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THE TREATMENT OF LANDFILL LEACHATE USING AN MF/UF MEMBRANE SYSTEM: FOCUSING ON MEMBRANE FOULING

by
Stacie Banks

A thesis submitted to the faculty of Graduate and Postdoctoral Studies
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ABSTRACT

The flow of precipitation and/or groundwater through landfills allows soluble materials to leach into the water. The resulting liquid is called leachate and can contain heavy metals, bacteria, chlorides, sulphides, organic material, industrial/household chemicals and other pollutants depending on the nature of the landfill and the materials housed within. The variable nature of leachate makes it difficult to treat through conventional means. Leachate constituents tend to fluctuate based on: precipitation rates, season, age of the landfill, area geology, and the leachate collection system used.

Membrane systems are being used increasingly throughout the western world to treat landfill leachate as environmental regulations tighten. This work examined leachate filtration using a bench-scale MF/UF membrane system, focussing on surface fouling and constituent reductions at the Trail Road Landfill in Ottawa, Ontario. Two experimental set-ups were used in this experiment, the first in the field at the Trail Road landfill and the second in the Hydraulics lab at University of Ottawa.

The study found that ultrafiltration membranes with a molecular weight cut-off of 10 KDa and below gave the best overall leachate treatment. A 1 KDa ultrafiltration membrane gave the highest percent removals overall of all the membranes tested, but had one of the lowest steady state fluxes ranging from 2 to 5 L/m^2h. The 5 KDa membrane tested gave similar but lower overall percent removals at a higher flux (5 to 14 L/m2h) and thus would require a smaller surface area in full scale operation. No membrane tested met all sewer-use bylaws defined by the City of Ottawa, but when the raw leachate parameters were above the bylaws, most were treated to the required concentration by at least one of the membranes used. The variable nature of the leachate made direct membrane comparisons and performance evaluations difficult.

Carbonates such as calcite and dolomite were determined to be one of the main foulants/scalants. Iron sulphides or iron oxides tended to form a general coating over the membrane surface and may have been the base for a surface coating of mixed-element origins observed in spring 2003. BOD concentrations seemed to have a direct impact on the flux, with fluxes decreasing with increasing BOD concentration. The fouling type was generally thought to be cake filtration based on flux results and basic fouling determination equations.

ABRÉGÉ

Le ruissellement de la précipitation et/ou d'eau souterraine à travers des enfouissements municipaux permet aux matériaux solubles de s'infiltrer dans l'eau. Le liquide résultant est appelé leachate et peut contenir de métaux lourds, des bactéries, chlorures, sulfides, matériaux organiques, de produits industriels ou domestiques ou autres polluants dépendant de la nature du l'enfouissement et les matériaux inclues dedans. La nature variable de ce leachate rends difficile son traitement par modes habituels. Les constituants du leachate varient en raison des taux de précipitation, la saison, l'age de l'enfouissement, la géologie de l'endroit et du type de système de collection du leachate.

Les systèmes de membranes se font utiliser de plus en plus souvent à l'occident pour traiter le leachate d'enfouissements municipaux grâce aux ordonances environmentales strictes. Le traitement biologique peut être effectif mais n'est pas aussi versatile que le traitement à la membrane. Ce travail a examiné la filtration du leachate en utilisant un système de microfiltration/ultrafiltration à petite échelle en misant le fouling de surface et les réductions de constituants tel que les métaux et le soufre au Trail Road Landfill à Ottawa, Ontario.

Cette étude a trouvé qu'une ultrafiltration membranaire avec un cut-off de 5 KDa et moins éprouvait les meilleurs résultant pour le traitement du leachate. Les pourcentages de réduction pour la membrane de 5 KDa étaient élevés comparés avec ceux des autres membranes. Il avait un flux à l'état stationnaire de 5 à 14 L/m^2h et requièrait une surface d'approximativement (1597 à 1917 m^2) a pleine échelle. Une membrane d'ultrafiltration de 1 KDa a permis les pourcentages de réduction les plus élevés au niveau global, mais avait un flux à l'état stationnaire (2 à 5 L/m^2h) que la membrane de 5 KDa et requièrerait donc une surface plus grande (1917 à 4792 m^2) pour traiter l'écoulement de leachate du Trail Road Landfill. Aucune membrane a exigences d'utilisation des égouts de la Ville d'Ottawa, mais quand les paramètres étaient au dessus des exigences avant le traitement, la majorité étaient traités pour répondre aux exigences par une des membranes utilisés.

Les carbonates tel que le calcite et la dolomite ont été déterminés comme étant les foulants/scalants principaux. Les sulfides et oxydes de fer avaient tendance à former une coating sur la surface de la membrane et pourrait être la base pour un revêtement superficielle d'origine d'éléments mixtes qui a été observé au printemps 2003. Les concentrations de DOB semblaient avoir un impacte direct sur le flux, avec des flux décroisant avec une concentration de DOB croissante. Le type de fouling était généralement du type de filtration à gâteau basé sur les résultats de flux et sur les équation de fouling de base.

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NOMENCLATURE

A	=	Surface Area of the Membrane (m^2)
c_b	=	Bulk Concentration (g/l) = C_b
c_m	=	Concentration at the Membrane Surface (g/L)
c_p	=	Concentration of Permeate (g/L)
D	=	Distance (m)
J	=	Flux ($L/m^2 \cdot h$)
J_0	=	Initial Filtrate Flux Through the Clean Membrane ($L/m^2 \cdot h$)
J_v	=	Instantaneous Filtrate Flux ($L/m^2 \cdot h$)
K	=	Constant
k	=	Mass Transfer Coefficient
m_{cake}	=	Cake Mass (g)
? P	=	Transmembrane Pressure (N/m^2)
Q	=	Volumetric Flow Rate (m^3/s)
r_a	=	Sulphide Production Rate ($g\ S/(m^2 \cdot h)$)
R_a	=	Resistance from Adsorb onto the Membrane Surface (m^{-1})
R_{cp}	=	Concentration Polarization Resistance (m^{-1})
R_g	=	Resistance from Gel Layer Formation (m^{-1})
R_{inter}	=	Resistance from Intermediate Blocking (m^{-1})
R_m	=	Membrane Hydraulic Resistance (m^{-1})
R_p	=	Resistance from Blocked Pores (m^{-1})
r_p	=	Pore Radius (m)
R_{tot}	=	Total Resistance (m^{-1})
t	=	Filtration Time (h)
T	=	Temperature (°C)
u	=	Flow Velocity (m/s)
μ	=	Viscosity of the Solution ($N \cdot s$)
a_{block}	=	Pore blockage efficiency (m^2/kg)
a_{pore}	=	Pore constriction efficiency (m^2/kg)
d_m	=	Cake thickness (m)

s_{inter} = Area blocked per unit of filtrate volume (m^2/m^3)

ACRONYMS

A/O	= Anoxic/oxic
BOD	= Biochemical Oxygen Demand
CBOD	= Carbonaceous Biochemical Oxygen Demand
CF	= Cross Flow
COD	= Chemical Oxygen Demand
CPU	= Central Processing Unit
CRA	= Conestoga-Rovers & Associates
Da	= Daltons
DOTM	= Direct Observation Through the Membrane
EDX	= Energy Dispersive X-ray
EM	= Electron Microscope
EPS	= Extracellular Polymetric Substances
GPEC	= Green Plan Environmental Corporation
GFD	= Gallons/ft^2day
HELP	= Hydraulic Evaluation of Landfill Performance
HRT	= Hydraulic Retention Time
ICP	= Inductively Coupled Plasma
MBR	= Membrane Bioreactors
MF	= Microfiltration
MPN	= Most Probable Number
MSW	= Municipal Solid Waste
MW	= Molecular Weight (Da)
MWCO	= Molecular Weight Cut-off (Da)
N	= Nitrogen
NF	=Nanofiltration
P	= Phosphorous
PEG	= Polyethylene glycol
PES	= Polyethersulphone
ppm	= parts per million

PS = Polysulphone

PVDF = Polyvinylide fluoride

PVC = Polyvinyl Chloride

RBC = Rotating Biological Contactor

redox = Reduction/Oxidation

RO = Reverse Osmosis

ROMC = Regional Municipality of Ottawa-Carleton

ROPEC = Robert O. Pickard Environmental Centre

SAIC = Science Applications International Corporation

SDI = Silt Density Index

SEM = Scanning Electron Microscope

SPR = Sulfide Production Rate

SRB = Sulphur Reducing Bacteria

TDS = Total Dissolved Solids

TF = Thin Film

TKN = Total Kjeldahl Nitrogen

TOC = Total Organic Carbon

TSS = Total Suspended Solids

UF = Ultrafiltration

UV = Ultraviolet

VFAs = Volatile Fatty Acids

VOC = Volatile Organic Carbon

WWTP = Wastewater Treatment Plant

XOCs = Xenobiotic Organic Compounds

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CHAPTER 1

INTRODUCTION

1.1 Background

Problems associated with waste disposal have existed for centuries. In medieval European towns disposal of waste consisted of dumping around homes and in the streets. Flea-bearing rats feeding on the waste, coupled with poor human hygiene, led to recurrent epidemics, including the bubonic plague. Growing awareness of the connection between refuse, pests, hygiene and disease resulted in changing individual habits, and the advent of large central dumps away from the main community. However, large-scale sanitary waste disposal with closed dumps and organized collection did not begin until the nineteenth century (Tchobanoglous *et al.*, 1993). The discovery and understanding of groundwater contamination and greenhouse gas emissions from landfills led to further improvements in solid waste disposal in the late 20th century. Currently, landfills are designed not only to decrease the presence of pests, but also to manage greenhouse gases and contaminated waters (Tchobanoglous *et al.*, 1993).

1.1.1 Landfill Leachate

Leachate is wastewater produced by water migrating through a landfill and becoming contaminated. The term leachate implies the leaching of materials/contaminants into the surrounding waters from the material in the landfill. The water source may be precipitation and/or groundwater, possibly augmented by the presence of liquid wastes within the landfill. Leachate varies in concentration depending on the waste material involved, the age of the landfill and the landfill management practices (Gierlich and Kollbach, 1998; Peters, 1996; Tchobanoglous *et al.,* 1993). In general landfill leachate contains various suspended solids, ammonia, organics, halogenated hydrocarbons, heavy metals and salts such as carbonates, sulfates and sodium chlorides (Gierlich and Kollbach, 1998; Tchobanoglous *et al.*, 1993; Trebouet *et al.*, 2001).

1.1.2 Membranes

Issues of water development and protection have led to a number of environmental studies, regulations, and technological advances concerning landfills. Landfill leachate should not be discharged directly into local water systems and normally cannot be held in the landfill indefinitely. Therefore, a number of treatment options for landfill leachate have been developed, each providing various levels of treatment.

Leachate treatment using membranes was developed in the last 15 years and has been proven effective in the removal of pollutants. Membrane systems essentially act to filter out targeted parameters from the leachate and concentrate them. The concentrated leachate can then be re-landfilled, dry or wet, and the filtered water discharged to the sewers or treated to surface water standards. Like most filters they can become clogged. This clogging or fouling decreases the life of the membrane. The causes of fouling and the effectiveness of membranes in the treatment of landfill leachate are dependant on landfill type, age and membrane used (Mulder, 1991; Trebouet *et al.*, 2001).

1.1.3 The Trail Road Landfill Facility

Trail Road landfill is the municipal solid waste facility for the City of Ottawa. There are four stages or sections to the landfill. The first two were filled and capped in 1988 and 1991 respectively, and had no leachate collection or liner system in place. The main protection against offsite contamination from these unlined stages is a well drawing enough water to prevent offsite groundwater migration. The third and fourth stages are currently being filled and are lined. They contain active leachate and gas collection systems. Since 1996, the collected leachate has been transported by tanker truck to the municipal wastewater treatment facility, the Robert O. Picard Environmental Centre (ROPEC). Approximately 185 m^3/day of leachate are taken to ROPEC for treatment. The leachate is also routinely recirculated into the landfill, as a form of volume management, to promote decomposition and to flush the holding tank. (Golder Associates, 2002; Hurd *et al.*, 2001; SAIC, 2001).

1.2 Motivation for Research

1.2.1 Sustainable Wastewater Treatment

The City of Ottawa has been examining alternative leachate treatment options. Several studies were commissioned to examine the feasibility of several different types of on-site treatment and pre-treatment. One preferred option was a sewage line extension with possible limited pre-treatment. Concerns surrounding straight sewage line injection included the heavy metal concentrations within the leachate, pipe corrosion by the leachate transformations and the route of the sewage line extension.

There was widespread public opposition to the sewage line extension through a small subdivision called Stonebridge, which halted the sewage line extension in July 2003 (CBC, 2003). Pretreating the leachate with membranes may provide some of the flexibility needed to allow for sewage line use, without having to compromise on sewage discharge standards. If further study concludes that total on-site treatment is the most desirable option, then this study focusing on large pore membrane pretreatment could be used to explore further reverse osmosis treatment or other complete treatment alternatives. A membrane treatment system may save the municipality from future sewage line replacement expense and improve the overall treatment process, by removing metals and other contaminants from the leachate.

1.2.2 Understanding Membrane Fouling in the Treatment of Landfill Leachate

Membrane treatment of wastewater streams is a relatively new area of study, and as such, all of the fouling mechanisms are not fully understood. Exploring the components and materials involved in fouling, the dynamics of flow needed to decrease fouling and the cleaning agents required are all very important areas of research. This project focussed mainly on the use of Microfiltration (MF) and Ultrafiltration (UF) membranes for pretreatment of real landfill leachate and aspects of fouling leading to deterioration of membrane performance.

1.3 Objectives and Scope

1.3.1 Main Objectives

The purpose of this project was to examine fouling in the context of treating real landfill leachate on-site using a laboratory scale system. The more specific goals of the study are given below:

- Design of a laboratory-scale in-field system for the treatment of leachate using membrane coupons, which could be recovered for fouling assessment.
- Examine what makes MF and UF membranes foul when leachate is treated.
- Preform membrane autopsies using a scanning electron microscope (SEM) to identify the main fouling components on the membrane surface.
- Explore the stages of membrane fouling over time.
- Evaluate the removal of various contaminants using MF and UF membranes.
- Discover how seasonal variations in leachate composition and strength can effect leachate treatment and membrane fouling.

1.3.2 The Scope of the Study

This laboratory scale study was conducted in two phases, the first in the field and the second within a controlled environment, both using freshly collected leachate from the Trail Road Landfill. The system tested flat sheet membrane coupons (14.5 by 9 cm), not full-scale commercial membrane units, as the effects of fouling could be augmented and forensic analysis could be conducted more easily. Much of the study was spent designing and redesigning the apparatus until optimum operating conditions were met.

The analysis of each test examined basic treatment and fouling parameters, as well as rudimentary pore size effects using several different membranes of varying pore size and composition. The main focus of the fouling studies were basic mineral species identification and confirmation. This study did not examine biological fouling (bio-fouling) in depth or examine the bacterial species involved.

1.3.3 Limitations

1.3.3.1 Trail Road Landfill Set-up

The first testing apparatus was developed with a limited power supply in mind. The mobile flat sheet membrane test system was housed in a shed on the landfill site, with one 15 Amp outlet supplying all of the operating power. The site was located approximately 55 km from the University of Ottawa, which resulted in a great deal of travel during operation for routine inspection and maintenance.

Temperatures in the field could not be regulated and limited the amount of work done on site. The heat of the late summer proved to be a problem. On days which reached 30°C or more the system was not run, due to possible pump, compressor and/or computer failure caused by overheating. The leachate temperatures within the system reached up to 45°C on warm days (>25°C), due to the constant recirculation through the four pumps involved. This led to the rupture of a feed line in an initial run and the eventual long term deformation of the PVC (polyvinyl chloride) piping, leading to significant overall leakage.

In late October and November freezing within the system between runs became an issue. The shed was made of wood and uninsulated, a heating unit was considered a fire hazard and would also have caused a significant power drain on the 15 Amp, 120 V supply. The system had to be moved into an insulated and heated facility for the project to continue. It was relocated to the Hydraulic Lab in the Colonel By building on the University of Ottawa Campus. With the move the piping was redesigned, a cooling system was installed, and one new pump replaced the four previously used. If a full-scale membrane treatment facility was to be implemented at the Trail Road Landfill a temperature controlled facility with an ample water supply and a means of ventilation with dust control would be required.

CHAPTER 2

LITERATURE REVIEW

2.1 Properties of Landfill Leachate

2.1.1 Factors in Leachate Generation

Leachate generation is a problem at landfills throughout the world. Prior to enhanced environmental regulations, waste types were unseparated and landfills unlined. Most westernised countries have implemented leachate collection legislation and separation of municipal solid waste (MSW) from industrial waste in the last two decades. Developing countries often do not separate their waste streams or line their landfills. Leachates produced from these landfills and older landfills in developed countries may contain not only MSW, but industrial waste as well, adding increased potential toxicity to the leachate generated (Tchobanoglous *et al.*, 1993).

In temperate or rainy climates the implications of water migration through the landfill are obvious, but even in arid countries leachate can be generated. Groundwater infiltration, capillary water and the actual moisture content of the waste all contribute moisture towards the formation of leachate in arid regions. In Kuwait, a rising water table combined with a high sludge and liquid waste content contribute to high leachate production despite arid conditions and an average annual rainfall of 110 mm (Al-Yaqout and Hamonda, 2003).

Computer models, such as the Hydraulic Evaluation of Landfill Performance (HELP) program, are used in the solid waste industry to calculate water balances and leachate flows through landfills and were used in predicting leachate generation at the Trail Road Landfill (Hurd, 1999 and Tchobanoglous *et al.*, 1993). Generic models often do not account for the advent of any channelling or short circuiting. This may occur early in the landfill's life when the landfill material is coarsest or with a heavy rainfall event. There may also be poor overall distribution of moisture through the waste. Some areas of the same landfill may be dry while others are saturated (Bendz *et al.*, 1997).

Leachate production in constant regular amounts does not generally occur until the landfill mass reaches a moisture content of approximately 45%, which is its field capacity

(Chu *et al.*, 1994). MSW can accumulate moisture for up to 10 years and will eventually lose some of its field capacity with degradation, compaction and age (Bendz *et al.*, 1997). MSW can absorb about 13.5 cm of water per metre of refuse height when compaction is fairly even and there is no avenue for channelling. Leachate production is generally greatest where the waste is less compact (Chu *et al.*, 1994).

A high moisture content facilitates the redistribution of nutrients and microorganisms within the landfill and is essential for hydrolysis. The moisture content may be the most important factor in the biodegradation process (Bendz *et al.*, 1997). Moisture content alone does not wholly control the generation and strength of leachate. The following factors also play a significant role: initial composition of the waste, particle size, degree of compaction, refuse decomposition factors (e.g. pH, water content, temperature, nutrients, oxygen concentrations, and mixing), landfill age, surface topography and the hydrology and hydrogeology of the site (Al-Yaqout and Hamonda, 2003).

2.1.2 Leachate Variation

The chemical composition of leachate changes depending upon the age and type of landfill. As water percolates through the landfill, decomposing materials along with various chemicals and metals leach into the water. There are several decompositional phases that landfilled materials undergo. The resulting gas production and leachate parameters are depicted in Figure 2-1. Phase I is the initial adjustment phase, where the biodegradable materials in the landfill undergo aerobic decomposition. Air exposure prior to and trapped air just after landfilling allows for this aerobic phase. Most of the leachate produced in this phase is due to compaction and subsequent dewatering or short circuiting in the roughly compacted waste. The primary sources of microbes are the soil used in the daily cover, wastewater sludge (where landfilled) and recycled leachate (where recycled) (Kjeldsen *et al.*, 2002 and Tchobanoglous *et al.*, 1993).

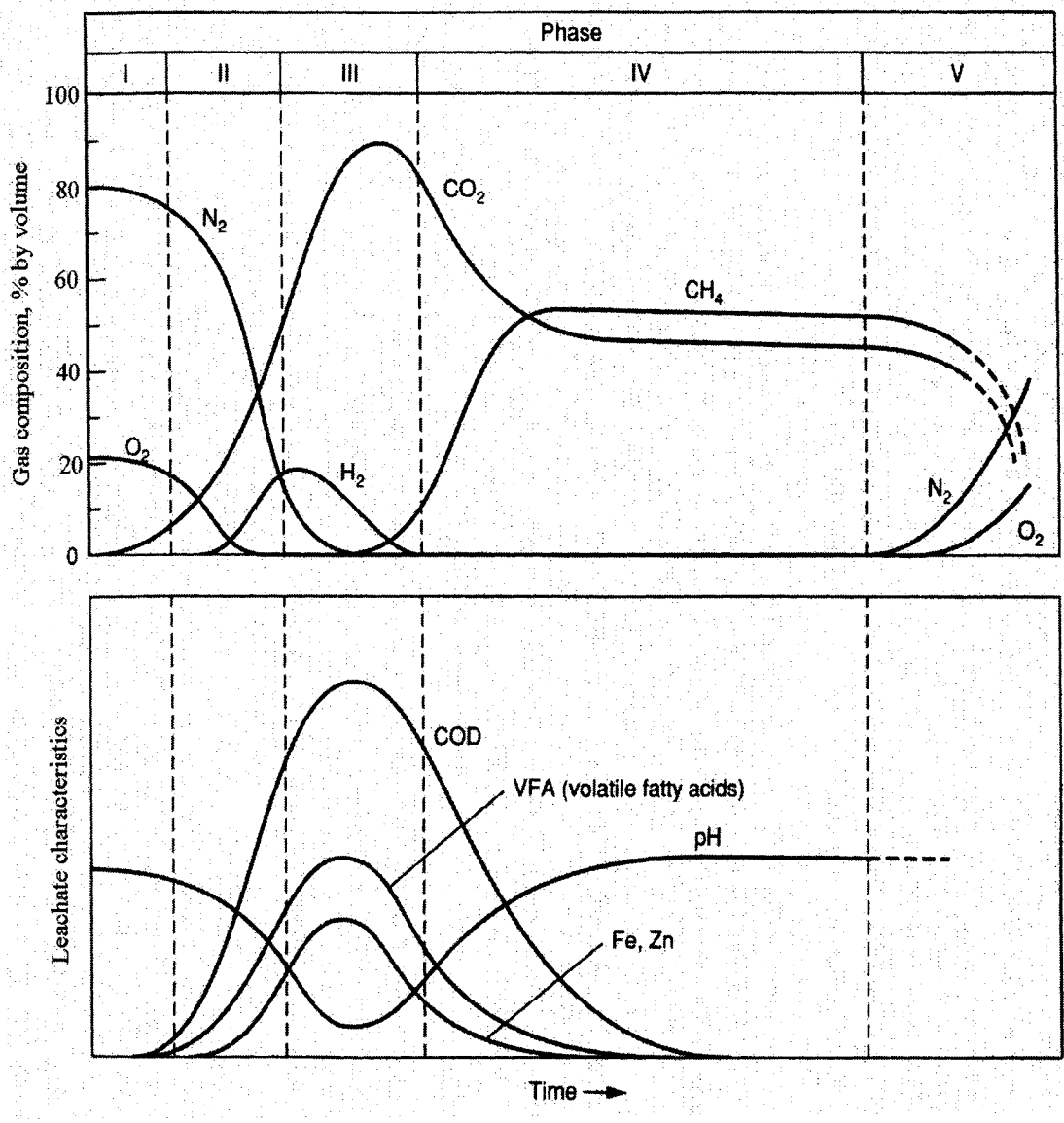


Figure 2-1 Phases of general landfill gas and leachate characteristics (Tchobanoglous *et al.*, 1993).

Phase II is the transitional phase where oxygen is depleted and anaerobic conditions begin to develop. Cellulose and hemicellulose comprise 45 to 60% (dry weight) of MSW and are the major biological constituents degraded in this phase (Kjeldsen *et al.*, 2002). Nitrates and sulphates are reduced, while hydrogen sulphide and nitrogen gases are produced. The oxygen concentration and redox potential decrease and anaerobic microbe activity increases. Complex organic matter is converted to organic acids and intermediate products. This causes

the pH of leachate to drop and continue to drop into Phase III with increased acid production (Tchobanoglous *et al.*, 1993). The highest Biochemical Oxygen Demand (BOD) and Chemical Oxygen Demand (COD) concentrations are seen Phase III (Kjeldsen *et al.*, 2002 and Tchobanoglous *et al.*, 1993).

Phase III is the acid phase where organic acid, CO_2 and H_2 production increases. As the pH drops to approximately 5, the BOD, COD and conductivity of the leachate increase significantly (Tchobanoglous *et al.*, 1993). The COD values can exceed 34,000 mg/L, when volatile fatty acids (VFAs) are the main source of COD (Chu *et al.*, 1994). Metals become more soluble and nutrients essential to degradation of the waste are dissolved into the leachate (Kjeldsen *et al.*, 2002; Tchobanoglous *et al.*, 1993).

Methane fermentation starts to occur in Phase IV as anaerobic methanogenic bacteria transform acids to methane and carbon dioxide. The rate of acid generation decreases and the pH increases (pH 6.8 to 8) with the transformation of acids to methane. As the pH increases metals become less soluble leading to a decrease in the metals concentration of the leachate. The final maturation phase occurs when most of the readily available organic materials are consumed; gas generation and nutrient concentrations decrease; and the more difficult to degrade organic materials leach out (Kjeldsen *et al.*, 2002; Tchobanoglous *et al.*, 1993; Wreford *et al.*, 2000). The organic matter remaining are hydroxyaromatic substances, difficult to degrade because of their high molecular weight, such as humic acid, fulvic acid, tannic acid, gallic acid, and pyrogallol (Chu *et al.*, 1994). The BOD/COD ratio, which is a general measure of biodegradability, drops from as high as 0.7 in Phase III to 0.1 in mature methanogenic leachates (Wreford *et al.*, 2000).

The final phase (V) or humic stage is a hypothetical case, as landfills have yet to be studied for longer than 40 years and this situation has yet to be seen. The landfill is thought to become an aerobic system again as the waste is highly decomposed allowing the rate of oxygen diffusion to exceed the rate of oxygen uptake. Most of the evidence for this is based on computer modeling and laboratory experiments (Kjeldsen *et al.*, 2002).

The length of time it takes for these phases to occur can be variable, some taking decades to occur. The factor which most consistently affects the rate of decomposition is the moisture content. It is quite common for different parts (lifts or cells) of a landfill to be in different phases of decomposition (Kjeldsen *et al.*, 2002). Ragle *et al.* (1995) found that older areas (16 years old) of the same landfill had stronger COD values than the most recently filled sections. TDS and manganese leached readily decreasing in concentration over time, while COD, Total Organic Carbon (TOC) and Fe all increased with age as they became more available with waste decomposition. The newer areas of the landfill more readily released particulate matter into the leachate, at rates three to four times higher than the older area. The mass of particulate matter in the leachate of the new area also increased three to six times with a dramatic increase in flow, normally caused by a significant rainfall event. Increased compaction and chanalized drainage in the older sections meant that mass was not emitted from the waste as readily, therefore the particulate levels would increase slowly with an increase in flow (Ragle *et al.*, 1995).

Seasonal variations in overall rainfall tend to cause the leachate strength to rise during the dry season and decrease in the wet season (Bendz *et al.*, 1997). Heavy rainfall events often result in an increased and more dilute leachate production after a few days lag time (7 to 14 days). The lag time results from a culmination of infiltration rate, saturation index and overcoming forces which retain the moisture in the MSW, such as surface tension and capillary action (Bendz *et al.*, 1997; Chu *et al.*, 1994). During dry periods the percolation rates are low and the evaporation high allowing for longer water contact time with smaller quantities of water (Chu *et al.*, 1994). Refuse buried in arid climates decomposes more slowly than areas which receive 50 to 100 cm or more annual infiltration, but tends to be highly concentrated (Kjeldsen *et al.*, 2002). Leachate variation occurs over the life of the landfill, from season to season and on a diurnal basis. Leachate composition can see a threefold change over the course of day-to-day or hour-to-hour monitoring, while negligible changes are seen from minute-to-minute. This often means that it is very difficult to get a consistent leachate characterization even over the course of a day (Ragle *et al.*, 1995).

2.1.3 Leachate Composition

Despite its complexity and variability the major leachate constituents can be divided into four major categories (Kjeldsen *et al.*, 2002):

1) Dissolved Organic Matter: COD, TOC, volatile fatty acids (VFAs), fulvic and humic compounds.
2) Inorganic Macrocomponents: calcium (Ca^{2+}), magnesium (Mg^{2+}), sodium (Na^{+}), ammonium (NH_4^{+}), iron (Fe^{2+}), manganese (Mn^{2+}), chloride (Cl^{-}), sulphate (SO_4^{2-}), and hydrogen carbonate (HCO^{3-}).
3) Heavy Metals: cadmium (Cd^{2+}), chromium (Cr^{3+}), copper (Cu^{2+}), lead (Pb^{2+}), nickel (Ni^{2+}), and zinc (Zn^{2+}).
4) Xenobiotic Organic Compounds (XOCs): These are chemicals which originate from household or industrial chemicals and are present in relatively low concentrations (<1mg/L). They consist of a variety of aromatic hydrocarbons, phenols, chlorinated aliphatics, pesticides and plasticizers.

(NOTE: Parameters of particular concern to this project and membrane fouling are discussed in greater detail later in this chapter)

Only a small number of the complex chemicals within leachate are well understood. It is estimated that 90% to 95% of the organic materials in a municipal landfill are of unknown composition. Most monitoring programs at landfills only measure up to 200 of the more than 60 000 chemicals in use today (Nascimento Filho *et al.*, 2003). The impact on those exposed to long-term sustained levels of landfill leachate contamination is unknown. Many of the larger polymers and long chained complex chemicals cannot be treated with conventional biological wastewater treatment and will remain in the effluent after treatment.

Another avenue to consider when examining the composition of leachate is how the samples are collected. The character of leachate changes depending on how the samples are handled. If the collection system involves air exposure then aerobic nitrification can occur and affect the ammonia concentrations. The colour of the leachate can also be affected by air exposure. The oxidation of ferrous ion (Fe^{2+}) to ferric form (Fe^{3+}) can change the leachate colour from light yellow to dark brown. Ferric iron tends to form ferric hydroxide colloids

and fulvic complexes which contribute to an overall brownish coloured leachate and increase the overall suspended particulate loading. This means that turbidity actually increases with leachate exposed to atmospheric oxygen in storage (Chu *et al.*, 1994).

2.2 Landfill Leachate Treatment

The changing nature of leachate over time indicates the need for a system which can be modified easily to accommodate that change. Current leachate treatment throughout the world varies from no treatment to highly technical treatment plants. When leachate is untreated it is generally allowed to discharge into the local watershed or is held in the landfill until a critical liquid volume is reached and drainage is required.

2.2.1 Leachate Management

The foremost method of dealing with leachate has been simple on-site management. Primary methods of leachate management consist of limiting the infiltration of fresh water into the landfill and containment of any escaping waters. The 'dry-tomb' method of waste disposal involves lining the bottom and top of the landfill with an impermeable substance and preventing water migration (Tchobanoglous *et al.*, 1993). In the last decade it has come to light that without water infiltration waste decomposition is extremely slow and if the liners are punctured over time the problem of leachate generation would continue. Studies suggest that while leachate is a high strength wastewater it is necessary to have water infiltration for the overall health of the landfill (Wreford *et al.*, 2000).

A high moisture content improves the availability of nutrients and stimulates bacterial growth, while diluting metabolic inhibitors. This is of paramount importance to landfills trying to use the methane generated in the landfill as an energy source. As mentioned previously, landfill waste decomposition goes through several overall phases, but only with water present. It is the flow of leachate downwards through the landfill that carries nutrients from the younger, higher layers of the landfill downward to the lower and older areas increasing degradation through the addition of nutrients (Wreford *et al.*, 2000).

Leachate recycling involves pumping the leachate back into the landfill, so that the

nutrients can be further utilized in degradation. By recirculating the leachate the moisture content in the refuse can increase from a typical 15 to 25% to 40 to 50% and nutrients lost to leachate migration can be reintroduced (Kjeldsen *et al.*, 2002). Treatment through recirculation alone is not common practice in North America, as there is often residual leachate which will always be produced, especially in large landfills. If the holding tanks, holding ponds, and pumps used do not have a large capacity there could be leachate migration off site as a result of large rainfalls. Leachate recirculation can lead to the attenuation of leachate constituents by biological, chemical and physical processes; precipitation of metals with increasing pH during methanogenesis; and increased landfill gas production for collection and use (Tchobanoglous *et al.*, 1993).

Evaporation is another simple method of leachate management. It involves leaving the leachate in a lined pond and allowing it to naturally evaporate. Geomembranes can be used to cover the ponds in winter and during rainy seasons to prevent the entry of precipitation. Any gases produced under the geomembrane can be vented to a soil or compost filter. The dried residual leachate is often re-landfilled once stable (Tchobanoglous *et al.*, 1993).

2.2.2 Co-treatment with Municipal Wastewaters

With city growth outwards towards landfill sites, direct sewage system injection has become more feasible. In Europe several cities have taken this route, some with pretreatment before entering the sewage system to meet sewage use regulations (Gierlich and Kollbach, 1998; Peters, 1996). Some believe that the high concentrations of organic and inorganic toxic compounds in leachate should preclude its direct introduction into the sewer system and that there should always be at least a pre-treatment stage (Bohdziewicz *et al.*, 2001). Late phase IV leachate with a BOD/COD ratio less than 0.5 is not amenable to biological treatment. When leachate consists of more than 2% of the total sewage volume entering the MWTP, treatment efficiencies are reduced and bulking sludge results (Chiang and Qasim, 1994).

Both Waterloo, Ontario and Winnipeg, Manitoba discharge their leachate into their municipal wastewater treatment plants (WWTPs). In Waterloo the Erb Street landfill had no

leachate collection system and was developing a leachate mound within the landfill. A toe-drain system and a force-main were constructed to drain the leachate and send it to the wastewater treatment plant. Winnipeg trucks its leachate to the wastewater treatment plant for introduction into the activated sludge process. Both municipal wastewater plants were operating well under capacity prior to leachate introduction (Booth *et al.*, 1996; Hombach *et al.*, 2003).

The Waterloo WWTP was treating approximately half of its designed hydraulic load and 20 to 40% of its designed pollution load, prior to leachate introduction. The leachate introduction would have only represented 0.14% of the volume and about 2% of the waste pollution load when mixed. The landfill produced approximately 46 m^3/d of leachate, which was pumped to the sewer once the holding tank was at capacity at 25.4 m^3/h. The maximum impact of leachate on the system was evaluated when the sewage flow was low (night) and the leachate pumping at maximum output. Here the leachate could represent up to 3.6% by volume of the total sewage. It was found that the metal input increase was significant especially for nickel, but since the overall metals concentrations were well below regulation this had little impact on the biosolids and was not considered a concern. The worst case scenario of high percentage leachate discharge could easily be avoided by prolonged discharge during the day and avoiding maximum output at night (Booth *et al.*, 1996).

2.2.3 On-Site Treatment

Modern landfill facilities which offer complete leachate treatment are generally modular and multi-staged approaches designed to deal with the variability in leachate production and characteristics (Bohdziewicz *et al.*, 2001 and Trebouet *et al.*, 2001). The first step is generally biological treatment like activated sludge for ammonia, COD and BOD removal. Biological processes are needed for leachates containing volatile fatty acids, but are less useful for older stabilized leachates. A stabilized leachate may still have high COD values (500 to 1500 mg/L), but is biologically difficult to break down. This generally indicates that the feasibility of biological treatment is only in the early stages of leachate generation and other avenues of treatment are required (Bohdziewicz *et al.*, 2001; Trebouet

et al., 2001). Activated sludge can be difficult to regulate based on seasonal and long-term leachate fluctuations and does not deal in general with salt and metals reduction (Gierlich and Kollbach, 1998). Coagulation/flocculation, evaporation, chemical oxidation and membrane pre-treatment have also been used as a first stage in multistaged treatment plants (Bohdziewicz *et al.*, 2001 and Palma *et al.*, 2002). Secondary treatment stages vary depending on the level of treatment required. The following table, modified from Tchobanoglous *et al.* (1993), briefly outlines a number of different treatment options which have been used to deal with leachate. The list involves biological, chemical and physical treatment options (see Table 2-1).

Table 2-1 Overview of leachate treatment technologies (Tchobanoglous *et al.*, 1993).

Treatment Process	Application	Comments
	Biological Processes	
Activated Sludge	Removal of Organics	Defoaming additives may be necessary; separate clarifier needed.
Sequencing Batch Reactors	Removal of Organics	Similar to activated sludge, but no separate clarifier needed; only applicable to relatively low flow rates.
Aeration Stabilization Basins	Removal of Organics	Requires large land area.
Fixed Film Processes (Trickling Filters, Rotating Biological Contactors)	Removal of Organics	Commonly used on industrial effluents similar to leachates.
Anaerobic Lagoons and Contactors	Removal of Organics	Lower power requirements and sludge production than aerobic systems; requires heating; greater potential for process instability; slower than aerobic.
Nitrification/Denitrification	Removal of Nitrogen	Nitrification/denitrification can be accomplished simultaneously with the removal of organics.
	Chemical Processes	
Neutralization	pH Control	Of limited applicability to most leachates.
Precipitation	Removal of Metals and Some Anions	Produces a sludge, possibly requiring disposal as a hazardous waste.
Coagulation	Removal of Suspended Matter	Generally does not remove heavy metals, unless able to achieve organic matter removal (Urase *et al.*, 1997)
Oxidation	Removal of Organics	Works best on dilute waste streams,; use of chlorine can result in formation of chlorinated hydrocarbons.
Wet Air Oxidation	Removal of Organics	Costly; works well on refractory hydrocarbons.

Treatment Process	Application	Comments
Physical Operations		
Sedimentation/Flotation	Removal of Suspended Matter	Of limited applicability alone; may be used in conjunction with other treatment processes
Filtration	Removal of Suspended Matter	Useful only as a polishing step.
Air Stripping	Removal of Ammonia or Volatile Organics	May require air pollution control equipment.
Steam Stripping	Removal of Volatile Organics	High energy costs; condensate steam requires further treatment.
Adsorption	Removal of Organics	Proven technology; variable costs depending on leachate.
Ion Exchange	Removal of Dissolved Inorganics	Useful only as a polishing step.
Ultrafiltration	Removal of Bacteria, High Molecular Weight Organics and Bivalent Ions	Subject to fouling.
Reverse Osmosis	Dilute Solutions of Inorganics	Costly and may require pretreatment.
Evaporation	Where leachate Discharge is not Permissible	Resulting sludge may be hazardous; can be costly except in arid regions.

2.3 Membrane Technology

2.3.1 Basic Membrane Composition and Terminology

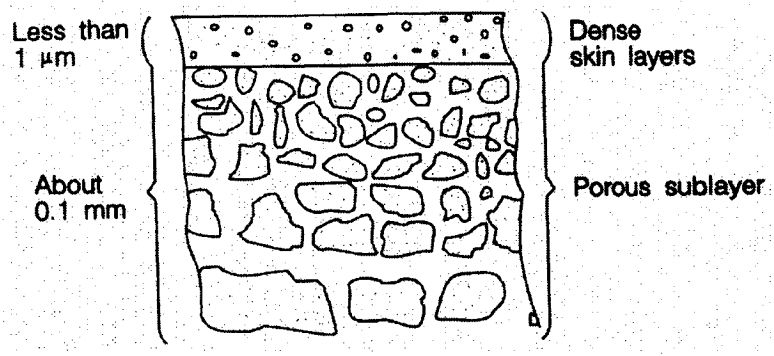


Figure 2-2 Asymmetric membrane cross section (Matsurra, 1994).

Synthetic membranes are a barrier to molecules based on their molecular weight. The molecular weight cut-off (MWCO) of a membrane determines the largest sized molecule able to permeate the membrane structure. There are membranes made of organic (e.g. polymetric or liquid) and inorganic materials (e.g. ceramic or metal). Polymetric industrial membranes are generally composed of a thin, dense top layer (thickness <0.5μm) supported by a porous sublayer (thickness 50-200 μm) (see Figure 2-2). The material of the top layer determines the *flux* or rate at which the water flows through the membrane. The top layer also determines the particle rejection size. These are called asymmetric membranes, because of the two different materials or layers in their structure. There are symmetric membranes composed of one material, but generally their fluxes are lower and they are not as resilient. The asymmetrical membrane have the benefit of high flux due to the thin nature of the upper layer, while having the selectivity of a thick membrane (Mulder, 1991).

The liquid or gas being filtered is called the *feed*. This project deals only with the filtration of liquids. The liquid able to permeate through the membrane is called the *permeate*. The permeate is the 'clean product' which has had the targeted particles and solutes filtered out. As the feed is circulated through the membrane housing the remaining liquid is concentrated and called the *concentrate*. Another word used to describe the

concentrate is *retentate*, as the liquid is retained and not able to permeate the membrane (Mulder, 1991; Peters, 1996).

Flow through a membrane can be driven by a number of different forces, such as differences in concentration, temperature, and pressure. For membranes used in liquid separation, changes in pressure across the membrane (ΔP) are generally the main driving force. Osmotic or hydrostatic pressures, caused by molecular interactions at the surface of the membrane, need to be overcome for filtration to occur. As the MWCO decreases those interactions become stronger and more pressure is needed to drive the process (Mulder, 1991).

For most industrial membrane wastewater applications the liquid enters into a membrane housing, possibly under pressure, and passes over the surface of the membranes housed within. In the case of polymetric membranes they may be flat sheets with a spacer behind to collect the permeate, or hollow fibres through which the permeate flows. There are a number of different pore sizes and materials available for each type of membrane (Matsuura, 1994; Mulder, 1991).

2.3.2 Microfiltration

The largest pore size classification for commercial membranes is microfiltration (MF). The pore size ranges from 0.1 μm (100 nm = 10^{-6} m) to several μm. The separation process is not necessarily controlled solely by the size of the pores involved. There are various microfiltration materials which are used to intentionally absorb targeted particles to their pores and form a secondary filtration layer. This layer accumulates and blocks the targeted molecule, which may be much smaller than the membrane pore size and thus changes the flux and selectivity of the membrane (Matsuura, 1994).

2.3.3 Reverse Osmosis

Reverse osmosis (RO) membranes have the smallest pore sizes at less than 1nm (1nm = 10^{-9} m). Water molecules are approximately one tenth of a nanometre, therefore they pass freely through the membrane. Organic solutes containing more than one hydrophilic functional group or an electrolyte solute (e.g. sodium chloride) cannot pass through the membrane pores.

Solutes targeted for removal are either rejected at the membrane surface by electrostatic forces or are simply not attracted to the surface and thus stay in solution. This leads to a layer of water at surface containing no solute. The water molecules travel along the pores, through the membrane, while the remaining solution becomes more concentrated. Mechanical pressure is applied to the feed to overcome and surpass osmotic pressures. That is why the process is called *reverse osmosis* (RO). One of the most successful applications of reverse osmosis is the desalination of sea or brackish waters in order to produce potable drinking water (Matsuura, 1994; Mulder, 1991).

2.3.4 Ultrafiltration and Nanofiltration

Ultrafiltration (UF) membranes have smaller pore sizes than MF, ranging from 1 to 100 nm. UF is mostly used in the separation of macromolecules and colloidal particles. The osmotic pressure of macromolecules is less than that for smaller molecules and therefore the pressure needed to overcome osmosis is not as great as needed in RO. Nanofiltration (NF) is often explained as the pore size cut-off, which lies between RO and UF (Matsuura, 1994). The following list shows the general pressure differences required and the fluxes to be expected for each membrane type. The fluxes are reported in volume per surface area, time and pressure, but standard fluxes in Canada are reported in $Lm^{-2}h^{-1}$ or LMH with no pressure component (Mulder, 1991):

Microfiltration:	$\Delta P \approx 0.0987$ to 1.974 atm
	(1.45 to 29.0 psi or 0.1 to 2 bar)
	Flux > 0.5 $m^3m^{-2}day^{-1}bar^{-1}$ (>20.8 $Lm^{-2}h^{-1}bar^{-1}$)
Ultrafiltration:	$\Delta P \approx 0.987$ to 4.94 atm
	(14.5 to 72.5 psi or 1 to 5 bar)
	Flux ≈ 0.1 - 0.5 $m^3m^{-2}day^{-1}bar^{-1}$
	(4.17 - 20.8 $Lm^{-2}h^{-1}bar^{-1}$)
Reverse Osmosis:	$\Delta P \approx 9.87$ to 98.7 atm
	(145 to 1450 psi or 10 to 100 bar)
	Flux < 0.05 $m^3m^{-2}day^{-1}bar^{-1}$
	(<2.08 $Lm^{-2}h^{-1}bar^{-1}$)

2.3.5 Membrane Applications for Leachate Treatment.

For total leachate treatment RO systems give the most complete contaminant removal. RO treatment can give approximately 80 percent to 90 percent contaminant removal/retention (Gierlich and Kollbach, 1998; Trebouet *et al.*, 2001). Reverse osmosis treatment has been used to deal with the salts and metals in leachate, either in conjunction with activated sludge or alone (Gierlich and Kollbach, 1998; Trebouet *et al.*, 2001). Rather than activated sludge, MF pretreatment is often used prior to RO treatment to decrease colloids and reduce biofouling on the RO membranes (Fane *et al.*, 2000). As of the year 2000 there were more than 100 RO leachate treatment plants in North Western Europe, North America and the Far East. Some membrane treatment facilities produce a permeate which meets with local discharge regulations (Bohdziewicz *et al.*, 2001; Gierlich and Kollbach, 1998). One of the major drawbacks to RO systems is the expense involved in pre and post treatment coupled with the energy costs. Pre-treatment cost may involve simple screening of larger particles, to seeding and precipitation, to an MF, UF or NF pre-treatment system depending on the waste stream. The post treatment costs are in the disposal of the concentrate (Trebouet *et al.*, 2001).

The treatment of leachate using RO alone was improved with the advent of the Rochem disc-tube module (Peters, 1996 and Peters, 1988). By 1996 Rochem disc-tube module systems composed 70% of the process capacity of existing leachate systems. This system is modular and offers flexible operating parameters, low energy costs (5 kWh/m^3 of permeate at an 80% recovery rate), and requires few cleaning agents. Each module is a pressure pipe vessel with membrane disks stacked one on top of the other. The disks are stacked along a central tension rod around which they rotate. They are composed of two octagonal membranes on each face of the disk, spaced with an internal fleece to allow for the permeate to drain. The disk rotation, coupled with the channel design, creates enough shear to minimize fouling. The stacking of the membrane disks allows for a compact system. Salt and organic rejection rates have been reported as high as 99% (Peters, 1996 and Peters, 1998).

For leachates with a high total suspended solids (TSS) concentrations pretreatment prior to the Rochem RO treatment system improved the overall plant performance. Leachates with high concentrations of soluble calcium sulphate were dealt with by using seeding and precipitation prior to RO treatment to avoid fouling and deposition. Pretreatment with partial TSS removal enabled a high pressure disc tube module to be designed, which gave higher recovery rates than RO alone. Another option for leachate pretreatment, in conjunction with seeding was the addition of a disk tube nanofiltration unit. NF allows for the separation of bivalent ions out of the leachate and the passage of monovalent ions to RO treatment. For example, the NF filtration leads to high rejection of sulphate ions and dissolved organic matter, with low chloride and sodium rejections. The former are then treated by RO. The combined NF and RO with seeding can result in a recovery rate of 95-97.5% (Peters, 1996 and Peters, 1998).

Spiral wound membrane modules have also been used in leachate treatment. These are long sheets of membrane with a spacer behind for permeate collection, rolled into a cylindrical unit. They provide a high surface area/volume ratio allowing for a compact membrane unit. This design is more conventional and readily available from multiple suppliers (Fane *et al.*, 2000).

NF has been proposed as an alternative to RO treatment where the required recoveries are not as stringent as discussed above. The more open structure in the NF membrane allows for higher fluxes, lower pressures and lower power requirements compared to RO. Most NF membranes are negatively charged and small uncharged particles pass through the membrane by pressure. Small charged particles are retained due to the electrostatic interaction and large particles are retained by sieving (Trebouet *et al.*, 2001).

Membrane Bioreactors (MBR) are a relatively new technology which combine the activated sludge and/or anaerobic digestion concept with submerged hollow fibre membranes. RO filtration often follows MBR treatment to remove the nitrification products. Negatively charged nitrate and nitrite produced in MBR treatment are more easily removed from water than positively charged ammonium ion or neutral ammonia found in leachate (Ahn, W.-Y. *et al.*, 2002).

2.4 Membrane Fouling

There is little published on membrane fouling with regards to landfill leachate. Fouling involved in the following areas are much more widely studied and understood in the academic literature: sea water desalination; milk, juice and other food processing; and surface, grey and groundwater treatment. The following section will review the general fouling hypotheses in the literature and examine their possible application to leachate treatment.

2.4.1 General Fouling

Membranes have pores through which a permeate of specific particle size flows. When those pores become blocked by organic or inorganic deposits, the flux declines and treatment efficiency decreases dramatically (Mulder, 1991; Peters, 1996). This deposition and blockage process is called *fouling*. Though the flux will decline naturally from membrane compaction based purely on flow and pressure, this will level off and the intrinsic membrane flux will remain. The decrease in flux from this point on may be due to fouling. When the permeate flow decreases under constant temperature and pressure fouling is often suspected (Tracey, 1996). The following graph shows a typical flux decline curve over time with fouling (Figure 2-3).

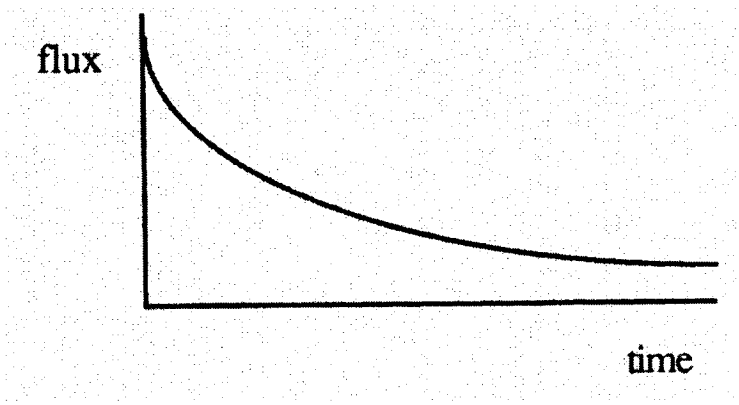


Figure 2-3 Typical flux decline curve (Mulder, 1991).

2.4.2 Mechanisms Involved

The flux (J) of a membrane is based on the driving force (? P), the viscosity (μ) of the liquid and the total resistance (R_{tot}) encountered.

$$J = \frac{\Delta P}{\mu R_{tot}} \qquad 2.1$$

The resistance can be composed of several different vectors (Figure 2-4). The initial total resistance is that of the membrane (R_m). With time other types of resistance can occur. Higher liquid concentration can occur near the membrane surface with the removal of permeate from the bulk solution. This acts as a form of mass transfer barrier to the filterable liquid in the bulk solution and is called concentration polarization (R_{cp}). There are also particles which will block pores (R_p) and adsorb onto the membrane surface (R_a) causing further resistance. Solutions that contain proteins can even form a gel layer over the membrane (R_g) . Figure 2-4 shows the various types of resistance that may occur.

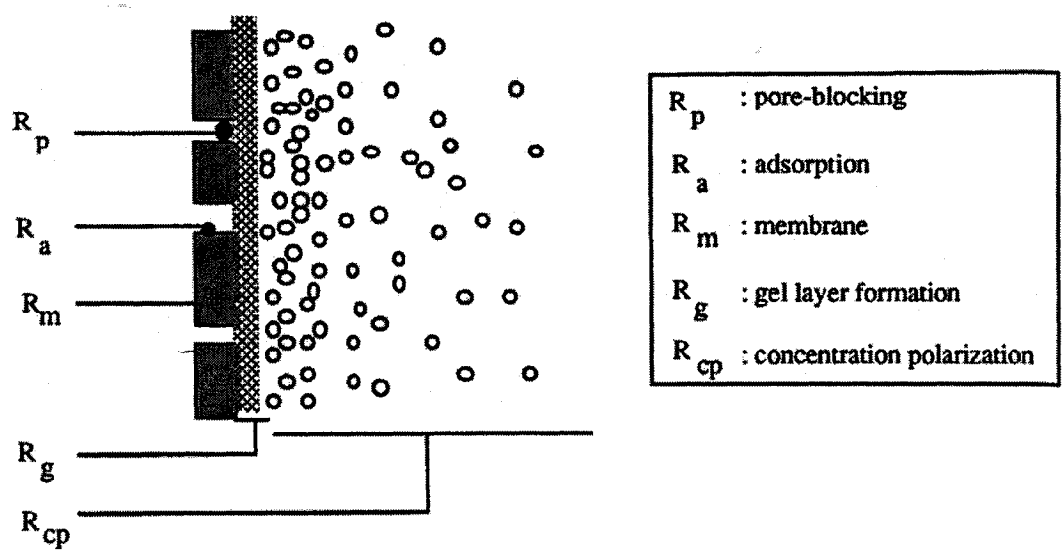


Figure 2-4 Various types of resistance in fouling (Mulder, 1991).

With UF, NF and RO membranes, fouling occurs mostly on the surface (Krack, 2000). Microfiltration membranes foul on the surface as well as within the pores themselves (Krack, 2000). Fouling tends to be most severe for MF and UF membranes, where the flux can decline to less than 5% of pure water filtration flux (Mulder, 1991). There are four

important types of fouling: 1) crystalline (inorganic mineral deposits), 2) organic (humic substances, oils and greases), 3) particulate and colloidal and 4) microbial (Bryers, 2000).

2.4.2.1 Concentration Polarization

Concentration polarization is not fouling. The solute retained by the membrane becomes concentrated at the membrane surface, but not necessarily on the membrane itself. This concentration at the surface is due to the removal of solvent and residual solute being concentrated. This effect will eventually reach a steady state, where there is a well defined boundary layer of concentrated solution.

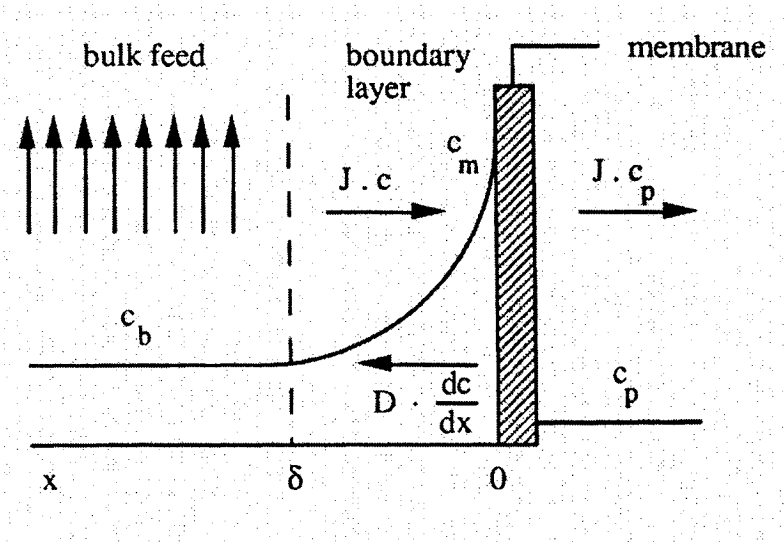


Figure 2-5 Concentration polarization profile (Mulder, 1991).

Concentration polarization can result in a *lower retention* of small molecules (such as salts), *higher retention* of larger molecules, and/or a *decrease in flux* when the polarization is well developed. The diffusion coefficients of retained macromolecules involved in MF and UF are small, and the fluxes are also quite high, when compared to RO. This leads to larger concentration polarization effects in MF and UF (Mulder, 1991). Figure 2-5 shows a typical concentration polarization concentration profile. This model assumes that at some distance (D) there is still a fully mixed bulk solution (c_b = bulk concentration), the exact point at which the concentration polarization begins is denoted by d. Within the boundary layer the

concentration increases from the bulk solution at the beginning of the boundary layer to a maximum at the surface of the membrane (c_m). The flow of solutes towards the membrane surface is denoted by J·c. If the solute is not fully retained by the membrane then the flow through the membrane of solute becomes $J \cdot c_p$ (c_p = concentration in the permeate). The accumulation at the surface eventually leads to a diffusive flow away from the membrane. Once the boundary layer has established steady state then the convective transport towards and the diffusive transport away, plus the solute passing through the membrane are equal (Mulder, 1991).

Generally it is acknowledged that the flux resulting from concentration polarization reaches a maximum and no increase in pressure will result in an increase in flux for UF. The flux increases with increasing pressure for RO, but with UF the flux increases for a small period and then levels off (Figure 2-6). Further decreases in flux are caused by fouling (see Figure 2-7) (Mulder, 1991). Fouling can actually lead to an increase in the concentration polarization as the fouling layer can then trap more ions near the membrane surface. One of the first signs in RO salt/brackish water treatment is an increase in salt content or conductivity in the permeate as more salts migrate through the membrane due to concentration polarization (Tracey, 1996).

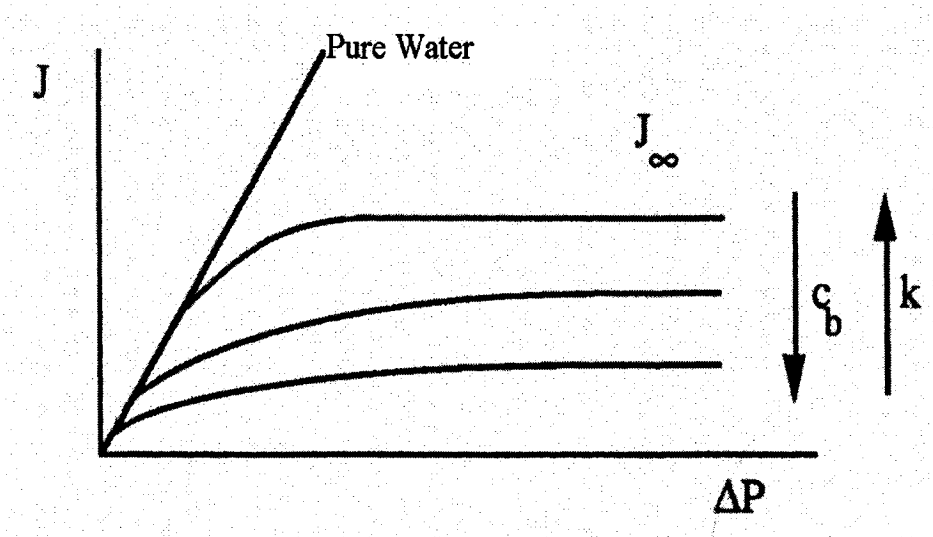


Figure 2-6 The effect of bulk concentration and mass transfer coefficient on flux with UF membranes (Mulder, 1991)

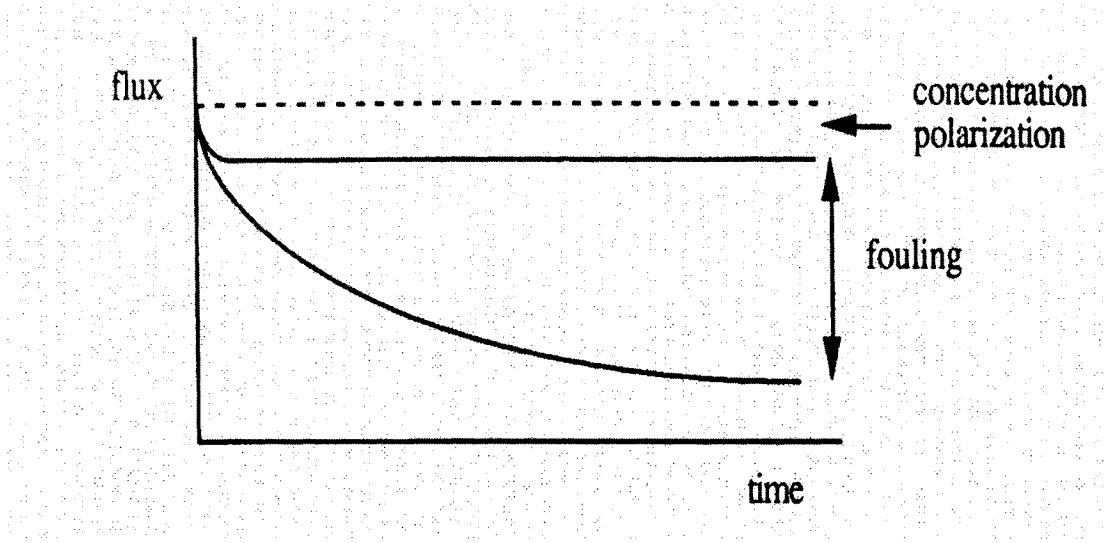


Figure 2-7 The effect of fouling on flux (Mulder, 1991).

2.4.2.2 Particulate Fouling

Particulate fouling arises when there are particles in the feed which are large enough to block, clog or accumulate in the entry of the membrane housing. The particles can then form a mass along the surface of the membrane clogging not only the inlet, but the membrane as well. Breakthrough from sand filters, incorrect placement or selection of filters, and concentrated waste streams with high TSS can all cause particulate fouling. Depending on the problem, modification of sand filters, the membrane unit inlet type or pre-filtration may resolve the problem. One way of estimating the particulate fouling potential of a feed is to measure the silt density index (SDI) (Tracey, 1996).

2.4.2.3 Colloidal Fouling

Colloidal fouling can occur when colloids exist in suspension. As the feed concentrates these molecules are retained and begin to coalesce. These groupings can then bind to the membrane surface and/or the housing material. Silica and iron tend to form colloids in water. Iron is soluble at pH 7 and below and insoluble at pH 8 and above. Many

leachate feeds have an approximately neutral pH which tends to increase as it is concentrated leading to more iron precipitation. Also, the increase in salt content in the concentrate can lead to the destabilization of dissolved ions resulting in deposition. Determining the extent to which a feed may foul colloidally can be difficult, as colloids are small enough to pass through a SDI filter (0.45μm pore size). Measurements of silica and iron in the feed and permeate may give some indication of colloidal fouling. Colloidal fouling can be complex as silica fouling can take more than one form and is influenced by the presence of transition metals like iron. It tends to occur at the feed end where the colloids are destabilized and can precipitate out. Coagulants and flocculents may be used to remove the unwanted parameters, but if not properly settled they may cause fouling themselves. Excessive coagulant addition can also lead to charge neutralization which may create a different type of colloid making coagulation ineffective (Tracey, 1996).

2.4.2.4 Chemical Scaling

This type of scaling only occurs in RO and tight NF membranes. Loose NF, UF and MF membranes do not suffer from this type of fouling as salts pass freely through the pores. Chemical scaling is the deposition of salts formed in the presence of concentrated ions. Calcium, strontium, barium, sulphate and carbonate can all cause sparingly soluble salts to develop, such as calcium carbonate, calcium sulphate, barium sulphate and strontium sulphate. As the feed moves along the membrane unit, it becomes increasingly concentrated and salts form more readily, therefore this type of fouling is generally strongest in the last element of a membrane system. Computer modeling programs have been developed to roughly predict the formation of salts and help develop a strategy towards combating their formation. A number of steps of varying complexity can be taken to prevent this type of fouling, depending on the salts being formed. Calcium carbonate can be managed simply by reducing the pH so as to prevent scaling (Tracey, 1996).

2.4.2.5 Biofouling

Most types of fouling can be managed in the liquid phase by reducing the foulant, but

the same may not be true of biofouling (Bryers, 2000; Flemming, 2000). Biofouling is the accumulation of biomass on a surface by growth and/or deposition to such a level that it causes operational problems (Vrouwenvelder and van der Kooij, 2002). It occurs due to the replication of microbes on the surface forming a biofilm or by attachment of a large number of microbes from solution. Eventually the growth of the microbes exceeds the membrane's tolerance or threshold and they affect membrane performance (Bryers, 2000 and Flemming, 2000). Microbes are one of the few foulants that can increase with time regardless of concentration, as long as there is nourishment (Flemming, 2000).

Where sterile conditions do not exist there will be some level of bacterial contamination and eventual biofilm formation (Flemming, 2000). Bacterial attachment and biofilm formation usually occur within the first few hours of operation, under non sterile conditions (Bryers, 2000; Flemming, 2000). In the case of surface water treatment there are between 10^4 and 10^6 cells per millilitre (Flemming, 2000). Microbes will adhere to surfaces in oligotrophic systems, regardless of hydrophobicity or hydrophilicity, smoothness or chemical constituents (Flemming, 2000). Biofouling can lead to areas of localized pH extremes causing membrane damage, which tends to start at the feed side and spread rapidly across the membrane surface (Tracey, 1996).

Biofouling is facilitated by the vertical transport vector through the membrane. There are a number of microbes that will adhere preferentially on the membrane surface. One example given by Flemming (2000) is the preferential colonization of polysulfone membranes by *Pseudomonas diminuta* and *Staphylococcus warneri*. Studies have shown that even when only a few microbial species may have preference for a type of membrane material, they will eventually form a coating of microbes and extracellular polymetric substances (EPS) that other microbes can then grow on (Flemming, 2000). A variety of substances fall under the heading of EPS: polysaccharides, proteins, glycoproteins, lipoproteins and other macromolecules of microbial origin. These substances adhere the microbe to the membrane surface and form a slime matrix which keeps the biofilm together (Flemming, 2000).

2.4.3 Fouling Minimization

Fouling can be minimized once the main fouling agents are known; the correct membrane is chosen; and the module design allows for high enough flows to lightly scour the surface (Peters, 1996). For a membrane leachate treatment system to work, open channel systems are required along with chemically resistant membranes. Open channel systems involve increased flow across the membrane system and thus less fouling and limited concentration polarization (Peters, 1996).

Pretreatment of feed solutions can be the easiest solution to the reduction of fouling (e.g. heat treatment, pH adjustment, complexing agents employed, chlorination, etc.). Feeds which are high in TSS or very concentrated, can be pre-treated with MF or UF before RO treatment. Table 2-2 gives examples of various foulants and ways to control them. Hydrophilic or phobic, charged or not, the membrane surface will be affected by the deposition of particles (Fane *et al.*, 2000).

Table 2-2 Foulants and their controls (Fane *et al.*, 2000)

Process	Foulant	Control
RO	General	Hydrodynamics/shear
	Inorganics ($CaSO_4$, $CaCO_3$ silica)	Avoid solubility limit. Water pretreatment, pH 4-6, avoid high recovery (or fluxes), add additives like polyphosphates
	Organics	Biological treatment, activated carbon, ozone
	Colloids (<0.5μm)	Coagulation filtration, microfiltration
	Biological solids	Chlorination/dechlorination, filtration, coagulation, microfiltration
UF/MF	General	Hydrodynamics/shear (e.g. crossflow, backflushing, bubble flow, sub-critical flux)
	Hydrocarbons, surfactants	Limit concentration in feed
	Proteins	Adjust pH and salts, hydrophilic and highly porous surface
	Biological Solids	Hydrophilicity, porosity control

Controlling the cross flow velocity can be very important in averting both concentration polarization and fouling deposition. If the cross flow is laminar, then a concentration profile can be observed over the cross-section, due to the gradual decrease of velocity from the center. The slower flows along the membrane surface allows the concentrated solution to linger and continue to concentrate longer than the flow through the center of the channel. When the flow is turbulent the concentration profile and the boundary layer are confined to near the surface. Many methods have been used to induce turbulence such as corrugated membranes and pulsating flow (Mulder, 1991). Cleaning a biofouled membrane can be very difficult, as the bonds between microbes and the EPS, and between the various EPS molecules themselves can be strong in combination. Targeting the combination of weak electrostatic interactions, hydrogen bonds and van der Waals interactions can be virtually impossible. Simply using commercially available cleansers can dramatically improve flux, but not completely remove the biofilm (Flemming, 2000).

Membrane cleaning is essential in most treatment applications. The correct cleaning agent is determined by the foulant and the membrane type (Krack, 2000). Knowing the type of cleanser to use, the correct temperature and the optimal time between cleansing will maximize the membrane's potential (Krack, 2000). When examining fouling, it is important to relate it back to a potential cleaning regimen. Cleaning can be either hydraulic, mechanical and/or chemical. Cleaning generally works best when the cleaning liquid is warmed within the limits of the membrane. When the cleaning involves chemical agents it often means the membrane will have a more limited life span (Krack, 2000; Tracey, 1996).

2.4.4 Fouling Analysis

Autopsy by Scanning Electron Microscope (SEM) is a generally accepted way to examine membranes after filtration (Fane *et al.*, 2000; Rimpelainen and Tremblay, 2000). Membrane samples can be cut from a larger fouled sample and dried. Gold, aluminum and some carbon are artifacts of the SEM/EDX technique. Energy dispersive X-ray (EDX) analysis using the SEM can then identify the elements involved in the fouling parameters. MINTEQA2, a water chemistry equilibrium computer program, can also be used in

conjunction with inductively coupled plasma (ICP) leachate analysis to identify compounds which may precipitate out of solution (Rimpelainen and Tremblay, 2000).

There are currently new, non-invasive techniques for monitoring fouling. Direct observation of the membrane surface has become more popular where modules can be modified to accommodate the imaging equipment. Direct observation through the membrane (DOTM) is a technique developed at the University of New South Wales (Fane *et al.*, 2000). It involves a transparent when wet MF membrane in a cross-flow test cell which can be optically observed. The feed and subsequent deposition can then be monitored over time. This system has observed that (Fane *et al.*, 2000):

- Smaller particles deposit first.
- The higher the cross-flow velocity the smaller the particles deposited.
- Surface coverage by particles correlates with increases in transmembrane pressure, the effect of which is greater for solutions with "non-visible" (e.g. cell debris) elements.
- Cakes composed of inert materials can be easily removed with an increase in cross flow or if the flux is reduced. Cakes of bacteria are removed in flocs due to the adhesive nature of bacteria.
- Information could be collected on the flux at the point when deposition occurs, relating it to the Reynold's number and the effect of spacers.

2.4.5 Modelling Fouling

There are several different theories concerning fouling formation available in the literature. The basic mathematical models of fouling are complete blocking, intermediate blocking, pore constriction and cake formation, which were reviewed by Harmia (1982). *Complete blocking* assumes that particles will completely block the pores without overlapping. This model focuses on the rate at which open pores will be blocked. *Intermediate blocking* does not assume that each particle will completely block each pore, but that it may also partially block a pore. This model also allows for one particle to settle on another creating layers of deposition, but again not necessarily direct pore blockage. *Pore*

constriction assumes that particles are deposited within evenly distributed equi-dimensional pores. Deposition is considered proportional to the volume of permeate passing through the membrane. The deposition would slowly diminishing the pore radius and thus decrease the flux. *Cake filtration* assumes deposition on the membrane in such as fashion that a layer is formed, which may build and create its own independent resistance on top of the particles already on or in the pores. This resistance increases with an increase in cake thickness (Harmia, 1982).

Many authors built further models upon the cake filtration model as it seems to fit a wide variety of feed circumstances. Waite *et al.* (1999) found that the cake formation most clearly suits haematite suspension filtration, while protein fouling models have been based on the cake filtration model as well (Belfort et al., 1994). There are a number of feed specific and more recent models available than the ones given below, such as Wiesner *et al.*(1989), Van Den Berg and Smolders (1990) and Ho and Zydney (2000), but they are not as applicable to leachate or they involve variables which were not measured during this project. To the author's knowledge there are no models that deal specifically with landfill leachate.

The following basic formulas were also developed for dead-end filtration, not crossflow. When examining cross flow membranes the particle back transport should be taken into account, however this effect does not become significant until the flux reaches steady state. Therefore, when applying these models to cross flow membrane flux data only the pre-steady-state flux conditions should be modelled (Harmia, 1982).

NOTE: Nomenclature not previously defined will be in tabular form after the four formulas are presented (Table 2-3).

Complete Blocking:

$$\frac{dN}{dt} = -\alpha_{block} A J_v C_b \qquad 2.2$$

Integrating 2.2 gives:

$$\frac{J_v}{J_0} = \exp\left(-\frac{\alpha_{block} A J_0 C_b}{N_0} t\right) \qquad 2.3$$

***Intermediate Blocking*:**

$$\frac{J_v}{J_0} = \frac{1}{1+(\sigma_{inter}\Delta P / \mu R_{inter})t} \qquad 2.4$$

Pore Constriction:

$$\frac{d}{dt}(\pi r_p^2 \delta_m) = -\alpha_{pore} A J_0 C_b \qquad 2.5$$

Integrating 2.5 gives:

$$\frac{J_v}{J_0} = \left(1 + \frac{\alpha_{pore} A J_0 C_b}{\pi r_p^2 \delta_m} t\right)^{-2} \qquad 2.6$$

Cake Filtration:

$$\frac{J_v}{J_0} = \left(1 + \frac{2\alpha_{cake} J_0 C_b}{\pi r_p^2 \delta_m} t\right)^{-1/2} \qquad 2.7$$

All of these models may be simplified with the use of a constant (K) to replace several constants (Table 2-4). By having all the models in terms of J_v/J_o and simplifying the formulas, the models may be compared and applied to experimental membrane flux data.

Table 2-3 Nomenclature for formulas 2.2 to 2.7 (Harmia, 1982)

Nomenclature	Definition	Nomenclature	Definition
J_v	Filtrate flux	R_{inter}	Resistance from intermediate blocking
J_0	Initial filtrate flux	K	Constant
A	Surface area of the membrane	r_p	pore radius
C_b	Bulk concentration	a_{pore}	Pore constriction efficiency
a_{block}	Pore blockage efficiency	d_m	Cake thickness
s_{inter}	Area blocked per unit of filtrate volume	m_{cake}	Cake mass

Table 2-4 Simplification of models to facilitate comparison (modified from Peng, 2002).

Model	Constant (K)	Equation
Complete blocking	$K_{block} = \left(\frac{\alpha_{block} A J_0 C_b}{N_0} \right)$	$\frac{J_v}{J_0} = \exp(-K_{block} t)$
Intermediate blocking	$K_{inter} = (\sigma_{inter} \Delta P / \mu R_{inter})$	$\frac{J_v}{J_0} = \frac{1}{1 + (K_{inter}) t}$
Pore constriction	$K_{constriction} = \left(\frac{\alpha_{pore} A J_0 C_b}{\pi r_p^2 \delta_m} \right)$	$\frac{J_v}{J_0} = (1 + K_{constriction} t)^{-2}$
Cake filtration	$K_{cake} = \left(\frac{2\alpha_{cake} J_0 C_b}{\pi r_p^2 \delta_m} \right)$	$\frac{J_v}{J_0} = (1 + K_{cake} t)^{-1/2}$

A combined cake filtration and pore blockage model was developed by Ho and Zydney (2000) for protein fouling involving MF (Equation 2.8). The applicability of the above models and the combined protein model to landfill leachate are discussed in Chapter 4, while the method of their application is briefly described in Chapter 3.

