Treatment of Arsenic Contaminated Groundwater using Oxidation and Membrane Filtration

by

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Abstract

Arsenic is a known carcinogen, causing cancers of the skin, lungs, bladder and kidney. Current research suggests that drinking water is the most common pathway for long-term low dose exposure. Arsenic contaminated drinking water has caused serious health problems in many countries including: India, Bangladesh, Argentina, Chile, Taiwan, the United States and Canada.

Nanofiltration (NF) is a promising technology for arsenic removal since it requires less energy than traditional reverse osmosis membranes. Several studies have shown that nanofiltration is capable of removing the oxidized form of arsenic [As(V)] while the reduced form of arsenic [As(III)] is poorly removed. To exploit this difference it has been suggested that a pretreatment step which oxidizes the As(III) to As(V) would improve the performance of membrane filtration, but this has never been demonstrated.

The research had three objectives: The first was to investigate the ability of NF membranes to treat arsenic contaminated groundwater and evaluate the influence of the membrane type and operating conditions. Secondly, the effectiveness of a solid phase oxidizing media (MnO_2) to oxidize arsenite to arsenate was investigated. Lastly, the MnO_2 was combined with NF membrane filtration to determine the benefit, if any, of oxidizing the arsenic prior to membrane filtration.

A pilot membrane system was installed to treat a naturally contaminated groundwater in Virden, Manitoba, Canada. The groundwater in Virden contains between 38 and 44 μg/L of arsenic, primarily made up of As(III), with little particulate arsenic.

In the first experiment three Filmtec® membranes were investigated: NF270, NF90 and XLE. Under all conditions tested the NF90 and NF270 membranes provided insufficient treatment of Virden's groundwater to meet Canada's recommended Interim Maximum Acceptable Concentration (IMAC) of 25 μg/L. The XLE membrane provided better arsenic removal and under the conditions of 25 Lmh flux and 70% recovery produced treated water with a total arsenic concentration of 21 μg/L. The XLE membrane is therefore able to sufficiently treat Virden's ground water. However treatment with the XLE membrane alone is insufficient to meet the USEPA's regulation of 10 μg/L or Canada's proposed Maximum Allowable Concentration (MAC) of 5 μg/L.

The effects of recovery and flux on total arsenic passage are consistent with accepted membrane theory. Increasing the flux increases the flow of pure water through the membrane; decreasing the overall passage of arsenic. Increasing the recovery increases the bulk concentration of arsenic, which leads to higher arsenic passage.

The second experiment investigated the arsenic oxidation capabilities of manganese dioxide (MnO_2) and the rate at which the oxidation occurs. The feed water contained primarily As(III), however, when filtered by MnO_2 at an Empty Bed Contact Time (EBCT) of only 1 minute, the dominant form of arsenic was the oxidized form [As(V)]. At an EBCT of 2 minutes the oxidation was nearly complete with the majority of the arsenic in the As(V) form. Little arsenic was removed by the MnO_2 filter.

The third and final experiment investigated the benefit, if any, to combining the membrane filtration and MnO_2 treatment investigated in the first and second experiments. The effect of MnO_2 pretreatment was dramatic. In Experiment I, the NF270 and NF90 membranes were unable to remove any arsenic while the XLE removed, at best, approximately 50% of the arsenic. Once pretreated with MnO_2 the passage of arsenic through all of the membranes dropped to less than 4 μg/L, corresponding to approximately 91% to 98% removal.

The dramatic improvement in arsenic removal can be attributed to charge. All three membranes are negatively charged. Through a charge exclusion effect the rejection of negatively charged ions is enhanced. During the first experiment, As(III) (which is neutrally charged) was the dominant form of arsenic, and was uninfluenced by the negative charge of the membrane. Once oxidized to As(V), the arsenic had a charge of -2, and was electrostatically repelled by the membrane. This greatly improved the arsenic rejection characteristics of the membrane.

Nanofiltration alone is not a suitable technology to remove arsenic contaminated waters where As(III) is the dominant species. When combined with MnO_2 pre-oxidation, the arsenic rejection performance of nanofiltration is dramatically improved.

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1 Introduction

Arsenic is a common, naturally occurring element. Widely recognized as a poison, long term exposure has also been shown to lead to a wide variety of health problems. Manifestations of exposure can range from skin problems (lesions and keritosis) to circulatory problems, degenerative diseases (targeting the respiratory, pulmonary and neurological systems) or even cancer (targeting bladder, kidney, liver, lungs and skin) (Mandal and Suzuki 2002; Ng et al. 2003).

Due to its mobility, drinking water is a common pathway for human exposure to arsenic. In general there are two causes of arsenic contamination of drinking water: natural geological formation and human activity. To limit the risk of cancer, in Canada the Interim Maximum Allowable Concentration (IMAC) is 25 μg/L, while in the United States the Maximum Concentration Limit (MCL) was recently lowered to 10 μg/L.

To remove arsenic from drinking water there are several broad categories of treatment options. The first is adsorption, which requires a media which has a high adsorption capacity and affinity for arsenic. Activated alumina and ion exchange resins are widely used, but are complicated by the need for highly acidic or basic solution to regenerate the media (Chwirka et al. 2000). In some cases the media is not regenerated but disposed of in a landfill. The second broad category is chemical precipitation. Iron or aluminum based coagulants are added to form hydroxides with which the arsenic will either co-precipitate or adsorb. The iron or aluminum hydroxide precipitates can then be removed through settling or filtration (Edwards 1994). The last category is membrane filtration which uses a selectively permeable membrane. The membrane allows the passage of water, but is impermeable to some of the other constituents. This is a promising technology for arsenic treatment due to its simple operation and minimal chemical requirements.

1.1 Research Motivation and Scope

Membrane filtration has been shown to be capable of removing arsenic; however, the majority of the research has been conducted using synthetic waters (Brandhuber and Amy 2001; Kang et al. 2000, 2001; Oh et al. 2000; Sato et al. 2002; Seidel et al. 2001; Urase et al. 1998; Vrijenhoek and Waypa 2000) or with natural water spiked with arsenic (Brandhuber and Amy 1998, 2001; Brandhuber et al. 1997; Kang et al. 2000, 2001; Oh et al. 2000; Sato et al. 2002; Seidel et al. 2001; Urase et al. 1998; Vrijenhoek and Waypa 2000). Since none of the work was performed with naturally contaminated groundwater and the arsenic composition of spiked or synthetic waters may not be representative, the performance predicted by these studies may be misleading.

Nevertheless the literature has consistently showen that membrane filtration removes the oxidized form of arsenic [As(V)] much more effectively than the reduced form [As(III)]. To exploit this difference several researchers have suggested that a pretreatment step which oxidizes the As(III) to As(V) would improve the performance of membrane filtration (Kartinen Jr and Martin 1995; Oh et al. 2000; Seidel et al. 2001), but it has not been demonstrated. There has been ample research into the oxidation of arsenic using MnO_2 (Ghurye and Clifford 2001; Manning et al. 2002), but an arsenic oxidation step has never been combined with membrane filtration.

To address these deficiencies in the literature, research was conducted using a pilot scale membrane system with two objectives:

1. The first objective was to investigate the application of membrane filtration to treat water with naturally occurring arsenic. Specifically, the feasibility of three different types of membranes, along with the impact of different operating conditions, was investigated.
2. The second objective was to verify the concept of introducing an arsenic oxidation step upstream of the membranes, which converts the As(III) to As(V), to improve the performance of membrane filtration. The performance of an oxidant (manganese dioxide or MnO_2) was investigated and the benefit was evaluated.

1.2 Thesis Organization

In Chapter 2, the sources, prevalence and chemical characteristics of arsenic contaminated ground waters are reviewed. The health implications of arsenic exposure and current exposure guidelines are also presented.

Arsenic treatment technologies, including membrane filtration, are described in detail. The advantages and disadvantages of each process are also discussed. The various techniques used to determine the concentration of each form of arsenic are reviewed, as are the issues concerning the preservation of arsenic prior to measurement.

The experiments which make up this research are described in detail in Chapter 3. The pilot site, apparatus and measurement methods are documented in Chapter 4

The results of the experimentation are presented in Chapter 5, along with a discussion of their significance. Finally, conclusions are made regarding the applicability of membrane filtration as an arsenic treatment process, the influence of the membrane operating conditions and the benefit of using a manganese dioxide oxidant step prior to membrane filtration.

2 Literature Review

The sources, prevalence and chemistry of arsenic are reviewed. The complications of exposure to arsenic are also discussed. A brief overview of membrane filtration is presented before reviewing the current methods employed to treat arsenic contaminated waters. The preservation, separation and measurement of arsenic are also discussed.

2.1 Arsenic Prevalence, Sources and Chemistry

Arsenic is a known carcinogen, causing cancers of the skin, lungs, bladder and kidney. The common exposure pathways include air, food and water. Current research suggests that drinking water is the most important pathways for long-term low dose exposure (Mandal and Suzuki 2002; Ng et al. 2003; Pontius et al. 1994).

Arsenic contaminated groundwater is found in many different parts of the world. The widespread arsenic contamination in India and Bangladesh is well known (Acharyya et al. 1999; Burgess et al. 2002; Das et al. 1994; Meng et al. 2001; Nickson et al. 1998). Reports of elevated arsenic concentrations (>50 µg//L) are common (Frey and Edwards 1997; Mandal and Suzuki 2002; Smedley and Kinniburgh 2002) and they highlight arsenic contamination problems in Canada (Alberta, British Columbia, Manitoba, Newfoundland, Nova Scotia, Ontario, Saskatchewan), the United States (Alaska, Arizona, California, Idaho, Maine, Michigan, Nevada, New Hampshire, Oregon, Texas, Utah, Wisconsin, Washington State) and around the world (Argentina, Chile, China, Hungary, Mexico, Taiwan, Thailand and Vietnam).

Arsenic is a common, naturally occurring element. The two primary sources of arsenic in drinking water are geological and anthropogenic. Geological sources of arsenic arise through the dissolution of arsenic bearing minerals (Boyle et al. 1998; Chowdhury et al. 1999; Welch et al. 1988) or iron oxides containing arsenic (Boyle et al. 1998; Chowdhury et al. 1999; Nickson et al. 1998; Smedley and Kinniburgh 2002; Welch et al. 1988). Arsenopyrite (FeAsS) is considered the most common arsenic bearing mineral, although other forms of arsenic minerals, such as realgar (AsS), orpiment (As_2S_3), claudetite (As_2O_3), arsenolite (As_4O_6), arsenic pentoxide (As_2O_5) and scorodite ($FeAsO_4$-$2H_2O$) have also been reported (Smedley and Kinniburgh 2002; Welch et al. 1988). Under the proper hydrogeological conditions, these minerals can dissolve and release arsenic into the water. Similarly, iron oxides, which have a strong affinity for arsenic, (Jain et al. 1999; Sadiq et al. 2002) can confine arsenic; however if the conditions change the iron oxide can release the arsenic. Anthropogenic sources, or sources associated with human activity, include the application of arsenic based insecticides and herbicides (Mandal and Suzuki 2002) and mining. Arsenic is commonly found in the same ore as iron and other metals. The mining processes employed to extract these metals alters the stability of the ore, leading to accelerated dissolution of the arsenic bearing minerals (Smedley and Kinniburgh 2002).

In natural waters arsenic can be found in two forms: inorganic and organic. Inorganic arsenic is primarily made up of trivalent arsenite [As(III)] or pentavalent arsenate [As(V)]. The relative concentrations of each are controlled by the redox potential (Eh) and pH, as shown in Figure 2-1. Under oxidizing conditions (positive Eh) As(V) is the primary form of arsenic, while under reducing conditions (negative Eh) the primary form is As(III). Although the redox potential provides an indication of which form of arsenic might be dominant, it has not proven to be an accurate predictor (Welch et al. 1988; Yan et al. 2000). Depending on the conditions, many authours have documented that either As(III) or As(V) can be the dominant species in groundwater. (Boyle et al. 1998; Burgess et al. 2002; Kim et al. 2002; Smedley and Kinniburgh 2002).

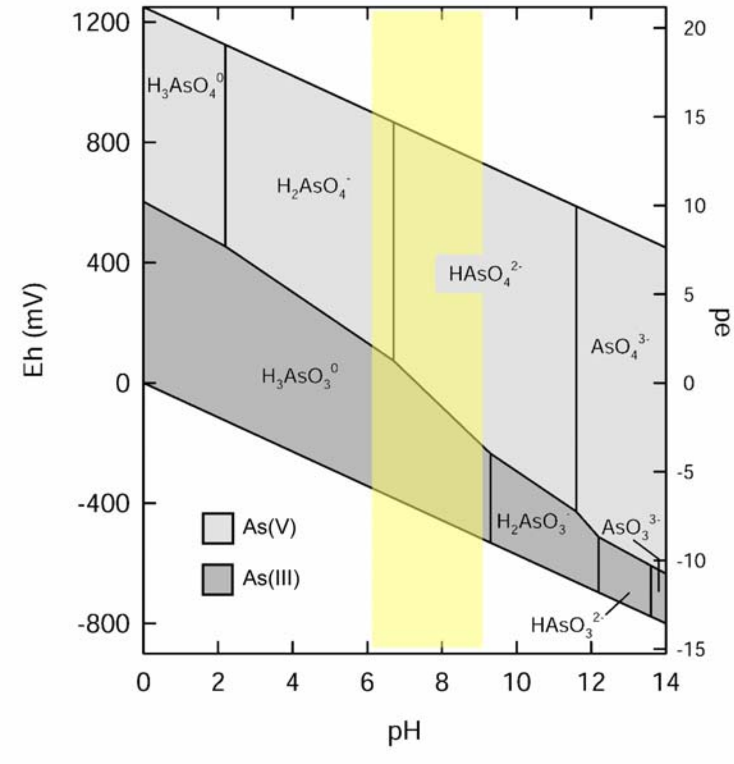


Figure 2-1 - Eh-pH diagrapm for inorganic arsenic. Adapted from Smedley and Kinniburgh 2002

The pH of the water controls the protonation and deprotonation of arsenic. At typical pH values for drinking water, between 6 and 9, only three forms of arsenic are thermodynamically possible. This is shown in Figure 2-1. As(V) (shaded in light gray) is as an anionic species ($HAsO_4^{2-}$ or AsO_4^{3-}) while As(III) (shaded in dark gray) is found primarily as a neutral species ($H_3A_SO_3$). This important characteristic of inorganic arsenic is exploited by both arsenic treatment and arsenic measurement techniques. Figure 2-2 shows the distribution of As(III) as a function of pH. It should be noted that although the pK_{a1} of arsenious acid is 9.22, it is thermodynamically possible for the ionic form of As(III) to make up more then 15% of the As(III) present at a pH of 8.5.

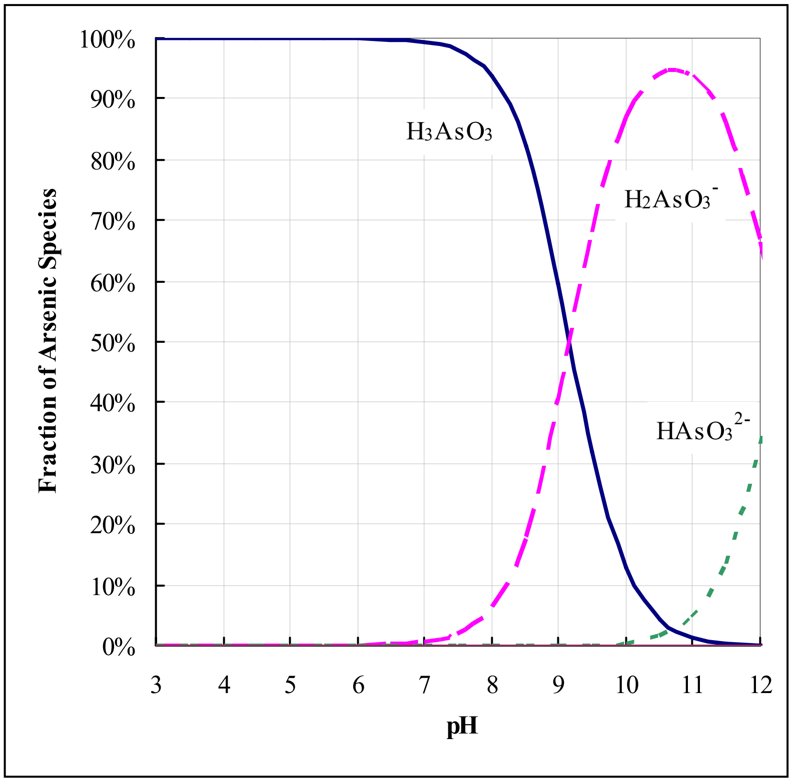


Figure 2-2 - Distribution of As(III) as a function of pH

Along with the inorganic forms of arsenic, organic arsenic may also be present. Inorganic arsenic can be methylated by microorganisms, producing monomethylarsonic acid (MMA) and dimethylarsinic acid (DMA) (Mandal and Suzuki 2002). Generally these are rare in groundwater (Bednar et al. 2004; Le et al. 2000) and considered not to be of quantitative importance (Smedley and Kinniburgh 2002).

Particulate arsenic (arsenic which is bound to particulate or other small particles) can account for a significant percentage of the arsenic. It has been reported to make up as much as 96% of the arsenic, or be completely absent in ground waters (Brandhuber and Amy 1998; Chen et al. 1999).

2.2 Arsenic Toxicity

Arsenic is commonly regarded as a poison. In high doses arsenic is very toxic. Acute exposure to arsenic can lead to gastrointestinal irritation, abnormally low blood pressure and convulsions. Death may also come from cardiovascular collapse. The lethal dose (LD_{50}) for humans has been reported to be between 1 to 4 mg / kg. (Pontius et al. 1994)

Due to its mobility, drinking water is a common pathway for human exposure to arsenic. Compared to acute doses, chronic exposure to concentrations in the order of 100 μg/L may cause health problems (Brown and Ross 2002). Blackfoot disease or gangrene of the feet has been reported in many people exposed to arsenic in their drinking water (Brown and Ross 2002; Das et al. 1994; Pontius et al. 1994; Viraraghavan et al. 1999). Skin lesions and keritosis (hardedning of the skin) have also been reported. Chronic exposure can also cause damage to the respiratory, pulmonary, renal and neurological systems (Mandal and Suzuki 2002; Ng et al. 2003). Cancers of the bladder, kidney, liver, lungs and skin have also been linked to arsenic exposure (Brown and Ross 2002; Smith et al. 1992).

Currently in the Canada, the Interim Maximum Allowable Concentration (IMAC) is 25 μg/L, while the proposed Maximum Allowable Concentration (MAC) is 5 μg/L. In the United States, the Maximum Concentration Limit (MCL) was recently lowered from 50 μg/L to 10 μg/L, which is in line with the World Health Organization (WHO) recommendation. The primary motivation for the revision of these regulation is to limit the risk of cancer. Critics such as the American Council on Science and Health have concluded that there is insufficient evidence to prove a carcinogenic or toxic risk, at the 50 μg/L exposure level (Brown and Ross 2002). Indeed studies have not found a link between arsenic exposure and adverse health effects. The studies, mainly performed in the Unites States, cite differences in diet and sociodemographics as reasons for the differences (Pontius et al. 1994).

Inorganic forms of arsenic (As(III) and As(V)) are considered more toxic then methylated forms (DMA or MMA) (Jain and Ali 2000). The toxicity scale has been presented as:

$$\text{As(III)} > \text{As(V)} > \text{MMA} > \text{DMA}$$

with As(III) reported to be 10 to 60 times more toxic then As(V) (Jain and Ali 2000; Pontius et al. 1994) and inorganic forms of arsenic approximately 100 times more toxic then organic forms (Jain and Ali 2000). Particulate arsenic and arsenic associated with complexes are also reported to be less toxic then inorganic forms of arsenic (Smedley and Kinniburgh 2002).

2.3 Membrane Filtration

Membrane filtration makes use of a membrane which is selectively permeable. The membrane allows the passage of water, but is impermeable to some of the other constituents. Which constituents are prevented from passing through the membrane depends on the characteristics of the membrane. In general, the more constituents a membrane is able to separate, the more pressure will be required to drive the treated water through the membrane. Historically, membranes have been divided into the four categories shown in Table 2-1 based on their selectivity.

Table 2-1 -Approximate operating pressures, pore sizes, molecular weight cutoffs and typical applications for different membrane categories.

Membrane Category	Approximate Operating Pressure (kPa)	Approximate pore size (Å)	Molecular Weight Cutoff (amu)	Typical Application
Reverse Osmosis	800-8000	< 10	< 500	desalination and removal of dissolved ions
Nanofiltration	350-1000	9 - 60	100 - 10 000	removal of larger dissolved ions or hardness
Ultrafiltration	50-700	30 - 2000	500 - 500 000	removal of colloids, viruses, and pathogens
Microfiltration	30-300	500 - 20 000	-	filtration of bacteria, cysts and suspended solids

Adapted from Mallevialle et al. 1996; Dow Liquid Separations 2004

During membrane filtration, solutes are transported to the surface of the membrane by the advective flow of water. At the membrane surface the solutes are rejected, which leads to an increased solute concentration at the surface of the membrane, termed concentration polarization. A representation is presented in Figure 2-3. The white arrows show the direction treated of water flow. The shading represents the concentration profile and is shown graphically on the right.

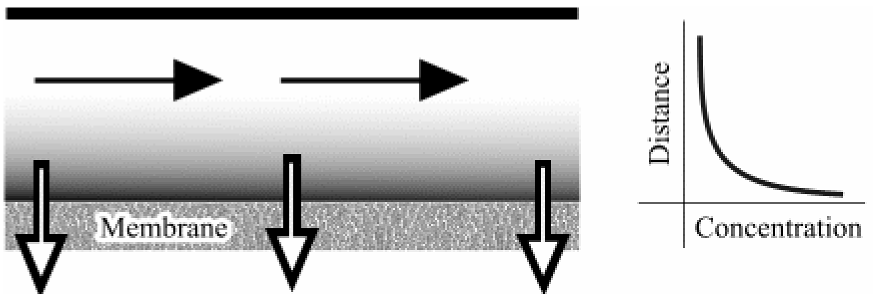


Figure 2-3 - Schematic of concentration profile during membrane filtration

Concentration polarization is undesirable, since the membrane must filter a solution with a higher solute concentration than the feed (or bulk) solution. This can cause precipitation and accelerate fouling that can lead to higher solute passage and poorer treated water quality. To minimize concentration polarization, reverse osmosis and nanofiltration membranes are configured to ensure that the direction of filtration is perpendicular to the direction of the feed flow, this is known as cross flow and is represented by the black arrows in Figure 2-3. The cross wise momentum of the water serves to limit the thickness of the concentration polarization layer. Thus, higher cross flow velocities reduce the thickness of the concentration polarization layer.

2.3.1 Definitions

Specific terminology exists to describe aspects of membrane filtration. Brief definitions of the terminology used are given here:

Bulk Concentration - the solute concentration on the feed side of the membrane, at a distance beyond the concentration polarization layer. The *bulk concentration* is always greater than the *feed concentration*.

Concentrate or Reject - The portion of the feed that is rejected by the membrane. The *concentrate* is the portion of the feed stream that does not pass through the membrane and is thus concentrated. It is also referred to as the *reject* stream.

Concentration Factor - defines how many more times concentrated the *concentrate* is compared to the *feed*. For example, for a membrane with 75% rejection, the *concentrate* will have a solute concentration of approximately 3 times that of the *feed* stream or a *concentration factor* of 3.

Cross-Flow - In the majority of membrane systems, the feed solution travels across the surface of the membrane tangentially to the membrane. This *cross flow* limits extent of concentration polarization and enhances the rejection.

Flux - a measure of the filtration rate standardized to the surface area of the membrane. It is measured as volume/time/area, for example $L/m^2/h$ which is frequently abbreviated to Lmh. The flux is often normalized to 20ºC.

Feed Concentration - the solute concentration of the stream to be treated.

Passage - the percentage of solutes which pass through the membrane. It is calculated as a ratio of the treated water concentration to the feed concentration. For example if the feed water concentration is 100 and the treated water concentration is 42, then the passage is 42%.

Permeability - a measure of the amount of pressure (or energy) required to drive water through the membrane. It is measured as flux/pressure, for example Lmh/bar.

Permeate - the treated water, or the water that has permeated through the membrane.

Recovery - the ratio of treated water flow rate to feed water flow rate.

Rejection - the percentage of solutes which do not pass through the membrane. It is calculated as 100% - *passage*.

Spiral Wound Membrane - The majority of nanofiltration and reverse osmosis membranes are configured as spiral wound membranes. In this configuration the membrane is rolled into a compact cylinder, making efficient use of space and allowing for large amounts of membrane surface area in a small volume

2.3.2 Predicting Rejection of Solutes

Predicting the performance of a nanofiltration membrane is challenging since so many factors influence its performance. From the various components of the feed water, to the composition of the membrane, to the operating conditions of the membrane, each can influence which solutes pass through the membrane and which are retained. As a very rough approximation, rejections follow the lytropic series as shown below; which predicts increased rejection based on increasing hydrated radius (Mallevialle et al. 1996). In general, divalent ions are rejected better then monovalent ions.

$$Mg^{2+} > Ca^{2+} > Sr^{2+} > Ba^{2+} > Ra^{+} > Li^{+} > Na^{+} > K^{+}$$

$$SO_4^{2-} > Cl^{-} > Br^{-} > NO_3^{-} > I^{-}$$

More accurate predictions can be made using models. Generally speaking there are two groups of models that have been used to describe filtration by a membrane. The first type is mechanical. Three mechanical models are summarized below; in each case the performance of the membrane is predicted in two separate components: the pure water flux and the solute flux.

Table 2-2 -Summary of models used to predict membrane filtration

<table>
<tr><th>Model</th><th>Pure Water Flux</th><th>Solute Flux</th></tr>
<tr><td rowspan="2">Preferential Sorption - Capillary Flow</td><td>$J_w = P_{PW}(\Delta p - \Delta\Pi)$</td><td>$J_i = \frac{c_m K_{d,i} D_i}{\delta_m}(x_{i,m} - x_{i,p})$</td></tr>
<tr><td colspan="2">Only thin layer of water, which is sorbed to the membrane surface, is permeating through the membrane pores. Preferential sorption of water (over the solute) leads to a solute deficit within the membrane</td></tr>
<tr><td rowspan="2">Irreversible Thermodynamics</td><td>$J_w = -K_W(\Delta p - \sigma \cdot \Delta\Pi)$</td><td>$J_s = \overline{c_s}\left(1-\sigma\right)J_v + \omega \cdot \Delta c_s$</td></tr>
<tr><td colspan="2">Membrane separation is an irreversible thermodynamic process. Free energy will be constantly dissipated and entropy constantly produced.</td></tr>
<tr><td rowspan="2">Solution Diffusion</td><td>$J_w = -K_W \frac{(\Delta p - \Delta\Pi)}{\delta_m}$</td><td>$J_s = -D \cdot K_d \frac{\Delta c_s}{\delta_m}$</td></tr>
<tr><td colspan="2">Describes the transport of solute and solvent in terms of affinity for the membrane and the diffusive transport within the membrane</td></tr>
</table>

Adapted from Mallevialle et al. 1996; Brandhuber 1999; Mohammad and Takriff 2003

Although not of direct importance in this discussion, for completeness the parameters used in the models summarized above are: J_W is the pure water permeability, K_w is the hydraulic permeability, Δp is the difference in applied pressure across the membrane, $\Delta\Pi$ is the difference in osmotic pressure across the membrane due to concentration differences, δ_m is the thickness of the membrane, J_i is the flux of solute i through the membrane, J_s is the total solute flux, c_m is the molar density, c_s is the solute concentration (note that $\overline{c_s}$ is the average concentration across the membrane while Δc_s represents the difference in concentration across the membrane), D is the total diffusivity, while D_i represents the diffusivity of solute i, similarly K_d is the total solute distribution coefficient, while $K_{d,i}$ represents the distribution coefficient of solute i, $x_{i,m}$ and $x_{i,p}$ represent the mole fraction in the membrane and permeate respectively, σ represents the "reflection co-efficient" which accounts for selectivity, ω is a parameters describing the interaction of the membrane and solute.

Of primary importance are the relationships which become evident through examination of the models. In each of the models summarized above the pure water flux is related primarily to the pressure (Δp), while the solute flux is a function of the difference in solute concentration across the membrane (Δc_s or $x_{i,m}$ - $x_{i,p}$). In the models, these relationships are considered independently of each other, implying that the effects of varying the pressure or the concentration act independently.

The general effects of the operating conditions can be deduced from the relationships in the models. The pure water flux is proportionally related to the pressure; therefore increasing the pressure will increase the pure water flux. If the solute flux is constant and the pure water flux is increased, the overall solute passage decreases (due to the "dilution" of the solutes).

The solute flux is proportionally related to the solute concentration gradient across the membrane. Many factors influence the concentration gradient across the membrane: feed solute concentration, the cross flow velocity and recovery. The table below summarizes the influence of each of these parameters on the overall solute passage assuming that the pure water flux is constant.

Table 2-3 - The impact of various operating parameters on solute passage

The effect of increasing the:	**Solute concentration gradient across membrane** (Δc_s)	**Solute Flux through membrane** (J_s)	**Overall Solute Passage**
Feed Concentration	↑	↑	↑
Recovery	↑	↑	↑
Cross Flow Velocity	↓	↓	↓

Increasing the recovery increases the concentration at the membrane surface and consequently the solute passage. This happens through two mechanisms. First, increasing the recovery increases the concentration factor and thus the concentration on the feed side of the membrane. Secondly, for spiral wound membranes the recovery is closely related to the cross flow velocity, because of their configuration. As the recovery is increased, more water is removed from the feed stream thus the cross velocity decreases and the amount of concentration polarization increases.

Left out of the models discussed above is the concept of charge. This is accounted for in another category of models that considers the solute transport across the membrane as a sum of the different forces driving solutes through the membrane. The pure water flux can be related to pressure using the Hagen-Poiseuille equation as shown in equation 1 (Bandini and Vezzani 2003; Bowen et al. 1997) which is a more fundamental version of the form presented in the "Preferential Sorption - Capillary Flow" model.

$$J_w = \frac{r_p^2 \Delta p}{8\mu\delta} \qquad 1$$

Solute flux is defined using in the Extended Nernst-Planck equation as shown in equation 2.

$$J_i = \left(-D_i \frac{dc_i}{dx} \right) - \left(D_i z_i c_i \frac{F}{RT} \frac{d\psi}{dx} \right) + \left(K_i c_i J_v \right) \qquad 2$$

Many of the symbols are described above, the additional symbols include: c_i - the concentration of solute *i* at the surface of the membrane, z_i - the valance of solute *i*, F - Faraday's constant, R - the gas constant, T - temperature and ψ - the electric potential and J_v is the volume flux and can be estimated based on the membrane area.

Each of the terms of the Nernst-Planck equation describes a different component of the solute flux. The first term describes diffusion (as a function of concentration gradient across the membrane), the second term quantifies the flux due to electrostatic forces (as a function of the charge gradient) and the last represents the convection of the solute (as a function of volume flux). In all three terms of the Extended Nerst Plank equation is found the term c_i, - the concentration of solute *i* at the surface of the membrane, revealing that it is the concentration at the surface of the membrane that dictates the solute passage through the membrane.

The concentration at the surface of the membrane can be estimated using the Donnan equilibrium as shown in equation 3.

$$\begin{gathered} c_i = C_i \exp\left(-z_i \frac{F}{RT} \Delta\psi_D \right), \\ \psi_D = \psi_m - \psi_s \end{gathered} \qquad 3$$

where C_i is the bulk (or feed) concentration of solute *i* and the Donnan potential (ψ_D) is the difference between the electrical potential of the solution (ψ_s) and the electrical potential of the membrane (ψ_m).

The Nernst-Plank equation coupled with the Donnan Equilibrium have been shown to accurately predict the rejection of various salts by nanofiltration and reverse osmosis membranes (Afonso and de Pinho 2000; Bandini and Vezzani 2003; Bowen and Mukhtar 1996; Mohammad and Takriff 2003; Peeters et al. 1998; Vezzani and Bandini 2002).

Interpretation of equation 2 and 3 shows that the solute concentration at the surface of the membrane determines the solute passage. If the charge (or electrical potential) of the membrane increases, the concentration of co-ions (ions with a similar charge) at the membrane surface decreases, while the concentration of counter ions (ions with the opposite charge) increases. If the ion is neutrally charged, then the concentration at the membrane surface is unaffected by the charge of the membrane.

The implication is that by altering the charge of the membrane (and consequently the solute concentration at the membranes surface) the passage of a particular solute is enhanced or reduced.

The charge of the membrane is difficult to ascertain, primarily because the charge of the membrane depends on its environment. The pH influences the charge of the membrane through the protonation and deprontonation of the membrane functional groups (Afonso et al. 2001; Childress and Deshmukh 1998; Childress and Elimelech 1996, 2000; Deshmukh and Childress 2001; Schaep and Vandecasteele 2001; Vrijenhoek et al. 2001). Changing the ionic constituents can also influence the charge of a membrane. Increasing the overall ionic strength of the solution can lessen the magnitude of the membrane's charge (Afonso et al. 2001), while complex formation between Ca^{2+} and any negatively charged groups on the surface of the membrane can make the membrane's charge more positive (Childress and Elimelech 1996; Deshmukh and Childress 2001). Similarly humic acids can influence the charge of membrane by adsorbing to the membrane surface and, because they have negative functional groups, make the overall charge more negative (Childress and Elimelech 1996; Deshmukh and Childress 2001).

2.4 Arsenic Treatment Methods

2.4.1 Precipitative Methods

In the simplest sense, these methods involve transforming the dissolved arsenic into larger filterable solids which can be more easily removed. Precipitative methods used to remove arsenic are comprised of three processes: coagulation, sorption and co-precipitation. Coagulation refers to altering the chemistry of the feed water to encourage small particles to join and form larger particles, which are more easily removed. Since it acts only on particles, only particulate arsenic is removed by this process. Co-precipitation involves initiating a precipitative reaction which will entrap other ions during the formation of the precipitates. Sorption occurs during both coagulation and co-precipitation since these processes create particles whose surface has a significant sorption capacity for dissolved arsenic.

To remove dissolved arsenic, iron or aluminum based coagulants are dosed at a concentration and pH that will initiate a precipitative reaction. Iron based coagulants have been shown to form iron hydroxide-arsenic co-precipitates (as have aluminum based coagulants). Not only do the coagulants co-precipitate with arsenic, the iron (or aluminum) hydroxides also have a sorption capacity for dissolved arsenic. Once formed, these hydroxides with particles can be removed from solution through a traditional sedimentation / filtration process or through membrane filtration (Brandhuber and Amy 1998; Chen et al. 2002; Cheng et al. 1994; Chwirka et al. 2004; Edwards 1994; Ghurye and Clifford 2004; Gregor 2001; Han et al. 2002). Of the co-precipitation and sorption processes, it has been shown that co-precipitation is the more important process. If the hydroxides are pre-formed, rather then formed in situ, overall arsenic removal is decreased, (Edwards 1994; Ghurye and Clifford 2004).

The type of coagulant, concentration and the pH have a significant effect on the successful removal of arsenic (Chen et al. 2002; Chwirka et al. 2004; Edwards 1994; Han et al. 2002); consequently, the control of these is important. It has been reported that aluminum and iron based coagulants are equally effective when compared on a molar basis; however, ferric coagulants are more effective at higher pHs then aluminum, due to the higher solubility of aluminum hydroxides (Edwards 1994; Kartinen Jr and Martin 1995). Generally, increasing the dose of coagulant will increase the amount of arsenic removed (Brandhuber and Amy 1998; Cheng et al. 1994; Han et al. 2002).

Much of the literature has shown that As(V) can be removed using precipitative methods, while they are less effective on As(III) (Chen et al. 2002; Chwirka et al. 2004; Chwirka et al. 2000; Ghurye and Clifford 2004; Gregor 2001; Kartinen Jr and Martin 1995). To enhance removal of As(III), pre-oxidation is suggested. The preferential removal of As(V) has been shown to result from the positive charge of the iron (or aluminum) hydroxides: negatively charged As(V) will adsorb preferentially to neutral As(III). This effect has been demonstrated by Ghurye and Clifford (2004), who noticed that a decrease in pH has the effect of increasing arsenic removal. This was attributed to: (1) increasing the number of positively charged adsorption sites on the hydroxide particle as suggested by Jain et al. 1999 and (2) decreasing OH^- concentration which is an excellent ligand to the adsorption sites (Ghurye and Clifford 2004). The effect of pH had been noted in previous studies as well (Chwirka et al. 2000).

As with standard water treatment, to be effective the precipitative processes must be combined with a filtration process. Traditional sedimentation and filtration as well as membrane filtration (using ultrafilters or microfilters) has been shown to be effective at removing arsenic when combined with the precipitative process discusses above. Membrane filtration, although more expensive, eliminates the need for a flocculation step since it is able to filter smaller particles than traditional sand filtration.

In addition to the similarity of the process to standard coagulation, another advantage of the precipitative processes is the absence of toxic residuals. Tests from ferric chloride coagulation found that the residuals pass the toxicity characteristic leaking procedure (TCLP) (Chen et al. 1999; Chwirka et al. 2004; Ghurye and Clifford 2004)

2.4.2 Media Based Process

Media based processes include any media which is configured in a flow-through bed. Activated alumina and ion exchange are the most widely used media for arsenic removal.

Activated alumina (AA) is a crystalline aluminum oxide, approximately Al_2O_3. It uses an adsorption mechanism to remove arsenic from solution (Chwirka et al. 2000). Arsenic is not the only ion able to adsorb onto AA; the approximate selectivity preference is reported as (Chwirka et al. 2000):

$$OH^- > H_2AsO_4^- > H_3SiO_4 > F^- > SO_4^{2-} > HCO_3^- > Cl^- > NO_3^-$$

Since only charged forms of arsenic will adsorb, As(III) must be converted to As(V) prior to treatment (Chwirka et al. 2000). Since the pH of zero point of charge of AA is 8.2, to have a high density of positive charges the pH must be significantly lowered (to approximately 6) prior to treatment (Chwirka et al. 2000; Kartinen Jr and Martin 1995). This also reduces the concentration of OH^-, for which AA has a greater affinity. The pH must then be adjusted after treatment. Additionally, AA is regenerated with caustic soda (NaOH); however, only 60-70% of the media's capacity is recoverable (Kartinen Jr and Martin 1995). The chemical costs of pH adjustment and regeneration are significant. The waste stream also presents a problem. Not only is it a very high pH solution, it also contains soluble arsenic which must be treated prior to disposal.

Ion exchange is a process of subsisting one ion in solution with another. A media with weakly adsorbed ions is used. If the media is presented with ions that are preferentially adsorbed, the weakly adsorbed ion will be released to solution and substituted with the more strongly adsorbed ion. The approximate selectivity sequence for ion exchange is reported as (Chwirka et al. 2000):

$$SO_4^{-2} > HAsO_4^{-2} > CO_3^{-2}, NO_3^- > H_2AsO_4^-, HCO_3^- >> Si(OH)_4, H_3AsO_3$$

Note that As(V) ($HAsO_4^{-2}$, H_2AsO_4) is preferentially sorbed to As(III) (H_3AsO_3). Consequently, As(V) removal is better than As(III) (Chen et al. 2002; Chwirka et al. 2000; Kartinen Jr and Martin 1995; Korngold et al. 2001). Even more significant is that sulphate is selected preferentially over arsenic. If sulphate is present in the water it will eventually displace and arsenic adsorbed by the ion exchange media and release it back in to solution (Chwirka et al. 2000). Ion exchange also removes carbonate (CO_3^{-2}) which reduces the pH and therefore necessitates pH adjustment before consumption (Chwirka et al. 2000). Residuals also present a problem since the brine used for regeneration becomes contaminated with arsenic and is therefore toxic. These disadvantages can be mediated. With an iron based coagulant it is possible to precipitate the arsenic and safely dispose of the sludge (Chwirka et al. 2000; Korngold et al. 2001). Using multiple treatment columns, it is possible to reduce the amount of arsenic contaminated brine (Kim et al. 2003). Regardless, these difficulties will significantly hinder the installation of ion exchange for arsenic treatment (Chwirka et al. 2000).

Other media based arsenic removal technologies exist, however, they are relatively new and not widely used. Ferric oxide coated alginnate beads are able to remove arsenic by reacting with As(V) to form ferric oxide which remains bound to the beads (Zouboulis and Katsoyiannis 2002). Unfortunately, the capacity is small compared to the other media discussed above. Another emerging technology known as hybrid ion exchanger (HIX) shows very selective removal of arsenic (both As(V) and As(III)) without changing the other water quality characteristics (DeMarco et al. 2003). HIX are beads made of nanoscale hydrated iron oxide particles. In an investigation by the developers, HIX beads significantly outperformed conventional ion exchange media.

2.4.3 Membrane Filtration

The atomic mass of arsenic is 74.9 amu. Of the categories of membranes presented in Table 2-1, only reverse osmosis membranes have a molecular weight cutoff small enough to filter arsenic. Indeed, reverse osmosis membranes are capable of removing As(III) and much of the As(V). Studies have shown that the this class of membrane typically remove 100% of As(V) while only removing 60% to 80% of As(III) (for example Brandhuber and Amy 1998). Yet, nanofiltration membranes are also capable of removing arsenic, even though their pores are seemingly too large. A summary of the arsenic rejection for nanofiltration results from the literature is shown in Table 2-4. This is not an exhaustive presentation of all the research involving the membrane filtration of arsenic; however, all of the membranes presented have appeared in at least two separate studies. In all of the studies the feed water was synthetic or a natural water spiked with arsenic.

