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AN INVESTIGATION INTO THE ORGANIC FOULING OF ION-EXCHANGE MEMBRANES

(Contract between the Division of Water Technology
and the Water Research Commission)

by

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EXECUTIVE SUMMARY

It is anticipated that, in future, electrodialysis (ED) will be used to a far greater extent than at present in South Africa for the treatment of industrial effluents; for the recovery of water or chemicals for reuse or for a reduction in the effluent volume. Industrial effluents usually contain a wide range of organic materials, some of which have the potential to foul ion-exchange membranes and hence may lead to the failure of the ED process. The organic fouling of ion-exchange membranes was, therefore, investigated to obtain a better understanding of the membrane fouling process.

The main objectives of the study were the following:

- To select industrial effluents which may be treated to good effect with ED.
- To investigate the fouling characteristics of selected foulants which affect membranes.
- To determine cleaning methods for fouled membranes.
- To identify methods for the pretreatment of membranes to prevent or minimize organic fouling.
- To study the surface characteristics of fouled membranes.

An earlier literature study has shown that fouling of ion-exchange membranes depends on the concentration of foulant in the feedwater, the pH of the feed solution, the linear flow velocity of the feed solution through an ED stack, the current density applied, the frequency of polarity reversal, membrane cleaning methods and pretreatment of the feedwater prior to ED treatment.

The most common ion-exchange membrane foulant found in surface waters in South Africa is humic acid. This acid was found to be present in fouled anion-exchange membranes obtained from Tutuka Power Station (Eskom).

Industrial effluents may contain a wide variety of organic materials which have the potential to foul ion-exchange membranes. The most common ion-exchange membrane foulants encountered in industrial effluents are detergents, dyes, certain hydrocarbons and organic additives added to electroplating baths.

Membrane fouling with humic acid and para-dodecylbenzene sulphonate (DBS, detergent), was found to increase with increasing current density, increasing concentration of foulant in the feedwater and decreasing flow velocity of the feedwater through the fouling cell.

Biocides used for water treatment can cause fouling of ion-exchange membranes. It was found that a biocide with a fixed positive charge caused fouling of a cation-exchange membrane. However, no fouling of anion-exchange membranes could be detected with a limited number of biocides that were tested.

Nickel and cadmium electroplating baths contain organic additives that can foul ion-exchange membranes. Some membranes, however, were found to be more resistant to organic fouling than others. Conventional ion-exchange membranes are not suitable for treatment of chromium rinse water because the membranes are oxidized by chromium. Therefore, specially designed membranes should be used for treatment of chromium rinse waters.

It was possible to control membrane fouling by humic acids through the use of polarity reversal and regular rinses of the membranes with dilute caustic soda solutions. The polarity reversal cycle, however, should be as short as possible. Fouling of ion-exchange membranes by detergents, however, will be more difficult to control because the detergent molecule is small enough to penetrate the pores of the anion-exchange

membrane to foul the membrane irreversibly. Fouling of anion-exchange membranes by detergents at low concentrations may be controlled by polarity reversal and regular cleaning of the membranes with salt/caustic soda solutions. It may, however, be preferable to remove the detergents with activated carbon, prior to ED treatment.

It should be possible to remove humic acids effectively from water with coagulation/flocculation with ferric chloride and oxidation with chlorine, prior to ED treatment. Ultraviolet oxidation, ultrafiltration and adsorption technology (carbon and resin) may also be used effectively to remove humic acids and organic materials occurring in sewage effluents from ED feedwaters. It should also be possible to remove detergents from effluents with adsorption technology (activated carbon and resin) prior to ED treatment. These latter two methods, however, warrant further investigation.

No difference could be detected in the scanning electron micrographs of fouled and unfouled ion-exchange membranes.

Most of the objectives, as set out in the original contract, have been achieved in this study.

The report includes the following items of interest for those dealing with ED technology:

- It describes a simple membrane fouling method which may be used to predict the fouling potential of selected foulants and industrial effluents.
- It describes pretreatment methods for ED feedwater to reduce or eliminate membrane fouling.
- It describes membrane cleaning methods that may be used to restore fouled membranes.
- It describes membranes which are more resistant to organic fouling than others.

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

- The membrane fouling cell will be evaluated further to predict the fouling potential of selected foulants and industrial effluents for different ion-exchange membranes.
- Pretreatment of nickel and cadmium electroplating rinse waters will be studied to reduce or eliminate fouling caused by organic additives in the plating rinse waters.
- A publication reflection the main results of the study will be compiled and submitted to a popular journal.

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

- The fouling potential of an effluent should always be evaluated first in a fouling cell, before ED treatment of the effluent is considered.
- The fouling potential of other effluents, such as whey, molasses, etc., likely to be treated with ED should be evaluated in the fouling cell and pretreatment and membrane cleaning methods should be developed, if required.
- Ultraviolet oxidation, ultrafiltration and adsorption technology (carbon and resin) may be applied effectively to remove organic materials from industrial and sewage effluents prior to ED treatment.
- A talk should be given at a local membrane symposium in South Africa (WISA-MTD) to transfer the technology to all parties interested in ED technology.

1. INTRODUCTION

Electrodialysis (ED),using ion-exchange membranes,will be used on a larger scale in future in South Africa for treatment of industrial effluents for water and chemical recovery for reuse and for effluent volume reduction. Industrial effluents usually contain a wide variety of organics in different concentrations. Some of the organics have the potential to foul ion-exchange membranes and this can lead to failure of the ED process.

It has been demonstrated that anion-exchange membranes can be very sensitive towards some organics which have the ability to penetrate and foul the membranes(1). Membrane fouling shortens membrane life and it affects the economics of the ED process adversely. Therefore, techniques and methods should be developed for cleaning of the membranes after fouling has occurred in an attempt to restore membrane performance or to prevent membrane fouling,by suitable pretreatment. The use of ED may be ruled out if the fouling potential of an effluent is too high for the ion-exchange membranes under consideration.

Not enough information is presently available in South Africa regarding the nature of organics that can cause fouling of ion-exchange membranes(2). Information regarding ways and means to clean fouled membranes or to prevent membrane fouling from taking place, is also lacking. Insufficient information is available regarding the type and character of organics occurring in effluents where ED is applied in South Africa and where ED has the potential to be applied(3).

Cooling tower blowdown is treated at Tutuka Power Station at Eskom with EDR for water recovery and effluent volume reduction. Fouling of the anion-exchange membranes is experienced. This fouling reduces plant availability and therefore has an adverse effect on desalination performance of the plant(3). It is suspected that naturally occurring organics in the feed water or biocides used in the process for bacteriological control, is responsible for the membrane fouling. The exact cause of the fouling, however, is unknown and there exists a need to identify the foulants and to investigate membrane cleaning methods to clean the fouled membranes. There is also a need to investigate methods to prevent fouling by suitable pretreatment techniques.

Electrodialysis may be applied in future in South Africa in the electroplating industry for water and chemical recovery from electroplating rinse waters. Plating baths contain organic additives which have the potential to foul ion-exchange membranes(4). Consequently, there is a need to identify these potential foulants so that the fouling potential of the organics for ED membranes can be determined and that methods can be developed to clean the fouled membranes.

Electrodialysis will also be increasingly applied in future in South Africa in the general chemical process industry for concentration/desalination applications. There is a need to identify the fouling potential of these effluents for ED membranes and to develop methods to clean the fouled membranes and to devise pretreatment techniques with which the fouling potential of the effluents can be reduced to acceptable levels.

It is claimed by the manufacturers of ion-exchange membranes that certain membranes have a higher resistance towards organic fouling than others. Consequently, there is a need to identify these membranes and also to evaluate the performance of these membranes when exposed to organic foulants.

The applied current density, linear flow velocity through an ED stack and pH of the feed solution can affect the fouling behaviour of foulants during ED treatment(5). Therefore, there exists a need to examine the effect of these parameters on membrane fouling.

The objectives of this study were therefore to:

a) conduct a literature survey regarding fouling of ion-exchange membranes (separate report);

b) study the membrane fouling behaviour of selected potential foulants and industrial effluents most likely to be treated with ED in South Africa;

c) determine membrane cleaning methods;

d) identify pretreatment methods to prevent or minimize organic fouling of ion-exchange membranes; and

e) study the surface characteristics of fouled membranes.

2. EXPERIMENTAL

2.1 Fouling Cell

Schematic diagrams of the fouling cell that were used are shown in Figures 1 and 2.

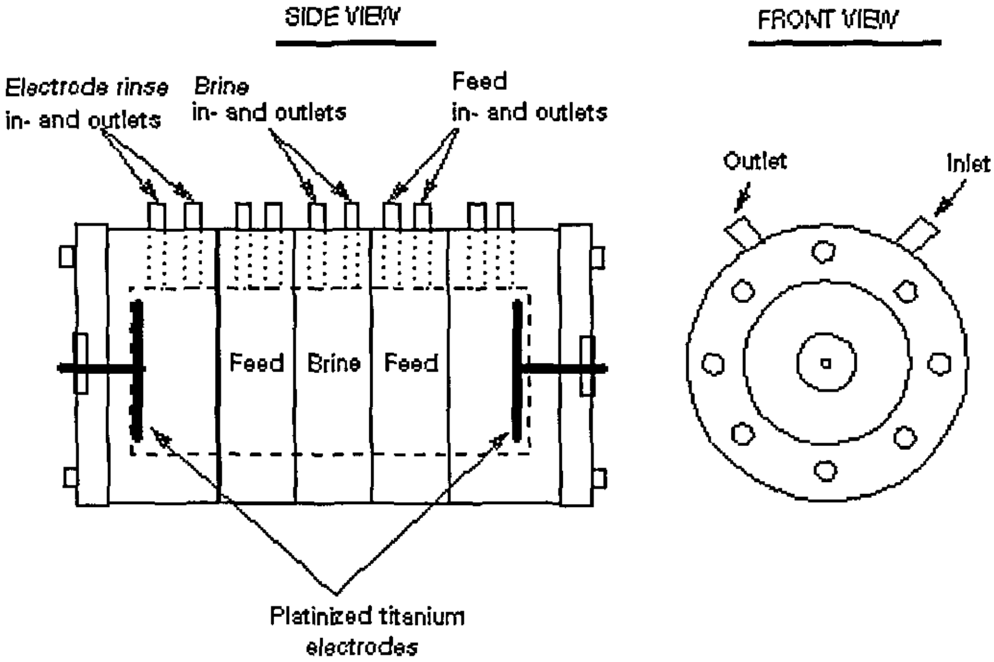

Figure 1: Schematic diagram of fouling cell.

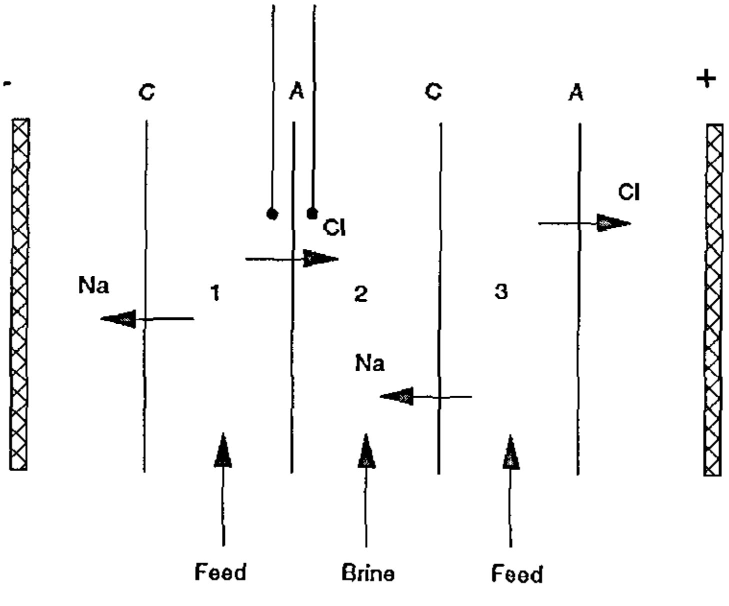

Figure 2: ***Simplified schematic diagram of fouling cell.*** **C = cationic membrane; A = anionic membrane.**

The fouling cell consists of five perspex cells which can be clamped together to hold the membranes (7,1 cm^2 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 ℓ/min and 0,7 ℓ/min were used through the feed and brine compartments, respectively. Pretoria tap water spiked with sodium chloride (2 000, 3 000 or 5 000 mg/ℓ) served as feed water. Para-dodecylbenzene sulphonate (DBS) (a common detergent) and humic acid (HA) were used as foulants in the feed water. DBS is a common foulant that can occur in many effluents and HA is representative of organics that can occur in surface waters as a result of natural decay of organic matter. Electroplating effluents and organic additives used in the plating process were used as potential foulants originating from electroplating processes. 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 consists of a carbon slurry (2%, pH ≈ 5) in 1 mol/ℓ sodium sulphate solution. This solution was circulated through the two electrode compartments.

A DC current density (20; 10 or 5 mA/cm^2) 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 before and after fouling were measured in 0,5 mol/ℓ sodium chloride solution.

3. RESULTS AND DISCUSSION

3.1 Membrane Fouling with p-Dodecyl Benzene Sulphonate (DBS)

3.1.1 Effect of current density and feed water salinity level on fouling of Selemion AMV membranes using 100 mg/ℓ DBS

The effect of current density on membrane fouling using Pretoria tap water as feed spiked with 100 mg/ℓ DBS and 5 000 mg/ℓ sodium chloride, is shown in Figure 3.1

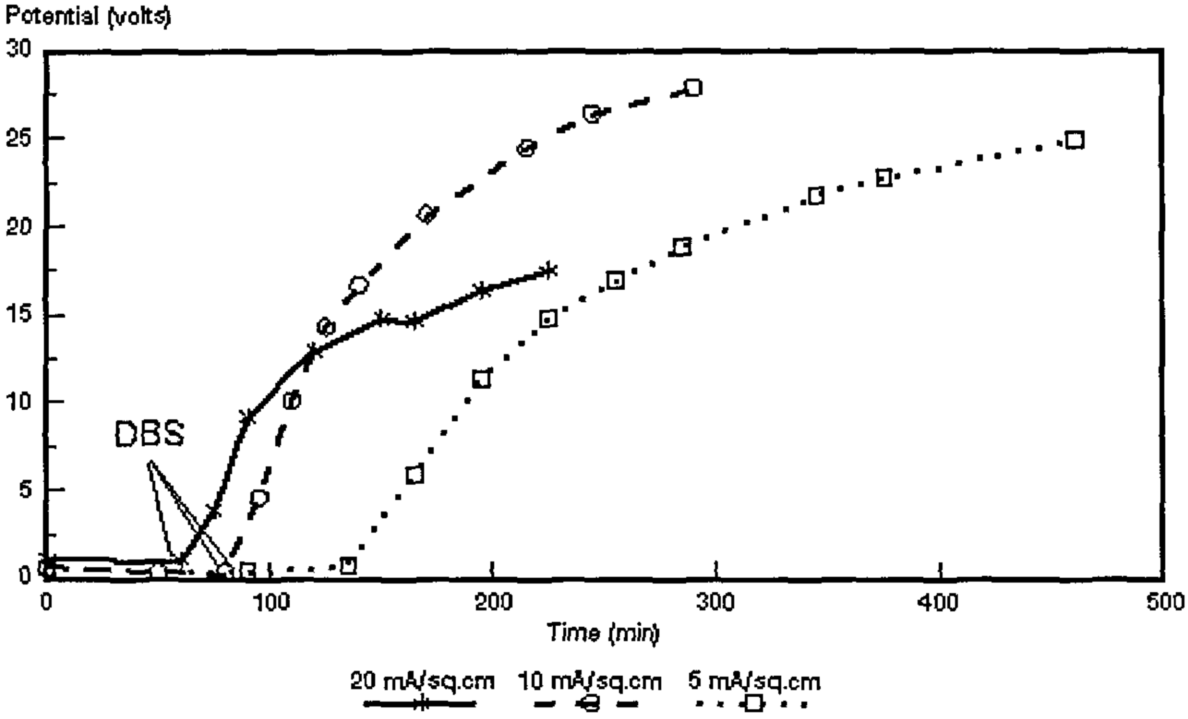

Figure 3.1: **Membrane potential as a function of time at different current densities (*100 mg/ℓ* DBS; *5 000 mg/ℓ* NaCl; *Selemion* AMV *membrane*).**

Membrane fouling (increase in membrane potential) increased with increasing current density. Membrane fouling immediately started to occur when DBS was added at current densities of 20 and 10 mA/cm^2. Membrane fouling, however, only started to occur sixty minutes after DBS had been added in the case of the lower current density (5 mA/cm^2). Consequently, it appears that less serious membrane fouling may be experienced at lower current density.

The effect of current density on membrane fouling using Pretoria tap water spiked with 100 mg/ℓ DBS and 2 000 mg/ℓ sodium chloride, is shown in Figure 3.2.

Higher membrane potentials were experienced at the lower feed water salt concentration (2 000 mg/ℓ NaCl; Figure 3.2). It is also interesting to note that membrane fouling has started immediately to occur when the foulant has been added in the case of the lowest current density (5 mA/cm^2) that has been used. This suggests that a higher salt concentration in the feed water (see Fig. 31.) inhibits membrane fouling to a certain degree.

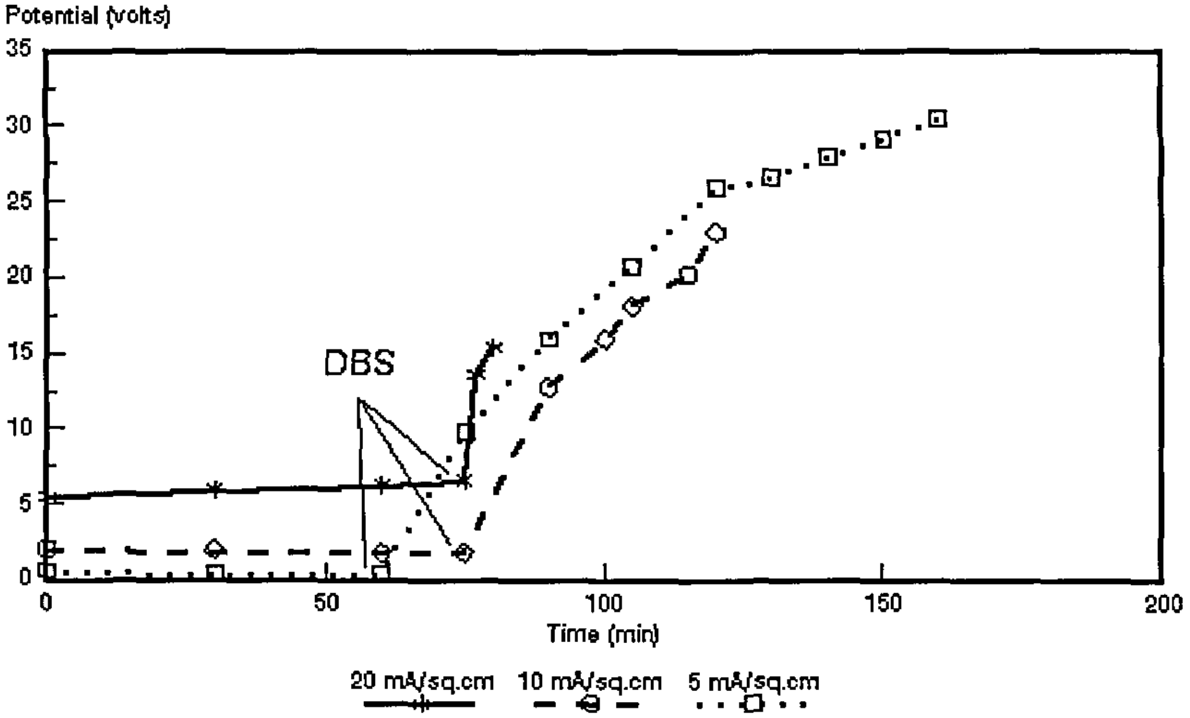

Figure 3.2: **Membrane potential as a function of time at different current densities (100 mg/ℓ DBS; 2 000 mg/ℓ NaCl; Selemion AMV membrane).**

Membrane resistance before and after fouling is shown in Table 3.1.

Table 3.1: **Membrane resistance before and after fouling with 100 mg/ℓ DBS.**

Membrane	Current Density mA/cm^2	Resistance ($ohm \cdot cm^2$)	
		Unused	Used
Selemion AMV	20(1)	3,1* 2,3**	371* 20**
Selemion AMV	10(1)	3,1* 2,0**	91* 31**
Selemion AMV	5(1)	2,6* 1,3**	274* 16*
Selemion AMV	20(2)	1,7* 1,3**	2,7* 1,4**
Selemion AMV	10(2)	1,9* 1,4**	63* 1,9**
Selemion AMV	5(2)	2,0* 1,0**	181* 18,0**

* Membrane resistance measured immediately after fouling (0,5 mol/ℓ NaCl)
** Membrane resistance measured after equilibration (overnight) in 0,5 mol/ℓ NaCl
(1) 5 000 mg/ℓ NaCl
(2) 2 000 mg/ℓ NaCl.

Membrane resistance increased significantly after membrane fouling. The increase in membrane resistance, however, was much lower (Table 3.1) after the membrane was equilibrated in 0,5 mol/ℓ sodium chloride solution. This can be ascribed to defouling of the membrane by the sodium chloride solution and to a decrease in resistance as a result of the higher salt concentration in contact with the membrane. An increase in membrane resistance is indicative of membrane fouling.

3.1.2 Effect of current density and feed water salinity level on fouling of Selemion AMV membranes using 50 mg/ℓ DBS

The effect of current density on membrane fouling using Pretoria tap water spiked with 50 mg/ℓ DBS and 2 000 mg/ℓ sodium chloride, is shown in Figure 3.3. The effect of current density on membrane fouling using Pretoria tap water spiked with 50 mg/ℓ DBS and 5 000 mg/ℓ sodium chloride, is shown in Figure 3.4.

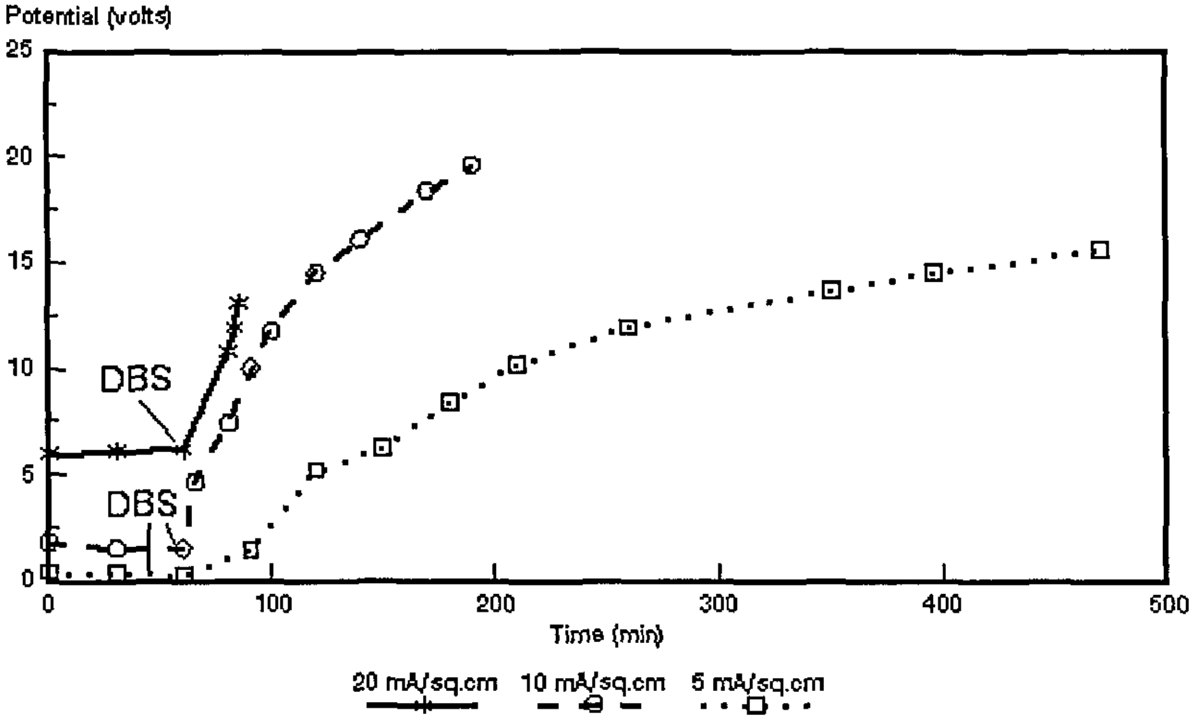

Figure 3.3: Membrane potential as a function of time at different current densities (50 mg/ℓ DBS; 2 000 mg/ℓ NaCl; Selemion AMV membrane).

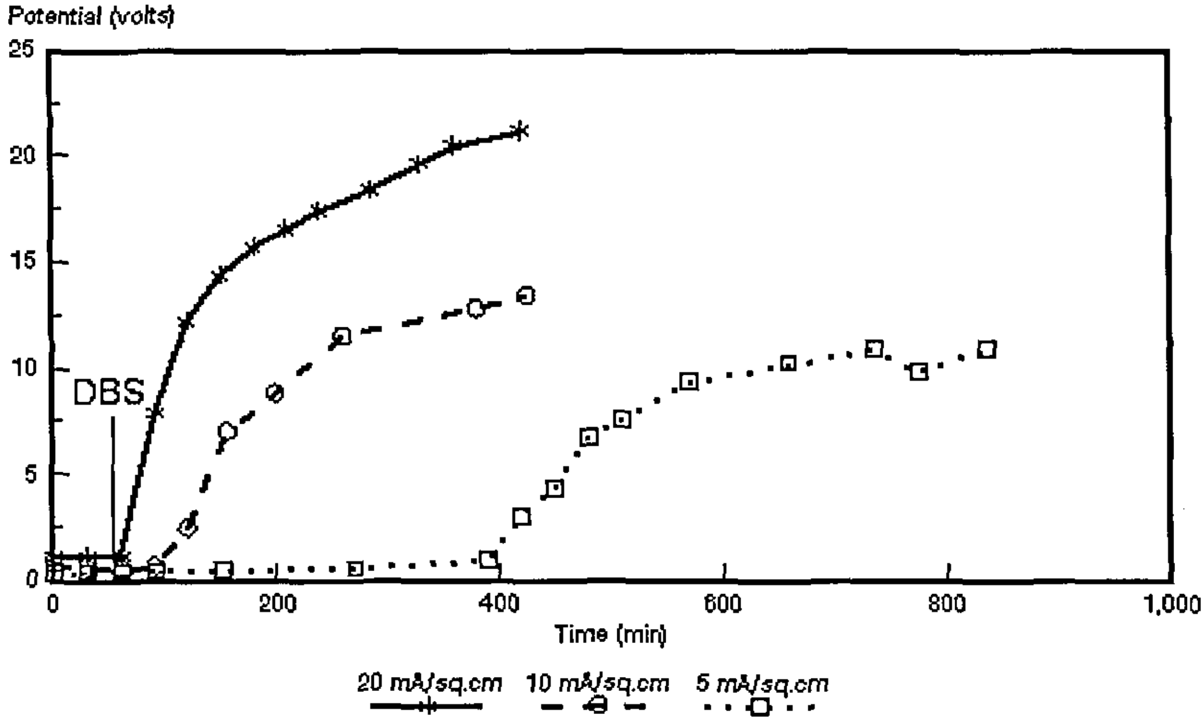

Figure 3.4: Membrane potential as a function of time at different current densities (50 mg/ℓ DBS; 5 000 mg/ℓ NaCl; Selemion AMV membrane).

A significantly higher membrane potential was again experienced at the lower feed water salinity level (Figs. 3.3 and 3.4). More severe membrane fouling was experienced at the higher current density. It is again shown that a higher feed water salinity level has the effect to postpone fouling to commence at lower current densities (Figs. 3.3 and 3.4). This may be ascribed to elution of the foulant anions with chloride ions or prevention of the foulant ions to accumulate at the membrane surface by the relatively high concentration of chloride ions.

Membrane resistance before and after fouling is shown in Table 3.2. High membrane resistances were experienced when the membranes became fouled. Membrane resistance could be significantly reduced after equilibration in sodium chloride solution. This showed that it should be possible to partly restore membrane performance with a sodium chloride rinse.

Table 3.2: **Membrane resistance before and after fouling with 50 mg/ℓ DBS.**

Membrane	**Current Density**	**Resistance ($ohm \cdot cm^2$)**	
	mA/cm^2	**Unused**	**Used**
Selemion AMV	$20^{(1)}$	0,4* 0,2**	1,5* 0,7**
Selemion AMV	$10^{(1)}$	0,3* 0,1**	76* 17**
Selemion AMV	$5^{(1)}$	1,6* 0,7**	118* 31**
Selemion AMV	$20^{(2)}$	1,0* 0,2**	192* 17**
Selemion AMV	$10^{(2)}$	1,2* 0,7**	144* 10,0**
Selemion AMV	$5^{(2)}$	2,9* 1,9**	175* 12,3**

* Membrane resistance measured immediately after fouling (0,5 mol/ℓ NaCl)

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

(1) 5 000 mg/ℓ NaCl

(2) 2 000 mg/ℓ NaCl.

3.1.3 Effect of current density on fouling of Selemion AMV membranes using 25 mg/ℓ DBS

The effect of current density on membrane fouling using Pretoria tap water spiked with 25 mg/ℓ DBS and 5 000 mg/ℓ sodium chloride, is shown in Figure 3.5. A sharp increase in membrane fouling was experienced at a current density of 20 mA/cm^2. Membrane fouling, however, took much longer to commence at a current density of 10 mA/cm^2 and no membrane fouling could be detected at a current density of 5 mA/cm^2 over the test period.

Membrane resistance before and after fouling is shown in Table 3.3.

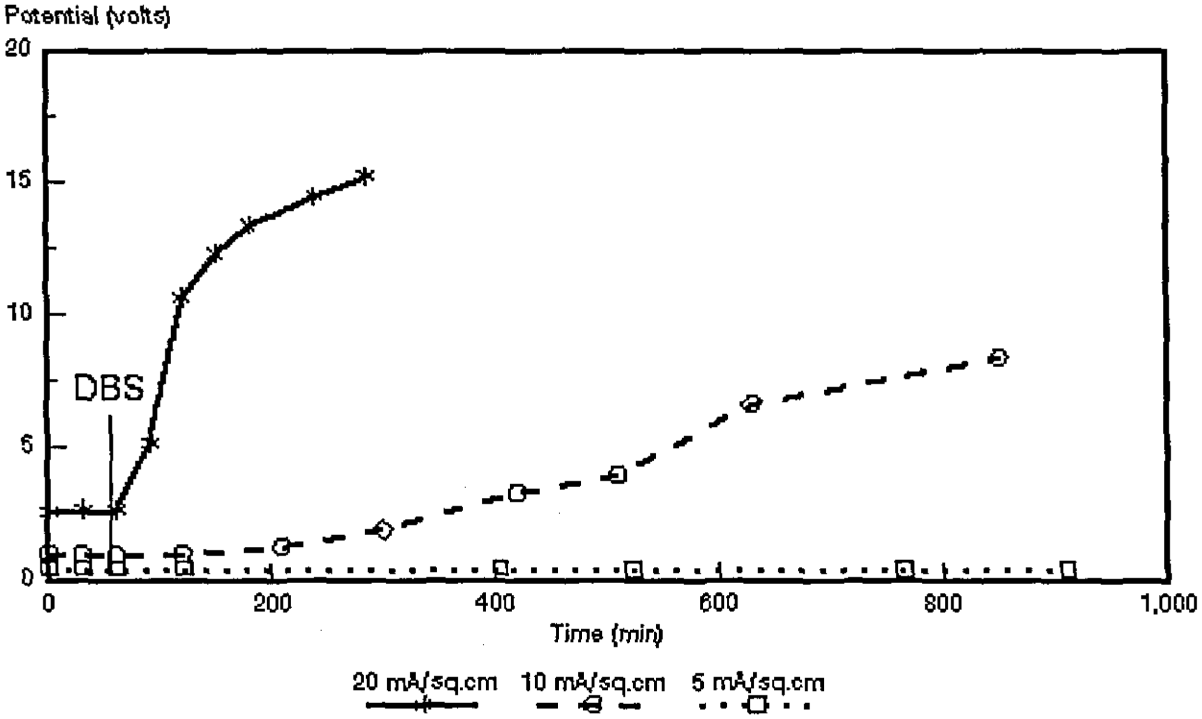

Figure 3.5: Membrane potential as a function of time at different current densities (25 mg/ℓ DBS; 5 000 mg/ℓ NaCl; Selemion AMV membrane).