Combined Pore Blockage and Cake Filtration Model (Ho and Zydney, 2000):

$$\frac{Q}{Q_0} = \frac{J_v}{J_0} = \left[\exp\left(-\frac{\alpha \Delta P C_b}{\mu R_m} t \right) + \frac{R_m}{R_m + R_p} \times \left(1 - \exp\left(-\frac{\alpha \Delta P C_b}{\mu R_m} t \right) \right) \right] \qquad 2.8$$

Which can be simplified by using the following:

$$K_1 = \left(\frac{\alpha \Delta P C_b}{\mu R_m} \right), \quad K_2 = \frac{R_m}{R_m + R_p} \tag{2.9}$$

To give:

$$\frac{J_v}{J_0} = \left[\exp(-K_1 t) + K_2 \times (1 - \exp(-K_1 t)) \right] \tag{2.10}$$

Where: Q = Volumetric flow rate

2.5 The Trail Road Landfill

The Trail Road Landfill is owned and operated by the City of Ottawa, formerly the Regional Municipality of Ottawa-Carleton (ROMC). The Trail Road Landfill was opened by ROMC in 1980 and continues to receive the City of Ottawa's MSW. In 2001 the landfill received 260,676 tonnes of gross waste, 153,541 tonnes of which were landfilled, 24,521 tonnes were diverted and 82,614 tonnes of fill material was used on site (Golder Associates, 2002).

As mentioned in Chapter 1 there are four stages to the landfill. The first two stages were filled and capped in 1988 and 1991 respectively with no leachate collection or liner system. The third and forth stages are active and have both leachate and gas collection systems (Golder Associates, 2002; Hurd *et al.*, 2001; SAIC, 2001). Approximately 185 m^3/day of leachate has been transported by tanker truck to ROPEC since 1996. In 2001 47,525,000 litres of leachate were transported off-site to ROPEC with none removed during August or September due to dry conditions (Golder Associates, 2002). The leachate is also routinely recirculated into the landfill, as a form of volume management, to promote decomposition (Golder Associates, 2002; Hurd, 1999; and SAIC, 2001).

The geological setting for a landfill can effect the leachate composition. The Trail Road Landfill is located on slightly rolling clays consisting of 30 to 35 m of glacial deposits overlaying limestone bedrock. There is a northwest-southeast trending sand and gravel ridge which is 38 m thick and runs through the area upon which the Trail Road Landfill sits on the east side. This ridge has led to the development of gravel and sand pits near the landfill area.

The ridge extends to the bedrock and contains a deep aquifer, while other areas overlain with clay contain a more shallow perched aquifer. Elevated chloride, alkalinity, iron, hardness, organic carbon and nitrogen concentrations in the local groundwater are considered to be from non-landfill sources, whereas bromide, boron and organic carbon are thought to appear with leachate infiltration on-site. There is some groundwater contamination in the shallow and deep aquifers near Stages 1 and 2 (the unlined stages) and is contained to the City of Ottawa property. There is also surface water discharge northeast of the property which does not show any evidence of leachate contamination (Golder Associates, 2002).

2.5.1 Leachate at the Trail Road Landfill

In general the BOD/COD ratio for the landfill leachate produced from the 3rd and 4th stages is characteristic of an older landfill even though it is still active. The leachate recirculation program resulting in enhanced decomposition led to this lower ratio. Golder Associates (2001) found that most leachate parameters were highly variable over time. The BOD ranged in 2001 from 200 to 5,900 mg/L, TKN ranged from 2 mg/L to 1,120 mg/L and TSS ranged from 7 to 1940 mg/L. The VOCs were in general below the detection limit and not of concern to treatment or groundwater contamination (Golder Associates, 2002).

Trail Road Landfill raw leachate quality data was given to the author in late 2003 by Peter Filiopovich at the Trail Road Landfill and spanned the project time period (summer 2002- summer 2003). This data is presented in Chapter 4, though it is not data collected by the author, its analysis belongs more readily in the discussion and results section for better comparison to the data collected by the author during project.

2.5.2 Leachate Parameters of Concern to this Project

The parameters of concern to this project were:

- Those with a high fouling potential
- Those with the ability to degrade pipes or block machinery
- Trace metals, due to their potential toxicity
- Organic matter

Factors such as leachate pH, conductivity, and chloride concentrations can effect aquatic toxicity, but are not covered below. Little work has been done on the chronic effects of leachate exposure, but there is some indication that it does exert genetic toxicity over time (Kjeldsen *et al.*, 2002)

2.5.2.1 Calcium Carbonate and Dolomite Precipitation in Landfills

Calcium carbonate and organic matter are major causes of clogging in leachate collection systems. Landfill leachates are typically supersaturated with carbonate minerals, which can precipitate within the collection system and on the aggregate above the piping (Bennett *et al.* 1999). Once the system is clogged it can no longer keep advective leachate transportation from occurring. High COD and Ca^{2+} concentrations (50,000 - 80,000 mg/L and 3,500mg/L respectively) were found to cause the most significant clogging (Rittmann *et al.*, 2003).

Calcium carbonate and calcium sulphate also causes scaling on membrane surfaces and within system piping (Peters, 1996). The degradation of organic acids under anaerobic conditions increases the leachate pH and leads to calcite precipitation. Dissolved CO_2 is the limiting factor in the production of $CaCO_3$ and therefore by encouraging CO_2 volatilization the amount of $CaCO_3$ which can be formed in the system is reduced (Fleming *et al.* 1999 and Rittmann *et al.*, 2003).

2.5.2.2 Ammonia

Ammonia often does not decrease with time and constitutes a major long-term pollutant in leachate. Ammonia-nitrogen is often found in concentrations of 500 to 2000 mg/L and will stay at those concentrations after the acidic phase, as there are no mechanisms for its degradation under methanogenic conditions that exist in the landfill. Ammonia is considered the most acutely toxic component in leachate (Kjeldsen *et al.*, 2002). Sensitive aquatic species can suffer from ammonia toxicity when leachate is discharged into surface waters (Kjeldsen *et al.*, 2002).

2.5.2.3 Sulphur

Anaerobic conditions may occur within the biofilm along sewage pipes. Pitting occurs within those strictly anaerobic conditions and involves sulphur reducing bacteria (SRB), such as *Desulfovibrio desulfurcans* (Bitton, 1999; Hvitved-Jacobsen and Neilsen, 2000; Geldreich, 1996). Pitting corrosion in iron pipes is characterised by small holes forming and expanding along the top or sides of pipes (Bitton, 1999; Hvitved-Jacobsen and Neilsen, 2000). The pitting mechanism may be linked to the metabolic function of SRBs, which can produce cathodic depolarization around the area of growth. The cathodic hydrogen is released by an enzyme called hydrogenase, this indicates the initiation of biocorrosion (Bitton, 1999). Depolarization around the bacteria releases Fe^{2+} and H^{+}. Free iron in combination with the sulphate forms FeS, which accumulates on the pipe surface (Bitton, 1999). As the process continues the pipe loses more iron and corrodes away (Bitton, 1999).

When dissolved oxygen and nitrate are depleted in wastewater, sulphate reducing bacteria will use sulphate as an electron acceptor and municipal sewage as an organic carbon source, leading to the formation of hydrogen sulphide (H_2S). Hydrogen sulphide (H_2S) can be oxidized in the biofilm, by sulphide oxidizing bacteria such as *Thiobacillus concretivorus*, to form sulfuric acid (H_2SO_4). The sulfuric acid formed can lead to pipe corrosion which is particularly detrimental to concrete pipes, as almost all of the acid produced will react with the cement in the concrete leaving only loosely bound particles (Bitton, 1999; Hvitved-Jacobsen and Neilsen, 2000).

Large slow-flowing (<30cm/s) gravity sewers with insufficient aeration and fairly high temperatures (>15 - 20°C) have the most problems with sulphide production. In pressure mains sulphide is produced even at low temperatures when the line is full and the residence time exceeds 0.5 - 2 hours. Sulphide concentrations of 0.5, 3 and 10 mg S/L are considered low, medium and high 'problem' concentrations for corrosion (Hvitved-Jacobsen and Neilsen, 2000).

Corrosion is not the only concern with sulphide production. There are health and odour issues as well. Hydrogen sulphide (H_2S) is a weak acid and tends not to form at higher pH:

$$H_2S \_ H^+ + HS^- \_ 2H^+ + S^{2-} \qquad 2.11$$

The density of hydrogen sulphide is slightly higher than atmospheric and can therefore accumulate in manholes and pump stations. Hydrogen sulfide concentrations above 150 ppm can no longer be smelled and instrumentation must be used to protect work crews before entering a sewer for maintenance. A pH increase may decrease the formation of H_2S as it tends to form in lower pH ranges. H_2S can be released into the atmosphere, but HS^- and S^{2-} will stay in the water phase if the pH conditions exist. The following table summarises some of the known exposure risks associated with H_2S exposure:

Table 2-5 Risks associated with hydrogen sulphide exposure (Hvitved-Jacobsen and Neilsen, 2000)

Odour or human effect	Concentration in atmosphere (ppm)
Odour limit	0.1 - 0.2
Unpleasant smell	3 - 5
Recommended criterion per workday	10
Effect on eyes	50 - 100
Inactivation of smell	150 - 250
Serious water accumulation in lungs	300 - 500
Deadly impact on nervous system	500 - 1000
Immediate cessation of respiration	1000 - 2000

2.5.2.4 Metals

Heavy metals are of particular interest, because of their potential toxicity. They leach into the water, soil and clay via ion exchange. Leaching increases as the soil's ion exchange capacity decreases with decreasing pH which occurs in the acid phase of decomposition. Trace metal concentrations then decrease in the methanogenic phase with the accompanying pH increase. The leachate from a younger landfill will have more trace metals than a stabilized older leachate. Trace metal amounts in leachate are therefore not only affected by the amount found in the landfill, but by the degradation processes occurring (Chu *et al.*, 1994).

In Japan, where a large percentage of the solid waste landfilled may be ash (≈20%) metals remaining in the ash are of particular concern. One study found that while the leachate from three landfills was biologically and chemicaly treated, the proportion of metals stayed the same before and after treatment. The effluent metals concentrations were not above discharge standards, but were 10 to 1000 times higher than the local surface water conditions. In general, coagulation was not very effective in removing metals at higher pH and was more effective at lower pH, but not substantially so. The metals removal was much more substantial when organic mater could be successfully removed, due to the metal complexes formed. Removal of organic and salt metal complexes was found to be best using a low retention nanofiltration membrane with the possibility of upgrading to a RO membrane system for more complete removals (Urase *et al.*, 1997).

Many studies have found that metal concentrations in general are fairly low in most landfills and do not pose a significant problem. In fact many leachate studies have shown metals concentrations at or below the US drinking water standards. Less than 0.02% of heavy metals received in the landfill are actually leached, as sorption and precipitation leads to metal immobilization. Soils in the neutral to high pH levels, such as in the methanogenic phase, have significant sorptive capacities and tend to trap metals. Metals are often not reported in terms of their complexes, but in ionic form making it difficult to fully understand in what forms metals are leaching. There is some concern over the long-term break through leaching, but that scenario has yet to be proven (Kjeldsen *et al.*, 2002).

2.5.2.5 Organic Matter

When degraded, organic matter can deplete oxygen concentrations in receiving waters, which can affect the stream bottom flora and fauna (Kjeldsen *et al.*, 2002). One study found that the BOD_5 of older landfill sites closed in 1987 was 420 mg/L (Hombach *et al.*, 2003), which rose to 8160 mg/L for a recently decommissioned site (closed 1998) and 10,630 mg/L for an active site. The max discharge found in active sites was 25,400 mg/L (Hombach *et al.*, 2003).

As the contaminants in leachate are composed almost exclusively of dissolved matter, much of the organic matter is very small. One study found 95% of the BOD exerted was less than 500 Da MWCO (Park *et al.*, 2001). Fresh leachate has been found to contain 80% hydrophilic organic substances and 20% humic and fulvic acids. After biological treatment the hydrophoilic substances decrease as they are more easily degraded, but most of the humic and fulvic acids remain (Park *et al.*, 2001). Humic-type substances are refractory anionic macromolecules of moderate (1000 Da MW-fulvic acids) to high (10,000 Da MW-humic acids) molecular weights. These can be important constituents of organic matter, the most difficult to degrade and may have significant fouling effects (Trebouet *et al.*, 2001).

Trace organics dissolved within the landfill tend to be adsorbed onto the landfill clay liner and those that do not, migrate out with the leachate. Some of the organics, and thus the COD, can be volatilized easily. A reduction in volatile organic compounds (VOCs) can occur simply from movement through pipes, from circulation in tanks and general agitation (CRA, 2001a).

CHAPTER 3

METHODOLOGY

3.1 Design Rationale and Operations

As stated in Chapter 1 the main goal of this project was to examine fouling in the context of treating real Trail Road Landfill leachate on-site. The first of five goals listed was the design and construction of a laboratory-scale, in-field membrane coupon system. The high variability of measured leachate parameters, combined with large fluctuations in values over time, presented a difficult design problem. The desire was to build a system, which could operate under realistic and representative field conditions. A complete ceramic membrane system was designed and built in spring 2002, but never used due to the limited power supply available on-site and concerns over field conditions. Ceramic membranes were initially considered because of their resistance to abrasion and tearing. They had proven very successful in the treatment of bilge water at the University of Ottawa (Peng, 2002), but had been used rarely in landfill leachate application. The fragility of the ceramic units; the need for a cooling system in a recirculating system of this design; and the power needed to run the pump for the unit made the design impractical once it became apparent that the power service would not be improved and the lack of readily available cool water was discovered.

The second design, and the design track which was followed for the rest of the project, involved a Sepa® flat sheet membrane testing cell from Osmonics Inc. (currently GE Osmonics Inc.). The flat sheet membranes were more flexible and easier to manipulate in the field. They were more susceptible to scouring and therefore a pre-filtration system of 100 and 30 microns was added to the feed line to remove sand and rocks. Several design improvements were made throughout the life of the project as problems were identified and rectified and will be covered later on in this chapter.

The next series of goals for the project were analytical ones, focusing on membrane fouling and membrane examination post experimental run. Membrane autopsies were done using a scanning electron microscope (SEM) to identify the main fouling components on the membrane surface. Another goal was to examine the stages of membrane fouling over time by performing a sequential membrane run using the same

membrane type, with leachate collected in the same time frame. The effect of how seasonal variations in leachate composition and strength affect leachate treatment and membrane fouling was also a goal of the project. Finally, the effectiveness of MF and UF membranes in the treatment of landfill leachate was to be examined by determining what parameters are removed and to what level. This chapter will review the methods used to attain the previously mentioned goals, beginning with the facilities available and the effect these had on the design.

3.1.1 Available Facilities

3.1.1.1 Trail Road Facilities

A lined, sloped gravel bed was available near the pump house filling station to locate the project (see Appendix A for a map of the Trail Road Landfill and project location). The bed was a relict from a previous leachate pre-treatment project and needed to be relined. Once relined a 3.7 m by 4.3 m (12 ft by 14 ft) shed was built on-site in May 2002 (Figure 3-1). The shed was not insulated and was without running water. A 120 V/15 Amp circuit was extended from the pumphouse to power the experimental set-up. The power supply proved to be susceptible to surges and also limited the strength of pump that could be used for the project. The pump house contained two pumps, which transferred leachate from an underground collection tank, through the transfer hose to a waiting tanker truck. Permission was given to house three large 227 L (60 gal) barrels under the pump house exterior gangplank. These barrels were used as primary receptacles for the leachate and were filled using the transfer hose (Figure 3-2).

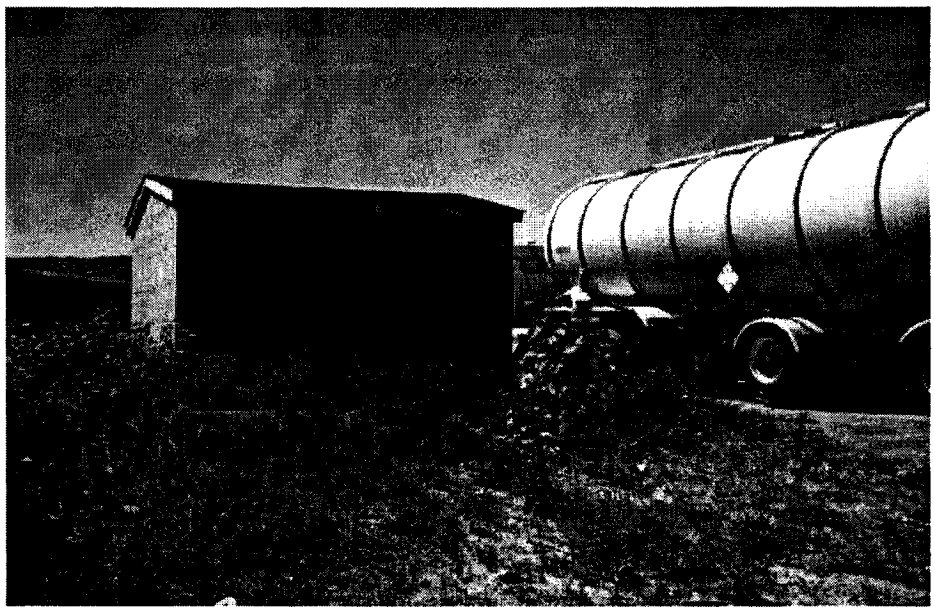


Figure 3 - 1 View of shed with a tanker truck filling in the background.

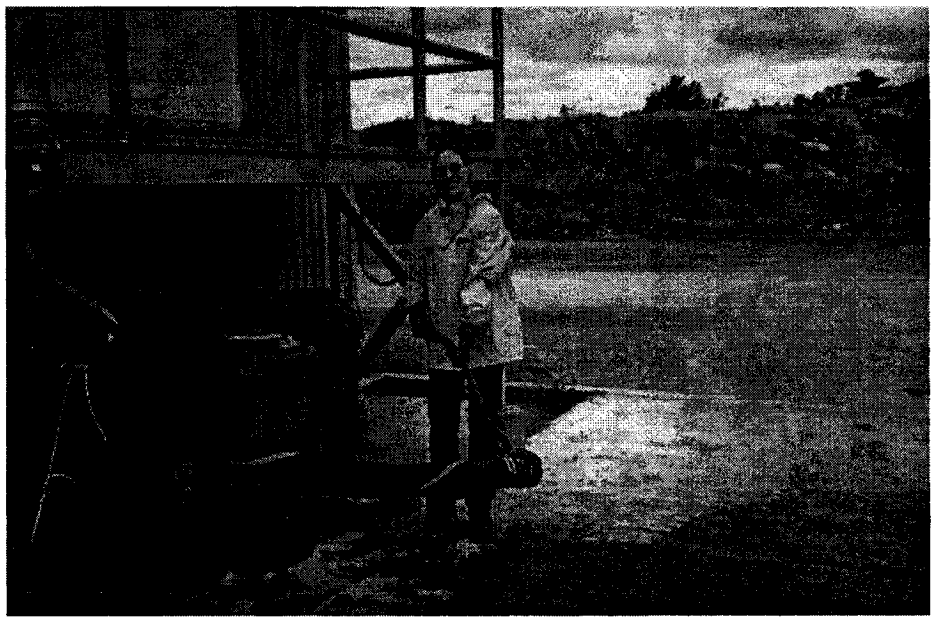


Figure 3 - 2 The author filling the transfer barrel with leachate using the transfer hose.

During a run the apparatus was checked every 6 hours to ensure that everything was operational, which was not always the case. The lack of running water and low power supply meant there was no way to cool the system during the hottest days of the summer or heat the system in the late fall when the system froze between runs (see Appendix A for a map of where the facility was located at the Trail Road Landfill and for brief descriptions of other projects run in the same location and the problems encountered).

3.1.1.2 University of Ottawa Facilities

No appropriate facilities could be found at the Trail Road Landfill, thus project relocation was required. The facilities at the University of Ottawa allowed for much easier system control. The project was set up in a small, unused area of the hydraulics lab located in the basement of the Colonel By building, on the University of Ottawa main campus. It operated there from winter of 2002 to summer of 2003. The hydraulics lab has a large reservoir of water, a small portion of which was used in a heat exchange cooling system to regulate the leachate temperature. There were floor drains to the sewer system in the event of a spill, a pressurized air supply of approximately 100 psi and a 120 V/15 Amp power supply was still used, but had a much more stable grid with more outlets available.

3.1.2 The Apparatus

3.1.2.1 Sepa® GE Osmonics Inc. Cell

The Sepa® membrane cell used was a cross-flow system, which allowed for coupon testing. It was designed to simulate flows in larger full-scale units. The system accepted most flat sheet membranes sized to approximately 19 cm by 14 cm, which gave an exposed membrane surface area of 155 cm^2. The membrane sat between two plastic plates, the lower of which had channels for fluid entry and exit. The cell had a pneumatic air driven piston mechanism, which applied pressure over the entire area of the membrane housing. O-rings completed the seal between the plates and were routinely replaced to insure a proper seal. The following figures show the cell and the positions of the inflow and outflows (Figures 3-3 and 3-4).

Figure 3 - 3 Osmonics Ltd. Sepa ® membrane cell with the inlet to the right, the outlet to the left and the permeate exiting the central hose.

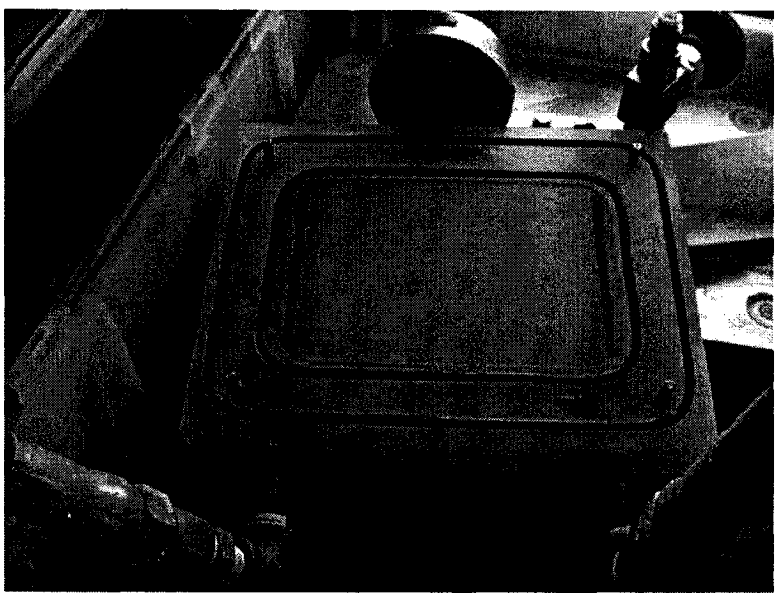


Figure 3 - 4 Bottom plate of the membrane housing with the inlet channel to the left and the outlet on the right. The membrane is positioned in the centre of the housing overlapping the inner, but not the outer O-ring.

3.1.2.2 Membranes Studied In This Work

One of the early objectives of this study was to test a wide variety of membranes with a range of MWCOs and find the most suitable membrane for leachate treatment. A number of available membrane were ordered from GE Osmonics Inc. and from those available a number were chosen for testing. The membranes chosen had to be UF or MF and not require pressures of over 75 psi as the system was not equipped to handle pressures above this. Unfortunately delays in sourcing the membranes, problems with the experimental set-up and the eventual relocation of the project meant that not all of the membranes were tested.

Of those tested not all were satisfactory runs. Most of the data from the preliminary studies were incomplete, as runs were interrupted by instrumental or hardware failure. The membranes from which complete runs were accomplished are listed in the table below (Table 3-1). A complete run was 48 hours long and had sample collection before and after the run.

The goal in testing multiple membranes was run to run each membrane at least twice and if possible more, but problems with the experimental set-up and time constraints did not allow all to be tested more than once. The MF membrane JX_{67200} was the most plentiful membrane available and was used not only for the sequential runs to be explained later in this chapter), but in multiple normal runs as well. JX_{67200} was the only MF made available by GE Osmonics Inc. for this study. See Appendix B for a complete list of membranes used and problems associated with certain runs. Most of the membranes examined in this project were procured from GE Osmonics Inc.. The membranes used in the initial testing were residuals from a previous study on bilgewater treatment and were a mixture of GE Osmonics Inc. and Koch Membrane Systems Inc. due to delays with Osmonics delivery.

Table 3-1 List of membranes used in complete runs. All GE Osmonics Inc. membranes with the exception of M-180 which is a Koch membrane.

COMMERCIAL NAME*	MEMBRANE MATERIAL**	REJECTION SIZE (KDALTONS)	CLASS	TYPICAL FLUX/PSI GFD@PSI	RUN DATE
JX_{62700}	PVDF	62700 (0.3 microns)	MF	130/30	Sept. 30, 2002 Oct. 22, 2002 Oct. 24, 2002 April 10, 2003 April 12, 2003 April 15, 2003
MW_{100}	Ultrafilic	100	UF	176/20	Oct. 9, 2002
EW_{60}	PS	60	UF	300/25	March 4, 2003
ER_{30}	PS	30	UF	325/50	Oct. 2, 2002 April 15, 2003
QW_{30}	N/A	30	UF	N/A	Sept. 12, 2002
GN_{10}	N/A	10	UF	N/A	Sept. 16, 2002
$M\text{-}180_{10}$	N/A	10	UF	N/A	August 13, 2002
PT_5	PES	5	UF	90/50	Oct. 7, 2002 March 17, 2003 April 7, 2003
GM_4	TF	4-PEG	UF	20/40	March 7, 2003
GK_2	TF	2-PEG	UF	17/75	Sept. 24, 2002 March 10, 2003
GH_1	TF	1-PEG	UF	20/150	Feb. 24, 2003 July 23, 2003

* Subscript number represents the MWCO (KDa).

** Membrane material was identified as the specific polymer used or an industry material type, those that were not available are listed as N/A.

Abbreviations:

PS = Polysulfone PES = Polyethersulfone TF = Thin Film

GFD = Gallons/ft^2day PVDF = Polyvinylide fluoride PEG = Polyethylene glycol

3.1.3 Operation of the Trail Road Landfill Apparatus

The basic apparatus was composed of two sloped-side tanks, one for the permeate and the other for the concentrate; a pump or series of pumps to circulate the leachate into the cell and back to the concentrate tank; the previously described Sepa® Cell to house the membrane; a permeate flow measuring device; and a series of in-line monitoring devices which sent data to a computer running systems operation software and controlling automation. The original apparatus design components are displayed in the following schematic, with flow directions (Figure 3-5). The role that each component played during a leachate run will be explained more clearly by discussing how the apparatus operated and what role each component played in the operation.

The original apparatus consisted of the membrane housing; an air compressor; a data acquisition unit with NuDAM® modules connected to the in-line temperature probes and pressure transducers and a computer; piping and pumps all installed upon a mobile scaffolding unit; and two tanks for the permeate and the feed. The scaffolding allowed for easy delivery to the Trail Road Landfill. The tanks and main computer were connected on-site. Water testing of the system was done in the Chemical Engineering Workshop and again at the landfill to make certain measuring devices were operational and the piping was watertight. Once it was clear that there were no leaks and all sensors were operating normally, then a test was conducted using fresh leachate.

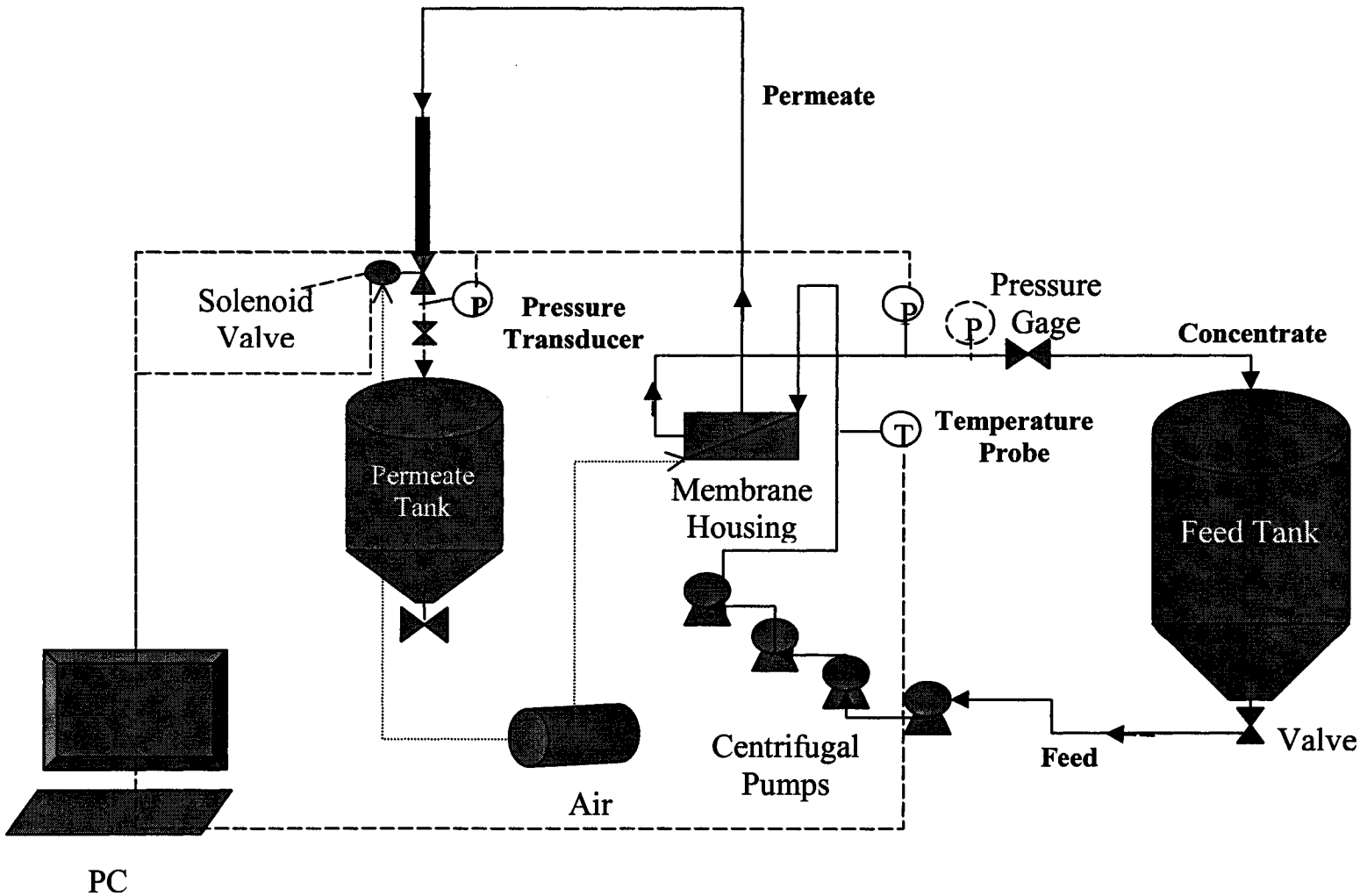


Figure 3-5 Schematic for the first apparatus.

The first step in beginning a fouling test was to collect leachate in the 227 L (60 gal) tank mentioned previously, using the leachate transfer hose to fill the barrel. Once full, a submersible pump was lowered into the tank and the leachate pumped through two preliminary bag filters. The filters were 100 and 30 micron filters attached to the outside of the shed in case of leakage or poor hose connection. These were installed to protect the down stream pumps and membranes from larger particulate matter that occasionally exited the transfer hose and to decrease precipitation of the solids within the system.

Ninety-five litres (25 gallons, the volume denotations on the tanks were in gallons) of pre-filtered leachate was drained into the feed tank via a hose through the shed wall. The submersible pump was then turned off and removed from the transfer barrel; the filter entry point valve closed to prevent back flow; and the hose connecting the filters to the pump disconnected and coiled. Once the leachate was delivered to the feed tank a sheet membrane was cut and placed in the Sepa® cell, the computer turned on and the LabVIEW™ program designed for the system engaged. The Osmonics cell was sealed by air pressure using an air compressor.

The following gives an outline of what occurred while the system was running:

1 Four small centrifugal pumps in series were used to circulate and pressurize the leachate (see Figure 3-6). The pumps were SHURflo® centrifugal circulating pumps with noryl® corrosion resistant housing, delivering 45.4 L./min of flow. Each pump delivered approximately 10 psi of pressure giving a max pressure of 40 psi. The four pumps were chosen for there low power draws and the ability to turn one or more off to adjust for pressure requirements below 40 psi.

2 Just before the pumps were started the LabVIEW™ data acquisition program was set to 'run' and recorded data (temperature and pressure results) every 10 or 20 seconds, depending on the membrane type.

3 Leachate flowed under pressure across the surface of the membrane within the cell. The filtered liquid (permeate) went to the permeate tank, while the unfiltered leachate was recirculated to the feed tank. The feed tank then became the concentrate tank as the bulk solution lost water and became more concentrated. A flow-through rather than a recirculating system was considered, but concerns over methane gas sparking in the leachate well precluded a flow-through system.

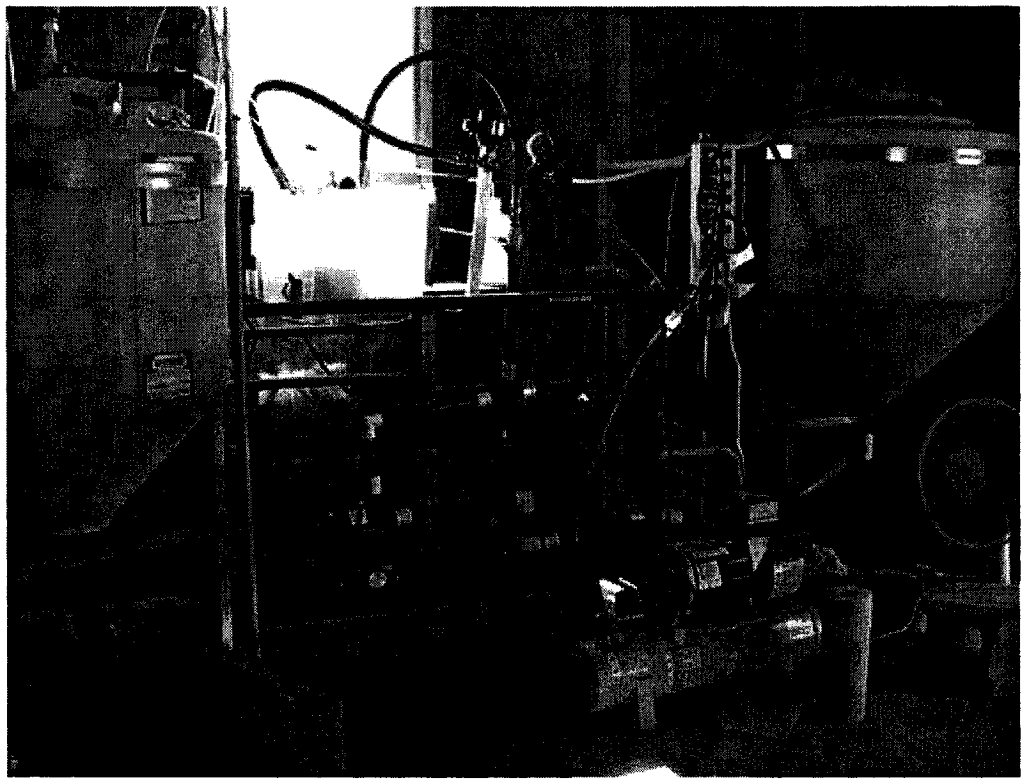


Figure 3- 6 The apparatus at the Trail Road Landfill. The feed tank is to the right, the permeate tank to the left, the cell is housed within the plastic container on top of the scaffolding, the four pumps are just below and the air compressor is on the floor.

Liquid temperatures and pressures were monitored using a temperature probe inserted near the cell inlet and pressure transducer just after the cell.

Permeate production was monitored using a vertical PVC (3/4"or 1.9 cm diameter) pipe which was filled and emptied based on 70 g of liquid filling the column. A pressure transducer at the bottom of the pipe monitored the weight of the permeate filling the column. Once it reached 70 g the LabVIEW^{tm} program was set to open the air pressure operated solenoid valve, just below the pressure transducer, and the column emptied. A ball valve attached below the solenoid valve was partially closed, so as to reduce the flow upon emptying and prevent the column from emptying past the pressure transducer (see Figure 3-7).

Figure 3- 7 Permeate production monitoring device. The permeate entered the pipe seen centre, filling the pipe and area pictured until 70 g above the pressure transducer was reached. The solenoid valve was then opened

6 The system was monitored by a number of NuDAM® data collection modules linked to a microprocessor and CPU (central processing unit) running LabVIEW^{tm}. The program monitored the room temperature, the process temperature, the operating pressure, the permeate mass being collected (from the pressure transducer in the permeate flow device) and the status of the NuDAM® modules. Figure 3-8 gives a sample of what the LabVIEW^{tm} screen looked like during a run.

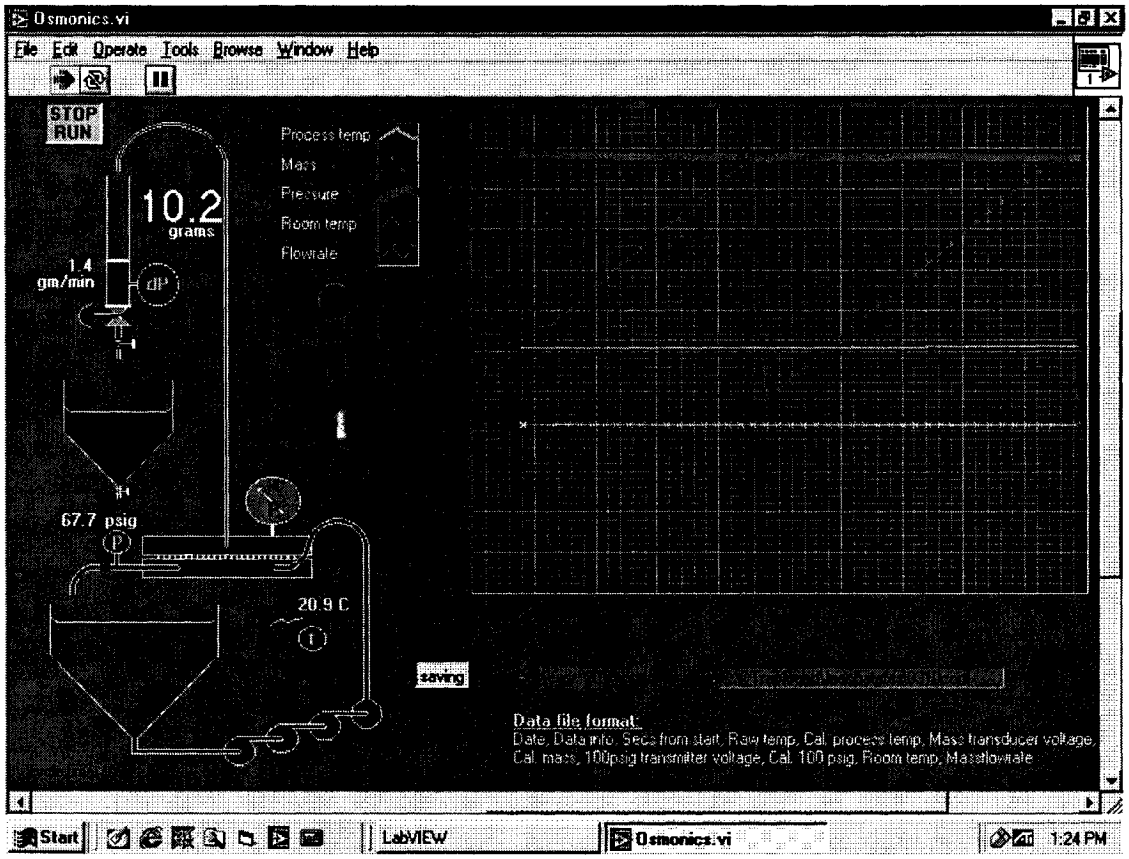


Figure 3-8 LabVIEW screen example.

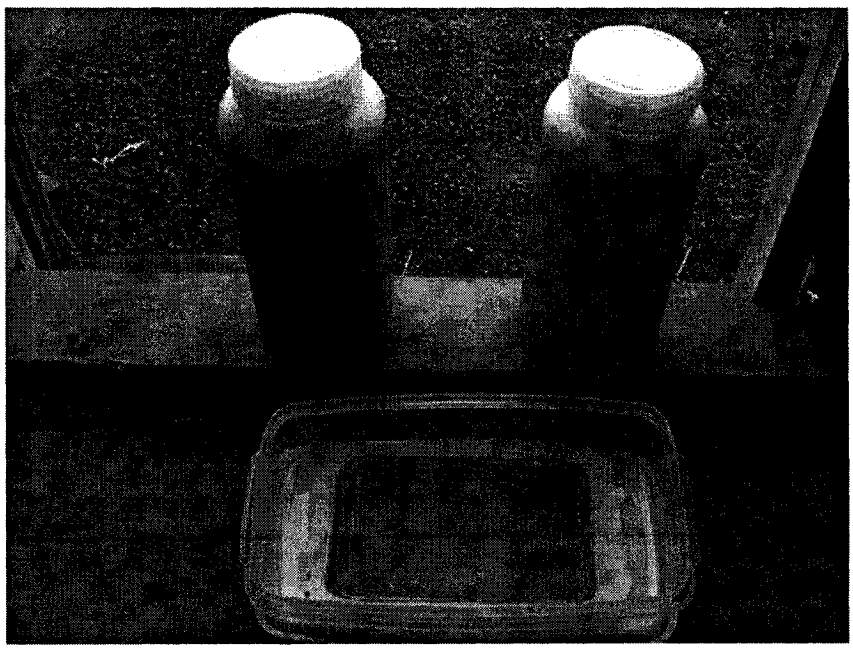


Figure 3- 9 Samples of membrane, concentrate and permeate samples collected at the end of a run

7 Samples were collected of the fresh pre-filtered leachate, concentrate and permeate liquid. The system was run for approximately 48 hours. This seemed to be an appropriate length of time based on preliminary trials discussed in Chapter 4. The membrane was also collected at the end of each run for analysis (see Figure 3-9). For the field trials, only COD, ICP and SEM analysis were performed.

3.1.3.1 Problems with the Trail Road Landfill Apparatus Design

The following is a list of problems with the original design and the remedies taken; most of these problems were corrected by the second apparatus design:

- An unreinforced Tygon tube ruptured within the first week of full operation. It had melted due to high leachate temperatures. Some damage was done to the pumps as there was no automatic shutdown and the author was between check-in times when it happened. Both the inlet and outlet lines from the cell were replaced with Swadgelok high pressure, high temperature reinforced tubing.
- The heat of the leachate also deformed the 1.9cm (3/4") PVC piping with time, causing significant leakage and coupling fusion by the end of the project stay at the Trail Road Landfill. In the second design the piping was replaced with 1.9 cm (3/4") stainless steel piping. The heat at the landfill may have also have effected some of the final results, which will be covered in Chapter 4.
- The four pumps in series necessitated more piping and connections than one larger pump. The extra connections made it harder to fix leaks without causing others. In the second design one pump with 7 impellers replaced the four as a more reliable power supply was available. The replacement pump was a Goulds 5GB03 - 7 Stage centrifugal pump with an output of approximately 1.9 to 2.1 m^3/hr at approximately 20 to 30 psi.
- In order to maintain and change the pressure, a valve was placed in the outflow stream leaving the cell. The valve was partially closed to varying degrees to control the pressure. By having the valve set away from the cell there would be no pressure drop over the length of the membrane. There was a danger that fouling would occur at the outlet if the point of pressure drop was too close too the cell

and the leachate destabilized. This fouling could then move backwards spreading along the length of the membrane. Though the location of the valve was correct, the type of valve was not. The GE Osmonics Inc. cell relied mostly on cross-flow velocity and the first valve used was a needle valve, which fouled very easily and decreased flow rates by blocking the outflow. It was replaced by a ball valve in the second design.

- The Osmonics cell itself caused pipe fouling at the inlet, as the flow took a dramatic directional change within the cell. This led to a build up of material just before the cell inlet, due to the unstable flow conditions. This could not be rectified.
- The first air compressor used was replaced by a more heavy duty model as the opening and closing of the solenoid valve combined with pressurizing the cell was too much demand for a light duty model. The air compressor was replaced completely by the pressurized air supply available in the Hydraulics Lab.
- The Osmonics cell had a small air leak due to a break in the air-driven sealing piston's O-ring. The reason for the leak was not discovered until October at which time it was rectified.
- Part way through the time at the Trail Road Landfill it was realized that the pre-filtration was not enough to manage the solids in the leachate. A 5 micron bag filter was introduced to the recycle line in the feed tank, which assisted in decreasing the overall solids in the system.
- There was no mixing within the concentration tank itself as the recirculation kept the tank well mixed, but for lower flows or in the case of a flow-through system this would be required to reduce sedimentation in the tank.

3.1.4 Apparatus at the University of Ottawa

The second apparatus design was an improvement on the first, not only in the changes mentioned previously, but also in the location and the ability to control the system more easily. Problems with the cell remained the same, but the piping, pumps, air compressor and pressure control valve were all replaced, making it much easier to locate any problems and fix leaks. A single tube heat exchanger was added, which had been

designed for the original ceramic system. The readily available supply of water in the hydraulics lab reservoir allowed for its addition (Figure 3-10).

The second system operated essentially the same as the first. Leachate was collected from the sampling tap at the Trail Road landfill in five gas containers ('jerry cans') of 20 L (5 gal) each and transported by car to the hydraulics lab. They were then emptied into the same large barrel used at the Trail Road landfill (Figure 3-11a). The leachate was then passed through a hose to the preliminary filters (Figures 3-11b to 11c). All three filters (100, 30 and 5 microns) were monitored for clogging and replaced every 3 or 4 runs depending on the strength of the leachate (Figure 3-11d to see spent filters).

The system was then run as before with the exception of the output from the pump being split into two streams. One stream was pumped through the cell and other was cooled and recycled (see schematic Figure 3-12). The heat exchanger had a 1.27 cm (½") stainless steel tube running through a larger 2.54 cm (1") stainless steel pipe. The unit was vertical with an inlet at the bottom and outlet at the top. A submersible pump was lowered into the reservoir and pumped water along the outer pipe. The leachate diverted for cooling was pumped through the inner tube and cooled by heat exchange.

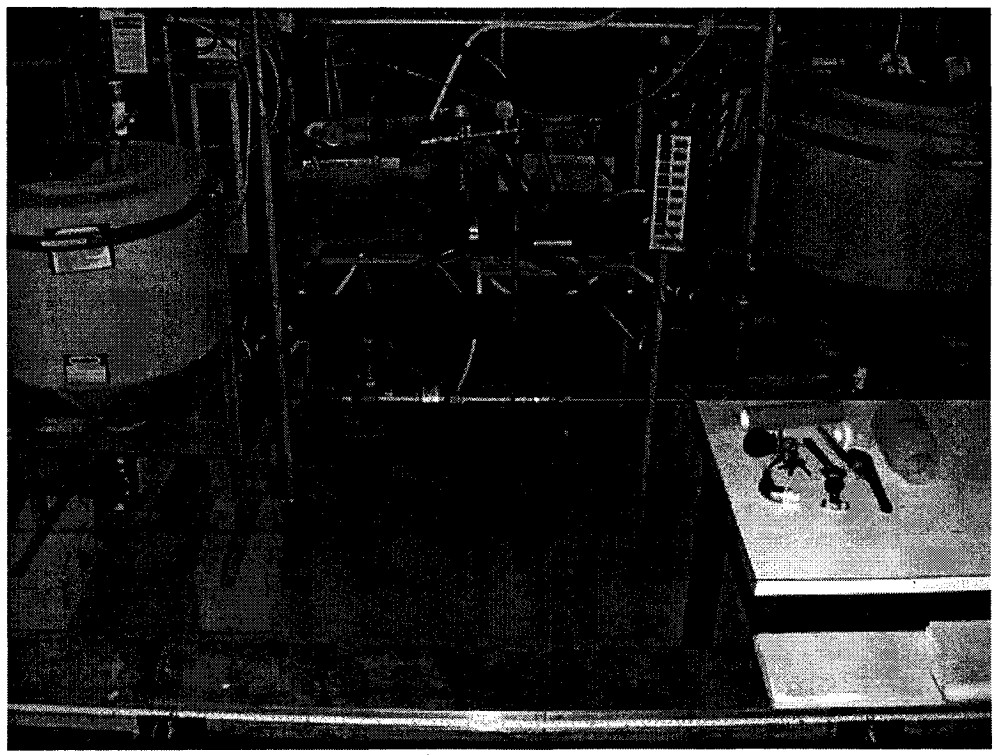


Figure 3-10 Apparatus in the hydraulics lab.

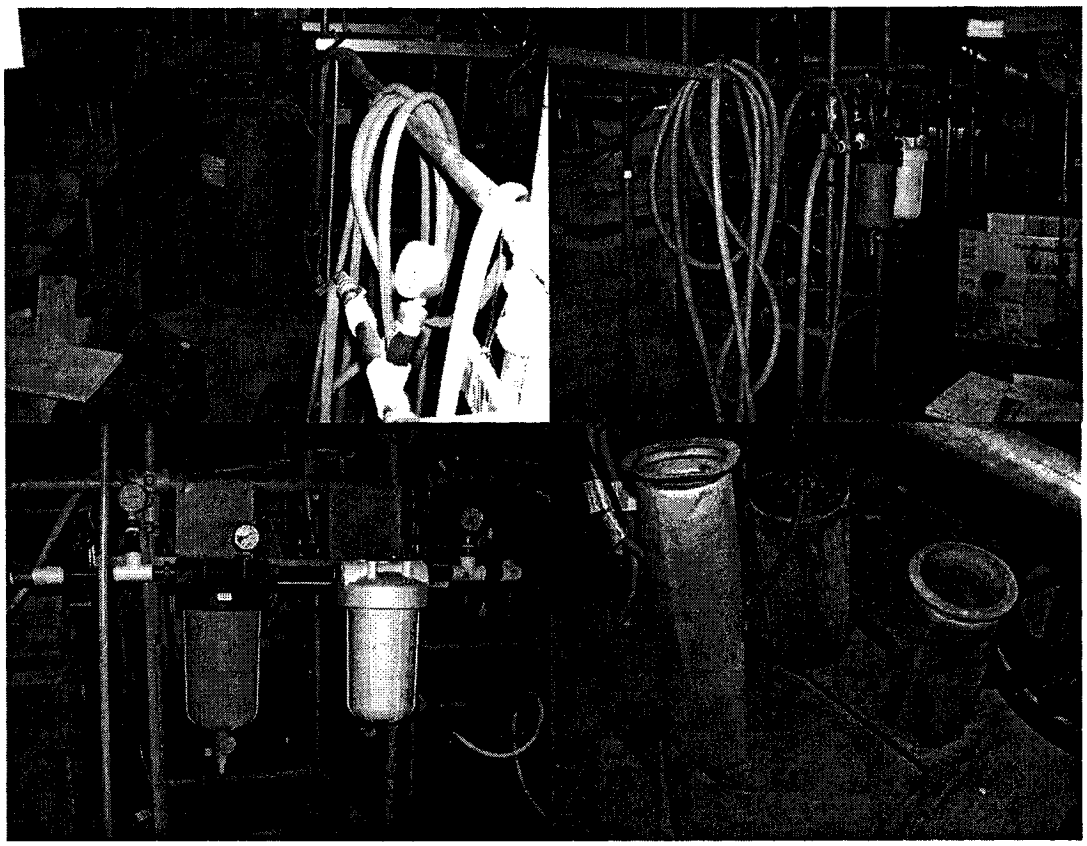


Figure 3-11a-b (top left to bottom right): a) Barrel with jerry cans, b) Hose attached to bag filters, c) Bag filers, 100 micron and 30 micron filter housings, d) 5 micron bag filter to the left, 30 micron centre and 100 micron to the right.

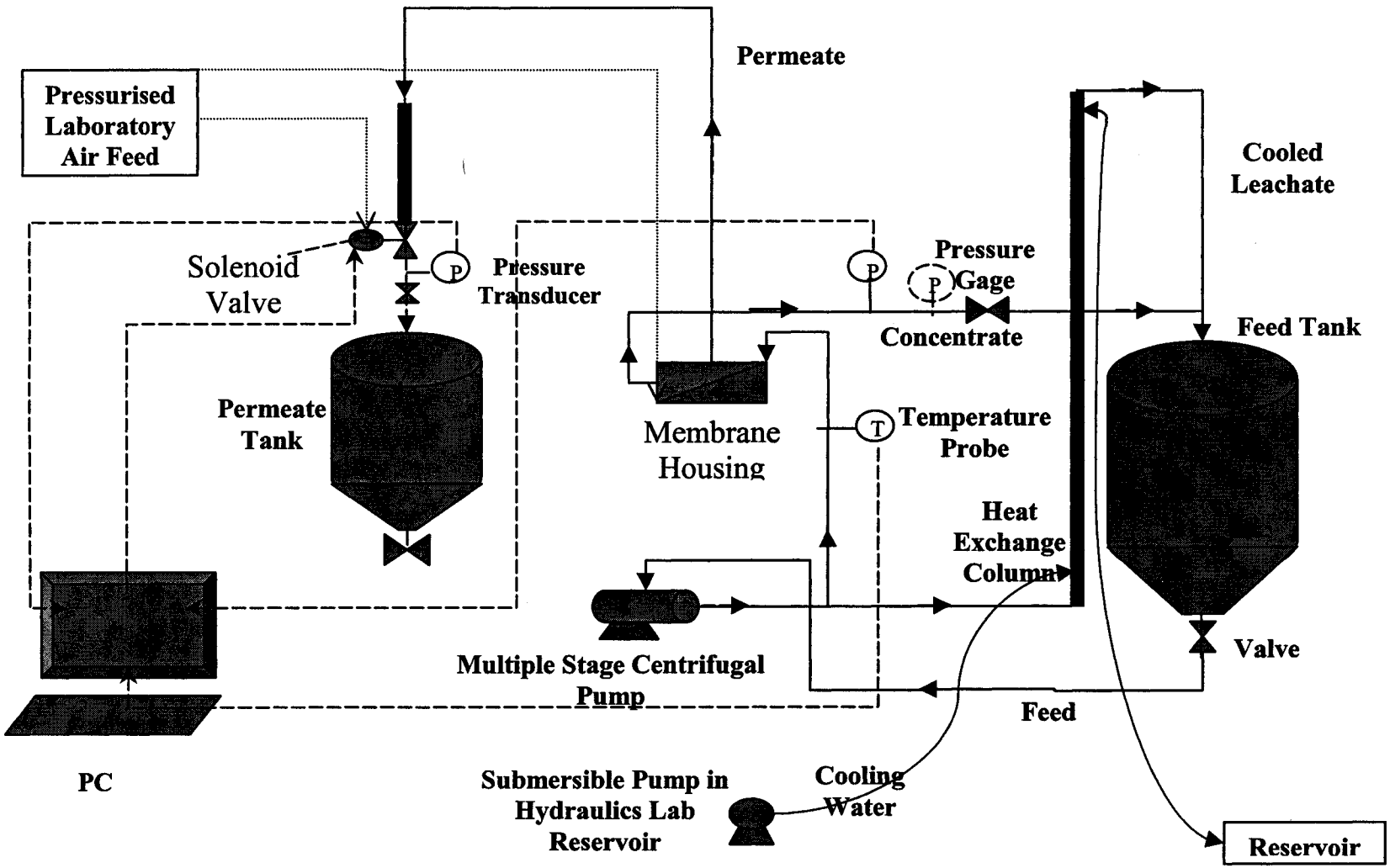


Figure 3-12 Schematic for the second apparatus.

3.1.4.1 Sequential Runs

Most of the runs were 48 hours long, but there was a desire to examine what level of fouling occurred over distinct sequential time intervals. The MF membrane (named JX_{62700}) was tested at a number of different time intervals: 5, 15 and 30 mins, along with 1, 2, 4, 6, 8, 12, 24, and 48 hours. This sequential run was performed at the Hydraulics lab near the end of the study, as a previous attempts to run this series at the Trail Road Landfill proved to be too difficult due to variable conditions. Once it was clear that the system was running consistently it became much easier to experiment with the length of runs.

One unexpected experiment was an unforeseen system shutdown in the middle of a full run, which was immediately restarted. The stop and immediate influx of flow resulted in an immediate increase in flux, which will be discussed in Chapter 4.

3.2 Data Collection

Data was collected during the run using in-line sensors and automated data collection for the flux, temperatures and pressure. Information regarding the material accumulated on the membrane and the characteristics of the liquid samples was collected post experiment.

3.2.1 Sampling

There are no standard protocols for sampling, filtration and storage of leachate (Kjeldsen *et al.*, 2002). Samples of fresh pre-filtered leachate were collected prior to the beginning of a run. Once the run was finished, samples of permeate and concentrate were also collected. A one litre and two 250 ml samples of each sample type were required for analysis. The fouled membrane was placed into a rectangular plastic container, which was deep enough to keep the membrane from sticking to the top and keep it from rolling in on itself.

3.2.2 Preliminary Data Collection on Liquid Samples

For the first half of the study COD and ICP analysis were the only analyses done on the liquid samples. The Closed Reflux, Colorimetric Method (method number 5220 D)

was used for total COD analysis as described in Standard Methods for Examination of Water and Wastewater (APHA, 1992).

ICP work was by Accutest Laboratories. Samples used for ICP analysis were prepared by adding 2% nitric acid to stabilise metals and any biological activity. Acidified samples were refrigerated at 4°C for 2 days to allow for complete reaction and dissolution of particulate matter. The samples were then filtered with a Whatman no.1 700mm filter paper to remove particulate mater. The filtering most likely removed some of the metals adhered onto particulates, but particulate matter would block the thin sampling tube of the ICP apparatus. Data was collected on the following metals in solution: magnesium, calcium, potassium, sodium, aluminium, barium, boron, cadmium, chromium, cobalt, copper, iron, lead, manganese, nickel, silicon, strontium, zinc, phosphorous and sulphur.

3.2.3 Membrane Data Collection

The tests done on the membranes were visual inspections using SEM and analysis by EDX. The SEM used was in the Carleton University Earth Sciences Department. Membrane samples were prepared for SEM analysis by cutting two small samples ($<1 cm^2$) from each coupon and freeze drying them to prevent any fluid contamination in the SEM vacuum, which was a key concern for the operator (Figure 3-13). The samples were mounted on slides and a map made as to the position of each sample. Two identical slides were produced with the same membrane samples on each. One was treated with carbon and the other with gold and silver (Figure 3-14).

The carbon coating was for EDX analysis and the gold coating was used for SEM photography. Clean membranes and scale/precipitate samples collected from the system were only coated with carbon for analysis. Gold reflects the X-rays better than the carbon giving better resolution. The carbon allowed for material grounding, while facilitating better beam penetration. With experience it became easier to identify and analyse surface particles using the SEM. The final samples were analysed using thin window beam setting so that carbon and oxygen could be partially analysed, improving plant or carbonate identification. The SEM system settings for the beam current were: 20 kV, ln A = 100, and the detector was set to 65.

Biological analysis of the sludge on the membrane was attempted using cultured heterotrophic bacterial growth and most probable number (MPN) counts, but the sludge attached on the membrane was difficult to remove in any consistent pattern and difficult to dilute due to the particulate matter present. Leachate dilution, which resulted in a sample relatively free of particulate matter, became unrepresentative given the margins of error involved. A DNA sequencing lab informed the author that a heterotrophic bacterial count would only identify the presence of microbes, but species separation using several culture media was needed before DNA identification of any bacteria could be used. No labs contacted by the author could offer the expertise needed to aid in or do the full species identification; therefore that stream of investigation was not pursued.

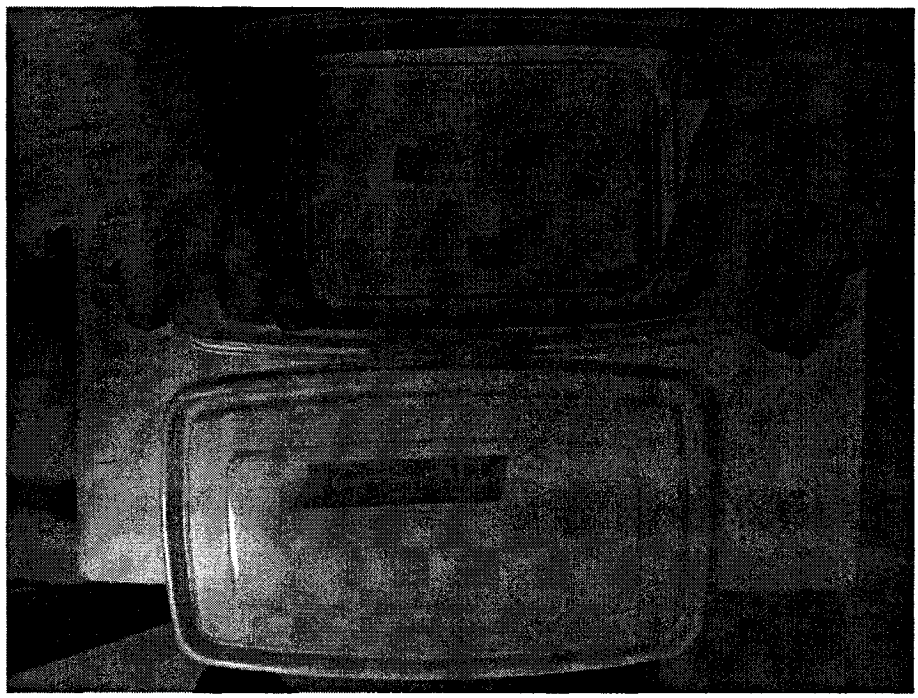


Figure 3- 13 Membrane sample with SEM samples taken.

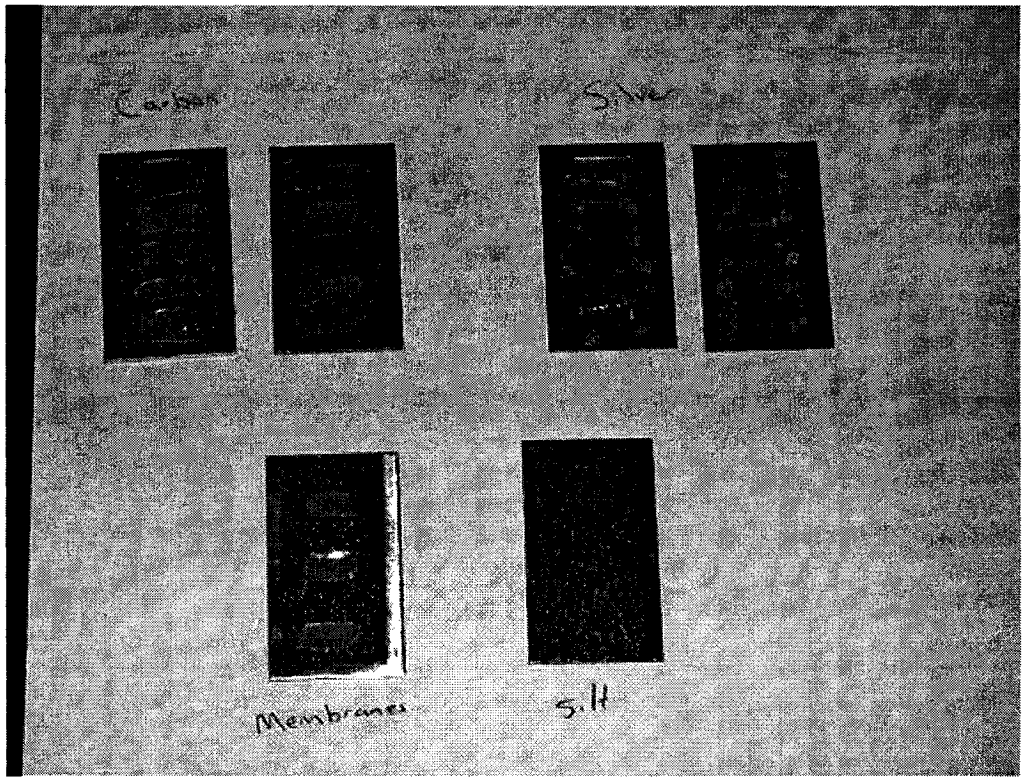


Figure 3- 14 Membrane and scale samples mounted and coated with gold and silver.

The scale samples previously mentioned were those collected from precipitate within the system and along the margins of membranes. There was inevitably a build-up of scale at the entrance and at times exit channels of the membrane housing, this can be seen on the right of the membrane shown in Figure 3-13. This scale build-up was thought to have occurred due tot he dramatic change in flow direction upon entering the cell, destabilising suspended particles. The scale was tested for $CaCO_3$ content by dropping a small amount of 10% HCl on the scale sample and watching for gas/bubble production indicating the presence of $CaCO_3$.

3.2.4 Parameters Examined by Accutest Laboratories

Accutest laboratories of Ottawa were hired to do the analysis of the liquid samples from the second set-up. They performed BOD, COD, sulfate, ammonia, total Kjeldahl nitrogen, ICP and total phosphorous analysis.

3.3 Data Analysis

LabVIEW™ was programmed to record data from the pressure gauges and the temperature probes, via the NuDAM® modules. Data was collected every ten seconds unless otherwise instructed. The raw data was calibrated according to each device and recorded. A sample of the raw data output for a run is given in Appendix C with a CD of raw data.

3.3.1 Flux Data Normalization and Application of the Fouling Equations

The raw data imported to an Excel spreadsheet was used to calculate the raw flux (L/m^2 hr). The first attempt to calculate flux involved dividing each successive mass reading difference by the 10-second interval (giving grams/second) and then converting to litres using water density based on temperature. This was not a feasible option as the number of data points was unmanageable and the noise created in those 10-second intervals was translated to graphs. The flux per-column filling was calculated rather than the flux per-10-second intervals which significantly reduced the data and noise incurred.

Fluxes from one run could not be compared directly to another due to the differences in operating temperature and pressure. The flux therefore had to be corrected for both temperature and pressure using equations 3.1 and 3.2 respectively (Peng, 2002). Both the raw and corrected fluxes are presented in the results. The steady state fluxes or the fluxes reached after two days, were compared between the membranes, for this comparison the 30 psi and 25EC corrected fluxes were used.

$$\text{Flux @ 25EC} = (\text{Flux@ Run Temp.})\times(1+(25-\text{Temp.})\times 0.03 \qquad 3\text{-}1$$

$$\text{Flux @ 30 psi} = (\text{Flux @ Run Pressure})\times 30/\ (\text{Run Pressure}) \qquad 3\text{-}2$$

The type of fouling was also examined by applying the fouling equations described in section 2.4.5. The four basic models were applied to each complete fouling run and as well to the first 10 hours of the same run to examine the type of basic fouling involved. The combined pore blockage was also applied to a few runs, but never resulted in a good fit and therefore was not presented within the results. The models were fit to the data using the method of least squares regression.

3.3.2 Determining Foulants

The components of fouling were examined by comparing EDX analysis with established geological standards, such as $CaCO_3$. The EDX data was also compared with possible precipitates determined by using the USEPA water solution chemistry program MINTEQA2.

MINTEQA2 provided equilibrium results for metal and chemical compound solubility using the ICP and sulphate data . Comprehensive data sets needed to run this program (i.e. eH, conductivity and turbidity) were not available. Data missing from the project data set were taken as average values from the City of Ottawa's Trail Road annual report data sets to give an approximation of leachate conditions and quality as needed. MINTEQA2's default equilibrium parameters (i.e. solubility constants) were used. This use of data approximation meant that the MINTEQA2 output could only be used to examine the possible precipitates, but the amount of those precipitates formed could not be reported with reliable accuracy. This program was essentially used to further substantiate EDX findings and help to explain EDX scans by identifying the possible precipitates involved.

3.3.2.1 EDX Background Measurements

EDX analysis used a powerful electron beam current to liberate ions and could therefore 'burn' through a membrane surface if left focussed on one section for too long. This would result in not only collecting information on the foulant being examined, but the membrane and eventually the supporting material as well. Background readings were therefore required for the clean membranes and for the glue used to adhere the membranes to the slide. Table 3-2 summarises the peaks seen for each and must be referred to when analyzing each of the membranes when fouled. Also, when preparing the samples for EDX analysis they were coated with carbon leading to higher carbon peaks than normal. The SEM pictures were taken using membranes with gold coating for improved resolution.

Table 3-2 General membrane composition as analysed by EDX.

Membrane or Material	High elemental peaks	FS*	Membrane Material or composition
Glue	No peaks	8K	N/A
JX_{62700}	C and F with occasional Cl and Si peaks	4K	Polyvinylide fluoride
MW_{100}	C peaks with occasional Si and O peaks	2K	Ultrafilic
EW_{60}	S and C with smaller P and F peak	8K	Polysulfone
ER_{30}	S and C peaks with smaller P and O, with occasional Ca and Si peaks	2K	Polysulfone
GN_{10}	O, S, Si and Ca with smaller C, Al and K peaks	8K	N/A
PT_5	Ca, S and C peaks	8K	Polyethersulfone
GM_4	S and C peaks with occasional Al, O and Si peaks	8K	Thin Film
GK_2	S and C with smaller F peak	8K	Thin Film
GH_1	S and C with smaller O and Ca peaks and occasional Al and Si peaks	1K	Thin Film

* FS = is full scale at which the graph was viewed, zooming in on a graph meant decreasing the K value given in the above table, therefore some peaks were much larger than others depending on the scale at which the graph was viewed.

3.3.3 Sulphide Production Rate Estimation

The methods for this portion of the study are presented in Chapter 4, Discussion of Results section 4.3.5.2, so as to enhance the readers understanding of the results presented.

CHAPTER 4

DISCUSSION OF RESULTS

This chapter was divided into 4 sections each discussing various aspects of the results. The leachate used in this study was briefly characterized in section 4.1, to give the reader an understanding of the variability of real leachate composition used for the study. Section 4.2 examined the basic flux results; how the length of a run was determined; the effect of temperature and pressure on flux; the noise inherent in the results; a brief examination of the steady state flux results; the flux results from the MF sequential runs; an accidental case of system flushing; and the basic fouling type determined from fouling equations.

In section 4.3 the liquid parameters measured (COD, BOD, ammonia, TP, TKN, sulphate and a number of elements using ICP analysis) were examined focusing on the seasonal variation of each and the removal levels of all parameters. Each parameter was examined individually and the results were related back to the sewer use bylaws and the effect of fouling on treatability. Section 4.4 discussed fouling parameters examined using SEM/EDX. The main elements involved in fouling and the visual aspects of this fouling were discussed.

4.1 Basic Leachate Characterization

Before entering into a discussion of the flux results characterization of the fresh leachate was necessary, to understand the quality and variation of fresh landfill leachate used during the experimental runs. The range of some basic parameters measured is given in Table 4-1. Some parameters had substantial variations in concentration. For example the COD had a minimum and maximum concentration of 545 and 2825 mg/L (a range of 2280 mg/L) and BOD had a range of 551 mg/L. It should be noted that BOD concentrations were both above and below the municipal sewer use bylaw limits. Some parameters did not have sewer use bylaw guidelines, for example ammonia which ranged from 267 to 775 mg/L and sulphate which ranged from 28 to 133 mg/L. Only TP was consistently below both the maximum allowable discharge and sewer use bylaw, with a maximum raw landfill leachate value of 5.33 mg/L.

The maximum allowable sewer discharge, given by the City of Ottawa, was a one-time only monthly discharge limit, while the sewer use bylaw value was the target concentration for a parameter that was not to be exceeded. A full discussion of each parameter in Table 4-1 is provided in section 4.2. The wide range of concentrations for the parameters were an indication of the variability of real Trail Road landfill leachate. This variability was reinforced throughout Chapter 4 as it affected the overall operation of the membrane experimental set-up, flux and treatment results. For some parameters this variability was seasonally based.

Table 4-1 Concentration ranges of fresh leachate used in study.

Parameter	Range (mg/L)	Maximum (mg/L)	Sewer use bylaws (mg/L)
COD	545 to 2825	1000	–
BOD	43 to 594	1000	300
Ammonia	267 to 775	–	–
TKN	80 to 822	250	100
TP	1.07 to 5.33	25	10
Sulphate	28 to133	–	–

4.2 Flux Data

In general a consistent flux decline was obvious over time in all membrane separation runs. Optimum flux decline curves were observed when temperatures and pressures during a run were fairly constant and the pumping system was operating properly. Figure 4-1 for membrane PT_5 was one of the best examples of 'textbook' flux decline with a steady state flux of approximately 5.5 L/m^2h after about 20 hours of operation. Not all flux results showed such a clear flux decline. When temperatures and pressures varied dramatically during a run, so did the raw flux data. Appendix D contains all flux graphs. Section 4.2.2 gives examples of non-ideal fluxes caused by temperature and pressure variation, while section 4.2.3 deals with the issue of noise inherent in permeate production.

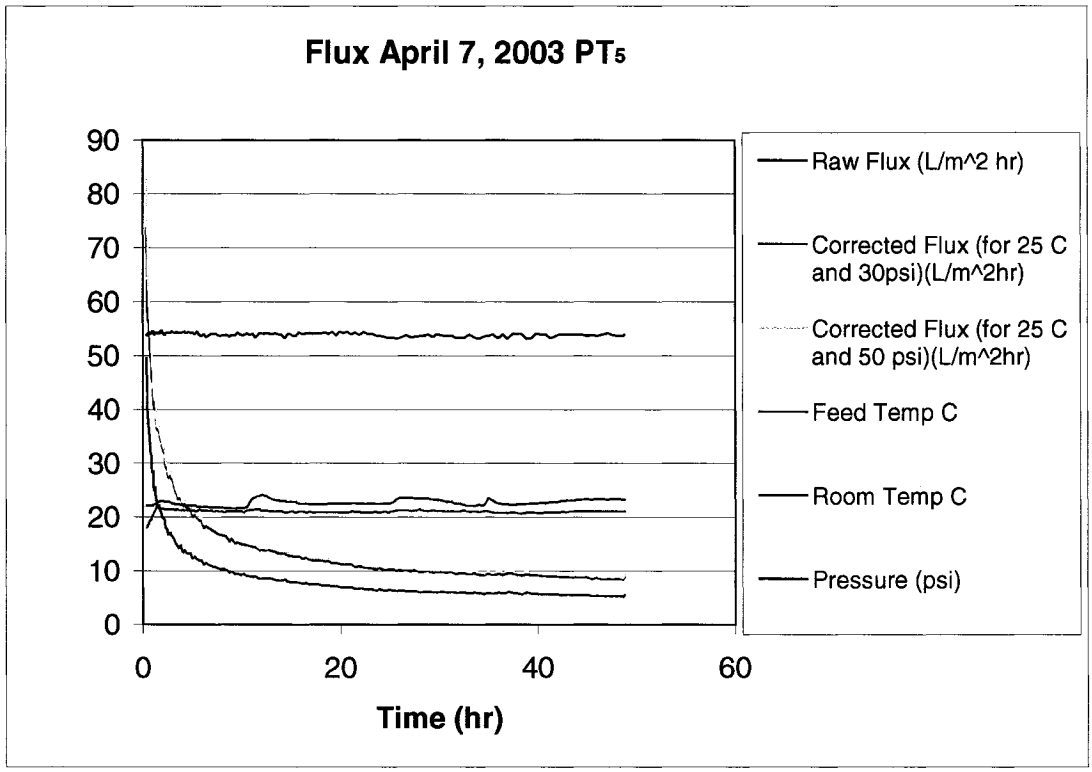


Figure 4-1 Good example of textbook flux decline from membrane PT_5.

NOTE: The Y-axis was unlabelled in Figure 4-1 and all proceeding flux graphs, as the units are given for each parameter in the legend and all values can be fitted to the same scale.

4.2.1 Determining the Length of a Run

The standard length of time used to examine leachate treatment and membrane fouling was 48 hours. This was determined by examining the flux data from a preliminary run of over 80 hours done on August 13, 2002 using membrane $M\text{-}180_{10}$ (Figure 4-2). Increases in pressure from approximately 16 psi to 30 psi at 16 hours caused the raw permeate flux data to increase slightly and then continue to decrease. Once corrected to 25EC and 30 psi, the flux continued to decline rather than increase.

The majority of the flux decline occurred in the first 48 hours and no significant decrease was seen after that point. Flux results observed at 24, 48 and 80 hours for the corrected flux was approximately 9.2 L/m^2h. Lower fluxes of 7.1 and 7.5 L/m^2h were seen at 29.5 and 72 hours. From Figure 4-2 it was determined that steady-state flux was achieved by 48 hours and there was no need to run for longer periods of time.

4.2.2 The Effect of Temperature and Pressure

As mentioned in the introduction to section 4.1, not all flux results were ideal. A comparison of Figures 4.1 and 4.3 showed the differences between an ideal flux graph with stable temperatures (Figure 4-1) and a flux resulting from unstable temperatures (Figure 4.3). Raw fluxes would often vary with changes in temperature as seen in Figure 4-3 for membrane JX_{62700}, giving them an undulating appearance with the diurnal temperature changes.

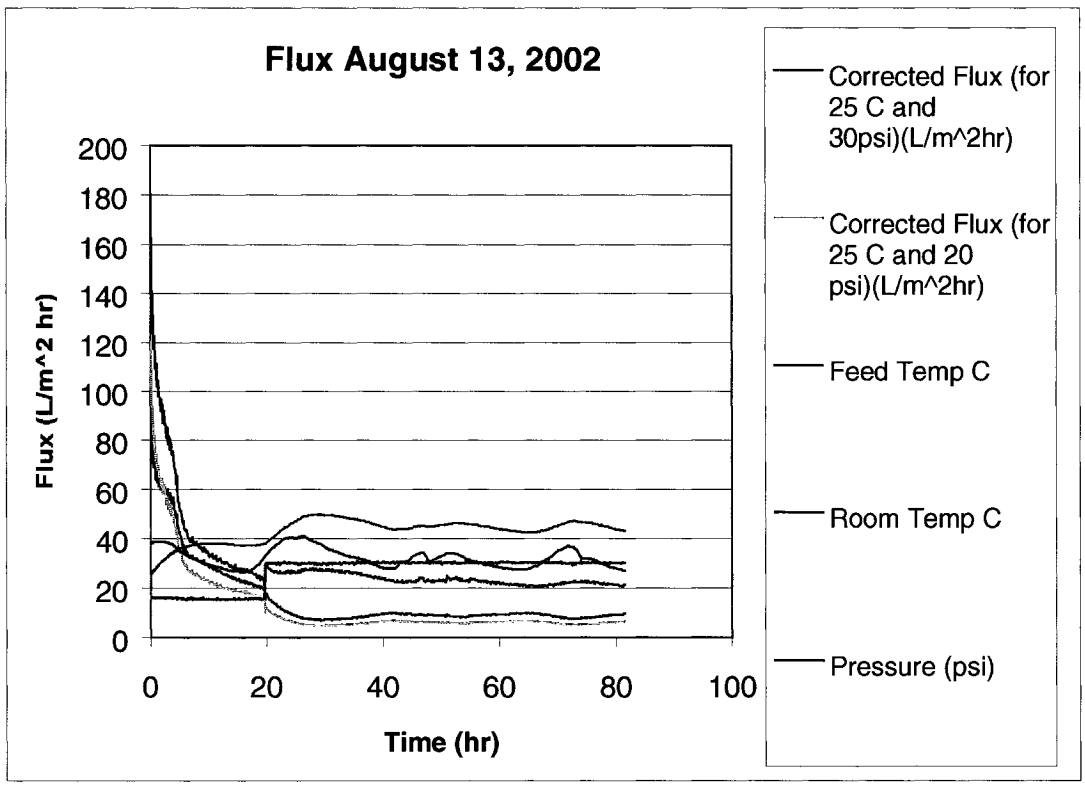


Figure 4-2 Initial run to determine the length of testing using KOCH membrane M-180, 10 KDa.

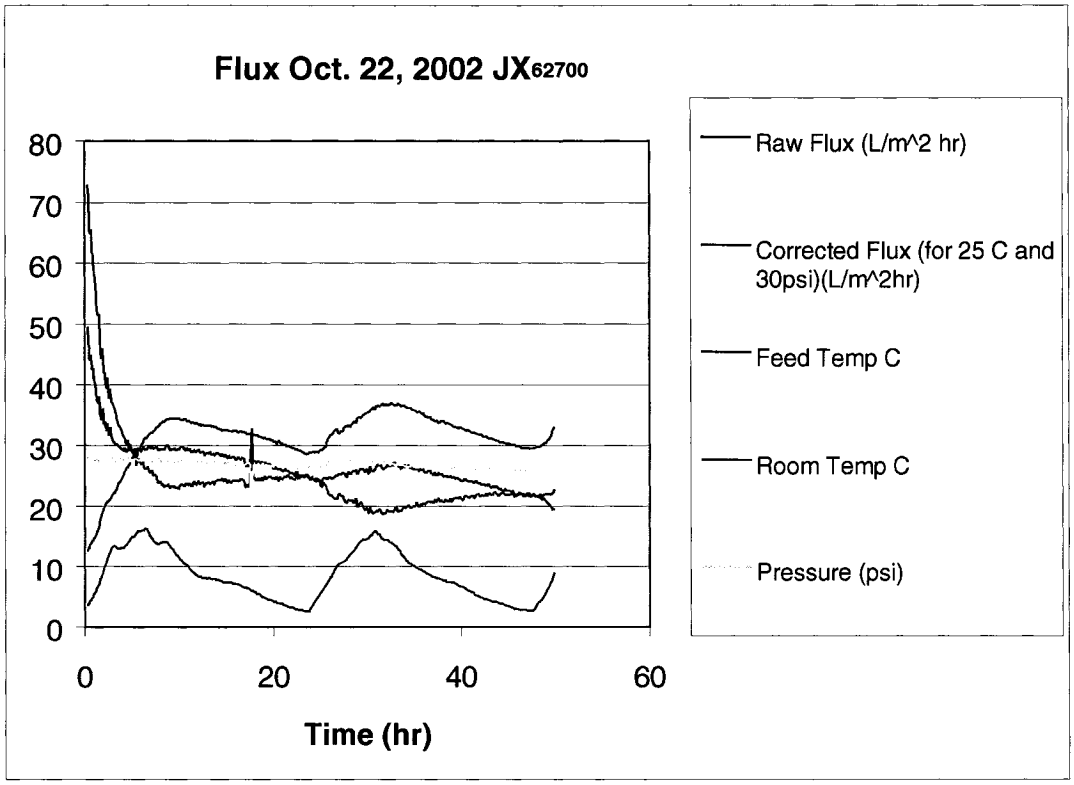


Figure 4-3 Flux graph showing the effect of temperature on flux of the MF membrane JX, 62700 KDa.

The raw flux in Figure 4-3 showed a fairly typical decline from 0 to 4 hours, but the flux undulated with temperature after this point peaking at 10 and 27 hours, corresponding with the temperature peaks. The corrected flux still showed a slight correlation with the temperature inherent in the raw data, but more closely emulated a flux that was produced under constant temperature. A temporary pressure drop from 27 to 19 psi at 18 hours translated into a flux spike caused by the pressure correction. In practice, a decrease in pressure would not result in an actual flux increase.

Another example of temperature affecting flux was observed in the flux data from the September 24, 2002 run at the Trail Road landfill using the UF membrane GK_2. This run had extremely high feed temperatures, brought on by a heat wave (Figure 4-4a and 4-4b). Figure 4-4a showed the temperatures involved and the associated fluxes, while Figure 4-4b allows closer inspection of the flux results. Again, the raw flux peaked with temperature peaks as seen previously. The peaks were seen at 8 hours and 32 hours with feed temperatures reaching 37EC and 43EC respectively. The raw flux varied diurnally and did not decrease significantly. Once the flux was corrected for temperature and

pressure (25EC and 30 psi) the overall decline became obvious, with smaller undulations ranging between 7 L/m^2h at both 23 and 44 hours and 5 L/m^2h at 31 hours. This reinforces the finding that temperature has a direct impact on flux results.

Pressure fluctuations also caused flux changes, but not to the same extent as temperature change. Short periods of pressure change were not expected to cause significant changes, but longer-term pressure alterations as seen in Figure 4-2 did cause a flux change in the raw flux which continued to exert an effect on the raw flux over the entire run. This increase in the raw flux was then corrected for by applying the pressure correction equation. Practically, pressure fluctuations or variations were not considered as important to the overall flux results as temperature fluctuations.

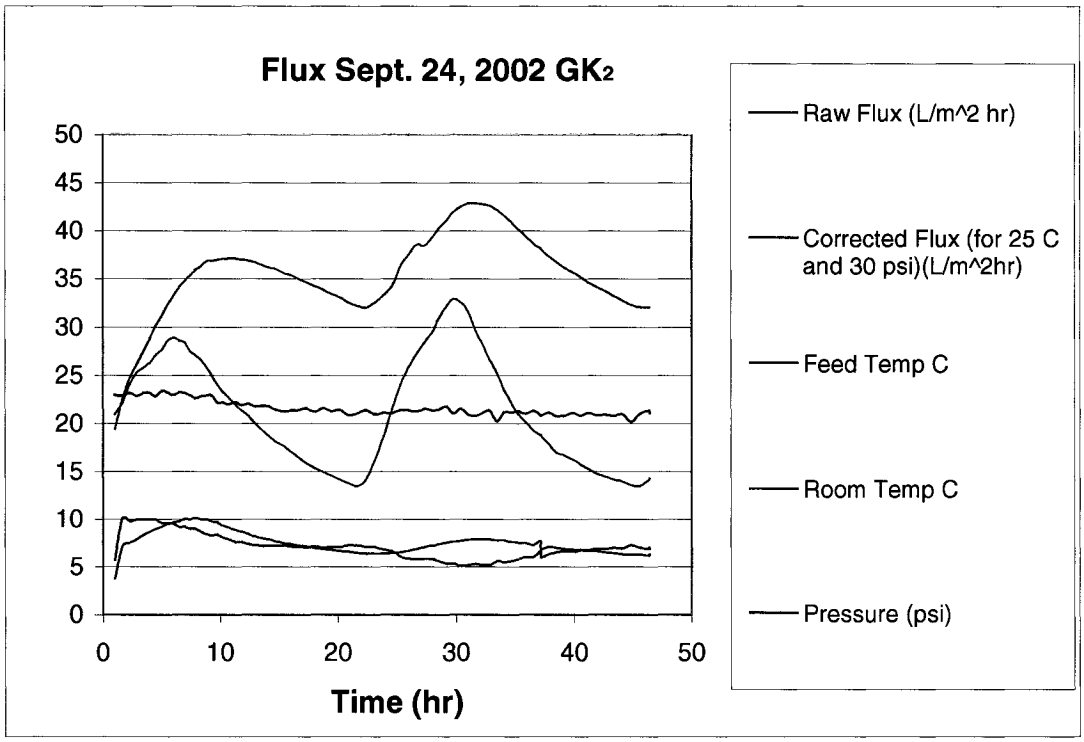


Figure 4-4a Flux graph showing temperature effects on flux during a heat wave (September 24, 2002 with the UF membrane GK (2 KDa)).

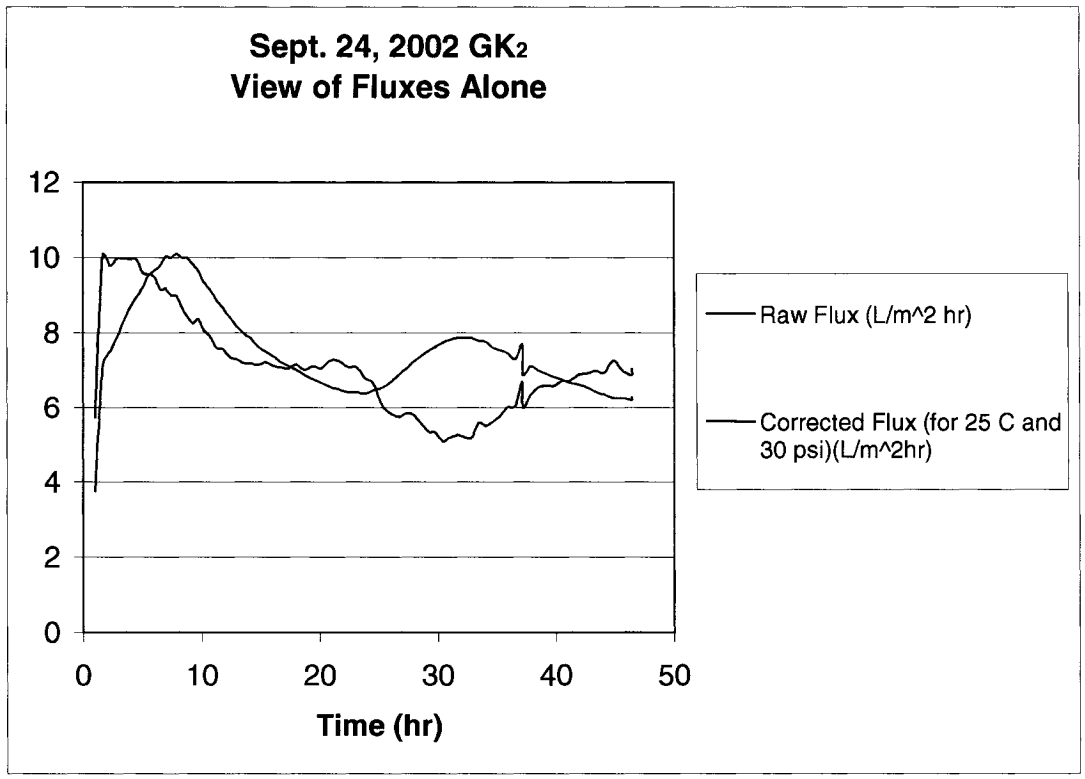


Figure 4-4b Closer view of GK_2 fluxes to accentuate the effect of temperature on flux (September 24, 2002 with the UF membrane GK (2 KDa)).

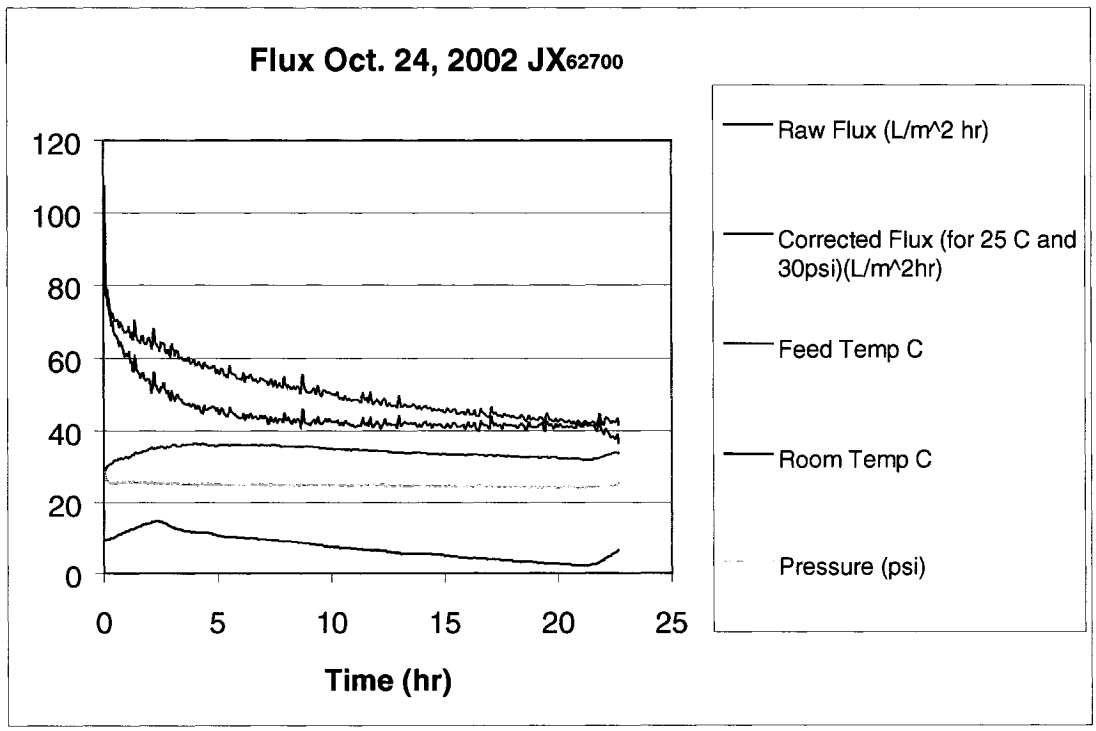


Figure 4-5 A good example of how, despite the noise, the flux trend can still be seen in the case of the MF membrane JX (62700 KDa) run on October 24, 2002.

4.2.3 Noise

In all of the flux decline examples discussed one may have noticed that the flux lines were not completely smooth and included small fluctuations or noise along the line itself. Figure 4-5 shows a clear example of residual 'noise' encountered during the October 24, 2002 JX_{62700} run. The action of permeate dripping into the permeate monitoring column above the pressure transducer caused noise as the drops fell and the surface of the water permeate in the column was disrupted. A flow meter was considered in lieu of the noise, but determined not to be feasible to measure permeate, because of the low flows, moderate TSS concentrations and possible corrosive content in the permeate.

Smoothing of the flux data was conducted by reducing the amount of information used to determine the flux. The system originally collected data every 10 or 20 seconds for 48 hours giving a large number of data points and noise to contend with. To reduce both the noise and the amount of data, the flux for each permeate column filling and emptying sequence was calculated using the time required to fill the liquid column to 70 grams (the point at which the column was set to empty) to give a grams per second reading. This reduced the amount of flux data to the number of column empty and fill sequences, rather than 172,800 flux points resulting from the 10 second data collection interval over 48 hours. The noise generated was still evident with the data reduction, but to a much lesser extent and the general flux trend could be easily seen through the noise (Figure 4-5).

4.2.4 Steady State Flux Results

The steady state flux was the flux value seen once the flux stopped decreasing and levelled off. Steady state flux can be achieved in pure water runs once membrane compaction has been fully achieved. In the case of a feed capable of fouling the membrane, the steady state flux occurs once the fouling layer reaches a stable mass and continues to impede flux at a relatively constant level. For this project the steady state flux was assumed to be achieved by 48 hours (see section 4.2.1). The steady state fluxes used for comparison between membranes were corrected to 30 psi and 25°C. Some

corrected fluxes were undulating due to temperature changes; the average flux value from these undulations near 48 hours was taken.

Steady state flux results did not show an overall trend with membrane MWCO (see Figure 4-6 and Table 4-6 in section 4.3.2). Figure 4-6 shows the steady state fluxes for all runs with landfill leachate. Steady state fluxes ranged from 0.6 to 32 L/m^2h with no trend evident between membrane MWCO and steady state flux. A general trend of steady state flux increase with MWCO increase was expected, but not seen. This may be due to a number of factors, which might include: membrane material type, temperature fluctuations, fouling variable and leachate characteristics and concentration.

Steady state flux results were highly variable for each MWCO, as well as over the range of MWCOs. This variability in flux may be explained by fouling, which may have occurred to various extents depending on leachate quality (i.e. size of the components, BOD/COD ratios, TSS concentration, etc.). Additionally, the characteristics of the leachate in terms of the types and sizes of organic constituents may be highly variable from run to run leading to a wide range of fluxes for similar membrane sizes. The relation of leachate parameters to MWCO, component removal and steady state flux will be discussed further in section 4.3.

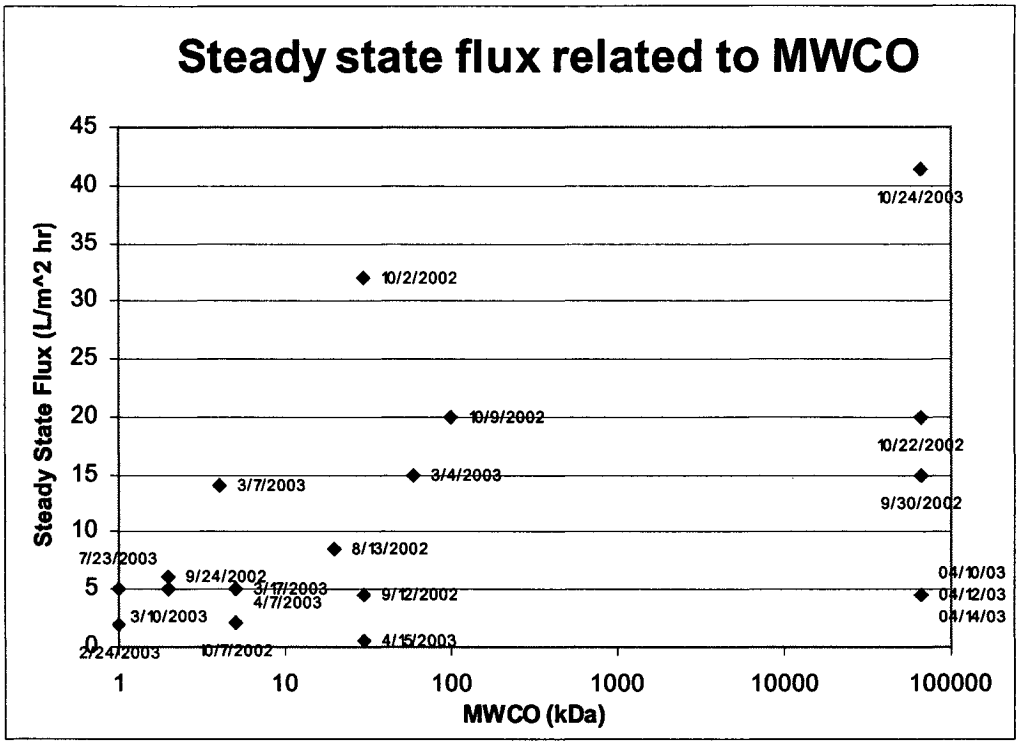


Figure 4-6 Steady state flux results with MWCO. NOTE: MWCO 5 KDa reached a steady state flux of 5 L/m^{2}hr twice (3/17/2003 and 4/7/2003).

4.2.5 MF Sequential Run Fluxes

Examination of the fluxes produced during the MF sequential runs with the JX_{62700} membrane showed that fluxes were reproducible when fairly consistent temperature and pressure settings were used with leachate of similar quality. Since sequential runs used the same raw leachate sample, the characteristics of the sample were also constant. Sequential runs occurred from April 10th to the 15th using the JX_{62700} membrane. Figures 4-7 a to c highlight the decreases seen in the first few minutes of a run and the general decrease over the hours leading to a full 48 hour run.

Most of the runs showed identical flux decline over time. Figure 4-7a showed the initial fluxes started at 188 L/m^{2}h for the 5 min run and decreased to 32 L/m^{2}h by the end of the 30 min run, with the 15 min run showing the same rate of flux decline. The intermediate flux period that examined runs of 1 to 12 hours also showed similar flux declines, starting at an initial flux of 79 L/m^{2}h and finishing at a final flux of 5.7 L/m^{2}h. The 2, 8 and 12 hour runs all seemed to start with a low flux and then rose to a maximum before starting their flux decline. This result was caused by an experimental error. Before

the 2, 8 and 12 hour sequential runs the permeate monitoring tube emptied fully and showed negative mass production until the column filled to above the pressure transducer, there was also a lag time as the permeate delivery tube emptied between runs and took time to fill and then empty into the column. The problem of column emptying was corrected by filling the column to the pressure transducer with distilled water.

The runs that did not conform to the overall decline of the other sequential runs were the 24 and 48 hour runs. Line blockages were visually observed after both runs and cleaned, as it was part of the standard operating procedure to check the inflow tube to the pump and the inflow and outflow hoses from the membrane housing and clean them if required. The outflow tube from the membrane housing was up to 75% blocked at the end of the 24 hour run and 50% blocked for the 48 hour run.

The reason for the increase in flux was thought, but not confirmed, to be caused by an increase in fluid pressure within the cell as the pump continued to pump at the same rate through a smaller orifice, thus increasing permeate production through pressure. Also, the noise in the 24 hour run may have been due to the flow variations due to pipe constrictions and/or the stripping of fouling layers due to increased flow friction. There was an attempt at line flushing and manual cleaning between the 24 and 48 hour runs, but there may have been residual blocking that was not removed.

Despite the problems in the 24 and 48 hour runs the sequential study did show flux decline reproducibility where operating conditions were stable (temperature and pressure), and the leachate had the same quality and characteristics. The sequential runs tend to indicate that variation in fluxes for similar MWCO membranes was influenced significantly by differences in the quality and characteristics of the leachate, as these runs all used leachates collected within days of each other and all had similar characteristics.

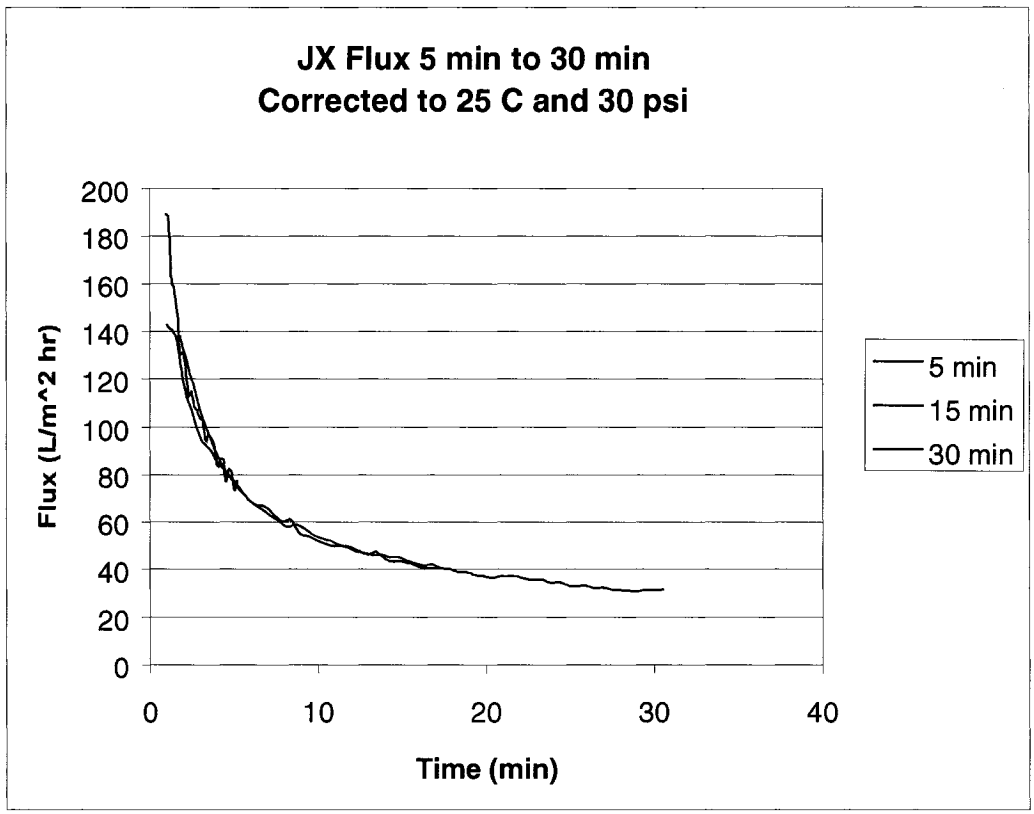


Figure 4-7a Sequential runs 5 to 30 minutes.

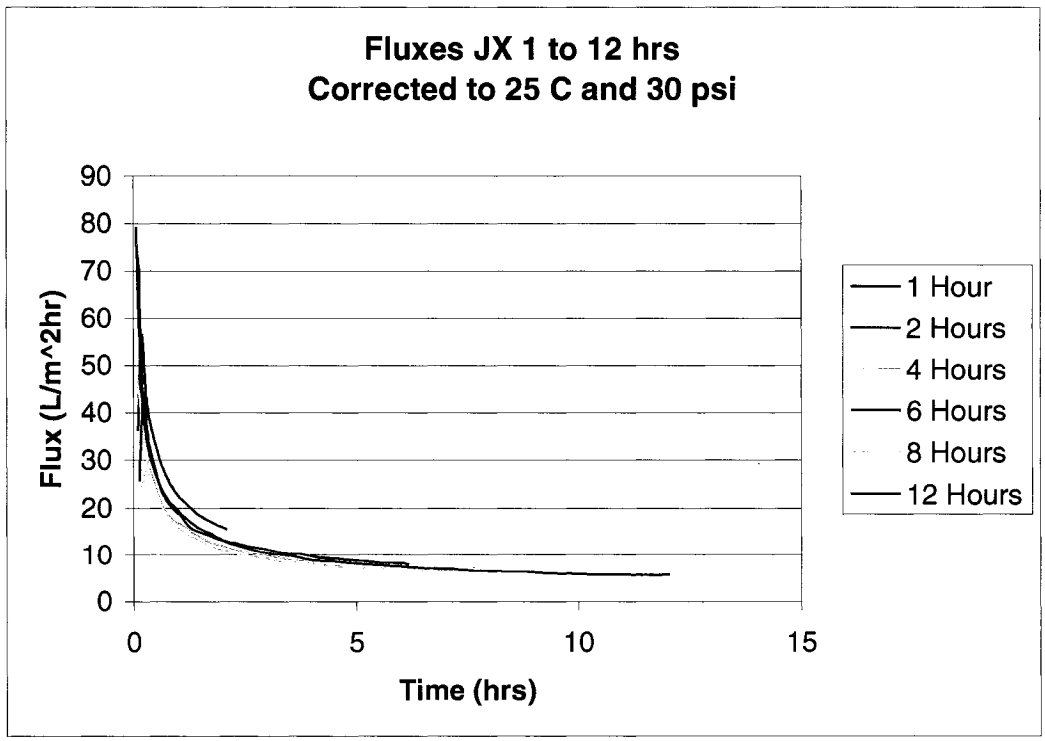


Figure 4-7b Sequential runs for 1 to 12 hours.

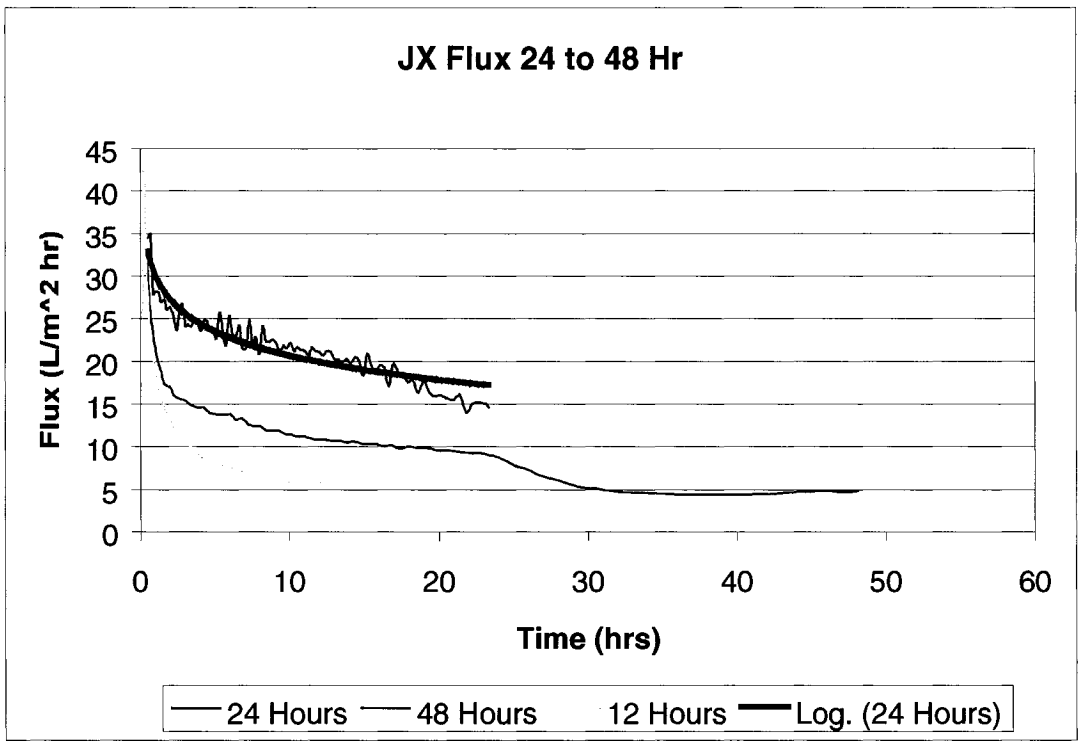


Figure 4-7c Sequential runs for 12 to 48 hours, with a logarithmic trend line outlining the decline in the 24-hour flux.

4.2.6 Application of Fouling Equations to Identify Fouling Type

As mentioned in Chapter 2 there are no models to the author's knowledge that are applied specifically to fouling and landfill leachate. Though this was not a modelling project, the application of basic equations for various types of fouling gave valuable insight into the way UF and MF membranes may foul during leachate treatment. The fouling equations described in Chapter 2 (equations 2.2 to 2.8) were applied to the corrected flux results of the full-length runs to identify the basic type of deposition (complete blocking, intermediate blocking, pore constriction, and cake filtration). The equations were designed for dead-end filtration and should only be applied to the initial flux decline in cross-flow systems (prior to steady state flux and back flow transport). The equations were applied separately to the entire run and to the initial flux decline (approximately 0 to 10 hours) to examine the fit to both sets of experimental flux results.

When the parameters of a run were stable (e.g. temperature and pressure) and the flux results showed a textbook flux decline, the fouling equation that best fit these runs was Equation 2.7, the cake filtration equation (Figure 4-8). For the PT_5 run on April 7,

2003 the cake filtration equation fit both the entire run and the initial flux declines as well. The same was true of the sequential MF membrane experimental runs using JX_{62700}. This suggested that back flow transport may not play a substantial role in our membrane experimental set-up for landfill leachate treatment where conditions are optimized (steady temperature and pressure).

In general, the cake filtration equation gave the best fit to the experimental results. The fit was not as good for fluxes which were slightly irregular and where temperature and pressure varied as the models were meant to fit curves rather than the irregular patterns seen in some runs. When full runs of slightly irregular fluxes were modelled, the fouling equation outputs conformed to the steady state flux and fouling area, rather than the active fouling period for which these models were designed. Therefore the fouling equations were applied to the initial flux period and the fit improved. Only the initial fouling periods were used for comparison purposes. Under these conditions the cake filtration equation gave the best fit for UF and MF membranes.

The MF membrane JX_{62700} gave consistent cake filtration fits. Membranes between 5 and 30 KDa mostly showed cake filtration fits, while none of the fouling equations matched results for membranes with 1 to 4 KDa MWCOs. Appendix D features the flux graphs with models applied to the initial flux decline for all full runs. Table 4-2 gives the fouling equations of best fit, with the resulting variables. There was no trend evident with respect to MWCO and the calculated K value for the cake deposition equation as seen in Figure 4-9, but these are different feeds/leachates and a variety of membrane sizes and types.

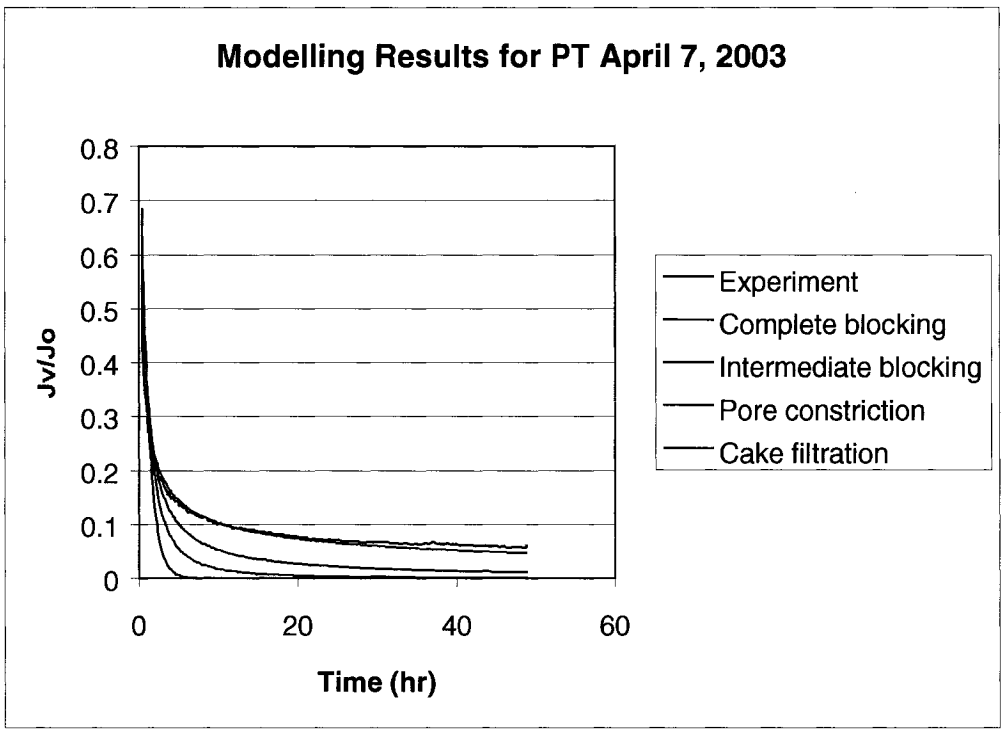


Figure 4-8 Example of flux decline with cake filtration model being the best fit.

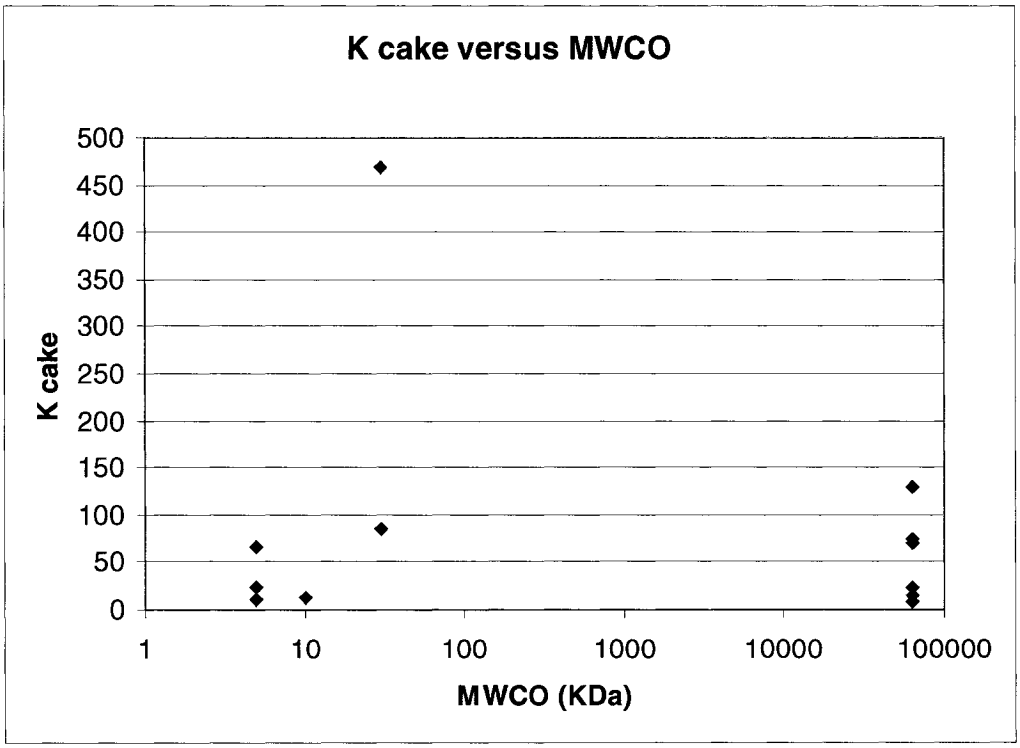


Figure 4-9 K cake from the cake filtration equation results versus MWCO.

Table 4-2 Fouling equations of best fit for each membrane and the resulting fouling flux- based equation

Membrane	Date	Fouling Equation of Best Fit	SSE*	K value	Resulting Equation
JX_{62700}	Sept. 30, 2002	Cake	0.012	23.7	$\frac{J_v}{J_0} = (1+23.7t)^{-1/2}$
	Oct. 22, 2002	Cake	0.039	13.9	$\frac{J_v}{J_0} = (1+13.9t)^{-1/2}$
	Oct. 24, 2002	Cake	1.04	9.39	$\frac{J_v}{J_0} = (1+9.39t)^{-1/2}$
	April 10, 2003 (6 hour run)	Cake	0.002	70.0	$\frac{J_v}{J_0} = (1+70.0t)^{-1/2}$
	April 12, 2003 (48 hour run)	Cake	0.005	74.4	$\frac{J_v}{J_0} = (1+74.4t)^{-1/2}$
	April 15, 2003 (2 hour run)	Cake	0.018	130	$\frac{J_v}{J_0} = (1+130t)^{-1/2}$
MW_{100}	Oct. 9, 2002	None			
EW_{60}	March 4, 2003	None			
ER_{30}	Oct. 2, 2002	None			
	April 15, 2003	Cake	$3.56*10^{-4}$	469	$\frac{J_v}{J_0} = (1+469t)^{-1/2}$
QW_{30}	Sept. 12, 2002	Cake	0.219	84.4	$\frac{J_v}{J_0} = (1+84.4t)^{-1/2}$
GN_{10}	Sept. 16, 2002	None			
$M\text{-}180_{10}$	Aug. 13, 2002	Cake	0.168	13.7	$\frac{J_v}{J_0} = (1+13.7t)^{-1/2}$

Membrane	Date	Fouling Equation of Best Fit	SSE*	K value	Resulting Equation
PT_5	Oct. 7, 2002	Cake	0.012	66.1	$\frac{J_v}{J_0} = (1+66.1t)^{-1/2}$
	March 17, 2003	Cake	0.182	23.1	$\frac{J_v}{J_0} = (1+23.1t)^{-1/2}$
		Intermediate	0.130	5.45	$\frac{J_v}{J_0} = \frac{1}{1+5.45t}$
	April 7, 203	Cake	0.008	9.58	$\frac{J_v}{J_0} = (1+9.58t)^{-1/2}$
GM_4	March 7, 2003	None			
GK_2	Sept. 24, 2002	None			
	March 10, 2003	None			
GH_1	Feb. 24, 2003	None			
	July 23, 2003	None			

***SSE = Sum of Squares Error**

As detailed in Chapter 2, section 2.4.5, cake filtration assumes a layer forms from deposition on the membrane. This layer then builds and forms its own resistance on top of any other particles deposited on or in the membrane pores and this resistance grows with an increase in layer thickness. Based on visual inspections of membranes after a run this description of a fouling layer seemed very appropriate as all the membranes demonstrated formation of a fairly homogeneous light brown to dark brown layer formed over the membrane's surface. This layer could be removed with light pressure from the author's finger wiping across the membrane surface. This would go towards further explaining how stopping and restarting the system as discussed in section 4.2.6 could have resulted in a 71% flux recovery. The composition and some of the visual aspects of this layer will be discussed in section 4.4.

4.3 Examination of Targeted Parameters

4.3.1 General Parameter Variations Over Time

Trail Road Landfill staff take leachate samples approximately every second day excluding weekends and test them for COD, TKN, and TSS; additionally BOD_5 is tested weekly. The COD, BOD, TKN, and TSS data from the Trail Road Landfill were placed into graphical form to examine seasonal changes (Figure 4-10, 4-11, 4-12 and 4-13)(Appendix E for raw landfill data). These raw leachate values are routinely compared to both sewer use bylaw target values and maximum allowable values that may not be exceeded more than once per month when discharging to the sewer system (Table 4-3 for bylaw and maximum values). Direct sewage discharge to a trunk sewer was the original plan for the Trail Road Landfill leachate management project, but some of the parameters at certain points of the year exceeded even the maximum discharge limits, which indicated the need for some level of pre-treatment to avoid fines and breaching sewer use protocols.

Figures 4-10 to 4-13 showed that COD, BOD and TSS seemed to vary seasonally with changing temperatures and precipitation, while TKN showed no such correlation. Figure 4-14 displayed the amount of precipitation recorded over the time span of the project, taken from Environment Canada's meteorological web service (Environment Canada, 2003). Figure 4-10 showed COD peaking with dry weather over the summer months (5800 mg/L) and again in spring (7400 mg/L) as the increased rainfall flushed out leachate held in the landfill over the winter. Soon after the COD peaks, the BOD peaked in summer and spring at 2100 and 2600 mg/L, which indicated that the microbial flora that were degrading the MSW in the landfill were responding to the increased nutrients, moisture and warmth (see Figure 4-13). The TSS concentration fluctuated with COD fluctuations with the exception of a peak in September and October 2002 (285 mg/L) which was noted in the author's field notes as a period of very dark and almost black leachate during a period of low precipitation (see Figures 4-10 and 4-11).

Table 4-3 Sewer use bylaw limits and maximum allowable sewer discharge limits for some of the parameters studied (City of Ottawa).

Parameter	Units	Maximum limit	Sewer bylaw limit
BOD	mg/L	1000	300
COD	mg/L	1000	---
TKN	mg/L	250	100
TP	mg/L	25	10
TSS	mg/L	500	350
Sulphate	mg/L	1500	1500

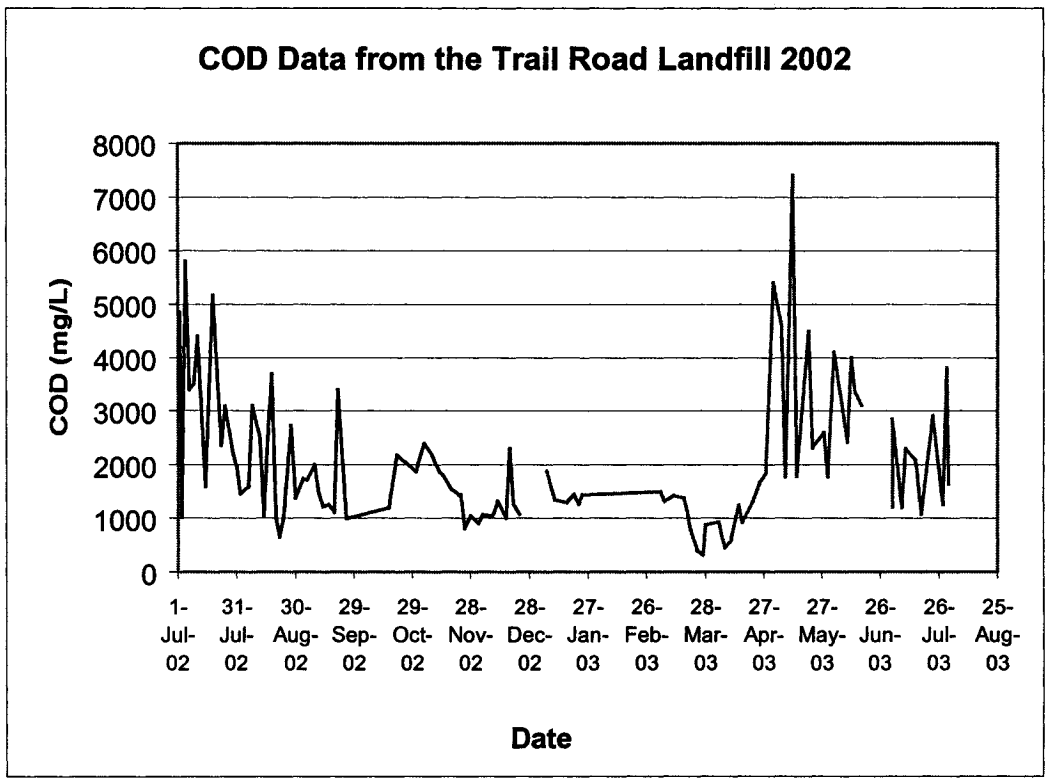


Figure 4-10 COD results from the Trail Road Landfill. Gaps in data are due to holidays (Data unpublished when this document was authored).

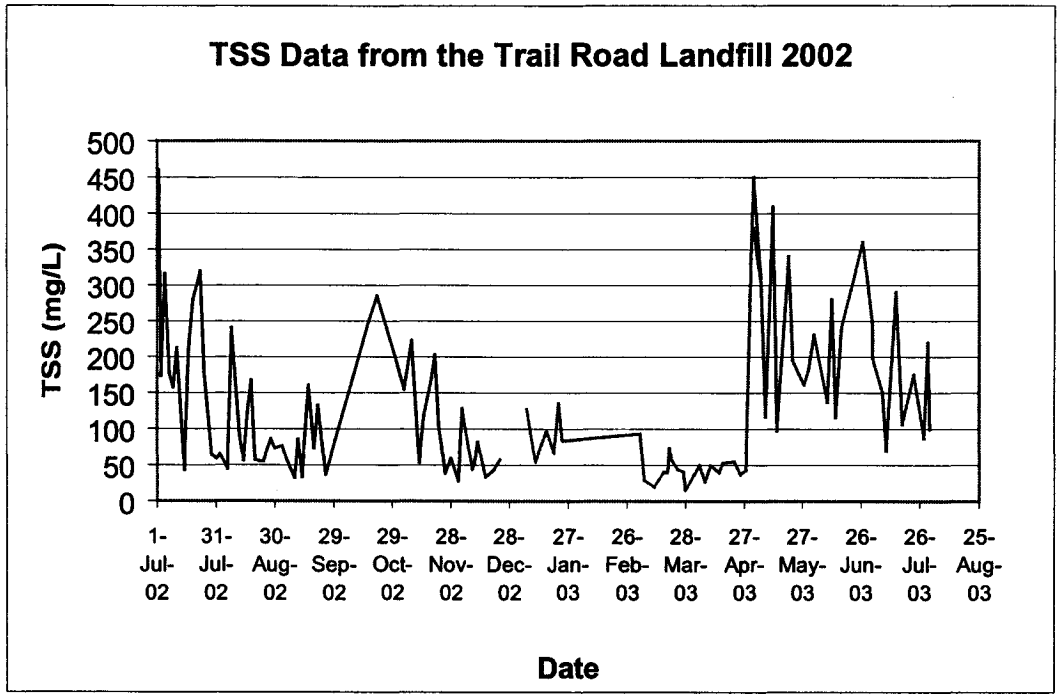


Figure 4-11 TSS Data from the Trail Road Landfill (Data unpublished).

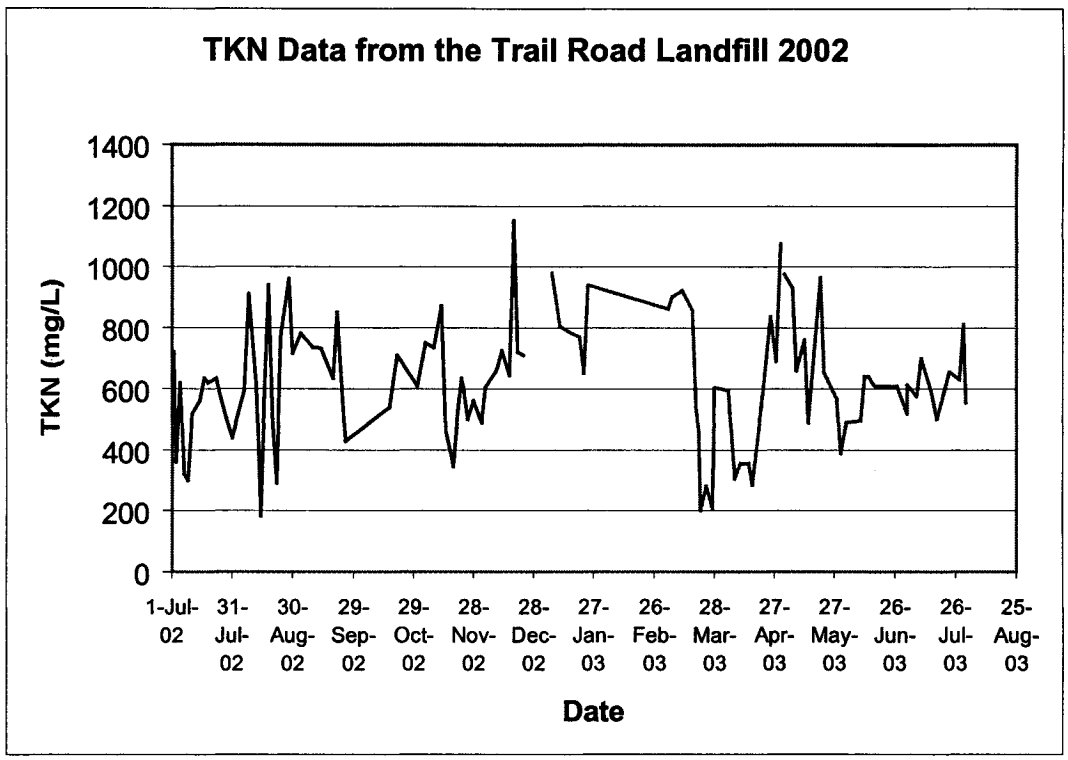


Figure 4-12 TKN data from the Trail Road Landfill (Data unpublished).

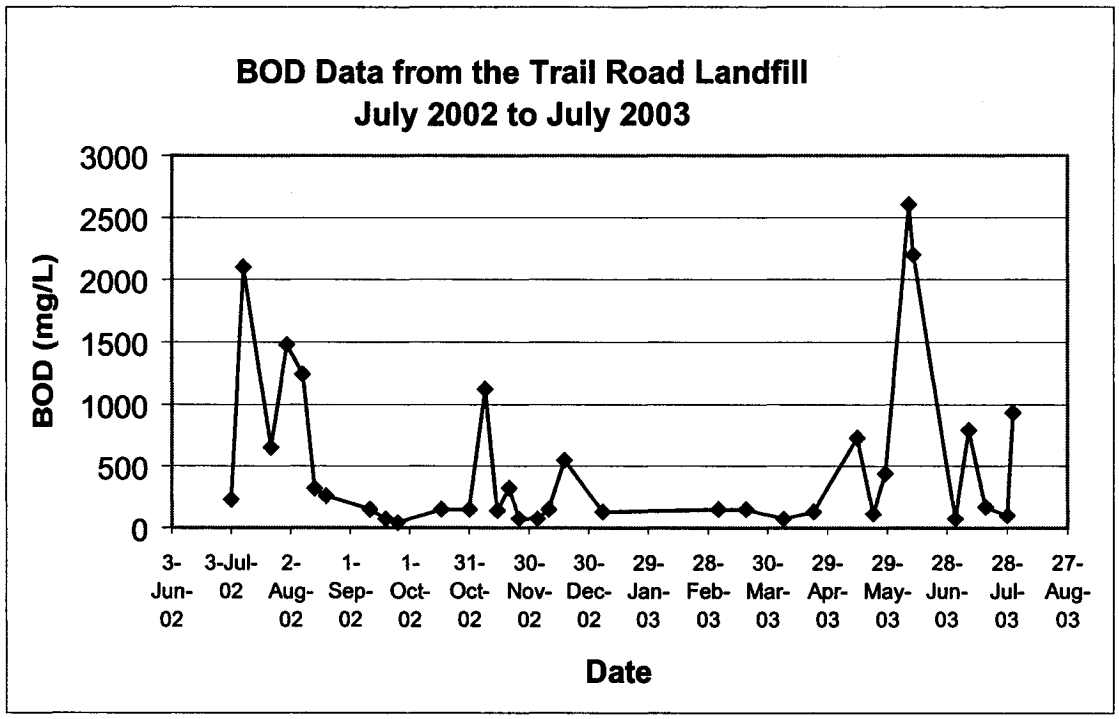


Figure 4-13 BOD Data from the Trail Road Landfill (Data unpublished).

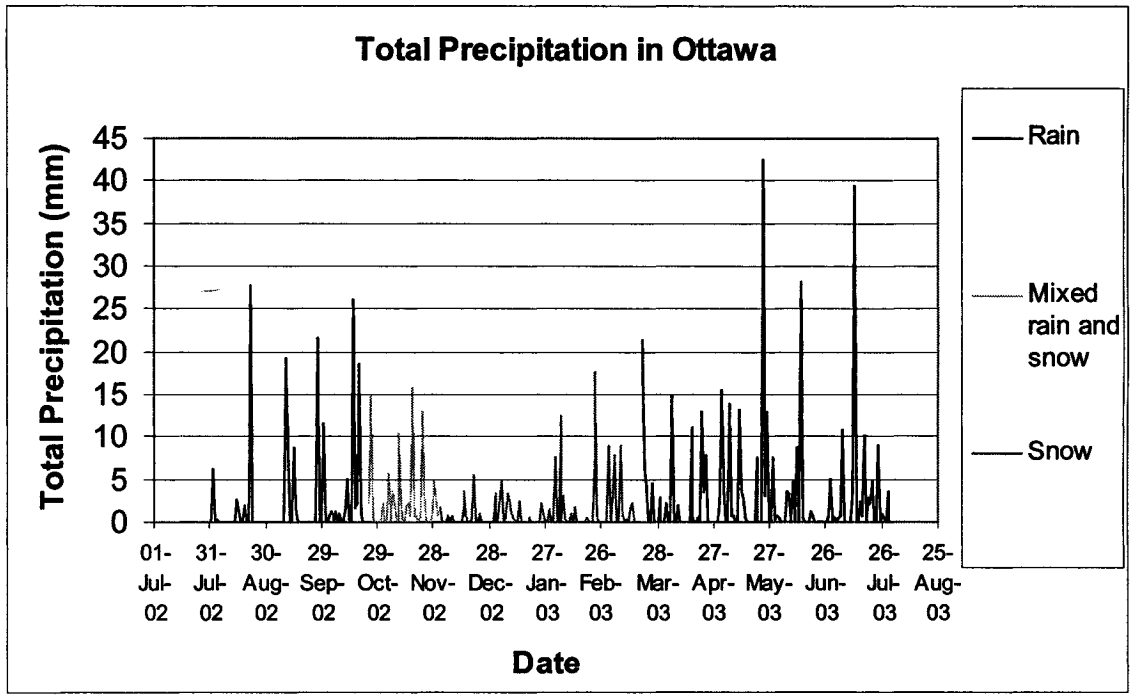


Figure 4-14 Precipitation data gathered from Environment Canada Website 2003 (Environment Canada, 2003).

From January 2003 to July 2003, COD, BOD, TKN, phosphorous, and ammonia were measured in liquid samples collected from the experimental runs. Figure 4-15 shows the concentrations of these parameters in the raw leachate used in this study. Ammonia, phosphorous and sulphate levels all decreased until mid April when they all began increasing. Increased dilution with snowmelt and rainfall may have caused this decrease in concentration. The eventual increase may have occurred due to rainfall decreases and thus longer liquid leachate residence times in the landfill. The BOD for the raw leachate rose between winter (<100 mg/L) and spring (.600 mg/L), when most other parameters decreased. The increased warmth and water content with spring conditions could have led to the increase in the BOD as the landfill flushed out what was held over winter. Increased microbial activity in spring and summer was expected. Increasing microbial concentrations in the landfill may explain the continuous decrease in TKN over time during spring and summer.

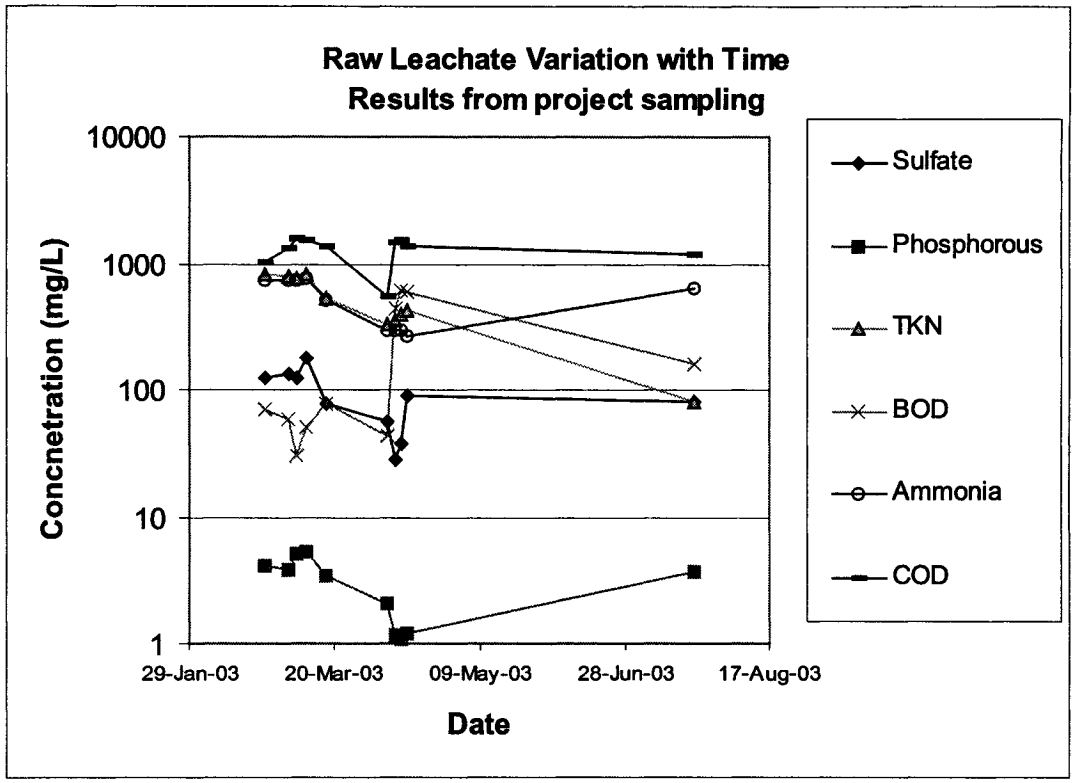


Figure 4-15 Raw leachate parameter results.

The varying characteristics of the leachate can affect its treatability, thus the treatment regime may need to be varied depending on the season. Ragle *et al.* (1995) found while examining an old landfill (16 years) and a young one (3.7 years) that there were much more dramatic hourly changes in the old landfill site, with a flow decrease of 63% and concentration increases of 47% COD, 74% iron, 53% Mn and 20% TDS in one 5 hour period. The young landfill also saw hourly variations, but they were to a much lesser extent. Maximum variations in the observed parameters for the older landfill were at least four times those observed in the new landfill (Ragle *et al.*, 1995). This further emphasises the need for a flexible system over the life of a landfill as the amount of variability can increase with time. Younger landfills have leachates which respond less directly to precipitation as channels have not yet formed and give stronger leachates with a longer lag period than older leachates which come from channels within the landfill and are actually more diluted with rainfall (Ragle *et al.*, 1995). Leachate can vary based on a number of circumstances such as season; the type and amount of MSW; age of landfill, method of compaction used; size of the landfill cells; and drainage patterns within the landfill. It should also be noted that while parameters such as BOD and COD are non-specific measures of pollution, it is possible that variation in these non-specific parameters, equal or greater variations in specific pollutant parameters and characteristics may occur (i.e. specific compounds, sizes of specific compounds). This leachate variability reflected part of the difficulty in describing membrane performance and fouling, and may have led to highly varied results.

The next sections examine each parameter measured for treatability using membranes, but the variable nature of the leachate coupled with equipment problems and a small data set, make drawing conclusions on treatment efficiency difficult. The effect of interactions between parameters measured and unmeasured in the system, the variability in particle size and the numerous unexamined chemical and biological interactions within the leachate all made it difficult to give a complete picture of the effectiveness of UF and MF membrane leachate treatment. However, some of the parameters examined in section 4.3 did show that membranes were effective for leachate pre-treatment.

4.3.2 COD

4.3.2.1 Leachate COD Variation

COD data was measured during the first (field) and second (lab) phase of the project. Thus COD was examined more closely than other measured liquid leachate parameters that were not sampled as often. Comparison of the Trail Road Landfill COD data and the project COD data revealed gaps in both data sets that only allowed for direct comparison in February and March 2003, where both data series correlated (Figure 4-16). The COD results determined by the author are the average of a minimum of two tests on each sample. Obvious outliers were expunged from the averaging. Where differences arose between the Trail Road data set and the data specific to this project, the project data was taken foremost (see Appendix F for all COD raw data).

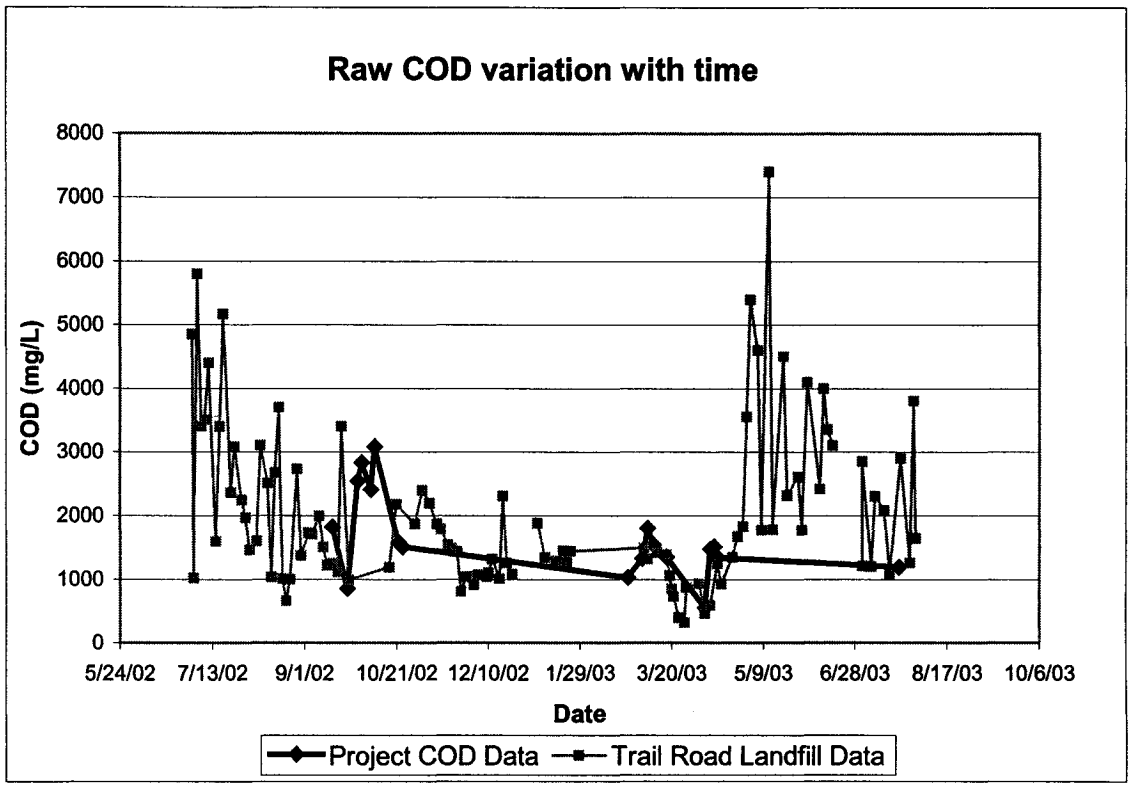


Figure 4-16 Raw COD fluctuation change with time.

As seen in Figure 4-16, the COD concentration range for the leachate tested during this project was in the low to mid range (545 to 3080 mg/L) when compared to the overall leachate strength for the year from the Trail Road Landfill (range of 315 to 7400

mg/L). Leachate COD concentrations can range from 140 to 152000 mg/L, with the methanogenic phase leachate producing a general range of 500-4500 mg/L and the acid phase 6000 to 60000 mg/L COD (Kjeldsen, *et al.*, 2002). COD results tend to indicate that the Trail Road landfill had some acid phase characteristics, but was mostly in the methanogenic phase category. One study that compared a 16 year old and a 3.7 year old landfill found that the average COD concentration for the older site was higher at 6544 mg/L than the new site at 3277 mg/L (Ragle *et al.*, 1995). This indicated that the Trail Road leachate would be considered young, but a landfill may still be in the acid phase after 16 years and recirculation of the leachate at Trail Road gave the leachate some properties of older landfill leachate, such as a decreased overall bio-degradability, which will be discussed in section 4.3.4.

The variability of the leachate COD concentration must be taken into consideration when examining COD removal rates and determining the effectiveness of treatment. Seasonal COD variation was easily seen in the Trail Road Landfill, but due to the small number of data points this overall view was missed within the project data. Gaps in the project data stemmed from periods when the membrane apparatus was not in operation due to environmental or equipment conditions.

However, the project data was easily correlated to weather patterns (Figure 4-17). There was a dry period the late summer and fall of 2002, during which the leachate became very dark and the number of leachate tanker trunks required diminished to one or none each day. It was during this time at the end of September that the COD concentration was the highest. The COD concentration seemed to increase with a lack of precipitation and high external temperatures. It decreased with the onset of more frequent rainfall events and lower temperatures.

The COD concentration in the leachate at the Trail Road Landfill showed trends with weather and seasonal changes. The leachate used in this study was typical of leachate found in the fall and early spring according to the Trail Road Landfill data (see Figure 4-17). Knowing that the leachate was typical of the two seasons meant that the membrane effectiveness in those seasons could be evaluated.

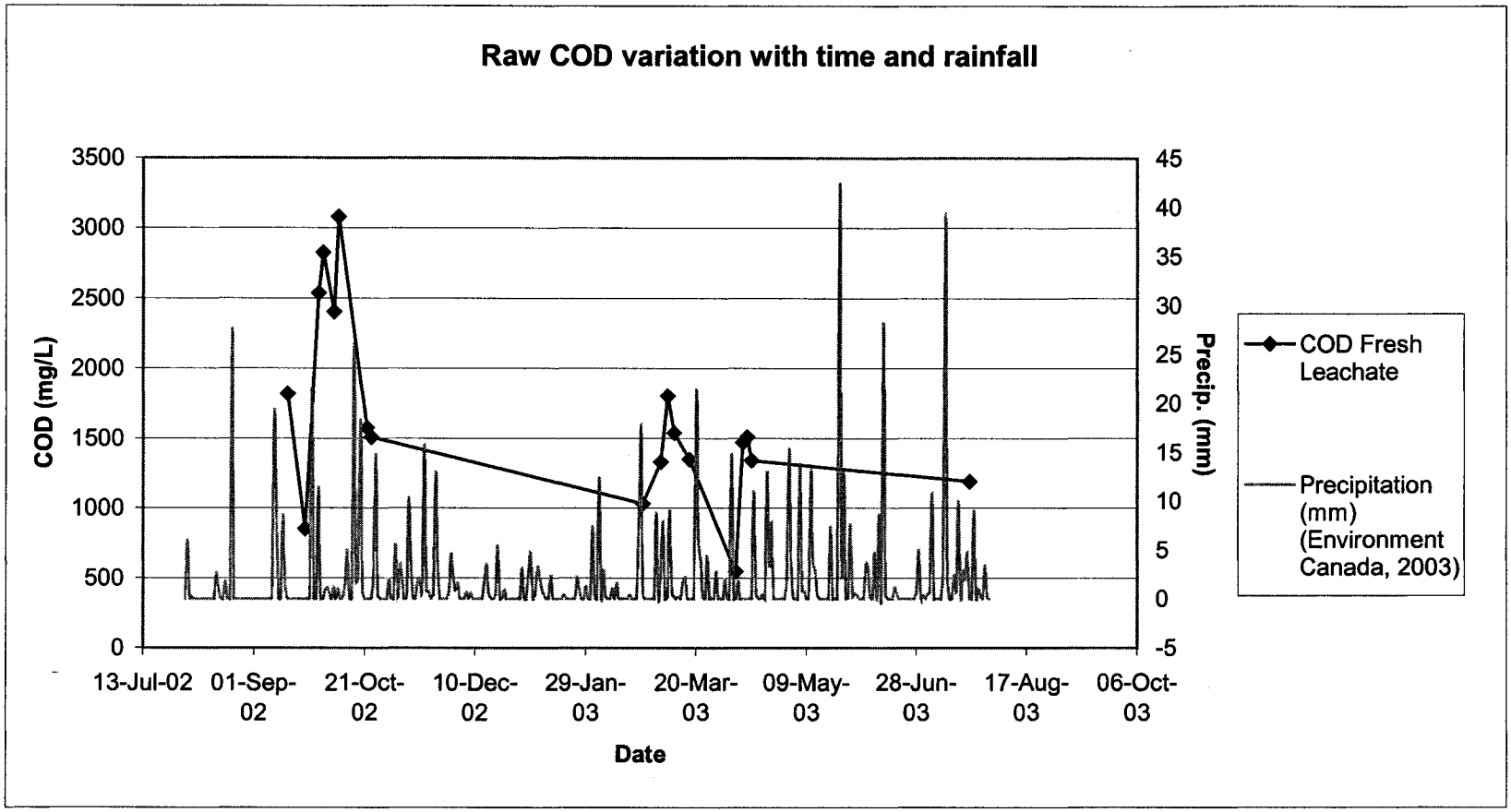


Figure 4-17 Variation in raw COD data for the project with time, temperature and rainfall.

4.3.2.2 COD Change Within an Experimental Run

A circulation study was conducted to examine the change in the COD of the leachate over the run time (48 hours) with recycling and no filtration at constant temperature and pressure (20°C and 20 psi). The stability of the COD concentration was examined independently of filtration, as the processes of precipitation and biological activity were not controlled. The leachate used in this experiment was of medium strength (1433 mg/L) when compared to the raw leachate used over the entire study (COD 545 to 3080 mg/L).

Figure 4-18 shows that during this experiment the COD concentration decreased a maximum of 14% over 48 hours. The COD concentration decrease may have been due to in situ biological activity or the presence of Fe (II), Mn(II), chloride and/or sulfide which can contribute to about a third of the COD values in leachate (Kjeldsen et al., 2002). When the leachate is exposed to oxygen the Fe (II) can be oxidize to Fe (III) and precipitate out, thus decreasing the COD (Kjeldsen et al., 2002). Nitrite ions in leachate have also been known to affect COD readings (Park *et al.*, 2001) This study was done in January and even further reductions in COD may be seen during the warmer months when higher microbial activity was likely.

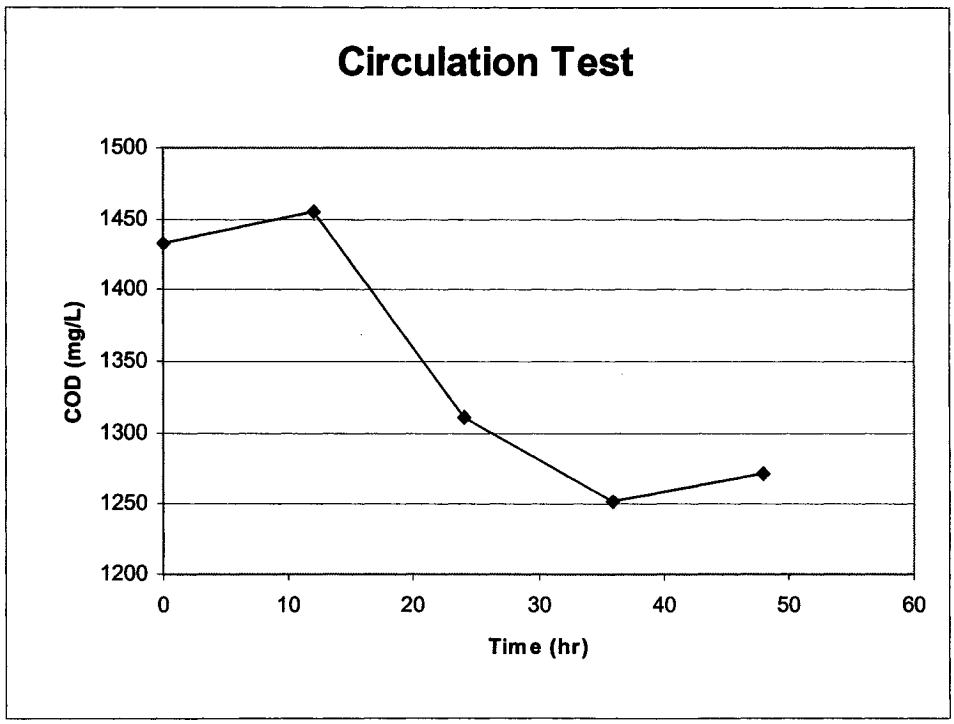


Figure 4-18 Examination of COD change over time with simple recycle.

To further emphasize the changes that may occur in the total COD over time, mass balances were performed on several experimental runs. COD data was collected from the fresh leachate, permeate and concentrate liquids for most 48 hour runs and the feed volume estimated based on a level indicator within the feed tank and the volume in apparatus piping. The mass of COD in the system was estimated based on the volumes recorded before and after the run; and the COD concentration results. Table 4-4 gives the mass balance results; see Appendix F for complete mass balance results.

In general the COD mass (COD START) in the fresh leachate was larger than the cumulative mass in the concentrate and permeate (COD END). For example the COD START for the September 30th JX_{62700} run was 231 g, while the COD END was 165 g, a decrease of 29%. The average percent decrease was 25%, which further substantiates the circulation study findings of a general COD decrease over time. Only two runs showed COD concentration increases and therefore a percent increase (MW_{100} and EW_{60}).
The circulation study found a maximum decrease in COD concentration of 14%, which was less than the average mass balance decrease. One reason for the increased percent loss in the mass balances may have been enhanced bio-activity of the leachate used in the runs, as the circulation study was done in January 2003 when the bio-activity would have been at its lowest for the study period.

Volume estimates from the denotations on the tanks may have added a possible source of error to the mass balance results, as the volumes were estimates and not exact measurements (tank denotations were in 10 gallons denotations, therefore ± approximately 2.5 gallons) . The standard deviation for COD is typically 17.76 mg/L COD with an accuracy as percent relative error (bias) of -4.7% (APHA, 1992). All of these errors may have had an effect on the overall mass balance to approximately ± 15%.

Table 4-4 COD mass balance results.

		COD (g)		
Membrane	Date	IN	OUT	% Difference
	30-Sep-02	231	165	-29
	22-Oct-02	179	163	-9
	24-Oct-02	171	154	-10
	10-Apr-03	147	127	-13
	12-Apr-03	165	106	-36
JX_{62700}	15-Apr-03	122	86	-29
MW_{100}	9-Oct-02	280	292	4
EW_{60}	4-Mar-03	121	159	32
ER_{30}	2-Oct-02	321	135	-58
GN_{10}	16-Sep-02	207	125	-39
	7-Oct-02	273	270	-1
	17-Mar-03	123	64	-48
PT_5	7-Apr-03	57	46	-20
GM_4	7-Mar-03	188	109	-42
GK_2	24-Sep-02	97	59	-39
	10-Mar-03	140	82	-41
GH_1	24-Feb-03	94	83	-11
	23-Jul-03	108	40	-63

4.3.2.3 COD Removal using MF and UF membranes

The realization that the COD concentration generally decreased rather than increased during a membrane run led to the concept of examining not only the percent removal between the fresh leachate and the permeate, but also the percent change between the fresh leachate and the concentrate. The percent change was given as negative where the COD decreased between the fresh leachate and concentrate, and positive where the COD increased. Equations 4-1 and 4-2 show how percent removal and percent concentration were calculated for the COD data. The same formulae were applied for the other measured parameters (BOD, ammonia, TKN, TP, sulphate and ICP data). Table 4-5 explains how the effectiveness of membrane treatment was evaluated.

$$REMOVAL\ \% = \left(\frac{FRESH - PERM}{FRESH}\right) \times 100 \qquad 4.1$$

$$CHANGE\ \% = -\left(\frac{FRESH - CONC}{FRESH}\right) \times 100 \qquad 4.2$$

Where: FRESH = Fresh Leachate COD (mg/L), CONC = Concentrate COD (mg/L), PERM = Permeate COD (mg/L)

Table 4-5 Determination of percent removal and membrane effectiveness

Scenario	**Effectiveness of membrane treatment**	**Corrected Removal %**
REMOVAL % = 0	No removal. Membrane not effective or broken	0
REMOVAL % > 0 CHANGE % >0 (i.e. concentration of parameter)	Removal. Membrane effective.	= REMOVAL %
REMOVAL % > 0 CHANGE % < 0 (i.e. removal of parameter) REMOVAL % > -CHANGE %	Removal. Effectiveness of the membrane can only be taken as the removal beyond any reduction in the concentrate	= REMOVAL % + CHANGE %
REMOVAL % > 0 CHANGE % < 0 (i.e. removal of parameter) REMOVAL % < -CHANGE %	No Removal. Not effective beyond the overall parameter decrease in the system	0

The calculated COD removal percentages are presented in Table 4-6. Initially, the possibility of COD decrease in the system was not considered. The difference between the fresh leachate and the concentrate was not thought to be significant as on average 16 L of permeate were produced from 102 L of fresh leachate, therefore in a few initial cases only concentrate and permeate samples were collected for analysis. It was not until after these initial runs that the amount of precipitate in the concentrate tank was noted and the fresh leachate began to be collected for analysis.

In three runs the fresh leachate results were not available and had to be estimated from field and concentrate data. These are indicated by the word None in the column labelled Raw leachate, followed by an approximate raw value. The percent removals for these cases were calculated as the difference between the permeate COD concentration and an approximated fresh leachate COD concentration. The approximate fresh leachate value was calculated using equation 4-2 and solving for *FRESH*, with a known *CONC*

value and a *CHANGE* % of –14% from the circulation study. The concentrate in all of these cases was significantly higher than the permeate and thus COD removal due to membrane treatment was assumed to have occurred.

The MW_{100} run and the PT_5 October 7th run both showed little to no initial percent removal, and it was therefore assumed that these membranes were damaged in some way. The JX_{62700} April 15th run was considered to have no clear percent removal as the COD reduction in the concentrate was more than the percent removal. This may not indicate a damaged membrane as there was removal, but the MWCO was very high which may have allowed a large portion of the COD to pass through the membrane.

Table 4-6 COD percent removals for each full run.

Membrane	Date	Raw Leachate COD (mg/L)	Removal %	Change %	Corrected Removal %
JX_{62700}	Sept. 30, 2002	2538	38	-0.79	37
	Oct. 22, 2002	1575	9.8	-4.3	5.5
	Oct. 24, 2002	1507	18	24	18
	April 10, 2003	1470	14	-5.4	8.6
	April 12, 2003	1510	36	-26	10
	April 15, 2003	1340	29	-34	0
MW_{100}	Oct. 9, 2002	3080	0.71	16	0
EW_{60}	March 4, 2003	1330	21	56	21
ER_{30}	Oct. 2, 2002	2825	59	-45	14
QW_{30}	Sept. 12, 2002	No Samples Taken			
GN_{10}	Sept. 16, 2002	None 1819	54	-14	40
$M\text{-}180_{10}$	Aug. 13, 2002	No Samples Taken			
PT_5	Oct. 7, 2002	2404	2.0	-11	0
	March 17, 2003	1350	52	-2.2	50
	April 7, 203	545	22	5.3	22
GM_4	March 7, 2003	None 1802	50	-14	36
GK_2	Sept. 24, 2002	None 852	40	-14	26
	March 10, 2003	1540	47	-7.8	39
GH_1	Feb. 24, 2003	1030	13	28	13
	July 23, 2003	1190	68	-10	58

Another run that encountered problems was the GH_1 February 24th run. During this run the outlet piping from the membrane cell was blocked, unfortunately this was only discovered after run completion. The constricted outlet may have caused a pressure build-up and forced particles through the membrane or caused tearing, thus raising the permeate COD concentration. The GH_1 membrane was rerun July 23, 2003 and showed substantial improvement in percent removal (58% versus 13%) with a similar COD strength. The GH_1 rerun gave the highest percent removal, which was the anticipated result for such a low MWCO membrane.

Figure 4-19 shows a general trend of percent COD removal increasing with MWCO decrease for the UF membranes. Membranes with MWCO of 10 KDa or less gave COD percent removals of 22 to 58 percent. Referring back to Table 4-6 the highest raw or fresh leachate COD in the UF series was 2825 mg/L for the ER_{30} membrane with a 14% removal and the lowest was 545 mg/L for PT_5 on April 5th with 22% removal. The rest of the fresh leachate CODs were between 1030 to 1350 mg/L, which in general indicated that on a COD basis the leachate characteristics may be similar and thus supported the MWCO and COD removal trend. The variability in COD removal within each individual MWCO was likely due to variability in characteristics other than COD concentration.

The MF membrane JX_{62700} was run in fall and spring. Figure 4-20 showed the fresh leachate, concentrate and permeate COD concentration results of these runs. The run numbers corresponded to the order in which the experiments were performed, corresponding to the dates given in Table 4-6. Runs 1-3 were the fall runs while 4-6 were the spring runs (i.e. Run #1 = Sept. 30th and Run #4 = April 12th).

Figure 4-19 shows that lower fresh leachate COD concentrations gave the lowest permeate COD concentrations, but not necessarily the highest COD percent removal. The highest strength leachate actually gave the best COD percent removal, but not the lowest COD permeate concentration. The JX_{62700} membrane was not very effective at COD removal as very few of the permeates met the maximum city bylaw allowable discharge of 1000 mg/L.

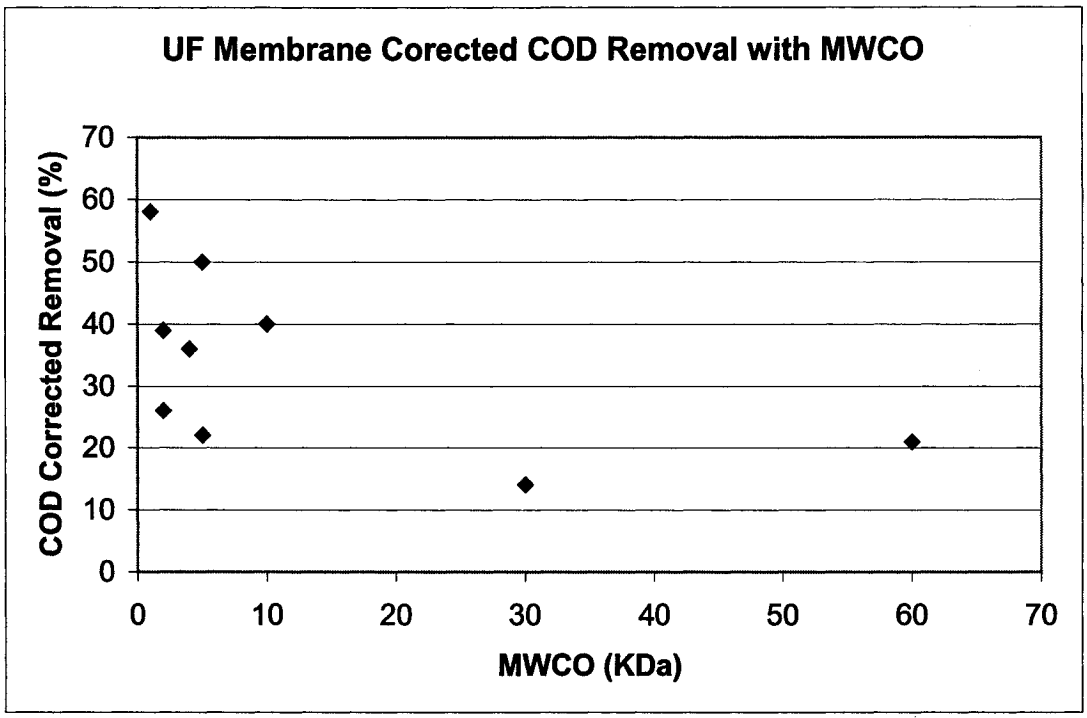


Figure 4-19 COD percent removal with UF MWCO.

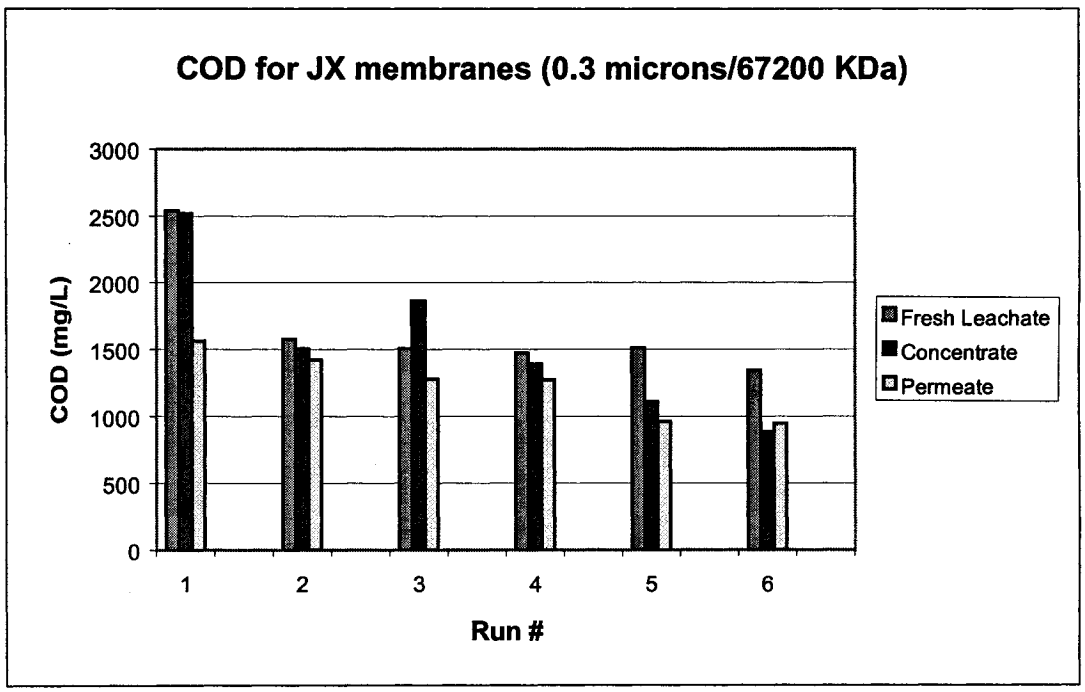


Figure 4-20 COD removal using MF membrane JX.

Table 4-7 Permeate COD, COD removal and flux with approximate membrane area.

Membrane	Date	Permeate COD (mg/L)	Corrected Removal %	Steady State Flux (L/m^2h)	Minimum Membrane Area Required (m^2) 2000 based
JX_{62700}	Sept. 30, 2002	1562	37	15	534
	Oct. 22, 2002	1421	5.5	20	400
	Oct. 24, 2002	1274	18	40	200
	April 10, 2003	1270	8.6	4.5	1780
	April 12, 2003	962	10	4.5	1780
	April 15, 2003	948	0	4.5	1780
MW_{100}	Oct. 9, 2002	3058	0	20	400
EW_{60}	March 4, 2003	1050	21	15	534
ER_{30}	Oct. 2, 2002	1163	14	0.6	13347
QW_{30}	Sept. 12, 2002	No Samples Taken		32	250
GN_{10}	Sept. 16, 2002	844	38	None-too variable	
$M\text{-}180_{10}$	Aug. 13, 2002	No Samples Taken		8.6	931
PT_5	Oct. 7, 2002	2357	0	3	2669
	March 17, 2003	652	50	14	572
	April 7, 203	425	22	5	1602
GM_4	March 7, 2003	897	35	14	572
GK_2	Sept. 24, 2002	512	25	6	1335
	March 10, 2003	818	39	5	1602
GH_1	Feb. 24, 2003	896	13	2	4004
	July 23, 2003	384	58	5	1602

The permeate COD concentration results and steady state fluxes of each membrane are presented in Table 4-7. All of the membranes which consistently produced permeates below the sewer use maximum of 1000 mg/L had MWCOs of =10 KDa. This would indicate that further pre-treatment prior to leachate discharge to the sewer would be needed if a higher MWCO membrane was to be used. The membrane with the best combination of flux, percent COD removal and permeate concentration (below the discharge criteria) was PT_5 on March 17th, with flux of 15 L/m^{2}hr, 50% COD removal, and 652 mg/L COD concentration in the permeate. GH_1 membrane gave the best percent COD removal at 58% with 384 mg/L COD permeate and a lower flux of 5 L/m^{2}hr.

Leachate COD concentration seemed to affect the overall removals seen, but there were other factors, discussed in section 4.2, which can further affect the run such as temperature and pressure. Membrane composition has also been shown to affect the removal process, as certain membrane materials are more effective when treating various feed types (Mulder, 1991). However, this study cannot draw conclusions based on membrane materials, as a change in composition usually meant a change in MWCO as well.

The size of the COD components may have affected the overall COD removals and may also have changed with season. One study found that a municipal landfill in use for three years produced a leachate with 37% of COD components above 3000 Da, 13% between 550 and 300 Da, and 50% below 500 Da (Park *et al.*, 2001). This same study found that fluvic acids composed 20% of the overall COD, while hydrophilic substances composed the remaining 80% (Park *et al.*, 2001). The Trail Road landfill mixed older and younger leachate, with landfill cell #3 operating from 1991 to present and landfill cell #4 from 1999 to present, but recirculation of the leachate allowed for greater overall degradation of the biodegradable components and thus an overall 'older' leachate (Golder Associates, 2002). Thus a larger percentage of humic and fulvic acids would be expected along with an overall increase in the molecular weight of the COD components (see section 4.3.3 for further discussion on this topic).

4.3.2.4 Size of Membrane Required

To briefly examine the full-scale application of these membranes an estimate was made of the area required to meet the flux requirements of the Trail Road Landfill leachate. The total leachate removed from the site for 2000 and 2001 was 70,150,000 L and 47,525,000 L respectively (Golder Associates, 2002), these values were used to estimate an average daily leachate production value and thus find an approximate minimum membrane area required in a full-scale application. 2001 was a very dry year and produced less leachate than normal therefore only the year 2000 value was applied. The average leachate production rate for 2000 was approximately 192,192 L/day.

A higher membrane area than calculated using the annual average would be required to handle the leachate production in the spring, thus the values given in Table 4-7 give an idea as to the relative area requirements of one membrane when compared to another. If these values were to be applied an appropriate scale-up safety factor would need to included in the calculation so as not to under size the unit. The highest daily leachate production volume was not available for this study, but could be determined if full scale membrane application or further piloting is done.

The highest membrane area calculated was for the ER_{30} membrane, due to its low flux (0.3 L/m^2h). The lowest membrane area was 240 m^2 for the MF membrane JX_{62700} with a flux of 40 L/m^2h. JX_{62700} membrane had a wide range of approximate membrane areas as its flux varied substantially from 40 to 4.5 L/m^2h giving areas of 200 to 1780 m^2. 1780 m^2 was higher than most UF membrane areas.

Based on the membrane area information the best membrane for COD removal was PT_5. GH_1 membrane gave COD removals between 13 and 58 %, but would require approximately 1602 to 4004 m^2 of membrane area, while PT_5 gave COD removals of 22 to 50% and only required 572 to 1602 m^2 membrane area, while still meeting the sewer-use bylaws. In further sections of 4.3 the removals of each examined parameter will be compared back to the area approximations in Table 4-7 to further examine each membrane's overall effectiveness.

4.3.3 BOD

4.3.3.1 BOD Characteristics of the Trail Road Leachate

As mentioned in section 4.3.1, the Trail Road BOD concentration data varied seasonally. The BOD range was 42 to 2600 mg/L for the Trail Road data and 30 to 600 mg/L BOD range for the raw leachate project data. This BOD range indicated a methanogenic phase leachate, which generally ranges from 500 to 4500 mg/L BOD concentration (Kjeldsen, *et al.* 2002).

Figure 4-21 showed the BOD peaks correlated with the COD peaks over time. The lower number of BOD data points (weekly versus bi-daily) hid some of the complexity seen in the COD results, but there was still a discernable trend which indicated that the BOD increased with increasing moisture and temperature in the spring and decreased as the rainfall events subsided in the late summer and as temperatures dropped in winter, as typically does leachate production. The direct correlation of leachate production to rain fall a Trail Road was typical of a recently filled landfill or a relatively young landfill with little canalization occurring within the landfilled MSW (Regale *et al.*, 1995).

A BOD/COD ratio was calculated from the fresh leachate data to give an idea of how biodegradable the leachate was and what component of the overall COD was constituted by the BOD. Both the project results and the landfill results showed that the BOD/COD ratio increased with an increase in BOD concentration. This indicated that BOD played a larger role in leachate oxygen demand during the wet warmer months of the year (see Figure 4-22 a and b). The BOD/COD ratio for the leachate used in this study varied from a BOD/COD ratio of <0.1 in the winter to >0.4 in the spring.

A BOD/COD ratio of approximately 0.7 is typical for acid Phase III landfill leachates, whereas mature methanogenic Phase IV landfills have a ratio of 0.1 (Wreford *et al.*, 2000). Other studies have found an average BOD/COD ratio of 0.58 BOD/COD for acidic phase leachates and 0.06 for methanogenic phase leachates (Kjeldsen, *et al.* 2002). The leachate recirculation program at the Trail Road Landfill increased the degradation within the landfill, thus decreasing the BOD/COD in the leachate to that of a more a mature landfill, but not fully mature as the landfill was still actively filling. Therefore, the

Trail Road leachate was in a different category than typically studied, because of the recycle.

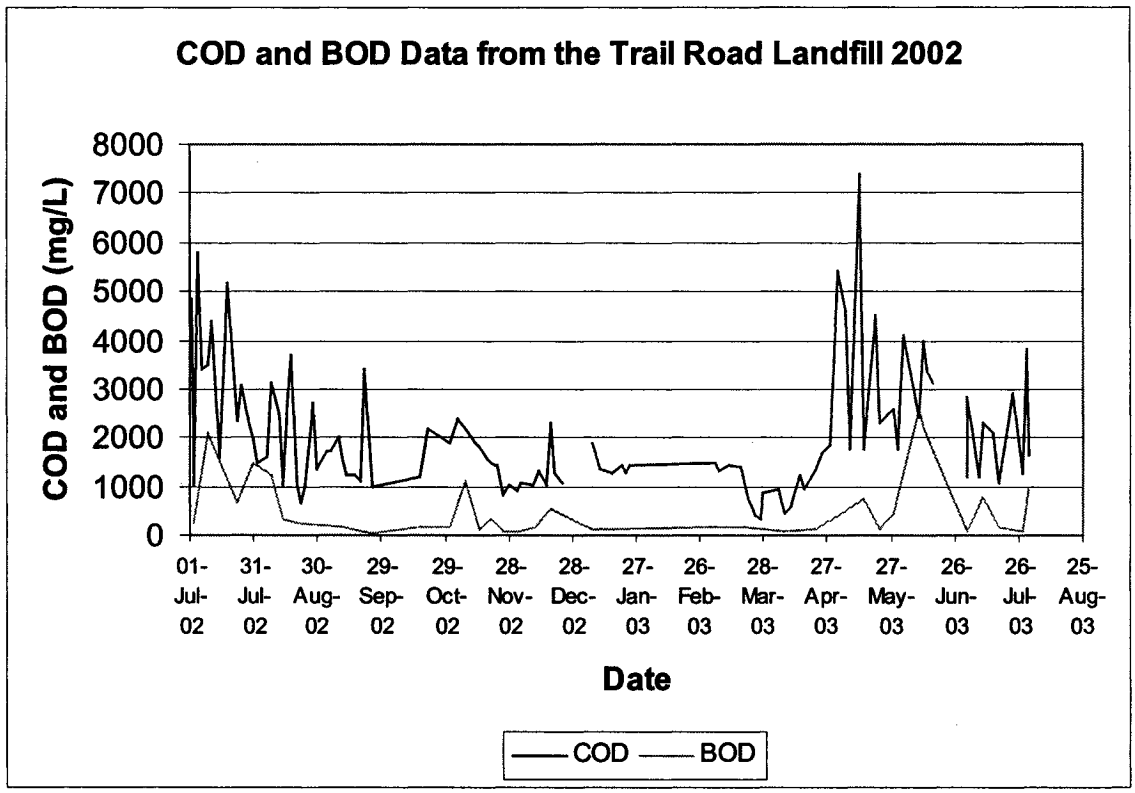


Figure 4-21 BOD and COD data from the Trail Road Landfill

The majority of the BOD/COD ratios seen in the Trail Road Landfill leachate tended to be below 0.5, which would make it difficult to treat biologically, above 0.5 the biological treatment is considered more feasible. A low BOD/COD ratio suggested a leachate with low volatile fatty acids and higher amounts of humic and fulvic-like compounds, which are difficult to biodegrade (Kjeldsen, *et al.* 2002). One study found that 95% of the BOD in landfill leachate was exerted by particles of less than 500 Da, while others found fresh leachate from relatively young landfills contained 80% smaller molecular weight hydrophilic substances and 20% humic and fluvic acids (which are also mostly hydrophilic) (Park, *et al.*, 2001). Humic and fulvic acid levels are thought to be higher than 20% for the Trail Road Landfill leachate used in this study based on the BOD/COD characteristics. Fulvic acids (1000 Da) and humic acids (100,000 Da) are large molecules making them harder to treat biologically, but easier to remove with membrane filtration. The biological degradation of organics in the leachate was enhanced

by the leachate recycle programme, making it more difficult than typical young leachates without recycle to treat biologically.

Hydrophilic substances are more easily consumed in biological treatment than either humic or fluvic acids and are generally of a lower molecular weight. Some of the hydrophilic substances may have been degraded in the leachate recycling program. Some studies have found that landfill leachate BOD/COD ratios for COD and BOD components above 500 Da tends to be between 0.02 to 0.03 rising to 0.44 for components below 500 Da, indicating an increased bio-degradability with decreasing molecular weight (Park *et al.*, 2001). Changes in the BOD/COD ratios of the leachate indicated the complexities incurred when trying to treat landfill leachate over the course of a year. Variations in membrane performance may be partly due to the variations in biological activity with seasonal changes.

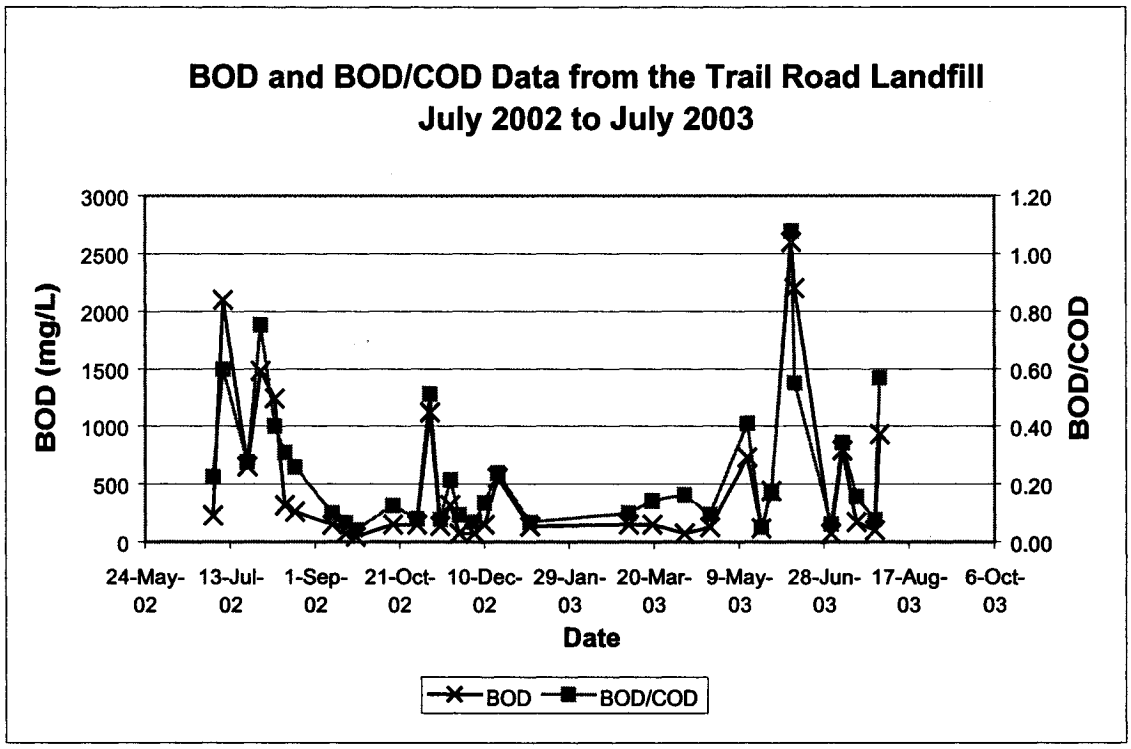


Figure 4-22a Trail Road Landfill data for BOD and BOD/COD results

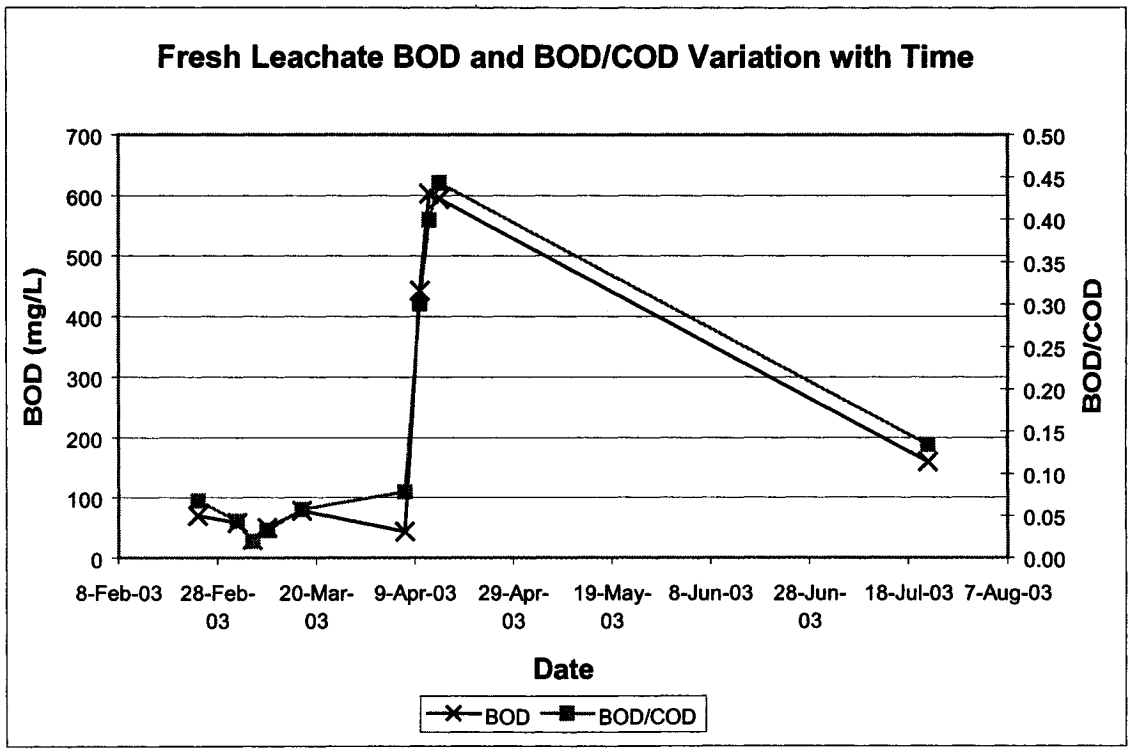


Figure 4-22b The project data on BOD and BOD/COD

4.3.3.2 BOD Removal using UF and MF Membranes

The BOD percent removal was determined using the same method outlined in the COD section 4.3.2.3 and Table 4-5 and are given in Table 4-8. The results were from the winter and spring runs as the COD and ICP data were the only liquid parameters measured in fall.

The MF membrane JX_{62700} did not show any significant BOD removal, but also had the highest BOD concentrations of all runs (Table 4-8). The overall COD composition in the leachate may have changed with spring as the BOD/COD ratio increased. As discussed in section 4.3.2.3 the COD percent change was the highest for the last two spring MF runs, when compared to all other winter and spring runs (Table 4-6). This higher COD percent change and the higher BOD/COD ratio indicated increased microbial activity. Also, the MF membrane fluxes decreased from 40 and 20 L/m^2h in the fall (BOD/COD <0.1) to 4.5 L/m^2h in the spring (BOD/COD >0.5), which may have resulted from increased fouling caused by microorganisms.

Though bio-fouling was not specifically examined, microbes and their excreted EPS can add another level of fouling beyond particulate deposition and thus decrease flux results and would be more prevalent when BOD/CODs are highest. Table 4-9 shows that the all the UF membranes, with the exception of one GH_1 run, than JX_{62700} in spring 2003, indicating a higher level of fouling when BOD/COD ratios are higher (>0.5).

Table 4-8 BOD percent removals for each full run.

Membrane	Date	Raw Leachate BOD (mg/L)	Removal %	Change %	Corrected Removal %
JX_{62700}	April 10, 2003	442	2	26	2
	April 12, 2003	603	40	-80	0
	April 15, 2003	594	33	-61	0
EW_{60}	March 4, 2003	58	84	-72	12
PT_5	March 17, 2003	78	59	-9	50
	April 7, 203	43	70	-35	36
GM_4	March 7, 2003	None	26	35	-34	0
GK_2	March 10, 2003	50	72	-14	58
GH_1	Feb. 24, 2003	70	89	-1	88
	July 23, 2003	160	91	-61	30

Table 4-9 BOD percent removals, permeate BOD and steady state flux.

Membrane	Date	Permeate BOD (mg/L)	Corrected Removal %	Steady State Flux (L/m^2h)
JX_{62700}	April 10, 2003	434	2	4.5
	April 12, 2003	362	0	4.5
	April 15, 2003	396	0	4.5
EW_{60}	March 4, 2003	9	12	15
PT_5	March 17, 2003	32	50	14
	April 7, 203	13	36	5
GM_4	March 7, 2003	17	0	14
GK_2	March 10, 2003	14	58	5
GH_1	Feb. 24, 2003	8	88	2
	July 23, 2003	15	30	5

The sewer use bylaw target for BOD_5 was 300 mg/L. Almost all fresh leachates and therefore the permeates were below the bylaw value, except for the JX_{62700} April 10th to 15th runs (the sequential runs). The JX_{62700} membrane gave 0% BOD removal resulted in a permeate above the bylaw for the sequential runs, but still below the 1000 mg/L maximum discharge value.

Membranes of 5 KDa or less gave the best BOD percent removals (excluding the GM_4 run). The highest BOD percent removal was 88% using the GH_1 membrane on February 24th, but the next run in July had a BOD percent removal of 30%. The July run had a slightly higher BOD than the other UF membrane runs at 160 mg/L, and was more than double the 70 mg/L BOD in the fresh leachate of the GH_1 February run.

Though GH_1 gave good percent removals the flux was low ranging from 2 to 5 L/m^2h. The PT_5 membrane had a BOD percent removal of 36% to 50% and a flux of 5 to 14 L/m^2h, giving excellent removals at a higher than average UF flux. The GK_2 membrane also gave good BOD percent removal at 58%, but with a lower flux of 5 L/m^2h. Both of these membranes would require roughly the same theoretical membrane area with PT_5 at 572 to 1602 m^2 and GK_2 at 1602 to 4004 m^2. Removal rates and resulting permeate BOD concentrations would probably change for all the UF membranes had they been tested at higher BOD concentrations in the spring. Even a slight increase in BOD to 160 mg/L from 70 mg/L seemed to have affected the corrected BOD percent removal rates in the case of GH_1.

Most of the UF runs used relatively the same fresh leachate BOD concentration and showed decreasing percent removals with an increase in MWCO, with the exception of the GM_4 membrane (Figure 4-23). GH_4 indicated by the X in Figure 4-23 showed 0% BOD removal, but had 35 % COD removal. The character of the leachate may have affected membrane performance even though the total COD or BOD values did not indicate any compositional difference. GH_1 showed that relatively small BOD concentrations when doubled could affect the overall percent removal. There was, however, no correlation between raw leachate BOD concentration and percent removal within individual membrane types. This data set was small as only JX_{62700}, PT_5 and GH_1 were tested more than once when the BOD was measured and the JX_{62700} membrane gave no BOD percent removal (see Figure 4-24 and Appendix G for BOD data).

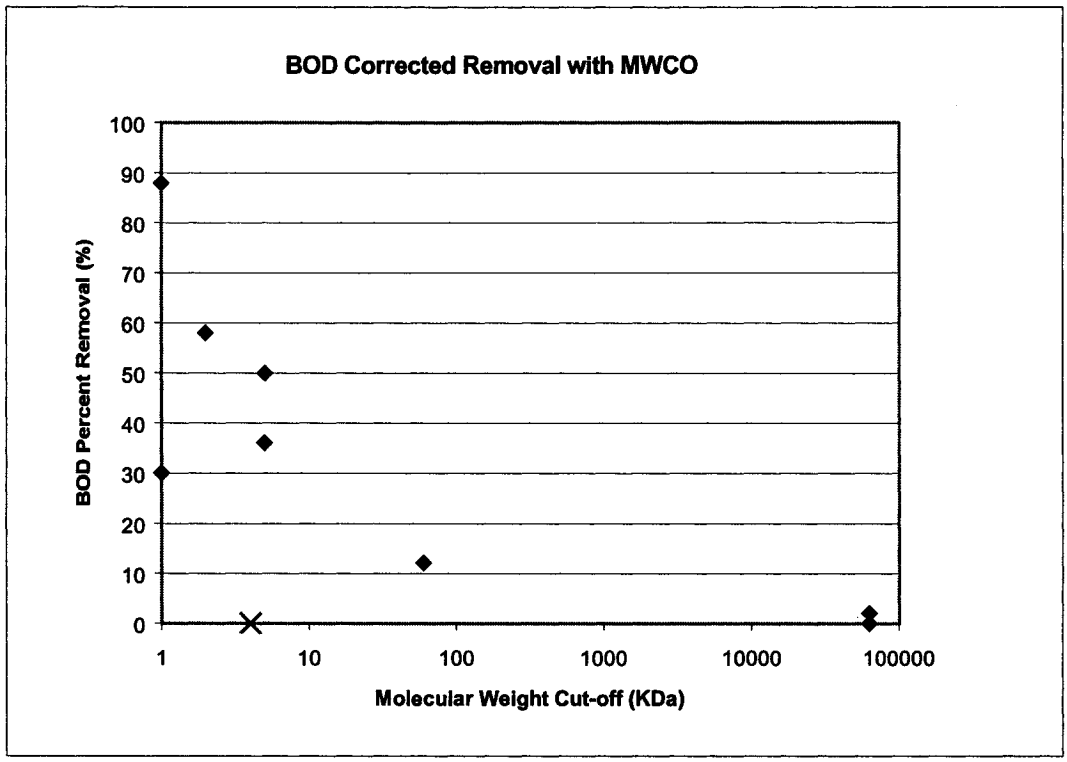


Figure 4-23 BOD percent removal with MWCO.

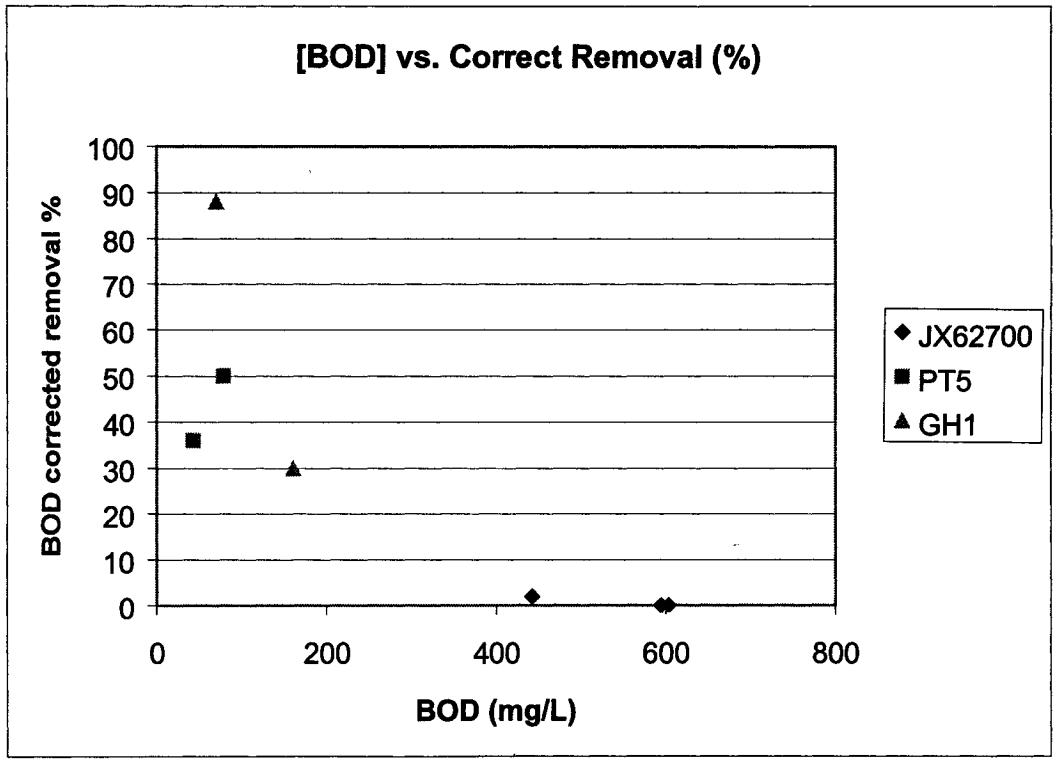


Figure 4-24 BOD concentration related to corrected BOD percent removal

4.3.4 Ammonia, Total Kjeldahl Nitrogen and Total Phosphorous

4.3.4.1 Leachate Characterization for Ammonia, Total Kjeldahl Nitrogen and Total Phosphorous

Of the raw leachate components ammonia, TKN and TP, only the TKN was consistently measured by the Trail Road Landfill and showed no seasonal variation. There were too few data points from the project data to draw any conclusions as to the seasonal variability of ammonia and TP (Figure 4-25). The three parameters did seem to follow the same increase and decrease patterns. Concentrations were higher in the winter 2003 when there was less dilution, decreasing in spring with greater dilution and increasing in mid-April(see Appendix H for raw ammonia, TKN, and TP data).

A BOD:N:P ratio for stabilised leachates is approximately 100:312:0.3 (Park *et al.*, 2001). The BOD:N:P ratios for the Trail Road landfill ranged from 100:66:0.2 to 100:3042:34 and none met the approximate stabilised criteria. The Trail Road Landfill was still being filled, with recycling involved which helped to stabilize the leachate in some, but not all parameters (Table 4-10).

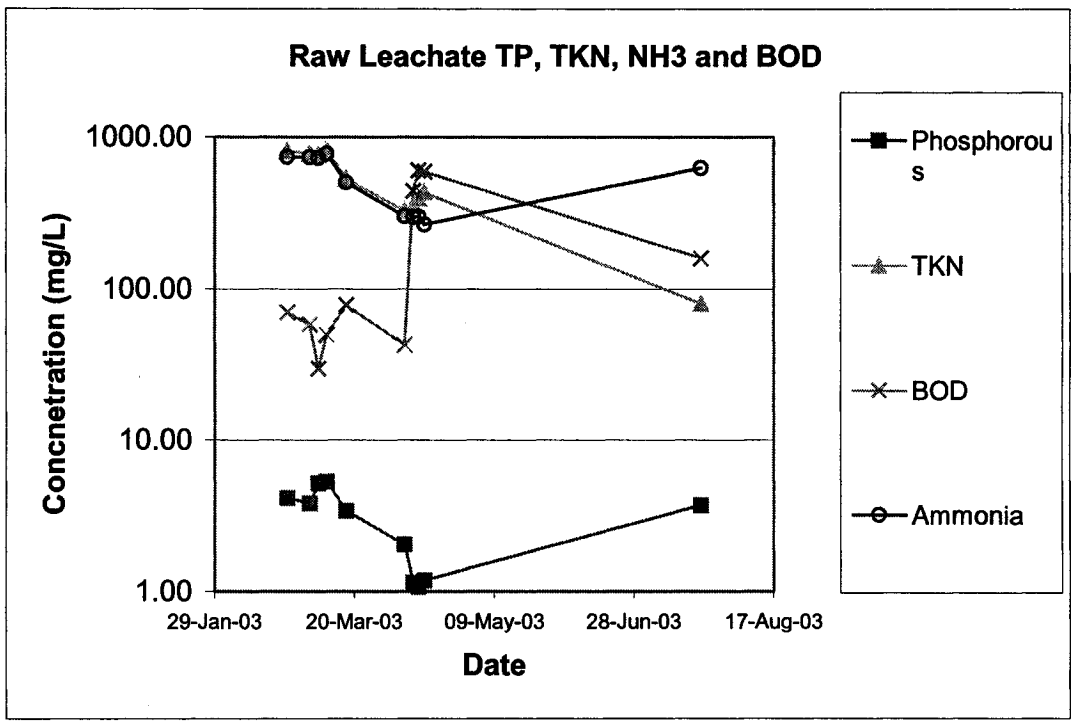


Figure 4-25 Project data for various raw leachate parameters

Table 4-10 BOD:N:P results for the leachate used in this project

Membrane	Date	BOD:	N:	P
	4/10/2003	100	80	0.3
	4/12/2003	100	66	0.2
JX_{62700}	4/14/2003	100	73	0.2
EW_{60}	3/4/2003	100	1340	6.6
	3/17/2003	100	683	4.4
PT_5	4/7/2003	100	763	4.7
GM_4	3/7/2003	100	3042	34.2
GK_2	3/10/2003	100	1644	10.7
	2/24/2003	100	1160	5.9
GH_1	7/22/2003	100	50	2.3

4.3.4.2 Ammonia, Total Kjeldahl Nitrogen and Total Phosphorous Removal

The percent removal of each of the components was compared once again to the percent change in the bulk liquid. As discussed previously there can be constituent decreases caused by precipitation, biological and/or chemical reactions. If the leachate was a stable feed the concentrate should be more concentrated, but this was not the case for many constituents.

Ammonia levels in the concentrate seemed to stay the same as the initial feed levels with a variation of +/- 5% (see Table 4-11). Ammonia levels tend to stabilize over the life of a landfill and average values do not generally vary from year to year substantially (Kjeldsen, *et al.* 2002). Other than one PT_5 run and one GH_1 run all of the ammonia percent removals were below 10%, therefore any ammonia removal by membrane treatment was considered marginal.

The best TKN removals were found when using the GH_1 membrane (17 to 41% removal) (see Table 4-11). Other than an MF membrane with 24% TKN removal, the percent removals for all other membranes were all at or below 10%. The high removals seen using the JX_{62700} MF membrane may have been due to biofilm formation, mentioned in the BOD section 4.3.3. The TKN removals were generally only marginally better than the NH_3 removals, as TKN includes NH_3, but also other nitrogen components which may have been of a lower molecular weight.

Table 4-11 Percent removals and change for ammonia, TKN and TP

		Ammonia			TKN		
Membrane	Date	Removal %	Change %	Corrected Removal %	Removal %	Change %	Corrected Removal %
	4/10/2003	6	3.3	6	-13	19	0
	4/12/2003	9	-5	4	30	-6.3	24
JX_{62700}	4/14/2003	-1	4.1	0	33	-23	10
EW_{60}	3/4/2003	12	-3.8	8	16	-8.9	7
	3/17/2003	11	1.4	11	5	11	5
PT_5	4/7/2003	6	4.3	6	-1	12	0
GM_4	3/7/2003	3	**n/a 0	3	9	n/a -3.7	5
GK_2	3/10/2003	5	2.6	5	8	2.1	8
	2/24/2003	22	-2.6	19	27	-10	17
GH_1	7/22/2003	10	-4	6	70	-29	41

		TP			
Membrane	Date	Removal %	Change %	Corrected Removal %	Steady State Flux (L/m^2h)
	4/10/2003	87	-62	25	4.5
	4/12/2003	80	-52	28	4.5
JX_{62700}	4/14/2003	77	-61	16	4.5
EW_{60}	3/4/2003	34	29	34	15
	3/17/2003	9	-72	0	14
PT_5	4/7/2003	89	-19	70	5
GM_4	3/7/2003	74	n/a -42	32	14
GK_2	3/10/2003	67	-40	27	5
	2/24/2003	59	-40	19	2
GH_1	7/22/2003	91	-58	33	5

***Where removal % was negative there was no removal, rather an increase in the component between the fresh leachate and permeate.**

****Where the percent change was unknown it was estimated based on an average of the other percent changes. The fresh leachate and thus the percent removal were estimated from this.**

The TP removal percentages were the highest of the three (Table 4-11), but the TP levels were in general 100 times less that the other two constituents (see Table 4-12). Also, the percent change between the fresh leachate and the concentrate was the highest of all three constituents in this section. The total phosphorus removals were high for all membranes, with the April 7th PT_5 run giving a 70% overall TP percent removal. The April 7, 2003 PT_5 run did have one of the smallest percent removals at –19% and if it had been higher or closer to average (42%) its percent removal would still have been high, but closer to the other removals seen at approximately 47%. The high removals by MF (16 to 28%) indicated again the possible importance of BOD levels to membrane effectiveness and fouling. The COD and TSS levels in mid-April 2003 were not significantly different than those found in winter. The BOD was the only measured parameter with a considerable increase during this period (see Figure 4-25 and Table 4-12).

The higher percent removal of TP over ammonia and TN stands to reason from a molecular weight point of view with phosphorous having more than twice the atomic weight of nitrogen (32.1 versus 14). The TP would generally consist of larger molecules than TKN, while TKN probably contains nitrogen compounds larger than ammonia leading to its higher overall removals than ammonia.

Table 4-12 Raw leachate and permeate results for ammonia, TKN and TP.

		Fresh Leachate			Permeate		
Membrane		Ammonia	TKN	TP	Ammonia	TKN	TP
	Date	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)
JX_{62700}	4/10/2003	299	353	1.14	282	398	0.15
	4/12/2003	300	398	1.07	272	277	0.21
	4/14/2003	267	433	1.18	269	290	0.27
EW_{60}	3/4/2003	736	777	3.81	650	650	2.50
PT_5	3/17/2003	504	533	3.40	447	507	3.11
	4/7/2003	302	328	2.03	283	331	0.22
GM_4	3/7/2003	728	791	8.9	707	723	2.29
GK_2	3/10/2003	775	822	5.33	733	758	1.74
GH_1	2/24/2003	739	812	4.14	577	595	1.71
	7/22/2003	628	80	3.69	565	24	0.33

There were sewer use bylaw values for TKN and TP, but not for ammonia. For TKN the maximum limit was 250 mg/L and the target was 100 mg/L and below. Only the second GH_1 run met both of these quality targets at 24 mg/L (Table 4-12). The fresh leachate TP concentration was already below the maximum of 25 mg/L TP and target of 10 mg/L, thus the permeate was also below both limits. The highest raw leachate TP value was just over 5 mg/L. The best overall removals for all variables was given by GH_1 with 6 to 19% ammonia removal, 17 to 41% TKN removal, 19 to 33% TP removal, a flux of 2 to 5 L/m^2h and an approximate area of 1602 to 4004 m^2.

Ammonia and TP did not show an overall trend with MWCO and percent removal for the UF membranes, but TKN did show a slight trend of percent removal increasing with decreasing MWCO (Figure 4-26a). Figure 4-26b shows that with the addition of the MF membrane JX_{62700} to the graph all trends disappear due to the high percent removals seen during those runs (Figure 4-26b). Figures 4-27a, b and c showed that ammonia removal seemed to increase with increasing raw leachate ammonia concentration, while TP showed the opposite relation and TKN no relation between percent removal and raw leachate TKN concentration. This indicates the varying nature of the leachate and how a number of factors may affect membrane effectiveness in leachate treatment.

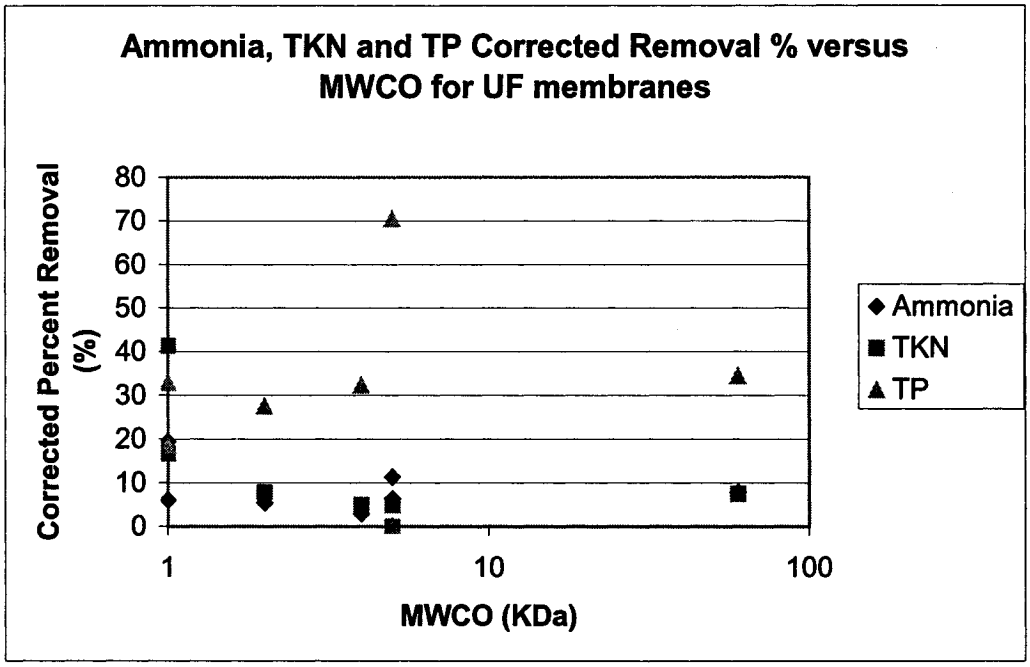


Figure 4-26a Ammonia, TKN and TP corrected percent removal with MWCO for UF membranes

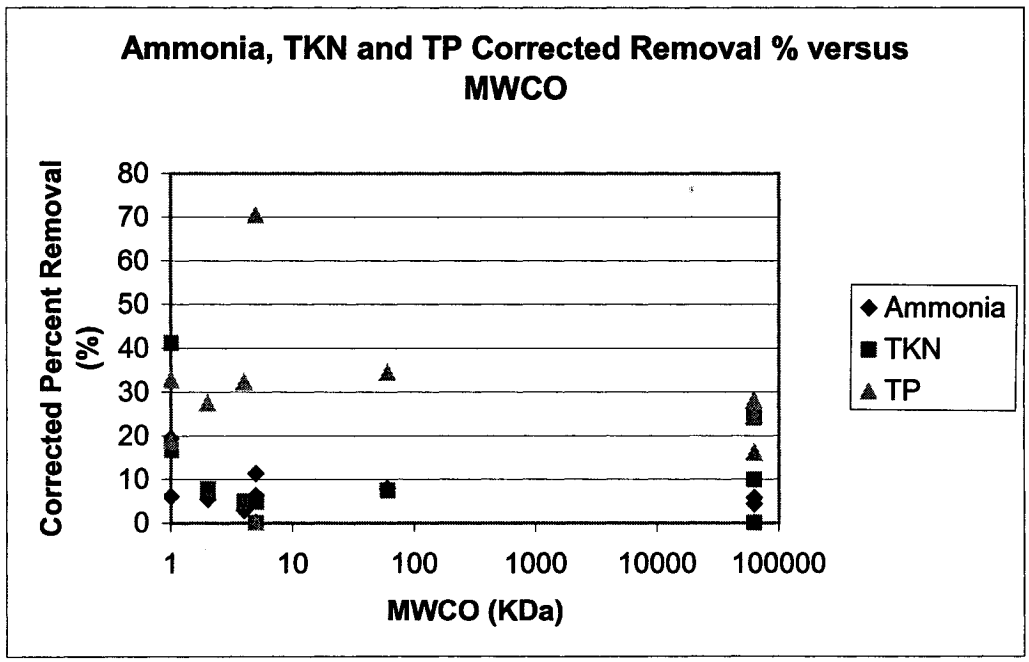
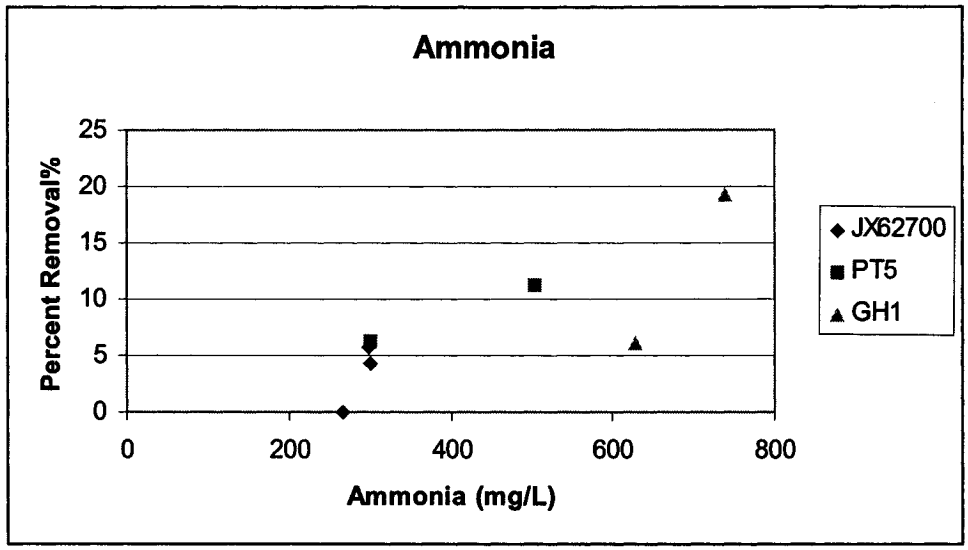
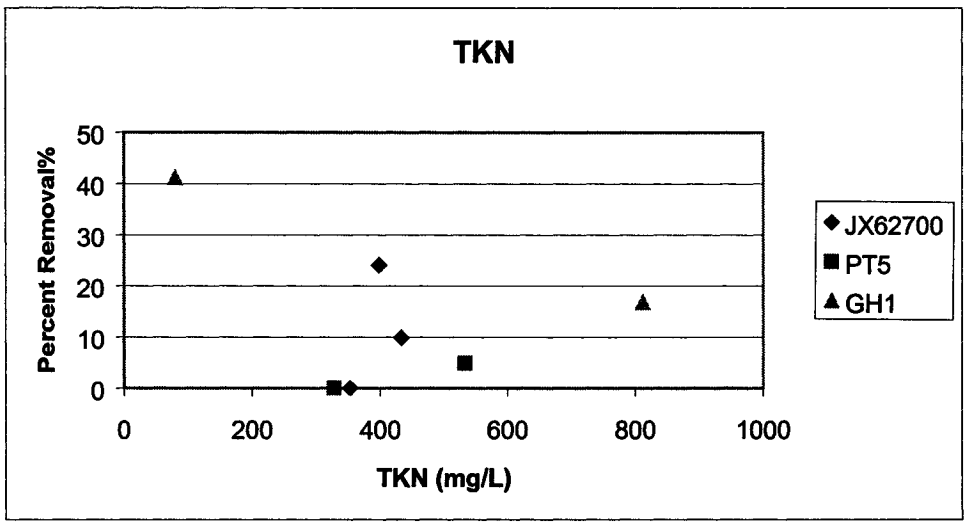
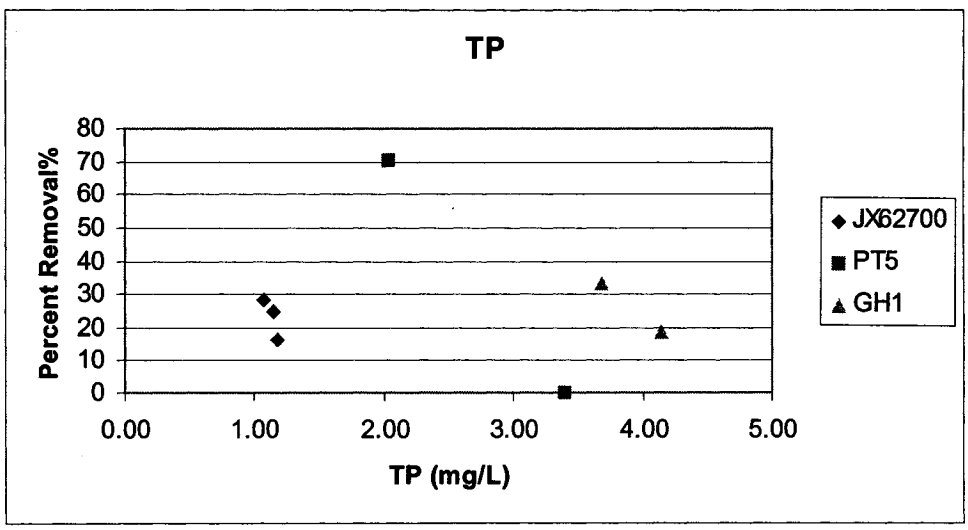


Figure 4-26b Ammonia, TKN and TP corrected percent removal with MWCO for all membranes.







Figures 4-27a, b and c. Comparison of ammonia, TKN and TP concentration to corrected percent removal.

4.3.5 Sulphate

The raw leachate data showed the same general patterns for sulphate as for ammonia, TKN and TP (Figure 4-25 and Appendix H for raw sulphate data). Sulphate concentrations decreased from winter to spring (124 to 28 mg/L) and increased during late spring (28 to 90 mg/L). The overall sulphate concentration range in the raw leachate was 28 to 133 mg/L. Kjeldsen *et al.* (2002) gave the sulphate ranges for methanogenic phased landfill as 10 to 420 mg/L (average 80 mg/L) and 70 to 1750 mg/L (average 500 mg/L) for an acid phase landfill, which indicated that the leachate used in this project was more closely aligned to a methanogenic leachate. Methanogenic leachates have lower sulphate concentrations as microbes reduce sulphate to sulphite (Kjeldsen *et al.,* 2002).

When considering sulphate treatment of landfill leachate there are two main concerns, the first being the treatment efficacy and the second being the implications of possible pipe corrosion if the permeate or raw leachate were discharged directly into the sewer system. The fresh leachate sulphate concentration was well below the sewer use bylaw maximum limit of 1500 mg/L, but sulphate removal as a by-product of membrane treatment was still considered valuable based on the possibility of decreasing sulphide production in sewer lines (Table 4-13).

4.3.5.1 Sulphate Removal

The best removals were obtained by PT_5 at 42% sulphate removal and GH_1 at 41% sulphate removal. Again the PT_5 membrane had the higher general flux (5 to 14 L/m^2h) and concomitant lower general membrane area requirement (572 m^2 to 1602 m^2) of the two membranes as mentioned in previous sections (Table 4-7). JX_{62700} removed little to no sulphate (0 to 11%), while the UF membranes gave removals between 3 and 42% (Table 4-14). There was no trend between sulphate removal and membrane MWCO, nor was there a trend between sulphate removal and raw leachate sulphate concentration.

Table 4-13 Fresh leachate and permeate sulphate concentrations with steady state flux.

Membrane	Date	Fresh Leachate (mg/L)	Permeate (mg/L)	Steady State Flux (L/m^2h)
	4/10/2003	28	25	4.5
	4/12/2003	37	43	4.5
JX_{62700}	4/14/2003	90	15	4.5
EW_{60}	3/4/2003	133	114	15
	3/17/2003	78	28	14
PT_5	4/7/2003	57	39	5
GM_4	3/7/2003	212	111	14
GK_2	3/10/2003	126	111	5
	2/24/2003	124	92	2
GH_1	7/22/2003	80	24	5

Table 4-14 Sulphate removal results

Membrane	Date	Removal %	Change %	Corrected Removal %
	4/10/2003	11	11	11
	4/12/2003	-16	19	0
JX_{62700}	4/14/2003	83	-80	3
EW_{60}	3/4/2003	14	1	14
	3/17/2003	64	-22	42
PT_5	4/7/2003	32	-26	6
GM_4*	3/7/2003	48	-17	31
GK_2	3/10/2003	12	-9	3
	2/24/2003	26	-16	10
GH_1	7/22/2003	70	-29	41

*** Based on the concentrated and average percent change value.**

4.3.5.2 Sulphide Production Rate Estimation

Simple empirical equations have been developed to predict hydrogen sulphide formation in pressure and gravity sewer mains (equations 4-1 and 4-2). There are complex models available to determine sulphide production in pipes, which include variables such as heterotrophic biomass growth; oxygen consumption; hydrolysis and fermentation; with pipe specification requirements, but these often require more information than is available (Hvitved-Jacobsen and Neilsen, 2000). For the purposes of this project most of the expanded and even some of the basic equations could not be used, as the force main specifications were required. The sewage line expansion project to the

Trail Road Landfill was suspended in July 2003 and therefore there were no firm sewage line designs confirmed.

Most of the expanded equations also focused mainly on municipal wastewaters and would have to be modified to accommodate leachate and the mixing of leachate with municipal waste further down the sewage line. The following two equations (4-1 and 4-2) were the only equations which did not involve pipe specifications or specific biological information beyond BOD and could give rough estimations of the sulphide production rates (SPRs).

Taken from Hvitved-Jacobsen and Neilsen, 2000 :

$$r_a = 0.228\ 10^{-3}\ [COD]\ 1.07^{\ T-20} \qquad 4.1$$

$$r_a = 1\ 10^{-3}\ [BOD]\ 1.07^{\ T-20} \qquad 4.2$$

Where: r_a = Sulphide production rate (g S/(m^2·h))

T = Temperature (EC)

[COD] = Chemical Oxygen Demand concentration (mg/L)

[BOD] = Biological Oxygen Demand concentration (mg/L)

Equations 4-1 and 4-2 which are dependent on BOD or COD concentration as well as wastewater temperature were applied to both treated and untreated leachate data, to compare the differences in resulting SPRs. The raw leachate data was applied at its initial temperature, while the permeate data was applied at the highest, lowest and average temperatures for each run. Equation 4-1 used the project COD concentrations, which were available for fall, winter and spring. Figure 4-28a shows the SPR results for fall 2002 using Equation 4-1. According to Figure 4-28a, SPRs in the fall would have been highest when the permeate was introduced at mid to high run temperatures, at 1.30 to 1.65 g S/(m^2·h). These mid to high temperature permeate SPRs were actually higher than simple raw leachate SPRs which averaged 0.55 g S/(m^2·h). The lowest temperature permeate SPRs were still the lowest production rates with an average of 0.30 g S/(m^2·h). This showed that temperature control or cooling within the system should be used in full-scale application prior to sewage line injection to keep SPRs in sewage pipes at a minimum. According to these equations the membrane treatment may only be effective at reducing SPRs in the sewage line extension when used in combination with temperature controls.

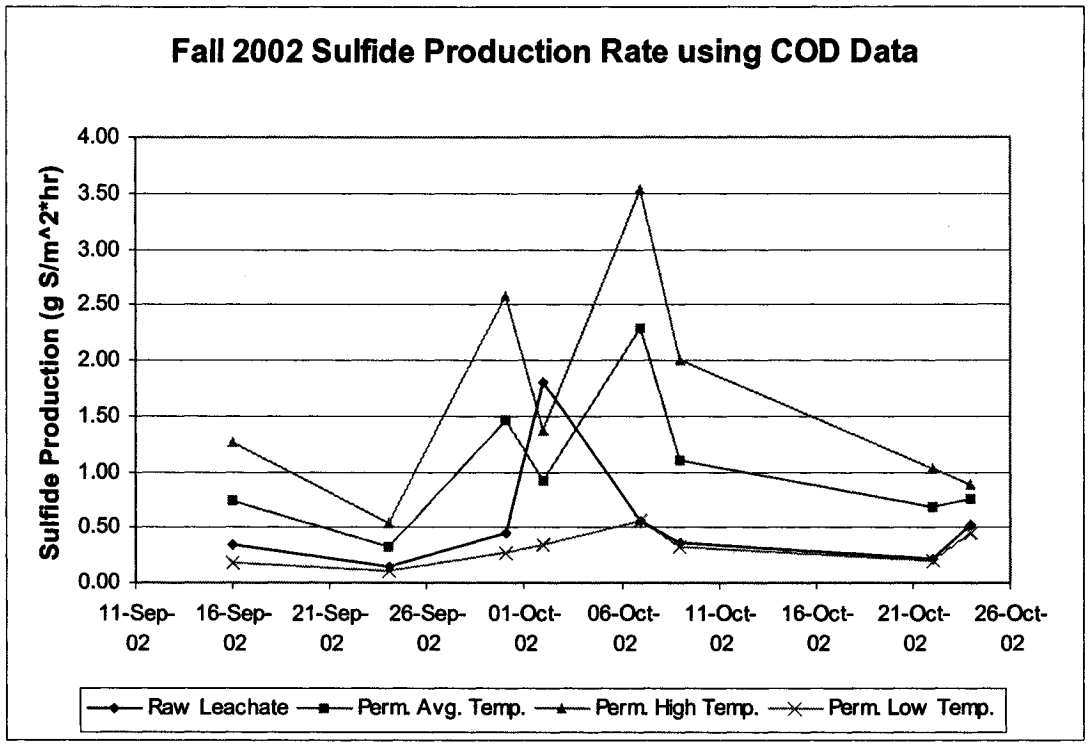


Figure 4-28a Sulphide production rate using fall 2002 [COD] data.

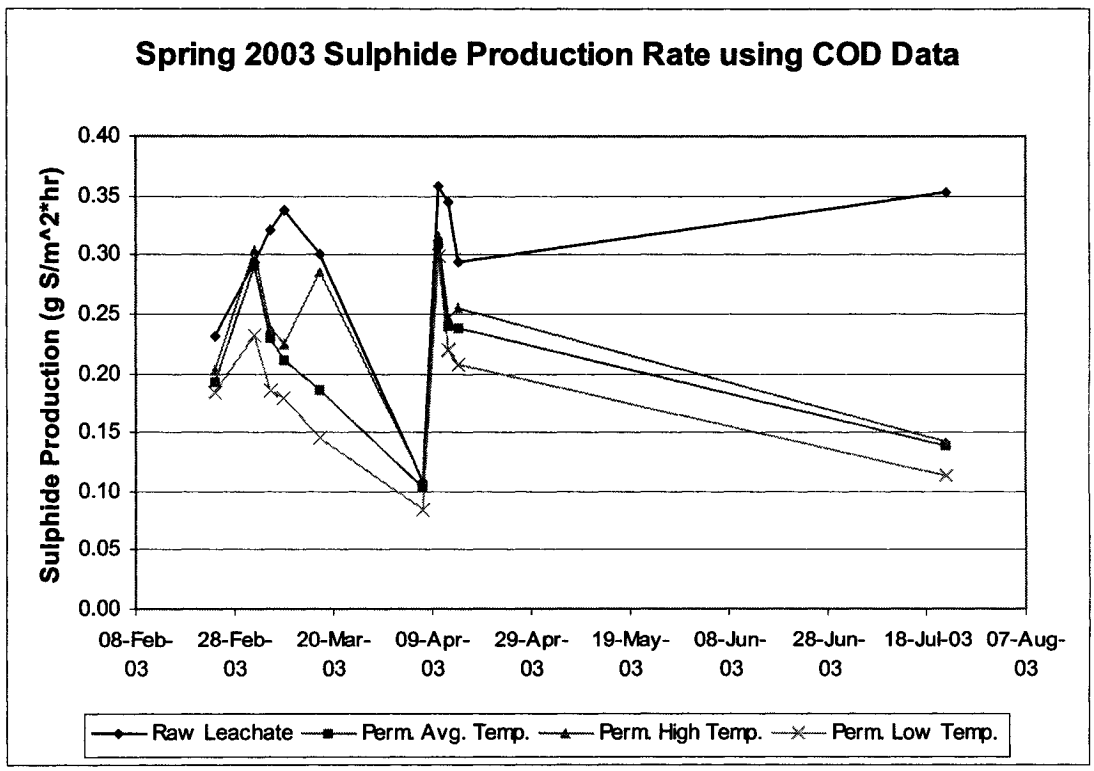


Figure 4-28b Sulphide production rate using spring 2003 [COD] data for the second experimental set-up

The spring SPR results calculated with equation 4-1 showed that generally the permeate-based SPRs were lower than the raw leachate SPR results (see Figure 4-28b). The lowest SPR calculated for Equation 4-1 was 0.8 g S/(m^2·h) given by PT_5 on April 7, 2003 using the low temperature permeate. There were a number of reasons for the difference between the fall and spring SPR results. The first reason was that the temperature did not fluctuate as widely in spring, as the second experimental set-up contained a cooling unit. Secondly, the raw leachate COD concentrations were generally higher in fall (average fall [COD] = 2150 mg/L) than spring (average spring [COD] = 1286 mg/L), and larger MWCO membranes were tested in fall. Only one membrane below 5 KDa was tested in fall (GK_2), but all membranes below 5 KDa were tested in spring. Finally, the combination of lower raw COD concentrations with lower MWCO membranes led to overall lower COD permeate concentrations in the spring and thus lower SPRs (average permeate [COD] for fall = 1543 mg/L and average permeate [COD] for spring = 830 mg/L).

Equation 4-2 used BOD concentration, (COD concentration used in Equation 4-1) and as such could only be applied to the spring 2003 data. Figure 4-29 shows that regardless of temperature the SPR would decrease with membrane leachate treatment. The average SPR for Equation 4-2 was 0.22 g S/(m^2·h) for the raw leachate and 0.14, 0.15 and 0.14 g S/(m^2·h) for the average, highest and lowest temperature permeate. An SPR of 0.02 g S/(m^2·h) or less was calculated for most of the membranes using Equation 4-2 regardless of which temperature was used with the permeate. The highest SPRs were seen in mid-April where the BOD was the highest and the resulting permeate SPRs were also highest as there was little to no removal of BOD at that point as JX_{62700} had a very large MWCO (SPR permeate range of 0.36 to 0.47 g S/(m^2·h) in mid April).

According to both equations, the keys to deterring sulphide formation were high COD and/or BOD reduction combined with temperatures of 20EC or less before injection to a sewer main. Low sulphide problem levels are considered to be less than 0.5 mg S/L. Most of the results found were within the low problem range. The exception to this was the high temperature permeate results for the COD based sulphide production. These were considered a medium problem concentration for corrosion at above 0.5 mg S/L and just above 3.0 mg S/L (Hvited-Jacobsen and Neilsen, 2000).

