An application of reverse osmosis process on effluent treatment for the rubber industry

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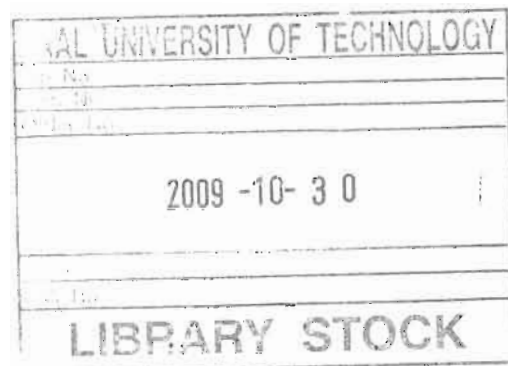
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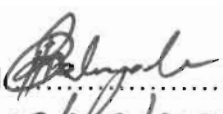
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G. F. Ralengole

DECLARATION

I declare that this dissertation "An application of reverse osmosis process on effluent treatment for the rubber industry" is my original work. All the sources used and quoted in this dissertation have been acknowledged accordingly.

Signed ....

Date ...02/09/2009......

ACKNOWLEDGEMENTS

you for you support, patience and always being there for me even in difficult times.

May God bless all who made this work possible!

ABSTRACT

The methods used to remove potassium sulphate (K_2SO_4) and other impurities contained within Karbochem finishing plant effluent were investigated. Reverse osmosis was explored for this application. The study was conducted in two steps. The first step focuses mainly on the effluent treatment using BW30 flat-sheet as well as BW30-2540 spiral-wound reverse osmosis membranes for the rejection of potassium and sulphate ions. The membranes were supplied by Filmtec. The second step reveals the possible use of potassium sulphate obtained from the brine stream in the fertiliser and fertigation industry by a literature search.

Reverse osmosis study was conducted on a laboratory scale unit using flat sheet membranes and also on a pilot plant scale using spiral wound membrane modules. The tests were conducted at a feed pressure of 20 bar(g) with the membrane rejections being 98% and 99.1% on flat sheet membrane, and 96.9% and 99.4% on spiral wound membrane for potassium and sulphates respectively.

The results show that both membranes have completely desalinated. Significant reduction in the concentrations of all problematic quality parameters, especially of potassium and the sulphate ions was noted.

Granular activated carbon (GAC) bed treatment was recommended for pre-treatment of the effluent prior to exposure of the membrane to avoid organic fouling of the membrane. GAC treatment was tested to illustrate its effectiveness to adsorb the COD's.

The silt density index (SDI) of the effluent was determined and was found to be 0.062 with the maximum recommended SDI of 5 or below for the membrane used.

ROSA design-software was used to simulate the plant design and the results obtained were used to estimate the running costs of the proposed reverse osmosis plant. The reverse osmosis running cost was estimated at R 0.42/m^3 of permeate.

One of the main problems of reverse osmosis membrane technology is that it generates waste in the form of a brine stream, and for this reason the brine stream was proposed for the use in the fertilizer industries as it contained substantial amounts of potassium. The results as discussed indicated that the brine stream could be used for irrigation purposes within Karbochem factory. The requirements of the fertilizer factories in South Africa should be established and the possibilities of developing brine stream to meet the industrial requirements should be evaluated.

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

NOMENCLATURE

A [l.m^{-2}.hr^{-1}.bar^{-1}]   Water permeability coefficient

B [l.m^{-2}.hr^{-1}.bar^{-1}]   Solute permeability coefficient

BQR   Big Quill Resources

C [mg/l]   Concentration

CAN   Calcium ammonium nitrate

COD [mg/l]   Chemical Oxygen Demand

c_w [kg/m^3]   Concentration of water

D_w [m^2/s]   Diffusivity of water

FM   Flow meter

GAC   Granular activated carbon

J [l.m^{-2}.hr^{-1}]   Flow/flux

K   Empirical constant particular to the contaminant

Lp   Hydrodynamic permeability

MF   Microfiltration

MOP   Muriate of potash (KCl)

n   Empirical constant particular to the contaminant

NF   Nanofiltration

NTU   Nephelometric turbidity units

P [Bar]   Pressure

PI   Pressure indicator

R [%]   Rejection coefficient

R [J/mol.K]   Gas constant

R_f Fouling resistance

R_m Hydrodynamic resistance of the membrane

RO   Reverse osmosis

R_T Total hydraulic resistance

R.W.B   Rand water board

SDI	Silt density index
SOP	Sulphate of potash (K_2SO_4)
t [hours]	Total running time
T[K]	Temperature
UF	Ultrafiltration
V_w [m^3/mol]	molar volume
x	Change in molar fraction

Greek letters

Δ	Change
σ [%]	Rejection coefficient of the membrane
∞	Infinity
η [Pa.s]	Viscosity
π [Bar]	Osmotic pressure

Subscripts

F	Feed
f	Final
i	Initial
s	Solute
w	Water

Chapter 1 – Introduction, Goals and Overview of the study

Karbochem, Projects Department (2005) reported that "The Department of Water Affairs and Forestry has indicated the tightening up effluent discharge regulations and levying charges for effluent that is discharged. These charges will depend on the quality of the effluent".

Presently the effluent from Karbochem factory is handled by Sasol for biological treatment. The stringent regulations might result in an increase in effluent treatment costs and it may become viable for Karbochem to do additional in-house water treatment. Potassium sulphate (K_2SO_4) in effluent could be a problem because it is available at levels exceeding discharge limits for both potassium ions and sulphate anions, and ways of removing it, should be investigated.

According to Engelbrecht *et al.* (2006:6) an understanding of the movement of water and solutes across membranes is important in many technical processes. These include a large variety of membrane filtration systems for the treatment of wastewater, membrane distillation in the desalination of seawater, and the delivery of drugs within the human body. Transport processes through the membranes are dynamic and dependent on the membrane structure (porosity), as well as the chemical state of the membrane and the materials being transported.

Membrane filtration is a major technology with many applications. These applications include clarification and fractionation of dairy products, desalination of seawater, purification of potable water, and treatment of a large range of wastewater products. Membrane filtration has the potential to become even

more prominent, provided that fouling of the membranes can be alleviated more effectively (Engelbrecht *et al.* 2006:6).

The principal objective of this investigation was therefore to prepare technically viable proposal to remove K_2SO_4 from the effluent obtained from Karbochem finishing plant. This would be achieved by exploring membrane technology and then doing a literature search on the possible uses of potassium sulphate resulting from the brine, as K_2SO_4 is mainly being imported in South Africa. The study should also ensure that the quality of water conforms to the discharge standards or the water can be reused within Karbochem factory.

All chemical elements used in the graphs and tables of this dissertation, are in ionic form.

Table 1: Summary of the water balance over the Karbochem factory[i].

IN		OUT	
	M^3/d		m^3/d
R.W.B water	650	Storm water	570
Process water	600	Rubber chemical product	100
Steam	585	Rubber reactors	110
Dilution	80	Rubber final treatment	360
TOTAL	**1915**	**TOTAL**	**1140**

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[i] *Information obtained from Keeve Steyn Resources conservation (KSRC) technical report no. 1432/1, page 5*

Table 2: Summary of water standards at Karbochem[ii].

	R.W.B WATER	PROCESS WATER
CONDUCTIVITY [mS/m]	58	
Ph	8.6	7
TDS [mg/l]	420	420
HARDNESS [mg/l CaCO$_3$]	220	10 or less
Na$^+$ [mg/l]	48	210
K$^+$ [mg/l]	9	9
SO$_4^{2-}$ [mg/l]	145	145
Cl$^-$ [mg/l]	51	51
COD [mg/l]	28	28

KSRC (1985:5) summarises the water balances and water standards at Karbochem on Table 1 and 2 respectively. The water movements at Karbochem finishing plant were schematically represented on Figure 1.
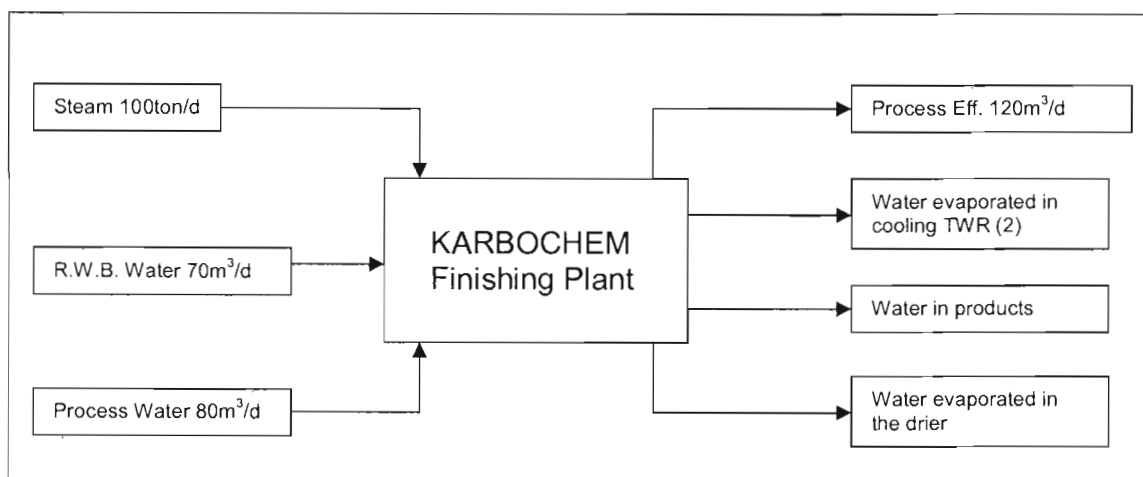
Figure 1: Schematic of water movement at Karbochem finishing plant[iii].

In Chapter 2 of this dissertation a brief introduction to membrane processes is given. Basic principles of membrane technology, activated carbon bed, and adsorption process are also discussed. Applicable legislation to Karbochem and around Vaal Dam, regarding water and wastewater management were also outlined.

Types and advantages of fluid fertilizers were discussed in Chapter 3, with emphasis given to potassium fertilizers. Fertigation and the application thereof were also discussed in Chapter 3.

A research methodology and apparatus used in all experiments were explained in Chapter 4, while Chapter 5 discussed experimental results obtained. Conclusions and recommendations were given in Chapter 6.

Chapter 2 – First Literature Review

2.1 Introduction to Membrane Processes

A lot of work has been done in membrane technology research, now towards the application in various industries for water treatment. UP (2005:2) states that "synthetic membranes have been used many years in many applications such as in blood dialysis and enrichment of uranium isotopes for nuclear fuels. However, it was not until the mid 1960's that perm-selective (semi-permeable) synthetic membranes were developed into a suitable form for economical use for desalination of water. The first membranes were cellulose-acetate membranes with relatively low fluxes and requiring high operating pressures".

Timmer (2001:2) reported already in the late sixties that membrane processes gradually have found their way into industrial applications and they serve as viable alternatives for more traditional processes like distillation, evaporation or extraction. Based on the main driving force, which is applied to accomplish the separation, many membrane processes can be distinguished. An overview of the driving forces and the related membrane separation processes is given in Table 3.

According to UP (2005:7) South Africa is considered as one of the pioneering countries as far as membrane treatment of saline effluents is concerned. Many new potential applications such as desalination of cooling water blow down, treatment and desalination of acid mine water and treatment of textile and other industrial effluents have been initiated and extensively researched in South Africa. As a result, a number of innovative full scale plants have been installed, for example at Sasol, Eskom, Mondi, Columbus Steel, and at a number of mines and industries.

Table 3: Driving forces and their related membrane separation processes

Driving force	Membrane process
Pressure difference	Microfiltration, ultrafiltration, nanofiltration, reverse osmosis or hyperfiltration
Chemical potential difference	Prevaporation, pertraction, dialysis, gas separation, vapour permeation, liquid membranes
Electrical potential difference	Electrodialysis, membrane electrophoresis, membrane electrolysis
Temperature difference	Membrane distillation

Every membrane separation is characterised by the use of a membrane to accomplish a particular separation. The membrane has the ability to transport one component more readily than other because of differences in physical and/or chemical properties between the membrane and the permeating components. Transport through the membrane takes place as a result of the driving force acting on the components in the feed solution (Mulder 1996:14).

Macedonio and Drioli (2008:399) reported that pressure driven membrane operations can be divided into four overlapping categories of increasing selectivity: microfiltration (MF), ultrafiltration (UF), nanofiltration (NF) and reverse osmosis (RO). Timmer (2001:2) agrees with Macedonio and Drioli (2008:399) and further explains each pressure driven membrane process as follows:

- Microfiltration (MF) is characterised by a membrane pore size between 0.05 and 2 µm and operating pressures below 2 bar. MF is primarily used to separate particles and bacteria from other smaller solutes.

- Ultrafiltration (UF) is characterised by a membrane pore size between 2 nm and 0.05 μm and operating pressures between 1 and 10 bar. UF is used to separate colloids such as proteins from small molecules for example, sugars and salts.

- Nanofiltration (NF) is characterised by membrane pore size between 0.5 and 2 nm and operating pressures between 5 and 40 bar. NF is used to achieve a separation between sugars, other organic molecules and multivalent salts on one hand and monovalent salts and water on the other.

- Reverse osmosis (RO) or hyperfiltration. RO membranes are considered not to have pores. Transport of solvent is accomplished through the free volume between the segments of the polymer of which the membrane is constituted. The operating pressures in RO are generally between 10 and 100 bar and this technique is mainly used to remove water.

In general, the driving pressure increases as selectivity increases. Separation is accomplished by MF and UF membranes via mechanical sieving, while capillary flow or solution diffusion is responsible for separation in NF and RO membranes. However, membrane composition combined with solvent and solute characteristics can influence rejection via electrostatic double layer interactions or other hindrances (Macedonio & Drioli 2008:399)

Timmer (2001:2) states that many textbooks have been written about the basic mechanisms and the various applications of these processes. Pressure-driven membrane separation processes, electrodialysis and gas separation are industrially implemented and are generally considered as proven technology. Given the main focus of this study which is pressure-driven membrane separation, no further comments will be given about other techniques.

UP (2005:6) states that a pressure-driven membrane process consists essentially of the following elements:

- Membranes engineered into modules, which form the basis of the process.
- High-pressure pumps to deliver feed water at the required pressure to the modules.
- Pre-treatment process to produce feed water of the required quality that would not damage or foul the membranes.
- Post-treatment process to produce water of the required quality for the specific use of the water.
- Process control equipment, including equipment and chemicals for membrane cleaning and preservation.
- Energy recovery systems, normally only for large-scale RO applications.
- Brine/concentrate and other residuals disposal/recovery systems.

2.2 Legislation

The various water quality standards that the final product needs to conform to were given in Table 1 and the current water quality of Karbochem finishing plant effluent were given in Table 2. The comparison between Karbochem finishing plant effluent and the in-stream water quality guidelines for the Vaal Dam catchment was shown in Figure 2. This figure clearly shows that Karbochem finishing plant effluent would need to undergo in-house water treatment in order to ensure compliance with the discharge standards.
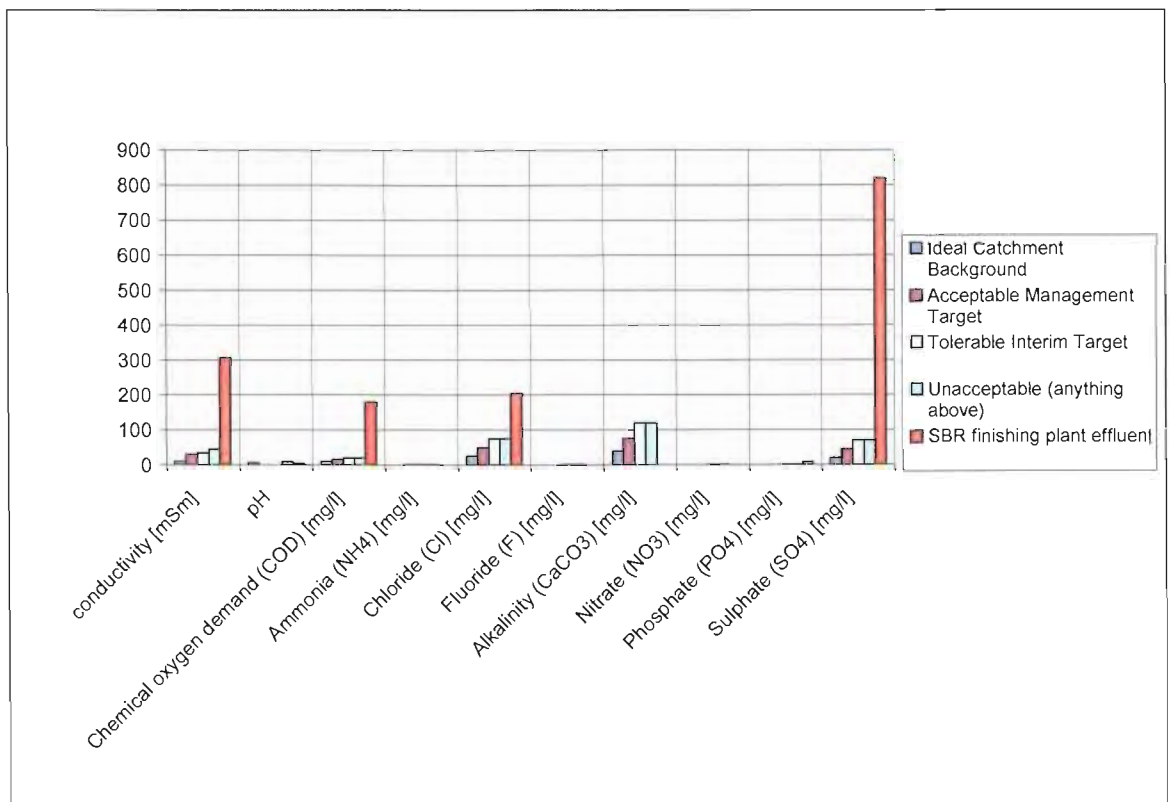
Figure 2: Karbochem finishing plant effluent v/s water quality guidelines [iv]

[iv] *The in-stream water quality guidelines for the Vaal Dam catchment were issued by Rand Water on www.reservoir.co.za*

2.3 Reverse osmosis (RO) and nanofiltration (NF) processes

Nataraj *et al.* (2006: 2352) reported that nanofiltration, in concept and in operation, is much the same as reverse osmosis. However, the key difference is the degree of removal of monovalent ions. NF is not as fine as RO filtration process, and it also does not require the same energy to perform the separation. In RO membrane process, separation performance of the membrane is judged by the percentage rejection (%R) of TDS, COD and other feed components.

Therefore, these parameters could be used as the performance indicators in the treatment of Karbochem effluent, and enable the evaluation of membrane process to be applied.

According to Mulder (1996:297), the difference between ultrafiltration and nanofiltration/reverse osmosis lies in the size of the solute. Consequently, denser membranes are required with much higher hydrodynamic resistance. Such low molecular solutes would pass freely through ultrafiltration membranes. In fact, the nanofiltration and reverse osmosis membranes can be considered as being intermediate between open porous types of membrane (microfiltration/ultrafiltration) and dense nonporous membranes (prevaporation/gas separation). Because of their higher membrane resistance, much higher pressure must be applied to force the same amount of solvent through the membrane. Moreover, the osmotic pressure has to be overcome (the osmotic pressure of seawater, for example, is about 25 bar).

Based on the definitions of RO and NF as discussed on Section 2.1, these two processes are more applicable to this study because they are both used to separate water from salts and other substances. However, nanofiltration cannot be used on this study because it separates multivalent salts on one hand and

monovalent salts and water on the other. The purpose of this project is to separate potassium sulphate and other substances from water, meaning both potassium ions and sulphate ions are required to be on the same side and water on the other.

This will be achieved by RO because its function is to separate impurities from water. This means that, with RO, the impurities will be on one side of the membrane and water on the other. Nanofiltration will not achieve this because it tends to separate sulphate anion on the one side of the membrane and potassium ion and water on the other.

