## **Evaluation of a PCI Reverse Osmosis**

## Membrane on Landfill Leachate

#### In fulfillment of the Masters Degree in Water and Environmental

Management

University of KwaZulu Natal

**Civil Engineering** 

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Declaration

I Vischal Rambridge hereby declare that this dissertation in my own work, unless stated in the text, and that it has not been submitted in part, or whole to any other University or Technikon. The research was carried out at the Bisasar Road Landfill site, Durban under the supervision of Dr. V L Pillay / Dr. C Trois

V Rambridge

## **Acknowledgements**

I wish to express my sincere gratitude to the following people for their contribution towards this dissertation:

- (i) Dr. Cristina Trois, for the supervision of the project.
- Gavin, for his invaluable support, and for providing the leachate for the project, which was a task on its own.
- (iii) Andre Swart, for his support and encouragement.
- (iv) Jappie Schoeman, who supplied the test unit.

## ABSTRACT

The specific objective of this study was to evaluate a PCI reverse osmosis membrane for determining the production rate of permeate, permeate quality, COD and BOD removal efficiency, ammonia removal efficiency, and whether the Department of Water Affairs and Forestry standards are achievable in the treatment of landfill leachate. The data collection was done by the author in 2001/2002. The chemical analysis was done by the CSIR in 2002 and the reporting on the findings were done in 2005/2006.

The equipment used was a reverse osmosis pilot plant supplied by the CSIR. The leachate used in the study was sourced from the Bisasar Road landfill site in Durban. The average COD of leachate used in the experiment was 2095 mg/l. The RO system was operated under a constant pressure of 4000 kPa, for over 500 hrs and monitored over 8 hrs/day to determine the permeate flux, conductivity, COD, BOD, pH, TDS, ammonia rejection and sodium rejection.

The results of the experiment showed that for a concentrated leachate an average COD removal efficiency of 97.7 % can be obtained. For other parameters such as total dissolved solids, ammonia, conductivity, the average removal efficiencies were 97.72 %, 88.97% and 95.0%, respectively.

The average clean water recovery during the eight hour experimental period was 70%, as suggested by local membrane suppliers. The percentage recovery was kept at 70% by adjusting the brine flow rate leaving the system. There was a drop in water recovery to below 70 % which was due to the flux decreasing during the night and the brine flow rate remaining constant.

The average clean water flux was 873  $l/m^2$ day versus the average normal flux of 542  $l/m^2$ day due to a clean water rinse being carried out before doing a clean water flux. The

clean water flux was achieved at the same operating pressures as the normal runs. The clean water flux was performed to give an indication of the performance of the membrane and also to set up the maintenance routine.

The average flux after a chemical clean was  $1158 \text{ l/m}^2$ day, Ultrasol 10 being the cleaning agent used in this study. The normal flux after the chemical cleaning cycles throughout the experiment dropped as expected due to the irreversible fouling layer formed on the membrane, which could not be removed by the Ultrasol 10 alone.

However the normal flux did increase at 500 hours when an Ultrasol 10 and HCl clean was done. This showed that the membrane was resilient to the leachate and could maintain a good rejection and recovery rate without drastic degradation.

These results indicate that leachate could be treated by the use of reverse osmosis, and high efficiencies of removal can be achieved, however still above the standard discharge limits stipulated by DWAF.

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### Abbreviations

- Ba Barium
- C.A. Cellulose Acetate
- Ca Calcium
- Cl Chlorine
- C.O.D. Chemical Oxygen Demand
- Cr Chromium total
- D.S.W. Durban Solid Waste
- D.W.A.F Department of Water Affairs and Forestry
- Fe iron
- HCI Hydrochloric Acid
- K Potassium
- Mg Magnesium
- MW Molecular Mass
- Mn Manganese
- Na Sodium
- NH<sub>3</sub> Ammonia Nitrate
- Ní Nickel
- NO<sub>3</sub> Nitrate
- P Total Phosphate

- P.A. Polyamide
- Pb Lead
- Si Silicon
- SO<sub>4</sub>
   Sulphate
- Sr Strontium
- T.D.S. Total Dissolved Solids
- T.O.C. Total Organic Carbon
- T.S.S. Total Suspended Solids

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## CHAPTER 1 INTRODUCTION

#### 1.1 Background

Toxic and hazardous compounds can originate from landfill leachate as a result of the soluble components of the solid and liquid wastes being leached into the surface and ground water. Therefore landfill leachate can be compared to complex industrial waste streams, which contain both toxic and inorganic contaminants.

The need for an environmental awareness towards the design of sustainable landfills, and a requirement to treat at source has led to the research into suitable leachate treatment strategies that could be applicable to the rural and semi-urban areas where sewer lines are not an option. In order to meet the stringent South African discharge standards, appropriate and cost effective treatment systems are required.

In general, the objective of leachate treatment at all landfill sites should be to attain the required standards for discharge, whether to sewer, watercourse, land or tidal water. A variety of physico-chemical and biological techniques are available for onsite treatment of leachate prior to discharge.

These techniques vary in cost, approach, applicability and effectiveness. Treatment strategies have to meet individual leachate volume, composition and discharge conditions and have to be site specific.

The major components in the leachate are:

- high concentrations of degradable and non-degradable organic materials,
- concentration of specific hazardous organics and inorganics
- ammonium and increasingly, nitrate ions
- sulphides
- odorous compounds
- suspended solids.

#### 1.2 Objectives

The Specific objectives of the study were as follows:

- To evaluate a PCI reverse osmosis membrane using the Bisasar Road Landfill Leachate for:
  - Production Rate
  - COD and BOD Removal
  - Ammonia removal
  - o Cleanability
  - o Economic Feasibility
- To investigate if the treated permeate meets the Department of Water affairs and Forestry (DWAF) discharge standards.

#### **Motivation**

To minimize the impact on the environment the Department of Water Affairs and Forestry (DWAF) have put in place a minimum effluent discharge standard that should be met. Therefore research has to be done in order to determine a means to treat leachate being discharged from landfills, therefore leachate treatment facilities should satisfy the following

- the leachate treatment system should be adequate for the varying volumes and compositions of the leachate generated through all stages of the landfill development and restoration.
- the treatment should be robust, to ensure that the performance requirements are maintained throughout and beyond the operational life of the landfill.
- Should be cost effective

#### 1.3 Approach

The approach for the literature review was to get as much insight into the following:

- Leachate generation
- Composition
- Leachate treatments
  - > Physical
  - > Biological
    - Problems with leachate treatment in South Africa
    - Reverse Osmosis

The experimental approach was as follows:

- Determination of the clean water flux for production rates and cleanability of the membrane
- Investigate the removal efficiencies of Total Dissolved Solids (TDS)
- Investigate the removal of Chemical Oxygen demands (COD)
- Investigate the removal of Ammonia and sodium and compare them to the Department of Water Affairs and Forestry (DWAF) standards.

#### 1.4 Thesis Outline

The remainder of the thesis is divided into five chapters:

Chapter 2 deals with literature review

Chapter 3 deals with the experimental system and procedures.

Chapter 4 deals with the results

Chapter 5 concludes the study

# CHAPTER 2 LITERATURE REVIEW

#### 2.1 Leachate generation and composition

#### 2.1.1 Leachate Generation

Leachate that is generated in landfills is a contaminated liquid that contains dissolved products from decomposing wastes. This liquid can be over 50 times as strong as industrial effluents. The leachate is formed as water permeates through the landfill. The source of the water is mainly from precipitation into an operating landfill, infiltration through the surface of a completed landfill, or to a lesser extent, water already contained in the waste, and runoff from exterior surrounding areas. (Robinson, 1986)

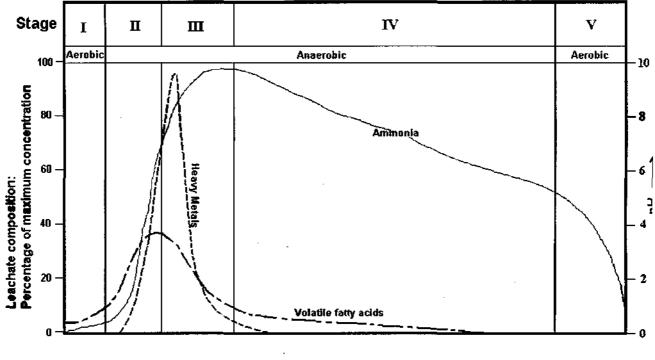
The best place to try to prevent the generation of leachate is at the surface of the landfill. Water entering the landfill will end up in one of three places:

- Surface runoff into drainage, which surround landfills.
- Evaporation from the landfill
- Percolating into the waste in the landfill.

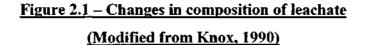
The water percolating through the landfill will react both biologically and chemically with the waste. Biological reactions take place on a continual basis, and will be either aerobic or anaerobic decomposition depending on the amount of oxygen available, and on the stage of decomposition of the landfill. Chemical decomposition in the waste itself will also add contaminants to the leachate.

#### 2.1.2 Leachate Composition

The composition of the leachate will be dependent on the materials that the waste is made up of, and the age, or level of decomposition of the waste. Evidence has been found that leachate compositions can vary significantly between landfills and at individual landfills over time (Kmet and McGinley, 1982) The results of reports submitted to the Wisconsin Department of Natural Resources by landfill operators who monitored leachate collection systems of sixteen landfills were summarized. Nine of which accepted industrial waste, and three accepting hazardous waste. They also found variations in the concentration of the leachate over time (Figure 2.1 and Figure 2.2). (Robinson, 1986)



Time  $\longrightarrow$ 



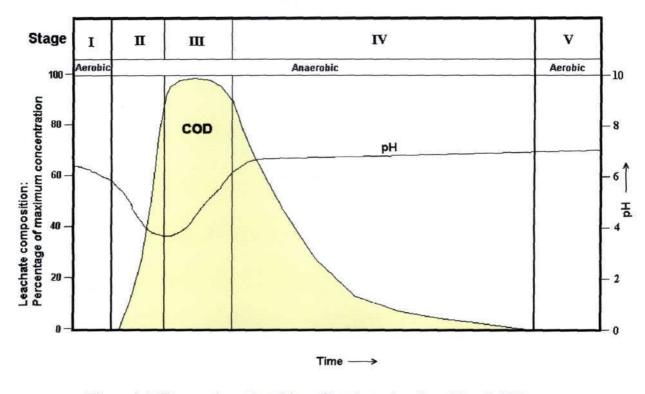


Figure 2.2 Changes in composition of leachate showing pH and COD (Modified from Knox, 1990)

The composition of leachate depends on the stage of degradation and type of leachate within a landfill (Figure 2.1 and 2.2). Leachates generated during the early stages of anaerobic degradation are characterized by high concentrations of volatile fatty acids, acidic pH, high BOD to COD ratio and high levels of ammoniacal nitrogen and organic nitrogen. Ammonia is mostly generated from the decomposition of proteinaceous materials. As the pH rises, precipitates of sulphides, hydroxides and carbonates are formed (Knox 1990).

After the onset of methanogenesis, many of the fatty acids responsible for the acidic pH and high BOD are converted to methane and carbon dioxide. Methanogenic leachates are characterized by low concentrations of fatty acids, neutral to alkaline pH, lower levels of ammoniacal nitrogen and low BOD to COD ratios. During the steady methanogenic stage, a dynamic equilibrium exists where organic compounds are consumed as fast as they are produced (Knox 1990).

The adsorptive capacity of the waste is also an important consideration affecting leachate generation. The capacity may be exceeded by rainwater or ground water flowing into the

landfill or generation of water by microbial processes and liquid waste input. Leachate generation can occur well before the adsorptive capacity has been reached.

Other factors may result in higher than normal contaminant concentrations. These may be because of certain industrial wastes being introduced into the landfill. In addition, as the weather changes throughout the year, this may affect solid waste characteristics. The amount of precipitation will affect the concentration of leachate. During the rainy season, the concentration of the leachate will be lower due to dilution. The introduction of hazardous materials into landfill may result in a leachate that could, itself end up being classified as a hazardous material. It may then require special handling.

Physical modification of solid waste may also have an impact on the leachate characteristics. Shredded refuse was shown (Ham 1980) to generate higher initial contaminant concentrations than unprocessed waste. After a period, the concentration of contaminants declined sharply. This is in contrast to unprocessed solid waste where it was found that leachate concentrations declined slowly (Robinson, 1986).

The operational procedures of the landfill will also affect the characteristics of the leachate. In an experiment, Ham placed solid waste in 1.2m deep test cells and placed different covers over each one. Over some, he placed an earth cover, others had a covering of more waste, while others were left uncovered. The test cells that were not covered, had high initial concentrations of chemical oxygen demand, but these concentrations declined rapidly when compared to those test cells where earth-covered material was placed over them (Ham, 1980). The objective of leachate treatments is to obtain the required discharge standards. Treatment strategies should meet individual leachate volume, composition and discharge conditions, and will be site specific. The components of the leachate that may need to be removed prior to discharge include:

- High concentrations of degradable and non-degradable organic and non-organic materials
- High concentrations of specific hazardous organics and inorganics
- Ammonium and nitrate ions
- Sulphides
- Odorous compounds
- Suspended solids

#### 2.2.1 Physical Treatment

#### Activated carbon adsorption

Granular activated carbon (GAC) is a highly porous material with a high surface to area ratio. GAC (and powdered activated carbon – PAC) have been used to adsorb residual quantities of organic materials from leachates which have previously had the majority of their organic contaminants removed using other treatment methods.

- suspended solids must be removed from the leachate prior to treatment, to prevent blockages on the carbon filter. This can be achieved by several means including plate separators and pressurized sand filters.
- The activated carbon can be regenerated after it becomes completely saturated with absorbent. The regeneration cycle cannot be taken in situ. In situations were small volumes of GAC (often in modular units) have been used, the GAC may be disposed of by incineration rather than sent for regeneration.

This method of treatment can be used in an effluent polishing situation to reduce COD loading, non-volatile organics and hazardous organics. The treatment can be highly effective with up to 99% removal attainable, but is generally very expensive in significant quantities of residual COD required treatment (Horan N. J et al:1996)

#### Air stripping of ammonia

Air stripping of ammonia is frequently considered as a treatment method for leachate. The process can be undertaken in a lagoon or in a purpose built stripping tower. The pH of the leachate is adjusted to values of 11 or above prior to being exposed to large amounts of air. Gaseous ammonia is then released to the atmosphere (Collivignarelli C. et al. 1998).

Several factors have to be considered when using air stripping of ammonia from leachate.

- the environmental impact of releasing gas into the atmosphere is difficult to mitigate. Considerable quantities of ammonia with significant ouder would be released unless removed by subsequent scrubbing. Gas scrubbing might be used to prevent this ammonia discharge to the atmosphere but the capital and running costs of such a system may render the overall process relatively expensive.
- The power costs associated with the provision of large amounts of air, which must be supplied for the stripping process, are likely to be high. In addition, because of the half-life nature of the reductions in ammonia values, it may well prove extremely expensive to achieve very low effluent concentrations, which are often required.
- The pH of the treated effluent will require adjustment prior to discharge in accordance with the discharge consent requirements. The adjustment of pH will also require potentially large quantities of alkali and acid reagents.

#### **Evaporation**

This is a two to four stage process in which leachate is concentrated by evaporation and distillation. Pre-treatment involves the addition of acid to reduce the pH levels, and turn ammonia into soluble ammonia salts. The leachate is evaporated, and separated into distillate and residual liquor. The concentrate is typically 1/20 of its original volume. The concentrated leachate is sometimes sent back to the landfill (Deborah R. Birchler et al. 1994)

#### 2.2.2 Physical / Chemical Treatment

#### Coagulation, flocculation and settling

This treatment involving the addition of reagents to the leachate followed by mixing and settling, results in a reduction in suspended solids, heavy metals, turbidity, colour and some organic loading concentrations. It may be used before or after other treatment methods. Reagents that are added to the leachate include lime, sodium and magnesium hydroxide, ferric chloride and sulphate, and polymeric coagulants (Galvez Perez et al. 2004)

#### Oxidation with hydrogen peroxide, hypochlorite solution and ozone

Oxidation of leachate by the addition of oxidizing agents and pH adjustments may be used for the removal of sulphides, sulphite, formaldehyde, cyanide, and phenolics. The principle use of this type of treatment is in situations where odours caused by sulphides are a particular problem (Wang F et al. 2003)

- the performance of the process depends on the reaction time and on the oxidizing agent chosen. Agents other than hydrogen peroxide may be used, including calcium and sodium hypochlorite, ozone and chlorine gas with caustic soda. Caution has to be exercised when using oxidizing agents to ensure safe handling.
- Treatment may be carried out in batch or continuous process, using dilute solutions of the oxidizing agents. A ratio of hydrogen peroxide to soluble sulphide of unity, at a neutral pH, with a contact time of about ten minutes is usually adequate to remove sulphides.

Organic compounds may also be removed by oxidizing agents such as ozone, although high dosages are often required to bring about significant reductions in COD. Ozone has been used in wastewater treatment plants to control odours, improve suspended solids removal, oxidize pesticides and improve biodegradability of other organic compounds (Wang F et al. 2003).

#### Wet air oxidation

This is a type of combustion process which may be suitable for leachates with high organic strength, for example with COD between 5000 and 150 000 mg/l. The process can be undertaken in conjunction with other physical-chemical or biological treatment processes, and used as a final or polishing stage of leachate treatment

The leachate is mixed with air, and is pumped into a series of heat exchangers under pressure. Oxidation takes place in a reactor at temperatures of up to 310 °C, and a pressure of up to 20000 kPa. The resulting gas phase is passed through an air purification system, and

vented at atmosphere, and the liquid phase is recycled into a heat exchanger(Cossu R et al. 1998). This technique is expensive but can be used to treat very high strength leachates.

#### 2.2.3 Biological Treatment

#### Aerobic biological treatment:

#### Trickling or percolating filters

This is an attached growth process. This type of treatment is limited, as it cannot readily be used as a single stage treatment for high strength leachates that contain high COD and ammoniacal-N. This is due to clogging that occurs because of a build up of slimes (microbial growth) and the precipitation of inorganic salts. If inorganic salts are responsible for the clogging, then this problem can be overcome by physico-chemical pretreatment (Robinson et al. 1999).

#### **Rotating biological contactors**

This is an attached growth process. This treatment consists of rows of rotating shaft-mounted disks. The disks rotate and in doing so, attached microorganisms are alternatively immersed in leachate, and then exposed to air. Rotating biological contactors are more successful in handling high strengths leachates than percolating filters (Robinson et al. 1999).

#### Non-attached processes

In this process, which can be performed in a lagoon or tank, aeration encourages the formation and growth of suspended biological flocs, which break down and metabolize the polluting components of the leachate. The average retention time for this treatment is from 10 to 20 days. High efficiencies in removal of COD and ammoniacial nitrogen can be achieved.

- Extended aeration treatment plants have been shown to be robust, both biologically and mechanically. Mechanically, extended aeration plants can be engineered to require little maintenance, and to provide automated discharge of treated leachate as appropriate to specific discharge consent.
- The microbial flocs are resilient to shock loads. They can acclimatize to the presence of toxins and metals as well as high ammoniacal-N and chloride levels, partly because of the large volume of the extended aeration system enables them to rapidly dilute incoming leachate dosages.
- The extended aeration plants developed for leachate treatment differ in their operation from standard activated sludge processes (which were initially developed for treatment of domestic sewage and have been installed at some

landfills). The short residence time of the activated sludge plants enables reduction of COD but only limited removal of ammoniacal nitrogen.

Phosphoric acid is generally added to the extended process to ensure sufficient phosphate levels for microbial growth. Regular inputs of alkali, preferably sodium hydroxide, may also be added to counteract reduction in pH, which occur during the nitrification process.

Extended aeration treatment lagoons, if operated correctly on a daily cycle in accordance with recent leachate treatment research, have been found to be a flexible form of leachate treatment (Robinson et al. 1999).

#### Anaerobic biological treatment

This treatment uses similar biodegradation processes to that of a landfill. High removal of BOD and COD can be achieved by degradation of organic materials to methane and carbon dioxide (Kettunen R H. et al 1999).

The main problems with anaerobic treatment of leachate are:

- Once landfill waste ultimately achieve subsequent methanogenic conditions, with effective conversion of organic compounds to landfill gases, an anaerobic plant could become redundant.
- Removal of ammoniacal nitrogen, perhaps the major long-term contaminant in many land fill leachate, cannot be achieved in any anaerobic system.

#### 2.3 The problem of leachate treatment in South Africa

Landfills containing municipal wastes can have serious economic implications, and in a struggling economy, thought should be given to providing cost effective leachate treatments. The benefits of certain leachate treatment processes should be weighed up against other social demands placed on local taxes. Leachate treatments thus not only have to meet discharge standards, but also have to be economically viable.

Due to South Africa being a semi arid area, water is often derived from aquifers. Any leachate being discharged into these aquifers may cause a serious environmental or health problem if standards are not met. Legislation thus has to be put in place in order to protect both man, and the natural environment.

#### 2.4 Legislation concerning leachate treatment in South Africa

Water quality criteria aim to define the limits for the use of water in various processes. These apply not only to industrial processes, but also to processes such as agricultural production and leachate generation. Generally, the criteria are the concentration of a contaminant above which the water cannot be used for its intended purpose.

In South Africa, the Uniform Effluent Standards (UES) has an approach that aims to regulate the effluents into river systems by way of uniform standards. The goal were to approach a zero discharge of effluent. The standards are set to treat contaminated effluents based on Best Available Technology Not Entailing Excessive Cost or BATNEEC. (Pulles et al, 1996)

The problem with this however is that the standards only take into account the effluents, and do not consider that the receiving water may already be polluted. It also doesn't take into account that different river systems have varying abilities to assimilate pollutants. The approach is however simple and straightforward. (Pulles et al, 1996)

Although the Uniform Effluent Standards lead to a decrease in the rate of water quality deterioration, deterioration of the resource is continued. A more advanced approach to water quality management was thus required. The Department of Water Affairs and Forestry (DWA&F) adopted an approach in 1990 to where the following principles would be included:

"The desired quality of a water resource is determined by its present and/or intended uses. This quality should be stated as a list of water quality objectives" (Pulles et al, 1996).

It is accepted that the water environment has a certain, usually quantifiable, capacity to assimilate pollutants without detriment to predetermined quality objectives.

The assimilative capacity of a water body is part of the water resource and, as such, must be managed judiciously and shared in an equitable manner amongst all water users for the disposal of wastes.

For those pollutants which pose the greatest threat to the environment, because of their toxicity, extent of bio-accumulation and persistence, a precautionary approach aimed at minimizing or preventing inputs to the water environment should be adopted."

The control of point source pollutants can be controlled by the use of regulations and permits. Monitoring programs of effluents is thus important to gather information of water quality, and how it changes over time. Effluent discharge into the natural environment is still restricted to the general effluent standards. (Table 2.1) Appendix B gives the standards for other countries.

Parameter	Standard		
	Shall not contain any substance in a concentration capable of producing		
Colour, odour or taste	Any colour, odour or taste		
РН	Shall be between 5.5 and 9.5		
Dissolved oxygen	Shall be at least 75 per cent saturation		
Typical (faecal) coliforms	Shall not contain any coliforms per 100 ml		
Temperature	Shall be a maximum of 35°C		
Chemical Oxygen Demand	Not to exceed 75mg/l after applying the chloride correction		
Ovugan abaanhad	The oxygen absorbed from acid N/80 KMnO4 in 4 hours at 27°C shall not		
Oxygen absorbed	exceed 10mg/l		
Suspended solids	Not to exceed 25mg/l		
Sodium	Not to be increased by more than 90mg/l above that of the intake water		
Soap, oil or grease	Not to exceed 2.5mg/l		

## <u>Table 2.1 - General Effluent Standards (Pulles et al 1996)</u>

Other Constituents	Maximum concentrations			
Residual chlorine	0.1mg/l			
Free and saline ammonia	10.0mg/l as N			
Arsenic	0.5mg/l as As			
Boron	1.0mg/l as B			
Hexavalent Chromium	0.05mg/l as Cr			
Total chromium	0.5mg/l as Cr			
Copper	1.0mg/l as Cu			
Phenolic compounds	0.1mg/l as phenol			
Lead	0.1mg/l as Pb			
Cyanides	0.5mg/l as CN			
Sulphides	1.0mg/l as S			
Fluoride	1.0mg/l as F			
Zinc	5.0mg/l as Zn			
Manganese	0.4mg/l as Mn			
Cadmium	0.05mg/l as Cd			
Мегсигу	0.02mg/l as Hg			
Selenium	0.05mg/l as Se			
	The waste water or effluent shall contain no other constituents in			
Other	concentrations which are poisonous or injurious to humans, animals, fish			
	deleterious to agricultural use			

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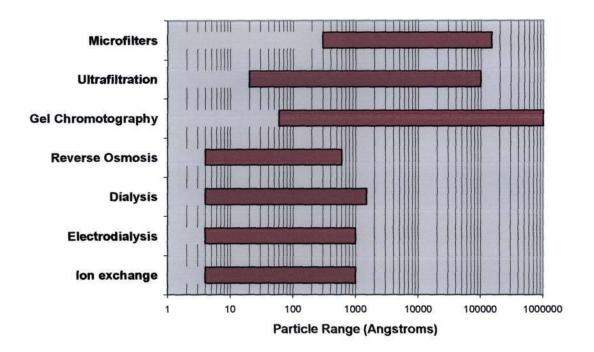
#### 2.5 Membrane Technology

#### 2.5.1 Introduction

The main purpose of a membrane process is to separate one or more components from a liquid that contains two or more components. This is achieved by using a differential driving potential across a membrane. Either the goal is to remove unwanted solutes such as dissolved organics and in-organics from the feed solution, or to make relatively clean water, and leave a more concentrated solute (Belfort G, 1984).