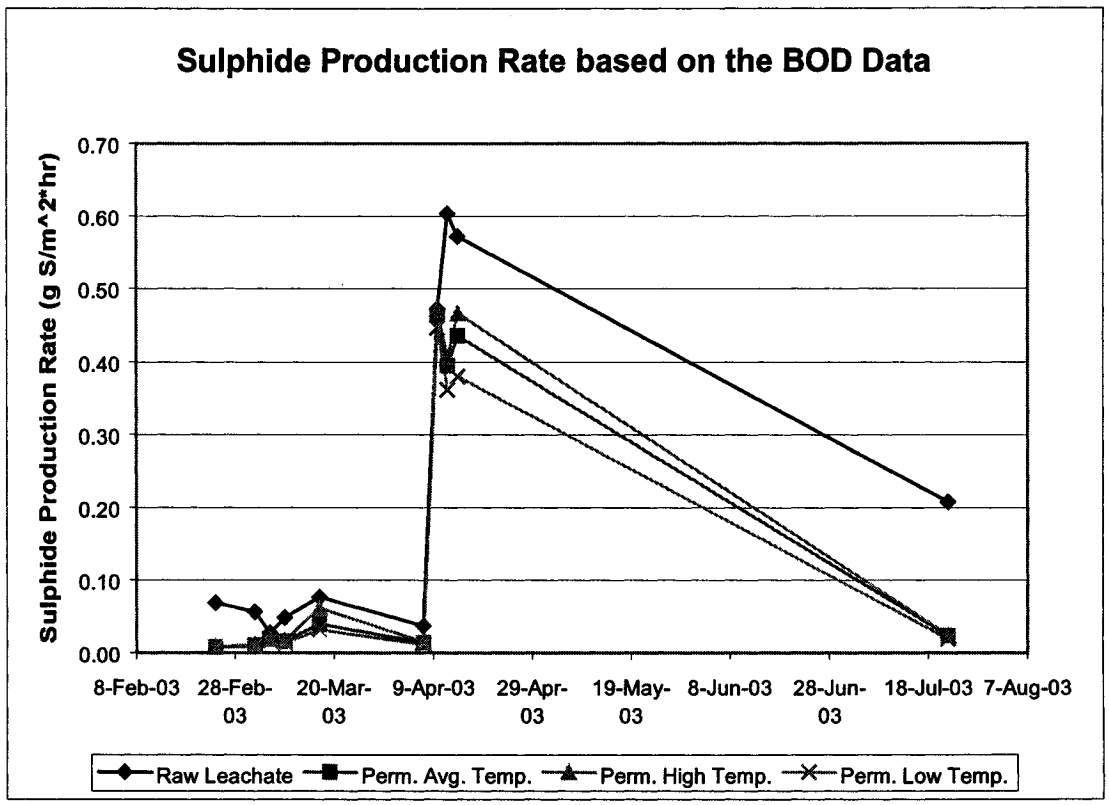


Figure 4-29 Sulphide production rate based on the BOD data

4.3.6 ICP Metal Analysis

4.3.6.1 Characterization of the Leachate Based on ICP Results

The leachate samples were analyzed for the following elements: magnesium (Mg), calcium (Ca), potassium (K), sodium (Na), aluminium (Al), barium (Ba), boron (B), cadmium (Cd), chromium (Cr), cobalt (Co), copper (Cu), iron (Fe), lead (Pb), manganese (Mn), nickel (Ni), silicon (Si), strontium (Sr), zinc (Zn), phosphorous (P) and sulphur (S). Of these elements most did not show any clear seasonal change (Appendix I for ICP data and seasonal graphs). Those elements that showed slight seasonal variations were: Al, Ba, Cd, B, Cr, Co, Mn and P. Some of the elements analyzed were below the ICP detection limit, for example Al and Cd were below detection limits in fall 2002, while Pb and Fe were below detection in winter spring and summer 2003 (Appendix I for all ICP data).

The most important cations in the leachate were the alkaline and alkaline-earth metals, which were also the findings of Park, *et al.* (2001) and these concentrations are highlighted in Table 4-15. Table 4-15 shows the average concentrations of ICP elemental results for both the 2002 and 2003 time frames of the project. Kjeldsen *et al.* (2002) gave the ranges for acid and methanogenic phase landfills for Ca, Mg, Fe, Mn and Zn (Table 4-15). According to these values this leachate was closely related to a methanogenic leachate which shows lower values of these parameters due to the increased pH and thus enhanced sorption and precipitation (Kjeldsen *et al.*,2002) .

There was a higher concentration of Sr than other heavy metals in the raw leachate (13.0 and 18.5 mg/L), but the low Fe concentrations (10.7 and 0.0 mg/L) were unexpected given the black colour of the leachate which was often attributed to Fe in the literature (Kjeldsen *et al.*, 2002). It was thought that Fe in the system might have existed as iron oxide in the suspended solids. Colloids have an affinity for heavy metals and though toxic metals or heavy metals levels in solution tested were generally low, there may have been a significant component adsorbed onto colloids which were removed prior to ICP analysis. No standard protocols for leachate sampling, filtration, and storage of leachate samples exist to date (Kjeldsen *et al.*, 2002). The two heavy metals of higher concentration were Sr and B (Table 4-15).

Table 4-15 Average concentrations of elements analyzed by ICP, with alkaline and alkaline-earth metals highlighted.

Element	Fall 2002	Spring 2003	Acid Phase*		Methanogenic Phase*	
			Range	Average	Range	Average
	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)
Magnesium	124	97	50-1150	470	40-350	180
Calcium	85	88	10-2500	1200	20-600	60
Potassium	736	477				
Sodium	1571	1122				
Aluminium	<0.01	0.72				
Barium	0.33	7.24				
Boron	11.34	0.06				
Cadmium	<0.001	1.17				
Chromium	0.07	4.60				
Cobalt	0.03	0.01				
Copper	0.13	0.13				
Iron	10.53	<0.01	20-2100	780	3-280	15
Lead	0.02	<0.001				
Manganese	0.17	0.03	0.3-65	25	0.03-45	0.7
Nickel	0.20	0.18				
Silicon	11.70	8.69				
Strontium	13.00	18.53				
Zinc	0.64	0.28				
Phosphorous	3.13	6.31				
Sulphur	12.98	22.64	0.1-120	5	0.03-4	0.6

***Acid phase and methanogenic phase values were taken from Kjeldsen *et al.*, 2002.**

A note must be made of the significance of heavy metals in leachate. Less than 0.02% of heavy metals received at landfills are found in leachate within a 30 year time span (Kjeldsen *et al.*, 2002). Both precipitation and sorption are believed to be significant for metal immobilization within the landfill, especially at the neutral to higher pHs of the methanogenic phase (landfill leachate is in reduced state) when sorptive capacity is higher. As sulphide is formed from sulphate reduction heavy metals form complexes and precipitate out of solution also leading to lower overall metal concentation in leachate (Kjeldsen *et al.*, 2002). The formation of precipitates within the landfill indicates again that a large portion of the metals in leachate would be complexed as metal sulphides or metal hydroxides.

4.3.6.2 Metals Removal

The majority of the elements studied were below the sewer use by-law requirements prior to treatment (i.e. Al, Co, Cu, Fe, Mn, Pb, Ni, and Zn) meaning that

treatment of these metals and those not listed in the bylaw (Mg, Ca, Na, Si, Sr, P and S-sulphate and hydrogen sulphide are monitored) was a non-issue in terms of sewage line discharge. Elements that showed concentration levels above the sewer use by-laws are summarised in Table 4-16.

Samples were taken during the circulation run to examine how the metals content in leachate changed over time in the system. Most elements studied were found to decrease over time or show little to no change over the circulation study. Only sulphur levels increased over the time of a run. The following elements generally decreased over time: Ca, K, Sr and P. Some elements showed a general decrease and then increased near the end of the run: Mg, Ba, B, Si, and Ni (see Appendix I for graphical representation of circulation results).

Table 4-16 List of elements that exceeded the sewer use bylaw values

Element	Sewer Use By-Law		Description of results
	Maximum (mg/L)	Limit (mg/L)	
Barium	1.2		• Fall 2002 all results below limits • Spring and winter 2003 all results above limits
Boron	2		• Fall 2002 all results above • Spring and winter 2003 all results below
Cadmium	1	1	• Fall 2002 all results below. • Spring and winter all permeate results above and all fresh leachate levels below.
Chromium	5	5	• Fall all results below • Spring and winter most results are below limits with the following exceptions:
March 10, 2003 – GK_2 – 5.80 mg Cr/L, Fresh – 0.56 mg Cr/L Permeate April 7, 2003 – PT_5 – 5.96 mg Cr/L Fresh – 0.34 mg Cr/L Permeate July 22, 2003 – GH_1 – 8.06 mg Cr/L Fresh – 0.08 mg Cr/L Permeate			

In general, most elements studied did not show any percent removal with the majority of membranes used, based on the concentrations reported, only those elements that showed positive corrected removals above 5% are presented in Table 4-17. The best percent removals were placed in bold for each element and the runs for which the raw leachate needed to be estimated from the concentrate were highlighted (the raw leachate

was estimated using methods previously described in the COD section 4.3.2). For all of the raw ICP data with calculated removals see Appendix I.

To examine how metals and other elements studied were removed their charge, atomic weight, ionic and atomic radii were examined (Table 4-18)(Petrucci and Harwood, 1993). The most readily removed elements are highlighted in Table 4-18, along with the 5 largest atomic masses and radii in bold. Neither charge, atomic mass, atomic or ionic radii seemed to effect the overall removal of the elements in question. The atomic properties were not thought to be of significance to removals in UF and MF membranes, thought they normally are considered in NF and RO. The pore size of the UF and MF membranes make size of molecules and particles more important to removals than charge and elemental size.

The reason for the broad range of membranes showing Cr and Ni removal was not determined based on either membrane material types, or atomic properties. GH_1 was the only membrane which removed some percentage of most elements, those corrected removal values are rewritten in Table 4-18. There was no correlation noted between the charge, atomic mass, or either radius for the level of removal shown by GH_1. Strontium for example had one of the highest concentrations in the raw leachate, along with one of the highest atomic weights, atomic radius and ionic radius and a charge of 2+, but it had one of the lowest correct removals (8%). The strontium corrected removal did not compare to the 75% B removal, an element with one of the lowest radii and mass. The 3+ charge on the boron may have been a reason for it's higher percent removal, but this would mean Al should have had a higher percent removal as well.

Table 4-17 Elements and membranes that gave positive corrected percent removals.

	Membrane	Date Run	Removal %	Change %	Corrected Removal %
Magnesium	GH_1	07/23/2003	22	-7	**16**
	GM4	03/07/2003	12	1	12
Calcium	GH_1	07/23/2003	87	-69	17
	PT_5	03/17/2003	53	-8	**46**
Potassium	GH_1	07/23/2003	14	-3	11
	ER_{30}	10/02/2002	16	4	**16**
Sodium	GH_1	07/23/2003	12	-3	9
	GM4	03/07/2003	10	5	**10**
	ER_{30}	10/02/2002	13	5	13
	JX_{62700}	10/22/2002	10	1	**10**
Aluminium	GH_1	02/24/2003	44	-26	18
	GH_1	07/23/2003	69	-61	8
	GK_2	03/10/2003	43	-17	**26**
	PT_5	03/17/2003	22	-1	21
Barium	GH_1	07/23/2003	8	-2	**6**
	MW_{100}	10/09/2002	56	-50	**6**
Boron	GH_1	02/24/2003	75	6	**75**
	GK_2	03/10/2003	76	14	**76**
	GM_4	03/07/2003	74	3	74
	PT_5	03/17/2003	60	17	60
	PT_5	04/07/2003	56	0	56
	ER_{30}	10/02/2002	10	3	10
	EW_{60}	03/04/2003	76	3	76
Cadmium	EW_{60}	03/04/2003	51	2	51
Chromium	GH_1	02/24/2003	92	-35	57
	GH_1	07/22/2003	99	-58	41
	GK_2	03/10/2003	90	-26	64
	GM_4	03/07/2003	84	-10	74
	PT_5	10/07/2002	51	-5	46
	PT_5	03/17/2003	85	-4	**81**
	PT_5	04/07/2003	94	-25	70
	ER_{30}	10/02/2002	48	-10	38
	EW_{60}	03/04/2003	87	-10	77
	MW_{100}	10/09/2002	36	78	36
	JX_{62700}	10/22/2002	33	0	33
Chromium	JX_{62700}	10/24/2002	36	19	36
	JX_{62700}	04/10/2003	71	-46	26
Cobalt	PT_5	10/07/2002	43	0	43
	MW_{100}	10/09/2002	41	18	41
	JX_{62700}	10/22/2002	31	27	31
	JX_{62700}	10/24/2002	45	30	**45**

	Membrane	Date Run	Removal %	Change %	Corrected Removal %
Copper	GH_1	02/24/2003	43	-14	**29**
	GK_2	03/10/2003	33	-11	22
	GM_4	03/07/2003	17	41	17
	PT_5	03/17/2003	33	-17	17
	EW_{60}	03/04/2003	29	41	29
Iron	PT_5	10/07/2002	90	-57	33
	ER_{30}	10/02/2002	68	-36	32
	MW_{100}	10/09/2002	79	-49	30
	JX_{62700}	10/22/2002	74	-60	14
	JX_{62700}	10/24/2002	52	21	**52**
Lead	No removal or below detection levels				
Manganese	GH_1	02/24/2003	58	19	58
	GK_2	03/10/2003	74	19	**74**
	GM_4	03/07/2003	65	-29	36
	PT_5	04/07/2003	8	15	8
	EW_{60}	03/04/2003	70	-29	41
	JX_{62700}	04/10/2003	14	0	14
Nickel	GH_1	07/22/2003	70	8	**70**
	GK_2	03/10/2003	54	22	54
	GM_4	03/07/2003	53	15	53
	PT_5	10/07/2002	27	3	27
	PT_5	03/17/2003	26	15	26
	PT_5	04/07/2003	15	10	15
	ER_{30}	10/02/2002	25	15	25
	EW_{60}	03/04/2003	63	15	63
	MW_{100}	10/09/2002	17	18	17
	JX_{62700}	10/22/2002	9	24	9
	JX_{62700}	10/24/2002	32	26	32
Silicon	GM_4	03/07/2003	8	-1	7
	ER_{30}	10/02/2002	14	-1	**13**
Strontium	GH_1	02/24/2003	14	-6	8
	GH_1	07/22/2003	47	-42	5
	GK_2	03/10/2003	14	-4	**10**
Zinc	PT_5	10/07/2002	58	-19	39
	ER_{30}	10/02/2002	68	14	**68**
	EW_{60}	03/04/2003	31	14	31
	MW_{100}	10/09/2002	78	-31	47
	JX_{62700}	10/24/2002	43	76	43
Phosphorous	GH_1	07/22/2003	74	-44	30
	GK_2	03/10/2003	11	5	11
	PT_5	03/17/2003	27	0	27
	PT_5	04/07/2003	11	13	11
	EW_{60}	03/04/2003	24	7	24

	Membrane	Date Run	Removal %	Change %	Corrected Removal %
Phosphorous	MW_{100}	10/09/2002	71	71	71
	JX_{62700}	10/22/2002	54	-6	48
	JX_{62700}	10/24/2002	55	41	**55**
Sulphur	GH_1	07/22/2003	52	10	**52**
	PT_5	10/07/2002	62	-37	25
	PT_5	03/17/2003	9	16	9
	PT_5	04/07/2003	23	3	23
	JX_{62700}	10/22/2002	13	20	13
	JX_{62700}	04/10/2003	7	-1	6

Table 4-18 Atomic information on elements studied (Most readily removed elements are highlighted and the largest masses and radii are in bold) (Petrucci and Harwood, 1993).

	Charge	Atomic Mass	Ionic Radius (pm)	Atomic Radius (pm)	GH_1 corrected Percent Removal (%)
Magnesium	2+	24.31	65	160	16
Calcium	2+	40.08	**99**	**197**	17
Potassium	1+	39.10	**133**	**227**	11
Sodium	1+	22.99	95	**186**	9
Aluminium	3+	26.98	50	143	18
Barium	2+	**137.33**	**149**	**217**	6
Boron	3+	10.81	---	88	**75**
Cadmium	2+	**112.41**	97	149	---
Chromium	2+	52.00	84	125	57
	3+	52.00	64	125	
Cobalt	2+	58.93	74	125	---
	3+	58.93	63	125	
Copper	1+	63.55	96	128	29
	2+	63.55	72	128	
Iron	2+	55.85	76	124	---
	3+	55.85	64	124	
Lead	2+	**207.20**	**133**	146	---
Manganese	2+	54.94	80	124	58
Nickel	2+	92.91	72	125	70
Silicon	4+	28.09	---	117	---
Strontium	2+	**87.62**	**113**	**215**	8
Zinc	2+	65.39	83	133	---
Phosphorous	3-	30.97	212	110	30
Sulphur	2-	32.07	---	117	52

The best overall percent removals were given by GH_1 and PT_5. GK_2 and GM_4 also gave good percent removals, but not for the same range of elements (see Table 4-15). The low molecular weight membranes, however, did not provide all of the metals removals as some of the larger MWCO UF membranes (>10 KDa) and the MF membrane used gave good removals for select elements. The elements most readily treated using UF and MF membranes were Cr and Ni, with Al, B, Co, Fe, Mn, Zn and P all being removed by a range of membrane sizes to varying degrees.

Cr was the most readily removed using all membrane MWCOs with a maximum percent removal of 81% using PT_5 at a raw leachate Cr concentration of 2.77 mg/L. The lowest Cr percent removal was 26% using JX_{62700} with a raw leachate Cr concentration of 2.24 mg/L. The Cr concentrations ranged from 0.06 mg/L to 8.06 mg/L. Ni was also readily removed with a wide range of membrane MWCOs. GH_1 gave the highest Ni percent removals at 70%, while the lowest percent Ni removal was 9% with JX_{62700}. Ni had a concentration range of 0.09 mg/L to 0.35 mg/L.

B was of particular concern to the Trail Road Landfill as it tended to be above the sewer-use bylaw maximum allowable discharge of 2 mg/L. Over the course of this project, however, only the samples taken in the fall 2002 were above 2 mg/L, while all samples taken in 2003 were below this. All of the positive B corrected percent removals happened in 2003, with most membranes at 5 KDa or below, though EW_{60} also showed a high percent removal at 75%. GH_1 and GK_2 gave B percent removals at 75 and 76%.

Only Cr and Ni had enough samples from runs of the same membrane MWCO to determine the effect of leachate Cr or Ni concentration on percent removal. Neither showed a correlation with concentration and percent correct removals for a given MWCO (see Figures 4-30a and b). None of the elements tested showed a correlation between percent removals and MWCO.

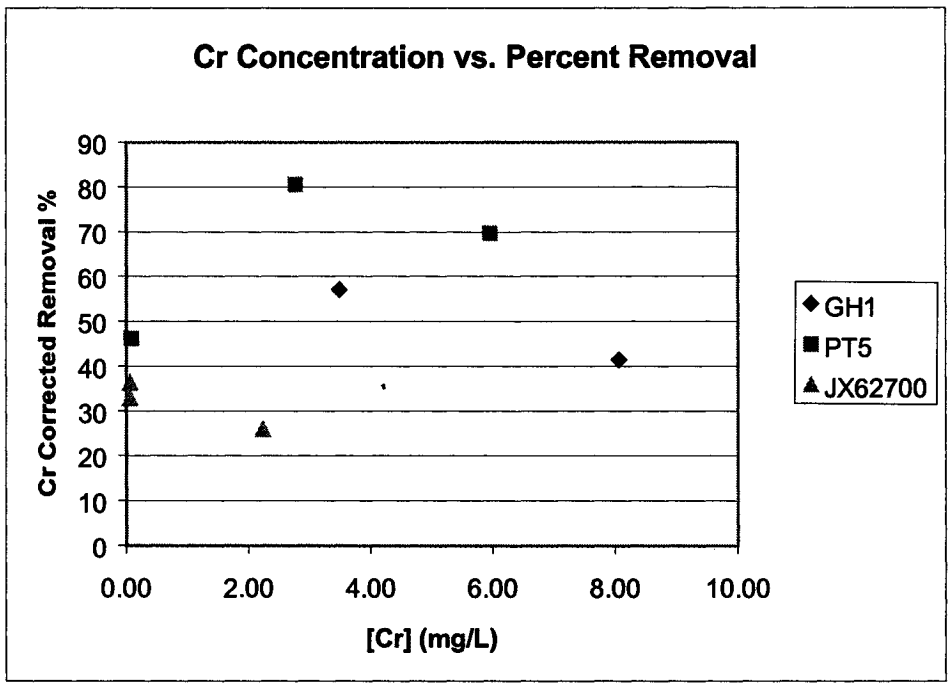


Figure 4-30a Raw leachate Cr concentration versus Cr percent removal.

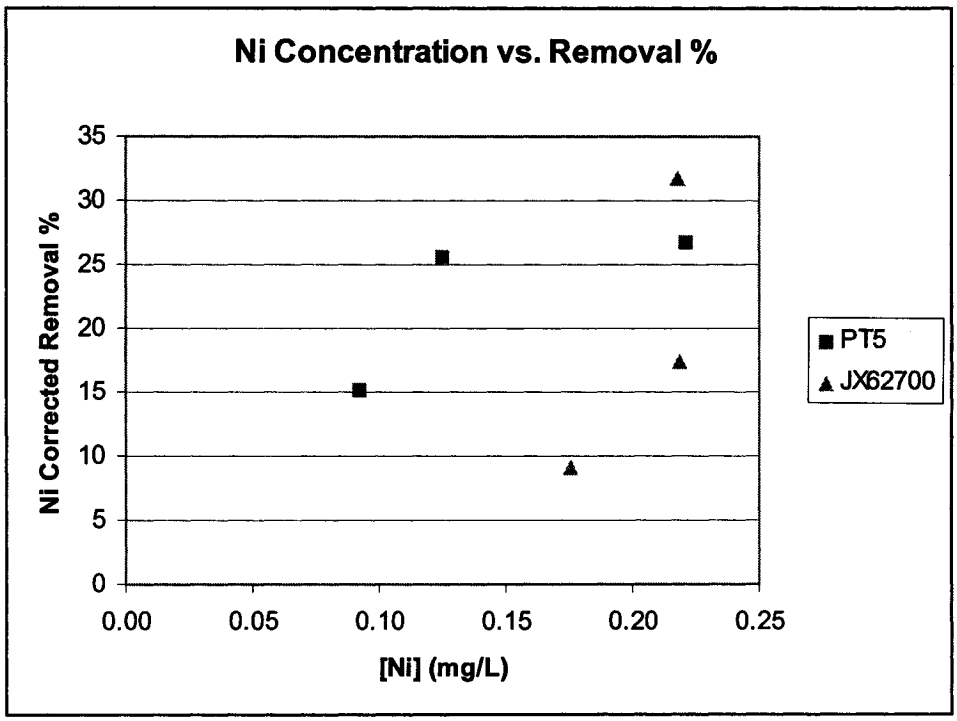


Figure 4-30b Raw leachate Ni concentration versus Ni percent removal.

4.4 Fouling Analysis

Membrane fouling analysis was performed using SEM images and EDX analysis. Only surface fouling could be examined using these methods as the membranes were mounted with the membrane backing adhered to a slide. The SEM data was mostly qualitative in nature. The size of the membrane coupons precluded SEM examination of their entire surfaces, and therefore only small samples were examined. The images gave approximate sizes for the foulants and evidence regarding foulant deposition.

EDX allowed elemental analysis of the foulants. EDX results give elemental peaks for each element in relative terms, not specific values or weights. This can be difficult in a slurry type situation, where various solids are mixed and thus there can be a number of elements in one EDX scan, with little to no indication of the overall chemical composition of the main foulant. Some of the foulants can be isolated and compared to geological mineral standards also examined using EDX. EDX was also used to analyze clean membranes for background readings and the scale deposits seen on the inside of tanks and pipes.

Figure 4-31a, b and c showed the clean JX_{62700} membrane at various magnifications. There were still some particles on the membrane, which were consistent with dust based on their Si content. In these photographs the membrane pore matrix was visible, and variations in the membrane surface and weaknesses in the overall structure were noted. Figure 4-32 showed the virgin GK_2 membrane at a similar magnification to Figure 4-31a, but the matrix was not visible. The particles on the membrane surface may have been due to the dusty conditions of the shed at the Trail Road Landfill, though the membranes were kept in sealed tubes the dust was all pervasive. Figure 4-33 showed the variation in membrane structures, as magnifications of 10μm showed that the PT_5 membrane had a needle-like structure, possibly caused by the membrane backing material. These needles-like structures were analysed via EDX and had the same composition as the membrane and therefore were not extraneous depositions.

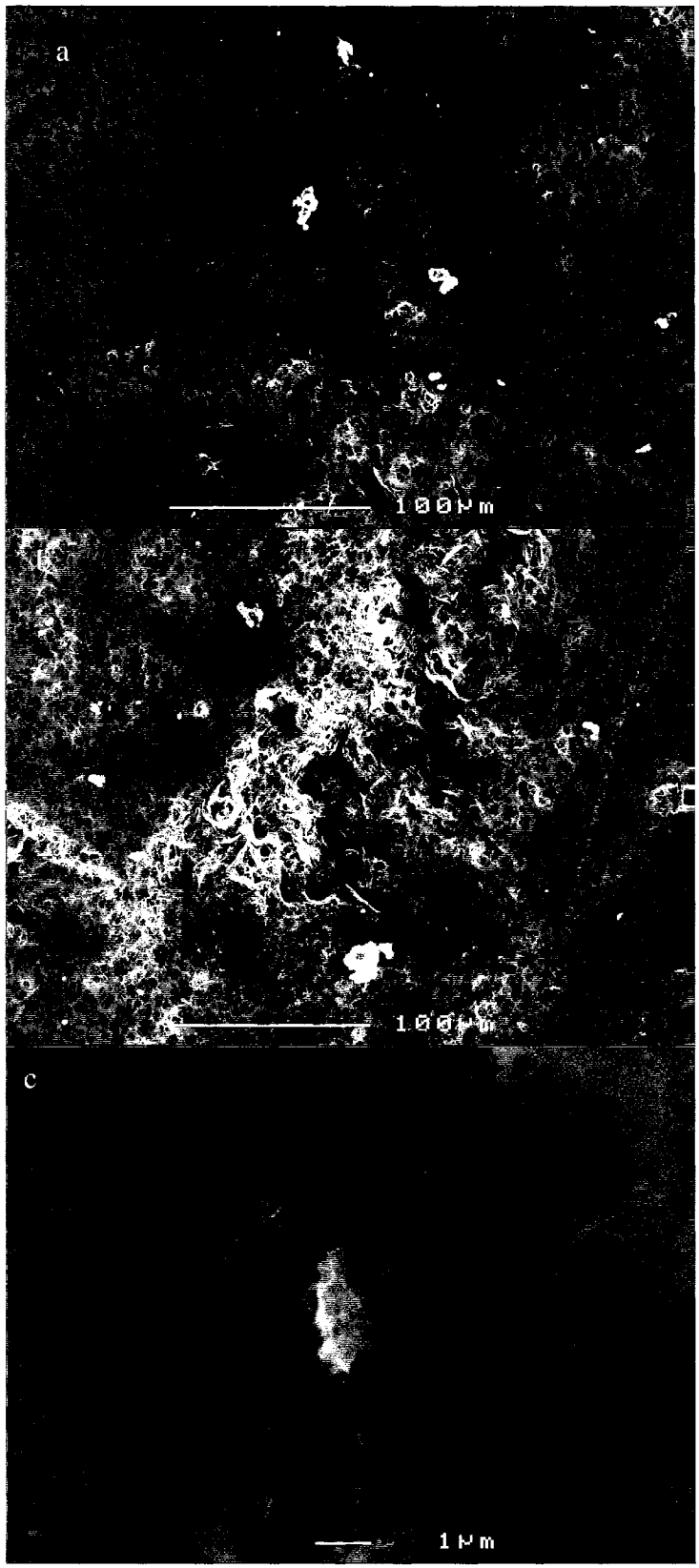


Figure 4-31 a, b, and c JX_{62700} SEM pictures of clean membranes.

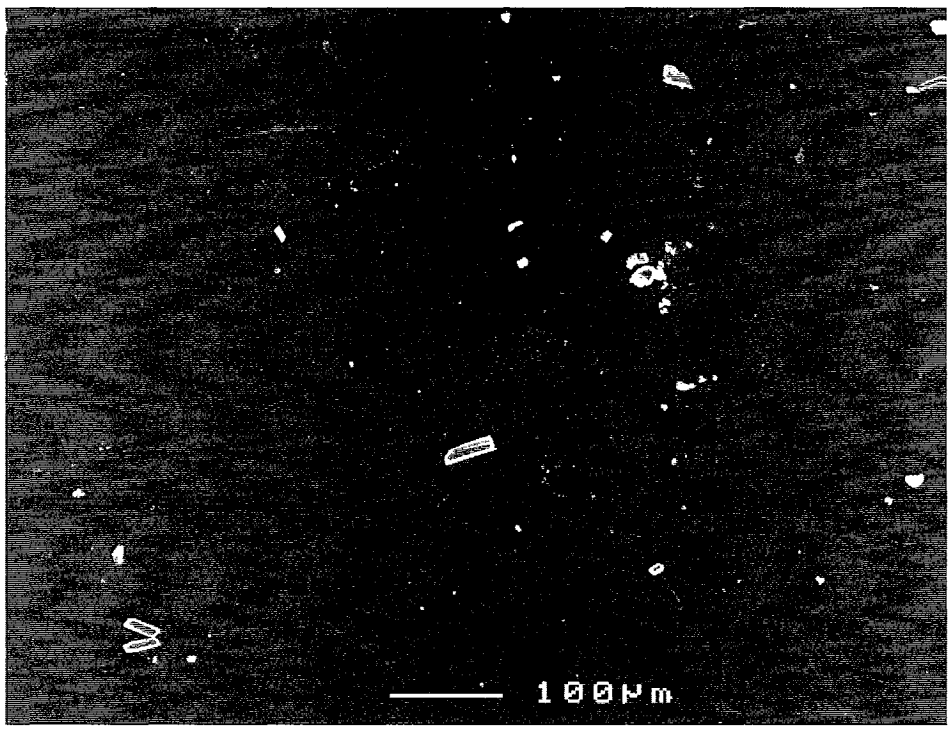


Figure 4-32 GK_2 'clean' membrane sample, showing signs of dust deposition using SEM.

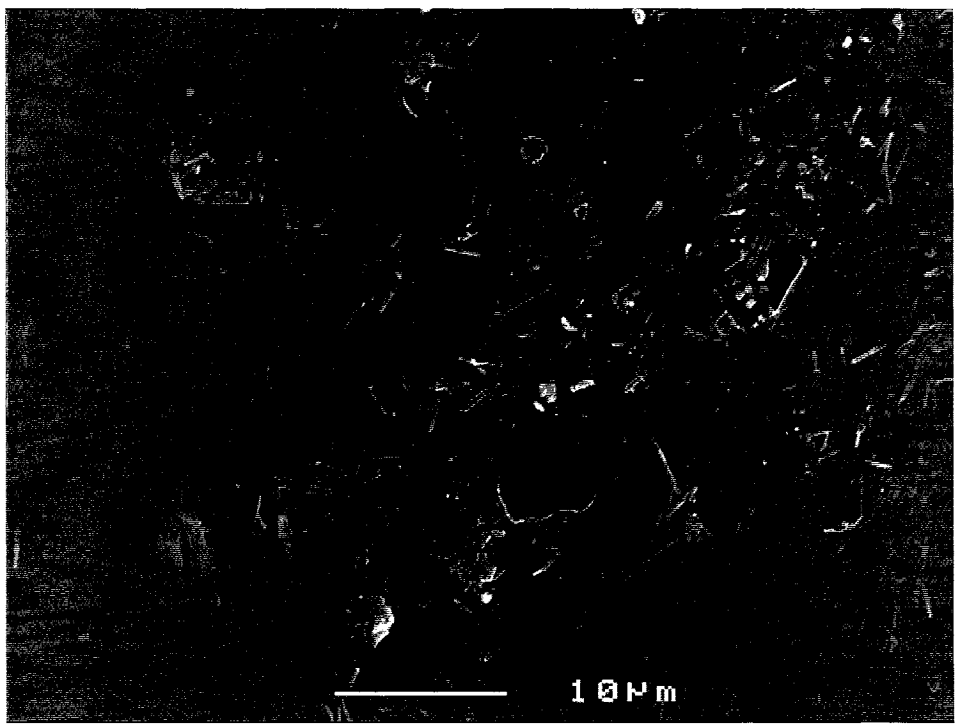


Figure 4-33 Clean PT_5 membrane showing an interesting needle-like matrix using SEM.

There were also particles which resembled plant matter on some membranes 'clean' and fouled, which in retrospect may have been small wood fibres from the board upon which the membranes were cut and dried. Some of the deposits on the 'clean' membranes were calcium based indicating that some part of the membrane curing process may have involved calcium-based solutions.

4.4.1 Scale Analysis using EDX

Samples of scale were taken from the feed tank, membrane, pump and pipe surfaces. The samples were collected on October 2, 2002 from the feed tank, October 4, 2002 from feed tank, October 24, 2002 from the membrane surface, and July 4, 2003 from the pump impellers. These samples generally had a flaky quality and tended to coat surfaces (Figure 4-34 for samples of scale collected from the bottom of the feed tank on October 2, 2003). Analysis of this material was deemed to be important to determine the main system scalants. All scale samples were tested with a drop of 10% HCl to examine if they effervesced and all but one did, indicating a proportion of the scale was likely composed of $CaCO_3$ (calcite). The EDX analysis supported this finding.

A large Ca peak was seen for all scale EDX analysis with the exception of one, which was an almost black sludge taken off the surface of a membrane in late October when the leachate was very dark. The black sludge was also the only non-effervescent scale sample. This scale showed a Fe peak with slightly smaller Ca, P, Cl and O peaks (Figure 4-35). This indicated that for the dark black leachate, iron oxide might have played a significant role in producing the black colour. Iron was not seen in the ICP analysis of this period, but iron oxides would have been removed in filtration of the ICP sample as only dissolved species were analysed. Metal sulphides may have also been a source of colour in the leachate, but the scan of this scale had too many peaks to positively identify a sulphide compound.

Figure 4-36 showed the EDX Ca peak for the scale sample taken in July, which was representative of the three brown scales tested. The first two scales tested were examined at a higher resolution and showed very small Sr and Fe peaks, which were just barely detectable.

The mulch used as a cover at the landfill was also sampled to examine if any of this fine organic matter was making its way into the leachate and depositing on the membranes during a run. The majority of the peaks seen in this analysis were Si and O or C, Ca, O, and K. As mentioned in the previous section, there were deposits of plant-like material on some membranes and it was not until the entire body of SEM data was analyzed that the possibility of deposition from the wooden cutting block and not the landfill mulch was realized. Once examined under SEM, the mulch plant fibre material looked more degraded than those seen on the membranes. Figure 4-37a showed the mulch SEM image and Figure 4-37b showed an example of the plant fibre seen on a 'clean' GK membrane.

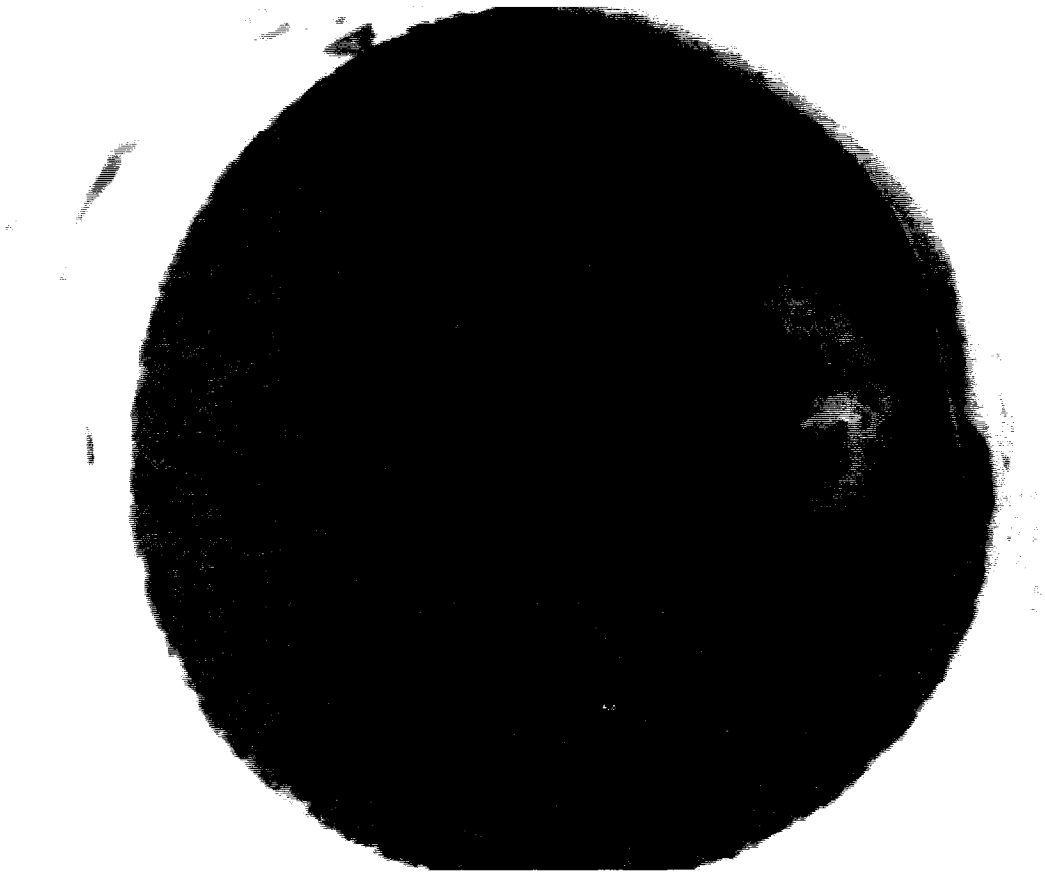


Figure 4-34 Scale sample taken from the bottom of the feed tank in the bottom of an 8 cm diameter bottle on October 2, 2003.

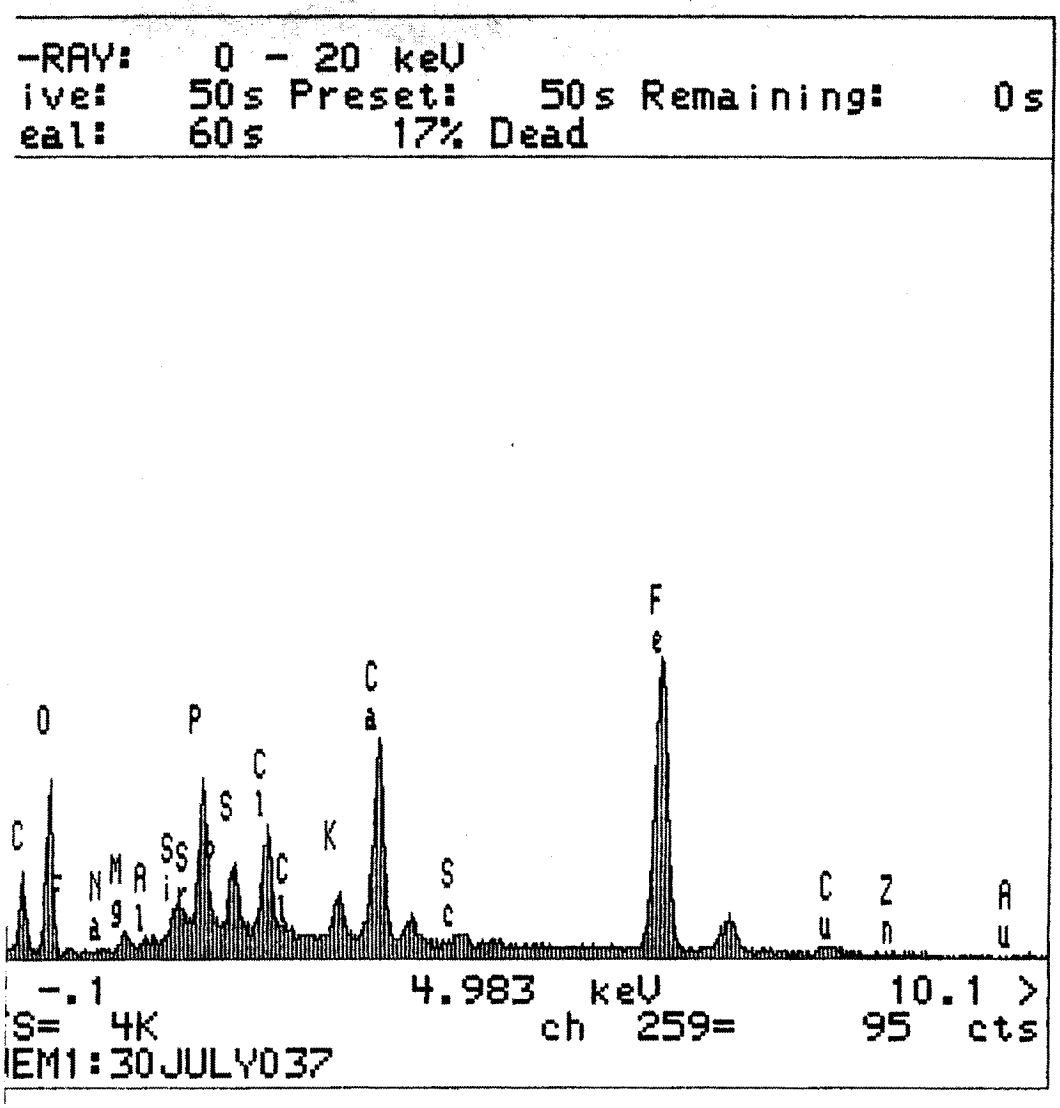


Figure 4-35 EDX scan for dark scale collected on October 24, 2002.

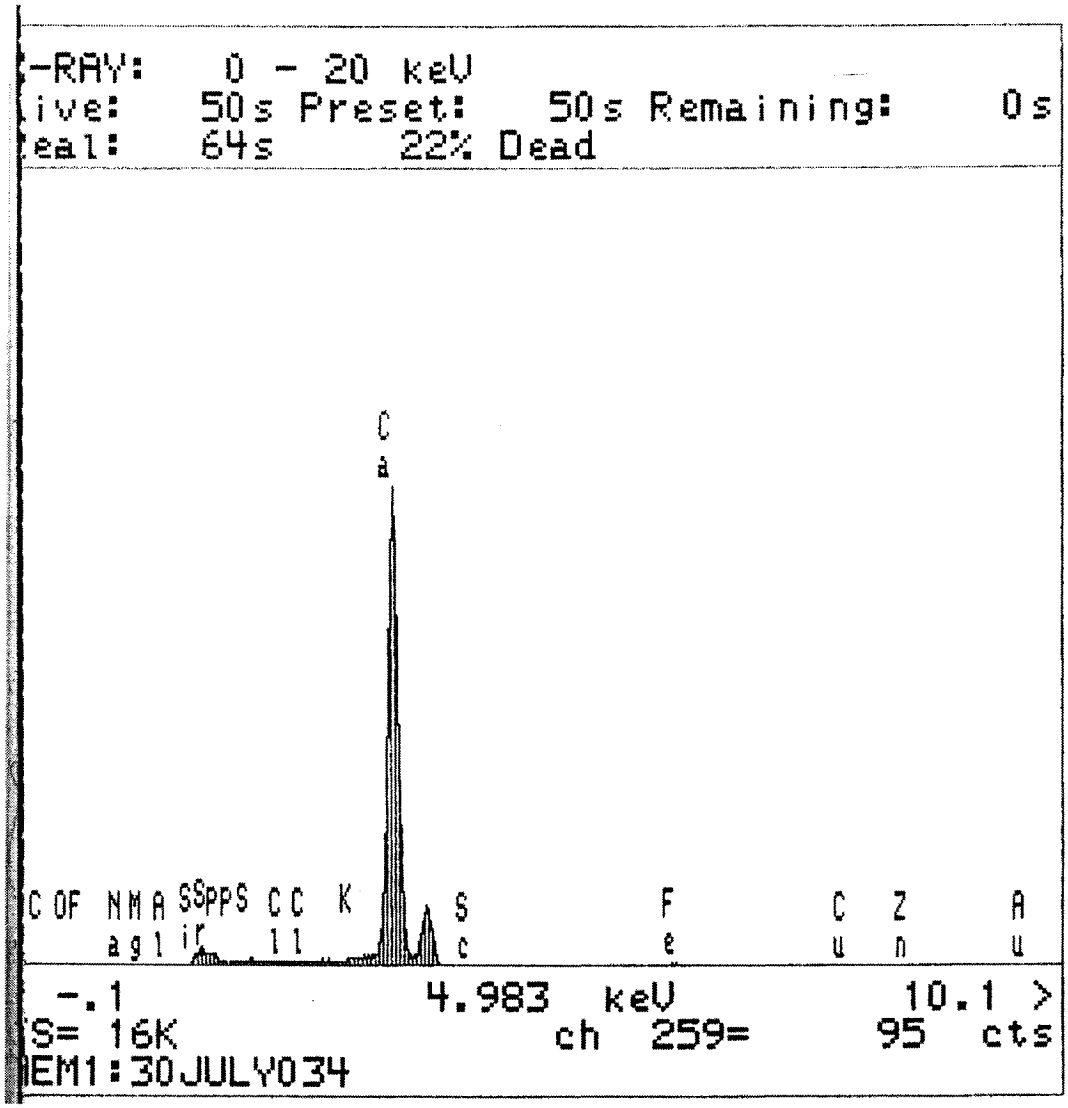


Figure 4-36 EDX scan for light scale collected on July 4, 2003.

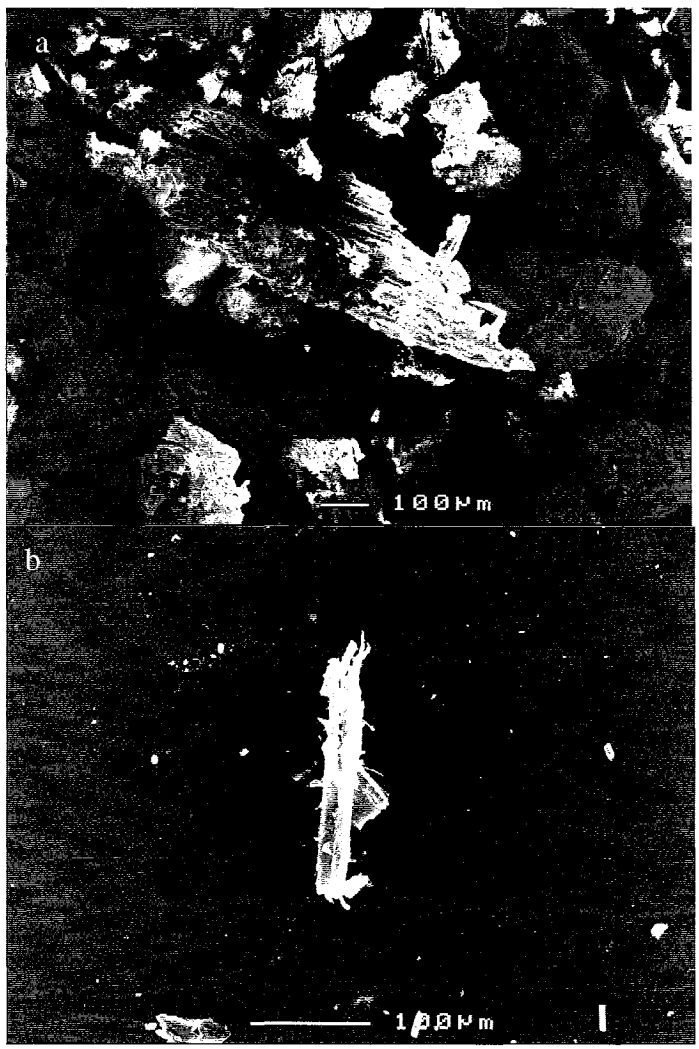


Figure 4-37a and b Plant material in the landfill mulch and the plant material seen on a 'clean' GK membrane, SEM photo.

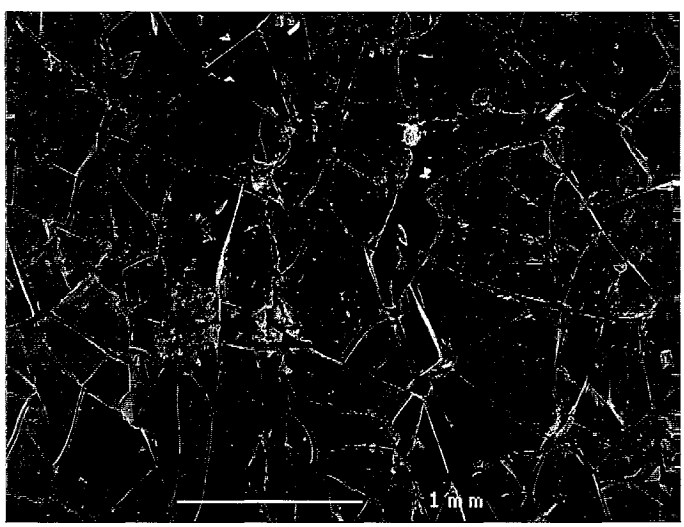


Figure 4-38 Black scale sample from October 24, 2002 SEM photo.

The scales gave interesting SEM photographs with flaky general structures and nodule formations which tested as Ca (EDX), with the exception of course of the black sludge scale sample which looked different from the other scales as it tended to form glassy sheets rather than flaky masses (Figure 4-39). It was on the October 2nd and 4th scales that the possibility of microorganisms in or on the scales was discovered. As the EDX analysis was done using a carbon coating this meant that analysing for organisms via EDX was impossible, but the appearance of rod like structures in the SEM indicated the presence of bacilli microorganisms. Figure 4-39 showed the flaky structure of the scale collected on October 2, 2002. Figures 4-40a, b, c and d showed the overall nodules of Ca and the exploration of an indentation in the scale in which rod like structures were noted.

Figure 4-39 October 2, 2002 scale showing an overall flaky structure in SEM photo.

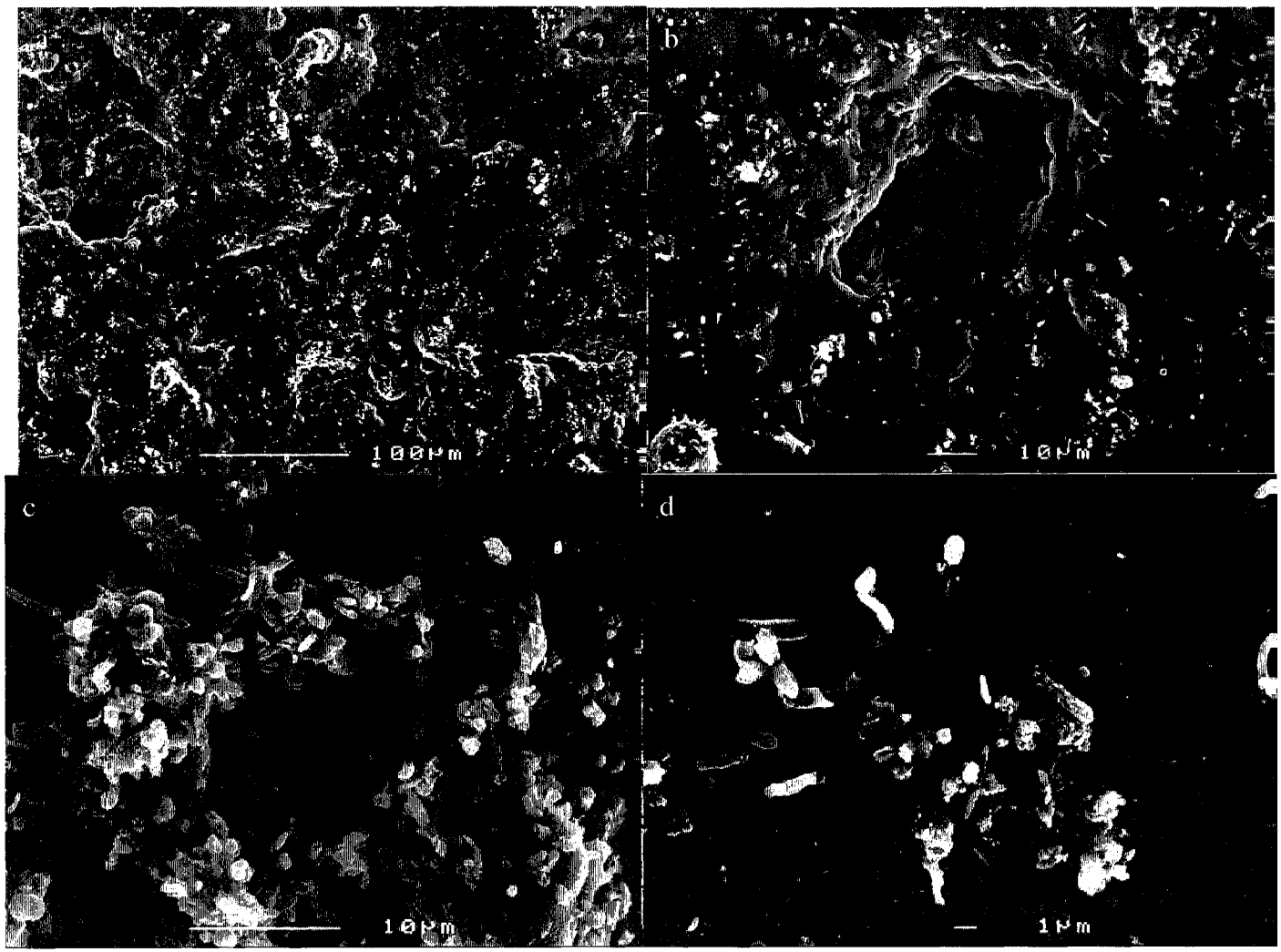


Figure 4-40a, b, c, and d October 4, 2002 scale sample with (a) overall view of scale showing a coating of calcite nodules, (b and c) magnification of depressions with rounded calcite nodules, (c and d) rod like structures seen that may be microorganisms (SEM photos).

4.4.2 Fouled Membrane SEM/EDX Results

4.4.2.1 Methods used in Determining Foulants

The first sample analysed using SEM was a trial run to examine whether the method of drying a fouled membrane would affect the sample quality, and for preliminary examinations of the deposits on the membranes. The M-180 membrane tested on August 7, 2002 was the first sample analyzed, and during this run a line ruptured ending the run at 9 hours 36 minutes, therefore the membrane could be sacrificed as the run was incomplete. The membrane was coated in a film of brown leachate deposit material and the entire membrane coupon was destroyed during the initial examination.

Three different methods of drying were employed: air-drying, freeze-drying, and freeze-drying with a heating plate. Despite the method of drying employed the foulant on the membrane cracked (Figure 4-41a, b and c). Therefore since all methods of drying lead to the development of cracks, future samples were freeze-dried as it was considered the safest method to avoid any possible liquid contamination of the SEM vacuum with leachate.

The deposits analysed by EDX were mainly Ca (3.8×10^4 counts) with smaller Fe and P peaks (5×10^3 counts)(Figure 4-42). The count levels represent the strength of signal returned to the SEM from EDX analysis. The coating over the entire membrane proved to be higher in Fe (3.4×10^3 counts) with a much smaller Ca peak (1.2×10^3) and even smaller P, Si and S peaks (8×10^2, 5×10^2, 4.5×10^2 respectively). The printouts from these preliminary EDX scans displayed the counts on the graph, but took 5 to 10 minutes per graph to print and could not be used when there were a number of samples to examine in a day due to time constraints and operator availability. A more basic and faster printout was used for the rest of the samples, therefore the counts could not be given, only relative abundances as seen in Figures 4-35 and 4-36.

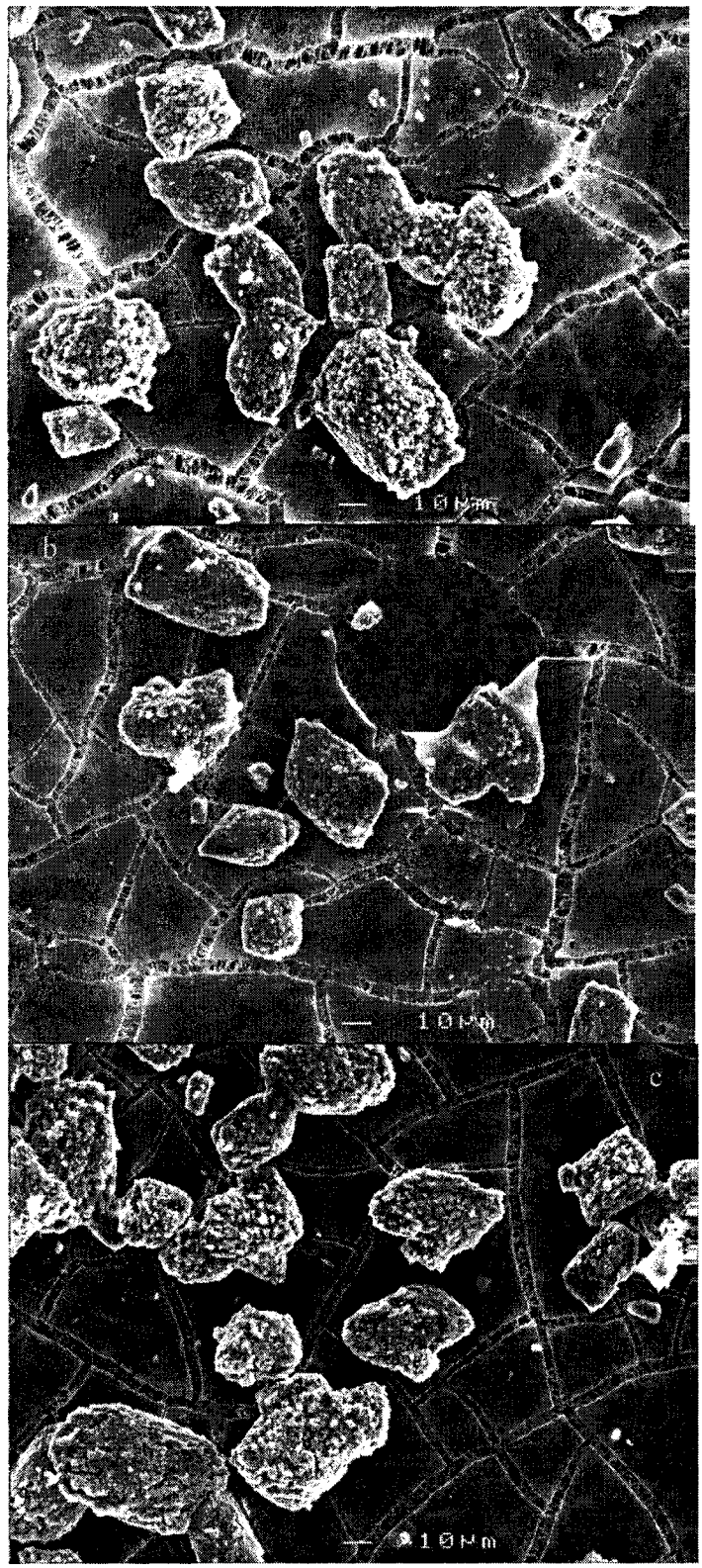


Figure 4-41 a, b and c. Preliminary fouled membrane examinations with three methods of drying used (a) air dried, (b) freeze-dried with heating element, and (c) freeze-dried without heat (SEM images).

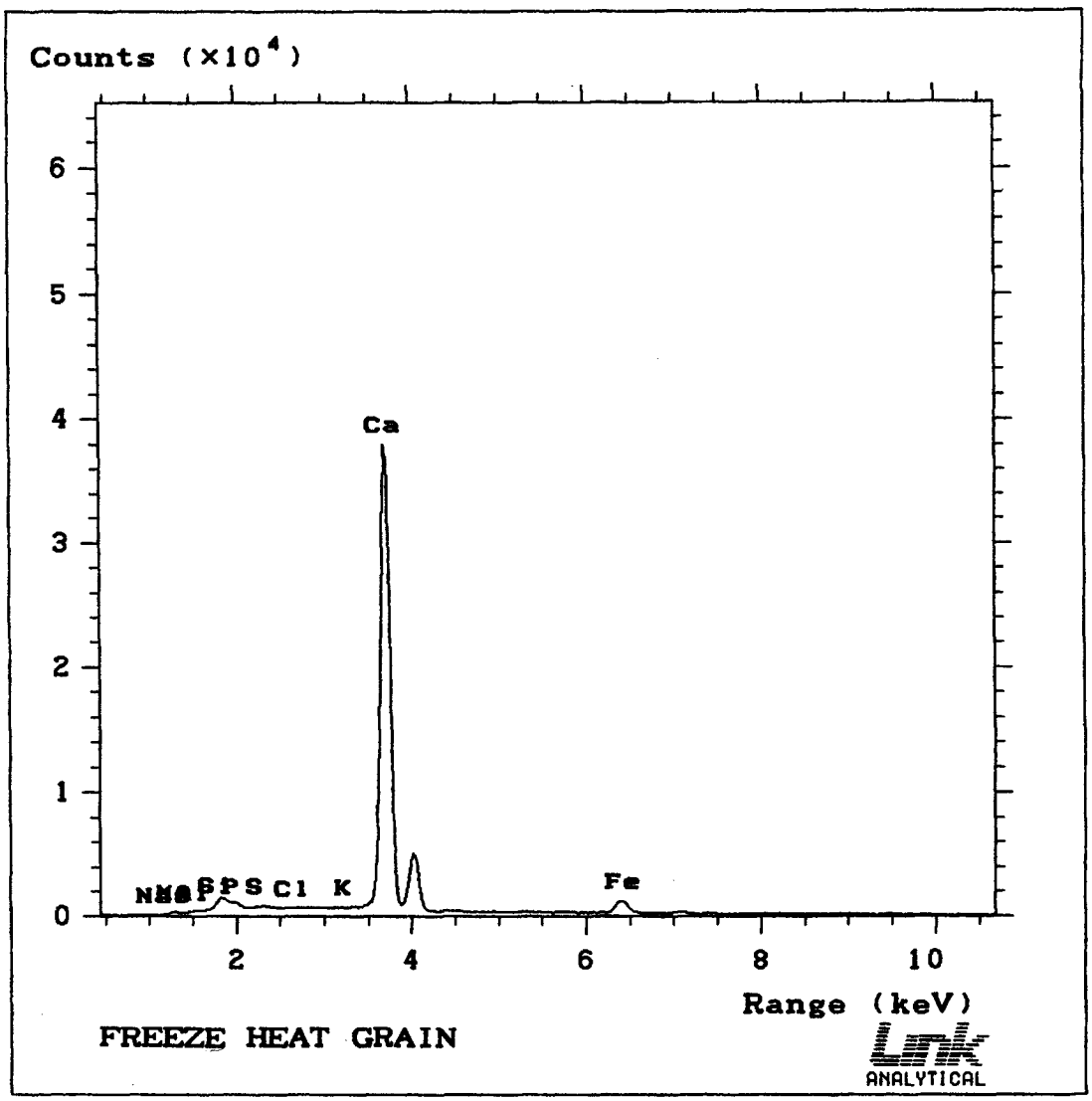


Figure 4-42 EDX scan of a calcite deposition on M-180 membrane run August 7, 2002 and freeze-dried with heating pad.

A standard examination protocol was developed from the preliminary samples. SEM photos were taken of the overall membrane sample at 100 μm and from there greater magnifications of specific deposits were examined. Given the number of samples and the number of pictures, only representative photos with the analysis of characteristic deposits were chosen to display in the main body of the thesis, however all of the SEM photos and EDX pictures were placed on the Appendix CD under Appendix K.

There were few standards that could be compared with the foulants analysed. The three geological standards used were calcite ($CaCO_3$), dolomite ($CaMg(CO_3)_2$) and iron sulphide (FeS_2) (see Appendix K for standards). These were compared to the EDX scans from the fouled membrane. Given that the leachate deposit was more of a slurry than discrete parts there were very few membrane foulant scans which matched any of the standards exactly.

4.4.2.2 Fall SEM/EDX Fouled Membrane Results

Due to the number of samples analysed and the format of this thesis, the fall 2002 membrane samples and spring 2003 samples will be examined separately. Deposits on the fall membrane samples were mostly calcite and/or iron sulphide. The calcite deposits appeared as bright distinct nodules under SEM while the iron sulphide was a general dark coating over the membrane surface. One problem with diagnosing either of these foulants was the compositions of the membranes. Some membranes contain C and/or S in their composition, which may have accentuated the counts of either element. For example when scanning the PT_5 PES membrane, the calcite deposit scans showed a small sulphur peak probably related to the membrane composition. However, when the fouling layer is fairly thick or dense the elements in the membrane composition do not appear in the scans.

The samples were stored wet in a refrigerator at 4°C before freeze drying during which time some crystals precipitated out. These perfectly formed structures were interesting and gave insight into what was precipitating out or seeding itself in or on the membrane, but they would not have formed in the turbulent flow conditions of the cell (Figure 4-43). The calcite nodules and the overall deposits seen were not thought to be part of this post filtration crystallization/formation due to their shape and distribution over the surface.

A summary of the fall membrane EDX findings was placed into Table 4-19. There was more complexity to each, and membranes of particular interest will be discussed further in this section. All scans and photos for each membrane were placed in Appendix K.

Table 4-19 Fall membrane EDX summary findings.

Membrane	Date	Membrane Material	Foulants
JX_{62700}	Sept. 30, 2002	PVDF (EDX scan gave: C and F with Ca, Cl, Si and S smaller peaks)	• Calcite nodules with small Fe peaks • Fe, Cl, S, and smaller K, Ca and P peaks in general area scans • Some strange seeded crystals of Mg and Cl noted (see Figure 4-43)
	Oct. 22, 2002	Same as above	• Fe peaks with smaller >Ca, >P, >Cl, >K and >S peaks • Some deposits with large P peaks and smaller >Mg and >Fe peaks • Little to no Ca
	Oct. 24, 2002	Same as above	• Mostly Cl and Fe deposits with smaller K • Some crystals with Ca> Ti >and >Si • Again little to no Ca only peaks • Some Mg based crystals were found • Other P and Fe crystals • One Aluminium deposit noted
MW_{100}	Oct. 9, 2002	Ultrafilic (EDX scan gave: C peak)	• Mostly iron sulphide deposits • Lower Ca deposits than normal, K, P and Cl also seen in EDX scan of foulants.
ER_{30}	Oct. 2, 2002	PS (EDX scan: S, C and P)	• Dark area of membrane gave S peaks • Lighter areas had large Ca peaks with smaller >>S and Fe peaks (see Figures 4-44a and b).
QW_{30}	Sept. 12, 2002	Unknown – No Scan	• Calcite nodules with some Fe • Dark area between nodules - Fe and Cl.
GN_{10}	Sept. 16, 2002	Unknown – (EDX scan: S, C and a smaller O peak)	• General scan of membrane area produced a S peak (probably membrane material) • Calcite nodules over surface
PT_5	Oct. 7, 2002	PES (EDX scan: S, C, and P)	• Calcite nodules • Iron Sulphide Coating
GK_2	Sept. 24, 2002	Thin Film (EDX S and C peaks)	• Calcite • The general coating reads as sulphur and the calcite scans showed S as well. The sulphur may be from the membrane itself.

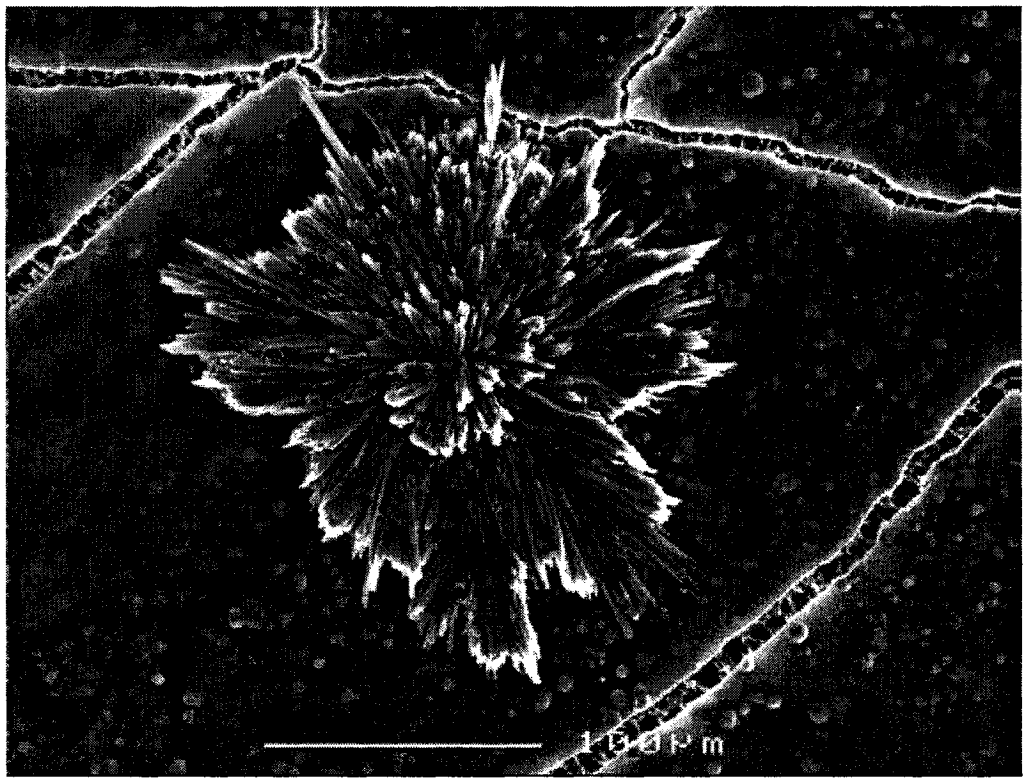


Figure 4-43 Mg and Cl precipitate crystal developed on the membrane after filtration and before drying of the Sept. 30, 2002 JX_{62700} (SEM images).

As mentioned in the ICP section (section 4.3.6) there were considerably higher levels of iron in the fall when compared to the spring, with concentrations ranging from 22 mg/L on October 9, 2002 to 2.80 mg/L on October 24, 2002 and below detection limits (0.01 mg/L) in spring. The iron content seemed to have been both dissolved and colloidal in nature as indicated by the black colour of some leachates in the fall. The colloidal or particulate iron component may have been the reason for iron deposition on the membranes, as few of the membranes were effective in removing elemental iron from the feed stream according to the ICP data.

While most samples showed some form of calcium present on the membranes the later October samples showed almost none (Oct. 22 and 24, 2002), again pointing towards an extremely changeable leachate composition. The October 22, 2003 fresh leachate did not have lower calcium concentrations when compared to other fall samples according to ICP analysis (122 mg/L), but the fresh October 24, 2002 sample did (15 mg/L).

Despite the late fall membranes' lack of calcium deposits, most fall samples were coated in calcium. One sample of interest was the ER_{30} (run September 30, 2002) for which

the calcite fouling was extensive. The sample analysed had a small section on which the fouling layer was removed and several layers of fouling were seen (Figure 4-44a). The darkest area, which was considered to be almost clean membrane, was mostly composed of S, which made sense given that the membrane was composed of PS. The lighter, smooth areas along the periphery of the dark area scanned as Ca with a small S peak, indicating calcite deposition with the underlying membrane itself also being analysed due to the thin nature of the deposit. The white textured areas were Ca with little to no S and some Fe, again indicating calcite, but a thicker deposit and therefore no S peaks originating from the membrane. Also within this thick depositional layer the bacilli-like rod shaped structures were noted, but not on any other Fall 2002 sample (see Figure 4-44b). This suggested that in situations of extreme scaling bio-fouling may occur, as the scale gives a media onto which the microbes can adhere (Figure 4-44b).

The ER_{30} membrane also had dark and light brown areas (35% dark, 65% light) outlining different types of fouling, and the SEM sample was taken on the border of these different coloured fouling deposits. Under SEM, the membrane sample did show different characteristics, with the darker brown area being relatively smooth, while the lighter brown area was textured. Figures 4-45a and b show the dark and the light areas, with the dark showing mostly iron under EDX scan and the light area calcium. The reason for this fouling variation may have been due to entrance and exit effects from the membrane cell or leachate properties which could not be fully explored in this project.

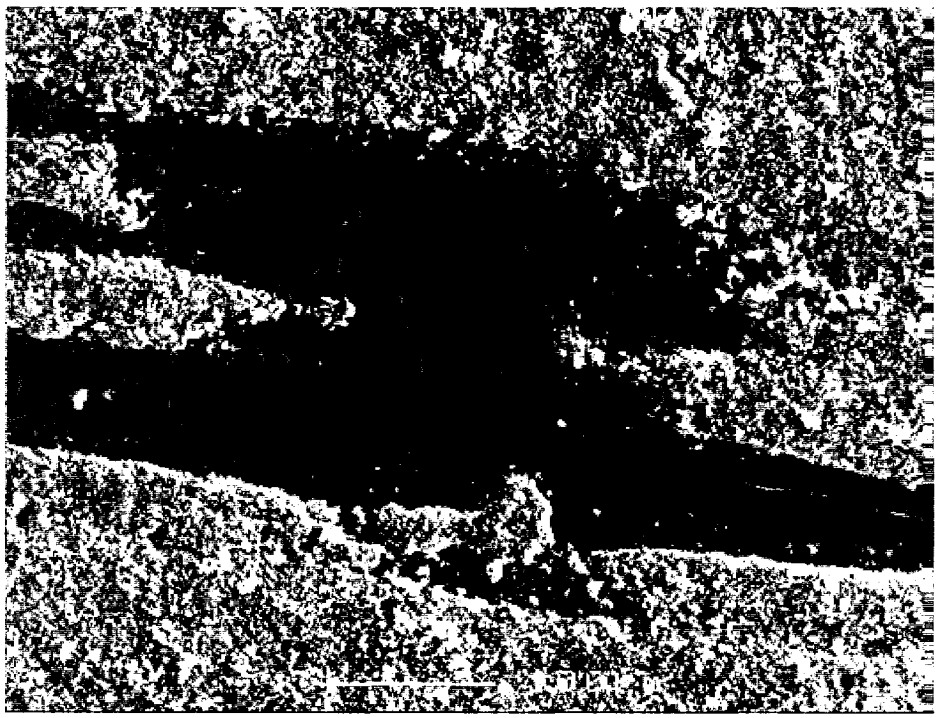


Figure 4-44a ER_{30} Oct. 2, 2002 membrane SEM image of cleaned area.