The most suitable technique for this purpose is thus reverse osmosis and will be explored in more detail. However, NF will also be discussed in conjunction with RO in literature review, as their principles are similar. No further comments will be made on the other pressure driven membrane processes.

Macedonio and Drioli (2008:399) states that when a solution containing ions is brought in contact with membranes possessing a fixed surface charge as the membrane (co-ion) can be inhibited. This condition is termed Donnan Exclusion. More specifically, when a solution with anionic arsenate is brought in contact with a membrane possessing a fixed negative charge, the rejection of arsenate may be greater than if the membrane is uncharged.

Karbochem effluent contains potassium ions and sulphate anions, therefore the Donnan Exclusion would occur in the treatment of Karbochem effluent based on the charge of the membranes to be used.
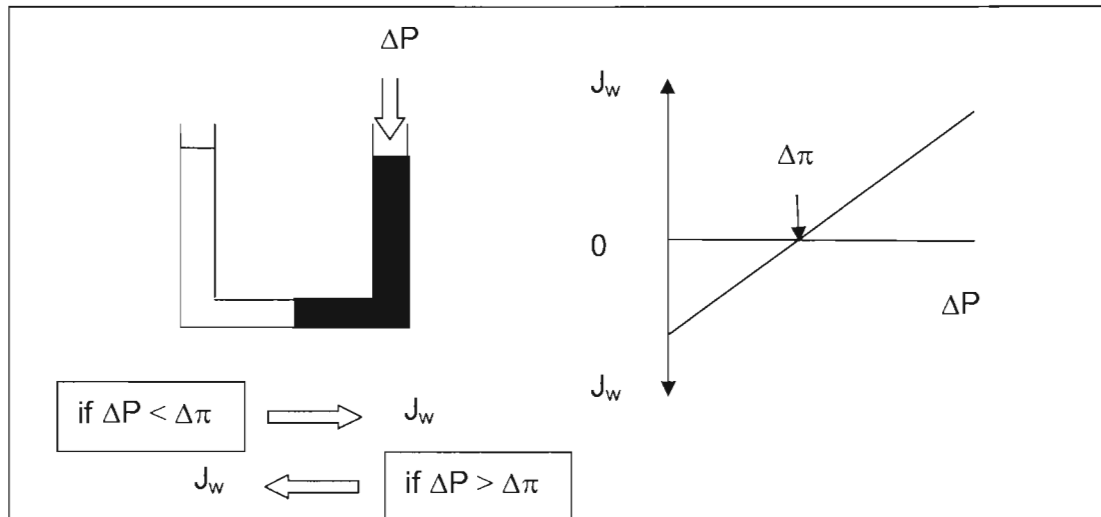
Figure 3: Schematic of water flow as a function of applied pressure

Figure 3 represents a schematic drawing of a membrane separating pure water from a salt solution. The membrane is permeable to the solvent (water) but not to the solute (salt). In order to allow water to pass through the membrane, the applied pressure must be higher than the osmotic pressure. As can be seen from Figure 3, water flows from the dilute solution (pure water) to the concentrated solution if the applied pressure is smaller than the osmotic pressure. When the applied pressure is higher than the osmotic pressure, water flows from the concentrated solution to the dilute solution (Mulder 1996:297).

This implies that, a membrane selected for this study should be permeable to water but not to potassium ions, sulphate anions, and the other impurities contained in the effluent from Karbochem factory. The applied pressure that is

greater than osmotic pressure of this effluent must be applied in order to allow water to pass through the membrane.

According to Weckesser and Konig (2007:3), the water flux J_w through a semi permeable membrane which is proportional to the net driving force in a reverse osmosis process is described by the following Equation:

$$J_w = A (\Delta P - \Delta \pi) \tag{1}$$

where: Jw = water flux $[l.m^{-2}.hr^{-1}]$

                                   A = water permeability coefficient $[l.m^{-2}.hr^{-1}.bar^{-1}]$

                                   ΔP = applied pressure [bar]

                                   $\Delta \pi$ = change in osmotic pressure [bar]

And $\Delta P = (P_F - P_p)$ is the hydraulic pressure difference across the membrane (from feed side to permeate side), $\Delta \pi = (\pi_F - \pi_p)$ is the osmotic pressure difference across the membrane. The "A" is temperature dependent and represents a unique constant for each membrane material type. It is referred to as "A" value, solvent transport coefficient, or water transport parameter. The "A" value (for a specific temperature) is easily obtained experimentally by measuring J_w and $(\Delta P - \Delta \pi)$ and then applying them to Equation 1. Once the "A" value for a specific membrane is known, permeate flux may be predicted for a variety of net driving pressures.

Therefore, the water flux could be modelled by equation 1 when the water permeability, applied pressure, and the change in osmotic pressure of Karbochem effluent are known.

Mulder (1996:298) states that in practice, the membrane may be a little permeable to low molecular solutes and hence the real osmotic pressure difference across the membrane is not $\Delta\pi$ but $\sigma\Delta\pi$, where σ is the reflection coefficient of the membrane towards that particular solute. When $R < 100\%$, then $\sigma < 1$ and Equation 1 become:

$$J_w = A\ (\Delta P - \sigma\Delta\pi) \tag{2}$$

In the description considered here, we assume that the solute is completely retained by the membrane.

The water permeability coefficient "A" (also defined as the hydrodynamic permeability coefficient) is a constant for a given membrane and contains the following parameters.

$$A = D_w.c_w.V_w / R.T.\Delta x \tag{3}$$

Where D_w is diffusivity of water, c_w is concentration of water, V_w is molar volume, R is a gas constant, T is temperature, and Δx is the change in molar fraction. The value of "A", which is a function of the distribution coefficient (solubility) and the diffusivity, lies roughly in the range $3.10^{-3} - 6.10^{-5}\ m^3.m^{-2}.h^{-1}.bar^{-1}$ for reverse osmosis while for nanofiltration the permeabilities range from 3.10^{-3} to $2.10^{-2}\ m^3.m^{-2}.h^{-1}.bar^{-1}$ (Mulder 1996:298).

Weckesser and Konig (2007:3) described the salt/solute flux in a reverse osmosis process by the following Equation:

$$J_s = B\ (c_F - c_p) \tag{4}$$

Where c_F is the salt concentration of the feed, c_p is the salt concentration of permeate. The driving force for the mass transfer of salt is the concentration difference from the feed side to permeate side ($c_F - c_p$). The "B" is often referred to as "B" value, the solute transport parameter, or the salt transport coefficient.

Similar to the water flux, Equation 4 enables the modelling of potassium sulphate when the transport coefficient of potassium sulphate, concentration of potassium sulphate both in the feed and permeate streams are known.

According to Mulder (1996:298) the value of "B" lies in the range $5.10^{-3} - 10^{-4}$ m.h^{-1} for reverse osmosis with NaCl as solute with the lowest value for high rejection membranes. The solute permeability coefficient "B" is a function of the diffusivity and the distribution coefficients as given by Equation 5.

$$B = D_s.K_s / \Delta x \hspace{4cm} (5)$$

From Equation 1, it can be seen that when the applied pressure is increased the water flux increases linearly. The solute flux (Equation 4) is hardly affected by the pressure difference and is only determined by the concentration difference across the membrane (Mulder 1996:298).

Williams (2003:3) states that the solute separation is measured in terms of rejection, R, defined as:

$$R = 1 - c_p/c_F \hspace{4cm} (6)$$

Consequently, as the pressure increases the selectivity also increases because the solute concentration in the permeate decreases. The limiting case R_{max} is

reached as $\Delta P \Rightarrow \infty$. With $c_p = J_s/J_w$ and combining Equations 1, 4 and 6, the rejection coefficient can be written as:

$R = A(\Delta P - \Delta\pi) / A(\Delta P - \Delta\pi) + B$ (Mulder 1996:299) (7)

Equation 7 is very illustrative since the only variable which appears in this Equation is ΔP, assuming that the constants A and B are independent of the pressure.

The pressures used in reverse osmosis range from 20 to 100 bar and in nanofiltration from about 10 to 20 bar, which are much higher than those used in ultrafiltration. In contrast to ultrafiltration and microfiltration, the choice of material directly influences the separation efficiency through the constants A and B (see Equation 6). In simple terms, this means that the constant A must be as high as possible whereas the constant B must be as low as possible to obtain an efficient separation. In other words the membrane (material) must have a high affinity for the solvent (mostly water) and a low affinity for the solute (Mulder 1996:299).

The rejection coefficient is an important parameter as it could be used to predict the separation efficiency of potassium ions and sulphate anions as well as other impurities.

2.3.1 Characteristic flux behaviour in pressure driven membrane operations

According to Gradison *et al.* (2000:166) by assuming that the osmotic pressure is very small the permeate flux (J) can be expressed as:

$$J = \Delta P / \eta.R_T \qquad\qquad (8)$$

where η is permeate viscosity, ΔP is the transmembrane pressure, and R_T is the total hydrodynamic resistance, comprising the membrane resistance (R_m) and the fouling resistance (R_f): $R_T = (R_m + R_f)$. R_m reflects the physical properties of the membrane.

The hydrodynamic resistance R_m is a membrane constant and does not depend on the feed composition or on the applied pressure. The flux-force relationship for pure water is given schematically in Figure 4. However, when solutes are added to the water the behaviour observed is completely different especially in microfiltration and ultrafiltration.
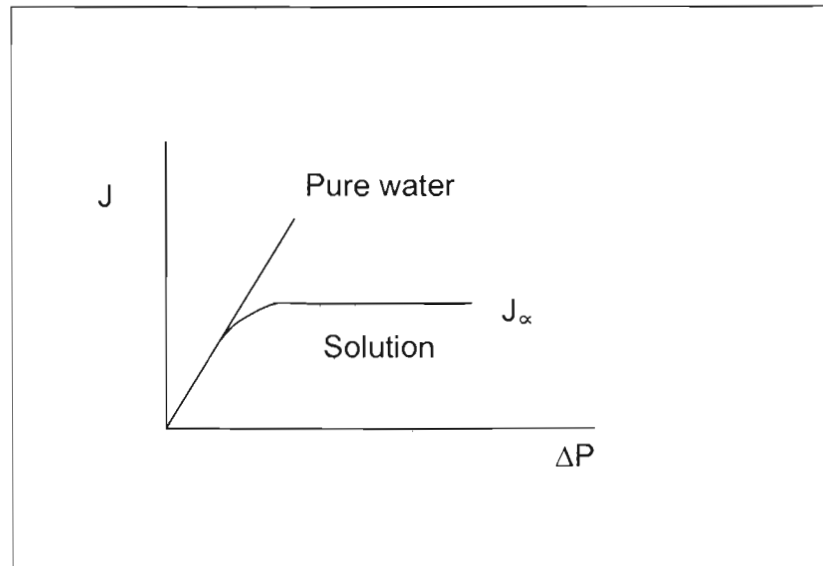
Figure 4: Water flux as a function of the applied pressure.

When the pressure is increased the flux increases, but after a finite (minimum) pressure has been attained the flux does not increase further on increasing the pressure. This maximum flux is called the limiting flux, J_∞(Mulder 1996:427).

2.3.2 Polarization phenomena and membrane fouling

In order to achieve a particular separation via a membrane process, the first step is to develop a suitable membrane. However, during an actual separation, for example, a pressure-driven process, the membrane performance (or better the system performance) can change very much with time, and often typical flux-time behaviour may be observed. This means the flux through the membrane decreases over time. This behaviour is shown schematically in Figure 5 and is mainly due to concentration polarization and fouling (Mulder 1996:416).
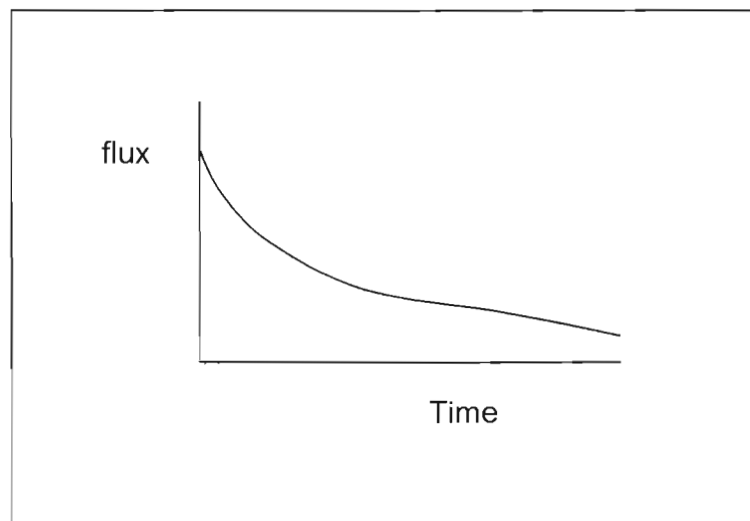
Figure 5: Flux behaviour as a function of time

Flux decline can be caused by several factors, such as concentration polarisation, adsorption, gel layer formation and plugging of the pores. All these

factors induce additional resistance on the feed side to the transport across the membrane. The extent of these phenomena is strongly dependent on the types of membrane processes and feed solution employed. As stated by Mulder (1996:416), the convective flux through the membrane is written as:

Flux = Driving force / Viscosity x Total resistance (9)

This implies that in order to achieve a high water flux, Karbochem effluent would require some pre-treatment prior to membrane treatment as it contains some rubber crumbs and a large amount of suspended solids. These impurities could plug the pores of the membrane and also promote concentration polarisation. All these factors would increase the total resistance and based on Equation 9, the water flux would be reduced.

2.4 Membranes for reverse osmosis (RO) and nanofiltration (NF)

Williams (2003:5) reported that most currently available membranes fall into two categories: asymmetric membranes containing one polymer, and thin-film composite membranes consisting of two or more polymer layers. Asymmetric RO membranes have a very thin, perm-selective skin layer supported on a more porous sublayer of the same polymer. The dense skin layer determines the fluxes and selectivities of these membranes, while the porous sublayer serves only as mechanical support for the skin layer and has little effect on the membrane separation properties.

Mulder (1996:299) gives two different types of membrane with an asymmetric structure and is distinguished as follows:

- (Integral) asymmetric membranes.
- Composite membranes.

In integral asymmetric membranes, both toplayer and the sublayer consist of the same material. These membranes are prepared by phase inversion techniques. For this reason, it is essential that the polymeric material from which the membrane is to be prepared is soluble in a solvent or a solvent mixture. Because most polymers are soluble in one or more solvents, asymmetric membranes can be prepared from almost any material. However, this certainly does not imply that such membranes are suitable for every reverse osmosis application because the material constants A and B must have optimal values for a given application. Thus for aqueous applications, for example, the desalination of seawater and brackish water, hydrophilic materials should be used (high A value) with a low solute permeability (Mulder 1996:300).

Based on theory above, a membrane made from hydrophilic materials and with a low solute permeability should be used for the treatment of Karbochem effluent. These characteristics would promote a better separation of water from potassium sulphate and other impurities.

Perry *et al.* (1997:22-50) states that the highest-rejection membranes are those designed for single pass production of potable water from the sea. The generally accepted criterion is 99.4 percent rejection of NaCl. Some membranes, notably cellulose triacetate fibres are rated even higher. A whole range of membranes is available as rejection requirements ease, and membrane with excellent chlorine resistance and hydrolytic stability can be made with salt rejection over 90 percent.

Although RO membranes have been formed and tested with a wide range of different materials and preparation techniques, the cellulosic polymers (cellulose acetate, cellulose triacetate, etc.), linear and cross-linked aromatic polyamide, and aryl-alky polyetherurea are among the most important RO membrane materials. Asymmetric cellulose acetate membranes continue to enjoy widespread use despite some of their disadvantages given below:

- A narrow pH operating range (4.5 – 7.5) since it is subject to hydrolysis.
- Susceptibility to biological attack.
- Compaction (mechanical compression) at high pressures which results in reduced water flux.
- Low upper temperature limits ($\approx 35^0 C$).

Polyamide and polyurea composite membranes typically have higher water fluxes and salt and organic rejections. They can withstand higher temperature and larger pH variations (4 – 11), and are immune to biological attack and compaction. However, these membranes tend to be less chlorine-resistant and more susceptible to oxidation compared to cellulose acetate membranes. According to Williams (2003:7-8) these can also be more expensive.

Other materials that have been used frequently for reverse osmosis membranes are aromatic polyamides. These materials also show high selectivities towards salts but their water flux is somewhat lower. Polyamides can be used over a wide pH range, approximately from 5 – 9. The main drawback of polyamides (or of polymers with an amide group –NH-CO in general) is their susceptibility against free chlorine Cl_2 which causes degradation of the amide group. Asymmetric membranes as well as symmetric membranes have been prepared from these polymers by melt or dry spinning to obtain hollow fibres with very small dimensions (outside diameters of such hollow fibres < 100 μm). The

membrane thickness of these fibres is about ≈ 20 μm with the result that the permeation rate has decreased dramatically. However, this effect is counteracted by the extremely high surface area in a given volume element, with values up to 30 000 m^2/m^3 (Mulder 1996:300).

2.4.1 FILMTEC Membranes

Dow (2008:14) reported that FILMTEC thin film composite membranes give excellent performance for a wide variety of application, chemical processing and waste treatment. These membranes exhibit excellent performance in terms of flux, salt and organics rejection, and microbiological resistance. FILMTEC elements can operate over pH range of 2 to 11, and are resistant to compaction and are suitable for temperatures up to 45^0 C. They can be effectively cleaned at pH 1 and pH 12. Their performance remains stable over several years, even under harsh operating conditions. Annexure A gives technical information about the FILMTEC membrane used in this study.

Therefore, FILMTEC's thin film composite membranes could be well suited for the application in the treatment of Karbochem effluent as it contains some salts, organics, and is within the recommended pH.

As a general rule, membranes with high water permeability (low feed pressure) also have a higher salt permeability compared to membranes with lower water permeability. The permeability of solutes decreases (the rejection increases) with an increase in the following (Dow 2008:15):

• Degree of dissociation: Weak acids, for example lactic acid, are rejected much better at higher pH when the dissociation is high.

- Ionic charge: For example, divalent ions are better rejected than monovalent ions.
- Molecular weight: Higher molecular weight species are better rejected.
- Nonpolarity: Less polar substances are rejected better.
- Degree of hydration: Highly hydrated species, e.g. chloride, are better rejected than less hydrated ones, for example,. nitrate.
- Degree of molecular branching: For example, iso-propanol is better rejected than n-propanol.

2.5 Membrane modules

RO membranes are exposed to feed water under very high pressure. The membrane being very thin and flimsy must therefore be structurally supported to withstand the high feed water pressures. The unit into which membranes are engineered for use is referred to as a module. This operational unit consists of the membranes, pressure support structures, feed inlet and concentrate outlet ports, and permeate draw-off points (UP 2005:14).

Williams (2003:8) and UP (2005:14) pointed out that the objectives of a membrane module include:

- That it offer mechanical support to the fragile RO membrane even at high operating pressures (up to 8Mpa).
- That the design minimise pressure drop across the module as well as fouling and concentration polarisation.
- That the module be relatively inexpensive and easy to replace in the membrane process.

- To produce a compact module, i.e., one providing a maximum membrane surface per unit volume (maximum packing density).
- To avoid any leak between the feed and the permeate compartments.

UP (2005:14) added that the membranes must also satisfy other requirements such as:

- Ease of cleaning (hydraulic, chemical)
- Ease of assembly and disassembly
- Low hold-up volume

The most common commercially available membrane modules include tubular, spiral-wound, capillary, hallow-fiber, and plate-and-frame elements (Williams 2003:8 & UP 2005:14)

2.5.1 Tubular modules

According to Mulder (1996:469-470), tubular membranes are not self-supporting. Such membranes are placed inside a porous stainless steel; ceramic or plastic tube with the diameter of the tube being, in general, more than 10 mm. The number of tubes put together in the module may vary from 4 to 18, but is not limited to this number. The fed solution always flows through the centre of the tubes while the permeate flows through the porous supporting tube into the module housing. Ceramic membranes are mostly assembled in such tubular module configurations. However, the packing density of the tubular module is rather low, being less than 300 m^2/m^3.