Table 3.3: **Membrane resistance before and after fouling with 25 mg/ℓ DBS.**

Membrane	**Current Density** mA/cm^2	**Resistance** (ohm·cm^2) Unused	**Resistance** (ohm·cm^2) Used
Selemion AMV	20$^{(1)}$	1,6* 0,5**	74* 6**
Selemion AMV	10$^{(1)}$	2,6* 1,0**	284* 16,1**
Selemion AMV	5$^{(1)}$	1,0* 0,5**	264* 52**

* Membrane resistance measured immediately after fouling (0,5 mol/ℓ NaCl)
** Membrane resistance measured after equilibration (overnight) in 0,5 mol/ℓ NaCl
(1) 5 000 mg/ℓ NaCl.

Membrane resistance again showed a significant decrease in resistance after equilibration in sodium chloride (0,5 M) solution.

3.1.4 Effect of current density and interruption of current on fouling of Selemion AMV membranes using 50 mg/ℓ DBS

The effect of current density and interruption of current on membrane fouling using Pretoria tap water spiked with 50 mg/ℓ DBS and 5 000 mg/ℓ sodium chloride, is shown in Figure 3.6. The fouling runs were terminated at the end of the day and started the next morning. A reduction in membrane potential was observed when the runs were started the next day. Membrane potential, however, again increased relatively fast as a function of time. The reduction in membrane potential as a result of interruption of the electric current may be ascribed to peeling off of the foulant from the membrane surface when the current was interrupted overnight.

Membrane resistance before and after fouling is shown in Table 3.4.

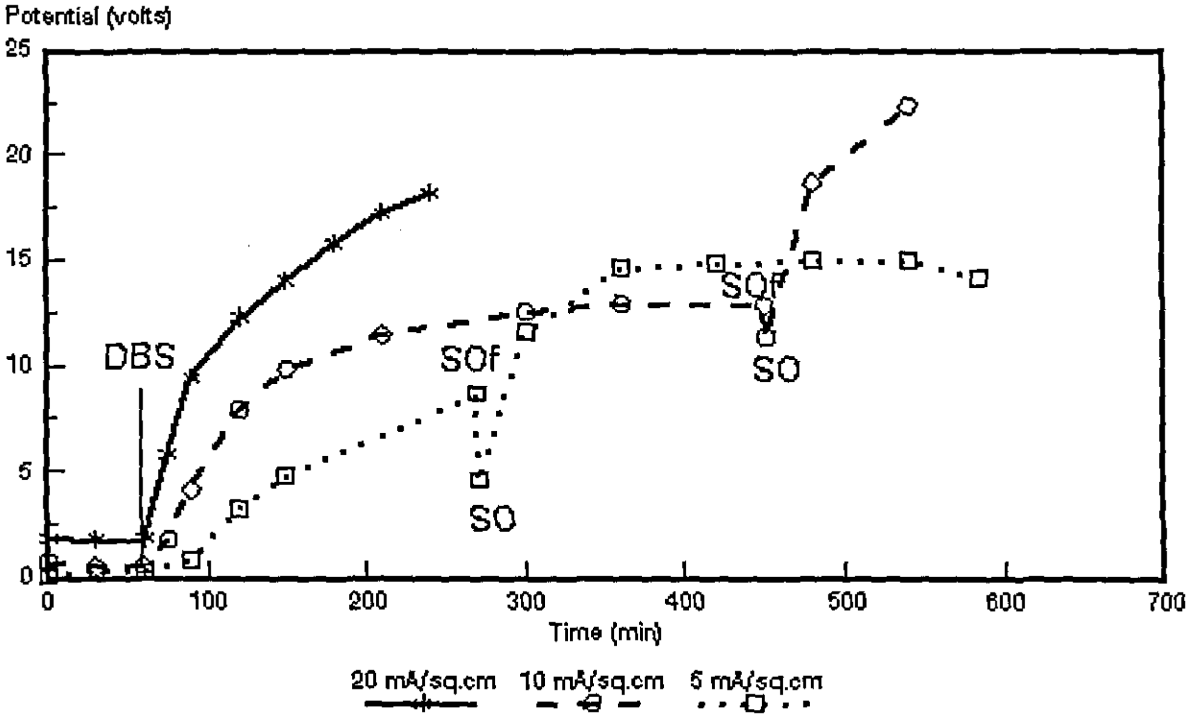

Figure 3.6: **Membrane potential as a function of time at different current densities when current was interrupted overnight (50 mg/ℓ DBS; 5 000 mg/ℓ NaCl; Selemion AMV membrane) SOF: switch off; SO: switch on.**

Table 3.4: **Membrane resistance before and after fouling with 50 mg/ℓ DBS.**

Membrane	Current Density	Resistance (ohm·cm^2)	
	mA/cm^2	Unused	Used
Selemion AMV	20$^{(1)}$	1,5* 0,4**	439* 8,0**
Selemion AMV	10$^{(1)}$	1,6* 0,6**	441* 48**
Selemion AMV	5$^{(1)}$	2,6* 1,1**	94* 32**

* Membrane resistance measured immediately after fouling (0,5 mol/ℓ NaCl)
** Membrane resistance measured after equilibration (overnight) in 0,5 mol/ℓ NaCl
(1) 5 000 mg/ℓ NaCl.

3.1.5 Effect of current density on fouling of Ionac MA-3475 and Ionics A-204-UZL-386 membranes using 50 mg/ℓ DBS

The effect of current density on fouling of Ionac MA-3475 and Ionics A-204- UZL-386 membranes using Pretoria tap water spiked with 50 mg/ℓ DBS and 5 000 mg/ℓ sodium chloride, is shown in Figures 3.7 and 3.8. Membrane fouling increased with increasing current density in the case of the Ionac membranes. It appears, however, that less fouling has taken place at lower current densities (5 and 10 mA/cm^2) using Ionac membranes (Fig. 3.6) than has been experienced with the Selemion membranes. It is further interesting to note that a higher membrane potential has been experienced when the run was started the next day. This indicated that membrane fouling took place overnight when the membrane was in contact with the feed solution.

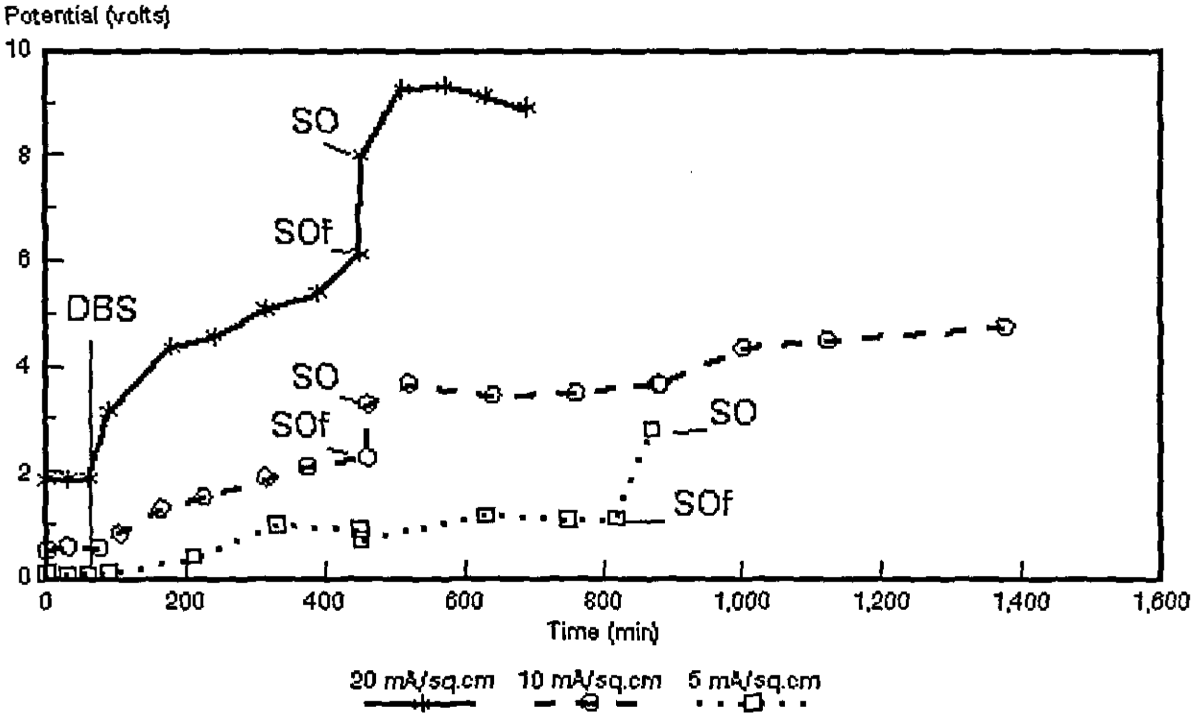

Figure 3.7: Membrane potential as a function of time at different current densities (50 mg/ℓ DBS; 5 000 mg/ℓ NaCl; Ionac MA-3475 membrane). SOF: Switch off; SO: switch on.

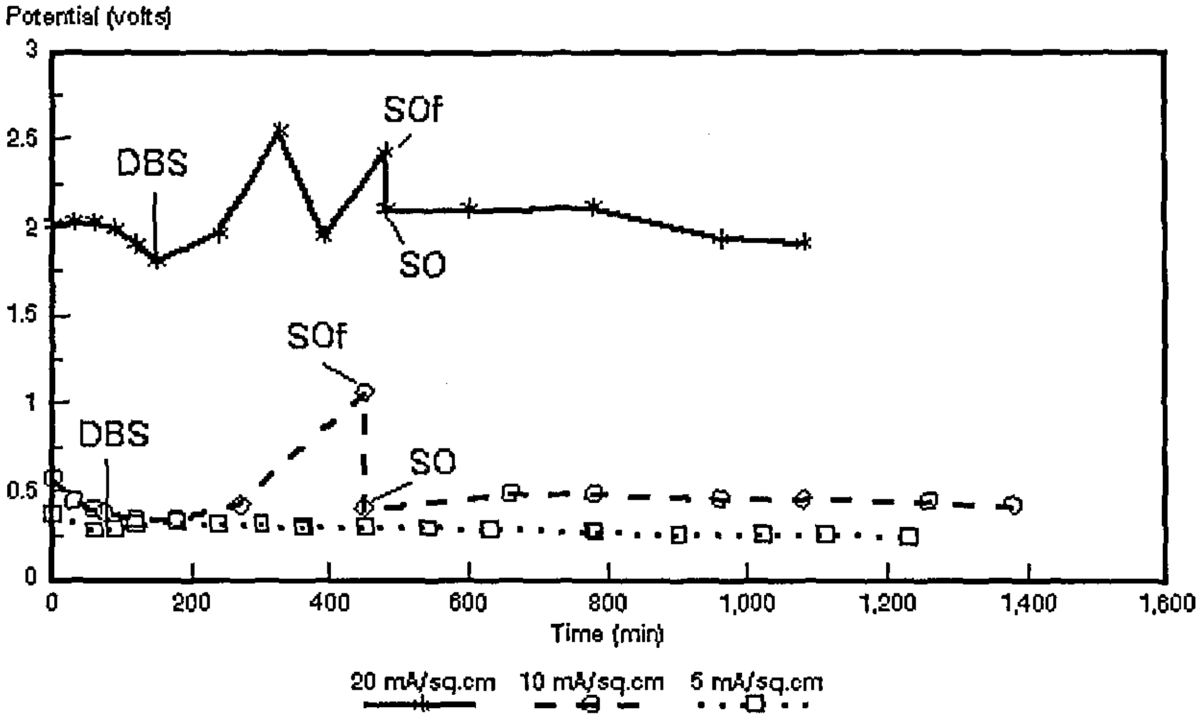

Figure 3.8: **Membrane potential as a function of time at different current densities (50 mg/ℓ DBS; 5 000 mg/ℓ NaCl; Ionics A-204-UZL-386 membranes). SOF: switch off; SO: switch on.**

Much less membrane fouling was encountered with the Ionics membrane than with the Selemion or Ionac membranes (Fig. 3.7). This shows that the Ionics membrane is much more resistant to DBS membrane fouling than the other two membrane types.

Membrane resistance before and after fouling is shown in Table 3.5. Membrane resistance again decreased significantly after exposure of the membrane to sodium chloride solution. It is also interesting to note that the Ionics membrane shows a significant increase in membrane resistance despite the fact that little increase in membrane potential has been experienced in comparison with the Selemion and Ionac membranes which show a significant increase in membrane potential. This might be explained by membrane surface fouling that took place.

Table 3.5: **Membrane resistance before and after fouling (Ionac MA-3475 and Ionics A-204-UZL-386 membranes).**

Membrane	Current Density	Resistance (ohm·cm²)	
	mA/cm²	Unused	Used
Ionac MA-3475	20⁽¹⁾	30* 26**	93* 41**
Ionac MA-3475	10⁽¹⁾	30* 26**	233* 161**
Ionac MA-3475	5⁽¹⁾	30* 26**	285* 216**
Ionics A-204-UZL-386	20⁽¹⁾	8* 4**	437* 82**
Ionics A-204-UZL-386	10⁽¹⁾	10* 5**	415* 45**
Ionics A-204-UZL-386	5⁽¹⁾	10* 4**	420* 46**

* Membrane resistance measured immediately after fouling (0,5 mol/ℓ NaCl)
** Membrane resistance measured after equilibration (overnight) in 0,5 mol/ℓ NaCl
(1) 5 000 mg/ℓ NaCl.

3.2 Membrane Fouling with Humic Acid (HA)

3.2.1 Effect of humic acid (HA) and polarity reversal on fouling of Selemion AMV, Ionac MA-3475 and Ionics A-204-UZL-386 membranes

The effect of Pretoria tap water spiked with 100 mg/ℓ HA and 3 000 mg/ℓ sodium chloride on membrane fouling of Selemion AMV, Ionac MA-3475 and Ionics A-204-UZL-386 membranes using a current density of 20 mA/cm², is shown in Figure 3.9. The Ionac and Selemion membranes were very sensitive to organic fouling. The membrane potential increased rapidly as a function of time. However, the Ionics membrane showed a very high resistance to organic fouling. No increase in membrane voltage was experienced over the test period.

Preliminary tests indicated that membrane fouling could be controlled with polarity reversal. The base line voltage could be maintained after the first polarity reversal cycle (Fig. 3.9). However, the base line voltage could not be maintained after the second polarity reversal cycle showing that irreversible fouling was taking place.

A shorter polarity reversal frequency may improve the situation. A brown precipitate had formed on the anion-exchange membrane facing the anode.

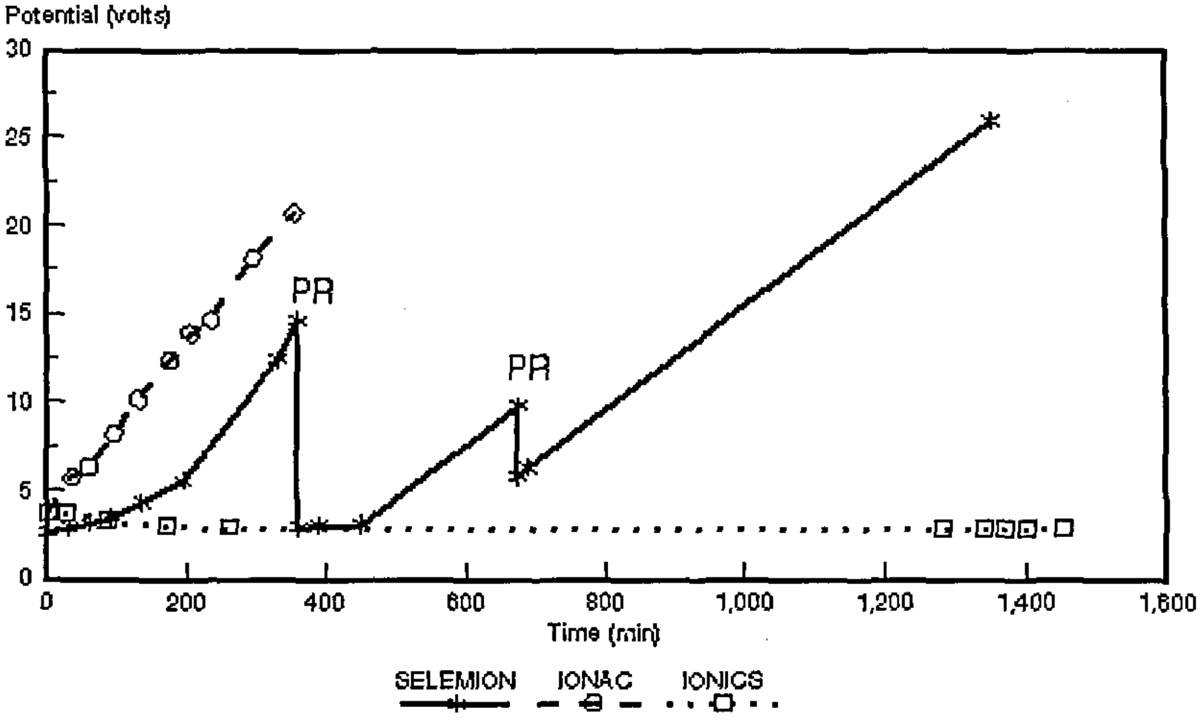

Figure 3.9: **Membrane potential as a function of time using different ion-exchange membranes and polarity reversal (PR) (Selemion AMV, Ionac MA-3475, Ionics A-204-UZL-386 membranes; 100 mg/ℓ HA, 3 000 mg/ℓ NaCl; 20 mA/cm^2).**

Membrane resistance before and after fouling is shown in Table 3.6.

Table 3.6: **Membrane resistances before and after fouling with humic acid (100 mg/ℓ) using different ion-exchange membranes.**

Membrane	Current Density mA/cm^2	Resistance (ohm·cm^2) Unused	Resistance (ohm·cm^2) Used
Selemion AMV	20$^{(1)}$	1,0* 0,5**	14,2* 3,6**
Ionac MA-3475	20$^{(1)}$	15,2* 9,1**	20,8* 9,1**
Ionics A-204-UZL-386	20$^{(1)}$	4,5* 1,5**	8,6* 1,5**

* Membrane resistance measured immediately after fouling (0,5 mol/ℓ NaCl)
** Membrane resistance measured after equilibration (overnight) in 0,5 mol/ℓ NaCl
(1) 3 000 mg/ℓ NaCl.

An increase in membrane resistance was experienced showing that membrane fouling was taking place. It is interesting to note that membrane resistance could be reduced to its original value after equilibration with sodium chloride solution in the case of the Ionac and Ionics membranes. This showed that the membrane's resistance could be restored after equilibration with sodium chloride solution to its initial level. This, however, did not happen with the Selemion membrane, showing that it would be more difficult to clean this membrane.

3.2.2 Effect of current interruption and caustic soda cleaning on membranes fouled with humic acid

The effect of current interruption and caustic soda cleaning on membrane fouling fouled with 100 mg/ℓ HA in Pretoria tap water (3 000 mg/ℓ NaCl), is shown in Figure 3.10. Membrane potential increased slowly in the beginning and then more rapidly after fouling has taken place for approximately 130 minutes.

The fouling run was terminated at the end of the day (approximately 220 minutes' fouling). The membrane potential was about the same as the base line voltage when the run was started the next day. This showed that the membrane defouled overnight. Membrane voltage, however, again increased and a caustic rinse was given in an attempt to clean the membrane. The caustic soda cleaning had a beneficial effect on membrane potential and the potential was almost reduced to its base line value. Fouling was again allowed to take place and membrane potential was high when the current was interrupted. Successive current interruption and caustic soda cleanings showed that the membrane could be cleaned. However, fouling rapidly started to occur after membrane cleaning. It also appeared that the base line voltage could not be maintained after the last caustic soda cleaning showing that membrane fouling was irreversible.

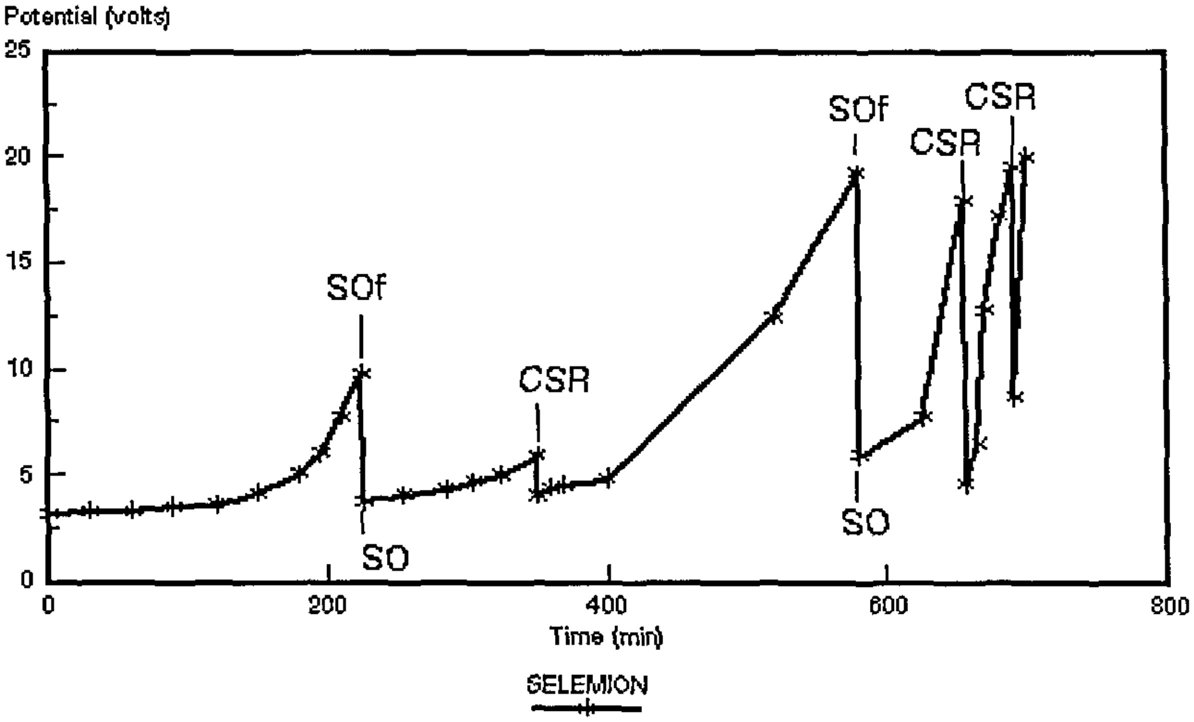

Figure 3.10: **Effect of caustic soda cleaning and current interruption on membrane fouling using 100 mg/ℓ humic acid as foulant (3 000 mg/ℓ NaCl; Selemion AMV membrane; CD 20 mA/cm^2; rinse 30 minutes with 0,1 mol/ℓ NaOH and 30 minutes with water).**
SOF: switch off; SO: switch on.

3.2.3 Effect of feed flow rate on membrane fouling

The effect of feed water flow rate on membrane fouling is shown in Figure 3.11. Pretoria tap water spiked with 100 mg/ℓ HA and 3 000 mg/ℓ sodium chloride was used as feed water. Feed flow rates of 600; 1 100 and 1 600 mℓ/min were used. Increasing feed flow rate from 600 to 1 600 mℓ/min had a dramatic effect on membrane fouling (Fig. 3.11). It took much longer for fouling to take place at the higher feed flow rate. Consequently, it will be advantageous to use the highest possible flow rates in an ED stack to inhibit membrane fouling.

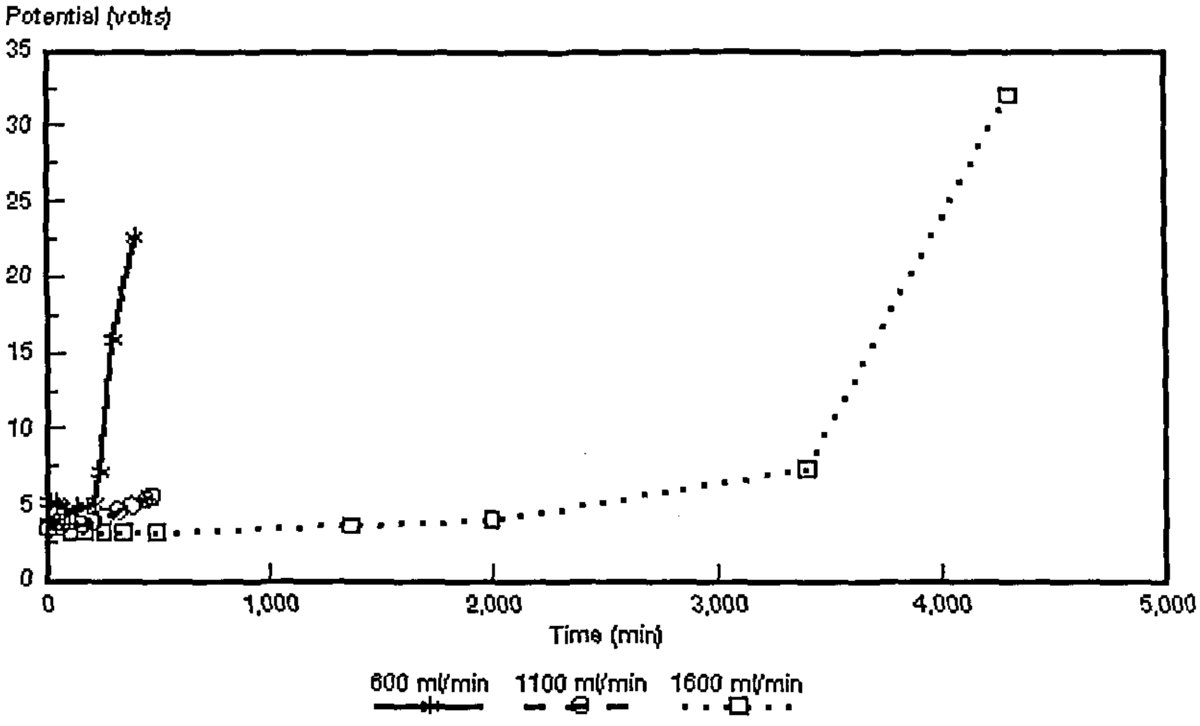

Figure 3.11: **Effect of feed flow rate on membrane fouling (100 mg/ℓ HA; 3 000 mg/ℓ NaCl; Selemion AMV membrane; CD 20 mA/cm^2).**

3.2.4 Effect of increasing current density on membrane fouling using Selemion AMV membranes and humic acid foulant

The effect of increasing current density on membrane fouling using Selemion AMV membranes and 100 mg/ℓ humic acid as foulant, is shown in Figure 3.12. Membrane fouling increased dramatically with increasing current density in the current density range from 5 to 20 mA/cm^2. No membrane fouling was experienced at a current density of 5 mA/cm^2 over the test period. Consequently, membrane fouling in ED applications might be reduced significantly by operating an ED stack at the lowest possible current density. This, however, will affect the economics of the process adversely because a larger membrane area will be required.

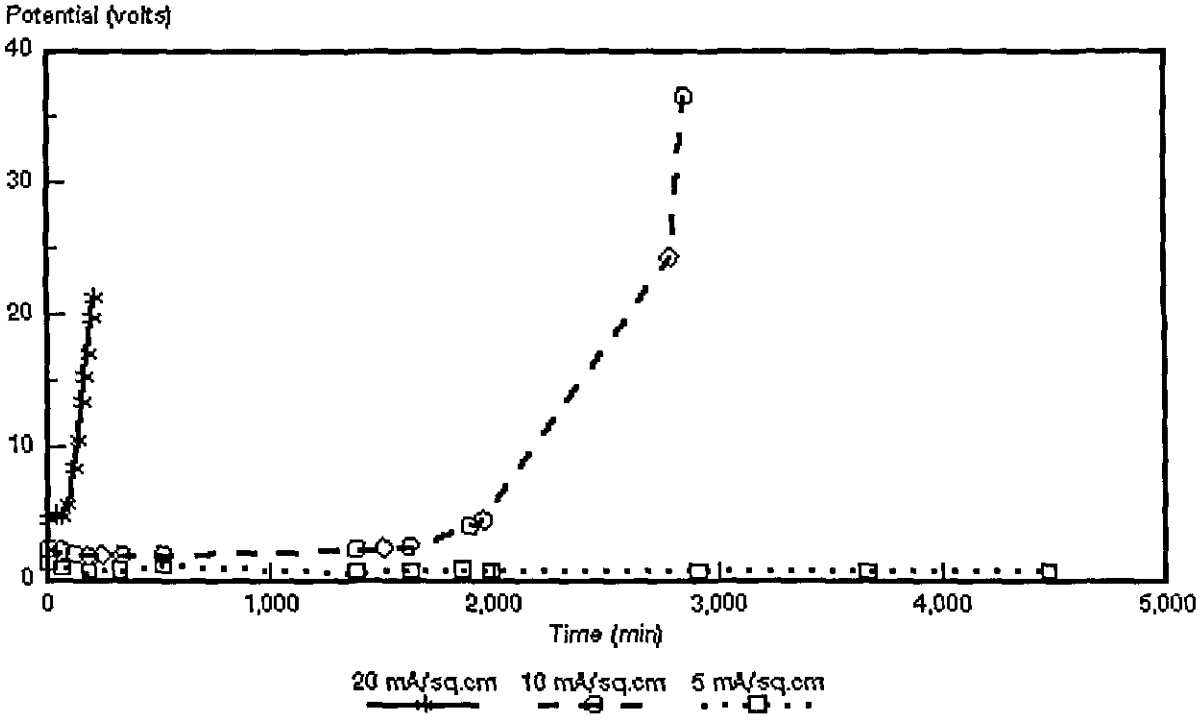

Figure 3.12: **Effect of current density on membrane fouling using Selemion AMV membrane and 100 mg/ℓ humic acid as foulant (3 000 mg/ℓ NaCl).**

3.2.5 Effect of polarity reversal, caustic soda and mechanical cleaning on membrane fouling using Ionac MA-3475 membranes and humic acid as foulant

The effect of polarity reversal, caustic soda and mechanical cleaning on membrane fouling using Ionac MA-3475 membranes and 100 mg/ℓ humic acid, is shown in Figure 3.13. It appeared that it should be possible to control membrane fouling by polarity reversal. However, the frequency of polarity reversal should be as short as possible. Membrane potential could be restored to its initial value after polarity reversal.

The power supply cut out (CO) on two occasions during this run. This happened when the membrane potential became too high. It is again interesting to note that the starting voltage in both cases has been much lower than the cut out voltage. This suggests that the membranes became defouled overnight.