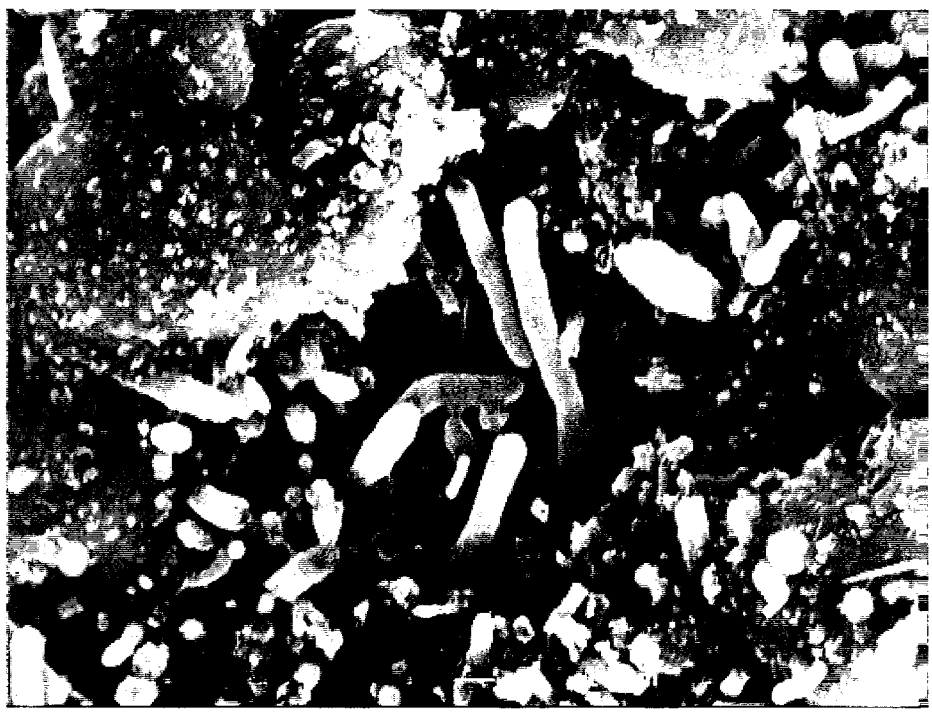


Figure 4-44b ER_{30} Oct. 2, 2002 membrane SEM image of rod-like structures in foulant.

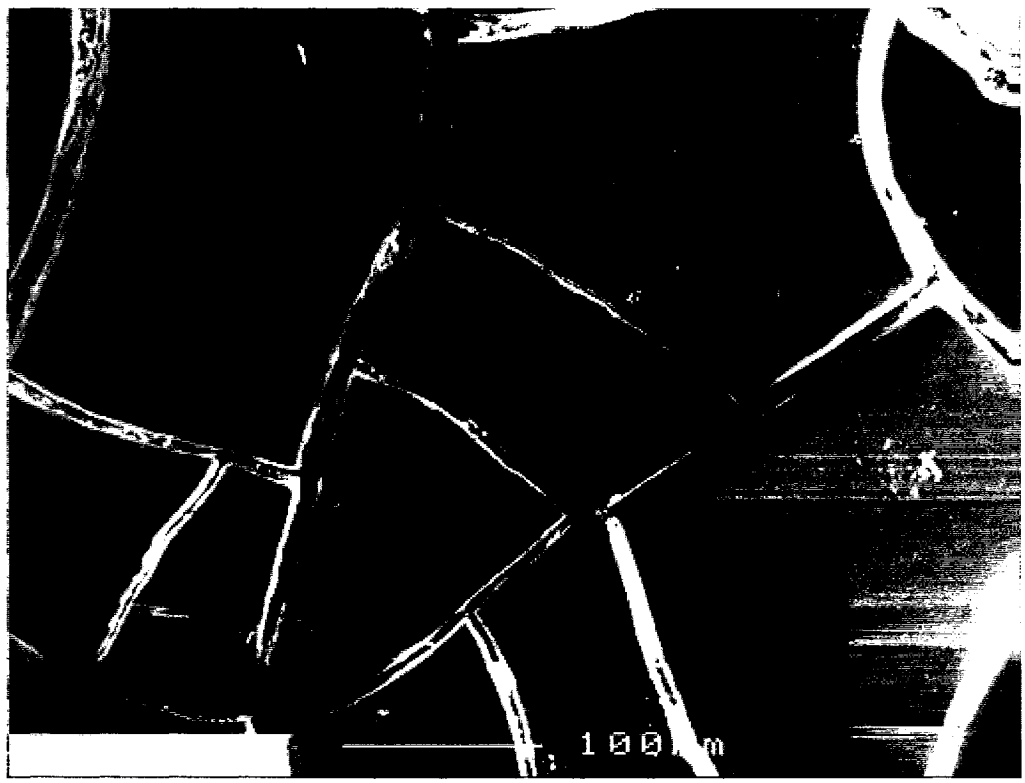


Figure 4-45a SEM image of dark section of ER_{30} membrane sample.

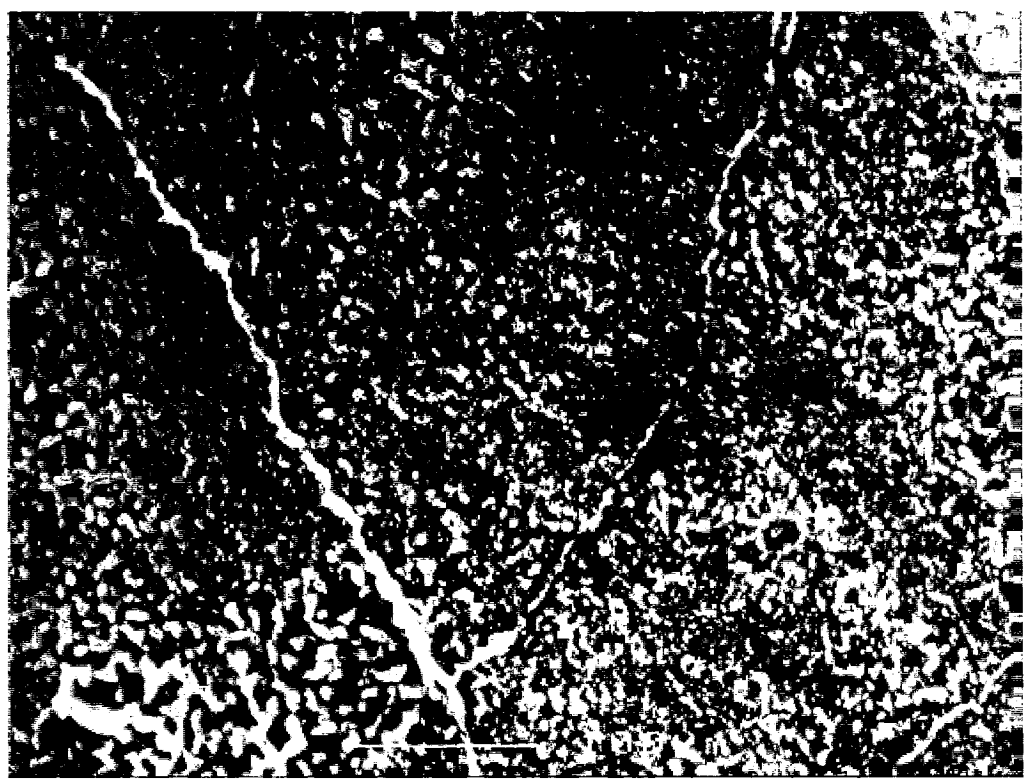


Figure 5-45b Light section of the ER_{30} membrane sample (SEM image).

4.4.2.3 Spring SEM/EDX results

The 'spring 2003' SEM/EDX results included all membranes run in the winter, spring and summer 2003 with the exception of the sequential run JX membranes which will be treated separately in the next section and the GK_2 membrane (run March 10, 2003) which could not be sampled due to extreme cracking and flaking when dried. It was during the spring membrane analysis that the thin window EDX beam current method was introduced to the author. Therefore, the scale samples (discussed in 4.4.1) and fall membrane samples (discussed in section 4.4.2.2) were not analyzed in thin window.

Thin window EDX changed the beam focus, such that C and O could be measured. Thin window scanning was used to scan the standards and most of the spring-run membranes. As mentioned in Chapter 3, standard EDX scans of the membrane samples involved coating them in carbon, which would then increase the amount of overall carbon measured. The calcite standard was not coated in carbon as it was an alternately prepared standard. Therefore, the membrane samples examined under thin-window may give high carbon peaks, but this may be a peak enhanced or caused by the carbon coating.

Overall, the spring membranes did not show as many calcium deposits and the analyses tended to give more general 'sludge-like' readings with few elements dominating, but rather a range of elements at approximately the same levels. This decrease in distinct deposits made it harder to draw conclusions as to the nature of the precipitate. Table 4-20 gives the results from the EDX analysis of the spring 2003 membranes. S, Fe, P, Cl and Ca figure largely throughout the 2003 runs. The spring membranes may have dolomite deposits rather than calcite given the increased geometric structures. Cl and S also figure more predominantly in the spring membranes than the fall samples. The S deposits may be artefact from the membrane composition, though the strength of the S peaks indicates a deposit.

Table 4-20 Spring 2003 EDX summary of results.

Membrane	Date	Membrane Material	Foulants
EW_{60}	March 4, 2003	PS (S and C peaks)	• S and C peaks (membrane) with either Cl>Fe>K>P; Cl>Na>K>Fe and P; or Ca>Cl>P>Fe. • The range of elements found in different areas of the membrane indicated a sludge deposit rather than distinct foulants. • Ca nodules appear to be there, but were covered by an overall deposit, which explained the presence of elements other than Ca in EDX scans of these areas (see Figure 4-46)
ER_{30}	April 15, 2003	PS (S and C peaks)	• Single high S peaks were noted without C, indicating a type of S deposit on the overall membrane. Some of the overall S peaks scans also had smaller P peaks accompanying. • There are very few light deposits on this mostly dark membrane with most identified being above 100 μm, some deposits had single Fe peaks, while most others had Ca peaks in combination with other elements (see Figure 4-47) • The Ca deposits did not appear as rounded as previous nodules and contain either: P, Si, Mg or S as elements of lesser concentration.
PT_5	March 17, 2003	PES (C and S peaks)	• Membrane appeared rougher than most other spring membrane samples as it seemed to have more distinct foulant deposits. • However, most scans showed a sludge-like character to even the distinct foulant deposits, with many equally concentrated elements being identified. • The overall deposit was a combination of C, O and S (membrane) with Ca>P>K>Fe>Ca. • Several strong Ca peaks were given for the distinct deposit in combination with S, C and O (membrane), Cl>Si>Mg>P>Al>Sr>Fe (with Mg this may be dolomite) • A coating of sludge seemed to be overall distinct deposits.

PT_5	April 7, 2003	PES (C and S peaks)	• This membrane had the most distinct deposits of all the spring membranes, most had Ca peaks with other elements in lesser concentration. This indicated again an overall sludge deposit. The Ca deposits were more geometrical than the Fall 2002 deposits (see Figures 4-48a and b). Dolomite tends to be more geometrical in formation than calcite. • The overall deposit on the membrane was found to be predominantly Fe and Cl.
GM_4	March 10, 2003	Thin Film (EDX S and C peaks)	• Mostly sludge deposits consisting of Ca>Fe>P>S>C>O (membrane), or S+C+O (membrane) with Cl>K>Na>Ca • Few bright individual deposits of S
GH_1	February 24, 2003	Thin Film (EDX S and C peaks)	• Not as much deposited on membrane, may be due to line blockages found later • Most scans show either S and C alone, probably membrane material or show them in combination with other elements such as Ca and Fe; and Cl>K>Na.
	July 25, 2003	Thin Film (EDX S and C peaks)	• Coating on membrane was sulphur based. • White deposits were found to be either Cl and Al; Fe; Si and >>Al; or Ca.

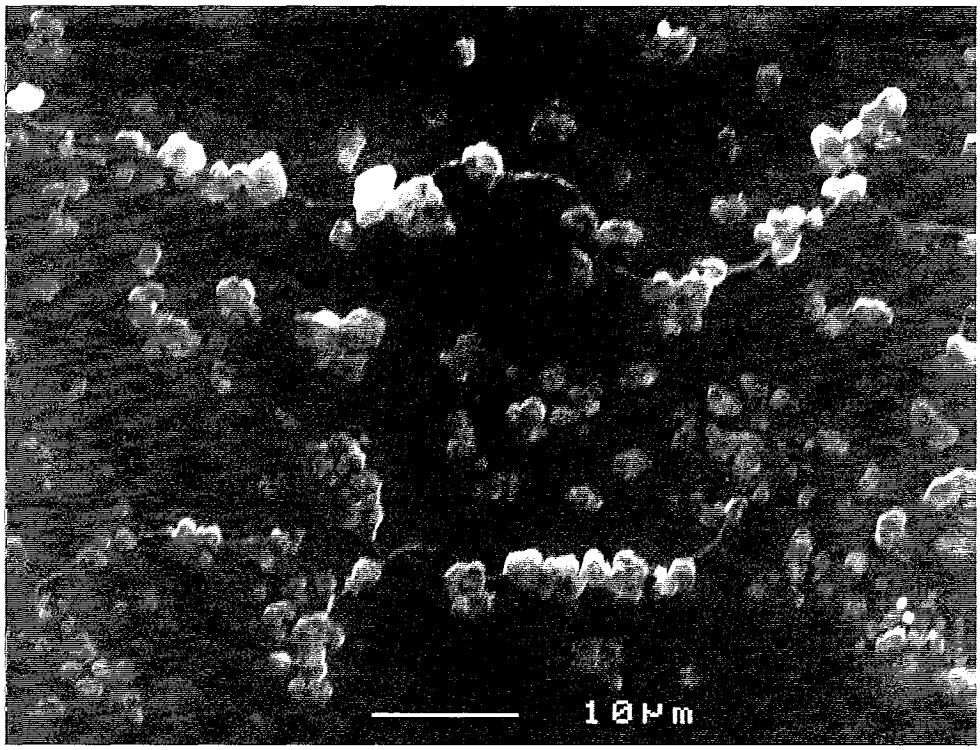


Figure 4-46 EW_{60} March 4. 2003 – Nodules of calcite seem to be present, but clear EDX readings were not obtained due an overall coating (SEM image).

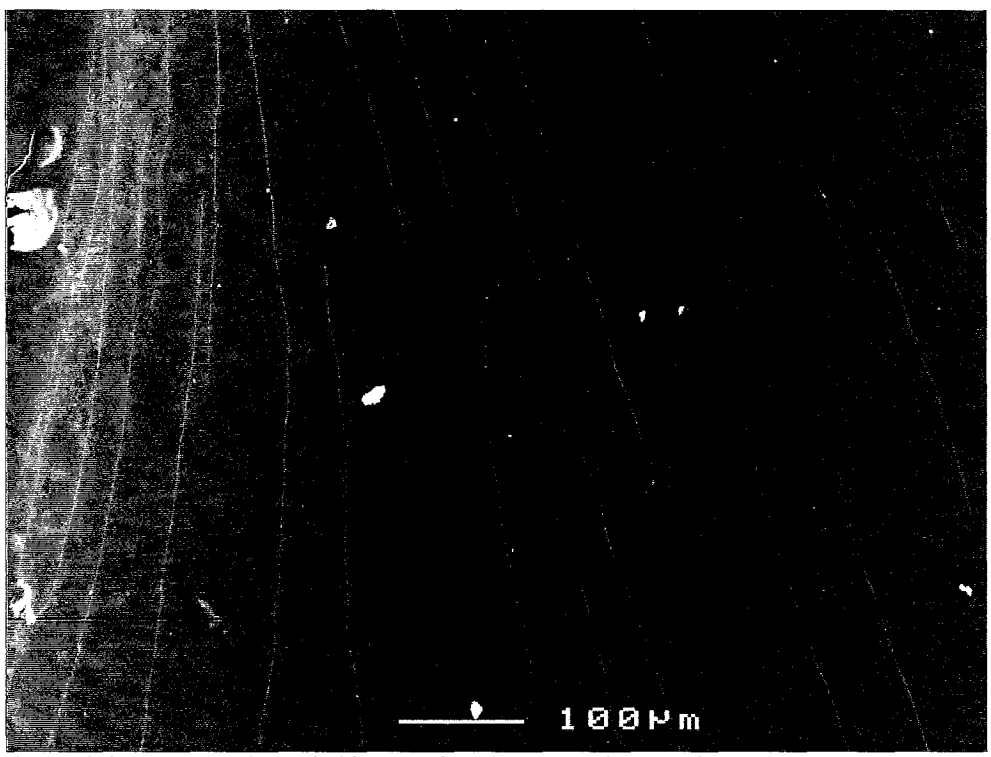


Figure 4-47 ER_{30}, April 15, 2003. Very few light deposits on this mostly dark membrane (SEM image).

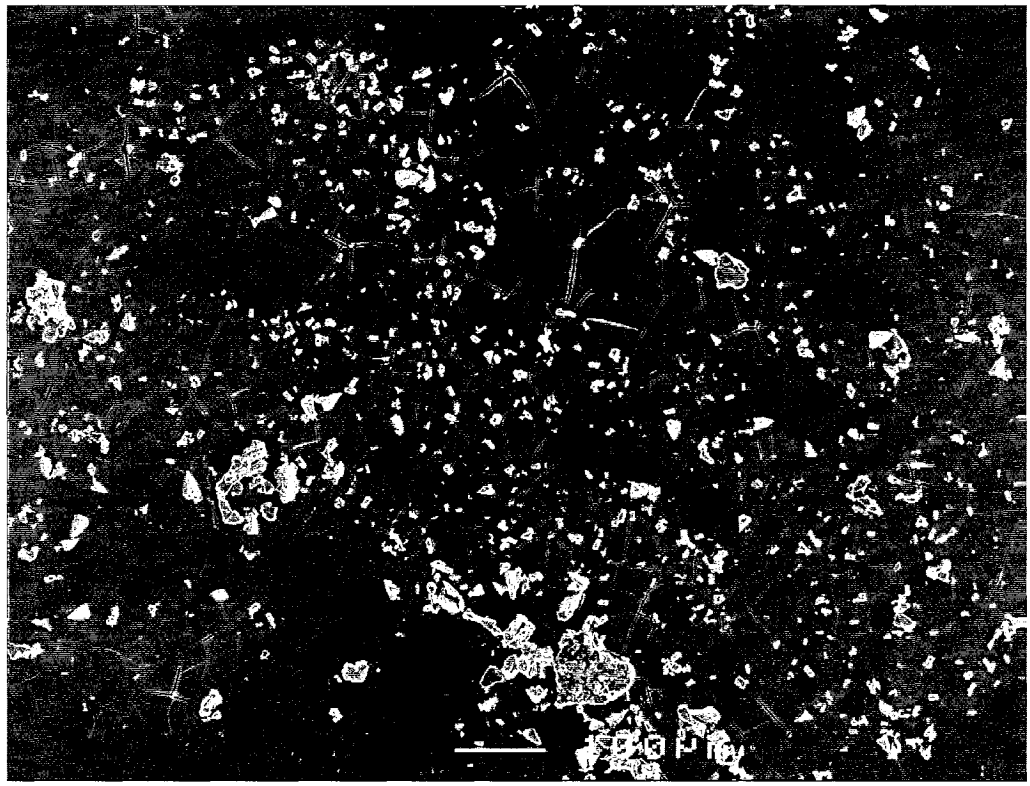


Figure 4-48a 100μm view of the PT_5, April 7, 2003 (SEM image).

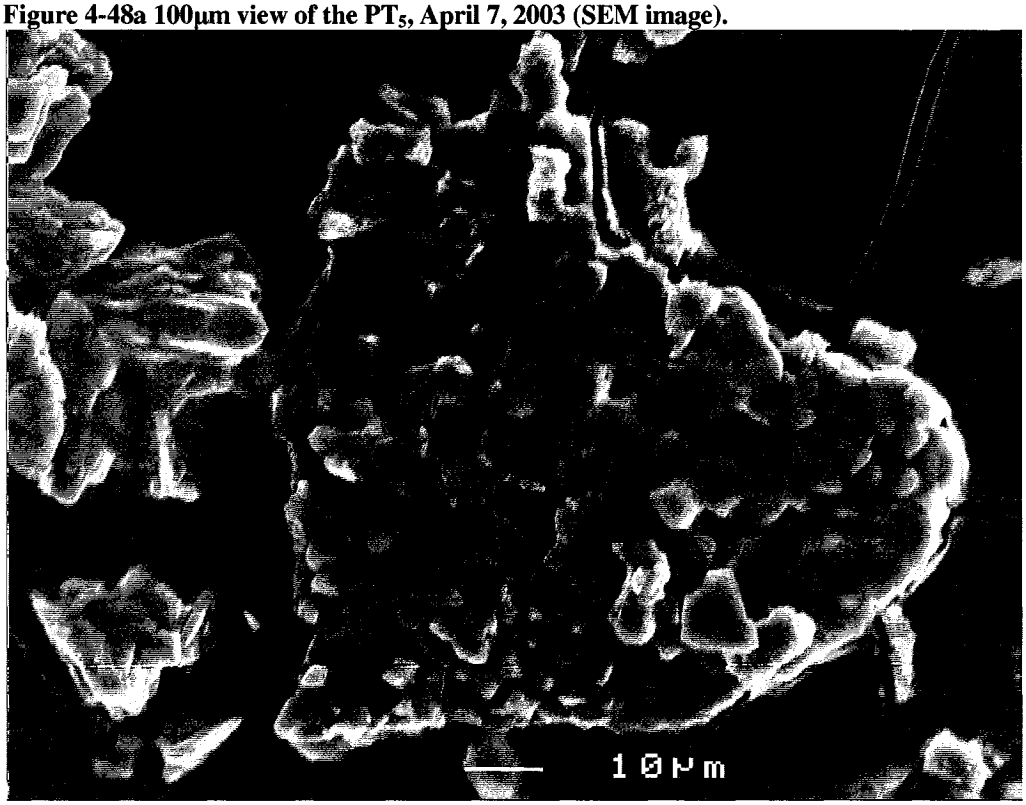


Figure 4-48b Close-up of calcium deposits which were more geometric than the fall 2002 deposits (SEM image).

4.4.2.4 Sequential Run SEM/EDX Results

Sequential runs of 5, 15 and 30 min, along with 1, 2, 4, 6, 8, 12, 24, and 48 hours were performed from April 10 to April 15, 2003 using an MF JX_{62700} membrane, as it ran fairly consistently without failure and was the most abundant of all the membranes received from Osmonics. The progression of foulants and amount of fouling was examined using SEM and EDX analysis. The purpose of this phase of the study was to examine whether foulants change over time. Table 4-21 summarised the foulants found. It must be remembered that these samples were small portions of samples taken from the overall membrane and though visually they appeared as a representative sample they may not actually represent the whole, as there tended to be areas of preferential deposit need the inflow of the cell.

Much of the variation between runs occurred in the first three runs 5, 15 and 30 min. Table 4-23 pays particular attention to these samples as they show that over time some structures appear and then are covered by other depositional layers. The initial fouling seems to be both calcium and chlorine based, with other less common deposits seen as well. One foulant of interest was a round, 'bubbled' feature seen in Figures 4-49a and b and 4-50 and described as a mostly Cl deposits.

The sequential runs seemed to indicate that calcite deposits are important in the initial fouling along with the round, 'bubbled' features. These can then be overtaken by a general sludge layer and eventually this layer allows for further calcite deposition after 24 and 48 hours. These membrane samples were examined along the surface, but not along the side relief, therefore the thickness of the fouling layers were unknown and thus the premise of overlapping deposition was an assumption, as fouling layers may have been removed and re-deposited over time due to the turbulent flow conditions within the cell.

Table 4-21 Summary of deposits on the sequential membranes for the JX_{62700} MF membrane.

Length of Run	Membrane Material	Foulants

5 min	JX - PVDF (EDX-C and F peaks)	• The overall deposition layer had very few peaks with Cl being the most prominent element.
		• Most of the distinct deposits were Ca (Calcite) only peak or Ca with Sr and Cl (˜ 10% area coverage)
		• Plant material was seen, but as mentioned previously this may have been due to the wooden surface upon which the membrane sample was cut.
		• Other less common distinct deposits were:
		  • Fe peak with a smaller Cl peak and the following other elements >K>Ca>S>P>Si>Zn>Mg>Na (small grain 3*2 μm)
		  • Si>K>Al (2 μm particles)
		  • Cl>K (7*4 μm)
		  • Fe>>Ca>Cl>K>Si>Zn

15 min		• The overall deposition layer again had very few peaks with Cl being the most prominent element. • Distinct deposits of Ca (Calcite) (˜ 10% area coverage) • There was an organic-like rounded deposit over the sample with a bubbled structure, which was not seen previously (see Figure 4-49a). The EDX analysis gave a Cl peak with smaller K>S>P peaks (˜ 15-20% area coverage). • There were also some flake-like deposits noted on the sample which were analysed as a Cl peak with smaller K>S>P>Ca>Fe peaks, this may be the same analysis as the bubble-like structures which could be seen in the same view as the specimen seemed quite thin (see Figure 4-49b). This sample could not be identified based on visuals or scans, the most likely possibility would be piece of membrane surface released when the sample was liberated. • Some less common deposits gave the following analysis: Zn>Fe>Ca>Cl>Na>K; or Fe>Ca>Cl>K
30 min		• The overall deposition layer had very few peaks with Cl being the most prominent element and K>S>P and Ca smaller peaks. • The round bubble-like structures are still seen, but have become harder to see because of other deposits overlaying them. Cl peak with smaller K>S>P as seen in the 15 min run (see Figure 4-50) (˜ 10% area coverage). • There are also a number of Ca deposits with small Sr peaks, some also occurred with Fe>Cl>K peaks as well (˜ 15% area coverage).
1 hr		• General coating of Fe>Cl>P>Ca • Calcite deposits over most of the membrane occupying approximately 25% of the overall area. • Figure 4-51a displayed rounded Ca deposits with on long piece of plant material, 4-58b gives an example of plant material (C and O peaks) overlapping membrane cracks, indicating post run deposition from cutting.

2 hr	JX - PVDF (EDX-C and F peaks)	• General deposit contained Cl=S=P>Na>Fe>Mg. • The round bubble-like structures are seen in the background, but have other deposits overlaying them. Cl peak with smaller K>S>P as seen in the 15 min run (see Figure 4-52a and b). Scanned as C>Cl>P>S • Few Ca deposits observed, those that were contain O>Si>Al>C as well (less than 1%). • There were other types of deposits identified in low amounts as well (less than 1% total area) C>Si >Al; Si>Al>Ca>O>Cl>C; and Fe>O>S>Cl>Ca (possibly an iron oxide)
4 hr		• General deposit contained C (probably coating) >Cl>O>S>K>P>Na>Ca>Mg>Fe • Very few distinct deposits, but in this case most were Ca based deposits (<5% surface area). The Ca deposits had a strong Ca peak with much smaller C and O peaks (from coating) and varied with either only a small Sr peak or a number of smaller peaks (Cl>S>P>Sr>Na>K>Mg)
6 hr		• General deposit contained C>O (probably coating) >S>P>Ca>Fe>P>Cl. • One very large (~ 500μm) Ca deposit noted with a number of smaller deposits (~ 10μm) (<10% surface area coverage). Ca peaks were accompanied by smaller O>C>Sr and cover approximately 15% of the surface area. • One large (~ 50μm) Fe peak deposit seen.
8 hr		• General deposit contained C >O (probably coating) >P>S>Cl>Ca>K. • No identifiable distinct deposits other than the plant material thought to be placed on the membrane after the run during membrane cutting.
12 hr		• General deposit contained C >O (probably coating) >S>P>Cl>Ca>K>Fe. • This sample was 'bumpier' than past sequential samples with general Ca>C>O (Calcite) over most of the membrane surface (~ 40 to 50% surface area) (see Figures 4-53 a and b). The deposits were also found to contain lesser amounts of S>Cl>P>Fe>Sr>Na>Mg.
24 hr		• General deposit contained C >O (probably coating) >Ca>S>P>Cl>Fe>K. • Again this sample had an overall bumpy texture as seen in the 12 hr sample. Most of the deposits were Ca>C>O (calcite) with smaller Sr>S >Fe>Cl peaks.
48 hr		• General deposit contained C >O (probably coating) >Ca>S. • This sample has the greatest amount of deposition on its surface and it was difficult to discern one deposit from another (see Figure 4-54). Most of the deposits are Ca>C>O (calcite) with smaller Sr>S >Fe>Cl peaks (~ 60 to 70% surface area coverage).

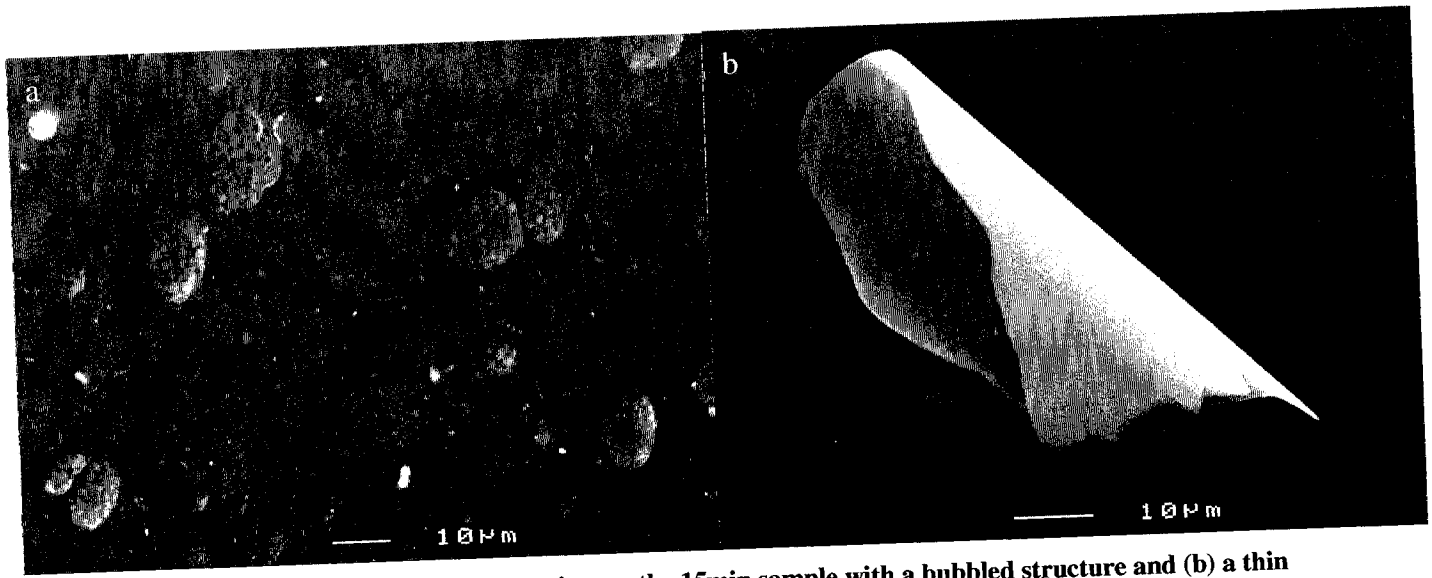


Figure 4-49a and b Organic-like rounded deposit over the 15min sample with a bubbled structure and (b) a thin film/plastic deposit.

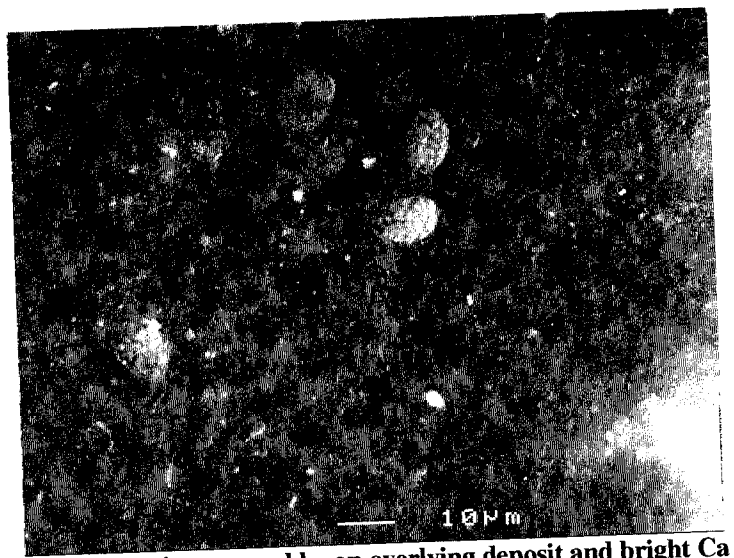


Figure 4-50 Round bubble-like structure being covered by an overlying deposit and bright Ca flecks from the 30 min sample.

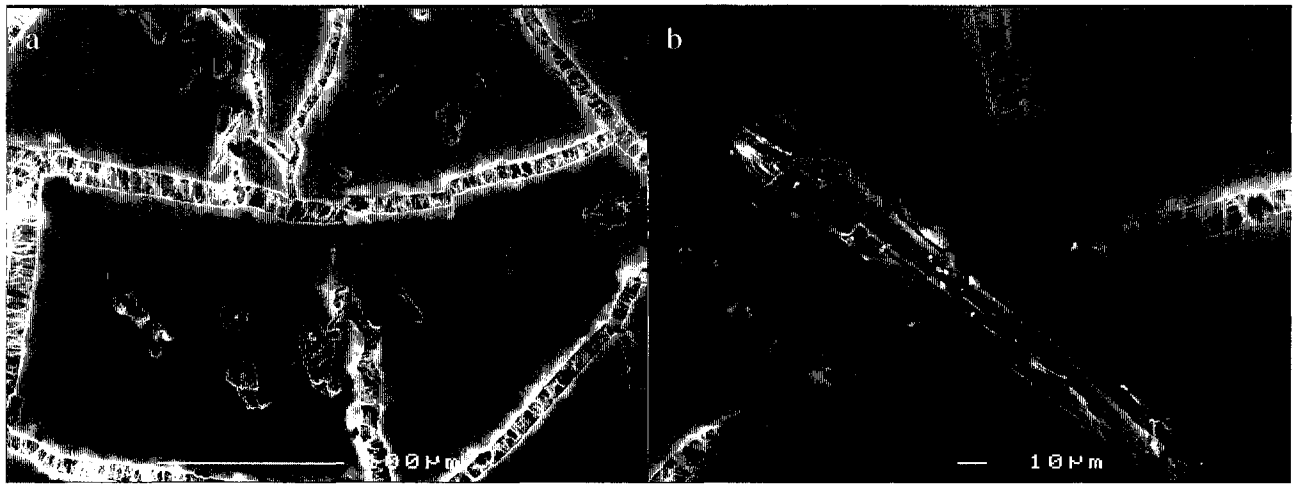


Figure 4-51a 1 hr run - rounded Ca deposits with one long piece of plant material right of centre. 4-51b Plant material overlapping membrane cracks.

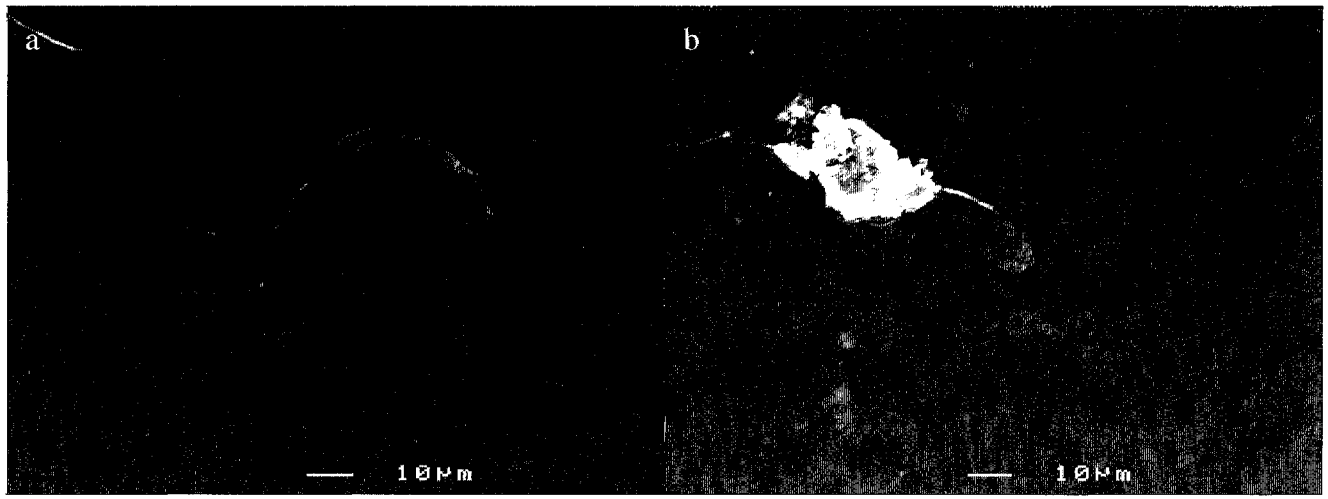
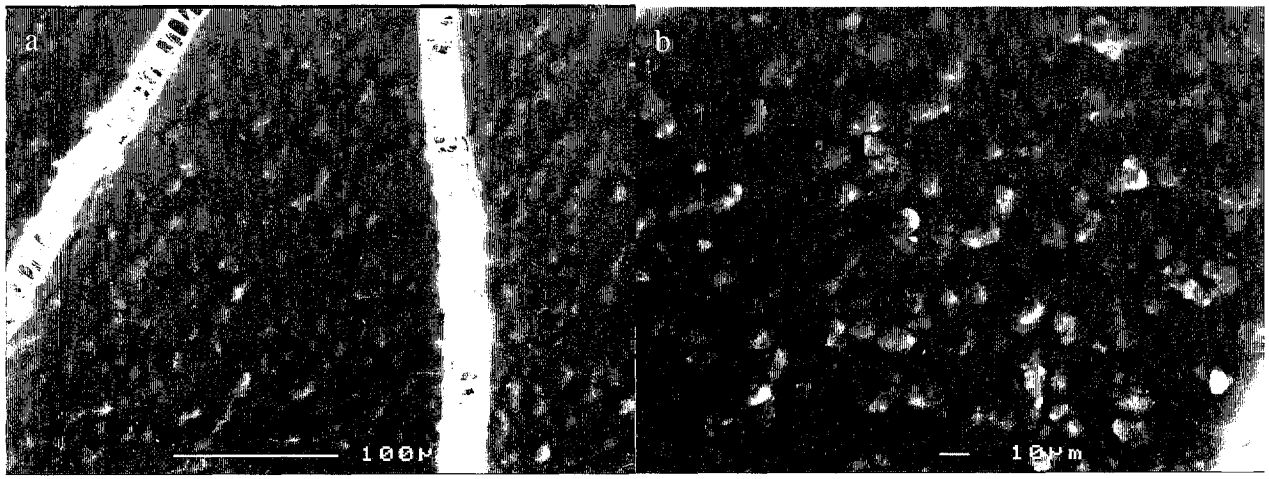


Figure 4-52a and b The round bubble-like structures seen on the 2 hour run membranes.



Figures 4-53 a and b 12 hr run- Possible calcite deposits over most of the membrane surface.

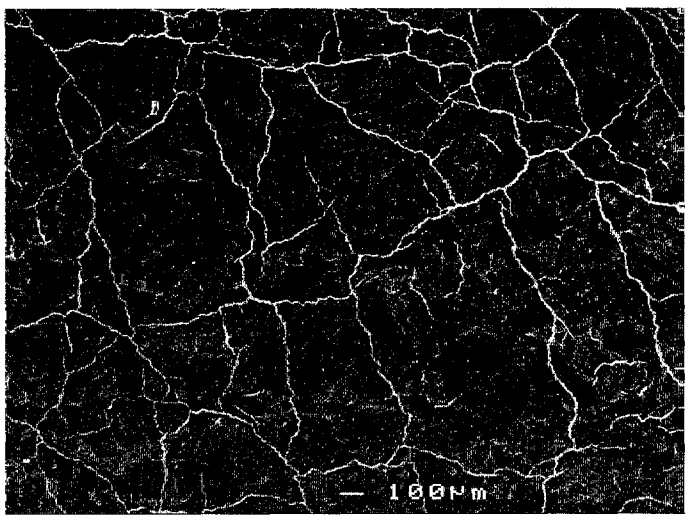


Figure 4-54 48 hr run-large amount of deposition on the 48 hour run surface, most of the deposits were calcite

Secondary 15 and 30 min run using JX_{62700} was done on July 27, 2003 to further examine the extent of short-term fouling. Both membranes again were fouled to a significant extent given the short period of the runs (Figures 4-55 and 4-56). The general sludge covering the membrane for both runs had only a slight Cl peak. Approximately half of the distinct deposits were Ca based (calcite) with Sr and Fe minor peaks. The other half were Cl>K based deposits or Cl>Na deposits, similar to the Cl deposits observed in the original 15 and 30min runs. Distinct deposits cover approximately 30% of the membrane area for the 15 min run and approximately 45% for the 30 min run.

The membrane used in the sequential run study was a PVDF membrane which may be more susceptible to calcite fouling than the Thin Film composite membranes for instance, thus the progression of the fouling seen can only be inferred to a similar membrane of composition and MWCO with a similar leachate. When the SEM/EDX results for all membranes tested were reviewed, it could be suggested that PVDF, 62700 KDa membranes and PES, 5 KDa membranes were more susceptible to calcite scaling; while PS membranes, 1 to 4 KDa were more susceptible to sulphur based foulants. However, this was not the case in late October 2002 when very few calcium deposits were found on the JX_{62700} membrane or on September 24, 2002 when broad calcite fouling was seen on a GK_4 a Thin Film composite membrane. The type of foulants deposited were therefore more likely influenced by a combination of leachate quality; membrane type and size; leachate flow within the cell; and environmental conditions.

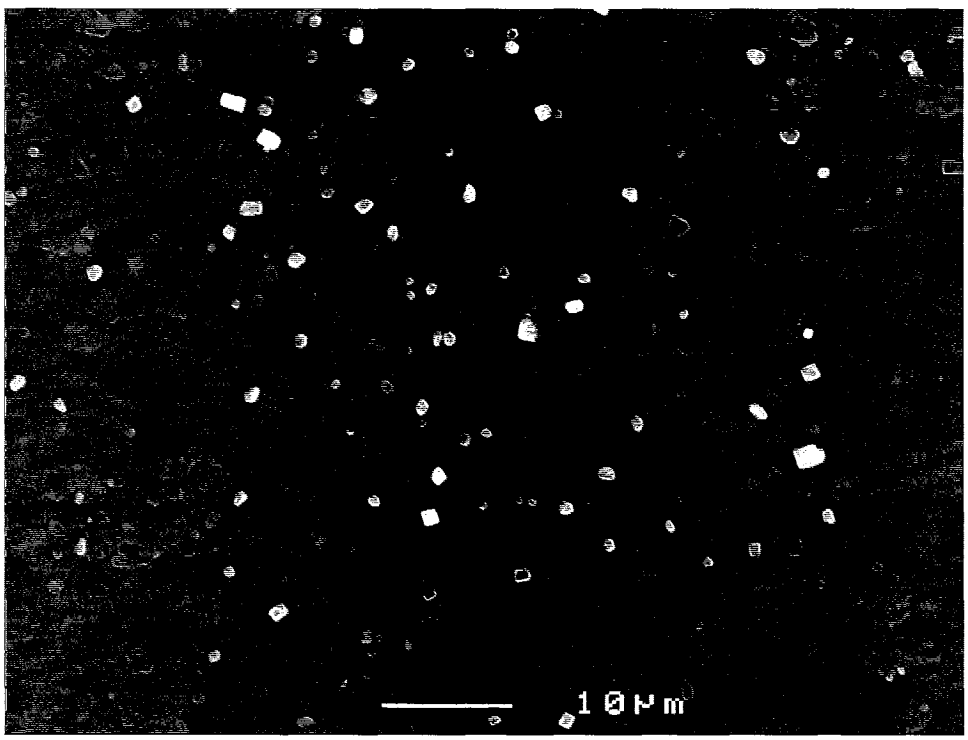


Figure 4-55 View of fouling on the JX_{62700} 15 min run on July 27, 2003.

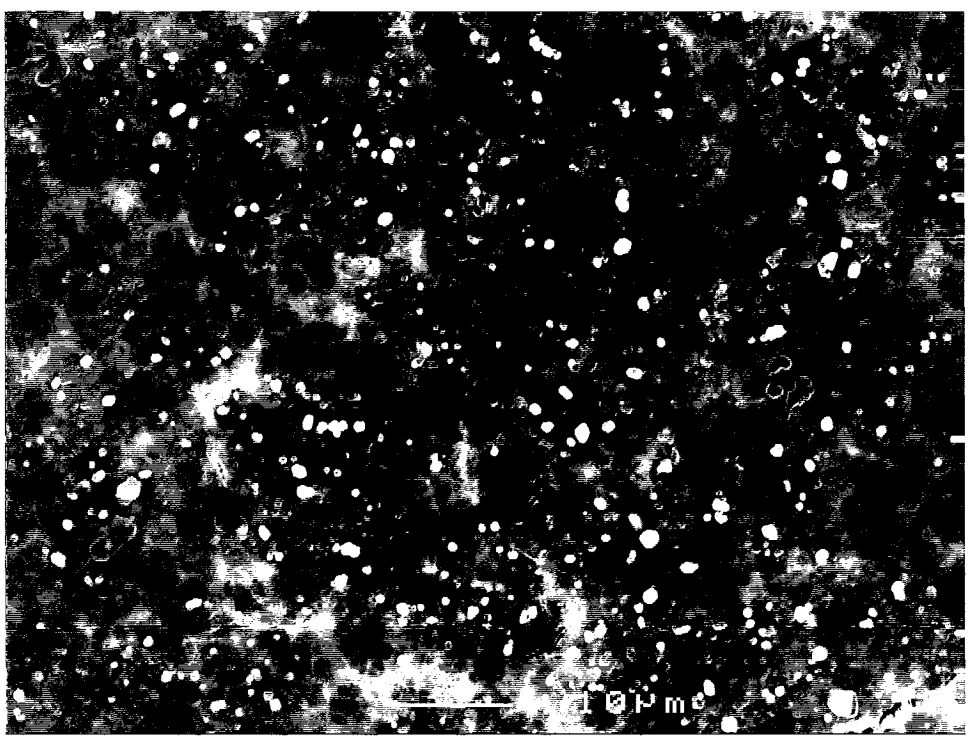


Figure 4-56 View of fouling on the JX_{62700} 30 min run on July 27, 2003.

4.4.3 Foulant and Precipitate Prediction

As mentioned in Chapter 3, MINTEQA2 was used to help determine what may precipitate out of the Trail Road landfill leachate. This program relied upon the concentration of each element dissolved in solution to determine what minerals precipitate out. The leachate did contain suspended solids which were not measured for elemental concentrations and therefore could not be used in the prediction. These suspended solids were thought to be the main cause of fouling and thus the precipitates predicted by MINTEQA2 would not be the only solids in solution.

MINTEQA2 was run using the ICP data along with the ammonia, TP and sulphate data for spring 2003. The only elements not contained within the MINTEQA2 database were B, Si and P. Data on the leachate quality was limited, therefore the results of this program can only be taken as a rough estimate of precipitated species. Table 4-22 lists the predicted outputs given by the program and their chemical formulas. One element that was not analyzed for in the standard ICP runs was Cl, and given its relative importance in the EDX results it is unfortunate that minerals involving Cl cannot be evaluated.

The precipitation of more than one carbonate can make identification of calcite based on HCl effervesces more difficult as strontianite, otavite and dolomite (to a limited extent) all effervesce with 10% HCl. The appearance of Ca in numerous EDX scans, which compared well to the calcite standard, indicated there was more calcite fouling than other carbonate species in the fall and possibly more dolomite in the spring due to the appearance of Mg in the scans and the change in mineral appearance (Klein and Hurlbut, 1993).

Table 4-22 Mineral precipitate predictions using MINTEQA2

Date	Membrane	Mineral Names	Chemical Formula
Oct. 2, 2002	ER_{30}	Dolomite Hematite ---------- Bixbyite	$(CaMg(CO_3)_2)$ Fe_2O_3 $Co(OH)_3$ $(Mn, Fe)_2O_3$
Oct. 7, 2002		Strontianite Dolomite Hematite ---------- Bixbyite	$SrCO_3$ $(CaMg(CO_3)_2)$ Fe_2O_3 $Co(OH)_3$ $(Mn, Fe)_2O_3$
Oct. 9, 2002		Dolomite Hematite ---------- Bixbyite Strontianite	$(CaMg(CO_3)_2)$ Fe_2O_3 $Co(OH)_3$ $(Mn, Fe)_2O_3$ $SrCO_3$
Oct. 22, 2002		Strontianite Dolomite ---------- Bixbyite	$SrCO_3$ $(CaMg(CO_3)_2)$ $Co(OH)_3$ $(Mn, Fe)_2O_3$
Oct. 24, 2002		Dolomite Hematite ---------- Bixbyite	$(CaMg(CO_3)_2)$ Fe_2O_3 $Co(OH)_3$ $(Mn, Fe)_2O_3$
Fall Average 2002		Strontianite Dolomite Hematite ---------- Bixbyite	$SrCO_3$ $(CaMg(CO_3)_2)$ Fe_2O_3 $Co(OH)_3$ $(Mn, Fe)_2O_3$
Feb. 24, 2003		Strontianite Dolomite Otavite Diaspore ---------- Bixbyite Barite	$SrCO_3$ $(CaMg(CO_3)_2)$ $CdCO_3$ aAl O(OH) $Co(OH)_3$ $(Mn, Fe)_2O_3$ $BaSO_4$
March 7, 2003		Strontianite Dolomite Barite Diaspore Otavite ---------- Bixbyite	$SrCO_3$ $(CaMg(CO_3)_2)$ $BaSO_4$ aAl O(OH) $CdCO_3$ $Co(OH)_3$ $(Mn, Fe)_2O_3$
March 17, 2003		Strontianite Dolomite Diaspore Barite Otavite ---------- Bixbyite	$SrCO_3$ $(CaMg(CO_3)_2)$ aAl O(OH) $BaSO_4$ $CdCO_3$ $Co(OH)_3$ $(Mn, Fe)_2O_3$

Date	Membrane	Mineral Names	
Feb. 24, 2003		Strontianite	$SrCO_3$
		Dolomite	$(CaMg(CO_3)_2)$
		Otavite	$CdCO_3$
		Diaspore	aAl O(OH)
		----------	$Co(OH)_3$
		Bixbyite	$(Mn, Fe)_2O_3$
		Barite	$BaSO_4$
March 7, 2003		Strontianite	$SrCO_3$
		Dolomite	$(CaMg(CO_3)_2)$
		Barite	$BaSO_4$
		Diaspore	aAl O(OH)
		Otavite	$CdCO_3$
		----------	$Co(OH)_3$
		Bixbyite	$(Mn, Fe)_2O_3$
March 17, 2003		Strontianite	$SrCO_3$
		Dolomite	$(CaMg(CO_3)_2)$
		Diaspore	aAl O(OH)
		Barite	$BaSO_4$
		Otavite	$CdCO_3$
		----------	$Co(OH)_3$
		Bixbyite	$(Mn, Fe)_2O_3$
April 7, 2003		Malachite	$Cu_2(PO_4)_3(OH)$
		Strontianite	$SrCO_3$
		Dolomite	$(CaMg(CO_3)_2)$
		Calcite	$CaCO_3$
		Hydroxylapatite	$Ca_5(PO_4)_3(OH)_2$
		Otavite	$CdCO_3$
		Barite	$BaSO_4$
		Diaspore	aAl O(OH)
		----------	$Co(OH)_3$
		Bixbyite	$(Mn, Fe)_2O_3$
April 10, 2003		Calcite	$CaCO_3$
		Strontianite	$SrCO_3$
		Dolomite	$(CaMg(CO_3)_2)$
		Hydroxylapatite	$Ca_5(PO_4)_3(OH)_2$
		Otavite	$CdCO_3$
		Barite	$BaSO_4$
		Diaspore	aAl O(OH)
		----------	$Co(OH)_3$
		Bixbyite	$(Mn, Fe)_2O_3$
July 22, 2003		Strontianite	$SrCO_3$
		Dolomite	$(CaMg(CO_3)_2)$
		Hydroxylapatite	$Ca_5(PO_4)_3(OH)_2$
		Otavite	$CdCO_3$
		Barite	$BaSO_4$
		Diaspore	aAl O(OH)
		----------	$Co(OH)_3$
		Bixbyite	$(Mn, Fe)_2O_3$
Spring Average 2003		Strontianite	$SrCO_3$
		Dolomite	$(CaMg(CO_3)_2)$
		Otavite	$CdCO_3$
		Diaspore	aAl O(OH)
		----------	$Co(OH)_3$
		Bixbyite	$(Mn, Fe)_2O_3$

Several of the minerals MINTEQA2 gave as precipitates are rarely seen in nature (i.e. strontianite, otavite, and bixbyite) (Klein and Hurlbut, 1993). Sr appeared primarily in conjunction with Ca in EDX analysis, indicating that Sr may have occupied the Ca position in a limited fashion within the calcite matrix, forming limited Strontianite. This was thought to occur due to the large concentrations of Sr in solution.

Neither Cd, Cu, Co nor Mn were noted on EDX scans as significant peaks, indicating that perhaps otavite, malachite, $Co(OH)_3$ and bixbyite were not in fact formed or existed in such small quantities within the depositional layer that they could not be identified by EDX scans. An iron hydroxide was expected to form in the late fall, as indicated by the dark nature of the leachate in the fall, therefore the prediction of hematite formation seemed plausible. Limited diaspore and hydroxylapatite formation was also considered to be reasonable given the occurrences of Al and P in the EDX scans, though during the running of MINTEQA2 hydroxylapatite would often move in and out of solution, only precipitating for the April7, 2003 run.

The formation of dolomite was not indicated on any EDX scan based on comparisons with the dolomite standard, as there was very little Mg in the fall and in the spring the Mg was hidden within a number of other elements in the 'sludge'. The April 7^{th} and 10^{th} runs were the only runs to have calcite listed as precipitating and were two of the few spring runs that showed significant Ca based fouling.

The ICP data for fall 2002 and spring 2002 were averaged to give a generic leachate for each time period and to examine the precipitates as seen in Table 4-22. Both the fall and spring data indicated that strontianite, dolomite, hematite, $Co(OH)_3$, and bixbyite precipitated, but the spring also precipitated otavite and diaspore.

The leachate formed depositional layers that were essentially a mixed-element sludge and thus many of these precipitate identifications cannot be truly applied to the melange. The predicted precipitates were considered estimates from a very complex and varied feed source and should only be used for general comparison to the EDX scans. More complete data sets with this program in mind would need to be developed, along with analysis of the exact solids content of the leachate in order to improve the estimation quality.

Another reason for not seeing the predicted precipitation may have been due to the constant flow within the apparatus preventing crystallization. Crystals with a Mg and Cl base were found on one membrane after it was stored wet before sampling and drying for SEM analysis (i.e. Sept. 30, 2002 JX_{62700} run). It was thought that these crystals formed out of the remaining solution and it indicated that precipitation would occur more readily from the leachate if it was not under constant flow. This form of deposition was not normally seen.

CHAPTER 5

CONCLUSIONS

Part of this study involved examining the characteristics of the raw leachate and how this may affect membrane treatment. It was found that several of the studied parameters varied seasonally and that the leachate composition can vary widely. The leachate type was also examined to determine the leachate phase. The Trail Road landfill leachate type was most closely aligned with a stabilised methanogenic leachate, though the landfill was filling at the time of testing. The leachate recycle, along with the mixing of leachates from several cells of differing ages, placed the Trail Road Landfill leachate outside the standard leachate categories. Leachate recylcing generally leads to greater organic removals and metals precipitation from the young leachate, which when mixed with the older cells, gives a more stabilized leachate characteristic.

Various membranes were able to decrease the concentrations of certain contaminants depending on the membrane size, leachate quality, and membrane type. For example, most of the raw COD concentrations were above or near the maximum discharge concentration. Membranes with MWCOs of 10 KDa or less were able to reduce the COD concentration in the leachate to meet the COD bylaw (i.e. GN_{10}, PT_5, GM_4, GK_2, and GH_1). Also, when B and Ba concentrations were above the bylaws, no membranes tested while these parameters were high were able to met the bylaw after treatment, but when Cr was above the bylaw concentrations all membranes tested while the concentrations were high met the bylaw (i.e. GK_2, PT_5, and GH_1).

Generally the UF membranes with MWCOs of 5KDa or less gave the best percent removals. The PT_5 membrane performed the best overall with a good steady state flux range (5 to 14 L/m^2h), reasonable removals of most parameters and would require approximately (1597 to 1917 m^2) in area for full-scale application. The GH_1 membrane generally gave the highest overall percent removals, but had a lower steady state flux (2 to 5 L/m^2h) than PT_5 and thus would require a higher surface area (1917 to 4792 m^2) to deal with the Trail Road Landfill's leachate output. The GH_1 membrane was also the only membrane that produced permeate with a TKN concentration below the sewer-use bylaw. No membranes tested were able to meet sewer-use bylaws for all targeted parameters and none met the bylaw, which was

a parameter of concern for the Trail Road Landfill. Though the membranes were not run head-to-head and the leachate characteristics changed, GH_1 and PT_5 consistently demonstrated the best removals. UF membrane pre-treatment (MWCO<10 KDa) was shown to reduced a number of parameters listed in the sewer-use bylaw.

Fouling was found to be a problem in the treatment of Trail Road leachate, resulting in a reduction of permeate flux. Based on the flux the fouling type was determined to be cake filtration. SEM images confirmed the existance of a significant film on the membranes. Carbonates such as calcite and/or dolomite seemed to be the main foulant/scalants, with carbonates such as strontianite making occasional substitutions within the scale. Iron sulphides or oxides tended to form a general coating over the membrane surface and may have been the base for the mixed-element deposits seen in the spring runs. Of all the raw leachate liquid parameters, BOD concentration seemed to have the most direct impact on the flux, causing flux decreases with BOD concentration increases.

CHAPTER 6

RECOMMENDATIONS FOR FURTHER STUDY

Perhaps this study was too ambitious in trying to deal with raw leachate under field conditions rather than examining individual leachate components via a laboratory produced synthetic leachate that would produce more definitive results. Real landfill leachate is very dynamic, does not have a set formula, changes constantly and involves various component interactions, which may change the nature of the leachate over time and even within the treatment system.

6.1 Operational Changes and Improvements

The following list suggests operational changes, which may improve any further study and provide further insight into the origins of fouling:

- More sequential runs to further examine fouling over time using lower MWCOs.
- Run membranes head-to-head for comparison with a second apparatus, so that comparisons can be made between membrane types at the same leachate quality.
- Run one type and size of membrane over the whole testing period, especially throughout seasonal changes, to better observe the effects of seasonal variations in leachate quality on fouling. It is difficult to draw conclusions regarding treatment efficacy when using a range of membrane types and MWCOs, with a range of testing dates and leachate qualities.
- More runs of each membrane type over a standard period of time (i.e. testing all membranes every three or four weeks). This may require a decrease in the number of membranes tested, but would improve the overall consistency of the data and allow for a more thorough examination of each membrane.
- An exploration of optimal pressure for each MWCO used would be beneficial to discover possible pressure ranges for full-scale applications.
- The transmembrane pressure should be monitored along with continuous recirculating flow monitoring using a flow meter after the cell.
- Stainless steel membrane-housing plates are available for the Sepa© Cell and should

be used in future as the intense scrubbing needed to clean the membrane housing between runs resulted in surface scouring and scratching of the plastic housing plates. The use of metal pipes and a metal membrane-housing unit may contribute to an increase in metals in the liquid, but not significantly so. Running deionised water through the system for a run length of 48 hours and taking samples for metal analysis before and after would allow correction for the background metals.

- The initial fouling test used to discover when steady state was reached was performed during a dry period when the leachate was very concentrated. It indicated that steady state fouling occurred at approximately 48 hours, but changes within the leachate may alter this value as well. Routine monthly steady state flux checks would help optimise the time used during a run.
- A materials study could be done to discover which membrane materials lead to the least amount of fouling, by testing membranes of various material types, but with similar pore sizes.
- Monitor conductivity, eH, alkalinity, turbidity and colour for all samples.
- Expanded testing parameters to fulfil more of the MINTEQA2 requested parameters and more effectively use this tool.

6.2 Recommended Changes in Testing and Interpretation

The low levels of metals in the Trail Road landfill leachate may require that atomic adsorption be used for metals testing rather than ICP, as the detection limits involved are too high for the low concentrations in the leachate (Urase *et al.*, 1997). Metals examination could also be extended to the solids within the leachate by examining the precipitate and TSS solids using ICP solid injection or atomic adsorption. Solids analysis may give insight into whether metals pass through MF and UF membranes as ions or attached to particles smaller than the MWCO and might allow more accurate predictive modelling via MINTEQA2. The reasons behind the metals removal noted at high MWCO should also be examined.

6.3 Leachate Pretreatment

Ideally there would be little to no need for optimisation of leachate characteristics, but due to the wide fluctuations in leachate quality this may not be the case. Further study is needed to clarify whether pH adjustments, coagulation, or aeration could improve the leachate treatment, without significantly increasing costs. These are a few pre-treatment suggestions, which may improve overall leachate treatment:

- Seeding with gypsum to encourage precipitation of TSS and scalants (Peters, 1996).
- Aeration prior to filtration may strip the leachate of ammonium and methane, while encouraging any cohesion or precipitation to occur. This may require a brief post-aeration settling period prior to membrane filtration post-aeration.

6.4 Biofouling Studies

A biofouling study should be done and methods determined for the separation and identification of microbes within the foulant on the membrane and the leachate itself. The best metals removals at high MWCOs were seen when the BOD was high. It was hypothesized that this increase in biological activity led to a layer of microbes and EPS in combination with calcium scaling acting as a secondary membrane layer effectively reducing the MWCO. Though biofouling was not specifically studied its effects may have been seen and should be studied in future.

6.5 Cleaning Studies

6.5.1 Flow Rate Variation and its Effects on Membrane Cleaning

Recirculation flow rate was not monitored, as pressure was considered to be the more important parameter in producing permeate. Higher flow rates lead to higher turbulence and more effective dispersal and emulsification (Krack, 2000). To discover the optimum cross flow velocity in preventing or minimizing fouling, a flow meter at the housing outlet is needed.

Flow rate can be very important to the effectiveness of a cleansing agent. A low flow rate is needed during cleaning, so that cleaner is not forced through the membrane causing deeper secondary fouling with scouring. For MF membranes a low pressure cleaning should

be followed by a high pressure run that will dissolve and push through any fouling within the membrane pores (Krack, 2000). Back flushing studies could also be considered for cleaning (Krack, 2000). A simple pure water cleaning regime may lead to better overall flux results and give a good indication of how effective and when chemical cleaning would be required.

6.5.2 Temperature Related to Cleaning Studies

Studies examining the optimal temperature ranges for treatment, fouling and cleaning would be an asset to determine the operational parameters for a full-scale treatment plant. An increase in temperature of 10°C approximately doubles the cleansing activity of the cleaning agent, which is why temperature is an important parameter to study and vary in future experiments. Temperature can have a dramatic impact on flux, as seen in Chapter 4. Some membrane materials are also temperature sensitive, even the glues involved in modern membrane modules can be sensitive to heat (Krack, 2000).

Given the need for decreased costs in wastewater treatment it may not be possible to increase the temperature of the cleaning agent or to regulate the treatment temperature of the system. If the cleaning agent is not at the same temperature as the feed then solidification of various proteins and chemical compounds may occur, thus making it more difficult to clean, therefore feed and cleaning agent temperature should be comparable (Krack, 2000).

6.5.3 Other Parameters Related to Cleaning Studies

The cleaning schedule, type of chemicals used, water quality used in cleaning, pH, anti-bacterial agents and enzyme derived cleaning products are all parameters which could be examined in a cleaning experiment (Krack, 2000). There are a number of physical and chemical considerations, along with the seasonal variations in the leachate quality to consider. This variation in the raw leachate means that cleaning schedules and possibly even products must change to accommodate the change in feed. Also, it would be of interest to use the leachate strength data with the corresponding fluxes and MWCO to develop a model for predicting the fouling over time with varying concentration and MWCO, leading to a more effective cleaning regimen.

CHAPTER 7

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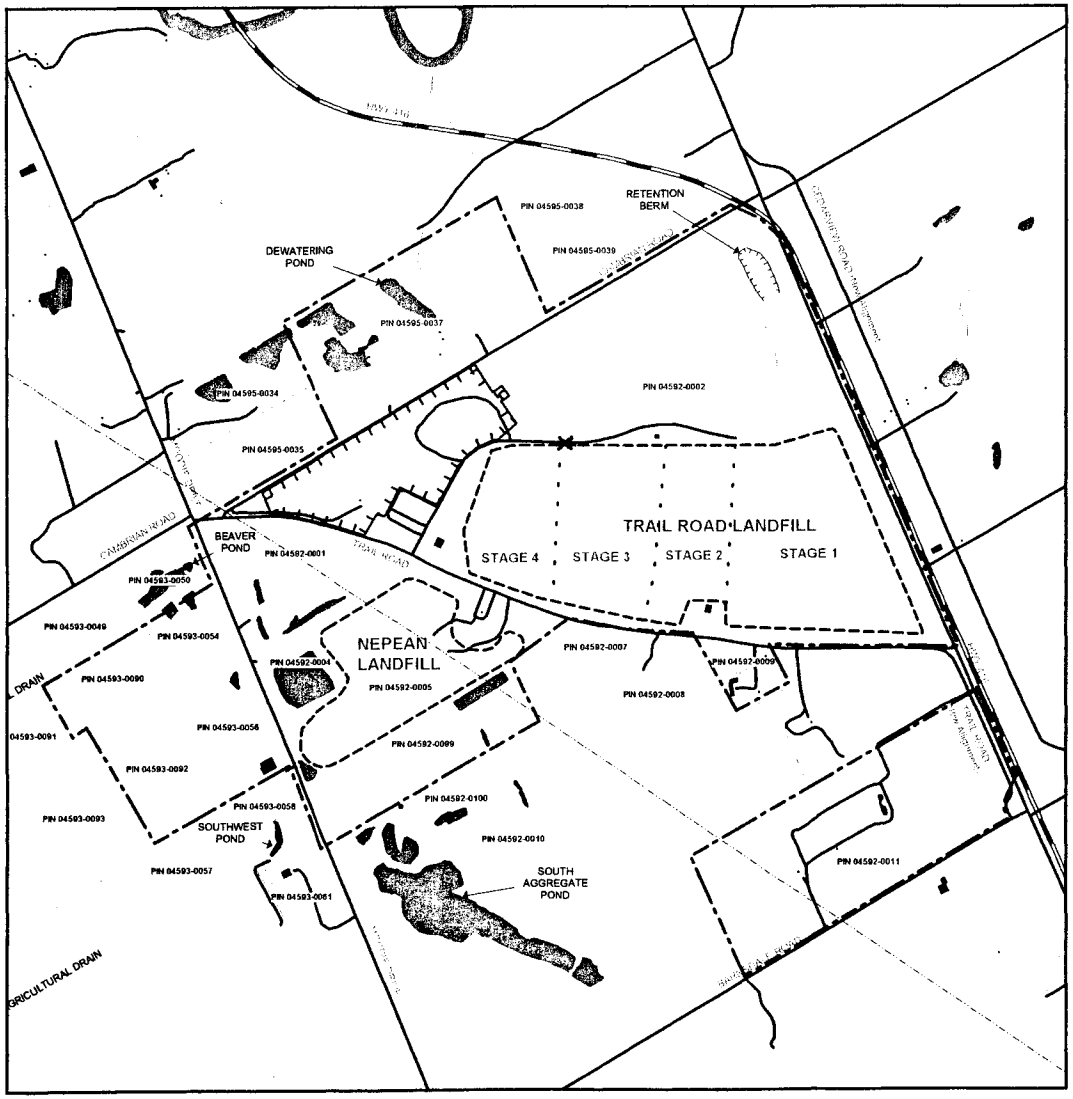
Appendix A

Map of the Trail Road Landfill

(Map not to scale from Golder, 2002)



LEGEND

- APPROXIMATE CITY OF OTTAWA PROPERTY LIMITS
- COMPOSTING AREA
- LANDFILL BOUNDARY
- LANDFILL STAGE BOUNDARY
- HYDRO LINE
- ROADWAY
- RAILWAY
- FENCE LINE
- WATER
- HEDGE
- BUILDING
- LANE
- HIGHWAY
- BERM
- WATER BODY

SPECIAL NOTE

THIS DRAWING TO BE READ IN CONJUNCTION WITH ACCOMPANYING REPORT

REFERENCE

BASE PLAN PRODUCED BY GOLDER ASSOCIATES LTD.
UNDER LICENCE WITH THE ONTARIO MINISTRY
OF NATURAL RESOURCES, QUEENS PRINTER, 1996

REVISION	DATE	DESCRIPTION	DRAWN	CHECKED	REVIEW

SCALE	1:15,000	
PROJECT	011-2818	
DESIGNED		
DRAWN	MRL	MAR/02
CHECKED	AMH	MAR/02
REVIEWED	BJV	MAR/02

PROJECT
TRAIL & NEPEAN LANDFILL SITES
2001 MONITORING & OPERATING PROGRAM

SHEET TITLE
SITE PLAN

N
W E
S

Golder Associates

FILE NO.
N:\Active\2001\011-2818 Trail Road 2001\GIs_Info\Maps

FIGURE NO.
1.2

A.1 Other Leachate Treatment and Pre-treatment Studies at the Trail Road Landfill

A number of grants were issued to several consultants and university groups to examine pre-treatment and treatment options for the Trail Road landfill. Abridged versions of four consultants reports were made available in late 2001, with full documents available to the public in early 2002. The treatment studies included an AutoFlash evaporator, a biological anoxic/oxic system, various adsorption processes, solar oxidation, enhanced membrane filtration, and steam stripping. A brief description of each is useful in describing the particular problems of operation at the Trail Road landfill.

A.1.1 AutoFlash

AutoFlash evaporation examined by CRA (Conestoga-Rovers & Associates) was chosen as an emergent technology capable of addressing the concerns associated with evaporation. The disadvantages of most evaporation techniques is the energy required to evaporate and difficulties in regulating pressure. This system was to use waste heat from the system itself and/or heat generated from landfill gas to bring temperatures close to evaporation prior to entering the evaporation column. Further energy is then used to 'top-up' the heat for evaporation. The control systems to prevent back migration used self regulating passive interstage pressure devices, as the pressures increased through each stage of the system, to simplify any automation (CRA, 2001a).

The CRA AutoFlash study was conducted between August 2001 and December 2001. The TDS in the initial runs were well beyond the optimum operational range of 250,000 mg/L at more than 400,000 mg/L. Fouling was a problem in the piping and passive interstage devices, which led to short circuiting. Mechanical problems were also discovered in dealing with the fouling and rectified. An anti-scalant was added to the feed along with a change in the acid used for pH adjustment. Despite the change, coupled with problems in the mechanisation of pH adjustment and anti-scalant addition, there was still considerable fouling occurring. Eventually CRA achieved one optimized test by adjusting the Total Dissolved Solids (TDS) concentration. It ran for 7 days and in that time took approximately 5 days to reach steady state, then the project was terminated. The resulting concentrate needed to be treated further, but this vector was not examined. The distillate did meet the sewer use by-laws, but the system relied on the assumption

that waste heat would be readily available and that a cleaning regimen could be found (CRA, 2001a).

CRA then further examined the possibility of polishing the resulting effluent using a rotating biological contactor (RBC). RBC involves a number of mechanically rotating, closely spaced rotating disks which are exposed in sequence to the atmosphere. Biomass attaches to the disks and aerobically proceeds to oxidize the organic matter. The flash evaporator distillate was essentially devoid of N and P, which needed to be added for biological activity. Activated sludge was also added to develop the biofilms. The time of the year during which the project was developed was too cold (5°C) to result in anymore than 30% COD removal which did not meet surface water discharge requirements. CRA also looked at simple chemical treatment in the addition of lime and crystalline limestone in a settling tank of distillate to complex VFAs and remove COD. The required dosage needed to come close to the discharge standard was shown to be impractical and not cost effective (CRA, 2001a).

A.1.2 Biological Anoxic/Oxic System

CRA also ran a biological anoxic/oxic system between May 2001 and November 2001. It consisted of an anoxic tank, an aeration (oxic) tank and a secondary clarifier, with recirculation between the oxic and anoxic tanks. The goals of the system were to degrade organic material and through proper recycle rates encourage nitrification and denitrification. It took 7 weeks to establish the biological activity using a leachate feed and activated sludge. During this time the aeration system needed to be replaced, as it was not effective. Once steady state was reached the system was run at increasing flow periods for 4 to 6 weeks at a time, to examine how changes in HRT effected the system (CRA, 2001b).

CRA found that BOD removal was excellent (up to 99% removal) at a flow rate of 3 m^3/d. COD removals ranged from 72% to 92%, which would indicate the presence of difficult to degrade or essentially non-biodegradable material. The uptake of ammonia nitrogen (92% removal), suspended solids removal, and heavy metal removal were all high, but phosphorous was minimally removed. The sludge accumulated metals and would in practice be dried and returned to the landfill. This system met the sewer use by-law standards and CRA claimed that

H_2S formation would be eliminated (CRA, 2001b).

Lentz (1996) examined the feasibility of treating the Trail Road leachate using a series of upflow anaerobic sludge blanket sequencing batch reactors. Sulphides, chlorides, metals, dissolved solids and BOD concentrations were not reduced sufficiently for sewage disposal and flow rates were difficult to control and sustain. This indicates that treating Trail Road Landfill leachate with a biologically driven system may not be practical due to leachate variations and the sensitivity of microbial populations to change.

A.1.3 Adsorption Studies

Green Plan Environmental Corporation (GPEC) International Ltd. working with the University of Ottawa examined the use of various absorption methods to treat landfill leachate. Sphagnum peat moss, compost from the Trail Road Landfill yard waste, two natural zeolites, vermiculite clay and activated carbon were all examined as adsorption media in bench scale studies. From these, peat moss was found to be the most cost-effective media and used in an on-site pilot scale study from August 1, 2001 to September 25, 2001. Over that period of time, with 570 L of leachate treated, clogging was noted as a problem. Most parameters met the project target of 50% less than all Sewer Use By-Law discharge limits. Nitrogen was the parameter which broke through the most quickly as it competes with boron for adsorption sites. Nitrogen break through, along with hydrogen sulphide and boron adsorption requirements were used to postulate a full-scale system. The spent peat moss was proposed as an alterative cover material or could simply be landfilled (GPEC, 2002).

A.1.4 Solar Oxidation, Enhanced Membrane Filtration and Steam Stripping

Science Applications International Corporation (SAIC Canada) conducted solar oxidation, enhanced membrane filtration, and steam stripping leachate treatment studies. Solar Oxidation uses solar ultraviolet (UV) light to split hydrogen peroxide molecules, producing highly reactive hydroxyl radicals. The hydroxyl radicals rapidly react with organic contaminants in water and break them down to carbon dioxide, salt and water. The goal of the first step was to remove xylene and toluene (SAIC, 2001).

The second step in their treatment process was to use a water soluble polymer to bind to boron and then filter the leachate through an NF membrane system. The membrane was used to target inorganic compounds and remove a large fraction of the BOD and TSS. The surfaces of the membranes used became negative at high pH which improved cation rejection. Boron removal was found to be significantly improved by an increase in pH up to 10 from approximately 7, rather than chemical sequestration. The enhanced filtration was found to be very effective at removing TSS, CBOD, boron and the non-ammonia total kjeldahl nitrogen (TKN) portion. SAIC used a low and high pressure system (145 psi and 1000 psi respectively). The high pressure system seemed to perform better under the field operating conditions (SAIC, 2001).

The final step was steam stripping to remove volatile organics like ammonia. The leachate fell from the top of a packed column as steam flowed upward from the bottom. As the steam encountered the leachate organics were volatilized, captured and condensed at the top of the column. The process was very effective with a high pH leachate permeate from the membrane system (SAIC, 2001).

