EVALUATION OF MEMBRANE TECHNOLOGY FOR ELECTROPLATING EFFLUENT TREATMENT

Report to the WATER RESEARCH COMMISSION

by

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EVALUATION OF MEMBRANE, ELECTROLYTIC AND ION-EXCHANGE TECHNOLOGIES FOR TREATMENT OF ELECTROPLATING EFFLUENTS

EXECUTIVE SUMMARY

Large volumes of wastewaters are produced in the electroplating industry as a result of the following activities:

- a) Plating of common and precious metals;
- b) Metal finishing and electroless plating; and
- c) The manufacture of printed circuit boards.

The major sources of waste that result from normal plating and metal finishing operations are alkaline cleanings, acid cleanings, spent plating-bath solutions and rinse waters. The largest portion (approximately 90%) of the water required in the plating process is for rinsing, where it is used to remove the process solution film (drag-out) from the surface of the work pieces. The water thus becomes contaminated with the constituents of the process solutions and is not directly reusable.

Common plating metals include nickel, chromium, copper, zinc, cadmium, lead, iron and tin. The metals originate from two types of waste streams in the electroplating process, viz., an acid stream (from Ni, Cr, Cu and Zn plating) and an alkaline stream (from Cu, Ag, Cd and Zn cyanide plating). These two streams are usually mixed before lime addition in a thickener/clarifier for removal of the toxic metals in the form of their metal hydroxide sludges. The toxic metal hydroxide sludges are usually filter pressed and removed by truck from plating shops for safe disposal, hence expensive plating metals are lost in this process. The clarified effluent is discharged into the sewer system and has to comply with the effluent discharge standards laid down by the authorities. Thus, large volumes of water are lost in this process.

Electroplating chemicals are expensive and some of them such as nickel, cadmium and chromium are also toxic. These chemicals can have adverse effects on biological processes and on soil at disposal sites. Electroplating chemicals can also increase the TDS of the water environment with its resultant economic implications. Therefore, it would be advantageous to recover these chemicals for reuse and thus prevent such undesired effects on the environment. An industry consultant has estimated that it would be technically possible to recover 80 to 90% copper; 30 to 40% zinc; 90 to 95% nickel; and 70 to 75% chromium from plating effluents.

Electroplating is said to be one of the most anti-ecological technologies in current use. The environment is annually polluted with around one cubic kilometre of toxic effluents, carrying 50 000 tons of heavy metals and 100 000 tons of acids and alkalis, 25 to 30% of which are released to natural aquifers. Chromium is carcinogenic and cadmium causes liver and kidney diseases.

The annual consumption of water by the electroplating industry in South Africa is approximately 9×10^6 m³ of which 80% is discharged as effluent. In an attempt to prevent water pollution the industry resorts dilution of their effluents, with consequent wastage of scare water resources. Ideally, this water should be recycled to decrease water intake by the industry. Recycling of recovered metals (Ni, Ag, Zn, Cr. etc.) to the plating process will reduce water pollution and sludge volumes dramatically. Consequently, the pollution load on the environment will be dramatically reduced with metal/water recovery technologies.

Reverse osmosis (RO), electrodialysis (ED), coupled transport, diffusion dialysis, electrolytic metal recovery, evaporation and ion-exhcange are processes that can be used for electroplating effluent treatment. Both RO and ED have been demonstrated to be effective for nickel and water recovery from nickel rinse waters. The coupled transport process has the potential to recover chromium from chromium waste-waters. Acids (HCI, H₂SO₄, HNO₃) can be successfully recovered from spent acid effluents with diffusion dialysis. Metals like nickel and silver can be cost effectively recovered from electroplating rinse waters with electrolytic metal recovery technology. Evaporation technology can be successfully applied for nickel and chromium recovery from electroplating wastewaters. Nickel, chromium and copper can be effectively recovered from electroplating rinse waters with ion-exchange technology.

No or very little experience is available in South Africa regarding the use of membrane and other technologies for treatment of electroplating effluents. In particular, the

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fouling potential of electroplating effluents for membranes and ways and means to clean fouled membranes, are unknown. A South African developed tubular RO system containing cellulose acetate membranes (TCARO system) has the potential to be successfully applied for treatment of electroplating effluents. The restriction of the South African membrane system is that the pH of the effluent must be slightly acidic (pH approximately 6,5) to prevent hydrolysis of the cellulose acetate RO membranes. Membrane life time will be shortened if the membranes are used at low (pH <4) and high pH (pH >8). However, other membranes (polyamide) and membrane configurations (spiral wrap) are available that should be successfully applied for treatment of high pH (pH >8) and low pH (pH <4) electroplating effluents.

Little experience also exists in South Africa regarding the use of ED for treatment of electroplating effluents. No South African developed ED system is presently available. However, ED systems that can be supplied by overseas companies can be effectively applied for electroplating effluent treatment. Little experience also exists in South Africa regarding the use of electrolytic, evaporation and ion-exchange technologies for treatment of electroplating effluents. Therefore, needs exist to :

- (a) Evaluate the above technologies for treatment of electroplating effluents;
- (b) Evaluate the fouling potential of the effluents for membranes and to develop membrane cleaning methods;
- (c) To identify the most suitable technologies for the South African situation;
- (d) Develop process design criteria for full scale application; and
- (e) Determine the economics of the processes.

The anticipated benefits of the research can be as follows:

- (a) That water can be saved and that plating chemicals can be economically recovered to reduce the pollution load on the environment;
- (b) That the most suitable processes can be identified for the economic treatment of electroplating effluents in South Africa; and
- (b) That a South African developed membrane system can be implemented for electroplating effluent treatment to prevent imports of overseas systems.

The objectives of the study were:

- (a) To evaluate RO and ED for metal and water recovery from electroplating rinse waters;
- (b) To evaluate RO and ED for treatment of mixed (before metal removal by precipitation) and final (after metal removal) electroplating effluents;
- (c) To determine the fouling potential of electroplating effluents for RO and ED membranes and to develop membrane cleaning methods;
- (d) To evaluate an electrolytic metal recovery process for metal recovery from electroplating rinse waters;
- (e) To evaluate diffusion dialysis for acid recovery from spent acid;
- (f) To evaluate ion-exchange for metal recovery from electroplating rinse water;
- (g) To develop process design criteria for electroplating effluent treatment; and
- (h) To determine the economics of the processes.
 - **Note**: The above work was carried out on specific selected effluents (Ni, Cr, Cd and other related metals) that were identified by an industry survey to have major environmental impact and containing high value recoverable materials.

Nickel drag-out (rinse water) can be cost effectively treated with a TCARO system for nickel and water recovery for reuse in the electroplating process. Payback periods for 5 m³/h; 5 m³/d; and 15 m³/d nickel/water recovery RO plants were determined at 1,3; 2,1; and 1,7 years, respectively. Nickel could be concentrated from 1300 mg/ ℓ in the inlet drag-out (13 500 mg/ ℓ Ni RO feed tank) to 14 400 mg/ ℓ in the RO brine at a water recovery 93 percent (feed and bleed system; concentration factor 11,1). The nickel concentration in the RO permeate was only $37,4 \text{ mg/}\ell$. Therefore, a nickel removal of 99,7 percent was obtained from the RO feed. Nickel could also be concentrated in a batch system from 1 760 mg/ ℓ in the feed to 7 400 mg/ ℓ in the brine at a water recovery of 93 percent (concentration factor 4,2). The RO permeate had a nickel concentration of only 38,9 mg/l. Therefore, nickel removal was 97,8 percent. Higher water recovery (approximately 95%) and therefore higher brine (Ni) concentration is possible. Very little membrane fouling took place when the fouling potential of nickel drag-out was determined for cellulose acetate RO membranes. It was demonstrated that it should be possible to control membrane fouling with regular chemical cleaning. Regular chemical cleaning is considered to be very important for trouble free operation of a nickel recovery RO system.

It appears that it will also be possible to use spiral wrap Filmtec membranes (high rejection seawater RO membranes) successfully for nickel and water recovery from nickel drag-out. Nickel could be concentrated from 635 mg/ ℓ in the RO feed (batch system) to 9 625 mg/ ℓ in the RO brine (concentration factor 15,2) at a water recovery of approximately 90 percent. The nickel concentration in the RO permeate was only 1,35 mg/ ℓ . Therefore, nickel removal was 99,8 percent. Higher water recovery should be possible (approximately 95%). It also seems that it will be possible to control membrane fouling with regular chemical cleaning. Better feed pretreatment, however, will be necessary with the spiral wrap Filmtec membranes than with tubular membranes. Cartridge filtration (5 to 10 μ m) should protect the membranes from fouling.

Chromium rinse water could be successfully treated with TCARO membranes for chromium and water recovery. Chromium in the inlet drag-out was concentrated from 740 mg/ ℓ (2 950 mg/ ℓ in RO feed tank) to 3 100 mg/ ℓ in the RO brine (concentration factor 4,2) at a water recovery of 80 percent (feed and bleed system). The chromium concentration in the RO permeate was 189 mg/l. Therefore, chromium removal was 93,6 percent. Chromium could also be concentrated from 469 mg/ ℓ in a batch system to 2 320 mg/ ℓ (concentration factor 4,9) in the RO brine at a water recovery of 92 percent. Chromium removal was 87 percent. The concentration level, however, of the recovered chromium is too low for direct use in the plating bath. However, it will be possible to increase its concentration level to the required strength (approximately 240 g/ ℓ CrO₃) with an evaporator prior to use. Membrane fouling took place during RO treatment of chromium rinse water. However, it appears that it should be possible to control membrane fouling with regular chemical cleaning. An evaporator can also be used to concentrate chromium in the drag-out to the required bath strength. This technology may be superior to RO technology for chromium recovery from chromium drag-out.

It appears that it will also be possible to apply spiral wrap Filmtec membranes for chromium and water recovery from chromium drag-out. Chromium was concentrated from 1 840 mg/ ℓ in the RO feed to 24 400 mg/ ℓ in the RO brine (concentration factor of 13,2) at a water recovery of approximately 90 percent. Therefore, a higher concentration could be obtained than with TCARO membranes. The chromium

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concentration level in the RO permeate was only 25,2 mg/ℓ Therefore, chromium removal was 98,6 percent. It also appears that it will be possible to control membrane fouling with regular chemical cleaning. It was noted that permeate flux increased after a number of batch runs. This phenomenon is of concern and warrants further investigation.

It appears that it will be possible to treat acidic zinc drag-out successfully with TCARO membranes. Zinc could be concentrated from 1 740 mg/ ℓ in the inlet drag-out (RO feed tank 5 090 mg/ ℓ) to 5 280 mg/ ℓ in the RO brine (concentration factor of 3) at a water recovery of 80 percent. The zinc concentration in the RO permeate was 323 mg/ ℓ . Therefore, zinc removal was 93,7 percent. Zinc could also be concentrated from 630 mg/ ℓ in the RO feed to 2 790 mg/ ℓ in the RO brine (batch systems; 91% water recovery) while the zinc concentration in the RO permeate was only 36 mg/ ℓ . Therefore, zinc removal was 94,3 percent. Membrane fouling was experienced during RO treatment of the zinc drag-out. However, it appears that it will be possible to control membrane fouling with regular chemical cleanings. Zinc has a low value compared to nickel. Therefore, a zinc recovery RO plant will not be very economic.

It appears that it will be possible to treat alkaline zinc cyanide rinse water successfully with PCI AFC 99 tubular RO membranes. The zinc in the inlet drag-out was concentrated from 420 mg/ ℓ (2 200 mg/ ℓ Zn in RO feed) to approximately 2 200 mg/ ℓ in the RO brine (concentration factor of 5,2) at a water recovery of 80 percent (feed and bleed system). The zinc concentration level in the RO permeate was only 29,9 mg/ ℓ . Therefore, zinc removal was 98,6 percent. Serious membrane fouling was experienced during treatment of the alkaline zinc drag-out. However, it was demonstrated that it should be possible to control membrane fouling with regular chemical cleaning.

It appears that it will be possible to treat alkaline cadmium rinse water successfully with spiral wrap Filmtec RO membranes. Cadmium was concentrated from 95 mg/l in the RO feed to 900 mg/l in the RO brine (concentration factor of 9,5) at a water recovery of approximately 90 percent (batch system). The RO permeate only contained 0,16 mg/l cadmium (99,8% Cd removal). Membrane fouling, however, was experienced during treatment of the cadmium rinse water. However, it was

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demonstrated that it should be possible to control membrane fouling with regular chemical cleaning.

It is possible to treat nickel drag-out cost effectively with ED for nickel and water recovery for reuse in the electroplating process. Plant payback period of approximately 1,5 year is possible (113 m² ED plant). Nickel in the ED feed was maintained between 0,5 and 1 g/ ℓ while nickel was concentrated to approximately 50 g/ ℓ in the ED brine. Nickel recovery of 97 percent was obtained.

It is possible to treat alkaline copper (1,2 kg Cu/h; 113 m² membrane area) and silver (113 m² ED plant) cost effectively with ED. Plant payback periods of approximately 1 and less than 2 years are possible, respectively. Metal recoveries of 92 and 95 percent were obtained, respectively.

Pilot plant results showed that nickel drag-out could be concentrated from approximately 3,5 g/ ℓ in the ED feed to 23 g/ ℓ in the ED brine (concentration factor of 6,5) at a water recovery of approximately 85 percent. The nickel concentration in the desalinated feed varied between approximately 700 and 1 000 mg/ ℓ . Nickel removal varied between 68 and 78 percent. Nickel loading rate was determined at 0,048 g nickel per hour per square metre membrane area at a nickel removal of 78,7 percent. Electrical energy consumption was determined at 2,35 kwh/kg Ni.

Selemion AMV anionic membranes were rapidly fouled with spent nickel plating bath solution in fouling tests while Ionics A-204-UZL and Ionac MA-3475 anionic membranes showed little signs of membrane fouling. Therefore, care should be taken in the selection of ion-exchange membranes for treatment of nickel drag-out. Alternatively, feedwater pretreatment with activated carbon should be practised to remove foulants prior to ED treatment to prevent process failure. Regular membrane cleanings with actid and caustic rinses should also be practised to clean fouled membranes.

It appears that it will be possible to treat chromium drag-out successfully with EED for chromium recovery. The recovered chromium from a feed chromium concentration of 48 g/ ℓ had a concentration level of 240 g/ ℓ . It will be possible to use the recovered chromium directly in the plating bath without further concentration. Electrical energy consumption, however, was high (38,3 kwh/kg Cr0₃). Further work, however, will be required to optimize this process for chromium recovery.

It will be possible to treat mixed electroplating effluent successfully with TCARO membranes for water recovery, effluent volume reduction and pollution control. Water recovery of more than 80 percent is possible (feed and bleed system). This means that the mixed plating effluent that must be treated for metal removal, is reduced significantly by RO treatment. The electrical conductivity of the mixed effluent (181 mS/m) was reduced from 831 mS/m in the RO feed (feed and bleed system) to 76 mS/m in the RO permeate (90,9% removal). Therefore, an excellent quality RO permeate can be produced that can be used as rinse water in the electroplating process. Excellent removals of heavy metals were also obtained. Nickel was reduced from 77 to 3.3 mg/ ℓ (95,7% removal); chromium from 51 to 3.1 mg/ ℓ (93,9% removal); zinc from 290 to 13,1 mg/l (95,5% removal); cadmium from 34 to 1,71 mg/l (95,0% removal). Membrane fouling took place during RO treatment of the effluent. However, it was demonstrated that it should be possible to control membrane fouling with regular chemical cleaning. Batch RO tests showed that the electrical conductivity of the RO feed could be reduced from 174 mS/m to 36,1 mS/m in the RO permeate (79,7% removal) at a water recovery of approximately 90 percent. Chromium was reduced from 8 to 0,92 mg/ ℓ (88,5% removal); zinc from 54 to 4,75 mg/ ℓ (91,2% removal); nickel from 15,4 to 1,35 mg/ ℓ (91,2% removal); and copper from 1,08 to 0,19 mg/*l* (82,4% removal).

It will be possible to treat mixed electroplating effluent successfully with ED for water recovery, effluent volume reduction and pollution control. The TDS of the ED feed could be reduced from 804 to 259 mg/ ℓ in the ED product (67,8% removal) at a water recovery of approximately 85 percent. Nickel was reduced from 12,8 to 0,96 mg/ ℓ (92,5% removal); zinc from 24,6 to 1,54 mg/ ℓ (93,7% removal); copper from 0,48 to 0,05 mg/ ℓ (89,6% removal); and cadmium from 2,8 to 0,19 mg/ ℓ (93,2% removal). It will also be possible to handle the much smaller brine volume easier with conventional lime precipitation treatment than the much larger mixed plating effluent.

Final effluent discharged by plating shops can be treated effectively with TCARO membranes for water recovery, effluent volume reduction and pollution control.

Electrical conductivity of the final effluent (130 mS/m) could be reduced from 529 mS/m in the RO feed to 29,1 mS/m in the RO permeate (94,5% removal) at a water recovery of 80 percent (feed and bleed system). Therefore, an excellent quality RO permeate was produced that could be used as rinse water in the electroplating process. Cadmium was reduced from 5,2 to 0,08 mg/ ℓ (98,5% removal); chromium from 7,1 to 0,2 mg/ ℓ (97,2% removal); copper from 3,8 to 0,7 mg/ ℓ (81,6% removal); nickel from 36,7 to 0,91 mg/ ℓ (97,5% removal); and zinc from 5,8 to 0,09 mg/ ℓ (98,4% removal).

It will be possible to apply a Chemelec electrolytic cell effectively for cadmium and cyanide removal from cadmium drag-out. Cadmium could be reduced in one case from 190 mg/ ℓ in the feed to only 4,2 mg/ ℓ in the product and cyanide from 862 mg/ ℓ to 429 mg/ ℓ . Better cyanide removals, however, will be possible if higher electric current is applied.

A Chemelec electrolytic cell can be cost effectively applied for nickel recovery from nickel drag-out. Plant payback period of less than 1,5 year is possible. Nickel, for example, was reduced in one case from 766 mg/ ℓ in the drag-out to approximately 6 mg/ ℓ (99,3% removal) in the treated water. Highest nickel removal took place when the pH of the feedwater was controlled between pH 4 and pH 4,8. It was demonstrated in pilot tests that nickel in a drag-out tank could be reduced from approximately 1 000 to 400 mg/ ℓ with ease with a Chemelec cell. Nickel recovery rate was determined at 2,1 g nickel per hour (electrode area 0,045 m²).