Table 2-4 - Summary of arsenic rejection studies involving nanofiltration membranes.

Membrane		Nominal Salt Rejection (%)	Reported Zeta Potential or Charge Density	Arsenic Rejection (%)	
				As(III)	As(V)
Filmtec	**NF45**	60 [A]	-12.5 mV [B]	5-20 [A]	50-90 [A]
	NF70	-	25mV [A] -18 mV [B] -15 to -20 mV [C]	65-95 [D]	95-99 [D]
Nitto Denko	**NTR-7250**	70 [E]	-2 mol/L [F]	10-30 [E]	80-85 [E]
	NTR-729HF	93 [G]	-0.15 mol/L [F]	20-50 [G]	90-95 [G]
	ES10	99.6 [G]	-1000 mol/L [F]	50-75 [H]	90-99 [G]

Sources: A - Vrijenhoek et al. 2001
B - Brandhuber 1999
C -Childress and Elimelech 1996
D - Waypa et al. 1997; Brandhuber and Amy 1998
E - Oh et al. 2000; Sato et al. 2002; Oh et al. 2004
F - Oh et al. 2000
G - Kang et al. 2000; Oh et al. 2000; Sato et al. 2002; Oh et al. 2004
H - Urase et al. 1998; Kang et al. 2000; Oh et al. 2000; Sato et al. 2002; Oh et al. 2004

The charge density and zeta potential are two different methods of expressing the charge of a surface and are not comparable to one another. Zeta potential is an approximation of the electrical potential of the membrane (expressed in mV), while charge density is a measure of the concentration of charged groups on the membranes surface (expressed in mol/L).

It is clear that As(V) is much more easily treated with nanofiltration membranes than As(III). The consensus is that the charge of nanofiltration membranes is able to enhance the rejection of the negatively charged As(V), and there is evidence in Table 2-4 which supports this. The Filmtec membranes have somewhat similar zeta potentials and achieve similar rejection of As(V), while the rejection of As(III) differs greatly between the membranes.

The membranes by Nitto-Denko have very different charge densities, but their As(V) rejections are similar. For example the charge density of ES10 is orders of magnitude larger than NTR-729HF, but their rejections of As(V) are similar. NTR-7250 and NTR-729HF are closer in charge density, yet their rejections of As(V) are dissimilar. Therefore factors other than charge must be influencing the passage of arsenic. For the Nitto-Denko membranes the arsenic rejection performance is more closely tied to the nominal salt rejection.

2.4.3.1 Factors Influencing Arsenic Passage through Membranes

Many factors have been shown to influence the passage of arsenic through membranes. These factors are summarized below.

Charge

Membrane charge has been shown to play a significant role in the arsenic removal of nanofiltration membranes. It has been shown in several studies, and it is summarized in Table 2-4, that As(V) is more easily removed then As(III) (Brandhuber and Amy 1998; Kang et al. 2000; Oh et al. 2000; Seidel et al. 2001; Urase et al. 1998; Vrijenhoek and Waypa 2000).

The Nernst Plank equation has been successfully employed to model the rejection of both As(III) and As(V) (Brandhuber 1999; Oh et al. 2004; Oh et al. 2000; Urase et al. 1998). This relationship shows that the concentration at the surface of the membrane determines the solute passage. It will be recalled from Section 2.3.2 that if a membrane is charged, the concentration of co-ions (ions with a similar charge) at the membrane surface decreases, while the concentration of counter ions (ions with the opposite charge) increases. If the ion is neutral, the concentration at the membrane surface is unaffected by the membrane's charge.

Nanofiltration membranes are, in general, negatively charged. Since As(V) is also negatively charged, its passage is inhibited, while the passage of the neutral As(III) is uninfluenced by the charge of the membrane.

Feed Arsenic Concentration

Increasing the concentration of As(III) to be treated has been shown to decrease rejection (Seidel et al. 2001). Seidel et al. hypothesized that since As(III) is neutrally charged, the diffusion of As(III) is proportional to the bulk concentration resulting in a reduced solute flux.

Some researches have found that increasing the concentration of As(V) has increased the passage of As(V) (Brandhuber and Amy 2001), while others have found the opposite (Seidel et al. 2001; Vrijenhoek and Waypa 2000). Brandhuber and Amy point out that this observation is consistent with the Nernst-Plank equation and Donnan theory as presented in Section 2.3.2. Seidel et al., and Vrijenhoek and Waypa state that their observations are due to the presence of the more permeable and more mobile bicarbonate ion that are therefore more likely to permeate than As(V).

Operating Conditions

The general effect of the membrane's operating conditions as discussed in 2.3.2 generally hold for arsenic. Increasing the flux will decrease the overall solute passage since the arsenic flux will remain constant while the pure water flux will increase. This is true for both As(III) and As(V) (Brandhuber and Amy 2001; Sato et al. 2002; Waypa et al. 1997).

In full scale membrane systems, recovery and average bulk concentration are interrelated. Increasing the recovery also increases the bulk concentration. As discussed above increasing the bulk concentration of As(III) increases the overall passage. While the literature is not consistent regarding the effects of increasing the concentration of As(V), one study did report that the passage of As(V) increases with recovery (Brandhuber and Amy 2001).

Ionic Strength

The presence of additional salts has been shown to have an impact on the rejection of As(V). Some reports show that increasing the concentration of anions or cations increased the passage of As(V) (Brandhuber and Amy 2001; Seidel et al. 2001). With the increased ionic strength the Donnan potential weakens, thus the As(V) concentration at the surface of the membrane increases. Brandhuber and Amy note that the effect of Ca^{2+} ions is particularly strong. This is consistent with the observation that complex formation between Ca^{2+} and the negatively charged groups on the surface of the membrane can make the membrane's charge more positive (Childress and Elimelech 1996; Deshmukh and Childress 2001).

One contradictory study showed that As(V) rejection increases with increasing feed salt concentration. This is hypothesized to be due to the presence of more mobile ions which preferentially permeate (Vrijenhoek and Waypa 2000).

The literature does not discuss the effect of ionic strength on the passage of As(III).

pH

The pH of the feed solution influences the rejection of arsenic since it controls the charge of the membrane and the protonation of arsenic. At higher pHs both the membrane and arsenic are more likely to be negatively charged.

Nanofiltration membranes are, in general, negatively charged. The zeta potential (or charge) of the membrane is influenced by the pH. As pH increases, the zeta potential of membranes has been shown to become more negative (Kang et al. 2000; Oh et al. 2000; Urase et al. 1998). This occurs since the charged groups within the membrane deprotonate as the pH increases.

It will be recalled from the discussion above that the charge of As(III) and As(V) is controlled by the pH. It is evident from Figure 2-1 that as the pH increases both As(III) and As(V) are more likely to be negatively charged. Increasing the charge of arsenic has been demonstrated to increase the rejection of arsenic (Brandhuber and Amy 2001; Kang et al. 2000; Oh et al. 2004; Oh et al. 2000; Seidel et al. 2001; Urase et al. 1998; Vrijenhoek and Waypa 2000).

Some researchers have seen a decrease of rejection of both As(III) and As(V) at higher pHs. However these observations are not clearly addressed (Waypa et al. 1997).

Natural Organic Matter (NOM)

The presence of organic matter has been shown to increase the rejection of As(V) (Brandhuber and Amy 1998, 2001). Initially a theory of co-rejection of DOC and As(V) was proposed to explain the increase in rejection. In the later study it was shown that although NOM improved the membranes ability to reject As(V), there was no As(V) associated with or bound to the NOM. The authours suggested that the NOM is sequestering divalent cations and altering the electrostatic equilibrium within the membrane and thus reducing the transport of arsenic through the membrane.

Alternatively, the rejection of As(V) may also be enhanced through the adsorption of humic acids which make the charge of the membrane more negative (Childress and Elimelech 1996; Deshmukh and Childress 2001) and thus inhibits the passage of As(V).

Permeability

Lower permeability membranes tend to have smaller pores making them more resistant to the passage of both water and solutes. Membrane permeability has been correlated with the passage of As(III), but no correlation was found with the passage of As(V) (Brandhuber and Amy 1998). This is because, unlike As(V), As(III) is unaffected by charge and must be removed through size exclusion mechanisms (Waypa et al. 1997).

2.4.3.2 Residuals

Residuals generation has been largely ignored in many of the studies investigating membrane processes for arsenic removal. It is a concern for any nanofiltration system treating water containing arsenic. The primary residual generated by nanofiltration is the reject stream. Depending on the operational parameters and membrane performance, the arsenic concentration in the reject stream could be between 2 to 10 times the concentration of the feed water. The residual flow could range from 20% - 45% of the treated water flow. (These estimates assume arsenic rejections between 50% and 90% and operational recoveries of 70% to 85%). The residuals are therefore a significant issue and must be considered when evaluating a membrane filtration process.

In a report by the American Water Works Association, possible dispositions for the residuals include: receiving streams, sanitary sewers and landfills (after precipitative coagulation) (Amy et al. 1999). To accommodate the discharge of the reject stream, the flow in the receiving stream would have to be large enough to provide sufficient dilution to meet the water quality standard governing the stream. Alternatively, a waste water treatment plant must have the capacity and the capability to remove arsenic to meet the local discharge regulations. Using precipitative coagulation to treat the reject stream will produce solids which pass the TCLP, but the size of such a facility may be impractical (Amy et al. 1999).

Investigating the disposition of the residuals generated by nanofiltration is not within the scope of this research, but may be the subject of future work.

2.4.4 Pre-Oxidation

The limited removal provided by reverse osmosis and nanofiltration membranes is not insignificant. Arsenite is more toxic and more mobile in the environment then arsenate (Jain and Ali 2000; Pontius et al. 1994; Smedley and Kinniburgh 2002). A successful treatment system must remove both As(III) and As(V).

Since As(V) is more easily rejected by membranes, oxidizing the dissolved arsenic from As(III) to As(V) would enhance the arsenic removal. Several studies have been done on different oxidizing materials including chlorine (Bissen and Frimmel 2003; Ghurye and Clifford 2001), hydrogen peroxide (Bissen and Frimmel 2003; Ghurye and Clifford 2001; Hug and Leupin 2003; Pettine et al. 1999; Pettine and Millero 2000), oxygen (Bissen and Frimmel 2003; Ghurye and Clifford 2001; Kim and Nriagu 2000), ozone (Bissen and Frimmel 2003; Ghurye and Clifford 2001; Kim and Nriagu 2000) and manganese oxides (Bissen and Frimmel 2003; Driehaus et al. 1995; Ghurye and Clifford 2001; Manning et al. 2002; Moore et al. 1990; Tournassat et al. 2002).

Chemical oxidants such as chlorine and permaganate are commonly used in water treatment. Both are effective at oxidizing As(III) to As(V) even in the presence of interfering reductants (Ghurye and Clifford 2001).

UV is an other popular technology which can achieve moderate oxidation of As(III); however, extremely high UV doses are required (Ghurye and Clifford 2001). When a photoabsorber such as sulphite is added, As(III) oxidation is achievable through a patented process (Khoe et al. 1997) using standard UV doses (Ghurye and Clifford 2001).

Ozone oxidizes As(III), although sulfite and TOC slow the oxidation rate considerably; complete oxidation is nevertheless achievable with sufficiently high doses (Ghurye and Clifford 2001). The presence of iron and manganese are reported to have no effect on the rate of oxidation by Ghuyre and Clifford. Meanwhile Kim and Nriagu (2000) report that the presence of iron can accelerate the oxidation rate and contribute to arsenic removal through the co-precipitation of iron and As(V) . Oxygen and air can also oxidize As(III); however, the rate of oxidation is very slow (Kim and Nriagu 2000; Scott and Morgan 1995) and in some cases only oxidizes a fraction of the dissolved arsenic (Hug and Leupin 2003).

There are disadvantage to all the oxidants discussed above: chlorine is incompatible with nanofiltration membranes, handling permanganate can be dangerous and ozone is toxic to humans and requires a costly ozone generator.

Manganese dioxide (MnO_2) is a solid oxidizing media which has been shown to oxidize As(III) under a variety of conditions (Bajpai and Chaudhuri 1999; Bissen and Frimmel 2003; Driehaus et al. 1995; Manning et al. 2002; Moore et al. 1990; Nesbitt et al. 1998; Oscarson et al. 1983; Scott and Morgan 1995; Tournassat et al. 2002). Due to the inert nature of MnO_2 based media, the long life and simple operation compared to the oxidants discussed above, MnO_2 was chosen as the companion oxidant for the membrane filtration of arsenic. The details of its operation are discussed below.

Oxidation of Arsenic Using Solid Manganese Dioxide Based Media

Manganese dioxide (MnO_2) is a solid oxidizing media which has been shown to oxidize As(III) under a variety of conditions (Bajpai and Chaudhuri 1999; Bissen and Frimmel 2003; Driehaus et al. 1995; Manning et al. 2002; Moore et al. 1990; Nesbitt et al. 1998; Oscarson et al. 1983; Scott and Morgan 1995; Tournassat et al. 2002). MnO_2 is the oxidant and not merely a catalyst for oxidation by (dissolved) oxygen. This is confirmed by research which shows that the dissolved oxygen in the feed water has only a limited effect on the oxidation rate of arsenic by MnO_2 (Ghurye and Clifford 2001; Scott and Morgan 1995).

Many authors have tried to define the stoichiometric reaction between As(III) and MnO_2 (Moore et al. 1990; Oscarson et al. 1983; Scott and Morgan 1995). The details are generally presented as shown in equation 4.

$$MnO_2 + H_3AsO_3 + 2H^+ \longrightarrow Mn^{2+} + H_3AsO_4 + H_2O \qquad 4$$

A more recent study by Nesbitt et al. (1998) has shown that there exists an intermediate form of manganese and the reaction proceeds in two steps:

$$\begin{aligned} 2MnO_2 + H_3AsO_3 &\longrightarrow 2MnOOH^* + H_3AsO_4 \\ 2MnOOH^* + H_3AsO_3 &\longrightarrow 2MnO + H_3AsO_4 + H_2O \end{aligned} \qquad 5$$

This reaction scheme has also been presented as shown in Figure 2-4. The consumption of H^+ by the oxidation reaction as shown in reaction 4, implies that the reaction will cause the pH to increase. If the product of reaction 5 is written as Mn^{2+} rather than MnO, consumption of H^+ is also noted.

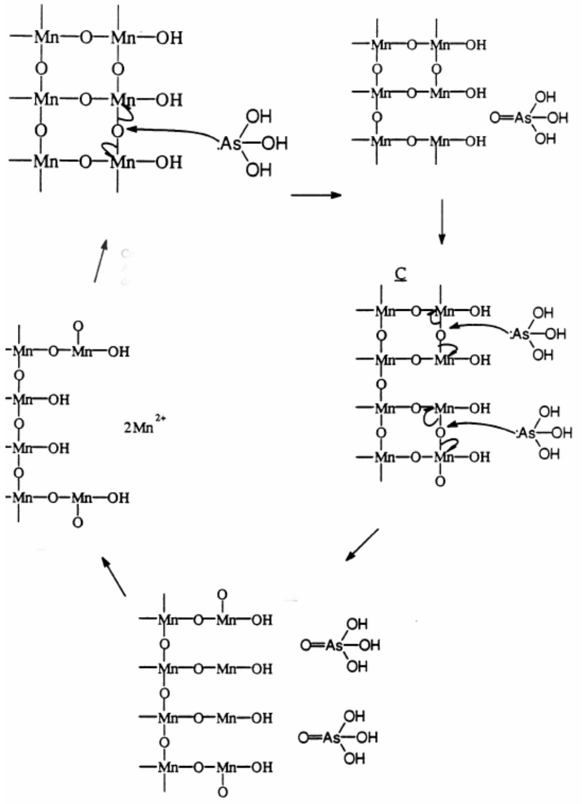


Figure 2-4 -Reaction scheme between As(III) and MnO2 (From Nesbitt et al. 1998)

Installing MnO_2 in a column configuration is a feasible method of oxidizing the As(V) to As(III) (Bajpai and Chaudhuri 1999; Driehaus et al. 1995; Ghurye and Clifford 2001). Investigators report that the filter is successful at oxidizing the As(III) to As(V). While excellent arsenic removal is reported by Bajpai and Chudhuri, others report only moderate removal of arsenic (Driehaus et al. 1995; Ghurye and Clifford 2001).

Early investigators showed that arsenic removal is possible through adsorption of arsenic to the surface of MnO_2. The neutral arsenic species, As(III), is adsorbed more easily then the negatively charged As(V). It is hypothesized that this is because the pH of zero charge (PZC) for MnO_2 is less then 6.4, so for most natural waters MnO_2 will have a negative charge (Oscarson et al. 1983; Subramanian et al. 1997). This makes sorption of negatively charged As(V) less likely. Removal of arsenic can also be achieved through co-precipitation of arsenic with the manganese released through reaction 5 (Oscarson et al. 1983; Tournassat et al. 2002).

Batch studies have shown that the rate of arsenic oxidation increases with temperature (Moore et al. 1990; Oscarson et al. 1983; Scott and Morgan 1995), while in column studies using MnO_2 as a media temperature has been shown to have little effect on the rate of arsenic oxidation (Ghurye and Clifford 2001). The effect of pH has been shown to be minimal (Ghurye and Clifford 2001; Moore et al. 1990; Scott and Morgan 1995).

The presence of other ions in the water reduces the efficiency of MnO_2. Cations such as manganese (Mn^{2+}) and calcium (Ca^{2+}) reduce the effectiveness of MnO_2 (Driehaus et al. 1995; Scott and Morgan 1995). Other reductants, such as Fe(II) or sulfide (S^{2-}), compete with As(III) and therefore reduce the oxidation rate (Ghurye and Clifford 2001).

It is clear from reaction 5 that the MnO_2 is consumed during the oxidation of arsenic. We can also see that dissolved manganese is released. Some researchers report an excess of dissolved manganese after As(V) oxidation (Scott and Morgan 1995) while others report that very little manganese is released into solution (Bajpai and Chaudhuri 1999; Driehaus et al. 1995; Moore et al. 1990; Nesbitt et al. 1998; Subramanian et al. 1997; Tournassat et al. 2002). There are two possible explanations for the lack of dissolved manganese in the treated water: (1) adsorption of the dissolved manganese to the surface of the remaining crystal (Nesbitt et al. 1998) and (2) the formation of arsenic-manganese precipitate which adsorbs to the MnO_2 crystal (Driehaus et al. 1995; Moore et al. 1990; Subramanian et al. 1997). This later pathway of an oxidative-precipitative reaction has been demonstrated by Tournassat et al. (2002). This would also explain the observation that little arsenic removal is seen when only As(V) is present (Bajpai and Chaudhuri 1999), since without As(III), dissolved manganese is not released.

2.5 Arsenic Measurement

2.5.1 Arsenic Stability in Water Samples

The distribution of arsenic varies depending on the water source. Since the treatability of arsenic depends on its speciation, determining which species are present in the water is crucial. If there is conversion between the species during shipment to the laboratory, the results may misrepresent the forms of arsenic present.

In studies which investigated the stability of arsenic in water samples, all have shown that conversion between the inorganic forms of arsenic As(III) and As(V) is likely (Bednar et al. 2002; Gallagher et al. 2004; Gallagher et al. 2001; Hall et al. 1999; Jokai et al. 1998). The rate and nature of the conversion depends on the characteristics of the water sample and the sample storage conditions.

Working with reagent grade water, studies have reported a reduction of As(V) to As(III) over time (Bednar et al. 2002; Hall et al. 1999). In both cases, microbiological activity is suggested as the cause for the change. In other studies researchers have observed oxidation from As(III) to As(V) as well as reduction from As(V) to As(III) (Jokai et al. 1998). In natural waters, arsenic has been found to undergo similar oxidation or reduction reactions (Hall et al. 1999). A comprehensive study showed that the change in arsenic distribution was unique for each water source. Random shifts in distribution were observed: oxidation of arsenic in some cases and reduction in others (Gallagher et al. 2004).

The storage temperature has been shown to have a significant influence on the stability of arsenic species. To varying degrees colder storage temperatures have been shown to lessen the conversion of species (Gallagher et al. 2004; Hall et al. 1999; Jokai et al. 1998).

Some studies have reported that lower arsenic concentrations result in more rapid conversion kinetics (Hall et al. 1999; Jokai et al. 1998); however, others report no relation between concentration and conversion kinetics (Gallagher et al. 2004).

The formation of iron precipitates or complexes containing arsenic has been shown to affect the concentration of water samples containing arsenic (Gallagher et al. 2004). Several studies have noted decreasing arsenic concentrations in solutions containing arsenic and iron (Bednar et al. 2002; Gallagher et al. 2004; Gallagher et al. 2001; Hall et al. 1999).

Due to the formation of iron precipitates and the unpredictable shifts in arsenic speciation, chemical preservation of arsenic samples is recommended (Bednar et al. 2002; Gallagher et al. 2004; Gallagher et al. 2001; Hall et al. 1999).

2.5.2 Stabilizing Arsenic Species for Analysis

There is no universally accepted method for preserving samples (Eaton et al. 1998; Edwards et al. 1998). Various acids have been investigated for their ability to maintain a stable distribution of inorganic arsenic species: ascorbic (Eaton et al. 1998), acetic (Gallagher et al. 2004), hydrochloric (Bednar et al. 2002; Eaton et al. 1998; Hall et al. 1999), sulphuric (Bednar et al. 2002) and nitric (Bednar et al. 2002; Hall et al. 1999). The acids tested preserved the total arsenic concentration; however, they can influence the speciation. Sulphuric and nitric acid were successful at preserving the arsenic speciation provided iron was not present.

To prevent the interference of iron in the preservation of arsenic species ethylenediaminetetraacetic acid (EDTA) has been used to sequester the iron that can co-precipitate with arsenic. This has been demonstrated in three separate studies (Bednar et al. 2002; Gallagher et al. 2004; Gallagher et al. 2001). In the later study, Gallagher et al. show that while EDTA is effective at preventing the formation of iron-arsenic co-precipitates, a change in speciation is still possible. Using acetic acid in conjunction with EDTA prevents the formation of iron-arsenic co-precipitates and the interconversion of arsenic species (Gallagher et al. 2004).

2.5.3 Field Separation Techniques

In light of the uncertainty surrounding the preservation of arsenic samples and the likelihood that speciation change or arsenic co-precipitation will occur, field separation was investigated as a means of eliminating the need for preservation.

Using small ion exchange cartridges in the field has proven to be a reliable method of separating different forms of arsenic. At pHs of natural waters, 6.5 to 8.5, As(V) is negatively charged while As(III) is neutral. This allows anion exchange media to retain the As(V), while allowing the neutral As(III) to pass through the column.

Several different trials have shown that field speciation methods match more sophisticated laboratory methods without the need for preservation (Bednar et al. 2004; Edwards et al. 1998; Ficklin 1983; Le et al. 2000; Miller et al. 2000; Yalcin and Le 2001) and at a relatively low cost (Le et al. 1998).

Using a 0.45 µm filter to prefilter the sample is recommended. This ensures that the capacity of the exchange media is not prematurely exhausted by arsenic co-precipitates which can form in the presence of iron, manganese and aluminum cations (Bednar et al. 2002; Edwards et al. 1998; Le et al. 2000). Rather then filter out solid arsenic co-precipitates, Bendar et al. suggested using EDTA to sequester the cations in order to prevent co-precipitation at the head of the exchange media (Bednar et al. 2002).

Once the species have been separated on the anion exchange column, the arsenic samples can be preserved with acid and the total arsenic concentrations measured. The uncharged species, such as As(III), can be determined by analyzing the treated sampled. The charged species can be determined directly by eluting them from exchange media using an acid such as hydrochloric acid (Le et al. 2000; Miller et al. 2000) or nitric acid (Bednar et al. 2002) or indirectly by calculating the difference between the total arsenic concentration and the concentration of uncharged arsenic species (Edwards et al. 1998).

Miller et al. have shown that a field separation technique based on anion exchange over estimates the concentration of As(III) since some forms of arsenic (dimethylarsinate (DMA) and monomethylarsonate (MMA)) are not retained by the column and thus included in the As(III) measurement (Miller et al. 2000). Other errors can be introduced if the capacity of the column is exceeded (Bednar et al. 2002).

2.5.4 Detection Methods

Once separated the samples must be analyzed. In the literature, the hydride generation (HG) and inductively coupled plasma - mass spectrometry (ICP-MS) are commonly used to detect and measure arsenic concentrations.

Hydride generation involves the production of volatile hydrides upon a chemical treatment with a strong reducing agent, typically sodium borohydride ($NaBH_4$) (Eaton et al. 1998; Gong et al. 2002; Le et al. 2000). Hydride generation can be coupled with various types of spectrometry: atomic absorption (HG-AAS), atomic fluorescence (HG-AFS), atomic emission (HG-AES) or mass spectrometry (HG-MS) (Eaton et al. 1998). The primary advantage of HG techniques is that only gaseous hydrides are introduced to the detector and the remaining sample matrix is discarded. As a result, chemical interferences are eliminated (Eaton et al. 1998; Guerin et al. 2000). Unfortunately, the complexity of this technique can be time consuming (Eaton et al. 1998) and thus costly. The detection limit of HG generation techniques have been reported as low as 0.05 µg/L (Le et al. 2000).

Inductively coupled mass spectroscopy (ICP-MS) is a very sensitive detection method which is generally combined with sophisticated separation methods, such as high performance liquid chromatography (HPLC), to achieve very low detection limits. (Edwards et al. 1998; Gong et al. 2002; Guerin et al. 2000). This is now the most effective tool in many arsenic research laboratories (Gong et al. 2002). Although ICP-MS provides rapid and sensitive arsenic measurements, interferences from chloride can present a problem (Edwards et al. 1998). For the majority of matrices, these interferences are not significant and can be accounted for (Edwards et al. 1998).

2.6 Summary and Needs

Arsenic Chemistry and Health Effects

The two primary sources of arsenic in drinking water are geological and anthropogenic. In natural waters arsenic can be found in two forms: inorganic and organic. In drinking waters (pHs between 6 and 9), inorganic arsenic is made up of two forms: As(V) as an anionic species ($HAsO_4^{2-}$ or AsO_4^{3-}) or As(III) as a neutral species ($H_3A_SO_3$). This important characteristic of inorganic arsenic is exploited by both arsenic treatment and arsenic measurement techniques. Organic forms of arsenic are rare in groundwater (Bednar et al. 2004; Le et al. 2000) and considered not to be of quantitative importance (Smedley and Kinniburgh 2002).

Current research suggests that drinking water is the most important pathways for long-term low dose exposure (Mandal and Suzuki 2002; Ng et al. 2003; Pontius et al. 1994). Chronic exposure to concentrations in order of 100 μg/L may cause health problems (Brown and Ross 2002). Blackfoot disease or gangrene of the feet, have been reported in many people exposed to arsenic in their drinking water (Brown and Ross 2002; Das et al. 1994; Pontius et al. 1994; Viraraghavan et al. 1999). Skin lesions and keritosis (hardedning of the skin) have also been reported. Currently in Canada, the Interim Maximum Allowable Concentration (IMAC) is 25 μg/L, while the proposed Maximum Allowable Concentration (MAC) is 5 μg/L. In the United States, the Maximum Concentration Limit (MCL) was recently lowered from 50 μg/L to 10 μg/L, which is in line with the WHO recommendation. The primary motivation for the reduction in these limits is to limit the risk of cancer.

Arsenic Treatment

Arsenic treatment technologies rely on one of three different processes: (1) transformation arsenic into a filterable form (2) adsorption of arsenic onto a media and (3) filtration of arsenic.

Precipitative methods involve transforming the dissolved arsenic into larger filterable solids which can be more easily removed. Iron based coagulants have been shown to form iron hydroxide-arsenic co-precipitates (as have aluminum based coagulants). Not only do the coagulants co-precipitate with arsenic, the iron (or aluminum) hydroxides also have a sorption capacity for dissolved arsenic. As with standard water treatment, to be effective precipitative processes must be combined with a filtration process to remove the precipitated arsenic. Traditional sedimentation and filtration as well as membrane filtration (using ultrafilters or microfilters) have been shown to be effective at removing arsenic when combined with the precipitative methods. Advantages of precipitative processes include their similarity to standard coagulation and the absence of toxic residuals.

Adsorption processes, such as activated alumina and ion exchange, can remove arsenic however only charged forms of arsenic will adsorb; therefore As(III) must be converted to As(V) prior to treatment. Activated alumina and ion exchange also require pH adjustment. Residuals present a problem since the regeneration solutions contain high concentrations of arsenic.

Filtration of arsenic requires a selectively permeable membrane. The membrane allows the passage of water, but is semi-permeable to arsenic. This is a promising technology for arsenic treatment due to its simple operation and lack of chemical dosing or chemical regeneration.

Membrane Treatment

Reverse osmosis membranes have been used to treat arsenic contaminated ground waters; but they require more energy and operate at higher pressures than nanofiltration membranes. Even though their pores are seemingly too large, nanofiltration membranes have been shown to remove between 50 and 99% of As(V) while providing anywhere from 5 to 95% removal of As(III). It is clear that As(V) is much more easily treated with nanofiltration membranes than As(III).

The consensus is that the charge of nanofiltration membranes enhances the rejection of the negatively charged As(V). Nanofiltration membranes are, in general, negatively charged. Since As(V) is also negatively charged, its passage is inhibited, while the passage of the neutral As(III) is uninfluenced by the charge of the membrane. This is consistent with the predictions of the Donnan equilibrium.

Membrane Operation

The quality of the treated water is a function of the ratio between the pure water flux and solute flux. The pure water flux is related primarily to the pressure applied to the membrane, while the solute flux is a function of the difference in solute concentration across the membrane. In the models presented in Section 2.3.2, these relationships are considered independently, implying that the effects of varying the pressure or the concentration act independently. The pure water flux is proportionally related to the pressure; therefore, increasing the pressure will increase the pure water flux. If the solute flux is constant and the pure water flux is increased, the overall solute passage decreases (due to the "dilution" of the solutes). Increasing the recovery increases the bulk concentration of arsenic, which leads to higher arsenic passage.

Pre-Oxidation of Arsenic

The difficulty reverse osmosis and nanofiltration have removing As(III) is not insignificant. Arsenite is more toxic and more mobile in the environment then arsenate (Jain and Ali 2000; Pontius et al. 1994; Smedley and Kinniburgh 2002). A successful treatment system must remove both As(III) and As(V). Since As(V) is more easily rejected by membranes, oxidizing the dissolved arsenic from As(III) to As(V) would enhance the arsenic removal. Several studies have been done on different oxidizing materials including chlorine, hydrogen peroxide, oxygen, ozone and manganese oxides. Of those mentioned each has its disadvantage: chlorine is incompatible with nanofiltration membranes, handling permanganate can be dangerous and ozone is toxic to humans.

Manganese dioxide (MnO_2) is a solid oxidizing media which has been shown to oxidize As(III) under a variety of conditions (Bajpai and Chaudhuri 1999; Bissen and Frimmel 2003; Driehaus et al. 1995; Ghurye and Clifford 2001; Manning et al. 2002; Moore et al. 1990; Nesbitt et al. 1998; Oscarson et al. 1983; Scott and Morgan 1995; Tournassat et al. 2002). Due to the inert nature of MnO_2 based media, its long life and simple operation compared to the oxidants discussed above, MnO_2 was chosen as the companion oxidant for the membrane filtration of arsenic.

Arsenic Measurement

Due to the influence of arsenic speciation on the effectiveness of membrane filtration, speciated arsenic analyses are necessary. In light of the uncertainty surrounding the preservation of arsenic samples and the likelihood that speciation change or arsenic co-precipitation will occur, field separation was determined to be the most appropriate method.

Once separated the preserved samples are very stable and easily analyzed by ICP-MS. This provides a cost effective (Le et al. 1998) and accurate analytical method (Bednar et al. 2004; Edwards et al. 1998; Ficklin 1983; Le et al. 2000; Miller et al. 2000) for determining the arsenic speciation.

Research Needs

Nanofiltration is an attractive treatment option due to its low energy requirement (compared to reverse osmosis), robustness and the lack of chemical regeneration requirements. Unfortunately, the majority of research involving membrane filtration has been conducted with synthetic feed waters or natural waters spiked with arsenic. Little research has investigated membrane filtration of waters containing naturally occurring arsenic. The performance of membrane filtration predicted by these studies may be misleading since the arsenic composition may not be accurately represented by spiked or synthetic waters.

As discussed above, the literature has consistently shown that membrane filtration removes As(V) much more effectively than the reduced form As(III). To exploit this difference several researches have suggested that a pretreatment step which oxidizes the As(III) to As(V) would improve the performance of membrane filtration (Kartinen Jr and Martin 1995; Oh et al. 2000; Seidel et al. 2001), but this has never been demonstrated. There have been several studies which show that oxidation of arsenic by MnO_2 is feasible (Ghurye and Clifford 2001; Manning et al. 2002), but it is has never been combined with membrane filtration.

To address these deficiencies in the literature, research was conducted using a pilot scale membrane system with two objectives:

1. The first objective was to investigate the application of membrane filtration to treat water with naturally occurring arsenic. Specifically, the feasibility of three different types of membranes, along with the impact of different operating conditions, was investigated.
2. The second objective was to the verify concept of introducing an arsenic oxidation step prior to the membranes, which converts the As(III) to As(V), to improve the performance of membrane filtration. The performance of an oxidant (manganese dioxide or MnO2) was investigated and the benefit was evaluated.

3 Experimental Design

Three experiments were conducted. The first (Experiment I) was done to quantify the amount of arsenic removal achieved using three different membranes. The second (Experiment II) investigated the arsenic oxidation capability of a solid media made of manganese dioxide (MnO_2). The last experiment (Experiment III) investigated the benefit, if any, of combining the MnO_2 treatment with the membrane filtration.

A preliminary experiment was planned prior to Experiment I. Starting with ten potential candidates, the goal was to select the membrane(s) with the best arsenic rejection characteristics for further testing in the field. Due to laboratory and time constraints this experimentation was not conducted. For completeness it is described at the end of this chapter in Section 3.4.

3.1 Experiment I: Removal of Arsenic by Membrane Filtration

The goal of Experiment I was to quantify the amount of arsenic removal achieved using three different membranes and the influence of the membrane operating conditions. The operating conditions investigated were flux and recovery. The flux is a measure of the filtration rate standardized to the surface area of the membrane. Recovery is the ratio of the treated water flow rate to the feed water flow rate.

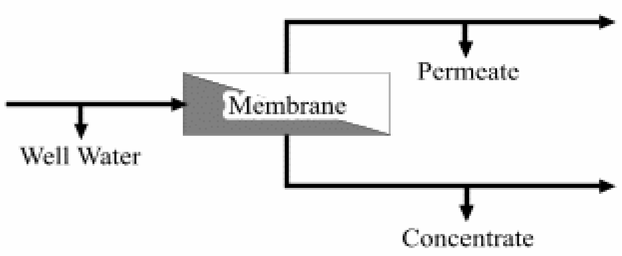


Figure 3-1 - Equipment layout used during Experiment I

The general equipment layout and sample point locations are shown in Figure 3-1. Three different membranes provided by Filmtec were investigated in this study: NF270, NF90 and XLE. The selection of these membranes is discussed in Section 4.3.1. The effects of the operating conditions were investigated as a 2^2 factorial experiment. The recovery was varied from 70 to 85 percent, while the flux was varied from 15 to 25 Lmh. A center point condition was also used. The combinations of operating conditions investigated are shown in Table 3-1. Also shown is the order in which the five different operating conditions were investigated. The order was randomly chosen except for the centre point condition (Recovery: 77.5%, Flux: 20 Lmh) which was investigated first and last. This provides an estimate of the experimental error and ensures that any experimental drift which occurred during the experimental runs was noted.

Table 3-1 - Order of experimental runs in Experiment I

		Recovery [%]		
		70	**77.5**	**85**
Flux [Lmh]	**25**	3rd		2nd
	20 (1)		1st	
	20 (2)		6th	
	15	4th		5th

While a perfect factorial experiment was designed, the experimental condition of 77.5% recovery and a flux of 25 Lmh was unachievable for the NF90 and XLE membranes due to a limitation of the experimental apparatus. In both cases, the experimental point was moved to the closest possible stable combination of recovery and flux. In the case of the NF90 membrane 77.5% recovery and a flux of 20 Lmh was used, while in the case of the XLE membrane 82% recovery and a flux of 22 Lmh was used. Relocating the experimental point introduces some confounding between the estimated effect of each parameter, but still allows for a statistical analysis.

Table 3-2 - Experiment I Arsenic Sampling Schedule

Condition	Flux (Lmh)	Recovery (%)	Samples Taken		
			Well Water	**Permeate**	**Concentrate**
1	**20**	**77.5**	As(Suspended) As(III) As(V)	As(III) As(V)	As(Total)
2	**25**	**85**	As(Total)	As(III) As(V)	As(Total)
3	**25**	**70**	As(Suspended) As(III) As(V)	As(III) As(V)	As(Total)
4	**15**	**70**	As(Suspended) As(III) As(V)	As(III) As(V)	As(Total)
5	**15**	**85**	As(Total)	As(III) As(V)	As(Total)
6	**20**	**77.5**	As(Suspended) As(III) As(V)	As(III) As(V)	As(Total)

During each of these experiments samples were taken to determine the speciation and concentration of arsenic in each process streams. Table 3-2 shows which samples were taken under each operating condition.

In one working day, three of the six experimental conditions for a given membrane were run. The following day, the final three experimental conditions were run. At the start and end of each day, the well water was sampled for suspended arsenic [As(Suspended)], As(III) and As(V). The arsenic concentration was assumed to vary insignificantly during the course of one day, thus during experimental conditions #2 and #5, the well water was sampled for total arsenic only. This assumption was found to be statistically valid at the 95% confidence interval, with the exception of the As(III) concentration on two days. This small daily variation impacted the results only minimally. The permeate was sampled for As(III) and As(V) under each separate condition. The permeate was not sampled for As(Suspended) since the membrane is tighter than 0.45 μm and would therefore remove any suspended arsenic.

Triplicate samples were taken to estimate the error associated with the arsenic measurements. The separation of arsenic concentrations into As(Suspended), As(III) and As(V) required labourious sample processing be done in the field (see Section 4.6.1), which likely introduced more variability into the measurement.

From the data collected the passage of As(III) and As(V) under different operating condition was calculated. Removal of particulate arsenic through mechanical sieving was calculated using the As(Suspended) concentration of the well water. Mass balances were calculated using the concentrate arsenic concentration.

Table 3-3 - Experiment I General Chemistry Sampling Schedule

Condition	Flux (Lmh)	Recovery (%)	Samples Taken	
			Well Water	Permeate
1	20	77.5	X	X
2	25	85		X
3	25	70	X	X
4	15	70	X	X
5	15	85		X
6	20	77.5	X	X

To confirm the proper function of each membrane, general chemistry samples were also taken. General chemistry analyses were performed by a laboratory (RPC, Fredericton, N.B., (506)452-1369) and included parameters such as turbidity, total organic carbon (TOC), alkalinity, pH, total dissolved solids (TDS), hardness, iron and ammonia. The schedule of general chemistry sampling is shown in

Table 3-3. As with the arsenic sampling, during conditions #2 and #5, the well water samples were not taken since the composition of the well water was not likely to change between condition #1 and #3 or #4 and #6.

3.2 Experiment II: Manganese Dioxide Column Study

The goal of Experiment II was to investigate the arsenic oxidation capability and rate of a solid media made of manganese dioxide (MnO_2). A pilot column was constructed which contained MnO_2 and was installed to treat the well water. The general equipment layout and sampling locations are shown in Figure 3-2.

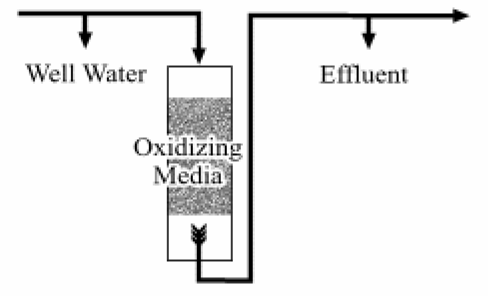


Figure 3-2 - Equipment layout used during experiment II

The parameter studied was the empty bed contact time (EBCT). The EBCT is calculated by dividing the volume of media by the flow rate. It is used as a standard indicator of how long the water is in contact with the media, in this case MnO_2. Due to the porosity of the media, the actual contact time is approximately 50% less than the EBCT. During Experiment II, the EBCT was varied between 1 and 8 minutes. The order in which the different EBCTs were investigated was chosen randomly.

The well water and the column effluent were tested for As(Suspended), As(III) and As(V). Table 3-4 shows which samples were taken during each experimental condition. Since all five experimental conditions could be run in a single day, the arsenic concentrations of the well water were only sampled during the first and last experimental conditions. Again, triplicate samples of the speciated arsenic measurements were taken in order to provide an estimate of error.

Table 3-4 - Experiment II Arsenic Sampling Schedule

Condition	EBCT (min)	Samples Taken	
		Well Water	Column Effluent
1	**1:00**	As(Suspended) As(III) As(V)	As(Suspended) As(III) As(V)
2	**2:00**		As(Suspended) As(III) As(V)
3	**8:00**		As(Suspended) As(III) As(V)
4	**6:00**		As(Suspended) As(III) As(V)
5	**4:00**	As(Suspended) As(III) As(V)	As(Suspended) As(III) As(V)

The effect of the varying the EBCT on the amount of arsenic oxidation was determined. Removal of particulate arsenic through filtration mechanisms was accounted for by measuring the suspended arsenic in the well water. Suspended arsenic concentrations were measured in the column effluent to determine if the MnO_2 causes particulate arsenic to form through the co-precipitation of iron or manganese present.