The first caustic soda rinse (0,1 mol/ℓ NaOH, 15 min) had a dramatic effect on membrane potential. Membrane potential was almost decreased to its initial value

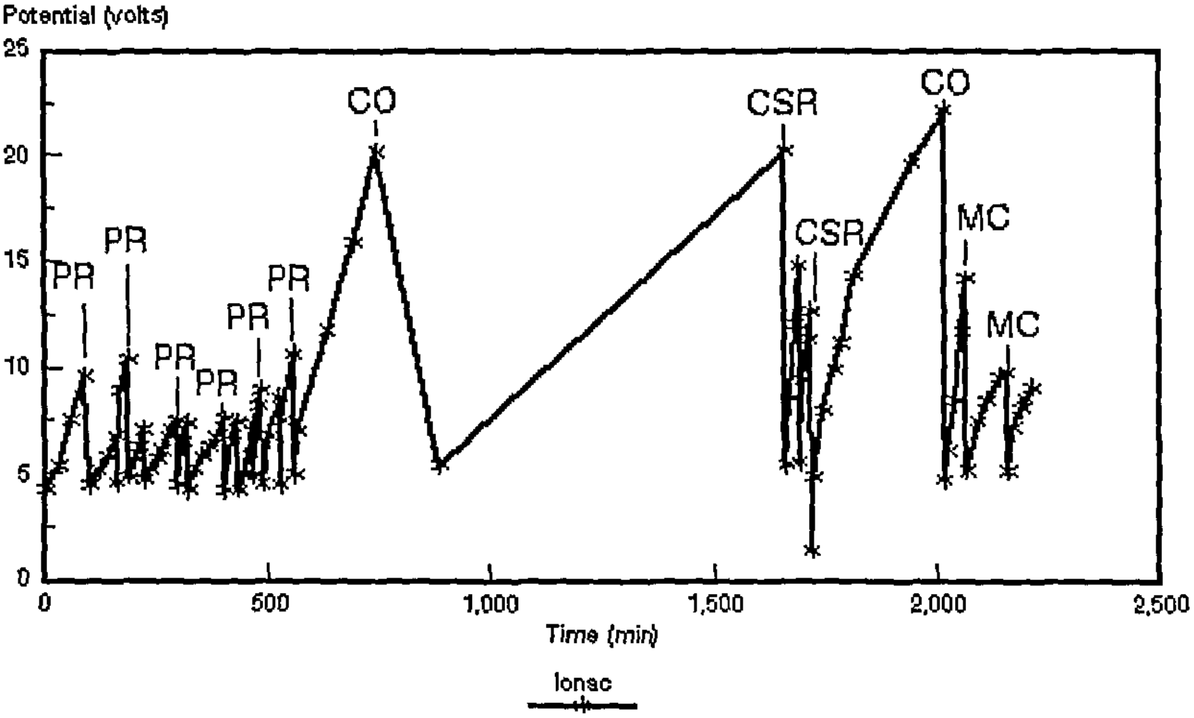

Figure 3.13: **Effect of polarity reversal, caustic soda (0,1 mol/ℓ NaOH - 15 min rinse) and mechanical cleaning on membrane fouling (Ionac MA-3475 membrane, 100 mg/ℓ HM; 3 000 mg/ℓ NaCl; CD 20 mA/cm^2) PR: polarity reversal; CO: cut out; CSR: caustic soda rinse; MC: mechanical cleaning.**

showing that it would be possible to defoul the membrane almost completely with electro-elution. Mechanical cleaning (cleaning membrane with tissue) also had a dramatic effect on membrane potential. This showed that membrane fouling with humic acid over a relatively short period was a surface phenomenon.

3.2.6 Effect of humic acid fouling on Ionic A-204-UZL membranes

The effect of humic acid fouling (500 mg/ℓ) on Ionics A-204-UZL membranes is shown in Figure 3.14. Almost no increase in voltage was experienced as a function of time. This showed that the Ionics membrane was very resistant towards humic acid fouling. Membrane resistance was determined at 2,6 ohm·cm^2 before and after fouling. This showed that no fouling took place.

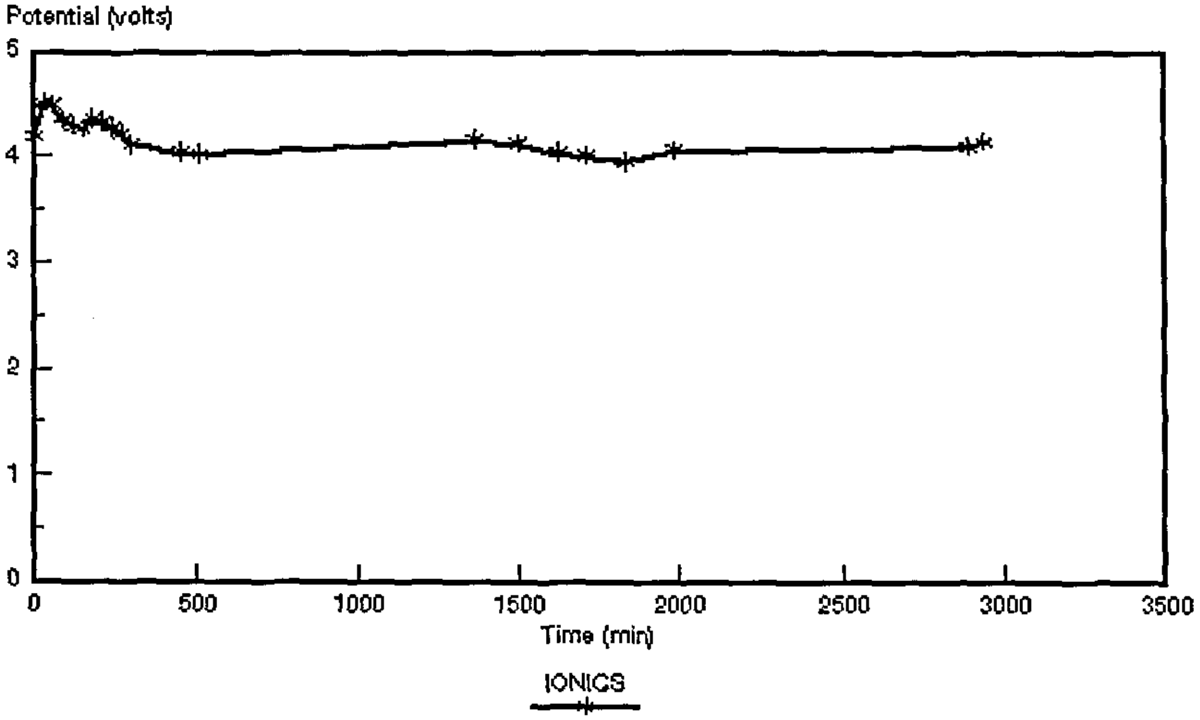

Figure 3.14: **Effect of humic acid fouling on Ionics A-204-UZL membranes (500 mg/ℓ humic acid; 3 000 mg/ℓ NaCl; 20 mA/cm^2).**

3.2.7 The effect of preflocculation of a humic acid solution on membrane fouling

The effect of preflocculation of a humic acid feed solution on membrane fouling using Selemion AMV membranes, is shown in Figure 3.15. Humic acid solution (100 mg/ℓ) was flocculated with 30 mg/ℓ ferric chloride solution. Well defined flocs formed which settled rapidly. The flocs were removed by filtration and the filtered water was used as feed water to the fouling cell.

The COD of the feed water before flocculation was 560 mg/ℓ. The COD after flocculation was 160 mg/ℓ. Therefore, a significant amount of humic acid could be removed by flocculation.

The flocculated water took much longer to foul the membrane than the unflocculated feed water. Consequently, it will be advantageous to remove humic acid from water supplies with ferric chloride flocculation prior to ED treatment to inhibit membrane fouling from taking place.

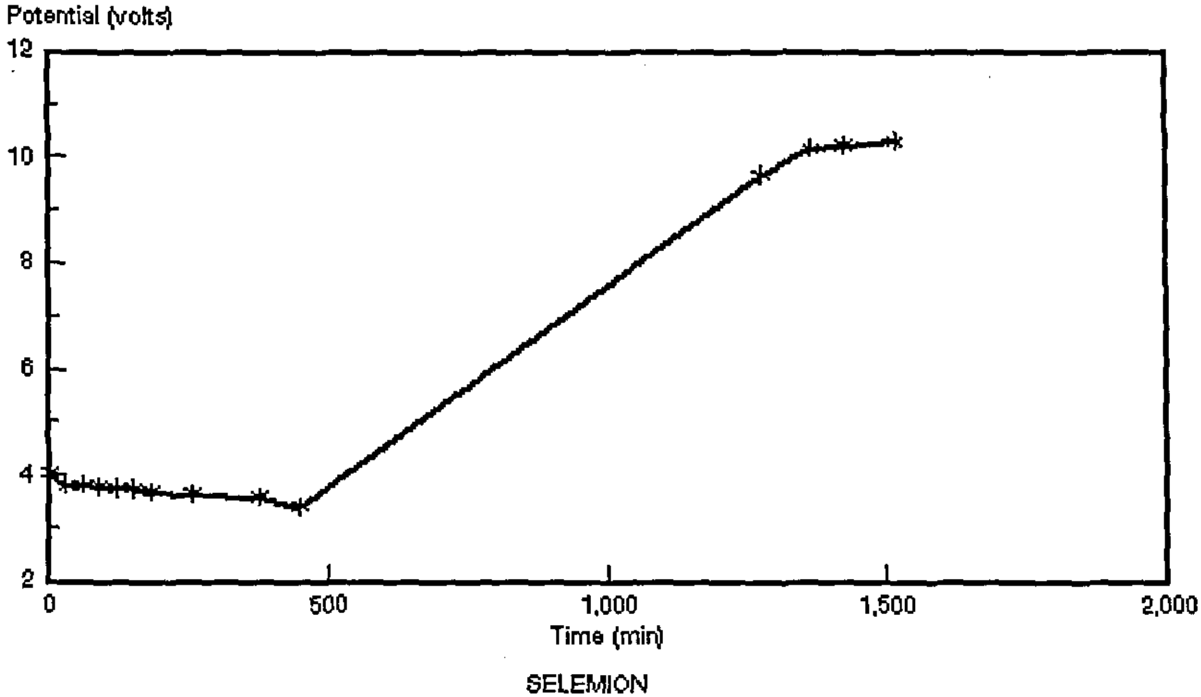

Figure 3.15: **Effect of preflocculation of humic acid feed with ferric chloride on membrane fouling using Selemion AMV membranes (100 mg/ℓ HA; CD 20 mA/cm^2).**

3.2.8 Effect of ultrafiltration pretreatment, polarity reversal and caustic soda rinse on membrane fouling

The effect of ultrafiltration (UF) pretreatment, polarity reversal and caustic soda rinse on membrane fouling using Selemion AMV membranes, is shown in Figure 3.16.

The COD of the humic acid solution (100 mg/ℓ) before and after UF pretreatment was 560 and 400 mg/ℓ, respectively. Polysulphone UF membranes with a molecular mass cut-off of approximately 40 000 were used. Only partial removal of the humic acid was obtained and rapid fouling of the Selemion AMV membrane took place (Fig. 3.16). A lower molecular mass cut-off UF membrane may give better results.

Polarity reversal and a caustic soda rinse decreased the membrane potential but it was not possible to decrease the membrane potential to its initial value. Therefore, it appeared that irreversible fouling had taken place.

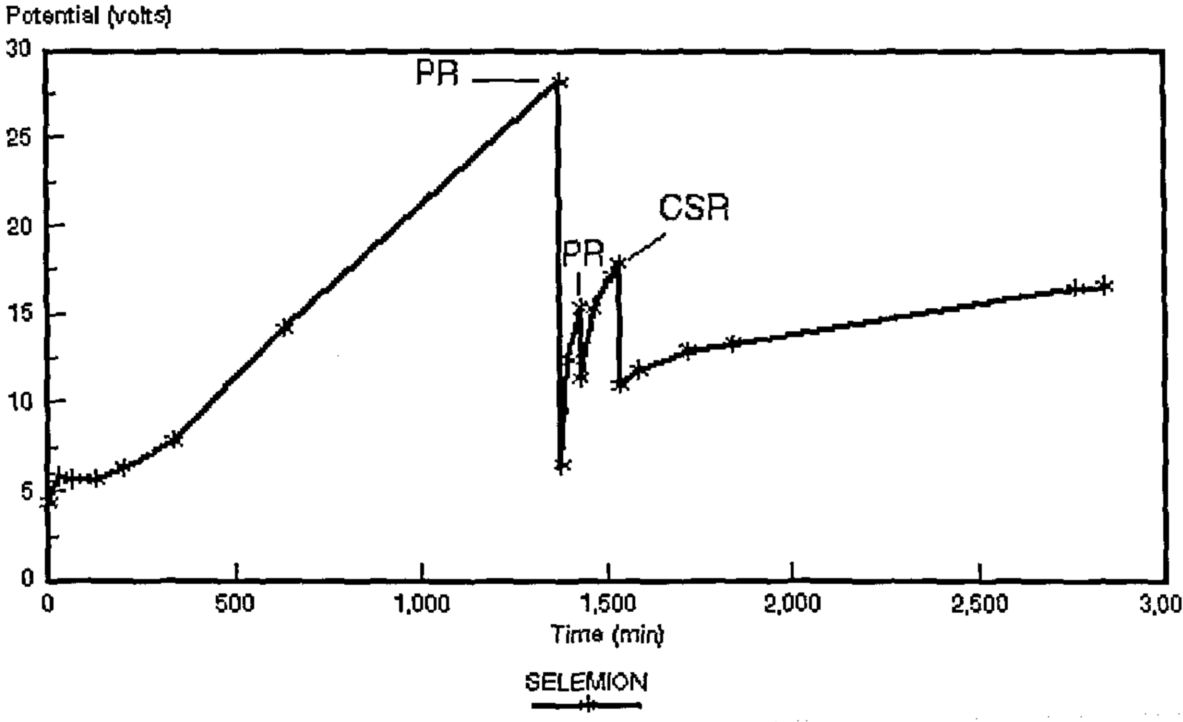

Figure 3.16: **Effect of ultrafiltration pretreatment, polarity reversal and caustic soda rinse on membrane fouling (100 mg/ℓ HA; 3 000 mg/ℓ NaCl; CD 20 mA/cm^2; Selemion AMV membrane). PR: polarity reversal; CSR: caustic soda rinse (0,1 mol/ℓ; 15 min).**

3.3 *Effect of Organics Extracted from Fouled Eskom Membranes on Membrane Fouling*

Cooling tower blow-down is treated at Tutuka Power Station at Eskom with EDR for water recovery and effluent volume reduction. An Ionics EDR stack and membranes are used. A steady increase in product water conductivity was experienced over the last two years, most probably as a result of membrane fouling caused by some of the constituents in the cooling tower blow-down. The feed water to the EDR unit contains biocides and organic matter of natural origin. These compounds may be responsible for the membrane fouling that is experienced with the EDR membranes. Consequently, the fouling potential of these two types of compounds for Ionics membranes was evaluated in the fouling cell.

Organics were extracted from fouled anion-exchange membranes obtained from Eskom with 0,1 mol/ℓ caustic soda solution and fouling tests were conducted by dissolving the extract (0,1 mol/ℓ NaOH) in Pretoria tap water spiked with 3 000 mg/ℓ sodium chloride solution (pH adjusted to approximately 7 with HCl). An attempt was also made to identify the organics extracted from the membranes and to examine the surface characteristics of the fouled membranes. The fouling potential of a few biocides commonly used in cooling tower water, was also evaluated for the membranes used at Eskom.

3.3.1 Effect of organics extracted from fouled membranes on membrane fouling

The effect of organics extracted from fouled membranes obtained from Eskom on membrane fouling, is shown in Figure 3.17. The COD of the feed solution was 370 mg/ℓ. Membrane fouling slowly occurred as could be seen from the increase in membrane potential that was experienced. Polarity reversal decreased membrane potential significantly. However, membrane potential could not be restored to its initial value, nor could caustic soda cleaning decrease the membrane potential significantly. Consequently, it appeared that irreversible membrane fouling had occurred with the Selemion AMV membrane.

A brown precipitate had formed on the surface of the anion-exchange membrane. This precipitate could be removed easily with mechanical cleaning of the membrane surface. Membrane resistances of the unused and used membranes after equilibration in 0,5 mol/ℓ sodium chloride solution were 0,5 and 5,1 ohm·cm^2, respectively. This showed that membrane fouling had taken place.

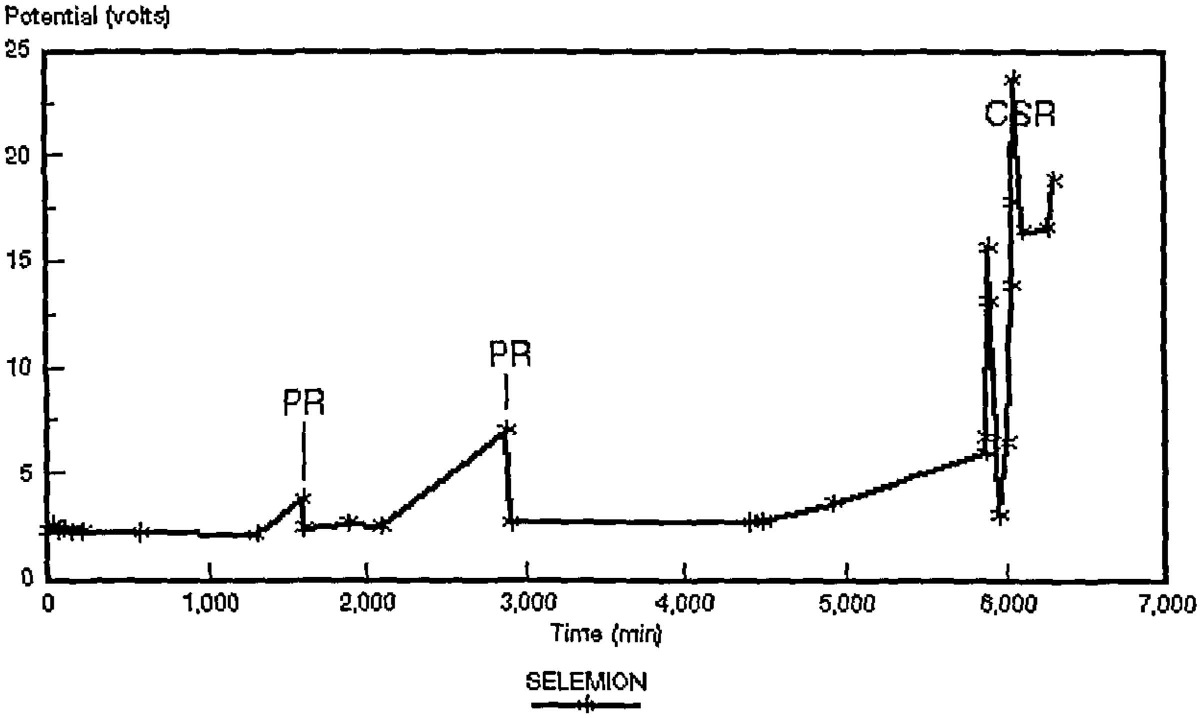

Figure 3.17: **Effect of organics extracted from fouled membranes on membrane fouling (3 000 mg/ℓ NaCl; CD 20 mA/cm^2; Selemion AMV membrane).**

3.3.2 Identification of organics extracted from fouled membranes

Capillary gas chromatography (CGC) and high pressure liquid chromatography (HPLC) analysis were conducted on a synthetic humic acid solution and on the organics extracted from the fouled membranes. Gas chromatography chromatograms have indicated that "*fingerprinting*" was not possible. However, HPLC chromatograms (Figs. 3.18 and 3.19) have shown that humic acid is present in the organic fraction that was removed from the fouled membranes. Consequently, humic acids in the cooling tower blow-down water are most probably responsible for the membrane fouling that is experienced with the EDR membranes at Tutuka Power Station. A relatively low molecular mass compound was also detected in the HPLC chromatogram (first peak, Fig. 3.18). This compound may also play a role in the membrane fouling that is experienced and needs to be identified.

Scanning electron micrographs (SEM) were taken of fouled and unfouled membranes. No differences, however, could be detected in the micrographs and further work may be required in this regard.

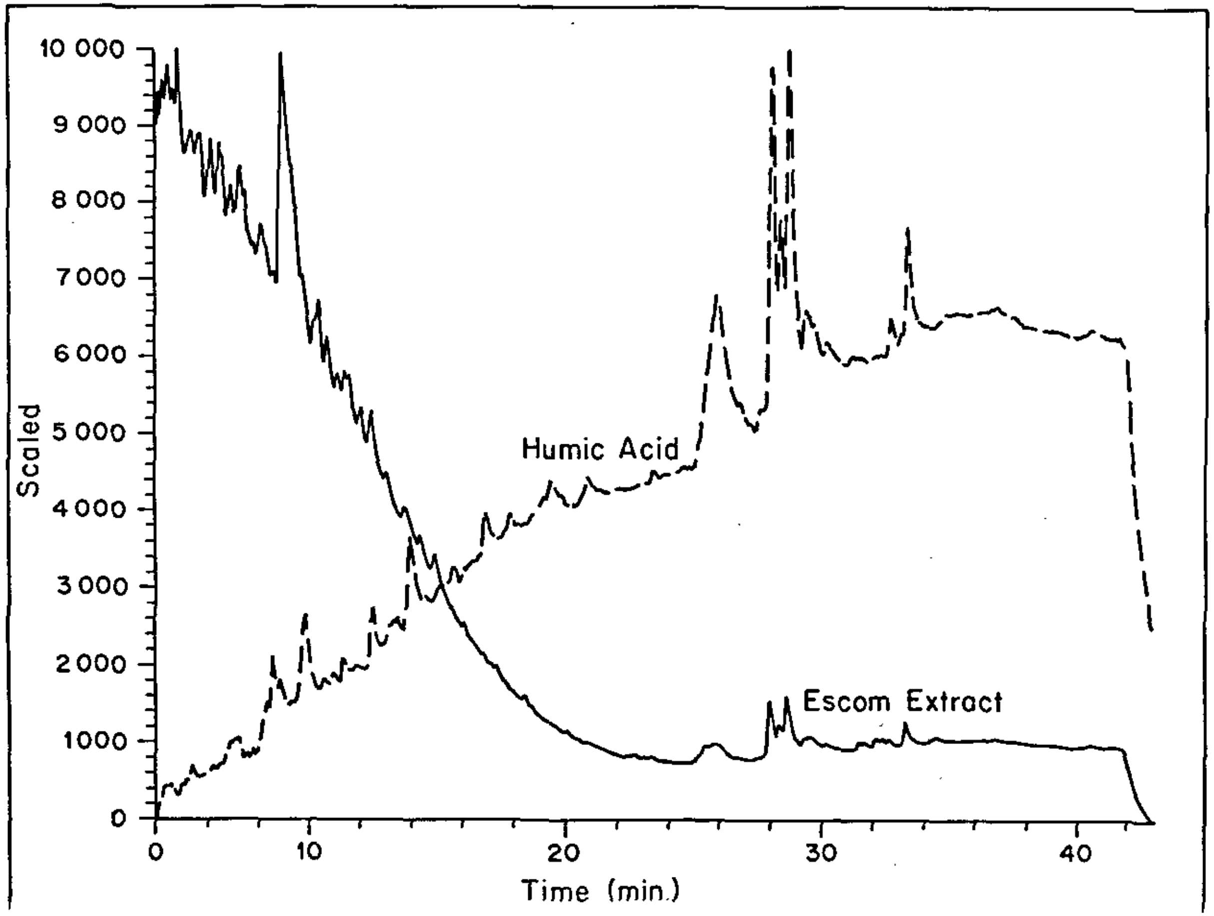

Figure 3.18: HPLC chromatogram of humic acid solution and of organics extracted from fouled membranes.

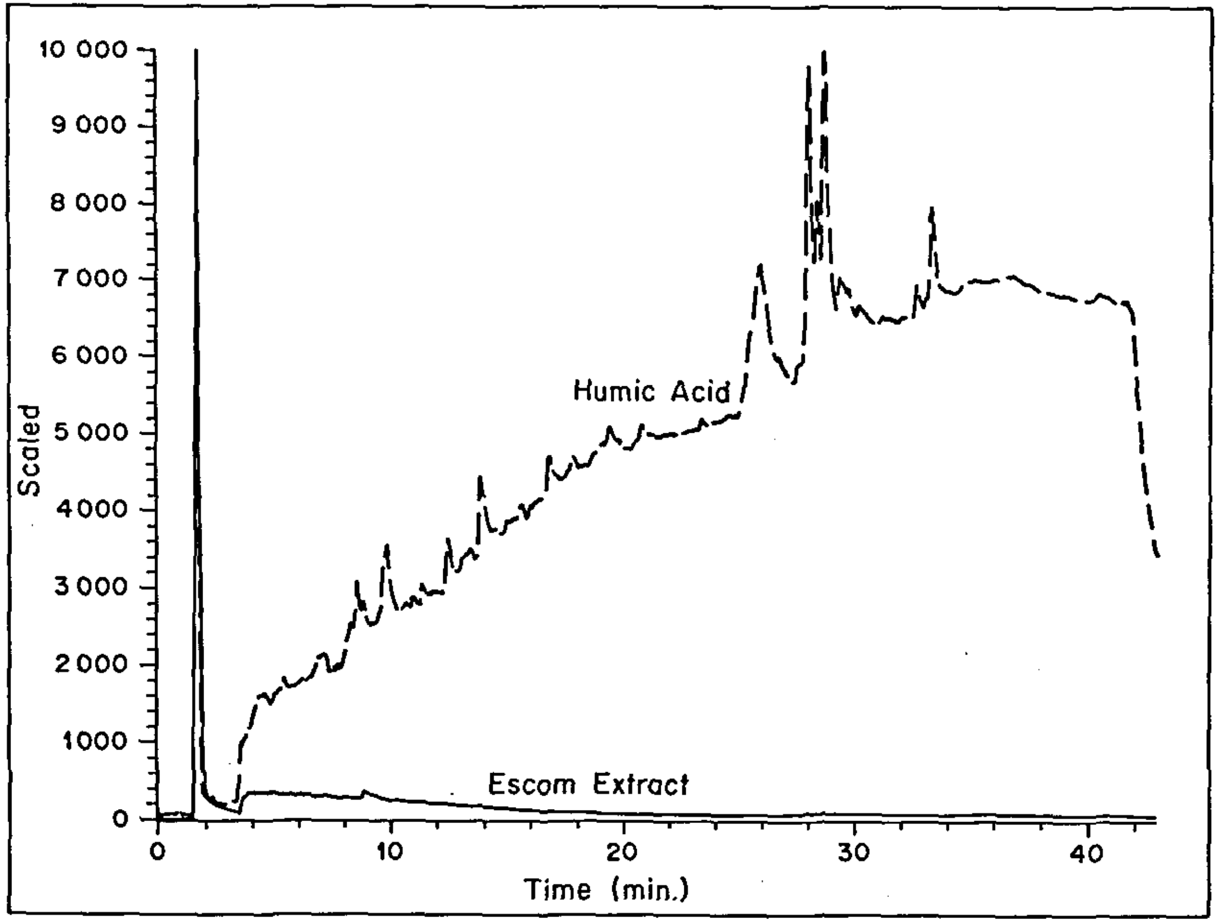

Figure 3.19: HPLC chromatogram of humic acid solution and of organics extracted from fouled membranes.

3.3.3 Effect of biocides on membrane fouling

Limited work was conducted in a previous study(6) on the effect of biocides, used in cooling tower blow-down, on membrane fouling. The fouling potential of Belclene 350 and Kathon WT 500 for Ionics cation-exchange membranes was determined. The fouling potential of Synperonic NP6 for Ionics anion-exchange membranes was also determined. It was found that Belclene 350 had the potential to foul Ionics cation-exchange membranes. However, no membrane fouling of the anion-exchange membrane could be detected.

3.4 Effect of Spent Plating Bath Water, Rinse Waters and Additives Added to the Plating Bath, on Membrane Fouling

3.4.1 Effect of spent plating bath water on membrane fouling

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 3.20. The Selemion AMV membrane was fouled with the spent plating solution. However, the Ionics and Ionac membranes showed no 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.

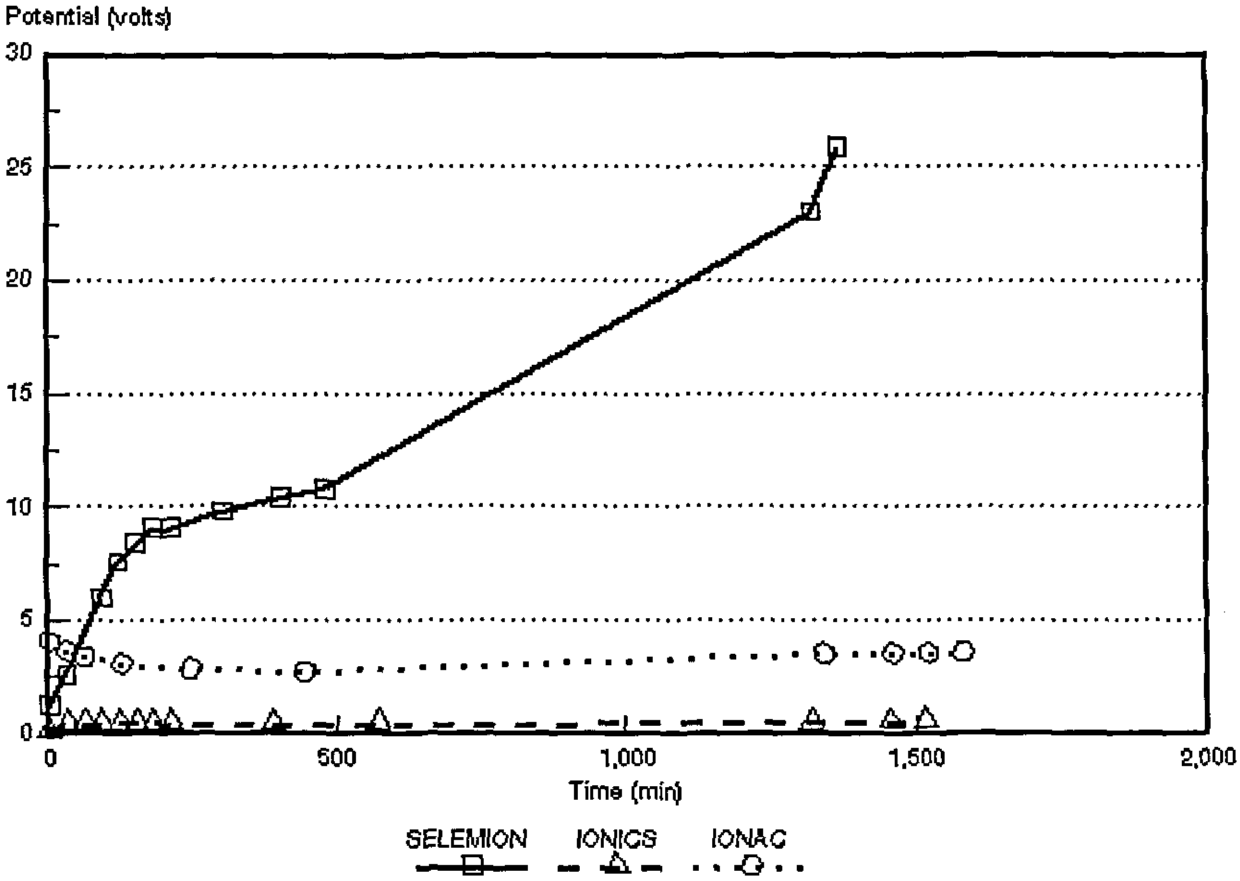

Figure 3.20: **Effect of spent nickel plating bath water on membrane fouling using Selemion, Ionics and Ionac membranes (CD 20 mA/cm^2; Conductivity of feed 5 300 mS/m; COD of feed 59 000 mg/ℓ).**

Membrane resistance before and after fouling is shown in Table 3.7.