It will be possible to use diffusion dialysis effectively in the electroplating industry for acid recovery from spent acid produced during cleaning of metals prior to plating. Acid recovery from sulphuric/hydrochloric acid mixture was determined at 58 percent. Hydrochloric acid recovery varied between 74 and 76 percent. Sulphuric acid recovery was approximately 75 percent. Approximately 95 percent of the metals (Fe, Ni, Cu) could be removed from the recovered acid. Zinc was not as effectively removed (14,4% removal) as the other metals. However, it may also be possible in this case to recover acid effectively with diffusion dialysis for reuse in the plating process.

It will be possible to use ion-exchange effectively for nickel recovery from dilute nickel rinse waters (150; 400 and 1 000 mg/ ℓ Ni). Most of the nickel could be removed from the exhausted resin with 2,5 to 3 bedvolumes dilute sulphuric acid regenerant. The recovered nickel solution can be used in the plating bath or the nickel can be electrolytically recovered for sale to scrap metal dealers. It might also be possible to use the treated rinse water as rinse water in the process. Chrome and copper electroplating rinse waters can also be effectively treated with ion-exchange.

Process design criteria for electroplating effluent treatment with membrane, electrolytic and ion-exchange technology can be derived from the experimental results. Demonstration plants should now be installed at selected plating shops to transfer metal/water/effluent volume reduction/pollution control technology to the electroplaters. Electrolytic nickel and zinc recovery plants as well as an evaporator for chromium recovery from chromium drag-out was recently installed in South Africa at plating shops.

Centralized treatment of electroplating effluents is successfully applied in the USA and elsewhere. A centralized facility for treatment of electroplating effluents should function effectively in South Africa. This will take the effluent treatment responsibility away from the electroplater by effluent treatment experts with an effluent treatment infrastructure. The electroplater will benefit from such an approach because it will not be necessary for them to have their own advanced effluent treatment system. However, the economics of such an approach should first be determined to determine whether such an approach would be economically feasible. Alternatively, effluent treatment can be conducted for electroplaters by effluent treatment experts on site.

The contract objectives have been achieved in this study. It was shown that:

- a) Reverse osmosis and ED can be effectively applied for metal (Ni, Cr, Zn, Cd, Cu) and water recovery from electroplating rinse waters.
- b) Reverse osmosis and ED can be effectively applied for treatment of mixed and final electroplating effluent for water recovery, effluent volume reduction and pollution control.

- c) Diffusion dialysis can be effectively applied for acid recovery from spent acid produced in the electroplating process.
- d) Membrane fouling can be controlled with chemical cleaning when treating electroplating effluents with RO and ED.
- e) An electrolytic cell can be effectively applied to recover metals (Ni, Cu, Ag, Zn) from electroplating drag-out.
- f) Electro-electrodialysis should be effectively applied to recover chromium from chromium drag-out for reuse.
- g) Ion-exchange can be effectively applied for treatment of final effluent produced by an electroplating shop as well as for the recovery of nickel and chromium from nickel and chromium rinse waters, respectively.
- h) A centralized treatment facility should function effectively for electroplating effluent treatment in South Africa.
- i) Process design criteria for treatment of electroplating effluents with RO, ED, an electrolytic cell, electro-electrodialysis and ion-exchange have been developed.

This report offers the following to potential users of membrane technology for electroplating effluent treatment:

- a) It identifies technologies that can be effectively applied for treatment of electroplating effluents.
- b) It presents process design criteria for treatment of electroplating effluents.
- c) It shows the economics of treatment of electroplating effluents with membrane and other technologies.
- d) It suggests how a centralized treatment facility can be applied for treatment of electroplating 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 electroplating effluents with membrane and other technologies will be presented to the South African Electroplating Society.
- c) Results of the investigation will be submitted for presentation at an overseas conference.

d) A consultancy service regarding treatment of electroplating effluents will be rendered to the South African Electroplating Community.

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

- a) Demonstration plants (RO, ED, electrolytic cell, evaporation and ion-exchange) should now be installed at selected electroplating shops to:
- Demonstrate performance of metal and water recovery technologies to electroplaters;
- Identify any operational problems that might occur;
- Demonstrate the economics of these processes to the electroplaters; and
- Develop process design criteria for full scale application.
- b) The economic feasibility of a central treatment facility for electroplaters should be determined and implemented if economical justifiable.
- c) Treatment of electroplating effluents on site for metal and water recovery by external water treatment companies who can render such a service to electroplaters should be investigated and implemented if benefits can be derived for the plater and the water treatment company.

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1. INTRODUCTION

Large volumes of wastewaters are produced in the electroplating industry as a result of the following activities⁽¹⁾:

- a) Plating of common and precious metals;
- b) Metal finishing and electroless plating; and
- c) The manufacture of printed circuit boards.

The major sources of waste that result from normal plating and metal finishing operations are alkaline cleanings, acid cleanings, spent plating-bath solutions and rinse waters. The largest portion (approximately 90%) of the water required in the plating process is for rinsing, where it is used to remove the process solution film (drag-out) from the surface of the work pieces. The water thus becomes contaminated with the constituents of the process solutions and is not directly reusable.

Common plating metals include nickel, chromium, copper, zinc, cadmium, lead, iron and tin⁽¹⁾. The metals originate from two types of waste streams in the electroplating process, viz., an acid stream (from Ni, Cr, Cu and Zn plating) and an alkaline stream (from Cu, Ag, Cd and Zn cyanide plating). These two streams are usually mixed before lime addition in a thickener/clarifier for removal of the toxic metals in the form of their metal hydroxide sludges. The toxic metal hydroxide sludges are usually filter pressed and removed by truck from plating shops for safe disposal, hence expensive plating metals are lost in this process. The clarified effluent is discharged into the sewer system and has to comply with the effluent discharge standards laid down by the authorities. Thus, large volumes of water are lost in this process.

Electroplating chemicals are expensive and some of them such as nickel, cadmium and chromium are also toxic⁽²⁾. These chemicals can have adverse effects on biological processes and on soil at disposal sites. Electroplating chemicals can also increase the TDS of the water environment with its resultant economic implications. Therefore, it would be advantageous to recover these chemicals for reuse and thus prevent such undesired effects on the environment. An industry consultant has estimated that it would be technically possible to recover 80 to 90% copper; 30 to 40% zinc; 90 to 95% nickel; and 70 to 75% chromium from plating effluents⁽³⁾. Electroplating is said to be one of the most anti-ecological technologies in current use. The environment is annually polluted with around one cubic kilometre of toxic effluents, carrying 50 000 tons of heavy metals and 100 000 tons of acids and alkalis, 25 to 30% of which are released to natural aquifers⁽²⁾. Chromium ^(v) is carcinogenic and cadmium causes liver and kidney diseases.

The annual consumption of water by the electroplating industry in South Africa is approximately 9 x 10⁶ m ³⁽⁴⁾ of which 80% is discharged as effluent. In an attempt to prevent water pollution the industry resort to dilution of their effluents, with consequent wastage of scare water resources. Ideally, this water should be recycled to decrease water intake by the industry. Recycling of recovered metals (Ni, Ag, Zn, Cr. etc.) to the plating process will reduce water pollution and sludge volumes dramatically. Consequently, the pollution load on the environment will be dramatically reduced with metal/water recovery technologies.

Reverse osmosis (RO), electrodialysis (ED), coupled transport, diffusion dialysis, electrolytic metal recovery, evaporation and ion-exhcange are processes that can be used for electroplating effluent treatment^(2,5,6,7). Both RO⁽⁶⁾ and ED⁽⁹⁾ have been demonstrated to be effective for nickel and water recovery from nickel rinse waters. The coupled transport process has the potential to recover chromium from chromium waste-waters⁽⁶⁾. Acids (HCl, H₂SO₄, HNO₃) can be successfully recovered from spent acid effluents with diffusion dialysis⁽¹⁰⁾. Metals like nickel and silver can be cost effectively recovered from electroplating rinse waters with electrolytic metal recovery technology⁽¹¹⁾. Evaporation technology can be successfully applied for nickel and chromium recovery from electroplating wastewaters⁽¹²⁾. Nickel, chromium and copper can be effectively recovered from electroplating rinse waters with ion-exchange technology⁽¹³⁾.

No or very little experience is available in South Africa regarding the use of membrane and other technologies for treatment of electroplating effluents. In particular, the fouling potential of electroplating effluents for membranes and ways and means to clean fouled membranes, are unknown. A South African developed tubular RO system containing cellulose acetate membranes has the potential to be successfully applied for treatment of electroplating effluents. The restriction of the South African membrane system is that the pH of the effluent mujst be slightly acidic (pH approximately 6,5) to prevent hydrolysis of the cellulose acetate RO membranes. Membrane life time will be shortened if the membranes are used at low (pH <4) and high ph (pH >8). However, other membranes (polyamide) and membrane configuration (spiral wrap) are available that should be successfully applied for treatment of high pH (pH >8) and low pH (pH <4) electroplating effluents.

Little experience also exists in South Africa regarding the use of ED for treatment of electroplating effluents. No South African developed ED system is presently available. However, ED systems that can be supplied by overseas companies can be effectively applied for electroplating effluent treatment. Little experience also exists in South Africa regarding the use of electrolytic, evaporation and ion-exchange technologies for treatment of electroplating effluents. Therefore, needs exist to :

- (a) Evaluate the above technologies for treatment of electroplating effluents;
- (b) Evaluate the fouling potential of the effluents for membranes and to develop membrane cleaning methods;
- (c) To identify the most suitable technologies for the South African situation;
- (d) Develop process design criteria for full scale application; and
- (e) Determine the economics of the processes.

The anticipated benefits of the research can be as follows:

- (a) That water can be saved and that plating chemicals can be economically recovered to reduce the pollution load on the environment;
- (b) That the most suitable processes can be identified for the economic treatment of electroplating effluents in South Africa; and
- (b) That a South African developed membrane system can be implemented for electroplating effluent treatment to prevent imports of overseas systems.

The objectives of the study were:

(a) To evaluate RO and ED for metal and water recovery from electroplating rinse waters;

- (b) To evaluate RO and ED for treatment of mixed (before metal removal by precipitation) and final (after metal removal) electroplating effluents;
- (c) To determine the fouling potential of electroplating effluents for RO and ED membranes and to develop membrane cleaning methods;
- (d) To evaluate an electrolytic metal recovery process for metal recovery from electroplating rinse waters;
- (e) To evaluate diffusion dialysis for acid recovery from spent acid;
- (f) To evaluate ion-exchange for metal recovery from electroplating rinse water;
- (g) To develop process design criteria for electroplating effluent treatment; and
- (h) To determine the economics of the processes.
 - **Note**: The above work was carried out on specific selected effluents (Ni, Cr, Cd and other related metals) that were identified by an industry survey to have major environmental impact and containing high value recoverable materials.

2. LITERATURE SURVEY

An extensive literature survey was carried out to identify and evaluate technologies that could be successfully applied for treatment of electroplating effluents^(14, 15, 16). These technologies include:

- (a) Reverse osmosis;
- (b) Electrodialysis;
- (c) Electrolytic metal recovery;
- (d) Evaporation; and
- (e) Ion-exchange.

It should be possible to recover acid effectively from spent acid solution with diffusion dialysis⁽¹⁰⁾. It should also be possible to recovcer chromium from chrome bearing electroplating effluents with the coupled transport process⁽⁶⁾. It also appears to be possible to use a centralized treatment facility effectively for treatment of electroplating effluents^(14,16). The literature survey, however, is presented in separate reports. A brief overview of membrane technologies for treatment of electroplating effluents is included in this report.

3. OVERVIEW OF MEMBRANE SEPARATION PROCESSES FOR METAL FINISHING⁽¹⁷⁾

Waste treatment problems in the metal finishing industry are certainly many, complex and severe. Probably no other industry has to reckon with as wide a variety of problems due to contaminants, including heavy metals, oily waste, chlorinated hydrocarbons, and sludges that defy description.

No less varied than the pollution problems are the motivating influences for considering membrane separation processes as remedial tools. Among these influences:

- 1. Waste water discharge limitations and Resource Conservation and Recovery Act regulations are strict in the USA, particularly with regard to toxic heavy metals and certain organics such as chlorinated hydrocarbons. Furthermore, it appears that these regulations will become even more restrictive over the next few years.
- 2. Enforcement activity is exacerbated by public concern in the USA over the quality of drinking water. The problem of carcinogenic contamination in drinking water supplies is probably not as bad as the media would have the people to believe. Regardless, there is not doubt that public concern will keep this issue in the spotlight for years to come.
- 3. There are numerous cases of solute recovery providing an economic benefit, either by virtue of reusing or selling the concentrated solution. With the increasing scarcity of raw materials, this will become an even more important consideration. Likewise, as the cost of water increases and it undoubtedly will the value of reclaiming it will provide an additional economic incentive.
- 4. When compared with distillation, ion-exchange and other means of removing or concentrating dissolved solids, membrane processes offer economic benefits in the area of energy conservation.

Will membrane processes become increasingly important for effluent treatment? The answer is an unqualified yes. However, it is extremely important to approach each application with knowledge and understanding. Knowledge of the characteristics,

analysis and constancy of the waste stream is critical, as is an understanding of exactly how the membrane process will work for a particular application and precisely which technology, membrane material and device are optimum for each case.

Another question also comes to mind: If membrane technology has so much to offer, why hasn't it shown greater penetration in the effluent treatment market? The answer is fourfold:

- There is a general lack of understanding on the part of industry. There has been and remains relatively poor communication among manufacturers of membrane systems and prospective users.
- There has been too little aggressive marketing. Of the 160-odd manufacturers of membrane systems in the USA today, more than 90 percent are oriented towards single applications in relatively small geographic regions and have total sales of less than \$1 million per year. Moreover, these manufacturers very often do not have the technical resources to investigate new application opportunities - much less market systems for them.
- Membrane elements are thermally and/or chemically incompatible with some effluent streams.
- Economic considerations have favoured the established treatment technologies, which have provided sufficient removal capabilities but which are now subject to great scrutiny for the reasons mentioned above.

Reverse osmosis, ultrafiltration (MF) and electrodialysis are the three commonly used membrane processes. Their mechanisms, strengths and weaknesses when applied to waste treatment in the metal finishing industry are outlined here.

3.1 Reverse Osmosis

The mechanisms involved during RO are as follows:

As the feed stream containing dissolved salts and organic materials is pumped between layers of semi-permable membrane, a high-pressure pump forces pure water (permeate) through the membranes that have the capability to reject salts and organics.

As more permeate is removed from the feed stream, the remaining dissolved materials become more concentrated. The existing stream that has not passed through the membrane is known as the 'concentrate stream'.

In RO pure water and low-molecular-weight organic molecules pass through the porous membrane 'skin' and rejection of salts and higher-molecular-weight organic materials occurs.

The capability of RO to separate salts from rinse water underscores its utility in electroplating plants. Assuming that counter-current rinsing and other water conservation practises are utilised, the RO unit can be positioned to accept water from the first flowing rinse with the concentrate returned to the plating bath and the permeate to the last counter-current rinse. As the concentration of the concentrate stream increases, the osmotic pressure of the solute rises, resulting in a reduced permeate flow. The phenomenon is known as the 'osmotic pressure effect' and is a limiting factor in the output of an RO system.

In practice, only those lines with heated plating baths can be treated directly using RO. This is because the evaporation rate of the heated process solution is high enough to allow the RO concentrate to be fed directly to the bath. Solutions operated at low temperature require supplemental evaporation of the concentrate stream to reduce the volume before returning to the plating bath. The 'zero discharge' application of RO to electroplating rinses is illustrated in Figure 1.



Figure 1: 'Zero discharge' approach of RO to plating rinses

Typically, the limits imposed by osmotic pressure on the degree of concentration by RO restrict the concentrate concentration to about one-tenth of that provided by ED, but the RO permeate is generally pure enough to be used in the final rinse.

RO systems are currently operating on rinses for Watts and sulfamate nickel, acid copper, acid zinc, copper cyanide, brass cyanide, and hexavalent chromium plating lines.

3.2 Ultrafiltration

Ultrafiltration involves the movement of water through a semi-permeable membrane. However, the UF membrane pores are considerably larger than those for RO and, as a result, salts are not rejected. Ultrafiltration membranes are employed to remove high-molecular-weight organics such as oily waste and colloidal materials. The large pores in UF membranes allow both ionic and high-molecular-weight organic materials to pass through the membrane to the permeate stream. In metal finishing operations, UF is typically employed to concentrate emulsified oils from rinses or to recover valuable detergents from cleaning rinse waters.

In general osmotic pressure is not a problem when using UF, and the only energy requirement stems from running a low-pressure pump. On the other hand, UF will not remove ionic materials such as plating salts. Today, UF is being used in a multitude of applications, including: cleaners for one-piece steel and aluminum cans; rinses for strip coil coating; cleaning rinses for automobile and aircraft chassis; and coolant recovery.

3.3 Electrodialysis

An electrodialysis 'stack', which consists of alternating ion-exchange membranes that are permeable to either anions or cations but not to both is illustrated in Figure 2.

The solutions containing ions to be concentrated is pumped through every other cell. By applying direct current to an anode and cathode positioned parallel to the membranes, salts are attracted through the membrane that is permeable to the particular ionic species and are held back by the impermeable membrane. In this way, two streams are produced - one containing the salts in concentrated form and the other relatively pure water.

The application of an electrodialysis (ED) stack to a rinse water recovery system is illustrated in Figure 3. This scheme is based on a drag-out rinse tank that supplies the water to be treated and that received the relatively pure water from the ED stack. In general, ED can concentrate the rinse water salts up to bath strength - approximately an order of magnitude greater than can reverse osmosis. On the other hand, ED will not remove non-ionic solutes such as organics, and the purified rinse water (permeate) is not as pure as that produced by RO.

Electrodialysis is being used successfully on rinses from the following types of electroplating baths: gold, platinum, nickel, tin, copper, silver, palladium, cadmium, tinlead and zinc.

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Figure 2: Electrodialysis stack features alternating ion-exchange membranes





3.4 **Process Comparison**

Some characteristics of the three membrane separation processes are compared in Table 1. It should be noted that membrane fouling by suspended or precipitated solids represents the single most common cause of system malfunction. A thorough evaluation of the feed stream is essential, and pretreatment systems should be designed to minimise the danger of fouling. As with any other type of continuous processing, maintenance is also important. While these systems do not require any special operating skills, neither can the maintenance requirements be ignored.