3.3 Experiment III: Removal by Membrane Filtration with pre-oxidization

The goal of Experiment III was to investigate the benefit, if any, to combining the MnO_2 treatment investigated in Experiment II with the membrane filtration used in Experiment I. An MnO_2 filter was set up with the same hydraulic characteristics as in Experiment II, but sized to provide the needed flow rate to the membrane filtration apparatus. The general equipment layout and sample points are shown in Figure 3-3. The sample point W is well water, MT is MnO_2 water, P is permeate and C is concentrate.

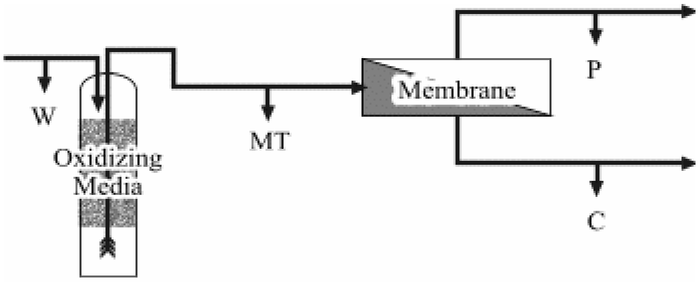


Figure 3-3 - Equipment layout used during experiment III

The same three membranes used in Experiment I were used in Experiment III. The experimental conditions were simplified. The same range of recoveries was used (70% to 85%); however, for this experiment the flux was held constant at 20 Lmh. Based on the results of Experiment II, the MnO_2 filter was operated at a constant EBCT of 7 minutes, ensuring complete oxidation.

Due to the extra sampling required only two experimental conditions were tested each day. During both experimental runs, the well water and MnO_2 treated water were sampled for As(Suspended), As(III) and As(V) while the permeate was sampled for As(III) and As(V). As explained previously, the permeate was not analyzed for suspended arsenic since the membrane is tighter than 0.45 µm and would therefore remove any suspended arsenic. All speciated arsenic samples were taken in triplicate to provide an estimate of the error.

Table 3-5 - Experiment III Arsenic Sampling Schedule

Condition	Flux (Lmh)	Recovery (%)	Samples Taken			
			Well Water	MnO_2 Treated	Permeate	Concentrate
1	20	70	As(Suspended) As(III) As(V)	As(Suspended) As(III) As(V)	As(III) As(V)	As(Total)
2	20	85	As(Suspended) As(III) As(V)	As(Suspended) As(III) As(V)	As(III) As(V)	As(Total)

The arsenic removal and oxidizing capabilities of the MnO_2 filter were confirmed by sampling for speciated arsenic before and after MnO_2 treatment. As in Experiment II, removal of particulate arsenic through filtration was accounted for by measuring the suspended arsenic in the well water and noting any loss of arsenic in the MnO_2 treated water. The suspended arsenic concentration of the MnO_2 treated water was taken to quantify the amount of particulate arsenic formed through the co-precipitation of iron and arsenic.

The passage of As(III) and As(V) under different recoveries was also calculated. These results were compared to the results from Experiment I to determine the improvement due to the addition of MnO_2 pretreatment. Mass balances were calculated using the concentrate arsenic concentration.

Table 3-6 - Experiment III General Chemistry Sampling Schedule

Condition	Flux (Lmh)	Recovery (%)	Samples Taken Well Water	 MnO_2 Treated	 Permeate
1	**20**	**70**	X	X	X
2	**20**	**85**	X	X	X

General chemistry samples were taken to investigate the impact of MnO_2 on other water quality parameters. These samples were also used to confirm the performance of each membrane. The schedule of general chemistry sampling is shown in Table 3-6.

3.4 Proposed Membrane Screening Experiment

Originally included in the scope of this research was a membrane screening experiment. Due to problems locating laboratory space and the waste disposal issues involved when working with arsenic in the laboratory, this experimentation was never carried out. For completeness, the experimental plan will be discussed here.

Starting with ten potential candidates, the purpose of the experiment was to select the membrane(s) with the best arsenic rejection characteristics for further testing in the field. The proposed experimentation was to take place in two parts. The first was a preliminary arsenic rejection test designed to screen the prospective membranes and select two or three potential candidates. The second part of the planned work was an investigation of the influence of pH, hardness and TDS on arsenic rejection and the impact of their interactions.

Experiment A: Preliminary Arsenic Rejection Test

Based on the information available in the literature and manufacturer's recommendation, ten membranes were selected. They included:

Filmtec	NF270, NF90, XLE, FT30, SW30, BW30
Osmonics	HL, AK
TriSep	TS-80, X-20
Sehan	NF, RO

In Experiment A, a solution with a pH of 7.5, hardness of 100 mg/L as $CaCO_3$, alkalinity of 100 mg/L as $CaCO_3$ and 100 mg/L of NaCl was to be created. To this solution 200 µg/L of As(V) was to be added in the form of sodium arsenate (Na_2HAsO_4).

The operating parameters were to be fixed. Depending on the actual conditions in the lab, the operating parameters may have varied; however, the target transmembrane pressure (TMP) was 700 kPa and the target cross flow velocity was 10 to 20 cm/s.

The performance of the membranes was to be judged based on two criteria: (1) the passage of As(V) and (2) the permeability or treated water production rate. From the ten membranes tested in Experiment A, two or three were to be selected for further testing in Experiment B.

Experiment B: Influence of Feed Water Characteristics on Arsenic Rejection

The membranes selected in Experiment A were to be challenged with several different synthetic waters in order to determine the influence of pH, hardness and TDS, on the passage of arsenic.

Experiment B1: As(III) Rejection

This experiment was designed to investigate the influence of pH, TDS and hardness on the passage of As(III).

Eight synthetic feed waters were to be created with the characteristics shown in Table 3-7. The membranes identified in the Experiment A were to be challenged by each of these solutions. Each of the synthetic waters would have been spiked with 200 ug/L As(III). The As(III) was to be added as arsenic trioxide (As_2O_3).

Table 3-7 - Synthetic water quality parameters

Synthetic Water*	1	2	3	4	5	6	7	8
pH	6.5	6.5	7.5	6.5	6.5	7.5	8.5	8.5
Hardness (mg/L as $CaCO_3$)	400	400	100	10	10	100	10	10
Alkalinity (mg/L as $CaCO_3$)	100	100	100	100	100	100	100	100
Additional TDS (mg/L)	0	200	100	0	200	100	0	200

* synthetic waters #3 and #6 are duplicates and will be used to provide an estimate of standard deviation.

The synthetic waters would have been created shortly before testing and allowed to equilibrate for one hour. The pH, TDS, hardness, arsenic concentration and arsenic speciation were to be verified before and after each experimental run to ensure that the synthetic water was stable.

Experiment B2: As(V) Rejection

This experiment is very similar to Experiment B1. The same eight synthetic feed waters were to be created; however, in this experiment As(V) was to be added to the synthetic waters instead of As(III). The arsenate was to be added as sodium arsenate (Na_2HAsO_4).

Membrane Conditioning

Prior to testing, the membrane was to be soaked in deionized water for 12 to 24 hours. Once installed in the membrane test cell, the membranes were to be flushed for 1 hour with deionized water. After the membranes had been sufficiently flushed, the membrane experimental run would commence.

After each experiment was completed the apparatus was to be washed with a 1% nitric acid solution for 30 minutes to ensure the arsenic was flushed from the apparatus. The equipment was to then be rinsed with deionized water prior to starting the next run.

Arsenic Sampling

After 90 and 120 minutes of operation, feed, concentrate and permeate samples were to be taken. The samples were to be analyzed as shown in Table 3-8.

Table 3-8 - Sampling schedule for membrane screening study

	Feed Tank	**Permeate**	**Concentrate**
As(III) (µg/L)	X*	X	-
As(V) (µg/L)	X*	X	-
As(Dissolved) (µg/L)	-	-	X
Hardness (mg/L as $CaCO_3$)	X	X	X
TDS (mg/L)	X	X	X

*If speciation change within the feed water is found to be insignificant during the first five experimental runs, the remainder of these samples would have been foregone to limit the number of speciated arsenic samples required.

The measurement of As(III) and As(V) concentration in the permeate would have been used to calculate the passage of each species through the membrane being tested. The arsenic passage characteristics of each membrane could then be compared. Any change in speciation due to membrane filtration could have been quantified. The measurement of As(III) and As(V) concentrations within the feed tank were to be used to verify that no oxidation or reduction of arsenic occurred during the experimental run. This was expected to be unlikely since the oxidation of arsenic by air is a slow process. Concentrate measurements of As(III) and As(V) concentrations were to be used to complete mass balance calculations

The hardness and TDS measurements were to be used to verify the performance of the membranes and compare it to published data.

System Blanks

Prior to any testing, the synthetic water presented in Experiment A, was to be run through the system for two hours. No membranes were to be installed for this test.

The arsenic concentrations of the permeate and concentrate streams as well as the feed tanks were to be measured. The goal of the test was to quantify the amount of arsenic lost through adsorption to the test apparatus.

Construction of Synthetic Waters

A model was developed and tested for calculating the required amount of each component necessary to create the synthetic waters for Experiments A and B. In summary, for a given volume, the necessary volume of sodium bicarbonate ($NaHCO_3$) was added to achieve the desired alkalinity. The pH was then adjusted using sodium hydroxide (NaOH) or hydrochloric acid (HCl). Appropriate amounts of calcium nitrate $Ca(NO_3)_2$ was then added to achieve the desired hardness. $Ca(NO_3)_2$ was chosen over calcium chloride ($CaCl_2$) since this would add chloride to the water, which could interfere with the arsenic analysis. To adjust the total dissolved solids (TDS) of the solution the appropriate amount of sodium chloride (NaCl) was added.

4 Materials and Methods

The process of selecting a site, the experimental apparatus used, the operation of the apparatus and the analytical methods employed are discussed in this section.

4.1 Site Selection

There were many factors which influenced selection of the site: water quality (including arsenic concentration), physical site conditions such as the availability of electrical power and space, local discharge requirements, and the degree of support of local site staff.

Several sites were investigated as potential candidates: Halifax, N.S., Cold Lake, AB, Deloro, ON, Pender Island, BC, and Viden, MB. Two towns, Deloro, ON and Cold Lake, AB, were eliminated due to the limited support of local staff and the administrative difficulties in obtaining approval for the research. Halifax, NS and Pender Island, BC were eliminated due to the limited amount of space available and approval difficulties. Virden, Manitoba was selected since there was ample physical space for the apparatus, an acceptable method of waste discharge and very supportive local staff.

4.2 Site Description

The research was conducted in Virden, Manitoba. The water was supplied to the pilot by the town's wells located 6 km North East of the town of Virden, in the valley of the Assiniboine River. The wells also supply the municipal drinking water system. The pilot was installed by the author, with the assistance of the Town of Virden staff. A map of the site location is shown in Figure 4-1.

(Created using Microsoft Streets and Trips and Xara X)

Figure 4-1 - Map of research site location, 6 km North-East of Virden, MB

Virden's drinking water is supplied by two wells, approximately 24 m deep. Photographs of the pump house location are shown in Figure 4-2. The wells are located between the pump house and the river. Well #1 is located approximately 200 m from the bank of the river, while well #2 is less than 100 m from the river. Based on the conductivity measurements, the composition of the water pumped from each well is slightly different. Well #1 had a conductivity of approximately 1950 μS/cm while well #2 had a conductivity of approximately 1680 μS/cm. For simplicity, all experiments were conducted using only water from well #1.

(Photos by Author)

Figure 4-2 - Photos of pump house location

4.3 Membrane Filtration System

A description of the construction and operation of the membrane filtration system can be found below.

4.3.1 Apparatus

Membrane Types

Three different membranes were used. The membranes were supplied by Filmtec (a division of Dow, Midland, Michigan, (800)447-4369) through a research agreement between Filmtec and Zenon Environmental Inc. The different membranes types were selected based on the literature results and manufacturer's recommendations.

As discussed in Section 3.4, six membranes by Filmtec were originally selected for the membrane screening experiment. Due to the large pressure requirements of the FT-30, SW-30 and BW-30 membranes, they were eliminated from the pilot study. The three membranes selected for evaluation were NF270, NF90 and XLE.

The NF270 membrane is designed to provide removal of divalent ions, colour and total organic carbon (TOC). The NF90 is a tighter membrane designed to provide removal of divalent ions and some monovalent ions, colour and TOC. The XLE membrane is a low energy reverse osmosis membrane designed to provide removal of both monovalent and divalent ions. Table 4-1 summarizes the general characteristics of each membrane along with the standard salt rejection and permeability specifications published by Filmtec (Dow Liquid Separations 2004). Zeta potential values are also shown (Krueger 2004; Manttari et al. 2004)

Table 4-1 -Characteristics of membranes used

Membrane Name	Description	Salt Rejection [A] (%)	Permeability [A] (Lmh/bar)	Zeta Potential [B] (mV)
NF270	"Loose" Nanofiltration	40-60	13	-5 to -16
NF90	"Tight" Nanofiltration	85-95	6.7	-15 to -30
XLE	"Low Energy" Reverse Osmosis	99	7.1	-10 to -25

Sources: A - Dow Liquid Separations 2004
B - Krueger 2004

Membrane Configuration

The majority of nanofiltration and reverse osmosis membranes are configured as spiral wound membranes. In this configuration the membrane is rolled into a compact cylinder, making efficient use of space and allowing for a large membrane surface area in a small volume. More importantly, the flow is oriented relative to the membrane such that the feed water travels parallel to the surface of the membrane. This results in a cross flow across the membrane surface. The momentum of the water serves to limit the thickness of the concentration polarization layer, as discussed in Section 2.3.2. This is desirable since it reduces the concentration at the surface of the membrane and thus the solute passage.

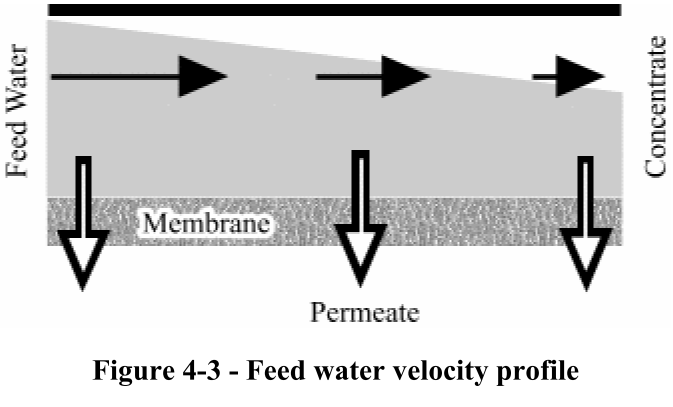


Figure 4-3 - Feed water velocity profile

Maintaining the crossflow limits the recovery of a single membrane, since as feed water permeates through the membrane, the velocity along the surface of the membrane decreases. A representation of the velocity profile is shown in Figure 4-3. The shaded gray area represents the decreasing flow of the feed water traveling along the surface of membrane, while the black arrows represent the magnitude of the cross flow velocity. In standard membrane systems the recovery from a single 40 inch long element is typically 15%, which minimizes the drop in cross flow velocity from the feed side to concentrate side of the membrane.

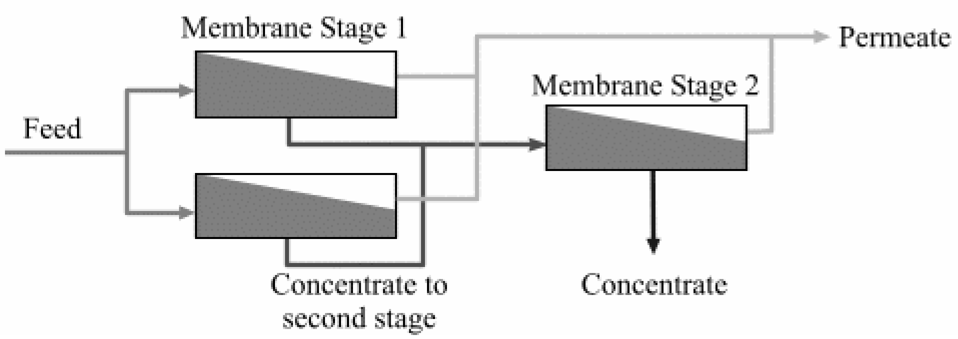


Figure 4-4 - Multistaging of membranes

To increase the recovery of standard membrane system, a technique called multistaging is used. This concept is shown in figure Figure 4-4. In a multistaged membrane system, concentrate from one or more membranes is collected and fed to a second or subsequent stage of membranes. In this way the cross flow velocity within each membrane element can be maintained and recoveries higher than 15% can be achieved.

Zenon Environmental Inc. (Oakville, Ontario, (905)465-3030) has developed a method of internalizing the multistaging concept, allowing higher recoveries to be achieved from a single element. This research uses an eight inch prototype membrane with internal staging. Zenon Environmental Inc. has patent pending on the internal multistage membranes used.

Equipment

A photograph of the membrane filtration system is shown in Figure 4-5. The system was constructed by Zenon Environmental Inc., under the direction of the authour. A schematic is shown in Figure 4-6 while a detailed process and instrumentation drawing can be found in Appendix A.

Figure 4-5 - Membrane filtration system used in Experiment I and III

The membrane was housed in a standard single element, eight inch membrane housing by Protec (Vista, California, model PRO-8-300EP). The feed pressure was supplied by a multistage centrifugal pump by Grundfos (Oakville, Ontario, (905) 829-9533, model CHN2-60). It is able to produce 26 L/m at 700 kPa. All the connecting pipes on the membrane system were made from schedule 80 poly vinyl chloride (PVC).

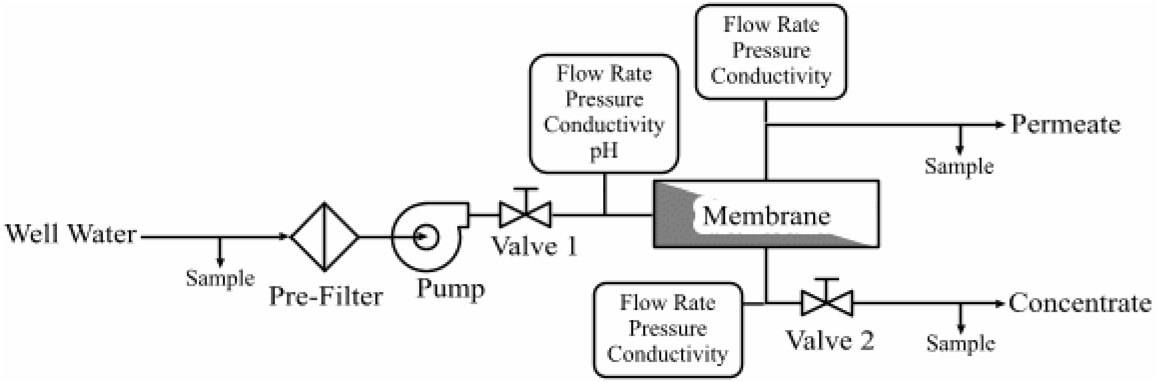


Figure 4-6 - Configuration of membrane filtration system

Data Logging

The membrane filtration system was controlled by a Micrologix 1500 programmable logic controller (PLC) by Allen Bradley (Milwaukee, Wisconsin, (414)382.2000). Online instrumentation was used to measure flow, pressure, conductivity, pH and temperature. The data was logged by the PLC every 5 seconds.

Magnetic flow meters by ABB (Zurich, Switzerland, model Copa-EX) were used to measure the permeate and concentrate flow rates. The feed flow was determined by adding the permeate flow and concentrate flow rates. The flow meters are capable of measuring flows between 0 and 50 ± 0.0175 L/s.

Membrane feed pressure, permeate pressure and concentrate pressure were measured with pressure transmitters by ABB (model 600T). The pressure transmitters are capable of measuring pressures from 0 to 1600 kPa ± 2.4 kPa.

Permeate conductivity was measured with a conductivity sensor by Hach/GLI (Loveland, Colorado, model PRO-C3A1N transmitter and model 3422 probe). Feed water and concentrate conductivity were measured with a conductivity sensor by ABB (model 4620 transmitter and model 2077 probe). In each process stream the conductivity was in a different range. To improve the accuracy of the conductivity measurement, the electrode constant of each conductivity probe was unique depending on which process stream the probe was analyzing. The manufacturer, cell constant and range of each probe is summarized below:

Table 4-2 - Conductivity sensor specifications

Process Stream	Measurement Range	Cell Constant	Manufacturer
Feed	0-2000 ± 2 μs/cm	1.0	Hach/GLI
Permeate	0 - 1000 ± 12.5 μs/cm	0.1	ABB
Concentrate	0-200000 ± 200 μs/cm	10	Hach/GLI

The feed pH of the water was measured with an online pH sensor. The pH sensor is made up of a model 4630 transmitter and model TB551 probe by ABB. The sensor is capable of measuring within 0.175 units.

The temperature was measured using a Synsycon temperature sensor by ABB. The sensor is capable of measuring temperatures in rage of 0 - 40 ± 0.5°C.

4.3.2 Operation

The flux and recovery of the system were controlled using manually operated hand valves and monitored using online instrumentation. The flux was set by controlling the feed pressure using the flow control valve on the down stream side of the pump (Valve 1 in Figure 4-6), while the reject flow was controlled using the valve on the concentrate stream (Valve 2 in Figure 4-6).

For each experimental run, the membrane filtration system was allowed to operate for a minimum of one hour prior to sampling. The operating conditions were monitored using data logging equipment and a performance chart was created to verify that the operating conditions were stable.

New membranes were flushed (operated at 0% recovery) for 10 minutes at 20 L/min to remove any residual manufacturing chemicals or shipping preservatives. To condition the membranes, they were operated under experimental conditions (e.g. 77.5% recovery and a flux of 20 Lmh) for a minimum of 10 hours over a period of two days. At the end of each experiment, the membrane was flushed for 10 minutes with 20 L/min of feed water to remove the concentrate from the membrane. A flush was also performed at the start of each day.

While not in operation, the membranes were stored in sealed plastic bags after being flushed with a solution of 5 mg/L of sodium meta-bisulfite ($Na_2S_2O_5$). $Na_2S_2O_5$ is used to scavenge oxygen, thereby limiting the growth of aerobic bacteria and preserving the membranes between experiments. $Na_2S_2O_5$ can make the charge of the membrane more negative; however, within the pH range of 6 to 9 the influence of $Na_2S_2O_5$ is not significant (Childress and Elimelech 1996).

4.4 Manganese Dioxide Column and Filter

4.4.1 Apparatus

Media

The manganese dioxide media used is made by American Minerals (King of Prussia, Pennsylvania, USA (610)337-8030) It is marketed under the name Pyrolox and contains 79% - 80% manganese dioxide (MnO_2) by weight. In this study, the media size used was a -8 / +20 mesh; the media was therefore between 0.8 mm and 2.3 mm. A close up photograph of the MnO_2 media is shown in Figure 4-7 with a 6.4 mm (¼ inch) grid in the background.

The drain of each column was covered with 100 mm of garnet to provide an underbed. The garnet was number 8 mesh (greater than 2.3 mm). The garnet was manufactured by International Garnet (Norfolk, Virginia, USA (757)857-5631).

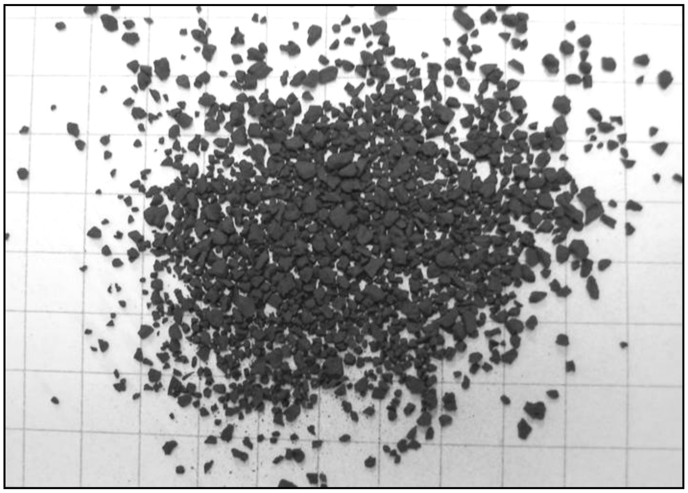


Figure 4-7 - Manganese dioxide media used in Experiment II and Experiment III

Filter

The full size filter used in Experiment III was a fiberglass wound tank, supplied by Waterite (Winnipeg, Manitoba (204)786-1604, model WC1865EN) and shown in Figure 4-8. The internal diameter of the filter was approximately 430 mm. The filter was loaded with 4 inches of garnet and 0.965 m of MnO_2.

Pilot Column

The pilot column used in Experiment II, was designed to operate at the same fluxes the filter used in Experiment III . The pilot column was manufactured by Zenon Environmental Inc. and was made from a clear acrylic pipe 100 mm in diameter and 1.5 m long. The internal diameter of the pipe was approximately 100 mm. A photo of the pilot column is shown in Figure 4-9. Like the full scale filter, the pilot column was loaded with 4 inches of garnet and 0.965 m of MnO_2.

Figure 4-8 - Manganese dioxide filter used in Experiment III

4.4.2 Operation

The pilot column and full size filter were operated in exactly the same manner. For simplicity, the following discussion will refer only to the full size filter.

After loading the filter with MnO_2 media, it was backwashed to remove any fine particles. The filter was backwashed at a flux of 86 m/h (35 USgpm/ft^2) (as recommended by the manufacturer) until there was no discolouration in the backwash water. This took between 2.5 and 3 hours.

Prior to operation, the filter was operated for 200 bed volumes to condition the filter and equilibrate arsenic adsorption capacity of the MnO_2 (Bajpai and Chaudhuri 1999; Driehaus et al. 1995; Ghurye and Clifford 2001).

For each experimental run, a minimum of 5 bed volumes were treated prior to sampling to allow the MnO_2 to acclimatize to the hydraulic conditions (Ghurye and Clifford 2001). During Experiment III the membrane system was operating for an hour to achieve steady state, resulting in between 5 and 11 bed volumes treated by the MnO_2 filter prior to the sampling.

Figure 4-9 - Manganese dioxide pilot column used in Experiment II

4.5 Ancillary Equipment

A prefilter was used to filter out any large particulate matter. The filter used was a dual density (5 µm with 50 µm prefilter) manufactured by Pentek (Upper Saddle River, New Jersey, USA, (201) 818-5900). A standard 4 inch diameter by 20 inches long prefilter was used (DGD-5005-20).

The interconnections between the feed water, MnO_2 filter and membrane system were made using PVC hose. One inch internal diameter Clearbraid® Series K3150 hose by Accuflex (Canton, Michigan, (734) 451-0080) was used.

The test apparatus water inlet pressure was regulated using a pressure regulator by Watts (Burlington, Ontario, Canada, (905)332-4090, model 25AUB).

4.6 Sampling Methodology

Two different sampling methodologies were employed. One method was used to determine the arsenic concentrations, the other to determine the general water quality parameters.

4.6.1 Arsenic

Sampling Materials

The samples for arsenic analysis were obtained and processed using 50 mL and 20 mL Norm-Ject® syringes made of polypropylene and polyethylene (Fisher catalogue numbers: 14-817-35, 14-817-33). The 0.45 µm filters were 25mm cellulose ester membranes by Millipore (Fisher cat#: HAWP 025 00). The filter holder was polypropylene and also by Millipore (Fisher cat#: SX00 025 00). To separate the arsenic species, anion exchange cartridges by Sep-Pak® were used (Waters catalogue number: WAT020545). The cartridges have an ion exchange capacity of 230 µeq/mL. The arsenic samples were preserved with nitric acid (HNO_3)and sent to the laboratory for analysis in 15 mL polypropylene sample tubes by Fisher Scientific (Fisher catalogue number: 05-539-5).

Sample Collection and Processing

Unless a separation procedure is performed, it is likely that even with preservation the speciation of the arsenic would change between the time the sample is taken and the analysis is performed. To prevent measurement errors due to shifts in speciation, separation of the various forms of arsenic was done in the field immediately after sampling. The separation of the sample into aliquots of suspended arsenic [As(Suspended)], As(III) and As(V) analysis was done using a field separation method similar to other methods described in the literature (Bednar et al. 2004; Edwards et al. 1998; Ficklin 1983; Le et al. 2000; Miller et al. 2000). Separating the As(Suspended) was done by passing an aliquot of the sample through the 0.45 µm filter. The separation of As(III) and As(V) was done using an anion exchange cartridge. Pre-filtering the sample ensures that the anion exchange media is not prematurely exhausted by arsenic co-precipitates (Edwards,'98, Le,'00, Bednar,'02). The validity of the method was discussed and confirmed by Dr. X. Chris Le (Department of Public Health Sciences, University of Alberta, Canada), who is an authority on the subject of arsenic analysis (Le 2004).

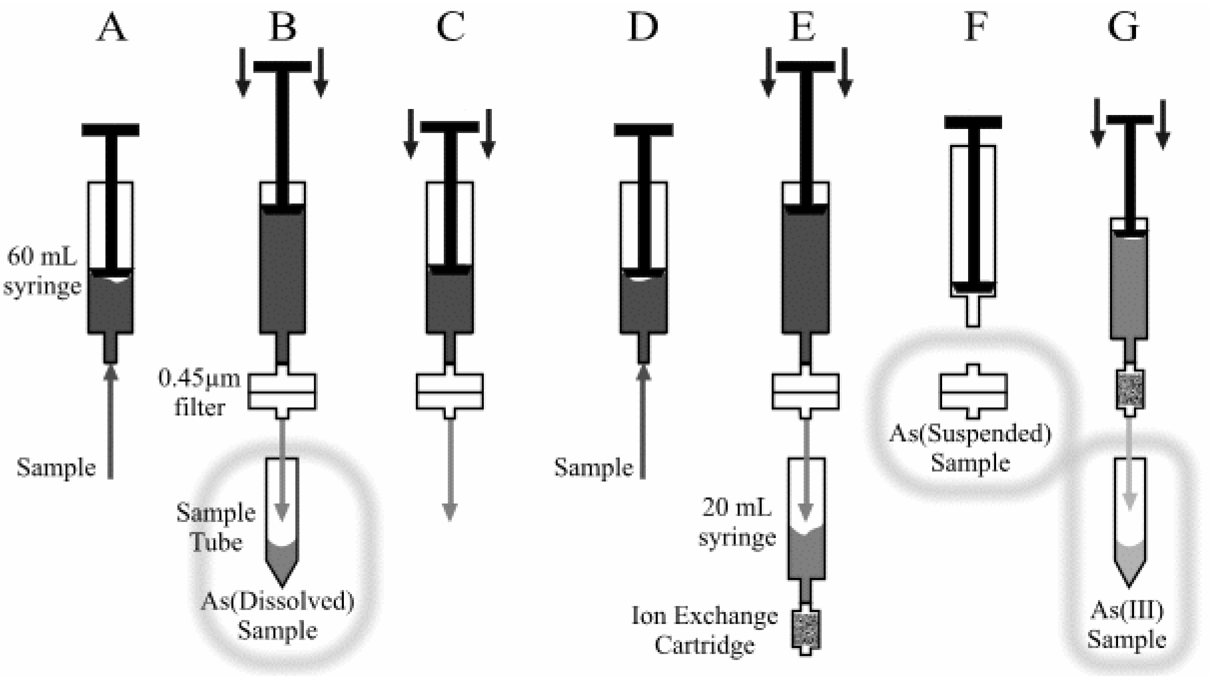


Figure 4-10 - Schematic of arsenic sample processing procedure

The separation of arsenic species was performed as shown in Figure 4-10. Prior to processing the samples, two empty 15 mL sample tubes were placed in a stand and two drops of 70% nitric acid (HNO_3) were added to each tube. Depending on the stream being sampled (well water, permeate, concentrate, column effluent or MnO_2 treated water) the appropriate sample port was opened (see figures Figure 3-1 trough Figure 3-3) and flushed for a minimum of 1 minute prior to sample collection.

The sample was collected using a sterile 60 mL syringe (Figure 4-10A). The pressure of the sample stream was allowed to fill the syringe. After discarding the first 5 mL, a 0.45µm filter was fitted to the end of the syringe and 15mL of the sample was filtered directly into one of the sample tubes (Figure 4-10B) which was saved for As(Dissolved) analysis. Then 35 mL was passed through the filter (Figure 4-10C) and the last 5 mL discarded. A second 60 mL sample was collected (Figure 4-10D) and after discarding the first 5 mL, 20 mL of sample was filtered directly into the body of a sterile 20 mL syringe (Figure 4-10E), 30 mL was passed through the filter (Figure 4-10C) and the remaining 5 mL was discarded. In total 100ml of sample was filtered through the 0.45 µm filter. The filter was removed from the filter holder, folded in quarters then placed within an air tight bag (Figure 4-10F). After installing the plunger in the 20ml syringe, the filtered sample was passed through the ion exchange cartridge at the rate of 2 - 3 mL/min. The first 3 mL from the ion exchanged cartridge was discarded, and the second sample tube was filled directly from the ion exchange cartridge (Figure 4-10G). The sample tubes were then sealed with an air tight lid.

It should be noted that HNO_3 was used at the preserving acid because using HCl would have introduced more chloride, which may have interfered the arsenic analysis (Edwards et al. 1998).

Sample Analysis

All the arsenic concentrations were determined using Inductively Coupled Plasma Mass Spectrometry (ICP-MS) according to EPA Method 200.8 (Environmental Monitoring Systems Laboratory (Cincinnati Ohio) 1992) by RPC (a private laboratory in Fredericton, N.B., (506)452-1369).

The concentration of suspended arsenic was determined by digesting the filters with nitric and hydrochloric acids prior to ICP-MS analysis. The total dissolved arsenic concentration [As(Dissolved)] was determined from the filtered aliquot and represents the combined concentration of As(III) and As(V) . The As(III) concentration was determined from the aliquot which passed through the ion exchange cartridge. The As(V) concentration was determined by subtracting the As(III) concentration from the As(Dissolved) concentration.

The minimum reporting limit (MRL) for suspended arsenic is 0.05 μg/filter. Since 100 mL of water was filtered through the sample, this equates to a MRL of 0.5 μg/L. None of the samples were reported to have suspended arsenic concentrations greater than 0.5 μg/L. These non-detect values were treated as 0 μg/L in the subsequent data analysis.

The MRL for the As(Dissolved) and As(III) concentrations was 1 μg/L. Some samples were reported by RPC as having concentrations "<1" μg/L. During the analysis of the results these values were treated as having 1 μg/L of arsenic. This is a conservative estimate.

4.6.2 General Chemistry

Sampling Materials

The general chemistry samples were collected in 250 mL high density polyethylene Nalgene bottles (Fisher catalogue number: 02-923D).

Sample Collection and Processing

The sample bottle was flushed three times. The bottles were filled minimizing aeration then sealed without head space. The sample was placed in a cooler and refrigerated until shipment. Shipment was done as soon as practical after the samples had been taken (typically within 2 days). However, due to the location of the test site and the logistics involved in shipping, the time between sampling and analysis in some cases was as long as 25 days.

Since the general chemistry sample was used for the determination of various water quality parameters, it was not preserved. This likely compromised the analytical accuracy of some parameters, such as ammonia, iron and total organic carbon, where preservation is recommended (American Public Health Association et al. 1995). Any effects due the lack of preservation are not critical to the results or their interpretation.

Sample Analysis

The inorganic constituents were determined by analyzing the general chemistry sample. The analysis was done by RPC (Fredericton, N.B., (506)452-1369). The methods used by RPC are summarized in Table 4-3, along with the minimum reporting limit (MRL).

From these values, RPC calculated the total dissolved solids (TDS) and hardness as per the standard method (American Public Health Association et al. 1995).

The pH, total organic carbon and turbidity were also determined from the analysis of the general chemistry sample. The analysis was done by RPC (Fredericton, N.B., (506)452-1369) and their methods are summarized in Table 4-4.

Table 4-3 -Minimum reporting limits (MRL) and analytical methods used for inorganic constituents

RPC ID	MRL (mg/L)	Reference [A]	Method Principle
Sodium	< 0.05	EPA 200.7	ICP-ES [B]
Potassium	< 0.02	EPA 200.7	ICP-ES
Calcium	< 0.05	EPA 200.7	ICP-ES
Magnesium	< 0.01	EPA 200.7	ICP-ES
Iron	< 0.02	EPA 200.7	ICP-ES
Manganese	< 0.001	EPA 200.7	ICP-ES
Copper	< 0.001	EPA 200.7	ICP-ES
Zinc	< 0.001	EPA 200.7	ICP-ES
Alkalinity (as $CaCO_3$)	< 1	EPA 310.2	Automated Methyl Orange Colourimetry
Chloride	< 0.5	SM 4500-Cl^- E	Automated Ferricyanide Colourimetry
Ammonia (as N)	< 0.05	SM 4500-NH_3 G	Automated "Phenate" Colourimetry

A - The Method Reference is the principal accepted reference for a procedure from which the RPC Standard Operating Procedures were derived.
SM - American Public Health Association et al. 1995.
EPA - Environmental Monitoring Systems Laboratory (Cincinnati Ohio) 1992

B - Inductively Coupled Plasma Emission Spectrometry

Table 4-4 -Minimum reporting limits (MRL) and analytical methods used for other constituents

RPC ID	MRL	Reference [A]	Method Principle
pH	-	SM 4500-H^+ B	pH Electrode - Electrometric
Total Organic Carbon (mg/L)	< 0.5	SM 5310 C	Auto. UV-Persulfate digestion, dialysis/colorimetry
Turbidity (NTU)	< 0.1	SM 2130 B	Manual nephelometry

A - The Method Reference is the principal accepted reference for a procedure from which the RPC Standard Operating Procedures were derived
SM - American Public Health Association et al. 1995.

4.7 Calculations

4.7.1 Arsenate Concentration

The arsenate concentration [As(V)] was calculated by difference. The average As(III) concentration (based on three replicate samples) was subtracted from the average total dissolved arsenic [As(Dissolved)] concentration (also based on three replicate samples). This calculation is shown below:

$$As(V) = \overline{As(Dissolved)} - \overline{As(III)} \tag{6}$$

4.7.2 Membrane Performance

Recovery was calculated as $\frac{Q_{Permeate}}{Q_{Permeate} + Q_{Concentrate}}$, where Q is the volumtric flow rate.

Passage was calculated as:

$$Passage = {C_{Permeate}} \big/ {C_{Feed}} \tag{7}$$

where C_{Feed} is the concentration in the feed and $C_{Permeate}$ is the concentration in the permeate.

4.7.3 Statistical Calculations

The statistical calculations used in this thesis are briefly discussed below; for a more detailed discussion consult an introductory statistics textbook (for example Clarke and Kempson (1997)) or an online mathematical resource (for example Weisstein (2005)).

All arsenic samples were taken in triplicate. The results of the triplicate samples were pooled to provide an estimate of the standard deviation. The standard deviation is estimated using equation 8.

$$s(x) = \sqrt{\frac{\sum_{i=1}^{n} (x_i - \overline{x})^2}{n-1}} \text{, where } \overline{x} \text{ represents the average of } x. \tag{8}$$

The well water arsenic concentrations were taken in triplicate twice per day; in this case all six samples were pooled.

Propagation of Variance

The standard deviation of calculated values, such as the As(V) concentration and passage, was calculated used the propagation of variance (Weisstein 2005). If *x=f(u,v)* then the variance of x can be calculated as shown in equation 9.

$$\sigma_x^2 = \sigma_u^2\left(\frac{\partial x}{\partial u}\right)^2 + \sigma_v^2\left(\frac{\partial x}{\partial v}\right)^2 + 2\sigma_{u,v}\left(\frac{\partial x}{\partial u}\right)\left(\frac{\partial x}{\partial v}\right) \qquad 9$$

The propagation of variance was used for two different calculations. The first was the concentration of As(V). It was calculated by subtracting the As(III) concentration from the As(Dissolved) concentration. If we call this relationship *P*, as shown in below:

$$P(As(Dissolved), As(III)) = As(Dissolved) - As(III) = As(V) \qquad 10$$

then using equation 9, the expression for the variance of As(V) can be calculated as shown in equation 11

$$\begin{aligned} s_{As(V)}^2 = s_{As(Dissolved)}^2\left(\frac{\partial P}{\partial As(Dissolved)}\right)^2 + s_{As(III)}^2\left(\frac{\partial P}{\partial As(III)}\right)^2 \cdots \\ +2\cdot s_{As(Dissolved),As(III)}\left(\frac{\partial P}{\partial As(Dissolved)}\right)\left(\frac{\partial P}{\partial As(III)}\right) \end{aligned} \qquad 11$$

where $s_{As(Dissolved),As(III)}$ represents the covariance between the As(Dissolved) and As(III). After calculating the partial derivatives $\frac{\partial P}{\partial As(Dissolved)}$ and $\frac{\partial P}{\partial As(III)}$, the expression becomes:

$$s_{As(V)}^2 = s_{As(Dissolved)}^2 + s_{As(III)}^2 - 2\cdot s_{As(Dissolved),As(III)} \qquad 12$$

During the analysis, it was assumed that $s_{As(Dissolved),As(III)}$ is 0. This was done for two reasons: first, from the data collected it was impossible to estimate the covariance, and secondly, the covariance is likely positive. Therefore this assumption results in a conservatively large estimate of the variance.