2.5.2 Spiral wound modules

An envelope of two flat-sheet membranes enclosing a flexible spacer (permeate collector) is sealed on three of is edges. The open edge is connected and rolled up onto a perforated tube which carries the permeate. Several "sandwiches" are thus fastened and separated from one another by a feed-side spacer. The spacer not only maintains an open flow channel for feed flow, but also fulfils the very important function of inducing turbulence, thus reducing concentration polarisation. The spacer may be a mesh or it may be a corrugated spacer. The feed flows parallel to the permeate tube axis. The diameter of an element can be as much as 300mm, and its length can be up to 1.5m. Several elements (two to six) can be inserted into a single cylindrical pressure vessel. These are much more compact (700 to 1000m^2/m^3) and cause a lower head loss than tubular or plate-and-frame modules. The spiral-wound module is, however, more sensitive to clogging than open-channel tubular and flat-sheet systems due to the restricted flow channels of spacer. The feed water must therefore comply with relative stringent quality specifications and require a fair amount of pre-treatment, depending on the raw water quality (UP 2005:15).

2.5.3 Capillary modules

Capillary module consists of a large number of capillaries assessed together in a module. The free ends of the fibres are potted with agents such as epoxy resins, polyurethanes, or silicone rubber. The membranes (capillaries) are self-supporting. Two types of module arrangement can be distinguished as follows, according to Mulder (1996:470):

- Where the feed solution passes through the bore of the capillary (lumen) whereas the permeate is collected on the outside of the capillaries.
- Where the feed solution enters the module on the shell side of the capillaries (external) and the permeate passes into the fibre bore (outside-in).

2.5.4 Hollow-fibre modules

According to Williams (2003:10) hollow-fiber elements consists of large number of fine hollow fiber membranes (with an outer diameter up to 200µm) placed in a pressure vessel and the feed flows outside the fibers and permeates through these. These elements have an extremely high packing density and can have high permeate production rates per module. However, these modules are highly prone to fouling and are not feasible for some applications.

2.5.5 Plate and frame modules

These modules are made of stacked flat-sheet membranes and support plates. Their design is derived from that of filter presses. The feed circulates between the membranes of two adjacent plates. The thickness of the liquid sheet is in the range of 0.5 to 3 mm. The packing density of plate-and-frame units is about 100 to 400 m^2/m^3. The plates may be corrugated on the feed side to improve mass transfer. Their arrangement makes it possible to bring about, in parallel and/or in series, circulation. Large assemblies with a surface of up to 100 m^2 can thus be formed. Units are easily disassembled to gain access for manual cleaning or replacement of the membranes. In some of the designs, permeate is collected from individual support plates, which makes the location of faulty membranes a simple matter (UP 2005:16).

2.6 Pre-treatment

To increase the efficiency and life of reverse osmosis and nanofiltration (RO/NF) systems, effective pre-treatment of the feed water is required. Selection of the proper pre-treatment will maximize efficiency and membrane life by minimising the following, as reported by Dow (2008:19):

- Fouling
- Scaling
- Membrane degradation

And by optimizing:

- Product flow
- Product quality (salt rejection)
- Product recovery
- Operating & maintenance costs

Kucera (1997:55) explained that fouling of RO membranes is as a result of suspended solids, microbes, and organic material, particularly long-chained species that deposit on the surface of the membrane modules in an RO system. Hence, these materials typically foul the first stage of an RO system. Microbes, if left untreated, can reproduce and spread, thereby fouling an entire RO system. Once deposited on the membranes, foulants attract additional solids, thereby accelerating any fouling problem that might already exist. In addition to solids, microbes, and organics, soluble heavy metals (such as iron) can foul RO membranes when oxidised within the membrane modules. Oxidation can occur in any stage of an RO system when the pH and dissolved oxygen concentration are suitable.

Karbochem effluent would therefore require pre-treatment since it contains solids and organics that could foul and scale the membrane. The pH and dissolved oxygen concentration of the effluent should be controlled to avoid oxidation soluble heavy metals which would then lead to membrane fouling.

Pre-treatment of feed water must involve a total system approach for continuous and reliable operation. For example, an improperly designed and/or operated clarifier will result in loading the sand or multimedia filter beyond its operating limits. Such inadequate pre-treatment often necessitates frequent cleaning of the membrane elements to restore productivity and salt rejection. The cost of cleaning, downtime and lost system performance can be significant. According to Dow (2008:19), the proper treatment scheme for feed water depends on:

- Feed water source
- Feed water consumption
- Application

Kucera (1997:56) states that pre-treatment to minimise scaling and fouling of membranes includes water treatment techniques such as clarification, filtration, and chemical additives such as coagulants, flocculants, biocides, and inhibitors. The selection of the appropriate technologies for a given feedwater should be site-specific. Several factors, such as capital and operating budgets, manpower, cost of utilities, space availability, and future expansion requirements, in addition to the efficacy of the specific techniques, must be considered in developing a pre-treatment system for a given application.

The type of pre-treatment system depends to a large extent on feed water source (i.e., well water surface water, and municipal wastewater). Industrial and

municipal wastewaters have a wide variety of organic and inorganic constituents. Some types of organic components may adversely affect RO/NF membranes, including severe flow loss and/or membrane degradation (organic fouling), making a well-designed pre-treatment scheme imperative. Once the feed source has been determined, a complete and accurate analysis of the feed water should be made. The importance of a feed water analysis cannot be overemphasized. It is critical in determining the proper pre-treatment and RO/NF system design (Dow 2008:19).

2.6.1 Chlorination and de-chlorination

Chlorine (Cl_2) has been used for many years to treat municipal and industrial water and waste waters to control micro organisms quickly. The effectiveness of chlorine is dependent on the chlorine concentration, time of exposure, and pH of the water. Chlorine is used for treating potable water where a residual chlorine concentration near 0.5 mg/l is commonly used. In an industrial water treatment scheme, fouling of water intake lines, heat exchangers, sand filters, etc., may be prevented by maintaining a free residual chlorine concentration of 0.5 – 1.0 mg/l or higher, dependent on the organic content of the incoming water (Dow 2008:58).

Chlorination for RO/NF pre-treatment has been applied especially where biological fouling prevention is required (i.e., typically for surface waters). Chlorine is added continuously at the intake, and a reaction time of 20 – 30 min should be allowed. A free residual chlorine concentration of 0.5 – 1.0 mg/l should be maintained through the whole pre-treatment line. Dechlorination upstream of the membranes is required, however, to protect the membranes from oxidation (Dow 2008:58).

FILMTEC membranes can withstand short-term exposure to free chlorine (hypochlorite); however, its resistance is limited. The membrane can be used successfully in installations where system upsets result in temporary exposure to free chlorine. Eventually, degradation may occur after approximately 200 – 1000 hours of exposure to 1 ppm concentrations of free chlorine (Dow 2008:58).

The rate of chlorine attack depends on various feed water characteristics. Under alkaline pH conditions, chlorine attack is faster than at a neutral or acidic pH. Chlorine attack is also faster when iron or other transition metals are present either in the water or on the membrane surface. These metals catalyse membrane degradation. Because of the risk of membrane oxidation, chlorine is not recommended for intentionally sanitizing membrane systems (Dow 2008:58).

Continuous chlorination and de-chlorination of feed water has been standard for years. It is believed that the chlorine reacts with the organic matter in the water and breaks it down to more biodegradable fragments. Since there is no chlorine present on the membranes, micro-organisms can grow with an enhanced nutrient offering, unless the system is sanitized very frequently. Therefore, the continuous chlorination/de-chlorination method is becoming less popular (Dow 2008:58).

Instead of continuous chlorination, chlorine is preferably applied off-line to the pre-treatment section periodically. During off-line chlorination, the feed water has to be sent to drain prior to reaching membranes. Before the system goes into operation again, all chlorine containing feed water has to be rinsed out carefully, and the absence of chlorine must be verified, for example, by monitoring of the oxidation-redox potential (ORP) (Dow 2008:58).

When RO or NF membrane is used in the RO/NF process, the feed must be de-chlorinated to prevent oxidation of the membrane. FILMTEC membranes have some chlorine tolerance before noticeable loss of salt rejection is observed. The first sign of chlorine attack on RO/NF membrane is loss of membrane flux followed by an increase flux and salt passage. An acid pH is preferred for better biocidal effect during chlorination. Chlorine attack is also faster at higher temperatures. Since oxidation damage is not covered under warranty, FILMTEC recommends removing residual free chlorine by pre-treatment prior to exposure of the feed water to the membrane. Other oxidizing agents such as chlorine oxide, hydrogen peroxide, ozone, and permanganate are capable of damaging RO/NF membranes also if not used properly (Dow 2008:60).

Residual free chlorine can be reduced to harmless chlorides by activated carbon or chemical reducing agents. An activated carbon bed as explained by Dow (2008:60) is very effective in the de-chlorination of RO feed water according to the following reaction:

$$C + 2Cl_2 + 2H_2O \rightarrow 4HCl + CO_2 \qquad (10)$$

Sodium metabisulfite (SMBS) is commonly used for the removal of free chlorine and as a biostatic. Other chemical reducing agents exist, for example, sulphur dioxide, but they are not as cost-effective as SMBS (Dow 2008:60).

When dissolved in water, sodium bisulphite (SBS) is formed from SMBS:

$$Na_2S_2O_5 + H_2O \rightarrow 2NaHSO_3 \qquad (11)$$

SBS then reduces hypochlorous acid according to:

$$2NaHSO_3 + 2HOCl \rightarrow H_2SO_4 + 2HCl + Na_2SO_4 \qquad\qquad (12)$$
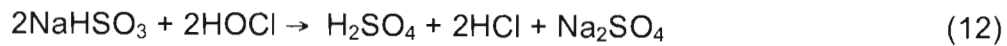
In theory, 1.34 mg of sodium metabisulfite will remove 1 mg of free chlorine. In practice, however, 3 mg of sodium metabisulfite is normally used to remove 1 mg of chlorine (Dow 2008:60).

2.6.2 Colloidal material

Colloidal material in water is present as very small particles just larger than dissolved particles in the range of about 50 – 200 nm and is determined as turbidity. Turbidity is expressed in nephelometric turbidity units (NTU). It is determined by comparing the intensity of light scattered by the water sample to the intensity of light scattered by a standard reference in the turbidity meter. For RO, the turbidity in the feed water is normally specified by manufacturers as < 0.1 NTU. This level can normally only be achieved by means of chemical pre-treatment including coagulation and filtration. UF is excellent to remove turbidity to almost zero (UP 2005:23).

Although turbidity is a good indication of the presence of colloidal material, low NTU values do not always reflect low fouling potential. For this reason, another parameter – the Silt Density Index (SDI) – was developed to give a better indication of the fouling potential of feed water (UP 2005:24).

Fouling indices are determined from simple membrane tests. The water to be tested is passed through a 0.45 μm Millipore filter with a 47 mm internal diameter at 210 kPa to determine the indices. Because of the effects of different filtration equipment, the Millipore filter apparatus is generally used to generate accurate index measurements (UP 2005:24).

The SDI is the most widely used fouling index. The test cell is used to determine three time intervals for calculation of the SDI. The first two time intervals are the times to collect an initial 500 ml and the final 500 ml of water that passes the filter. The third time interval is 5, 10, or 15 minutes and is the time between the collection of the initial and final sample. The 15 minutes interval is used unless the water is highly fouling that the filter plugs before the 15 minutes interval is realized. The interval between the initial and final sample collection is decreased until a final 500 ml sample can be collected (UP 2005:24).

$$SDI = \frac{100\left[1 - \frac{t_i}{t_f}\right]}{t} \quad (13)$$

where: t_i = time to collect initial 500 ml of sample

t_f = time to collect final 500 ml of sample

t = total running time of test

The SDI is a static measurement of resistance that is determined by samples taken at the beginning and at the end of the test. The SDI is not reflective of a continuously operated membrane process. It is, however, generally used to specify the quality of feed water to membranes. Typical values specified by manufacturers vary from around 2 to 5 for spiral wound systems (UP 2005:24). Therefore, the SDI could be used to assess the intensity of Karbochem effluent to foul the membrane. This could be modelled by Equation 13 as discussed by UP (2005:24).

2.6.3 Activated Carbon Bed

The removal of toxic compounds represents a problem, particularly when they are present at low concentrations. The methods commonly employed are either destructive oxidation by means of ozone, hydrogen peroxide, manganese oxides or adsorption by porous solids such as activated carbon, fly ash and natural or pillared clays (Solisio *et al.* 2001: 33).

Carbon has been used as an adsorbent for centuries. Early uses of carbon were reported for water filtration and for sugar solution purification. Activated carbons ability to remove a large variety of compounds from contaminated waters has led to its increased use in the last thirty years. Recent changes in water discharge standards regarding toxic pollutants have placed an additional emphasis on this technology (Carbtrol 2008:2).

According to Solisio *et al.* (2001:33), granular activated carbon (GAC) is considered the most effective adsorbent, especially for those substances containing refractory organic compounds that persist in the environment and resist biodegradation. The granular activated carbon (GAC) could therefore be used to remove the organic compounds from Karbochem effluent prior to feeding into the membrane system.

Kucera (1997:59) states that carbon is generally replaced when exhausted. Regeneration of carbon using acid, caustic, or solvents has had very limited success. Steaming is effective for killing microbiological growth in carbon filters but rather ineffective for removing naturally occurring organics from the carbon.

2.6.3.1 Adsorption

Adsorption is a natural process by which molecules of a dissolved compound collect on and adhere to the surface of an adsorbent solid. Adsorption occurs when the attractive forces at the carbon surface overcome the attractive forces of the liquid (Carbtrol 2008:2).

Solisio *et al.* (2001:33) reported that in the adsorption process, the choice of GAC is justified by its good adsorbing capacity due to the high surface area resulting from the high porosity. Because of these characteristics, it is used in the filtration process of macromolecular organic substances present in wastewaters coming from food or pharmaceutical industries. According to Carbtrol (2008:2) one gram of a typical commercial activated carbon will have a surface area equivalent to 1000 square meters. This high surface area permits the accumulation of a large number of contaminant molecules

2.6.3.2 Adsorption Capacity

The specific capacity of a granular activated carbon to adsorb organic compounds is related to: molecular surface attraction, the total surface area available per unit weight of carbon, and the concentration of contaminants in the waste water stream (Carbtrol 2008:2).

Kucera (1997:59) reported that up to 95% of the organic loading can be removed via adsorption on the medium. Virtually 100% of chlorine can be removed via catalytic destruction. Organic loading is approximately 5 – 15 lb per 100 lb of carbon; chlorine loading is virtually unlimited. This makes activated carbon a suitable adsorbent for the removal of both organic compounds and free chlorine from Karbochem effluent.

The basic instrument for evaluating activated carbon use is the adsorption isotherm. The isotherm represents an empirical relationship between the amount of contaminant adsorbed per unit weight of carbon and its equilibrium water concentration (Carbtrol 2008:2).

This relationship can be expressed in the following form:

$$X/M = K.C^{1/n} \qquad \qquad (14)$$

Where:

X/M	= Amount of contaminant adsorbed per unit weight of carbon.
C	= Concentration of contaminant in the water stream.
K, n	= Empirical constants particular to the contaminant.

The constants K and n are determined by plotting experimental results on log-log paper with the concentration of contaminant on the X axis and the amount adsorbed on the Y axis. The slope of the line developed is equal to 1/n and the intercept equal to K. These dimensionless, empirical constants are useful for comparing the adsorption capacities for different compounds or for assessing the adsorption capacities of various activated carbons (Carbtrol 2008:2). The amount of organics adsorbed from Karbochem effluent per unit weight of carbon could be determined by Equation 14. The same equation should be used also for the free chlorine.

Liquid phase adsorption isotherms have been developed for most commercial activated carbons for a variety of specific compounds. Figure 19 presents a typical adsorption isotherm used to predict activated carbon adsorption capacity.

An isotherm is specific to a particular contaminant and the type of activated carbon used (Carbtrol 2008:2).

2.6.3.3 Design Consideration

As contaminated water stream passes through a confined bed of activated carbon, a dynamic condition develops which establishes a mass transfer zone. This "mass transfer zone" is defined as the carbon bed depth required to reduce the contaminant concentration from the initial to the final level, at a given flow rate, see Figure 6 (Carbtrol 2008:3).

As the mass transfer zone moves through a carbon bed and reaches its exit boundary, contamination begins to show in the effluent. This condition is classified as "breakthrough" and the amount of material adsorbed is considered the breakthrough capacity. If the bed continues to be exposed to the water stream, the mass transfer zone will pass completely through the bed and the effluent contaminant level will equal the influent. At this point, saturation capacity is reached. The saturated capacity is that which is represented by the isotherm (Carbtrol 2008:3).

To take full advantage of the adsorption capacity difference between breakthrough and saturation, several carbon beds are often operated in series. This allows the mass transfer zone to pass completely through the first bed prior to its removal from service. Effluent quality is maintained by the subsequent beds in the series (Carbtrol 2008:3).

When sizing an activated carbon system, it is necessary to choose an appropriate contact time for the wastewater and the carbon. Empty Bed Contact time (EBCT) is the terminology used to describe this parameter. EBCT is

defined as the total volume of the activated carbon bed divided by the liquid flow rate and is usually expressed in minutes (Carbtrol 2008:3).

2.6.3.4 Choice of technologies

Carbon adsorption is an extremely versatile technology. For water treatment applications, it has proved to be the least expensive treatment option. Adsorption is particularly effective in treating low concentration waste streams and in meeting stringent treatment levels (Carbtrol 2008:3).

One of the major attributes of activated carbon treatment is its ability to remove a wide variety of toxic organic compounds to non-detectable levels (99.99%). Its suitability on a specific application will normally depend on costs as they relate to the amount of carbon consumed (Carbtrol 2008:3).
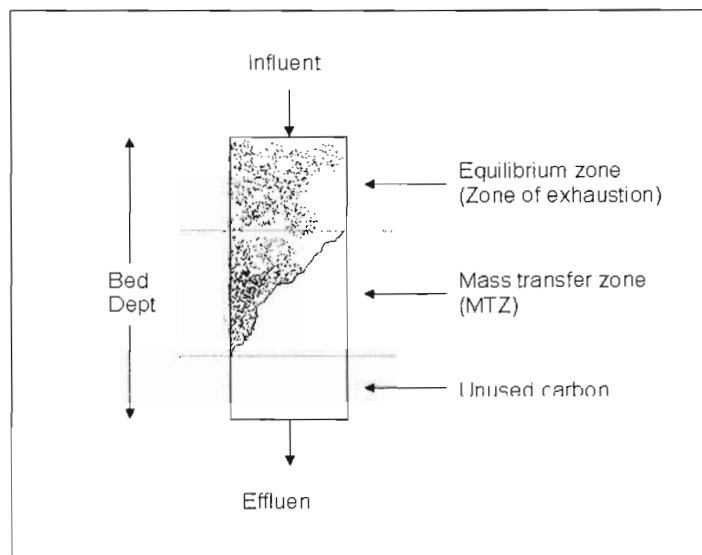
Figure 6: Flow diagram of zones within a carbon bed.

2.7 RO system design

Most RO filtration systems are based on spiral-wound membranes being mounted inside pressure vessels. Such vessels can be arranged in parallel and/or in series to produce a matrix of membranes with a sufficient total membrane surface area in order to obtain a specified total permeate flow and permeate quality at an acceptable cost level. To realise this objective, existing RO design software packages are valuable tools. Such software enables ready simulation of numerous RO configurations or conditions by changing RO parameter values (UP 2005:47).

Several RO design-software packages exist as membrane producers freely offer their RO software to the customer. In Table 4, actual RO software packages from different RO membrane suppliers are displayed. All companies have websites through which the software may be requested. Commercial detail of these and university software are available in Table 4 (UP 2005: 47).