It should now be clear that there is no single membrane process optimum for all applications. It is incumbent upon the responsible individual to understand the alternative technologies such as membrane processes, then select the most effective and economical treatment or recovery system for his situation.

Feature	ED	RO	UF
Continuous process	Yes	Yes	Yes
Concentration capability	High	Moderate	High
Ionic separation	Yes	Yes	No
Organic separation	No	Yes	Yes
Energy usage	Moderate	Moderate	Low
Permeate purity	Moderate	High	High
Membrane stability	High	Moderate	High

Table 1: Comparison of membrane separation processes

4. **EXPERIMENTAL**

4.1 Treatment of electroplating waste waters with RO

A simplified diagram of the experimental set-up that was used to determine flux curves and the fouling potential of electroplating rinse waters (Ni, Cr, Zn, Cd) and other electroplating waste waters for RO membranes, is shown in Figure 4.



Figure 4: Experimental set-up for treatment of electroplating rinse waters

Drag-out from the plating shop was pumped into a 3 000 litre storage tank where it was diluted to a predetermined concentration level. The RO feed tank was then filled with 200 litre rinse water and the rinse water was pumped through two cellulose acetate membrane modules in series (1,75 m² each) at a feed inlet pressure of 4 000 kPa. Sponge ball cleaning with flow reversal was applied (30 to 60 minutes). Brine was returned to the feed tank and the volume of the feed tank was kept constant at 200 litre with a level controller. Brine and permeate was withdrawn from the RO modules to give a water recovery of approximately 80% (feed and bleed system). Water flux (corrected to 25°C) was determined as a function of time to determine the fouling potential of the rinse water for the membranes. This experimental set-up was also used to determine the fouling potential of mixed and final electroplating effluent for RO membranes. Membrane modules could be interchanged to evaluate different membrane modules.

Batch tests were also conducted with the experimental set-up shown in Figure 4. Plating effluent (200 ℓ) was circulated through the RO membranes at a feed inlet pressure of 4 000 kPa and permeate was withdrawn until a water recovery of approximately 90% was obtained. Permeate flux (corrected to 25°C) was determined as a function of time and percentage water recovery. The chemical composition of the feed, permeate and brine was determined with automated methods at the end of the runs. Analysis was conducted on a composite sample of the permeate in the case of batch experiments.

Membrane cleaning was studied by circulating cleaning solutions (2% citric acid, pH 4,5; EDTA 0,5% normal pH; EDTA 0,5% pH 11; 0,5% Biotec, etc) through the membranes for one hour. Clean water fluxes were determined before and after cleaning.

4.2 Treatment of electroplating waste waters with ED

4.2.1 ED pilot plant

The experimental set-up of the ED pilot plant that was used for the investigation is shown in Figure 5.



Figure 5: Electrodialysis pilot plant

50 ℓ Polyethylene tank; 2. Product recirculation pump; 3. Brine recirculation tank;
 4. Brine recirculation pump; 5. Electrode recirculation tank; 6. Electrodes;
 7. Flow meters; 8. Mano meters; 9. Stack with 75 cell pairs; 10. Discharge valves;
 11. Adjusting valves; 12. Raw product input; 13. Treated product output;
 14. Reversal valves; 15. Make-up valve.

A polarization curve was first established on real effluent as feed by increasing cell pair voltage and measuring electrical current (conducted at approximately 90% demineralization of feed). This data were plotted and the operating cell pair voltage was taken as 80 percent of the limiting voltage (limiting voltage determined from the inflection point on curve).
Nickel drag-out (30 ℓ) and brine (5 ℓ drag-out) were circulated through the ED stack (75 cell pairs, 204 cm² per membrane) at a flow rate of 700 ℓ /h. A sodium sulphate solution (10 g/ ℓ) was used as electrode rinse. Electrodialysis was conducted by applying constant voltage across the stack and determining electrical current as a function of time. The ED feed was discarded after approximately 70 minutes of operation when little more demineralization took place and the procedure was repeated with three more new feed batches. The pH of the brine and electrode rinse was kept constant at a pH between 2 and 3 during a run by addition of sulphuric acid. The pH of the feed varied between pH 2 and 3.

The chemical composition of the ED feed, product and brine was determined at the end of the runs. Electrical energy consumption and the nickel loading rate were determined from the results.

Mixed electroplating rinse water was also treated with ED. The same experimental procedure was followed as for the nickel rinse water.

4.2.2 Fouling cell

A schematic diagram of the fouling cell that was used for the ED membrane fouling tests is shows in Figures 6 and 7.



Figure 6: Schematic diagram of fouling cell



Figure 7: Simplified schematic diagram of fouling cell

C = cationic membrane; A = anionic membrane

The fouling cell consisted of five perspex cells which could be clamped together to hold the membranes (7,1 cm² exposed area) in position. Water containing foulant (approximately 60 ℓ) was circulated through the feed (2 x) and brine compartments (1 x) of the fouling cell and returned to the feed tank. Flow rates of 1,1 and 0,7 ℓ /min were used through the feed and brine compartments, respectively. The fouling potential of nickel electroplating bath effluent was evaluated in the fouling cell. Selemion AMV and CMV; Ionac MA-3475 and MC-3470 and Ionics A-204-UZL-386 and C-61-CZL-386 membranes were used. The electrode rinse water consisted of a carbon slurry (2%, pH = 5) in a 1 mol/ ℓ sodium sulphate solution. This solution was circulated through the two electrode compartments.

A DC current density of 20 mA/cm² was used (Hewlett Packard power source, 0 - 60 volt; 0 - 15 amp) to supply the motive force for ion migration. The voltage drop across the anion-exchange membrane was measured with platinum electrodes connected to a Hewlett Packard multimeter. An increase in potential drop across the membrane indicated fouling. The AC membrane resistances of the unused and used membranes were measured in 0,5 mol/ ℓ sodium chloride solution. Platinized titionium electrodes were used in the resistance measurement cell.

4.2.3 Ion-exchange membrane reactor

The experimental set-up for treatment of chromium rinse water with electroelectrodialysis (EED) is shown in Figure 8.



Figure 8: Experimental set-up for treatment of chromium rinse water with EED

Chromium drag-out (20 ℓ) and tap water (2 ℓ) were circulated at a flow rate of 920 m ℓ /min through the membrane stack. Morgane ARA anion-exchange membrane was 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 platinized titanium anode were used.

4.3 Treatment of electroplating rinse waters with a Chemelec electrolytic cell

The experimental set-up for treatment of nickel and cadmium rinse waters with a Chemelec electrolytic cell is shown in Figure 9.



Figure 9: Experimental set-up for treatment of nickel rinse water with an electrolytic cell

One hundred litre nickel drag-out (approximately 1 000 mg/ ℓ Ni) was circulated through the cell. The solution left the cell by an overflow and was circulated back to a simulated drag-out tank. Electric current (5 amp) was applied and the nickel concentration of the feed was determined as a function of time. The nickel concentration level of the feed was increased to approximately 1 000 mg/ ℓ when the concentration level in the feed tank was reduced to approximately 500 mg/ ℓ . The pH of the feed solution was kept between pH 4,0 and 4,8 with addition of a 5 percent caustic soda solution. Titanium mesh (chloride resistant) cathodes (2 x) and anodes (3 x) were used. The area of one cathode (both sides) was approximately 0,045m². The run was conducted for approximately 550 hours.

The electrolytic recovery of nickel and cadmium was beforehand studied in the experimental set-up shown in Figure 9 without the 100 litre drag-out tank. Feed (10 or 15 litre) was put in the reservoir tank, electrical current applied (different electrical currents) and the metal concentrations were determined after certain time intervals.

Stainless steel mesh cathodes and anodes were used for cadmium removal/recovery studies.

The deposited metal can either be removed from the cathode by anodic stripping or by removing it with a wire brush. Nickel and cadmium were removed from the cathodes with a wire brush in this investigation.

4.4 Treatment of spent acid with diffusion dialysis

The experimental set-up for treatment of spent acid solution with diffusion dialysis is shown in Figure 10.



Figure 10: Experimental apparatus for diffusion dialysis

M: anion-exchange membrane; A: dialysate cell; B: diffusate cell; WT: water tank; FT: feed tank; RAT: recovered acid tank; WAT: waste acid tank. The dialyzer contained 19 Selemion DSV membranes containing 10 dialysate and 10 diffusate chambers. The effective membrane area was $172 \text{ cm}^2/\text{sheet}$ or 0,327 m²/unit.

Spent acid was fed from the bottom inlet (feed tank) and rises up, passing through each (dialysate) chamber and discharged in the dialysate tank (waste acid tank) from the top outlet on the same side as the inlet (feed tank). Water was fed from the top inlet (water tank) and flowed down, passing through each diffusate chamber and discharging from the bottom outlet (recovered acid tank) on the same side as the inlet (note: acid and water flow rates of approximately 1,0 ℓ/m^2 .h were used). Acid and metal concentration levels in the feed, dialysate and diffusate were determined by titration and atomic absorption analysis, respectively.

4.5 **Treatment of nickel rinse water with ion-exchange**

The experimental set-up for treatment of nickel rinse water with ion-exchange (IX) is shown in Figure 11.



Figure 11: Experimental set-up for treatment of nickel rinse water with ionexchange

Nickel rinse water from a 200 litre feed tank was passed at a flow rate of 10 bedvolumes per hour (10 BV's/h) through 105 mℓ resin (Duolite C20; 75 cm x 2.5 cm glass column). The nickel concentration in the product water was measured at regular time intervals (atomic absorption analysis) and breakthrough curves were established. The resin was regenerated with 10 BV's 4% sulphuric acid solution at a flow rate of 5 BV's/h and elution curves were established. The resin was rinsed with tap water to remove excess acid prior to the following loading run.

5. **RESULTS AND DISCUSSION**

5.1 Treatment of nickel rinse water with RO

Nickel rinse water was treated continuously (feed and bleed system, see Figure 4) with tubular cellulose acetate RO membranes (TCARO) at a plating shop to determine the fouling potential of the effluent for the membranes⁽¹⁵⁾. A batch test (see Figure 4) was conducted to establish process design criteria for a full scale application. Nickel rinse water was also treated (batch system) with spiral wrap filmtec membranes (seawater RO; 240 mm x 50 mm membrane; membrane area 1,022 m²) to evaluate this membrane type for effluent treatment⁽¹⁵⁾.

5.1.1 Evaluation of the fouling potential of nickel rinse water for tubular cellulose acetate RO membranes through pilot tests with a continuous RO system

Pilot tests (feed and bleed RO system) were conducted for approximately 336 hours at a plating shop⁽¹⁵⁾. Water recovery was set at approximately 82 percent for the first 100 hours of operation whereafter water recovery was increased to approximately 93% for the remainder of the run.

Permeate flux as a function of time is shown in Figure 12. The pH of the drag-out, RO feed tank, permeate and brine as a function of time is shown in Figures, 13, 14, 15 and 16. The conductivity of the drag-out, RO feed, permeate and brine as a function of time is shown in Figures 17, 18, 19 and 20. Water recovery as a function of time is shown in Figure 21. The clean water flux (CWF) is shown in Figure 22. The chemical composition of the RO feed, permeate and brine at 82 and 93% water recovery is shown in Tables 2 and 3, respectively.



Figure 12: Permeate flux as a function of time



Figure 13: pH of inlet drag-out as a function of time



Figure 14: pH of drag-out in RO feed tank as a function of time



Figure 15: pH of RO permeate as a function of time.



Figure 16: pH of RO brine as a function of time



Figure 17: Conductivity of inlet drag-out as a function of time



Figure 18: Conductivity of RO feed as a function of time



Figure 19: Conductivity of RO permeate as a function of time



Figure 20: Conductivity of RO brine as a function of time



Figure 21: Water recovery as a function of time



Figure 22: Clean water flux as a function of time (3 000 mg/l NaCl in Pretoria tap water)

Constituent	Inlet Drag-out	Feed Tank	Permeate	Brine	% Rejection
Sodium	174	1 115	11	1 197	99,0
Potassium	3	21	< 1	23	95,2
Calcium	23	41	2	45	95,1
Magnesium	16	80	1	87	98, 8
Ammonia-Nitrogen	7,3	72,1	1,6	75,5	97,8
Nitrate + Nitrite	< 0,2	0,6	< 0,2	< 0,2	66,7
Sulphate	2 969	7 516	74	11 404	99, 0
Chloride	184	961	69	1 290	92,8
СОР	664	2 520	344	1 640	86,3
Nickel	1 370	3 260	7,8	3 670	99,8
Iron	2,17	15,9	0,2	16,7	98,7
TDS	4 612	33 906	455	32 542	98,7
рН	1,8	1,4	1,5	1,4	
Conductivity mS/m	1 010	2 960	114	3 160	96,2

Table 2:Chemical Composition* of RO feed, permeate and brine (Run 4;
82% water recovery)

*

Concentration in mg/ unless otherwise stated

Table 3:Chemical Composition* of RO feed, permeate and brine (Run 21;
93% water recovery)

Constituent	Inlet Drag-out	Feed Tank	Permeate	Brine	% Rejection
Sodium	699	4 806	150	5 337	96,88
Potassium	6	51	2	46	96,08
Calcium	29	313	2	313	99,36
Magnesium	27	856	1	597	99,88
Ammonia-Nitrogen	33,5	200,5	11,5	220,8	94,26
Nitrate + Nitrite	7,8	13,4	7,5	13,2	44,03
Sulphate	4 943	68 723	< 5	73 509	
Chloride	986	5 420	556	5 006	89,74
COD	2 909	12 227	1 318	14 727	89,22
Nickel	1 300	13 500	37,4	14 400	99,72
Iron	4,07	37,4	0,13	38,8	99,65
TDS	10 279	107 093	1 384	114 523	98,70
рН	3,8	3,6	4,4	3,6	
Conductivity mS/m	768	4 010	141	4 260	96,5

*

Concentration in mg/e unless otherwise stated

Permeate flux remained almost constant at approximately 500 ℓ/m^2 .d when a water recovery of approximately 82% was used (first 110 hours of operation) (Figure 12). This showed that serious membrane fouling was not taking place. Water recovery was increased to approximately 93% after 110 hours of operation. Permeate flux decreased to approximately 280 ℓ/m^2 .h when the conductivity of the RO feed stabilized after approximately 140 hours of operation (Figure 18).

It appeared that permeate flux steadily declined from approximately 180 hours of operation till nearly 300 hours of operation. This normally indicated that membrane fouling took place. However, membrane fouling did not appear to be very serious. It is also interesting to note that there has been a steady increase in the conductivity of the RO feed water from approximately 180 hours of operation till nearly 300 hours of operation (Figure 18). This might explain the steady decrease in permeate flux that was experienced (Figure 12). Nevertheless, it appears that serious membrane fouling will not take place when nickel rinse water is treated with TCARO membranes when flow reversal with sponge ball cleaning is applied. (Note: The higher flux values between 160 and 180 hours of operation are ascribed to a faulty pressure gauge).

The steady decline in permeate flux that was experienced might also be ascribed to metal or organic fouling or to a slow degradation of the cellulose acetate membranes when exposed to a relatively low pH feed water (Figures 13 and 14). A citric ash cleaning (2%, pH 4,5) had no effect on permeate flux (Figure 12). A Biotex cleaning (0,5%) also appeared to have very little effect. The pH of the feed water was increased to approximately 3,5 by addition of sodium hydroxide to the holding tank after approximately 30 hours of operation to prevent rapid degradation of the cellulose acetate membranes (Figures 13 and 14). The spikes in the pH versus time graph (Figure 15) can be ascribed to the presence of dilution water in the system after the membranes have been rinsed with tap water at the end of each day.

The initial conductivity of the drag-out was approximately 1 000 mS/m (Figure 17). However, conductivity of the drag-out decreased to approximately 700 mS/m after 30 hours of operation. The conductivity of the RO feed water was approximately 1 000 mS/m when a water recovery of approximately 82% was used and approximately 4 000 mS/m when a water recovery of approximately 93% was used (Figure 18).

(Varying conductivity between 164 hours and 198 hours (Figures 18 and 20) of operation is ascribed to a faulty conductivity meter). Permeate conductivity was approximately 50 mS/m at a water recovery of 82%. Permeate conductivity, however, increased to approximately 100 mS/m at a water recovery of approximately 93%. It is interesting to note that permeate conductivity remains almost constant when a water recovery of approximately 93% has been applied (Figure 19). This showed that serious membrane fouling was not experienced over the test period. This was confirmed by the clean water flux that was conducted after approximately 151 hours of operation at 93% recovery) (see Figure 22).

The chemical composition of the RO permeate showed that a very good quality permeate could be produced (Tables 2 and 3). Ion rejections were excellent. The TDS of the RO feed was reduced from 33 906 to 455 mg/ ℓ (98,7% reduction) in the case when a water recovery of 82% was used. The nickel in the brine had a concentration of 3 670 mg/ ℓ . The TDS of the RO feed was reduced from 107 093 to 1 384 mg/ ℓ (98,7% reduction) in the case when a water recovery of 93% was used. The nickel in the brine had a concentration of 14 400 mg/ ℓ . Organic additives were also significantly concentrated in the RO brine. This means that both nickel and organic additives can be recovered for reuse in the plating process. It should be possible to reuse the RO brine (7% of feed) and permeate in the plating process. Consequently, valuable nickel, plating additives and water (rinse water) can be recovered for reuse.

5.1.2 Batch treatment of nickel rinse water with tubular cellulose acetate RO membranes

Permeate flux as a function of time and percentage water recovery is shown in Figures 23 and 24.



Figure 23: Permeate flux as a function of time



Figure 24: Permeate flux as a function of percentage water recovery

Permeate flux was high in the beginning of the run (approximately 640 ℓ/m^2 .d) and decreased as a function of time and was measured at 401 ℓ/m^2 .d when the run was terminated at 93% water recovery⁽¹⁵⁾. Clean water flux before and after the run was 842 ℓ/m^2 .d and 835 ℓ/m^2 .d respectively. This showed that little membrane fouling took place during treatment of nickel rinse water (also see 4.1.1). This batch run was conducted immediately after the membrane fouling studies to determine permeate flux for design purposes.