The second calculated parameter was passage. The variance of the passage was calculated in a similar fashion. Passage was calculated as shown in equation 7. After calculating the partial derivatives, the expression for the variance of the passage calculations becomes:

$$s_{Passage}^2 = s_{Permeate}^2 \left(\frac{1}{C_{Feed}}\right)^2 + s_{Feed}^2 \left(\frac{C_{Permeate}}{C_{Feed}^2}\right)^2 - 2s_{Feed,\mathrm{P}ermeate}\left(\frac{1}{C_{Feed}}\right)\left(\frac{C_{Permeate}}{C_{Feed}^2}\right) \qquad 13$$

Again, C_{Feed} is the average feed concentration and $C_{Permeate}$ is the average permeate concentration. s^2_{Feed} is the variance of the feed concentration, $s^2_{Permeate}$ is the standard deviation of the permeate concentration and $s_{Feed,Permeate}$ is the covariance of the feed and permeate concentrations.

As with the calculation of the variance of As(V), it was assumed that $s_{Feed,Permeate}$ is equal to 0. From the data collected it was impossible to estimate the covariance, but the covariance is likely positive; therefore, this assumption results in a conservatively large estimate of the standard deviation.

Confidence Intervals

Once the standard deviation is known the confidence interval can be calculated. The 95% confidence interval for the mean was calculated as:

$$95\%C.I. = t_{95\%,n-1}\frac{s}{\sqrt{n}} \qquad 14$$

Difference of Means

Standard t tests were performed to determine if there was a difference in the feed water arsenic concentrations. The average As(Dissolved) and As(III) concentrations in the well water were compared at the start and end of each day. T tests were also performed to detect experimental drift by comparing the permeate arsenic concentrations at the start and end of each group of experiments.

The hypothesis test was set up as shown in equation 15, where x_1 and x_2 are the arsenic concentrations at the start and the end of the day, or the start and end of the group of experiments. x_1 and x_2 were chosen such that $x_1 > x_2$.

$$H_0 : \overline{x_1} - \overline{x_2} = 0 \qquad\qquad H_1 : \overline{x_1} - \overline{x_2} \neq 0 \qquad 15$$

$$t_{observed} = \frac{\overline{x_1} - \overline{x_2}}{\sqrt{s_p^2\left(\frac{1}{n_1} + \frac{1}{n_2}\right)}} \qquad 16$$

where the pooled variance , s_p^2, is calculated as $s_p^2 = \frac{(n_1 - 1)s_1^2 + (n_2 - 1)s_2^2}{v}$ and $v = n_1 + n_2 - 2$

If the test statistic $t_{\alpha/2,v}$ was greater than $t_{observed}$, then there null hypothesis was not rejected and the difference between arsenic concentrations was found to be statistically significant. If the test statistic $t_{\alpha/2,v}$ was less than $t_{observed}$, then the null hypothesis was rejected. $t_{\alpha/2,v}$ was found in standard statistical tables. All t tests were conducted at a 95% confidence level.

Linear Regression

The linear regression was performed using coded variables. The flux was coded from -1=15 Lmh to 1=25 Lmh and the recovery was coded from -1=70% to 1=85%. Using matrix algebra the regression parameters were calculated using:

$$\hat{\beta} = (X'X)^{-1}(X'y) \qquad 17$$

where $\hat{\beta}$ is the vector of linearly regressed parameter estimates, X is the matrix of coded independent variables, and y is the vector of response variables. For the regressions presented in Section 5.2.4, there were 6 experimental runs, therefore the X and y matrices have 6 rows each and take the forms:

$$X = \begin{bmatrix} 1 & X^1_{Flux} & X^1_{Recovery} & X^1_{Flux,Recovery} \\ 1 & X^2_{Flux} & X^2_{Recovery} & X^2_{Flux,Recovery} \\ 1 & X^3_{Flux} & X^3_{Recovery} & X^3_{Flux,Recovery} \\ 1 & X^4_{Flux} & X^4_{Recovery} & X^4_{Flux,Recovery} \\ 1 & X^5_{Flux} & X^5_{Recovery} & X^5_{Flux,Recovery} \\ 1 & X^6_{Flux} & X^6_{Recovery} & X^6_{Flux,Recovery} \end{bmatrix} \qquad y = \begin{bmatrix} Y^1_{Passage} \\ Y^2_{Passage} \\ Y^3_{Passage} \\ Y^4_{Passage} \\ Y^5_{Passage} \\ Y^6_{Passage} \end{bmatrix} \qquad 18$$

where X^n_{Flux} are the coded flux values, $X^n_{Recovery}$ are the coded recovery values and $X^n_{Flux,Permeate}$ are the coded interaction terms. The values in the y matrix are made up of the measured passage for each experimental condition.

ANOVA

An analysis of variance (ANOVA) of the linear regression described above was done to determine which of the parameters studied were most significant.

The *main effects* were calculated from the parameter estimates as shown below, where *i* is the parameter number.

$$Main\,Effect_i = 2\hat{\beta}_i \qquad 19$$

The *sum of squares* was calculated as:

$$Sum\,of\;\;Squares = 2^{n-2} \cdot \left(Main\,Effect_i \right)^2 \qquad 20$$

where *n* is the number of factors. In this investigation *n*=2.

The *mean square* for each parameter was calculated by dividing the *sum of squares* by the *degrees of freedom*, which was equal to 1 in this investigation. The observed F statistic (F_{obs}) was calculated by dividing the *mean square* by the variance estimate made from the two centre point replicates (experimental runs #1 and #6).

The F test statistics were used to determine which of the factors were significant. In order to be considered statistically significant, F_{obs} must be greater then the standard tabulated F value. All F tests were conducted at a 95% confidence level.

4.7.4 Modeling Software

A software model from Filmtec called Reverse Osmosis System Analysis (ROSA) was used to predict the solute passage through each of the membranes. The software is freely available from Filmtec's website (http://www.dow.com/liquidseps/) and can be used to simulate the operation of any Filmtec product. Version 6.0 was used.

Since the membranes used in this research were prototypes with internal-multistaging, ROSA was not directly applicable. The internal staging of the membrane was simulated with 26 standard membranes in an externally staged configuration. The operating conditions were scaled from the single prototype element to match the simulation in ROSA.

5 Results and Discussion

To investigate the application of nanofiltration as a technology for arsenic treatment, a pilot study was conducted on a ground water with naturally occurring arsenic. The pilot study took place during the fall of 2004 in Virden, Manitoba.

The results and discussion that follow are based on values calculated as described in Section 4.7. The analytical data is tabulated and presented in Appendix B.

5.1 Virden groundwater characteristics

Arsenic

The groundwater in Virden contains between 38 to 44 μg/L of arsenic. This is made up entirely of dissolved arsenic; particulate arsenic analyses were performed but none was detected. The arsenic profile is presented in Figure 5-1. The total arsenic concentration is shown, along with the concentrations of As(III) and As(V). The dashed lines indicate the overall average concentration of each species of arsenic. It is clear that the majority of the arsenic in Virden's groundwater is found in the reduced form [As(III)]. The As(III) concentration ranged from 34 to 41 μg/L. The As(V) concentration was smaller ranging from 3 to 7 μg/L.

The error bars indicate the 95% confidence intervals based on six replicate samples each day. The replicate samples were pooled to determine the average concentration for each day. The large confidence interval attributed to the As(V) measurements is caused by two things: the small concentration of As(V) compared to the total concentration of arsenic and that the As(V) concentration was determined by the difference between the total dissolved arsenic concentration and As(III). Looking at the As(V) concentration, on many days the 95% confidence interval includes 0, indicating that there was not a statistically significant concentration of As(V).

There is some day to day variation in the concentration of arsenic in Virden's ground water. Other then the small variations, an overall trend in the arsenic profile is not evident. In early November, however, the arsenic concentration dropped off slightly. This corresponds to the changes in other water quality parameters which are discussed below.

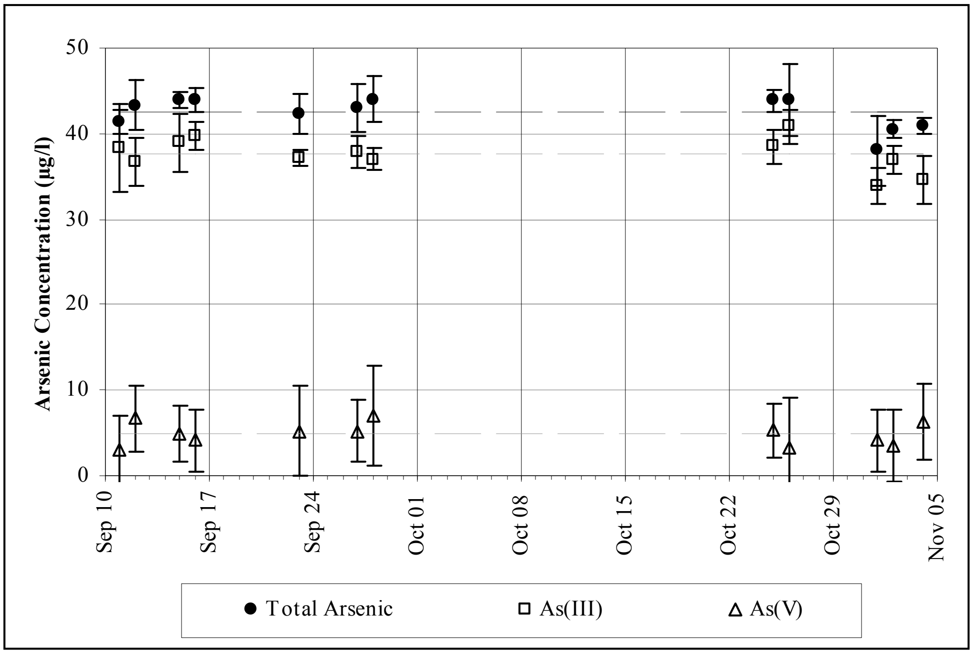


Figure 5-1 - Arsenic concentrations of Virden well water during fall 2004 experimental work

General Chemistry

The general water chemistry parameters were more stable than the arsenic concentrations discussed above. The average parameter values (based on 22 samples) over the time the experiments took place are shown in Table 5-1 along with the observed range of each parameter. The individual trends of each parameter are discussed below.

Table 5-1 -Average concentrations of various parameters during experimental work

	Average	Range
Tubidity (NTU)	0.9	*0.3 - 1.2*
TOC (mg C/L)	15.0	*13.8 - 15.9*
Alkalinity (mg/L as $CaCO_3$)	650	*640 - 680*
pH	8.3	*7.9 - 8.4*
Sodium (mg/L)	409	*392 - 420*
Chloride (mg/L)	236	*230 - 244*
TDS (g/L)	1.10	*1.08 - 1.13*
Hardness (mg/L as $CaCO_3$)	45.6	*42.2 - 47.9*
Iron (mg/L)	0.58	*0.48 - 0.64*
NH_3 (mg/L as N)	1.02	*0.35 - 1.79*

Turbidity and Total and Dissolved Organic Carbon (TOC/DOC)

The turbidity is higher than expected for a groundwater. Given that the turbidity analysis was not performed immediately after sampling, the trend presented in Figure 5-2 show relatively stable turbidities ranging from 0.6 to 1.2. During the early part of November 2005, however there is greater variation in the turbidity results with turbidities reported as high as 1.9. The variability of the observations could be a result of changes within the sample during shipment. The samples were analyzed between 13 to 22 days after sampling. A turbidity measurement is not stable over this time scale since settling or flocculation is possible; either would impact the turbidity measurement (American Public Health Association et al. 1995). Alternatively, the variability could result from surface water influence of the underlying aquifer. Little is known of the hydrogeological characteristics, and the aquifer may be connected to the nearby (200 m) Assiniboine River.

The groundwater in Virden, Manitoba has elevated total organic carbon (TOC) levels. The TOC concentration ranged from 14 to 16 mg C/L as shown in Figure 5-2. Again, this could be due to the proximity of the well to the Assiniboine River. These results are consistent with analysis performed by the Town of Virden, who reported 16.9 mg C/L in April 2003.

As discussed in Section 4.6.2, the samples were not collected in glass bottles or preserved with acid as recommended (American Public Health Association et al. 1995). This may have influenced the analytical results.

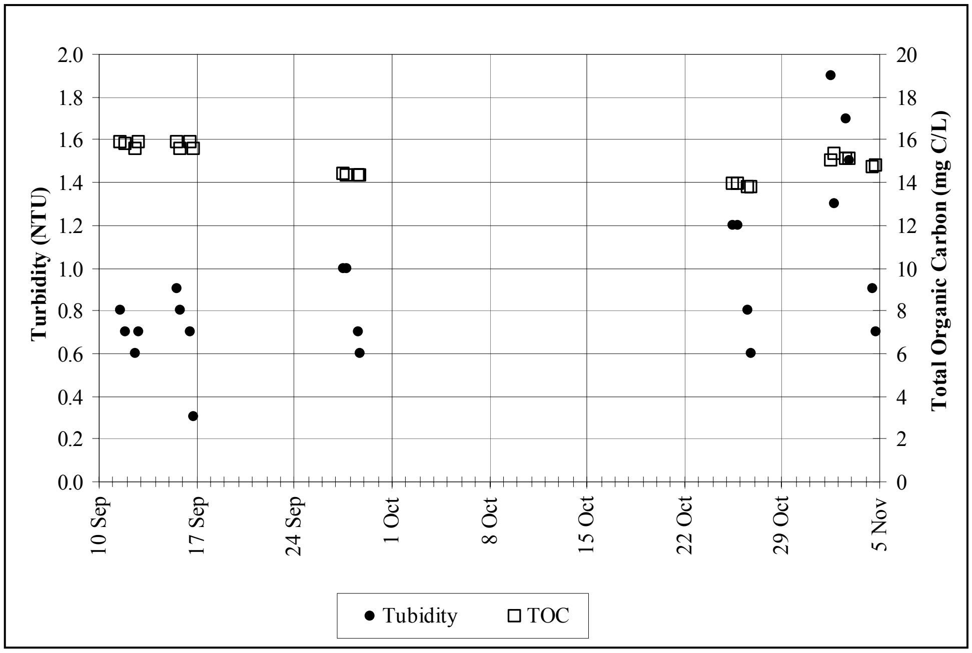


Figure 5-2 - Turbidity and TOC during fall 2004 experimental work

pH and Alkalinity

As can be seen in Figure 5-3, Virden's groundwater has a slightly alkali pH (approximately 8.2) and a high alkalinity. Both were very consistent, with exception of the period starting in early November, at which time the pH dropped to approximately 7.7. Again, this could be an indication that the groundwater is influenced by surface water.

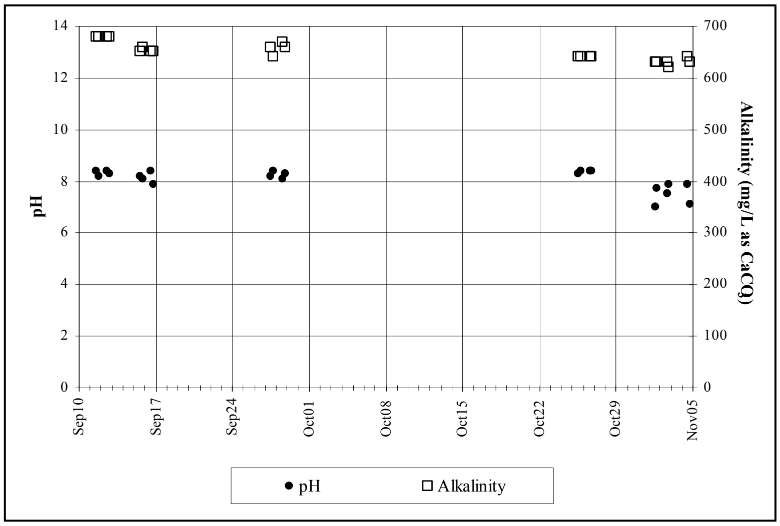


Figure 5-3 - Alkalinity and pH profiles during fall 2004 experimental work

Total Dissolved Solids (TDS), Hardness and Iron

A total dissolved solids of 1100 mg/L (Figure 5-4) is moderately high for a groundwater. This is mainly due to the high concentrations of sodium and chloride in the water (see Table 5-1). For the duration of the experiments, the TDS remained stable.

Virden's groundwater is quite soft with an average hardness of approximately 45 mg/L as $CaCO_3$. During the experiments this remained consistent.

The concentration of iron in the water is high for a drinking water (averaging 0.6 mg/L) but not unusual for a groundwater. During the experimental work the iron concentration was stable. More variability in the iron concentration was noted near 12 September and 2 November, which as mentioned previously, could indicate the groundwater is influenced by surface water.

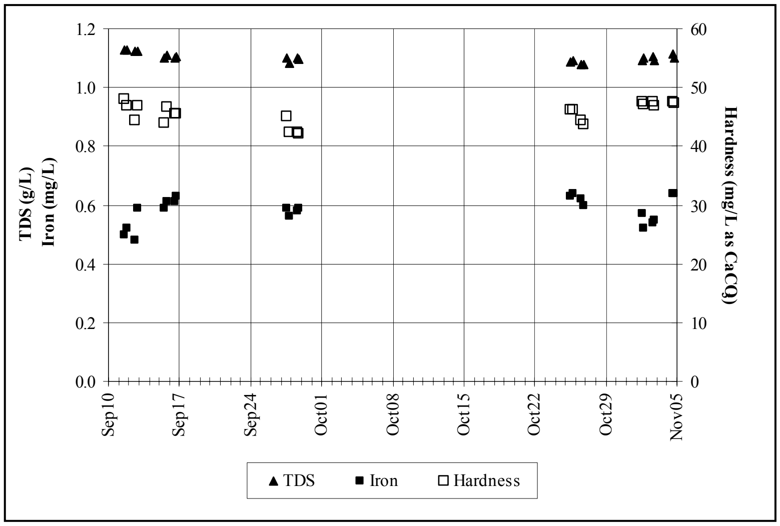


Figure 5-4 - Total Dissolved Solids, Hardness and Iron profiles during fall 2004 experimental work

Ammonia

Presented in Figure 5-5 is the ammonia trend. The ammonia concentrations are inconsistent, with the results clustered near 0.6 mg/L or 1.7 m/L. As discussed in Section 4.6.2, the samples were not preserved with acid as recommended (American Public Health Association et al. 1995). Since fluctuations of groundwater constituents are unlikely, the variability in ammonia results is suspected to be caused by changes during shipment. In an attempt to quantify the change, the ammonia concentration was plotted against the delay between sampling and analysis. This is shown in Figure 5-6. It is clear that the storage time does not correlate to the ammonia concentration.

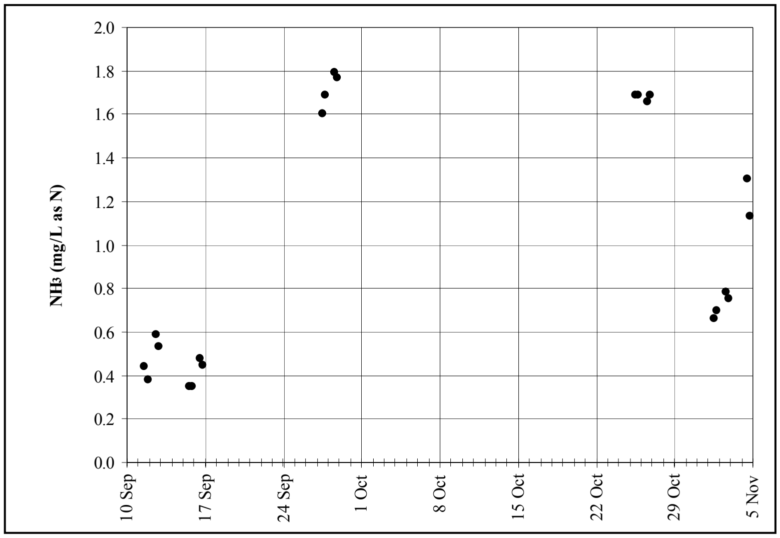


Figure 5-5 - Ammonia profiles during fall 2004 experimental work

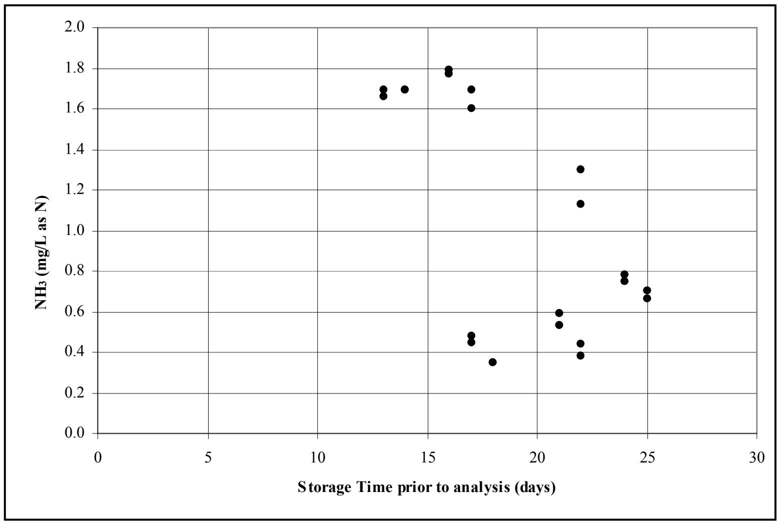


Figure 5-6 - Ammonia concentration versus storage time

Temperature

The groundwater temperature was measured on a continuous basis during the experimentation. The temperature was stable, varying between 7.5°C and 8.5°C

5.2 Experiment I: Membrane Filtration

The goal of this experiment was to quantify the amount of arsenic removal, if any, by three different membranes. The effects of the operating conditions and the type of membrane were investigated.

5.2.1 Performance Stability

Each of the three membranes was operated under 5 different operating conditions as described in Section 3.1. The process was controlled manually and was subject to operator error. The variation between the target operating conditions and the actual operating conditions was less than 2%. A summary of the actual operating conditions is presented in Appendix C.

Prior to sampling, the membrane was run for at least an hour to allow the process to stabilize. To monitor process stability, parameters such as conductivity rejection and normalized permeate flow were recorded with data logging equipment. The operating conditions were also recorded. For each membrane and experimental condition a performance chart was created to verify that the operating conditions were stable. The performance trend for the NF270 membrane's first experimental condition is shown in Figure 5-7. Conductivity rejection is calculated from the feed and permeate conductivity and is an approximation of the salt rejection. Normalized permeate flow is a calculated value which standardizes membrane performance based on the temperature and conductivity as recommended by Dow/Filmtec (Dow Liquid Separations 2004).

The other 5 performance graphs for the NF270 membrane are shown in Appendix D, along with 6 performance graphs each for the NF90 and the XLE membranes, all of which show steady state conditions during sampling.

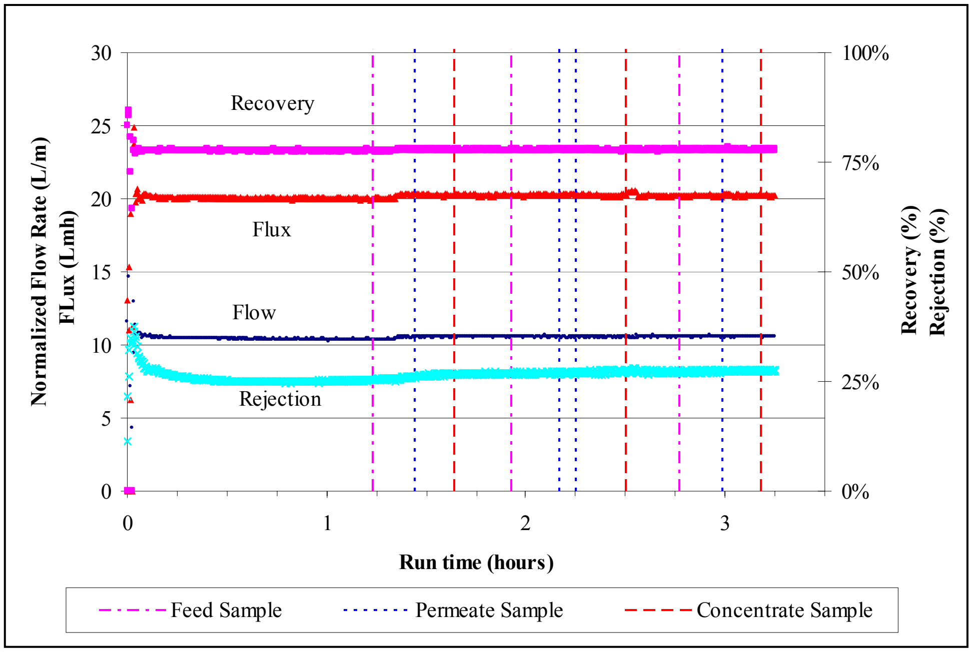


Figure 5-7 - Performance trends for NF270, experimental condition 1

After the first hour of stable operation, the sampling process was started. As detailed in Section 4.6, two types of samples were taken: samples for arsenic analysis (taken in triplicate) and samples for general chemistry analysis.

The sampling times in relation to the experiment run time are also shown in Figure 5-7. This was done to confirm that the act of sampling did not have an effect on the performance or operation of the membrane. Between the samples, approximately 15 minutes elapses. During this time the arsenic sample was being passed through an ion exchange cartridge to separate the different species.

In some instances there were performance variations. In the example shown in Figure 5-7 there is a temporary flux increase after 2.5 hours of operation. Since only three replicate samples were taken, detecting variations in arsenic passage was not statistically possible. The analytical results were inspected to determine if the variations had an impact on the membranes performance. Careful examination showed that these small variations in operating conditions did not impact arsenic passage through the membrane. Comments and discussion similar to that above accompany each of the 18 performance graphs in Appendix D.

5.2.2 NF270 Results

Performance validation

The NF270 is designed to remove divalent ions, thus hardness is used to evaluate the overall performance of the membrane. Shown in Table 5-2 are the measured hardness passage results. The 95% confidence interval is calculated to be between 10% and 12% passage depending on the operating conditions. For comparison, the hardness passage predicted by ROSA is also shown. ROSA is a membrane filtration modeling software available from Filmtec and is discussed in Section 4.7.4. The hardness passage observed is 7 to 16 times higher than that predicted by the ROSA model. In light of these results the membrane was removed and the apparatus inspected to ensure that all connections and internal seals were intact. No problems were found.

Observing passage which is twice that predicted by ROSA is not unusual (Johnson 2005). For "loose" nanofiltration membranes (like the NF270), it is also important to consider that the accuracy of the ROSA model decreases as the ionic strength of the solution increases (Johnson 2005). It is possible that the elevated ionic strength of the well water (and its concentration during filtration) causes inaccuracies in the predictions made by ROSA.

Although the hardness passage results differ from the model, no physical problems or other indications that the apparatus was functioning improperly were found.

Table 5-2 - Measured and predicted hardness passage (%) through NF270 membrane under various operating conditions

		Recovery [%]					
		70		**77.5**		**85**	
		Measured	***Predicted***	**Measured**	***Predicted***	**Measured**	***Predicted***
Flux [Lmh]	**25**	51	*3*			65	5
	20 (1)			63	*6*		
	20 (2)			67			
	15	65	*7*			74	*11*

The values of the two central experimental conditions show some variation in the hardness passage. Statistical t tests show no difference in rejection between the replicates at 95% significance; therefore, no experimental drift was observed.

Table 5-3 - Arsenic concentration (µg/L)of NF270 permeate under various operating conditions

			Recovery [%]					
			70		77.5		85	
			Concentration	*95% C.I*	Concentration	*95% C.I. (%)*	Concentration	*95% C.I. (%)*
Flux [Lmh]	**25**	As(Dissolved)	43	*7*			41	*8*
		As(III)	39	*0*			39	*4*
		As(V)	4	*7*			3	*4*
	20 (1)	As(Dissolved)			46	*5*		
		As(III)			41	*8*		
		As(V)			5	*11*		
	20 (2)	As(Dissolved)			45	*4*		
		As(III)			41	*1*		
		As(V)			4	*4*		
	15	As(Dissolved)	42	*5*			44	*4*
		As(III)	40	*4*			39	*6*
		As(V)	2	*4*			5	*7*

Arsenic passage with NF270 membrane

The concentration of total arsenic under each different operating condition is shown in Table 5-3. The total arsenic concentration in the permeate varied from 44 to 46 µg/L depending on the operating conditions. Under all conditions, the treated water exceeds Canada's recommended IMAC of 25 µg/L.

The arsenic passage results using the NF270 membrane are shown in Table 5-4. For each experimental condition, the percent passage of arsenic is presented along with the 95% confidence interval. The confidence interval was calculated as described in Section 4.7.3.

In all cases the 95% confidence interval includes 100 percent passage. Therefore, under all the conditions tested, the NF270 membrane does not provide any statistically significant removal of arsenic.

Table 5-4 - Arsenic passage (%) through NF270 under various operating conditions

			Recovery [%]					
			70		77.5		85	
			Passage (%)	*95% C.I. (%)*	**Passage (%)**	*95% C.I. (%)*	**Passage (%)**	*95% C.I. (%)*
Flux [Lmh]	**25**	As(Dissolved)	99	*22*			93	*18*
		As(III)	101	*12*			102	*16*
		As(V)	75	*145*			56	*169*
	20 (1)	As(Dissolved)			106	*13*		
		As(III)			107	*24*		
		As(V)			100	*192*		
	20 (2)	As(Dissolved)			102	*20*		
		As(III)			100	*24*		
		As(V)			72	*559*		
	15	As(Dissolved)	94	*20*			102	*20*
		As(III)	97	*25*			96	*28*
		As(V)	63	*321*			147	*629*

5.2.3 NF90 Results

Process Validation

As with the NF270 membrane, the NF90 membrane was operated at 5 different conditions. Recall from Section 3.1 that one of the experimental points (recovery of 85% and flux of 25 Lmh) was modified to 77.5% recovery and 20 Lmh due to limitations of the apparatus.

The NF90 is a tighter membrane designed to remove divalent ions and some monovalent ions. Again, hardness was used to evaluate the overall performance of the membrane. Shown in Table 5-5 is the measured hardness passage under different operating conditions. The 95% confidence interval of the values shown is between 2 and 4 percentage points. The hardness passage predicted by ROSA is also shown for comparison. The measured passage is twice that predicted by ROSA for all experimental conditions; this is not unusual (Johnson 2005). Based on these passage results the membrane is functioning properly and there are no equipment failures or problems with the apparatus.

Table 5-5 - Measured and predicted hardness passage (%) through NF90 membrane under various operating conditions

		Recovery [%]					
		70		**77.5**		**85**	
		Measured	***Predicted***	**Measured**	***Predicted***	**Measured**	***Predicted***
Flux [Lmh]	**25**	3	*2*	5	2		
	20 (1)			5	*3*		
	20 (2)			5			
	15	6	*3*			9	*4*

Replicates of the central experimental condition show minimal variation in the hardness passage. Statistical t tests indicate no difference in rejection between the replicates at 95% confidence; therefore, no experimental drift was observed.

Arsenic passage with NF90 membrane

The concentration of each form of arsenic after filtration by the NF90 membrane is shown in Table 5-6. The total arsenic concentration of the treated water using NF90 is not noticeably different from NF270 with concentrations ranging from 40 to 44 μg/L. Under all conditions, the treated water exceeds Canada's recommended IMAC of 25 μg/L.

The arsenic passage results using an NF90 membrane are shown in Table 5-7. For each experimental condition, the percent passage of each form of arsenic is presented along with the 95% confidence interval. The confidence intervals were calculated as described in Section 4.7.3.

In all but a few cases the 95% confidence interval includes 100 percent passage. Operating at the lowest flux of 15 Lmh minimal arsenic removal was observed. We can therefore conclude that under the conditions tested the NF90 membrane does not provide any significant removal of arsenic.

Table 5-6 - Arsenic concentration (µg/L) of NF90 permeate under various operating conditions

			Recovery [%]					
			70		77.5		85	
			Concentration	*95% C.I*	Concentration	*95% C.I. (%)*	Concentration	*95% C.I. (%)*
Flux [Lmh]	25	As(Dissolved)	43	*3*	44	*1*		
		As(III)	36	*4*	40	*1*		
		As(V)	7	*7*	5	*1*		
	20 (1)	As(Dissolved)			40	*4*		
		As(III)			35	*5*		
		As(V)			6	*9*		
	20 (2)	As(Dissolved)			43	*2*		
		As(III)			40	*3*		
		As(V)			3	*4*		
	15	As(Dissolved)	41	*1*			40	*2*
		As(III)	36	*4*			37	*2*
		As(V)	5	*5*			3	*5*

Table 5-7 - Arsenic passage (%) through NF90 under various operating conditions

			Recovery [%]					
			70		77.5		85	
			Passage (%)	*95% C.I. (%)*	Passage (%)	*95% C.I. (%)*	Passage (%)	*95% C.I. (%)*
Flux [Lmh]	25	As(Dissolved)	96	*8*	100	*6*		
		As(III)	92	*22*	102	*21*		
		As(V)	133	*245*	93	*160*		
	20 (1)	As(Dissolved)			91	*10*		
		As(III)			89	*23*		
		As(V)			77	*228*		
	20 (2)	As(Dissolved)			97	*7*		
		As(III)			102	*10*		
		As(V)			53	*101*		
	15	As(Dissolved)	93	*4*			91	*6*
		As(III)	92	*11*			93	*9*
		As(V)	120	*128*			72	*98*

5.2.4 XLE Results

Process Validation

As with the other two membranes, the XLE membrane was tested under 5 different operating conditions. It will be recalled that one of the experimental points (85% recovery and 25 Lmh) was modified to 82% recovery and 22 Lmh due to limitations of the apparatus.

Table 5-8 - Measured and predicted hardness passage (%) through XLE membrane under various operating conditions

		Recovery [%]							
		70		**77.5**		**82**		**85**	
		Measured	***Predicted***	**Measured**	***Predicted***	**Measured**	***Predicted***	**Measured**	***Predicted***
Flux [Lmh]	**25**	4	*2*						
	22					7	*2*		
	20 (1)			6	*2*				
	20 (2)			6					
	15	6	*2*					11	*4*

The XLE is designed to remove monovalent and divalent ions, thus TDS is used to evaluate the overall performance of the membrane. Shown in Table 5-8 are the total dissolved solids (TDS) passage results. The 95% confidence intervals were between 3 and 8 percent. Also shown is the TDS passage predicted by the ROSA model. As with the NF90 membranes, the passage predicted by the ROSA model is less than the measured values. The differences are not extremely large and we can conclude that the XLE membrane is functioning properly and there are no equipment failures or problems with the apparatus.

The rejection measured at the replicate conditions (77.5% recovery and 20 Lmh) are identical. Statistical t tests indicate no difference in rejection between the replicates at 95% confidence; therefore, no experimental drift was observed.

Arsenic passage with XLE membrane

The total arsenic concentration of the treated water using an XLE membrane is shown in Table 5-9. The total arsenic concentration in the treated water ranges from 21 to 33 µg/L. This is significantly better than the two nanofiltration membranes discussed above. Operating under the conditions of

70% recovery and 25 Lmh, the XLE membrane provides sufficient arsenic removal to meet Canada's current IMAC of 25 µg/L, indicating that the XLE membrane has the ability to sufficiently treat Virden's ground water. However treatment with the XLE membrane alone is insufficient to meet the USEPA's regulation of 10 µg/L or Canada's proposed MAC of 5 µg/L.

Table 5-9 - Total arsenic concentration (µg/L) of XLE permeate under various operating conditions

			Recovery [%]							
			70		**77.5**		**82**		**85**	
			Concentration	*95% C.I*	**Concentration**	*95% C.I*	**Concentration**	*95% C.I*	**Concentration**	*95% C.I*
Flux [Lmh]	**25**	As(Dissolved)	21	*2*						
		As(III)	19	*1*						
		As(V)	2	*3*						
	22	As(Dissolved)					27	*1*		
		As(III)					24	*0*		
		As(V)					3	*1*		
	20 (1)	As(Dissolved)			26	*0*				
		As(III)			23	*4*				
		As(V)			3	*4*				
	20 (2)	As(Dissolved)			28	*0*				
		As(III)			24	*0*				
		As(V)			4	*0*				
	15	As(Dissolved)	26	*4*					33	*0*
		As(III)	23	*2*					26	*0*
		As(V)	3	*5*					6	*1*

The arsenic passage results using an XLE membrane are shown in Table 5-10. For each experimental condition, the percent passage of arsenic is presented along with the 95% confidence interval. The confidence interval was calculated as described in Section 4.7. The replicates of the centre point condition show similar removal. At 95% significance, t tests indicate no difference in rejection for all forms of arsenic. This confirms experimental drift was not observed.

The XLE provides statistically significant arsenic removal. The amount of arsenic passage varies depending on the operating condition. The removal of total arsenic closely parallels the removal of As(III), because the majority of the arsenic in the feed water is in the reduced [As(III)] form.

Table 5-10 - Arsenic passage (%) through XLE under various operating conditions

		Recovery [%]							
		70		77.5		82		85	
Flux [Lmh]		Passage (%)	*95% C.I. (%)*	Passage (%)	*95% C.I. (%)*	Passage (%)	*95% C.I. (%)*	Passage (%)	*95% C.I. (%)*
25	As(Dissolved)	49	*9*						
	As(III)	49	*7*						
	As(V)	45	*88*						
22	As(Dissolved)					64	*10*		
	As(III)					63	*7*		
	As(V)					65	*101*		
20 (1)	As(Dissolved)			61	*9*				
	As(III)			62	*12*				
	As(V)			52	*107*				
20 (2)	As(Dissolved)			65	*9*				
	As(III)			65	*6*				
	As(V)			57	*57*				
15	As(Dissolved)	61	*12*					77	*17*
	As(III)	62	*9*					70	*6*
	As(V)	48	*81*					86	*119*

The effects of recovery and flux are consistent with the membrane theory presented in Section 2.3.2. This is also consistent with the literature where increasing fluxes result in decreased passage (Sato et al. 2002; Vrijenhoek et al. 2001). This is because increasing the flux increases the pure water flux through the membrane which dilutes the arsenic on the permeate side of the membrane, decreasing the overall arsenic passage.

Recovery also influences the arsenic passage: increasing the recovery increases the solute passage through the membrane. At higher recoveries the solute concentration on the feed side of the membrane is higher. As predicted by the models presented in Section 2.3.2, this increase in concentration directly increases the solute flux through the membrane.

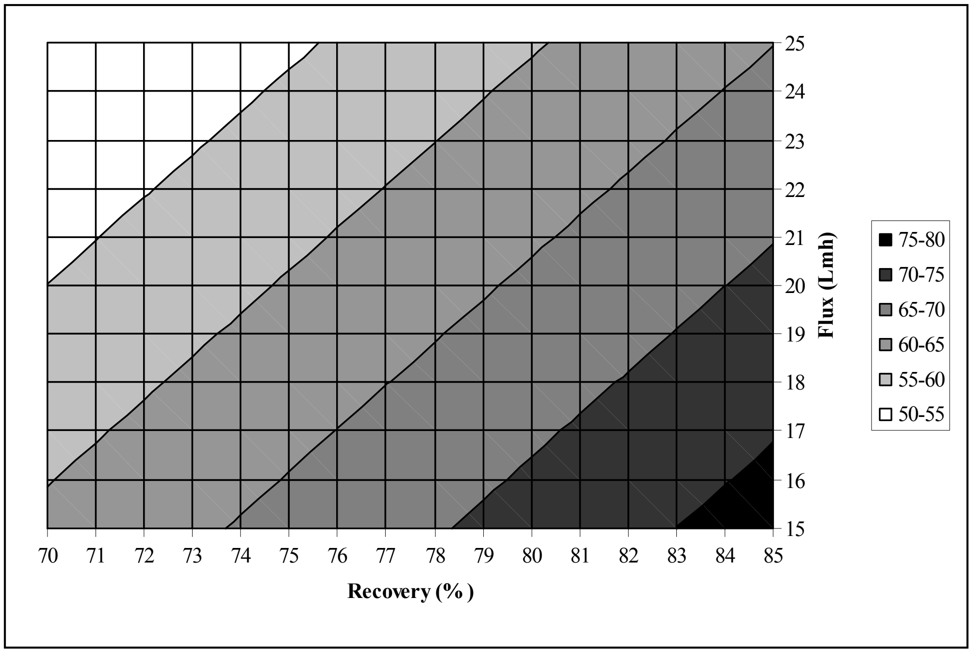


Figure 5-8 - Total arsenic passage (%) through XLE as a function of flux and recovery

The passage of total arsenic shown in Table 5-10 is presented graphically in Figure 5-8. A linear regression was used to create the contours shown. The model for the linear regression is shown in equation 21. The results of the regression and the analysis of variance are shown in Table 5-11.

$$P_{As} = \beta_0 + \beta_1 \left(Flux \right) + \beta_2 \left(Recovery \right) + \beta_{1,2} \left(Flux \cdot Recovery \right) \qquad 21$$

Using the methods described in Section 4.7.3, the main effects and observed F statistics were calculated. The F test statistics were used to investigate which of the factors are significant. In order to be considered statistically significant, the observed F statistic must be greater then the standard F value. At 95% confidence and with 1 degree of freedom the test statistic is approximately 161. Using this comparison, none of the parameters calculated are statistically significant. The lack of any statistically significant terms is due to the very large test statistic, which in turn is due to the limited degrees of freedom. Unfortunately, only two center point replicates were performed leaving one degree of freedom. The single degree of freedom makes it difficult to determine which terms are statistically significant.

Although statistically significance cannot be shown, an investigation into the relative importance of the terms is possible with the information presented in Table 5-11. The main effect of recovery (β_2) is slightly larger than flux (β_1). The interaction term, $\beta_{1,2,}$ has an effect which is an order of magnitude smaller then both flux and recovery. We can conclude that while the interaction between flux and recovery is not significant, the effect of flux and recovery independently are important. These results are as expected and consistent with the model assumptions presented in Section 2.3.2. The models assume independence between the solute flux (which is indirectly related to the recovery via the concentration gradient) and pure water flux (which is directly related to the flux).