Table 4: RO design-software packages

Company	Membrane name	RO-Softwares	Homepages
Dow	Filmtec	Rosa	www.dow.com/
Hydranautics	Hydranautics	Rodesign, Rodata	www.membranes.com/
Koch	Fluid systems	Ropro 6.1, Costpro	www.kochmembrane.com/
Osmonics	Osmonics, Desal	WinFlows	www.osmonics.com/
Toray, Ropur, Trisep	Toray, ropur, Trisep	WinCarol 1, 2p flows	www.ropur.com/
University	**Membrane name**	**RO-Software**	**Homepage**
RWTH Aachen, Germany	-	-RoDesign	
		-USRRO for Aspen	www.ivt.rwth-aachen.de/

2.8 Conclusion from the quoted first literature review.

Based on above literature review, it can be concluded that a reverse osmosis is a candidate unit process to separate sulphate from the target effluent and potassium sulphate probably retained in the brine would be available for application in the future.

BW30 membranes supplied by Filmtec should used during experimentation. A flux equation presented as Equation 1 can be used to model and evaluate the

process dynamics of reverse osmosis. An activated carbon bed adsorption should be incorporated in the pre-treatment of effluent to reduce concentration of organic materials in the effluent. The ROSA programme designed by Filmtec can be used as RO design and simulation tool in this study.

Chapter 3 – Second Literature Review

3.1 The use of K_2SO_4 in fertilizer industry – Introduction

Potassium hydroxide is used in the batch make-up at Karbochem. The resulting product is used to produce latex which is later coagulated by the addition of 98% sulphuric acid in the finishing plant. At this stage, potassium sulphate is formed as a by-product and is washed away with plant water. Eventually, potassium sulphate formed, ends up in the effluent.

The removal of potassium sulphate from the effluent by reverse osmosis was envisaged in Chapter 2. In this Chapter, the possible uses of potassium sulphate in fertilizer and fertigation industry will be revealed by a literature search in the following Sections.

3.2 Fertilizers

In ancient times farmers discovered that excreta of animals and their decomposing bodies are food for plant life. American-Indians used wood ashes for fertilizer. The Chinese have maintained the fertility of their soil for 5000 years by the application of this principle. Manures have been applied on a large scale to maintain better plant yields (Austin 1984:477). This implies that the fertilizers are required in order to increase the plant yields.

EFMA (1997) states that, mineral fertilizers are made from naturally-occurring raw materials containing nutrients which have normally been transformed into a more plant-available form by industrial processing. Although the number of chemical processes used is relatively small, there is a wide variety of finished products. This diversity facilitates site-specific application, which takes account

of factors such as soil type, the requirements of the crop, and weather conditions, thus making it possible to achieve optimal plant nutrition and minimal environmental impact.

According to Austin (1984:477) the composition of commercial fertilizer mixes are generally expressed in terms of nitrogen as N_2, phosphorus as P_2O_5, and potassium as K_2O. Thus a 30:12:6 formula would contain 30% total nitrogen, 12% available phosphate (P_2O_5 – equivalent to 5.23% P), and 6% soluble potash (K_2O – equivalent to 5% K). These three components (NPK) of fertilizers are available in the brine stream in liquid form (refer to Table 14).

3.2.1 Fluid Fertilizers

The production of fluid fertilizers is a relatively new development in the South African fertilizer industry. This is not the case in some overseas countries such as USA, which is the primary source of fluid fertilizer technology to South Africa. The term fluid fertilizer can be applied to any fertilizing material capable of flowing, but this chapter is restricted to Suspensions and Solutions, the two principal types of fluid fertilizer available in South Africa (Dickinson *et al.* 1989:95).

3.2.1.1 Types of fluid fertilizer

The two types of fluid fertilizers are as follows:

3.2.1.1.1 Suspensions

Suspensions are fluid fertilizers that contain plant nutrients both in solution (solution phase) and as a fine undissolved particles (solid phase). The term

suspended solution implies that the solid phase particles are suspended in the solution phase whose viscosity has been increased by the addition of a thickening agent (usually gelling clay) to prevent the particles from settling out (Dickinson *et al.* 1989:95).

Mixed NPK suspensions rated satisfactory are at least 98% pourable, contain no crystals larger than 850μ with no crystals settled and packed on the bottom of the storage container. Loose crystals and/or synersis are considered undesirable but the suspension is not necessarily rated unsatisfactory if recirculation or air sparging will easily reconstitute the suspension (Dickinson *et al.* 1989:95).

3.2.1.1.2 Solutions

Solutions are fluid fertilizers in which the plant nutrients are dissolved in solution. In other words, solutions are not always clear (Dickinson *et al.* 1989:95).The brine stream from Karbochem effluent treatment might fit well in this category as no solid phase is expected.

The major advantage of solution fertilizer over suspension is the absence of a solid phase which sometimes results in troublesome precipitates settling in storage tanks and blockages in application equipment. The principal disadvantage of mixed NPK & NK solutions is their low plant food content in relation to suspensions. Nitrogen solutions on the other hand generally have relatively high plant food content (Dickinson *et al.* 1989:95).

3.2.1.2 Advantages of fluid fertilizers

According to Dickinson *et al.* (1989:96) the growing use of fluid fertilizer in South Africa can be attributed largely to:

- Ease of handling.
- Product uniformity.
- Labour saving.
- Uniformity of application (the pattern of spray broadcast or band placed fluid fertilizer is very uniform).
- Versatility of application (can easily be placed at any desired depth in the soil and Fertigation).

3.2.1.3 Potassium Fertilizers

Dickinson *et al.* (1989:84) states that the following potassium fertilizers are available in South Africa:

Potassium chloride (KCl) – 50% K

Potassium sulphate (K_2SO_4) – 40% K

Potash magnesia – 21.5% K (5.5% Mg; 16% S)

Potassium nitrate (KNO_3) – 38% K; 13% N

The element potassium (K) occurs in nature in salts and mixtures of salts and minerals (Dickinson *et al.* 1989:84). According to EFMA (1997) the most commonly used product is potassium chloride, otherwise known as murate of potash (MOP), which contains 40% to 60% K_2O. For plants which are particularly sensitive to chlorine, for example tobacco, potatoes, fruits and vegetables, potassium sulphate, which contains 50% K_2O and 18% sulphur, is

recommended. For use on Mg-deficient soils, potassium magnesium sulphate, containing 30% K_2O, 10% magnesium oxide (MgO) and 18% sulphur (S) is recommended.

There are presently two commercial methods of producing potassium sulphate. Magnesium sulphate is used in one process and sulphuric acid in the other. The two processes as indicated by Dickinson *et al.* (1989:86) are as follows:

- The magnesium sulphate process

The mineral kieserite $MgSO_4.H_2O$ is converted to $MgSO_4.7H_2O$ by addition of warm water. When potassium chloride is added, crystals of the double sulphate of potassium and magnesium $K_2SO_4.MgSO_4$ are formed. This product is known as potash-magnesia. When this double salt is further treated with potassium chloride, potassium sulphate crystallizes out, and the very soluble magnesium chloride remains in solution, see Equation 15.

$$K_2SO_4.MgSO_4 + 2KCl = 2K_2SO_4 + MgCl_2 \qquad (15)$$

- The sulphuric acid process

In this process in which sulphuric acid provides the sulphate ions, use is made of natural crude salt which does not contain magnesium sulphate. Potassium chloride is heated together with sulphuric acid in special ovens at up to 350°C, and eventually to 850°C, in order to complete the conversion to potassium sulphate, with hydrochloric acid as by-product. The following chemical reactions take place:

$$KCl + H_2SO_4 = KHSO_4 + HCl \qquad (16)$$
$$KCl + KHSO_4 = K_2SO_4 + HCl \qquad (17)$$

3.2.2 Potassium Sulphate

According to Tandon and Roy (2004), sulphate of potash (SOP) is an important source of potassium and sulphate. About 50% K_2O and 18% sulphur and they are both are in the form that is readily available to the plant. These are particularly suitable for crops sensitive to chlorine in stead of potassium chloride. SOP has a very low salt index (46.1) as compared to 116.3 in case of MOP on material basis. It also stores well under damp conditions. SOP should not be mixed with calcium ammonium nitrate (CAN) or urea.

Standard specifications of potassium sulphate (SOP) based on the Indian experience are given in Table 5. Typical internationally accepted technical specifications of SOP include maximum moisture content of 1% by weight and maximum sodium content as NaCl of 1% by weight. In addition, particle size specifications are that 90% of material shall pass through 4mm IS sieve and be retained on 1mm IS sieve. Further, not more than 5% material shall be below 1 mm size (Tandon & Roy 2004).

As stated by Alley and Wysor (2005), potassium sulphate is widely used in tobacco and potato production. It is a dry granular product that is water soluble and is an excellent sulphur source as well as K source.

Table 5: Standard specifications of potassium sulphate (SOP)

Moisture, percent by weight, maximum	1.5
Potash (as K_2O), percent by weight, minimum	50
Sulphur (as S), percent by weight, minimum	17.5
Total chlorides (as Cl), percent by weight (on dry basis), maximum	2.5
Sodium (as NaCl), percent by weight (on dry basis), maximum	2

3.2.3 Straight fertilizers

All fertilizers contain at least one major plant nutrient. The term 'straight fertilizers' is used in connection with fertilizers which have a declarable content of only one of the major plant nutrients, namely nitrogen, phosphorus and potassium (EFMA 1997). The brine stream also has a potential of being used as a straight fertilizer since it contains a declarable content of potassium above those of nitrogen and phosphorus (refer to Table 14).

3.2.4 Fertigation

The correct combination of water and nutrients (macro and micro) is imperative for increased product yield as well as product quality. Waterman (2001:1) defines fertigation as the application of fertilizers through an irrigation system by the use of "T" tape, drippers, micro-jets, sprinklers, etc. Therefore, the brine stream could be used in fertigation if it contains nutrients in right quantities.

According to Dickinson et al. (1989:120) although fertigation is a relatively new concept in South Africa it has been applied in various forms elsewhere since the turn of the century. Attention will be given here mainly to the application of

fertilizers through irrigation systems, but the basic principles also apply to the use of herbicides, insecticides, fungicides and acids in irrigation.

Chemicals applied in this manner must meet the following requirements as listed by Dickinson *et al.* (1989:120):

- Be non-corrosive and not cause blockages;
- Must be safe for field use;
- Not lower yields;
- Be water soluble and compatible;
- Not have a detrimental effect on the salts and other chemicals in the irrigation water.

3.2.4.1 Advantages of Fertigation

- Very accurate and specific fertilization. Macro- and micro-nutrients can be applied separately or in combination to satisfy very specific requirements of plants.
- Deficiency symptoms can be corrected at a late stage when crops are tall.
- Fertilizers and other chemicals can be combined.
- Leaching in sandy soils can be limited.
- Higher usage efficiency – less fertilizer can often give the same or higher yields.
- Prevent soil compaction due to less traffic.
- Greater flexibility to reduce risk. Fertilization can be discontinued at any stage, for example, after hail, wind or insect damage.
- Computerization is very practical.
- Higher management level often leads to higher yields.
- Less theft of fertilizer (Dickinson *et al.* 1989:120).

3.2.4.2 Application of Fertigation

The accuracy of application will always be influenced by the quality of design and management of the irrigation system. The distribution of chemicals will obviously be as accurate as the distribution of water. Even the level of water distribution must never be taken for granted and is influenced by several independent factors (Dickinson *et al.* 1989:121):

- Climatic factors – wind speed and direction.
- Sprinkler variables – nozzle size, angle, rotation tempo, type of nozzle and the pressure at the nozzle.
- Distribution variables – sprinkler spacing on laterals, spacing of laterals, height of sprinklers above ground or crop, stability of riser pipes, pressure differentials across the system.
- Management variables – time of irrigation, tempo of movement of laterals and sprinklers over the area by mobile systems.

A lowering of pressure or increase in the speed of the system or a decrease of the application rate of water will have a detrimental effect on the coefficient of uniformity (CU) of mobile systems (Dickinson *et al.* 1989:121).

One nozzle with a poor application will have a strip or circle effect on either over (injurious) or under application of chemicals (Dickinson *et al.* 1989:121).

Wind is an important factor to be considered. Wind speed with permanent systems should be below 8 km/h, whilst 24 km/h is the maximum for mobile systems. Anything above these speeds or during periods of gusty winds, irrigation should be ceased (Dickinson *et al.* 1989:121).

3.2.4.3 Injection methods in fertigation

Various methods have been devised to introduce fertilizers and other chemicals into irrigation systems. The final choice must ultimately be with the farmer. The following can be used; venture systems, pressure displacement tanks, electrical and water driven pumps. The latter two are probably the most accurate and reliable with the least trouble. It is however possible that the correct application will provide the same accuracy with the first two options (Dickinson *et al.* 1989:121).

Furthermore, a mixing tank and storage tank is required. Mild steel, stainless steel, glass fibre, polyethylene and rubber are some of the more popular materials used by tank manufacturers. Tank choice can be based on quantity, type of chemicals and length of storage. These factors will determine the size and materials from which the tanks are to be made, and thus ultimately influence the price in cents per litre of the final product (Dickinson *et al.* 1989:121).

3.2.5 Fertilization

The principle of fertilization is based on the general S-growth curve of plants. This generally applies to all plants and crops with adjustments for time and quantity of fertilizer applications. For the sake of generalisation the programming of Fertigation can be done in three phases as designated on the graph, with appropriate percentages of the NPK balance after deducting planter fertilizer (Dickinson *et al.* 1989:123).

3.2.5.1 Potassium (K)

According to BQR (2007) potassium is an immobile nutrient in the soil, moving slowly for only short distance (by diffusion) through moisture films on soil particle surfaces. It can leach in very sandy or organic soils, but seldom leached out of the crop root zones.

Nearly every aspect of plant growth is dependent upon adequate supply of potassium (K). Potassium helps to improve plant's disease resistance, tolerance to water stress, winter hardiness, tolerance to crop pests, and increased efficiency of (N) use (BRQ 2007).

Providing adequate amounts of potassium in fertilizer to meet current crop needs and to build soil (K) levels is critical to sustain profitable crop production. This essential nutrient is required in greater amounts than any other nutrient except (N) and some crops take up more (K) than (N). Only when the soil is adequately supplied with (K) can optimum crop production be sustained (BRQ 2007).

Problems are seldom if ever encountered with this nutrient. The general sources of K namely potassium sulphate (K_2SO_4), potassium chloride (KCl) and potassium nitrate (KNO_3) are fairly soluble in water (see Table 6). Temperature must always be taken into consideration. A decrease in temperature overnight should be compensated for to prevent crystallization (Dickinson *et al.* 1989:125).

When potassium is applied, the cation, K^+ is absorbed by the clay complex. When the clay becomes saturated movement of K^+ can occur until it is eventually adsorbed by another exchange complex. Plants require substantial amounts of K and on a dry mass-basis; leaves should contain about 1% or more

K. The 1% will vary for different crops and must be regarded as a guideline. Generally, it has been found that a 1:1 N:K mixture is very good for fertigation. Potassium has however not received much attention in the RSA and could be investigated in the fertigation context (Dickinson *et al.* 1989:125).

Table 6: Solubility of potassium salts in water

Temperature [^{0}C]	Solubility in water [g/kg]		
	KNO_3	KCl	K_2SO_4
0	133	276	74
10	209	310	92
20	316	340	111
30	458	370	130

3.2.5.2 Sulphur (S)

Sulphur fulfils several important functions in the plant as stated by BQR (2007). There can be no protein without (S). This nutrient is needed to make chlorophyll, enzymes, vitamins and other essential compounds in the plant. Sulphur deficient plants are often uniformly chlorotic, stunted, thin-stemmed, and spindly.

Sulphur is present in SOP in the sulphate ion (SO_4^{2-}) form. The sulphate is metabolized by the plant, and the (S) becomes an integral part of plant compounds, vital to plant metabolism (BQR 2007). Therefore, the brine stream could also serve as a source of sulphur when used in the fertiliser and fertigation industry.

3.2.5.3 The agricultural advantages of SOP

It supplies the crop with both (K) and (S). It has the lowest salt index among conventional potash fertilizers. Preferred for (Cl) sensitive crops such as potatoes, canola, tomatoes, clover, peas, beans, oats, wheat, alfalfa, tobacco, cool season grasses, ornamental plants, etc. It is compatible with late (K) applications just before planting. Recognition of the increasing needs for supplemental sulphur in crop production, combined with the established roles of (K) and (S) in plant physiology makes SOP a component of choice in balanced plant nutrition (BQR 2007)

3.3 Conclusion from the quoted second literature review

The brine stream from reverse osmosis process should be assessed for the concentrations of potassium and sulphates. If potassium and sulphates are available in 50% K_2O and 18% sulphur, then the brine stream could be used for crops that are sensitive to chlorine as stated by Tandon and Roy (2004), as well as in BQR (2007). However, brine stream might require additional treatment to remove other impurities present. If dry granular potassium sulphate is desired, the standard specifications given in Table 5 should be used as a guide and the product can be used in tobacco and potato productions. If this product does not comply with any of afore mentioned specifications, it could also be considered for irrigation purposes at Karbochem factory.

Chapter 4 – Research Methodology

4.1 Membrane selection trial

In Section 2.4.1, Dow reported that FILMTEC thin film composite membranes give excellent performance (in terms of flux, salt and organics rejections, and microbiological resistance) for a wide variety of application, chemical processing and waste treatment. It was also reported that FILMTEC elements can operate over pH range of 2 to 11 and are resistant to compaction and are suitable for temperatures up to 45^0 C.

For this reasons mentioned above a simulation was done using the ROSA software to evaluate the rejection of potassium ions and sulphate anions by various Filmtec membrane modules. The trial was done using the following Filmtec membrane modules: SW30-2540, BW30-2540, TW30-2540, LP-2540, XLE-2540, NF200-2540, and NF90-2540. All these modules were manufactured from polyamide thin film composite. The simulations were performed with the following process conditions: feed pressure and temperature of 15 Bar and 25°C respectively. The data was used to select a membrane module to be tested on a pilot scale. The results of this simulation were presented and discussed in Section 5.1.

4.2 Laboratory scale RO unit – Flat sheet membrane evaluation

Annexure A recommends Filmtec brackish water reverse osmosis membrane elements for consistent, outstanding system performance in light industrial applications. In this experiment, a laboratory scale experiment was conducted with the aim to evaluate the rejection of both potassium and sulphate ions by BW30 flat sheet membrane on the effluent obtained from Karbochem finishing

Figure 8 illustrates the cross-sectional view of a dead-end module. This Figure describes the fittings and the internals of a dead-end module.
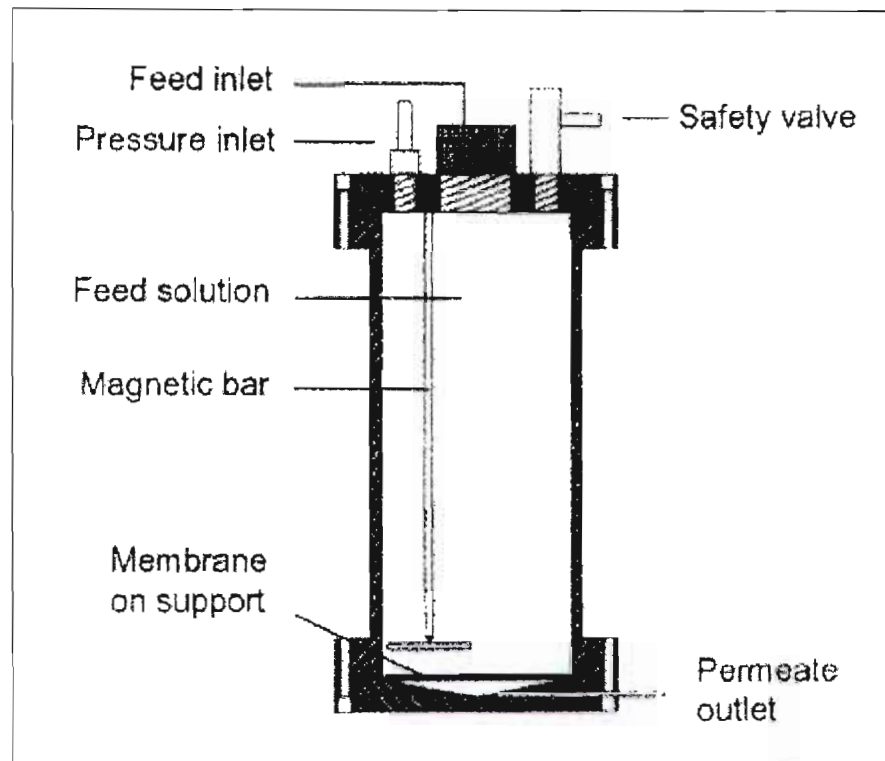
Figure 8: Schematic representation of flat-sheet module (drawing adopted from Krieg *et al.* (2004:206)).

4.2.2 Experimental Procedure

The membrane was immersed in distilled water for approximately 1 hour before the experiment was started. A fixed volume (approximately 1500 ml) of effluent sample from Karbochem Finishing plant was filtered to remove rubber crumbs and other suspended solids prior to feeding into the RO unit. Applied pressure of 2000 kPa was introduced to the unit, using pressurized nitrogen gas as a driving force. A magnetic agitator was used to homogenise the feed solution and prevent premature blinding or concentration polarisation. The agitator speed

was set at 500rpm. This experiment was performed at room temperature. Samples of 500ml of the feed, permeate and brine solutions were collected and then sent to CSIR water laboratories for elemental analysis. The methods of analysis used at CSIR were detailed on Annexure D.

4.3 Pilot plant tests – Spiral wound element evaluation

Following the results obtained from experiment with BW30 flat sheet module, the same experiment was performed using a BW30-2540 element. This was to evaluate the performance of this polymer membrane on a larger scale. A BW30-2540 element was designed to achieve the following:

- Active area = 2.6 m^2
- Applied pressure = 15.5 Bar
- Permeate flow rate = 3.2 m^3/d
- Stabilized salt rejection = 99.5 %

The difference between the two experiments was that, one used a flat sheet membrane element while the other used a spiral wound membrane element. Spiral wound membrane element has got a larger surface area than the flat sheet membrane element used, thereby allowing for higher permeate flux .

4.3.1 Apparatus

The apparatus used for this experiment were as follows:

- 100 litres Plastic tank used as a reservoir.
- 1 x Mono pump.
- Pressure relieve valve set at 2500 kPa.

- Ball valves for flow control.
- Pressure indicators (PI).
- Feed and permeate flow meters (FM).
- 2,5 inch membrane module fitted with BW30-2540 membrane element.
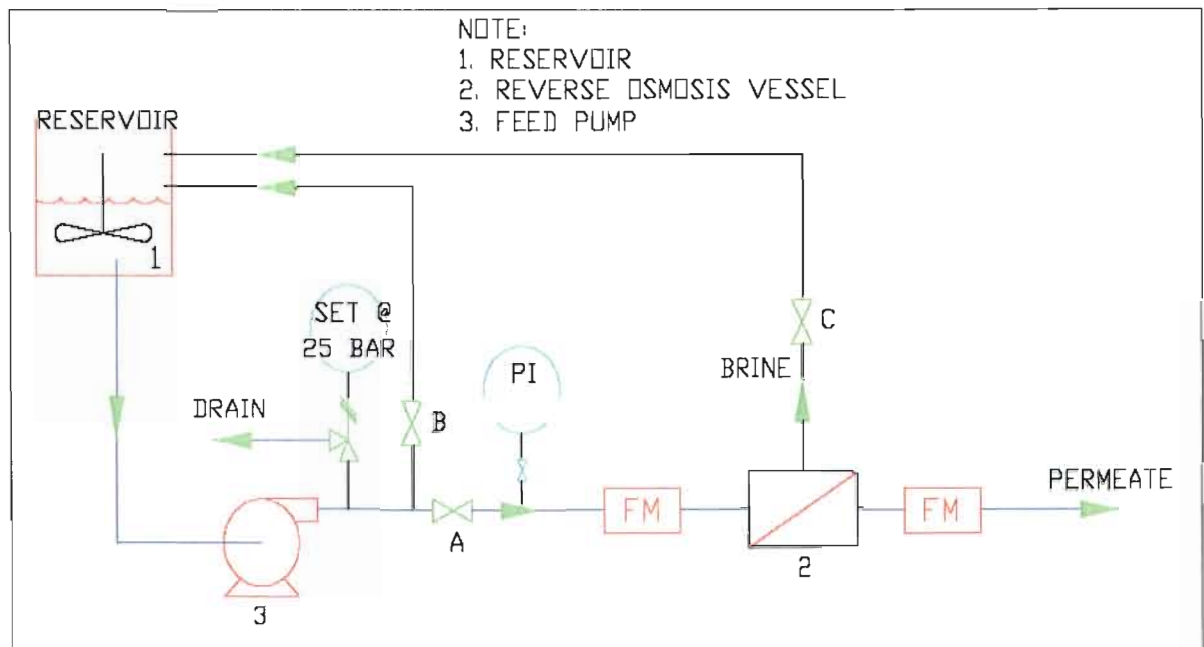
Figure 9: Experimental set-up for BW30-2540 membrane module in pilot plant (AUTOCAD drawing).

4.3.2 Experimental procedure

A sample of 40 000 ml effluent from Karbochem Finishing plant was first filtered with a filter paper to remove rubber crumbs and other suspended solids. This was done prior to feeding the effluent into the reservoir indicated on Figure 9. BW30-2540 membrane element (effective membrane area is 2.6 m^2) was fitted into a stainless steel pressure vessel as labelled 2 on Figure 9. A sample of 500 ml was taken from the reservoir to represent the feed solution. The pump was started and the feed pressure to the membrane was regulated at 2000 kPa

using ball valves labelled B and C on Figure 9. The bucket and stopwatch method was used to determine the streams flow rates and the following were obtained:

Feed = 11.133 l/min
Permeate = 0.263 l/min
Brine = 10.87 l/min

Effluent was stirred constantly and the system was allowed to run for approximately 40 minutes before 500 ml permeate and brine samples were taken. These experiments were performed at room temperature. The feed, permeate and brine samples were sent to CSIR water laboratories in Pretoria for the elemental analysis. Refer to Annexure D for the analytical methods used at CSIR. The same experiment was repeated. However, in the second time the experiment was allowed to run for 1 hour before 500 ml permeate and brine samples were taken.

4.4 Silt Density Index (SDI) tests

The silt density index (SDI) of the effluent was measured to establish the fouling potential of the effluent. The same apparatus as in Section 3.2.1 were used and the procedure was as follows:

4.4.1 Experimental procedure

The feed pump was started and feed pressure regulated at 2000 kPa using ball valves labelled A and B on Figure 9. The system was allowed to run continuously for approximately 30 min at the feed rate of 11.133 l/min before the first permeate sample was taken. A sample of 500 ml was collected from

permeate stream and the time taken was recorded. The system was allowed to run continuously for 15 min after the first sample was collected and before the final sample was collected. The final 500 ml sample was then collected and the time taken was noted. The SDI was calculated using Equation 13. This procedure was repeated twice to check the accuracy of the results.

4.5 Activated carbon treatment

This experiment was performed to demonstrate the effectiveness of activated carbon treatment on the adsorption of COD's and free chlorine. This technology was recommended on literature to be used in the pre-treatment of the effluent. Granular activated carbon (GAC) with a porosity of 0.6 and density of 50g/100ml was used. Cactus Carbon Ltd situated in Midrand, South Africa supplied this activated carbon.

4.5.1 Apparatus

Figure 10 is a photograph of the experimental setup used. This Figure also defines each apparatus used.
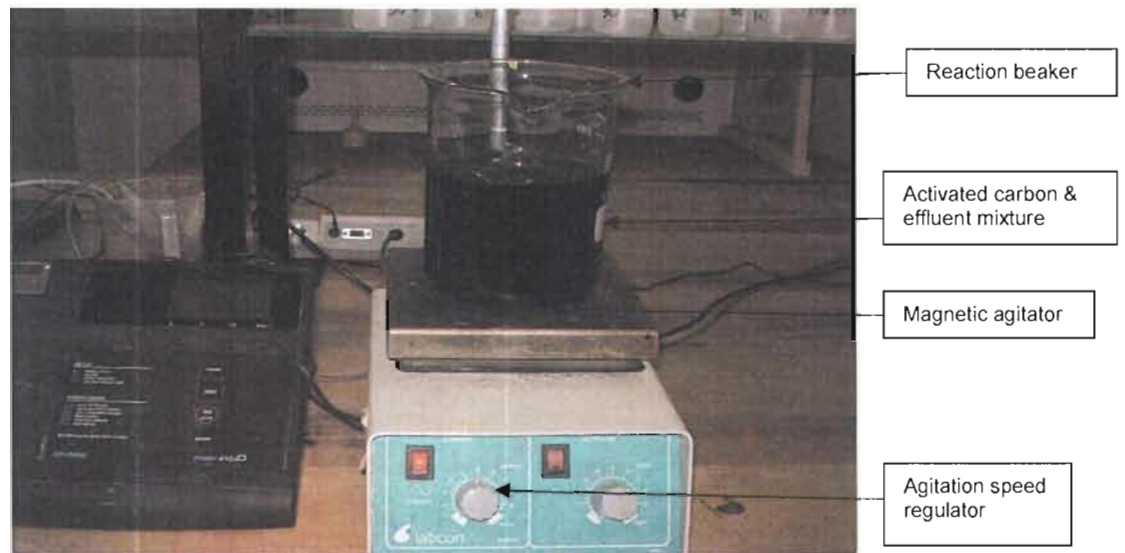
Figure 10: Apparatus used for activated carbon adsorption

Figure 11 below, shows the granular activated carbon (GAC) that was used in this experiment.
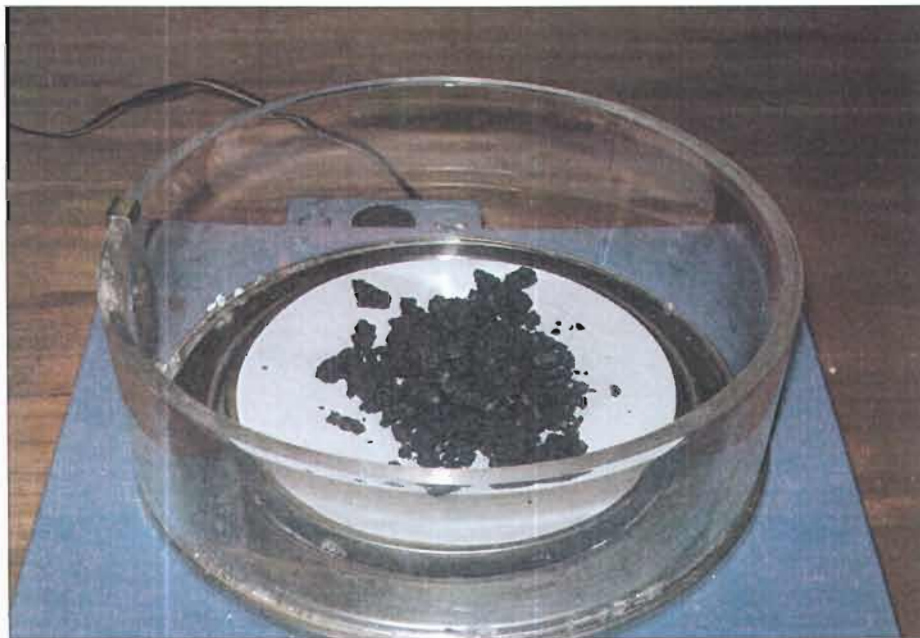
Figure 11: Granular Activated Carbon

4.5.2 Experimental Procedure

A sample of 600 ml effluent was poured into the reaction beaker. 10 g of granular activated carbon was weighed and then poured into the reaction beaker. Magnetic agitator was started and maintained at 500 rpm. The process was allowed to run for about 30 minutes at a room temperature. The same procedure was repeated varying the mass of granular activated carbon to 20 g and 30 g respectively. The slurry was then filtered to remove spent activated carbon.

4.6 Filtration process

Filtration was applied to separate the slurry into filtrate and spent activated carbon.

4.6.1 Apparatus

The photograph on Figure 12, illustrates the experimental setup and apparatus used.
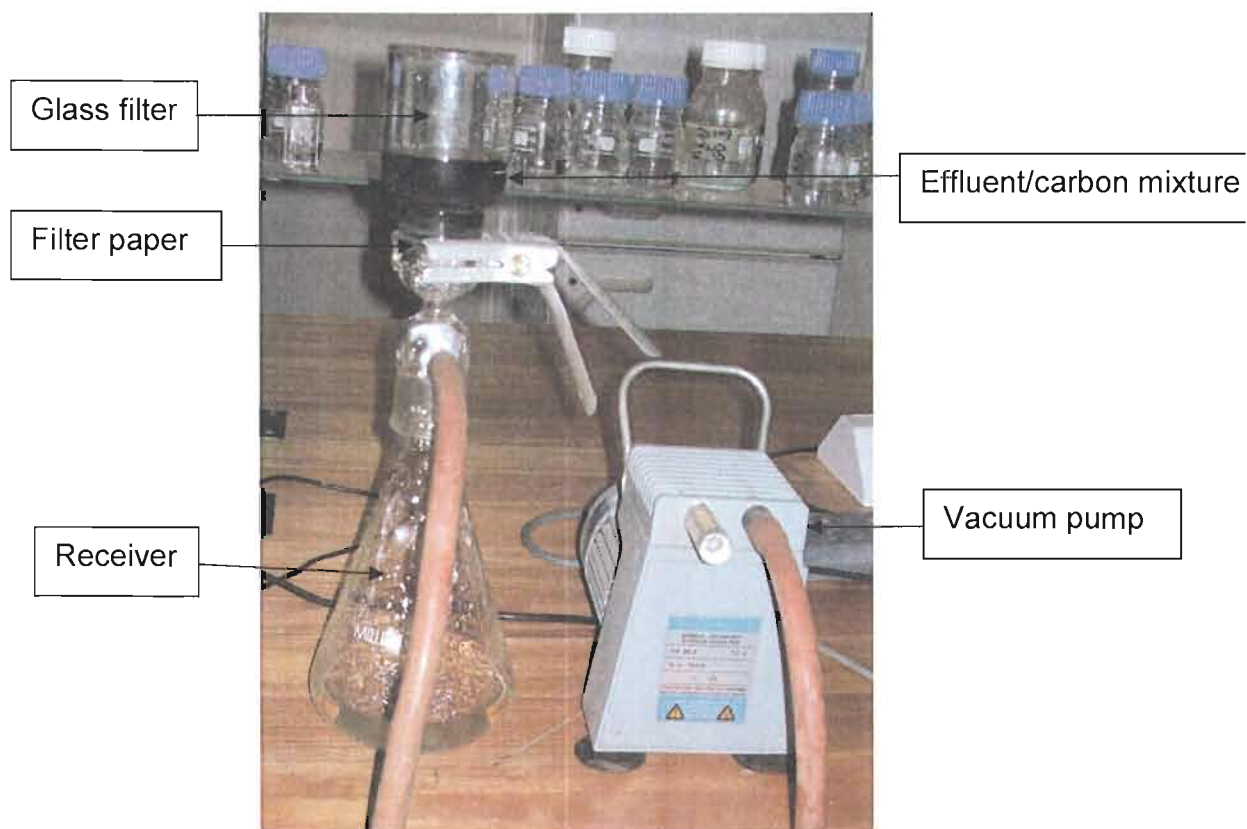
Figure 12: Apparatus used for filtration

4.6.2 Experimental Procedure

The slurry was filtered through the filter paper and filtrate collected in the receiver while spent activated carbon settled on the filter paper. Filtrate samples were then sent to CSIR water laboratories for the analysis of COD and free chlorine. The results were obtained and reported in Table 9. Refer to Annexure D for the analytical methods used at CSIR.

4.7 Sensitivity Analysis

A sensitivity analysis was performed using FILMTEC ROSA simulation software to evaluate the performance of BW30-2540 FILMTEC membrane on variable

operating conditions. The results of effluent feed quality obtained during experiment conducted under Section 4.2 above were used as input data to the software. The feed flow rate was kept constant at 0.5 m^3/hr while the feed pressure of the system was varied. The pressures used were as follows: 2.5 bar, 5 bar, 10 bar, 15 bar, 20 bar, and 25 bar. Temperature was assumed to be at $25^{\circ}C$.

Chapter 5 – Experimental Results and Discussion

The results of all experiments and simulations conducted in Chapter 4 were reported and discussed on this Chapter. This was done in order to relate both experimental as well as simulation results in terms of their significance with regard to theoretical basis of this research.

5.1 Simulation Results of Membrane Selection trial

The objective was to obtain permeate stream conforming to RWB and Karbochem process water specifications regarding potassium ions and sulphate anions. Based on data recorded in Table 7, it is clear that LP-2540, XLE-2540, NF200-2540, and NF90-2540 modules would achieve desired permeate specifications ($9mg/l$ K^+ and $145mg/l$ SO_4^{2-}). The desired permeate specifications would be achieved using SW30-2540, BW30-2540, or TW30-2540 modules.

The SW30-2540 module seems to be the best in terms of potassium ion and sulphate anion rejections; however, this module gives the lowest recovery and the highest specific power which would then result in an increased effluent treatment cost.

Table 7: Performance Evaluation of Various Filmtec Modules

	Membrane Module:	SW30-2540	BW30-2540	TW30-2540	LP-2540	XLE-2540	NF200-2540	NF90-2540
	Feed Pressure [Bar]	15	15	15	15	15	15	15
	Operating Temp [$^\circ$C]	25	25	25	25	25	25	25
	Feed Flow [m^3/hr]	0.67	0.67	0.67	0.67	0.67	0.67	0.67
Feed	K^+ [mg/l]	701	701	701	701	701	701	701
	SO_4^{2-} [mg/l]	819	819	819	819	819	819	819
Permeate	K^+ [mg/l]	1.41	4.73	4.73	10.51	11.03	28.46	8.44
	SO_4^{2-} [mg/l]	1.33	5.41	5.41	12.06	12.69	9.8	8.87
Brine	K^+ [mg/l]	783.4	846.8	846.8	966.3	1040	968.3	1184
	SO_4^{2-} [mg/l]	915.3	989.3	989.3	1129	1215	1141	1384
	Recovery [%]	10.54	17.31	17.31	27.76	32.95	28.44	41.07
	Specific Power [kWh/m^3]	4.94	3.01	3.01	1.88	1.58	1.83	1.27

The choice should be between BW30-2540 and TW30-2540 modules for this application. Both modules have achieved similar results. However, Dow (2008:17) states that BW30 membranes are used for brackish water while TW30 membranes are used for tap water.

Therefore, the life span of TW30-2540 module might deteriorate very rapidly as compared to that of BW30-2540 as the TW30 membranes are not designed to handle high salt composition which could result in precipitation and promote rapid scale formation. The BW30 membranes are designed to treat brackish water and therefore BW30-2540 is recommended for the treatment of Karbochem effluent.

5.2 Experimental Results of a Laboratory Scale RO Unit

Figure 13 below shows that BW30 flat-sheet membrane has a high rejection for most of the species contained in Karbochem Finishing plant effluent. The percentage rejection of each component was calculated using Equation 6. Focusing primarily on potassium sulphate rejection, 98% and 99.1% were obtained for potassium and sulphate respectively. This agrees with literature reviewed in the sense that higher rejections are obtained for multivalent ions than for monovalent ions. The COD rejection was also high at 98.3%. Observing the feed and permeate streams, all the elements contained in the feed solution were significantly rejected.

It was also observed that, the concentration of all the elements contained in the feed solution were almost doubled and thereby making the brine stream very rich in potassium sulphate. As Section 3.2 in the literature discusses the role and uses of potassium sulphate within the fertilizer industry, the brine stream might be disposed by eliminating undesirable components such as the COD and Cl in the stream and then use K_2SO_4 as a fertilizer. The undesirable components could be controlled in the pre-treatment stages.
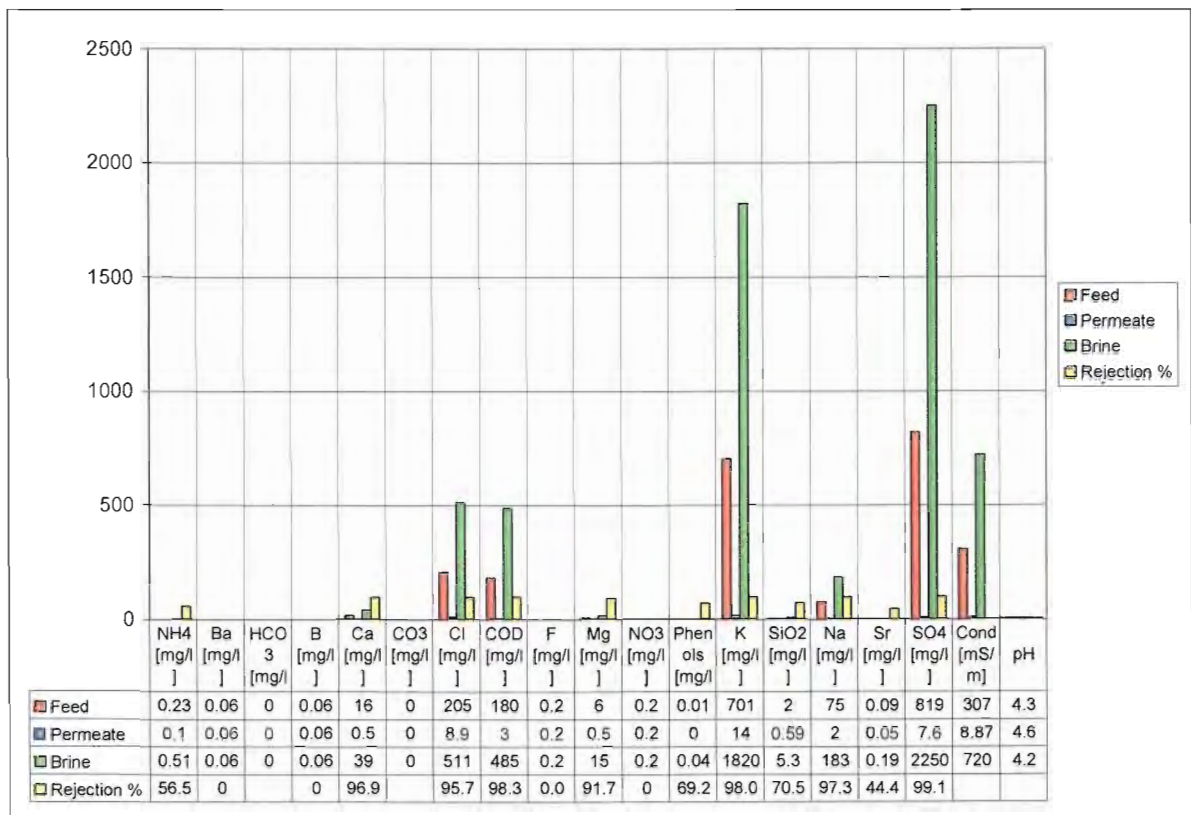
Figure 13: Water quality after treatment with flat-sheet module

	NH4 [mg/l]	Ba [mg/l]	HCO3 [mg/l]	B [mg/l]	Ca [mg/l]	CO3 [mg/l]	Cl [mg/l]	COD [mg/l]	F [mg/l]	Mg [mg/l]	NO3 [mg/l]	Phenols [mg/l]	K [mg/l]	SiO2 [mg/l]	Na [mg/l]	Sr [mg/l]	SO4 [mg/l]	Cond [mS/m]	pH
Feed	0.23	0.06	0	0.06	16	0	205	180	0.2	6	0.2	0.01	701	2	75	0.09	819	307	4.3
Permeate	0.1	0.06	0	0.06	0.5	0	8.9	3	0.2	0.5	0.2	0	14	0.59	2	0.05	7.6	8.87	4.6
Brine	0.51	0.06	0	0.06	39	0	511	485	0.2	15	0.2	0.04	1820	5.3	183	0.19	2250	720	4.2
Rejection %	56.5	0		0	96.9		95.7	98.3	0.0	91.7	0	69.2	98.0	70.5	97.3	44.4	99.1		

5.3 Experimental Results of Pilot Plant Tests

The trends observed in the previous experiment were again seen on Figure 14 and therefore, discussions about Figure 13 are also applicable to Figure 14. These results were obtained using BW30-2540 membrane module. The differences in the two experiments were noted only on the brine streams. On Figure 13, the concentrations of each component were significantly increased while it almost remained constant on Figure 14. This is because the first experiment was on a very small scale and the experiment was run until the feed solution was halved, while the second experiment was performed on a larger

69

scale and the brine sample was taken before the feed solution was halved in the reservoir.

	NH4 [mg/l]	Ba [mg/l]	HCO3 [mg/l]	B [mg/l]	Ca [mg/l]	CO3 [mg/l]	Cl [mg/l]	COD [mg/l]	F [mg/l]	Mg [mg/l]	NO3 [mg/l]	Phenols [mg/l]	P [mg/l]	K [mg/l]	SiO2 [mg/l]	Na [mg/l]	Sr [mg/l]	SO4 [mg/l]	Cond [mS/m]	pH
Feed	0.5	0.06	0	0.06	13	0	158	136	0.93	6	0.2	0.006	8.1	545	2.2	69	0.09	870	299	4.1
Permeate	0.1	0.06	0	0.06	0.5	0	22	99	0.85	0.5	0.2	0.004	0.2	17	0.59	2	0.05	5	9.45	5.6
Brine	0.7	0.06	0	0.06	22	0	202	304	1	7	0.2	0.007	9	550	2.8	73	0.12	879	310	6.1
Rejection %	80	0		0	96.2		86.1	27.2	8.6	91.7	0	33.3	97.5	96.9	73.2	97.1	44.4	99.4		

Figure 14: Water quality after treatment with spiral wound module (Test 1)

Figure 15 also shows similar trends observed on Figure 13 and 14. These results were obtained with the same set-up used to obtain the results on Figure 14. The only notable difference between Figure 14 and 15 was the brine concentrations. On Figure 15, the concentration of each element increased better than on Figure 14 because the experiment performed to yield Figure 15 results was run a little longer than on Figure 14. This shows that the more the brine stream is recycled, the more concentrated the brine becomes.

Figure 15: Water quality after treatment with spiral wound module (Test 2)

	NH4 [mg/l]	Ba [mg/l]	HCO3 [mg/l]	B [mg/l]	Ca [mg/l]	CO3 [mg/l]	Cl [mg/l]	COD [mg/l]	F [mg/l]	Mg [mg/l]	NO3 [mg/l]	Phenols [mg/l]	P [mg/l]	K [mg/l]	SiO2 [mg/l]	Na [mg/l]	Sr [mg/l]	SO4 [mg/l]	Cond [mS/m]	pH
Feed	0.37	0.1	13.7	0.06	32	0.02		136		8	0.98			777	3.6	158	0.09	1360	441	6.5
Permeate	0.1	0.1	5.9	0.06	4.9	0.003		4		2.3	0.54			15	0.39	3	0.08	5.1	13.2	6.5
Brine	0.85	0.1	35.6	0.06	40	0.03		149		9	3.9			861	3.7	181	0.11	1520	472	7
Rejection [%]	73.0		56.9		84.7	85.0		97.1		71.3	44.9			98.1	89.2	98.1	11.1	99.6		
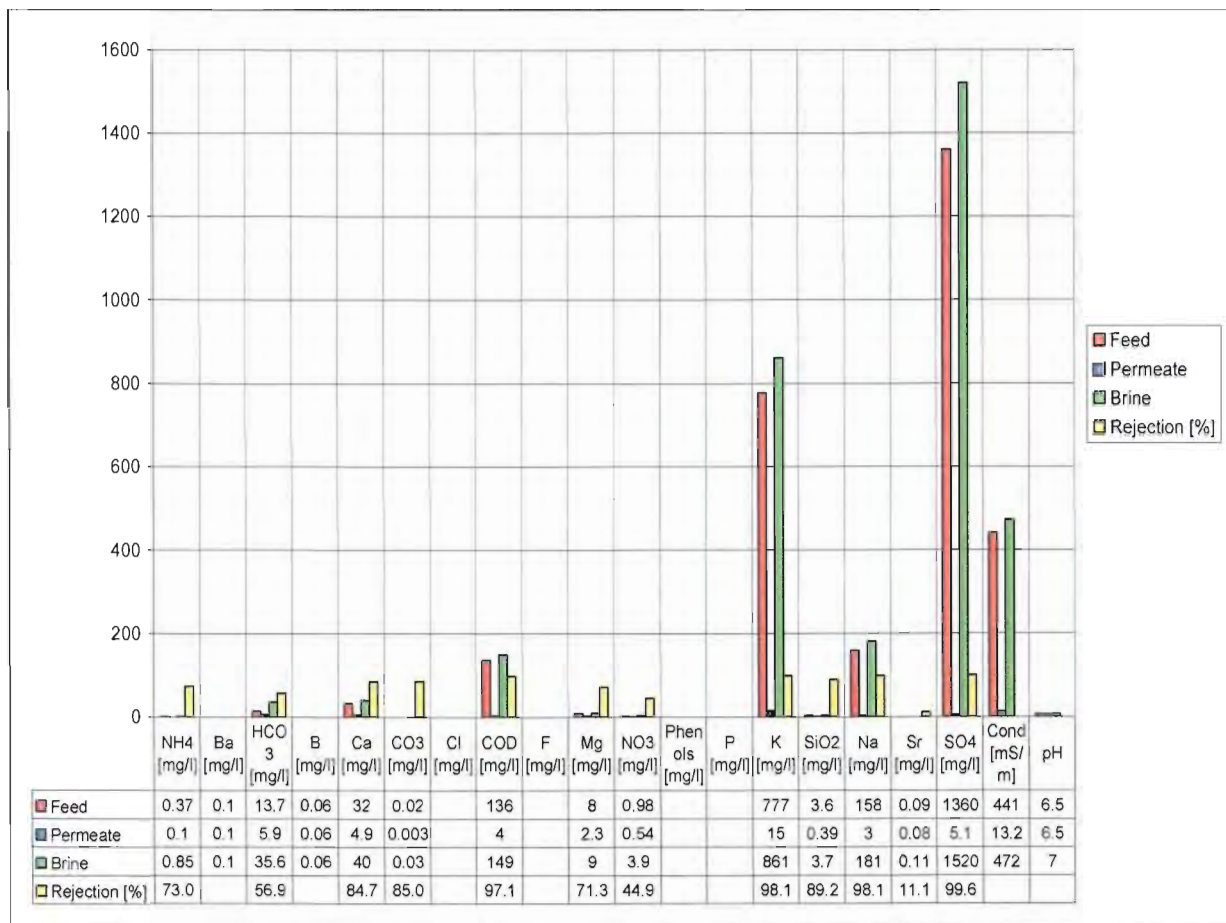
The permeate quality from all experiments compares well with Karbochem water standards as given on Table 2, except for the TDS which could not be measured and potassium ion which is slightly high.

Reverse osmosis seems to be effective mitigating effluent problems that Karbochem had as previously indicated on Figure 2. However, it creates another problem as it generates waste in the form of brine and ways of disposing or recovering the brine stream will be necessary.

5.4 Experimental Results of the Silt Density Index (SDI) Tests

The SDI values were calculated using Equation 13 and the values recorded on Table 8. The following is a sample calculation done for Test 1 (Run 1):

$$SDI = \frac{100\left[1 - \dfrac{t_i}{t_f}\right]}{t}$$

$$SDI = \frac{100\left[1 - \dfrac{4.22}{4.27}\right]}{15}$$

$$SDI = 0.078$$

Table 8: Determination of the feed water SDI

	Run 1	Run 2
t_i [min]	4.22	4.27
t_f [min]	4.27	4.3
t [min]	15	15
SDI	0.078	0.047

The difference in the two values obtained could be associated with the human error when operating the stop watch. These values on both runs were however, way too low as compared to the maximum recommended SDI of 5 for the BW30-2540 membrane as given on Annexure A. This means that the fouling potential of the feed water to BW30-2540 membranes is significantly low.

5.5 Experimental Results of Activated Carbon Treatment

Table 9 show the results obtained from the activated carbon treatment. These results indicate that no pre-treatment is required for the free chlorine as the effluent from Karbochem finishing plant contained free chlorine at concentrations

below 0.01 mg/l. The free chlorine tolerance of the membrane used is <0.1 mg/l, meaning that the membrane was not under any threats from chlorine attack of the effluent.

Table 9: Results of activated carbon bed treatment.

Run	Weight of carbon [g]	Effluent vol [ml]	Initial concentration [mg/l]		Final concentration [mg/l]		Contaminant adsorbed [mg/l]	
			COD	Free Cl_2	COD	Free Cl_2	COD	free Cl_2
1	10.071	600	482	<0.01	344	<0.01	138	-
2	20.122	600	482	<0.01	242	<0.01	240	-
3	30.214	600	482	<0.01	143	<0.01	339	-

The results above illustrates that activated carbon is capable of adsorbing the COD and chlorine from the effluent and thereby reducing them to the required levels. Pre-treating the effluent with activated carbon bed prior to RO treatment should definitely reduce the risk of free chlorine attack as well as organic fouling of the membrane.

5.6 Experimental Results of a Sensitivity Analysis

Sensitivity analysis was performed to evaluate the performance of BW30-2540 membrane module when varying the feed pressure. Figure 16 shows the results obtained for the rejections of both potassium and sulphate ions at different pressures.
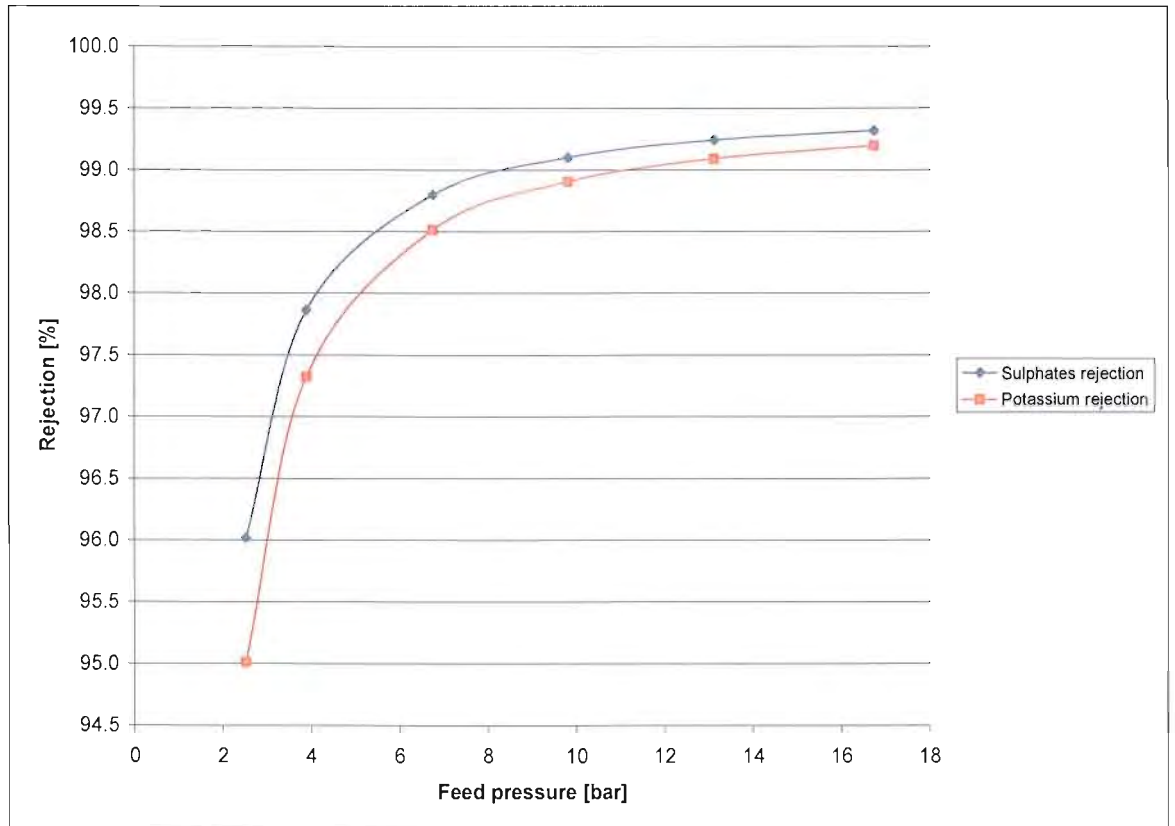
Figure 16: Rejection Curves – Sensitivity Analysis

The focus was more on the rejections of potassium and the sulphate as they form the main objective of this study. Both curves showed that solute rejection rises with the feed pressure.

Figure 17 summarises the results obtained for permeate flux at different pressures during sensitivity analysis.
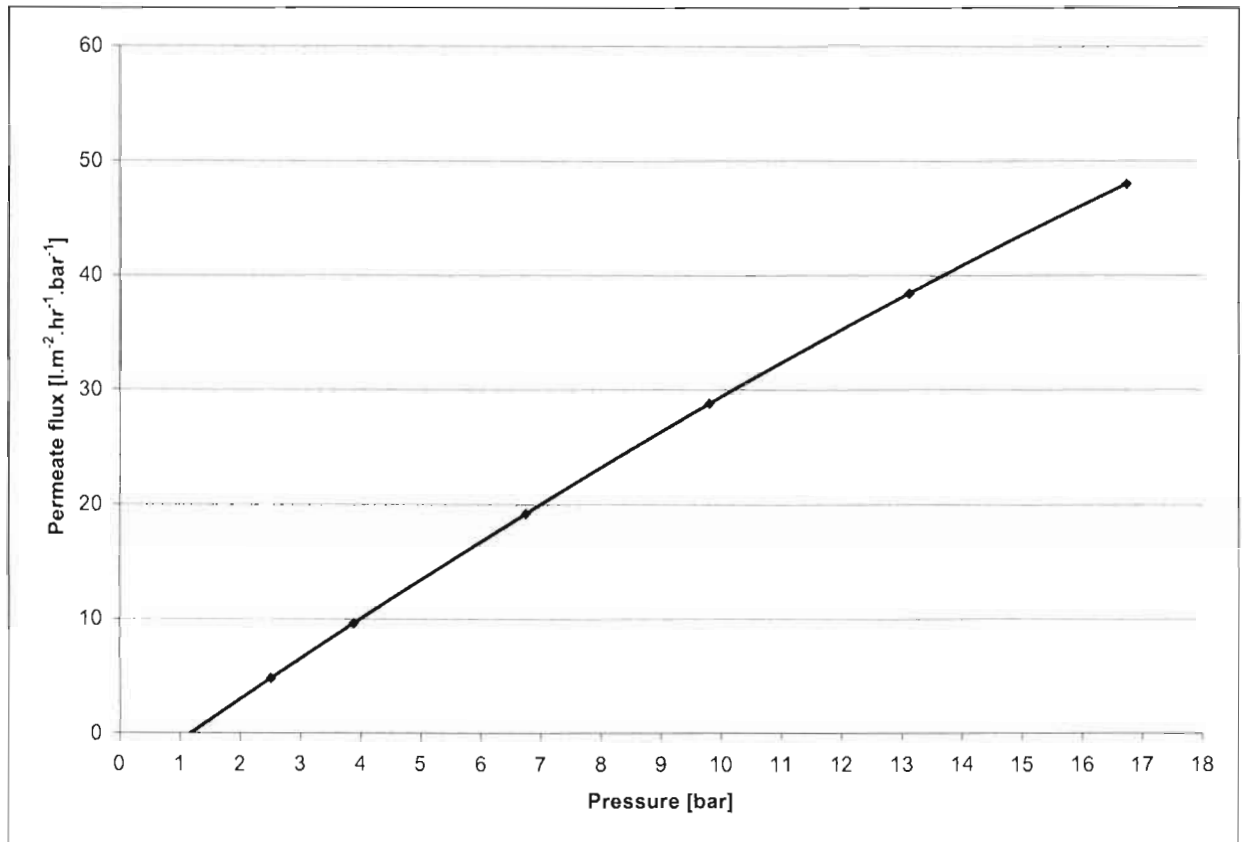
Figure 17: Flux Curve - Sensitivity Analysis

The flux curve shows that the higher the pressure the more water permeates through the membrane. This illustrates that the water flux equation is applicable where water flux is directly proportional to the applied pressure (refer to Equation 1). The point where the graph cuts through the x-axis represents osmotic pressure of the solution. This means that in order for water to permeate through the membrane, the applied pressure must be higher than the osmotic pressure of the solution. This flux curve is of the order 1.2 bar at zero flow.

Figure 18 shows the relationship between water recovery and the applied pressure.
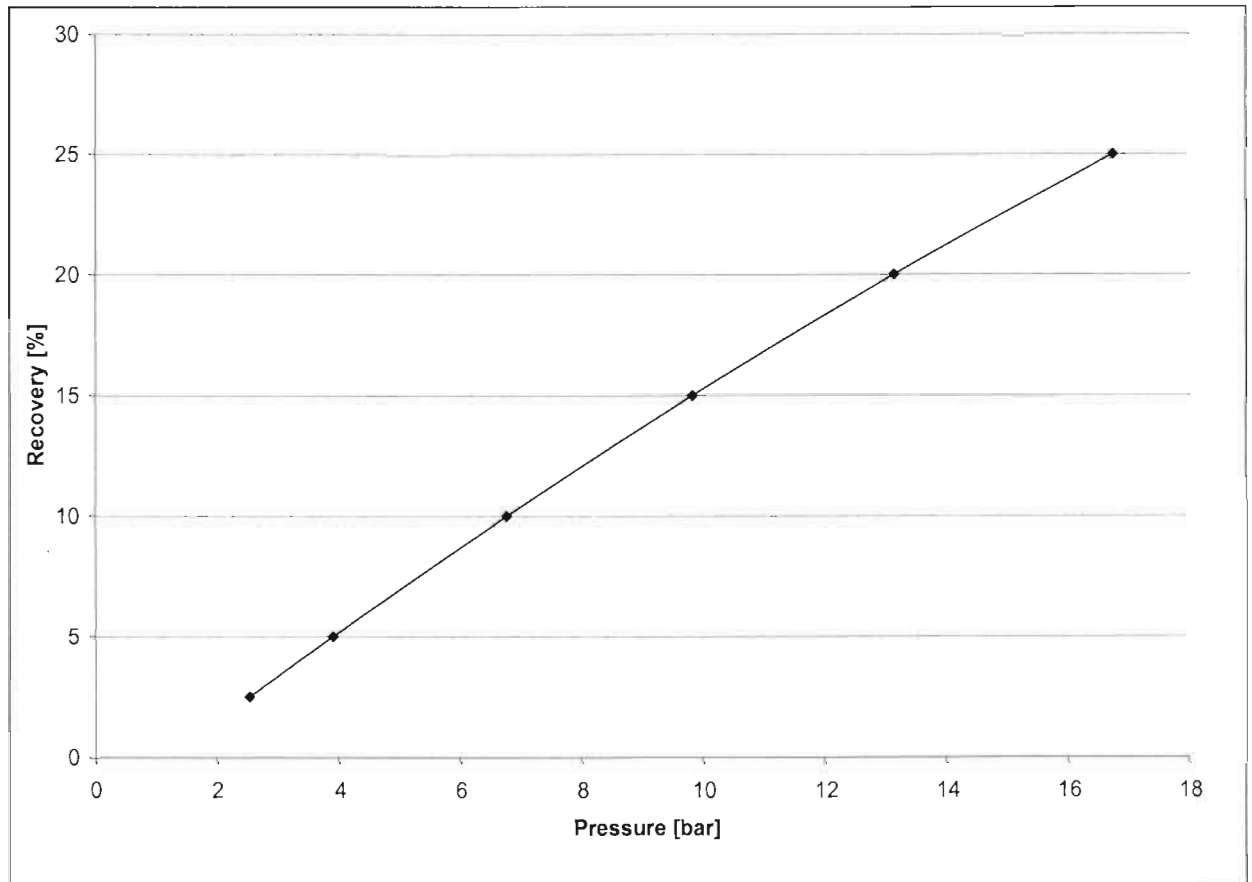
Figure 18: Recovery Curve – Sensitivity Analysis

Water recovery increases with an increase in applied pressure. This means that the higher the pressure, the more water recovery will be attained. Refer to Table 17 to observe the effect of pressure increase on element rejection.

The feed results obtained from Experiment 4.2 were used to approximate the expected performance of a similar spiral membrane system using Rosa RO design-software package with BW30-4040 module. The results of this simulation were recorded on Table 10 and conform to Karbochem water standards. These

membranes, however, requires pre-treatment to protect against organic fouling and free chlorine attacks. Annexure B displays detailed design report by ROSA design-software.

Table 10: Performance results of spiral-wound membrane.

Parameter	Feed	Brine	Permeate
NH_4^+ [mg/l]	0.23	0.32	0.02
K^+ [mg/l]	701	998.29	7.3
Na^+ [mg/l]	75	118.67	0.77
Mg^{2+} [mg/l]	6	8.56	0.04
Ca^{2+} [mg/l]	16	22.82	0.09
Sr^{2+} [mg/l]	0.09	0.13	0
Ba^{2+} [mg/l]	0.06	0.09	0
CO_3^{2-} [mg/l]	0	0	0
HCO_3^- [mg/l]	0	0	0
NO_3^- [mg/l]	0.2	0.27	0.05
Cl^- [mg/l]	205	291.71	2.66
F^- [mg/l]	0.2	0.28	0
SO_4^{2-} [mg/l]	819	1166.85	7.34
SiO_2 [mg/l]	2	2.85	0.01
Boron [mg/l]	0.06	0.07	0.03
CO_2 [mg/l]	0	0	0
TDS [mg/l]	1825.12	2611.25	18.48
pH	4.3	4.3	4.3

The above results were used to extrapolate the running costs to treat 120 m^3/day of effluent, based on a 30% recovery of the water. Refer to Table 11 for detail.

Table 11: Running costs for spiral-wound RO treatment

Power required [kW]	1.26
Specific energy [kWh/m^3]	1.68
Energy charge [c/kWh]	25.05
RO running cost [R/m^3]	0.42

Power and specific energy required were estimated by ROSA design-software. At the time this report was issued, the energy charge was 25.05 cents/kWh during high season, for large customers within the vicinity of Gauteng province (refer to annexure C). Using the information aforementioned, the running costs of the RO plant with 5 elements were estimated at 42 cents/m^3 of permeate.

The operating costs of activated carbon bed treatment could not be quantified as this process would still need to be optimized. However, Carbtrol (2008) states that "for many water treatment applications it has proved to be the least expensive treatment option". The loading capacity of granular activated carbon could be determined using the adsorption isotherms. The systems should also be sized properly and the number of times activated carbon can be regenerated should also be determined.

Table 12 compares the treatment costs by the existing and proposed effluent treatment systems. When this report was compiled, the variable treatment charge for Karbochem effluent treatment was R 0.26/m^3 and a penalty charge of R 1.60/m^3 was imposed based on the agreed quality specification as per contract number SCI 726 REV 3 of the 13th August 2003 between Karbochem and Sasol. The raw water cost was assumed to be R 3.15/m^3.

Table 12 also illustrates that the proposed RO system would pay itself out for the operating costs as opposed to the existing system at Karbochem. Some saving would be achieved because the amount of raw water currently purchased by Karbochem would be reduced as permeate from the RO treatment would be re-used within Karbochem factory.

Table 12: Treatment costs of existing system vs. proposed system

EXISTING SYSTEM	
Variable treatment charge [R/m^3]	0.26
Flow rate of finishing effluent [m^3/d]	120
Treatment costs [R/d]	31.2
R.W.B Water usage [m^3/d]	70
Process water [m^3/d]	80
Raw water cost [R/m^3]	3.15
Finishing plant expenses on raw water [R/d]	472.5
Total expenses on water [R/d]	503.7
PROPOSED SYSTEM	
RO running costs [R/m^3]	0.42
Flow rate of finishing effluent [m^3/d]	120
Treatment costs [R/d]	50.4
Water to be re-used [m^3/d]	36
Raw water cost [R/m^3]	3.15
Savings on raw water [R/d]	113.4
Total savings [R/d]	63

Chapter 6 – Conclusions and Recommendations

To conclude, reverse osmosis is a technically suitable process for treating the effluent from Karbochem finishing plant. However, pre-treatment of this effluent is necessary as it contains significant concentration of COD and Cl_2 which could attack the membrane and shorten its life span. Significant amounts of rubber crumbs were also noted which could block the system completely or cause colloidal fouling of the membranes. The membrane is under a minimal risk of free chlorine attack as this is available at low levels in the effluent (refer to Table 9). This implies that, no treatment to remove Cl_2 is necessary.

Flat-sheet and spiral-wound reverse osmosis treatments have completely desalinated and significantly reduced the concentrations of all problematic quality parameters at Karbochem, especially of potassium and the sulphates. Both solute rejection and water passage through the membrane rise with pressure, however, care should be taken not to exceed the maximum recommended element permeate flow rate and feed pressure, which are $0.13 m^3/hr$ and 41.37 bar respectively for BW30-2540 element. There is no significant difference in terms of rejection between flat-sheet and spiral wound membranes of the same type, except that spiral-wound offers more active area and thus allows for higher permeate flow rates and feed pressures.

The quality of treated water (permeate) complies with Karbochem process water standards except only for potassium which slightly exceeds the specification. This means that permeate can be used as process water at Karbochem only if potassium could be controlled to acceptable specification (< 10 mg/l) else, this water can be used for cleaning purposes in the plant.

The concentrations of potassium and sulphate ions noted in the brine stream are too low for recovery (550 – 1820 mg/l K^+ and 879 – 2250 mg/l SO_4^{2-} in brine stream). The amount of effluent available at Karbochem finishing plant is approximately, 120 m^3/day. This implies that it is not financially viable to produce dry granular potassium sulphate from the brine stream. This brine can be used and sold as a liquid fertiliser provided other impurities are removed to acceptable levels required by the users. The brine could be used for plants which are sensitive to chlorine, for example tobacco, potatoes, fruits and vegetables as recommended by Dickinson *et al.* (1988:84). This conclusion is also supported by Tandon and Roy (2004). The brine stream can also be used for irrigation purposes within Karbochem factory.

The following is a concise summary of recommendations:

- A strainer followed by a sand filter is recommended for the pre-treatment of the effluent to remove rubber crumbs and suspended solids respectively, in order to prevent blockages and colloidal fouling of the membranes.

- An activated carbon bed filter is recommended to reduce the COD concentration to acceptable levels and reduce the risk of membrane attack.

- The membrane with a higher recovery should be used in order to achieve higher permeate flow rate for water re-use at Karbochem factory.

- It is recommended that the requirements of fertilizer and fertigation industries such as Omnia in South Africa be established and the possibilities of developing the brine stream to meet those requirements should be evaluated.

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FIGURES

Figure 19: Adsorption Isotherm
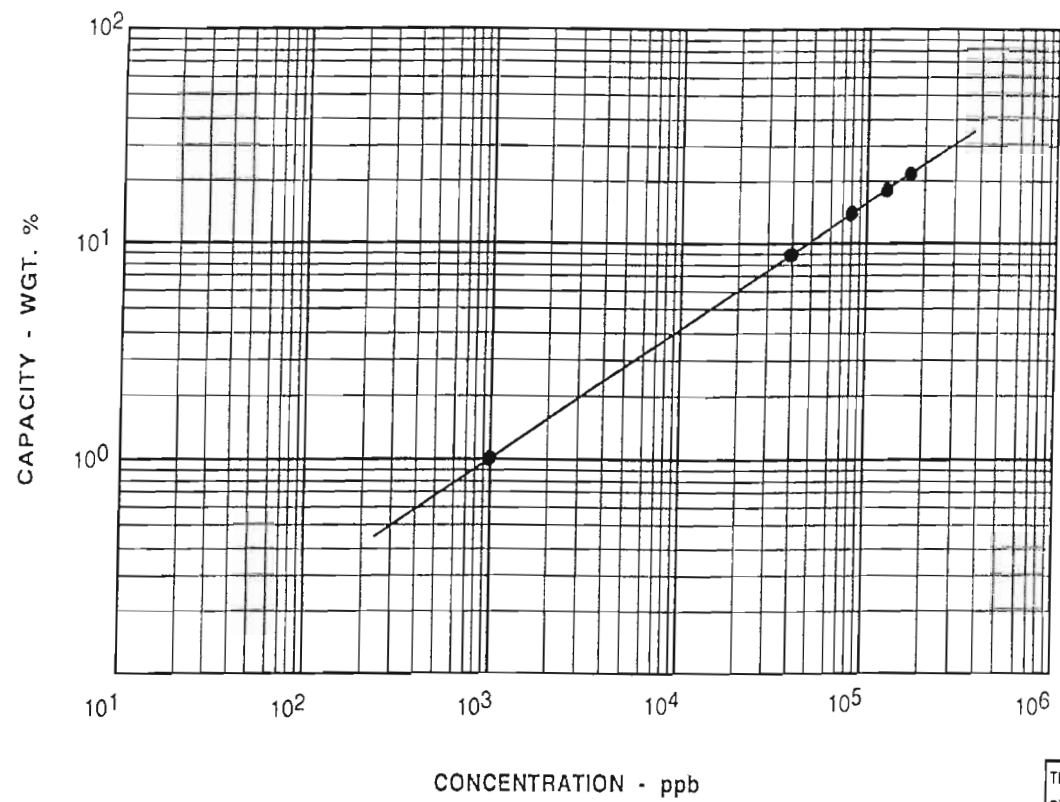
CAPACITY - WGT. %

CONCENTRATION - ppb
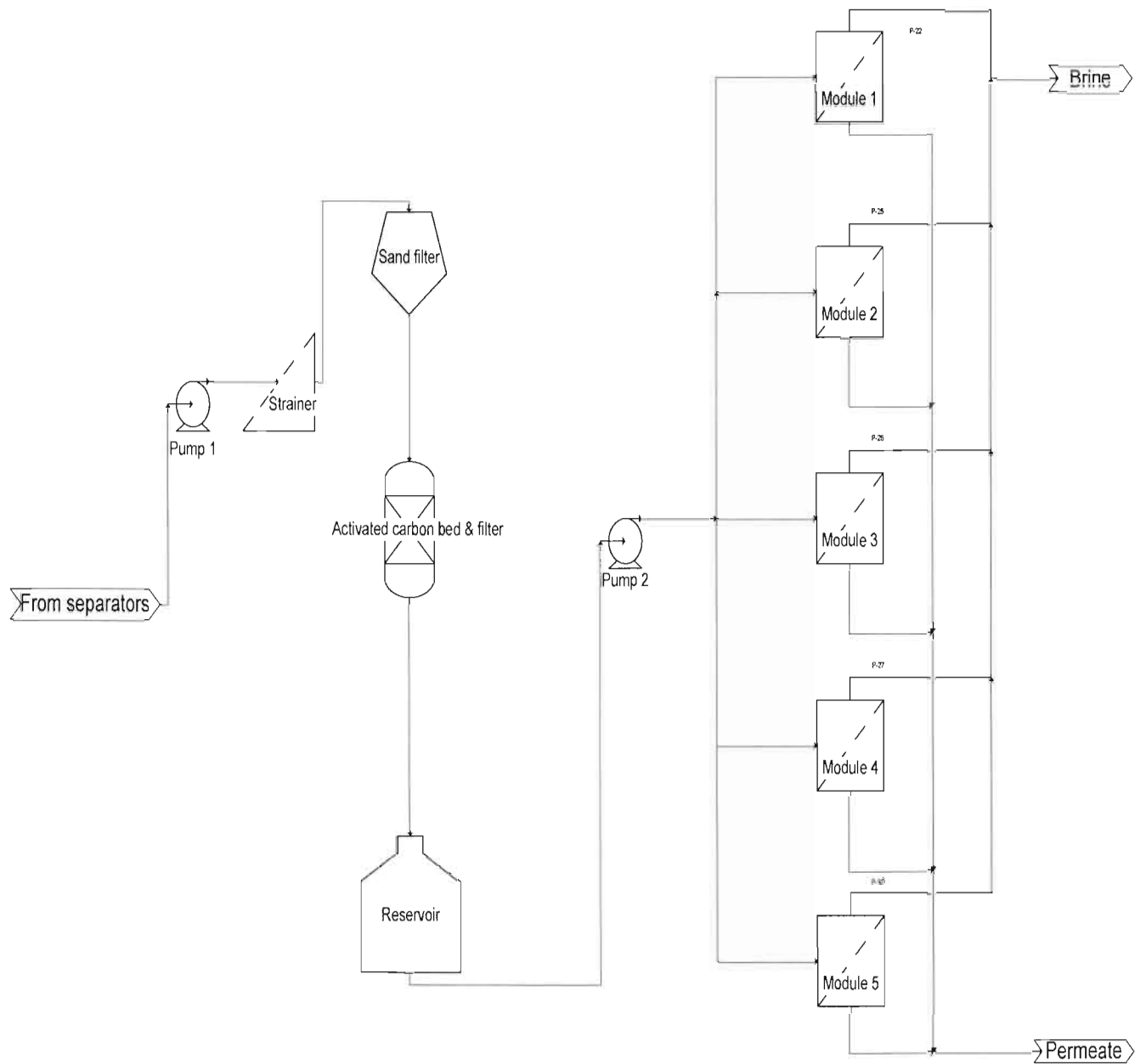
Figure 20: Process flow diagram (PFD)

TABLES

Table 13: In-stream water quality guidelines for the Vaal Dam Catchment

Variables Physical	Measured as	Ideal Catchment Background	Acceptable Management Target	Tolerable Interim Target	Unacceptable
Conductivity	mS/m	< 10	10 - 30	30 - 45	> 45
pH	pH units	6.5 - 8.5			< 6.5; > 8.5
Organic					
Chemical Oxygen Demand (COD)	mg/l	< 10	10 - 15	15 - 20	> 20
Macro Elements					
Ammonia (NH_4)	mg/l	< 0.2	0.2 - 0.5	0.5 - 1.0	> 1
Chloride (Cl)	mg/l	< 25	25 - 50	50 - 75	> 75
Fluoride (F)	mg/l	< 0.05	0.05 - 0.20	0.2 - 0.4	> 0.4
Alkalinity	$CaCO3$ mg/l	< 40	40 - 75	75 - 120	> 120
Nitrate (NO_3)	mg/l	< 0.1	0.1 - 0.2	0.2 - 0.3	> 0.3
Phosphate (PO_4)	mg/l	0.05	0.05 - 0.25	0.25 - 0.50	> 0.5
Sulphate (SO_4)	mg/l	< 20	20 - 45	45 - 70	> 70
Bacteriological					
Faecal coliforms	counts/100ml		< 126	126 - 1000	> 1000

Table 14: Effluent quality before and after flat-sheet membrane treatment

Parameter	Feed	Permeate	Brine
Ammonia [mg/l]	0.23	0.1	0.51
Barium [mg/l]	0.06	0.06	0.06
Bicarbonates [mg/l]	0	0	0
Boron [mg/l]	0.06	0.06	0.06
Calcium [mg/l]	16	0.5	39
Carbonates [mg/l]	0	0	0
Chloride [mg/l]	205	8.9	511
COD [mg/l]	180	3	485
Fluoride [mg/l]	0.2	0.2	0.2
Magnesium [mg/l]	6	0.5	15
Nitrate nitrogen [mg/l]	0.2	0.2	0.2
Phenols [mg/l]	0.013	0.004	0.041
Potassium [mg/l]	701	14	1820
Silicon [mg/l]	2	0.59	5.3
Sodium [mg/l]	75	2	183
Strontium [mg/l]	0.09	0.05	0.19
Sulphate [mg/l]	819	7.6	2250
Conductivity [mS/m]	307	8.87	720
pH	4.3	4.6	4.2

Table 15: Water quality after pilot test using spiral-wound module (Test 1)

Parameter	Feed	Permeate	Brine
Ammonia [mg/l]	0.5	0.1	0.7
Barium [mg/l]	0.06	0.06	0.06
Bicarbonates [mg/l]	0	0	0
Boron [mg/l]	0.06	0.06	0.06
Calcium [mg/l]	13	0.5	22
Carbonates [mg/l]	0	0	0
Chloride [mg/l]	158	22	202
COD [mg/l]	136	99	304
Fluoride [mg/l]	0.93	0.85	1
Magnesium [mg/l]	6	0.5	7
Nitrate nitrogen [mg/l]	0.2	0.2	0.2
Phenols [mg/l]	0.006	0.004	0.007
Phosphate - (tot) [mg/l]	8.1	0.2	9
Potassium [mg/l]	545	17	550
Silicon [mg/l]	2.2	0.59	2.8
Sodium [mg/l]	69	2	73
Strontium [mg/l]	0.09	0.05	0.12
Sulphate [mg/l]	870	5	879
Conductivity [mS/m]	299	9.45	310
pH	4.1	5.6	6.1

Table 16: Water quality after pilot test using spiral-wound module (Test 2)

Parameter	Feed	Permeate	Brine
Ammonia [mg/l]	0.37	<0.1	0.85
Barium [mg/l]	<0.1	<0.1	<0.1
Bicarbonates [mg/l]	13.7	5.9	35.6
Boron [mg/l]	<0.06	<0.06	<0.06
Calcium [mg/l]	32	<4.9	40
Carbonates [mg/l]	0.02	0.003	0.03
Chloride [mg/l]	368	20	400
COD [mg/l]	136	4	149
Fluoride [mg/l]	<0.2	<0.2	<0.2
Magnesium [mg/l]	8	<2.3	9
Nitrate nitrogen [mg/l]	0.98	0.54	3.9
Phenols [mg/l]			
Phosphate - (tot) [mg/l]			
Potassium [mg/l]	777	15	861
Silicon [mg/l]	3.6	<0.39	3.7
Sodium [mg/l]	158	3	181
Strontium [mg/l]	0.09	<0.08	0.11
Sulphate [mg/l]	1360	5.1	1520
Conductivity [mS/m]	441	13.2	472
pH	6.5	6.5	7

Table 17: Results of Sensitivity analysis by ROSA software

	Feed	Permeate					
Feed pressure [bar]		2.52	3.89	6.75	9.81	13.12	16.73
Recovery [%]		2.5	5	10	15	20	25
SO_4^{2-} Rejection [%]		96.0	97.9	98.8	99.1	99.2	99.3
K^+ Rejection [%]		95.0	97.3	98.5	98.9	99.1	99.2
Flow rate [m^3/hr]	0.5	0.013	0.026	0.052	0.08	0.1	0.13
Permeate flux [$l.m^{-2}.hr^{-1}.bar^{-1}$]		4.81	9.61	19.22	28.83	38.44	48.05
$NH4^+$ [mg/l]	0.5	0.07	0.05	0.03	0.02	0.02	0.02
K^+ [mg/l]	545	27.16	14.57	8.09	5.95	4.93	4.36
Na^+ [mg/l]	172.95	6.88	3.7	2.09	1.57	1.32	1.2
Mg^{2+} [mg/l]	6	0.13	0.07	0.04	0.03	0.03	0.03
Ca^{2+} [mg/l]	13	0.27	0.15	0.09	0.07	0.06	0.05
Sr^+ [mg/l]	0.09	0	0	0	0	0	0
Ba^{2+} [mg/l]	0.06	0	0	0	0	0	0
CO_3^{2-} [mg/l]	0	0	0	0	0	0	0
HCO_3^- [mg/l]	0	0	0	0	0	0	0
NO_3^- [mg/l]	0.2	0.13	0.1	0.07	0.06	0.05	0.04
Cl^- [mg/l]	158	10.46	5.62	3.09	2.25	1.84	1.61
F^- [mg/l]	0.93	0.07	0.04	0.02	0.02	0.01	0.01
SO_4^{2-} [mg/l]	870	34.6	18.59	10.45	7.8	6.56	5.9
SiO_2 [mg/l]	2.2	0.07	0.04	0.02	0.01	0.01	0.01
Boron [mg/l]	0.06	0.05	0.04	0.04	0.03	0.03	0.03
CO_2 [mg/l]	0	0	0	0	0	0	0
TDS [mg/l]	1769.3	80.12	43.17	24.2	17.97	15.01	13.4
pH	4.1	4.1	4.1	4.1	4.1	4.1	4.1

ANNEXURES

ANNEXURE A – BW30 Product information

The information on this annexure was obtained from Filmtec, the manufacturer of BW30 type of membranes.

DOW

FILMTEC Membranes

FILMTEC Fiberglassed Elements for Light Industrial Systems

Features

FILMTEC™ brackish water reverse osmosis membrane elements provide consistent, outstanding system performance in light industrial applications.

- FILMTEC BW30LE-4040 delivers highest performance at lowest pressure resulting in less energy usage and lower costs.
- FILMTEC BW30-4040 is the industry standard for reliable operation and production of the highest quality water.
- FILMTEC BW30-2540 elements are designed for systems smaller than 1 gpm (0.2 m³/h) offering a hard shell exterior for extra strength

Elements with a hard shell exterior are recommended for systems with multiple-element housings containing three or more membranes, as they are designed to withstand higher pressure drops.

Product Specifications

| Product	Part Number	Active Area ft² (m²)	Applied Pressure psig (bar)	Permeate Flow Rate gpd (m³/d)	Stabilized Salt Rejection (%)
BW30LE-4040	80604	82 (7.6)	150 (10.3)	2,300 (8.7)	99.2
BW30-4040	80763	82 (7.6)	225 (15.5)	2,400 (9.1)	99.5
BW30-2540	80766	28 (2.6)	225 (15.5)	850 (3.2)	99.5

1. Permeate flow and salt rejection based on the following test conditions: 2,000 ppm NaCl, pressure specified above, 77°F (25°C) and 15% recovery
2. Permeate flows for individual elements may vary ±20%
3. For the purpose of improvement, specifications may be updated periodically
4. BW30LE-4040 was previously named BW30HP-4040

Figure 1
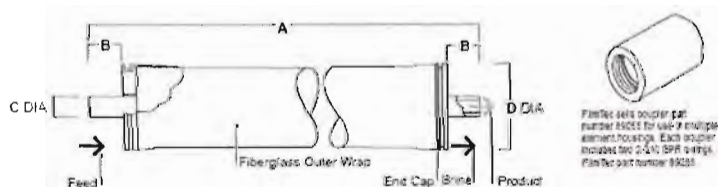
Product	Dimensions – Inches (mm)			
	A	B	C	D
BW30LE-4040	40.0 (1,016)	1.05 (26.7)	0.75 (19)	3.9 (99)
BW30-4040	40.0 (1,016)	1.05 (26.7)	0.75 (19)	3.9 (99)
BW30-2540	40.0 (1,016)	1.19 (30.2)	0.75 (19)	2.4 (61)

1. Refer to FilmTec Design Guidelines for multiple-element systems.
2. BW30-2540 elements fit nominal 2.5-inch I.D. pressure vessel. BW30LE-4040 and BW30-4040 elements fit nominal 4-inch I.D. pressure vessel

1 inch = 25.4 mm

* Trademark of The Dow Chemical Company
FILMTEC Membranes

Form No. 609-00350-803

Operating Limits	• Membrane Type	Polyamide Thin-Film Composite
	• Maximum Operating Temperature	113°F (45°C)
	• Maximum Operating Pressure	600 psi (41 bar)
	• Maximum Feed Flow Rate - 4040 elements	16 gpm (3.6 m³/h)
	- 2540 elements	6 gpm (1.4 m³/h)
	• Maximum Pressure Drop	15 psig (1.0 bar)
	• pH Range, Continuous Operation[a]	2 – 11
	• pH Range, Short-Term Cleaning[b]	1 – 12
	• Maximum Feed Silt Density Index	SDI 5
	• Free Chlorine Tolerance[c]	<0.1 ppm

[a] Maximum temperature for continuous operation above pH 10 is 95°F (35°C).
[b] Refer to Cleaning Guidelines in specification sheet 609-23010
[c] Under certain conditions, the presence of free chlorine and other oxidizing agents will cause premature membrane failure. Since oxidation damage is not covered under warranty, FilmTec recommends removing residual free chlorine by pretreatment prior to membrane exposure. Please refer to technical bulletin 609-22010 for more information.

Important Information

Proper start-up of reverse osmosis water treatment systems is essential to prepare the membranes for operating service and to prevent membrane damage due to overfeeding or hydraulic shock. Following the proper start-up sequence also helps ensure that system operating parameters conform to design specifications so that system water quality and productivity goals can be achieved.

Before initiating system start-up procedures, membrane pretreatment, loading of the membrane elements, instrument calibration and other system checks should be completed

Please refer to the application information literature entitled "Start-Up Sequence" (Form No. 609-00298) for more information.

Operation Guidelines

Avoid any abrupt pressure or cross-flow variations on the spiral elements during start-up, shutdown, cleaning or other sequences to prevent possible membrane damage. During start-up, a gradual change from a standstill to operating state is recommended as follows:
• Feed pressure should be increased gradually over a 30-60 second time frame.
• Cross-flow velocity at set operating point should be achieved gradually over 15-20 seconds
• Permeate obtained from first hour of operation should be discarded.

General Information

• Keep elements moist at all times after initial wetting.
• If operating limits and guidelines given in this bulletin are not strictly followed, the limited warranty will be null and void
• To prevent biological growth during prolonged system shutdowns, it is recommended that membrane elements be immersed in a preservative solution
• The customer is fully responsible for the effects of incompatible chemicals and lubricants on elements.
• Maximum pressure drop across an entire pressure vessel (housing) is 50 psi (3.4 bar).
• Avoid static permeate-side backpressure at all times

DOW

* Trademark of The Dow Chemical Company
Form No. 609-00350-803

ANNEXURE B – ROSA detailed report for RO system design.

The information contained on this annexure was obtained from the process simulation using ROSA design software

Reverse Osmosis System Analysis for FILMTEC™ Membranes   ROSA v6.1.5 ConfigDB U238786_55
Project: Proposed plant design 1   Case: 1
Gale Ralengole, Vaal University of Technology   1 20 2008

Project Information: Proposed RO plant design

System Details

Feed Flow to Stage 1	120.00 m³ d	Pass 1 Permeate Flow	36.00 m³ d	Osmotic Pressure:
Raw Water Flow to System	120.00 m³ d	Pass 1 Recovery	30.00 %	Feed 0.83 bar
Feed Pressure	14.39 bar	Feed Temperature	25.0 C	Concentrate 1.16 bar
Fouling Factor	0.85	Feed TDS	1833.43 mg l	Average 1.00 bar
Chem. Dose	None	Number of Elements	5	Average NDP 13.03 bar
Total Active Area	36.23 M²	Average Pass 1 Flux	41.40 lmh	Power 2.50 kW
Water Classification: RO Permeate SDI < 1				Specific Energy 1.67 kWh m³

Stage	Element	#PV	#Ele	Feed Flow (m³ d)	Feed Press (bar)	Recirc Flow (m³ d)	Conc Flow (m³ d)	Conc Press (bar)	Perm Flow (m³ d)	Avg Flux (lmh)	Perm Press (bar)	Boost Press (bar)	Perm TDS (mg l)
1	BW30-4040	5	1	120.00	14.04	0.00	84.00	13.99	36.00	41.40	0.00	0.00	18.48

Pass Streams (mg l as Ion)					
Name	Feed	Adjusted Feed	Concentrate	Permeate	
			Stage 1	Stage 1	Total
NH4	0.23	0.23	0.32	0.02	0.02
K	701.00	701.00	998.29	7.30	7.30
Na	75.00	83.30	118.67	0.77	0.77
Mg	6.00	6.00	8.56	0.04	0.04
Ca	16.00	16.00	22.82	0.09	0.09
Sr	0.09	0.09	0.13	0.00	0.00
Ba	0.06	0.06	0.09	0.00	0.00
CO3	0.00	0.00	0.00	0.00	0.00
HCO3	0.00	0.00	0.00	0.00	0.00
NO3	0.20	0.20	0.27	0.05	0.05
Cl	205.00	205.00	291.71	2.66	2.66
F	0.20	0.20	0.28	0.00	0.00
SO4	819.00	819.00	1166.85	7.34	7.34
SiO2	2.00	2.00	2.85	0.01	0.01
Boron	0.06	0.06	0.07	0.03	0.03
CO2	0.00	0.00	0.00	0.00	0.00
TDS	1825.12	1833.43	2611.25	18.48	18.48
pH	4.30	4.30	4.30	4.30	4.30

Design Warnings

-None-

Solubility Warnings

BaSO4 (% Saturation) - 100%
Antiscalants may be required. Consult your antiscalant manufacturer for dosing and maximum allowable system recovery.

Stage Details

Stage	Element	Recovery	Perm Flow (m³ d)	Perm TDS (mg l)	Feed Flow (m³ d)	Feed TDS (mg l)	Feed Press (bar)
1		0.30	7.20	18.48	24.00	1833.43	14.04

Permeate Flux reported by ROSA is calculated based on ACTIVE membrane area. DISCLAIMER- NO WARRANTY, EXPRESSED OR IMPLIED, AND NO WARRANTY OF MERCHANTABILITY OR FITNESS, IS GIVEN. Neither FilmTec Corporation nor The Dow Chemical Company assume liability for results obtained or damages incurred from the application of this information. FilmTec Corporation and The Dow Chemical Company assume no liability, if, as a result of customer's use of the ROSA membrane design software, the customer should be sued for alleged infringement of any patent not owned or controlled by the FilmTec Corporation nor The Dow Chemical Company.

Scaling Calculations

	Raw Water	Adjusted Feed	Concentrate
pH	4.30	4.30	4.30
Langelier Saturation Index	-11.13	-11.13	-10.95
Stiff & Davis Stability Index	-10.93	-10.93	-10.89
Ionic Strength (Molal)	0.03	0.03	0.05
TDS (mg l)	1825.12	1833.43	2611.25
HCO3	0.00	0.00	0.00
CO2	0.00	0.00	0.00
CO3	0.00	0.00	0.00
CaSO4 (% Saturation)	2.27	2.27	3.85
BaSO4 (% Saturation)	1298.12	1298.12	1789.82
SrSO4 (% Saturation)	0.84	0.84	1.23
CaF2 (% Saturation)	0.09	0.09	0.25
SiO2 (% Saturation)	1.20	1.20	1.71
Mg(OH)2 (% Saturation)	0.00	0.00	0.00

To balance: 8.30 mg l Na added to feed.

ANNEXURE C – Electricity tariffs in Gauteng Province

This information was found from the City power website

CURRENT TARIFFS				2007/2008					
	Supply Position	Service Charge	Network Charge	Maximum Demand		Energy Charge			
SEGMENT				Summer Winter					
		R/Month	R/Month	R/kVA	R/kVA	TOU		c/kWh	
							Non seasonal	Low Season	High Season
Large Customer - TOU	MV- kVA	3,626.28		38.75	40.95	Peak		23.75	55.07
						Standard		17.52	21.39
						Off - Peak		14.52	15.33
Large Customer - TOU	LV- kVA	2,948.67		43.07	45.52	Peak		26.40	61.23
						Standard		19.49	23.79
						Off - Peak		16.14	17.05
Large Customer	MV- kVA	805.01		52.12	54.38			15.81	23.38
Large Customer	LV- kVA	402.51		52.33	54.95			16.94	25.05
Business	400 V	85.34	66.00					33.85	50.96
< 100 kVA		94.94	84.50					33.85	50.96
< 500 kVA		120.42	109.85					33.85	50.96
> 500 kVA		175.63	164.78					33.85	50.96
Business Prepaid < 50 kVA							46.12		
Business Prepaid > 100 kVA							48.00		
Agricultural	400 V	96.23	65.00					26.28	39.57
> 50 kVA		111.75	76.70					26.28	39.57
Domestic 3 Ø Optional 60A	230 V	88.80	53.06					27.77	41.80
80 A		88.80	62.61					27.77	41.80
Domestic 1 Ø Optional 60A	230 V	88.80	33.19					27.77	41.80
80 A		88.80	38.83					27.77	41.80
Domestic 3 Ø 60A	230 V	88.80	53.06				33.02		
80 A		88.80	62.61				33.02		
Domestic 1 Ø 60A	230 V	88.80	33.19				33.02		
80 A		88.80	38.83				33.02		
Prepaid three phase							45.54		
Prepaid single phase							45.54		
Life Line conventional	230V						45.54		
Life Line Prepaid	230 V						43.23		
Robot intersection							43.84		
Streetlights & Billboard per luminaire							49.15		

ANNEXURE D – Analytical methods used

These are the methods used for the sample analysis at CSIR water laboratories

Determinand	Method Used	Method No.
pH Electrical conductivity Turbidity Colour Total dissolved solids Total suspended solids	Electrometric Conductimetric (25°C) Nephelometric Visual comparison Gravimetric (180°C) Gravimetric (103°C-105°C)	CMP 11 CMP 14 CMP 13 CMP 12 CMP 15 CMP 16
Kjeldahl nitrogen, ammonia nitrogen, nitrate & nitrite nitrogen, nitrate nitrogen, nitrite nitrogen, orthophosphate, free cyanide, cyanide (tot) chloride, sulphate, phenol	Automated Flow Injection	CMP 26 (a – k)
Alkalinity	Potentiometric titration	CMP 17
Bromide , Chromium (hexavalent)	Manual colorimetric	CMP 22, CMP 5
Fluoride	Ion - selective electrode	CMP 21
Sulphide*	Idiometric titration	CMP 23
Chemical oxygen demand	Colorimetric	CMP 24
Oxygen absorbed	Titrimetric	CMP 25
Aluminium, barium, lithium, strontium, calcium, magnesium, potassium, sodium, cadmium, chromium, cobalt, copper, gold, iron, lead, manganese, nickel, silver, zinc, silicon, boron, molybdenum, vanadium, antimony, titanium, total phosphorus, zirconium	Inductively - coupled plasma atomic emission spectrometry	CMP 1 CMP 26a
Arsenic, selenium	Hydride generation / inductively - coupled plasma atomic emission spectrometry	CMP 2
Mercury	Cold vapour generation / atomic absorption spectrometry	CMP 3
Total Hardness	Calculation	CMP 4
TOC, DOC	Aquadoc - IR spectroscopy	CMP 29
Salmonella	Presence / Absence	MMP 6
Somatic Coliphage*	Single /Double layer	MMP 7
Escherichia Coli	Indole Test	MMP 8
Heterotrophic plate count	Pour plate	MMP 1
Pseudomonas *Clostridia* Yeast & Moulds Faecal Streptococci Total & Faecal coliforms	Membrane Filtration	MMP 2, MMP 3. MMP 5, MMP 9, MMP 10, MMP 11
Legionella	MPN Assay	MMP 4

* = not accredited
09 March 2006

105