Microfiltration of Synthetic metalworking fluids using Aluminum Oxide Membranes

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Abstract

Metalworking fluids (MWFs) are used in manufacturing as coolants, lubricants, and corrosion inhibitors. Growing MWF acquisition and disposal costs, together with concerns about microbiological health hazards and environmental impact have led to increased interest in MWF recycling, contaminant control, and alternative application strategies. Membrane filtration can remove microbes, particulate, and tramp oils that contaminate metalworking fluids and has the potential to reduce health risks and extend MWF life in the machine tool industry. However, poorly understood relationships between the compatibility of metalworking fluid ingredients, contaminants, membrane materials, and membrane pore-size distributions have precluded the widespread industrial application of the technology.

This research assesses the mechanisms of productivity decline during the microfiltration of an uncontaminated synthetic MWF using aluminum oxide membranes. It is revealed that while the majority of synthetic MWF ingredients have a negligible impact on microfiltration productivity, specialty additives such as lubricants, defoamers, and biocides can significantly reduce productivity. This is due to adsorption of these ingredients to the membrane surface that serves to increase resistance to MWF flow through the membrane pores. MWF ingredient characteristics such as hydrophilic/hydrophobic content and electrostatic charge can influence adsorption and productivity-loss during microfiltration. These findings demonstrate that the chemistry and concentration of specialty additives are important to account for during the design of membrane filtration systems for MWF recycling.

List of Figures

List of Tables

Table of Contents

Chapter 1

Introduction

1.1. Metalworking Fluid Functionality and Formulation

Metalworking fluids (MWFs) benefit a variety of metal cutting and shaping processes by cooling and lubricating the workpiece and tool, transporting chips out of the cutting zone, and imparting corrosion protection. Approximately 1 billion gallons of MWF were used in 1998. MWF usage increased 5.3% between 1997 and 1998 (ILMA, 1998).

Metalworking fluids can be divided into four basic categories: straight oils, soluble oils, semi-synthetics, and synthetics. According to the Independent Lubricant Manufacturers Association, there are no strict definitions that distinguish these types of fluids (ILMA, 1990). Generally they are differentiated by the amount of mineral oil present in the formulation. Straight oils have no water in their formulation and are typically mineral oils with or without extreme pressure and polar additives (Oberwalleney and Sheng, 1996). The need for more cooling in higher speed machining operations led to the introduction of water-soluble formulations (Springborn, 1967). Water-soluble fluids are sold in a concentrated form that is typically diluted 80-95% before use in manufacturing. Soluble oil, semi-synthetic, and synthetic fluids are water-soluble fluids that have varying ratios of water to mineral oil in their concentrated forms. A soluble oil typically consists of 60-90% mineral oil in the concentrate with the balance made up mostly of emulsifiers to keep the oil stable in the water phase. Semi-synthetic fluids are similar, except they typically contain 2-30% oil in the concentrated form.

Synthetic MWFs contain no mineral oil. As a result synthetics have excellent cooling characteristics, but inherently have low lubrication capability. Consequently, synthetic fluids must be formulated with lubricant additives to provide the metalworking performance of oil-containing products (ILMA, 1990; Sutherland et al., 1997). Oil-containing products also tend to exhibit less corrosion than synthetic MWFs. Thus synthetic MWFs often contain multiple corrosion inhibitors to prevent the fluid from chemically attacking the workpiece. Other specialty ingredients that can be found in water-soluble metalworking fluids include wetting agents, chelating agents, pH buffers, defoamers, and biocides. A typical synthetic MWF can contain all these types of additives. Figure 1.1 illustrates the relative percentage of oil, water, and additives found in the concentrate of different types of water-soluble MWFs (Sheng and Oberwalleney, 1997).

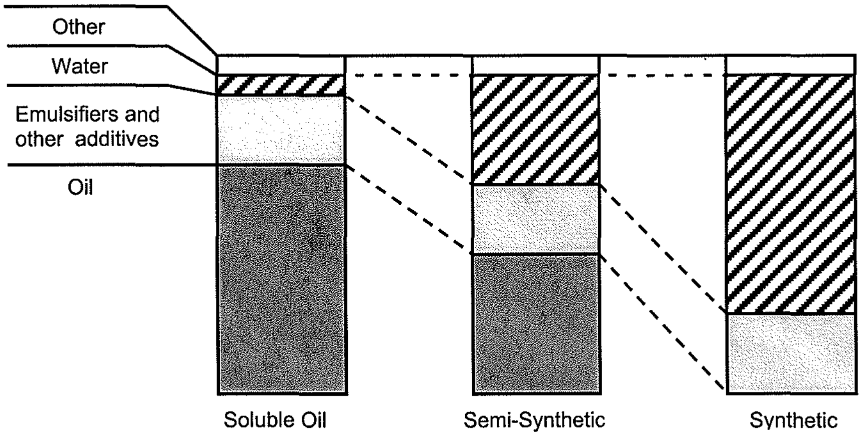


Figure 1.1. Relative proportion of water, oil, and additives in the concentrated form of water-soluble MWFs. Adapted from Oberwalleney and Sheng (1996).

Before the 1970s, most metalworking operations employed either straight oils or soluble oils. Since then, straight oil consumption has decreased since they can create hazardous oil mists and have inherent fire risks. Semi-synthetic and synthetic MWFs have gained marketshare because of 1) the transition to higher speed machining, 2) the increase in petroleum costs during the 1970s, and 3) the reduced susceptibility of synthetics to microbial proliferation.

1.2. Metalworking Fluid Concerns

Four major concerns have been raised about the state-of-the-art application of MWFs (Skerlos et al., 1999a). First, particulate, tramp oils, and bacteria are known to reduce the quality of metalworking operations over time (Marano et al., 1991; Byers et al., 1994). Second, these contaminants eventually render the fluid ineffective for metalworking operations, creating significant acquisition and disposal costs that reduce profitability (Klocke and Eisenblatter, 1997; Rajagopalan et al., 1998a). Third, the disposal of MWF places a significant burden on the environment (Skerlos et al., 1998). Fourth, bacteria and the biocides used to control their growth in MWFs can be a significant health hazard (NIOSH, 1998). Sections 1.2.1 and 1.2.2 review what is currently known about environmental and health impacts of MWF usage.

1.2.1. Environmental Impacts of Metalworking Fluids

The level of environmental impact at each stage of the MWF life-cycle depends on 1) the level of raw material, energy, and water resource consumption, and 2) the level of ecosystem alteration that occurs. The life-cycle stages of a MWF are listed in Table 1.1,

Table 1.1. Life-Cycle Stages of Metalworking Fluids.

- Refining and production;
- Transportation;
- Preparation;
- Use at the machine tool;
- Recycling and maintenance;
- Treatment;
- Oil recovery;
- Disposal.

Of the life-cycle stages directly influenced by MWF end-users, the disposal stage is believed to have the most significant impact on the environment.

MWF disposal results from a breakdown of the product by metal residuals, microorganisms, leak oils, and excesses in heat, water hardness, and water evaporation. MWF disposal can negatively impact the environment by serving as a carrier for hazardous metal carry-off, hazardous metal constituents, and oil. MWFs may also be the source of oxygen depletion and nutrient loading in receiving waters. The impacts of MWF disposal on the environment are illustrated in Figure 1.2 and are discussed in the following paragraphs.

Hazardous Metal Carry-Off. A non-hazardous MWF can become hazardous at the machine tool by carrying metal residuals containing inclusions of heavy metals such as lead, chromium, or cadmium. Disposal of MWF containing excesses of hazardous metals can exceed $250 per 55-gallon drum and is strictly regulated.

Hazardous Chemical Constituents. A MWF may contain known hazardous ingredients that are reported on its accompanying Material Safety Data Sheet (MSDS). Generally, hazardous ingredients found on an MSDS may have one or more of the following characteristics: combustibility, flammability, oxidativity, instability, reactivity, carcinogenicity, toxicity, or corrosivity. MWFs with hazardous ingredients can be subject to special regulatory requirements.

Biochemical Oxygen Demand. When MWF is disposed to a receiving water, the MWF is subject to biodegradation by microorganisms that consume oxygen in the process. To account for this form of pollution, the biochemical oxygen demand (BOD) of a MWF is measured as a metric of its oxygen depleting capacity. Maximum permissible levels of BOD (measured over 5 days) in sewered MWF is commonly 200 mg/l, although large variation exists between localities. Untreated MWFs can have BOD concentrations over 4000 mg/l (Rajagopalan et al., 1998a).

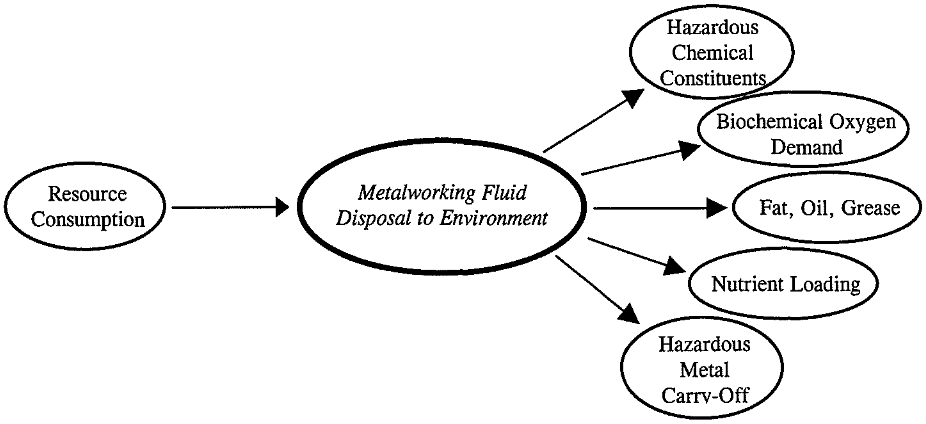


Figure 1.2. Categories of environmental consideration due to MWF disposal.

Oil and Grease. Fat, oil, and grease (FOG) contaminants in MWFs come from petroleum, mineral, animal, or vegetable sources. FOG can lead to taste, odor, and other aesthetic problems in water at relatively low concentrations. At elevated concentrations, FOG can be toxic.

Nutrients. MWFs can also have elevated levels of nutrients such as nitrogen and phosphorous. Excessive nutrient concentrations can lead to excessive microbial growth and ecosystem disruption in receiving waters.

The United States Environmental Protection Agency (EPA) has become increasingly interested in the regulation of MWF disposal. In 1995, the agency proposed effluent limitation guidelines and standards for the machine tool industry. The proposed Metal Products and Machinery Rule would require oil and grease disposals below 17 mg/l (EPA, 1995). Since untreated MWFs typically contain levels of oil and grease above 2000 mg/l, achieving this standard would increase on-site treatment and disposal costs significantly (Kulowiec, 1979). The proposed Metal Products and Machinery Rule has served to heighten recent interest in MWF recycling.

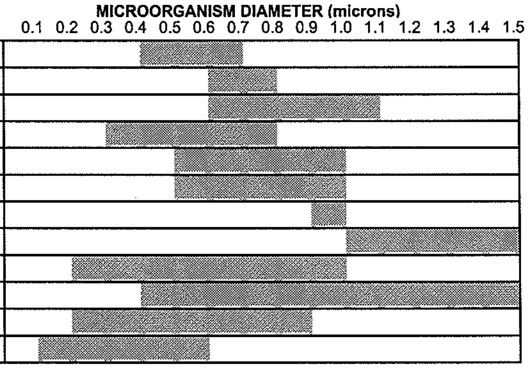
1.2.2. Human Health Impacts of Metalworking Fluids

Metalworking fluids can contain health hazards. Common MWFs used in the 1970s and 1980s were found to contain potentially carcinogenic nitrosamines (Byers et al., 1994). The addition of nitrosamine forming ingredients such as sodium nitrite has since been prohibited. Triethanolamine, a common ingredient in current MWFs, has been associated with occupational asthma and is a suspected carcinogen (NIOSH, 1998; Savonius, 1994). Several other ingredients found in MWF formulations are listed as potential exposure hazards and must be listed on the MSDS provided with MWF formulations.

Apart from inherent hazards that may be associated with MWF chemistry, health hazards may exist due to microbial contamination. Bacterial populations of 10^5 to 10^9 organisms per milliliter of MWF are not uncommon in poorly maintained MWF systems and are the primary reason biocides are used in water-soluble MWF formulations. Without adequate control, bacterial populations can reach these levels in as short as 48 to 72 hours. Table 1.2 lists typical MWF bacteria, their survivability in MWF, and their relative sizes (Rossmoore, 1981; Holt et al., 1989).

Table 1.2. Bacterial Species Found in MWFs and their Survivability, Length, and Diameter.

Species	**Survival/ Growth**	**Length (um)**
Pseudomonas aeruginosa	Excellent	1.5-3.0
Pseudomonas fluorescens	Good	2.3-2.8
Pseudomonas putida	Good	2.0-4.0
Proteus mirabilis	Excellent	1.0-3.0
Enterobacter cloacae	Very Good	1.2-3.0
Enterobacter agglomerans	Good	1.2-3.0
Citrobacter frueundii	Very Good	2.0-6.0
Escherichia coli	Good	2.0-6.0
Klebsiella pneumonia	Very Good	0.6-6.0
Desulfovibrio sp.	Fair-Good	2.5-10
Legionella sp.	Not known	2-20
Mycobacterium sp.	Good	1.0-10



Microbial contamination has been recognized as a cause of deterioration of MWFs and has been studied extensively (Lee and Chandler, 1941; Bennett, 1972). The primary reasons for the study of microbes in the past were directly concerned with reducing biodegradation of MWF ingredients. However, pathogenic or potentially pathogenic organisms such as *Pseudomonas aeruginosa*, *Escherichia coli*, *Legionella sp.*, and *Mycobacteria sp.* have been isolated from MWFs in recent years (NIOSH, 1998). This has raised concern about worker safety. Fortunately, infections directly attributable to microorganisms in MWFs appear to be rare. One notable exception is an outbreak of Pontiac fever in an engine manufacturing plant that was caused by MWF aerosol contaminated with *Legionella sp.* (Herwaldt et al., 1984).

Increasing attention has been paid to bacterial by-products in MWFs, such as endotoxins that have been detected in MWF mists. Endotoxins are functional components of the cell wall of many bacteria found in Table 1.2. Endotoxins are generally released by microbial lysis or by destabilization of the bacterial cell wall. They can cause allergic responses in the upper respiratory tract, airways, or the distal portions of the lungs (e.g., HP, also known as allergic alveolitis). HP has been associated with microbially contaminated MWFs in several recent studies, and more generally, heightened incidence of asthma and other disorders of the pulmonary airways have been reported by individuals exposed to MWFs (NIOSH, 1998).

Biocides used to control bacterial populations in MWFs also have health risks associated with them. Biocides have been linked to allergic contact dermatitis (Zugerman, 1986; Byers et al., 1994). Some biocides have also been linked to nitrosamine formation in MWFs (Mackerer, 1989).

After a comprehensive review of respiratory disorders associated with MWF exposure, the National Institute for Occupational Safety and Health (NIOSH) has recommended that exposure to MWF aerosols be limited to 0.5 mg/m^3. This is an order of magnitude below the current standard. In addition, NIOSH has recommended that dermal exposure to MWFs be limited where possible (NIOSH, 1998).