Table 5-11 - Analysis of variance of model used to predict total arsenic passage through XLE membrane

Parameter	Regression Estimate	Main Effect	Sum of Squares	Degrees of Freedom	Mean Square	F statistic
β_0	0.630					
β_1	-6.05E-02	-0.12	0.015	1	1.5E-02	0.0
β_2	8.01E-02	0.16	0.026	1	2.6E-02	0.0
$\beta_{1,2}$	-6.26E-04	-1.25E-03	1.6E-06	1	1.6E-06	0.0
MS(Error)				1	7.3E+00	

The model explains the observations well (R^2=0.98) and it appears to be valid for the ranges over which it was performed (70-85% recovery and 15-25 Lmh). The residuals from this model are presented below. A pattern to the residuals is not obvious. However given that the model's simplicity and linearity differ greatly from the relationships which have been used to model membrane treatment (see Section 2.3.2), it is unlikely the model presented is ideal for predicting arsenic passage.

Table 5-12 - Residuals from linear regression of total arsenic passage through XLE membrane

		Recovery [%]			
		70	**77.5**	**82**	**85**
Flux [Lmh]	**25**	-6			
	22			6	
	20 (1)		-2		
	20 (2)		2		
	15	6			0

5.2.5 Effect of membrane type

Neither nanofiltration membranes (NF270 or NF90) removed significant amounts of arsenic. The low pressure reverse osmosis membrane (XLE) was able to remove up to 50% of the arsenic. It is clear that the membrane type has an influence on its ability to remove arsenic.

Permeability is a measure of the amount of energy required to drive water through the membrane. Higher permeability membranes require less energy to treat the same amount of water than low permeability membranes. In general, membranes with low permeabilities have smaller pores and allow less solute passage. The results from Experiment I support this hypothesis; the measured permeability values are presented in Table 5-13 along with the average passage of hardness and TDS measured onsite.

Table 5-13 - Summary of Permeability, TDS and hardness for each membrane

Membrane	Measured Permeability (Lmh/bar at 25°C)	Average Passage (%)	
		TDS	Hardness
NF270	9.1	83	65
NF90	5.1	35	5
XLE	4.3	6	0

It has been shown that membranes with lower permeabilities remove more As(III) than those with higher permeabilities (Brandhuber and Amy 1998). This relationship applies only to As(III) since it is neutral and not influenced by charge.

The average arsenic passage of each membrane operating under the same conditions (77.5% recovery and a flux of 20 LMH) is shown in Figure 5-9. The relationship noted in the literature is not obvious. There is a large decrease in permeability between the NF270 and NF90, but only a very slight decrease in the passage of arsenic; statistically speaking, the change is insignificant. The XLE membrane, meanwhile, is only slightly less permeable than the NF90, but the arsenic passage is much less. While the permeability of the membrane is a general indicator of its arsenic removal characteristics, it is clear that other unique properties of the membrane play a significant role.

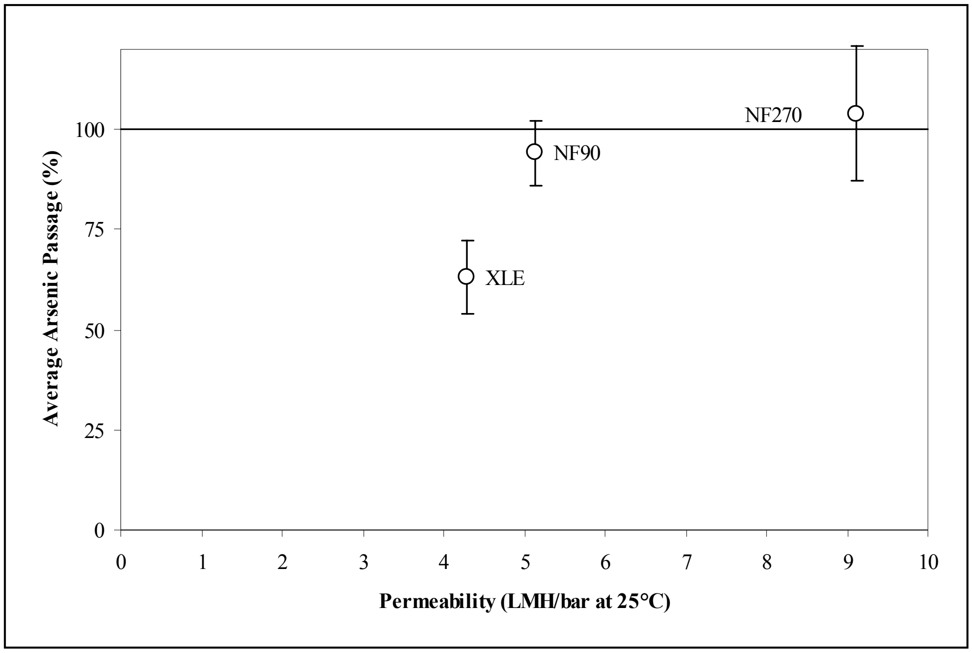


Figure 5-9 - Average arsenic passage versus membrane permeability

5.2.6 Comparison of results to literature

The performance of the membranes tested is poorer than suggested in the literature. A summary of the literature involving similar membranes is shown in Table 5-14. Since the dominant form of arsenic in Virden is As(III), only these results are summarized here. The NF270 membrane is a new version of the NF70 and arsenic passage was expected to be similar; however, much more arsenic passage was observed. The arsenic passage through NF90 observed in this work was much greater than reported in the literature. It should be noted that results summarized for the NF90 are not presented in the literature but briefly mentioned; they are, therefore, presented for rough comparison only. The performance of the XLE membrane is in agreement with the results presented in the literature. The reported salt passage of the ES10 membrane (0.4%) is half that of the XLE membrane (1%). When looking at the As(III) passage, the reported passage through the ES10 membrane is roughly half that of the XLE membrane.

Table 5-14 - Comparison of measured As(III) passage with literature results

Membrane	Nominal Salt Passage (%)	Zeta Potential (mV)	Reported As(III) Passage (%)	Observed As(III) Passage (%)
NF70	-	-15 to -20 [A], -25 [B]	5-45 [C]	-
NF270	40-60 [D]	-5 to -16 [E]	-	100
NF90	5-15 [D]	-15 to -30 [F]	< 10 [G]	100
ES10	0.4 [H]	-	25-50 [H]	-
XLE	1 [D]	-10 to -25 [F]		49-70

Sources:
A -Childress and Elimelech 1996
B - Vrijenhoek et al. 2001
C - Waypa et al. 1997; Brandhuber and Amy 1998
D - Dow Liquid Separations 2004
E - Manttari et al. 2004
F - Krueger 2004
G - Vrijenhoek and Waypa 2000
H - Oh et al. 2000; Sato et al. 2002

The differences between the results reported in the literature and the arsenic passage observed in this study are likely related to the feed water chemistry. All of the literature cited above was done with synthetic waters or natural waters spiked with arsenic. Compared to the water in Virden, Manitoba, which was found to have cation and anion sums of approximately 20 meq/L, these waters have a low ionic strength. It is likely that the added ionic strength of Virden's water enhanced the passage of arsenic. This contradicts the theory that increased ionic strength should inhibit the passage of arsenic since dissolved solids are preferentially permeated through the membrane (Mallevialle et al. 1996).

5.3 Experiment II: Manganese Dioxide Column Study

The goal of this experiment was to investigate the arsenic oxidation capabilities of manganese dioxide (MnO_2) and the rate at which oxidation occurs. As described in Section 3.2, five different experiments were conducted in which the empty bed contact time was varied between 1 and 8 minutes. The particulate arsenic, total dissolved arsenic, As(III) and As(V) concentrations were measured.

The results of Experiment II are shown in Figure 5-10. The total arsenic concentration is indicated by the dark line. The circles represent the As(III) concentration while the triangles represent the As(V) concentration. The error bars represent the 95% confidence interval. Particulate arsenic was not detected.

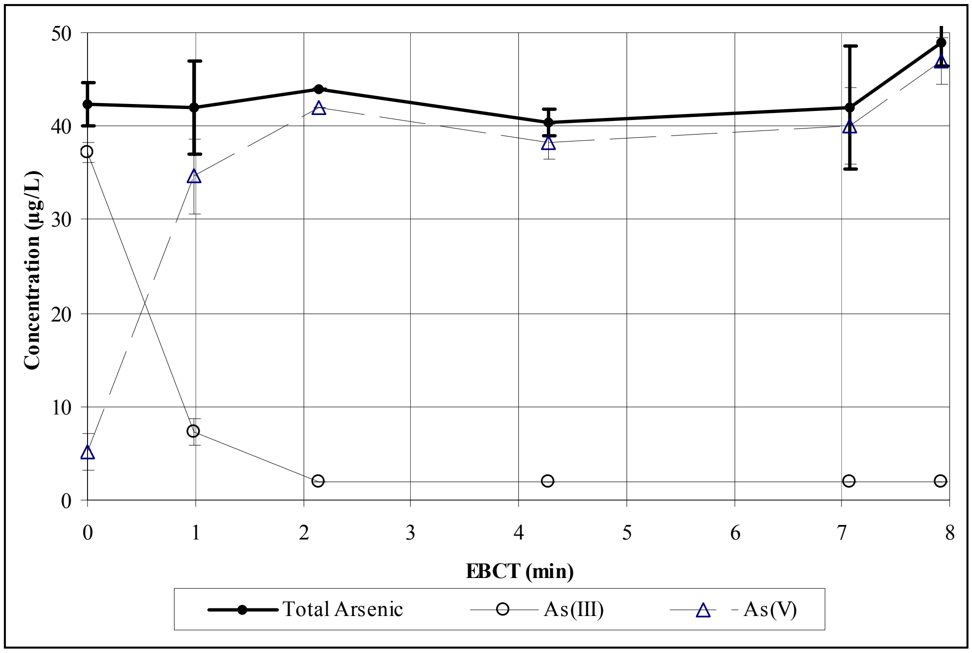


Figure 5-10 - Arsenic speciation as a function EBCT

The arsenic in the feed water was primarily in the reduced form [As(III)]. After 1 minute in the presence of MnO_2 the primary form of arsenic was the oxidized form [As(V)]. At an EBCT of 2 minutes the oxidation is nearly complete. Based on these results, a contact time of 7 minutes was used as a conservative run time for Experiment III.

Little arsenic is removed by the MnO_2 filter. The concentration of As(III) does not drop to 0, since the "< 1 µg/L" results were interpreted conservatively as "1 µg/L".

5.4 Experiment III: Membrane Filtration with Pre-oxidation

The goal of Experiment III was to investigate the benefit, if any, to combining the MnO_2 treatment investigated in Experiment II with the membrane filtration of Experiment I. As described in Section 3.3, an MnO_2 filter was set up with the same hydraulic characteristics as in Experiment II, but sized to provide the needed flow rate to the membrane filtration apparatus. The MnO_2 filter was operated at an EBCT of 7 minutes, which provides ample oxidation of the As(III) to As(V), as discussed in Section 5.3.

5.4.1 Effect of pre-oxidation on membrane feed water

The chemical constituents in Virden's ground water were monitored to determine if filtration through MnO_2 had an effect. The average removals of different chemical constituents through MnO_2 filtration are shown in Figure 5-11, along with the influent concentrations. The error bars represent the 95% confidence interval for the calculated removals.

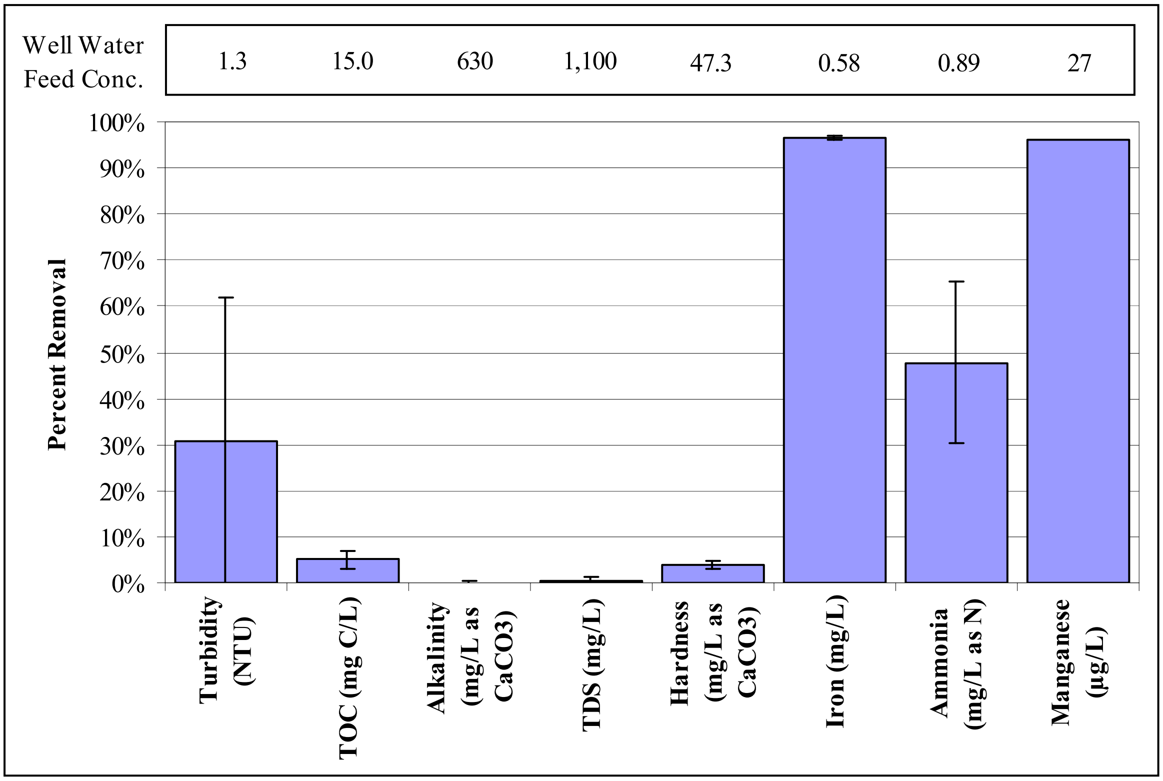


Figure 5-11 - Removals of other constituents due to MnO2 filtration

Statistically insignificant amounts of total dissolved solids (TDS) and alkalinity were removed by the MnO_2 filter. Total organic carbon (TOC) and hardness were removed in small amounts; 5% and 4% respectively.

Complete iron removal was also measured. This is not surprising since MnO_2 is frequently employed as an iron removal media. The iron in the water is oxidized by the MnO_2 and forms very small particulate. This particulate iron either sorbs to the surface of the MnO_2 or is removed through filtration mechanisms within the MnO_2 bed.

Although the concentration of Manganese (Mn^{2+}) in the well water was very small (27 µg/L), complete removal of Mn^{2+} was measured. This confirms the findings in the literature (discussed in

Section 2.4.4) which report that since dissolved Mn^{2+} adsorbs to MnO_2, little Mn^{2+} is released during the oxidation of As(III) by MnO_2 .

Relatively large amounts of turbidity and ammonia were also removed; 31% and 48% respectively. The large error bars indicate that this measurement has a large amount of variability. These parameters were plotted as time series to determine the nature of the variability.

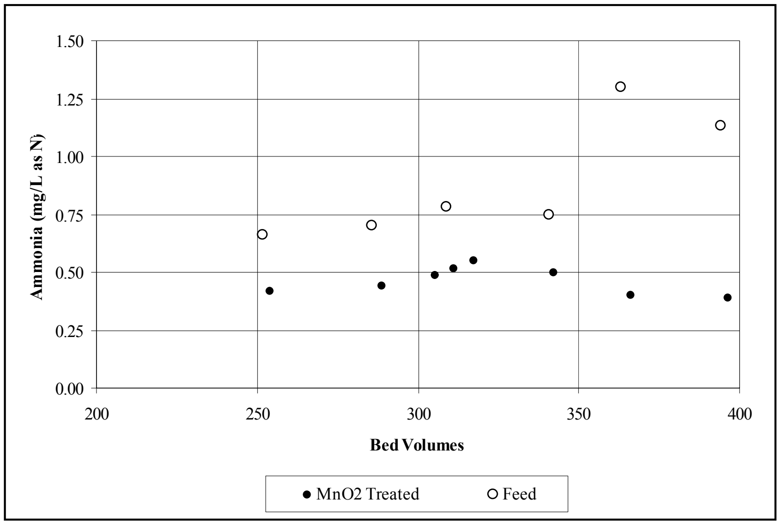


Figure 5-12 - Ammonia concentrations before and after MnO2 filtration

In Figure 5-12 the feed ammonia concentration was plotted with the ammonia concentration after MnO_2 filtration as a function of the number of empty bed volumes. Some removal (approximately 0.25 mg/L) of ammonia is noted. The feed ammonia concentration is initially stable near 0.75 mg/L but increases after 350 bed volumes. The increase could be due to actual changes of the feed water composition; but it is more likely that changes within the samples during shipment occurred. As discussed in Section 4.6.2, the samples were not preserved with acid as recommended (American Public Health Association et al. 1995).

The MnO_2 treated water turbidity varied between 1.4 and 0.5 NTU (Figure 5-13). The increasing trend of the turbidity in the MnO_2 treated water is the opposite of the trend visible in the feed water, which is decreasing. It is difficult to draw meaningful conclusions from this data other than to observe that in general some turbidity removal was achieved. The variability could be due to the long delay between sampling and measurement of the turbidity (20 to 25 days). In this time it is possible that settling or flocculation may have occurred which would affect the reliability of the sample measurement (American Public Health Association et al. 1995). Another possibility is the breakthrough of the precipitated particulate iron, but this is unlikely since, no iron (dissolved or particulate) was found in the MnO_2 treated water.

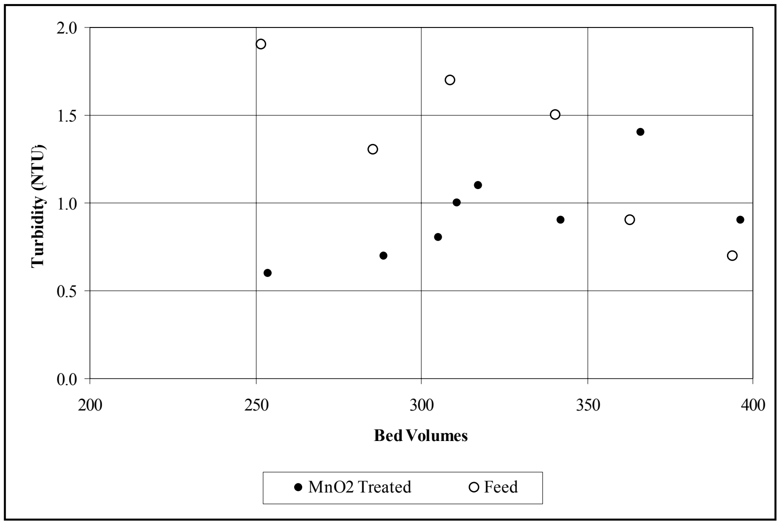


Figure 5-13 - Turbidity before and after MnO2 filtration

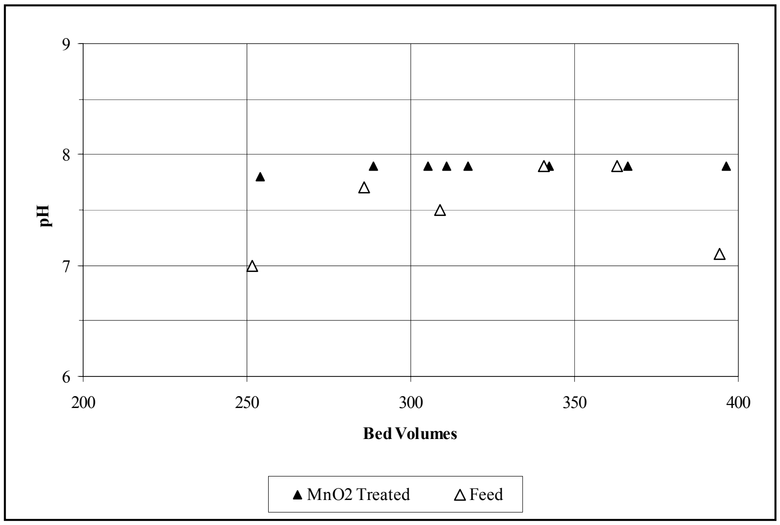


Figure 5-14 - pH before and after MnO2 filtration

As seen in Figure 5-14, the treated water pH is extremely stable at 7.9 while the feed pH varies unpredictably between 7.0 and 7.9. Recall that H^+ is consumed by MnO_2 as part of the process of converting As(III) to As(V). (Refer to Section 2.4.4 for a more detailed discussion of oxidation of arsenic by MnO_2.) Given the concentration of arsenic and the ionic strength of the water, ideal chemical equilibrium calculations predict an increase in pH from 6.7 to 7.0 (Snoeyink and Jenkins

1980). Given that the treated pH is 7.9, not 7.0 and that the magnitude of the pH increase shown in Figure 5-14 is inconsistent, it is unlikely that the oxidation of arsenic is causing the change in pH. Since the samples were shipped to the lab for analysis, the variability in the observations is more likely a result of changes within the sample during shipment.

5.4.2 Effect of pre-oxidation on arsenic composition and concentration

The MnO_2 media was configured to filter the water at an EBCT of 7 minutes. Based on the results of Experiment II, this should ensure that the arsenic is completely oxidized to As(V). The arsenic concentrations were measured to verify the results from Experiment II.

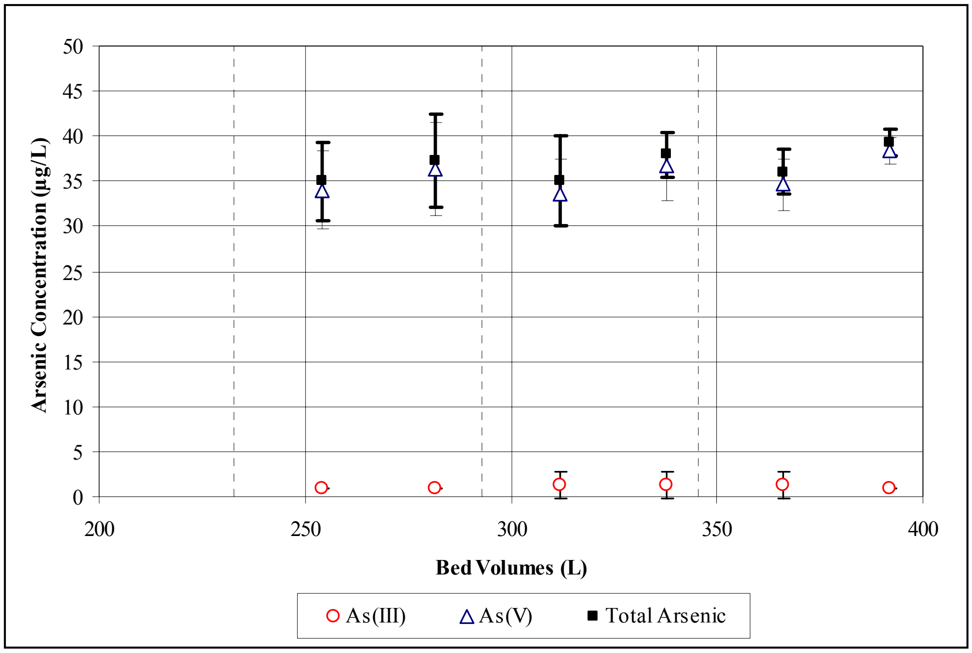


Figure 5-15 - Arsenic composition of MnO2 filtered water during Experiment III

Figure 5-15 shows the arsenic concentration of the MnO_2 filtered water during Experiment III. The arsenic concentrations are plotted versus the number of bed volumes treated. It is clear that the arsenic is almost completely oxidized by the MnO_2. The filter treated almost 400 bed volumes and showed no signs of reduced oxidation capacity.

The experiments were run over several days. As a result, the filter was shut off over night and the water was allowed to remain in contact with the MnO_2. This occurred three times, first at 233 bed volumes, again at 290 bed volumes and a finally at 345 bed volumes. This is noted in Figure 5-15 and Figure 5-16 using dashed lines. The effect of these stagnant periods can be deduced from slightly lower arsenic concentrations afterwards. Comparing the total arsenic concentrations in the feed water with the treated water in Figure 5-16, it is clear that the arsenic removal capacity after the stagnant period increased.

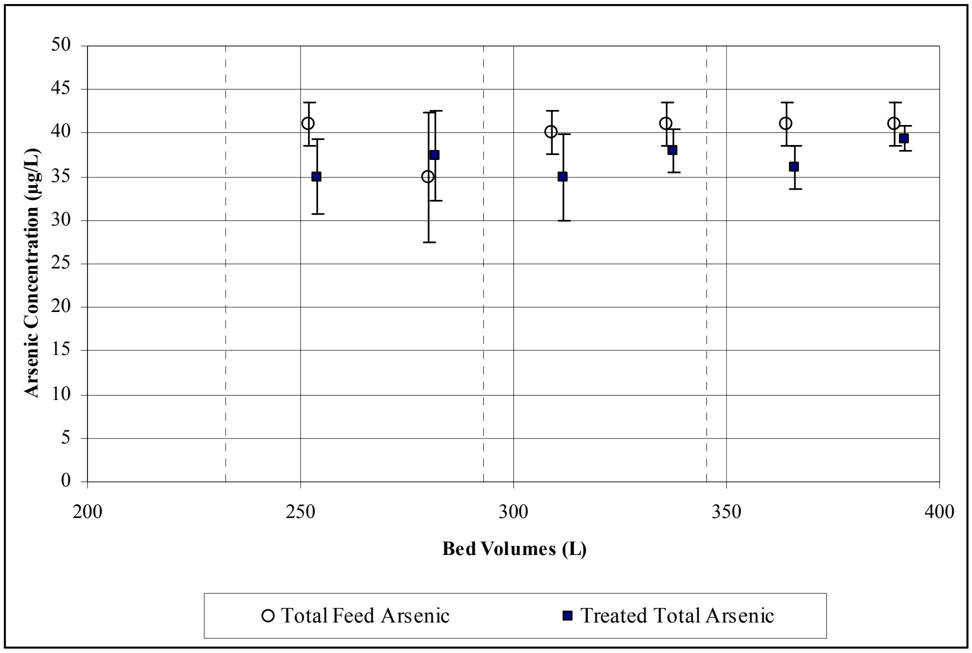


Figure 5-16 - Feed and MnO_2 treated arsenic concentrations during Experiment III

Although no arsenic removal was noted in Experiment II, arsenic removal using MnO_2 is not unexpected and has been reported in the literature (Driehaus et al. 1995; Ghurye and Clifford 2001; Ghurye and Clifford 2004). The cause of the increased removal capacity after a stagnant period is unclear. The literature refers to using backwash as a regeneration technique; however, no reference to "self regeneration" was found. It is hypothesized that during the stagnant periods some of the oxidation sites, which were previously occluded, are able to return to an active state while the filter is stagnant. This could occur if the dissolved iron, which had sorbed to the MnO_2 media after oxidation, precipitated into particulate iron during stagnant periods and desorbed.

5.4.3 Membrane Performance Validation

Performance Stability

Each of the three membranes was operated under 2 different operating conditions as described in Section 3.3. The process was controlled manually, and was subject to operator error. The variation between the target operating conditions and the actual operating conditions was less than 2%. A summary of the actual operating conditions is presented in Appendix C.

The same procedure used in Experiment I was used to ensure that the operation was at steady state prior to sampling. Please refer to Section 5.2.1 for details. In summary, both MnO_2 filters and the membrane system were run for a least an hour to allow the process to stabilize prior to sampling. For each membrane and experimental condition a performance chart was created to verify that the operating conditions were stable. All 6 performance graphs can be found in Appendix D.

Process Validation

The performance of each of the membranes was verified by comparing the measured passage with the passage predicted by the ROSA model as was done in Experiment I (see Section 5.2). The measured passage and predicted passage for each of the three membranes is shown in Table 5-15.

Table 5-15- Measured and predicted passage (%) for three different membranes at different recoveries operated at 20 Lmh

		Recovery [%]	
		70	85
NF270 **Hardness Passage (%)**	**Measured**	56	68
	Predicted	*5*	*8*
NF90 **Hardness Passage (%)**	**Measured**	1	4
	Predicted	*2*	*3*
XLE **TDS Passage (%)**	**Measured**	4	9
	Predicted	*3*	*4*

The hardness passage through the NF270 membrane observed is approximately 10 times that predicted by ROSA. Although considered unusual, it is consistent with the results of Experiment I (see Section 5.2.2). The measured passage is much closer to the predicted passage for the NF90 and XLE membranes. At the low recovery condition, the NF90 membrane shows less passage than predicted. This is based on only one sample and may be anomalous. The XLE performance is slightly poorer than expected with passages ranging from 125% to 225% of that predicted by ROSA. Again this is not unusual (Johnson 2005).

In general, the measured passage is very close to the values measured in Experiment I, indicating that the properties of the membranes did not change between Experiments I and Experiment III.

5.4.4 Arsenic passage

As stated earlier the goal of Experiment III was to evaluate the benefit of combining MnO_2 pre-treatment with membrane filtration. The effect of MnO_2 pretreatment is quite dramatic. In Experiment I, the NF270 and NF90 membranes were unable to remove any arsenic while the XLE membrane removed, at best, approximately 50% of the arsenic (Table 5-10). Once pretreated with MnO_2, to oxidize the arsenic, the passage of arsenic dropped considerably. The total arsenic concentrations of the treated water were less than 4 μg/L. The average results of the three triplicate samples at different stages of treatment are shown in Table 5-16. Shown in Figure 5-17 are the percent removals with error bars representing the 95% confidence intervals.

Table 5-16- Total arsenic (μg/L) concentrations of at different stages of treatment

	Recovery (%)					
	NF270		NF90		XLE	
Treatment Stage	**70**	**85**	**70**	**85**	**70**	**85**
Feed Well Water	41.0	35.0	40.0	41.0	41.0	41.0
MnO_2 Treated	35.0	37.3	35.0	38.0	36.0	39.3
MnO_2 and Membrane Treated	2.7	3.3	1.0	1.3	1.0	2.0

The dramatic improvement in arsenic removal between Experiment I and Experiment III can be attributed to charge. As discussed in Section 2.3.2, it has been demonstrated that the charge of a membrane will affect the solute concentration at the membrane surface. Recall that if the charge (or electrical potential) of the membrane increases, the concentration of co-ions (ions with a similar charge) at the membrane surface decreases, while the concentration of counter ions (ions with the opposite charge) increases. This is significant since the concentration at the surface of the membrane determines the solute flux through the membrane.

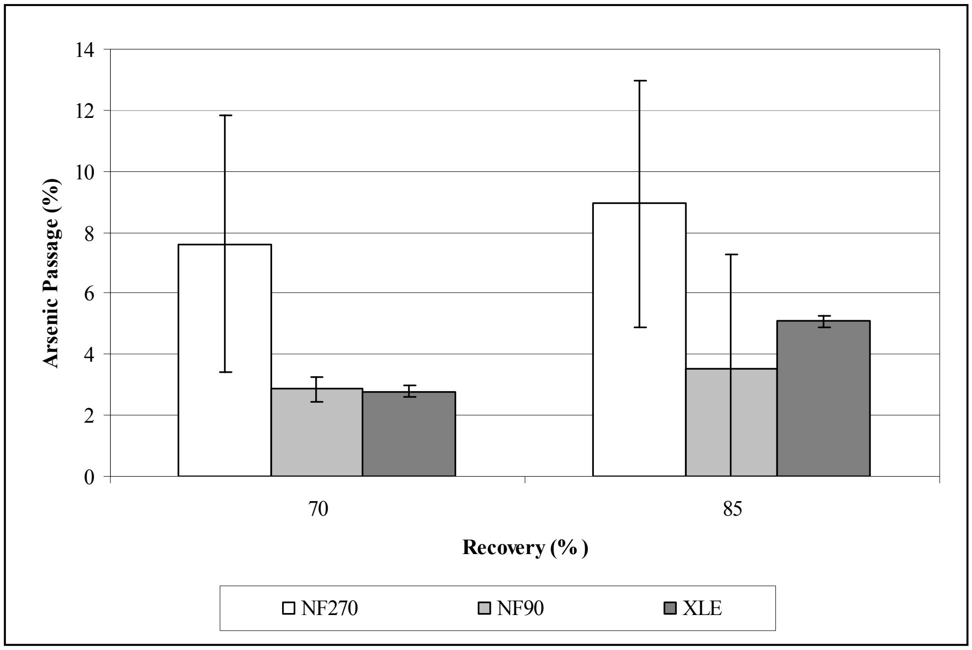


Figure 5-17 - Total arsenic passage (%) through each membrane, after MnO_2 pretreatment

As mentioned in Section 4.3, all three membranes are negatively charged; therefore, negatively charged ions will have a lower concentration at the membrane surface than if the membranes were neutral. Since As(III) is uncharged at pHs near 8, the As(III) which was predominant in Experiment I, was uninfluenced by the negative charge of the membrane. Once oxidized to As(V), the arsenic becomes ionic and has a charge of -2, which greatly reduces the concentration at the membrane surface.

An alternative explanation for the reduced passage of arsenic exists. As suggested by Tournassat et al. (2002), after being oxidizing to As(V) the arsenic could precipitate as an insoluble As-Mn complex. This complex would be easily removed by any of the membranes used. If the As-Mn complex was smaller than 0.45 µm, the analytical methods used (see Section 4.6.1) would be unable to differentiate the As-Mn complex from As(V). It is therefore not possible to determine through which mechanism the arsenic is removed. Regardless, using MnO_2 as a pretreatment step reduced the passage of arsenic through the membranes tested.

Increasing the recovery has the expected effect of increasing the passage (Figure 5-17), as was seen in the results of Experiment I. This is also consistent with one report from the literature which reported that the passage of As(V) increases dramatically as the system recovery increased (Vrijenhoek et al. 2001).

The difference in arsenic removals between the NF90 and XLE membranes is not statistically significant. On average, the arsenic passage through the NF90 membrane is slightly less than the XLE membrane. This is unexpected since the XLE membrane is a tighter membrane and able to remove more dissolved solids than the NF90 membrane (as shown by the TDS). The more negative surface charge of the NF90 membranes may account for this difference. Since NF90 has a greater negative charge than the XLE membrane, the charge exclusion of As(V) is enhanced. This reduces the concentration of arsenic at the surface of the membrane, inhibiting arsenic passage.

5.4.5 Comparison of results to literature

The membranes tested had similar results to the literature once the arsenic was in the oxidized form [As(V)]. A summary of the literature involving similar membranes is shown in Table 5-17. The NF270 membrane is a new version of the NF70, and As(V) passage is similar. The As(V) passage for NF90 membrane is similar to the results presented in the literature. The ES10 is a similar membrane to the XLE in terms of is salt passage, and the As(V)passage observed is in the same range.

All of the literature cited below was done working with synthetic waters or natural waters spiked with arsenic. Compared to the water in Virden, Manitoba, which has a dissolved solids concentration of 20 meq/L due to the sodium and chloride in the water (see Table 5-1), the waters used in the literature have a relatively low ionic strength. Dissolved solids will diminish the strength of the charge exclusion effect thereby allowing greater passage of As(V), however the type of salt is therefore important. Seidel *et al.* observed only a 5% increase in the As(V) passage with the addition of 10^{-2} mol/L of NaCl (Seidel et al. 2001). Brandhuber and Amy were able to increase the passage from 10% to 99% through the addition of 10^{-2} mol/L of Ca^{2+} (Brandhuber and Amy 2001). The increase in passage is due to complex formation between Ca^{2+} and the negatively charged groups on the surface of the membrane, reducing the magnitude of the membrane's charge (Childress and Elimelech 1996; Deshmukh and Childress 2001). The water in Virden has small concentrations of Ca^{2+} or Mg^{2+} ($\sim 2 \cdot 10^{-4}$ mol/L each); therefore, the extent that the charge of the membranes was influenced by the dissolved solids was minimal.

Table 5-17 - Comparison of observed As(V) passage with literature results

Membrane	Nominal Salt Passage (%)	Zeta Potential mV	Reported As(V) Passage (%)	Observed As(V) Passage (%)
NF70	-	-15 to -20 [A], -25 [B]	1-5 [C]	
NF270	40-60 [D]	-5mV to -16 [E]		10
NF90	5-15 [D]	-15 to -30 [F]	< 10 [G]	4
ES10	0.4 [H]	-	1-10 [H]	
XLE	1 [D]	-10 to -25 [F]		5

Sources:
A -Childress and Elimelech 1996
B - Vrijenhoek et al. 2001
C - Waypa et al. 1997; Brandhuber and Amy 1998
D - Dow Liquid Separations 2004
E - Manttari et al. 2004
F - Krueger 2004
G - Vrijenhoek and Waypa 2000
H - Oh et al. 2000; Sato et al. 2002)

5.5 Method Verifications

5.5.1 Variability of General Chemistry Parameters

During Experiment I and Experiment III, triplicate samples were taken to assess the variability in the laboratory measurements of the general chemistry parameters. These were taken at predetermined random times. Table 5-18 summarizes the 95% confidence intervals for each parameter. With the exception of ammonia, all of the parameters exhibit very small confidence intervals compared to the measured values.

In total, 60 general chemistry samples were analyzed by the laboratory. Each analysis was verified through an ion balance and erred on average 2% in favour of cations. Over all samples, the ion balance ranged from 5% greater cations to 2% greater anions. This is within acceptable limits.

Table 5-18 - 95% confidence intervals calculated based on three replicated samples.

Sample Stream	**Turbidity** (NTU)		**TOC** (mg C/L)		**Iron** (mg/L)		**Ammonia** (mg/L as N)	
	95% C.I.	**Range**	**95% C.I.**	**Range**	**95% C.I.**	**Range**	**95% C.I.**	**Range**
NF270 Permeate	0.7	0.5 - 1.0	0.5	1.6 - 1.9	0.05	0.23 - 0.27	0.07	01.4 - 1.43
NF90 Permeate	0.0	0.1 - 0.1	0.2	1.5 - 1.7	0.02	0.04 - 0.06	0.05	00.9 - 0.95
XLE Permeate	0.5	0.3 - 0.7	0.0	0.5 - 0.5	0.00	0.02 - 0.02	0.02	00.2 - 0.20
MnO_2 Filtered Water	0.5	0.8 - 1.1	0.2	14.1 - 14.2	0.00	0.02 - 0.02	0.07	00.5 - 0.55
Sample Stream	**pH**		**Alkalinity** (mg/L as $CaCO_3$)		**TDS** (g/L)		**Hardness** (mg/L as $CaCO_3$)	
	95% C.I.	**Range**	**95% C.I.**	**Range**	**95% C.I.**	**Range**	**95% C.I.**	**Range**
NF270 Permeate	0.1	8.3 - 8.4	29	500 - 520	0.02	0.92 - 0.93	2.4	29.5 - 31.4
NF90 Permeate	0.3	8.2 - 8.4	14	225 - 236	0.01	0.54 - 0.55	0.5	3.9 - 4.3
XLE Permeate	0.2	7.4 - 7.6	0	15 - 15	0.00	0.04 - 0.05	0.0	0.1 - 0.1
MnO_2 Filtered Water	0.0	7.9 - 7.9	14	630 - 640	0.01	1.10 - 1.10	0.3	45.3 - 45.5

5.5.2 Arsenic Stability

All of the arsenic samples were preserved with nitric acid (HNO_3) onsite. This was done to prevent species interconversion and precipitation of arsenic with iron which adversely affect the accuracy of the arsenic measurement. To confirm that speciation was required, six samples were taken in duplicate. One of the duplicates was preserved, while the other was left unpreserved. When the difference between the samples is compared, as in Figure 5-18, it is clear that sample preservation is required and that approximately 3 to 4 μg/L of total arsenic is lost without preservation.

5.5.3 Column Capacity

As discussed in Section 4.6.1, the speciation of arsenic was performed by separating the charged As(V) from the uncharged As(III) using ion exchange cartridges. It is critical that the capacity of the cartridges is not exceeded (Bednar et al. 2002). If the capacity of the cartridge is exceeded not all of the As(V) will be separated, leading to erroneously high As(III) values. To verify that the capacity of the cartridges was sufficient for the analytical method chosen, a sample of Virden's water was spiked with known quantities of As(III) and As(V) and processed. The results from this study are shown in Table 5-19.