The chemical composition of the RO feed, permeate and brine is shown in Table 4.

Constituent	RO Feed (Initial)	RO Permeate	RO Brine	% Rejection
Sodium	450	39,9	1 980	91,1
Potassium	6,0	0,66	33,5	89
Calcium	57,7	1,29	244	97,8
Magnesium	35,8	0,88	188	97,5
Sulphate	4 435	16	16 159	99,6
COD	1 430	140	6 060	90,2
Ammonia	20,5	3,3	80,7	83,9
Nitrate/Nitrite(N)	5	2	6,2	60
Chloride	423	99	2 288	76,6
TDS	10 128	708	42 335	93,0
Nickel	1 760	38,9	7 400	97,8
Iron	10,2	0,42	39,7	95,9
рH	3,6	3,4	3,1	
Conductivity mS/m	680	60	2 960	91,1

Table 4: Chemical composition^{*} of RO feed, permeate and brine (nickel drag-out)

All results expressed in mg/t unless otherwise stated.

Nickel was concentrated from 1 760 mg/ ℓ in the RO feed to 7 400 mg/ ℓ in the RO brine (4,2 times concentrated). Nickel removal by the cellulose acetate RO membranes was 97,8 percent.

The COD removal was determined at 90.2 percent. Therefore, a large percentage of the organics used in the plating process can be recovered for reuse.

Conductivity removal was determined at 91,1 percent and it should be possible to reuse both the RO permeate and brine (7% of feed) in the plating process. Consequently, valuable water and chemicals can be recovered for reuse in the plating process. Metal recovery will also lead to reduced sludge disposal costs and pollution prevention.

5.1.3 Batch treatment of nickel rinse water with spiral wrap filmtec membranes

Permeate flux as a function of time and percentage water recovery is shown in Figures 25 and 26. Clean water fluxes are shown in Figures 27 and 28. The chemical composition of the RO feed, permeate and brine is shown in Table 5.

The initial water flux during run 1 was high (Figures 25 and 26). Permeate flux was approximately 1 190 ℓ/m^2 .d. Permeate flux, however, decreased for subsequent runs (run 1 to 4). This indicated that membrane fouling took place. Permeate flux, however, increased during run 6 and remained more or less the same for runs 7 and 8.

The clean water fluxes clearly showed that membrane fouling took place (Figures 27 and 28). The clean water flux after run 8 was significantly lower than before the runs. It also appeared that membrane performance could be restored with a citric acid cleaning.



Figure 25: Permeate flux as a function of time



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Figure 26: Permeate flux as a function of percentage water recovery



Figure 27: Clean water flux as a function of time (3 000 mg/l NaCl in Pretoria tap water)



Figure 28:Clean water flux as a function of percentage water recovery
(3 000 mg/l NaCl in Pretoria tap water)

Constituent	Feed	Permeate	Brine	% Rejection
Sodium	183	< 2	2 678	98,9
Potassium	3	< 1	42	66,7
Calcium	24	1	349	95,8
Magnesium	16	11	213	93,8
Ammonia-Nitrogen	10,6	< 0,2	123,5	98,1
Nitrate + Nitrite	1,6	1,1	6,7	31,3
Sulphate	1 739	9	24 935	99,5
Chloride	210	48	2 126	77,1
COD	802	100	14 880	87,5
Nickel	635	1,35	9 625	99,8
Iron	1,67	< 0,03	27,55	98,2
TDS	4 198	31	< 50 000	99,3

 Table 5:
 Chemical Composition* of RO feed, permeate and brine (Nickel drag-out; 4 000 kPa)

*

All results expressed in mg/t unless otherwise stated.

Conductivity rejection was high (Table 5). Conductivity rejection was approximately 99% during run 1 and decreased somewhat for subsequent runs. Conductivity rejection was approximately 96% during run 8⁽¹⁵⁾.

A very good quality permeate was again produced (Table 5). TDS was only 31 mg/ ℓ . The nickel in the feed was reduced from 635 mg/ ℓ to approximately 1 mg/ ℓ in the permeate. Therefore, excellent removals of nickel can be obtained with Filmtec membranes. Nickel was concentrated from 635 mg/ ℓ in the feed to 9 625 mg/ ℓ in the RO brine (concentration factor of 15). Both the RO permeate and brine can be recovered for reuse in the plating process. Sludge volume will also be significantly reduced when metal recovery is practised. Metal pollution of the municipal sewer system will also be reduced through metal recovery at electroplating shops. This will ensure that toxic nickel will be kept out of the water environment to a large extent.

5.2 Treatment of chromium rinse water with RO

Chromium rinse water was treated with a feed and bleed system (Figure 4) with TCARO membranes to determine the fouling potential of the effluent for the membranes. A batch test (Figure 4) was conducted to establish process design criteria. Chromium rinse water was also treated (batch system) with spiral wrap Filmtec membranes (seawater RO, 240 mm x 50 mm membrane) to evaluate this membrane type for effluent treatment⁽¹⁵⁾.

5.2.1 Evaluation of the fouling potential of chromium rinse water for tubular cellulose acetate RO membranes through pilot tests with a continuous RO system

Pilot tests were conducted for approximately 480 hours at a plating shop. Water recovery was set at approximately 80 percent.

Permeate flux as a function of time is shown in Figure 29. The initial permeate flux was 825 ℓ/m^2 .d and it declined rapidly and was approximately 400 ℓ/m^2 .d after 73 hours of operation. Clean water flux was determined at approximately 554 ℓ/m^2 .d after 73 hours of operation. The membranes were then cleaned with 2 percent citric acid (pH 4,5 with ammonia) and permeate flux increased to 585 ℓ/m^2 .d. Further cleaning with 0,5 percent EDTA solution (normal pH and pH 11 with ammonia) increased CWF to approximately 600 and 654 ℓ/m^2 .d, respectively. The initial CWF was determined at approximately 840 ℓ/m^2 .d. Therefore, it appeared that some irreversible fouling took place or that the membranes were not properly cleaned. However, it was possible to increase permeate flux from approximately 400 ℓ/m^2 .d to 535 ℓ/m^2 .d after cleaning.



Figure 29: Permeate flux as a function of time at 80% water recovery

Permeate flux again declined when the run was started and was determined at $367 \ \ell/m^2$.d after 200 hours of operation. Clean water flux was $588 \ \ell/m^2$.d and was determined at $565 \ \ell/m^2$.d after cleaning with a 1 percent sodium hexametaphosphate solution. Therefore, it appeared that sodium hexametaphosphate solution had no effect on membrane cleaning. The membranes were then cleaned with a 2 percent citric acid solution (pH 4,5) and permeate flux increased to 604 $\ \ell/m^2$.d. Further cleaning of the membranes with 0,5 percent EDTA solution increased CWF flux to 620 $\ \ell/m^2$.d. This flux was somewhat lower than the CWF of 654 $\ \ell/m^2$.d (after 73 hours of operation) showing that the membranes were not completely cleaned.

Permeate flux declined when the run was commenced and was determined at $300 \ \ell/m^2$.d after 296 hours of operation. Clean water flux was determined at 495 ℓ/m^2 .d. No improvement in CWF was obtained after cleaning with 1 percent sodium hexa-metaphosphate solution (CWF 493 ℓ/m^2 .d). Clean water flux, however, increased to 529 ℓ/m^2 .d after cleaning with a 2 percent citric acid solution (pH 4,5). A further increase to 549 ℓ/m^2 .d in CWF was experienced after cleaning with a 0,5% EDTA solution (pH 11). This CWF, however, was again lower than the CWF of 620 ℓ/m^2 .d that was obtained after 200 hours of operation. This again showed that the membranes were not completely cleaned after chemical cleaning.

Permeate flux declined when the run was commenced and was determined at 285 ℓ/m^2 .d after 386 hours of operation. Clean water flux was determined at 487 ℓ/m^2 .d. Cleaning with citric acid (2% solution, pH 4,5) increased CWF to 522 ℓ/m^2 .d. Further cleaning with EDTA solution (0,5% solution, pH 11) increased CWF to 532 ℓ/m^2 .d. Three further consecutive one hour citric acid cleanings increased CWF to 628 ℓ/m^2 .d. This showed that it should be possible to clean the membranes with chemical cleaning (CWF after 200 hours was 620 ℓ/m^2 .d.

Permeate flux again declined when the run was commenced and was determined at 280 ℓ/m^2 d when the run was terminated. The membranes were cleaned with three consecutive citric acid cleanings and CWF was determined at 627 ℓ/m^2 .d. This again showed that it should be possible to control membrane fouling with chemical cleanings. Permeate conductivity also remained almost constant over the test period showing that serious membrane fouling did not take place.

The chemical composition of the RO feed, permeate and brine at 80 percent water recovery is shown in Table 6.

Constituent*	Cr Drag-out	Feed	Permeate	Brine	% Rejection
Sodium	159	790	45,7	880	94,2
Potassium	5,3	23,8	0,9	25,2	96,2
Calcium	42	244	5,8	259	97,6
Magnesium	8,9	25,9	2,7	27,5	89,6
Nitrate/Nitrite(N)	3,49	0,82	4,54	0,96	
Sulphate	11,5	256,8	31,3	294,7	87,8
COD	49	163	43	174	73,6
Nickel	24,9	138	1,1	155	99,2
Iron	1,7	1,9	0,9	2,3	52,6
Dissolved salts	1 480	7 440	355	8 313	95,2
Chloride	19	110	11	121	90,0
Chromium	740	2 950	189	3 100	93,6
Conductivity (mS/m)	121	520	31,5	575	93,9
рН	3,5	3,5	4,4	3,5	

Table 6:Chemical composition of RO feed, permeate and brine
(80% recovery; 200 hours of operation)

*

All results expressed in mg/t unless otherwise stated.

Excellent ion rejections were obtained (Table 6). Conductivity and chromium rejection were both 93,6 percent. Nickel showed a rejection of 99,2 percent.

An excellent quality permeate was also produced (Table 6). The TDS of the permeate was only 355 mg/ ℓ . It should be possible to use the RO permeate for rinsing in the plating process. It should also be possible to recover the chromium in the RO brine for reuse after ion-exchange treatment to remove sodium and further concentration in an evaporator.

5.2.2 Batch treatment of chromium rinse water with tubular cellulose acetate RO membranes

Permeate flux as a function of time and percentage water recovery is shown in Figures 30 and 31.



Figure 30: Permeate flux as a function of time.



Figure 31: Permeate flux as a function of percentage recovery

The initial permeate flux was 468 ℓ/m^2 .d. Flux, however, decreased as a function of time and was 288 ℓ/m^2 .d when the run was terminated at 91,5% water recovery.

The initial clean water flux was 627 ℓ/m^2 .d. Clean water flux after three batch runs was 600 ℓ/m^2 .d. Therefore, it appears that a certain degree of membrane fouling has taken place.

The chemical composition of the RO feed, permeate and brine is shown in Table 7. Chromium was concentrated from 469 mg/ ℓ in the RO feed to 2 320 mg/ ℓ in the RO brine (4,95 times concentrated). This concentration level of chromium in the brine, however, is nog high enough to put it directly back into the plating bath. However, it should be possible to increase the chromium concentration level in the brine to the required strength with an evaporator.

The pH of the chromium drag-out was less than 2. A pH of less than 2, however, will affect cellulose acetate membranes adversely. Therefore, the pH of the chromium rinse water was increased to a pH of approximately 3,5 with caustic soda prior to RO treatment. The sodium, however, should be removed from the brine by cation-exchange prior to reuse on the plating bath.

The ion rejections (Table 7) were not as high as during feed and bleed treatment (Table 6). A composite sample of the RO permeate was taken for analysis. Therefore, lower ion rejections were obtained.

Constituent*	RO Feed (Initial)	RO Permeate (Composite)	RO Brine (Remaining)	% Rejection
Sodium	109	25	629	77,1
Potassium	2,2	1,06	27,7	51,8
Calcium	41	7,8	252	81,0
Magnesium	10,5	0,81	72	92,3
COD	27	7	205	74.0
Ammonia	1,3	1,2	7,0	7,6
Nitrate/Nitrite(N)	0,5	0,3	6,2	40,0
Iron	0,19	0,04	3,5	63,2
Chromium	469	61	2 320	87,0
Sulphate	651	65	4 281	90,0
Chloride	14	7	82	50
TDS	1 225	225	7 592	81,6
рН	3,9	5,8	2,9	52,6
Conductivity (mS/m)	101	23,5	680	67,7

 Table 7:
 Chemical composition of RO feed, permeate and brine

* All results expressed in mg/t unless otherwise stated.

5.2.3 Batch treatment of chromium rinse water with spiral wrap Filmtec membranes

Permeate flux as a function of time and percentage water recovery is shown in Figures 32 and 33. Clean water fluxes are shown in Figures 34 and 35. The chemical composition of the RO feed, permeate and brine is shown in Table 8.

Initial permeate flux for the first four runs was approximately 1 000 ℓ/m^2 .d (Figures 32 and 33). Flux, however, decreased to approximately 400 ℓ/m^2 .d at the end of the runs at approximately 90% water recovery. Permeate flux was almost the same for the first four runs in the percentage water recovery range from 0 to approximately 90 percent. However, permeate flux increased dramatically during runs 5, 6, 7 and 8. Another feed

batch was used for runs 5 to 8. Conductivity rejection was also lower for runs 5 to 8 $(97\% \text{ versus } 99\% \text{ for runs } 1 \text{ to } 4)^{(15)}$. This might indicate that membrane fouling had started to take place. Consequently, the increased permeate flux might be ascribed to a changed membrane. This could have been brought about by the chromium in solution. Conductivity rejection, however, was still high.

It appeared that CWF before the chromium runs was less than the CWF after the chromium run (except for first point Figure 35). This showed that permeate flux could be higher during run 8. It also appeared that membrane cleaning with a citric acid solution had little effect on CWF.



Figure 32: Permeate flux as a function of time



Figure 33: Permeate flux as a function of percentage water recovery



Figure 34: Clean water as a function of time (3 000 mg/l NaCI in Pretoria tap water)



Figure 35: Clean water flux as a function of percentage water recovery (3 000 mg/l NaCI in Pretoria tap water)

Constituent	Feed	Permeate	Brine	% Rejection
Sodium	77	< 2	1 423	97,4
Potassium	4	1	61	75,0
Calcium	29	1	96	96,6
Magnesium	15	< 1	240	93.3
Ammonia-Nitrogen	3,0	0,6	32,1	80,0
Nitrate + Nitrite	4,6	0,4	82,4	91,3
Sulphate	1 835	140	26 124	92,4
Chloride	186	80	576	57,0
Chromium	1 840	25,2	24 400	88,6
Iron	25,4	0,05	405	99,8
TDS	3103,9	575,9	82 359	81,4

Table 8:Chemical composition* of RO feed, permeate and brine (Chromium
rinse water; 4 000 kPa)

*

Concentration in mg/t unless otherwise stated.

Excellent conductivity rejections were obtained. Conductivity rejection was approximately 99% during the first four runs. However, conductivity rejection decreased to approximately 98% towards the end of runs 5 to 8⁽¹⁵⁾.

A very good quality permeate was produced (Table 8). The TDS of the permeate was only 576 mg/ ℓ . Chromium was reduced from 1 840 mg/ ℓ in the RO feed to 25 mg/ ℓ in the permeate. Therefore, Filmtec membranes appear to be very effective for chromium removal. The chromium in the brine had a concentration of 24 400 mg/ ℓ . Therefore, chromium was concentrated by a factor of approximately 13. It should be possible to reuse both the permeate and brine in the plating process. Consequently, a significant amount of water (90% of feed) can be recovered for reuse. Sludge volume will also be dramatically reduced if chromium can be recovered for reuse. Chromium pollution of the municipal sewer system will be reduced if chromium recovery is practiced. Therefore, toxic chromium will be to a large extent kept out of the environment.

5.3 Treatment of zinc rinse waters with RO

Zinc rinse waters (both acid and alkaline) were treated with a feed and bleed RO

system (Figure 4) to determine the fouling potential of the effluent for the membranes. Tubular cellulose acetate membranes were used for the acid zinc rinse water while PCI AFC 99 membranes (tubular) were used on the alkaline zinc rinse water. A batch test was also conducted to establish process design criteria.

5.3.1 Evaluation of the fouling potential of acid zinc rinse water for tubular cellulose acetate RO membranes through pilot tests with a continuous RO system

Pilot tests were conducted for approximately 200 hours at a plating shop at a water recovery of approximately 80 percent.

Permeate flux as a function of time is shown in Figure 36. Permeate flux was 188 ℓ/m^2 .d when the run was commenced and decreased to 96 ℓ/m^2 .d after 4 hours of operation. The RO unit was switched off overnight and permeate flux was higher (129 ℓ/m^2 .d) when the RO unit was switched on the next morning. This pattern was followed for approximately 70 hours of operation when flux started to decline and was



Figure 36: Permeate flux as a function of time at 80% water recovery

measured at approximately 50 ℓ/m^2 .d after 90 hours of operation. Permeate flux increased to approximately 100 ℓ/m^2 .d after 100 hours of operation and decreased to approximately 30 ℓ/m^2 .d when the run was terminated after 207 hours of operation

The initial clean water flux was 587 ℓ/m^2 .d. Clean water flux, however, decreased to 370 ℓ/m^2 .d after 15 hours of operation showing that membrane fouling took place. Clean water flux declined further and was determined at 213 ℓ/m^2 .d after 110 hours of operation. A citric acid cleaning, however, increased CWF to 518 ℓ/m^2 .d (after 110 hours). Clean water flux was determined at 205 ℓ/m^2 .d after 207 hours of operation and increased to 528 ℓ/m^2 .d after citric acid cleanings. This showed that CWF could be maintained. Therefore, it should be possible to control membrane fouling with regular chemical cleaning. Permeate conductivity also remained constant during the run showing that serious membrane fouling did not take place.

The chemical composition of the RO feed, permeate and brine is shown in Table 9. Conductivity rejection was 76 percent. The TDS rejection, however, was 88,4 percent.