The United States Office of Saline Water in the late 1950's provided the impetus to develop a new desalinating process by reversing the osmotic flow through a selective membrane. UCLA was given the task, and thereafter developed a practical reverse osmosis membrane with sufficiently high water flux to make the process economically viable.

Although membrane process is a new science, several new processes for water and wastewater treatment have been developed since the late 1960s. These include the membrane processes as a group, which can be divided into the pressure driven Reverse Osmosis and Ultra-filtration, and electrically driven Electro-dialysis and Transport-depletion. These separation processes are characterized by their ability to filter, or remove matter from the feed. Figure 2.3 shows the useful range of particle size separation of various processes.



#### Figure 2.3 – Useful range of various separation processes

It can be seen from Figure 2.3 that there is overlap in the particle size separation. The reason for this is mainly that both Reverse Osmosis and Ultra-filtration membranes can be "tailor-made" for rejection of larger or smaller particles. The upper molecular mass cutoff for Ultra-filtration is in the region of about 400 000. Above this molecular mass, micro-filtration can be used. It allows the passage of solvent and solute molecules, but prevents the passage of small particulate matter.

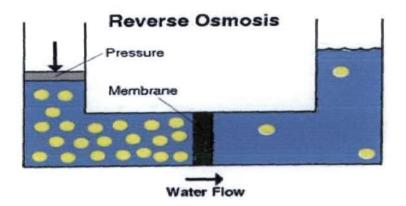
Table 2.2 shows various membrane processes, the pressure at which the membrane can operate (dictated by the Osmotic pressure), the constituents removed from the feed water and the constituents remaining in the product.

			1	Possible size of
Durante	Driving Potential	Constituents removed	Constituents remaining in	permeable
Process		from feed water	product (other than water)	species
				(Angstroms)
Reverse Osmosis (Hyper- filtration)	Pressure (as high as 40atm)	Water without dissolved and non- dissolved inorganic and organic	Little salt (owing to membrane leakage) BO <sub>3</sub> , NO <sub>3</sub> , urea, and low MW organics.	4-300
Ultra-filtration	Pressure (usually below 10atm)	constituents Water without non- dissolved organic constituents	All the salt and low molecular weight organics	20-100000
Electro-dialysis	Electrical	Dissolved inorganic ions	Little salt, all the organics (dissolved and non- dissolved) including viruses, bacteria, etc.	4-300
Transport depletion	Electrical	Dissolved inorganic ions	More than a little salt, all the organics (dissolved and non-dissolved) including viruses, bacteria, etc.	10-1000

#### Table 2.2 - Classification of Membrane Processes - (Belfort 1984)

#### 2.5.2 Reverse Osmosis

Osmosis is a process in which a solvent is transported through a membrane as a result of a difference in trans-membrane concentration. Figure 2.4 shows a dilute solution (in the outer tank) separated from a concentrate solution (inner tank) that may contain salts for example. A natural flow or flux will occur through the membrane from the dilute solution to the concentrated solution, even though a pressure difference will develop to try to prevent this – due to the increased head of liquid. This extra head of pressure – once stabilised, is called the Osmotic pressure of this system. It must be noted however that once the head difference has stabilised, solvent still passes through the membrane, but fluxes are statistically the same in both directions. (Rautenbach 1989)



#### Figure 2.4: Diagram Illustrating Reverse Osmosis

van't Hoff discovered in 1885 that the relationship between osmotic pressure and concentration (or another measure of concentration such as molar fraction or mass content) is linear, at least for highly dilute solutions, and is given by equation 2.2.

 $\pi = v_i c_i R T \tag{2.2}$ 

Where:

 $\pi$  is the Osmotic pressure  $c_i$  is the molar concentration of the solute  $v_i$  is the number of ions formed if the solute dissociates (e.g., for NaCl,  $v_i = 2$ ; for BaCl<sub>2</sub>,  $v_i = 3$ ) R is the gas constant

T is the absolute temperature

It can be seen from the equation 2.2 that if the temperature is raised, the Osmotic pressure will increase. This is due to the increase in flux passing through the membrane.

If pressure is applied to the more concentrated solution (Figure 2.4), and if that pressure exceeds the osmotic pressure, water flows through the membrane from the more concentrated solution toward the dilute solution. This process, called Reverse Osmosis removes a high

percentage of dissolved minerals, and an even higher percentage of colloidal and suspended matter. Reverse Osmosis can thus produce high quality water at low cost compared to other purifications processes, such as evaporation purification in which a large amount of energy is required to cause a change of state from liquid to gas.

The water transport (at constant temperature) due to Reverse Osmosis through a semipermeable membrane is described by the equation 2.3. (Rautenbach 1989)

$$Q_w = K_w (\Delta P - \Delta \pi) A / \tau \qquad (2.3)$$

Where:

 $Q_w$  is the water flow rate through the membrane

K<sub>w</sub> is the membrane permeability through the membrane

 $\Delta P$  is the hydraulic pressure differential across the membrane

 $\Delta \pi$  is the osmotic pressure differential across the membrane

A is the membrane surface area

 $\tau$  is the membrane thickness

It can be seen from equation 2.3 that in order to increase the amount of flow through the membrane, the surface area of the membrane simply has to be increased. Other options are to decrease the thickness of the membrane, or to increase the hydraulic pressure differential across the membrane.

Membranes need to be physically strong so that they are not destroyed when the high Osmotic pressures are applied to it. As an example - in the case of seawater,  $2500 \text{ kg/m}^2$  (Rautenbach et al. 1989) Most Reverse Osmosis membranes are made of either cellulose acetate or polyamide composites. These are cast into a thin film, either as a sheet or fine hollow fibres and then constructed into a cartridge called a Reverse Osmosis module. Pores in reverse osmosis membranes are so small they have not yet been resolved, even with electron microscopes. They are generally regarded to be in the 4 to 8 Å range.



Plate 2.1 – Reverse Osmosis module

After filtration to remove suspended particles, the incoming liquid is pressurized with a pump up to 4000kPa depending on the Reverse Osmotic pressure of the liquid and the system as a whole. This pressure will exceed the waters osmotic pressure. A portion of the water (called permeate) diffuses through the membrane leaving dissolved salts and other contaminants behind with the remaining water where they become more concentrated (often called brine or concentrate).

In order for the membrane to last, pretreatment is important. This is also necessary as it influences permeate quality and quantity. It affects the module's life because many waterborne contaminants can deposit on the membrane and foul it. Generally, the need for pretreatment increases as the system become larger and operates at higher pressures, and as permeate quality requirements become more demanding. This pretreatment is often simply the adjusting of the pH of the feed to a level that is suitable to the relevant membrane, as well as the addition of an anti- scalant to the feed in order to prevent premature fouling of the membrane.

#### 2.5.3 Membrane materials

The ideal membrane has the following characteristics: (Rautenbach 1989)

- High water flux rates
- High salt rejection
- Tolerant to chlorine and other oxidants
- Resistant to biological attack
- · Resistant to fouling by colloidal and suspended material
- Inexpensive
- Easy to form into thin or hollow fibers
- Mechanically strong, e.g., tolerates high pressures
- Chemically stable
- Able to withstand high temperatures

Since Reverse osmosis membranes need to have extremely small pores and significant water sorption tendency, only two materials are commonly used. As mentioned before, these are cellulose acetate (CA) and polyamide (PA) polymers. The CA membranes tolerate chlorine at levels used for microbial control, however at this level of chlorine, PA membranes will be destroyed. PA membranes do produce both higher rejection and flux, and tolerate a wider pH range on a continuous basis and a higher continuous temperature than CA membranes. The pH range that CA membranes can tolerate is between 2-8, while for PA membranes it is below  $40^{\circ}$ C, while for PA membranes it is below  $65^{\circ}$ C.

#### 2.5.4 Fouling of membranes

The definition of membrane fouling is not precise, however it is concerned with long-term flux decline and eventually retention decrease because of the accumulation of some fouling material. Gel formation on the membrane surface, membrane compaction, and membrane hydrolysis result in a similar phenomena and it is often impossible to distinguish between them. The main difference between gel formation and fouling is that the gel layer if formed on the membrane surface because the gel concentration is reached, whereas fouling is formed by another mechanism, and is more closely bound to the membrane surface. (Belfort 1984)

Fouling may be caused by a variety of compounds. These foulants may be classified as: (Belfort 1984)

- Dissolved organics, including humic substances, biological slimes and macromolecules.
- Dissolved inorganics, including inorganic precipitates such as CaSO<sub>4</sub>, CaCO<sub>3</sub>, Mg(OH)<sub>2</sub>, Fe(OH)<sub>3</sub>, and other metal hydroxides.
- Particulate matter.

The fouling mechanism is probably similar for most foulants, and thus in order to gain insight, only a few foulants need to be looked at (Jackson et al. 1973) followed this reasoning. They looked at the rate of fouling by deposition of iron hydroxide on tubular reverse osmosis membranes and postulated that the fouling occurred from a two-step nucleation growth mechanism. In the nucleation phase, foulants are deposited in pores and surface cavities of the membrane. This attachment is caused by the mechanical force acting from the convection of the foulants to the membrane surface and van der Waals' forces of attraction. The number of nucleation sites being dependent on the relative size of the foulants and pores in the membrane, as well as surface changes. The second step in this process is once sufficient amounts of foulant are trapped on the membrane surface, they act as nuclei from which growth proceeds by a polymerization reaction similar to those in flocculation. Large particles build up on the membrane surface forming a thin porous layer. The rate of growth depends on the number of nuclei, the rate of polymerization reactions, and the transport of foulants to the membrane surface. (Belfort 1984)

Fouling can also be explained by the fact that it is normally caused by materials that have large surface areas and are hydrophobic, therefore repelling water. When a hydrophobic substance is in an aqueous environment, it can reduce its total energy by reducing the area exposed to water. Therefore, it will be held to the surface of the membrane by the elimination of repulsive interactions with the surrounding water. (Gregor and Gregor, 1978)

There are three main ways to prevent fouling. These are:

- Hydrodynamics of the Membrane Module Fouling generally decreases with decreasing concentration polarization, so that a high flow velocity and a high Reynolds number is useful in slowing down the rate of fouling.
- Pretreatment of the feed Solution These include:
  - 1) Filtration prior to RO
  - 2) Chemical clarification
  - 3) pH adjustment.
  - 4) Chlorination

- 5) Adsorption on active carbon
- Properties of the membrane The pore size distribution of the membrane influences the fouling tendency. Dense membranes are normally less exposed to fouling than open membranes. (Belfort 1984) In addition, by creating a hydroscopic membrane, which has a strong affinity to water, the membrane will remain wetted even in the presence of hydrophobic particles. These particles thus cannot adhere to the surface.

## 2.5.5 Cleaning methods

When the flux has decreased to unacceptable values, the membrane must be cleaned. The cleaning method and frequency depend on the type of foulant and the chemical resistance of the membrane. There are three basic ways to clean a membrane: (Belfort, 1984)

- Hydraulic cleaning Sometimes a depressurizing followed by flushing with water at high linear velocity. This is sufficient to remove a fouling layer. Chemical cleaning then only needs to be used rarely.
- Chemical cleaning The following is a list of chemicals that can be used in cleaning:
  - 1) Acids (HNO<sub>3</sub>, H<sub>3</sub>PO<sub>4</sub>, citric acid)
  - 2) Bases (NaOH)
  - 3) Complexing agents (EDTA)
  - 4) Enzymes
  - 5) Detergents
  - 6) Disinfectants
- Mechanical cleaning This is often done in tubular modules. In situ mechanical cleaning can be performed by passing a sponge ball over the surface of the membrane.