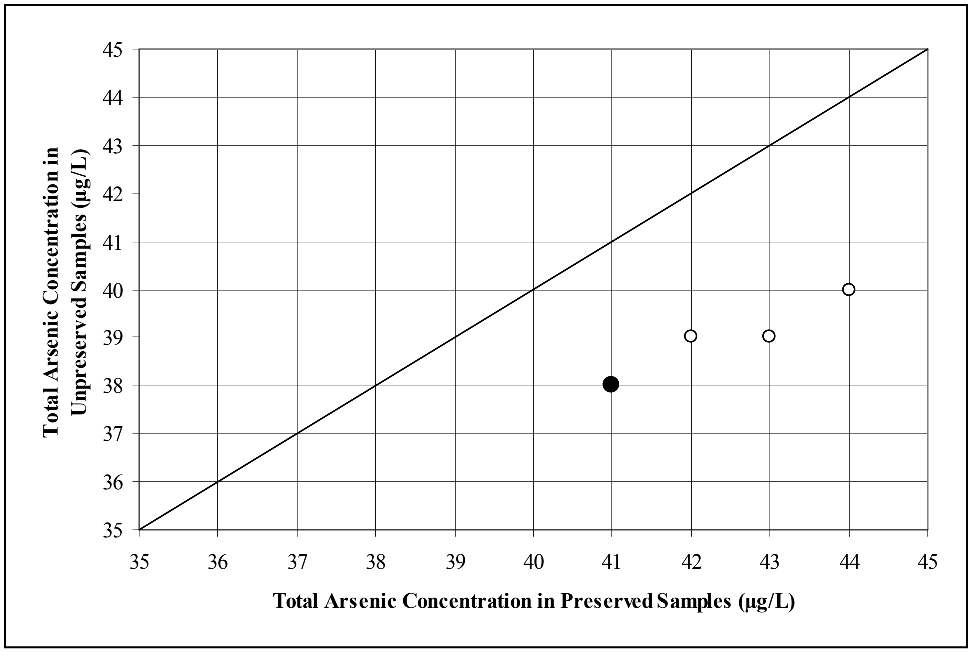


Figure 5-18 - Comparison of preserved and unpreserved arsenic concentrations. (solid dot ● indicates three data points)

The unpreserved sample is comprised primarily of As(V) which is not surprising since the sample was sent to the laboratory unpreserved. One aliquot of the sample was spiked with 46 µg/L of As(V). The additional As(V) was successfully removed by the ion exchange cartridge with no increase in the As(III) concentration however, approximately 6 µg/L of total arsenic is unaccounted for. A second aliquot was spiked with 39 µg/L of As(III). The additional As(III) was passed through the ion exchange cartridge and no change in the As(V) concentration is observed. Again, a small amount of the total arsenic was lost. The speciation study shows that the ion exchange cartridge can be successfully used to separate the different forms of arsenic present in Virden's groundwater.

Table 5-19 - Results from ion exchange cartridge capacity study

	Concentration(µg/L)		
	As(Total)	**As(III)**	**As(V)**
Unpreserved sample	44	1	43
Sample spiked with 46 µg/L As(V)	95	1	94
Sample spiked with 39 µg/L As(III)	89	46	43

5.5.4 Mass Balance

In order to verify that no arsenic was lost through adsorption to the experimental apparatus, mass balances were calculated and are presented below. Depending on the experimental conditions the arsenic recovery ranged from 85% to 109%, with most of the recoveries falling between 90% and 110%. During three experimental conditions the arsenic recovery was less than 90%.

Table 5-20 - Experiment I and III Arsenic Recoveries

Experiment	Condition	Flux (Lmh)	Recovery (%)	Total Arsenic Recovery (%)		
				NF270	NF90	XLE
I	1	20	78	107%	97%	98%
	2	25*	85*	97%	109%	99%
	3	25	70	103%	106%	101%
	4	15	70	100%	101%	98%
	5	15	85	102%	95%	97%
	6	20	78	103%	106%	99%
III	1	20	70	87%	87%	85%
	2	20	85	107%	91%	96%

"* Operating conditions differed for two of the membranes:
The NF90 was operated at 77.5% recovery and 25Lmh
The XLE membrane was operated at 82% recovery and 22 Lmh

5.6 Summary of Results

Virden's Groundwater Characteristics

The groundwater in Virden contains between 38 to 44 µg/L of arsenic, primarily made up of As(III), with little particulate arsenic. The turbidity (average 0.9 NTU), total organic carbon (average 15 mg C/L), iron (average 0.6 mg/L) and total dissolved solids (average 1100 mg/L) are elevated for a ground water. The groundwater is soft with a hardness of only 45 mg/L as $CaCO_3$. The alkalinity is high (650 mg/L as $CaCO_3$) which is unusual given the hardness. The pH is approximately 8.2.

Experiment I: Membrane Filtration

The goal of this experiment was to quantify the amount of arsenic removal, if any, by three different membranes.

Under all conditions the NF90 and NF270 membranes provided insufficient treatment of Virden's groundwater to meet Canada's recommended IMAC of 25 μg/L. Under the conditions of 25 Lmh and 70% recovery, the XLE membrane produced treated water with a total arsenic concentration of 21 μg/L, indicating is has the ability to sufficiently treat Virden's ground water. However, treatment with the XLE membrane alone is insufficient to meet the USEPA's regulation of 10 μg/L or Canada's proposed MAC of 5 μg/L.

The effects of recovery and flux on total arsenic passage are consistent with the membrane theory presented in Section 2.3.2: increasing the pressure increases the pure water flux through the membrane, decreasing the overall passage of arsenic. Increasing the recovery increases the bulk concentration of arsenic, which leads to higher arsenic passage. A statistical analysis indicated that while the interaction between flux and recovery is not significant, the effect of flux and recovery independently are important.

Experiment II: Manganese Dioxide Column Study

The goal of this experiment was to investigate the arsenic oxidation capabilities of manganese dioxide (MnO_2) and the rate at which the oxidation occurs.

The arsenic in the feed water was primarily in the reduced form [As(III)]. After 1 minute in the presence of MnO_2 the primary form of arsenic was the oxidized form [As(V)]. At an EBCT of 2 minutes the oxidation is nearly complete while little arsenic is removed by the MnO_2 filter.

Experiment III: Membrane Filtration with Pre-oxidation

The goal of Experiment III was to investigate the benefit, if any, to combining the MnO_2 treatment investigated in Experiment II with the membrane filtration of Experiment I.

The effect of MnO_2 pretreatment is quite dramatic. In Experiment I, the NF270 and NF90 membranes were unable to remove any arsenic while the XLE removed, at best, approximately 50% of the arsenic. Once pretreated with MnO_2, to oxidize the arsenic, the passage of arsenic dropped to less than 4 μg/L, corresponding to approximately 91% removal. These results confirm the suggestions of other authors that a pre-oxidation step would improve the performance of membrane filtration (Kartinen Jr and Martin 1995; Oh et al. 2000; Seidel et al. 2001).

The dramatic improvement in arsenic removal can be attributed to charge. All three membranes are negatively charged; therefore, negatively charged ions such as arsenic have a lower concentration at the membrane surface then in the bulk solution. This inhibits their passage through the membrane.

During Experiment I, As(III) (which is neutrally charged) was the dominant form of arsenic, and was uninfluenced by the negative charge of the membrane. Once oxidized to As(V), the arsenic had a charge of -2, which greatly reduced the concentration at the membrane surface and consequently the permeation through the membrane.

Comparison of Results to Literature

Based on the results of Experiment I, the passage of As(III) was much greater than suggested by the results in the literature. This is likely because the studies in the literature were conducted using a coupon testing apparatus rather than the full size membranes. Perhaps more importantly, the studies reported in the literature were conducted with synthetic waters or natural waters spiked with arsenic. Compared to the water in Virden, Manitoba, which has an ion sum of 20 meq/L, these waters have a low ionic strength which would influence the performance of the membrane.

During Experiment III the water was pretreated with MnO_2 and the arsenic converted to As(V). The performance of the membranes treating water with As(V) are similar to those reported in the literature.

6 Conclusions and Recommendations

6.1 Conclusions

The arsenic rejection capability of three different membranes was tested on a naturally contaminated groundwater in Virden, Manitoba using a pilot scale membrane filtration system. Virden's groundwater contains on average 42 μg/L of arsenic, primarily in the reduced form [As(III)]. The arsenic oxidizing performance of manganese dioxide (MnO_2) was also investigated and the advantages of using MnO_2 as an oxidation step prior to membrane filtration, was also investigated.

From the research conducted, the following conclusions are made:

1. The type of membrane had a significant impact on the total passage of arsenic.
2. The nanofiltration membranes tested (NF270 and NF90) removed statistically insignificant amount of arsenic from Virden's groundwater.
3. The low pressure reverse osmosis membrane (XLE) removed significantly more arsenic than the nanofiltration membranes. The arsenic concentration in the permeate of the XLE membrane ranged from 21 - 33 μg/L depending on the operating conditions. Operating under the conditions of 70% recovery and a flux of 25 Lmh, the XLE membrane provided sufficient arsenic removal to treat Virden's water and meet Canada's current IMAC of 25 μg/L. Treatment with the XLE membrane alone was insufficient to meet the USEPA's regulation of 10 μg/L or Canada's proposed MAC of 5 μg/L.
4. Manganese dioxide (MnO_2) is very effective oxidizing media for arsenic. Increasing the contact time between the water and MnO_2 increased the extent of arsenic oxidation. At empty bed contact times greater than 2 minutes, complete oxidation of As(III) to As(V) was observed.
5. Combining MnO_2 as a pre-oxidation step with reverse osmosis and nanofiltration membranes significantly enhances the removal of arsenic. Arsenic removals greater than 90% and treated water arsenic concentrations less than 5 μg/L were achieved by all three membranes once the pre-oxidation step was introduced. This confirms the suggestions in the literature that a pre-oxidation step would improve the performance of membrane filtration (Kartinen Jr and Martin 1995; Oh et al. 2000; Seidel et al. 2001).

6. The form of arsenic, whether reduced [As(III)] or oxidized [(As(V)], has a greater impact on the ability of membrane filtration to remove arsenic than does the type of membrane or the operating conditions.

7. Recovery and flux both influence the rejection of arsenic over the range tested (70% to 80% recovery, fluxes between 15 and 25 Lmh). The effect of these parameters on the performance of the membrane was found to be similar to their effect on other dissolved solutes. Increasing recovery or decreasing flux will increase the arsenic passage through the membrane.

These observations indicate that membrane filtration using low pressure membranes is likely to be successful where the oxidized form of arsenic [As(V)] dominates. If, however, the reduced species of arsenic [As(III)] dominates, low pressure membrane filtration alone is likely to be inadequate, unless combined with an oxidizing pretreatment step like manganese dioxide filtration.

6.2 Recommendations

Outside the scope of this work, but meriting further investigation are several research questions:

1. The experiments conducted in Virden were very short term. The long term operational stability of membrane filtration and MnO_2 oxidation processes are unknown. Fouling and scaling may influence the charge or surface properties of the membrane, which could impact its arsenic rejection performance. The arsenic oxidizing capacity of MnO_2 should be quantified and the operational lifetime estimated. The long term performance problems such as increased headloss associated with long term MnO_2 operation should also be investigated.

2. Seasonal variation of arsenic or the other constituents in Virden's groundwater may impact the applicability of nanofiltration and should be investigated further. Changes in the speciation and concentration of arsenic, ionic strength, pH, temperature or TOC concentration would influence the performance of membrane filtration.

3. The type of membrane was shown to have a significant influence on the passage of arsenic. An investigation of which membrane characteristics (charge, permeability etc.) most influence arsenic passage would be valuable.

4. The operating conditions not only influence the passage of arsenic, but also the membrane system's productivity (quantity of water produced) and long term stability (rate fouling).

Optimization of the operating conditions to minimize the passage of arsenic, while maximizing the productivity and stability, would be worthy of study.

5. It was not possible to determine which mechanism was responsible for the decreased arsenic passage once MnO_2 pretreatment was introduced: charge exclusion of As(V) or mechanical straining of an As-Mn complex. Using more sensitive arsenic separation methods, the mechanisms of arsenic rejection should be more thoroughly investigated.

6. The residuals from membrane filtration are a more concentrated waste. Depending on the operational parameters and membrane performance, the arsenic concentration in the reject stream could be anywhere from 2 to 10 times the concentration of the feed water. For membrane filtration to operate successfully, the residuals must be disposed of safely and economically. The technical feasibility and economics of suitable residual handling processes requires further investigation.

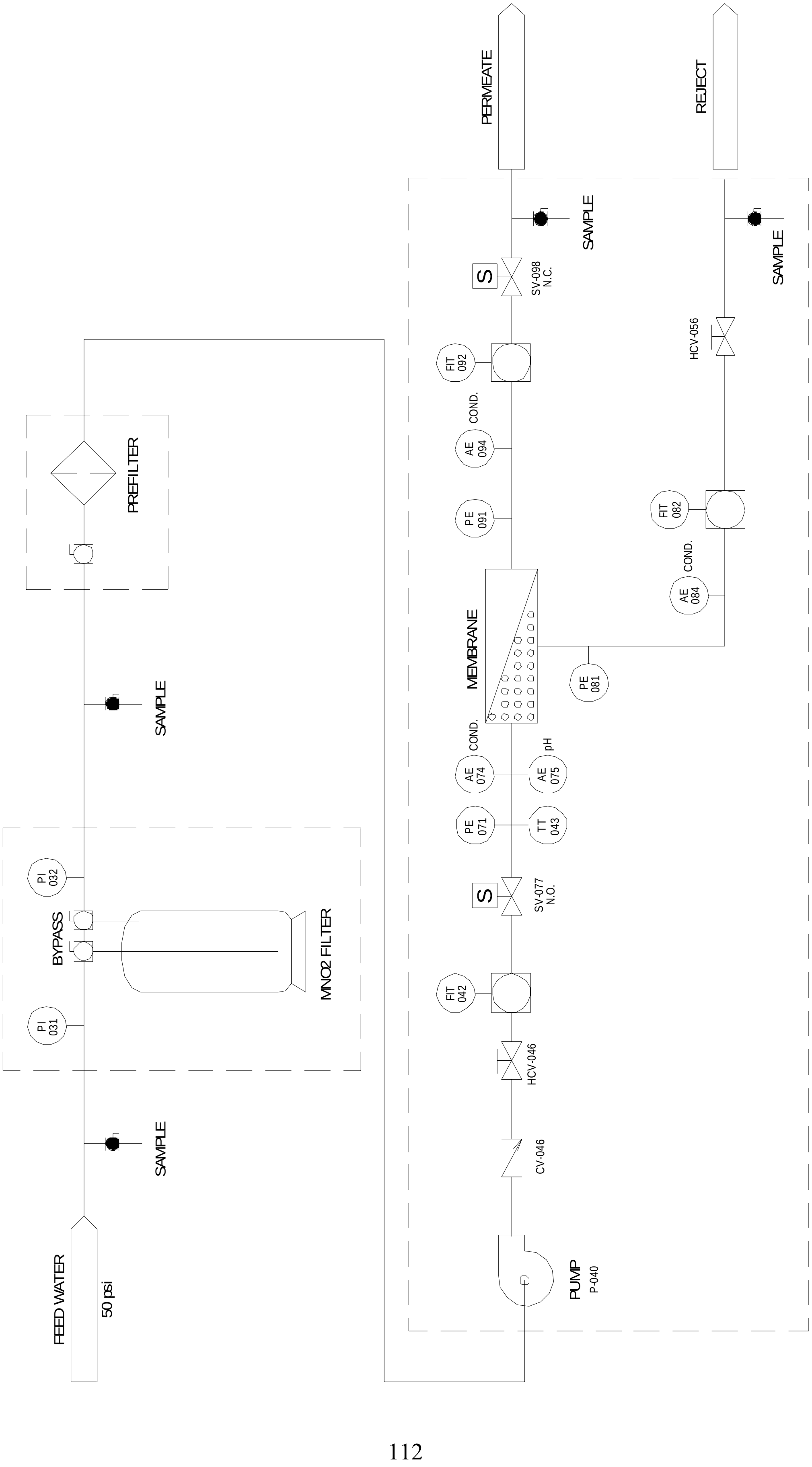
Appendices

Appendix A Process and Instrumentation Drawing of Membrane Apparatus

The process and instrumentation drawing of the membrane apparatus describes the process flow, the instrumentation and equipment used and the connecting piping.

The following abbreviations are used before the instrument number:

AE	Analyzing Element (with Type)
FIT	Flow indicating transmitter
PE	Pressure Element
PI	Pressure Indicator
HCV	Hand Control Valve
SV	Solenoid Valve
CV	Check Valve
TT	Temperature Transmitter


FEED WATER
50 psi
SAMPLE
PI 031
BYPASS
PI 032
MNO2 FILTER
SAMPLE
PREFILTER
PUMP
P-040
CV-046
HCV-046
FIT 042
SV-077
N.O.
S
PE 071
TT 043
AE 074
COND.
AE 075
pH
MEMBRANE
PE 081
AE 084
COND.
FIT 082
HCV-056
SAMPLE
REJECT
PE 091
AE 094
COND.
FIT 092
SV-098
N.C.
S
SAMPLE
PERMEATE

Appendix B Analytical Results

The tables below summarize the analytical results. They are presented in the same order the experiments are discussed.

The tables use the following abbreviations:

As(Sus.)	Suspended Arsenic
As(Dis.)	Dissolved Arsenic

Suspended arsenic is the arsenic greater than 0.45 μm, while dissolved arsenic is less than 0.45 μm. The concentration of As(III) was determined directly. The concentration of As(V) was determined by subtracting the As(III) concentration from the dissolved arsenic concentration.

B.1 Experiment I

Shown in Table B-1 and Table B-2 are the results from the well water samples taken on 11 and 12 September 2004.

Table B-1 - Arsenic concentrations of Well Water during preliminary experimentation in μg/L

Sample	**Well Water**		
	As(Sus.)	**As(Dis.)**	**As(III)**
1	N.D.	42	39
	N.D.	41	40
	N.D.	41	36
2	N.D.	42	36
	N.D.	44	36
	N.D.	44	38

Table B-2 - General chemistry analysis of Well Water during preliminary experimentation in mg/L

Sample	1	2	3	4
Turbidity (NTU)	0.8	0.7	0.6	0.7
Total Organic Carbon	15.9	15.8	15.6	15.9
Alkalinity (as $CaCO_3$)	680	680	680	680
pH	8.4	8.2	8.4	8.3
Sodium	420	418	417	416
Chloride	235	236	235	236
Calcium	11.6	11.6	10.9	11.4
Magnesium	4.61	4.35	4.18	4.48
TDS	1128	1128	1123	1124
Hardness (as $CaCO_3$)	47.9	46.9	44.4	46.9
Iron	0.50	0.52	0.48	0.59
Ammonia (as N)	0.44	0.38	0.59	0.53
Manganese	0.026	0.026	0.025	0.027

B.1.1 NF270 Results

Shown in Table B-3 through Table B-6 are the results from the experiments performed on the NF270 membrane. Experimental conditions 1, 2 and 3 took place on 25 October 2004, while conditions 4, 5 and 6 took place on and 26 October 2004.

Table B-3 - Arsenic Concentrations of Well Water during experimentation with NF270 membrane in µg/L

Condition	Flux	Recovery	Well Water			
			As(Total)	As(Sus.)	As(Dis.)	As(III)
1	20	77.5		N.D.	44	41
				N.D.	45	39
				N.D.	45	40
2	25	85	40			
3	25	70		N.D.	42	36
				N.D.	43	38
				N.D.	44	37
4	15	70		N.D.	42	39
				N.D.	44	40
				N.D.	38	44
5	15	85	46			
6	20	77.5		N.D.	50	41
				N.D.	44	39
				N.D.	46	42

Table B-4 - Arsenic Concentrations of Permeate and Concentrate during experimentation with NF270 membrane in µg/L

Condition	Flux	Recovery	Permeate		Concentrate			
			As(Dis.)	As(III)	As(Total)	As(Sus.)	As(Dis.)	As(III)
1	**20**	**77.5**	44	42		N.D.	52	49
			46	44		N.D.	47	44
			48	38		N.D.	46	43
2	**25**	**85**	44	41	45			
			42	39				
			38	38				
3	**25**	**70**	45	39	49			
			44	39				
			40	39				
4	**15**	**70**	41	38	50			
			40	40				
			44	41				
5	**15**	**85**	45	37	51			
			45	42				
			42	39				
6	**20**	**77.5**	44	40	48			
			44	41				
			47	41				

Table B-5 - General chemistry analysis of Well Water during experimentation with NF270 membrane in mg/L

Condition	**1**	**3**	**4**	**6**
Flux (Lmh)	**20**	**25**	**15**	**20**
Recovery (%)	**77**	**70**	**70**	**78**
Turbidity (NTU)	1.2	1.2	0.8	0.6
Total Organic Carbon	13.9	13.9	13.8	13.8
Alkalinity (as $CaCO_3$)	640	640	640	640
pH	8.3	8.4	8.4	8.4
Sodium	405	408	396	392
Chloride	235	235	237	238
Calcium	11.4	11.5	10.9	10.8
Magnesium	4.28	4.23	4.16	4.05
TDS	1086	1091	1080	1077
Hardness (as $CaCO_3$)	46.1	46.1	44.3	43.6
Iron	0.63	0.64	0.62	0.60
Ammonia (as N)	1.69	1.69	1.66	1.69
Manganese	0.028	0.028	0.026	0.026

Table B-6 - General chemistry analysis of Permeate during experimentation with NF270 membrane in mg/L

Condition	1	2	2	2	3	4	5	6
Flux (Lmh)	**20**	**25**	**25**	**25**	**25**	**15**	**15**	**20**
Recovery (%)	**77**	**85**	**85**	**85**	**70**	**70**	**85**	**78**
Turbidity (NTU)	0.5	0.9	1.0	0.5	0.8	0.6	0.9	0.6
Total Organic Carbon	1.5	1.9	1.7	1.6	1.7	1.5	2.0	1.9
Alkalinity (as $CaCO_3$)	480	500	520	500	430	470	540	480
pH	8.4	8.4	8.4	8.3	8.4	8.3	8.3	8.3
Sodium	329	351	342	336	299	332	348	334
Chloride	231	228	228	233	222	234	238	228
Calcium	6.99	7.68	7.33	7.23	5.79	6.95	7.90	7.13
Magnesium	2.77	2.97	2.85	2.78	2.25	2.74	3.11	2.83
TDS	894	927	929	916	822	893	958	896
Hardness (as $CaCO_3$)	28.9	31.4	30.0	29.5	23.7	28.6	32.5	29.5
Iron	0.21	0.23	0.27	0.26	0.16	0.22	0.26	0.22
Ammonia (as N)	1.41	1.43	1.40	1.37	1.32	1.34	1.49	1.34
Manganese	0.017	0.018	0.017	0.017	0.014	0.017	0.019	0.017

B.1.2 NF90 Results

Shown in Table B-7 through Table B-10 are the results from the experiments performed on the NF90 membrane. Experimental conditions 1, 2 and 3 took place on 15 September 2004, while conditions 4, 5 and 6 took place on and 16 September 2004.

Table B-7 - Arsenic Concentrations of Well Water during experimentation with NF90 membrane in µg/L

Condition	Flux	Recovery	Well Water			
			As(Total)	As(Sus.)	As(Dis.)	As(III)
1	**20**	**77.5**		N.D.	43	36
				N.D.	43	36
				N.D.	45	37
2	**25**	**77.5**	47			
3	**25**	**70**		N.D.	44	40
				N.D.	45	41
				N.D.	44	44
4	**15**	**70**		N.D.	42	39
				N.D.	43	39
				N.D.	44	41
5	**15**	**85**	46			
6	**20**	**77.5**		N.D.	44	39
				N.D.	46	42
				N.D.	44	38

Table B-8 - Arsenic Concentrations of Permeate and Concentrate during experimentation with NF90 membrane in µg/L

Condition	Flux	Recovery	Permeate		Concentrate			
			As(Dis.)	As(III)	As(Total)	As(Sus.)	As(Dis.)	As(III)
1	**20**	**77.5**	42	33		N.D.	51	48
			40	34		N.D.	52	50
			39	37		N.D.	58	52
2	**25**	**77.5**	44	39	63			
			45	40				
			44	40				
3	**25**	**70**	42	37	58			
			44	34				
			42	37				
4	**15**	**70**	41	38	52			
			42	35				
			41	36				
5	**15**	**85**	40	37	54			
			41	36				
			39	38				
6	**20**	**77.5**	42	41	59			
			43	39				
			44	41				

Table B-9 - General chemistry analysis Well Water during experimentation with NF90 membrane in mg/L

Condition	1	3	4	6
Flux (Lmh)	**20**	**25**	**15**	**20**
Recovery (%)	**77**	**70**	**70**	**78**
Turbidity (NTU)	0.9	0.8	0.7	0.3
Total Organic Carbon	15.9	15.6	15.9	15.6
Alkalinity (as $CaCO_3$)	650	660	650	650
pH	8.2	8.1	8.4	7.9
Sodium	417	418	415	419
Chloride	232	233	230	232
Calcium	10.7	11.5	11.2	11.2
Magnesium	4.16	4.34	4.27	4.27
TDS (mg/L)	1101	1110	1098	1105
Hardness (as $CaCO_3$)	43.8	46.6	45.6	45.6
Iron	0.59	0.61	0.61	0.63
Ammonia (as N)	0.35	0.35	0.48	1.19
Manganese	0.026	0.028	0.026	0.026

Table B-10 - General Chemistry analysis of Permeate during experimentation with NF90 membrane in mg/L

Condition	**1**	**2**	**3**	**4**	**5**	**5**	**5**	**6**
Flux (Lmh)	**20**	**25**	**25**	**15**	**15**	**15**	**15**	**20**
Recovery (%)	**77**	**77**	**70**	**70**	**85**	**85**	**85**	**78**
Turbidity (NTU)	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1
Total Organic Carbon	1.0	1.4	0.9	1.0	1.7	1.5	1.7	1.2
Alkalinity (as $CaCO_3$)	148	150	96	127	236	229	225	139
pH	8.2	8.3	8.2	8.5	8.4	8.2	8.2	8.4
Sodium	149	152	106	136	203	210	203	144
Chloride	140	139	104	127	178	178	180	138
Calcium	0.58	0.59	0.39	0.65	1.09	1.05	1.00	0.590
Magnesium	0.19	0.20	0.12	0.22	0.38	0.36	0.34	0.20
TDS	394	397	279	354	545	548	540	381
Hardness (as $CaCO_3$)	2.2	2.3	1.5	2.5	4.3	4.1	3.9	2.3
Iron	0.02	0.06	0.03	0.04	0.06	0.05	0.04	0.04
Ammonia (as N)	0.72	0.72	0.53	0.66	0.95	0.92	0.92	0.72
Manganese	< 0.001	0.001	< 0.001	0.001	0.002	0.002	0.002	< 0.001

B.1.3 XLE Results

Shown in Table B-11 through Table B-14 are the results from the experiments performed on the XLE membrane. Experimental conditions 1, 2 and 3 took place on 27 September 2004, while conditions 4, 5 and 6 took place on and 28 September 2004.

Table B-11 - Arsenic Concentrations of Well Water during experimentation with XLE membrane in µg/L

Condition	**Flux**	**Recovery**	**Well Water**			
			As(Total)	**As(Sus.)**	**As(Dis.)**	**As(III)**
1	**20**	**77.5**		N.D.	44	39
				N.D.	43	39
				N.D.	46	40
2	**22**	**82**	40			
3	**25**	**70**		N.D.	41	36
				N.D.	39	37
				N.D.	45	36
4	**15**	**70**		N.D.	40	38
				N.D.	44	36
				N.D.	48	35
5	**15**	**85**	38			
6	**20**	**77.5**		N.D.	44	38
				N.D.	44	37
				N.D.	44	38

Table B-12 - Arsenic Concentrations of Permeate and Concentrate during experimentation with XLE membrane in µg/L

Condition	**Flux**	**Recovery**	**Permeate**		**Concentrate**			
			As(Dis.)	**As(III)**	**As(Total)**	**As(Sus.)**	**As(Dis.)**	**As(III)**
1	**20**	**77.5**	26	23		N.D.	86	104
			26	22		N.D.	107	112
			26	25		N.D.	94	100
2	**22**	**82**	28	24	106			
			27	24				
			27	24				
3	**25**	**70**	22	19	95			
			20	19				
			21	18				
4	**15**	**70**	25	24	80			
			26	22				
			28	23				
5	**15**	**85**	36	26	91			
			32	26				
			32	26				
6	**20**	**77.5**	28	24	93			
			28	24				
			28	24				

Table B-13 - General Chemistry analysis of Well Water during experimentation with XLE membrane in mg/L

Condition	**1**	**3**	**4**	**6**
Flux (Lmh)	**20**	**25**	**15**	**20**
Recovery (%)	**77**	**70**	**70**	**78**
Turbidity (NTU)	1.0	1.0	0.7	0.6
Total Organic Carbon	14.4	14.3	14.3	14.3
Alkalinity (as $CaCO_3$)	660	640	670	660
pH	8.2	8.4	8.1	8.3
Sodium	401	397	399	398
Chloride	239	244	238	241
Calcium	11.1	10.5	10.5	10.4
Magnesium	4.22	3.93	3.92	3.94
TDS	1100	1085	1102	1098
Hardness (as $CaCO_3$)	45.1	42.4	42.4	42.2
Iron	0.59	0.56	0.58	0.59
Ammonia (as N)	1.60	1.69	1.79	1.77
Manganese	0.026	0.024	0.024	0.024

Table B-14 - General Chemistry analysis of Permeate during experimentation with XLE membrane in mg/L

Condition	1	2	3	3	3	4	5	6
Flux (Lmh)	**20**	**22**	**25**	**25**	**25**	**15**	**15**	**20**
Recovery (%)	**77**	**81**	**70**	**70**	**70**	**70**	**85**	**78**
Turbidity (NTU)	0.8	1.0	0.3	0.5	0.7	0.2	0.7	1.2
Total Organic Carbon	< 0.5	0.5	< 0.5	< 0.5	< 0.5	< 0.5	0.6	0.5
Alkalinity (as $CaCO_3$)	23	25	15	15	15	23	41	24
pH	7.4	7.9	7.6	7.5	7.4	7.3	7.5	7.8
Sodium	24.0	27.4	16.3	16.5	16.4	24.2	47.9	24.4
Chloride	27.5	29.3	17.8	17.6	18.0	27.4	49.1	27.2
Calcium	< 0.05	0.06	< 0.05	< 0.05	< 0.05	< 0.05	0.10	< 0.05
Magnesium	0.02	0.02	< 0.01	< 0.01	< 0.01	0.01	0.03	0.02
TDS	68	74	45	45	45	68	125	68
Hardness (as $CaCO_3$)	0.2	0.2	0.1	0.1	0.1	0.2	0.4	0.2
Iron	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02
Ammonia (as N)	0.27	0.28	0.20	0.20	0.18	0.25	0.43	0.28
Manganese	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001

B.2 Experiment II

Shown in Table B-15 are the results from Experiment II, which was performed on 23 September 2004.

Table B-15 - Arsenic Concentrations before and after MnO_2 Filtration in µg/L

Condition	EBCT (min)	Well Water			MnO_2 Filtered		
		As(Sus.)	As(Dis.)	As(III)	As(Sus.)	As(Dis.)	As(III)
1	**0.99**	N.D.	42	38	N.D.	40	7
		N.D.	39	36	N.D.	44	7
		N.D.	46	37	N.D.	42	8
2	**2.15**				N.D.	44	2
					N.D.	44	< 2
					N.D.	44	< 2
3	**7.93**				N.D.	49	< 2
					N.D.	50	< 2
					N.D.	48	< 2
4	**7.07**				N.D.	40	< 2
					N.D.	45	< 2
					N.D.	41	< 2
5	**4.28**	N.D.	42	36	N.D.	41	< 2
		N.D.	43	38	N.D.	40	< 2
		N.D.	42	38	N.D.	40	< 2

B.3 Experiment III

B.3.1 NF270 Results

Shown in Table B-16 through Table B-19 are the results from the experiment performed on the NF270 membrane with MnO_2 pretreatment. The experiment took place on 2 November 2004.

Table B-16 - Arsenic Concentrations of Well Water during experimentation with NF270 membrane in µg/L

Condition	Flux (Lmh)	Recovery (%)	Well Water		
			As(Sus.)	As(Dis.)	As(III)
1	20	77.5	N.D.	41	36
			N.D.	40	34
			N.D.	42	36
2	20	85	N.D.	32	34
			N.D.	38	32
			N.D.	35	31

Table B-17 - Arsenic Concentrations of MnO_2 Treated water during experimentation with NF270 membrane in µg/L

Condition	Flux (Lmh)	Recovery (%)	MnO_2 Treated		
			As(Sus.)	As(Dis.)	As(III)
1	20	77.5	N.D.	33	< 1
			N.D.	36	1
			N.D.	36	< 1
2	20	85	N.D.	38	< 1
			N.D.	39	< 1
			N.D.	35	< 1

Table B-18 - Arsenic Concentrations of Permeate and Concentrate during experimentation with NF270 membrane in µg/L

Condition	Flux (Lmh)	Recovery (%)	Permeate		Concentrate
			As(Dis.)	As(III)	As(Total)
1	**20**	**77.5**	3	< 1	113
			3	< 1	
			2	< 1	
2	**20**	**85**	4	1	237
			3	< 1	
			3	< 1	

Table B-19 - General chemistry analysis during experimentation with NF270 membrane in µg/L

Stream	Well Water	Well Water	MnO_2 Filtered	MnO_2 Filtered	Permeate	Permeate
Condition	**1**	**2**	**1**	**2**	**1**	**2**
Recovery (%)	**20**	**20**	**20**	**20**	**20**	**20**
Flux (Lmh)	**70**	**85**	**70**	**85**	**70**	**85**
Turbidity (NTU)	1.9	1.3	0.6	0.7	0.5	0.4
Total Organic Carbon	15.0	15.3	14.1	14.4	2.1	2.2
Alkalinity (as $CaCO_3$)	630	630	630	630	440	530
pH	7.0	7.7	7.8	7.9	7.8	7.8
Sodium	417	424	421	421	332	368
Chloride	233	236	231	231	231	235
Calcium	11.8	11.6	11.0	11.1	6.01	7.41
Magnesium	4.40	4.38	4.36	4.30	2.48	2.96
TDS (mg/L)	1091	1102	1093	1093	871	969
Hardness (as $CaCO_3$)	47.6	47.0	45.4	45.4	25.2	30.7
Iron	0.57	0.52	< 0.02	< 0.02	< 0.02	< 0.02
Ammonia (as N)	0.66	0.70	0.42	0.44	0.82	0.91
Manganese	0.027	0.026	0.001	0.001	< 0.001	0.001

B.3.2 NF90 Results

Shown in Table B-20 through Table B-23 are the results from the experiment performed on the NF90 membrane with MnO_2 pretreatment. The experiment took place on 2 November 2004.

Table B-20 - Arsenic Concentrations of Well Water during experimentation with NF90 membrane in µg/L

Condition	Flux (Lmh)	Recovery (%)	Well Water		
			As(Sus.)	As(Dis.)	As(III)
1	20	77.5	N.D.	41	35
			N.D.	40	38
			N.D.	39	35
2	20	85	N.D.	40	38
			N.D.	42	38
			N.D.	41	38

Table B-21 - Arsenic Concentrations of MnO_2 Treated water during experimentation with NF90 membrane in µg/L

Condition	Flux (Lmh)	Recovery (%)	MnO_2 Treated		
			As(Sus.)	As(Dis.)	As(III)
1	20	77.5	N.D.	33	< 1
			N.D.	35	< 1
			N.D.	37	2
2	20	85	N.D.	37	2
			N.D.	39	< 1
			N.D.	38	< 1

Table B-22 - Arsenic Concentration of Permeate and Concentrate during experimentation with NF90 membrane in µg/L

Condition	Flux (Lmh)	Recovery (%)	Permeate		Concentrate
			As(Dis.)	As(III)	As(Total)
1	20	77.5	< 1	< 1	115
			< 1	< 1	
			< 1	< 1	
2	20	85	2	< 1	247
			1	< 1	
			< 1	< 1	

Table B-23 - General chemistry analysis during experimentation with NF90 membrane in µg/L

Stream	Well Water	Well Water	MnO_2 Filtered	MnO_2 Filtered	MnO_2 Filtered	MnO_2 Filtered	Permeate	Permeate
Condition	**1**	**2**	**1**	**1**	**1**	**2**	**1**	**2**
Recovery (%)	**20**	**20**	**20**	**20**	**20**	**20**	**20**	**20**
Flux (Lmh)	**70**	**85**	**70**	**70**	**70**	**85**	**70**	**85**
Turbidity (NTU)	1.7	1.5	0.8	1.0	1.1	0.9	0.5	0.8
Total Organic Carbon	15.1	15.1	14.1	14.1	14.2	14.1	0.6	1.0
Alkalinity (as $CaCO_3$)	630	620	640	630	640	640	39	72
pH	7.5	7.9	7.9	7.9	7.9	7.9	7.5	7.8
Sodium	426	421	420	421	420	427	39.7	74.2
Chloride	237	235	232	233	234	233	37.1	72.3
Calcium	11.7	11.6	11.0	11.0	11.0	11.1	0.17	0.41
Magnesium	4.46	4.35	4.39	4.32	4.36	4.32	0.06	0.14
TDS (mg/L)	1105	1092	1099	1095	1101	1107	106	199
Hardness (as $CaCO_3$)	47.6	46.9	45.5	45.3	45.4	45.5	0.7	1.6
Iron	0.54	0.55	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02
Ammonia (as N)	0.78	0.75	0.49	0.52	0.55	0.50	0.07	< 0.05
Manganese	0.027	0.026	0.001	0.001	0.001	0.001	< 0.001	< 0.001

B.3.3 XLE Results

Shown in Table B-24 through Table B-27 are the results from the experiment performed on the XLE membrane with MnO_2 pretreatment. The experiment took place on 2 November 2004.

Table B-24 - Arsenic Concentration of Well Water during experimentation with XLE membrane in µg/L

Condition	Flux (Lmh)	Recovery (%)	Well Water		
			As(Sus.)	As(Dis.)	As(III)
1	**20**	**77.5**	N.D.	40	36
			N.D.	41	32
			N.D.	42	32
2	**20**	**85**	N.D.	41	35
			N.D.	42	39
			N.D.	40	34

Table B-25 - Arsenic Concentration of MnO_2 Treated water during experimentation with XLE membrane in µg/L

Condition	Flux (Lmh)	Recovery (%)	MnO_2 Treated		
			As(Sus.)	As(Dis.)	As(III)
1	20	77.5	N.D.	35	< 1
			N.D.	36	2
			N.D.	37	< 1
2	20	82	N.D.	39	< 1
			N.D.	40	< 1
			N.D.	39	< 1

Table B-26 - Arsenic Concentration of Permeate and Concentrate during experimentation with XLE membrane in µg/L

Condition	Flux (Lmh)	Recovery (%)	Permeate		Concentrate
			As(Dis.)	As(III)	As(Total)
1	20	77.5	1	< 1	115
			< 1	< 1	
			< 1	< 1	
2	20	85	2	< 1	255
			2	< 1	
			2	< 1	

Table B-27 - General chemistry analysis during experimentation with XLE membrane in µg/L

Stream	**Well Water**	**Well Water**	**MnO_2 Filtered**	**MnO_2 Filtered**	**Permeate**	**Permeate**
Condition	**1**	**2**	**1**	**2**	**1**	**2**
Recovery (%)	**20**	**20**	**20**	**20**	**20**	**20**
Flux (Lmh)	**70**	**85**	**70**	**85**	**70**	**85**
Turbidity (NTU)	0.9	0.7	1.4	0.9	1.2	0.6
Total Organic Carbon	14.7	14.8	14.4	14.6	0.5	1.2
Alkalinity (as $CaCO_3$)	640	630	630	640	23	46
pH	7.9	7.1	7.9	7.9	7.2	7.2
Sodium	426	423	418	424	18.2	39.2
Chloride	237	235	232	231	13.6	29.2
Calcium	11.7	11.7	10.8	11.2	0.24	0.58
Magnesium	4.46	4.40	4.35	4.42	0.07	0.20
TDS (mg/L)	1112	1100	1090	1101	48	100
Hardness (as $CaCO_3$)	47.6	47.3	44.9	46.2	0.9	2.3
Iron	0.64	0.64	< 0.02	< 0.02	< 0.02	< 0.02
Ammonia (as N)	1.30	1.13	0.40	0.39	0.13	< 0.05
Manganese	0.027	0.027	0.001	0.001	< 0.001	< 0.001

Appendix C Membrane Operating Conditions

The process was controlled manually and was therefore subject to operator error. The variation between the target operating conditions and the actual operating conditions was less than 2%. A summary of the actual operating conditions during the time the samples were taken is presented below.

C.1 Experiment I

Table C-1 - NF270 membrane Operating Conditions

Experimental Condition	**Target Experimental Conditions**		**Actual Experimental Conditions**		**Operational Error (%)**	
	Flux (Lmh)	**Recovery (%)**	**Flux (Lmh)**	**Recovery (%)**	**Flux**	**Recovery**
1	**20**	**77.5**	20.2	77.8	1.2%	0.3%
2	**25**	**85**	25.2	85.3	0.9%	0.4%
3	**25**	**70**	25.0	70.0	0.1%	0.0%
4	**15**	**70**	15.1	70.3	0.5%	0.5%
5	**15**	**85**	15.1	85.5	0.7%	0.6%
6	**20**	**77.5**	20.1	77.7	0.4%	0.2%

Table C-2 - NF90 membrane Operating Conditions

Experimental Condition	**Target Experimental Conditions**		**Actual Experimental Conditions**		**Operational Error (%)**	
	Flux (Lmh)	**Recovery (%)**	**Flux (Lmh)**	**Recovery (%)**	**Flux**	**Recovery**
1	**20**	**77.5**	20.5	77.8	2.7%	0.4%
2	**25**	**77.5**	25.1	77.6	0.3%	0.1%
3	**25**	**70**	25.3	70.3	1.1%	0.4%
4	**15**	**70**	15.1	70.2	0.5%	0.3%
5	**15**	**85**	15.2	85.1	1.2%	0.1%
6	**20**	**77.5**	20.2	77.4	0.8%	-0.1%

Table C-3 - XLE membrane Operating Conditions

Experimental Condition	Target Experimental Conditions		Actual Experimental Conditions		Operational Error (%)	
	Flux (Lmh)	Recovery (%)	Flux (Lmh)	Recovery (%)	Flux	Recovery
1	**20**	**77.5**	20.1	77.6	0.5%	0.2%
2	**23**	**82**	22.5	81.4	-0.2%	-0.7%
3	**25**	**70**	25.1	70.4	0.3%	0.5%
4	**15**	**70**	15.3	70.3	1.7%	0.4%
5	**15**	**85**	15.2	85.3	1.4%	0.4%
6	**20**	**77.5**	20.2	77.6	1.0%	0.1%

C.2 Experiment III

Table C-4 - membrane Operating Conditions during Experiment III

Membrane	Experimental Condition	Target Experimental Conditions		Actual Experimental Conditions		Operational Error (%)	
		Flux (Lmh)	Recovery (%)	Flux (Lmh)	Recovery (%)	Flux	Recovery
NF270	**1**	**20**	**70**	20.4	70.2	1.8%	0.4%
	2	**20**	**85**	20.2	85.4	1.1%	0.4%
NF90	**1**	**20**	**70**	20.3	70.3	1.4%	0.5%
	2	**20**	**85**	20.1	85.3	0.7%	0.3%
XLE	**1**	**20**	**70**	20.1	70.1	0.5%	0.2%
	2	**20**	**85**	20.0	85.2	0.2%	0.3%

Appendix D Performance Graphs

Prior to sampling, the membrane system was run for a least an hour to allow the process to stabilize. To monitor process stability, parameters such as conductivity rejection and normalized permeate flow were recorded with data logging equipment. The operating conditions were also recorded. For each membrane and experimental condition a performance chart was created to verify that the operating conditions were stable.