Constituent*	Zn Drag- out	Feed Tank	Permeate	Brine	% Rejection
Sodium	339	840	85,9	830	89,8
Potassium	6,7	14,6	2,77	14,9	81,0
Calcium	45,2	134	18,7	117	86,0
Magnesium	24,2	61,2	5,37	65,3	91,2
Sulphate	166,29	532	30	530	94,4
COD	4 480	9 170	1 090	9 990	88,1
Ammonia (N)	3 427	3 792	905	7 048	86,7
Nitrate/Nitrite (N)	5,2	7	4,1	10	41,4
Zinc	1 740	5 090	323	5 280	93,7
lron	0,04	0,38	0,01	0,39	97,4
Chloride	9 648	23 598	3 809	25 123	83,9
TDS	20 716	44 861	5 214	44 861	88,4
рН	6,6	6,1	7,0	6,1	
Conductivity (mS/m)	3 870	7 570	1 820	7 620	76,0

Table 9:Chemical composition of RO feed, permeate and brine
(after 207 hours of operation)

All results expressed in mg/t unless otherwise stated.

*

This indicated that something could have gone wrong with the conductivity measurement. High percentage ion rejections were obtained with the other ions. Zinc showed an ion rejection of approximately 94 percent.

5.3.2 Batch treatment of acid zinc rinse water with tubular cellulose acetate RO membranes

Permeate flux as a function of time and percentage water recovery is shown in Figures 37 and 38. Permeate flux was 407 ℓ/m^2 .d when the run was commenced and decreased to 124 ℓ/m^2 .d when the run was terminated at 91 percent water recovery. The CWF was 528 ℓ/m^2 .d before the run and was determined at 521 ℓ/m^2 .d after the run. This showed that a certain degree of membrane fouling took place.

The chemical composition of the RO feed, permeate and brine is shown in Table 10. The TDS rejection was approximately 90 percent. Conductivity rejection was again lower (approximately 72%). Excellent zinc removal was obtained. Zinc was removed from 630 mg/ ℓ in the RO feed to 36 mg/ ℓ in the RO permeate (94,3% removal). Zinc was at the same time concentrated from 630 mg/ ℓ in the RO feed to 2 790 mg/ ℓ in the RO brine (4,14 times concentrated). It should be possible to reuse both the RO permeate and brine in the plating process.


Figure 37: Permeate flux as a function of time



Figure 38: Permeate flux as a function of percentage water recovery

Constituent	RO Feed (Initial)	RO Permeate (Composite)	RO Brine (Remaining)	% Rejection
Sodium	109	16	502	85, 3
Potassium	1,85	0,38	8,7	79,5
Calcium	31	2,19	179	92,9
Magnesium	19	1,16	118	93,9
COD	1 240	416	5 800	66,5
Ammonia	1 690	537	7 833	66,6
Nitrate + Nitrite	2,4	1,7	2,7	29,2
Iron	0,67	0	22,3	100,0
Zinc	630	36	2 790	94, 3
Sulphate	244	26	418	89,3
Chloride	7 304	78	29 368	98, 9
TDS	4 382	448	33 538	89,8
рН	6,5	6,9	6,2	
Conductivity (m/Sm)	1 260	355	5 540	71,8

Table 10: Chemical composition of RO feed, permeate and brine

* Concentration in mg/*l* unless otherwise stated.

5.3.3 Evaluation of the fouling potential of alkaline zinc rinse water for tubular PCI AFC 99 RO membranes through pilot tests with a continuous RO system

Pilot tests were conducted for approximately 200 hours at a plating shop at a water recovery of approximately 80 percent. A PCI membrane module with a membrane area of 0,848 m² was used for the investigation. The zinc cyanide rinse water had a pH of approximately 11. Therefore, PCI AFC 99 tubular RO membranes with a high pH tolerance was used for this application.

Permeate flux as a function of time is shown in Figure 39.



Figure 39: Permeate flux as a function of time

The initial permeate flux was 1 218 ℓ/m^2 .d and this flux dropped to 403 ℓ/m^2 .d after 4 hours of operation. The RO plant was switched off overnight and the membranes were left in tap water. Flux was 1064 ℓ/m^2 .d the following day when the run was started and dropped to 406 ℓ/m^2 .d after 11 hours of operation. The RO membranes were again left in tap water overnight and flux was 294 ℓ/m^2 .d after 1 hour of operation (12 hours) the next day and decreased to 183 ℓ/m^2 .d after 17 hours of operation. Clean water flux was determined at 327 ℓ/m^2 .d (initial CWF 1 436 ℓ/m^2 .d). Therefore, it was obvious that serious membrane fouling had taken place.

The membranes were cleaned with a 2 percent citric acid solution (pH 4,5) and CWF was determined at 1 395 ℓ/m^2 .d (17 hours of operation). Therefore, it appeared that CWF could almost be restored. Permeate flux was 884 ℓ/m^2 .d (after 18 hours) when the run was commenced and dropped to 329 ℓ/m^2 .d after 46 hours of operation.

The membranes were again cleaned with citric acid and CWF was determined at 1400 ℓ/m^2 .d (46 hours of operation). Permeate flux was 903 ℓ/m^2 .d when the run was commenced (47 hours of operation) and decreased to 337 ℓ/m^2 .d after 95 hours of operation. The membranes were again cleaned with citric acid and CWF was determined at 1450 ℓ/m^2 .d.

Permeate flux increased to 934 ℓ/m^2 .d after cleaning (96 hours) and decreased to 315 ℓ/m^2 .d after 144 hours of operation. Clean water flux after a citric acid cleaning was 1440 ℓ/m^2 .d. Permeate flux was 923 ℓ/m^2 .d when the run was commenced (145 hours) and decreased to 233 ℓ/m^2 .d when the run was terminated. Clean water flux after a citric acid cleaning was 1455 ℓ/m^2 .d. Therefore, it appeared that it should be possible to control membrane fouling with regular citric acid cleanings. Permeate conductivity also remained almost constant during the run showing that serious membrane fouling was not taking place.

The chemical composition of the RO feed, permeate and brine is shown in Table 11. Conductivity rejection was determined at approximately 84 percent. The TDS rejection was almost 97 percent. This discrepancy can not be explained at this stage. Excellent zinc removals were obtained. Zinc was removed from 2 200 mg/ ℓ in the feed to 30 mg/ ℓ in the permeate (98,6% removal). It should be possible to reuse the RO permeate as rinse water in the plating process.

Constituent*	Drag-out	Feed Tank	Permeate	% Rejection
Sodium	2 840	11 900	540	95,5
Potassium	22,1	75	0,59	99,2
Calcium	27,7	25,0	3,25	87
Magnesium	0,3	1,29	0,19	85,3
Sulphate	25	5 085	188	96,3
COD	1 193	5 380	442	91,8
Ammonia	1	3,1	2,3	25,8
Nitrate/Nitrite(N)	0	0,06	0	100
Zinc	420	2 200	29,9	98,6
iron	64	311	2,6	99,2
TDS	12 126	51 498	1 786	96,5
рН	10,7	10,5	9,3	
Conductivity (mS/m)	1 400	4 610	755	83,6

 Table 11:
 Chemical composition of the drag-out, RO feed and RO permeate

All units in mg/t unless otherwise stated.

5.4 Treatment of cadium rinse water with RO

Cadmium rinse water has a high pH (pH approximately 11). Therefore, Filmtec polyamide membranes were evaluated for this application.⁽¹⁵⁾

5.4.1 Batch treatment of cadmium rinse water with spiral wrap Filmtec RO membranes

Permeate flux as a function of time and percentage water recovery is shown in Figures 40 and 41. Clean water fluxes are shown in Figures 42 and 43. The chemical composition of the RO feed, permeate and brine is shown in Table 12.



Figure 40: Permeate flux as a function time



Figure 41: Permeate flux as a function of percentage water recovery

The initial permeate flux was high (Figures 40 and 41). Permeate flux was approximately 1800 ℓ/m^2 .d in the beginning of run 1 and declined as a function of time. However, permeate flux decreased significantly during run 2. The initial permeate flux was approximately 1300 ℓ/m^2 .d when run 2 was commenced and again declined as a function of time. This showed that membrane fouling took place and the membranes were cleaned with citric acid. Permeate flux was restored (run 3) but again decreased significantly during run 4. It was again possible to restore permeate flux with a citric acid cleaning (after run 5).

Conductivity rejection was high. Conductivity rejection was approximately 98% during run 1. However, conductivity rejection decreased somewhat to approximately 97% during runs 3, 5 and 7 (after cleaning).



Figure 42: Clean water flux as a function time (3 000 mg/l NaCI in Pretoria tap water)



Figure 43: Clean water flux as a function of percentage water recovery (3 000 mg/ℓ NaCl in Pretoria tap water)

Constituent	Feed	Permeate	Brine	% Rejection
Sodium	707	22	5 854	96,9
Potassium	2	< 1	22	50,0
Calcium	2	1	2	50,0
Magnesium	1	1	1	-
Ammonia-Nitrogen	2,7	0,5	0,8	81,5
Nitrate + Nitrite	0,3	0,2	2,7	33,3
Sulphate	37	7	267	81,1
Chloride	668	96	8 898	85,6
COD	510	41	3 367	92,0
Cadmium	95	0,16	900	99,8
lron	9,1	< 0,03	57,5	99,7
TDS	2 416	57,3	18 371	97,6

Table 12:Chemical composition* of RO feed, permeate and brine
(Cadmium rinse water; 4 000 kPa)

* Concentration in mg/*l* unless otherwise stated.

The clean water fluxes showed that little membrane fouling took place after cleaning of the membranes with citric acid solution (Figures 42 and 43).

A very good quality permeate was again produced (Table 12). The TDS of the permeate was only 57 mg/ ℓ . Cadmium was reduced from 95 mg/ ℓ in the feed to approximately 0,2 mg/ ℓ in the permeate. The brine had a cadmium concentration of approximately 900 mg/ ℓ (concentration factor of 9,5). Consequently, it appears that it should be possible to use Filmtec RO membranes successfully for cadmium and water recovery and for pollution control.

5.5 Treatment of electroplating rinse waters with ED

Batch tests were conducted on real effluent with the ED pilot plant shown in Figure 5⁽¹⁸⁾. Results are also presented of treatment of nickel, copper and silver electroplating effluents with ED. This work was conducted by a commercial company in France.

The fouling potential of electroplating effluents for ED membranes is described with the fouling cell shown in Figure 7⁽¹⁵⁾. Treatment of chromium rinse water with electroelectrodialysis is described lastly with the cell shown in Figure 8.

5.5.1 Treatment of nickel electroplating rinse water with ED

The nickel concentration in the ED Feed and brine for four batch runs is shown in Figures 44, 45, 46 and 47 (note: fresh feed was used for each unit, 0,77 volt/cell pair). The chemical composition of the ED feed in the beginning and at the end of the runs is shown in Tables 13, 14, 15 and 16. The nickel, COD, calcium and sulphate concentration levels in the ED brine are shown in Table 17 for the different feed batches.

Nickel could be concentration from approximately 3,5 g/l in the ED feed to 23 g/l in the ED brine (6,6 times concentrated) (Figures 44 to 47 and Table 17). Nickel concentration could be reduced from 3,1 to 3,7 g/l in the ED feed to between 700 and 1 000 mg/l in the desalinated feed (Figures 44 to 47 and Tables 13 to 16). It should be possible to recycle both the ED brine and desalinated ED feed in the plating process.

The chemical composition of the ED brine after four feed water batches is shown in Table 18.



Figure 44: Nickel concentration in ED feed and brine during 1st batch run



Figure 45: Nickel concentration in ED feed and brine during 2nd batch run



Figure 46: Nickel concentration in ED feed and bring during 3rd batch run



Figure 47: Nickel concentration in ED feed and brine during 4th batch run

Constituent	Feed Begin	Feed End	Rejection(%)
COD	1 050	790	24,76
Ammonia (N)	35,6	2,1	94,10
Nitrate (N)	0,04	0,05	-
Nickel	3 520	980	72,16
Iron	12,8	4,1	67,97
Sodium	800	34,7	95,66
Potassium	9,1	0,38	95,82
Calcium	74,4	18,9	74,60
Magnesium	47,4	19,9	58,02
Sulphate Total	7 076	1 949	72,46
Chloride	1 366	149	89,09
TDS	17 460	5 877	66,34
Conductivity (mS/m)	1 182	315	73,35
рН	2,48	2,64	-

Table 13:Chemical composition of ED feed in the beginning and at the end
of the run (1st run)

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Constituent	Feed Begin	Feed End	Rejection (%)
COD	1 0450	940	9,62
Ammonia (N)	24,2	3,1	87,19
Nitrate (N)	0,02	0,09	-
Nickel	3 140	960	69,43
Iron	18,2	6,2	65,93
Sodium	709	71	89,99
Potassium	7,8	0,75	90,38
Calcium	63,4	16,7	73,66
Magnesium	44	18,4	58,18
Sulphate Total	5 713	1888,42	66,95
Chloride	1 299	210	83,83
TDS	16 313	6 019	63,10
Conductivity (mS/m)	1 168	339	70,98
рН	2,39	2,71	-

Table 14:Chemical composition of ED feed in the beginning and at the end
of the run (2nd run)

Table 15:Chemical composition of ED feed in the beginning and at the end
of the run (3rd run)

Constituent	Feed Begin	Feed End	Rejection(%)
COD	1 200	930	30,83
Ammonia (N)	39	3,3	91,54
Nitrate (N)	0,05	0	100,00
Nickel	3 730	890	76,14
Iron	26,2	8,9	66,03
Sodium	830	66	92,05
Potassium	9,8	0,61	93,78
Calcium	83	13,2	84,11
Magnesium	49,6	21,7	56,25
Sulphate Total	7 020	2 213	68,48
Chloride	1 433	177	87,65
TDS	16 848	5 921	64,86
Conductivity (mS/m)	1 340	361	73,06
рН	2,38	2,86	-

Constituent	Feed Begin	Feed End	Rejection(%)
COD	1 030	770	25,24
Ammonia (N)	35,2	2,5	92,90
Nitrate (N)	0	0,05	-
Nickel	3 560	760	78,65
Iron	15,6	5,3	66,03
Sodium	771	58	92,48
Potassium	8,3	0,58	93,01
Calcium	89	8,3	91,53
Magnesium	47	15	68,09
Sulphate Total	6 859	1496,58	78,18
Chloride	1 179	162	86,26
TDS	15 980	4,883	69,44
Conductivity (mS/m)	1 239	291	76,51
рН	2,55	2,80	-

Table 16:Chemical composition of ED feed in the beginning and at the end
of the run (4th run)

	Table 17:	Chemical com	position of the E	ED brine for the	different feed batches
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Constituents	Feed Ba (B	l Water htch 1 brine)	Feed Ba (B	d Water htch 2 krine)	Feed Ba (E	d Water atch 3 Brine)	Feed Ba (B	l Water tch 3 rine)
(mg/ฦ	Begin	End	Begin	End	Begin	End	Begin	End
COD	1 050	1 700	1 650	2 100	2 170	3 315	3 370	3 450
Nickel	3 520	8 800	9 000	9 000	17 000	16 900	19 000	23 000
Calcium	74,4	810	646	1 150	920	1 270	1 190	851
Sulphate	7 076	25 334	25 198	39 308	34 900	40 221	50 759	66 061
Conductivity mS/m	1 182	3 930	3 930	5 340	4 980	6 930	6 870	7 510
рН	2,48	2,12	2,16	2,02	2,14	1,91	1,77	1,65

Constituents	Concentration (mg/ℓ)
COD	3 450
Ammonia (N)	300,8
Nitrate (N)	4,5
Nickel	23 000
Iron	66,3
Sodium	7 180
Potassium	9,7
Calcium	851
Magnesium	389
Sulphate Total	66 062
Chloride	12 513
TDS	> 50 000
Conductivity (mS/m)	7 510
рН	1,65

Table 18:Chemical composition of ED brine after desalination
of 4 feed water batches

Not nickel only is concentrated in the ED process, but other cations and anions present in the feed water are also concentrated. The concentration of calcium for example in the ED brine, was determined at 851 mg/ ℓ (Table 18). Calcium was concentrated in the ED feed from approximately 60 to 100 mg/ ℓ to 851 mg/ ℓ in the ED brine. Care should therefore be taken that the solubility limit of calcium sulphate is not exceeded in the ED brine because it will cause scaling of the ED membranes. It would be possible to recycle the brine back to the plating bath if the other ions present in the brine would not adversely affect the plating process. The desalinated water can be used as rinse water in the process. Approximately 85 percent of the rinse water can be recovered for reuse. Brine comprises approximately 15 percent of the treated water.

The electrical energy consumption for nickel transport and the loading rate for nickel removal are shown in Table 19 for the different feed water batches.

Feed Batch No	Energy Consumption kWh/kg Ni	Loading Rate kg Ni/m².h	% NI Removal
1	1,87	0,044	72,16
2	2,4	0,038	69,43
3	2,5	0,042	76,14
4	2,35	0,048	78,65

Table 19:Electrical energy consumption for nickel transport and the loading
rate for nickel removal

The economics of the ED process for nickel recovery and the membrane area required for a certain size plant can be determined from the date in Table 19.

A flow diagram for nickel recovery from plating rinse waters as practiced in France is shown in Figure 48. The nickel concentration in the rinse bath was kept between 0,5 and 2 g/ ℓ while the nickel was concentrated to 50 g/ ℓ in the brine. Drag-out recovery was 97 percent.

5.5.2 Treatment of copper cyanide rinse water with ED

A flow diagram for treatment of copper cyanide, rinse water with ED is shown in Figure 49.



Figure 48: Flow diagram of ED plant for nickel and water recovery from nickel rinse water (I = electric current; U = voltage)



Figure 49: Flow diagram of ED plant for copper and water recovery from copper cyanide rinse water

The copper concentration level was kept between 0,5 and 1 g/ ℓ in the rinse tank while the copper was concentrated to 60 g/ ℓ in the ED brine. Approximately 92 percent of the drag-out was recovered in the process.

5.5.3 Treatment of silver cyanide rinse water with ED

The silver concentration level in the rinsing bath was kept between 0,3 and 1 g/ ℓ while the silver was concentrated to 27 g/ ℓ in the ED brine. Approximately 95 percent of the drag-out could be recovered in the process.