1.3. Membrane Filtration of MWFs

To alleviate the environmental and health concerns associated with MWF use described above, dry machining and minimal MWF research has been gaining momentum in the industry. However, these technologies have yet to resolve issues of chip evacuation, temperature control, and tool wear in more severe operations (Aronson, 1995; Klocke and Eisenblatter, 1997). As a result, there has been increased attention paid to MWF management in recent years. Oil skimmers, centrifuges, coalescers, settling tanks, depth filtration, magnetic separation, and floatation technologies have been used in the metalworking industry to various extents (Byers et al., 1994; ILMA, 1990). However, these technologies have yet to economically alleviate all the environmental, health, and performance issues associated with MWF contamination. This is in large part because these conventional technologies do not efficiently remove small particulate ($<10\mu$m) and bacteria.

Membrane filtration (MF) technology is capable of removing small particulate, bacteria, and oils from MWFs. For MWFs compatible with MF, the technology can reduce microbiological hazards and dependence on biocides for microbiological control. In addition, it can improve MWF performance and extend its useful life.

Several comprehensive sources exist that describe the general application of MF technology (Cheryan, 1986; Bhave et al., 1991; Ho and Sirkar et al., 1992). MF refers to the family of pressure-driven membrane separation methods that includes reverse osmosis, nanofiltration, ultrafiltration, and microfiltration. These technologies utilize a semi-permeable barrier or "membrane" capable of separating feed stream constituents according to their particle size relative to the pore size of the membrane. The membrane

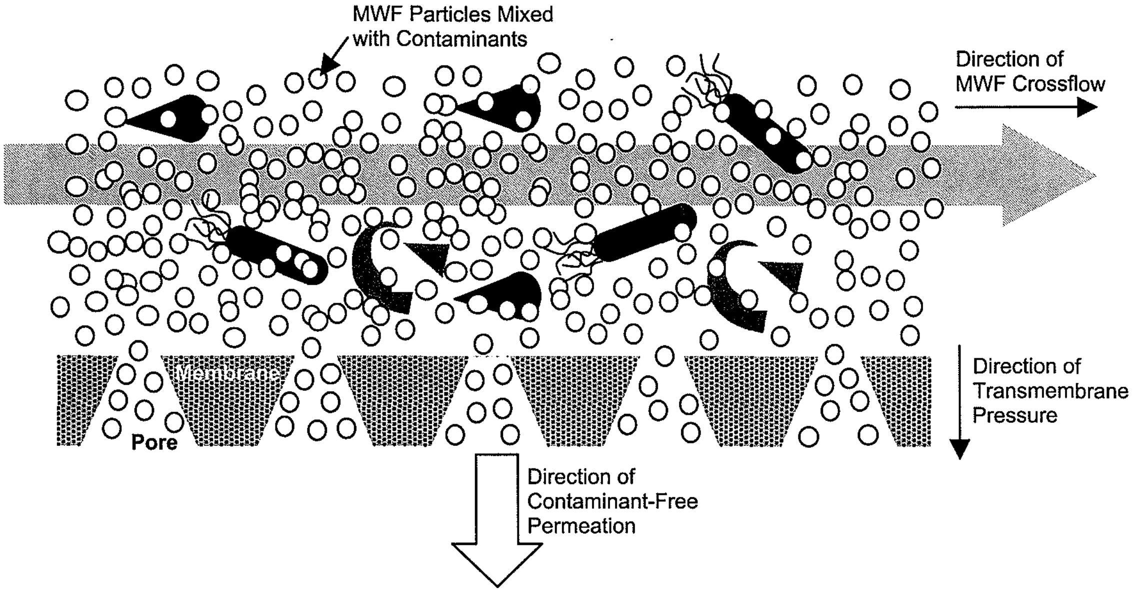


Figure 1.3. Cross-flow membrane filtration concept.

separates MWF ingredients from larger contaminants such as bacteria, tramp oils, and chips. The different membrane filtration technologies are differentiated by membrane pore size.

A major difference between conventional filtration and membrane filtration is that conventional filters operate by capturing particles within the filter matrix. Thus the filters cannot be regenerated after use. Membrane filtration can be performed with filtration tangential to the channels of bulk fluid flow. This discourages the accumulation of particles within the filter matrix and increases productivity. The cross-flow membrane filtration concept is illustrated in Figure 1.3.

The volumetric rate at which contaminant-free solution is produced divided by the surface area of the membrane is called the *flux*, or productivity, of the membrane. Flux is a function of the contamination level, fluid chemistry, and operating parameters. The capital cost of a MF system is highly dependent on flux. A membrane is *fouled* when it experiences a reduction in flux that cannot be increased without cleaning.

Membrane filters are usually sized to have pores that are too small for contaminant particles to enter, but large enough for the MWF ingredients to pass through. Therefore, the separation between MWF and contaminants occurs at the surface of the filter and consequently flushing or cleaning can regenerate the filter. Ceramic membrane filters, for instance, can thus last up to ten years or longer. The contaminant-free MWF filtrate is called the *permeate*, the residual stream is called the *retentate*. Both ultrafiltration and microfiltration have been considered for use in MWF recycling. Ultrafiltration membranes have pore sizes that range from approximately 1 to 100 nanometers (10^{-9} m). Microfiltration membranes have pore sizes that range from approximately 0.05 to 10 (10^{-6} m) (Mulder, 1991).

1.4. Research Objectives, Scope, and Overview of Report

1.4.1 Research Objectives

While the ability of membrane filtration to separate bacteria, small particulate, and oils from used MWFs is well proven, the extent to which membrane filtration can achieve a separation of contaminants without disruption of MWF chemistry is not currently known. This uncertainty is compounded by the multitude of different MWF chemistries and formulations currently used in the machine tool industry. The characteristics of MWFs that determine the degree of compatibility with membrane filters are poorly understood at this time. In addition, for MWFs that are compatible with membrane filtration, models do not currently exist to appropriately size membrane filtration systems to control microbial growth.

The overarching goal of this research is to understand the relationship between MWF selection and membrane filtration system design. Toward this goal, the research has two specific objectives:

- Experimentally isolate MWF ingredients that cause productivity loss during membrane filtration recycling;
- Study the mechanisms of productivity loss during the membrane filtration recycling of MWFs;

These objectives are met by accomplishing the following four specific tasks:

1. Design and construct an experimental testbed to study the membrane filtration recycling of MWFs;
2. Assess membrane filtration productivity during MWF recycling and isolate the contribution of individual MWF ingredients to productivity loss through experimentation;
3. Understand the mechanisms of productivity loss during MWF recycling;

4. Identify the chemical characteristics of MWF ingredients that influence the mechanisms of productivity loss during MWF recycling;

1.4.2 Scope of Research

The productivity of the membrane filtration process can be lowered either by the uncontaminated MWF or by contaminants later introduced at the machine tool. A MWF containing contaminants typically will have lower productivity than the same MWF without contaminants. However, there is evidence in the literature that MWF chemistry, for example, the presence of certain functional additives, can alone cause a significant amount of productivity loss. Therefore, this research examines an uncontaminated MWF to reveal and understand the baseline issues that determine the maximum achievable productivity of the recycling process for a given MWF/membrane combination.

The MWF investigated during this research is a fully formulated synthetic MWF. The formulation contains representatives from the spectrum of ingredients used in synthetic formulations such as lubricant additives, defoamers, chelating agents, and corrosion inhibitors. The specific chemistry selected is considered to be a general representative of MWF formulations widely used in the machine tool industry. The composition of the MWF will be discussed in Chapter 3.

The membrane filtration of this uncontaminated synthetic MWF is investigated using aluminum oxide (α-alumina) membranes. Despite their higher cost relative to polymeric membranes, α-alumina membranes were chosen for this research since they may hold significant performance advantages over organic membranes in the harsh environment of MWF systems. These include chemical and biological stability, ability to withstand vigorous and repeated cleaning procedures, and resistance to mechanical damage by machining particulate.

Microfiltration using a nominal pore-size of 0.2μm was chosen for this research. This pore-size was selected to provide a balance between a pore-size large enough to permit the transport of MWF ingredients and one small enough to retain bacteria (see Table 1.2) and most contaminant metal chips and oils.

1.4.3 Overview of Report

Chapter 2 provides an overview of the available literature describing membrane filtration in the application of MWF recycling. Previous research of MWF/membrane compatibility and contaminant removal using membrane filtration is described. Chapter 2 also discusses aspects of previous microbiology research relevant to microbial population growth in MWF systems. This includes empirical models describing microbial population growth and traditional forms of microbiological control used in the machine tool industry.

Chapter 3 describes the design and construction of the Membrane Filtration Hardware Testbed (MFHT) used in this research to investigate the interactions between MWFs and membrane filters. The testbed is used for an experimental investigation of uncontaminated synthetic MWF flux during microfiltration using 0.2μm aluminum oxide membranes. In addition to the flux of the full synthetic MWF formulation, the flux of each ingredient in the formulation is provided. These data are used to isolate the types of MWF ingredients that are responsible for productivity loss during the microfiltration process and that can be of concern when cleaning the membrane.

In Chapter 4, a mechanistic understanding of flux decline caused by the MWF investigated in Chapter 3 is pursued to help reveal the chemical characteristics of MWF specialty additives that contribute to membrane filtration productivity loss and that can contribute to residual effects that reduce flux between experiments. The chapter provides an overview of general mechanisms of productivity loss during microfiltration. Then, productivity data from Chapter 3 are used to propose the predominant mechanism of productivity loss for the uncontaminated synthetic MWF. The mechanism is verified directly using electron microscopy. Contributions of the individual MWF ingredients to flux decline are also verified using electron microscopy.

Chapter 5 investigates chemical characteristics of metalworking fluids that can influence the mechanism of productivity decline during microfiltration using aluminum oxide membranes. The family of polyoxyalkylene diblock copolymers comprised of ethylene oxide and propylene oxide are utilized for this purpose. These copolymers are commonly used as lubricant additives in metalworking fluids and possess several of the characteristics believed to contribute to flux decline observed during the microfiltration of synthetic MWFs. Therefore, this class of copolymers serves as a model for beginning to understand the relationship between metalworking fluid formulation and microfiltration flux. Specifically, relationships between ethylene oxide/propylene oxide ratio in the copolymer, acid modification of the copolymer, cleaning methods, solution conditions (e.g., pH and ionic strength), and flux are described.

Chapter 2

Literature Review

This chapter describes previous research of MWF recycling using membrane filtration, models that have been developed to describe microbial population growth, and the traditional control of microbial growth in MWF systems. Section 2.1 provides a brief overview of the membrane filtration technologies. Section 2.2 details previous compatibility studies, contaminant removal studies, and industrial case studies regarding the use of membrane filtration to recycle MWFs. Section 2.3 discusses equations that have been previously developed to describe microbial population growth and the traditional methodologies used to control microbial population growth in MWFs.

2.1. Membrane Filtration Technologies

A large number of industrial processes utilize membranes for the separation of mixtures. Ho and Sirkar et al. (1992) describe eight membrane separation processes in detail, including gas permeation, pervaporation, dialysis, electrodialysis, reverse osmosis (including nanofiltration), ultrafiltration, microfiltration, and emulsion liquid membrane separation. These technologies are briefly defined in Table 2.1.

Table 2.1. Common Membrane Separation Technologies (Ho and Sirkar et al., 1992).

Membrane Filtration Technology	Basic Concept
Ultrafiltration	Primarily a size exclusion-based pressure-driven separation process generally used to separate sugars, biomolecules, polymers, and colloids.
Microfiltration	Primarily a size exclusion-based pressure-driven separation process generally used to separate micron-sized particles from fluids.
Reverse Osmosis (including nanofiltration)	Separation of microsolutes (e.g., salts) from solvent (e.g., water) using high pressure.
Dialysis	Separation of microsolutes from solvent using concentration gradients.
Electrodialysis	Electrochemical separation process in which electrically charged membranes and an electrical potential difference are used to separate ionic species from an aqueous solution and other uncharged components.

The criteria to select among these technologies for a desired separation have been specified by Kesting (1985) and are summarized in Table 2.2.

Table 2.2. Factors Governing the Selection of a Membrane Filtration Technology for a Given Separation Application (Kesting, 1985).

- Separation goal
- Size of species retained
- Minor or major species of the feed solution transported through membrane
- Phase of feed and permeate streams
- Mechanism for transport/selectivity
- Driving force
- Nature of the species transported through the membrane (e.g., aqueous solvent or solution)

As discussed in Chapter 1, both ultrafiltration and microfiltration have been considered for application to MWF recycling in the machine tool industry. Although these technologies have different pore-sizes, they have several characteristics in common. They both separate aqueous mixtures using a sieving process and can operate at relatively low pressures (Vansant et al., 1994). Many of the same membrane materials and geometric configurations are used for both ultrafiltration and microfiltration membranes (Chenoweth et al., 1986).

Several comprehensive sources describe the transport mechanics and industrial applications of ultrafiltration and microfiltration (Cheryan, 1986; Ho and Sirkar et al., 1992; Rautenbach and Albrecht, 1989; Flinn et al., 1970; Bhave et al., 1991; Rushton, 1985; Vansant, 1994). Mulder (1991) has provided the characteristics of ultrafiltration and microfiltration summarized in Table 2.3.

Table 2.3. Characteristics of Ultrafiltration and Microfiltration (Mulder, 1991)

Characteristics	Ultrafiltration	Microfiltration
Thickness (approx.)	150 μm	10 - 150 μm
Pore Sizes (approx.)	1 - 100 nm	0.05 - 10 μm
Driving Force (pressure)	15-150 psi	0 - 30 psi
Separation Principle	Sieving mechanism	Sieving mechanism
Membrane Material	Polymeric or ceramic	Polymeric or ceramic
Main Applications	– Dairy (milk, whey, cheese making) – Food (potato starch and proteins) – Manufacturing (wastewater treatment, electropaint recovery) – Textile (indigo) – Pharmaceutical (enzymes and antibiotics)	– Analytical applications – Ultrapure water (semiconductors) – Cell harvesting and membrane bioreactor (biotechnology) – Clarification (beverages) – Sterilization (food, pharmaceuticals) – Plasmapheresis (medical)

Membrane fouling due to deposition and accumulation of macromolecules, colloids, and particles onto and into the membrane is the major concern during the membrane filtration separation process (Belfort et al., 1994; Cheryan, 1986). Fouling results in flux decline and productivity loss, and thus a primary objective of membrane filtration research is to better understand the mechanisms of fouling that may be applicable during a given separation process. Understanding fouling mechanisms can lead to process improvements that improve the performance of membrane filtration processes. Belfort et al. (1994) provides a comprehensive review of microfiltration flux decline mechanisms for characteristic solutions and particle suspensions. Cheryan (1986) provides a similar review for ultrafiltration. Chapter 4 discusses the mechanisms of flux decline most relevant to MWF recycling applications.

2.2. Membrane Filtration of MWFs

Ultrafiltration has been utilized in the machine tool industry as a means to remove the bulk of oil and oxygen demanding ingredients from MWFs prior to disposal (ILMA, 1990; Byers et al., 1994; Cheryan, 1986). When utilizing ultrafiltration for this purpose, membrane removal of MWF ingredients is desired to the largest degree possible. The permeate from the process is suitable for disposal. The retentate from the process has a much higher concentration of oil and oxygen demanding ingredients in a volume typically 3-5% of the original MWF volume disposed. The concentrated waste is less expensive to treat and is a candidate for incineration.

In contrast to the use of ultrafiltration as a pre-treatment to MWF disposal, using membrane filtration to recycle MWFs back to metalworking operations requires the selective separation of particulate, oil, and bacteria without removing any of the MWF ingredients. The related problem of oil and grease removal from alkaline cleaners used in parts washing machines has recently been proven feasible and economical in several industrial applications (Lindsey et al., 1995; Rajagopalan et al., 1998b; Lindsey and Montemurro, 1994; Barkan, 1997; Lindsey, 1997). However, little has been done at the academic level to remove the underlying sources of uncertainty that preclude wide-spread industrial application of membrane filtration for MWF recycling applications. Fundamental research is lacking to guide selection of MWFs, membrane materials, membrane configurations, and membrane pore-sizes during manufacturing process design for membrane filtration recycling.

The available studies of MWF recycling using membrane filtration can be put into three categories: chemical compatibility and productivity studies, contaminant removal studies, and industrial pilot studies. Chemical compatibility and productivity studies describe chemical characteristics of MWF ingredients that lead to reduced flux and increased membrane retention. Contaminant removal studies discuss contaminant characteristics that lead to reduced flux and increased membrane retention. Pilot studies describe chemical compatibility, productivity, and contaminant removal issues in a specific industrial application.

The following sections review the previous literature related to recycling MWFs using membrane filtration. Section 2.3.1 describes compatibility and productivity research. Section 2.3.2 discusses contaminant removal research. Section 2.3.3 describes industrial pilot studies.

2.2.1. Compatibility and Productivity Studies

Mahdi and Sköld (1990) contributed the first documented research in the literature describing the application of membrane filtration for MWF recycling. In this work, specific MWF ingredients and different types of membranes were investigated for compatibility and productivity. Three ultrafiltration membranes with a molecular weight cut off (MWCO) of 20,000 daltons were investigated for flux and retention of straight chain carboxylic acids used as corrosion inhibitors in synthetic MWFs. It was discovered for all three membranes that increasing the molecular chain length from 9 to 13 carbon atoms lowered flux and increased rejection. Fluoropolymer membranes were shown to have the highest flux when compared with cellulose acetate and polysulfone membranes. Since fluoropolymer membranes are also more robust to variations in pH, temperature, and different chemicals, these membranes were considered optimal in this application and selected for continued research.

Using the fluoropolymer membranes, the relationship between MWF ingredient concentration, flux, and membrane retention was then investigated. Specifically, the concentration of dodecanoic acid (a 12-carbon chain carboxylic acid used as a corrosion inhibitor) was raised from 0.25% to 2.0% in aqueous solution while measuring flux and retention. It was observed that below the critical micelle concentration (CMC) of the solution (the concentration at which the acid forms stable aggregate units containing multiple molecules, see Hunter, 1986), flux remained high and rejection of the acid did not occur. At concentrations above the CMC, flux decreased substantially and rejection was observed. In other words, once the carboxylic acid was introduced at concentrations large enough to permit self-aggregation, the dodecanoic acid became less compatible with the membrane. Thus, it was concluded that size-based characteristics play a strong role in determining the compatibility and productivity of MWF ingredients when using 20,000 MWCO fluoropolymer membranes.

The study of flux and rejection was also extended to hydrodynamic lubricant additives found in MWFs (Mahdi and Sköld, 1990). The lubricant additives investigated were from the family of polyoxyalkylene glycols that will be described in greater detail in Chapter 5. For these lubricant additives, flux was found to decrease corresponding to increased molecular weight and concentration. In addition, flux was independent of chemical composition. These data suggested once again that size-based interactions have a significant effect on the retention and flux characteristics of MWF ingredients when using 20,000 MWCO fluoropolymer membranes.

For the same polyoxyalkylene glycol lubricant additives, the effect of increased temperature was investigated for its impact on ultrafiltration flux and retention. These lubricant additives exhibit a characteristic temperature called the cloud point that corresponds to the temperature at which the lubricant will become insoluble in water and form a separate phase. The cloud point is important in metalworking applications since it serves as an activation temperature above which a lubricant additive leaves solution and forms a boundary lubrication film between contacting metal surfaces (this characteristic is termed inverse solubility). During filtration research with these inversely soluble lubricants using the 20,000 MWCO fluoropolymer membranes, maximum flux was observed at temperatures below the cloud point of the additives. Membrane retention of the lubricant additives was not observed at temperatures below the cloud point. As the temperature was raised above the cloud point, flux was reduced significantly and retention of the lubricant additives was observed. As the temperature was raised further above the cloud point, rejection continued to increase, but flux also increased. The flux increase with temperature above the cloud point was presumably due to reduced viscosity. The observations indicated that membrane filtration process temperatures are important to consider, since productivity and compatibility of MWF lubricants can fall significantly at temperatures above the cloud point. Otherwise productivity can be improved at elevated temperatures due to reduced viscosity.

More recently, the investigation of synthetic MWF formulations containing inversely soluble lubricants was expanded (Misra and Sköld, 1999). The investigation included different synthetic MWF base formulations containing alkanolamines (used as pH buffers and corrosion inhibitors), phosphate esters (used to improve the wetting ability of MWF formulations), and 9-10 carbon chain length carboxylic acids (used as corrosion inhibitors). An inversely soluble lubricating agent, polypropylene glycol (average molecular weight 1800), was added to the base MWF formulations at variable concentrations. Polymeric membranes with pore sizes in both the ultrafiltration and microfiltration range were investigated.

At normal temperatures (20-25°C), the polypropylene glycol lubricant additive was retained by the smallest pore-size membrane (MWCO 10,000), but permeated through the larger MWCO membranes. This supported the previous conclusions that size-based characteristics of MWF ingredients have a significant impact on flux and retention during low MWCO ultrafiltration. The same 10,000 MWCO membrane also retained a significant proportion of alkanolamine with molecular weight approximately 500. It was proposed that the highly branched chemical structure of the alkanolamine was responsible for its retention by a membrane with pore size an order of magnitude larger (MWCO is generally measured using linear molecules). Therefore, in addition to size, the authors proposed that the conformation (or spatial molecular arrangement) of MWF ingredient molecules also plays an important role in determining membrane compatibility during ultrafiltration of MWF ingredients.

The cloud point of the polypropylene glycol was also investigated in this study for its role in causing rejection of other MWF ingredients (Misra and Sköld, 1999). It was found that above the cloud point of the polypropylene glycol, certain ingredients of the MWF that ordinarily permeate through the membrane were retained by the membrane along with the polypropylene glycol. This effect, termed cosolubilization, was observed for polyoxyalkylene glycols (similar to those used in Mahdi and Sköld, 1990) in the presence of the polypropylene glycol. Since both these ingredients are lubricants used in synthetic MWFs, the authors proposed to use the cosolubilization phenomenon to formulate synthetic MWFs with greater levels of lubricity than could be offered by formulations containing either lubricant alone. However, no data was provided to support the hypothesized synergistic effects of cosolubilization on improved lubricity during metalworking operations. Regardless of possible benefits of cosolubilization to the manufacturing process, these observations again supported the conclusions of earlier work that cloud point must be considered during membrane filtration process design. Cosoulbilization can cause the retention of ingredients that otherwise would not be retained by the membrane.

Mahdi and Sköld (1991a) investigated three commercially available MWFs for their compatibility with membrane filtration using 20,000 MWCO membranes. The first MWF, an oil-water emulsion, was found to be incompatible the membranes. For the other two MWFs, it was found that water flux for the membranes could not be completely recovered after filtration and cleaning. In fact, when contaminants were present in the MWF to be filtered, water flux for the membranes could not be restored to within 50% of its original value after cleaning. The source of these observed residual effects causing flux-erosion in subsequent experiments was not investigated. These data served to raise doubt regarding the robustness of the 20,000 MWCO fluoropolymer membranes during industrial applications.

2.2.2 Contaminant Studies

Mahdi and Sköld (1991b) showed that for a model synthetic MWF 1) contaminant oils can be removed using 20,000 MWCO fluoropolymer membranes, 2) frequent membrane cleaning can improve the productivity of the recycling process significantly, and 3) a two process-tank system design may be advantageous when implementing membrane filtration for microbial control. Regarding the last point, the paper claimed that single-tank membrane filtration systems designed to recycle permeate back into the contaminated fluid tank are inefficient for larger system volumes and inadequate if the objective is to keep the numbers of microorganisms low. Evidence for this claim was not provided, but a two process-tank design was proposed as an improvement and was modeled for its effectiveness in maintaining microbial populations below a specified level. The microbial model used to describe the performance of the two-tank design assumed continuous exponential growth of the microorganisms and perfect membrane removal. The concentration of micrroorganisms in the process tank, the concentration of growth substrate, and the impact of non-exponential microbial growth were not considered in the model. It was concluded that control of microbial growth depended on the switching frequency between the two process tanks. The relationship between other membrane filtration system variables (e.g., flux and membrane rejection) and microbial control were not investigated.

Mahdi and Sköld (1991a) investigated contaminant removal from a commercially available MWF. The removal of contaminants from this MWF was performed using a fluorpolymer ultrafiltration membrane (20,000 MWCO), a polyvinylidene fluoride ultrafiltration membrane (pore-size not provided), and a polypropylene microfiltration membrane (0.2-0.8 μm pore-size). The sample MWF was collected from a field-study and was known to contain elevated levels of bacteria, fungi, and mineral oil. It was found that all three membranes completely removed the contaminants. Of the three membranes, the microfiltration membrane exhibited the highest flux.

Sato et al. (1996) performed a more detailed investigation of MWF contaminant removal using membranes. This study focused on the removal of ceramic chips from grinding fluids. The motivation for the research was the detrimental impact that ceramic chips have on surface finish during grinding operations. Ceramic chips are difficult to remove from grinding fluids by other means since they possess low specific gravity, have small diameter, and are nonmagnetic.

The objective of the research was to assess trends in flux through 1μm pore-size polymeric microfitlration membranes as the grain-size and concentration of the chips were altered. Chip sizes investigated ranged from 2μm to 8μm. Chip concentrations ranged from 3 grams/liter to 20 grams/liter. The grinding fluid used was deionized water without any additives. Since a formulated MWF was not used, the research naturally avoided the issues of MWF chemistry that can strongly influence membrane filtration flux.

The research showed that ceramic chip removal was readily achieved using microfiltration. It was revealed that for a constant chip concentration, flux decreases with decreasing grain size due to increasing resistance of a layer (termed a cake layer) of rejected chips that forms at the surface of the membrane. Cake-layer resistance increases non-linearly as grain-size is reduced. Regardless of particle grain-size or concentration, flux increases substantially when turbulence promoters are placed in the flow of the chip-laden MWF at the entrance to the membrane. Turbulence promoters discourage the formation of chip layers at the membrane surface. Experimental evidence revealed that the selection of turbulence promoter should not be performed arbitrarily, as an optimal blockage ratio (defined as the ratio of turbulence promoter height to the diameter of the membrane channel) can exist.

Sato et al. (1996) also compared the permeation resistance caused by three sources in the membrane filtration system: the membrane itself, the cake layer formed by chips at the membrane surface, and the pore-plugging caused by the lodging of ceramic chips inside membrane pores during the chip-removal process. It was found that pore-plugging due to the physical lodging of ceramic chips inside pores was negligible compared to the other two sources of membrane resistance. Because of this, the membranes could be cleaned and reused. It was also found that as chip sizes decreased the proportion of the total permeation resistance attributable to the cake layer increased significantly relative to the membrane resistance.

2.2.3 Pilot Investigations

Sköld (1991) described the industrial application of a model MWF that was optimized for membrane filtration based on results from the component study described in Mahdi and Sköld (1990). The model synthetic MWF used in this study was designed to inhibit the emulsification of leak oils and to have a high critical micelle concentration to avoid surfactant aggregates that would be retained by the membrane. During this seven-week study, approximately half of the MWF volume being used in a 4-axis grinding center (100 liters) was removed from the system each week and replaced with MWF that was treated during the previous week using a 20,000 MWCO fluoropolymer membrane. Before the ultrafiltration process was conducted, the MWF was first pre-filtered with a relatively coarse paper filter. This presumably improved the productivity of the process, but the impact of pre-filtration was not discussed.

The model MWF used in this study differed from synthetics commonly used in practice because it was formulated at pH=7 (instead of pH approximately equal to 9) and because it did not contain biocides. The neutral pH and absence of biocides were the essential elements of the claim that the health hazards associated with this MWF were lower than those typically found in other MWFs. However, the use of benzotriazole in the formulation may contradict this claim. Benzotriazole is listed by the Handbook of Toxic and Hazardous Chemicals and Carcinogens as a severe respiratory hazard (Sittig, 1985). Justification for the use of benzotriazole was not provided.

The model MWF formulation did not contain a defoaming agent. Instead, the defoamer was added separately at the machine tool because it was retained by the membrane. Adding the defoaming agent at the machine tool proved successful in controlling foaming and demonstrated the feasibility of metering specific ingredients into the MWF that may be retained by the membrane. However, it was suggested that the defoamer retention also caused substantial retention of an extreme pressure lubricant additive used in the formulation. This was proposed but not proven to be due to cosolubilization.

This study offered data describing the change in concentration of contaminant electrolytes over time during the ultrafiltration process (Sköld, 1991). Contaminant electrolytes found in MWFs include calcium, magnesium, and chloride. Calcium and magnesium can cause excessive soap formation that can destabilize MWFs. Chloride can promote corrosion of parts. The concentration of these ions was shown to be stable over time during ultrafiltration, but the role of the ultrafiltration process in controlling these ions was not clearly shown. The data suggested that the stable concentrations of these electrolytes followed from the use of deionized water for making up MWF losses instead of the tap water that was used in the original loading of the system.

The study also offered data of microbial concentrations over the seven-week period. The infrequent and batch-wise treatment of the MWF precluded the assessment of the microbial control capabilities offered by ultrafiltration in the absence of biocides. Microbial growth was observed to increase exponentially through the first three days of field-testing, then remained stationary at a concentration of approximately 10^7 CFU per milliliter (colony forming units per milliliter, widely used as a surrogate for actual number of microorganisms per milliliter) through the remainder of the study. This concentration of microorganisms is several orders of magnitude higher than the concentration of microorganisms that would be expected from a well-controlled MWF system, but the population was stable and did not increase to higher levels (e.g., 10^9 CFU/ml) that have been observed in poorly maintained MWF systems. The author noted that the stable bacterial population was not due to the ultrafiltration process. Presumably, it was due to the chemical composition of the MWF and low contaminant levels.

Rajagopalan et al. (1998a) described the use of 0.1μm aluminum oxide microfiltration membranes for removing sub-micron size aluminum chips from a grinding fluid used during polishing operations. For the MWF tested, no irreversible fouling was observed and the membrane was easily cleaned using acid washing. It was found beneficial during the microfiltration process to throttle the permeate flow deliberately to impose a back-pressure on the membrane that served to retard the formation of a cake layer of aluminum chips. The productivity loss from the reduced filtration rate caused by throttling was offset by longer intervals between membrane cleanings. The recycled MWF produced during using the aluminum oxide microfiltration membranes was reusable and contained no suspended solids that might damage polished surfaces. After three cycles of use, 1% of the fresh MWF concentrate was added to the coolant to replace surfactant additives in the formulation that were removed by the membrane over time. An economic analysis was performed that concluded significant cost savings were achievable over the current practice if membrane filtration recycling were performed throughout the facility.

2.3. Summary

Membrane filtration is capable of removing chips, bacteria, and oil from MWFs that are the cause of frequent MWF disposal and growing health concerns. Only a handful of studies have been conducted that have been directed toward understanding the fundamental compatibility of MWFs and membrane filters. These studies have focused on ultrafiltration membranes made of organic polymers. It has been shown that for 20,000 MWCO ultrafiltration, size and molecular conformation of MWF ingredients determine flux and retention characteristics. Process temperatures, cosolubilization, and circulation system design can impact the technical feasibility and economics of the process. For a model MWF specifically designed for use with ultrafiltration membranes, it has been shown that it is possible to remove MWF contaminants without disrupting the formulation. However, questions were also raised regarding polymer membrane robustness to the chemicals found in MWFs and the manufacturing environment in general.

Aluminum oxide microfiltration membranes were shown to remove contaminants from a commercially available MWF during an industrial application. In addition, aluminum oxide membranes proved robust to the machine tool environment and to cleaning chemicals required to periodically restore membrane flux. However, the chemical characteristics of MWFs that cause productivity loss during microfiltration using aluminum oxide membranes are not currently understood. Understanding these chemical characteristics is required to select MWFs that are amenable to microfiltration using aluminum oxide membranes without extensive trial-and-error testing during system design. Chapters 3-5 will discuss synthetic MWF ingredients that cause productivity decline during microfiltration using aluminum oxide membranes.

Chapter 3

Experimental Investigation of Synthetic MWF Ingredients that Cause Flux Decline During Microfiltration Using Aluminum Oxide Membranes

Chapter 3 describes an experimental investigation of synthetic MWF ingredients that cause flux decline during microfiltration using aluminum oxide membranes. Section 3.1 describes the experimental testbed developed and the procedure and materials used to collect MF productivity data. Section 3.2 reports productivity observations for a synthetic MWF in a ceramic membrane. Sections 3.3 and 3.4 identify the ingredients of the synthetic MWF responsible for the productivity decline witnessed in Section 3.2.

3.1. Testbed, Materials, and Procedure

3.1.1. Membrane Filtration Hardware Testbed

The first objective of this research was to construct an experimental testbed with the ability to acquire microfiltration research data in flexible operating environments. From the engineering perspective, the membrane filtration response variables of greatest interest are (1) permeate flux, (2) energy consumption, (3) disruption of the chemical integrity of the process fluid, and (4) contaminant removal. Permeate flux and energy consumption relate to the economic viability of the MF process. Contaminant removal and chemical depletion relate to the performance of the process.

The Membrane Filtration Hardware Testbed (MFHT) was designed and constructed to research these variables. A schematic of the MFHT is provided in Figure 3.1. The MFHT is mobile to facilitate use in field operations and to assess contamination conditions that cannot be adequately simulated in the laboratory. A computer control and data acquisition system facilitates laboratory experimentation and remote operation.

The reconfigurable design of the testbed permits modification to run membranes of a variety of sizes, geometries, and materials. The MFHT is currently configured to house ceramic membranes of the same configuration and material used in larger ceramic membrane systems employed in industrial applications.

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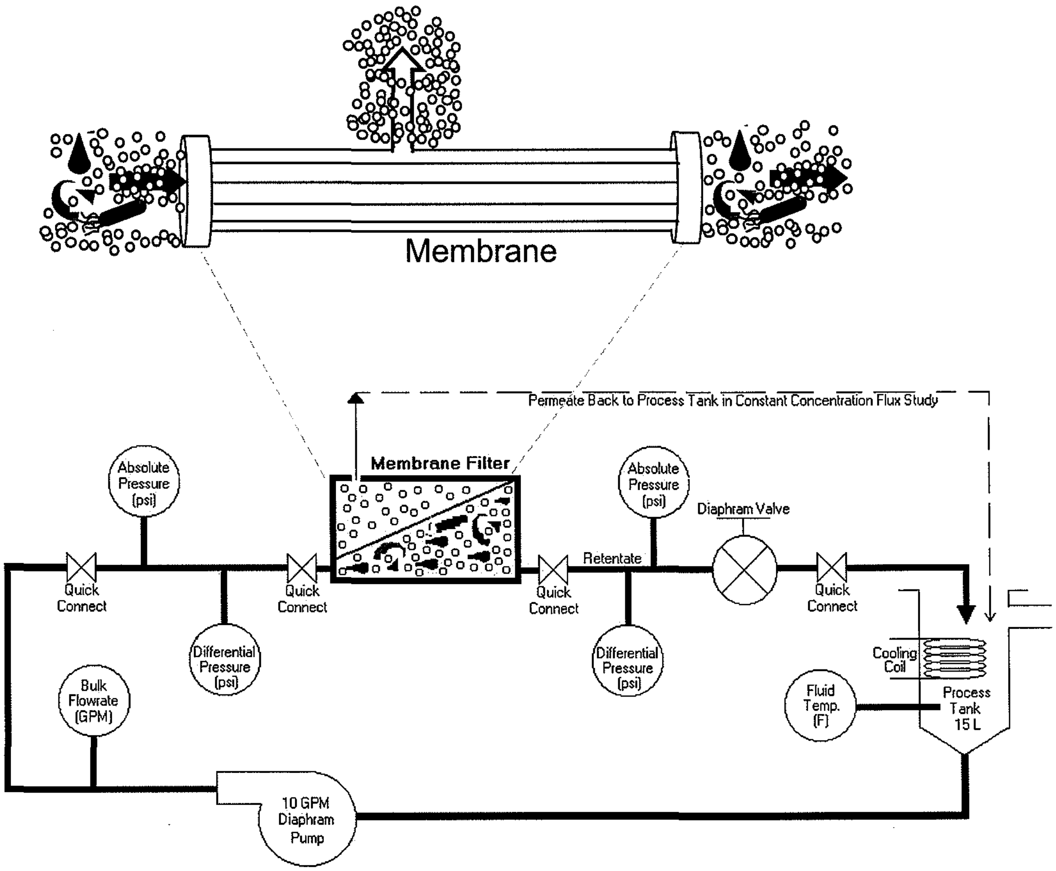


Figure 3.1. Membrane filtration concept and schematic for Membrane Filtration Hardware Testbed (MFHT). The testbed is designed to assess membrane filters and metalworking fluids for their compatibility in recycling applications.

computer control and data acquisition system facilitates laboratory experimentation and remote operation.

3.1.2. Materials

Two ceramic membranes provided by Cercor Separations (Corning, NY) were used in this study. The two membranes were labeled A and C. Both membranes were produced from the same manufacturing process and consist of alpha-phase aluminum oxide (α-alumina) with a nominal pore-size rated at 0.2 μm. Despite their higher cost, ceramic membranes were chosen for this research since they may hold significant performance advantages over organic membranes in the MWF recycling application. These include chemical and biological stability, ability to withstand harsh cleaning procedures, and resistance to mechanical damage by machining particulate.

A total of 28 experiments were conducted with Membrane A. These experiments were labeled A1-A28. Experiments A1-A9 observed the flux vs. time and pressure for a synthetic MWF. Experiments A10-A27 assessed the flux-eroding contributions of individual ingredients comprising the synthetic MWF. Experiment A28 again observed the flux vs. time of the synthetic fluid. A total of 9 experiments were conducted with Membrane C. These experiments were labeled C1-C9. They served as baseline data for MWF ingredient fluxes in a new membrane. The full list of experiments and their benchmark water fluxes is provided in Table 3.1.

Table 3.1. Experimental Titles, Run Order, and Associated Benchmark Water Fluxes.

Experiment Number	Avg. 40psi H_2O Flux (LMH)	Experiment Title
A1-A6	560	Full synthetic MWF flux vs. time and pressure
A7	574	Full synthetic flux vs. time under both constant and variable pressure
A8	563	Full synthetic flux vs. time with pH artificially raised from 9.2 to approx. 12
A9	550	Full synthetic flux vs. time after minor reformulation
A10-A12	561	Flux before/after lubricant and defoamer addition to base fluid + 2 biocides
A13-A14	552	Biocide flux vs. time, flowrate, and dilution
A15	562	Base fluid flux vs. time
A16	563	Biocide flux at low pH vs. time
A17-A19	555	Base fluid flux vs. time
A20	570	Lubricant additive flux vs. time, flowrate, and dilution
A21	566	Defoamer flux vs. time, flowrate, and dilution
A22-A27	574	Base fluid (and single ingredient) flux vs. time, flowrate, and dilution
A27	577	Base fluid flux vs. pressure
A28	552	Full synthetic MWF flux vs. time, flowrate, and dilution
C1	680	Flux vs. water flux and pH (5-12)
C2-C7	673	Base fluid (and single ingredient) flux vs. time, flowrate, and dilution
C7	669	Base fluid flux vs. pressure

The MWF used in this study was a water-soluble synthetic fluid provided by IRMCO Advanced Lubricant Technologies (Evanston, IL). Although the precise fluid formulation is confidential, the generalized formulation is provided in Table 3.2.

Table 3.2. Generalized Synthetic MWF Formulation.

Component	Concentration (%)
Water	50 - 80
Triethanolamine	5 - 20
Amine	5 - 20
Lubricant	<5
Defoamer	<0.5
Biocides (1-3	<2
Chelating agent	<2
pH Buffer	<5
Wetting agent	<1

This fluid is considered exemplary of a fully functional synthetic MWF capable of use in a variety of operations. It has a formulation similar to typical synthetic MWFs, but also has several specialty additives that improve its performance and extend its life. The concentrate formulation was diluted to 5% in all experiments.

3.1.3. Experimental Procedure

Data Collection. Filtration rate data was obtained using the MFHT by collecting MWF permeate in a graduated cylinder and measuring the time to obtain a certain volume of fluid (usually 250 mL). This measured filtration rate (liters/hour) was divided by the membrane surface area in contact with the fluid (m^2) to arrive at permeate flux expressed as LMH (liters/m^2/hour). For the membranes used in this study, the surface area was equal to 0.14 m^2. The permeate was returned to the process tank to maintain constant concentration of MWF during the experiments.

In addition to measuring flux as a function of pressure, the impact of cross-flow velocity and dilution on flux was also measured. The impact of cross-flow velocity was assessed by altering the flowrate of the fluid through the membrane, since the cross-flow velocity and flowrate are proportional by a factor equal to the inverse of the membrane channel area ($4mm^2$). Flowrate alterations were conducted in the range of 0.4 to 15 liters per minute over a 30-minute period after the establishment of a steady-state flux. This corresponded to a cross-flow velocity variation of 0.028 to 1.05 m/s. Flowrates were held constant for ten minutes before recording data. After flowrate variation, a dilution analysis immediately followed. The dilution analysis was conducted by adding 4 liters of water every five minutes over a 60-minute period to the process tank. This served to reduce the concentration of the MWF ingredients approximately five-fold. Flux measurements were recorded every five minutes.

Operating Parameter Control. Under the conditions of flow described above, flow inside the membrane pores is laminar, and flux is inversely proportional to fluid viscosity (Rushton, 1985). Since it was not the intention of this study to further study this relationship, the fluid temperature was controlled in these experiments at 68°F±2°F and temperature was measured to 0.1°F. Within that range, viscosity corrections were used to effectively standardize the fluid temperature at 68°F. Accuracy of the pressure gauges was ±0.5psi, and unless otherwise stated the operating pressure used in experimentation was 40psi. Accuracy of flowrate measurements was better than 0.1gpm, and flowrate was held to 9.5 liters per minute for all experiments unless otherwise stated. The water used in experimentation was filtered to remove ions and contaminants. In general, the water resistance was at least 18 MΩ.

Cleaning Procedure. A ninety-minute cleaning procedure was conducted after each experiment. To determine if the membrane was clean, the flux of deionized water (pH=5.5) was measured and compared to the water flux obtained when the membrane was new. If the water flux was at that benchmark level or higher, the membrane was considered clean. The cleaning solution contained 8 liters of water at 150°F, 50mL of a 1% solution of KochKleen detergent (Koch Membrane Systems, Wilmington, MA), and Ultrasil 11 (Klenzade, St.Paul, MN) added until the pH of the solution reached 12.

Water Flux. Experiments A1 and C1 measured the water flux as a function of pressure. It was observed that both membranes exhibited a linear trend for flux vs. pressure, but Membrane C has a benchmark water flux approximately 10% higher than that for Membrane A. This difference is an indication of manufacturing variation, and is known from previous experience to be typical for these membranes. Comparisons between data acquired from Membranes A and C in Section 3.4 are normalized to pre-experimental water flux to remove this source of variation from consideration.

3.2. Synthetic MWF Flux Data

This section describes flux data for the synthetic MWF. Flux is measured as a function of time, pressure, flowrate, and dilution. The section concludes with a brief description of MWF flux after minor reformulation of the synthetic MWF.

Experiments A1-A6 observed flux vs. time data for the synthetic fluid at a 5% concentration in water at several pressures, each for 150 minutes. The flux measurements for each of the six experiments were taken at 5-minute intervals for the first 90 minutes and 15-minute intervals for the remaining 60 minutes. The experiments were conducted in randomized order, and the experimental error based upon an independent analysis was less than 5%. The flux data are provided in Figure 3.2.

Figure 3.2 shows that at 5 minutes no flux measurement was above 300 LMH. From this point, it is seen that all flux measurements decreased over the first 60 minutes with incremental flux decline decreasing over that period before reaching a steady condition of slight flux decline. For comparisons between the fluxes in Figure 3.2, the steady-state condition is defined by time invariance of flux data between experiments. In Figure 3.2, this condition is held after 90 minutes. Prior to that time, it is observed that the slope of flux decline increases with pressure. The average fluxes at 150 minutes for 40psi, 25psi, and 15psi are 131 LMH, 115 LMH, and 74 LMH, respectively.

Since the average water flux at 40psi was approximately 560 LMH for Membrane A, it is interesting to note that the flux drops 75% for this fluid despite a lack of contamination in the fluid. This means that to achieve the same filtration rate of

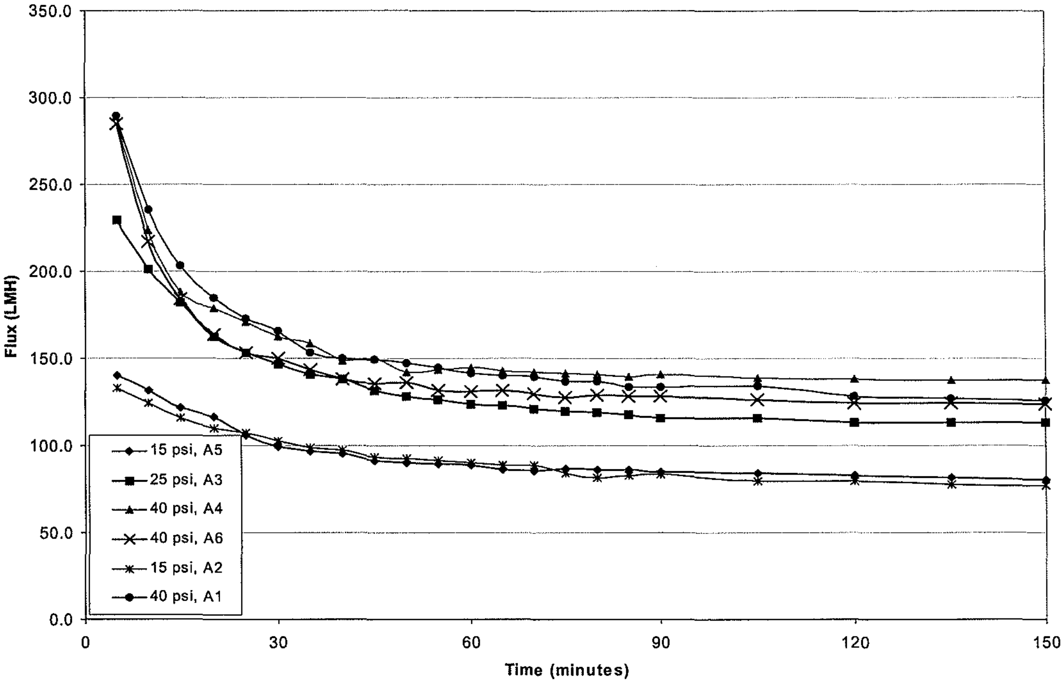


Figure 3.2. Flux vs. time of synthetic MWF in ceramic membrane at 15, 25, and 40psi (A1-A6).

water, approximately four times more membrane area would be required to filter this uncontaminated synthetic MWF. Since the viscosity of water at 25°C is 0.89 cSt and the viscosity of the synthetic MWF at 25°C is 0.95 cSt, the magnitude of difference between the flux of water and the flux of the synthetic fluid is not attributable to viscosity alone (Dean, 1985).

Experiments C1 and A8 were conducted to determine if the difference between the flux of the synthetic MWF and water could be explained by pH alone. Experiment C1 increased the pH of water from 5 to 12 by sodium hydroxide additions. Experiment A8 increased the pH of the synthetic MWF from 9 to 12 using sodium hydroxide additions. The experiments found that flux for both water and the MWF was independent of pH, within the range of experimental error. Therefore, differences between water flux and synthetic MWF flux cannot be attributed to variations in pH independent of the presence of MWF ingredients in the system.

Several other tests were designed to explore the nature of flux-erosion in the uncontaminated MWF. The effects of cross-flow velocity (i.e., flowrate) and dilution on steady-state flux were studied for the synthetic MWF in Experiment A28. After achieving steady-state, the procedures described in Section 3.3 were followed. It was observed that variations in flowrate between 0.4 and 15 liters per minute did not impact the flux significantly. Following the flowrate variation, a dilution sequence was conducted to reduce the concentration of MWF from 5% to 1%. The dilution had no significant impact on steady-state flux.

Experiment A9 measured flux vs. time for the synthetic fluid after slight modification of the formulation (less than 0.3%). Although it was previously observed that dilution will not improve flux after a steady-state has been established, Experiment A9 showed that initially reducing the concentration of some active ingredients within the manufacturer's specifications increased flux over 45%. This observation suggests that optimizing MWF formulations for ceramic membrane filtration will require: (1) the use of flux-eroding ingredients at concentrations no higher than that actually required by the metalworking process, and (2) the search for substitutes for flux-eroding MWF ingredients. To begin that process, the next two sections provide analysis of the ingredients responsible for the flux decline.

3.3. Specialty Additive Flux Data

Each chemical ingredient of the synthetic fluid was categorized as either part of the base fluid or as a specialty additive. The lubricant additive, defoamer, and three biocides were considered the specialty additives. The rest of the fluid, called the base fluid, included a corrosion inhibitor, a general lubricant, a pH buffer, a wetting agent, and a chelating agent. This section provides flux data for the specialty additives.

3.3.1. Flux of Lubricant Additive and Defoamer

Experiments A20 and A21 observed the impact of the lubricant additive and defoamer respectively on flux. Flux measurements were taken in 5-minute intervals for 70 minutes. Pressure was held at 40psi for both experiments. The concentration for the lubricant additive was 0.25%, and the concentration for the defoamer was 0.025%. Figure 3.3 shows the experimental results for the lubricant additive (A20) and defoamer (A21) flux. The initial water flux for each experiment corresponds to that at time zero. The steady-state flux for the lubricant additive was approximately 120 LMH, while that for the defoamer was approximately 410 LMH. Both flux declines are significant, with the defoamer having a larger flux-decline on a concentration basis. However, at typical MWF concentrations the lubricant additive is a more potent flux-eroding ingredient. Flowrate variations and MWF dilution performed as described in Section 3.3 after 70 minutes did not alter the steady-state fluxes.

3.3.2. Biocide Flux

Experiments C8 and C9 revealed the independent impacts of addition of Biocide 1 (0.5%) and Biocide 2 (0.5%) to water. In both experiments, Biocide 3 was added later to determine its overall impact in concert with the other two biocides. The results

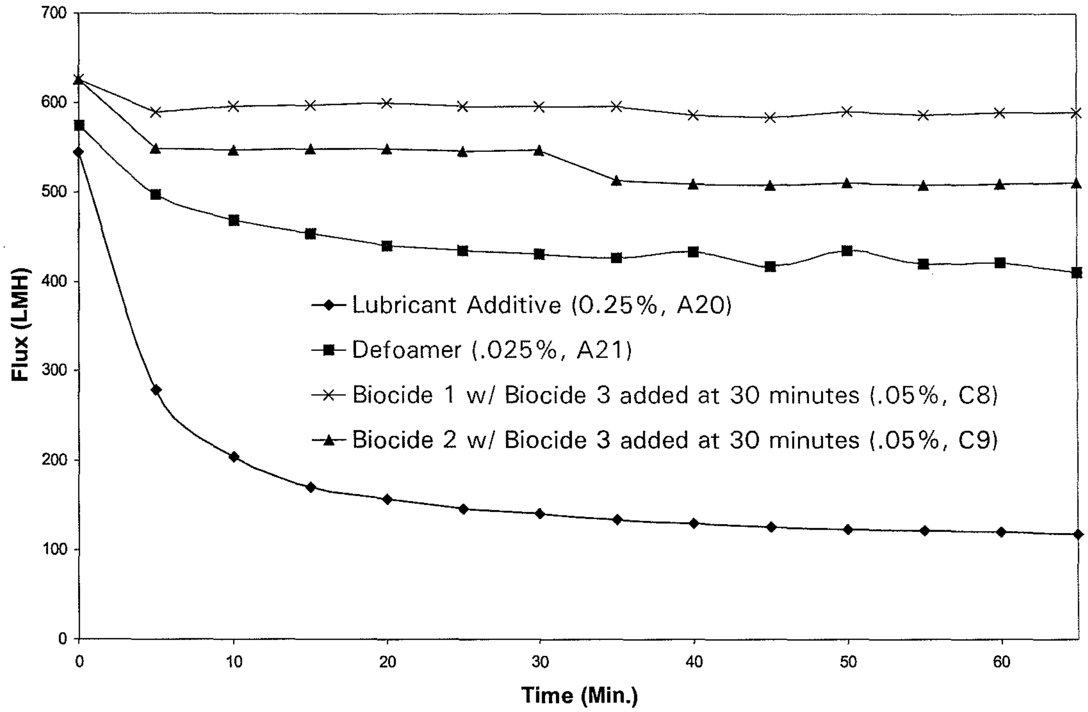


Figure 3.3. Specialty additive flux vs. time. Flux measured at 40psi.

shown in Figure 3.3 indicate that Biocide 1 had a flux approximately 5% lower than water flux and the addition of Biocide 3 did not further lower flux. Biocide 2 reduced flux 12% relative to water flux and the addition of Biocide 3 reduced flux another 6%. A flowrate and dilution study showed no significant impact on steady-state flux. These data show that biocides can reduce flux during microfiltration, and the degree of impact is dependent on the biocide chemistry.

3.3.3. Lubricant Additive and Defoamer Impact on Base Fluid/Biocide Flux

Experiments A10, A11, and A12 demonstrated the impact of lubricant additive and defoamer addition on the flux of a mixture of the base fluid and two biocides. In these experiments, the lubricant additive and defoamer were used at 0.25% and 0.025% respectively, and pressure was held constant at 40psi. Flux was measured in 5-minute intervals throughout all three experiments for 260 minutes. In all three experiments, the flux of the same base fluid/biocide mixture was measured for the first 65 minutes. In experiments A10 and A12, the lubricant was added to the MWF mixture at 65 minutes and the defoamer was added at 150 minutes. In experiment A11, they were added in reverse order.

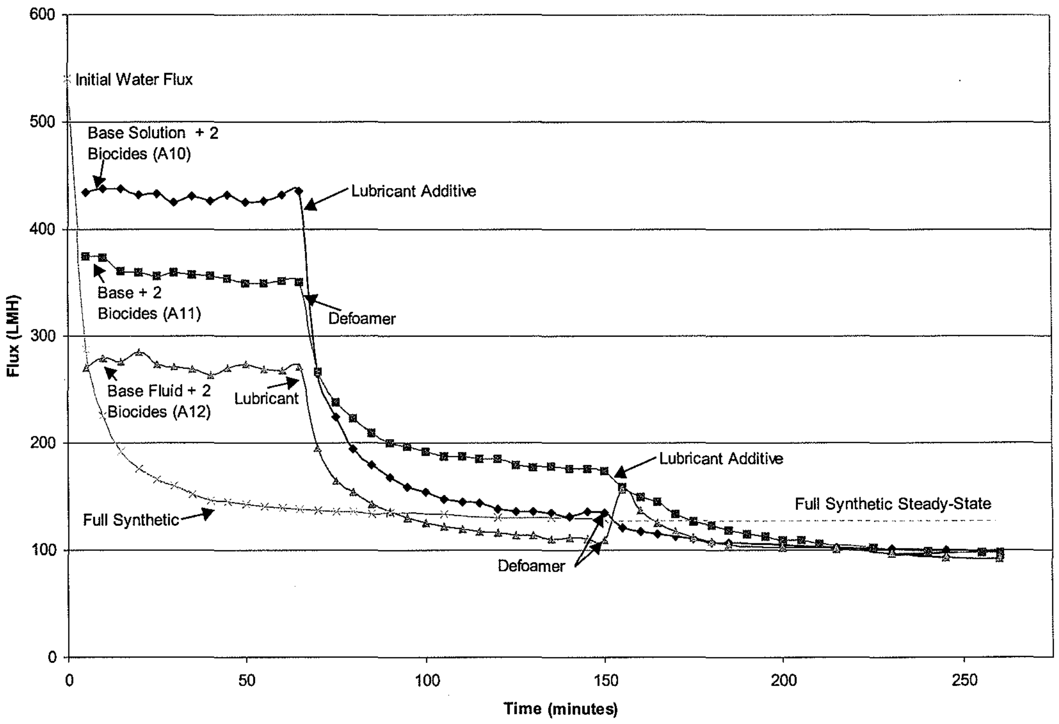


Figure 3.4. Lubricant additive and defoamer addition to mixture of base fluid and 2 biocides and comparison to flux of full synthetic fluid (A10-A12). Pressure held to 40psi.

Figure 3.4 illustrates the results of the experiments and compares them to the data for the full synthetic MWF at 40psi. Evidence shows that the lubricant additive and defoamer define the characteristic flux vs. time shape seen for the full synthetic fluid. The figure also shows that the magnitude of the flux erosion is clearly driven by the defoamer and lubricant additive, regardless of their order of addition and regardless of the initial flux of the base fluid/biocide mixture. In all experiments the final steady-state flux was between 93 and 97 LMH, significantly lower than the steady-state flux of the full fluid.

It is also noted that the initial mixtures of base fluid and two biocides had a declining flux between experiments. A flux decrease of 15% between Experiments A10 and A11 and a decrease of 25% between A11 and A12 was seen. Between each experiment, the membrane was cleaned and the water flux was maintained. It is concluded that the membrane surface characteristics were altered during the course of these experiments in a manner undetectable by water flux.

One last point of interest in Figure 3.4 is the spike in experiment A12 at 150 minutes. This should not be interpreted as an increase in flux due to the defoamer. In fact, at steady-state it is clear that the defoamer has reduced flux. However, in that experiment, the system was turned off for ten minutes intentionally during the addition of the defoamer. The increase in flux was due to the fact that the pressure relaxation changed the structure of the pore constriction to allow for an immediate and temporary increase in flow through the pores. The effect of this, although relatively minor, may suggest that enhanced removal of pore fouling material by mechanisms such as ultrasonic technology or backpulsing in MWF systems could be a useful tool to help maintain higher flux.

3.4. Base Fluid Flux Data

This section describes the flux of the base fluid independent of the specialty additives. The base fluid flux is analyzed in two contexts: before the ceramic membrane has been exposed to specialty additives and after. The comparison will determine if previous exposure of specialty additives to the membrane can reduce subsequent flux characteristics.

As shown in Figure 3.5, Experiments A22-A27 observed the flux of the base fluid and each of its ingredients with Membrane A. Experiments C2-C7 also measured the flux of the base fluid and each of its ingredients, but used Membrane C. Besides their different initial water fluxes discussed in Section 3.3, the only known difference between these membranes was that Membrane C had not been exposed to the specialty additives. Figure 3.5 shows the results of separate flux experiments with the corrosion inhibitor, general lubricant, chelating agent, pH buffer, wetting agent, and full base fluid in Membranes A and C. The fluxes are normalized to the initial water flux at 40psi before each experiment.

It is observed that previous exposure to specialty additives can significantly reduce flux of the full base fluid and each of its ingredients. The full base fluid has a flux 70% lower than the initial water flux in Membrane A. The same base fluid has a flux only 7% lower than water in Membrane C. It was previously proven in Experiments A15-A19 that the microfiltration of the base fluid ingredients themselves does not contribute to this change in flux observed over time.

Since the base fluid exhibited significant flux-erosion in Membrane A at Experiment A27, it was expected that the full synthetic fluid should also have a much lower flux than it did initially. Experiment A28 measured the flux vs. time for the full synthetic at 40psi. The results are provided in Figure 3.6 and are compared to previous data from Experiments A1-A6 at 40psi. The steady-state flux in experiment A28 was 68 LMH, approximately 50% lower than the level of observed in Experiments A1-A6.

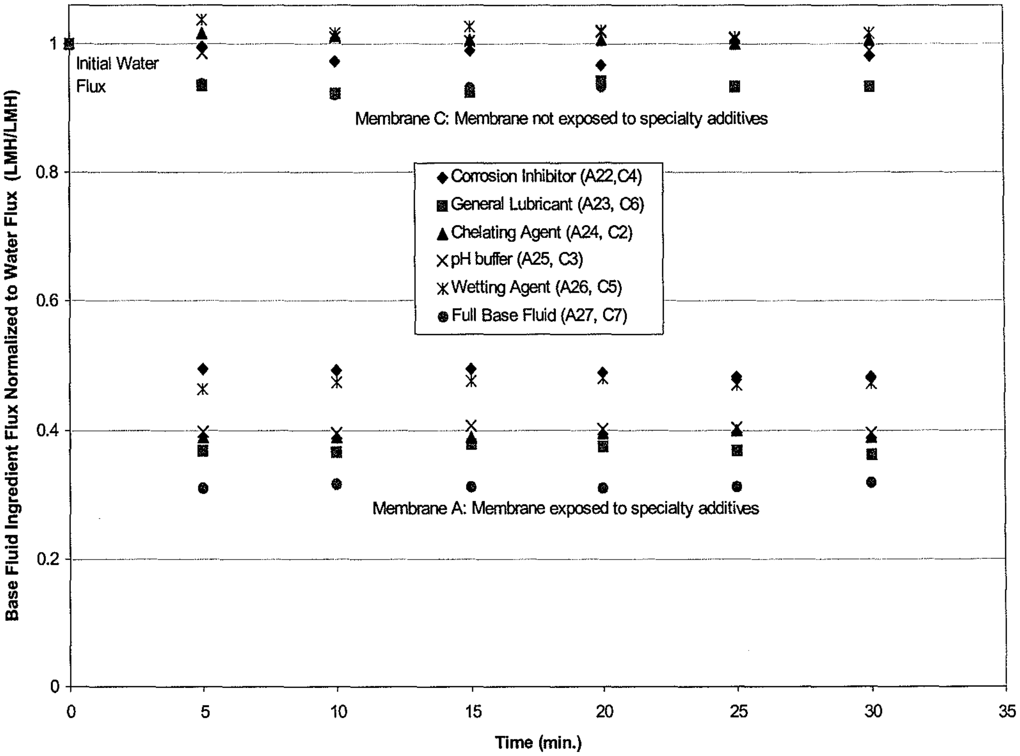


Figure 3.5. Fluxes of full base fluid and single ingredients in separate experiments before and after membrane exposure to specialty additives (A22-A27, C2-C7).

3.5. Conclusions

This chapter has described the utilization of a specialized testbed for studying the membrane filtration recycling of MWFs. Controlled experimentation with aluminum oxide membranes revealed that uncontaminated synthetic MWFs can cause significant flux-erosion compared to water. In the process of studying synthetic MWF ingredients that can cause these differences, the following conclusions were reached:

- Flux-erosion in uncontaminated synthetic MWFs results from low concentration specialty additives such as lubricant additives, biocides, and defoamers.
- Base fluid constituents common to many synthetic MWF chemistries do not cause flux-erosion independent of previous membrane exposure to specialty additives, even though base fluid ingredients comprise the majority of typical synthetic MWF formulations.

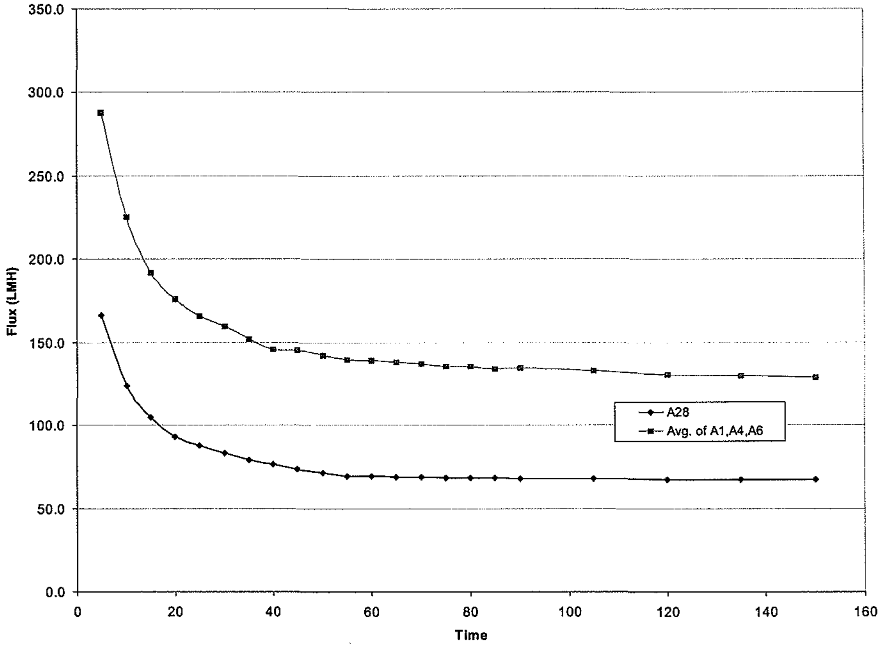


Figure 3.6. Comparison of 40psi flux vs. time data for full synthetic fluid in new membrane (A1, A4, A8) and in membrane after exposure to specialty additives (A28).

- Specialty additives can impart changes to the surface behavior of aluminum oxide membranes that remain after cleaning and are undetectable with water flux measurements. These residual effects reduce the subsequent flux of base fluid ingredients.

- Due to the sensitivity of membrane filtration productivity to low concentration specialty additives, specialty additives require particular attention with respect to their chemistry and use concentration when optimizing MWF formulations with respect to membrane filtration recycling.

Chapter 4

Analysis of Flux Decline Mechanisms During Microfiltration of a Synthetic Metalworking Fluid Using Aluminum Oxide Membranes

Chapter 3 isolated ingredients from a synthetic MWF formulation that impact productivity during microfiltration using aluminum oxide membranes. It was found that base fluid ingredients such as triethanolamine and amine dicarboxylate and general examples of a chelating agent, pH buffer, and wetting agent do not cause flux decline in previously unused aluminum oxide membranes. Specialty additives such as hydrodynamic lubricity agents, defoamers, and biocides determine the productivity of the microfiltration process, although they typically comprise less than 0.5% of the formulation. These additives can impart residual effects on the membrane surface that can lead to flux decline during base fluid permeation in subsequent applications.

This chapter describes the predominant mechanism of flux decline for the synthetic MWF. Section 4.1 describes the general mechanisms of flux decline known from the literature. Section 4.2 analyzes flux data from the previous paper to isolate the predominant mechanism of flux decline. Section 4.3 discusses the contribution of the lubricant additive and defoamer to the mechanism of flux decline. Section 4.4 discusses base fluid flux decline after membrane exposure to specialty additives caused by residual effects on the membrane surface.

4.1. Review of Flux Decline Mechanisms

Flux decline can occur due to physical obstruction or electrokinetic retardation of permeation. Physical obstruction to permeation can take the form of (a) *pore constriction*, (b) *pore blockage*, or (c) *cake formation* (Belfort et al., 1994). These three phenomena arise during particle convection due to either the size-based restriction of particle transport at the membrane surface or adsorptive interaction between particles and the membrane. Figure 4.1 illustrates the categories of physical obstruction to permeation that lead to flux decline.

The ratio (R) between the size of the particles comprising the feed stream and the pores of the membrane will generally determine the type of physical obstruction that occurs. Pore constriction arises if $R < 1$ and the particles comprising the permeate adsorb to the inner and outer-surfaces of the membrane pores. Adsorption can occur either as a monolayer or as multiple layers on the surface. If multiple layers of adsorption form or the adsorbing particles are large, the fouling layer can bridge across and completely block off pores.

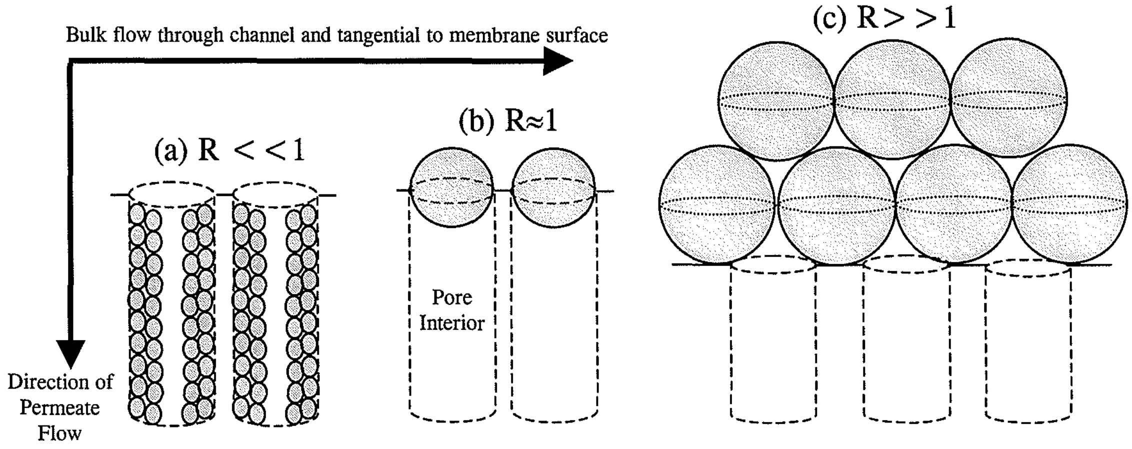


Figure 4.1. Types of physical obstruction to permeation. (a) pore constriction due to adsorption. (b) pore blocking due to physical lodging of particulate. (c) cake formation due to size-exclusion.

Pore constriction generally refers to a reduction of pore diameter caused by adsorption, while pore blockage refers to a percentage of pores that have lost their ability to conduct permeate. Pore constriction requires adsorption, while pore blockage can either occur due to adsorption or due to the physical lodging of particles with $R \approx 1$ at the entrance of membrane pores. Figure 4.2a provides an example of the latter type of pore blockage that was observed during microfiltration of 0.22μm polystyrene beads using an aluminum oxide membrane with 0.20μm pores.

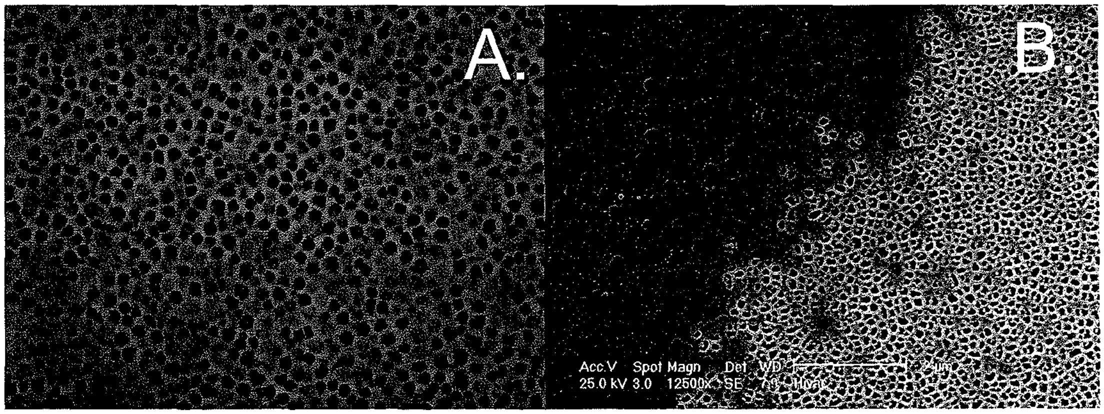


Figure 4.2. Electron microscopy images of pore blocking and cake formation. (a) Example of pore blocking caused by 0.22μm polystyrene beads on a membrane of 0.20μm pore size. (b) Transition region between cake layer formed by a 0.025% dispersion of defoamer in water and portion of membrane not exposed to defoamer.

Cake formation is observed when particles with $R > 1$ form a cohesive layer on the top of the membrane surface outside the pores. The level of resistance to permeation posed by a given cake layer depends on inter-particle interactions, the level of particle interaction with the surface, and the spacing between particles in the cake layer. Large attractive forces among particles and between particles and the surface lead to increased resistance to permeation. Tight packing of non-interacting particles also leads to increased resistance. Generally, cake layers are immobile at the membrane surface due to low crossflow shearing forces in the velocity boundary layer. Figure 4.2b illustrates a cake layer formed during microfiltration of a 0.025% defoamer dispersion in water using an aluminum oxide membrane with 0.20μm pores.

If solute cannot pass through the membrane pores ($R > 1$), the solute concentration builds up at the surface to create a concentration boundary layer as shown in Figure 4.3. This concentration layer can pose a considerable resistance to permeation that is observable in short time-scales (Ho and Sirkar et al., 1992). When the concentration boundary layer is the dominant source of flux decline, flux exhibits a non-linear response to pressure due to increased resistance to flow caused by compression of the boundary layer at elevated pressures. This mechanism of flux decline is called *concentration polarization* (Cheryan, 1986).

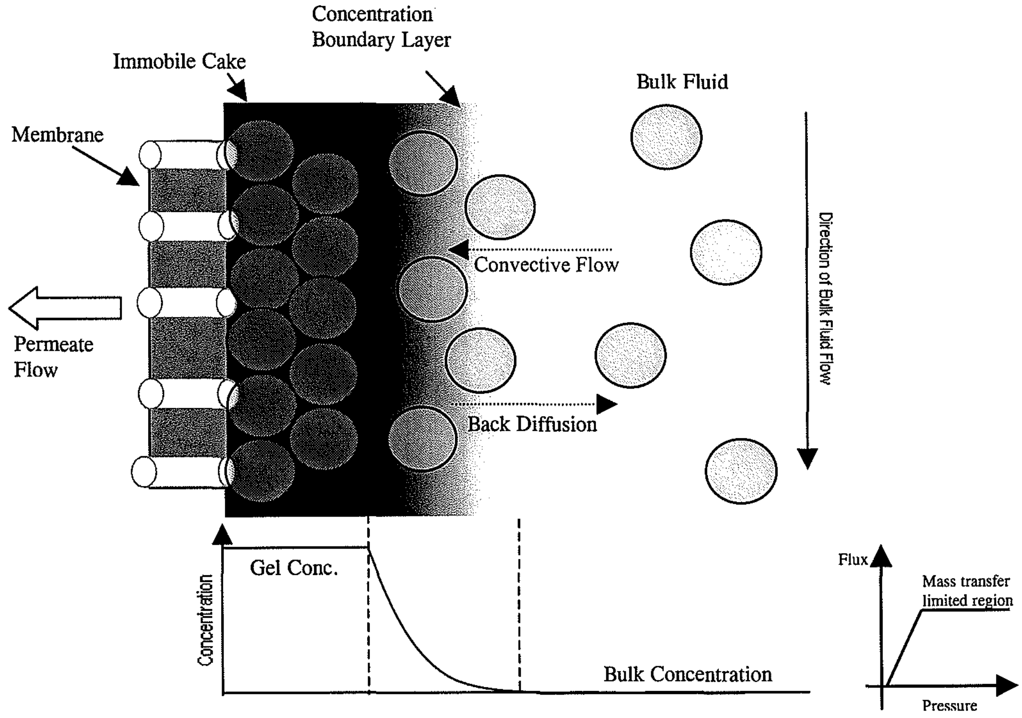


Figure 4.3. Illustration of the concentration polarization phenomenon and characteristic flux vs. pressure response.

The flux decline observed when concentration polarization exists is sensitive to variations of crossflow velocity and process fluid dilution as illustrated in Figure 4.3. Increasing crossflow velocity raises flux since the shearing forces created near the membrane surface reduce the thickness of the concentration boundary layer. Diluting the process fluid raises flux since the concentration gradient at the surface increases and results in increased diffusion of particles away from the membrane surface.

Electrokinetic retardation caused by electroviscous effects or osmotic concentration gradients can also cause flux decline (Levine, 1975; Cheryan, 1986). The electroviscous effect is a consequence of directional transport of ions during permeation. This transport creates an electrical field that resists the ion flow and increases the apparent viscosity of the permeating fluid. It has been shown that electroviscous effects are negligible in typical microfiltration applications (Bowen and Cao, 1998; Nazzal and Weisner, 1994). The same is not always true for osmotic flux decline. It has been reported that inorganic (e.g., titanium dioxide) microfiltration membranes can reject ions much smaller than the nominal pore size of the membrane (Porter and Zhuang, 1996). This can lead to an osmotic counter-pressure that reduces flux significantly.

4.2. Evidence of Pore Constriction for Synthetic MWF

Figure 4.4 graphs steady-state flux values for the synthetic MWF as a function of pressure. For reference to the specific nature of the experiments discussed herein, refer to Table 1 of Part 1, which defines the specific nature of the experiments. In Figure 4.4, it is observed that flux versus pressure is non-linear. The steady-state flux data are compared to transient flux data acquired during the experimental investigation. The transient flux data were measured at 5psi increments between 10psi and 35psi every 2 minutes after the achievement of steady-state flux at 40psi. Figure 4.4 shows that a linear model fits these data well. Thus, observations show that for the synthetic MWF, flux between experiments (long time-scale) has a non-linear response to pressure, while flux within an experiment (short time-scale) has a linear response to pressure.

The non-linear relationship of pressure and steady-state flux might at first suggest evidence of concentration polarization acting in the system. However, concentration polarization is a phenomenon that manifests itself in short-time scales. Under short time-scales flux was found to be linear in Figure 4.4. In addition, it was observed during the experimental investigation that crossflow velocity and MWF dilution had no impact on steady-state flux. These facts are inconsistent with the concentration polarization phenomenon. The fact that steady-state flux between experiments is non-linear with respect to pressure signifies that the flux-erosion

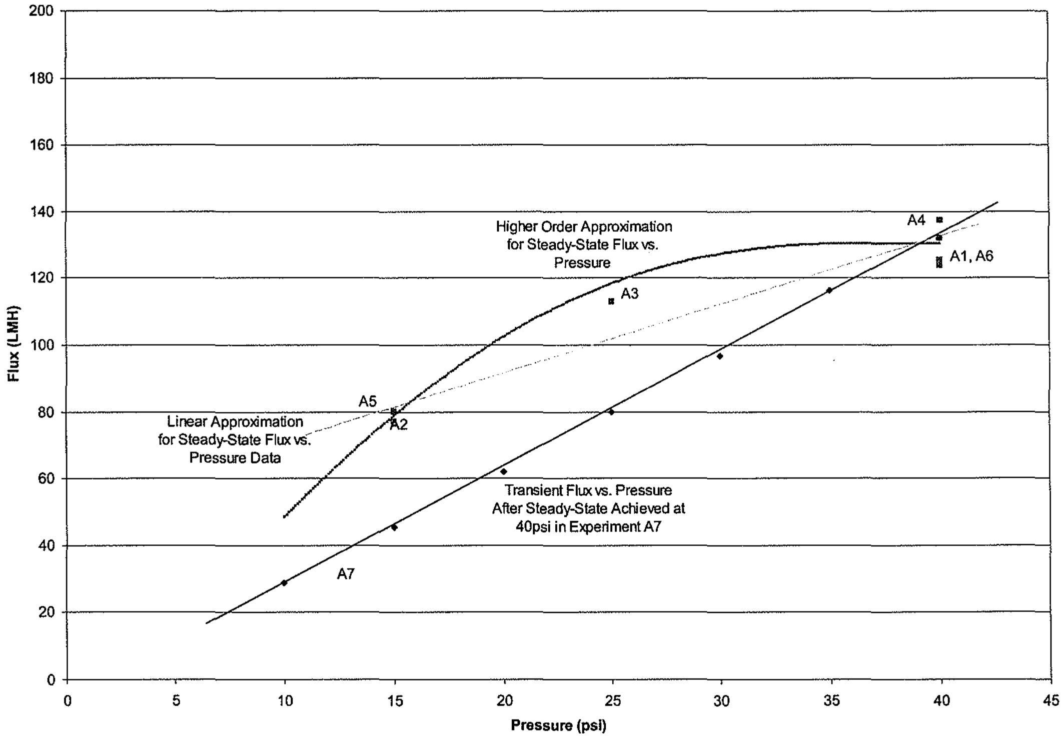


Figure 4.4. Linear and higher-order models for steady-state flux vs. pressure data. Also, comparison of steady-state flux vs. pressure (A1-A6) to transient flux vs. pressure after steady-state flux was achieved at 40psi (A7).

mechanism itself has a pressure dependence. This was supported by experimental observations that revealed the slope of flux decline prior to steady-state increases with pressure.

Similar to concentration polarization, relatively thick cake layers are also subject to the shearing forces imposed by crossflow filtration. For example, Sato et al. (1996) found that the flux of water through a cake layer of grinding swarf (approximately 1mm) was influenced by Reynolds number to the 0.75 power. For this synthetic MWF it was determined that Reynolds number alterations ranging over a factor of forty do not impact flux. It thus can be concluded that if a cake layer forms for the uncontaminated synthetic MWF, it is thin enough to remain well inside the velocity boundary layer.

With a thick cake layer and concentration polarization eliminated from consideration, only a relatively thin cake layer, pore blocking, or pore constriction could have been responsible for the flux decline caused by the synthetic MWF. As described in Section 4.2, all three mechanisms manifest themselves on the membrane surface. It was also known that regardless of the conformation of the physical obstruction, adsorption was an important underlying force driving the flux decline. This was evident from the level of chemical cleaning required to restore water flux after membrane exposure to MWF. Since adsorption was occurring as an important component of some physical obstruction mechanism at the membrane surface, it was presumed that the fouling structure could be directly observed using electron microscopy.

The Cercor membranes used during the experimental investigation could not be observed using electron microscopy without destructive testing. Consequently, direct observation of a similar aluminum oxide membrane surface was conducted with Anodisc membranes produced by Whatman® (Springfield Mill, UK). The membranes have been well characterized elsewhere, having a nominal pore size of 0.20μm and cylindrical pores (Hernández et al., 1995).

The major difference between the Cercor and Anodisc membranes important for consideration here is the crystal structure of the membrane. The Cercor membrane features α-phase alumina while the Anodisc features γ-phase alumina. The differences in crystal structure could have some difference in the magnitude of fouling in the two membranes, but is not expected to change the fundamental mechanism of interaction. Thus, the Anodisc membranes serve as a good model for understanding the fouling mechanisms for the membranes used during the experimental investigation using electron microscopy.

The membrane surface imaging was conducted using Field Emission Environmental Scanning Electron Microscopy (FE-ESEM). The major benefit of FE-ESEM relative to traditional SEM for this application is derived from the fact that non-conductive samples (e.g., aluminum oxide) can be imaged without the use of conductive coatings that could disrupt fouling layers. FE-ESEM also permits the use of reduced electron beam accelerating voltages, since high beam voltages can disrupt fouling layers during imaging. Figure 4.5 provides an FE-ESEM image of an Anodisc membrane exposed to the synthetic MWF compared to one that was not exposed to the MWF. The comparison reveals a significant amount of adsorption leading to pore constriction for the membrane exposed to MWF. Image analysis of Figure 4.5 estimated a nearly 50% decline in available surface area for permeation after exposure to MWF. It can be conclusively stated that the predominant resistance to MWF flow was due to pore constriction caused by adsorption. This pore constriction resulted in complete blockage of some pores. Cake formation was not observed.

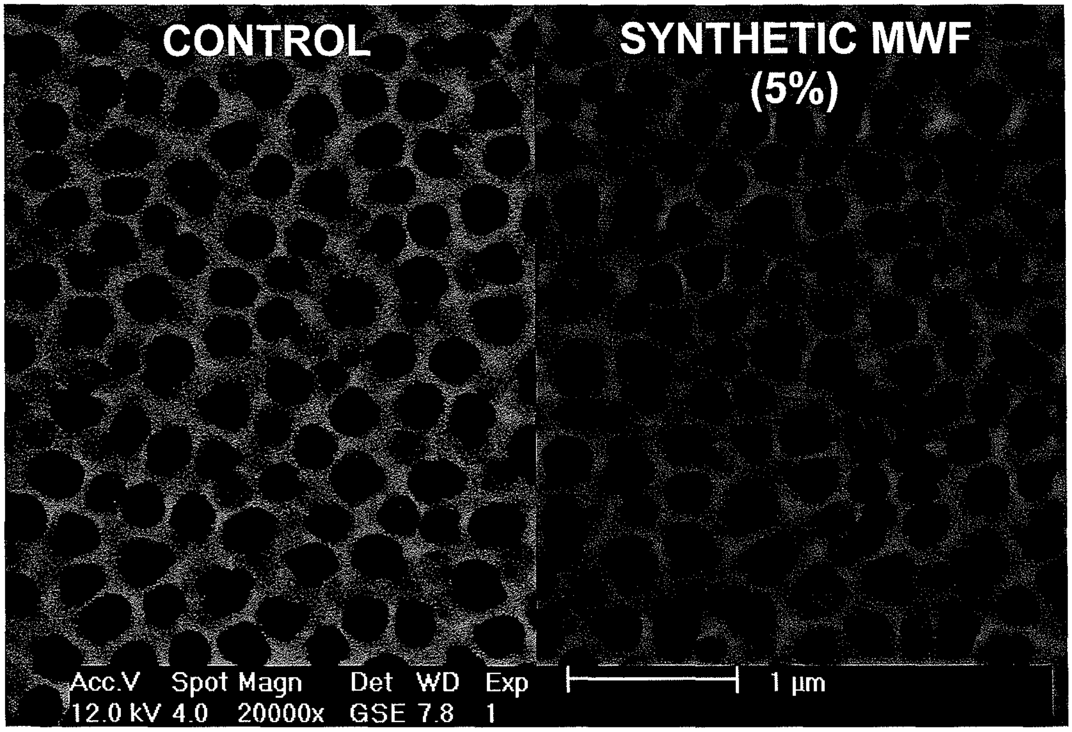


Figure 4.5. FE-ESEM image of an aluminum oxide membrane exposed to synthetic MWF (5%) compared to a new membrane.

4.3. Lubricant Additive and Defoamer Adsorption

Figure 4.6 provides a FE-ESEM image of an Anodisc surface after exposure to a 0.25% solution of the lubricant additive. The image is compared to the same membrane imaged in Figure 4.5 after exposure to the full MWF. The comparison shows approximately the same amount of pore constriction caused by the lubricant additive and the full MWF. Thus, it would appear from flux data and from direct imaging that the lubricant additive dominates the flux-eroding interaction between the MWF and the membrane surface at its use concentration. This interaction leads to pore constriction and reduced flux.

In isolation from the lubricant additive, it was seen in Figure 4.2 that the defoamer causes the formation of a cake layer. It is interesting to note that Figure 4.5 offered no evidence of cake layer formation, although the microfiltration conditions and concentration of defoamer (0.025%) were the same in both Figure 4.2 and Figure 4.5. The apparent inconsistency arises from the distinct solubility characteristics that the defoamer exhibits in the presence and absence of the lubricant additive. In water alone, the defoamer is a dispersion with a tendency to aggregate and form relatively large particles. When the lubricant additive (which possesses surfactant properties) is present

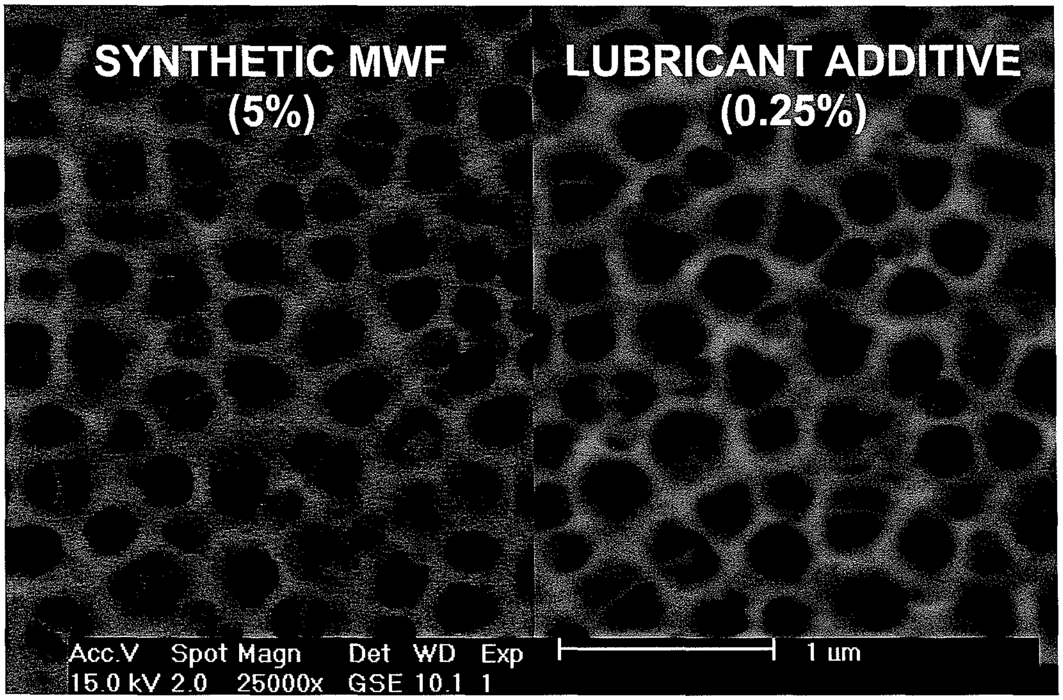


Figure 4.6. FE-ESEM image of an aluminum oxide membrane exposed to synthetic MWF (5%) compared to similar membrane exposed to lubricant additive (0.25%).

in solution, the defoamer becomes more soluble and loses a much its self-aggregation ability. Thus the defoamer is unable to form a cake layer at the membrane surface.

Photon correlation spectroscopy data supported the conclusion that defoamer solubility increases in the presence of the lubricant additive. The data indicated that the effective particle size of the defoamer (0.025%) in water is reduced nearly two orders of magnitude in the presence of the lubricant additive at 0.25%. The mixture of lubricant additive and defoamer exhibited approximately the same particle size as the lubricant additive alone.

Although the defoamer does not form a cake layer at the membrane surface in the presence of the lubricant additive, it cannot be stated that this ingredient therefore transports through the membrane unhindered. Foam tests conducted after microfiltration revealed a significant increase in MWF foaming, presumably due to adsorption of the defoamer to the membrane surface along with the lubricant additive. Adsorption of the lubricant additive in contrast was found to result in only a minor amount of loss (by percentage) to the membrane surface. Analysis using Fourier Transform Infrared Spectroscopy (FTIR) showed the adsorptive removal of lubricant additive from solution was less than 10% of the original concentration (0.25%).

Evidence from the membrane and surface science literature supports the conclusion that the lubricant additive and defoamer can adsorb to membrane surfaces to reduce flux. The lubricant additive is an example of a common variety of diblock copolymer used in synthetic MWFs that has been noted to exhibit flux-eroding interactions during ultrafiltration (Sköld, 1991; Misra and Sköld, 1999). Adsorptive surface interactions of diblock copolymers to inorganic surfaces have been researched extensively due to their ability to stabilize colloidal suspensions (deGennes, 1980; Marques et al., 1988; Munch and Gast, 1988).

Similarly, the defoaming agent is derived from the family of organosiloxane polymers that has been noted in the literature to demonstrate adsorptive interactions with inorganic surfaces (Bascom, 1968). Silicone-based defoaming agents in general are well known for their flux-eroding interactions with membranes (Liew et al., 1996; McGregor and Weaver, 1988). These flux-eroding interactions have been shown to increase the foaming tendencies of solutions under investigation, as was observed for the synthetic MWF.

4.4. Discussion of Base Fluid Flux Decline

One possible explanation for the base fluid flux decline observed after membrane exposure to specialty additives is that the electrical nature of the membrane surface was altered by the specialty additives to cause increased adsorption of the base fluid ingredients to the membrane. In this scenario, the level of adsorption would need to be large enough for notable pore constriction to occur. It is possible to assess the amount of pore constriction that would be required to account for the flux decline by analyzing flux versus pressure data. This section conducts this analysis for the flux versus pressure data provided in Figure 4.7.

Assuming laminar and time-invariant permeation with all pores equally sized and cylindrical, flux can be characterized by the *Hagen-Poiseuille* Equation given in Equation 4.1 for stream-line flow (Cheryan, 1986),

$$J = \frac{\varepsilon \, r^2 \, \Delta P}{8 \, \eta \, \Delta x} . \tag{4.1}$$

In Equation 4.1, J is the flux, ε is the porosity of the membrane, r is the pore radius, ΔP is the average pressure applied across the membrane, η is the viscosity of the permeate, and Δx the pore length. The Hagen-Poiseuille Equation provides a starting point for analyzing flux observations. In typical membrane processes the Hagen-Poiseuille Equation does not sufficiently describe flux data. Its assumptions do

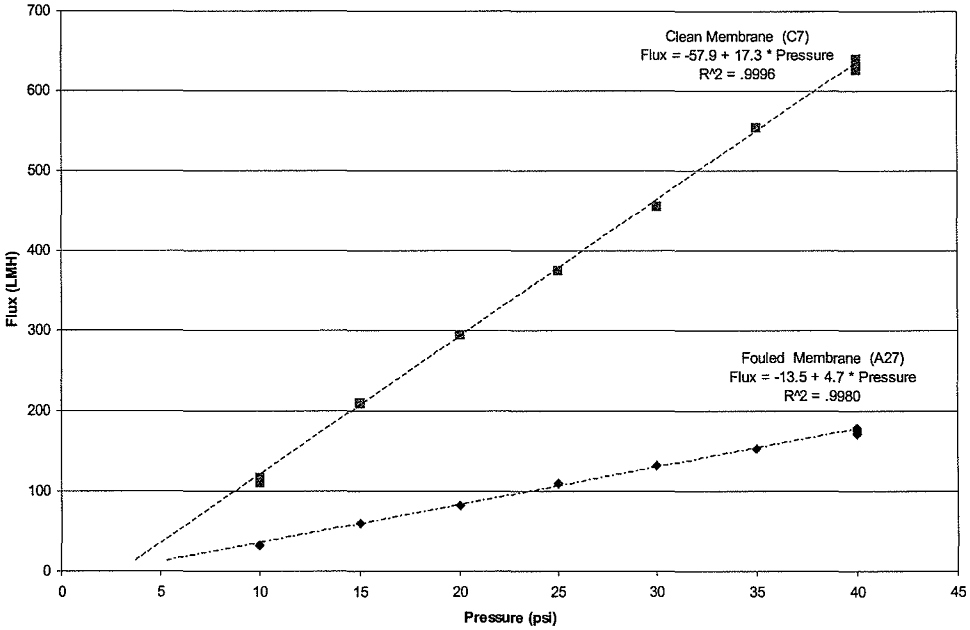


Figure 4.7. Flux vs. pressure of base fluid mixture in a new membrane (Experiment C7) versus after significant exposure to specialty additives (Experiment A27).

not account for the fact that membranes differ in their relative affinity for water (hydrophilicity) and that membrane pores are non-uniform and tortuously curved with respect to Δx. Usually the porosity of the membrane is unknown. Despite this, the flux response to pressure always remains linear for water.

Discrepancies between the slope of the Hagen-Poiseuille predictions and actual membrane observations are typically accounted for by introducing an empirical membrane resistance, R_m (Cheryan, 1986). Using this linear slope parameter, the flux can be conceptualized by Equation 4.2,

$$J = \frac{\Delta P}{R_m}. \tag{4.2}$$

For Membranes A and C, R_m (psiLMH^{-1}) was found to be 0.066 and 0.058 respectively by linear regression of water flux vs. pressure data when the membranes were new.

In Figure 4.7, it is observed that the flux of the base fluid in Membrane A has been reduced significantly due to previous exposure of the membrane to specialty additives (A27). In the language of the resistance model, the specialty additive exposure resulted in increased membrane resistance to base fluid permeation due to increased propensity to foul. Using the idea expressed in Equation 4.2, the fouling can be expressed as an additional resistance, R_f, in series with the inherent membrane resistance, R_m. This results in Equation 4.3 (Cheryan, 1986),

$$J = \frac{\Delta P}{R_m + R_f}. \tag{4.3}$$

Since the inherent R_m for Membrane A is 0.066, R_f can be back-calculated from the slope of the linear regression provided in Figure 4.7. This results in a calculated R_f of 0.147. If it were assumed that all pores of the membrane were equally sized at 0.2 μm and that this fouling resistance, R_f, were due to pore constriction, Equation 4.1 would predict this fouling resistance to be an effective reduction of pore diameter of 0.09μm.

Particle size estimation of the base fluid conducted using photon correlation spectroscopy demonstrated the absence of ingredients larger than 0.01μm. This is further supported by the known structural formulas of the base fluid ingredients. Thus at least nine monolayers of adsorption would be required to account for the magnitude of the pore constriction observed in Figure 4.7 if the base fluid were to cause flux decline by directly adsorbing to the membrane. This is unlikely given the known structures and behavior of the base fluid ingredients.

Further investigation revealed that sodium chloride (0.01 molar) at the pH of this MWF caused the same level of flux-decline as the base fluid ingredients. Salts such as sodium chloride are well known to posess an electrolytic nature, and their adsorption to alumiunum oxide is governed by electrical double-layer theory. The theory predicts that a rigid ion accumulation within the membrane pores to nine monolayers is highly improbable (Hunter, 1982).

In addition, the level of electrostatic attraction between membrane and solute depends strongly on the solute itself. For instance, elevated salt concentrations reduce the reach of the membrane electrical field into solution. Variations in ion valence and mobility also impact the strength of the electrical field caused by charged membrane surfaces. Thus, it is even more improbable that MWF ingredients with distinct chemistry and electrical characteristics (e.g., triethanolamine and amine dicarboxylate) would adsorb to the membrane to the exact same degree. However, the experimental investigation revealed that these and all the base fluid ingredients (either individually or in combination) exhibited approximately the same level of flux decline. Thus it can be concluded that base fluid flux decline does not arise due to pore constriction caused by direct adsorption of base fluid ingredients.

4.5. Conclusions

This chapter has discussed general flux-erosion mechanisms as they apply to the microfiltration of a synthetic MWF using aluminum oxide membranes. Analysis of flux data and Field Emission Environmental Scanning Electron Microscopy (FE-ESEM) images revealed:

- Adsorption of MWF ingredients leads to a reduction of pore diameter that serves to reduce flux.
- The bulk of the pore constriction and flux decline caused by the synthetic MWF is accounted for by a diblock copolymer used as a hydrodynamic lubricity additive.
- Organosiloxane defoamer dispersions in water cause flux decline by cake layer formation at the membrane surface.
- A mixture of defoamer and synthetic MWF does not cause the formation of a cake layer, but the defoamer still adsorbs to the membrane surface resulting in increased foaming tendency for the MWF.
- Base fluid ingredient flux decline observed in membranes previously exposed to specialty additives is not caused by these ingredients adsorbing to the membrane to cause pore constriction.

Chapter 5

Microfiltration of Polyoxyalkylene Metalworking Fluid Lubricant Additives Using Aluminum Oxide Membranes

5.1. Introduction

As described in Chapter 2, previous research discovered that polyoxyalkylene lubricant additives comprised of ethylene oxide (EO) and propylene oxide (PO) can lower the productivity of ultrafiltration processes. Ethylene oxide/propylene oxide (EO/PO) copolymers are widely used as lubricant additives in synthetic, semi-synthetic, and soluble oils that require improved boundary lubrication. These copolymers feature several of the chemical characteristics believed to contribute to productivity decline during membrane filtration. Thus, a study of the relationship between different EO/PO chemistries and flux can serve as a model for beginning to understand the interactions of other MWF ingredients with membrane filters.

Mahdi and Sköld (1990) researched the membrane filtration of ethylene oxide/propylene oxide (EO/PO) copolymers using 20,000 molecular weight cut off (MWCO) fluoropolymer ultrafiltration membranes. It was found that 1) increased molecular weight of the copolymer caused lower flux and 2) the ratio of ethylene oxide to propylene oxide in the copolymer did not significantly impact flux. The work concluded that during ultrafiltration, flux is closely related to size-based characteristics such as molecular weight and conformation and the tendency of MWF ingredients to aggregate in solution. Recent research using a wider variety of membranes also supported these conclusions (Misra and Sköld, 1999). A 10,000 MWCO membrane was found to remove a propylene glycol lubricant additive with an average molecular weight of 1,800 from solution. Microfiltration membranes (0.1μm pore-size) did not remove the same polymer from solution. Membrane adsorption was hypothesized to explain the flux decline observed using the microfiltration membranes, but was not specifically investigated.

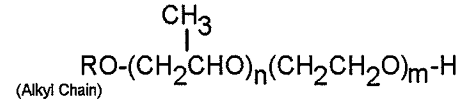
In Chapter 4, membrane adsorption of a similar copolymer lubricant additive was observed during microfiltration. It was revealed that adsorption of the copolymer to 0.2μm aluminum oxide membranes constricts membrane pores and plays the dominant role in determining the maximum achievable flux of the recycling process. It was also discovered that the copolymer can contribute to residual effects at the membrane surface that reduce the permeability of non-fouling solutions in subsequent experiments. However, the chemical characteristics of the copolymer that caused pore-constriction, flux-decline, and residual effects were not investigated.

This chapter describes chemical characteristics of EO/PO copolymers that lead to adsorption, flux-decline, and residual effects during microfiltration using 0.2μm aluminum oxide membranes. Section 5.2 provides a review of EO/PO copolymer chemistry and functionality relevant to MWFs and membrane filtration. Section 5.3 describes the materials and methods used to acquire flux data in Sections 5.4 and 5.5. Section 5.4 provides flux data for different EO/PO copolymer chemistries and discusses the role of EO/PO ratio in determining flux. Section 5.5 isolates residual effects caused by EO/PO copolymers and describes the mechanism by which EO/PO modification can lead to residual effects.

5.2. Ethylene Oxide/Propylene Oxide Copolymer Chemistry And Functionality

Polyoxyalkylene glycols (polyglycols) comprised of ethylene oxide (EO) and propylene oxide (PO) have been utilized in many industries since their introduction in the early 1940's (Mueller and Martin, 1974). Their dual hydrophilic and hydrophobic characteristics govern surfactant properties that serve useful emulsifying, detergent, and wetting functions (Nance, 1996). In water-soluble MWFs, polyglycols serve as hydrodynamic lubricity additives.

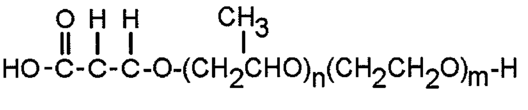
The hydrodynamic lubricity offered by polyglycols is derived from their inverse solubility (i.e., reduced solubility at increased temperature). Temperature rise at the point of contact causes the lubricant to leave solution and form a hydrodynamic boundary layer that reduces friction at the tool-workpiece interface. At the lower temperatures of the MWF circulation system and reservoir, the lubricant becomes soluble again. Equation 5.1 is a general formula for a linear ethylene oxide/propylene oxide copolymer,



$$\underset{\text{(Alkyl Chain)}}{RO}\text{-}(CH_2\overset{\overset{\textstyle CH_3}{|}}{C}HO)_n(CH_2CH_2O)_m\text{-}H \quad . \quad (5.1)$$

Ethylene oxide (*m*) is characterized by two carbon atoms and is water-soluble. Propylene oxide (*n*) is characterized by three carbon atoms and is water-insoluble. The variables *m* and *n* are the number of monomer units of ethylene oxide and propylene oxide per copolymer. The copolymer has variable solubility depending on the ratio of propylene oxide (hydrophobic) to ethylene oxide (hydrophilic). The percentage of ethylene oxide or propylene oxide in the copolymer can range from 0 to 100%.

The diblock copolymer described by Equation 5.1 is electrically neutral (i.e., nonionic) in solution and can be modified in several ways. The ratio *m:n*, the molecular weight, and the type of side chain (R in Equation 5.1) can affect the adsorption and self-aggregation properties of the polymer (Lipatov and Sergeeva, 1974). The side-chain R is typically an alkyl chain, but it can be acid-modified to produce an anionic copolymer. Equation 5.2 describes acrylic acid modification of Equation 5.1,



$$\mathrm{HO\text{-}\overset{\overset{O}{\|}}{C}\text{-}\overset{\overset{H}{|}}{C}\text{-}\overset{\overset{H}{|}}{C}\text{-}O\text{-}(CH_2\overset{\overset{CH_3}{|}}{C}HO)_n(CH_2CH_2O)_m\text{-}H} \quad . \quad (5.2)$$

In solution, the carboxylic acid functional group (COOH) found in Equation 5.2 dissociates to form a negatively charged (anionic) copolymer. Since MWFs are typically formulated at elevated pH, anionic copolymers must be neutralized in MWF formulations, typically with triethanolamine. An example of carboxylic acid modification of an EO/PO copolymer has been described by Laemmle (1984) for metalworking applications.

5.3 Experimental Methods

The objective of this research was to reveal the relationship between microfiltration flux-decline, hydrophobic/hydrophilic balance, and anionic modification. The membranes used for the study were 0.2μm α-alumina membranes produced by Keranor AS (Oslo, Norway). Table 5.1 describes the three EO/PO copolymers used during the research.

Table 5.1. EO/PO Polyglycol Characteristics.

Copolymer	Anionic vs. Nonionic	EO:PO Monomer Ratio	EO:PO Mass Ratio (calculated)	Average Molecular Weight	Molarity of 0.25 v/v% Solution (calculated)
UCON® base lubricant 75-H-450	Nonionic	3:1	681:299	980	$2.8\text{x}10^{-3}$
UCON® base lubricant 50-HB-660	Nonionic	1:1	685:905	1590	$1.6\text{x}10^{-3}$
UCON® MWF lubricant EPML-483	Anionic	1:1	2600:3400 to 8600:11,400	6,000-20,000 (estimated)	$1.3\text{x}10^{-4}$ to $4.2\text{x}10^{-4}$

The hydrophobic contribution to flux-decline was determined by comparing flux data for UCON® lubricants 75-H-450 and 50-HB-660 (Union Carbide, Danbury, CT). Both lubricants are nonionic with an equal mass content of ethylene oxide, but the former has a higher EO/PO ratio than the latter. The anionic contribution to flux decline was assessed by acquiring flux data for UCON® EPML-483 at different pH levels and after the addition of various salts (i.e., after changing the ionic strength of the solution). Salt addition and pH-modification altered copolymer-copolymer and copolymer-membrane interactions that are believed to be important to the anionic contribution to flux-decline. Therefore, the impact of variable ionic strength and pH on UCON® EPML-483 flux assisted in determining the mechanism by which anionic modification can contribute to flux-decline.

Flux data for the three EO/PO copolymers (0.25% solutions) in Table 5.1 were collected at pH=5.5 and pH=10.5 in six separate experiments. For each experiment, a new membrane was used and flux was measured once after every 150ml volume of permeate produced. A total of 16 flux measurements were collected during each experiment. The first four (4) measurements of flux were obtained for the copolymer solutions in the absence of supplemental salts. After the fourth measurement, the ionic strength of the copolymer solutions was modified by adding selected salts at a concentration of 10^{-2} M (moles/liter). Solutions of copolymer and sodium chloride (NaCl), sodium sulfate (Na_2SO_4), and calcium chloride ($CaCl_2$) were filtered consecutively. After obtaining four (4) flux measurements with each salt/copolymer solution, the membrane was flushed with 150ml of the next salt/copolymer solution to remove any unbound ions from the membrane before conducting flux measurements with the next salt/copolymer solution.

The remaining experiments performed in this study were designed to reveal the characteristics of copolymers that can lead to residual effects at the membrane surface that reduce the flux of non-fouling solutions in subsequent experiments after cleaning. Flux was measured as a function of cleaning conditions, pH, and the concentration of various salts. Section 5 describes these experiments in detail.

The membrane filtration system used in the research consisted of a vacuum pump, 1-liter receiving flask with vacuum-line intake, 47mm-membrane fixture, and 300mL fluid intake vessel. Transmembrane pressure during filtration was approximately 10psi. Flux was calculated by measuring the time to filter 150ml of solution and dividing by the surface area available for permeation ($22.1 cm^2$). Initial water flux for the membranes used in the research ranged from 1100 to 1500 LMH (liters/m^2/hour).

In the figures presented in this paper, flux is normalized to deionized water flux (pH=5.5) measured before each experiment unless otherwise stated. