levels of chromium (approximately 400 mg/ℓ). Consequently, ion-exchange treatment of the ED product water will be required to reduce the chromium concentration level to low values (< 0,1 mg/ℓ). It should be possible to treat the ED brine with ferrous sulphate and lime for chromium removal from the much reduced original effluent volume.

Membrane life time is an unknown factor when treating chromium rinse water with ED. Chromium may oxidise ion-exchange membranes to affect membrane properties (permselectivity, capacity, membrane resistance) adversely. Consequently, long term studies should be undertaken to evaluate the effect of chromium rinse water on ED membranes.

It appears that EED can be effectively applied for treatment of chromium drag-out. High concentration levels of chromium was obtained in the recovered chromium solution (240 g/ℓ CrO_3). This concentration level is of sufficient strength to be directly added to the plating bath. Electrical energy consumption, however, is high (approximately 38 kWh/kg CrO_3). Membrane life time and plant payback are unknown factors. However, it appears that this process will be too expensive for the electroplater.

It appears that the BED process should function effectively for treatment of spent pickling acid effluent produced by stainless steel manufacturers. It also appears that the diffusion dialysis process should function satisfactory for treatment of the spent pickling acid effluent[16]. However, effluent with a high nitrate concentration level (approximately

10 000 mg/ℓ) is produced by the diffusion dialysis process. Almost no effluent is produced with the BED process because all the products produced in the process can be recycled in the acid recovery process. Consequently, the BED process should be the ideal solution to solve the effluent problems caused by the pickling of acid.

Preliminary economics of the BED and a combination of the diffusion and BED processes have shown that it should be more economic to use a combination of diffusion dialysis and BED for effluent treatment[16]. Free acids (HNO_3 and HF) will be recovered by diffusion dialysis and complexed acids (HNO_3 and HF)) by BED. It is claimed that the BED process functions more efficiently when most of the free nitric acid is removed by diffusion dialysis and the ratio of nitric acid to hydrofluoric acid in the feed to the BED process is low. A high ratio of nitric acid to hydrofluoric acid in the feed water makes the BED process less efficient due to the relatively low permselectivity of the anion-exchange membranes for nitric acid.

It is claimed that a relatively large membrane area will be required if BED is used alone to recover the free and complexed acids from spent pickling acid effluent. Less membrane area will be required if the free acid is recovered by diffusion dialysis. Consequently, it seems that a combination of BED and diffusion dialysis is more economic than BED alone for treatment of spent pickling acid effluent.

The chemical composition of the spent pickling acid has shown that bound nitric and hydrofluoric acids are present in the effluent. Large dilution factors were used when the nitrate-nitrogen and fluoride concentration levels were determined. Consequently, inaccurate results could have been obtained and this matter warrents further investigation. The presence of relatively large quantities of bound acid in the spent pickling acid will justify the use of BED for acid recovery.

Membrane fouling can lead to the failure of membrane separation processes such as ED and BED for effluent treatment. Consequently, the fouling potential of the effluent for the ion-exchange membranes used in the process should be determined. This can only be properly studied through long term laboratory or pilot studies on real effluent. Membrane cleaning methods and the frequency of membrane cleaning can be determined in such a study. It is therefore suggested that long term laboratory or pilot studies be undertaken to evaluate the fouling potential of effluents when ion-exchange membranes are considered for effluent treatment.

Electrodialysis equipment suppliers suggest that feed water to an ED unit should be properly pretreated prior to ED to minimise membrane fouling as far as possible. Suspended solids for example, must be reduced to less than 1 NTU prior to ED treatment. Iron and manganese must be removed to less than 0,3 and 0,1 mg/ℓ in the

ED feed water, respectively. Barium and strontium must also be removed to very low concentration levels in the ED feed (< 0,1 mg/ℓ) to prevent membrane scaling. Charged organics with molecular mass less than approximately 500 must be removed from an ED feed water to protect especially the anionic membranes from fouling. Standard water treatment technologies can be applied to remove the above chemicals from effluents to acceptable levels for ED treatment.

The quality of the feed water for BED treatment should fall within certain criteria regarding the presence of metal contaminants such as iron, magnesium, calcium, chromium, nickel, etc. The concentration levels of these contaminants in BED feedwater should be below 2 mg/ℓ . Metals such as iron, chromium and nickel can be removed with simple pH adjustment followed by filtration. The presence of calcium and magnesium will necessitate further treatment with ion-exchange. The main consideration is to minimise the formation of insoluble impurities inside the BED stack and to avoid fouling of the membranes by multi-valent cationic and high molecular weight anionic material.

It appears that it should also be possible to apply BED technology effectively for acid and caustic soda recovery from sodium nitrate, sodium sulphate and sodium sulphate effluents. Effluents containing these chemicals are generated by industry and are considered as a pollution hazard. However, valuable caustic soda and acid can be recovered from these effluents with BED technology to turn pollution into profit.

The BED process is not at this stage considered to be an economic process for recovery of regenerant from waste ion-exchange regenerant. However, BED can be effectively applied for recovery of acid and caustic soda from spent ion-exchange regenerant. A lower membrane cost will be required to make the BED process an economic proposition for treatment of ion-exchange regenerant waste water.

5. CONCLUSIONS

Nickel drag-out can be cost-effectively treated with ED for nickel and water recovery in the electroplating industry. Plant payback period of approximately 2 years is possible. Pilot studies on nickel drag-out showed that nickel in the ED feed could be concentrated from 3,5 g/ℓ to approximately 28 g/ℓ in the ED brine. Nickel recovery rates varied between 0,83 and 1,0 kg Ni/m^2.d. Full-scale ED nickel / water recovery plant data showed that a nickel concentration level of approximately 50 g/ℓ could be reached in the ED brine. Approximately 97 percent of the drag-out can be recovered for reuse. Therefore, ED can be effectively applied as a metal / water recovery technology in the electroplating industry.

Chromium can be recovered from chromium rinse water with ED. Chromium in the ED feed could be concentrated from 1 300 mg/ℓ to 6 900 mg/ℓ in the ED brine. Brine volume comprised approximately 20 percent of the treated feed water volume. Therefore, effluent volume can be significantly decreased for subsequent further treatment of the ED brine for chromium removal with conventional precipitation technology. The chromium concentration level of the ED product is high (approximately 400 mg/ℓ). Ion-exchange treatment will be required to reduce the chromium level in the ED product to low concentration levels (<0,1 mg/ℓ). Electrical energy consumption for chromium recovery / removal was determined at 8,7 kWh/kg Cr. Chromium recovery rate varied between 0,12 and 0,26 kg Cr/m^2.d. Membrane life time and the economics of the process are unknown factors. Therefore, more work will be required to evaluate this process properly for treatment of chromium rinse waters.

- It appears that it should be possible to use the EED process effectively for chromium recovery from chromium drag-out for reuse in the plating bath. Chromium could be concentrated from 48 g/ℓ (CrO_3) to 240 g/ℓ (CrO_3) in the EED product. This concentration level is of sufficient strength for direct reuse in the plating bath. Electrical energy consumption, however, was high (38 kWh/kg Cr). Membrane life time and the economics of the process are unknown. However, it appears that this process will be too expensive for the electroplater to use. Further work will be required to evaluate this process properly for treatment of chromium drag-out.

- The bipolar electrodialysis process appears to function effectively for treatment of spent pickling acid effluent for acid recovery for reuse in the pickling process. A nitric acid concentration level between approximately 2,0 and 2,5 mol/ℓ could be obtained with ease. Hydrofluoric acid recovery, however, was poor when the nitrate concentration level in the feed water was high. However, the hydrofluoric acid concentration level in the acid product increased dramatically when most of the nitrate was removed from the feed. A hydrofluoric acid concentration level of approximately 2,5 mol/ℓ could be obtained towards the end of a run. Almost no effluent will be produced when BED is used for treatment of spent pickling acid effluent. All the chemicals produced in the process (acids and bases) can be reused in the process itself or in the pickling process. Consequently, the BED process should be the ideal solution to solve the spent pickling acid effluent problem experienced by stainless steel manufacturers. A combination of the diffusion dialysis and BED processes will function more effectively than BED alone for treatment of spent pickling acid effluent. This, however, will depend on the quantity of bound or complexed acids present in the spent pickling acid effluent. It appears that there is a significant amount of bound acid present in spent pickling acid effluent.

- Membrane fouling can lead to the failure of membrane separation process for effluent treatment. The fouling potential of the effluent for the BED membranes should therefore be determined through long term laboratory or pilot studies. This will ensure that proper process design criteria will be developed for treatment of the spent pickling acid effluent. Preliminary results have shown that the capital cost for a 1 750 ℓ/h BED plant for treatment of spent pickling acid will amount to approximately R14,8 million. The annual membrane cost will amount to approximately R2,7 million. Electrical energy required for the process will amount to approximately 2 600 kW. Preliminary results have shown that the capital cost for a combination of the diffusion dialysis and BED processes for a 1 750 ℓ/h plant will amount to approximately R11,5 million. (R2,3 million for diffusion dialysis and R9,2 million for BED). Operating expenses for the diffusion dialysis process will amount to R1,3 million for membrane replacement (annual cost), approximately R35 000 for spare parts for pumps and approximately 14 kW electrical energy will be used in the process. Operating expenses for BED will amount to approximately R1,4 million for membrane replacement (annual cost) and approximately 1 290 kW electrical energy will be consumed in the process.

- Preliminary tests showed that it would be possible to convert sodium nitrate effectively into nitric acid and caustic soda with the BED process. Acid and caustic soda concentration levels of approximately 2 mol/ℓ could be obtained with ease when sodium nitrate solution (approximately 10%) was treated with BED. Electrical energy consumption for acid production was determined at approximately 2 000 kWh/ton acid. Electrical energy consumption for caustic soda production was determined at approximately 3 000 kWh/ton caustic soda. The capital cost for a BED plant to treat 3 600 kg per day sodium nitrate solution (10 to 15%) is estimated at $ 450 000. This cost excludes membranes at an estimated cost of $ 20 000/set with one year life time and any pretreatment or site specific cost. The expected DC power consumption would be (average) 27 kW.

- Preliminary tests showed that it would be possible to convert sodium sulphate effectively into acid and caustic soda with BED. Acid and caustic soda concentration levels of approximately 2 mol/ℓ could be obtained with ease when sodium sulphate solutions (approximately 10 and 20%) were treated with BED. Electrical energy consumption for acid production varied between approximately 3 800 and 4 600 kWh/ton acid and between approximately 3 700 and 4 200 kWh/ton acid for two runs that were conducted. The electrical energy consumption for base production baried between approximately 3 500 and 6 500 kWh/ton caustic soda and between approximately 3 700 and 4 200 kWh/ton caustic soda for two runs that were conducted. Current efficiency was lower than expected and this matter warranted further investigation.

- Preliminary tests showed that it would be possible to convert sodium acetate effectively into acetic acid and caustic soda with BED. An acid concentration level of 1,875 mol/ℓ and a caustic soda concentration level of approximately 2 mol/ℓ could be obtained with ease when a sodium acetate solution (approximately 10%) was treated with BED. The concentration of sodium in the acid product was 1 528 mg/ℓ . Electrical energy consumption for base production varied between approximately 3 100 and 3 500 kWh/ton caustic soda. Current efficiencies for the two caustic soda batch runs that were conducted were 56,87 and 58,81%, respectively. Current efficiency, however, was lower than expected and this matter warranted further investigation.

6. LITERATURE

1. U.S.A.I.D. Manual (1980) : CH&M International Corporation, 7201, NW, 11th Place, Gainesville, Florida, USA, 32601.

2. Melzer, J. and Van Deventer, D. (1983) : Electrodialysis for Desalination of Waste Water in an Eskom Power Station. Presented at a Symposium on Desalination: New Developments and Industrial Application. CSIR Conference Centre, Pretoria, 27 October 1983.

3. Itoi, S., Nakamura, I. and Kawahara, T. (1980) : Recovery of Metals from Plating Rinse Waters. Desalination, 32, 383.

4. Schoeman, J.J., Vorster, W.A. and Steyn, A. (1992) : Evaluation of Reverse Osmosis, Electrodialysis, An Electrolytic Cell Process and Diffusion Dialysis for Electroplating Effluent Treatment, Progress Report to the WRC, Project No. 67034140, File No. 10/8/4/3/34140.

5. Schoeman, J.J. (1992) : Electrodialysis of Salts, Acids and Bases by Electro-Osmotic Pumping. Final Report Submitted to the WRC, April 1992.

6. Chiapello, L. (1990) : E.I.V.S. S.A., Filiale de Corning France, 11, Chemin de Ronde, BP36, 78110 Le Vesinet, France.

7. McArdle, John, C. and Piccari, A. (1991) : Aquatech Systems Pickle Liquor Recovery Process - Washington Steel Reduces Waste Disposal Costs and Liability. Iron and Steel Engineer, May 1991, pp. 39 - 43.

8. Mani, K.N., Chlanda, F.P. and Byszewski, C.H. (1990) : Aquatech Membrane Technology for Recovery of Acid / Base Values from Salt Streams. Allied-Signal Inc. 7 Powder Horn Drive, Mt. Bethel, NJ 07060.

9. Pollution Research Group (1984) : Pollution Research Group, Department of Chemical Engineering, University of Natal. Survey on Water Management and Effluent Treatment in the South African Metal Finishing Industry. Report prepared for the WRC, 1984.

10. Chiapello, J.M. and Gal, J.Y. (1992) : Recovery by Electrodialysis of Cyanide Electroplating Rinse Waters. Journal of Membrane Science, 68 (1992) 283 - 291.

11. Pamphlet on Ion-Exchange Regeneration. Aquatech Systems, Allied Signal Inc., 7 Powder Horn Drive, P O Box 4904, Warren, NJ 07059-5191 USA.

12. Schoeman, J.J. and Steyn, A. (1992) : Evaluation of Bipolar Electrodialysis for Acid Recovery from Spent Pickling Acid. Contract Report, September 1992.

13. Bar, D. (1992). Private Communication, Aquatech Systems, U S A.

14. Tran, T.V. and Clemens, P.B. (1986) : Recovery of Nickel Salts by EDR. Presented at the 73rd Annual AESF Technical Conference and Exhibit of Surface Finishing. Philadelphia, P A, June 23 - 26, 1986. Bulletin : T P 334 - ST.

15. Fromonot, G. (1992) : E.I.V.S. S. A., Filiale de Coming France, 11, Chemin de Ronde, BP 36, 78110 Le Vesinet, France.

16. Schoeman, J.J. and Steyn, A. (1992) : An Investigation into the Treatment of Spent Pickling Acid Effluent Produced by Columbus Stainless with Diffusion Dialysis. Contract Report.