Figure 50: Flow diagram of ED plant for silver and water recovery from silver cyanide rinse water

5.5.4 Fouling potential of spent plating bath water for ED membranes

The effect of spent nickel plating bath water on membrane fouling using Selemion AMV, Ionics A-204-UZL and Ionac MA-3475 membranes, is shown in Figure 51⁽¹⁵⁾. The Selemion AMV membrane was rapidly fouled with the spent plating bath solution. However, the Ionics and Ionac membranes showed little signs of membrane fouling over the test period. Consequently, it will be necessary to pretreat nickel rinse water prior to ED treatment when using Selemion AMV membranes. Activated carbon should be able to reduce the foulants to low levels. This matter, however needs further investigation. Frequent acid cleanings should also be considered for membrane cleaning.



Figure 51: Effect of spent nickel plating bath water on membrane fouling using Selemion, Ionics and Ionac membranes (CD 20 mA/cm²; Conductivity of feed 5 300 mS/m; COD of feed 59 000 mg/ℓ)

Membrane resistance before and after fouling is shown in Table 20.

Table 20:Membrane resistance before and after fouling with spent nickel
plating bath water using different ion-exchange membranes

	Resistance (ohm.cm ²)			
Membrane ⁽¹⁾	Unused	Used		
Selemion AMV	4,6* 0,51**	331* 5,8**		
Ionics A-204-UZL	7,6* 4,1**	23,6* 6,9**		
Ionac MA-3475	30* 25,9**	66,5* 29,4**		

Membrane resistance measured immediately after fouling (0,5 mol/l NaCl)
 Membrane resistance measured after equilibration (overnight) in 0,5 mol/l NaCl

(1) CD 20 mA/cm².

The resistances of the used membranes were all higher than that of the unused membranes. This showed that membrane fouling took place. However, membrane fouling was more severe in the case of the Selemion membranes. The lonics and lonac membranes showed less severe membrane fouling. However, membrane fouling took place and pretreatment will be necessary to protect the membranes from fouling.

5.5.5 Treatment of chromium rinse waters with electro-electrodialysis

Chromium oxide (Cr0₃) concentration levels in the treated feed and recovered product during EED treatment of chromium rinse water are shown in Figure 52 and Table 21. The initial concentration of chromium oxide in the EED feed was approximately 48 g/ ℓ . A chromium oxide concentration of approximately 240 g/ ℓ was obtained in the EED product when the run was terminated. It should be possible to reuse the recovered chromic acid without further concentration in the chromium plating bath.

Electrical energy consumption for chromium recovery was determined at 38,33 kwh/kg Cr0₃. Current efficiency was calculated as 58,7 percent.



Figure 52: Chromium oxide concentration as a function of time during EED treatment of chromium rinse water. (Morgane ARA; CD 80 mA/cm²; feed volume 20 ℓ; product volume 2 ℓ)

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Time	Current	Volt	Feed			Product			
(h)	(A)	(V)	Cr ^{s+} (g/ <i>t</i>)	CrO ₃ (g/ <i>l</i>)	Conduct (mS/m)	Cr⁵+ (g/ℓ)	CrO ₃ (g/ /)	Conduct (mS/m)	
0	5,78	78	25	48,08	12460	0	0,00	22,4	
10	-	20,35	25	48,08	10990	10	19,23	7220	
20		17,35	25	48,08	10140	20	38,46	10480	
30		18,25	23,25	44,71	9940	12,5	24,04	996 0	
40		16,08	22,5	43,27	10010	17,5	33,65	12890	
50		14,25	21,25	40,87	9460	25	48,08	16200	
60		13,89	20	38,46	9050	32,5	62,50	19400	
70		13,16	18,75	36,06	8670	40	76,92	22500	
80		12,5	21,1	40,58	8360	57,5	110,58	25800	
90		14,25	20,1	38,65	8110	60,21	115,79	29200	
100		12,58	20	38,46	7680	67,5	129,81	31200	
110		11,09	16,25	31,25	7660	72	138,46	37500	
120		10,47	18,75	36,06	7450	82,5	158,65	40000	
130		9,28	16,25	31,25	7120	80	153,85	44500	
140		8,35	13,75	26,44	6750	87,5	168,27	46600	
150		8,5	11,25	21,63	6530	92,5	177,88	49300	
160		8,21	15	28,85	6400	100	192,31	50800	
170		7,36	15	28,85	5970	97,5	187,50	51400	
180	-	7,48	12,5	24,04	5660	115	221,15	52900	
190		6,64	15	28,85	5290	125	240,38	52700	

Table 21:Chromium oxide concentration as a function of time during EED
treatment of chromium rinse water

5.6 **Treatment of mixed electroplating effluent**

The fouling potential of mixed electroplating effluent for tubular cellulose acetate membranes was first determined through pilot studies whereafter a batch run was conducted to establish process design criteria. Electrodialysis was also evaluated for treatment of the mixed plating effluent.

5.6.1 Evaluation of the fouling potential of mixed electroplating effluent for tubular cellulose acetate RO membranes through pilot tests with a continuous RO system

Pilot tests (feed and bleed RO system (Figure 4)) were conducted for approximately

340 hours at 80 percent water recovery at a plating shop. Permeate flux as a function of time is shown in Figure 53. The initial permeate flux was 521 ℓ/m^2 .d and permeate flux dropped rapidly to approximately 383 ℓ/m^2 .d after 16 hours of operation and then dropped much slower to approximately 313 ℓ/m^2 .d when the membranes were cleaned with citric acid (2%; pH 4,5) after 110 hours of operation.



Figure 53: Permeate flux as a function of time

The initial CWF was 555 ℓ/m^2 .d. Clean water flux after 110 hours of operation was 370 ℓ/m^2 .d. Therefore, membrane fouling took place. However, it was almost possible to restore CWF with a citric acid cleaning (CWF 531 ℓ/m^2 .d).

Permeate flux was 407 ℓ/m^2 .d when the run was commenced and decreased slowly and was determined at 283 ℓ/m^2 .d when the run was terminated after 316 hours of operation. Clean water flux was measured at 302 ℓ/m^2 .d. CWF, however, could be increased to 535 ℓ/m^2 .d with a citric acid cleaning. This showed that it should be possible to control membrane fouling with regular chemical cleaning of the membranes. The conductivity of the RO permeate remained constant over the run showing that serious membrane fouling did not take place. The chemical composition of the RO feed, permeate and brine and ion rejections are shown in Table 22.

Excellent ion rejections were obtained. Conductivity rejection was approximately 91 percent. Ion rejections of more than 94 percent were obtained for cadmium, chromium, copper, nickel, zinc and iron. The conductivity of the RO permeate was only 76 mS/m and it should be possible to reuse the RO permeate as rinse water in the plating process. The RO brine comprised approximately 20 percent of the feed. It should be easier to handle the much smaller brine volume for metal removal with conventional lime precipitation than the original mixed effluent.

Constituent	Inlet Drag-out	Feed Tank	Permeate	% Rejection	Brine
Calcium	35,6	209	9,8	95,31	234
Magnesium	19,22	108,8	3,18	97,1	117,6
Potassium	1,89	8,3	0,81	90,2	9,1
Sodium	160,8	724	57,4	92,1	764
Ammonia	30,1	100,7	11,1	89,0	111,3
Nitrate	7,6	17,5	6,4	63,4	18,0
COD	. 30	290	80	72,4	250
Cadmium	5,9	34	1,71	95,0	35
Chromium	7,7	51	0,71	93,9	54
Copper	0,85	15,0	0,71	95,3	15,8
Nickel	16,4	77	3,3	95,7	80
Zinc	51,5	290	13,1	95,5	319
Sulphate	408,3	2494	1,7	99,9	2656
Iron	7,62	33,4	0,61	98,2	33,8
рН	3,4	3,4	3,4	4,6	3,4
Conductivity (mS/m)	181	831	76	90,9	860

Table 22:Chemical composition* of RO feed, permeate and brine (316 hours
of operation)

* All units in mg/t unless otherwise stated.

5.6.2 Batch treatment of mixed electroplating with tubular cellulose acetate membranes

Permeate flux as a function of time and percentage water recovery is shown in Figures 54 and 55, respectively (run 1). Permeate flux was 574 ℓ/m^2 .d in the beginning of the run and decreased to 413 ℓ/m^2 .d at the end of the run (approximately 90% water recovery). Clean water flux was 535 ℓ/m^2 .d before the run and 529 ℓ/m^2 .d after 3 batch runs. Therefore, little membrane fouling took place.

The chemical composition of the RO feed, permeate and brine is shown in Table 23. Conductivity was reduced from 174 mS/m in the RO feed to 36,1 mS/m in the composite RO permeate. Therefore, an excellent quality permeate could be produced and it should be possible to recover this water for reuse (rinsing) in the plating process. Good removals of chromium, zinc, nickel and copper were also obtained. The RO brine which comprises approximately 10 percent of the feed can be treated with lime for metal removal prior to disposal to the municipal sewer system.



Figure 54: Permeate flux (l/m^2 .day) as a function of time (run 1)



Figure 55: Permeate flux (1/m².d) as a function of percentage water recovery (run 1)

Constituent	RO feed (Initial)	RO permeate	RO brine	% Rejection
Sodium	162	28	1,133	82,7
Potassium	2,1	0,34	14,5	83,8
Calcium	30,5	2,63	287	91,4
Magnesium	21	1,09	159	94,8
COD	90	90	300	0
Ammonia	31,7	7	207,3	77,9
Nitrate & nitrite	8,3	4	32	51,8
Iron	7,88	0,39	59,7	95,1
Chromium	8,0	0,92	60	88,5
Sulphate	420	21	3 322	95,0
Zinc	54	4,75	385	91,2
рН	3,4	4,4	3,2	-
Conductivity (mS/m)	174	36,1	925	79,3
Nickel	15,4	1,35	115	91,2
Copper	1.08	0,19	8,63	82,4

Table 23: Chemical composition^{*} of RO feed, permeate and brine

All units in mg/ℓ , unless otherwise stated.

5.6.3 Evaluation of ED for treatment of mixed electroplating effluent

A batch ED run was conducted with the ED pilot plant shown in Figure 5⁽¹⁸⁾.

The chemical composition of the ED feed, product and brine is shown in Table 24. An excellent quality product water was produced. Conductivity rejection was 77,2 percent. Excellent removals of cadmium, chromium, copper, nickel and zinc were obtained. It should be possible to reuse the ED product water as rinse water in the electroplating process.

The ED brine comprised 14 percent of the treated water. However, a higher water recovery (approximately 90%) should be possible which means that brine volume would only comprises approximately 10 percent of the treated feed. It should be

possible to treat this much reduced mixed plating effluent (ED brine) very effectively with lime for metal removal. Smaller treatment equipment will be required than for the much larger untreated mixed plating effluent.

Constituent (mg/ℓ)	Feed	Product	Brine	Rejection (%)
COD	80	10	100	87,50
Nitrate (N)	3,2	0,49	27,9	84,69
Total Sulphate	159,7	47,75	390,2	70,10
Cadmium	2,8	0,19	12,2	93,21
Calcium	34,8	1,86	195	94,66
Chromium	2,04	0,2	5,0	90,20
Copper	0,48	0,05	0,06	89,58
Iron	0	0,01	0	
Magnesium	19,4	0,3	85,0	98,45
Nickel	12,8	0,96	42	92,50
Potassium	3,53	0,43	5,4	87,82
Sodium	133	44,3	369	66,69
Zinc	24,6	1,54	91	93,74
Fluoride	-	0,6	5,8	-
Chloride	220	36	511	83,64
TDS	804	259	2 748	67,79
Conductivity (mS/m)	141	32,2	416	77,16
рН	6,10	6,08	7,18	

 Table 24:
 Chemical composition of ED feed, product and brine

5.7 Treatment of final electroplating effluent

Pilot tests were conducted for approximately 230 hours with tubular cellulose acetate RO membranes on final electroplating effluent (lime clarified effluent) at approximately 80 percent water recovery. Permeate flux as a function of time is shown in Figure 56. Initial permeate flux was 596 ℓ/m^2 .d. Flux, however, dropped rapidly in the beginning

and then started to decline (from 18 hours) at a much slower rate. Permeate flux was 378 ℓ/m^2 d when the run was terminated after 288 hours of operation.

Initial CWF was 643 ℓ/m^2 .d. Clean water flux was measured at 610 ℓ/m^2 .d after 228 hours of operation. This showed that some membrane fouling took place. Clean water flux was 630 ℓ/m^2 .d after a citric acid cleaning (22 hours of operation). This showed that it should be possible to control membrane fouling with regular chemical cleanings. The permeate conductivity remained constant during the test run showing that serious membrane fouling was not taking place.

The chemical composition of the RO feed and permeate is shown in Table 25. An excellent quality permeate was produced. Conductivity was only 29,1 mS/m (feed 529 mS/m, 94,5% rejection). Excellent cadmium, chromium, copper, nickel and zinc removals were also obtained. The RO permeate can be either used as rinse water in the plating process or discharged into the municipal sewerage system. The heavy metal concentration content of the RO permeate is very low with the result that it will not upset biological treatment systems.



Figure 56: Permeate flux as a function of time

Constituent	Drag-Out	RO Feed	RO Permeate	% Rejection
Calcium	72	378	7,4	98,0
Magnesium	23,1	144	2,3	98,4
Potassium	2,4	8,5	0,58	93,2
Sodium	96	462	31,8	93,1
Chloride	144	672	57	91,5
Ammonia	15,9	64,7	7,8	87,9
Nitrate	0,5	13,3	3,7	72,2
COD	90	250	90	64
Cadmium	1,7	5,2	0,08	98,5
Chromium	4,3	7,1	0,2	97,2
Copper	0,6	3,8	0,7	81,6
Nickel	13,8	36,7	0,91	97,5
Zinc	1,9	5,8	0,09	98,4
TDS	920	4 190	180	95,7
Sulphate	249	655	0	100
Iron	0,7	6,2	0	100
рН	6,4	7,0	6,3	
Conductivity (mS/m)	130	529	29,1	94,5

Table 25:Chemical composition* of drag-out, RO feed and RO permeate after
228 hours of operation

* All units in mg/ℓ unless otherwise stated

5.8 Treatment of nickel and cadmium electroplating rinse waters with an electrolytic cell

Batch tests were first conducted in a Chemelec electrolytic cell to evaluate this cell for cadmium and nickel recovery from cadmium and nickel rinse waters⁽¹⁵⁾. Nickel recovery from nickel rinse water was then studied over an approximately 550 hour period by circulating nickel rinse water (approximately 1 000 mg/ ℓ Ni) from a drag-out tank (simmulation of real process) through the cell to reduce the nickel concentration level to approximately 500 mg/ ℓ prior to the next run⁽¹⁸⁾.

5.8.1 Treatment of cadmium eletroplating rinse water with a Chemelec electrolytic cell

The cadmium removal/recovery results are shown in Table 26. Cadmium removal/recovery increased with increasing current applied. Cadmium recovery increased from 55,6 percent to 97,3 percent when current was increased from 0,5 to 8 ampere.

Excellent cadmium removals were obtained when higher electric current was applied. Cadmium for example was reduced from 190 mg/ ℓ in the feed to 4,2 mg/ ℓ in the final treated water when an electric current of 11 amps was applied. It is also interesting to note that the cyanide concentration level in the feed of 862 mg/ ℓ could be reduced to 429 mg/ ℓ when relatively low electric current was applied. Therefore, it appears that it will be possible to apply this technology very effectively for treatment of cadmium rinse waters for cadmium and cyanide removal.

Feed volume and feed concentration	Initial Cd concentration mg/ℓ	Current amp	Final Cd concentration mg/ℓ	% Cd Recovery
Volume 10 litre; Concentration ± 800 mS/m	200	3	5,2	97,4
	150	5	3,45	97,7
	248	8	6,70	97,3
	190	11	4,18	97,8
Volume 14 litre; Concentration ± 800 mS/m	180	0,5	79,9	55,6
	180	1,0	66,1	63. 3
	245	1,5	88,2	64,0
	160	2,0	27,0	83,1
	220	5,0	10,8	95,1
	220	8,0	5,9	97,3
	210	11,0	10,3	95,1
Volume 14 litre; Concentration ± 400 mS/m	150	0,5	40,1	73,3
	164	1,0	24,9	84,8
	158	1,5	31,0	80,4
	110*	2,0	17,1	84,5

Table 26: Cadmium removal/recovery from cadmium rinse water with a Chemelec electrolytic cell

*

Cyanide was reduced from 862 to 429 mg/L

5.8.2 Treatment of nickel electroplating rinse water with a Chemelec electrolytic cell

5.8.2.1 Batch tests

The nickel removal/recovery results are shown in Table 27. The feed water had a nickel concentration of approximately 1300 mg/l during the first 7 runs. The nickel concentration in the feed was approximately 350 mg/l for runs 8 to 19. Runs 11 to 14 were conducted on a nickel rinse water with an initial concentration of approximately 1000 mg/l. The pH of the feed was controlled to between pH 4 and 4,8 (runs 11 to 14) with addition of caustic soda solution with a pipette to the feed tank. However, it was not easy to control the pH accurately and caustic soda solution (20% NaOH) was added with a burette during runs 16 to 20. The pH was much better controlled in this case.

Table 27.	Nickel/removal	recovery	results	with a	Chemelec	cell

Description of Experiments	Run Number	Initial Nickel Concentration (mg/Ø	Current (amp)	Final Ni Concentration (mg/l)	% Ni Recovery
Feed volume 14 litre; feed concentration ± 600 mS/m; pH of feed solution not kept constant.	1 2 4 3 6 7 5	1 290 1 380 1 330 1 260 1 210 1 170 1 370	0,5 1,0 2,0 5,0 5,0 8,0	1 230 1 260 980 1 200 1 020 750 750	4,7 10,1 26,3 4,8 15,7 35,9 42,3
Feed volume 14 litre; feed concentration ± 300 mS/m; pH of feed solution not kept constant.	10 9 8	320 428 340	1,0 2,0 5,0	280 351 210	12,5 18,0 38,2
Feed volume 14 litre; feed concentration \pm 600 mS/m; pH of feed solution controlled between 4 and 4,8.	13 14 11 12	900 1 010 950 1 025	0.5 1,0 2,0 5,0	460 530 630 438	48,9 47,5 33,7 57,3
Feed volume 14 litre; feed solution 6 410 mS/m (45 300 mg/ℓ Ni); plating bath solution. pH of feed solution not controlled.	15	45 300	5,0	43 800	3,3
Feed volume 10 litre; feed solution 450 mg/ℓ Ni; pH controlled between 4 and 4,8.	16 17	445 454	5,0 5,0	7,7 3,7	98,3 99,2
Feed volume 10 litre; feed solution 766 mg/ℓ Ni; pH controlled between 4 and 4,8.	18	766	5,0	5,6	99,3
Feed volume 10 litre; feed solution 960 mg/ℓ Ni; pH controlled between 4 and 4,8.	19	960	5,0	65	93,2
Feed volume 10 litre; feed solution 4 230 mg/ℓ Ni; pH controlled between 4 and 4,8.	20	4 230	5,0	4 160	1,6

Excellent nickel removal/recoveries were obtained when the pH of the feed water was controlled to between pH 4 and 4,8 with a burette (runs 16 to 19; Table 27). Nickel recovery varied between 99 and 93 percent. Nickel for example was reduced from 766 mg/ ℓ to approximately 6 mg/ ℓ at the end of run 18 (99,3% removal). However, poor nickel removal was obtained during run 20 despite pH control of the feed water. This may be ascribed to poor mixing of the feed water. Poor nickel removals were also obtained when caustic soda was added with a pipette to the feed water in the tank to control the pH. This may also be ascribed to poor mixing of the feed water. Very poor nickel removals were obtained when the pH of the feed water was not controlled to between pH 4 and 4,8. Consequently, pH control of the feed water when nickel is electrolytically recovered, is very important. Nickel recovery also increases with increasing amount of electrical current applied. Satisfactory results were obtained when electric current of 5 amp was applied, pH controlled and nickel feed concentration was in the range from 445 to 960 mg/ ℓ .