## **CHAPTER 3**

# **Experimental Apparatus and Procedures**

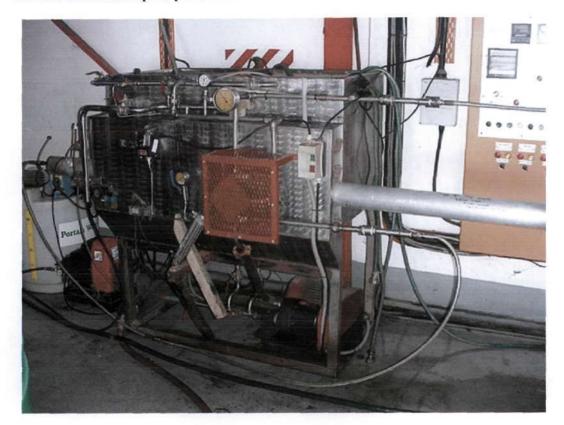
## 3.1.1 Leachate Collection and Storage

The apparatus used for the experimentation in this dissertation was a Reverse Osmosis pilot plant supplied by the CSIR. On an almost weekly basis, leachate was drawn from the collection point at the base of Bisasar Road Landfill and brought by tanker to a 10000-liter Jojo tank into which it was pumped. Plate 3.1 shows the main Jojo tank.



Plate 3.1 - Tanks containing un-treated leachate

## 3.2 Pilot Plant Description



The Reverse osmosis pilot plant used is shown in Plate 3.2.

Plate 3.2 - Reverse osmosis plant

The pilot plant consisted of two tanks, constructed of stainless steel, and welded together, which was housed on a steel frame. A motor and pump were located on the lower right of the frame, under the tanks. A membrane module holding a PCI membrane, was placed in position in front of the tanks (horizontal cylinder in plate 3.2), and connected up so that the liquid from the tanks would be pumped from one tank and through the membrane module. The 1000-liter Jojo tanks were connected to a main feed pipe by a valve, so that the leachate from each Jojo tank could be fed into the pilot plant in turn. The leachate being used could thus be recorded. The leachate

was fed into the tank on the right of the plant (feed tank) by a small pump that had a cut off circuit, so that once the tank reached a specific level, the feed would automatically switch off. Leachate could then be pumped into the membrane.

## 3.3 Flow Configurations

The membrane module was constructed in such a way that once the feed had flowed over the membrane it could be returned to the tanks. This meant that a substantial amount of brine was sent back into the feed tank. The feed in the feed tank thus became more concentrated. The reason for this action was to simulate how a membrane would react to the concentrated leachate in the last stage of a full-scale reverse osmosis plant.

An adjustable timer was located on the side of the unit (Plate 3.3). This timer was used to operate a compressor (Plate 3.4), which was attached to a valve assembly on the front of the plant. This could be set such that a switch would cause a piston to move three levers, which changed the flow direction through the membrane module. Changing the direction of flow caused a sponge ball, which was placed in the module to pass through the module, thus removing deposited material from the surface of the membrane.

The apparatus consisted of ten ball valves positioned such that various directions of flow could be achieved through the plant.



Plate 3.3 - Side View of Reverse Osmosis Pilot Plant

## 3.4 Cooling Elements

As the feed in the reverse osmosis plant passes through the plant several times the leachate tends to heat up, however this could be a problem, as the membranes are very sensitive to temperature. In order to solve this problem, a cooling coil was placed in the feed tank, and connected up to a water supply. This coil allowed water to pass through it – thus cooling the feed. Two pressure gauges were also located on the plant that indicated both the pressure on the inlet and outlet side of the membrane.

## 3.5 Anti Scalant Dosing Package

A 120-liter polyethylene tank with a dosing pump was used for the anti-scalant dosing into the main feed tank. The antiscalant solution was made up once a week and dosed at the required flowrate. The dosing pump had a 0-100 % manual stroke adjustment for dosing at different rates.

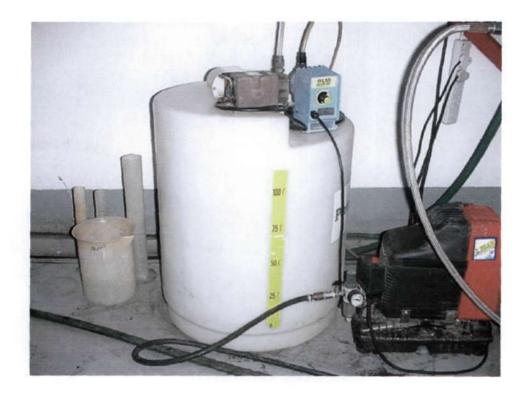


Plate 3.4 – Anti- scalant tank showing dosing pumps on top with air compressor on the right

## 3.6 pH and Conductivity Measurements

Other equipment used for measurements were the pH meter and the conductivity meter. They are shown in plate 3.5.



## Plate 3.5 - Conductivity meter (left) and pH meter

## **Conductivity Meter**

The LF 318 hand held conductivity meter, manufactured and supplied by Wissenschaftlich-Technische Werkstatten GmbH, was used for conductivity measurements.

## pH meter

The model 230 hand held pH meter, manufactured and supplied by Therm Orion was used for the pH monitoring of the plant.

Both instruments were calibrated regularly using standard calibration methods.

## 3.7 Experimental Procedure

#### 3.7.1 pH Adjustment

The feed pH had to be first adjusted to between 7.0 and 7.2. This was done by adding approximately 2.5 liters of a 30% concentrated hydrochloric acid into each of the small jo-jo tanks, and continually mixing and checking the pH level while adding 100ml of acid at a time.

#### 3.7.2 Anti-Scalant

In addition, before the RO plant was started, the amount of antiscalant was checked. If more was needed, it could be made from a commercially available product called Flocon. It was in concentrated form, and for every 100ml of Flocon, 100 liters of tap water was added to it. Once mixed, for every 1 liter of pH-adjusted leachate entering the feed tank, 12.5 ml of antiscalant was added to it.

The dosing rate for antiscalant was calculated as follows:

Feed flow rate = Permeate flow rate + Brine to waste flow rate

For example: Feed flow rate = 0.55 l/min (Permeate) + 0.225 l/min (Brine)

= 0.775 l/min

Therefore antiscalant rate =  $12.5 \text{ ml} \times 0.775 \text{ l/min}$ 

= 9.69 ml/min

#### The percentage water recovery

The percentage water recovery was determined using the following equation: Percentage Recovery =  $\frac{\text{Rate of Flux out } x - 100}{(\text{Rate of Flux out}) + (\text{Rate of brine out})}$  The percentage recovery was kept at 70% (requested by membrane manufacturer) by adjusting the brine flow rate leaving the system. The drop in water recovery to bellow 70 % was due to the flux decreasing during the night and the brine flow rate remaining the same. Unfortunately there was no one available at night to adjust the brine flow rate so as to maintain the water recovery at 70 %.

The rejection is given equation 3.2, and shows the membranes ability to stop salt passage through it.

$$\eta = \underline{\text{Pin} - \text{Pout}} \times 100 \tag{4.2}$$
Pin

Where:

Pin is the Pollution concentration in (conductivity)
Pout is the pollution concentration out (conductivity)
η Is the treatment efficiency or rejection.

#### 3.8 Daily procedure

#### 3.8.1 Start up:

- Water rinse no sponge ball recycle (timer and compressor off)
- Perform a Clean Water Flux (CWF)

#### 3.8.2 Effluent run:

- Start on effluent Feed and bleed mode
- Take readings every hour

#### 3.8.3 Shut down:

- Water rinse for 30 min (Tap water) No sponge ball.
- Perform a clean water flux
- Preserve with formaldehyde.

## 3.8 Water Rinse

In order to do a water rinse of the membrane, valves on the RO plant were orientated correctly so that the left tank of the RO plant fed into the main pump and went to the membrane. The tank needed to be filled up with clean water from the municipal supply line. Once the water had passed through the membrane, it was then sent to drain. The clean water rinse was performed for 30 minutes. The level in the left tank was continuously monitored in case the tank overflowed, or the level became too low which could damage the main feed pump.

## 3.9 Clean Water Flux

After a clean water rinse was performed a clean water flux was determined. Clean water was allowed to pass through the membrane for at least five minutes. The system pressure was increased until the pressure in the membrane was 4000 kPa. The system was allowed to run for fifteen minutes so that an equilibrium situation could be reached, and to ensure that measurements were taken in a homogenous way. Permeate flow rate (ml/min), brine flow rate (liters/5sec), temperature (°C), and pressure (inlet and outlet) were measured and recorded. The pressure was then slowly decreased so that the membrane was not subjected to any high forces due to sudden pressure changes.

#### 3.10 Feed and Bleed Mode

For the feed and bleed mode, the appropriate valves were moved into position to allow the leachate to flow through the module. The feed and dosing pump were switched on and adjusted to give the correct flows. The timer was also switched on and adjusted to give a 30-minute sponge ball cycle. At this point the compressor was switched on and the pressure checked.

The system was allowed to run for several minutes at low pressure to allow the leachate to displace the clean water from the module. The inlet pressure was then increased to 4000kPa. The cooling coil was then connected up to a water supply to keep the leachate cool.

#### 3.11 Brine Flow Adjustment

The manufacturer of the membrane had advised from their experience that a recovery of 70% was required for this project; the amount of brine being discharged had to be

adjusted until the required recovery was achieved. This was a sensitive process, as a small movement in the discharge valve often resulted in a drastic change in recovery. With each adjustment, volumes being discharged had to be measured in order to calculate recovery (Equation 3.1). Once the brine flowrate vs. rejection flow was correct a startup time was recorded. The system pressure and flowrates were closely monitored and adjusted if necessary until it reached an equilibrium condition, which normally took 30 minutes.

#### 3.12 Measurements and Data Recording

Once the startup procedure was completed and the system was running at constant pressure of 4000 kPa, readings were taken at two hours intervals. The following were recorded:

- Temperature of concentrated leachate.
- Inlet and outlet pressure (either side of the membrane)
- Permeate flowrate in ml/min
- Brine flowrate in ml/min
- Feed Conductivity
- Brine Conductivity
- Permeate Conductivity
- pH of the feed in tank, brine and product
- Samples of the feed in tank (concentrated leachate), brine and permeate were taken

#### 3.13 Shut Down

During shut down, the pressure of the RO plant was slowly decreased and the pumps, timer and compressor turned off. A 30minute water rinse was again carried out, and the membrane then preserved with formaldehyde.

## 3.14 Membrane Preservation

Formaldehyde was used for membrane preservation. This was a necessary procedure because biological growth would attack the membrane if left standing for long periods of time, which would inevitably destroy the membrane. For the preservation, 50ml of 40% formaldehyde solution was added to 20 liters of tap water. The mix was then placed in the left tank of the RO plant, and the associated valves adjusted to create a recirculation of the formaldehyde mix over the membrane and back into the tank. The cycle was run for 15-20 minutes. The plant was then turned off.

#### 3.15 Membrane Cleaning

This was a time consuming exercise (Taking approximately 6 hours), however a necessary one. The cleaning procedure was performed when necessary – usually when the clean water flux dropped to 70% of the value obtained after the last clean. The cleaning procedure was as follows:

- Perform a clean water flux.
- Water rinse for 30 minutes with a 5-minute sponge ball recycle.
- Perform a clean water flux.
- One-hour acid clean with Nitric acid (HNO<sub>3</sub>). The acid clean involved the following:
  - Mixing 110ml of acid with 50 liters of water,
  - Placing the mix in the left tank, and circulating through the membrane in much the same way as the formaldehyde preservation.
  - A 5-minute sponge ball recycle was used during this procedure i.e. the system would switch over every five minutes to allow the sponge ball to move through the membrane, thus dislodging any particles on the membrane.
- Water rinse for 30 minutes with no sponge ball recycle.
- Perform a clean water flux.
- One-hour clean with STPP (Sodium Tripolyphosphate) and EDTA (Complexing agent). This clean involved mixing 1000g of STPP and 250g of EDTA with 50 liters of water. Sodium hydroxide (NaOH) was then added until the pH of the mix was 10.8. No sponge ball recycle was used. Again, the mix was placed in the left tank, passed through the membrane, and recycled back into the tank.

- Water rinse for 30 minutes with no sponge ball recycle.
- Perform a clean water flux.

A schematic layout of the membrane separation system is shown in figure 3.3

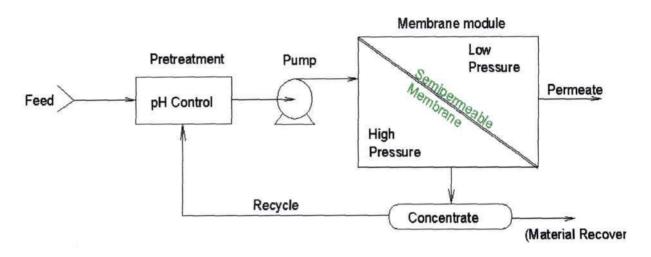


Figure 3.3 - Schematic of the membrane separation system used



Plate 3.7 - Showing the raw leachate, permeate and brine

Plate 3.7 indicates the colour removal due to reverse osmosis treatment. The plate shows raw leachate; permeate after reverse osmosis treatment and the concentrated brine.

## 3.16 Parameters measured

Analyses on permeate, feed, and brine samples were conducted by the CSIR. Some of the types of water analyses tested and their descriptions (Amjad 1993) were:

## Barium

Barium is a divalent ion, which forms a low solubility compound with sulfate. It requires the feed of a crystal growth inhibitor.

## Calcium

Calcium is always present as a divalent ion and forms insoluble or slightly soluble salts with common ions such as carbonate and sulfate. Both can be adequately controlled through crystal growth inhibitors or, if the precipitate is allowed to form, can readily be cleaned from the reverse osmosis membrane. Calcium concentration, in conjunction with alkalinity and sulfate concentrations, often establishes the upper limit to the water recovery of the RO system.

## Chloride

Chloride is relatively safe, having no negative effects on the life of the membranes, nor generating insoluble salts. Because it passes through RO membranes more easily than most anions, it is one of the predominant permeate ions.

#### Iron

Iron is generally present in the dissolved ferrous form, but can oxidize to the ferric state and precipitate as the hydroxide. Prior to use in an RO system, a supply containing iron should be pretreated to remove the iron, or steps taken to avoid contact of the supply with air or oxidizing substances such as chlorine.

## Magnesium

Magnesium forms sparingly soluble salts such as magnesium silicate and, under high pH conditions, magnesium hydroxide. Both are uncommon in RO systems.

## Manganese

Manganese is usually present at a level of less than 0.3ppm in public water supplies. Steps should be taken to eliminate contact with air or oxidants to assure that the manganese remains soluble.

#### Nitrate

Nitrate  $(NO_3)$  is similar to chloride in that it is not aggressive to the membrane, nor does it tend to form insoluble salts.

The pH, or measure of the concentration of hydrogen ions in the water, determines the percentage of inorganic carbon that is in the form of carbon dioxide, bicarbonate or carbonate. pH determines the extent to which carbon dioxide will appear in the permeate water, or whether calcium carbonate is likely to precipitate.

## **Pressure and Velocity**

The pressure chosen to run the Reverse Osmosis plant was 4000 kPa. Higher-pressure causes higher permeate flux and would thus increase efficiency, however it also causes more severe fouling by retained substances. Higher cross flow velocity reduces fouling, so a balance of flow and pressure had to be achieved. The optimum balance will generally vary depending on membrane type and feed solution characteristics. The strength of the membrane will determine the maximum hydraulic pressure and cross flow rate.

## Phosphate

Phosphate forms a low solubility salt with calcium. Liquids containing phosphate generally require the addition of an antiscalant.

#### Potassium

Potassium is chemically similar to sodium. No operating problems or fouling problems are caused by potassium.

pĦ

## Sodium

Sodium is monovalent and thus forms relatively soluble salts with most anions, including bicarbonate, sulfate, and chloride. This means that it seldom presents a fouling problem. Sodium is, however, the cation that passes most readily through an RO membrane. It will thus be present at high concentrations in the permeate, and will generally control overall rejection.

## Strontium

Strontium is a divalent ion. It forms a salt with sulfate that is soluble to the level of 1ppm, and requires the feed to be treated with a crystal growth inhibitor whenever strontium is present.

## Sulfate

Sulfate (SO  $_{4}^{-2}$ ) forms a sparingly soluble salt with calcium, strontium or barium. Sulfate does not usually limit the cycles of concentration, unless one or more of these cations are present at high levels.

#### Temperature

Temperature is important in determining the pressure drop through the membrane at the intended flux rate. It may also be important in determining the rate at which salts will precipitate in the membrane, and thus the extent to which these salts could become a major fouling problem.

## **Total Dissolved Solids**

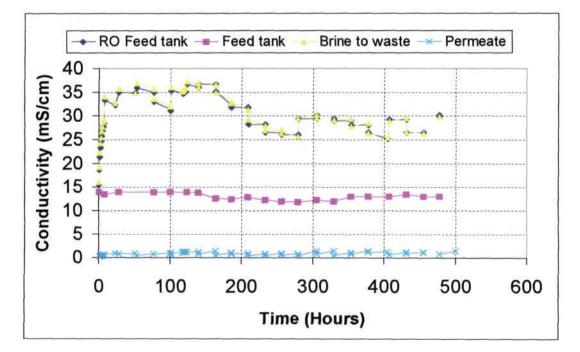
Total Dissolved Solids (TDS) is a measure of the total weight of impurities found in a supply. The measure is too general to predict key operational features of a unit, but does permit a quick, rough estimate of permeate quality.

Explanations of the main analyses studied - COD, TDS, Sodium and ammonia are given in appendix C.

# CHAPTER 4 RESULTS AND DISCUSSION

The data collection for this study was conducted in December 2001 to January 2002 by the author. The reporting of the findings of this study was done in 2005/2006 due to relocation of the author.

The raw data of flux rates, pH, conductivity and pressure were taken every 2-3 hours are given in Appendix A, while the data from the chemical analysis from samples taken approximately every 100 hours is given in Appendix B. The chemical analysis was performed by the CSIR Water Laboratories in Pretoria which comply with the general requirements of ISO/IEC 17025:2005, with the initial accreditation in February 1995.



## 4.1 Conductivity

Fig: 4.1 Conductivity vs. Time

Figure 4.1 shows changes in conductivity of the feed, brine to waste and permeate with time. The conductivity being a measure of the amount of salt or ion concentrations found in a sample. The graph shows that a high conductivity removal was achieved. The initial low values for the conductivity in the RO feed tank were due to the startup of the pilot plant and the concentration of the leachate gradually building up over time. pH adjusted leachate was then placed into the feed tank, and this caused a reduction in conductivity seen here. The gradual decline in conductivity after 170 hours was due to the raw leachate quality. The gradual drop in the feed conductivity was due to the runs being done in the summer period i.e. November to January, which is a high rainfall period. This caused the leachate to be at a lower concentration than it was initially.

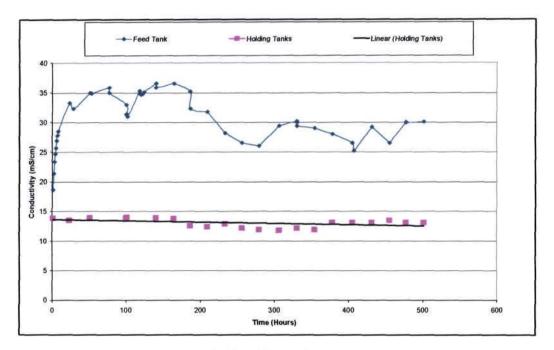


Fig. 4.2 Conductivity vs. Time

Figure 4.2 shows the effect of increased rainfall on the raw leachate over time. The leachate peaked at 14 mS/cm and dropped to a low of 11.8 mS/cm. The average leachate conductivity during the same periods in the main feed tank was 35 mS/cm and 26 mS/cm respectively.

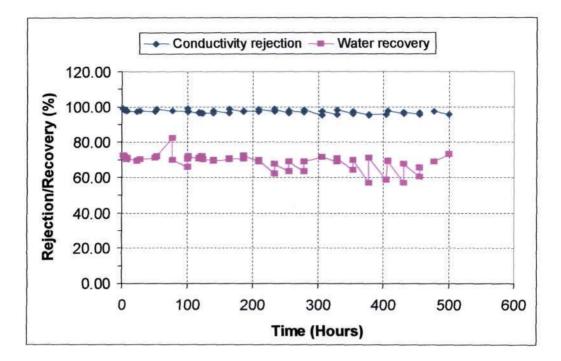


Fig. 4.3 Rejection/Recovery vs. Time

The graph shows that the conductivity rejection achieved was on average around 95 % and the water recovery achieved was on average 60-70 %. The desired water recovery was 70 % although a 100% water recovery could be achieved it would not be advantageous considering that the higher the water recovery the greater the effects of fouling. The conductivity rejection achieved was high and shows that the membrane can maintain a desired water recovery while achieving an efficient water recovery.

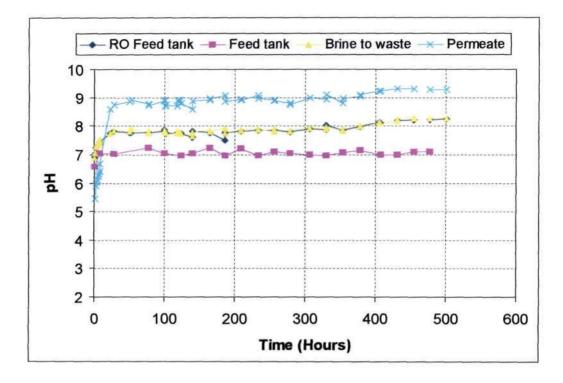


Fig. 4.4 pH vs. Time

The variation of pH with time is shown in Figure 4.4. The initial pH of the product, brine and feed were fairly low, and gradually increased as the concentration of the feed increased. The reason that the pH of the product is higher than the feed is due to the ability of the membrane to remove hydrogen ions. This would account for the slightly higher pH of the brine and feed, as compared to the pH in the holding tanks. The pH in the holding tanks was kept in a range between 7 and 7.2 as recommended by the manufacturer of the membrane.

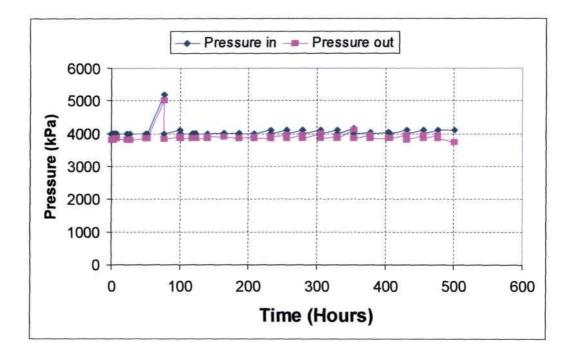
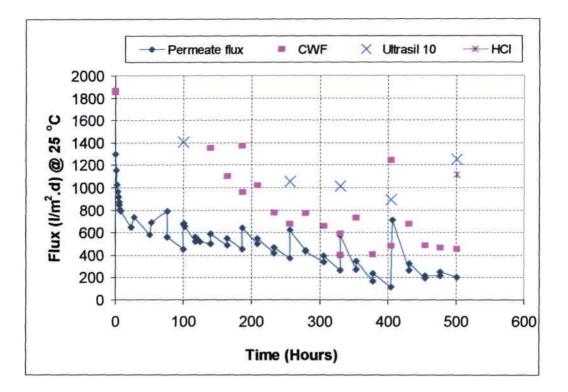


Fig 4.5 Pressure vs. time

Figure 4.5 Shows changes in pressure with time. It was decided to use a constant pressure of 4000 kPa in order to keep results consistent. The manufacturers again determined the maximum pressure that the membrane could be loaded to.

The graph shows that the inlet pressure remained fairly constant over the duration of the experimental work; except for the one time it peaked to over 5000 kPa. The outlet pressure also remained fairly constant throughout the experimental period with the exceptions of the time the pressure peaked. This was due to the sponge ball. As stated earlier the sponge ball is in place to act as a physical cleaning mechanism, and moves back and forward through the membrane. The pressure variations occurred when the sponge ball moved through the membrane every second cycle and got blocked in one of the pipes. The sponge ball was moved when the system was restarted and the pressure was decreased during the clean water rinse.

Sometimes the fouling rate can be determined by studying the differences in pressure on either side of the membrane, however in this case the pressures in and out are very close together, and any comparison would be misleading.



#### Figure 4.6 - Changes normalized permeate flux with time

Figure 4.6 shows the normalized flux rate of the leachate. The normalization of the flux rate is important because the flux rate is dependent on temperature (Equation 2.2). The normalization takes into account the changes in temperature, and converts the flux to a unit area of membrane.

The initial decline in flux is due to a compression of the membrane this being a new membrane it is expected that this compression will take place. Equation 2.3 showed that the flux rate is inversely proportional to the thickness of the membrane, however it should be remembered that this is for comparisons of different membranes, while in this case the actual membrane is compressed.