Table 3.7: ***Membrane resistances before and after fouling with spent nickel plating bath water using different ion-exchange membranes.***

Membrane[1]	**Resistance (ohm·cm^2)**	
	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/cm^3.

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

3.4.2 The effect of nickel rinse water on membrane fouling

The effect of nickel rinse water on membrane fouling using Selemion AMV, Ionics A-204-UZL and Ionac MA-3475 membranes, is shown in Figure 3.21. The nickel rinse water as received from the plating shop had a pH of approximately 2 and a conductivity of 839 mS/m. It appeared that little membrane fouling took place with the Selemion AMV membrane at this pH level (Fig. 3.21). The pH of the nickel rinse water was then adjusted to a pH of approximately 7 prior to fouling because the Selemion membranes were more stable at this pH level. However, severe membrane fouling was experienced at this elevated pH level. Little membrane fouling, on the other hand, took place with the Ionac and Ionics membranes (also elevated pH). Ultrafiltration of the nickel rinse water (elevated pH) had almost no effect in preventing membrane fouling from taking place. The iron concentration of the nickel rinse water was reduced from 5,7 before UF to 0,4 mg/ℓ after UF treatment. The COD of the feed water was reduced from 2 740 mg/ℓ (before UF) to 2 070 mg/ℓ (after UF). Despite this, serious membrane fouling was still taking place and pretreatment could be required prior to ED treatment of nickel rinse water. Activated carbon or resin should be able to reduce the foulants to low levels. This matter, however, needs further investigation.

Membrane resistances before and after fouling, are shown in Table 3.8.

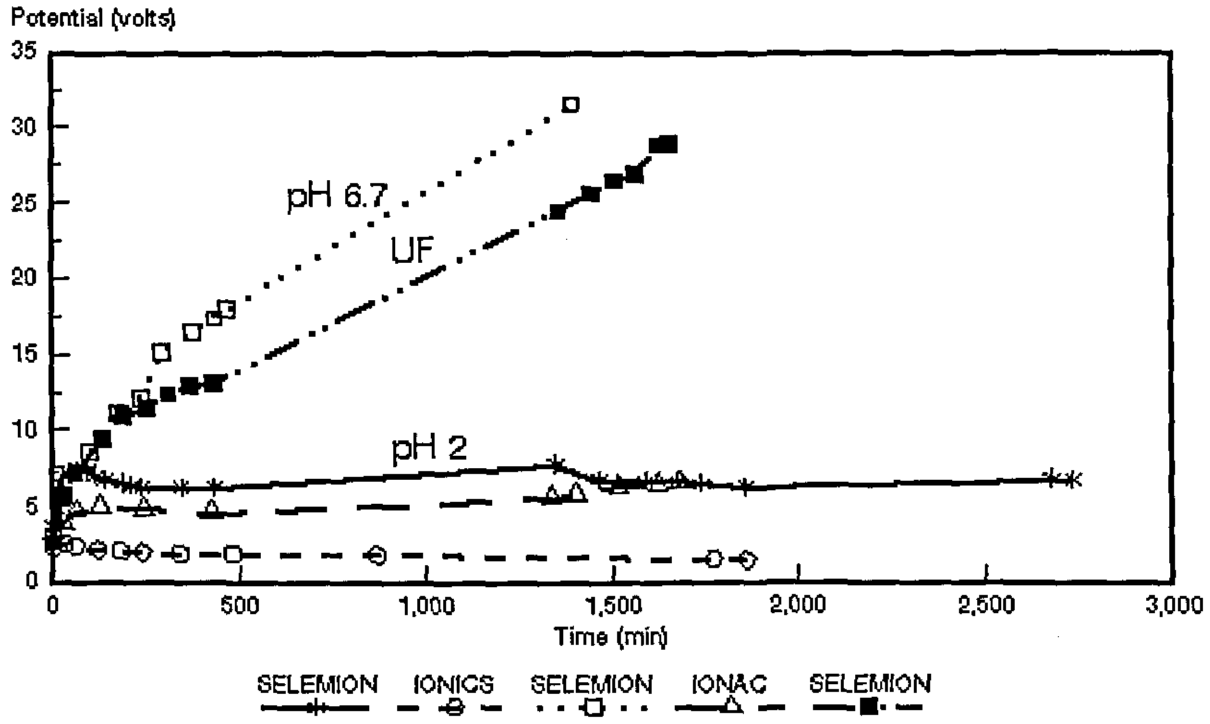

Figure 3.21: **Effect of nickel rinse water on membrane fouling using Selemion, Ionics and Ionac membranes (CD 20 mA/cm^2).**

Table 3.8: **Membrane resistances before and after fouling with nickel rinse water using different ion-exchange membranes.**

Membrane(1)	Resistance (ohm·cm^2)	
	Unused	Used
Selemion AMV (pH 2)	2,5* 0,5**	27,4* 25,4**
Ionics A-204-UZL (pH 7)	7,6* 4,1**	17,3* 7,6**
Selemion AMV (pH 7)	3,0* 1,0**	424* 37,8**
Ionac MA-3475 (pH 7)	12,2* 7,1**	236* 16,2**
Selemion AMV (pH 7; UF)	3,0* 1,5**	312* 17,2**

* 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/cm^2.

Membrane fouling was more severe in the case of the Selemion membranes. Membrane fouling, however, was experienced with the Ionics and Ionac membranes according to the membrane resistance values. A light precipitate had formed on the anionic membranes in all the cases. The precipitate could be nickel hydroxide. Nickel salts hydrolyze at relatively low pH to form nickel hydroxide. This can happen under polarizing conditions when the current density is too high. Nickel hydroxide fouling, however, should be countered by working at a lower current density. It should also be possible to clean the membranes with a dilute hydrochloric acid solution.

3.4.3 The effect of additives added to the plating bath on membrane fouling

A variety of additives are usually added to a plating bath to improve the quality of plating. These additives are usually proprietary chemicals. The additives are in most cases organic compounds and therefore have the potential to foul ion-exchange membranes. Consequently, the fouling potential was evaluated of additives used in a typical nickel plating bath.

The following additives are used in a typical nickel plating bath:

a) 612A wetting agent (5 mℓ/ℓ);
b) 660G (1,75 mℓ/ℓ);
c) nickel leveller 41 (10 mℓ/ℓ);
d) 63 agent (9,5 mℓ/ℓ).

The fouling potential of the above plating bath additives for Selemion AMV membranes, is shown in Figure 3.22. It appears that all the additives used in the nickel plating bath will cause membrane fouling when Selemion AMV membranes are used. Therefore, the foulants should be removed by proper pretreatment prior to ED of nickel plating solutions (Note: a precipitate had formed on the anion-exchange membrane). Activated carbon may remove the foulants effectively. However, this matter needs further investigation.

Membrane resistances before and after fouling is shown in Table 3.9.

Table 3.9: **Membrane resistances before and after fouling with additives used in nickel plating baths.**

Membrane	Additive	Resistance (ohm·cm^2)*	
		Unused	Used
Selemion AMV	612 A	0,51	6,6
	660 G	0,51	5,1
	63	0,51	20,3
	Ni Leveller 41	0,51	4,1

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

The membrane resistance values also showed that membrane fouling was experienced. It appears that additive 63 caused the most serious fouling.

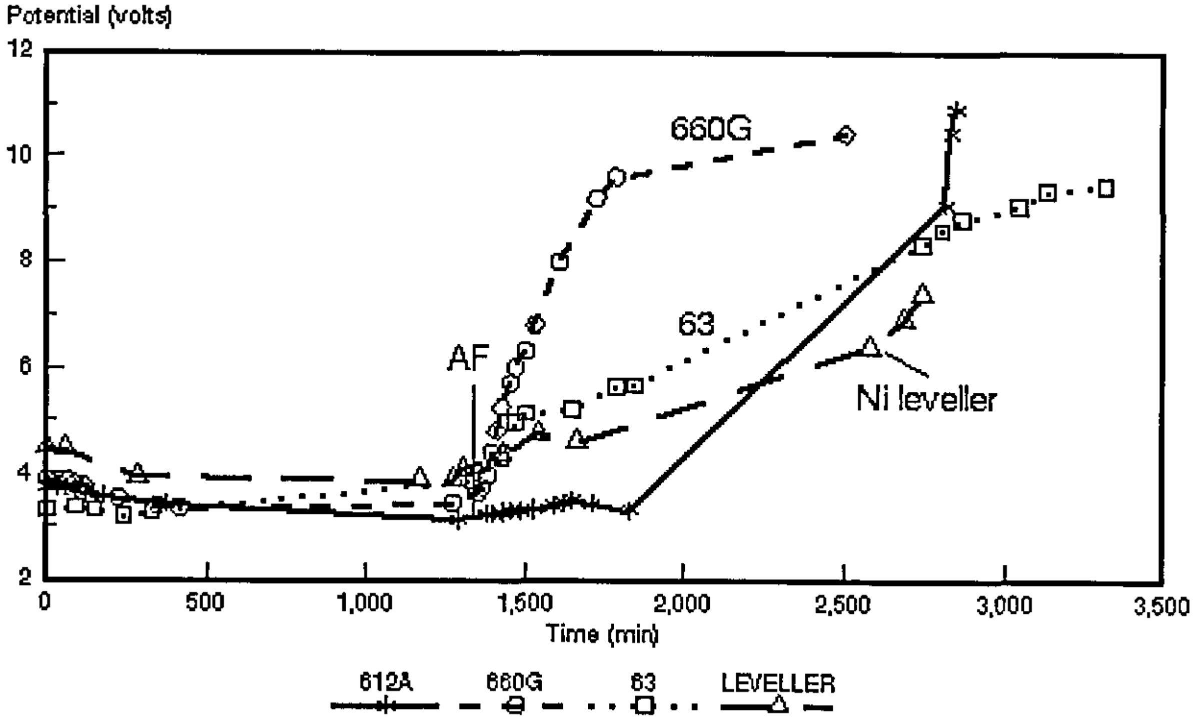

Figure 3.22: **Effect of different additives added in nickel plating bath on membrane fouling (Pretoria tap water; 3 000 mg/ℓ NaCl; CD 20 mA/cm^2; Selemion AMV membrane).**

3.4.4 The effect of cadmium rinse water on membrane fouling

The effect of cadmium rinse water on membrane fouling using Selemion AMV, Ionics A-204-UZL and Ionac MA-3475 membranes, is shown in Figure 3.23. The cadmium rinse water (cadmium cyanide) had a COD of approximately 1 000 mg/ℓ and a pH of 11. Severe membrane fouling was experienced with the Selemion and Ionac membranes (CD 20 mA/cm^2). However, almost no membrane fouling was experienced with the Ionics membranes. Less fouling was also experienced with the Selemion AMV membranes at a current density of 10 mA/cm^2. A precipitate had formed on the surface of the anion-exchange membrane in all cases where membrane fouling was encountered. Consequently, cadmium rinse water should be pretreated prior to ED treatment to remove the foulants. Activated carbon may be suitable for removing the foulants from solution. This matter, however, needs further investigation.

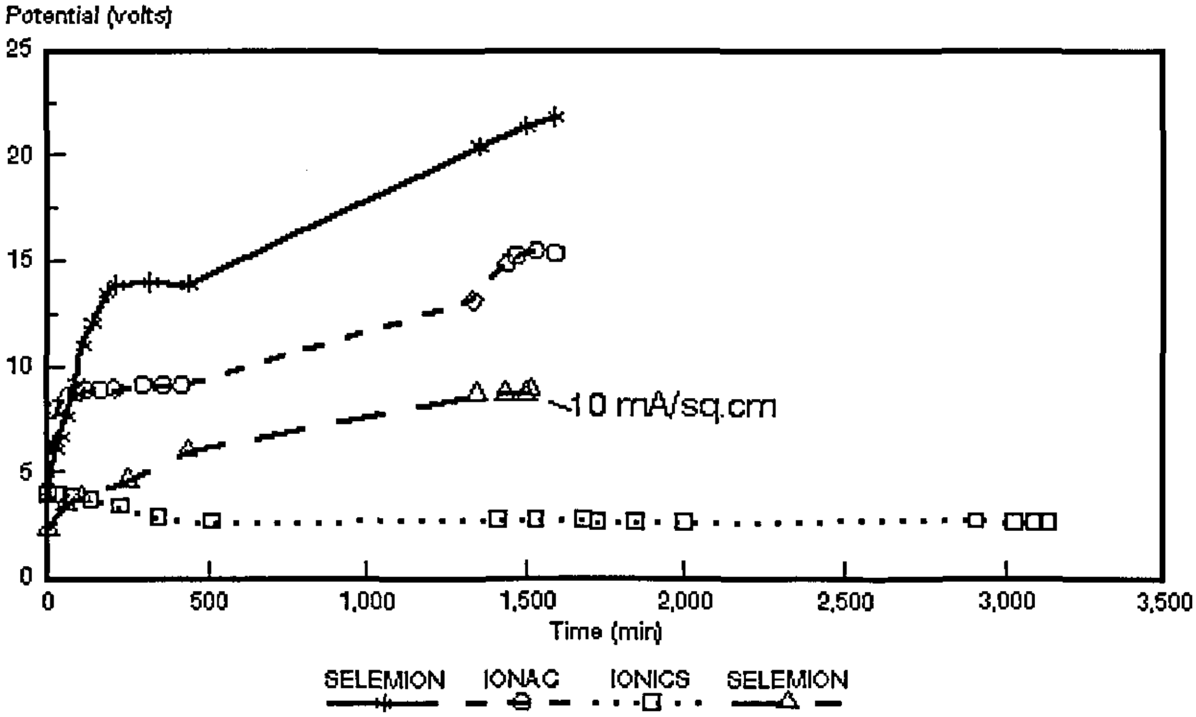

Figure 3.23: **Effect of cadmium rinse water on membrane fouling using Selemion, Ionac and Ionics membranes (Conductivity of rinse water 765 mS/m; CD 20 mA/cm^2).**

Membrane resistances before and after fouling with cadmium rinse water is shown in Table 3.10.

Table 3.10: Membrane resistances before and after fouling with cadmium rinse water.

Membrane	Resistance* (ohm·cm^2)	
	Unused	Used
Selemion AMV (20 mA/cm^2)	0,51	51,3
Selemion AMV (10 mA/cm^2)	0,51	15,8
Ionac MA-3475	12,2	28,4
Ionics A-204-UZL	2,5	3,0

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

The membrane resistance data clearly showed that the Ionics membrane was much more resistant towards fouling by cadmium rinse water than the other membranes. Less membrane fouling was also experienced at the lower current density.

3.4.5 The effect of cadmium brightener on membrane fouling

The effect of cadmium brightener on membrane fouling using Selemion AMV, Ionac MA-3475 and Ionics A_204-UZL membranes, is shown in Figure 3.24. The brightener caused fouling of the Selemion AMV membrane at a current density of 20 mA/cm^2. Far less fouling was observed in the case of the Ionac membrane at a current density of 10 mA/cm^2 while almost no fouling was observed with the Ionics membrane at the same current density.

Membrane resistances before and after fouling with the cadmium brightener is shown in Table 3.11.

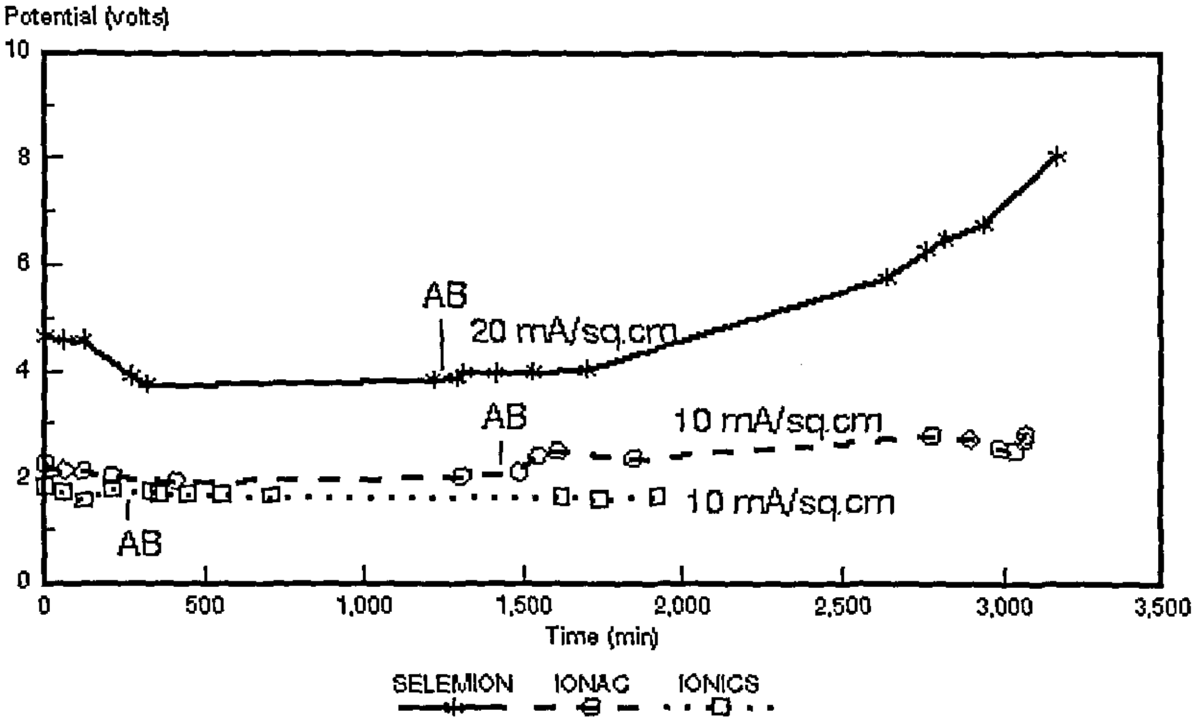

Figure 3.24: **Effect of cadmium brightener on membrane fouling using Selemion, Ionac and Ionics membranes (Pretoria tap water spiked with 3 000 mg/ℓ NaCl and 1,75 mℓ brightener/ℓ; conductivity 562 mS/m). AB: add brightener.**

Table 3.11: **Membrane resistances before and after fouling with cadmium brightener.**

Membrane	Resistance* (ohm·cm^2)	
	Unused	Used
Selemion AMV	0,51	11,2
Ionac MA-3475	10,2	10,2
Ionics A-204-UZL	5,6	6,1

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

Membrane resistance showed that the Selemion AMV membrane was fouled by the brightener at a current density of 20 mA/cm^2. However, the Ionac and Ionics membranes were not affected at a current density of 10 mA/cm^2.

3.4.6 Effect of chromium rinse water on membrane fouling using Ionac MA-3475 membranes

The effect of chromium rinse water on membrane fouling is shown in Figure 3.25. The chrome rinse water fouled the Ionac MA-3475 membranes. Fouling was more severe at the higher current density. The membrane was decolorized after the experiment and was also swollen. Chromium is a strong oxidizing agent and it appeared that the membrane has been attacked by the chromium. The membrane resistance was very high after the fouling experiment showing that the membrane properties had changed. Therefore, more suitable membranes for chromium rinse water treatment by ED should be identified prior to further testing.

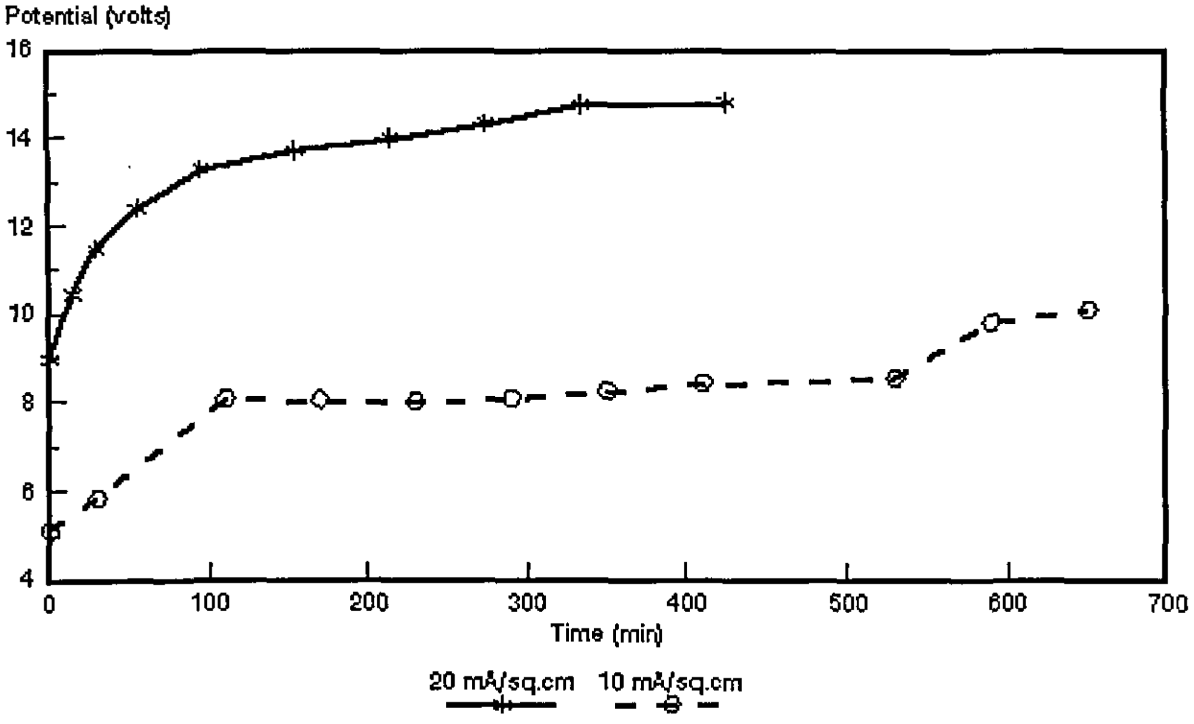

Figure 3.25: Effect of chromium rinse water on membrane fouling using Ionac membranes (Conductivity 710 mS/m; pH 2,4; CD 20 mA/cm^2).

3.5 General Discussion

The ion-exchange membrane fouling tests that have been conducted in this study are accelerated fouling tests. The membranes were exposed to much higher concentrations of foulants than would normally take place in practise. However, it should be possible to predict the fouling behaviour of ion-exchange membranes with this method when the membranes are exposed to low concentrations of foulants for a long period , as is happening under practical ED conditions.

The most common ion-exchange membrane foulant encountered in surface waters in South Africa, is humic acid. Humic acid results from the natural decay of organic matter present in surface waters. Humic acids have the potential to foul anion-exchange membranes. Fouling of anion-exchange membranes in ED can affect the economics of the ED process adversely because it shortens membrane life time and it increases the electrical energy consumption of the ED process. It can also affect the quality of the ED product water that is produced, adversely. This is what is happening with the ED process at Tutuka Power Station.

It should be possible to control humic acid fouling of ion-exchange membrane by suitable pretreatment of the feed water to an ED stack and/or by polarity reversal and chemical cleaning of the membranes. Low concentrations of humic acids should be effectively removed from water with ferric chloride coagulation - flocculation or with chlorination(7) prior to ED treatment. It should also be possible to control humic acid fouling of ion-exchange membranes with polarity reversal and chemical cleaning of the membranes with dilute caustic soda solution. The shorter the polarity reversal frequency and the more often the membranes are rinsed with a dilute caustic soda solution, the better are the results expected to be.

It may also be possible to control humic acid fouling of ion-exchange membranes with ultraviolet light oxidation, activated carbon and resin adsorption and by UF treatment. However, more work should be conducted to evaluate the effectiveness of these methods to remove humic acid from water. Preliminary studies had indicated that a UF membrane with a molecular mass cut-off of approximately 40 000 Dalton was not very effective for the removal of humic acid from water. However, UF membranes are available with much lower molecular mass cut-off values (< 10 000 Dalton) and these membranes may have a much better chance to remove humic acid effectively from water. Ultraviolet irridation equipment is also now readily available for water sterilization and possibly for the effective control of humic acid fouling of ion-exchange membranes. Ultraviolet treatment of humic acids in water may result in the fragmentation of the complex humic acid molecule into smaller units which may not be able to foul anion-exchange membranes. This matter and the removal of humic acid by activated carbon and ion-exchange resins, however, warrant further investigation.

Industrial effluents can contain a wide variety of organics that have the potential to foul ion-exchange membranes. The most common ion-exchange membrane foulants encountered in industrial effluents are detergents (DBS), dyes, certain hydrocarbons, phenolic compounds, organic additives added to plating baths, etc(7, 8). However, it may be possible to control fouling of ion-exchange membranes by these compounds by pretreatment with activated carbon and resins. Polarity reversal and periodic salt/caustic cleaning of the membranes should also be capable of controlling such fouling by these compounds. The fouling potential of an effluent, however, should always first be determined in a fouling cell as described in this study, prior to ED treatment, so that the correct pretreatment can be specified for a particular application.

Inorganic fouling of ion-exchange membranes is caused by the precipitation (scaling) of slightly soluble inorganic compounds (such as $CaSO_4$ and $CaCO_3$) in the brine compartments and the fixation of multivalent cations (such as Fe and Mn) on the cation-permeable membranes. Organic anions or multivalent cations can neutralize or even reverse the fixed charge of the membranes, with a significant reduction in efficiency. Fouling also causes an increase in membrane stack resistance which, in turn, increases electrical consumption and adversely effects the economics of the process.

The following constituents are also, to a greater or lesser extent, responsible for membrane fouling in ED(9):

a) Traces of heavy metals such as Fe, Mn and Cu;
b) dissolved gases such as O_2, CO_2 and H_2S;
c) silica in diverse polymeric and chemical forms;
d) inorganic colloids;
e) fine particulates of a wide range of sizes and composition;
f) alkaline earths such as Cu, Ba and Sr;
g) biological materials - viruses, fungi, algae, bacteria - all in varying stages of reproduction and life cycles.

Suspended and colloidal matter, bacteria, fungi, algae, etc., can penetrate the small water passages in an ED stack to affect the water flow through the stack adversely and to foul the membrane surfaces. These substances, however, can normally be easily removed from water with coagulation/flocculation and/or with microfiltration. Barium and strontium present in low concentrations in water can foul ion-exchange membranes because barium and strontium sulphates are sparsely soluble in water. Membrane fouling, however, of these compounds can usually be controlled by ion-exchange pretreatment of the feed water or by polarity reversal. Heavy metals like iron, manganese and copper and hydrogen sulphide can also foul ion-exchange membranes. Membrane fouling by these compounds are usually controlled by oxidation, aeration, pH adjustment and filtration prior to ED treatment. The development of the EDR process has helped to solve the pretreatment problem more readily in that it provides self-cleaning of the vital membrane surfaces as an integral part of the desalting process.

4. CONCLUSIONS

- Membrane fouling by DBS (detergent) increased with increasing current density, increasing DBS concentration and decreased at higher feed salinity levels (2 000 to 5 000 mg/ℓ). Ionics A-204-UZL-386 anion-exchange membranes appear to be much more resistant to DBS fouling than has been the case with Selemion AMV and Ionac MA-3475 membranes. It also appears that membranes fouled with DBS should be partly defouled with a sodium chloride solution. However, it may be very difficult to clean membranes fouled with DBS because the DBS molecule can penetrate the membrane pores. Consequently, it may be better to remove DBS by activated carbon or resin prior to ED treatment. This matter, however, needs further investigation.

- Membrane fouling by humic acid also increased with increasing current density. Ionics A-204-UZL-386 membranes are much more resistant to humic acid fouling than has been the case with the Selemion AMV and Ionac MA-3475 membranes. Polarity reversal and mechanical cleaning of the membrane surface help to control fouling. Caustic soda rinse of the membranes showed that humic acid fouling could be controlled by regular caustic soda rinses. Increased feed flow rate decreased membrane fouling. It took much longer for membrane fouling to take place at a flow rate of 1 600 mℓ/min than at a flow rate of 600 mℓ/min. Consequently, it will be advantageous to use the highest possible flow rate in an ED stack to inhibit membrane fouling. This matter also warrents further investigation under practical ED conditions in an ED membrane stack.

- Ferric chloride coagulation/flocculation of humic acid solution retarded membrane fouling. Consequently, it will be advantageous to remove humic acid from water supplies with ferric chloride and filtration prior to ED treatment.

- Ultrafiltration (40 000 cut-off membranes) has very little effect to prevent membrane fouling by humic acids. Lower molecular mass cut-off membranes (8 000 Dalton) should be evaluated for this purpose.

- Organics extracted from ion-exchange membranes used at Tutuka Power Station can foul ion-exchange membranes. However, it should be possible to control membrane fouling by these organics with polarity reversal and caustic soda cleanings of the membranes. The frequency of polarity reversal should be as short as possible. Cleaning of the membranes with dilute caustic solution should be performed regularly.

- Humic acid is present in the organics extracted from the membranes used at Tutuka Power Station. Consequently, humic acid is responsible for the membrane fouling that is experienced at the Power Station. A relatively low molecular mass compound was also detected in the extracted organics that could play a role in the membrane fouling that was encountered. This compound should be identified and its fouling potential should be evaluated for ion-exchange membranes.

- No difference could be detected in the scanning electron micrographs (SEM) of fouled and unfouled ion-exchange membranes. Further work will be required in this regard.

- Certain biocides can foul cation-exchange membranes. Belclene 350, fouled cation-exchange membranes. This compound has a fixed positive charge. No membrane fouling of the anion-exchange membranes could be detected with the biocide Synperonic NP6. This biocide has a fixed negative charge. The fouling potential of more biocides for ion-exchange membranes should be investigated.

- Spent nickel plating effluent has the potential to foul Selemion AMV membranes. Ionics A-204-UZL-386 and Ionac MA-3475 membranes showed far less fouling than has been the case with the Selemion AMV membranes. Consequently, it will be necessary to pretreat nickel plating effluent prior to ED treatment.

- Nickel plating rinse water has the potential to foul Selemion AMV membranes. However, little fouling took place with Ionac MA-3475 and Ionics A-204-UZL-386 membranes.

Activated carbon treatment of nickel rinse water has the potential to control membrane fouling. This matter, however, needs further investigation.

- Additives added to the nickel plating bath to improve the quality of plating have the potential to foul Selemion AMV membranes. Therefore, these additives should be removed prior to ED treatment. This may be accomplished with activated carbon or resin treatment of the effluent. This matter, however, also needs further investigation.

- Cadmium plating rinse water has the potential to foul Selemion AMV and Ionac MA-3475 membranes. However, almost no membrane fouling was experienced with the Ionics A-204-UZL-386 membranes. Consequently, cadmium plating rinse water should be pretreated prior to ED treatment. This may also be accomplished with activated carbon and/or resin treatment. This matter also needs further investigation.

- Cadmium brightener can foul Selemion AMV membranes. Therefore, the brightener used in the plating process should be removed prior to ED treatment. This may also be accomplished with activated carbon and/or resin adsorption. This matter also needs further investigation.

- Conventional ion-exchange membranes are not suitable for treatment of chromium plating rinse water because the membranes are oxidized by chromium. Therefore, specially designed ion-exchange membranes should be used for chromium rinse water treatment.

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AN INVESTIGATION INTO THE ORGANIC FOULING OF ION-EXCHANGE MEMBRANES

(Contract between the Division of Water Technology
and the Water Research Commission)

by

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WRC Project No. 396

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AN INVESTIGATION INTO THE ORGANIC FOULING OF ION-EXCHANGE MEMBRANES

EXECUTIVE SUMMARY

It is anticipated that, in future, electrodialysis (ED) will be used to a far greater extent than at present in South Africa for the treatment of industrial effluents; for the recovery of water or chemicals for reuse or for a reduction in the effluent volume. Industrial effluents usually contain a wide range of organic materials, some of which have the potential to foul ion-exchange membranes and hence may lead to the failure of the ED process. The organic fouling of ion-exchange membranes was, therefore, investigated to obtain a better understanding of the membrane fouling process.

The main objectives of the study were the following:

- To select industrial effluents which may be treated to good effect with ED.
- To investigate the fouling characteristics of selected foulants which affect membranes.
- To determine cleaning methods for fouled membranes.
- To identify methods for the pretreatment of membranes to prevent or minimize organic fouling.
- To study the surface characteristics of fouled membranes.

An earlier literature study has shown that fouling of ion-exchange membranes depends on the concentration of foulant in the feedwater, the pH of the feed solution, the linear flow velocity of the feed solution through an ED stack, the current density applied, the frequency of polarity reversal, membrane cleaning methods and pretreatment of the feedwater prior to ED treatment.

The most common ion-exchange membrane foulant found in surface waters in South Africa is humic acid. This acid was found to be present in fouled anion-exchange membranes obtained from Tutuka Power Station (Eskom).

Industrial effluents may contain a wide variety of organic materials which have the potential to foul ion-exchange membranes. The most common ion-exchange membrane foulants encountered in industrial effluents are detergents, dyes, certain hydrocarbons and organic additives added to electroplating baths.

Membrane fouling with humic acid and para-dodecylbenzene sulphonate (DBS, detergent), was found to increase with increasing current density, increasing concentration of foulant in the feedwater and decreasing flow velocity of the feedwater through the fouling cell.

Biocides used for water treatment can cause fouling of ion-exchange membranes. It was found that a biocide with a fixed positive charge caused fouling of a cation-exchange membrane. However, no fouling of anion-exchange membranes could be detected with a limited number of biocides that were tested.

Nickel and cadmium electroplating baths contain organic additives that can foul ion-exchange membranes. Some membranes, however, were found to be more resistant to organic fouling than others. Conventional ion-exchange membranes are not suitable for treatment of chromium rinse water because the membranes are oxidized by chromium. Therefore, specially designed membranes should be used for treatment of chromium rinse waters.

It was possible to control membrane fouling by humic acids through the use of polarity reversal and regular rinses of the membranes with dilute caustic soda solutions. The polarity reversal cycle, however, should be as short as possible. Fouling of ion-exchange membranes by detergents, however, will be more difficult to control because the detergent molecule is small enough to penetrate the pores of the anion-exchange membrane to foul the membrane irreversibly. Fouling of anion-exchange membranes by detergents at low concentrations may be controlled by polarity reversal and regular cleaning of the membranes with salt/caustic soda solutions. It may, however, be preferable to remove the detergents with activated carbon, prior to ED treatment.

It should be possible to remove humic acids effectively from water with coagulation/flocculation with ferric chloride and oxidation with chlorine, prior to ED treatment. Ultraviolet oxidation, ultrafiltration and adsorption technology (carbon and resin) may also be used effectively to remove humic acids and organic materials occurring in sewage effluents from ED feedwaters. It should also be possible to remove detergents from effluents with adsorption technology (activated carbon and resin) prior to ED treatment. These latter two methods, however, warrant further investigation.

No difference could be detected in the scanning electron micrographs of fouled and unfouled ion-exchange membranes.

Most of the objectives, as set out in the original contract, have been achieved in this study.

The report includes the following items of interest for those dealing with ED technology:

- It describes a simple membrane fouling method which may be used to predict the fouling potential of selected foulants and industrial effluents.
- It describes pretreatment methods for ED feedwater to reduce or eliminate membrane fouling.
- It describes membrane cleaning methods that may be used to restore fouled membranes.
- It describes membranes which are more resistant to organic fouling than others.

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

- The membrane fouling cell will be evaluated further to predict the fouling potential of selected foulants and industrial effluents for different ion-exchange membranes.
- Pretreatment of nickel and cadmium electroplating rinse waters will be studied to reduce or eliminate fouling caused by organic additives in the plating rinse waters.
- A publication reflection the main results of the study will be compiled and submitted to a popular journal.

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

- The fouling potential of an effluent should always be evaluated first in a fouling cell, before ED treatment of the effluent is considered.
- The fouling potential of other effluents, such as whey, molasses, etc., likely to be treated with ED should be evaluated in the fouling cell and pretreatment and membrane cleaning methods should be developed, if required.
- Ultraviolet oxidation, ultrafiltration and adsorption technology (carbon and resin) may be applied effectively to remove organic materials from industrial and sewage effluents prior to ED treatment.
- A talk should be given at a local membrane symposium in South Africa (WISA-MTD) to transfer the technology to all parties interested in ED technology.

1. INTRODUCTION

Electrodialysis (ED),using ion-exchange membranes,will be used on a larger scale in future in South Africa for treatment of industrial effluents for water and chemical recovery for reuse and for effluent volume reduction. Industrial effluents usually contain a wide variety of organics in different concentrations. Some of the organics have the potential to foul ion-exchange membranes and this can lead to failure of the ED process.

It has been demonstrated that anion-exchange membranes can be very sensitive towards some organics which have the ability to penetrate and foul the membranes(1). Membrane fouling shortens membrane life and it affects the economics of the ED process adversely. Therefore, techniques and methods should be developed for cleaning of the membranes after fouling has occurred in an attempt to restore membrane performance or to prevent membrane fouling,by suitable pretreatment. The use of ED may be ruled out if the fouling potential of an effluent is too high for the ion-exchange membranes under consideration.

Not enough information is presently available in South Africa regarding the nature of organics that can cause fouling of ion-exchange membranes(2). Information regarding ways and means to clean fouled membranes or to prevent membrane fouling from taking place, is also lacking. Insufficient information is available regarding the type and character of organics occurring in effluents where ED is applied in South Africa and where ED has the potential to be applied(3).

Cooling tower blowdown is treated at Tutuka Power Station at Eskom with EDR for water recovery and effluent volume reduction. Fouling of the anion-exchange membranes is experienced. This fouling reduces plant availability and therefore has an adverse effect on desalination performance of the plant(3). It is suspected that naturally occurring organics in the feed water or biocides used in the process for bacteriological control, is responsible for the membrane fouling. The exact cause of the fouling, however, is unknown and there exists a need to identify the foulants and to investigate membrane cleaning methods to clean the fouled membranes. There is also a need to investigate methods to prevent fouling by suitable pretreatment techniques.

Electrodialysis may be applied in future in South Africa in the electroplating industry for water and chemical recovery from electroplating rinse waters. Plating baths contain organic additives which have the potential to foul ion-exchange membranes(4). Consequently, there is a need to identify these potential foulants so that the fouling potential of the organics for ED membranes can be determined and that methods can be developed to clean the fouled membranes.

Electrodialysis will also be increasingly applied in future in South Africa in the general chemical process industry for concentration/desalination applications. There is a need to identify the fouling potential of these effluents for ED membranes and to develop methods to clean the fouled membranes and to devise pretreatment techniques with which the fouling potential of the effluents can be reduced to acceptable levels.

It is claimed by the manufacturers of ion-exchange membranes that certain membranes have a higher resistance towards organic fouling than others. Consequently, there is a need to identify these membranes and also to evaluate the performance of these membranes when exposed to organic foulants.

The applied current density, linear flow velocity through an ED stack and pH of the feed solution can affect the fouling behaviour of foulants during ED treatment(5). Therefore, there exists a need to examine the effect of these parameters on membrane fouling.

The objectives of this study were therefore to:

a) conduct a literature survey regarding fouling of ion-exchange membranes (separate report);

b) study the membrane fouling behaviour of selected potential foulants and industrial effluents most likely to be treated with ED in South Africa;

c) determine membrane cleaning methods;

d) identify pretreatment methods to prevent or minimize organic fouling of ion-exchange membranes; and

e) study the surface characteristics of fouled membranes.

2. EXPERIMENTAL

2.1 Fouling Cell

Schematic diagrams of the fouling cell that were used are shown in Figures 1 and 2.

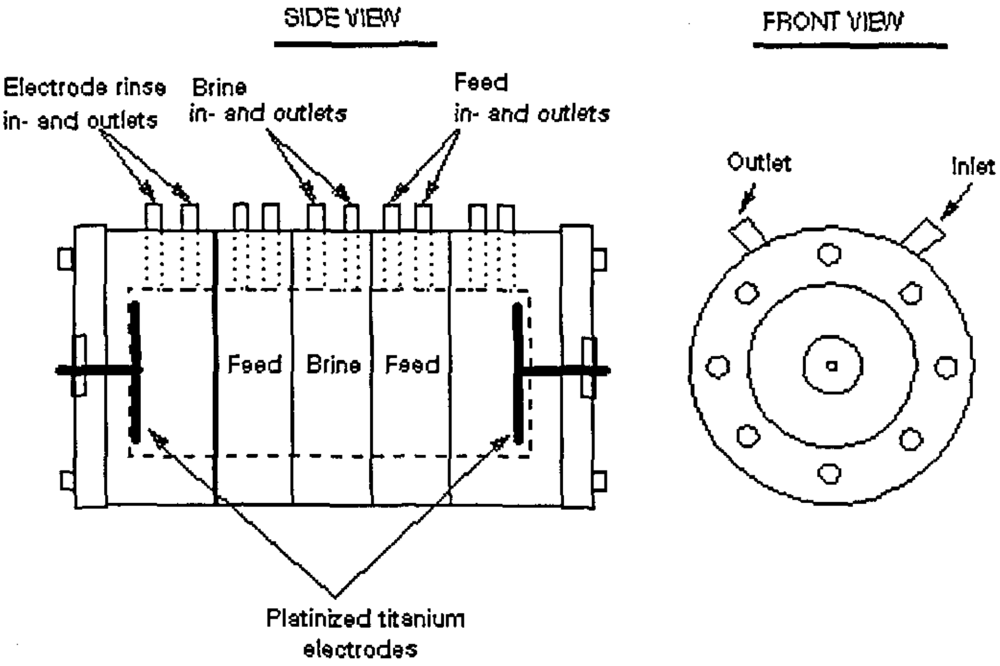

Figure 1: Schematic diagram of fouling cell.

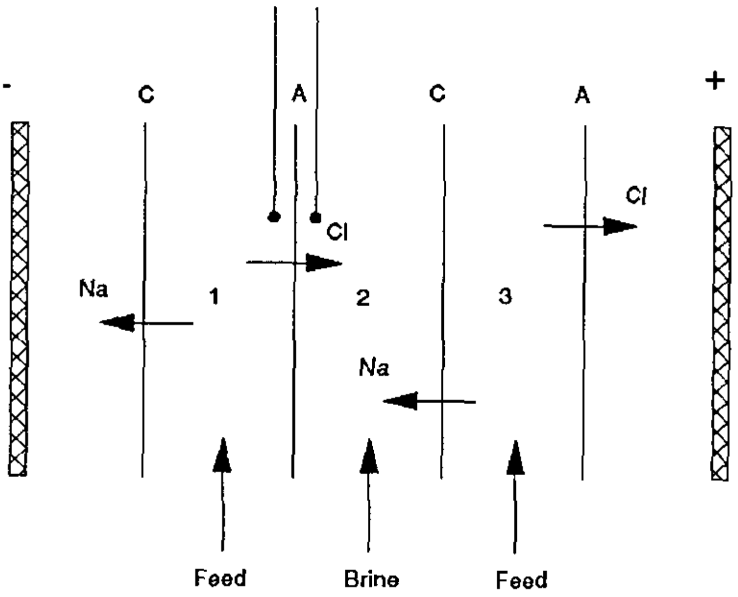

Figure 2: Simplified schematic diagram of fouling cell. C = cationic membrane; A = anionic membrane.

The fouling cell consists of five perspex cells which can be clamped together to hold the membranes (7,1 cm^2 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 ℓ/min and 0,7 ℓ/min were used through the feed and brine compartments, respectively. Pretoria tap water spiked with sodium chloride (2 000, 3 000 or 5 000 mg/ℓ) served as feed water. Para-dodecylbenzene sulphonate (DBS) (a common detergent) and humic acid (HA) were used as foulants in the feed water. DBS is a common foulant that can occur in many effluents and HA is representative of organics that can occur in surface waters as a result of natural decay of organic matter. Electroplating effluents and organic additives used in the plating process were used as potential foulants originating from electroplating processes. 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 consists of a carbon slurry (2%, pH ≈ 5) in 1 mol/ℓ sodium sulphate solution. This solution was circulated through the two electrode compartments.

A DC current density (20; 10 or 5 mA/cm^2) 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 before and after fouling were measured in 0,5 mol/ℓ sodium chloride solution.

3. RESULTS AND DISCUSSION

3.1 Membrane Fouling with p-Dodecyl Benzene Sulphonate (DBS)

3.1.1 Effect of current density and feed water salinity level on fouling of Selemion AMV membranes using 100 mg/ℓ DBS

The effect of current density on membrane fouling using Pretoria tap water as feed spiked with 100 mg/ℓ DBS and 5 000 mg/ℓ sodium chloride, is shown in Figure 3.1

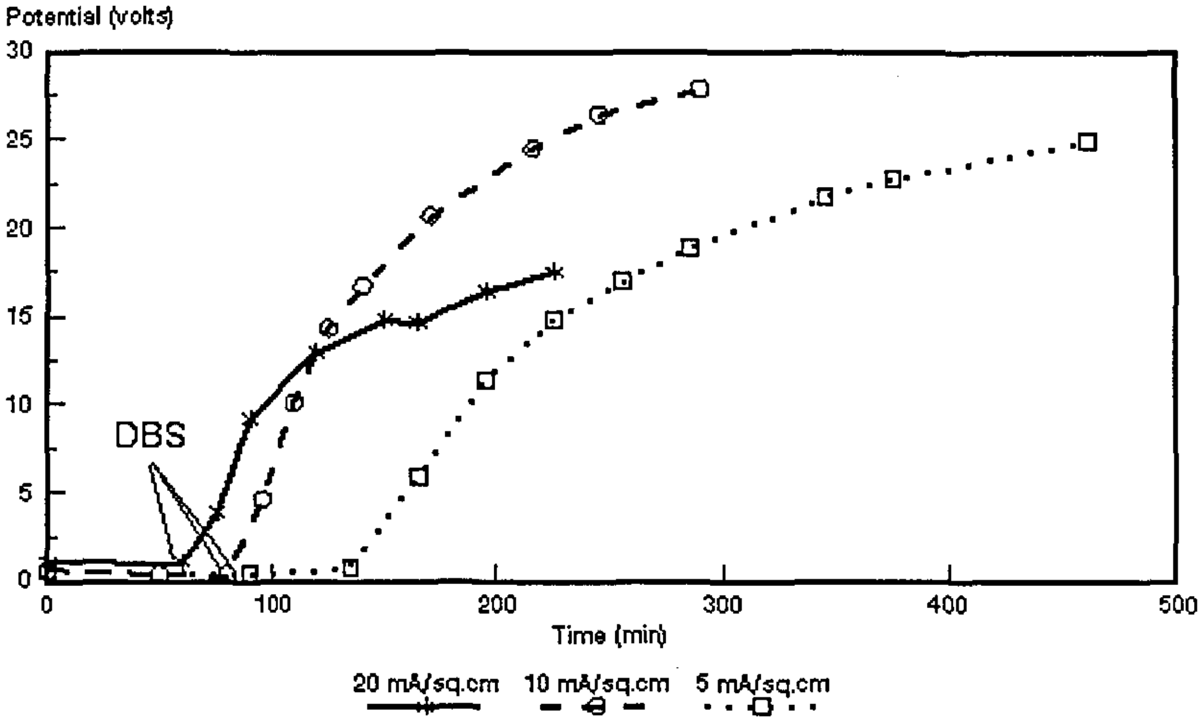

Figure 3.1: **Membrane potential as a function of time at different current densities (100 mg/ℓ DBS; 5 000 mg/ℓ NaCl; Selemion AMV membrane).**

Membrane fouling (increase in membrane potential) increased with increasing current density. Membrane fouling immediately started to occur when DBS was added at current densities of 20 and 10 mA/cm^2. Membrane fouling, however, only started to occur sixty minutes after DBS had been added in the case of the lower current density (5 mA/cm^2). Consequently, it appears that less serious membrane fouling may be experienced at lower current density.

The effect of current density on membrane fouling using Pretoria tap water spiked with 100 mg/ℓ DBS and 2 000 mg/ℓ sodium chloride, is shown in Figure 3.2.

Higher membrane potentials were experienced at the lower feed water salt concentration (2 000 mg/ℓ NaCl; Figure 3.2). It is also interesting to note that membrane fouling has started immediately to occur when the foulant has been added in the case of the lowest current density (5 mA/cm^2) that has been used. This suggests that a higher salt concentration in the feed water (see Fig. 31.) inhibits membrane fouling to a certain degree.

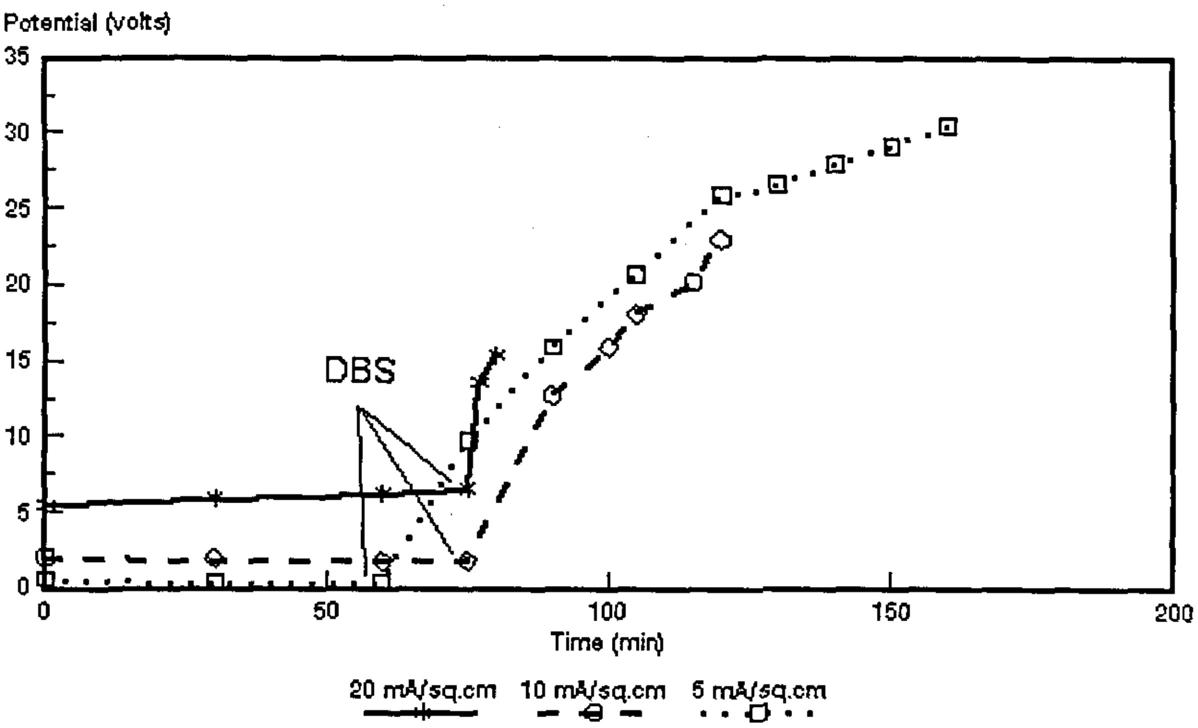

Figure 3.2: **Membrane potential as a function of time at different current densities (100 mg/ℓ DBS; 2 000 mg/ℓ NaCl; Selemion AMV membrane).**

Membrane resistance before and after fouling is shown in Table 3.1.

Table 3.1: Membrane resistance before and after fouling with 100 mg/ℓ DBS.

Membrane	Current Density mA/cm^2	Resistance ($ohm \cdot cm^2$) Unused	 Used
Selemion AMV	$20^{(1)}$	3,1* 2,3**	371* 20**
Selemion AMV	$10^{(1)}$	3,1* 2,0**	91* 31**
Selemion AMV	$5^{(1)}$	2,6* 1,3**	274* 16*
Selemion AMV	$20^{(2)}$	1,7* 1,3**	2,7* 1,4**
Selemion AMV	$10^{(2)}$	1,9* 1,4**	63* 1,9**
Selemion AMV	$5^{(2)}$	2,0* 1,0**	181* 18,0**

* Membrane resistance measured immediately after fouling (0,5 mol/ℓ NaCl)
** Membrane resistance measured after equilibration (overnight) in 0,5 mol/ℓ NaCl
(1) 5 000 mg/ℓ NaCl
(2) 2 000 mg/ℓ NaCl.

Membrane resistance increased significantly after membrane fouling. The increase in membrane resistance, however, was much lower (Table 3.1) after the membrane was equilibrated in 0,5 mol/ℓ sodium chloride solution. This can be ascribed to defouling of the membrane by the sodium chloride solution and to a decrease in resistance as a result of the higher salt concentration in contact with the membrane. An increase in membrane resistance is indicative of membrane fouling.

3.1.2 Effect of current density and feed water salinity level on fouling of Selemion AMV membranes using 50 mg/ℓ DBS

The effect of current density on membrane fouling using Pretoria tap water spiked with 50 mg/ℓ DBS and 2 000 mg/ℓ sodium chloride, is shown in Figure 3.3. The effect of current density on membrane fouling using Pretoria tap water spiked with 50 mg/ℓ DBS and 5 000 mg/ℓ sodium chloride, is shown in Figure 3.4.

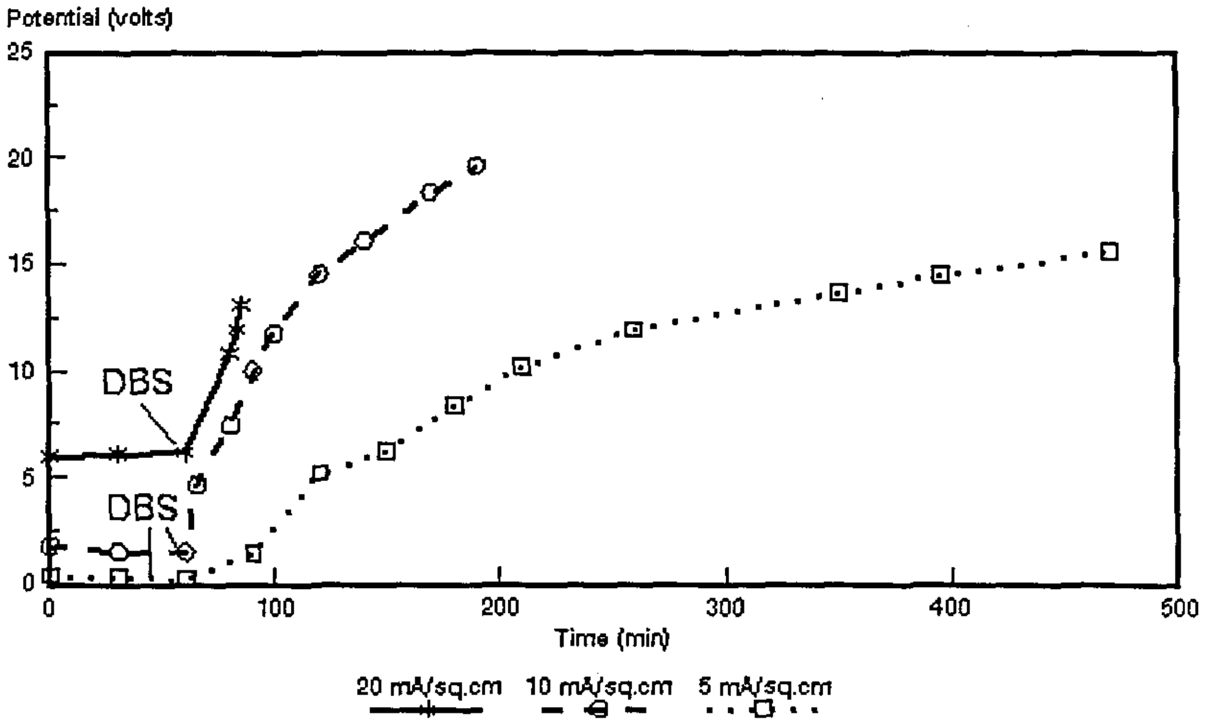

Figure 3.3: Membrane potential as a function of time at different current densities (50 mg/ℓ DBS; 2 000 mg/ℓ NaCl; Selemion AMV membrane).

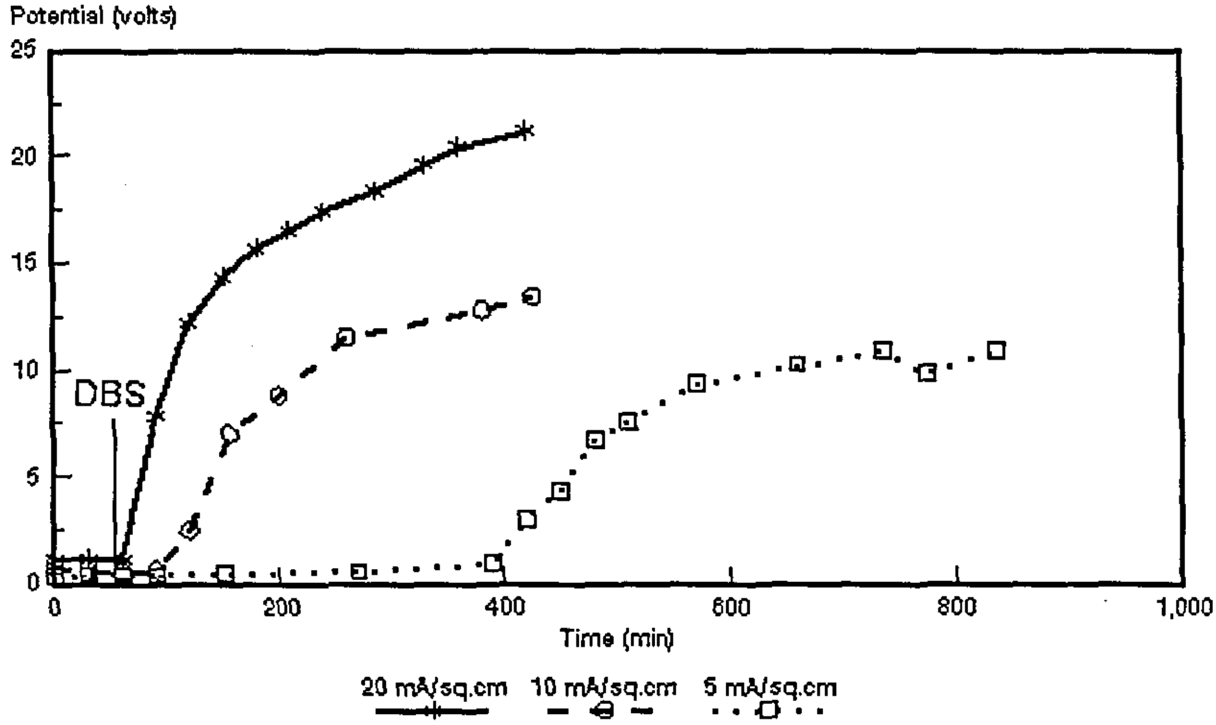

Figure 3.4: Membrane potential as a function of time at different current densities (50 mg/ℓ DBS; 5 000 mg/ℓ NaCl; Selemion AMV membrane).

A significantly higher membrane potential was again experienced at the lower feed water salinity level (Figs. 3.3 and 3.4). More severe membrane fouling was experienced at the higher current density. It is again shown that a higher feed water salinity level has the effect to postpone fouling to commence at lower current densities (Figs. 3.3 and 3.4). This may be ascribed to elution of the foulant anions with chloride ions or prevention of the foulant ions to accumulate at the membrane surface by the relatively high concentration of chloride ions.

Membrane resistance before and after fouling is shown in Table 3.2. High membrane resistances were experienced when the membranes became fouled. Membrane resistance could be significantly reduced after equilibration in sodium chloride solution. This showed that it should be possible to partly restore membrane performance with a sodium chloride rinse.

Table 3.2: **Membrane resistance before and after fouling with 50 mg/ℓ DBS.**

Membrane	**Current Density**	**Resistance (ohm·cm^2)**	
	mA/cm^2	**Unused**	**Used**
Selemion AMV	20$^{(1)}$	0,4* 0,2**	1,5* 0,7**
Selemion AMV	10$^{(1)}$	0,3* 0,1**	76* 17**
Selemion AMV	5$^{(1)}$	1,6* 0,7**	118* 31**
Selemion AMV	20$^{(2)}$	1,0* 0,2**	192* 17**
Selemion AMV	10$^{(2)}$	1,2* 0,7**	144* 10,0**
Selemion AMV	5$^{(2)}$	2,9* 1,9**	175* 12,3**

* Membrane resistance measured immediately after fouling (0,5 mol/ℓ NaCl)
** Membrane resistance measured after equilibration (overnight) in 0,5 mol/ℓ NaCl
(1) 5 000 mg/ℓ NaCl
(2) 2 000 mg/ℓ NaCl.

3.1.3 Effect of current density on fouling of Selemion AMV membranes using 25 mg/ℓ DBS

The effect of current density on membrane fouling using Pretoria tap water spiked with 25 mg/ℓ DBS and 5 000 mg/ℓ sodium chloride, is shown in Figure 3.5. A sharp increase in membrane fouling was experienced at a current density of 20 mA/cm². Membrane fouling, however, took much longer to commence at a current density of 10 mA/cm² and no membrane fouling could be detected at a current density of 5 mA/cm² over the test period.

Membrane resistance before and after fouling is shown in Table 3.3.

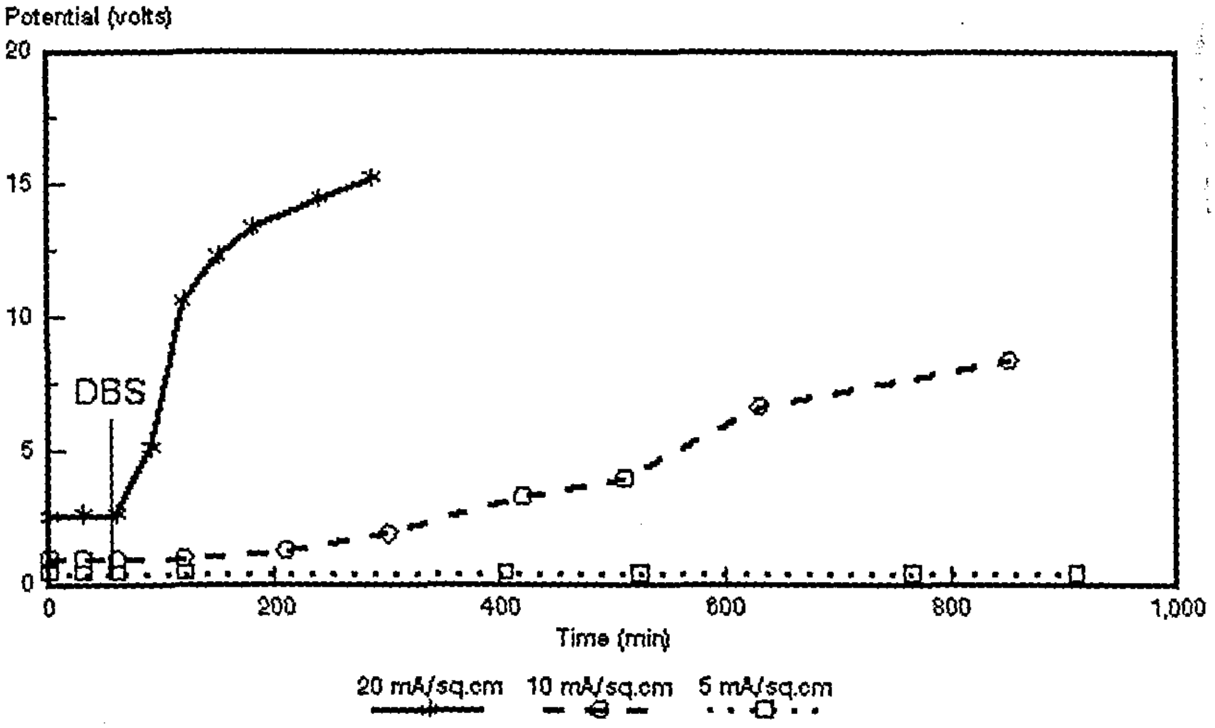

Figure 3.5: **Membrane potential as a function of time at different current densities (25 mg/ℓ DBS; 5 000 mg/ℓ NaCl; Selemion AMV membrane).**

Table 3.3: Membrane resistance before and after fouling with 25 mg/ℓ DBS.

Membrane	**Current Density mA/cm²**	**Resistance (ohm·cm²)**	
		Unused	**Used**
Selemion AMV	20(1)	1,6* 0,5**	74* 6**
Selemion AMV	10(1)	2,6* 1,0**	284* 16,1**
Selemion AMV	5(1)	1,0* 0,5**	264* 52**

* Membrane resistance measured immediately after fouling (0,5 mol/ℓ NaCl)
** Membrane resistance measured after equilibration (overnight) in 0,5 mol/ℓ NaCl
(1) 5 000 mg/ℓ NaCl.

Membrane resistance again showed a significant decrease in resistance after equilibration in sodium chloride (0,5 M) solution.

3.1.4 Effect of current density and interruption of current on fouling of Selemion AMV membranes using 50 mg/ℓ DBS

The effect of current density and interruption of current on membrane fouling using Pretoria tap water spiked with 50 mg/ℓ DBS and 5 000 mg/ℓ sodium chloride, is shown in Figure 3.6. The fouling runs were terminated at the end of the day and started the next morning. A reduction in membrane potential was observed when the runs were started the next day. Membrane potential, however, again increased relatively fast as a function of time. The reduction in membrane potential as a result of interruption of the electric current may be ascribed to peeling off of the foulant from the membrane surface when the current was interrupted overnight.

Membrane resistance before and after fouling is shown in Table 3.4.

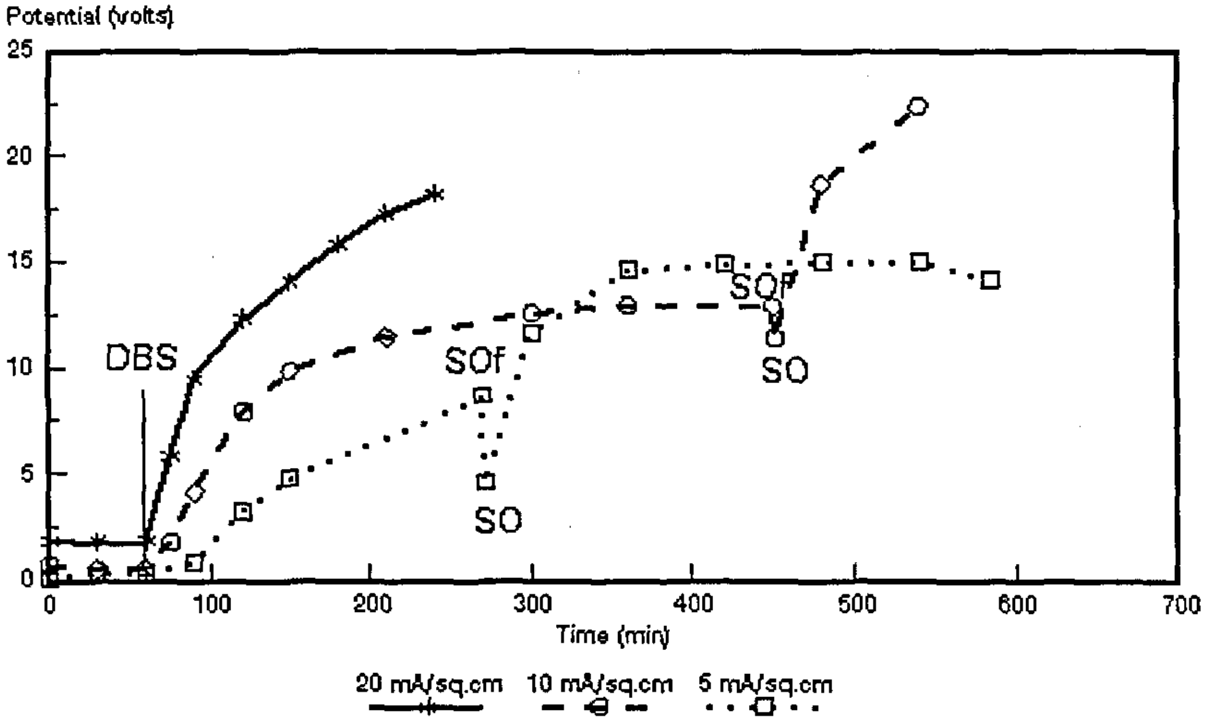

Figure 3.6: Membrane potential as a function of time at different current densities when current was interrupted overnight (50 mg/ℓ DBS; 5 000 mg/ℓ NaCl; Selemion AMV membrane) SOF: switch off; SO: switch on.

Table 3.4: Membrane resistance before and after fouling with 50 mg/ℓ DBS.

Membrane	Current Density mA/cm^2	Resistance (ohm·cm^2) Unused	Resistance (ohm·cm^2) Used
Selemion AMV	20$^{(1)}$	1,5* 0,4**	439* 8,0**
Selemion AMV	10$^{(1)}$	1,6* 0,6**	441* 48**
Selemion AMV	5$^{(1)}$	2,6* 1,1**	94* 32**

* Membrane resistance measured immediately after fouling (0,5 mol/ℓ NaCl)

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

(1) 5 000 mg/ℓ NaCl.

3.1.5 Effect of current density on fouling of Ionac MA-3475 and Ionics A-204-UZL-386 membranes using 50 mg/ℓ DBS

The effect of current density on fouling of Ionac MA-3475 and Ionics A-204- UZL-386 membranes using Pretoria tap water spiked with 50 mg/ℓ DBS and 5 000 mg/ℓ sodium chloride, is shown in Figures 3.7 and 3.8. Membrane fouling increased with increasing current density in the case of the Ionac membranes. It appears, however, that less fouling has taken place at lower current densities (5 and 10 mA/cm^2) using Ionac membranes (Fig. 3.6) than has been experienced with the Selemion membranes. It is further interesting to note that a higher membrane potential has been experienced when the run was started the next day. This indicated that membrane fouling took place overnight when the membrane was in contact with the feed solution.

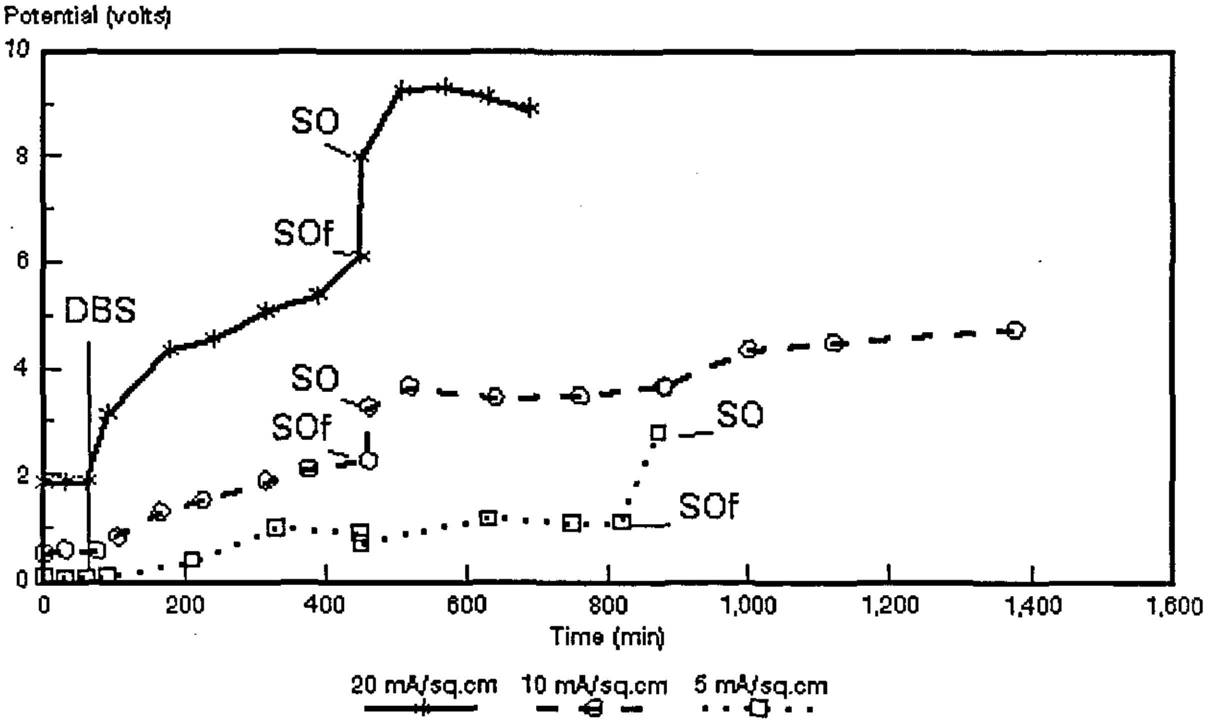

Figure 3.7: Membrane potential as a function of time at different current densities (50 mg/ℓ DBS; 5 000 mg/ℓ NaCl; Ionac MA-3475 membrane). SOF: Switch off; SO: switch on.

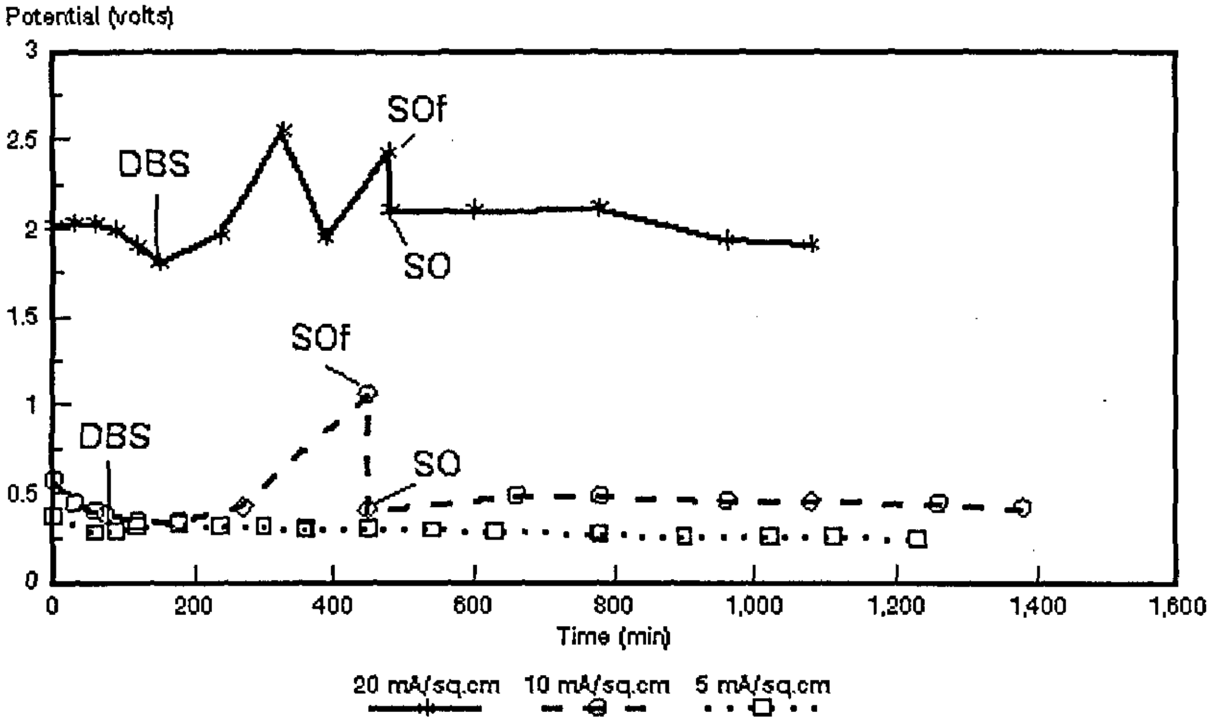

Figure 3.8: **Membrane potential as a function of time at different current densities (50 mg/ℓ DBS; 5 000 mg/ℓ NaCl; Ionics A-204-UZL-386 membranes). SOF: switch off; SO: switch on.**

Much less membrane fouling was encountered with the Ionics membrane than with the Selemion or Ionac membranes (Fig. 3.7). This shows that the Ionics membrane is much more resistant to DBS membrane fouling than the other two membrane types.

Membrane resistance before and after fouling is shown in Table 3.5. Membrane resistance again decreased significantly after exposure of the membrane to sodium chloride solution. It is also interesting to note that the Ionics membrane shows a significant increase in membrane resistance despite the fact that little increase in membrane potential has been experienced in comparison with the Selemion and Ionac membranes which show a significant increase in membrane potential. This might be explained by membrane surface fouling that took place.

Table 3.5: **Membrane resistance before and after fouling (Ionac MA-3475 and Ionics A-204-UZL-386 membranes).**

Membrane	*Current Density* mA/cm^2	*Resistance* (ohm·cm^2) *Unused*	*Used*
Ionac MA-3475	20(1)	30* 26**	93* 41**
Ionac MA-3475	10(1)	30* 26**	233* 161**
Ionac MA-3475	5(1)	30* 26**	285* 216**
Ionics A-204-UZL-386	20(1)	8* 4**	437* 82**
Ionics A-204-UZL-386	10(1)	10* 5**	415* 45**
Ionics A-204-UZL-386	5(1)	10* 4**	420* 46**

* Membrane resistance measured immediately after fouling (0,5 mol/ℓ NaCl)
** Membrane resistance measured after equilibration (overnight) in 0,5 mol/ℓ NaCl
(1) 5 000 mg/ℓ NaCl.

3.2 Membrane Fouling with Humic Acid (HA)

3.2.1 Effect of humic acid (HA) and polarity reversal on fouling of Selemion AMV, Ionac MA-3475 and Ionics A-204-UZL-386 membranes

The effect of Pretoria tap water spiked with 100 mg/ℓ HA and 3 000 mg/ℓ sodium chloride on membrane fouling of Selemion AMV, Ionac MA-3475 and Ionics A-204-UZL-386 membranes using a current density of 20 mA/cm^2, is shown in Figure 3.9. The Ionac and Selemion membranes were very sensitive to organic fouling. The membrane potential increased rapidly as a function of time. However, the Ionics membrane showed a very high resistance to organic fouling. No increase in membrane voltage was experienced over the test period.

Preliminary tests indicated that membrane fouling could be controlled with polarity reversal. The base line voltage could be maintained after the first polarity reversal cycle (Fig. 3.9). However, the base line voltage could not be maintained after the second polarity reversal cycle showing that irreversible fouling was taking place.

A shorter polarity reversal frequency may improve the situation. A brown precipitate had formed on the anion-exchange membrane facing the anode.

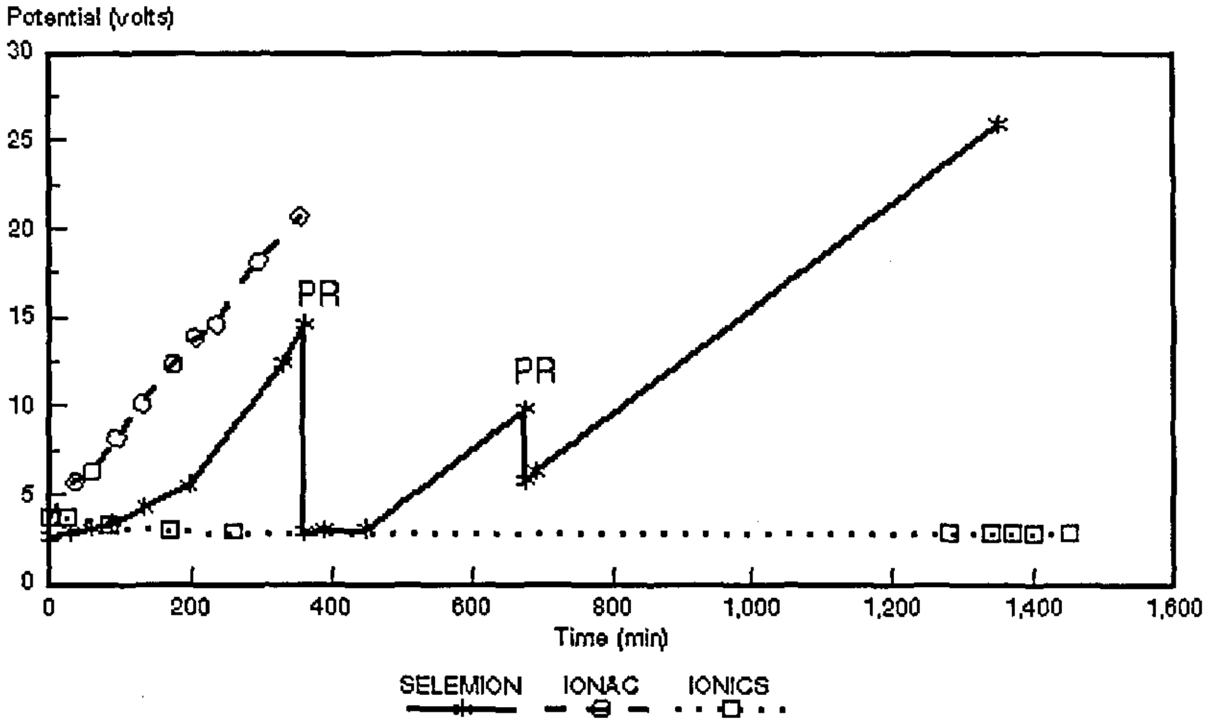

Figure 3.9: **Membrane potential as a function of time using different ion-exchange membranes and polarity reversal (PR) (Selemion AMV, Ionac MA-3475, Ionics A-204-UZL-386 membranes; 100 mg/ℓ HA, 3 000 mg/ℓ NaCl; 20 mA/cm^2).**

Membrane resistance before and after fouling is shown in Table 3.6.

Table 3.6: **Membrane resistances before and after fouling with humic acid (100 mg/ℓ) using different ion-exchange membranes.**

Membrane	Current Density mA/cm^2	Resistance (ohm·cm^2) Unused	Resistance (ohm·cm^2) Used
Selemion AMV	20$^{(1)}$	1,0* 0,5**	14,2* 3,6**
Ionac MA-3475	20$^{(1)}$	15,2* 9,1**	20,8* 9,1**
Ionics A-204-UZL-386	20$^{(1)}$	4,5* 1,5**	8,6* 1,5**

* *Membrane resistance measured immediately after fouling (0,5 mol/ℓ* NaCl)
** Membrane resistance measured after equilibration (overnight) in 0,5 mol/ℓ NaCl
(1) 3 000 mg/ℓ NaCl.

An increase in membrane resistance was experienced showing that membrane fouling was taking place. It is interesting to note that membrane resistance could be reduced to its original value after equilibration with sodium chloride solution in the case of the Ionac and Ionics membranes. This showed that the membrane's resistance could be restored after equilibration with sodium chloride solution to its initial level. This, however, did not happen with the Selemion membrane, showing that it would be more difficult to clean this membrane.

3.2.2 Effect of current interruption and caustic soda cleaning on membranes fouled with humic acid

The effect of current interruption and caustic soda cleaning on membrane fouling fouled with 100 mg/ℓ HA in Pretoria tap water (3 000 mg/ℓ NaCl), is shown in Figure 3.10. Membrane potential increased slowly in the beginning and then more rapidly after fouling has taken place for approximately 130 minutes.

The fouling run was terminated at the end of the day (approximately 220 minutes' fouling). The membrane potential was about the same as the base line voltage when the run was started the next day. This showed that the membrane defouled overnight. Membrane voltage, however, again increased and a caustic rinse was given in an attempt to clean the membrane. The caustic soda cleaning had a beneficial effect on membrane potential and the potential was almost reduced to its base line value. Fouling was again allowed to take place and membrane potential was high when the current was interrupted. Successive current interruption and caustic soda cleanings showed that the membrane could be cleaned. However, fouling rapidly started to occur after membrane cleaning. It also appeared that the base line voltage could not be maintained after the last caustic soda cleaning showing that membrane fouling was irreversible.

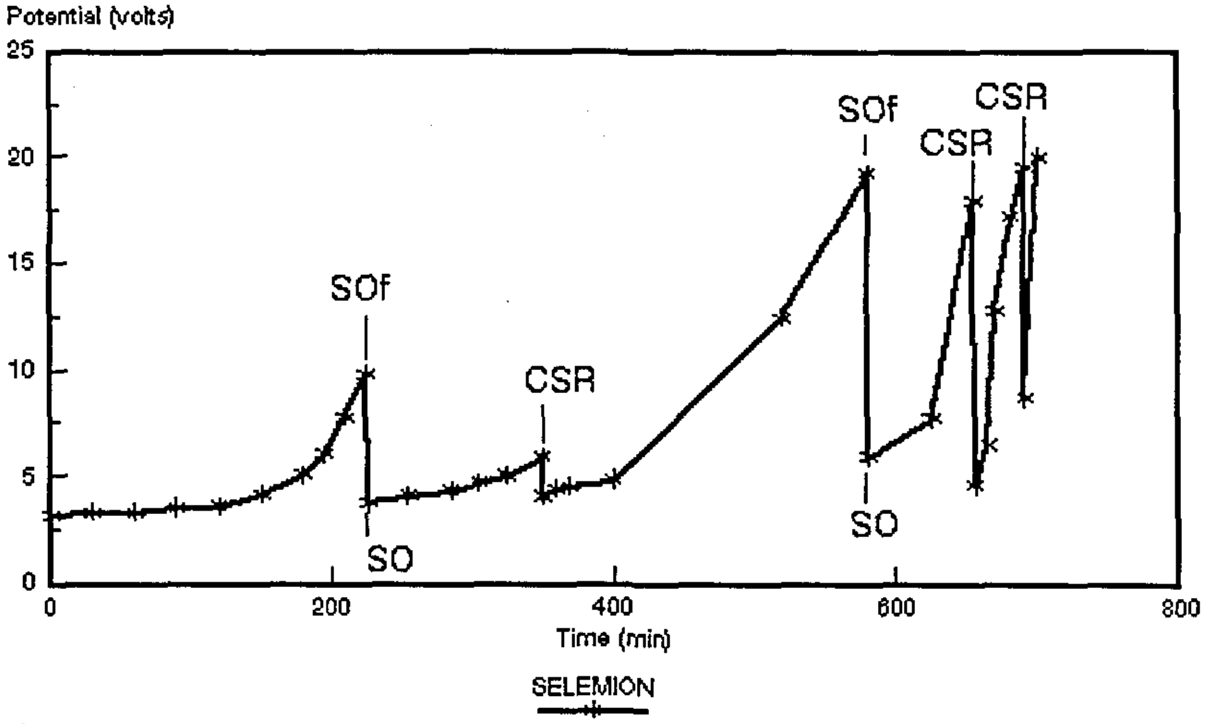

Figure 3.10: **Effect of caustic soda cleaning and current interruption on membrane fouling using 100 mg/ℓ humic acid as foulant (3 000 mg/ℓ NaCl; Selemion AMV membrane; CD 20 mA/cm^2; rinse 30 minutes with 0,1 mol/ℓ NaOH and 30 minutes with water).**
SOF: switch off; SO: switch on.

3.2.3 Effect of feed flow rate on membrane fouling

The effect of feed water flow rate on membrane fouling is shown in Figure 3.11. Pretoria tap water spiked with 100 mg/ℓ HA and 3 000 mg/ℓ sodium chloride was used as feed water. Feed flow rates of 600; 1 100 and 1 600 mℓ/min were used. Increasing feed flow rate from 600 to 1 600 mℓ/min had a dramatic effect on membrane fouling (Fig. 3.11). It took much longer for fouling to take place at the higher feed flow rate. Consequently, it will be advantageous to use the highest possible flow rates in an ED stack to inhibit membrane fouling.

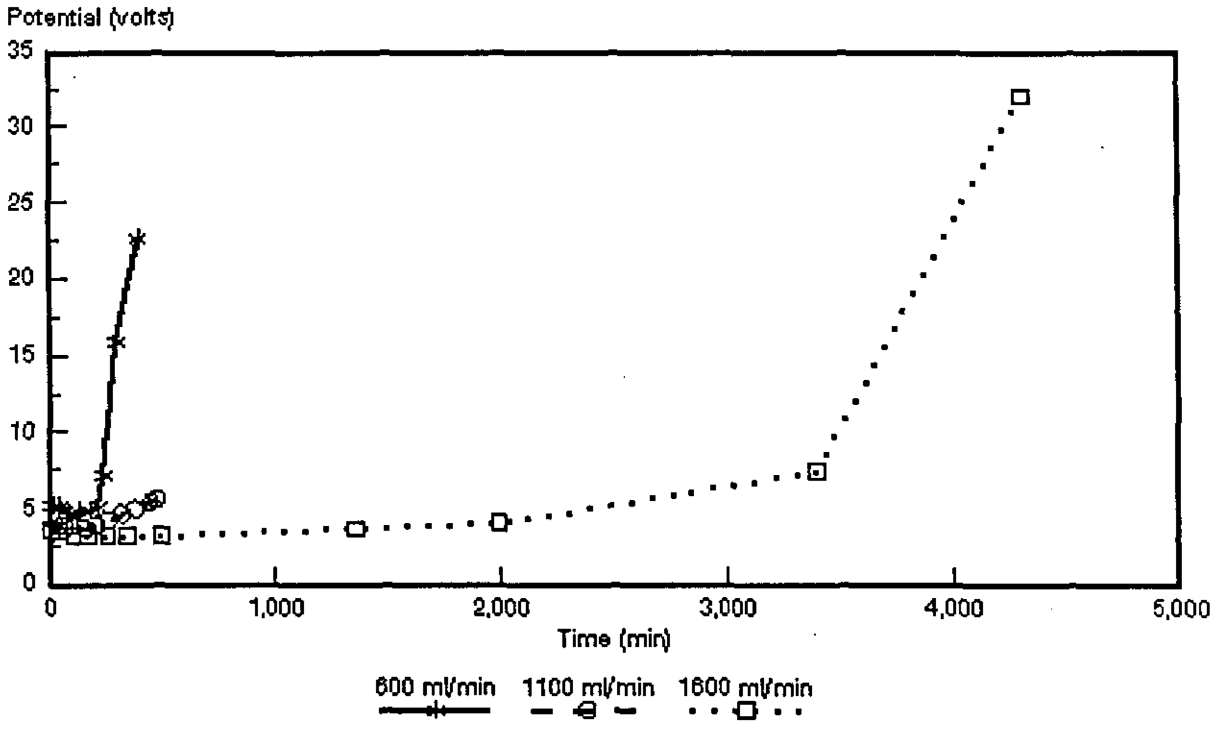

Figure 3.11: **Effect of feed flow rate on membrane fouling (100 mg/ℓ HA; 3 000 mg/ℓ NaCl; Selemion AMV membrane; CD 20 mA/cm^2).**

3.2.4 Effect of increasing current density on membrane fouling using Selemion AMV membranes and humic acid foulant

The effect of increasing current density on membrane fouling using Selemion AMV membranes and 100 mg/ℓ humic acid as foulant, is shown in Figure 3.12. Membrane fouling increased dramatically with increasing current density in the current density range from 5 to 20 mA/cm^2. No membrane fouling was experienced at a current density of 5 mA/cm^2 over the test period. Consequently, membrane fouling in ED applications might be reduced significantly by operating an ED stack at the lowest possible current density. This, however, will affect the economics of the process adversely because a larger membrane area will be required.

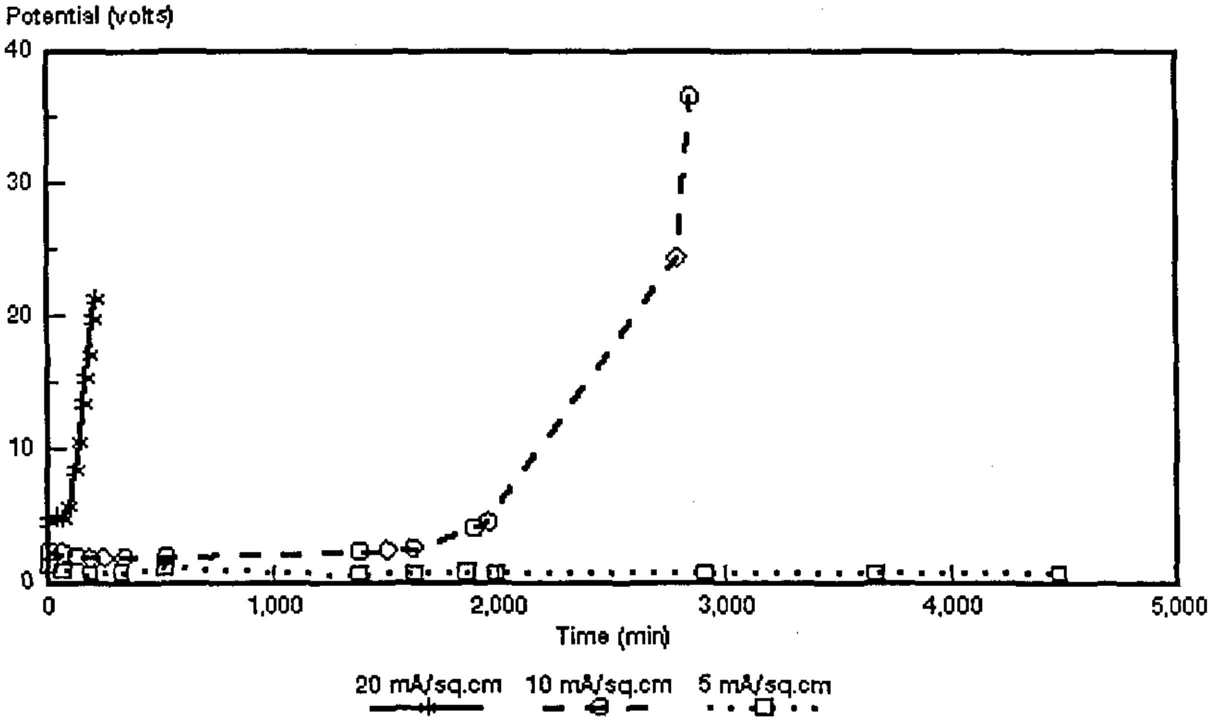

Figure 3.12: **Effect of current density on membrane fouling using Selemion AMV membrane and 100 mg/ℓ humic acid as foulant (3 000 mg/ℓ NaCl).**

3.2.5 Effect of polarity reversal, caustic soda and mechanical cleaning on membrane fouling using Ionac MA-3475 membranes and humic acid as foulant

The effect of polarity reversal, caustic soda and mechanical cleaning on membrane fouling using Ionac MA-3475 membranes and 100 mg/ℓ humic acid, is shown in Figure 3.13. It appeared that it should be possible to control membrane fouling by polarity reversal. However, the frequency of polarity reversal should be as short as possible. Membrane potential could be restored to its initial value after polarity reversal.

The power supply cut out (CO) on two occasions during this run. This happened when the membrane potential became too high. It is again interesting to note that the starting voltage in both cases has been much lower than the cut out voltage. This suggests that the membranes became defouled overnight.

The first caustic soda rinse (0,1 mol/ℓ NaOH, 15 min) had a dramatic effect on membrane potential. Membrane potential was almost decreased to its initial value

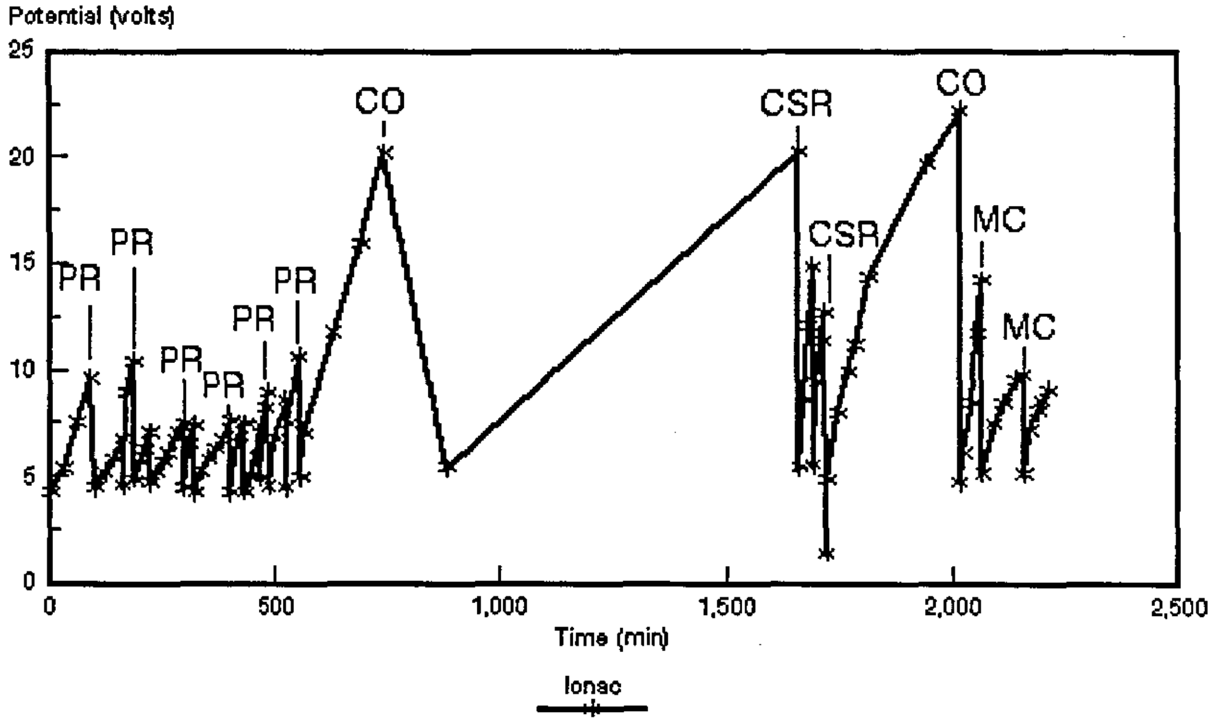

Figure 3.13: **Effect of polarity reversal, caustic soda (0,1 mol/ℓ NaOH - 15 min rinse) and mechanical cleaning on membrane fouling (Ionac MA-3475 membrane, 100 mg/ℓ HM; 3 000 mg/ℓ NaCl; CD 20 mA/cm^2) PR: polarity reversal; CO: cut out; CSR: caustic soda rinse; MC: mechanical cleaning.**

showing that it would be possible to defoul the membrane almost completely with electro-elution. Mechanical cleaning (cleaning membrane with tissue) also had a dramatic effect on membrane potential. This showed that membrane fouling with humic acid over a relatively short period was a surface phenomenon.

3.2.6 Effect of humic acid fouling on Ionic A-204-UZL membranes

The effect of humic acid fouling (500 mg/ℓ) on Ionics A-204-UZL membranes is shown in Figure 3.14. Almost no increase in voltage was experienced as a function of time. This showed that the Ionics membrane was very resistant towards humic acid fouling. Membrane resistance was determined at 2,6 ohm·cm^2 before and after fouling. This showed that no fouling took place.

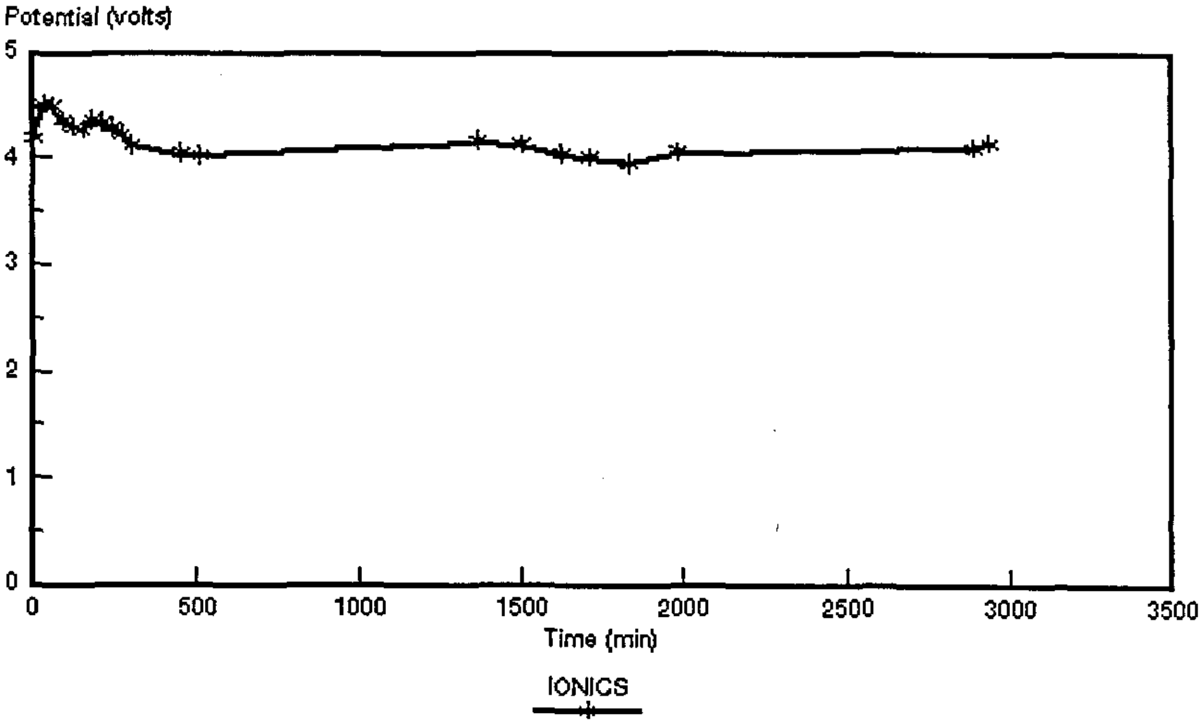

Figure 3.14: **Effect of humic acid fouling on Ionics A-204-UZL membranes (500 mg/ℓ humic acid; 3 000 mg/ℓ NaCl; 20 mA/cm^2).**

3.2.7 The effect of preflocculation of a humic acid solution on membrane fouling

The effect of preflocculation of a humic acid feed solution on membrane fouling using Selemion AMV membranes, is shown in Figure 3.15. Humic acid solution (100 mg/ℓ) was flocculated with 30 mg/ℓ ferric chloride solution. Well defined flocs formed which settled rapidly. The flocs were removed by filtration and the filtered water was used as feed water to the fouling cell.

The COD of the feed water before flocculation was 560 mg/ℓ. The COD after flocculation was 160 mg/ℓ. Therefore, a significant amount of humic acid could be removed by flocculation.

The flocculated water took much longer to foul the membrane than the unflocculated feed water. Consequently, it will be advantageous to remove humic acid from water supplies with ferric chloride flocculation prior to ED treatment to inhibit membrane fouling from taking place.

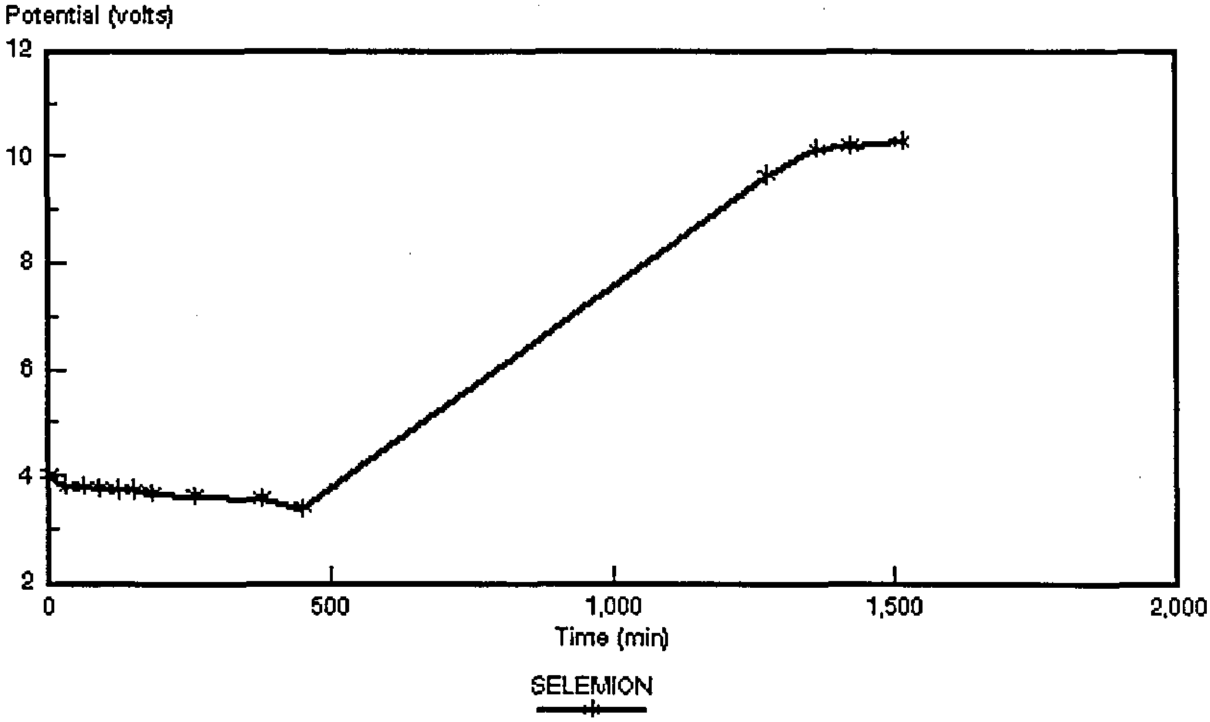

Figure 3.15: **Effect of preflocculation of humic acid feed with ferric chloride on membrane fouling using Selemion AMV membranes (100 mg/ℓ HA; CD 20 mA/cm^2).**

3.2.8 Effect of ultrafiltration pretreatment, polarity reversal and caustic soda rinse on membrane fouling

The effect of ultrafiltration (UF) pretreatment, polarity reversal and caustic soda rinse on membrane fouling using Selemion AMV membranes, is shown in Figure 3.16.

The COD of the humic acid solution (100 mg/ℓ) before and after UF pretreatment was 560 and 400 mg/ℓ, respectively. Polysulphone UF membranes with a molecular mass cut-off of approximately 40 000 were used. Only partial removal of the humic acid was obtained and rapid fouling of the Selemion AMV membrane took place (Fig. 3.16). A lower molecular mass cut-off UF membrane may give better results.

Polarity reversal and a caustic soda rinse decreased the membrane potential but it was not possible to decrease the membrane potential to its initial value. Therefore, it appeared that irreversible fouling had taken place.

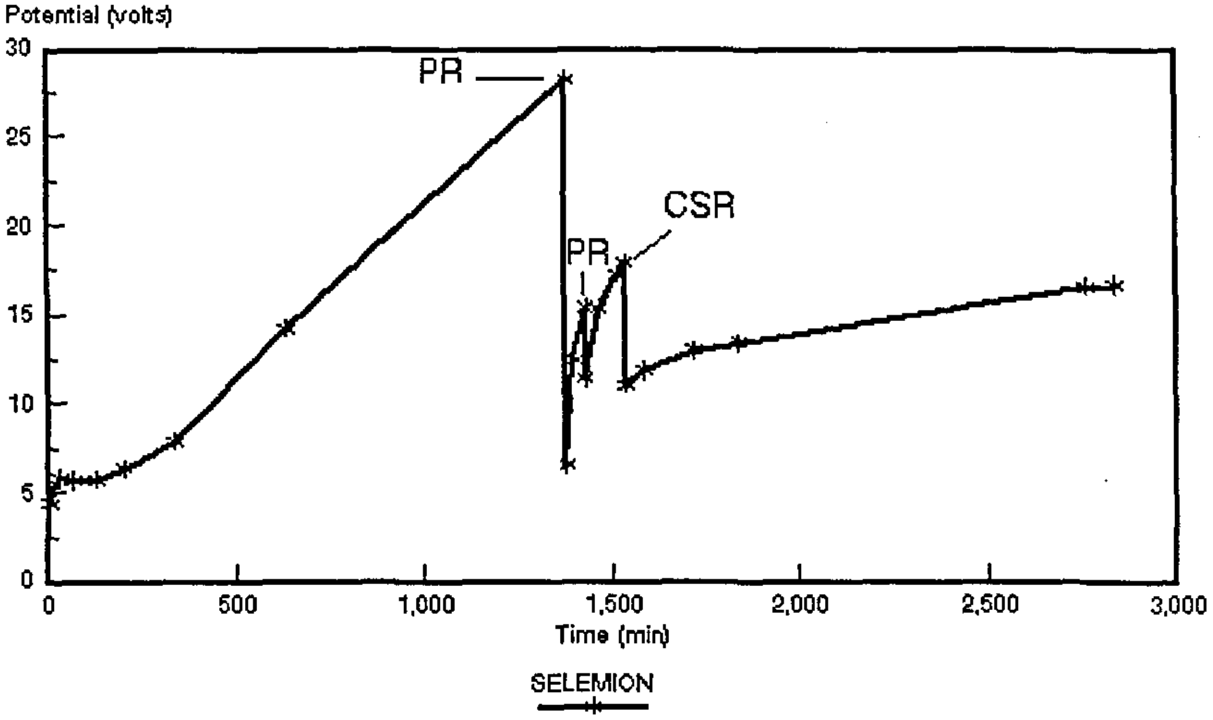

Figure 3.16: **Effect of ultrafiltration pretreatment, polarity reversal and caustic soda rinse on membrane fouling (100 mg/ℓ HA; 3 000 mg/ℓ NaCl; CD 20 mA/cm^2; Selemion AMV *membrane*). PR: *polarity reversal;* CSR: caustic soda rinse (0,1 mol/ℓ; 15 min).**

3.3 Effect of Organics Extracted from Fouled Eskom Membranes on Membrane Fouling

Cooling tower blow-down is treated at Tutuka Power Station at Eskom with EDR for water recovery and effluent volume reduction. An Ionics EDR stack and membranes are used. A steady increase in product water conductivity was experienced over the last two years, most probably as a result of membrane fouling caused by some of the constituents in the cooling tower blow-down. The feed water to the EDR unit contains biocides and organic matter of natural origin. These compounds may be responsible for the membrane fouling that is experienced with the EDR membranes. Consequently, the fouling potential of these two types of compounds for Ionics membranes was evaluated in the fouling cell.

Organics were extracted from fouled anion-exchange membranes obtained from Eskom with 0,1 mol/ℓ caustic soda solution and fouling tests were conducted by dissolving the extract (0,1 mol/ℓ NaOH) in Pretoria tap water spiked with 3 000 mg/ℓ sodium chloride solution (pH adjusted to approximately 7 with HCl). An attempt was also made to identify the organics extracted from the membranes and to examine the surface characteristics of the fouled membranes. The fouling potential of a few biocides commonly used in cooling tower water, was also evaluated for the membranes used at Eskom.

3.3.1 Effect of organics extracted from fouled membranes on membrane fouling

The effect of organics extracted from fouled membranes obtained from Eskom on membrane fouling, is shown in Figure 3.17. The COD of the feed solution was 370 mg/ℓ. Membrane fouling slowly occurred as could be seen from the increase in membrane potential that was experienced. Polarity reversal decreased membrane potential significantly. However, membrane potential could not be restored to its initial value, nor could caustic soda cleaning decrease the membrane potential significantly. Consequently, it appeared that irreversible membrane fouling had occurred with the Selemion AMV membrane.

A brown precipitate had formed on the surface of the anion-exchange membrane. This precipitate could be removed easily with mechanical cleaning of the membrane surface. Membrane resistances of the unused and used membranes after equilibration in 0,5 mol/ℓ sodium chloride solution were 0,5 and 5,1 ohm·cm^2, respectively. This showed that membrane fouling had taken place.

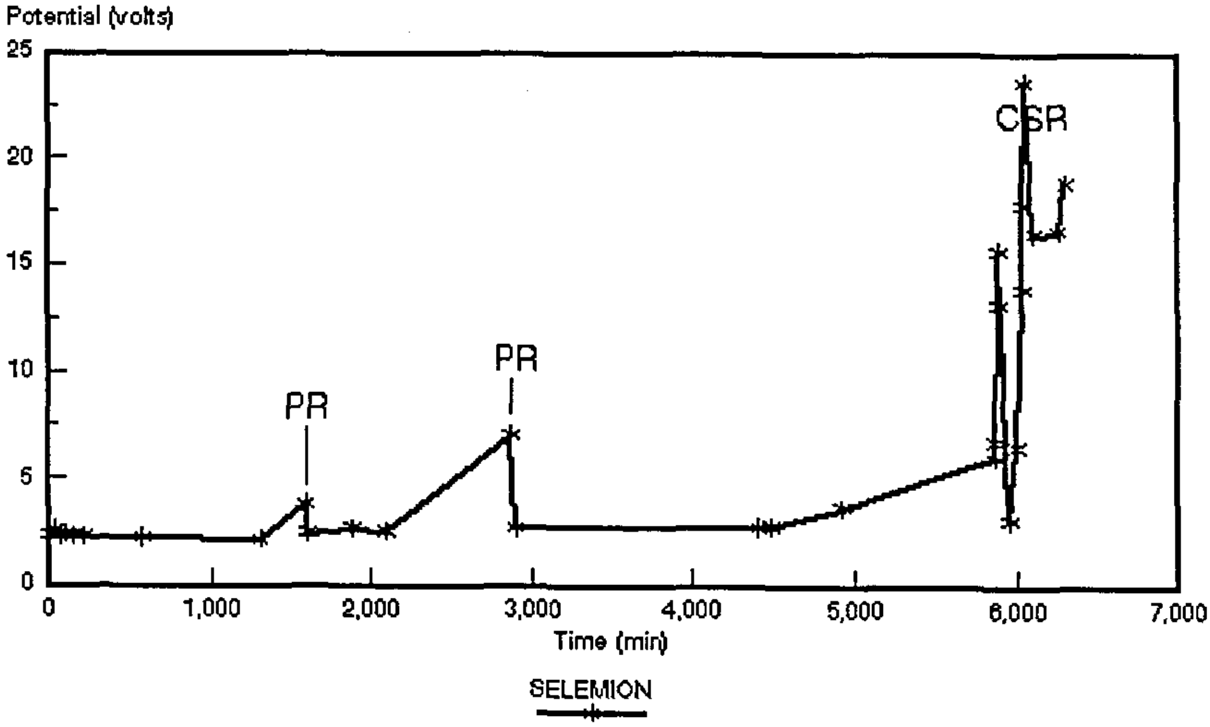

Figure 3.17: **Effect of organics extracted from fouled membranes on membrane fouling (3 000 mg/ℓ NaCl; CD 20 mA/cm^2; Selemion AMV membrane).**

3.3.2 Identification of organics extracted from fouled membranes

Capillary gas chromatography (CGC) and high pressure liquid chromatography (HPLC) analysis were conducted on a synthetic humic acid solution and on the organics extracted from the fouled membranes. Gas chromatography chromatograms have indicated that "fingerprinting" was not possible. However, HPLC chromatograms (Figs. 3.18 and 3.19) have shown that humic acid is present in the organic fraction that was removed from the fouled membranes. Consequently, humic acids in the cooling tower blow-down water are most probably responsible for the membrane fouling that is experienced with the EDR membranes at Tutuka Power Station. A relatively low molecular mass compound was also detected in the HPLC chromatogram (first peak, Fig. 3.18). This compound may also play a role in the membrane fouling that is experienced and needs to be identified.

Scanning electron micrographs (SEM) were taken of fouled and unfouled membranes. No differences, however, could be detected in the micrographs and further work may be required in this regard.

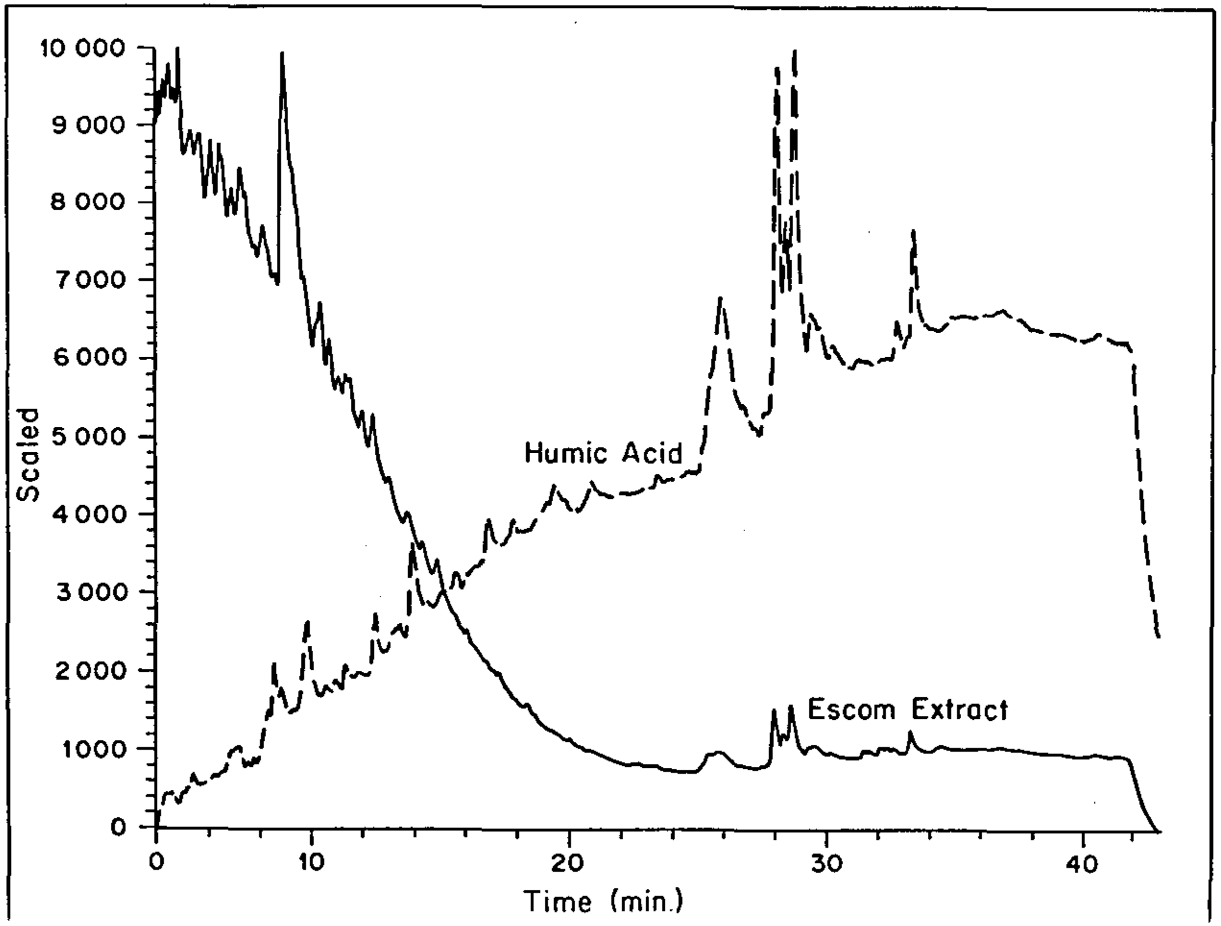

Figure 3.18: HPLC chromatogram of humic acid solution and of organics extracted from fouled membranes.

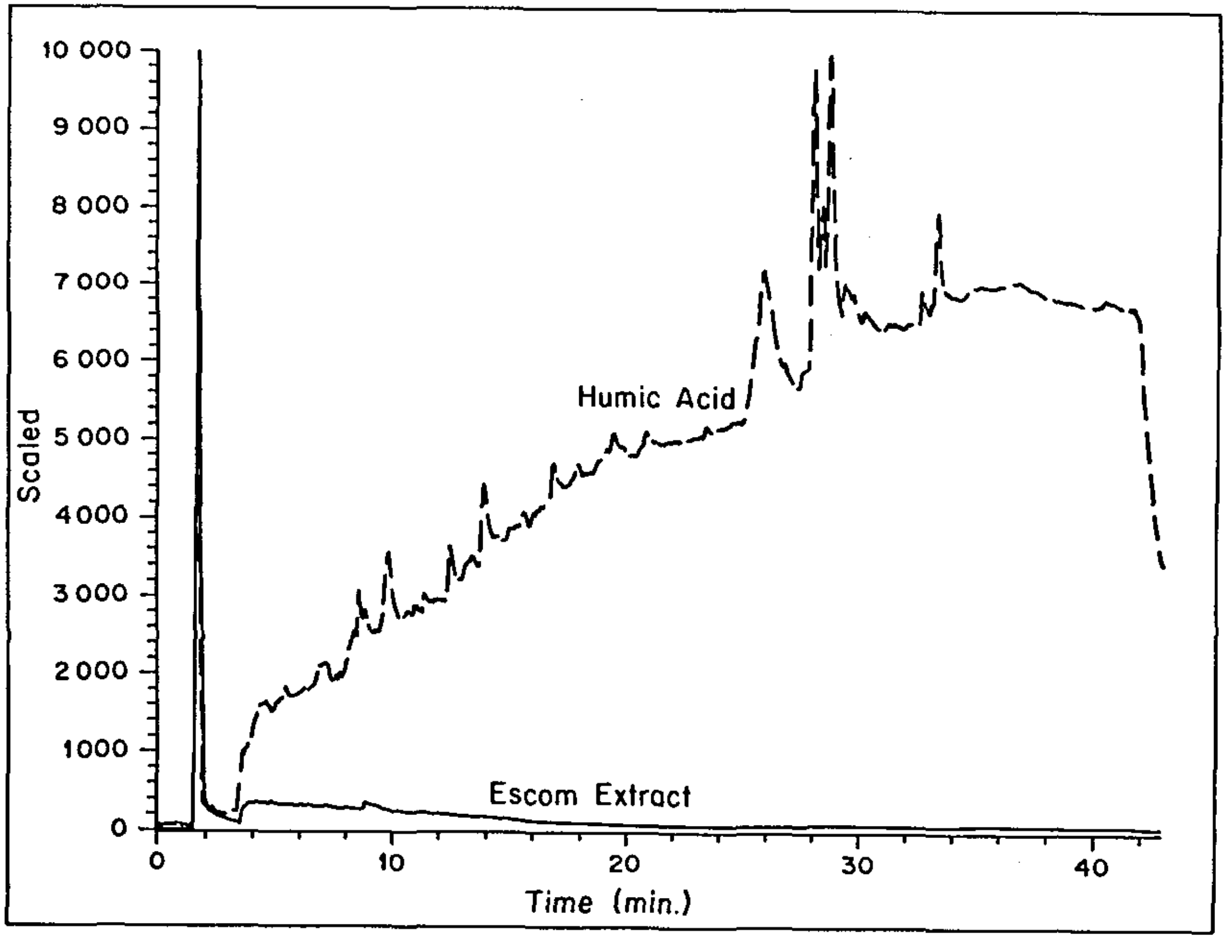

Figure 3.19: HPLC chromatogram of humic acid solution and of organics extracted from fouled membranes.

3.3.3 Effect of biocides on membrane fouling

Limited work was conducted in a previous study(6) on the effect of biocides, used in cooling tower blow-down, on membrane fouling. The fouling potential of Belclene 350 and Kathon WT 500 for Ionics cation-exchange membranes was determined. The fouling potential of Synperonic NP6 for Ionics anion-exchange membranes was also determined. It was found that Belclene 350 had the potential to foul Ionics cation-exchange membranes. However, no membrane fouling of the anion-exchange membrane could be detected.

3.4 Effect of Spent Plating Bath Water, Rinse Waters and Additives Added to the Plating Bath, on Membrane Fouling

3.4.1 Effect of spent plating bath water on membrane fouling

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 3.20. The Selemion AMV membrane was fouled with the spent plating solution. However, the Ionics and Ionac membranes showed no 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.

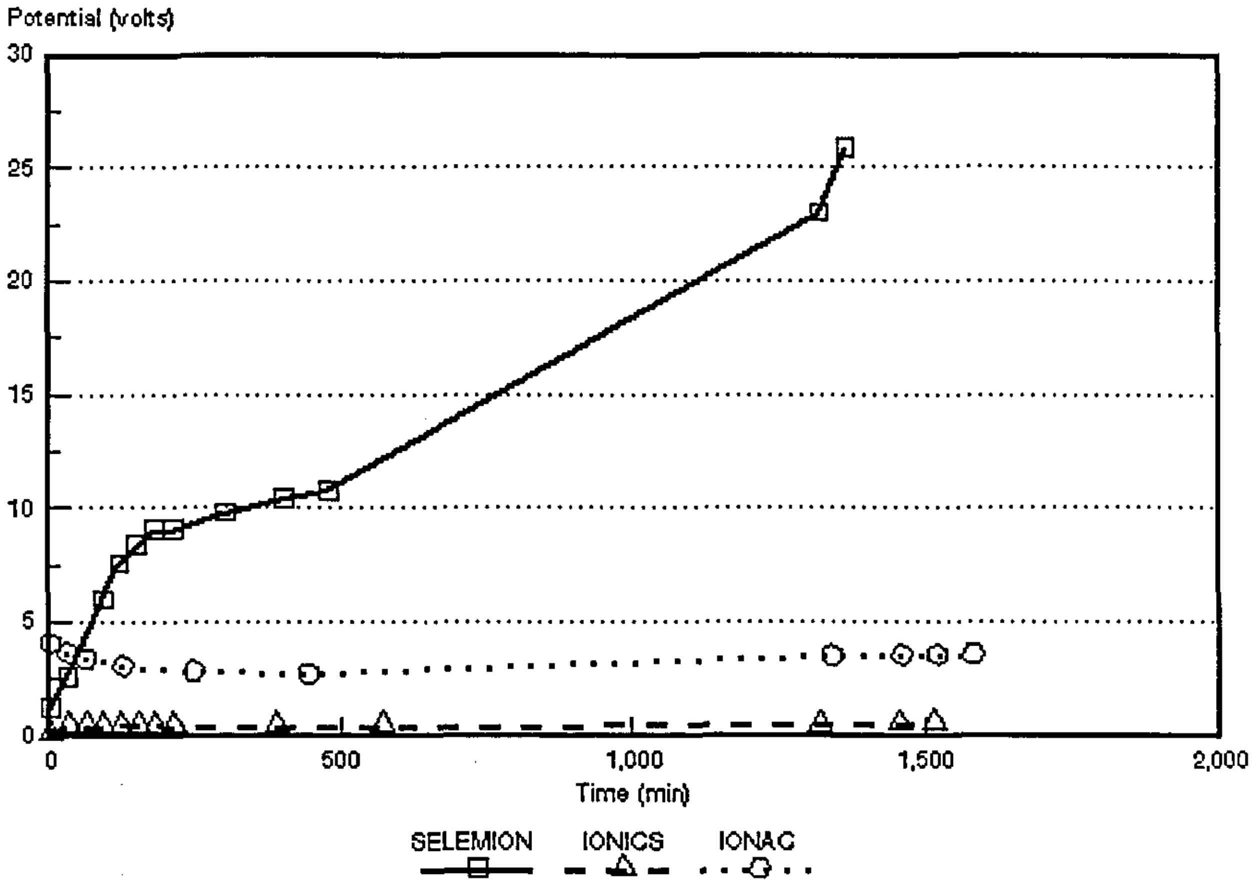

Figure 3.20: **Effect of spent nickel plating bath water on membrane fouling using Selemion, Ionics and Ionac membranes (CD 20 mA/cm^2; Conductivity of feed 5 300 mS/m; COD of feed 59 000 mg/ℓ).**

Membrane resistance before and after fouling is shown in Table 3.7.

Table 3.7: **Membrane resistances before and after fouling with spent nickel plating bath water using different ion-exchange membranes.**

Membrane$^{(1)}$	Resistance (ohm·cm^2)	
	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/cm^3.

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

3.4.2 The effect of nickel rinse water on membrane fouling

The effect of nickel rinse water on membrane fouling using Selemion AMV, Ionics A-204-UZL and Ionac MA-3475 membranes, is shown in Figure 3.21. The nickel rinse water as received from the plating shop had a pH of approximately 2 and a conductivity of 839 mS/m. It appeared that little membrane fouling took place with the Selemion AMV membrane at this pH level (Fig. 3.21). The pH of the nickel rinse water was then adjusted to a pH of approximately 7 prior to fouling because the Selemion membranes were more stable at this pH level. However, severe membrane fouling was experienced at this elevated pH level. Little membrane fouling, on the other hand, took place with the Ionac and Ionics membranes (also elevated pH). Ultrafiltration of the nickel rinse water (elevated pH) had almost no effect in preventing membrane fouling from taking place. The iron concentration of the nickel rinse water was reduced from 5,7 before UF to 0,4 mg/ℓ after UF treatment. The COD of the feed water was reduced from 2 740 mg/ℓ (before UF) to 2 070 mg/ℓ (after UF). Despite this, serious membrane fouling was still taking place and pretreatment could be required prior to ED treatment of nickel rinse water. Activated carbon or resin should be able to reduce the foulants to low levels. This matter, however, needs further investigation.

Membrane resistances before and after fouling, are shown in Table 3.8.

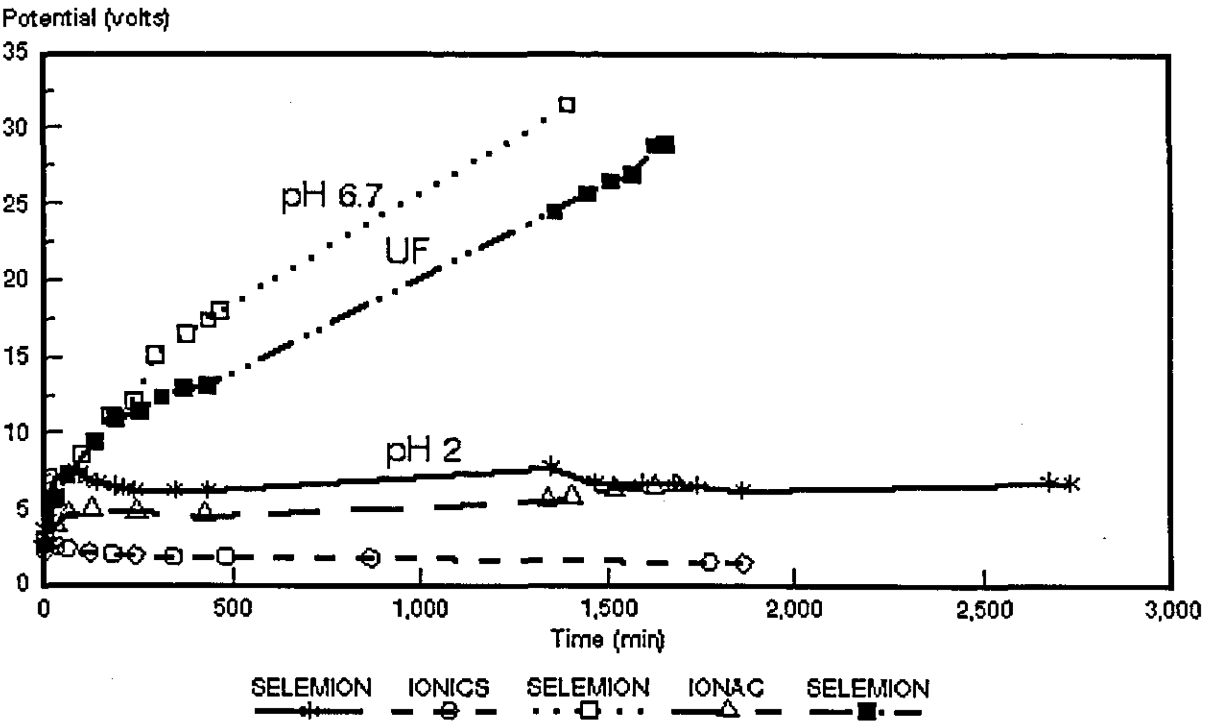

Figure 3.21: **Effect of nickel rinse water on membrane fouling using Selemion, Ionics and Ionac membranes (CD 20 mA/cm^2).**

Table 3.8: **Membrane resistances before and after fouling with nickel rinse water using different ion-exchange membranes.**

Membrane⁽¹⁾	**Resistance (ohm·cm^2)**	
	Unused	**Used**
Selemion AMV (pH 2)	2,5* 0,5**	27,4* 25,4**
Ionics A-204-UZL (pH 7)	7,6* 4,1**	17,3* 7,6**
Selemion AMV (pH 7)	3,0* 1,0**	424* 37,8**
Ionac MA-3475 (pH 7)	12,2* 7,1**	236* 16,2**
Selemion AMV (pH 7; UF)	3,0* 1,5**	312* 17,2**

* 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/cm^2.

Membrane fouling was more severe in the case of the Selemion membranes. Membrane fouling, however, was experienced with the Ionics and Ionac membranes according to the membrane resistance values. A light precipitate had formed on the anionic membranes in all the cases. The precipitate could be nickel hydroxide. Nickel salts hydrolyze at relatively low pH to form nickel hydroxide. This can happen under polarizing conditions when the current density is too high. Nickel hydroxide fouling, however, should be countered by working at a lower current density. It should also be possible to clean the membranes with a dilute hydrochloric acid solution.

3.4.3 The effect of additives added to the plating bath on membrane fouling

A variety of additives are usually added to a plating bath to improve the quality of plating. These additives are usually proprietary chemicals. The additives are in most cases organic compounds and therefore have the potential to foul ion-exchange membranes. Consequently, the fouling potential was evaluated of additives used in a typical nickel plating bath.

The following additives are used in a typical nickel plating bath:

a) 612A wetting agent (5 mℓ/ℓ);
b) 660G (1,75 mℓ/ℓ);
c) nickel leveller 41 (10 mℓ/ℓ);
d) 63 agent (9,5 mℓ/ℓ).

The fouling potential of the above plating bath additives for Selemion AMV membranes, is shown in Figure 3.22. It appears that all the additives used in the nickel plating bath will cause membrane fouling when Selemion AMV membranes are used. Therefore, the foulants should be removed by proper pretreatment prior to ED of nickel plating solutions (Note: a precipitate had formed on the anion-exchange membrane). Activated carbon may remove the foulants effectively. However, this matter needs further investigation.

Membrane resistances before and after fouling is shown in Table 3.9.

Table 3.9: Membrane resistances before and after fouling with additives used in nickel plating baths.

Membrane	Additive	Resistance ($\text{ohm}\cdot\text{cm}^2$)*	
		Unused	Used
Selemion AMV	612 A	0,51	6,6
	660 G	0,51	5,1
	63	0,51	20,3
	Ni Leveller 41	0,51	4,1

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

The membrane resistance values also showed that membrane fouling was experienced. It appears that additive 63 caused the most serious fouling.

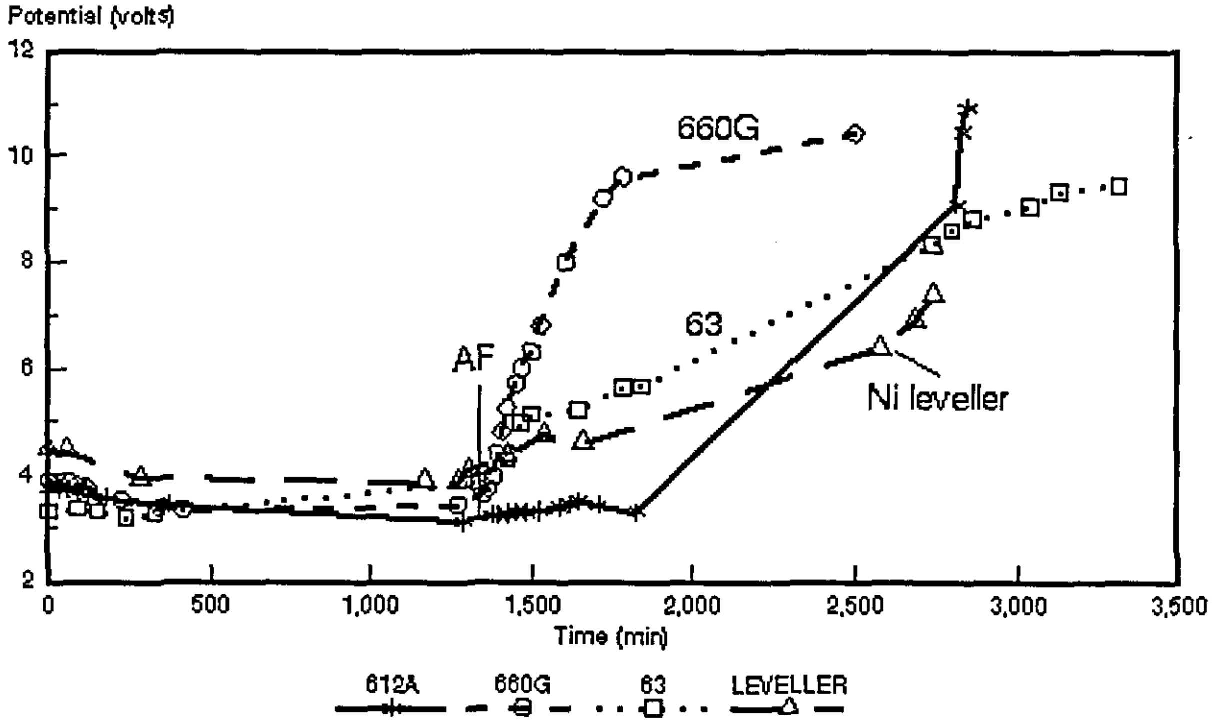

Figure 3.22: Effect of different additives added in nickel plating bath on membrane fouling (Pretoria tap water; 3 000 mg/ℓ NaCl; CD 20 mA/cm^2; Selemion AMV membrane).

3.4.4 The effect of cadmium rinse water on membrane fouling

The effect of cadmium rinse water on membrane fouling using Selemion AMV, Ionics A-204-UZL and Ionac MA-3475 membranes, is shown in Figure 3.23. The cadmium rinse water (cadmium cyanide) had a COD of approximately 1 000 mg/ℓ and a pH of 11. Severe membrane fouling was experienced with the Selemion and Ionac membranes (CD 20 mA/cm^2). However, almost no membrane fouling was experienced with the Ionics membranes. Less fouling was also experienced with the Selemion AMV membranes at a current density of 10 mA/cm^2. A precipitate had formed on the surface of the anion-exchange membrane in all cases where membrane fouling was encountered. Consequently, cadmium rinse water should be pretreated prior to ED treatment to remove the foulants. Activated carbon may be suitable for removing the foulants from solution. This matter, however, needs further investigation.

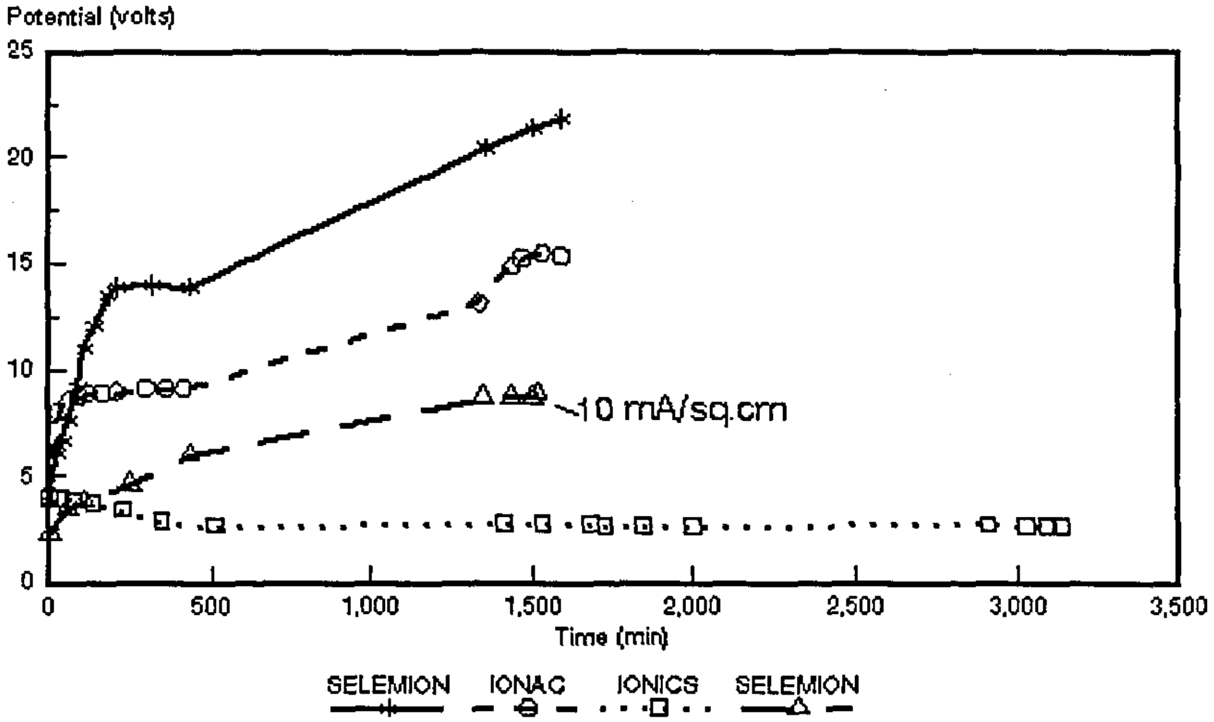

Figure 3.23: **Effect of cadmium rinse water on membrane fouling using Selemion, Ionac and Ionics membranes (Conductivity of rinse water 765 mS/m; CD 20 mA/cm^2).**

Membrane resistances before and after fouling with cadmium rinse water is shown in Table 3.10.

Table 3.10: **Membrane resistances before and after fouling with cadmium rinse water.**

Membrane	Resistance* (ohm·cm^2)	
	Unused	Used
Selemion AMV (20 mA/cm^2)	0,51	51,3
Selemion AMV (10 mA/cm^2)	0,51	15,8
Ionac MA-3475	12,2	28,4
Ionics A-204-UZL	2,5	3,0

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

The membrane resistance data clearly showed that the Ionics membrane was much more resistant towards fouling by cadmium rinse water than the other membranes. Less membrane fouling was also experienced at the lower current density.

3.4.5 The effect of cadmium brightener on membrane fouling

The effect of cadmium brightener on membrane fouling using Selemion AMV, Ionac MA-3475 and Ionics A_204-UZL membranes, is shown in Figure 3.24. The brightener caused fouling of the Selemion AMV membrane at a current density of 20 mA/cm^2. Far less fouling was observed in the case of the Ionac membrane at a current density of 10 mA/cm^2 while almost no fouling was observed with the Ionics membrane at the same current density.

Membrane resistances before and after fouling with the cadmium brightener is shown in Table 3.11.

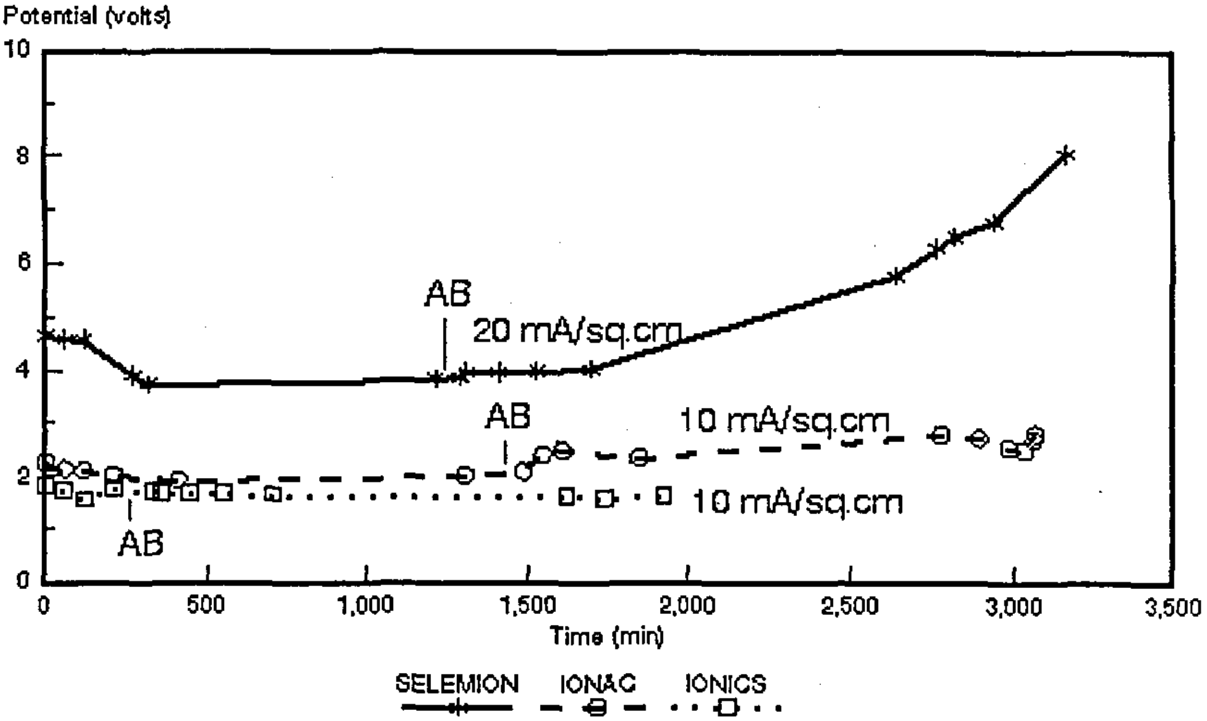

Figure 3.24: **Effect of cadmium brightener on membrane fouling using Selemion, Ionac and Ionics membranes (Pretoria tap water spiked with 3 000 mg/ℓ NaCl and 1,75 mℓ brightener/ℓ; conductivity 562 mS/m). AB: add brightener.**

Table 3.11: **Membrane resistances before and after fouling with cadmium brightener.**

Membrane	Resistance* (ohm·cm^2)	
	Unused	Used
Selemion AMV	0,51	11,2
Ionac MA-3475	10,2	10,2
Ionics A-204-UZL	5,6	6,1

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

Membrane resistance showed that the Selemion AMV membrane was fouled by the brightener at a current density of 20 mA/cm^2. However, the Ionac and Ionics membranes were not affected at a current density of 10 mA/cm^2.

3.4.6 Effect of chromium rinse water on membrane fouling using Ionac MA-3475 membranes

The effect of chromium rinse water on membrane fouling is shown in Figure 3.25. The chrome rinse water fouled the Ionac MA-3475 membranes. Fouling was more severe at the higher current density. The membrane was decolorized after the experiment and was also swollen. Chromium is a strong oxidizing agent and it appeared that the membrane has been attacked by the chromium. The membrane resistance was very high after the fouling experiment showing that the membrane properties had changed. Therefore, more suitable membranes for chromium rinse water treatment by ED should be identified prior to further testing.

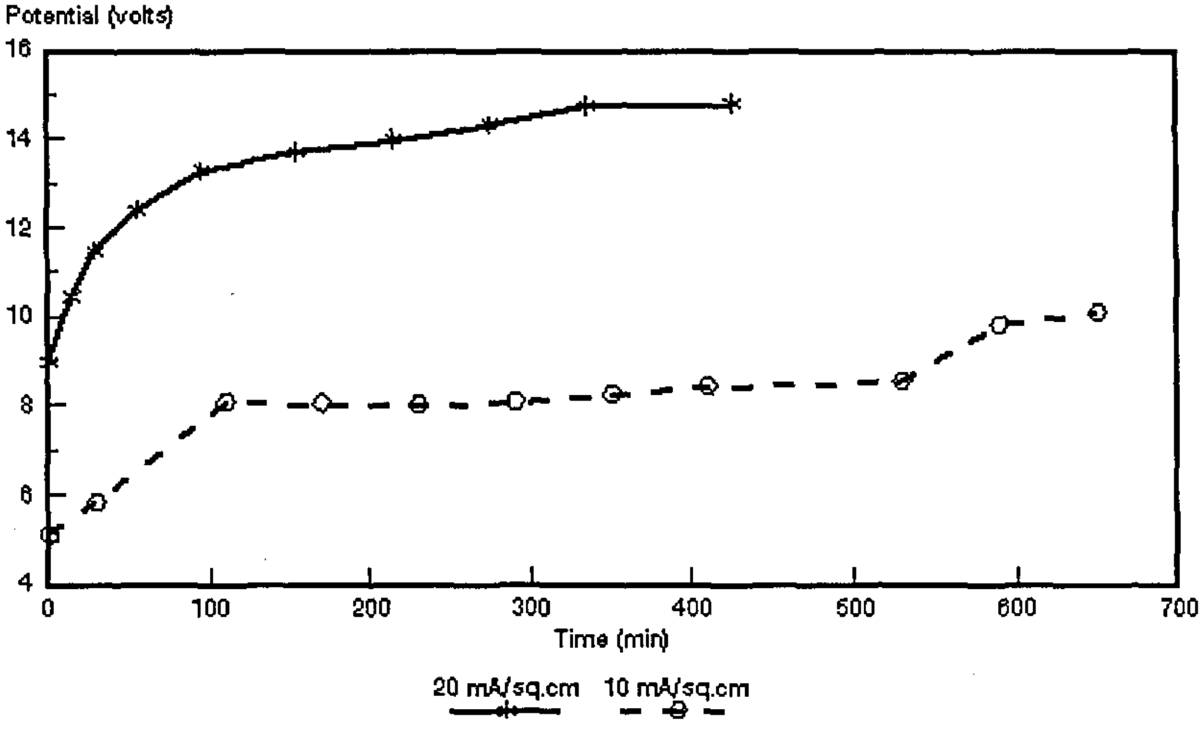

Figure 3.25: **Effect of chromium rinse water on membrane fouling using Ionac membranes (Conductivity 710 mS/m; pH 2,4; CD 20 mA/cm^2).**

3.5 General Discussion

The ion-exchange membrane fouling tests that have been conducted in this study are accelerated fouling tests. The membranes were exposed to much higher concentrations of foulants than would normally take place in practise. However, it should be possible to predict the fouling behaviour of ion-exchange membranes with this method when the membranes are exposed to low concentrations of foulants for a long period , as is happening under practical ED conditions.

The most common ion-exchange membrane foulant encountered in surface waters in South Africa, is humic acid. Humic acid results from the natural decay of organic matter present in surface waters. Humic acids have the potential to foul anion-exchange membranes. Fouling of anion-exchange membranes in ED can affect the economics of the ED process adversely because it shortens membrane life time and it increases the electrical energy consumption of the ED process. It can also affect the quality of the ED product water that is produced, adversely. This is what is happening with the ED process at Tutuka Power Station.

It should be possible to control humic acid fouling of ion-exchange membrane by suitable pretreatment of the feed water to an ED stack and/or by polarity reversal and chemical cleaning of the membranes. Low concentrations of humic acids should be effectively removed from water with ferric chloride coagulation - flocculation or with chlorination(7) prior to ED treatment. It should also be possible to control humic acid fouling of ion-exchange membranes with polarity reversal and chemical cleaning of the membranes with dilute caustic soda solution. The shorter the polarity reversal frequency and the more often the membranes are rinsed with a dilute caustic soda solution, the better are the results expected to be.

It may also be possible to control humic acid fouling of ion-exchange membranes with ultraviolet light oxidation, activated carbon and resin adsorption and by UF treatment. However, more work should be conducted to evaluate the effectiveness of these methods to remove humic acid from water. Preliminary studies had indicated that a UF membrane with a molecular mass cut-off of approximately 40 000 Dalton was not very effective for the removal of humic acid from water. However, UF membranes are available with much lower molecular mass cut-off values (< 10 000 Dalton) and these membranes may have a much better chance to remove humic acid effectively from water. Ultraviolet irridation equipment is also now readily available for water sterilization and possibly for the effective control of humic acid fouling of ion-exchange membranes. Ultraviolet treatment of humic acids in water may result in the fragmentation of the complex humic acid molecule into smaller units which may not be able to foul anion-exchange membranes. This matter and the removal of humic acid by activated carbon and ion-exchange resins, however, warrant further investigation.

Industrial effluents can contain a wide variety of organics that have the potential to foul ion-exchange membranes. The most common ion-exchange membrane foulants encountered in industrial effluents are detergents (DBS), dyes, certain hydrocarbons, phenolic compounds, organic additives added to plating baths, etc(7, 8). However, it may be possible to control fouling of ion-exchange membranes by these compounds by pretreatment with activated carbon and resins. Polarity reversal and periodic salt/caustic cleaning of the membranes should also be capable of controlling such fouling by these compounds. The fouling potential of an effluent, however, should always first be determined in a fouling cell as described in this study, prior to ED treatment, so that the correct pretreatment can be specified for a particular application.

Inorganic fouling of ion-exchange membranes is caused by the precipitation (scaling) of slightly soluble inorganic compounds (such as $CaSO_4$ and $CaCO_3$) in the brine compartments and the fixation of multivalent cations (such as Fe and Mn) on the cation-permeable membranes. Organic anions or multivalent cations can neutralize or even reverse the fixed charge of the membranes, with a significant reduction in efficiency. Fouling also causes an increase in membrane stack resistance which, in turn, increases electrical consumption and adversely effects the economics of the process.

The following constituents are also, to a greater or lesser extent, responsible for membrane fouling in ED(9):

a) Traces of heavy metals such as Fe, Mn and Cu;
b) dissolved gases such as O_2, CO_2 and H_2S;
c) silica in diverse polymeric and chemical forms;
d) inorganic colloids;
e) fine particulates of a wide range of sizes and composition;
f) alkaline earths such as Cu, Ba and Sr;
g) biological materials - viruses, fungi, algae, bacteria - all in varying stages of reproduction and life cycles.

Suspended and colloidal matter, bacteria, fungi, algae, etc., can penetrate the small water passages in an ED stack to affect the water flow through the stack adversely and to foul the membrane surfaces. These substances, however, can normally be easily removed from water with coagulation/flocculation and/or with microfiltration. Barium and strontium present in low concentrations in water can foul ion-exchange membranes because barium and strontium sulphates are sparsely soluble in water. Membrane fouling, however, of these compounds can usually be controlled by ion-exchange pretreatment of the feed water or by polarity reversal. Heavy metals like iron, manganese and copper and hydrogen sulphide can also foul ion-exchange membranes. Membrane fouling by these compounds are usually controlled by oxidation, aeration, pH adjustment and filtration prior to ED treatment. The development of the EDR process has helped to solve the pretreatment problem more readily in that it provides self-cleaning of the vital membrane surfaces as an integral part of the desalting process.

4. CONCLUSIONS

- Membrane fouling by DBS (detergent) increased with increasing current density, increasing DBS concentration and decreased at higher feed salinity levels (2 000 to 5 000 mg/ℓ). Ionics A-204-UZL-386 anion-exchange membranes appear to be much more resistant to DBS fouling than has been the case with Selemion AMV and Ionac MA-3475 membranes. It also appears that membranes fouled with DBS should be partly defouled with a sodium chloride solution. However, it may be very difficult to clean membranes fouled with DBS because the DBS molecule can penetrate the membrane pores. Consequently, it may be better to remove DBS by activated carbon or resin prior to ED treatment. This matter, however, needs further investigation.

- Membrane fouling by humic acid also increased with increasing current density. Ionics A-204-UZL-386 membranes are much more resistant to humic acid fouling than has been the case with the Selemion AMV and Ionac MA-3475 membranes. Polarity reversal and mechanical cleaning of the membrane surface help to control fouling. Caustic soda rinse of the membranes showed that humic acid fouling could be controlled by regular caustic soda rinses. Increased feed flow rate decreased membrane fouling. It took much longer for membrane fouling to take place at a flow rate of 1 600 mℓ/min than at a flow rate of 600 mℓ/min. Consequently, it will be advantageous to use the highest possible flow rate in an ED stack to inhibit membrane fouling. This matter also warrents further investigation under practical ED conditions in an ED membrane stack.

- Ferric chloride coagulation/flocculation of humic acid solution retarded membrane fouling. Consequently, it will be advantageous to remove humic acid from water supplies with ferric chloride and filtration prior to ED treatment.

- Ultrafiltration (40 000 cut-off membranes) has very little effect to prevent membrane fouling by humic acids. Lower molecular mass cut-off membranes (8 000 Dalton) should be evaluated for this purpose.

- Organics extracted from ion-exchange membranes used at Tutuka Power Station can foul ion-exchange membranes. However, it should be possible to control membrane fouling by these organics with polarity reversal and caustic soda cleanings of the membranes. The frequency of polarity reversal should be as short as possible. Cleaning of the membranes with dilute caustic solution should be performed regularly.

- Humic acid is present in the organics extracted from the membranes used at Tutuka Power Station. Consequently, humic acid is responsible for the membrane fouling that is experienced at the Power Station. A relatively low molecular mass compound was also detected in the extracted organics that could play a role in the membrane fouling that was encountered. This compound should be identified and its fouling potential should be evaluated for ion-exchange membranes.

- No difference could be detected in the scanning electron micrographs (SEM) of fouled and unfouled ion-exchange membranes. Further work will be required in this regard.

- Certain biocides can foul cation-exchange membranes. Belclene 350, fouled cation-exchange membranes. This compound has a fixed positive charge. No membrane fouling of the anion-exchange membranes could be detected with the biocide Synperonic NP6. This biocide has a fixed negative charge. The fouling potential of more biocides for ion-exchange membranes should be investigated.

- Spent nickel plating effluent has the potential to foul Selemion AMV membranes. Ionics A-204-UZL-386 and Ionac MA-3475 membranes showed far less fouling than has been the case with the Selemion AMV membranes. Consequently, it will be necessary to pretreat nickel plating effluent prior to ED treatment.

- Nickel plating rinse water has the potential to foul Selemion AMV membranes. However, little fouling took place with Ionac MA-3475 and Ionics A-204-UZL-386 membranes.

Activated carbon treatment of nickel rinse water has the potential to control membrane fouling. This matter, however, needs further investigation.

- Additives added to the nickel plating bath to improve the quality of plating have the potential to foul Selemion AMV membranes. Therefore, these additives should be removed prior to ED treatment. This may be accomplished with activated carbon or resin treatment of the effluent. This matter, however, also needs further investigation.

- Cadmium plating rinse water has the potential to foul Selemion AMV and Ionac MA-3475 membranes. However, almost no membrane fouling was experienced with the Ionics A-204-UZL-386 membranes. Consequently, cadmium plating rinse water should be pretreated prior to ED treatment. This may also be accomplished with activated carbon and/or resin treatment. This matter also needs further investigation.

- Cadmium brightener can foul Selemion AMV membranes. Therefore, the brightener used in the plating process should be removed prior to ED treatment. This may also be accomplished with activated carbon and/or resin adsorption. This matter also needs further investigation.

- Conventional ion-exchange membranes are not suitable for treatment of chromium plating rinse water because the membranes are oxidized by chromium. Therefore, specially designed ion-exchange membranes should be used for chromium rinse water treatment.

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