SAIC (2001) found that the leachate quality varied. The pilot scale experiment ran for 9 weeks between July and September 2001 and during that time one pump needed to be replaced. The hot dry summer caused the leachate to be quite concentrated and excessive foaming occurred with in the treatment process. The TSS concentrations were found to double over the dry season when compared to leachate collected in June, which was used as a template in preparing for the pilot study. The caustic or acid volumes needed increased dramatically for pH adjustment as the TSS interfered with the effectiveness of the acid. The optical density of the raw leachate also increased making the Ultra Violet (UV) treatment much more difficult and taxing (SAIC, 2001).

Appendix B

Membrane List

and

Determination of JX Pore Radius

Table B-1 Membranes used and dates tested

Date	Membrane Tested	Size of membrane (KDaltons)	Data Available	Notes
31-Jul-02			flux	Water Test
6-Aug-02			flux	Water Test
7-Aug-02	M-180	100	flux	Ruptured Line
13-Aug-02	M-180	100	flux	
30-Aug-02	GK	3.5	flux	Power Surge Turned Computer off
3-Sep-02	QW	30	flux	O-Ring Slippage, break in system
5-Sep-02	QX		flux	O-Ring Slippage, break in system
9-Sep-02	QW		flux, COD	Air Leaking From Cell
11-Sep-02	QX		flux	Air Compressor Turned Off
12-Sep-02	QW	30	flux	
16-Sep-02	GN	10	flux, COD	
23-Sep-02			flux	Power Surge Turned Computer off
24-Sep-02	GK	2	flux, COD	
30-Sep-02	JX	67200	flux, COD	
2-Oct-02	ER	30	flux, COD, ICP	
7-Oct-02	PT	5	flux, COD, ICP	
9-Oct-02	MW	100	flux, ICP	
22-Oct-02	JX		flux, COD, ICP	
24-Oct-02	JX	67200	flux, COD, ICP	
20-Nov-02			flux	Water Test
26-Nov-02	GK		flux	Freezing
21-Jan-03			flux	Water Test
22-Jan-03			flux	Water Test
28-Jan-03	Circulation test	N/A	flux, COD, ICP	
24-Feb-03	GH	1	flux, Accu, ICP	Problem with blockage in the valve

Date	Membrane Tested	Size of membrane (KDaltons)	Data Available	Notes
1-Mar-03	GM	4	flux	Computer Off during run
4-Mar-03	EW	60	flux, Accu, ICP	
7-Mar-03	GM	4	flux, ICP	
10-Mar-03	GK	2	flux, Accu, ICP	
17-Mar-03	PT	5	flux, Accu, ICP	
7-Apr-03	PT	5	flux, Accu, ICP	
10-Apr-03	JX	67200	flux, Accu, ICP	
12-Apr-03	JX	67200	flux	
15-Apr-03	JX	67200	flux, Accu, ICP	
15-Apr-03	ER	30	flux	Easter weekend lab closed
22-July-03	GH	1	flux, Accu, ICP88	

The microfiltration membrane used (JX) had a pore radius of 0.3 μm, but the molecular weight cut-off was not given. The following data was used to approximate the MWCO for comparison purposes with other membranes.

Table B-2 Membranes used to find the pore radius of JX (Peng, 2003)

Membrane		
	MWCO	**Pore Radius**
Name	**Daltons**	**nm**
GN	10000	3.7
M100	20000	5.2
QW	30000	6.4
P707	150000	14
QX	3600000	70

The trend line in the graph below gave the equation for the JX MWCO determination:

$$y = 735.69x^{2.0027}$$

When x = pore radius = 0.3 μm = 300 nm for JX

$$y \approx 67200 \text{ KDaltons}$$

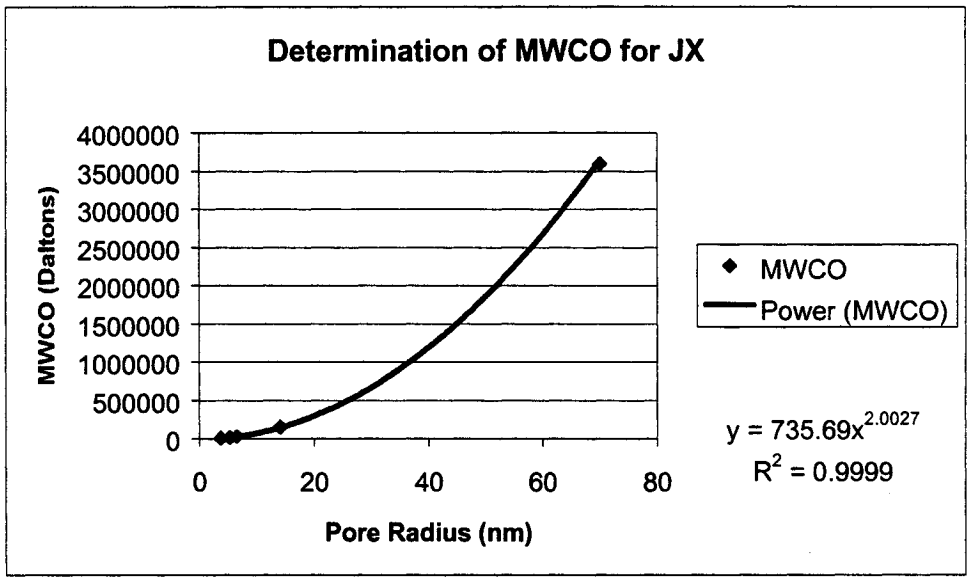


Figure B-1 Determination of MWCO for 0.3 microns.

Appendix C

Raw Data Output from LabVIEW

The attached CD of appendices at the end of the thesis contains several files of raw out-put data as the files are too large to append in printed form. The files are named leachatetest(MO)(DA).xls, where MO = month, DA = day for the leachate runs and watertest(MO)(DA).xls for water tests, the 2003 files also include 03 at the end of the file name. The following list explains some of the column headings:

Data Info – OK when all sensors are working the data was recording correctly and CHECK NUDAM MODULE when there are problems with the information stream

Cal Temp – Calibrated temperature

Mass trans V – The volts relayed from the pressure transducer monitoring the permeate mass.

Cal Mass – Calibrated mass based on the volts in milligrams

100 psig V - In-line pressure transducer monitoring flow pressure voltages

Cal 100psig - Calibrated pressure

Massflowrate - The mass flow rate calculation often did not operate properly and therefore these values are often incorrect.

See folder Appendix C in the CD for the complete excel files for all runs. Some runs are contained within their own folders listed by date as they were split into two or three separate files, to enable saving on a floppy disk.