The performance trends are shown in this appendix, all of which show steady state conditions during sampling. The rejection shown is conductivity rejection (calculated from the feed and permeate conductivity) and is an approximation of the salt rejection. Normalized permeate flow is a calculated value which standardizes membrane performance based on the temperature and conductivity as recommended by Dow/Filmtec (Dow Liquid Separations 2004).

After the first hour of stable operation, the sampling process was stared. As detailed in Chapter 3, two types of samples were taken: samples for arsenic analysis (taken in triplicate), and samples for general chemistry analysis.

The sampling times in relation to the experiment run time are also shown. This was done to confirm that the act of sampling did not have an effect on the performance or operation of the membrane. Between the samples, approximately 15 minutes elapses. During this time the arsenic sample was being passed through an ion exchange cartridge to separate the different species.

In some instances there were variations in the flux; frequently caused by variations in the feed pressure to the membrane system. The water was supplied by two wells (#1 or #2) each with a separate well pump (#1 and #2). Generally, only one of the two pumps was on; however, in periods of high demand (from Virden's drinking water treatment plant) both pumps were required. The transition from one well pump to two well pumps caused the majority of variations in the process conditions.

Since only three replicate samples were taken, detecting statistically significant variations in arsenic passage was not possible. The analytical results were inspected to determine if the variations had an impact on the membranes performance. Careful examination showed that these small variations in operating conditions did not impact arsenic passage through the membrane.

D.1 Experiment I

Shown below are the performance graphs from Experiment I

D.1.1 NF 270 Performance

Shown in Figure D-1 is the performance graph for condition 1 (77.5% recovery and a flux of 20 Lmh). During the time samples were collected, steady state performance of the membrane system is noted. Shortly after a run time of 2:30 there is a slight increase in flux. This was attributed to the second well pump turning on and increasing the feed pressure. The operating conditions were adjusted shortly afterwards to compensate for the increased pressure.

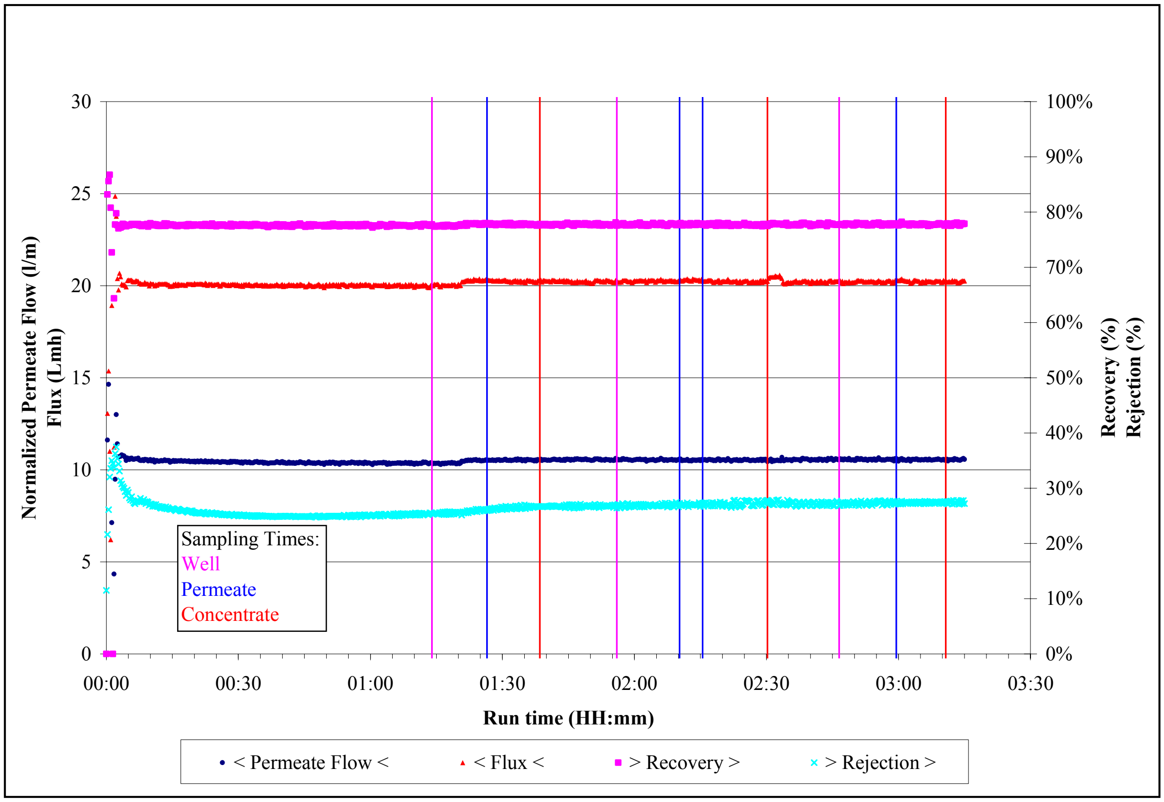


Figure D-1 - Performance graph of NF270 membrane operating under Condition 1 (20 Lmh and 77.5% recovery)

Shown in Figure D-2 is the performance graph for condition 2 (85% recovery and a flux of 25 Lmh). During the time samples were collected, steady state performance of the membrane system is noted. Shortly after a run time of 2:00 there is a slight increase in flux. This was attributed to the second well pump turning on and increasing the feed pressure.

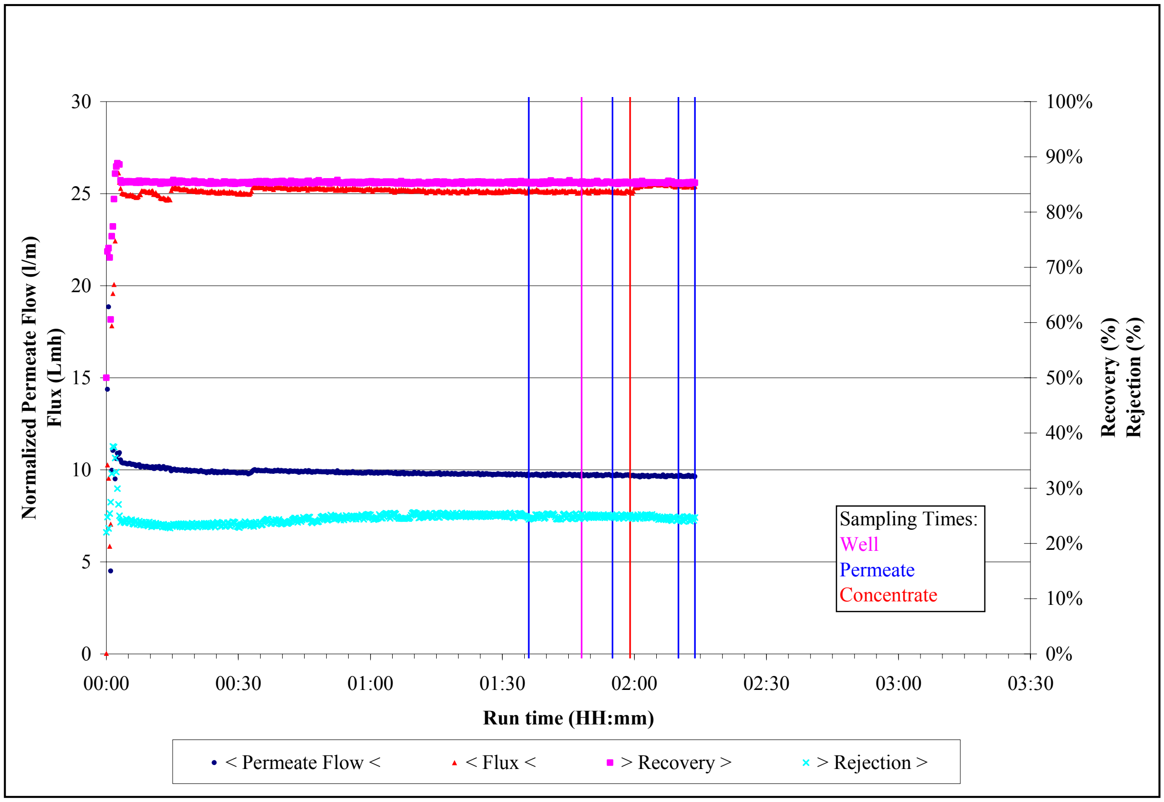


Figure D-2 - Performance graph of NF270 membrane operating under Condition 2 (25 Lmh and 85% recovery)

Shown in Figure D-3 is the performance graph for condition 3 (70% recovery and a flux of 25 Lmh). During the time samples were collected, steady state performance of the membrane system is noted. A slight change in flux is noted at a run time of 1:50, which is due to poor operator control. At a run time of 2:04, well pump #2 turned on an increased the pressure slightly. The operating conditions were adjusted shortly afterwards.

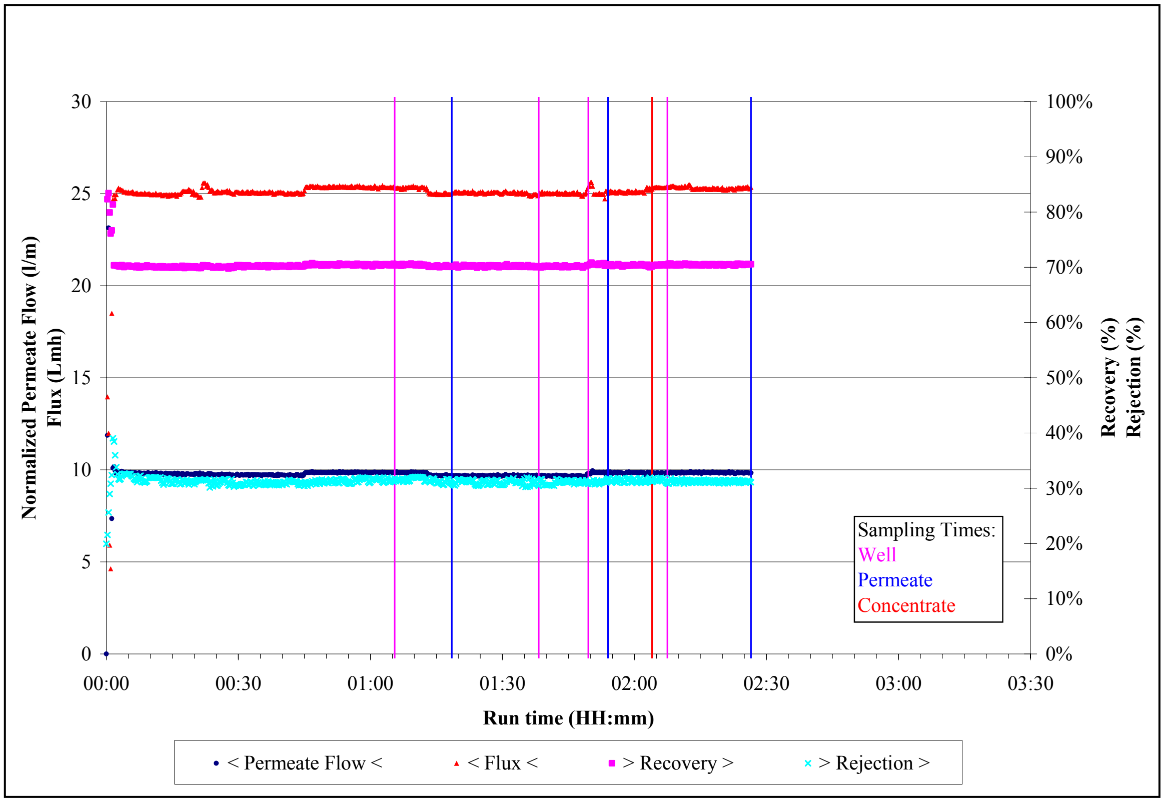


Figure D-3 - Performance graph of NF270 membrane operating under Condition 3 (25 Lmh and 70% recovery)

Shown in Figure D-4 is the performance graph for condition 4 (70% recovery and a flux of 15 Lmh). During the time samples were collected, steady state performance of the membrane system is noted.

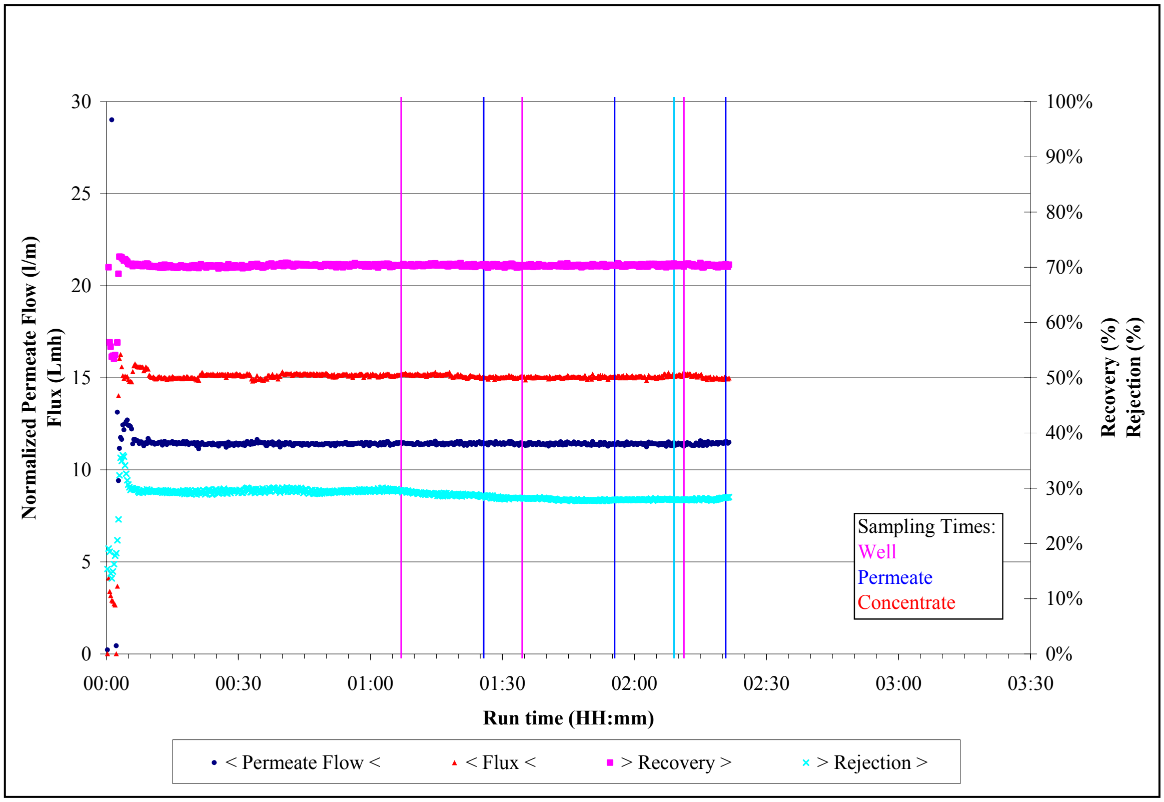


Figure D-4 - Performance graph of NF270 membrane operating under Condition 4 (15 Lmh and 70% recovery)

Shown in Figure D-5 is the performance graph for condition 5 (85% recovery and a flux of 15 Lmh). During the time samples were collected, steady state performance of the membrane system is noted. Starting at a run time of 1:15, erratic conductivity rejection readings are noted but considered false. These are attributed to erroneous permeate conductivity measurements caused by trapped air around the probe.

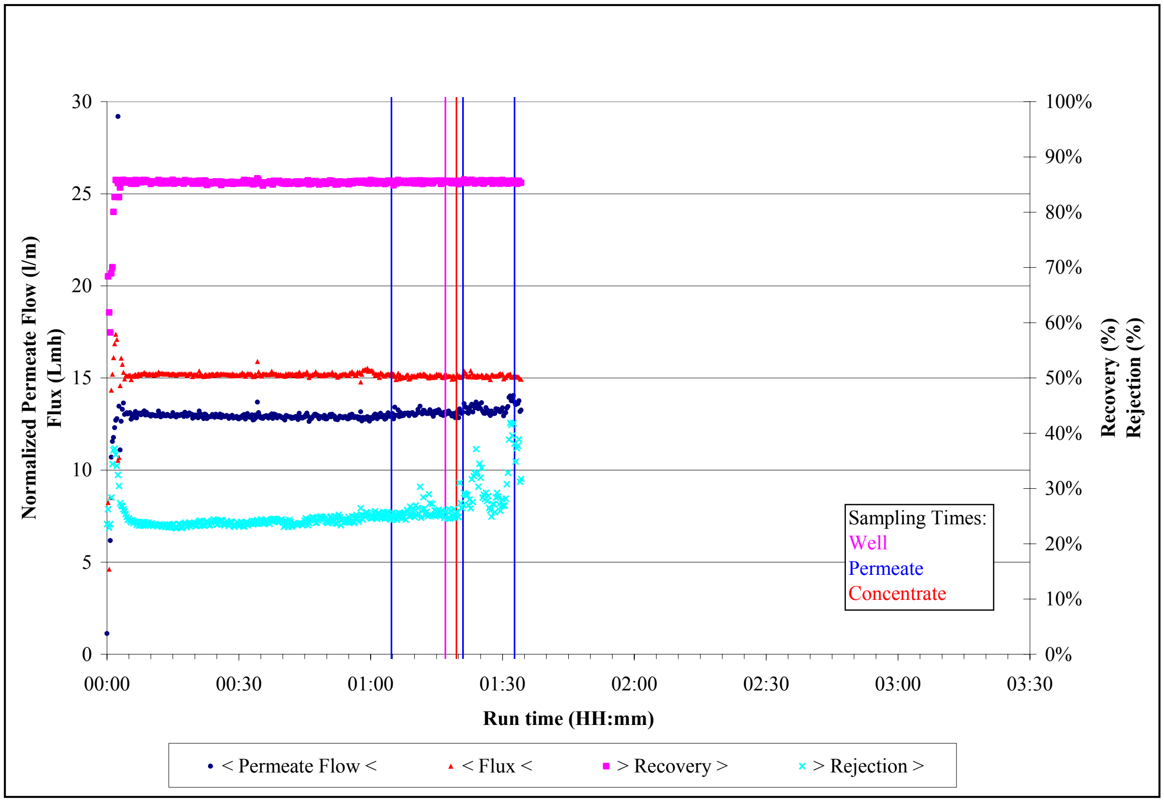


Figure D-5 - Performance graph of NF270 membrane operating under Condition 5 (15 Lmh and 85% recovery)

Shown in Figure D-6 is the performance graph for condition 6 (77.5% recovery and a flux of 20 Lmh). During the time samples were collected, steady state performance of the membrane system is noted. A slight change in flux is noted at a run time of 1:48, which is due to poor operator control.

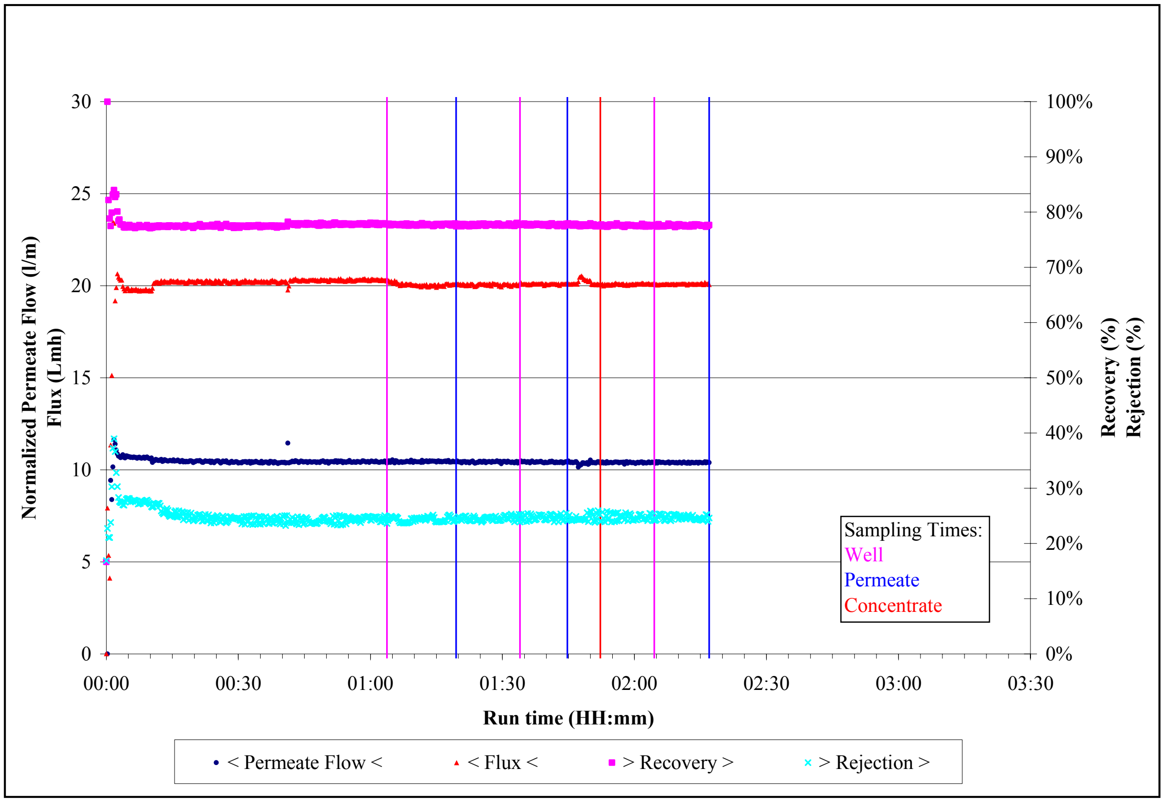


Figure D-6 - Performance graph of NF270 membrane operating under Condition 6 (20 Lmh and 77.5% recovery)

NF90 membrane

Shown in Figure D-7 is the performance graph for condition 1 (77.5% recovery and a flux of 20 Lmh). During the time samples were collected, steady state performance of the membrane system is noted. A slight increasing trend is noted in the conductivity rejection rising from 65% at the start of the sampling to 67% near the end. The flux varies between 20.1 and 20.9 Lmh and is caused by poor operator control.

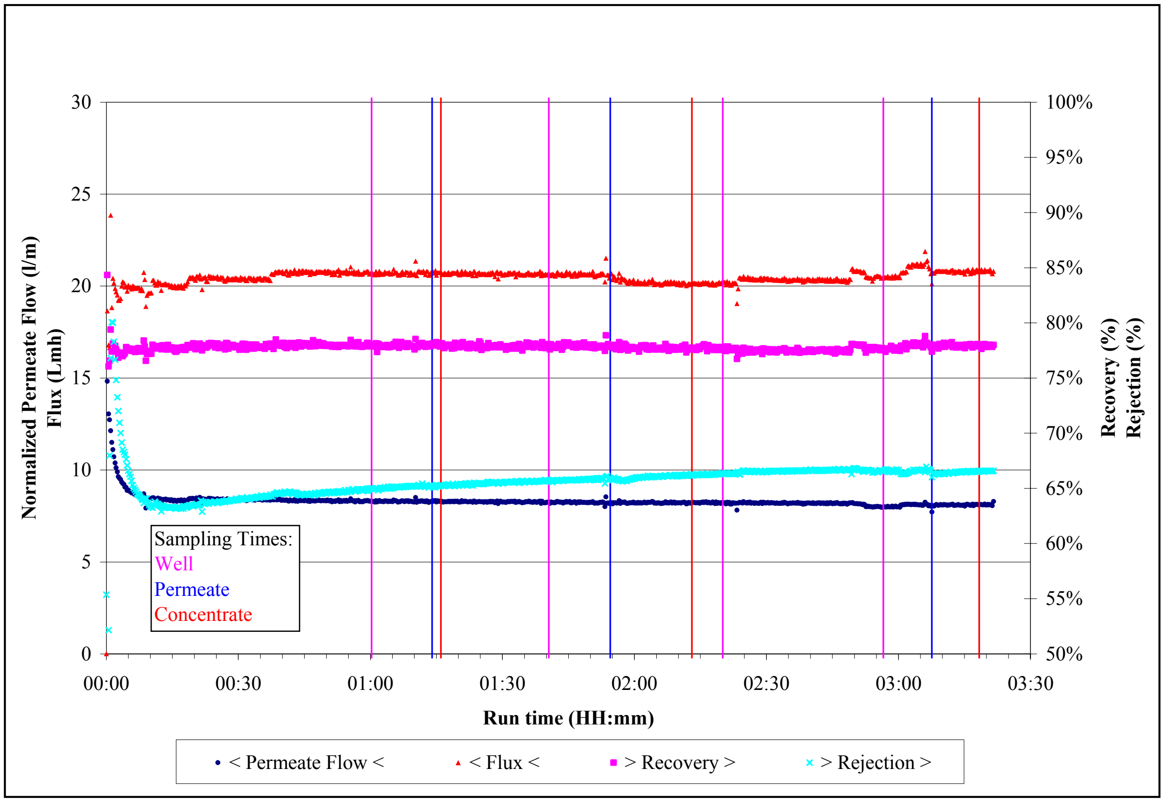


Figure D-7 - Performance graph of NF90 membrane operating under Condition 1 (20 Lmh and 77.5% recovery)

Shown in Figure D-8 is the performance graph for condition 2 (77.5% recovery and a flux of 25 Lmh). During the time samples were collected, steady state performance of the membrane system is noted. A slight increase in flux (from 20.1 to 20.6 Lmh) is observed shortly after the last permeate sample is taken. This had no obvious impact on the arsenic concentration of this sample (see Table B-8).

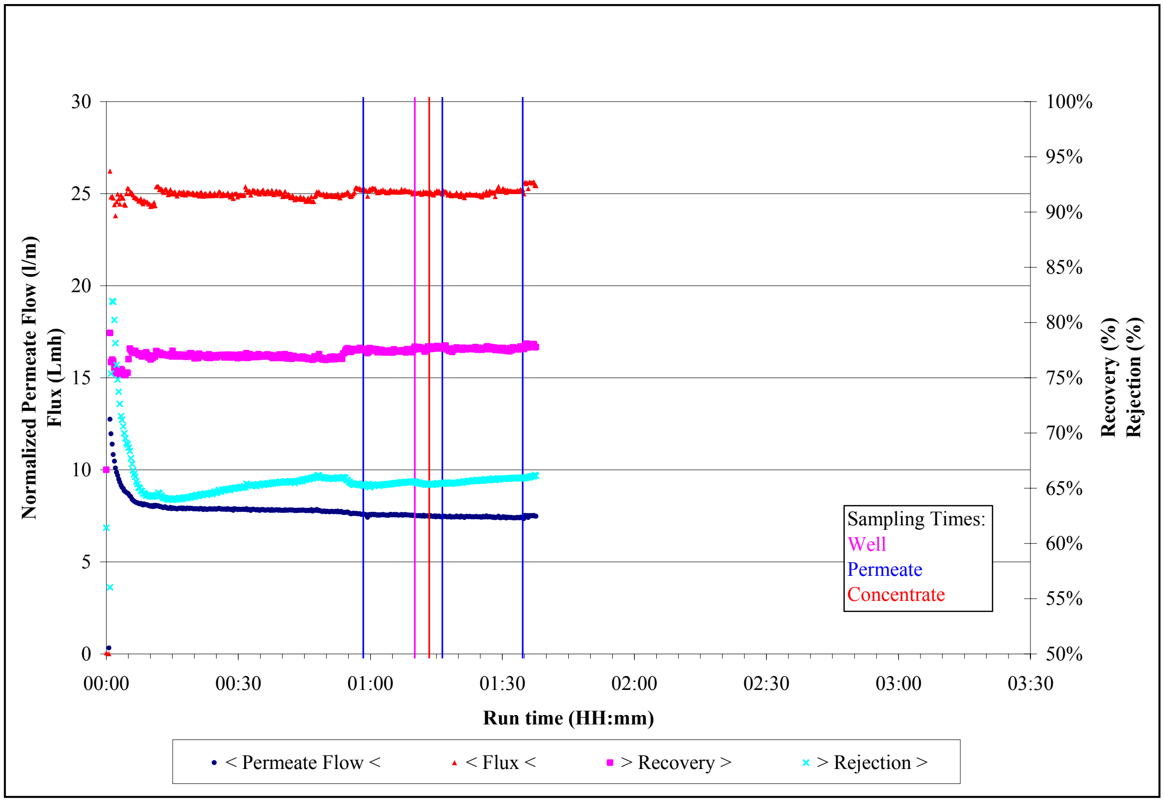


Figure D-8 - Performance graph of NF90 membrane operating under Condition 2 (25 Lmh and 77.5% recovery)

Shown in Figure D-9 is the performance graph for condition 3 (70% recovery and a flux of 25 Lmh). During the time samples were collected, steady state performance of the membrane system is noted. A slight increase in flux at run time 2:03 is noted. This did not have an obvious impact on the arsenic concentration of this sample (see Table B-8).

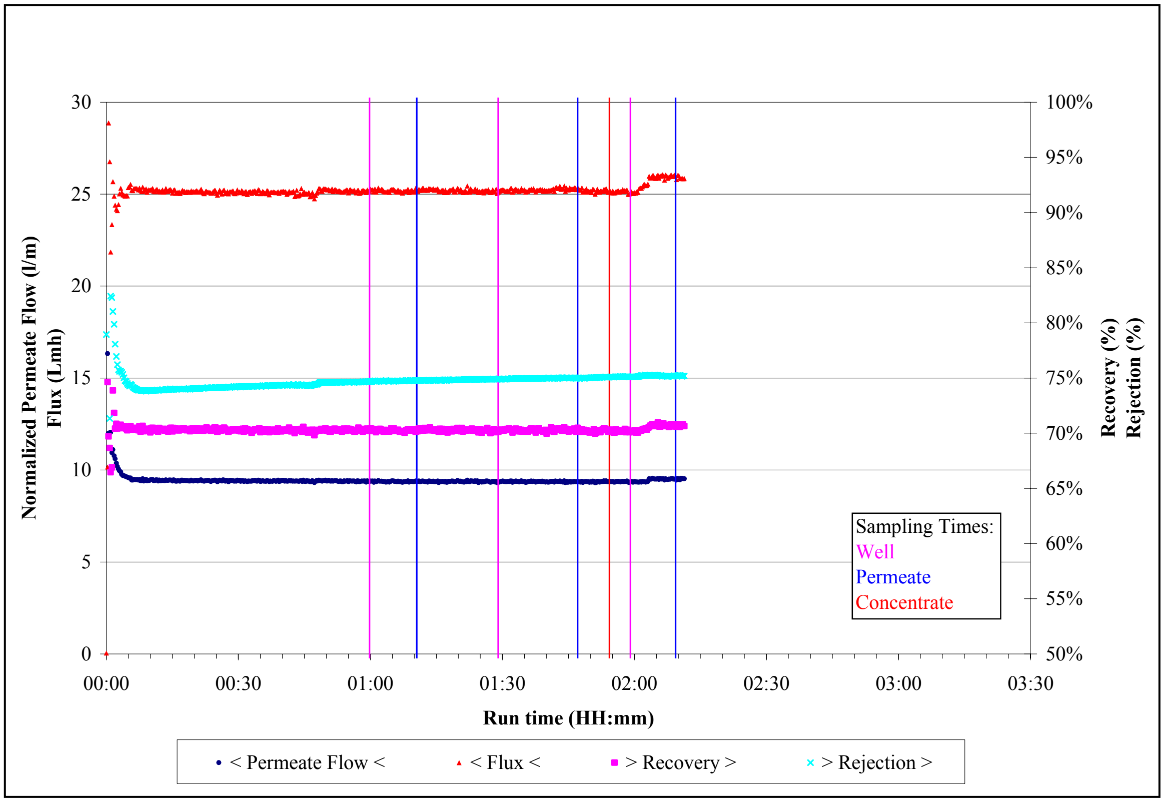


Figure D-9 - Performance graph of NF90 membrane operating under Condition 3 (25 Lmh and 70% recovery)

Shown in Figure D-10 is the performance graph for condition 4 (70% recovery and a flux of 15 Lmh). During the time samples were collected, steady state performance of the membrane system is noted. A slight decrease in flux is noted between 1:13 and 2:18. During this time well pump #2 turned off.

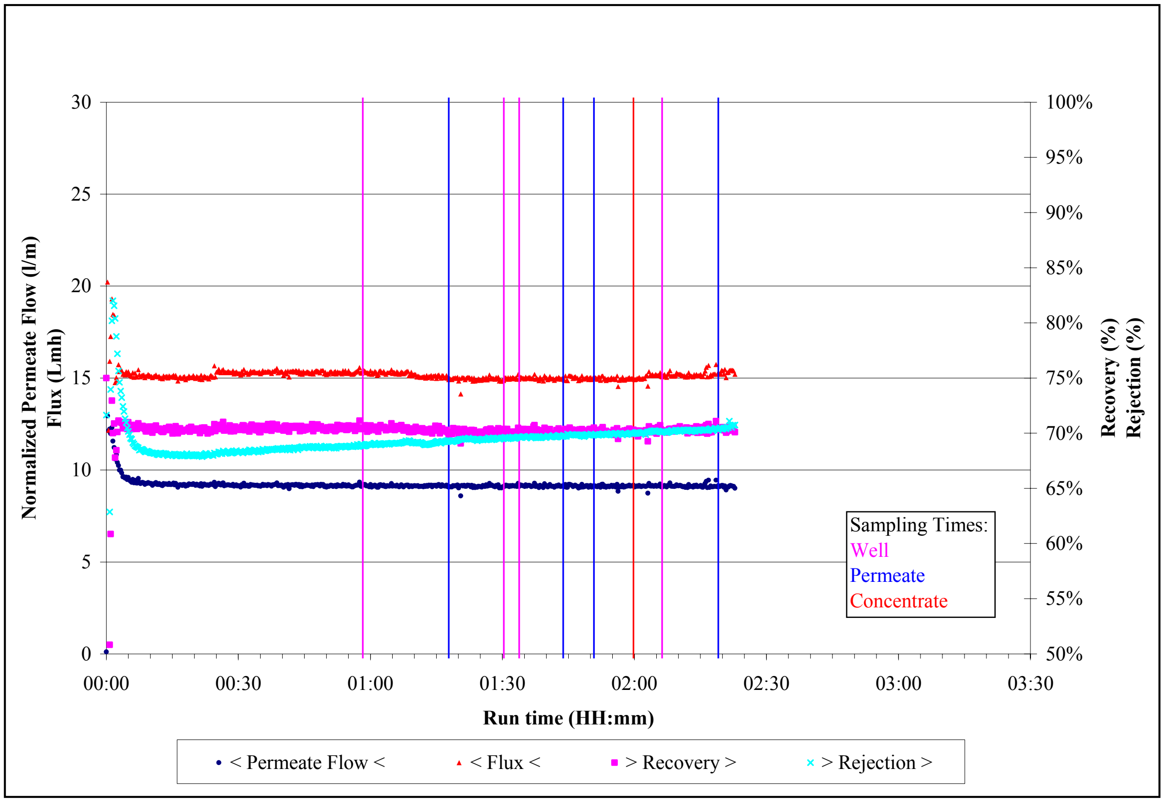


Figure D-10 - Performance graph of NF90 membrane operating under Condition 4 (15 Lmh and 70% recovery)

Shown in Figure D-11 is the performance graph for condition 5 (85% recovery and a flux of 15 Lmh). With the exception of conductivity rejection, steady state performance of the membrane system is noted during the time samples were collected. At a run time of 1:03, the conductivity rejection becomes erratic but the readings are considered false. These is attributed to erroneous permeate conductivity measurements caused by trapped air around the probe.

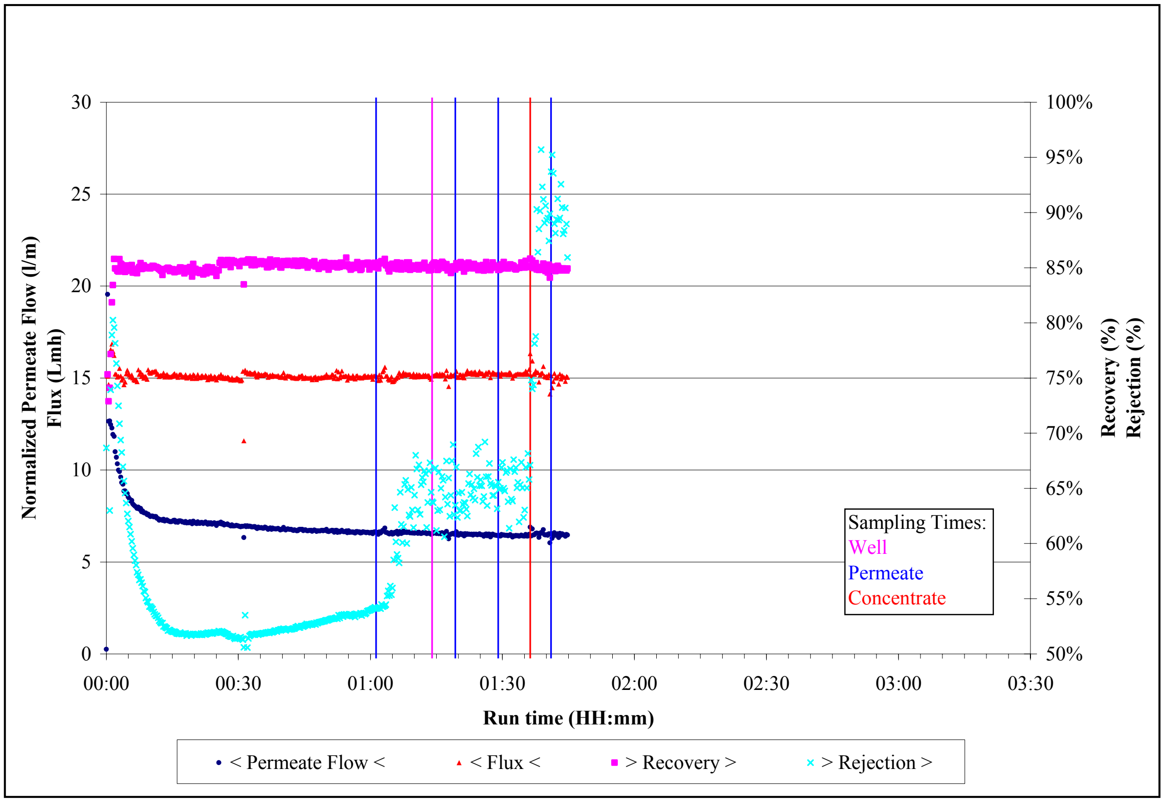


Figure D-11 - Performance graph of NF90 membrane operating under Condition 5 (15 Lmh and 85% recovery)

Shown in Figure D-12 is the performance graph for condition 6 (77.5% recovery and a flux of 20 Lmh). Steady state performance of the membrane system is noted during the time samples were collected. At a run time of 1:13 well pump #2 turned off causing a slight decrease in flux. The operating conditions were adjusted to compensate for the decreased feed pressure. At a run time of 2:20, well pump #2 turned back on causing the flux to increase.

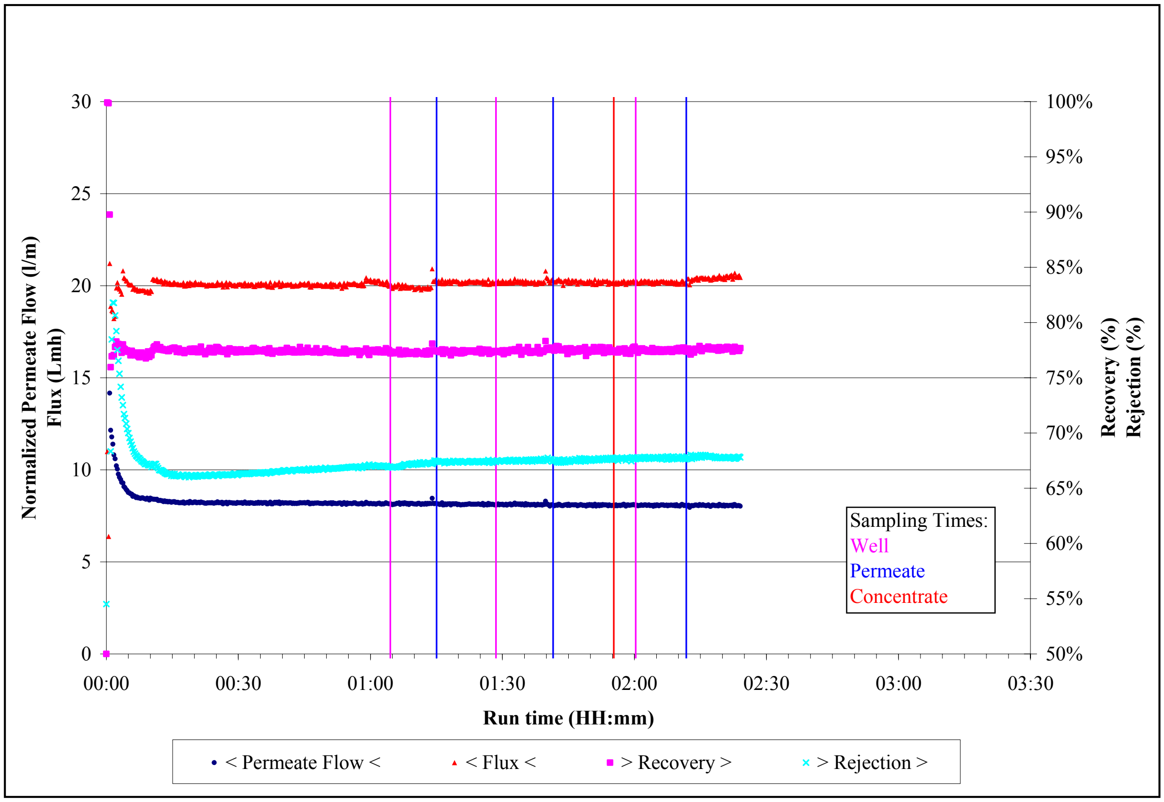


Figure D-12 - Performance graph of NF90 membrane operating under Condition 6 (20 Lmh and 77.5% recovery)

XLE membrane

Shown in Figure D-14 is the performance graph for condition 1 (77.5% recovery and a flux of 20 Lmh). Steady state performance of the membrane system is noted during the time samples were collected, with the exception of a sharp decrease in flux at a run time of 1:15. This was caused by poor operator control.

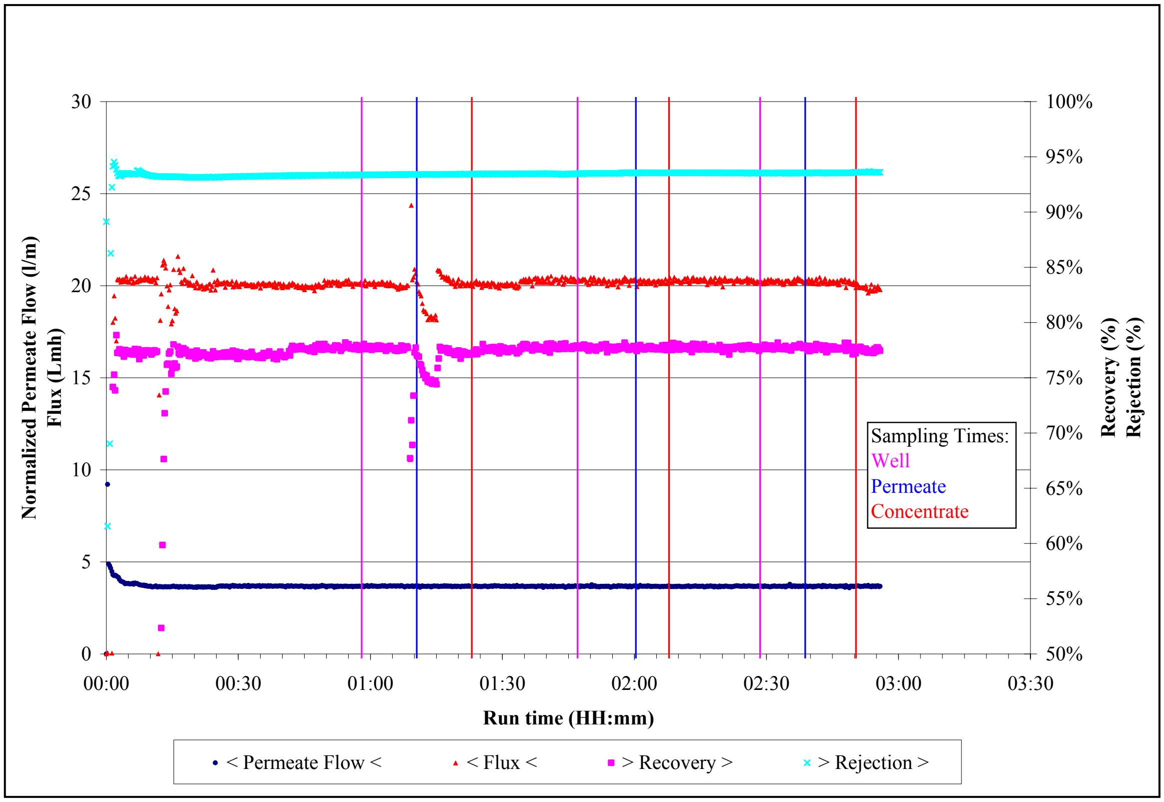


Figure D-13 - Performance graph of XLE membrane operating under Condition 1 (20 Lmh and 77.5% recovery)

Shown in Figure D-15 is the performance graph for condition 2 (82% recovery and a flux of 22 Lmh). Steady state performance of the membrane system is noted during the time samples were collected.

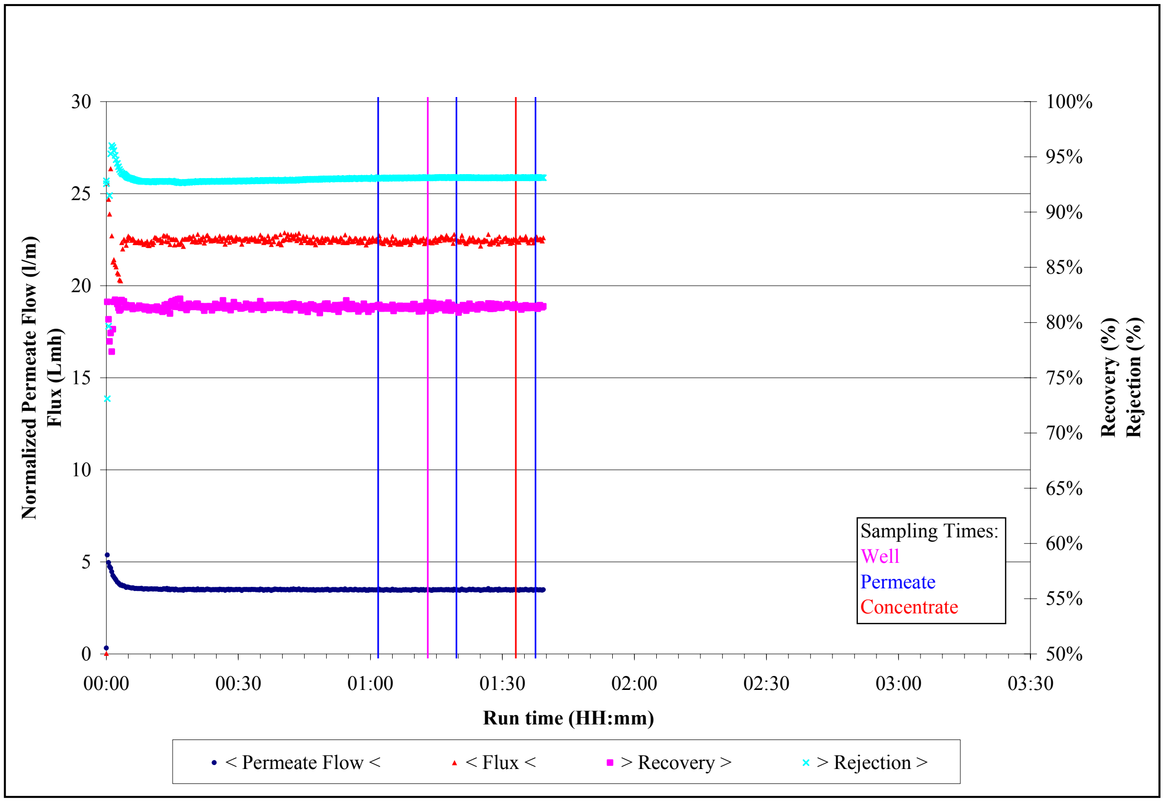


Figure D-14 - Performance graph of XLE membrane operating under Condition 2 (22 Lmh and 82% recovery)

Shown in Figure D-15 is the performance graph for condition 3 (70% recovery and a flux of 25 Lmh). During the time samples were collected, steady state performance of the membrane system is noted. A slight increase in pressure at run 2:10 is noted, which was caused by well pump #2 turning on.

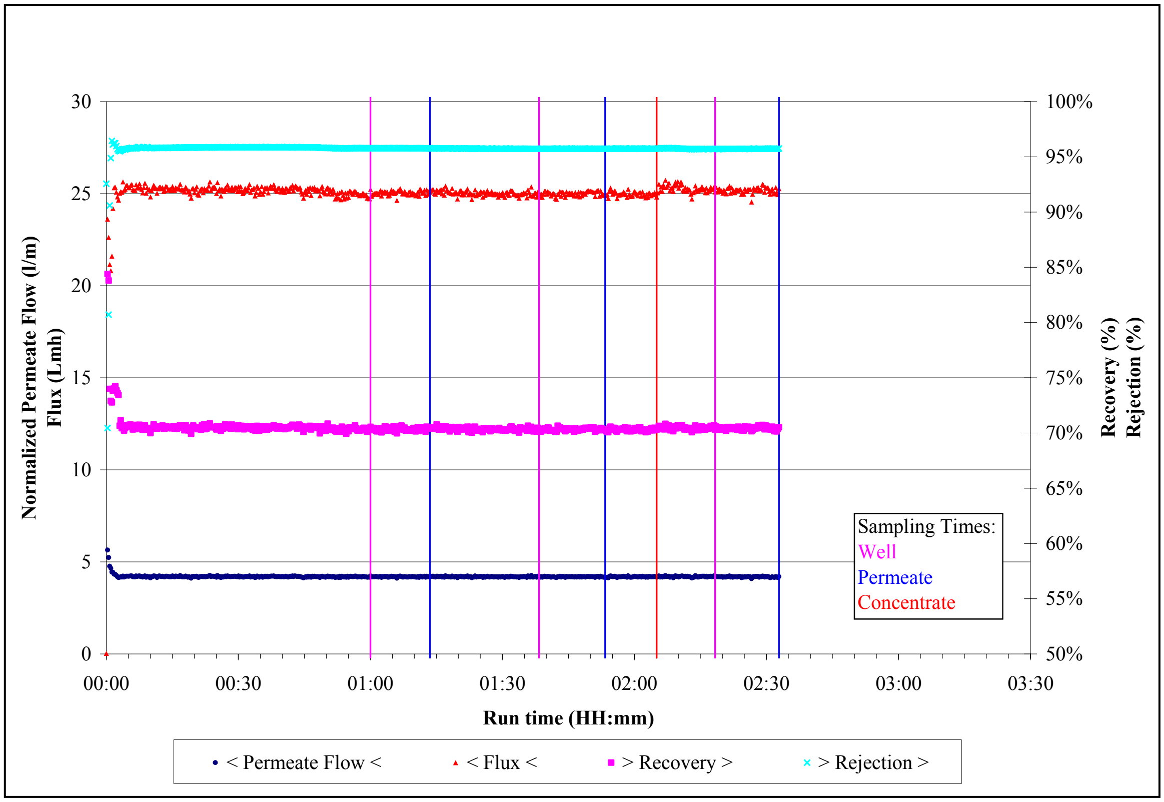


Figure D-15 - Performance graph of XLE membrane operating under Condition 3 (25 Lmh and 70% recovery)

Shown in Figure D-16 is the performance graph for condition 4 (70% recovery and a flux of 15 Lmh). During the time samples were collected, steady state performance of the membrane system is noted. A slight decrease in flux (from 15.3 to 14.9 Lmh) is noted after each permeate sample was taken (run times: 1:51, 2:09, 2:33) and is likely the results of the sampling process. No impact from these variations is seen the arsenic concentrations (see Table B-12).

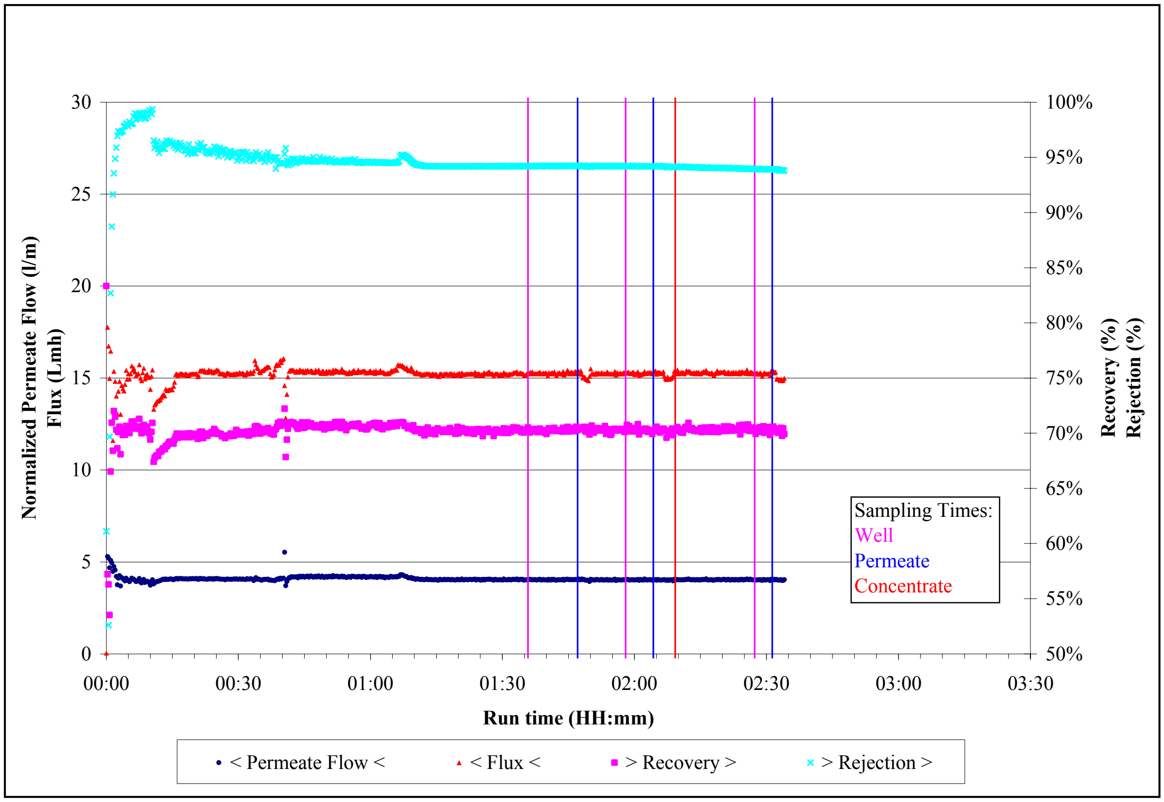


Figure D-16 - Performance graph of XLE membrane operating under Condition 4 (15 Lmh and 70% recovery)

Shown in Figure D-17 is the performance graph for condition 5 (85% recovery and a flux of 15 Lmh). During the time samples were collected, steady state performance of the membrane system is noted. At a run time of 1:29, very erratic readings are noted and were caused by poor operator control. Slight increases in flux are noted at runtimes of 1:19 and 1:39. These were caused by varying feed pressure as well pump #2 turned on and off. The impact of these variations was not evident when examining the arsenic concentrations (see Table B-12).

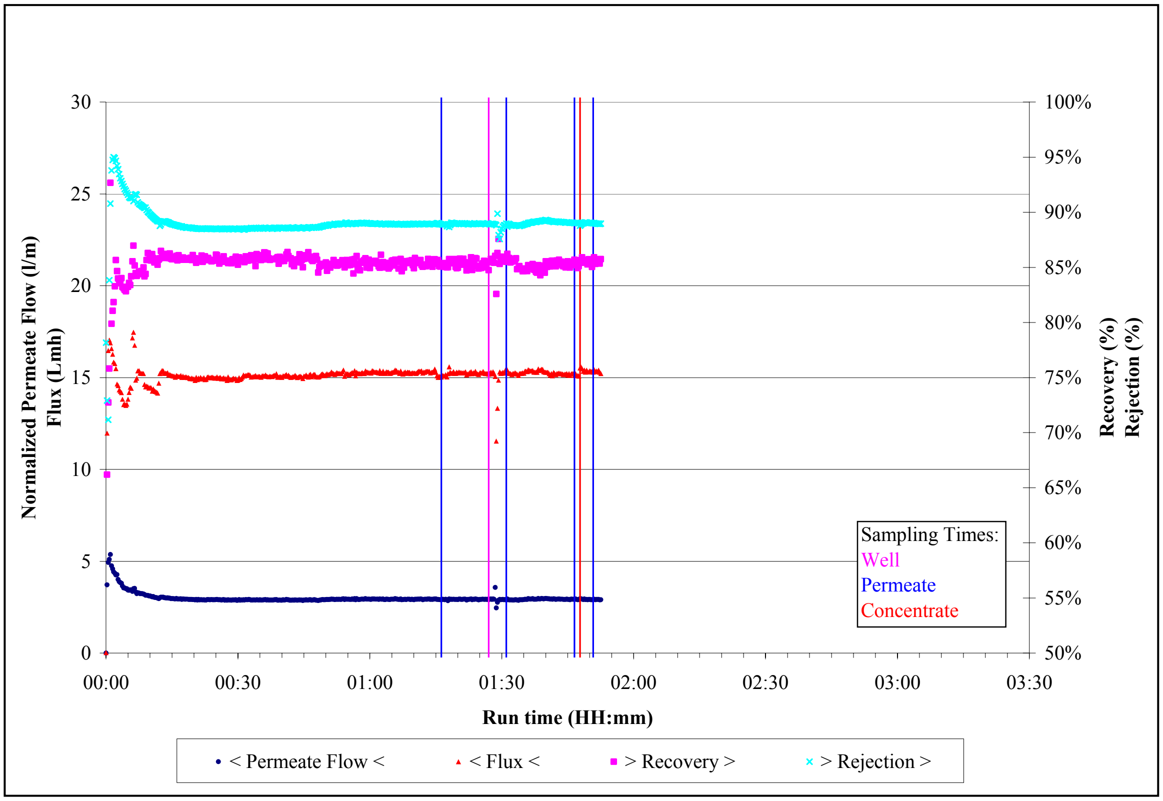


Figure D-17 - Performance graph of XLE membrane operating under Condition 5 (15 Lmh and 85% recovery)

Shown in Figure D-18 is the performance graph for condition 6 (77.5% recovery and a flux of 20 Lmh). During the time samples were collected, steady state performance of the membrane system is noted. After 1:47, more variability in the recovery is noted as it ranged from 76 to 79%. This variation did not obviously influence the arsenic concentrations of the permeate (see Table B-12).

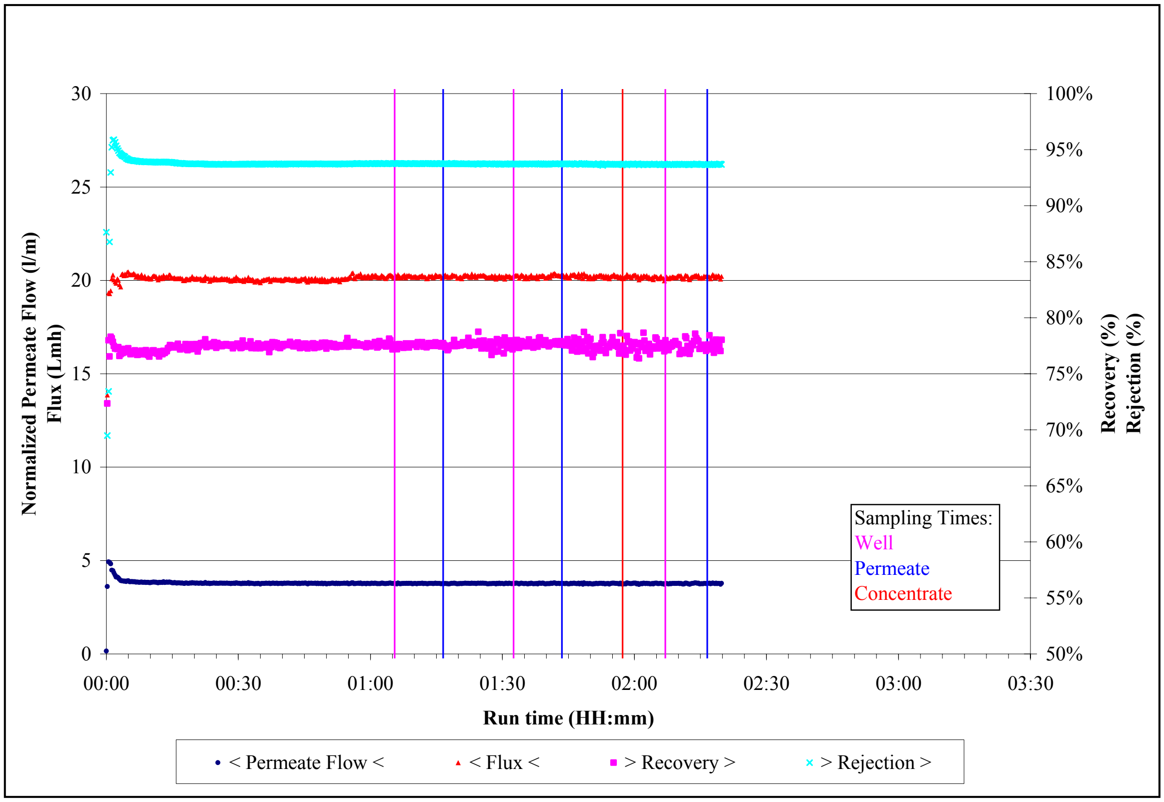


Figure D-18 - Performance graph of XLE membrane operating under Condition 6 (20 Lmh and 77.5% recovery)

D.2 Experiment III

NF270

Shown in Figure D-19 is the performance graph for condition 1 (70% recovery and a flux of 20 Lmh). During the time samples were collected, steady state performance of the membrane system is noted.

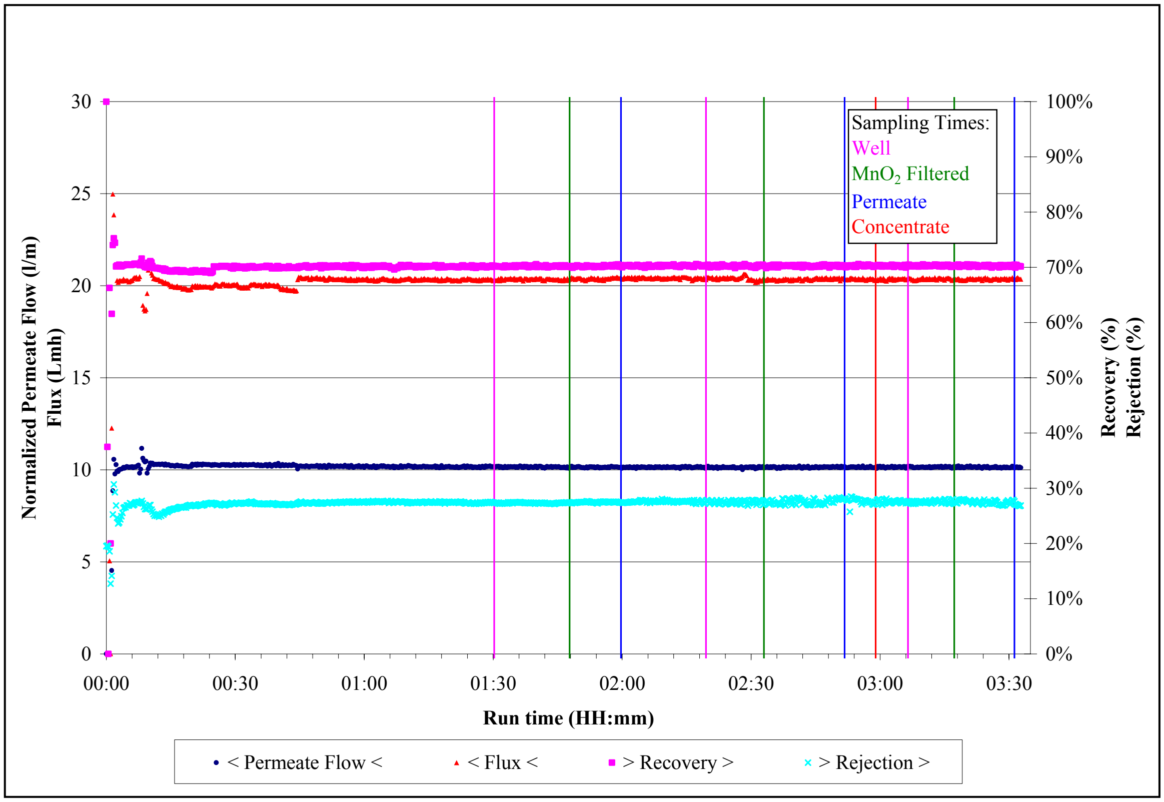


Figure D-19 - Performance graph of NF270 membrane with MnO_2 pretreatment operating under Condition 1 (20 Lmh and 70% recovery)

Shown in Figure D-20 is the performance graph for condition 2 (85% recovery and a flux of 20 Lmh). During the time samples were collected, steady state performance of the membrane system is noted with only small variations in the flux. At a run time of 2:08 well pump #2 turned on, while operator adjustment wasn't made until 2:38

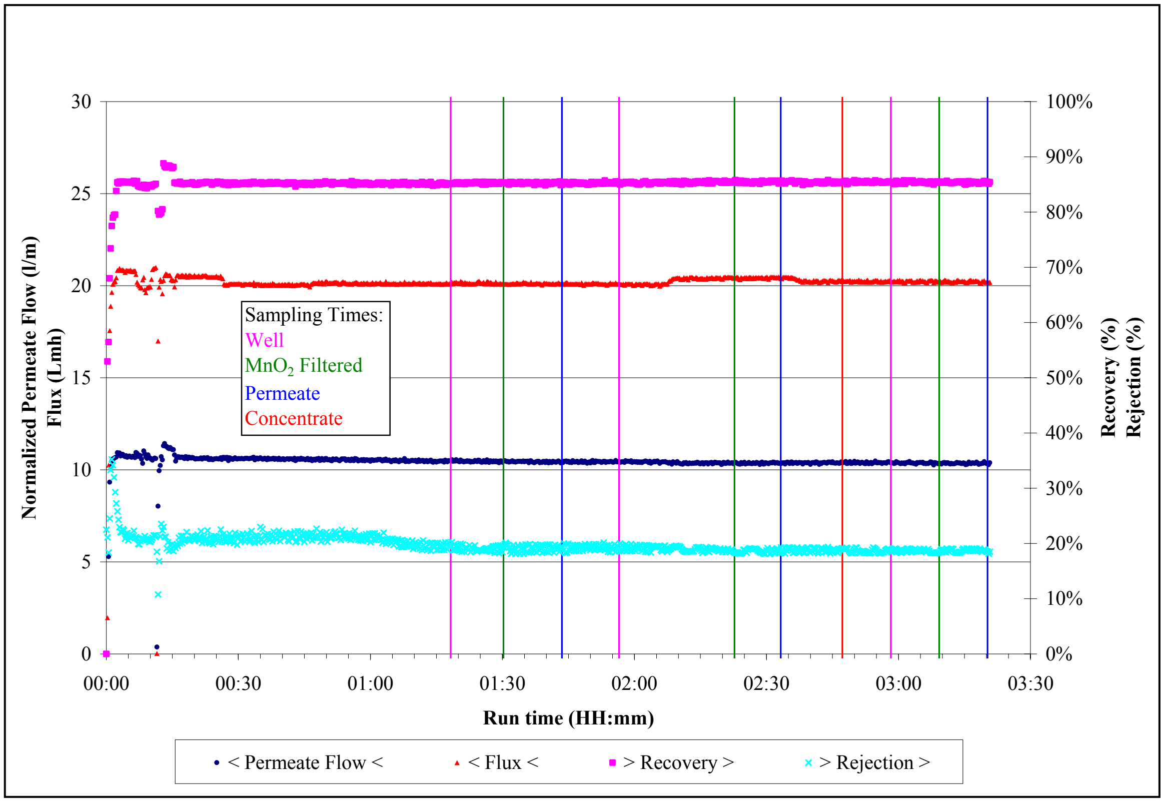


Figure D-20 - Performance graph of NF270 membrane with MnO_2 pretreatment operating under Condition 2 (20 Lmh and 85% recovery)

NF90

Shown in Figure D-21 is the performance graph for condition 1 (70% recovery and a flux of 20 Lmh). During the time samples were collected, steady state performance of the membrane system is noted.

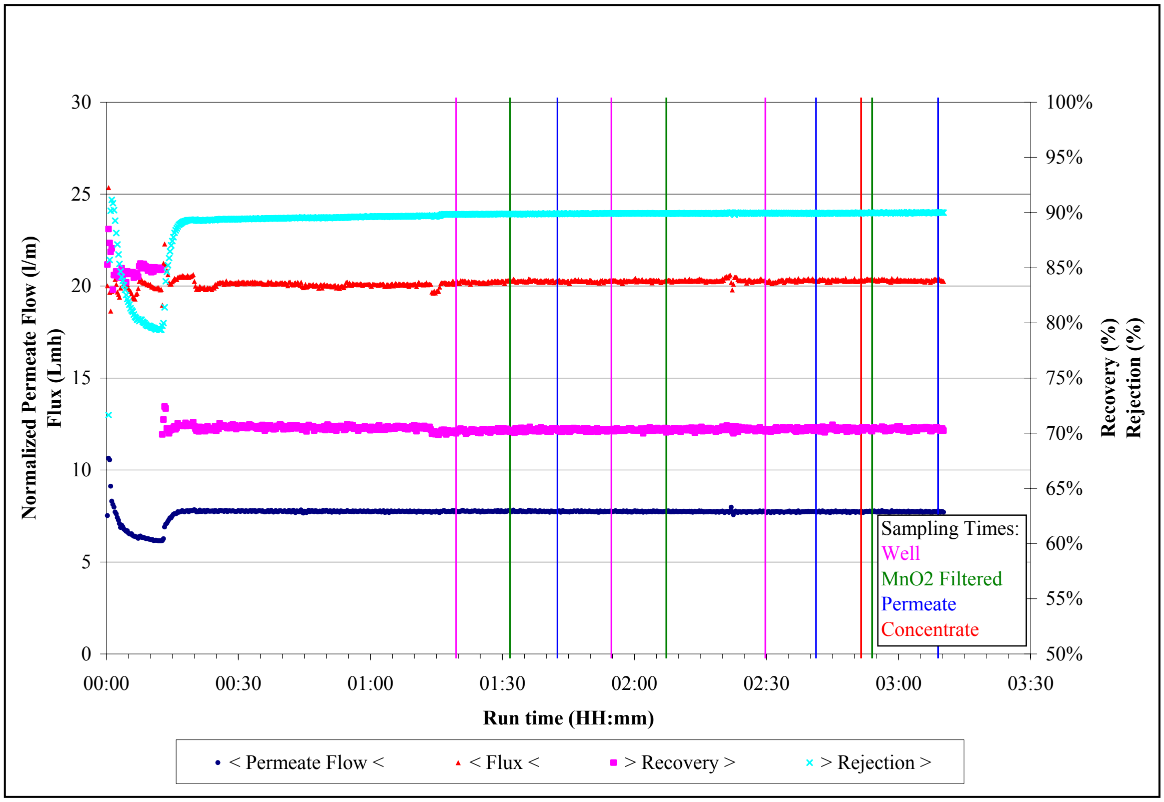


Figure D-21 - Performance graph of NF90 membrane with MnO_2 pretreatment operating under Condition 1 (20 Lmh and 70% recovery)

Shown in Figure D-22 is the performance graph for condition 2 (85% recovery and a flux of 20 Lmh). During the time samples were collected, steady state performance of the membrane system is noted.

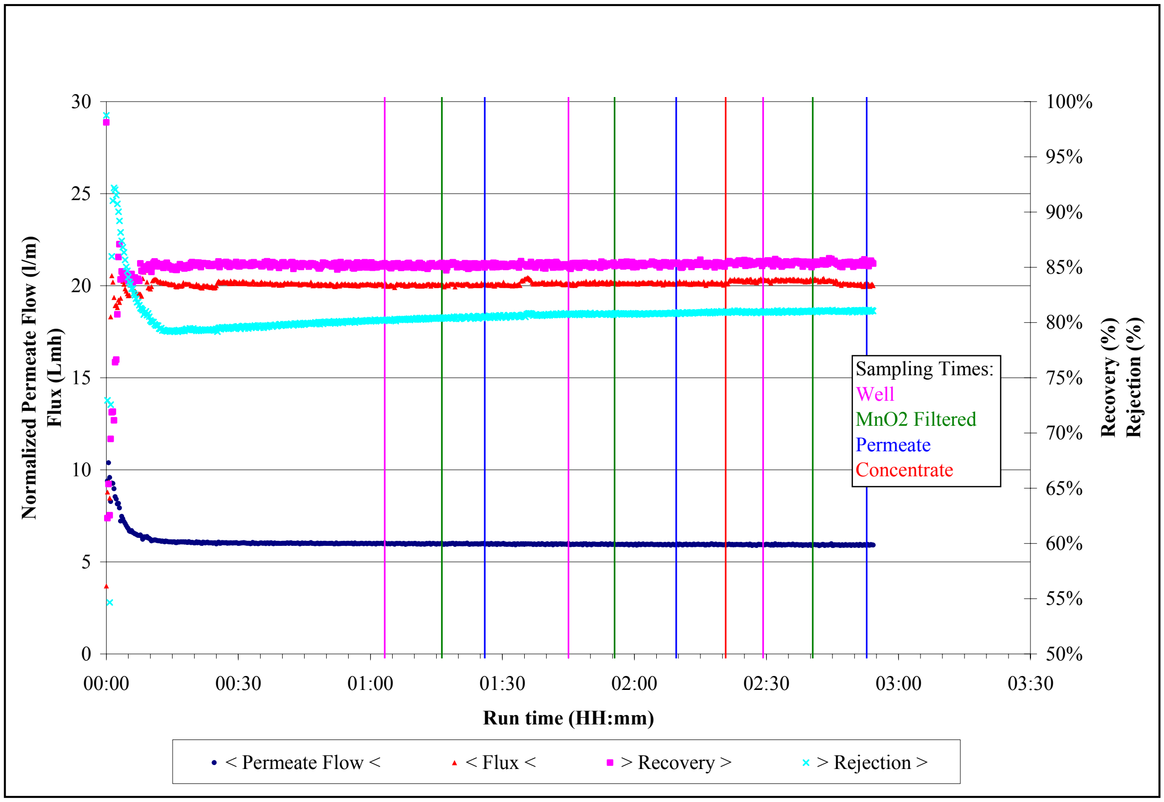


Figure D-22 - Performance graph of NF90 membrane with MnO_2 pretreatment operating under Condition 2 (20 Lmh and 85% recovery)

XLE

Shown in Figure D-23 is the performance graph for condition 1 (70% recovery and a flux of 20 Lmh). During the time samples were collected, steady state performance of the membrane system is noted.

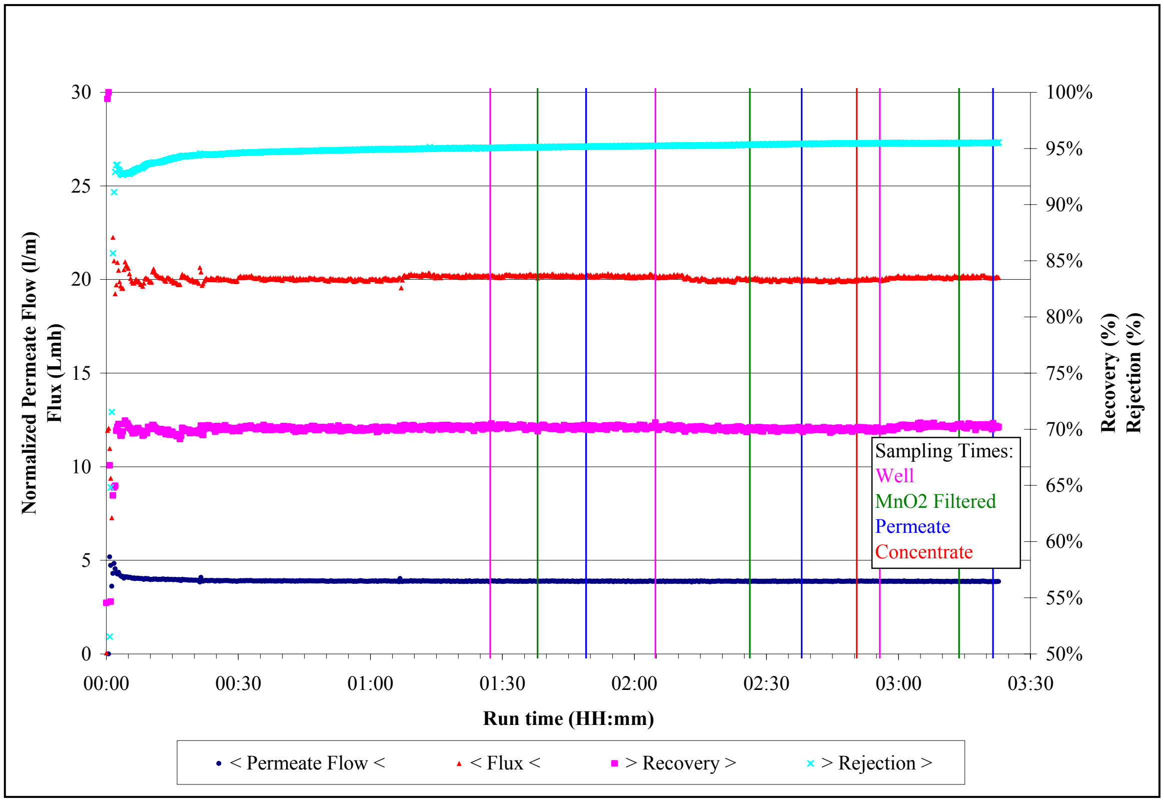


Figure D-23 - Performance graph of XLE membrane with MnO_2 pretreatment operating under Condition 1 (20 Lmh and 70% recovery)

Shown in Figure D-24 is the performance graph for condition 2 (85% recovery and a flux of 20 Lmh). During the time samples were collected, steady state performance of the membrane system is noted.

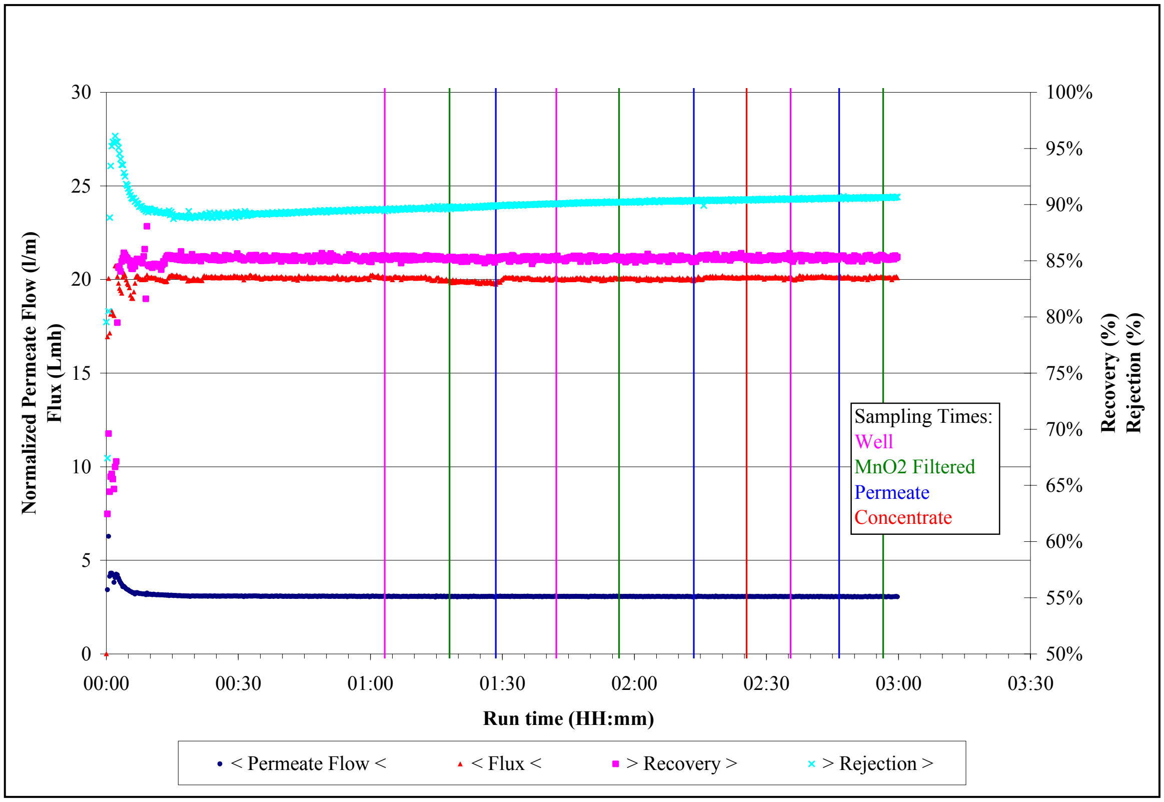


Figure D-24 - Performance graph of XLE membrane with MnO_2 pretreatment operating under Condition 2 (20 Lmh and 85% recovery)

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