5.8.2.2 Continuous tests

Nickel removal/recovery tests from an approximately 100 litre sample of nickel rinse were conducted for approximately 550 hours. The initial nickel concentration in the drag-out tank was approximately 1000 mg/ ℓ and nickel was removed from the drag-out with the Chemelec cell until the nickel concentration was reduced to approximately 400 mg/ ℓ . Nickel was then added to the drag-out tank to increase its concentration level to approximately 1000 mg/ ℓ prior to the next run. Nickel concentration in the drag-out tank as a function of time is shown in Figure 57.

The nickel concentration in the drag-out tank was 940 mg/ ℓ when the first run was started and it took approximately 26 hours to reduce the nickel concentration level in the tank to 370 mg/ ℓ . One litre plating bath solution was then added to the feed tank to increase its concentration level to approximately 1000 mg/ ℓ . Nickel concentration was reduced from 970 to 340 mg/ ℓ during the next run in a 24 hour period. Many more similar runs were conducted (Figure 57). An average time period of 24 hours was required to remove nickel from approximately 900 to 350 mg/ ℓ . The cathodes were replaced after 77 hours, 318 hours and 549 hours of operation.



Figure 57: Nickel concentration (mg/l) in drag-out tank as a function of time (hours)

Approximately 1,16 kg nickel was recovered over the 549 hours test period. This gives a nickel recovery rate of 2,1 g nickel per hour. The sodium content of the drag-out was increased from 382 mg/ ℓ to 1030 mg/ ℓ due to caustic soda addition (5% NaOH) for pH control (pH 4 to 4,8).

5.9 Treatment of spent acid effluent with diffusion dialysis

A mixture of sulphuric and hydrochloric acid solution and hydrochloric acid solution alone are used for cleaning of metal components prior to electroplating. The acid solutions becomes spent after use and must be discarded because the concentration level of dissolved metals (Fe, Zn, etc.) becomes too high for further processing. Acid recovery for reuse was therefore investigated with diffusion dialysis⁽¹⁶⁾. Spent acid samples were collected at different electroplating shops and dialyzed. The diffusion dialysis results are shown in Table 28.

Acid recovery varied between approximately 58 and 76 percent for the four spent acid samples that were investigated. Metal (Fe, Ni, Cu) leakage ratios were low (< 5,2%). This shows that the metals can be effectively removed from the recovered acid.

Parameters	Techniplate	Autoplate Chrome plant	Autoplate Copper plant	Smith's Wheels
Acid type	H₂SO₄/HCI	HCI	HCI	H₂SO₄
Diffusate flow rate (ℓ.m ⁻² h ⁻¹)	0,917	1,028	1,101	1,064
Feed acid flow rate (<i>t</i> .m ⁻² h ⁻¹)	1,083	1,028	1,229	0,862
Tap water flow rate (<i>l</i> .m ⁻² h ⁻¹)	1,138	1,028	1,229	1,046
Dialysate flow rate (ℓ.m ⁻² h ⁻¹)	1,248	1,028	1,229	1,248
FEED ACID				
Total acid concentration (mol/#)	1,98	1,03	1,005	0,55
Iron concentration (mg/#)	11 000	201	970	80 900
Zinc concentration (mg/ℓ)	61 000			
Nickel concentration (mg/#)				18,4
Copper concentration (mg/l)		361	47,5	<u> </u>
DIFFUSATE (Product)				
Total acid concentration (mg/ℓ)	1,14	0,763	0,768	0,41
Sulphuric acid concentration (g/l)				19,98
Hydrochloric acid concentration (g/ℓ)		27,8	27,98	
Acid recovery (%)*	57,58	74,03	76,42	74,55
Acid recovery ratio (%)**	48,75	74,03	68,41	60,03
Metal leakage ratio Iron (%)	2,18	3,83	2,59	1,83
Metal leakage ratio Copper (%)		4,63	5,22	
Metal leakage ratio Zinc (%)	14,37			
Metal leakage ratio Nickel (%)				2,29
Iron concentration (mg/ŧ)	284	7,7	28	1 820
Copper concentration (mg/ <i>t</i>)		16,8	2,76	
Zinc concentration (mg//)	10 350			
Nickel concentration (mg/ŧ)				0,52
DIALYSATE (Waste)				
Total acid concentration (mol/ℓ)	0,78	0,228	0,215	0,123
Sulphuric acid concentration (g/ŧ)				6,01
Hydrochloric acid concentration (g/t)		8,29	7,84	
Iron concentration (mg/ŧ)	9 050	166	930	62 800
Copper concentration (mg/ℓ)		332	45,2	
Zinc concentration (mg/ <i>t</i>)	46 000			
Nickel concentration (mg/ℓ)				16,5

Table 28: Acid recovery from spent acid with diffusion dialysis

* Diffusate acid concentration/Feed acid concentration

** Diffusate acid concentration x Diffusate flow rate/Feed concentration x Feed acid flow rate
Therefore, it will be possible to recover acid for reuse in the metal cleaning process. It should be noted that zinc was not as effectively removed from the recovered acid as the other metals (metal leakage ratio 14,4%). However, it should also be possible in this case to recover the acid effectively for reuse.

The metal concentration levels in the dialysate are high. The metals can be removed from the dialysate with lime precipitation followed by discharge of the clarified water into the municipal sewer system.

5.10 Treatment of nickel rinse water with ion-exchange

Nickel rinse waters containing approximately 1000; 400 and 150 mg/l nickel were passed through a strong acid cation-exchange resin (150 ml duolite C20) and breakthrough curves were established. The loading and elution curves are shown in Figures 58 to 63.

Nickel leakage started to occur after approximately 20, 80 and 100 BV's of rinse water had been passed through the resin column where the feed contained approximately 1000; 400 and 150 mg/ ℓ nickel, respectively. The elution curves showed that most of the nickel could be removed from the resin with 2,5 to 3 BV's regenerant. The waste regenerant containing nickel sulphate may be reused in the plating bath or the nickel can be electrolytically recovered and sold.

Process design criteria for nickel removal from nickel rinse water can be derived from Figures 58 to 63. The operating capacities for nickel removal at feed concentration levels of approximately 1000; 400 and 150 mg/ℓ can be determined from Figures 58; 60 and 62.



Figure 58: Nickel concentration in regenerant as a function of BV's regnerant passed through the column



Figure 59: Nickel concentration as a function of BV's rinse water passed through the resin column



Figure 60: Nickel concentration in regenerant as a function of BV's regenerant passed through the column



Figure 61: Nickel concentration as a function of BV's rinse water passed through the resin column



Figure 62: Nickel concentration in regenerant as a function of BV's regenerant passed through the column



Figure 63: Nickel concentration in regenerant as a function of BV's regenerant passed through the column

5.11 Economics

The economics of metal recovery technologies can be derived from the results presented under 4.1 to 4.10. Capital and operational costs can be obtained from plant suppliers. The economics of RO, ED and an electrolytic cell for nickel recovery were previously determined and would be presented in this section^(15, 19).

5.11.1 Economics of the RO process for nickel and water recovery from electroplating rinse water

The economics of a tubular cellulose acetate RO system for nickel and water recovery from electroplating rinse waters are shown in Tables 29, 30 and 31 for three different flows. Ultrafiltration was included as a pretreatment step to protect the membranes from colloidal fouling. However, it is doubtful whether UF will be required in practice together with tubular cellulose RO acetate membranes to protect the membranes from fouling.

Plant payback periods for $5 \text{ m}^3/\text{h}$; $5 \text{ m}^3/\text{d}$ and $15 \text{ m}^3/\text{d}$ were determined at 1,3 year; 2,1 year; and 1,7 year, respectively. Therefore, it appears that nickel recovery from electroplating rinse water will be an economic proposition.

5.11.2 Economics of the ED process for copper and water recovery from electroplating rinse water

Payback period for a 1,2 kg copper/h ED plant (113 m²) is presented in Table 32. Payback period was determined to be approximately 1 year.

Table 29:Economics of the RO process (tubular cellulose acetate
membranes) for nickel and water recovery from electroplating rinse
water (5 m³/hour; 2 035 mg/t Nickel drag-out)

	Items	Reverse Osmosis Plant
1.	Installed cost - Equipment (investment) - Installation, labour and materials (15% of investment)	340 000 <u>51 000</u> 391 000
2.	 Annual operating cost (Estimated) Labour, 1 080 hours/year @ R6,00/hour Maintenance @ 2¹/₂% of investment Raw materials Membrane replacement (2 year lifetime) Electricity 	6 480 8 500 42 500 <u>6 000</u> 63 480
3.	 Annual fixed cost Depreciation, 10% of investment Tax and insurance, 1% of investment Total fixed cost 	34 000 <u>4 400</u> 37 400
4.	Total cost of operation	100 880
5.	 Annual savings Plating chemicals Sludge disposal cost Water treatment chemicals Water usage 	506 864,4 3 600 26 400 <u>40 000</u> 576 864.4
6.	Net savings {(Annual savings - operating & fixed cost)}	475 984
7.	Net savings after tax (45% tax rate)	261 791
8.	Average ROI (%) (Net savings after tax/total investment)	67,0
9.	Cash flow from investment (Net savings after tax + depreciation)	295 791
10.	Payback period = Total Investment/Cash flow	1,3 year

Table 30:Economics of the RO process (tubular cellulose acetate
membranes) for nickel and water recovery from electroplating rinse
water (5 m³/day; 2 035 mg/ℓ Nickel drag-out)

Items		Reverse Osmosis Plant
1.	Installed cost - Equipment (investment) - Installation, labour and materials (15% of investment)	65 000 <u>9 750</u> 74 750
2.	 Annual operating cost (Estimated) Labour, 1 080 hours/year @ R6,00/hour Maintenance @ 2¹/₂% of investment Raw materials Membrane replacement (2 year lifetime) Electricity 	810 1 625 8 125 <u>750</u> 11 310
3.	 Annual fixed cost Depreciation, 10% of investment Tax and insurance, 1% of investment Total fixed cost 	6 500 <u>650</u> 7 150
4.	Total cost of operation	18 460
5.	 Annual savings Plating chemicals Sludge disposal cost Water treatment chemicals Water usage 	63 358,05 450 3 300 <u>5 000</u> 72 108,05
6.	Net savings {(Annual savings - operating & fixed cost)}	53 648
7.	Net savings after tax (45% tax rate)	29 506
8.	Average ROI (%) (Net savings after tax/total investment)	39,5
9.	Cash flow from investment (Net savings after tax + depreciation)	36 006
10.	Payback period = Total Investment/Cash flow	2,1 year

Table 31:Economics of the RO process (tubular cellulose acetate
membranes) for Nickel and water recovery from electroplating rinse
water (5 m³/hour; 2 035 mg/t Nickel drag-out)

	Items	Reverse Osmosis Plant
1.	Installed cost - Equipment (investment) - Installation, labour and materials (15% of investment)	165 000 <u>24 750</u> 189 750
2.	 Annual operating cost (Estimated) Labour, 1 080 hours/year @ R6,00/hour Maintenance @ 2¹/₂% of investment Raw materials Membrane replacement (2 year lifetime) Electricity 	3 456 4 125 20 625 <u>2 247</u> 30 453
3.	 Annual fixed cost Depreciation, 10% of investment Tax and insurance, 1% of investment Total fixed cost 	16 500 <u>1 650</u> 18 150
4.	Total cost of operation	48 603
5.	 Annual savings Plating chemicals Sludge disposal cost Water treatment chemicals Water usage 	190 074,15 1 350 9 900 <u>15 000</u> 216 324,15
6.	Net savings {(Annual savings - operating & fixed cost)}	167 721
7.	Net savings after tax (45% tax rate)	92 247
8.	Average ROI (%) (Net savings after tax/total investment)	48,6
9.	Cash flow from investment (Net savings after tax + depreciation)	108 747
10.	Payback period = Total Investment/Cash flow	1,7 year

Table 32:Economics of recycling of alkaline copper cyanide
with ED (1,2 kg Copper/h) (113m²)

Investment	R542 000,00 (113 m ²)	
Operating costs	R/year	
 Energy consumption (15,7 kW) 	7 229	
Maintenance	10 241	
Cell pairs replacement	42 169	
Total amour	nt 59 639	
Savings		
Copper cyanide solution	331 325	
Wastes treatment	268 072	
Total amour	nt 599 398	
Pay back about 12 months		

5.11.3 Economics of an electrolytic cell process for nickel recovery

The economics of the electrolytic cell process for nickel recovery from electroplating rinse waters (18 k ℓ /d rinse water containing 1 000 mg/ ℓ Ni) are summarised in Tables 33 and 34. Plant payback periods based on nickel prices of R21/kg and R30/kg were determined at 1,9 and 1,4 years, respectively. Consequently, it appears that it will be economical to recover nickel from plating rinse waters with an electrolytic cell.

Table 33:	Electrolytic recovery unit for nickel rinse water
	(based on nickel price of R21/kg)

Item	Amount
Cost factors	
Capital cost	R299 750,00
Installation cost (1/7 of capital cost)	42 821,00
Operating cost (1/10 of capital cost)	29 975,00
NaOH cost (for maintaining pH between 4 and 4,8)***	86 339,00
Chemical savings	
Nickel*	R137 970,00
Treatment and solid waste savings**	160 550,00
Net annual savings	182 206,00
Return on investment (%)	53,2
Payback period (Total investment/Net savings)	1,9 year

* Based on R21/kg for nickel: 18 kg nickel recovery per day; 365 days

** 2 470 kℓ Ni (OH)₂; R50/kℓ disposal cost; R15/kℓ lime; Density of Ni (OH)₂ 4,2 *** NaOH cost based on R2,80/kg

Table 34:Electrolytic recovery unit for nickel rinse water
(based on nickel price of R30/kg)

Item	Amount
Cost factors	
Capital cost	R299 750,00
Installation cost (1/7 of capital cost)	42 821,00
Operating cost (1/10 of capital cost)	29 975,00
NaOH cost (for maintaining pH between 4 and 4,8)***	86 339,00
Chemical savings (R/y)	
Nickel*	R197 100,00
Treatment and solid waste savings**	160 550,00
Net annual savings	241 336,00
Return on investment (%)	70,4
Payback period (Total investment/Net savings)	1,4 year

* Based on R21/kg for nickel: 18 kg nickel recovery per day; 365 days

** 2 470 kt Ni (OH)₂; R50/kt disposal cost; R15/kt lime; Density of Ni (OH)₂ 4,2

*** NaOH cost based on R2,80/kg

5.12.1 General Discussion

Membrane technologies like RO, ED, UF and diffusion dialysis can be effectively applied for treatment of electroplating effluents. Reverse osmosis using cellulose acetate membranes can be very effectively applied for treatment of nickel, chromium and zinc electroplating rinse waters. These rinse waters are acidic with the result that cellulose acetate membranes are suitable for this application. Electroplating rinse waters with a high pH (Zn, Cd, Cu) cannot be treated with cellulose acetate membranes. Polyamide membranes, however, are suitable for this application.

Reverse osmosis using cellulose acetate membranes is particularly suitable for treatment of nickel drag-out (nickel rinse water). Reverse osmosis can be costeffectively applied for water and metal recovery from nickel electroplating rinse waters. Metal removal of more than 98 percent is possible. This can be accomplished through feed and bleed or batch treatment. Care, however, should be taken that membrane fouling will not cause problems. It was demonstrated through pilot studies that membrane fouling occurred during RO treatment of electroplating rinse waters (Ni, Cr, Zn, Cd). However, it was also demonstrated that it would be possible to control membrane fouling with regular chemical cleaning. No pre-treatment will be required when TCARO membranes are used. However, cartridge filters (5 - 10 μ m) should be used to remove colloidal material before treatment with spiral wrap RO membranes.

Electrodialysis can be cost effectively applied for treatment of nickel, copper and silver rinse waters for metal and water recovery in the electroplating industry. Electrodialysis is particularly suitable for treatment of nickel rinse waters. Plant payback is less than 1,5 years. Electrodialysis, however, is a much more expensive technology than RO for small scale applications. Therefore, RO will be the preferred technology for small scale usage in the electroplating industry.

Electroplating effluents have the potential to foul ion-exchange membranes. Additives in the plating solutions are the culprits. Some ion-exchange membranes are more resistant to fouling than others. Therefore, membranes with the highest resistance towards fouling should be selected when ED technology is considered for electroplating effluent treatment. The membranes should also be regularly cleaned with acid and base to ensure satisfactory performance of the membranes.

It is usually organic additives in plating rinse waters that are responsible for fouling of ion-exchange membranes. These organics can usually be removed with activated carbon prior to ED treatment. Removal of these foulants prior to ED is considered to be very important for the successful operation of an ED system for metal and water recovery from plating drag-out.

It appears that it will be possible to apply the EED process effectively for chromium recovery from chromium drag-out. The concentration of the recovered chromium (240 g/ ℓ Cr0₃) is such that it can be directly added to the plating bath. Such high concentration level of chromium can not be obtained with RO or ion-exchange. The process, however, appears to be very expensive. Membrane life time may also be very short. More work will therefore be required for evaluation of the EED process for treatment of chromium rinse waters. This process was applied in the USA for treatment of chromium drag-out for chromium recovery.