Appendix D

Flux and Model Graphs

D.1 Flux Graphs

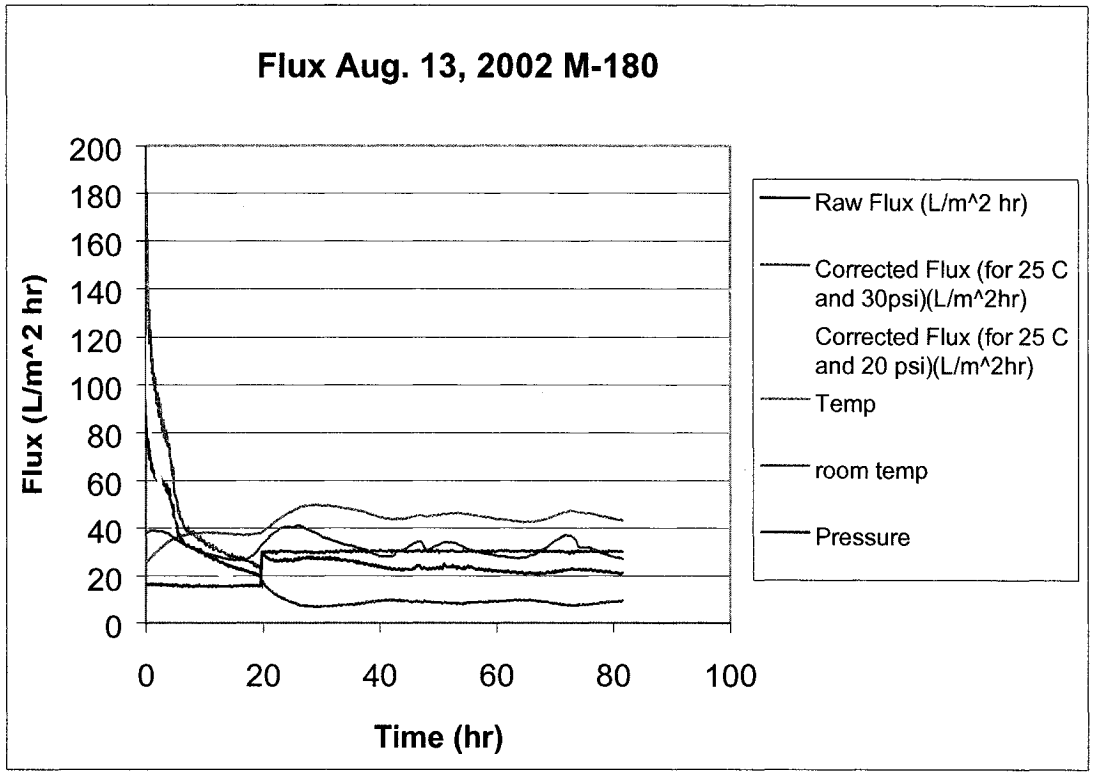


Figure D-1 Flux results for membrane M-180 run Aug. 13, 2002

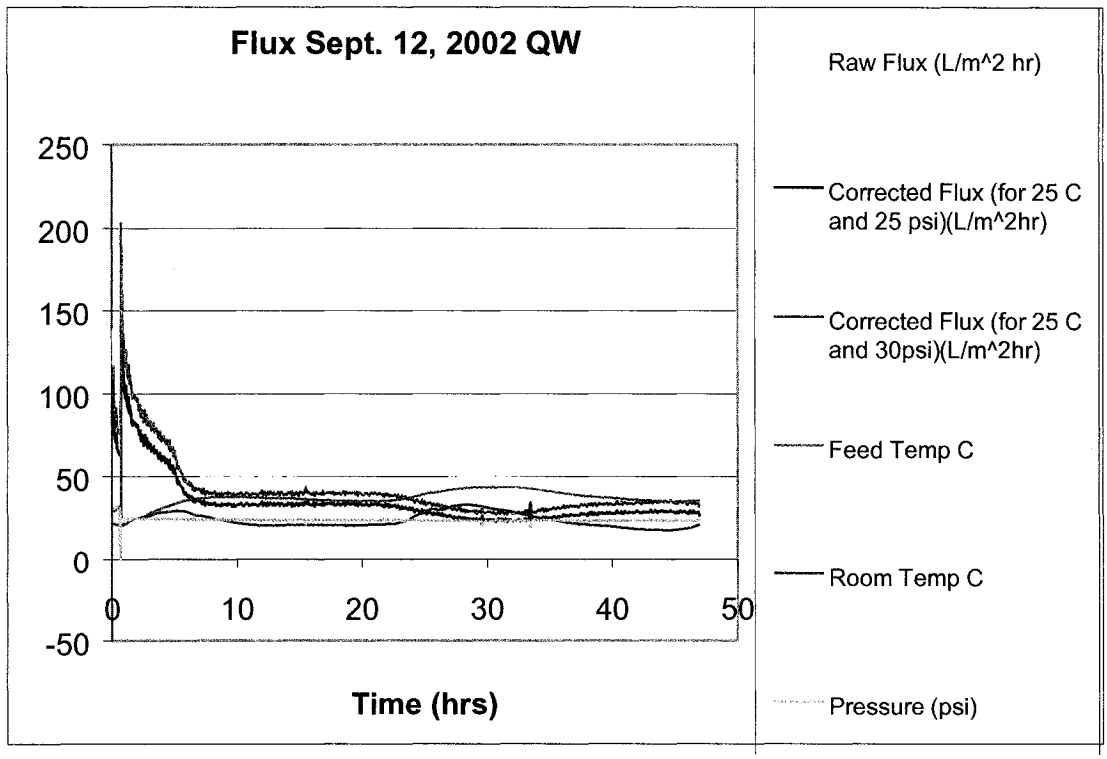


Figure D-2 Flux results for membrane QW run Sept. 12, 2002

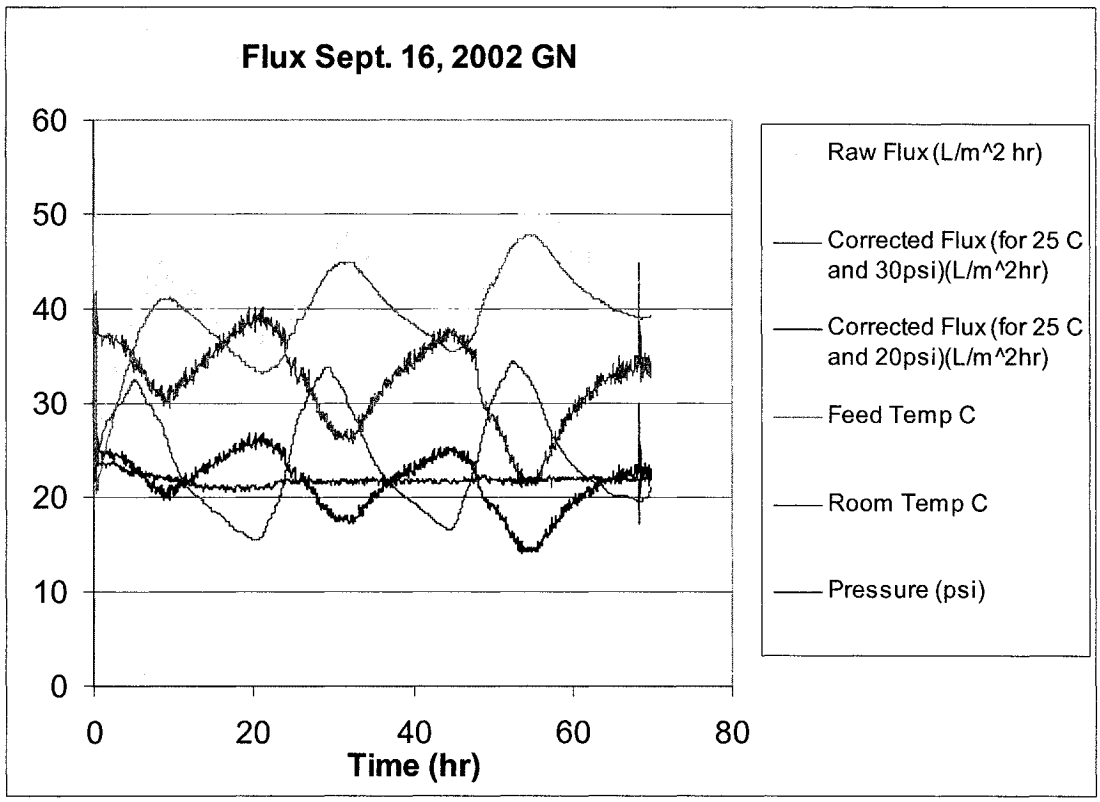


Figure D-3 Flux results for membrane GN run Sept. 16, 2002

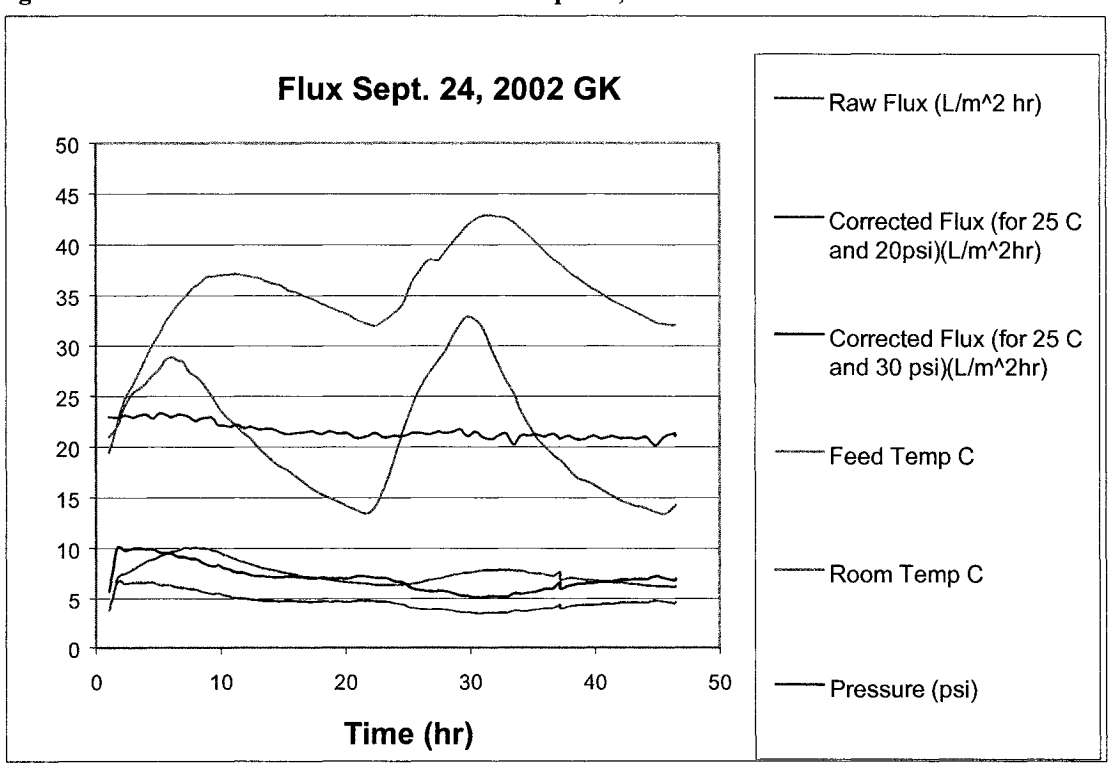


Figure D-4 Flux results for membrane GK run Sept. 24, 2002

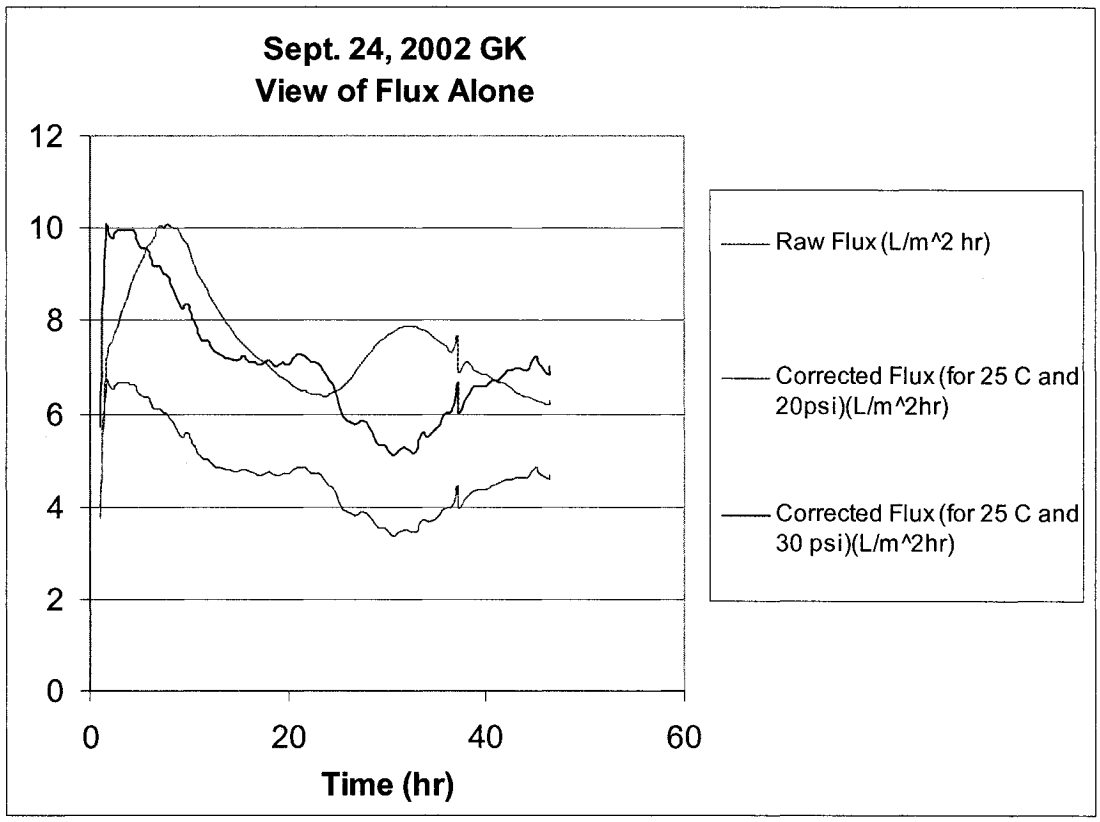


Figure D-5 Flux results alone for membrane GK run Sept. 24, 2002

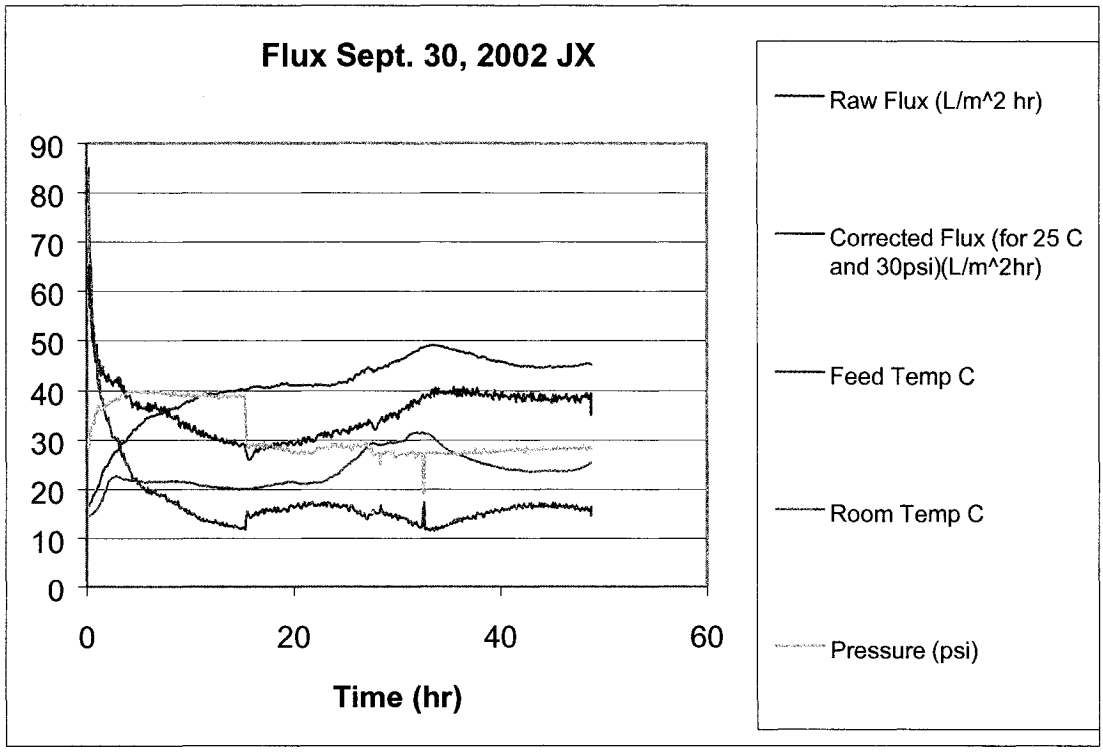


Figure D-6 Flux results for membrane JX run Sept. 30, 2002

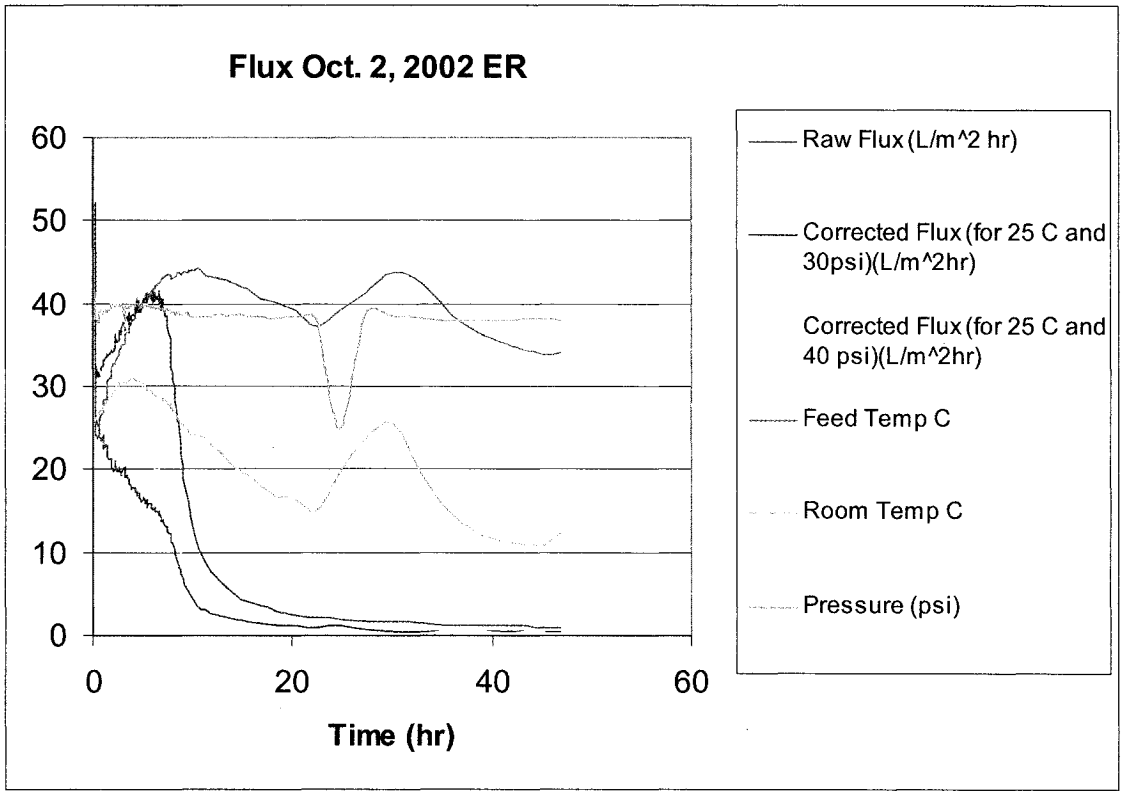


Figure D-7 Flux results for membrane ER run Oct. 2, 2002

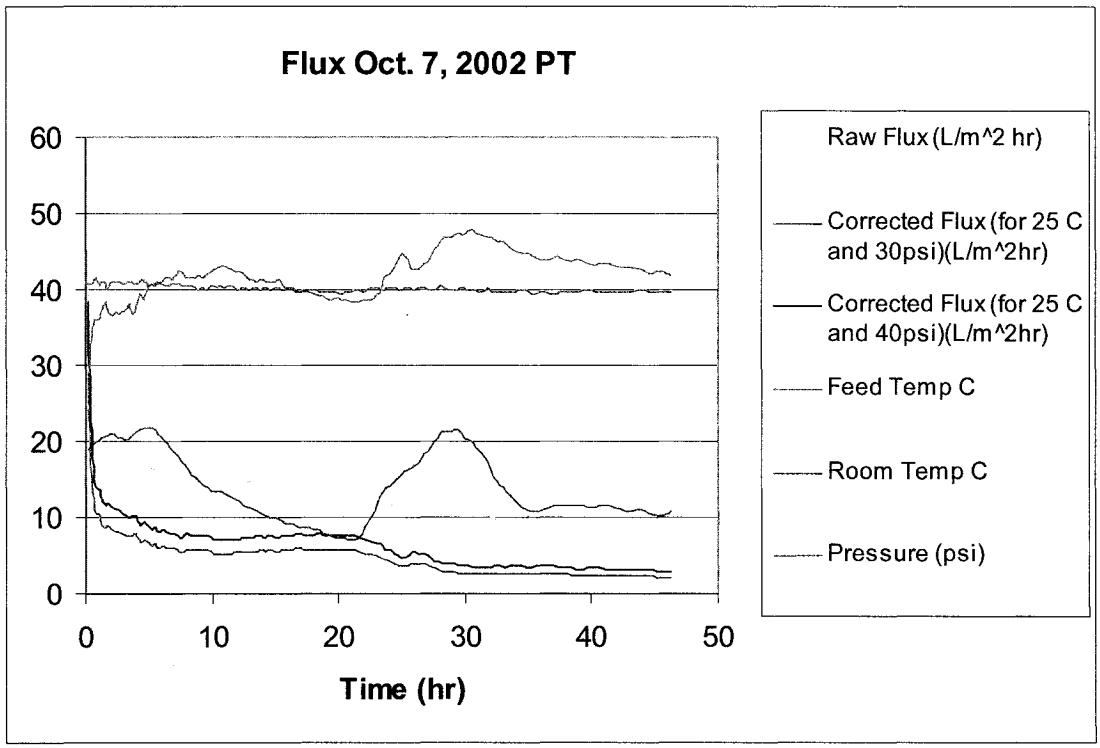


Figure D-8 Flux results for membrane PT run Oct. 7, 2002

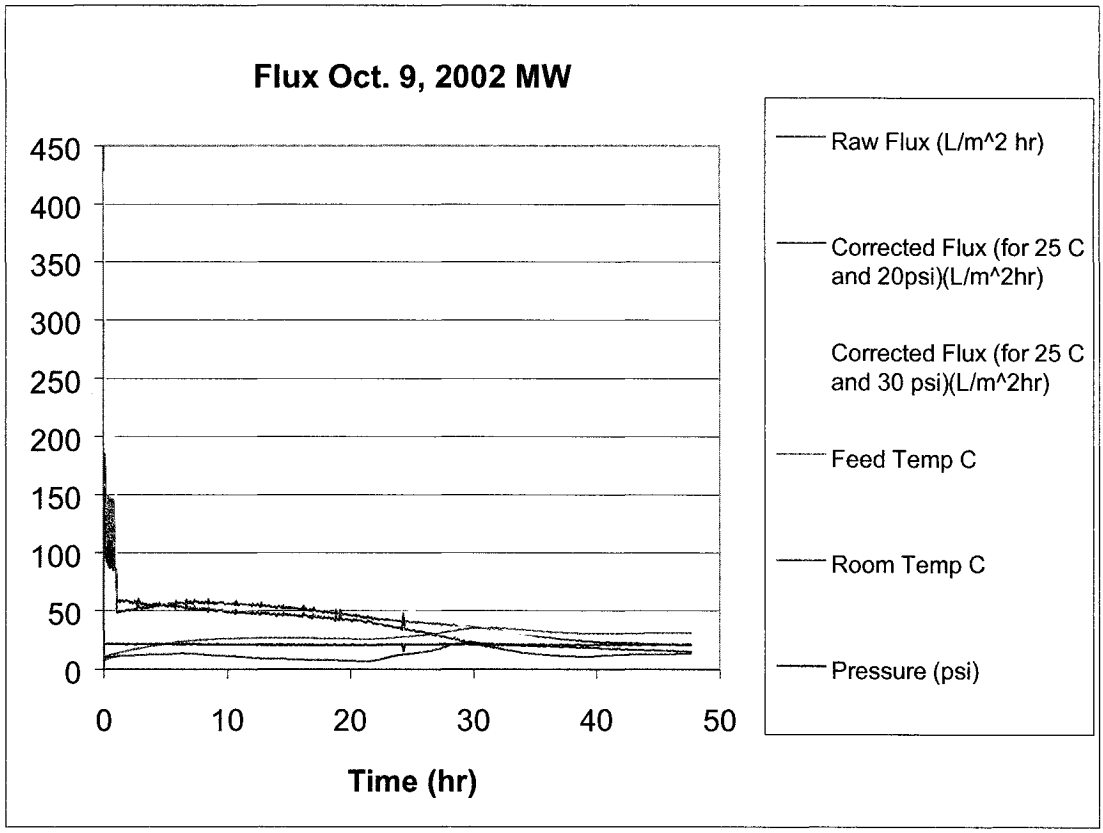


Figure D-9 Flux results for membrane MW run Oct. 9, 2002

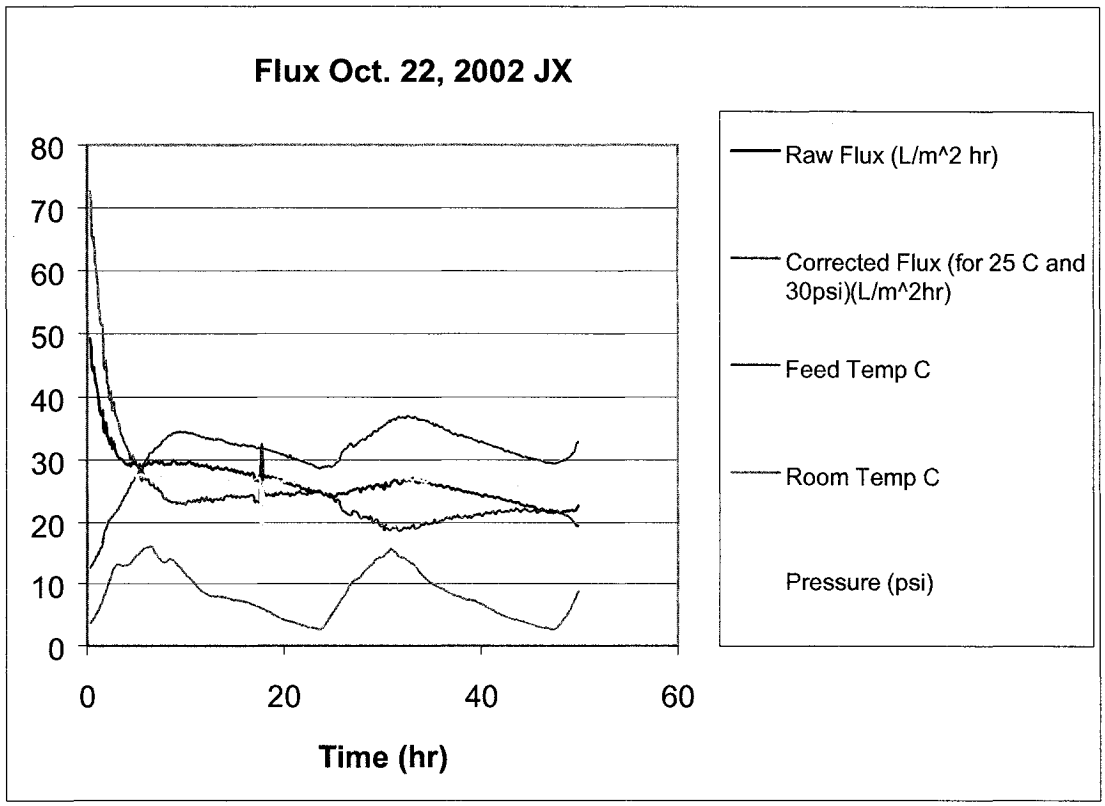


Figure D-10 Flux results for membrane JX run Oct. 22, 2002

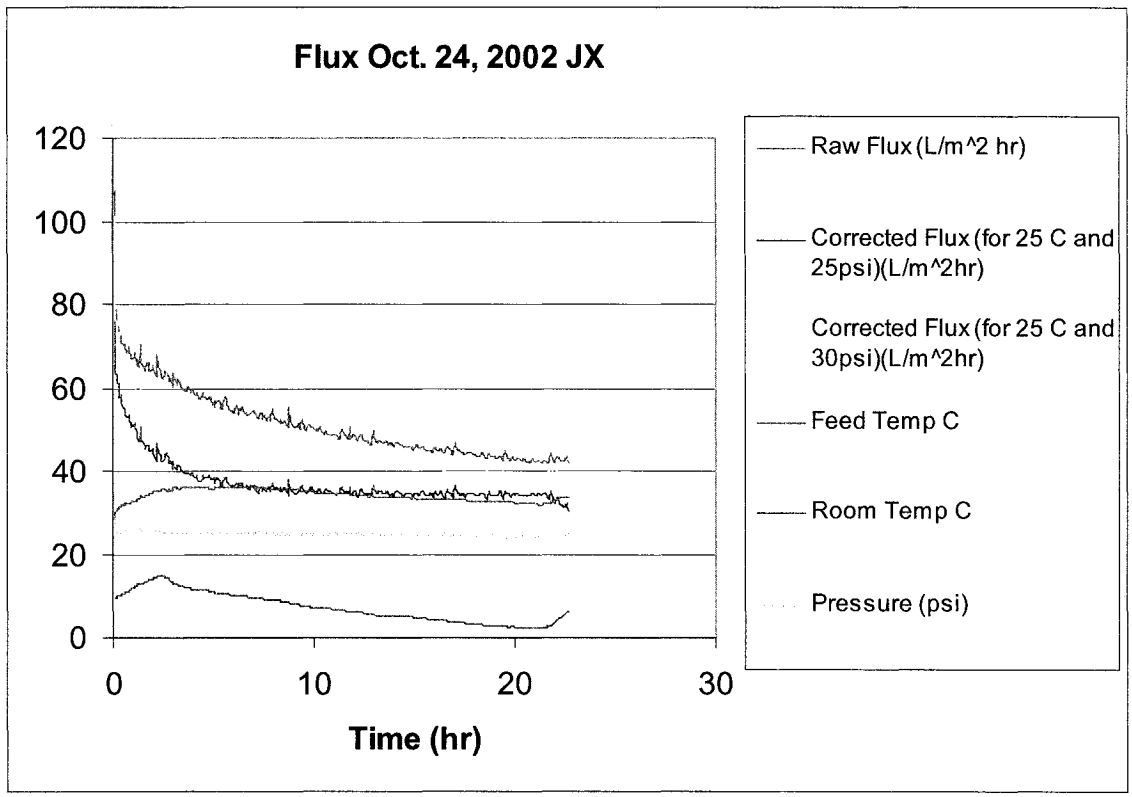


Figure D-11 Flux results for membrane JX run Oct. 24, 2002

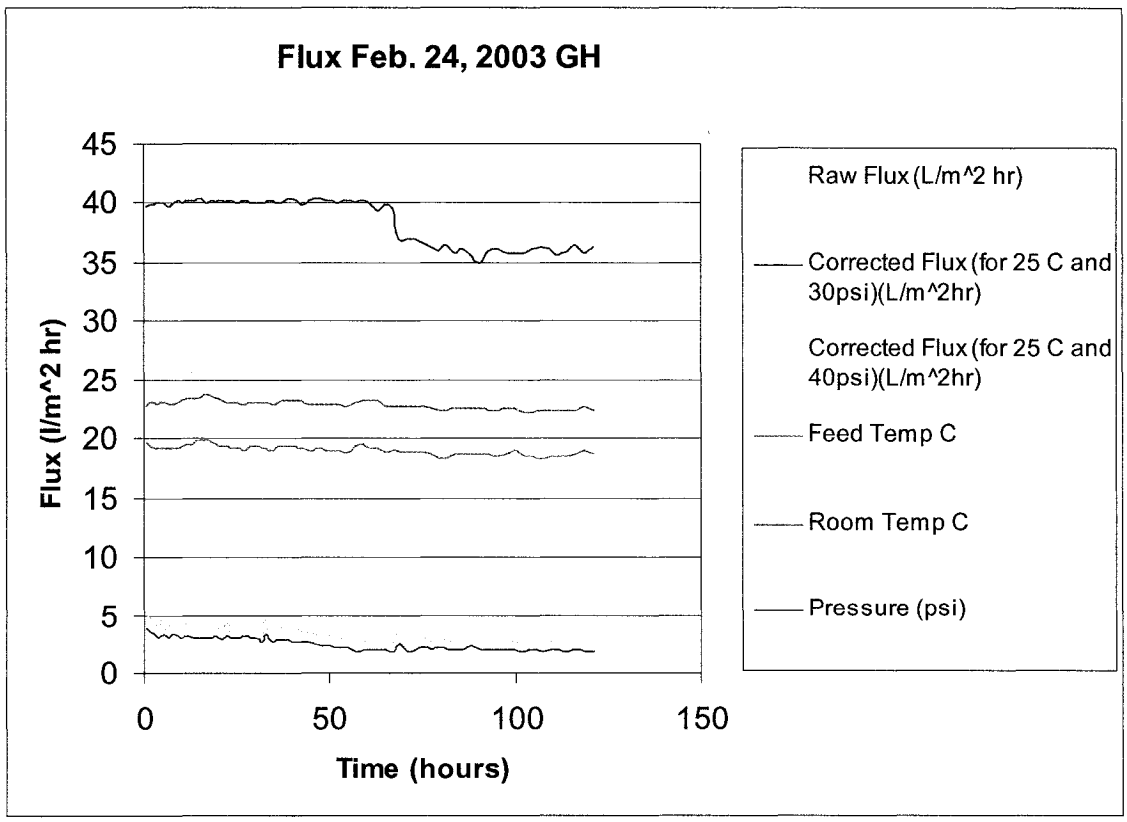


Figure D-12 Flux results for membrane GH run Feb. 24, 2003

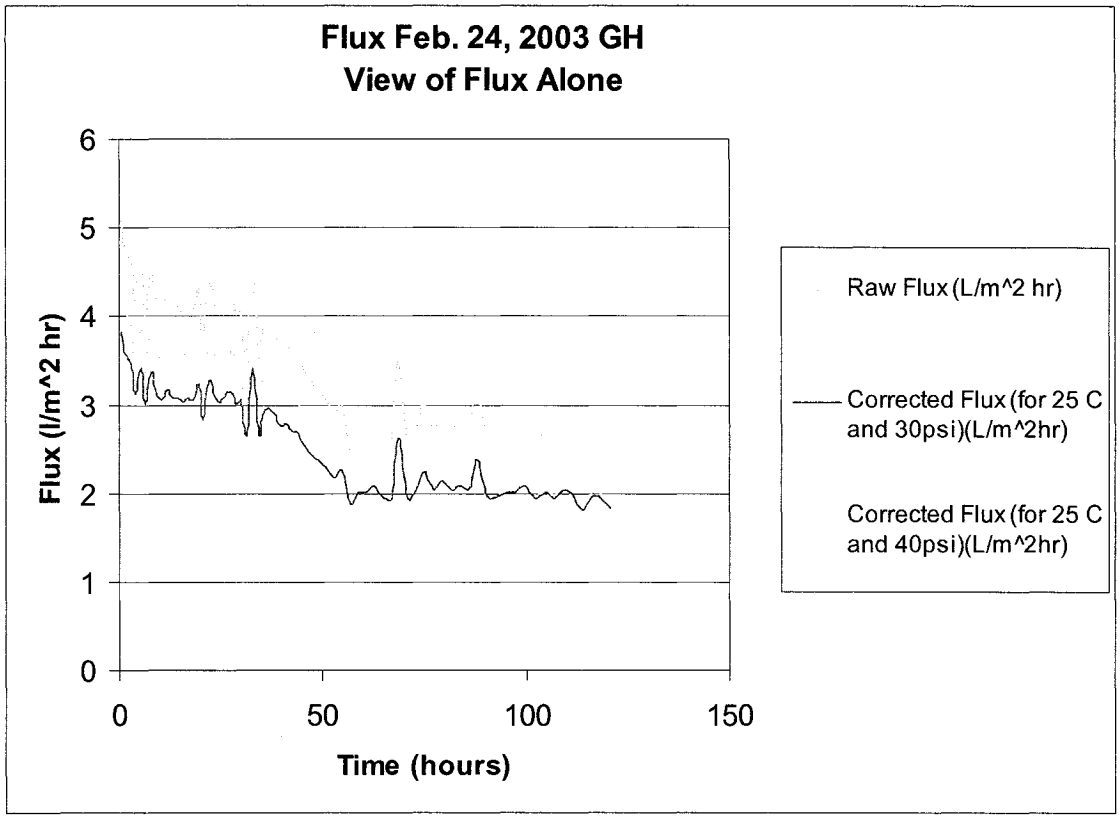


Figure D-13 Flux results alone for membrane GH run Feb. 24, 2003

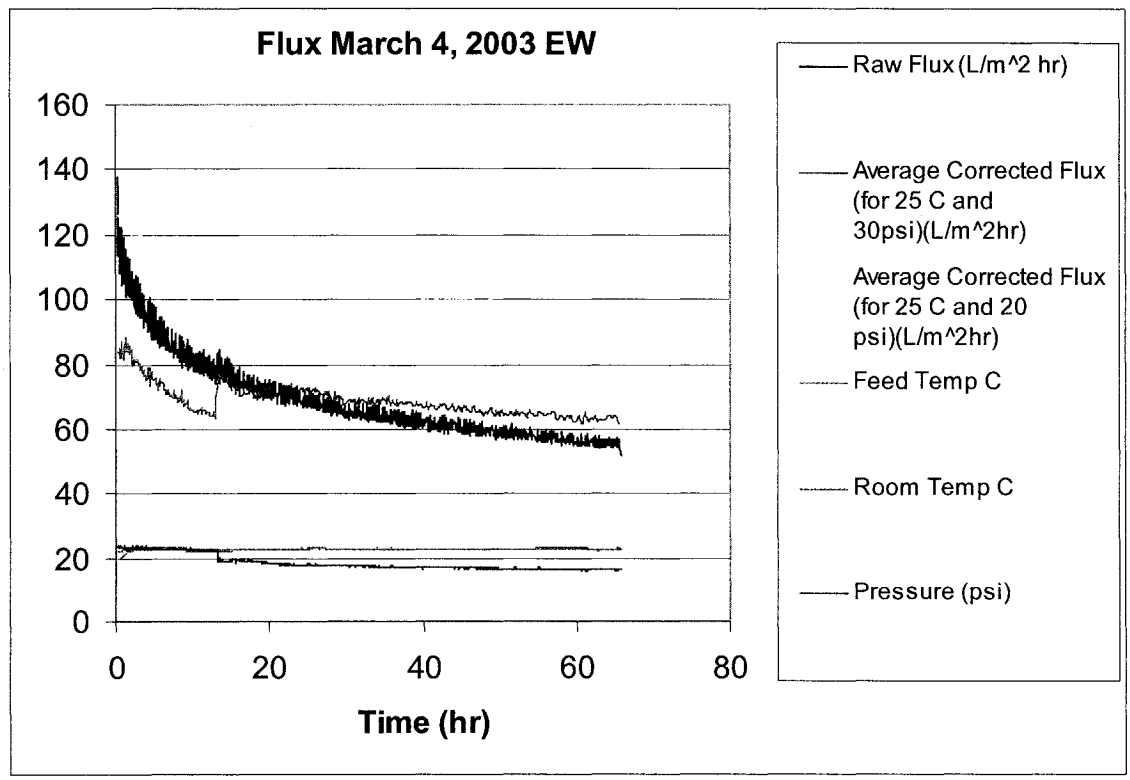


Figure D-14 Flux results for membrane EW run March 4, 2003

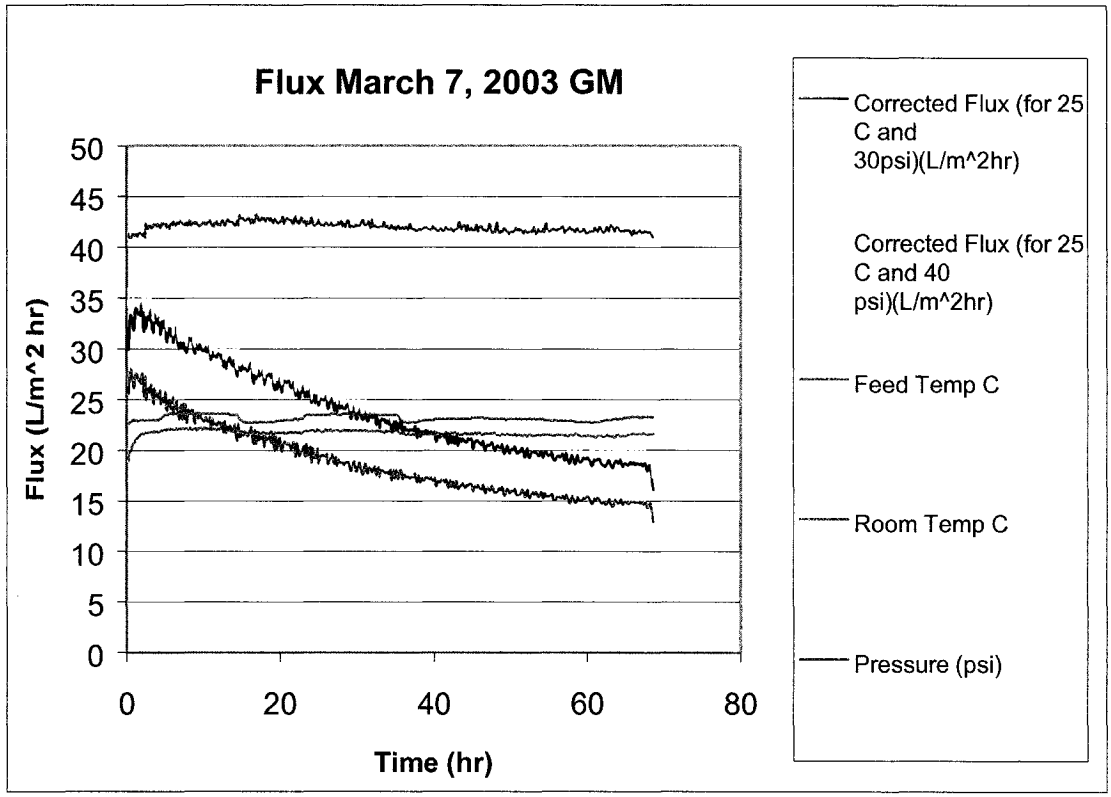


Figure D-15 Flux results for membrane GM run March 7, 2003

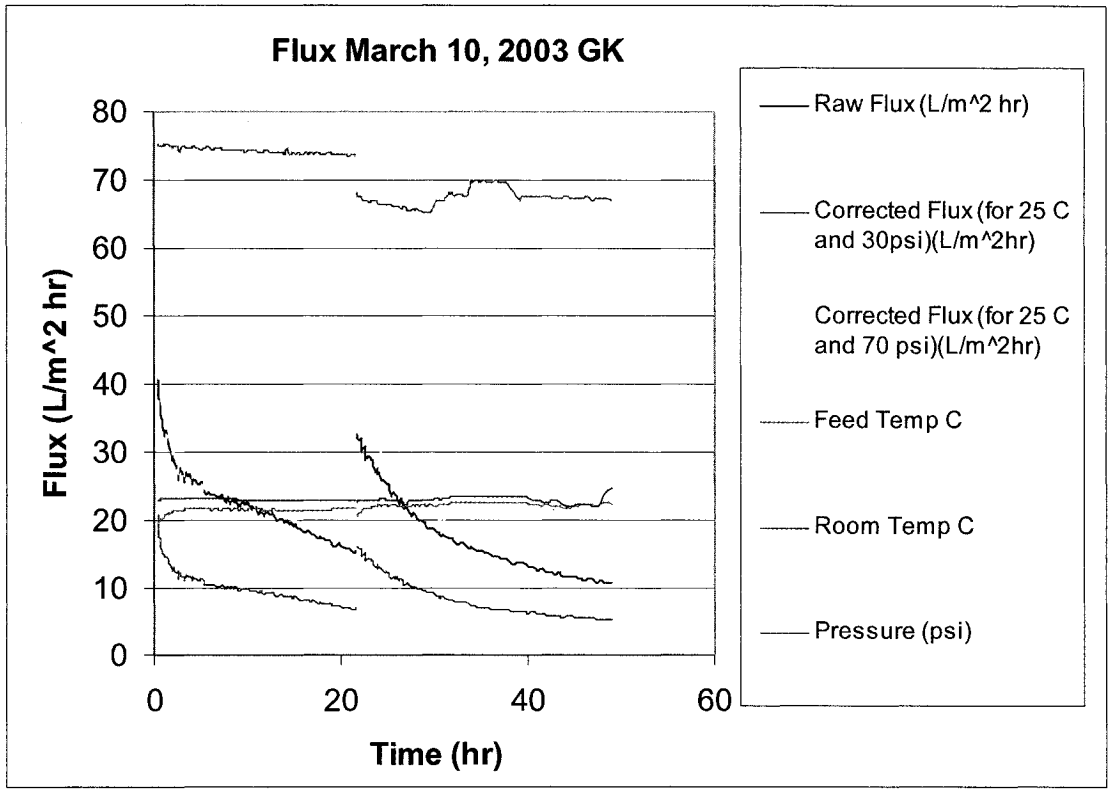


Figure D-16 Flux results for membrane GK run March 10, 2003

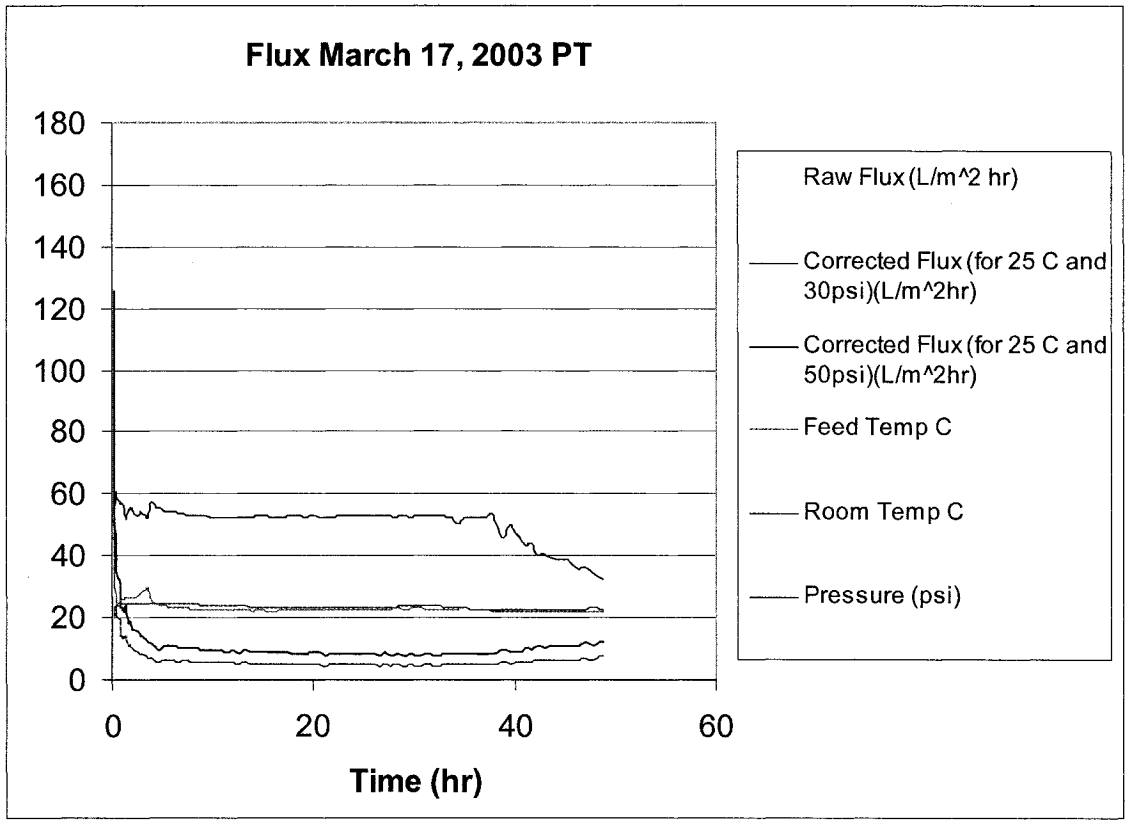


Figure D-17 Flux results for membrane PT run March 17, 2003

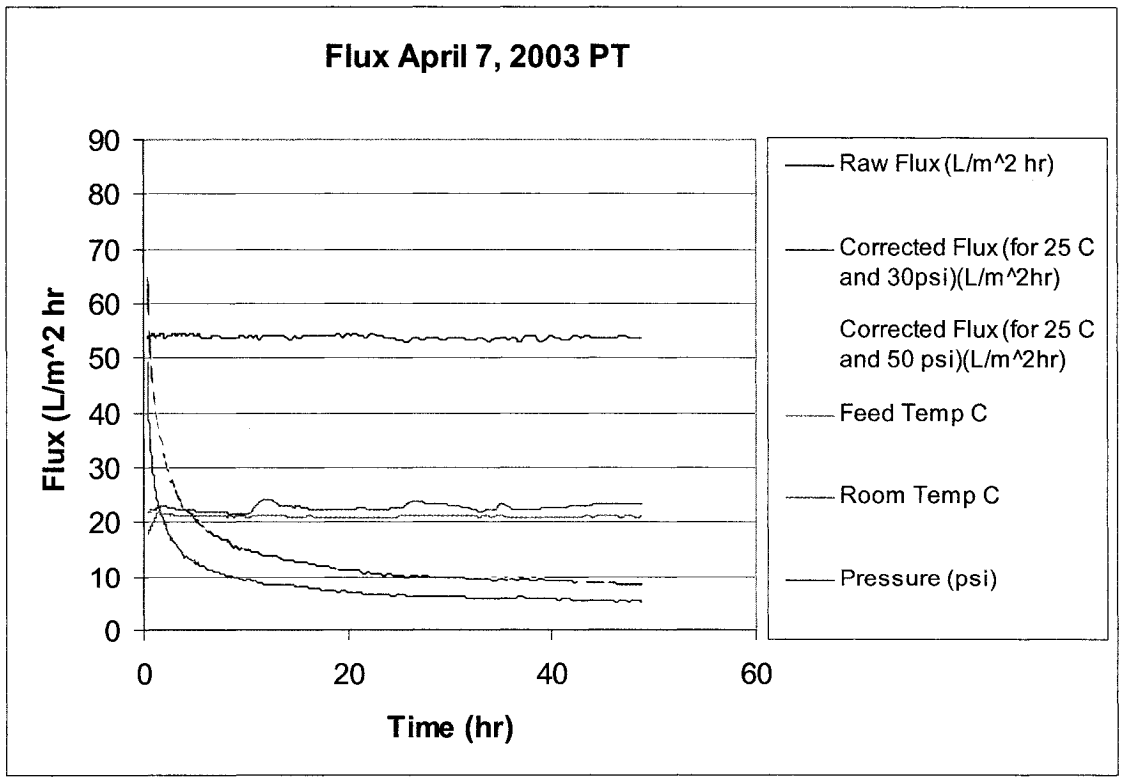


Figure D-18 Flux results for membrane PT run April 7, 2003

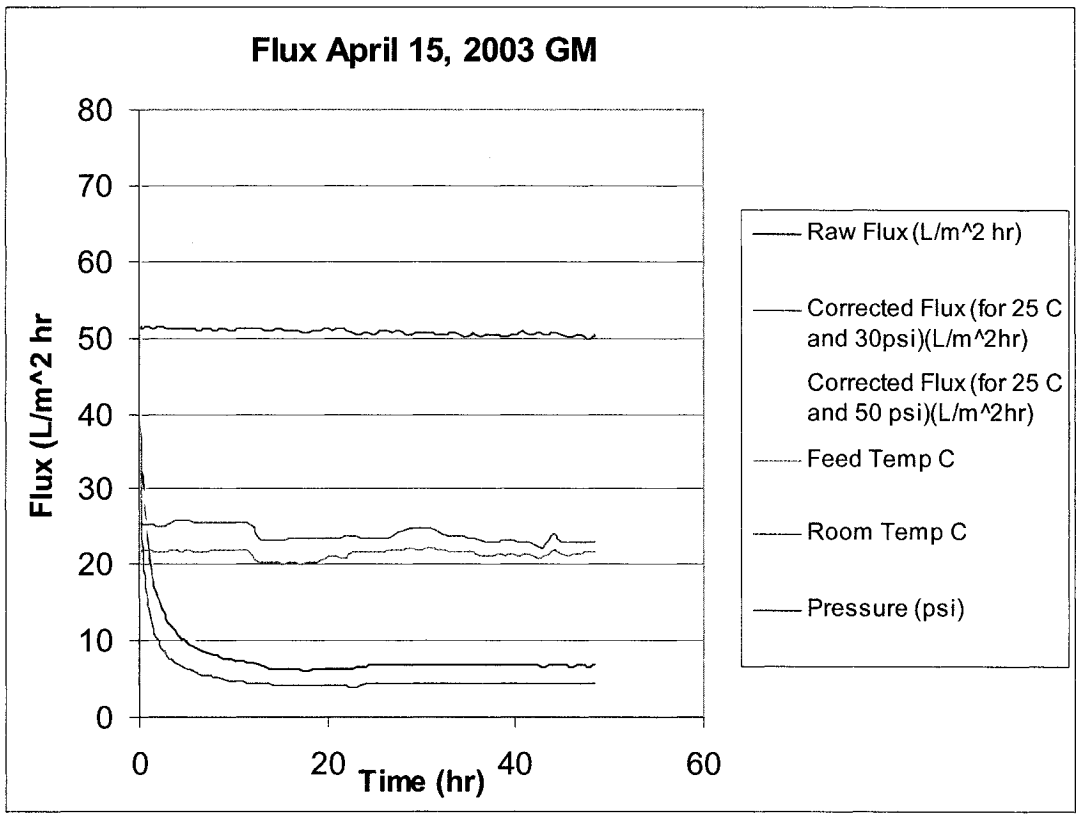


Figure D-19 Flux results for membrane GM run April 15, 2003

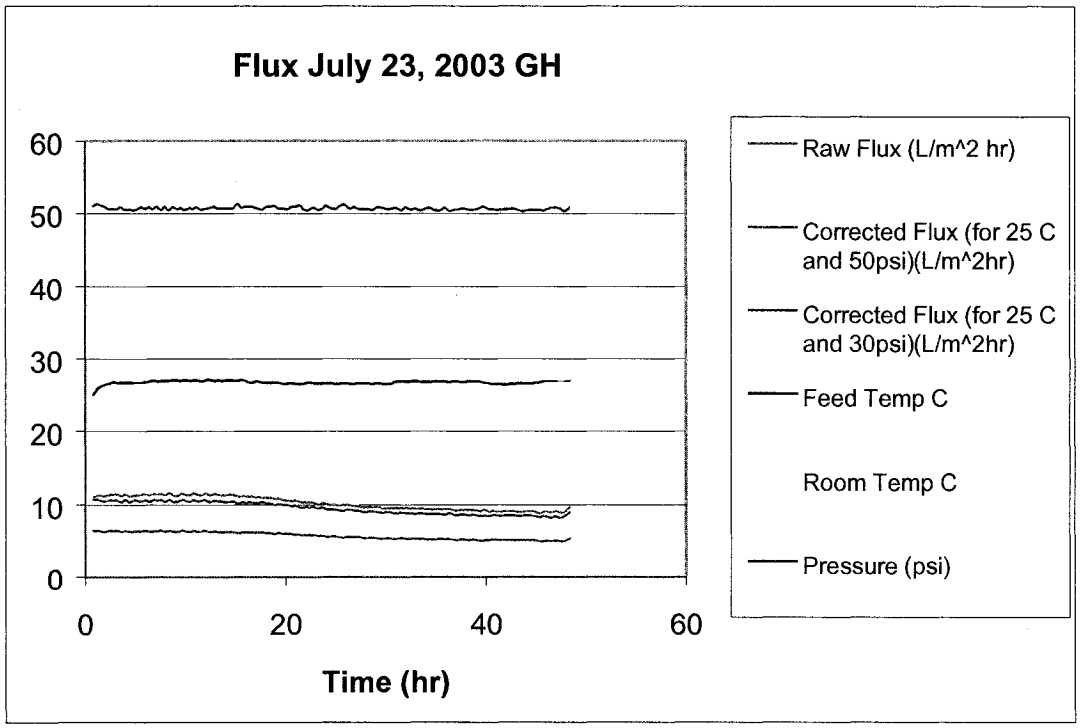


Figure D-20 Flux results for membrane GH run July 23, 2003

D.2 Modelling Graphs

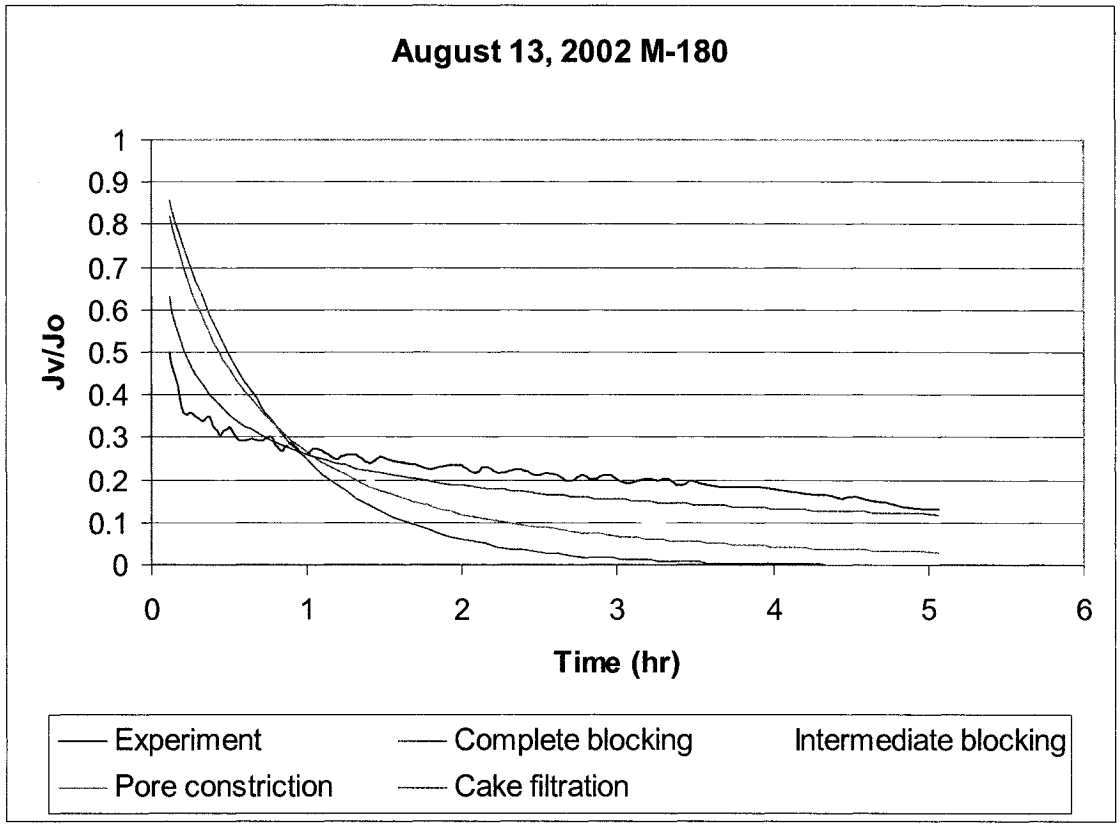


Figure D-21 Flux modelling results for membrane M-180 run Aug. 13, 2002

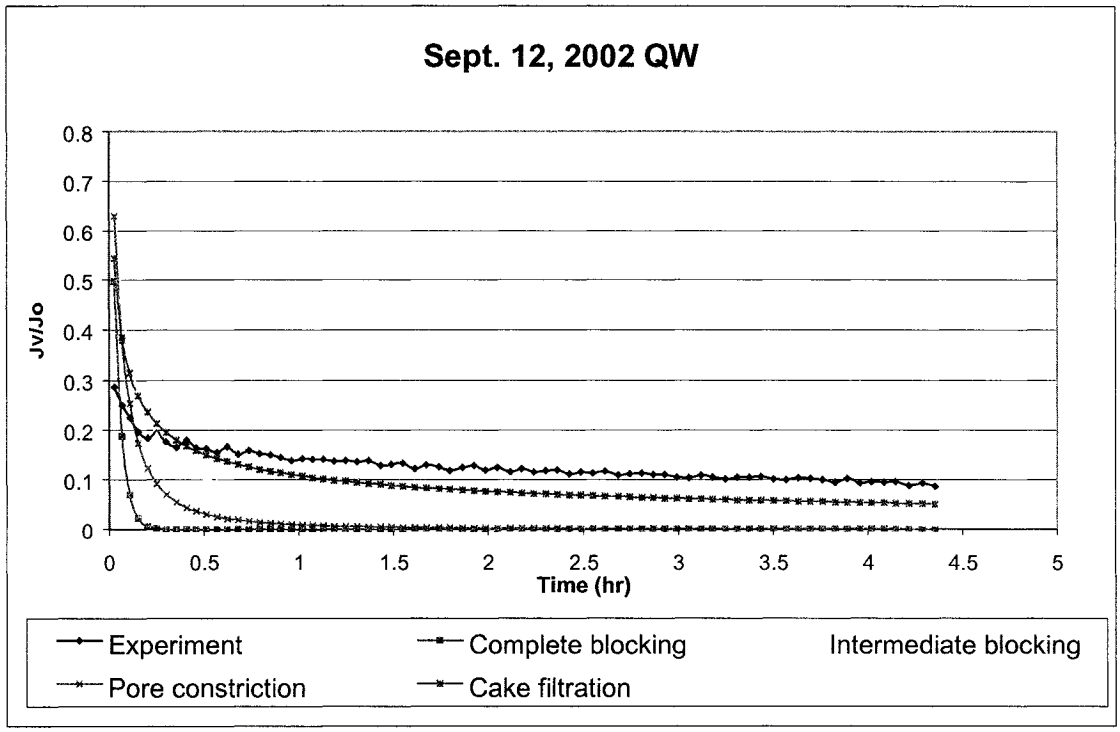


Figure D-22 Flux modelling results for membrane QW run Sept. 12, 2002

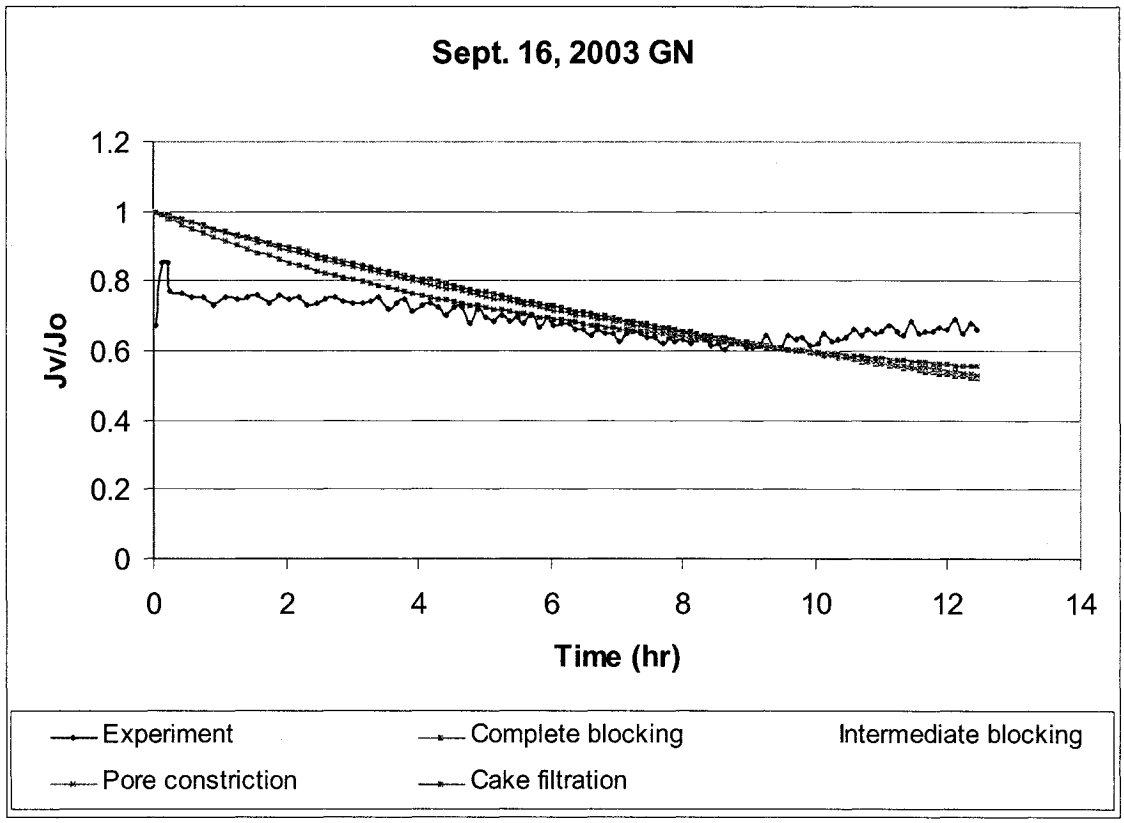


Figure D-23 Flux modelling results for membrane GN run Sept. 16, 2002

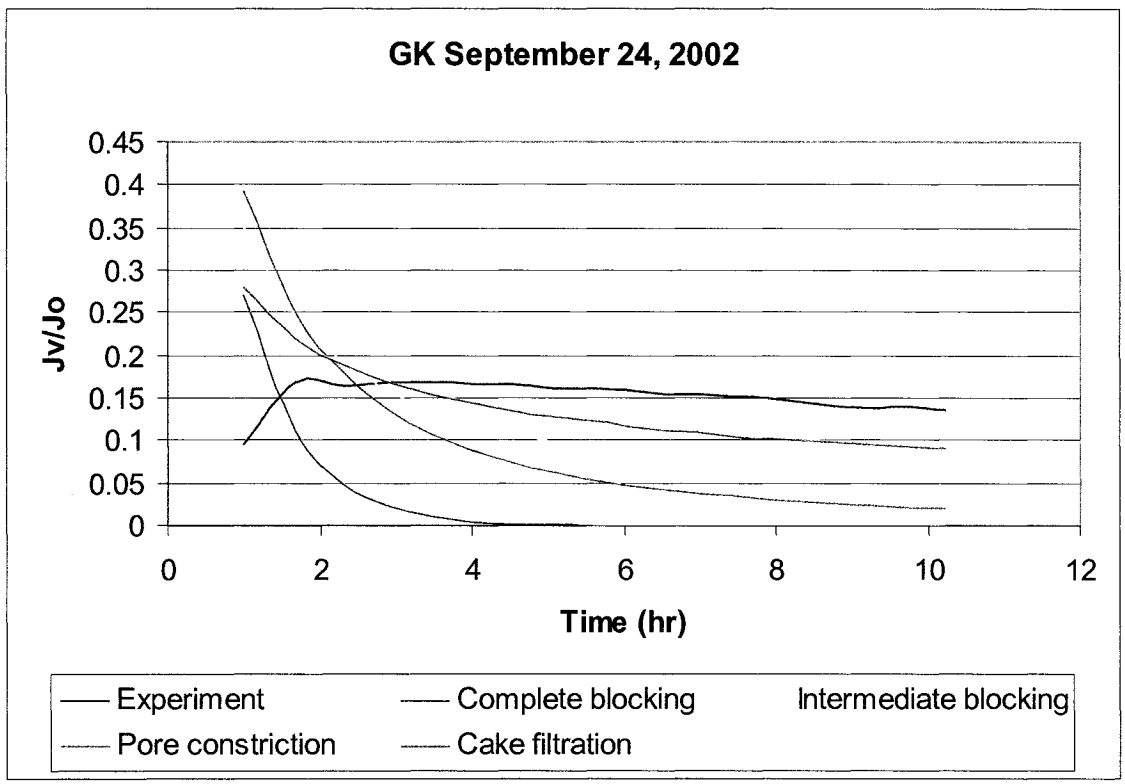


Figure D-24 Flux modelling results for membrane GK run Sept. 24, 2002

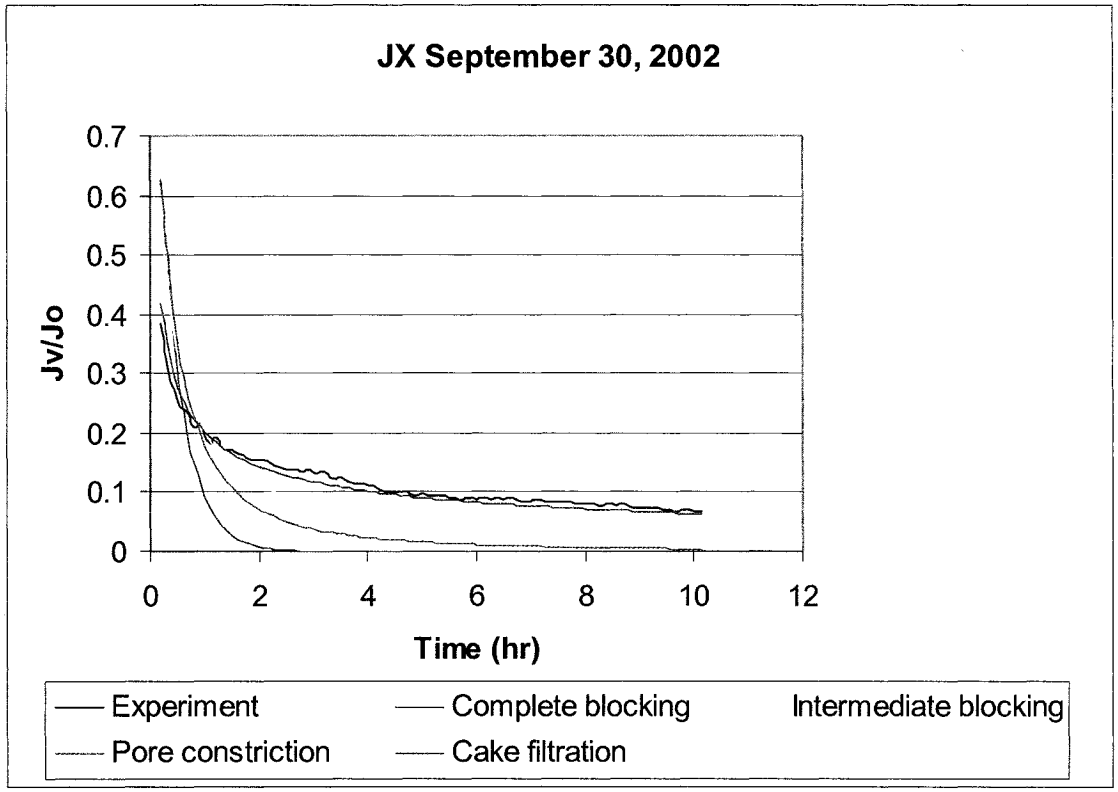


Figure D-25 Flux modelling results for membrane JX run Sept. 30, 2002

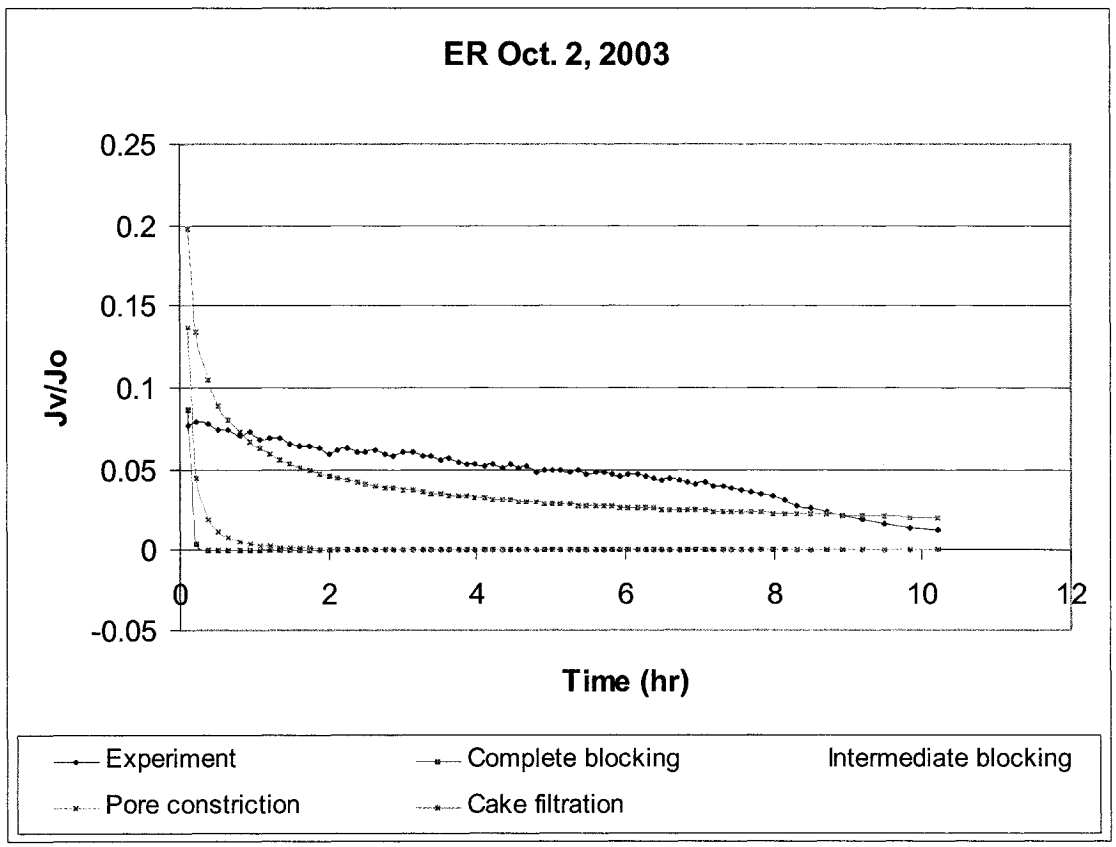


Figure D-26 Flux modelling results for membrane ER run Oct. 2, 2002

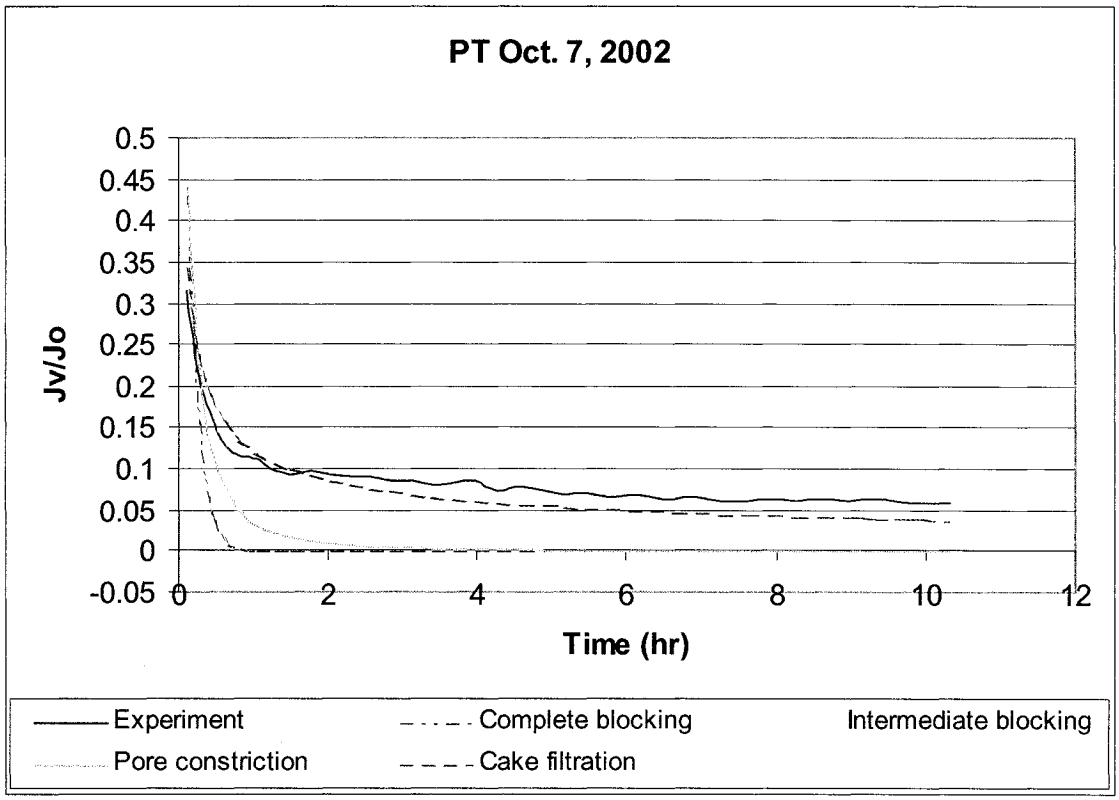


Figure D-27 Flux modelling results for membrane PT run Oct. 7, 2002

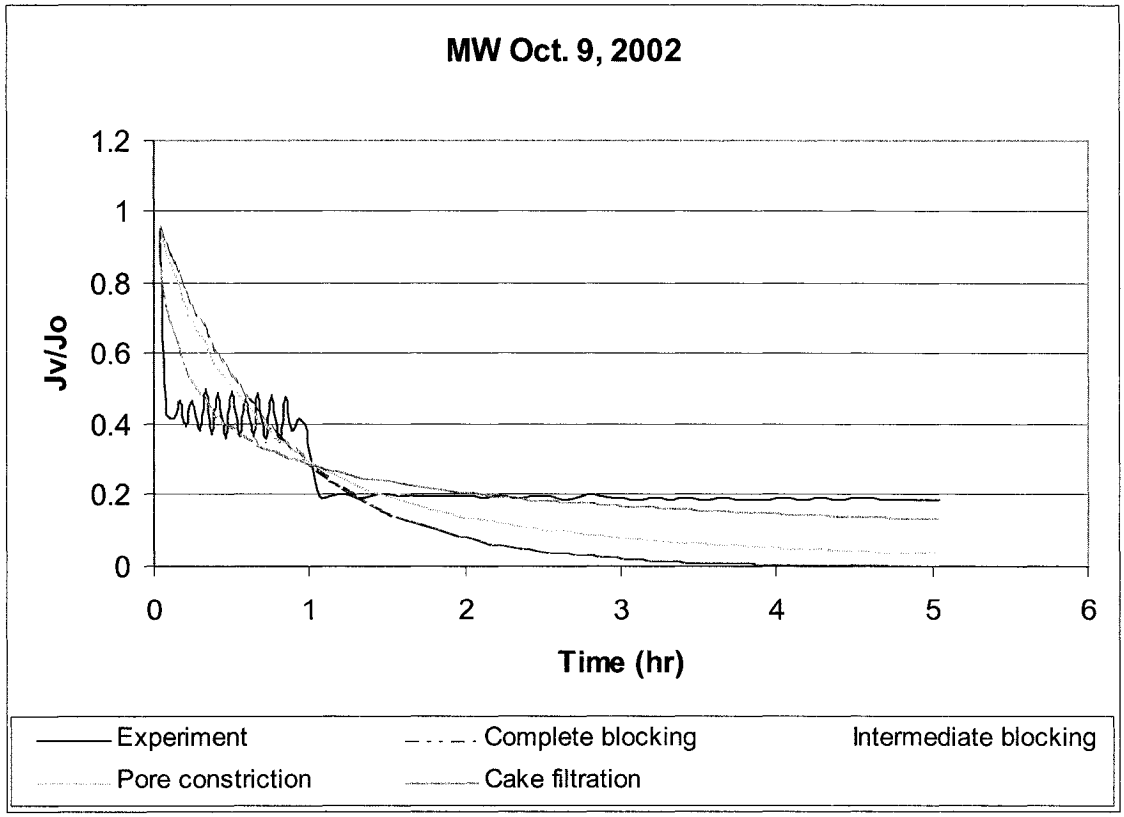


Figure D-28 Flux modelling results for membrane MW run Oct. 9, 2002

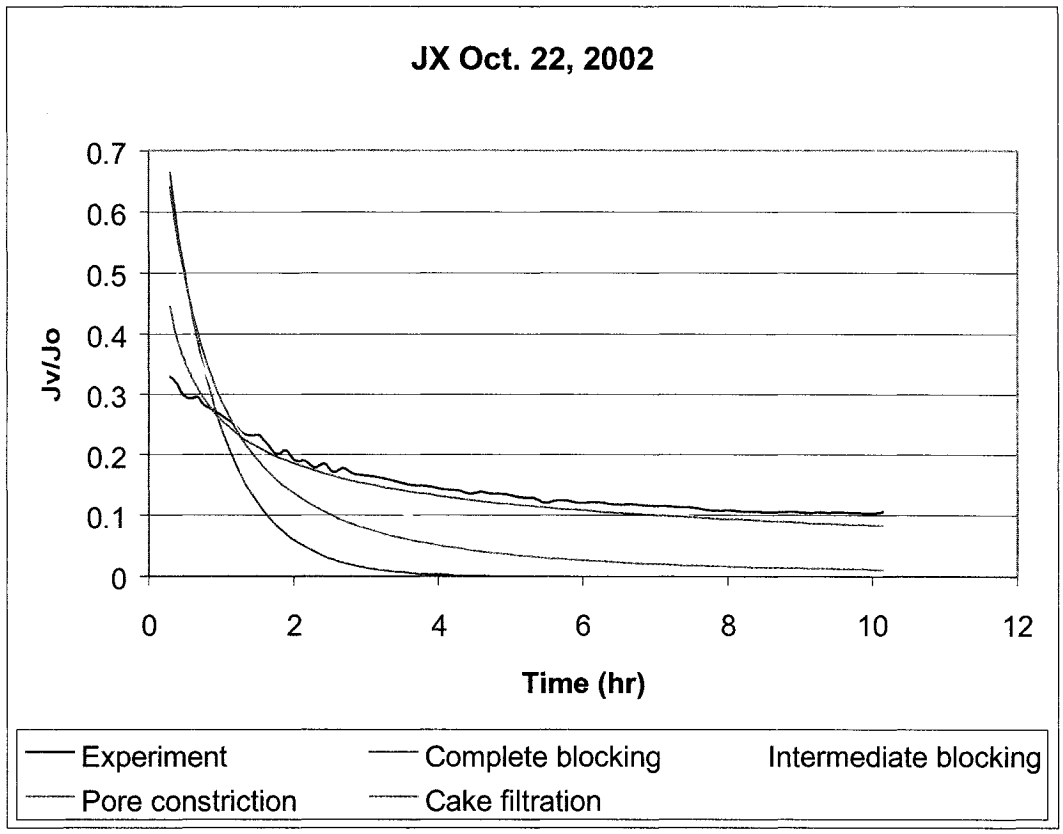


Figure D-29 Flux modelling results for membrane JX run Oct. 22, 2002

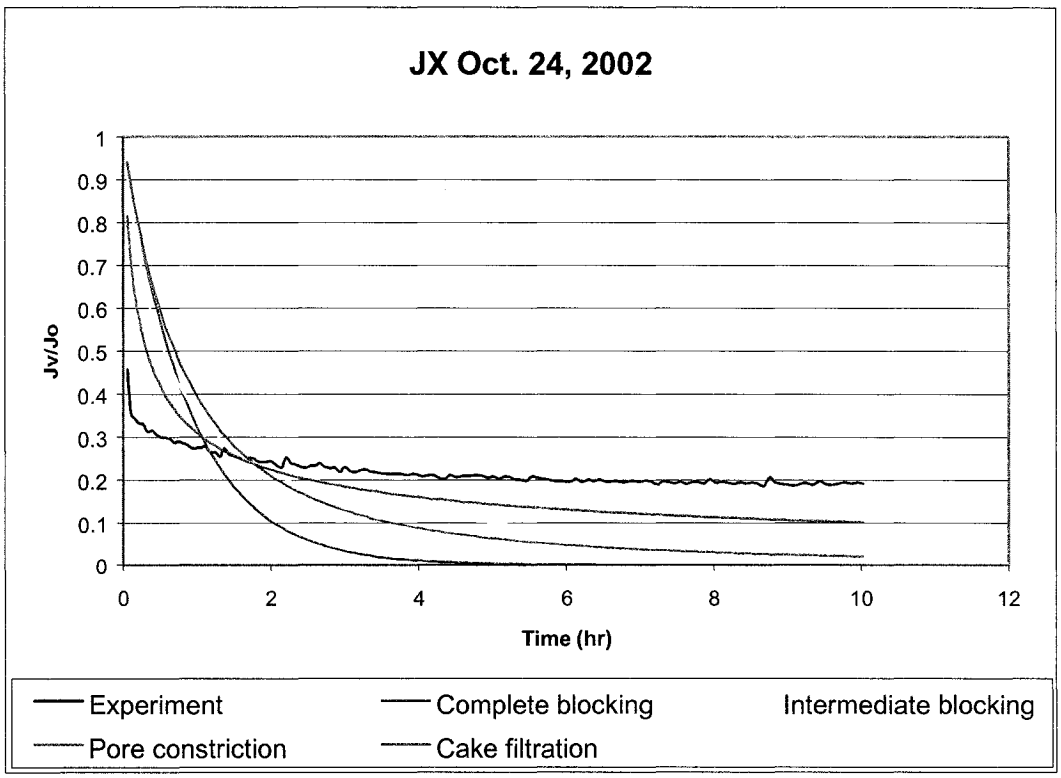


Figure D-30 Flux modelling results for membrane JX run Oct. 24, 2002

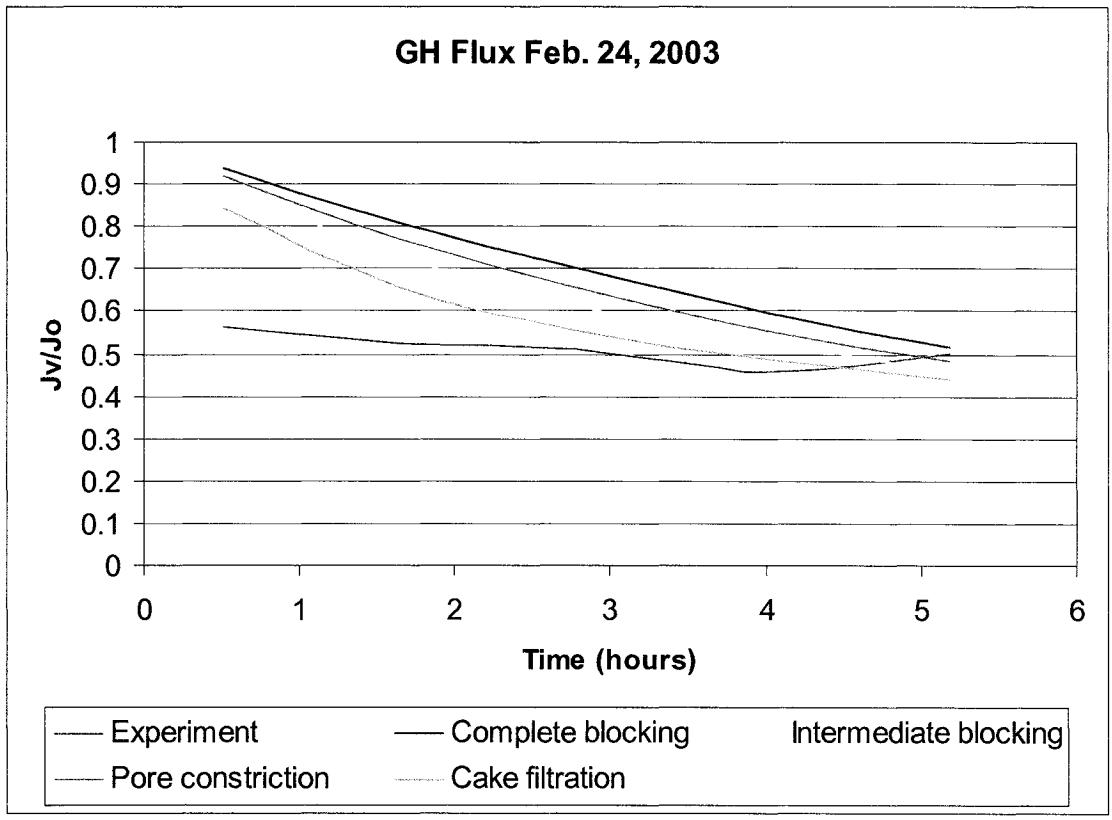


Figure D-31 Flux modelling results for membrane GH run Feb. 24, 2003

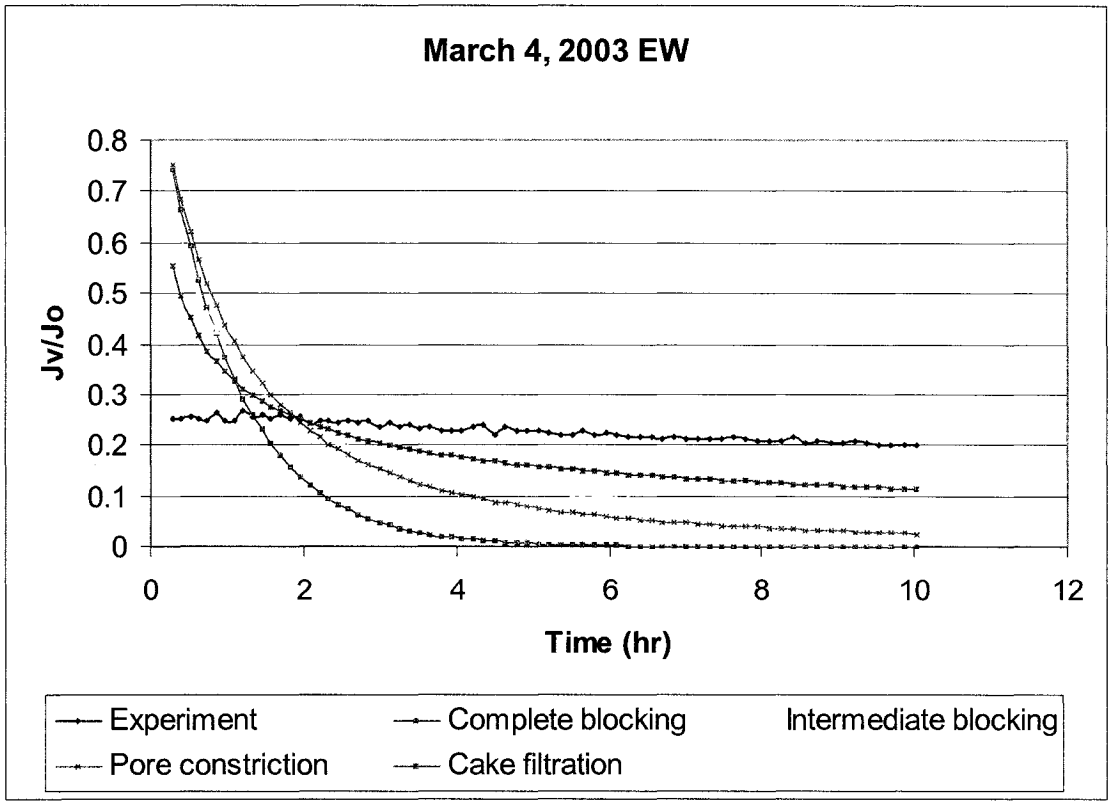


Figure D-32 Flux modelling results for membrane EW run March 4, 2003

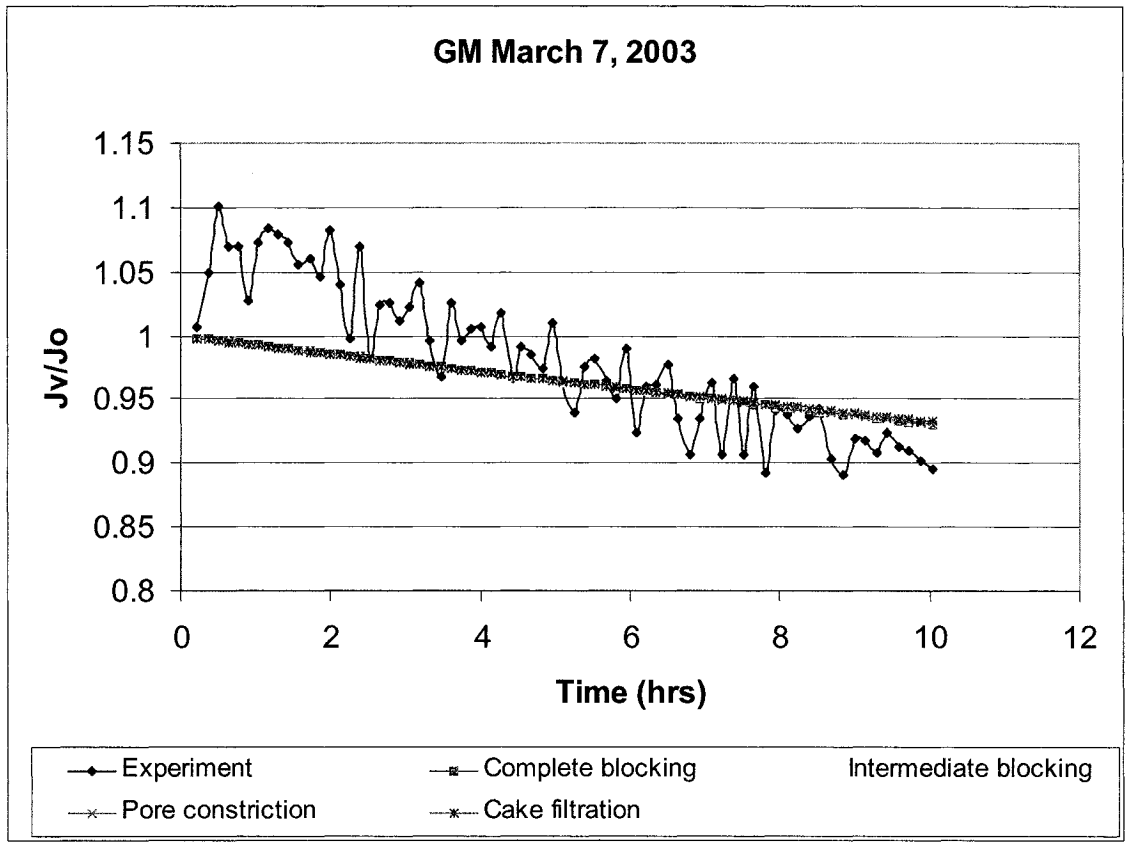


Figure D-33 Flux modelling results for membrane GM run March 7, 2003

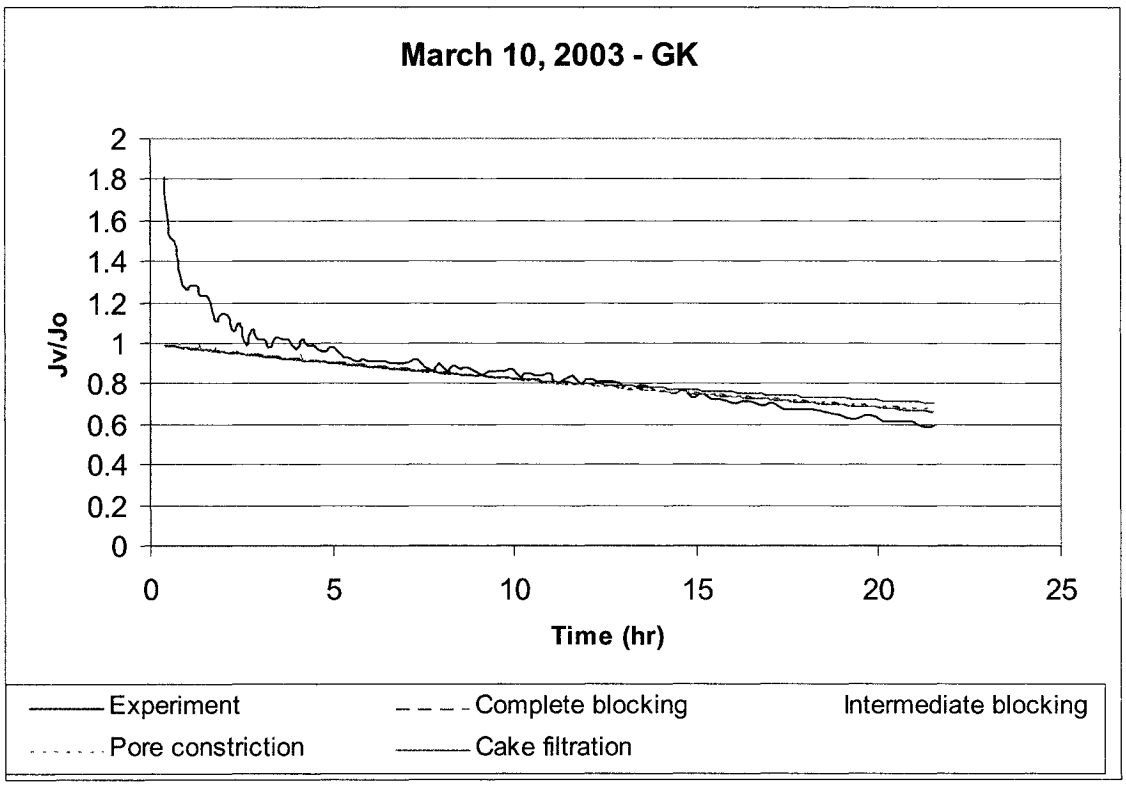


Figure D-34 Flux modelling results for membrane GK run March 10, 2003

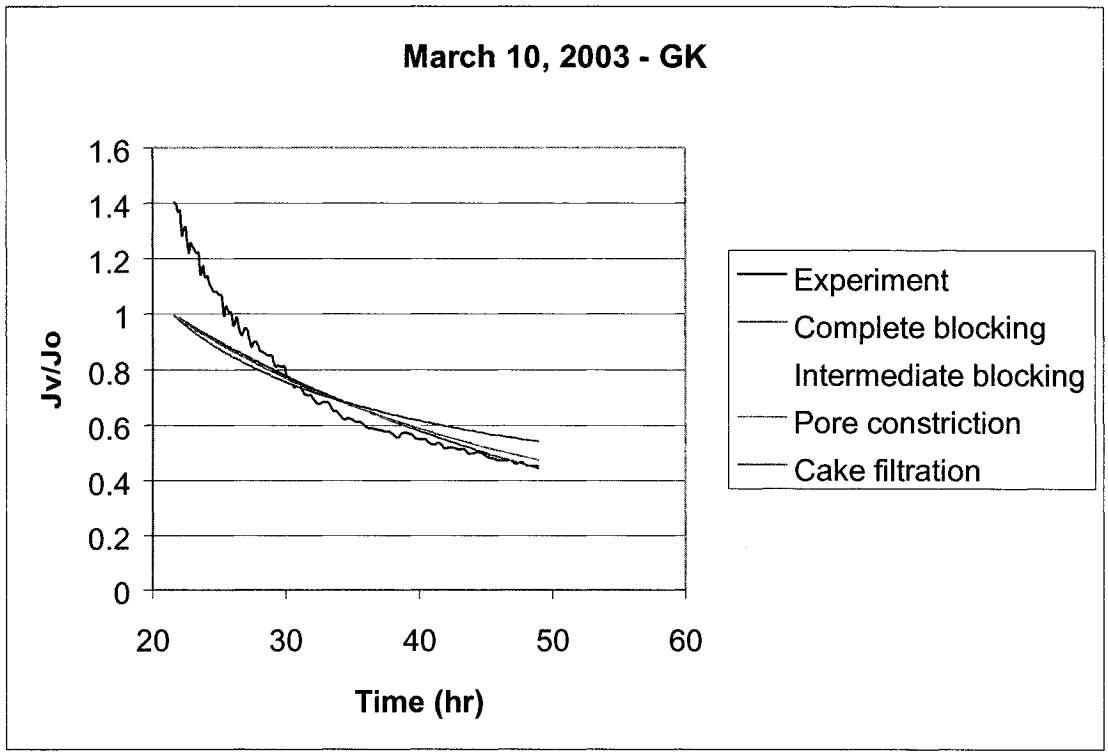


Figure D-35 Flux modelling results for membrane GK overall run March 10, 2003

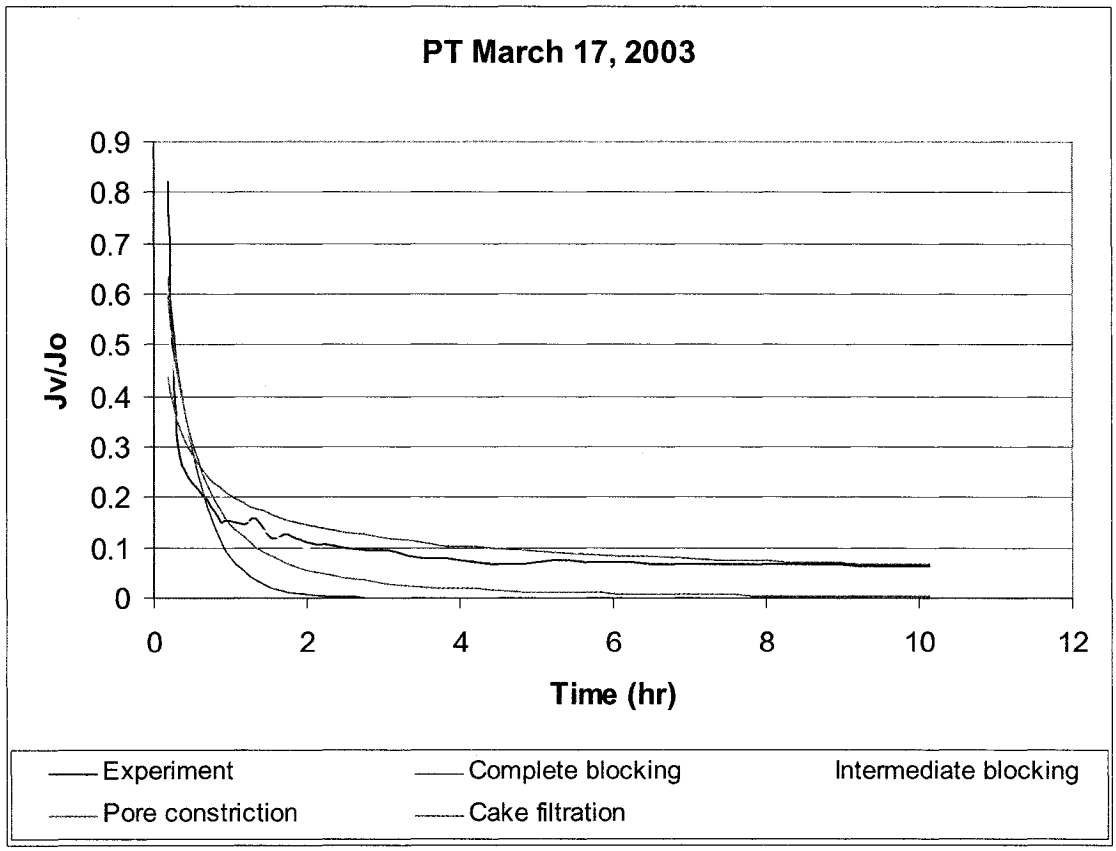


Figure D-36 Flux modelling results for membrane PT run March 17, 2003

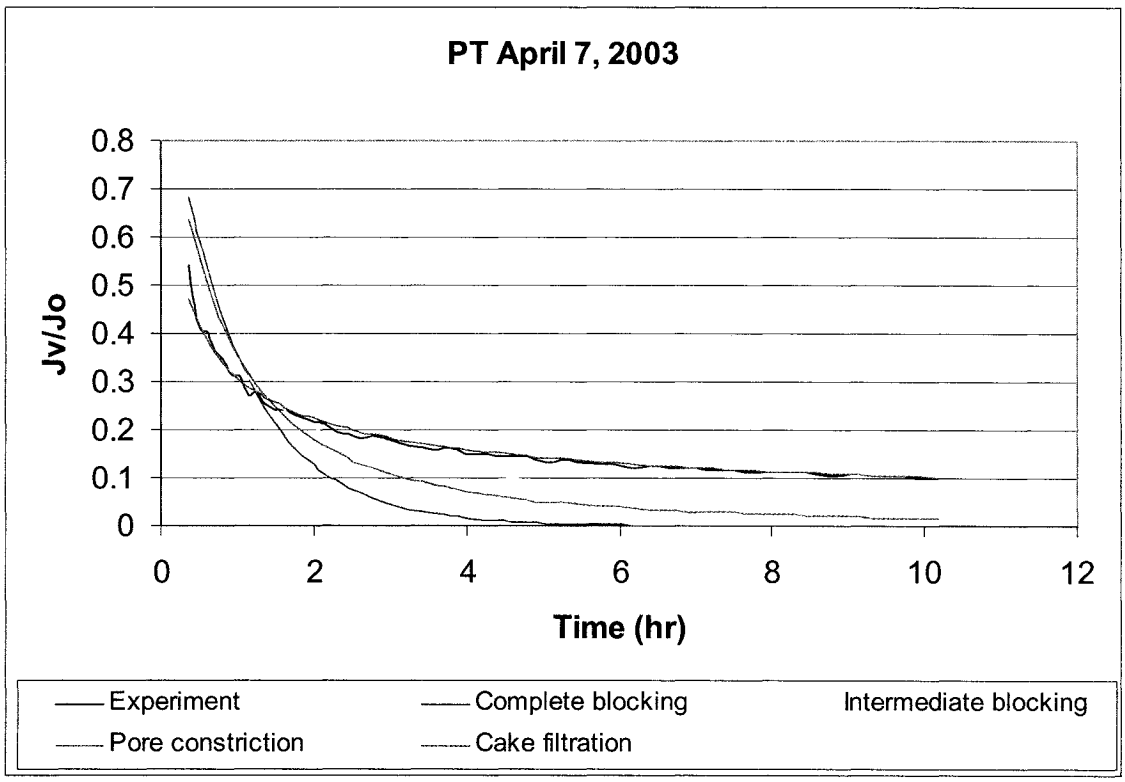


Figure D-37 Flux modelling results for membrane PT run April 7, 2003

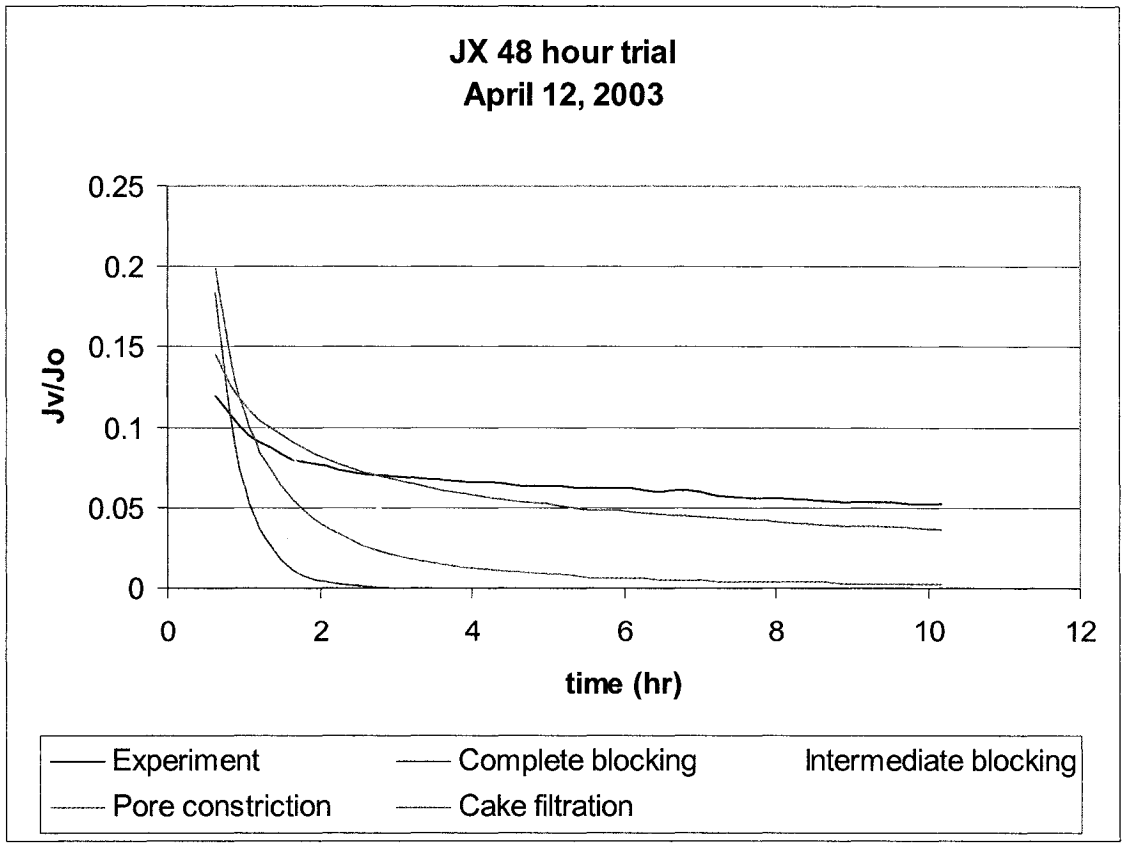


Figure D-38 Flux modelling results for membrane JX run April 12, 2003

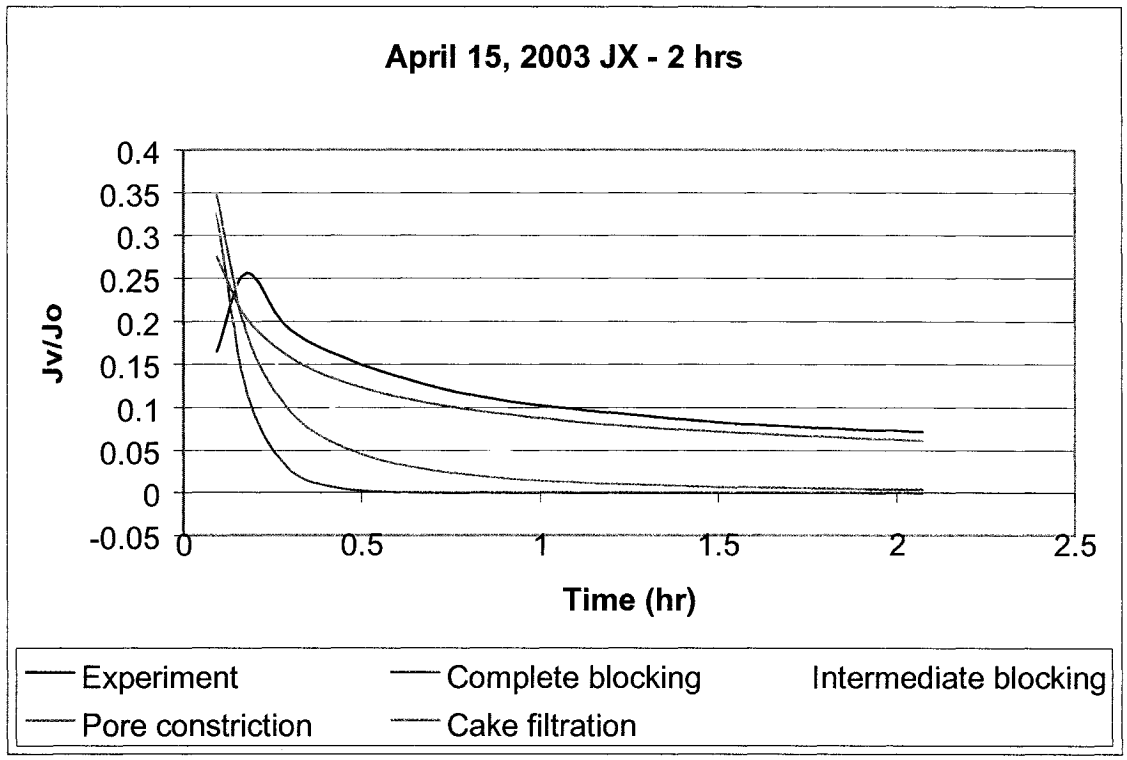


Figure D-39 Flux modelling results for membrane JX-2hr run April 15, 2003

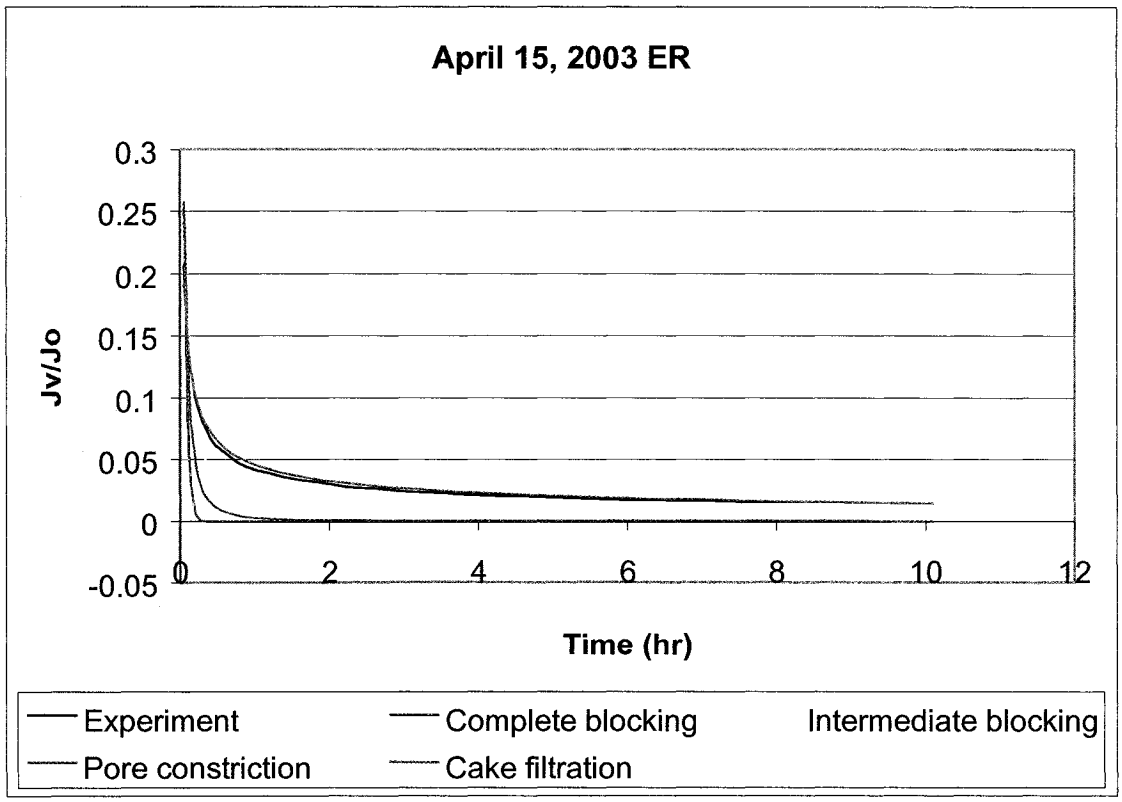


Figure D-40 Flux modelling results for membrane ER run April 15, 2003

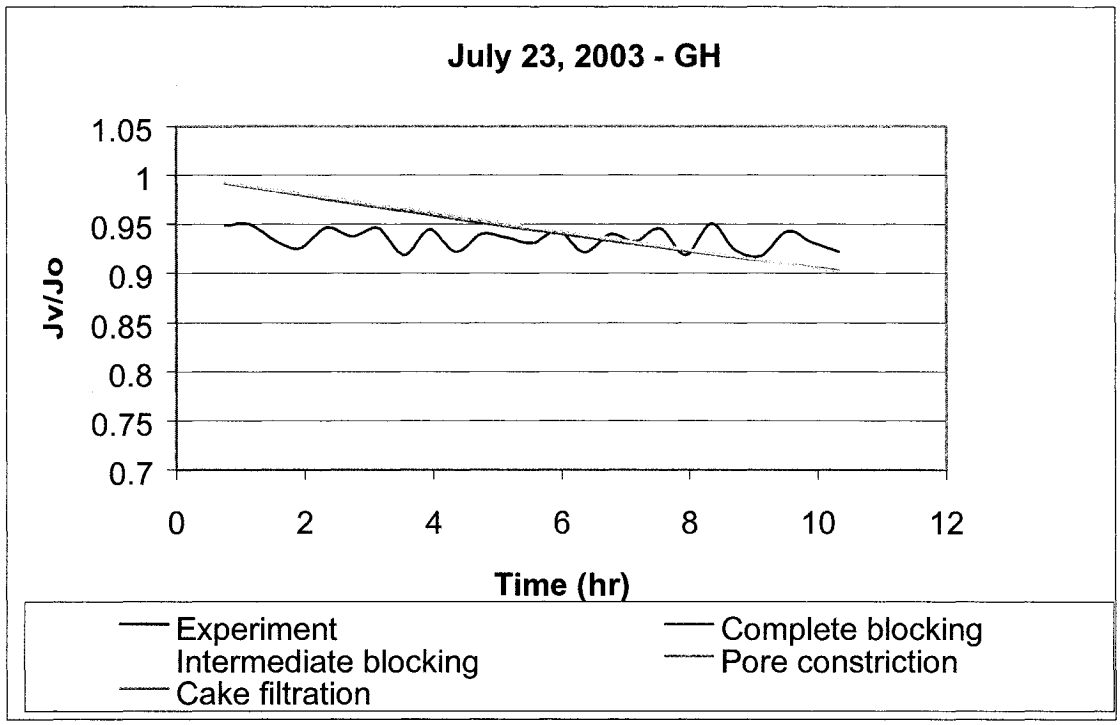


Figure D-41 Flux modelling results for membrane GH run July 23, 2003

Appendix E

Trail Road Landfill Fresh Leachate Data

Table E-1 Fresh leachate analyzed liquid parameters, excluding ICP data.

	Concentration (mg/L)					
Date	Sulfate	Phosphorous	TKN	BOD	Ammonia	COD
24-Feb-03	124	4.14	812	70	739	1030
4-Mar-03	133	3.81	777	58	736	1330
7-Mar-03	126	5.16	762	30	728	1550
10-Mar-03	176	5.33	822	50	775	1540
17-Mar-03	78	3.40	533	78	504	1350
7-Apr-03	57	2.03	328	43	302	545
10-Apr-03	28	1.14	353	442	299	1470
12-Apr-03	37	1.07	398	603	300	1510
14-Apr-03	90	1.18	433	594	267	1340
22-Jul-03	80	3.69	80	160	628	1190

Table E-2 containing the fresh leachate data provided by the Trail Road Landfill is on the Appendix CD under Appendix E, along with a paired-down version of the data by the author labelled Table E-3.

Appendix F

COD

Table F-1 Raw COD concentration data for all samples

COD

MDL = 5 mg/L

				COD (mg/L)	
Membrane Size	**Type**	**Date**	**Fresh Leachate**	**Concentrate**	**Permeate**
67200	JX	30-Sep-02	2538		
		2-Oct-02		2518	1562
		22-Oct-02	1575		
		24-Oct-02		1507	1421
		24-Oct-02	1507		
		25-Oct-02		1862	1274
		10-Apr-03	1470		
		11-Apr-03		1390	1270
		12-Apr-03	1510		
		14-Apr-03		1110	962
		14-Apr-03	1340		
		15-Apr-03		884	948
100	MW	9-Oct-02	3080		
		11-Oct-02		3582	3058
60	EW	4-Mar-03	1330		
		7-Mar-03		2080	1050
30	ER	10-Feb-02			
		2-Oct-02	2825		
		4-Oct-02		1546	1163
10	GN	16-Sep-02	N/A		
		19-Sep-02		1564	844
5	PT	7-Oct-02	2404		
				2673	2357
		17-Mar-03	1350		
		19-Mar-03		1320	652
		7-Apr-03	545		
		9-Apr-03		574	425
4	GM	7-Mar-03			
		10-Mar-03		1550	897
2	GK	24-Sep-02	N/A		
		26-Sep-02		733	512
		10-Mar-03	1540		
		12-Mar-03		1420	818

				COD (mg/L)	
Membrane Size	**Type**	**Date**	**Fresh Leachate**	**Concentrate**	**Permeate**
1	GH	24-Feb-03	1030		
		28-Feb-03		1320	896
		22-Jul-03	1190		
		25-Jul-03		1070	384
Circulation		28-Jan-02	1433		
		28-Jan-02		899	
		28-Jan-02		1455	
		29-Jan-02		1310	
		29-Jan-02		1257	
		30-Jan-02		1271	

Table F-2 Mass Balance Data for the COD concentration

			COD (mg/L)			Volume		
Membrane		**Date**	**Raw Leachate**	**Concentrate**	**Permeate**	**Feed (L)**	**Permeate (L)**	**Concentrate (L)**
	62700	Sept. 30, 2002	2538	2518	1562	91	24	67
	62700	Oct. 22, 2002	1575	1507	1421	114	18	96
	62700	Oct. 24, 2002	1507	1862	1274	114	16	98
	62700	April 10, 2003	1470	1390	1270	100	2	98
	62700	April 12, 2003	1510	1110	962	109	5	104
JX_{62700}	62700	April 15, 2003	1340	884	948	91	4	87
MW_{100}	100	Oct. 9, 2002	3080	3582	3058	91	27	64
EW_{60}	60	March 4, 2003	1330	2080	1050	91	62	29
ER_{30}	30	Oct. 2, 2002	2825	1546	1163	114	6	108
QW_{30}	30	Sept. 12, 2002	No Samples Taken			114	32	82
GN_{10}	10	Sept. 16, 2002	1819	1564	844	114	41	73
$M\text{-}180_{10}$	10	Aug. 13, 2002	No Samples Taken			105		105
	5	Oct. 7, 2002	2404	2673	2357	114	8	106
	5	March 17, 2003	1350	1320	652	91	6.5	84
PT_5	5	April 7, 203	545	574	425	105	9	96
GM_4	4	March 7, 2003	1802	1550	897	105	23	82
GK_2	2	Sept. 24, 2002	852	733	512	114	5	109
	2	March 10, 2003	1540	1420	818	91	13	78
GH_1	1	Feb. 24, 2003	1030	1320	896	91	4.5	86
	1	July 23, 2003	1190	1070	384	91	7	84

Table F-2 Continued

			COD (g)			COD (g)		
Membrane		**Date**	**Fresh Leachate**	**Permeate**	**Concentrate**	**IN**	**OUT**	**% Difference**
	62700	Sept. 30, 2002	231	60	105	231	165	-29
	62700	Oct. 22, 2002	179	27	136	179	163	-9
	62700	Oct. 24, 2002	171	30	124	171	154	-10
	62700	April 10, 2003	147	3	125	147	127	-13
	62700	April 12, 2003	165	6	100	165	106	-36
JX_{62700}	62700	April 15, 2003	122	4	82	122	86	-29
MW_{100}	100	Oct. 9, 2002	280	97	196	280	292	4
EW_{60}	60	March 4, 2003	121	129	30	121	159	32
ER_{30}	30	Oct. 2, 2002	321	9	125	321	135	-58
QW_{30}	30	Sept. 12, 2002						
GN_{10}	10	Sept. 16, 2002	207	64	61	207	125	-39
$M\text{-}180_{10}$	10	Aug. 13, 2002						
	5	Oct. 7, 2002	273	21	249	273	270	-1
	5	March 17, 2003	123	9	55	123	64	-48
PT_5	5	April 7, 203	57	5	41	57	46	-20
GM_4	4	March 7, 2003	188	36	73	188	109	-42
GK_2	2	Sept. 24, 2002	97	4	56	97	59	-39
	2	March 10, 2003	140	18	64	140	82	-41
GH_1	1	Feb. 24, 2003	94	6	77	94	83	-11
	1	July 23, 2003	108	7	32	108	40	-63

Appendix G

BOD

Table G-1 BOD concentration data with percent removal results

BOD

MDL = 1 mg/L

				BOD (mg/L)		Removal %	Change %	Corrected Removal %
Membrane Size	**Type**	**Date**	**Fresh Leachate**	**Concentrate**	**Permeate BOD**			
67200	JX	2003-04-10	442					
		2003-04-11		555	434	2	26	2
		2003-04-12	603					
		2003-04-14		121	362	40	-80	0
		2003-04-14	594					
		2003-04-15		229	396	33	-61	0
60	EW	2003-03-04	58					
		2003-03-07		16	9	84	-72	12
5	PT	2003-03-17	78					
		2003-03-19		71	32	59	-9	50
		2003-04-07	43					
		2003-04-09		28	13	70	-35	35
4	GM	2003-03-10		30	17	43		43
2	GK	2003-03-10	50					
		2003-03-12		43	14	72	-14	58
1	GH	2003-02-24	70					
		2003-02-28		69	8	89	-1	87
1	GH	2003-07-22	160					
		2003-07-25		63	15	91	-61	30

Table G-2 BOD/COD data

			Fresh Leachate		
Membrane Size	**Type**	**Date**	**[BOD] (mg/L)**	**[COD](mg/L)**	**BOD/COD**
1	GH	24-Feb-03	70	1030	0.07
1	GH	22-Jul-03	160	1190	0.13
2	GK	10-Mar-03	50	1540	0.03
4	GM	7-Mar-03	30	1550	0.02
5	PT	17-Mar-03	78	1350	0.06
5	PT	7-Apr-03	43	545	0.08
60	EW	4-Mar-03	58	1330	0.04
62700	JX	10-Apr-03	442	1470	0.30
62700	JX	12-Apr-03	603	1510	0.40
62700	JX	14-Apr-03	594	1340	0.44

Appendix H

Sulphate, Ammonia, TP and TKN

Table H-1 Raw ammonia concentration data

				Ammonia (mg/L)	
Membrane Size	**Type**	**Date**	**Fresh Leachate**	**Concentrate**	**Permeate**
67,200	JX	2003-04-10	299		
		2003-04-11		309	282
		2003-04-12	300		
		2003-04-14		285	272
		2003-04-14	267		
		2003-04-15		278	269
60	EW	2003-03-04	736		
		2003-03-07		708	650
5	PT	2003-03-17	504		
		2003-03-19		511	447
		2003-04-07	302		
		2003-04-09		315	283
4	GM	2003-03-10		728	707
2	GK	2003-03-10	775		
		2003-03-12		795	733
1	GH	2003-02-24	739		
		2003-02-28		720	577
		2003-07-22	628		
		2003-07-26		603	565

Table H-2 Raw nitrogen concentration data

				Nitrogen (mg/L)	
Membrane Size	**Type**	**Date**	**Fresh Leachate**	**Concentrate**	**Permeate**
0.3	JX	2003-04-10	353		
		2003-04-11		420	398
		2003-04-12	398		
		2003-04-14		373	277
		2003-04-14	433		
		2003-04-15		333	290
60	EW	2003-03-04	777		
		2003-03-07		708	650
5	PT	2003-03-17	533		
		2003-03-19		591	507
		2003-04-07	328		
		2003-04-09		368	331
4	GM	2003-03-10		762	723
2	GK	2003-03-10	822		
		2003-03-12		839	758
1	GH	2003-02-24	812		
		2003-02-28		731	595
		2003-07-22	80		
		2003-07-25		57	24

Table H-3 Raw phosphorous concentration data

				Phosphorous (mg/L)	
Membrane Size	Type	Date	Fresh Leachate	Concentrate	Permeate
0.3	JX	2003-04-10	1.14		
		2003-04-11		0.43	0.15
		2003-04-12	1.07		
		2003-04-14		0.51	0.21
		2003-04-14	1.18		
		2003-04-15		0.46	0.27
60	EW	2003-03-04	3.81		
		2003-03-07		4.90	2.50
5	PT	2003-03-17	3.40		
		2003-03-19		0.96	3.11
		2003-04-07	2.03		
		2003-04-09		1.65	0.22
4	GM	2003-03-10		5.16	2.29
2	GK	2003-03-10	5.33		
		2003-03-12		3.20	1.74
1	GH	2003-02-24	4.14		
		2003-02-28		2.48	1.71
		2003-07-22	3.69		
		2003-07-25		1.54	0.33

Table H-4 Raw sulphate concentration data

				Sulphate (mg/L)	
Membrane Size	Type	Date	Fresh Leachate	Concentrate	Permeate
67200	JX	2003-04-10	28		
		2003-04-11		31	25
		2003-04-12	37		
		2003-04-14		44	43
		2003-04-14	90		
		2003-04-15		18	15
60	EW	2003-03-04	133		
		2003-03-07		134	114
5	PT	2003-03-17	78		
		2003-03-19		61	28
		2003-04-07	57		
		2003-04-09		42	39
4	GM	2003-03-10		176	157
2	GK	2003-03-10	126		
		2003-03-12		115	111
1	GH	2003-02-24	124		
		2003-02-28		104	92
		2003-07-22	80		
		2003-07-25		57	24

Appendix I

ICP

All the ICP data are on the CD of Appendices under Appendix I. File named ICP.xls contains Tables I-1 to I-5 and a number of figures for the circulation and fresh concentrations for each element examined.

Appendix J

Colour and Membrane Pictures

There are limited digital images archiving the colour variations between samples as a colleague in error destroyed some of the samples. Those samples that were documented are presented on the CD of Appendices under Appendix J in a folder titled 'colour'. Table J-1 describes the origins of the images beyond the name of the file.

Table J-1 Image file descriptions for the appended CD.

File Name	Membrane Run	Description
Aug7top.jpg	M-180_{100} August 7, 2002	Top view of concentrate and permeate.
Aug7side.jpg	M-180_{100} August 7, 2002	Side view of concentrate and permeate.
Sept16 and Sept24side.jpg	GN_{10} September 16, 2002 GK_2 September 22, 2002	Side view of fresh leachate, permeate and concentrate for the run for Sept. 16 and concentrate with permeate of Sept. 22.
Sept16 and Sept24top.jpg	GN_{10} September 16, 2002 GK_2 September 24, 2002	Top view of fresh leachate, permeate and concentrate for the run for Sept. 16 and concentrate with permeate of Sept. 24.
Oct2side.jpg	ER_{30} October 2, 2002	Side view of fresh leachate, permeate and concentrate for the run
Oct2top.jpg	ER_{30} October 2, 2002	Top view of fresh leachate, permeate and concentrate for the run
Oct24 and Sept12.jpg	JX_{62700} October 24, 2002 QW_{30} September 12, 2002	Top and side view of fresh leachate, permeate and concentrate for the run for Oct. 24 and concentrate with permeate of Sept. 12.
Feb24side.jpg	GH_1 February 24, 2003	Side view of concentrate and permeate
Feb24top.jpg	GH_1 February 24, 2003	Top view of concentrate and permeate.
April 15 side.JPG	ER_{30} April 15, 2003	Side view of concentrate and permeate.
April 15 top.JPG	ER_{30} April 15, 2003	Top view of concentrate and permeate.
July 22 top.JPG	GH_1 July 22, 2003	Top view of fresh leachate, raw unfiltered leachate, permeate and concentrate
July 22 side.JPG	GH_1 July 22, 2003	Side view of fresh leachate, raw unfiltered leachate, permeate and concentrate

The fouled membranes images are also given under Appendix J on the CD under a folder named 'fouled membranes'. Some of the membranes dried and cracked during sample preparation prior to taking the digital image, but the membranes were not removed from the apparatus after a run damaged or cracked in an obvious way. The dates on the lids of the membrane containers are the dates on which they were collected. Each membrane image file is named by date followed by the membrane name (i.e. Oct9 – MW100.jpg).

Appendix K

SEM/EDX

There were numerous SEM photos and graphs produced during this study. The images are contained on the CD of appendices categorized by the following folder names: 2002 Membranes, 2003 Membranes, Clean Membranes, Scale and Sequential Membranes. Within each of these folders will be other folders for each specific run or sample identified by date or in the case of the sequential membranes time. These folders contain the images for those runs. The file names for each picture correspond to the day of SEM analysis and the number of photos. For example 3July_34.tif was the 34^{th} picture taken on the third of July. The graphs were hard-copy only printouts and could not be appended due to the sheer volume. The SEM scales of particular importance are featured within the main body of the text. The SEM/EDX standards for calcite, dolomite, and iron sulphide are given in Figures K-1 to K-3.

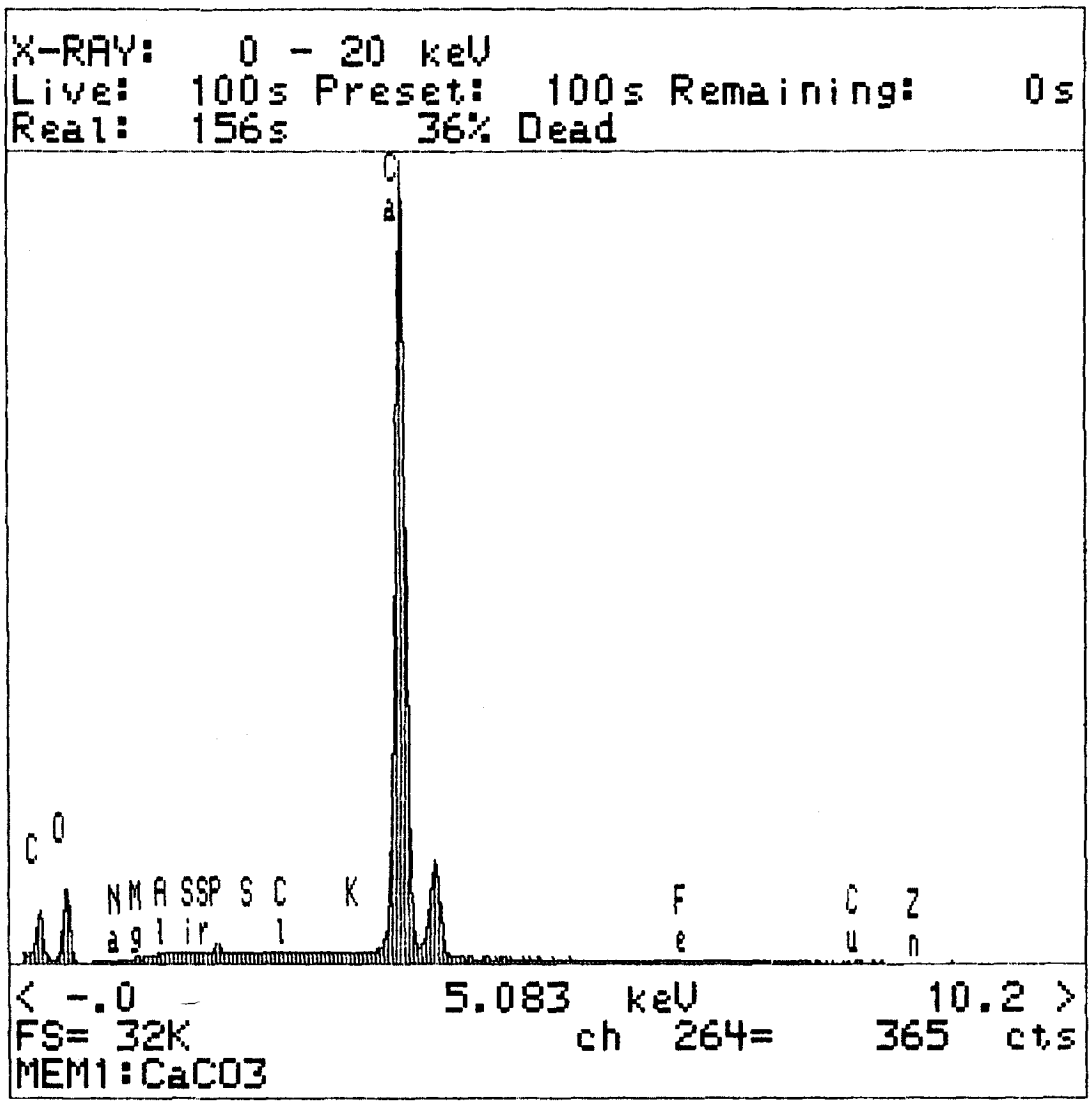


Figure 4-47 EDX scan of calcite standard.

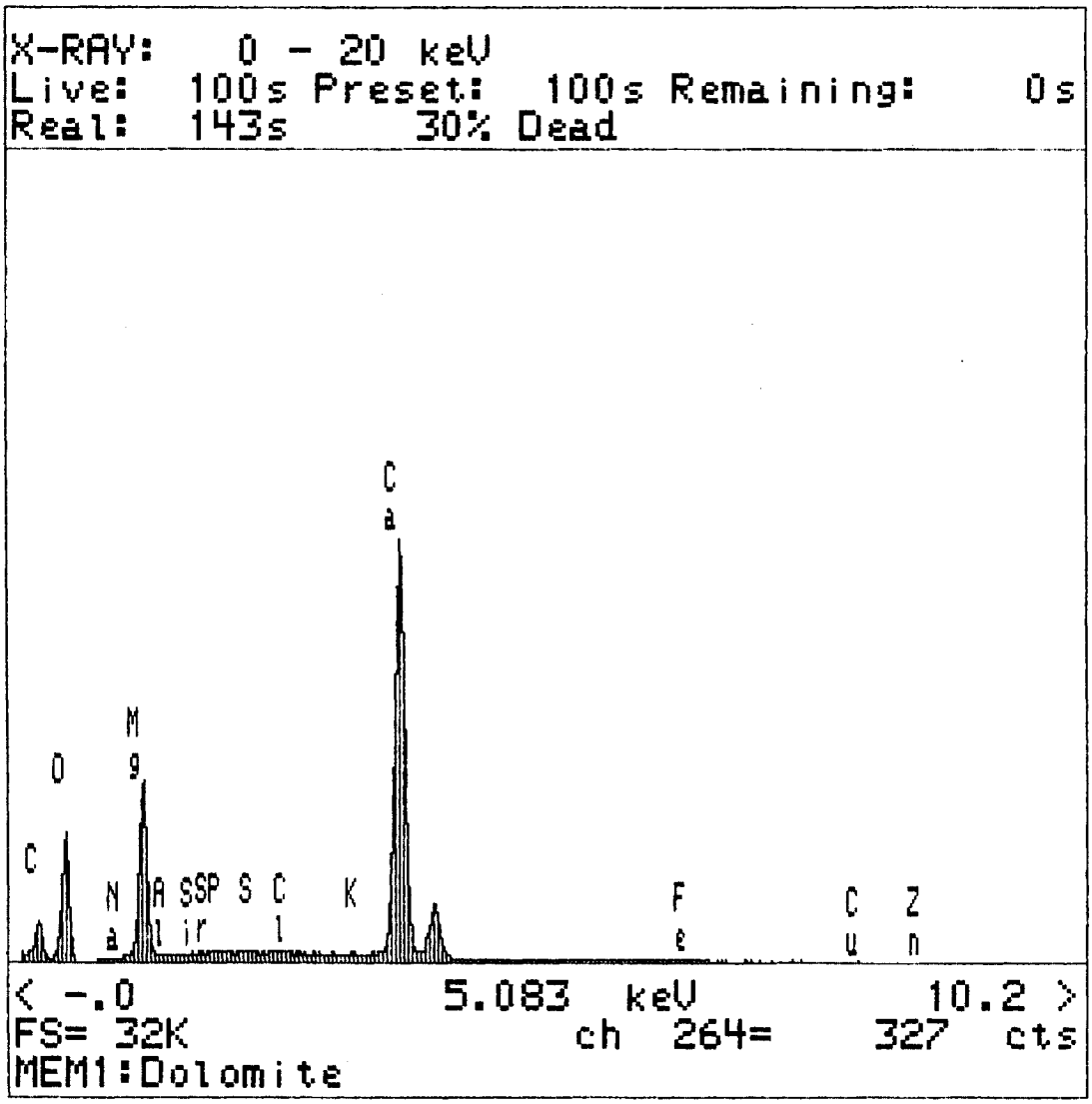


Figure 4-48 EDX scan of dolomite standard

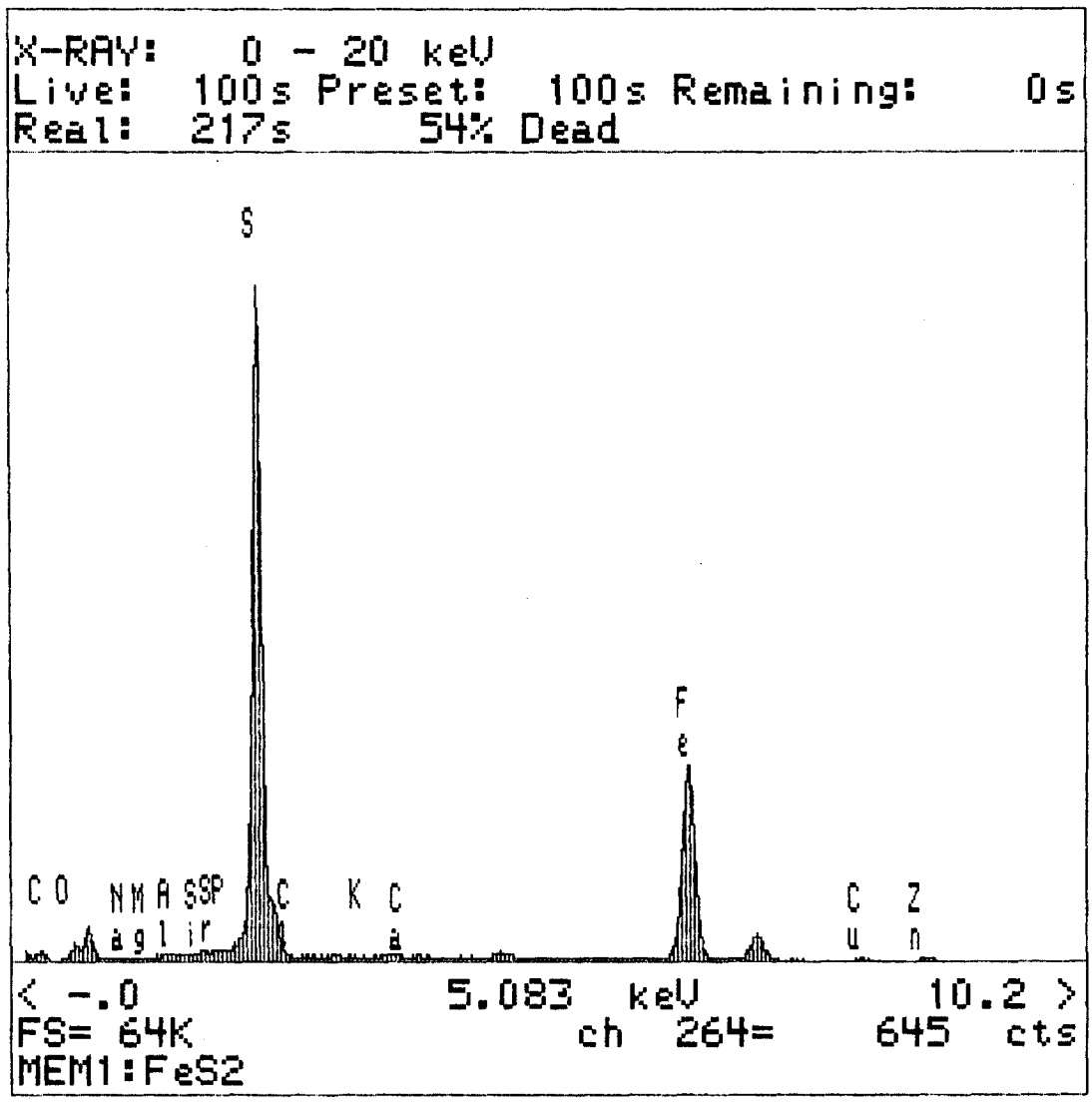


Figure 4-49 EDX scan of iron sulphide standard.