The sudden increase in water flux seen in Figure 4.6 is due to the membrane standing for several days without a run taking place. It was noted that the longer the experimental rig stood idol the greater the flux would be on start up. The reasons for no runs being carried out during these periods were the lack of leachate and lectures being held in the workshop in which the experiments were carried out. The clean water fluxes seen here are much higher than the normal flux because a clean water rise is carried out before doing a clean water flux. The clean water flux was done at the same operating pressures as the normal runs. The clean water flux is an indication of how well the membrane is operating and also determines when a chemical clean on the membrane should be carried out.

The graph also shows the resultant flux after a chemical clean, Ultrasol 10 being the cleaning agent. It can be seen that the flux after the cleaning cycles throughout the experiment dropped as expected due to an irreversible fouling layer forming on the membrane, which could not be removed by the Ultrasol 10, but did increase at 500 hours when an Ultrasol 10 and HCl clean was done. This shows that the membrane is resilient to the leachate and can maintain good rejection and recovery rates without drastic degradation.

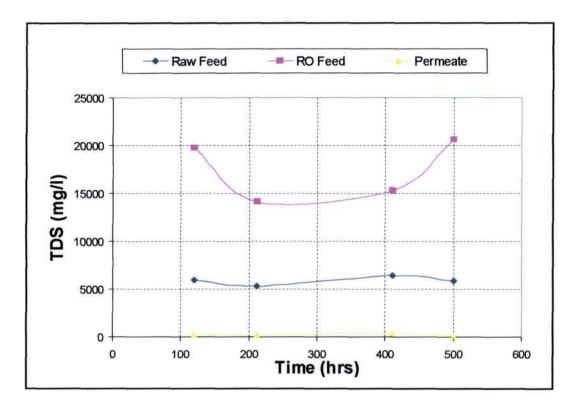


Fig. 4.7 Graph of Total Dissolved Solids (TDS) vs. Time

Figure 4.7 shows the graph of total dissolved solids vs. time for the raw feed, the RO feed and the permeate. It can be seen that the RO feed concentration is much higher than the actual raw feed from the landfill. This is because of the concentration effect of the RO feed. The average permeate concentration is 277 mg/l whilst the actual feed concentration is 17469 mg/l. It was observed that the permeate concentration did increase gradually over time and can be attributed to the membrane fouling as well as the increase in feed concentration over time. However at 500 hours due to the membrane being cleaned with the Ultrasol 10 and with the HCL solution the permeate concentration remained high.

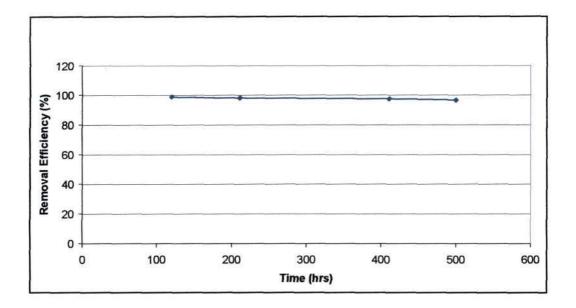


Fig. 4.8 Graph of TDS Removal Efficiency vs. Time

Figure 4.8 shows the drop in total dissolved solids removal efficiency over time due to the irreversible fouling layer that forms on the membrane. However it can be seen that the membrane does have excellent removal efficiencies for the total dissolved solids in the leachate even after 500 hours of operation.

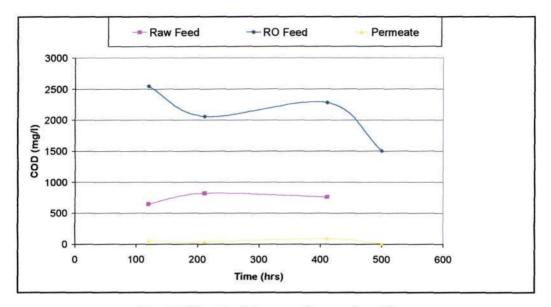


Fig 4.9 Chemical Oxygen Demand vs. Time

Figure 4.9 shows the graph of chemical oxygen demand (COD) vs. time for the raw feed, RO feed and the permeate. The average permeate COD over 500 hours was 48 mg/l. This value is the actual COD and does not include a chloride correction. The COD removal was below the general effluent standard which is not to exceed 75 mg/l after applying the chloride correction (Pulles et al 1996).

The average feed concentration was 2095 mg/l while the average COD removal efficiency was 97.7 %. This proved that the membrane was capable of achieving excellent COD removal not only for landfill leachate but also industrial effluents with similar feed COD concentrations.

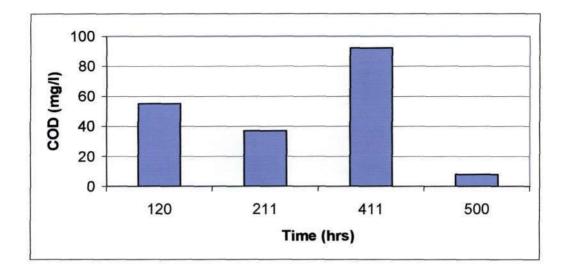


Fig 4.10 Permeate COD Concentrations vs. Time

Figure 4.10 shows the graph of permeates COD concentration vs. time. The average COD concentration was 48 mg/l. Only one of the concentrations was higher than the general effluent standard of 75 mg/l. This is not a big concern because the permeate was not treated with chlorine and it can be expected that the COD will drop after chlorine treatment.

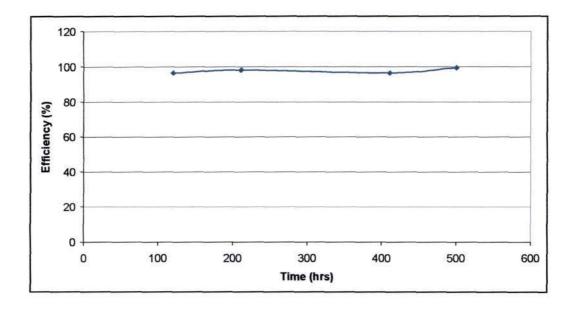


Fig. 4.11 COD Removal Efficiency vs. Time

Figure 4.11 shows the graph of permeates COD removal efficiency vs. time. The effect of membrane fouling can be seen on the COD removal efficiencies. The first chemical clean with Ultrasol 10 was done at 100 hours and hence the increase in COD removal. The second and third chemical cleans were done at 256 and 330 hrs respectively but did not make a difference on COD removal. The final chemical clean done using both Ultrasol 10 and HCl showed a marked increase in COD removal and shows that the membrane is resilient and can still achieve high COD removal efficiencies after long operating times, provided the membrane is cleaned regularly.

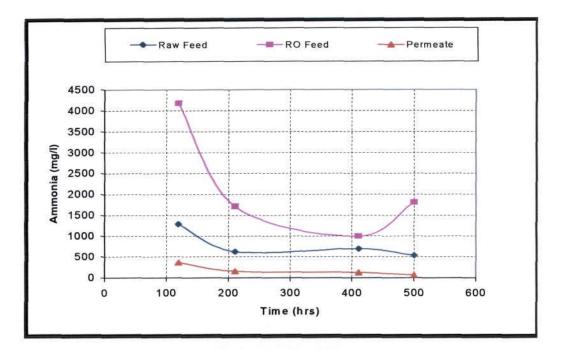
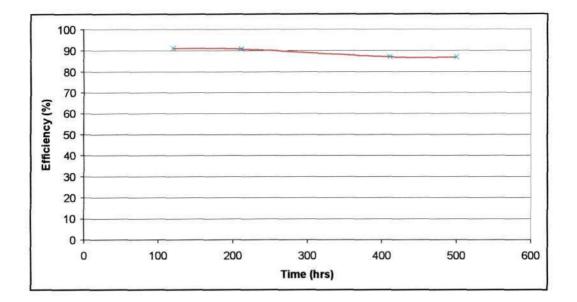


Fig 4.12: Level of Ammonia in Raw Feed, RO Feed and Permeate vs. Time

The concentration of ammonia in the raw feed and RO feed was initially high but then stabilised as the RO feed tank stabilized and reached steady state, Figure 4.12. However the ammonia concentration in the permeate dropped over the experimental period. This showed that the membrane is resilient to varying concentrations of ammonia.

The average ammonia concentration in the permeate was 180 mg/l and the average ammonia concentration in the RO feed was 2174 mg/l.

However the maximum permissible concentration for ammonia discharge is 10 mg/l. This is 18 time less than the average permeate level, it is therefore recommended that further treatment be carried out before the permeate is discharged to the environment.



## Fig 4.13 Ammonia Removal Efficiency vs. Time

The removal efficiency decreased as the membrane-fouling layer became larger, this was confirmed with the last ammonia removal efficiency dropping to below 88 %. After the membrane had a chemical clean with Ultrasol 10 and HCl the efficiency started to increase. The previous cleans where done with Ultrasol 10 only.

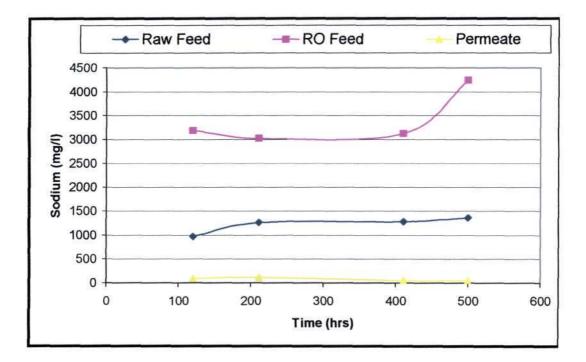
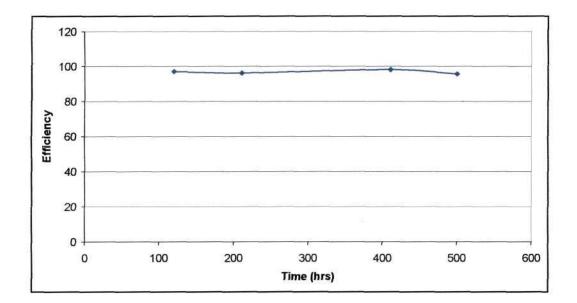


Fig 4.14 Concentration of Sodium in Raw Feed, RO Feed and Permeate vs. Time

The sodium concentration in the raw feed and RO feed remained fairly stable while the permeate concentration showed a steady drop over time. The average sodium concentration in the permeate was 89 mg/l while the average concentration in the RO feed was 3398 mg/l. The average removal efficiency was 97 %.



#### Fig 4.15: Sodium Removal Efficiency vs. Time

Figure 4.15 shows the graph of sodium removal efficiency over the experimental period. Here, like the ammonia removal, the effectiveness of sodium removal is due to the fouling layer that forms on the membrane. The larger the fouling layer the better the removal. The average sodium efficiency was 97 %.

# CHAPTER 5 CONCLUSION

The average COD of leachate used in the experiment was 2095 mg/l representing a strong leachate concentration. The RO system was operated under a constant pressure of 4000 kPa. Long term experiment was performed over 500 hrs and monitored over 8 hrs/day to determine permeate flux, conductivity, COD, BOD, pH, TDS, ammonia and sodium rejection.

The results of the experiment showed that for concentrated leachate, average COD removal efficiency 97.7 %. Other parameters such as total dissolved solids, ammonia, conductivity, the average removal efficiencies were 97.72 %, 88.97% and 95.0% respectively.

The average concentration for COD in the permeate was 100 mg/l which is still higher than discharge standards released by DWAF of 75 mg/l. It should be remembered however that the reverse osmosis pilot plant was treating concentrated leachate in order to accelerate fouling and simulate the last stage in a full-scale reverse osmosis plant.

The average value for efficiency of removal of ammonia was approximately 83%. The average concentration was 275mg/l N for the permeate, which is 28 times over the discharge limit.

The average value for efficiency of removal of TDS was approximately 92%. The average value for efficiency of removal of Sodium was approximately 93%,

The permeate had an average pH of 9.1 which meets discharge standards of between 5.5 and 9.5. Conductivity was too high with a value of 480ms/m while the standards are 250ms/m.

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The membrane supplier suggested that a water recovery of 70 % should be achieved, although a 100% water recovery could have been achieved. The reasoning behind the lower water recovery was that it was not advantageous to aim for a higher recovery, considering that the higher the water recovery the greater the effects of fouling. The average clean water recovery during the eight hour experimental period was 70%. The percentage recovery was kept at 70% by adjusting the brine flow rate leaving the system. There was a drop in water recovery to bellow 70 % which was due to the flux decreasing during the night and the brine flow rate remaining constant.

The average clean water flux was  $873 \ l/m^2$ day, verses the average normal flux of 542  $l/m^2$ day. The clean water flux was done at the same operating pressures as the normal runs. The clean water flux was performed to give an indication of the performance of the membrane and also determined when the chemical clean on the membrane was carried out.

The average flux after a chemical clean was  $1158 \text{ l/m}^2 \text{day}$ , Ultrasol 10 being the cleaning agent used in this study. The normal flux after the chemical cleaning cycles throughout the experiment dropped as expected due to the irreversible fouling layer formed on the membrane, which could not be removed by the Ultrasol 10 alone.

However the normal flux did increase at 500 hours when an Ultrasol 10 and HCl clean was done. This showed that the membrane was resilient to the leachate and could maintain a good rejection and recovery rate without drastic degradation.

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# **APPENDIX** A

## **RAW DATA AND RESULTS**

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WF flux conduc						Membrane area		0.81 m2		Membrane AFC99		Page No		Dosing concentration				Permatreat 391		0.5 mg/l make-ur Dosing rate	
Date	Time	Time	Pres		Temp	Flux	Flux Normai	Fe			in tank		o waste	-	duct	Brin		Recovery	Rejection	Measured	
		(h)	(kPa) in	(kPa) out	(deg C)	(ml/min)	(1/m2.d)	(mS/cm)	(pH)	(mS/cm)	(pH)	(mS/cm)	(pH)	(mS/cm)	(pH)	(ml/min) out	(V5 s)	(%)	(%)	(ml/min)	(ml/min)
24/Oct/01	CWF	0	4000	3800	22.25	980	1862				1997 - 19						1.27				
25/Oct/01	CWF	0	4000	3800	22	970	1854	Tan									1.25				
	09:00	0	4000	3800	22	680	1300	13.88	6.58	15.4	6.92	16.1	6.89								15.0
	10:00	1	4000	3800	25.5	660	1159			18.68	7.06	19.28	7.07	0.22	5.45				98.82	15	14.5
	11:00	2	4000	3800	27	610	1030			21.4	7.24	22.3	7.28	0.32	5.9	234		72.27	98.50	15	18.6
	12:00	3	4000	3800	27.25	575	965			23.4	7.27	24.2	7.35	0.4	6.04	222		72.15	98.29	15	17.5
	13:00	4	4000	3850	27.5	550	917			24.7	7.3	25.5	7.38	0.45	6.13	214		71.99	98.18	13.5	16.8
	14:00	5	4000	3850	28	530	872			25.7	7.32	26.8	7.4	0.5	6.24	210		71.62	98.05	13.5	16.3
	15:00	6	4000	3850	28	515	847			26.9	7.37	27.7	7.42	0.54	6.32	208		71.23	97.99	13.5	15.9
	16:00	7	4000	3850	28	490	806	Tar	nk 2	27.8	7.36	28.8	7.44	0.59	6.41	208		70.20	97.88	13.5	15.4
	17:00	8	4000	3850	28	480	789	13.49	7.05	28.5	7.45	29.3	7.53	0.67	6.67	196		71.01	97.65	13.5	14.9
26-Oct-2001	08:00	23	4000	3800	28.5	400	649			33.3	7.74	34.1	7.75	0.95	8.59	176		69.44	97.15	11.5	12.7
Rinse 30 min	CWF	23	4000	3800	22.5	740	1398										1.29				
	Preserve w	ith 0.25 %	SMBS				0														
29-Oct-2001	CWF	23	4000	3900	23	845	1577	Tar	nk 3		1						1.25	1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1			
	10:30	28	4000	3800	22.5	390	737	13.9	7.01	32.3	7.83	32.8	7.84	0.8	8.76	165		70.27	97.52	12	12.2
30/Oct/2001	09:00	51	4000	3850	29.5	370	584			35	7.78	35.8	7.82	0.9	8.86	149	100	71.29	97.43		11.4
Rinse 30 min	CWF	53	4000	3800	22	710	1357										1.25				
	10:00	53	4000	3850	24	380	692			34.9	7.77	34.9	7.89	0.5	8.92	147		72.11	98.57		11.6
31/Oct/2001	10:00	77	5190	5000	30	510	793			35.9	7.77	37	7.76	0.8	8.78	110		82.26	97.77	-	13.6
Rinse 30 min	CWF	77	4000	3800	24	680	1239	Tar	nk 3								1.25			1	1.00
	11:30	77	4000	3820	29	350	560	13.9	7.23	35	7.78	35.8	7.83	0.8	8.73	150		70.00	97.71	14.5	11.0
1/Nov/2001	09:45	100	4100	3900	30	290	451	1010		33	7.83	33.7	7.85	0.9	8.88	148		66.21	97.27		9.6
Rinse 30 min	CWF	100	4000	3850	23	590	1101				1.00		1.00		0.00		1.3		- Criter		1
	Preserve w																				-
	O LEACHA		1								1									-	-
21/Nov/2001	CWF	100	4000	3850	25	775	1378			-							1.3				
Lintericou		ur with 0.2		10 - pH 11		1.10	0										1.0				
Rinse 30 min	CWF	100	4000	3850	25	790	1404	Ta	nk 2								1.3				
Start	15:15	100	4000	3850	25	380	676	14	7.06	31.4	7.88	32	7.85	0.36	8.9	156	1.0	70.90	98.85	11	11.8
Otart	16:00	101	4000	3850	27.5	410	683	14	1.00	31.4	7.77	32.2	7.81	0.8	8.69	170		70.69	97.45	11	12.8
	17:00	102	4000	3850	29	410	656			31	7.74	32.3	7.78	0.9	8.76	158		72.18	97.10	11	12.5
22/Nov/2001	09:00	118	4000	3850	32.5	360	520			35.3	7.77	36.1	7.78	1.24	8.71	148		70.87	96.49	11	11.2
Rinse 30 min	CWF	118	4000	3850	25	680	1209			35.5	1.11	30.1	1.10	1.24	0.71	140	1.3	10.07	30.45	1	11.4
141150 30 11101	10:00	118	4000	3850	30	360	560			34.9	7.78	35.2	7.82	1.1	8.9	148	1.0	70.87	96.85	10.5	11.2
Samples	12:00	120	4000	3850	31	360	544			34.9	7.75	35.5	7.76	1.2	8.85	140		71.71	96.54	10.5	11.0
Samples	14:00	120	4000	3850	31.5	360	536	Ta	nk 3							142				10.5	11.0
	16:00	122	4000	3850	31.5	350				34.8	7.76	35.6	7.8	1.18	8.9	140		72.00	96.61	10.5	11.0
23/Nov/01	08:00	124					521	13.9	6.96	35.1	7.73	35.9	7.75	1.21	8.81		-	70.14	96.55		
Rinse 30 min	CWF	140	4000	3850	31.75	340	502			36.6	7.61	37.2	7.65	1.25	8.59	146		69.96	96.58	10.5	10.7
Ninse 30 min				3850	25	670	1191										-				
00/11- 100004		ith 0.25%		0000		100	0					-		-							4
26/Nov/2001	CWF	140	4000	3900	25	760	1351	tank 3	-	1					-	1 110	1.4		07.77	1-0-	10 -
07/01- 10000	08:40	140	4000	3900	25	330	587	1380	7.05	35.9	7.81	36.1	7.8	0.8	8.88	146		69.33	97.77	9	10.5
27/Nov/2001	08:40	164	4010	3900	31	320	484			3660	7.76	37	7.85	1.3	8.9	134		70.48	99.96	10	10.0
and the second	CWF	164	4000	3900	25	620	1102	Tank 2						_			1.5	-			
	09:40	164	4000	3900	29	340	544	12.6	7.23	36.6	7.77	36.6	7.83	0.5	8.97	140		70.83	98.63	10	10.6
28/Nov/2001	07:30	186	4010	3850	30	290	451			35.2	7.5	35	7.94	1	9.08	120		70.73	97.16	10	9.0
	CWF	186 with 0.25%	4000	3900	25	540	960						1				1.4				

Preserve with 0.25% SMBS

		eing held @																			
Dale	Time	_ <u></u> ime	Pres		qmeT		Flux Norma		ed	Feed i			o waste	Pro		Brir			Rejection	Measured	
1015 10014		(h)	(kPa) In	(kPa) out	(deg C)	(ml/min)	(l/m2.d)	(mS/cm)	(pH)	(mS/cm)	(pH)	(mS/cm)	(pH)	(mS/cm)	(pH)	(ml/min) ou		. (%)	(%)	(ml/mi <u>n)</u>	( <u>ml/min)</u>
10/Dec/2001	CWF 10:00	186	4000	3850	25.5	780	1369	Tank 1	0.00		7.70				8.87	I	<u>1,3</u>	72.52	97.52		11.5
11/Dec/2001	09:40	209	4000	3850 3900	-21	380 340	<u>642</u> 499	12.4	6.98	32.3	7.76	33	7.78	0.8	8.87	144		68.83	97.52		10.9
TINDE02001	CWF	209	4000	3850	25.5	580	1018	Tank3		31.0	1.01	32.3	1.64	- <u>0.</u> 9	0.94	104	1,4	99.03	80.07	- <u>''</u>	10.8
	10:30	- 209	4000	3850	31	360	544	12.89	7.2	31.8	7.81	31,4	7.87	0.5	8.9	154		70.04	98.43	11	11.3
12/Dec/2001	10:00	233	4100	3850	31.5	280	417	14.03	<u>_</u>	28.2	7.86	29.2	7.89	0.8	9.07	170		62.22	97.16	8	9.9
	CWF	233	4000	3900	26	450	780	Tank 2		·		2.4.4	1.00	<u> </u>	<u></u>	<u> </u>	1.3	VLIEL			
	11:00	233	4000	3900	30	300	467	12.2	6.98	28.2	7.86	28.1	7.88	0.4	8.96	142		67.87	98.58	11	9,7
13/Dec/2001	10:00	256	4100	3950	33	260	370			26.5	7.85	27	7.83	0.9	8.91	150		63.41	96.60	8	9.0
	CWF	256	4000	3900	26	390	676										1.5				
Chen	nical Clean	with 0.25 %	Ultrasil 10	for 1 t																	
	CWF	256	4000	3850	_27	625	1056	Tank 1									1.5				<u> </u>
	12:30	256	4000	3850	30	400	622	11.9	7.09	26.5	7.85	_ 27.1	7.91	0.6	8.88	178		69.20	97.74	11	12.7
14/Dec/2001	11:30	279	4100	3950	32	300	440			26	7 79	26.3	7.81	0.8	8.8	172		63.56	96.92	30	10.4
		CWF	4000	3850	25	435	773	Tank 2								<u> </u>	1.5		<b>\</b>		
	12:20	279	4000	3850	30	280	436	11.8	7.06	26	7,79	25.7	7.84	0.5	8.74	128		68.97	I	8	8.9
15/Dec/2001	15:00	306	4100	4000	33.5	240	336			29.4	7.9	29.5	7,94	1.4	8,98	<sup></sup> 96		71.43	<b> </b>	8	7.4
	CWF_		4000	3850	25	<u>370</u> 250	658	Tank 3		29.4			7.05		8.99	100		71.43		8	7.7
16/Dec/2001	15:40 15:30	306 330	4000	<u>3850</u> 3900	30 35	250	389	12.2	6.99	29.4	7,9	29.6	7.95	0.8	8.99 8.95	90	┝╼──┼	68.97	<b>↓</b> .		<u> </u>
10/Dec/2001	CWF	330	4000	3850		310	537			30.2	1.00	<u> </u>	1.9	1.3	0.33	<u>+</u>		1. 00.91	<u> </u>	<u> </u>	<b>├</b> ─· ··
	Ibrane presi		4000		- <u></u>	- 210		┟┅────				<u> </u>			<u> </u>			<u> </u>	<u> </u>	+	——
18/Dec/2001	CWF	330	4000	3850	_25	330	587	┝╼───┈		]		╉━┅━━━					1.25	<u> </u>		1	<u> </u>
clean with	1 % Ultrasi		4000					<u> </u>	┢╼╍╍╍	·		<u> </u>				1	1.4.4				
significant significant	CWF	330	4000	3850	25	570	1013	Tank 1 & 2	2	1		<u> </u>		1	·		·		<u> </u>		
	12:00	330	4000	3850	24	315	574	11.9	6.98	29.4	8.04	29.3	7.98	0.5	9,1	130		70.79		T –	
19/Dec/2001	10:50	354	4150	4100	35	205	273	L		29	7.84	29.1	7.98	1.1	8.8	114		64.26		8	7.0
	CWF	354	4000	3850	26	420	728										1.4				
	11:30	354	4000	3850	31	230	348	13.1	7.07	29	7.84	29.4	7.9	0.8	8.96	100		69.70		1	<u></u>
20/Dec/2001	11:30	378	4050	3950	34	125	172			28	7.99	27.9	8	1,4	9.04	94		57.08		8	4.8
	CWF	378	4000	3850	25.5	230	404	Tank 1		<u> </u>	L						1.4	I	<u> </u>	I	
	12:00	378	4000	3850	32	160	235	13.1	7.16	28	7,99	28.5	8.04	1.2	9.1	65	<b>↓</b>	71,11	<u> </u>	8	5.0
21/Dec/2001	15:00	405	4050	3850	35	85	113			26.5	8,13	26.4	8.15	1.2	9.23	60	·	58.62	<u> </u>	8	3.2
Class	with 0.1 %	405	4000	3850	25	270	480	╉╼╾╍	<u> </u>	·	Ì	<u> </u>	──	-l	┣──	1	1.4	-		-}	┣──
Ciean	CWF	405	4000	3850	- 25	500	889			───		·	+			· <b> </b>	1.4				
	brane pres		4000	3030	20		- <u></u>		╀╼┅━━━		í <u> </u>			┥───	┢────		1.4			+ -	<u>+</u>
7/Jan/2002		405	4000	3850	25	700	1244	Tank 2					┼┶──╼┶			╺╆╴╼╼╸	1-14				<u>†                                    </u>
Hedrizoot	09:00	407	4000	3850	26	410	711	13.1	7	25.2	8.1	25.5	8.1	0.6	9.23	180	<u> </u>	69.49		11	13.0
8/Jan/2002	09:30	431	4100	3950	35	200	267		<u> </u>	29.2	8.18	28.9	8.2	1,2	9.32	150	·	57,14		8	7.7
	CWF_	431	4000	3850	_25	380	676	Tank 1	<u> </u>			<u></u>		<u> </u>			1.4				
	10:30	431	4000	3800	36	250	322	13,5	7	29.2	8.18	29.5	8.25	0.9	9.32	120		67.57		9	8.1
9/Jan/2002	10:30	455	4100	3950	36	150	193	L		26.5	8.23	26.6	8.29	1.2	9,31	98		60.48		8	5.5
	CWF	455	4000	3850	26	280	485	Tank 2							1		1.3				
1011-10000	11:00	455	4000	3850	36	170	219	13.1	7.1	26.5	8.23	26.3	8.28	<u> </u>	9.31	90	+	65.38		<u> </u>	+
10/Jan/2002		477	4100	3950	36	170	219	· — —			─~─		<u> </u>		<u> </u>	+	+	1	<b></b>	8	3.7
	000 CWF	477	4000	3850 3850	26	270	468	40 4			- 0.00	20.0	0.07	+				69.09		8	6.1
11/Jan/2002		501	4100	3850	35		253	13.1	7,1	29.9	<u>8.22</u> 8.25	29.8	8.27	0.8	9.28	85		73.46		+	+ 0.1
11/3/02/02	CWF	501	4000	3750	26	155 260	451		<u> </u>	30.1	0.29	29.9	0.28	1,3	<u>,<!--</u--></u>	- <del> </del>	1.4	-1.73.46			+
29/Jan/2002		servation		3030	40	400		+			┨────	+					1 1.4	+		+ -	· - · · ·
2.5.00.02.002	CWF	501	4000	3850	26.5	430	736	Preservel	live waler h	nin no nwor	Sin				+	-					1
lean membra				+			1	1			<u> </u>		<u> </u>		+	-1		1		+ -	· <b>  -</b>
	CWF	501	4000	3850	26.5	700	1198				<u></u>		╌┤──╼──	-	1		<u>+</u>	<u> + ·-−</u> ··		·   · · · · · · · · · · · · · · · · · ·	+
lean with 0.1			1			- <u></u>	1	1	1		1	1	1		-		1		1		<b>—</b>
	CWF	501	4000	3850	26.5	730	_ 1249		1_		T	1									<u> </u>
lean with 0.2	5% Ultrasil	10 for 0.5																_			
_	CWF	501	4000	3850	26.5	730	1249			1									1		
tiler preserva							Q Q														
	CWF	501	400	0 3850	26.5	730	1249		1		1									-	

## **APPENDIX B**

# **CHEMICAL ANALYSIS**

### **Chemical Analysis After 120 hours of Operation**

Constituent	Raw Feed	<b>RO</b> Feed	Permeate	Removal %
Alkalinity	3450	7621	758	90.1
Ammonia(Free)	1284	4176	366	91.2
Barium	0.3	0.8	<0.1	
Calcium	66	60	<5.0	99.6
Chloride	3904	19995	82	99.6
Chrome	<0.1	<0.1	<0.1	97.8
COD	650	2545	55	96.5
Conductivity(ms/m)	1168	3500	124	
Iron	1.2	5.4	<0.1	
Lead	< 0.05	< 0.05	< 0.05	
Magnesium	100	298	3.6	
Manganese	0.28	0.44	<0.1	
Nikel	<0.1	<0.1	<0.1	
Nitrate	0.13	0.6	0.16	
pH	7.8	7.9	9.2	
Phenols	3.2	20	0.1	
Potassium	608	2326	50	
Silicon	16	50	0.1	
Sodium	966	3190	96	97
Strotium	0.72	2	<0.1	
Sulphate	80	294	15	
Suspended Solids	51	212	2	
TDS	5931	19791	244	98.8
Total phosphates	4.8	4.8	0.15	

Constituent	Raw Feed	RO Feed	Permeate	Removal %
Alkalinity	3624	7015	650	90.7
Ammonia(Free)	626	1714	157	90.8
Barium	0.32	0.77	<0.1	
Calcium	72	40	<5.0	99.6
Chloride	1756	6560	71	98.9
Chrome	<0.1	<0.1	<0.1	97.8
COD	820	2055	37	98.2
Conductivity(ms/m)	1142	2830	103	96.4
Iron	1.4	3.9	<0.1	
Lead	<0.05	0.13	< 0.05	
Magnesium	110	318	4.7	
Manganese	0.24	0.49	<0.1	
Nikel	<0.1	0.15	<0.1	
Nitrate	4.9	25	0.12	
pH	8	8	9.4	
Phenols	3.9	12	0.1	
Potassium	660	705	751	
Silicon	20	49	2.3	
Sodium	1260	3027	114	96.2
Strotium	0.8	1.8	<0.1	1
Sulphate	106	120	<10	
Suspended Solids	77	210	7	<u> </u>
IDS	5320	14146	262	98.1
Total phosphates	3.6	2.8	3.8	<u> </u>

### Chemical Analysis After 210 hours of Operation

Constituent	Raw Feed	RO Feed	Permeate	Removal %
Alkalinity	4600	5600	500	91.1
Ammonia(Free)	693	998	130	87
Barium	0.34	0.6	<0.1	••••••••••••••••••••••••••••••••••••••
Calcium	68	18	<5.0	
Chloride	1962	5866	132	97.7
Chrome	<0.1	0.11	<0.1	96
COD	762	2280	92	96.5
Conductivity(ms/m)	1304	2550	89	
Iron	2.4	4.2	<0.1	
Lead	<0.05	0.13	<0.05	
Magnesium	113	331	3.1	
Manganese	0.22	0.5	<0.1	1
Nikel	<0.1	0.21	<0.1	1
Nitrate	0.7	61	0.56	
pН	8.2	8.5	9.7	
Phenols	5	12	0.1	
Potassium	708	1748	31	
Silicon	20	45	3.1	
Sodium	1281	3126	60	98.1
Strotium	0.83	1.5	<0.1	
Sulphate	81	176	23	
Suspended Solids	72	159	8	
TDS	6412	15322	404	97.4
Total phosphates	4.2	1.3	0.08	

## Chemical Analysis After 407 hours of Operation

Constituent	Feed	Product	Brine	Removal %
TDS	5882	198	20620	96.6
Suspended Solids	41	1	575	97.6
Ammonia(Free)	534	69.7	1808	86.9
Nitrate nitrogen	0.09	0	0.38	100
Total phosphates	5.81	0.152	19.5	97.4
Alkalinity	2628	311	8.025	88.4
Chloride	2320	105	9.286	95.5
Sulphate	164	0	397	100
Flouride	0.948	0	2.89	100
Silicon	22.1	0.44	83.1	98
Calcium	81.4	0.617	71.5	99.2
Magnesium	133	0.995	437	99.3
Potassium	754	35.9	2260	95.2
Sodium	1360	59.5	4250	95.6
Barium	0.384	0	0.61	100
Strotium	0.944	0.007	2.27	99.3
Iron	1.98	0.014	3.51	99.3
Lead	0.147	0	0.297	100
Manganese	0.297	0.012	0.49	96
Nickel	0.169	0.006	0.525	96.4
Fotal organic Carbon	532	7.43	1266	98.6
Chemcial Oxygen Demand	1850	89	1890	97
Phenols	0.17	0.01	0.5	94.1
Conductivity	1310	86	3879	93.4
Н	7.03	8.21	7.65	

### Chemical Analysis After 500 hours of Operation

# **APPENDIX C**

## COD TDS Ammonia

### CHEMICAL OXYGEN DEMAND

Chemical Oxygen Demand (COD) is defined as the quantity of specified oxidant which reacts with a sample under controlled conditions. The quantity of oxidant consumed is expressed in terms of its oxygen equivalence. COD is expressed in mg/L Oxygen.

COD is often used as a measurement of pollutants in natural and waste waters and to assess the strength of waste such as sewerage and industrial effluent waters. COD has further applications in power plant operations, chemical manufacturing, commercial laundries, pulp and paper mills, and environmental impact studies.

#### How is it measured?

COD can be measured using the closed reflux colorimetric method, which is the approved standard method adopted by the US Environmental Protection Agency and equivalent national organisations across the world.

A sample of water to be measured is taken and added to a strongly acidic solution which has a known excess of potassium dichromate. The sample is heated to +150C for 2 hours and allowed to cool. After this 'digestion' time, the COD material in the sample is oxidised by the dichromate ion. The result of this reaction is a change in the 'state' of the chromium from hexavalent to the trivalent state. Both chromium's exhibit a colour and absorb light in the visible region of the spectrum By measuring the colour using a spectrophotometer it is possible to obtain the COD value in mg/L for that sample.

### TOTAL DISSOLVED SOLIDS

#### Source

Total Dissolved Solids (TDS) consist mainly of carbonates, bicarbonates, chlorides, sulfates, phosphates, nitrates, calcium, magnesium, sodium, potassium, iron, manganese, and a few others. They do not include gases, colloids, or sediment. The TDS can be estimated by measuring the specific conductance of the water. Dissolved solids in natural waters range from less than 10 mg/i for rain to more than 100,000 mg/I for brines. Since TDS is the sum of all materials dissolved in the water, it has many different mineral sources. The chart below indicates the TDS from various sources.

Total Disolved Solid (mg/l) Distilled Water (0) Two-column Deionizer Water (8) Rain and Snow (10) Oceans (35,000) Brine Well (125,000) Dead Sea (250,000)

High levels of total dissolved solids can adversely industrial applications requiring the use of water such as cooling tower operations; boiler feed water, food and beverage industries, and electronics manufacturers. High levels of chloride and sulfate will accelerate corrosion of metals. The US EPA has a suggested level of 500 mg/l listed in the Secondary Drinking Water Standards.

#### Treatment

TDS reduction is accomplished by reducing the total amount in the water. This is done during the process of deionisation or with reverse osmosis. Electrodialysis will also reduce the TDS.

**C2** 

### AMMONIA

#### Source

Ammonia (NH<sub>3</sub>) gas, usually expressed as nitrogen, is extremely soluble in water. It is the natural product of decay of organic nitrogen compounds. Ammonia finds its way to surface supplies from the runoff in agricultural areas where it is applied as fertilizer. It can also find its way to underground aquifers from animal feed lots. Ammonia is oxidized to nitrate by bacterial action. A concentration of 0.1 to 1.0 ppm is typically found in most surface water supplies, and is expressed as N. Ammonia is not usually found in well water supplies because the bacteria in the soil converts it nitrates. The concentration of Ammonia is not restricted by drinking water standards. Since Ammonia is corrosive to copper alloys it is a concern in cooling systems and in boiler feed.

#### Treatment

Ammonia can be destroyed chemically by chlorination. The initial reaction forms chloramines, and must be completely broken down before there is a chlorine residual. The chlorine will destroy organic contaminants in the waste stream before it will react with the ammonia. Ammonia can also be removed by cation exchange resin in the hydrogen form, which is the utilization of acid as a regenerant. Degasification will also remove Ammonia.