Reverse osmosis and ED technology are very suitable for treatment of mixed electroplating effluent. Approximately 90 percent water of good quality can be recovered with RO and ED which means that the brine will only comprises approximately 10 percent of the treated water. Much smaller metal precipitation equipment will be required to handle the smaller brine volume than will be the case without RO or ED treatment. It should also be possible to use the RO or ED product water as rinse water in the electroplating process. Therefore, a significant amount of water can be recovered for reuse in the electroplating process. Pollution of the environment will also be reduced with metal/water recovery technologies.

Final effluent (after conventional metal removal with lime) produced by electroplaters can also be effectively treated with RO, ED or ion-exchange for detoxification of the effluent, water recovery for reuse and pollution prevention of the water environment. Ion-exchange was not evaluated in this study for treatment of final electroplating effluent. However, ion-exchange is effectively applied in Germany for end of pipe treatment in the electroplating industry.

Evaporation technology can be effectively applied for treatment of chromium drag-out. It is possible to produce a very pure distillate with this technology and to concentrate drag-out to bath strength. Evaporation technology, however, is expensive but it may be the best available technology for treatment of chromium drag-out.

Electrolytic metal recovery in electrolytic cells can be very effectively applied for treatment of electroplating drag-out. This technology is particularly suitable for treatment of nickel, silver, copper, cadmium and zinc drag-out. Drag-out solution is pumped through the electrolytic cell where the metal is removed and water is circulated back to the drag-out tank. Metal is removed from the cathodes when the cathodes are saturated with the metal. The recovered metal can be either sold to scrap metal dealers or the cathode can be used as an anode in the plating bath (for Ni, Cu). Electrolytic metal recovery technology would ensure that metal pollution caused by the electroplating industry, would be minimized.

The electroplater is familiar with power sources and electrodes. These components form part of an electrolytic metal recovery system. It is therefore foreseen that this technology will be used more by electroplaters in future to solve their problems.

Ion-exchange technology can be effectively applied for nickel and chromium recovery from the corresponding rinse waters. The waste regenerant (dilute H_2SO_4) containing the recovered nickel in the case of nickel recovery can be circulated back to the plating bath. The ion-exchange product water may also be used as rinse water in the process. Nickel in the waste regenerant can also be electrolytically recovered and sold to scrap metal dealers. Recovered chromium in the regenerant in the case of chromium recovery will not be of efficient strength for direct use in the chrome plating bath. However, the concentration level of the recovered chrome can be increased sufficiently with evaporation for direct addition to the plating bath. Diffusion dialysis can be effectively applied for acid recovery from spent acid produced by the electroplating industry. Acid (HCI, H_2SO_4 and mixtures of HCI and H_2SO_4) recoveries between 60 and 80 are possible. More than 94 percent of the metals in the spent acid can be removed from the acid. Therefore, acid suitable for reuse will be produced. The diffusion dialysis process is a very simple process to operate and it should be possible for electroplaters to handle this process easily.

Process design criteria for treatment of electroplating effluents with membrane and other technologies are presented in this report. This information can be used for the design of metal/water recovery systems for the electroplating industry. The information presented in this report can also be used to determine the preliminary economics of metal/water recovery systems for the electroplating industry.

Demonstration metal/water recovery plants should now be installed at selected electroplating shops to demonstrate these technologies to prospective users. The RO, ED, electrolytic metal recovery, ion-exchange and evaporation processes should be considered for demonstration. Plant demonstration will demonstrate performance and economics of metal/water recovery technologies to the electroplaters and to the authorities.

The business of electroplaters is to conduct plating with the objective to make profit. Effluent treatment is not always seriously considered to be part of their business. However, platers are forced to treat their effluents so that it can comply to the discharge quality requirements laid down by the authorities. Consequently, treatment of electroplating effluents by outside effluent treatment companies might be welcomed by electroplaters especially if they could benefit from it. Outside effluent treatment companies have an infrastructure for effluent treatment. Most platers have no effluent treatment facilities except conventional lime metal precipitation/clarification equipment. Therefore, platers will benefit from it if outside companies can treat their effluents for them. Effluent streams for example can be collected at plating shops, transported to a central treatment facility and the effluents detoxified and metals recovered. Centralized treatment of electroplating effluents is successfully practised overseas. Alternatively, metal/water recovery technologies can be implemented by outside companies at electroplating shops and the technologies can be operated for the plater by the external companies.

6. CONCLUSIONS

- Nickel drag-out (rinse water) can be cost effectively treated with a TCARO system for nickel and water recovery for reuse in the electroplating process. Payback periods for $5 \text{ m}^3/\text{h}$; $5 \text{ m}^3/\text{d}$; and $15 \text{ m}^3/\text{d}$ nickel/water recovery RO plants were determined at 1,3; 2,1; and 1,7 years, respectively. Nickel could be concentrated from 1300 mg/ ℓ in the inlet drag-out (13 500 mg/l Ni RO feed tank) to 14 400 mg/l in the RO brine at a water recovery 93 percent (feed and bleed system; concentration factor 11,1). The nickel concentration in the RO permeate was only 37,4 mg/l. Therefore, a nickel removal of 99,7 percent was obtained from the RO feed. Nickel could also be concentrated in a batch system from 1 760 mg/ ℓ in the feed to 7 400 mg/ ℓ in the brine at a water recovery of 93 percent (concentration factor 4,2). The RO permeate had a nickel concentration of only 38,9 mg/l. Therefore, nickel removal was 97,8 percent. Higher water recovery (approximately 95%) and therefore higher brine (Ni) concentration is possible. Very little membrane fouling took place when the fouling potential of nickel drag-out was determined for cellulose acetate RO membranes. It was demonstrated that it should be possible to control membrane fouling with regular chemical cleaning. Regular chemical cleaning is considered to be very important for trouble free operation of a nickel recovery RO system.
- It appears that it will also be possible to use spiral wrap Filmtec membranes (high rejection seawater RO membranes) successfully for nickel and water recovery from nickel drag-out. Nickel could be concentrated from 635 mg/ℓ in the RO feed (batch system) to 9 625 mg/ℓ in the RO brine (concentration factor 15,2) at a water recovery of approximately 90 percent. The nickel concentration in the RO permeate was only 1,35 mg/ℓ. Therefore, nickel removal was 99,8 percent. Higher water recovery should be possible (approximately 95%). It also seems that it will be possible to control membrane fouling with regular chemical cleaning. Better feed pretreatment, however, will be necessary with the spiral wrap Filmtec membranes than with tubular membranes. Cartridge filtration (5 to 10 µm) should protect the membranes from fouling.
- Chromium rinse water could be successfully treated with TCARO membranes for chromium and water recovery. Chromium in the inlet drag-out was concentrated from

740 mg/ℓ (2 950 mg/ℓ in RO feed tank) to 3 100 mg/ℓ in the RO brine (concentration factor 4,2) at a water recovery of 80 percent (feed and bleed system). The chromium concentration in the RO permeate was 189 mg/ℓ. Therefore, chromium removal was 93,6 percent. Chromium could also be concentrated from 469 mg/ℓ in a batch system to 2 320 mg/ℓ (concentration factor 4,9) in the RO brine at a water recovery of 92 percent. Chromium removal was 87 percent. The concentration level, however, of the recovered chromium is too low for direct use in the plating bath. However, it will be possible to increase its concentration level to the required strength (approximately 240 g/ℓ CrO₃) with an evaporator prior to use. Membrane fouling took place during RO treatment of chromium rinse water. However, it appears that it should be possible to concentrate chromium in the drag-out to the required bath strength. This technology may be superior to RO technology for chromium recovery from chromium drag-out.

- It appears that it will also be possible to apply spiral wrap Filmtec membranes for chromium and water recovery from chromium drag-out. Chromium was concentrated from 1 840 mg/l in the RO feed to 24 400 mg/l in the RO brine (concentration factor of 13,2) at a water recovery of approximately 90 percent. Therefore, a higher concentration could be obtained than with TCARO membranes. The chromium concentration level in the RO permeate was only 25,2 mg/l. Therefore, chromium removal was 98,6 percent. It also appears that it will be possible to control membrane fouling with regular chemical cleaning. It was noted that permeate flux increased after a number of batch runs. This phenomenon is of concern and warrants further investigation.
- It appears that it will be possible to treat acidic zinc drag-out successfully with TCARO membranes. Zinc could be concentrated from 1 740 mg/l in the inlet drag-out (RO feed tank 5 090 mg/l) to 5 280 mg/l in the RO brine (concentration factor of 3) at a water recovery of 80 percent. The zinc concentration in the RO permeate was 323 mg/l. Therefore, zinc removal was 93,7 percent. Zinc could also be concentrated from 630 mg/l in the RO feed to 2 790 mg/l in the RO brine (batch systems; 91% water recovery) while the zinc concentration in the RO permeate was only 36 mg/l. Therefore, zinc removal was 94,3 percent. Membrane fouling was experienced during

RO treatment of the zinc drag-out. However, it appears that it will be possible to control membrane fouling with regular chemical cleanings. Zinc has a low value compared to nickel. Therefore, a zinc recovery RO plant will not be very economic.

- It appears that it will be possible to treat alkaline zinc cyanide rinse water successfully with PCI AFC 99 tubular RO membranes. The zinc in the inlet drag-out was concentrated from 420 mg/l (2 200 mg/l Zn in RO feed) to approximately 2 200 mg/l in the RO brine (concentration factor of 5,2) at a water recovery of 80 percent (feed and bleed system). The zinc concentration level in the RO permeate was only 29,9 mg/l. Therefore, zinc removal was 98,6 percent. Serious membrane fouling was experienced during treatment of the alkaline zinc drag-out. However, it was demonstrated that it should be possible to control membrane fouling with regular chemical cleaning.
- It appears that it will be possible to treat alkaline cadmium rinse water successfully with spiral wrap Filmtec RO membranes. Cadmium was concentrated from 95 mg/l in the RO feed to 900 mg/l in the RO brine (concentration factor of 9,5) at a water recovery of approximately 90 percent (batch system). The RO permeate only contained 0,16 mg/l cadmium (99,8% Cd removal). Membrane fouling, however, was experienced during treatment of the cadmium rinse water. However, it was demonstrated that it should be possible to control membrane fouling with regular chemical cleaning.
- It is possible to treat nickel drag-out cost effectively with ED for nickel and water recovery for reuse in the electroplating process. Plant payback period of approximately 1,5 year is possible (113 m² ED plant). Nickel in the ED feed was maintained between 0,5 and 1 g/ℓ while nickel was concentrated to approximately 50 g/ℓ in the ED brine. Nickel recovery of 97 percent was obtained.
- It is possible to treat alkaline copper (1,2 kg Cu/h; 113 m² membrane area) and silver (113 m² ED plant) cost effectively with ED. Plant payback periods of approximately 1 and less than 2 years are possible, respectively. Metal recoveries of 92 and 95 percent were obtained, respectively.

- Pilot plant results showed that nickel drag-out could be concentrated from approximately 3,5 g/l in the ED feed to 23 g/l in the ED brine (concentration factor of 6,5) at a water recovery of approximately 85 percent. The nickel concentration in the desalinated feed varied between approximately 700 and 1 000 mg/l. Nickel removal varied between 68 and 78 percent. Nickel loading rate was determined at 0,048 g nickel per hour per square metre membrane area at a nickel removal of 78,7 percent. Electrical energy consumption was determined at 2,35 kwh/kg Ni.
- Selemion AMV anionic membranes were rapidly fouled with spent nickel plating bath solution in fouling tests while lonics A-204-UZL and lonac MA-3475 anionic membranes showed little signs of membrane fouling. Therefore, care should be taken in the selection of ion-exchange membranes for treatment of nickel drag-out. Alternatively, feedwater pretreatment with activated carbon should be practised to remove foulants prior to ED treatment to prevent process failure. Regular membrane cleanings with acid and caustic rinses should also be practised to clean fouled membranes.
- It appears that it will be possible to treat chromium drag-out successfully with EED for chromium recovery. The recovered chromium from a feed chromium concentration of 48 g/ℓ had a concentration level of 240 g/ℓ. It will be possible to use the recovered chromium directly in the plating bath without further concentration. Electrical energy consumption, however, was high (38,3 kwh/kg Cr0₃). Further work, however, will be required to optimize this process for chromium recovery.
- It will be possible to treat mixed electroplating effluent successfully with TCARO membranes for water recovery, effluent volume reduction and pollution control. Water recovery of more than 80 percent is possible (feed and bleed system). This means that the mixed plating effluent that must be treated for metal removal, is reduced significantly by RO treatment. The electrical conductivity of the mixed effluent (181 mS/m) was reduced from 831 mS/m in the RO feed (feed and bleed system) to 76 mS/m in the RO permeate (90,9% removal). Therefore, an excellent quality RO permeate can be produced that can be used as rinse water in the electroplating process. Excellent removals of heavy metals were also obtained. Nickel was reduced from 77 to 3,3 mg/ℓ (95,7% removal); chromium from 51 to 3,1 mg/ℓ (93,9% removal); zinc from 290 to 13,1 mg/ℓ (95,5% removal); cadmium from 34 to 1,71 mg/ℓ (95,0%)

removal). Membrane fouling took place during RO treatment of the effluent. However, it was demonstrated that it should be possible to control membrane fouling with regular chemical cleaning. Batch RO tests showed that the electrical conductivity of the RO feed could be reduced from 174 mS/m to 36,1 mS/m in the RO permeate (79,7% removal) at a water recovery of approximately 90 percent. Chromium was reduced from 8 to 0,92 mg/ ℓ (88,5% removal); zinc from 54 to 4,75 mg/ ℓ (91,2% removal); nickel from 15,4 to 1,35 mg/ ℓ (91,2% removal); and copper from 1,08 to 0,19 mg/ ℓ (82,4% removal).

- It will be possible to treat mixed electroplating effluent successfully with ED for water recovery, effluent volume reduction and pollution control. The TDS of the ED feed could be reduced from 804 to 259 mg/l in the ED product (67,8% removal) at a water recovery of approximately 85 percent. Nickel was reduced from 12,8 to 0,96 mg/l (92,5% removal); zinc from 24,6 to 1,54 mg/l (93,7% removal); copper from 0,48 to 0,05 mg/l (89,6% removal); and cadmium from 2,8 to 0,19 mg/l (93,2% removal). It will also be possible to handle the much smaller brine volume easier with conventional lime precipitation treatment than the much larger mixed plating effluent.
- Final effluent discharged by plating shops can be treated effectively with TCARO membranes for water recovery, effluent volume reduction and pollution control. Electrical conductivity of the final effluent (130 mS/m) could be reduced from 529 mS/m in the RO feed to 29,1 mS/m in the RO permeate (94,5% removal) at a water recovery of 80 percent (feed and bleed system). Therefore, an excellent quality RO permeate was produced that could be used as rinse water in the electroplating process. Cadmium was reduced from 5,2 to 0,08 mg/ℓ (98,5% removal); chromium from 7,1 to 0,2 mg/ℓ (97,2% removal); copper from 3,8 to 0,7 mg/ℓ (81,6% removal); nickel from 36,7 to 0,91 mg/ℓ (97,5% removal); and zinc from 5,8 to 0,09 mg/ℓ (98,4% removal).
- It will be possible to apply a Chemelec electrolytic cell effectively for cadmium and cyanide removal from cadmium drag-out. Cadmium could be reduced in one case from 190 mg/l in the feed to only 4,2 mg/l in the product and cyanide from 862 mg/l to 429 mg/l. Better cyanide removals, however, will be possible if higher electric current is applied.

- A Chemelec electrolytic cell can be cost effectively applied for nickel recovery from nickel drag-out. Plant payback period of less than 1,5 year is possible. Nickel, for example, was reduced in one case from 766 mg/ℓ in the drag-out to approximately 6 mg/ℓ (99,3% removal) in the treated water. Highest nickel removal took place when the pH of the feedwater was controlled between pH 4 and pH 4,8. It was demonstrated in pilot tests that nickel in a drag-out tank could be reduced from approximately 1 000 to 400 mg/ℓ with ease with a Chemelec cell. Nickel recovery rate was determined at 2,1 g nickel per hour (electrode area 0,045 m²).
- It will be possible to use diffusion dialysis effectively in the electroplating industry for acid recovery from spent acid produced during cleaning of metals prior to plating. Acid recovery from sulphuric/hydrochloric acid mixture was determined at 58 percent. Hydrochloric acid recovery varied between 74 and 76 percent. Sulphuric acid recovery was approximately 75 percent. Approximately 95 percent of the metals (Fe, Ni, Cu) could be removed from the recovered acid. Zinc was not as effectively removed (14,4% removal) as the other metals. However, it may also be possible in this case to recover acid effectively with diffusion dialysis for reuse in the plating process.
- It will be possible to use ion-exchange effectively for nickel recovery from dilute nickel rinse waters (150; 400 and 1 000 mg/ℓ Ni). Most of the nickel could be removed from the exhausted resin with 2,5 to 3 bedvolumes dilute sulphuric acid regenerant. The recovered nickel solution can be used in the plating bath or the nickel can be electrolytically recovered for sale to scrap metal dealers. It might also be possible to use the treated rinse water as rinse water in the process. Chrome and copper electroplating rinse waters can also be effectively treated with ion-exchange.
- Process design criteria for electroplating effluent treatment with membrane, electrolytic and ion-exchange technology can be derived from the experimental results. Demonstration plants should now be installed at selected plating shops to transfer metal/water/effluentvolume reduction/pollution control technology to the electroplaters. Electrolytic nickel and zinc recovery plants as well as an evaporator for chromium recovery from chromium drag-out was recently installed in South Africa at plating shops.

Centralized treatment of electroplating effluents is successfully applied in the USA and elsewhere. A centralized facility for treatment of electroplating effluents should function effectively in South Africa. This will take the effluent treatment responsibility away from the electroplater by effluent treatment experts with an effluent treatment infrastructure. The electroplater will benefit from such an approach because it will not be necessary for them to have their own advanced effluent treatment system. However, the economics of such an approach should first be determined to determine whether such an approach would be economically feasible. Alternatively, effluent treatment can be conducted for electroplaters by effluent treatment experts on site.

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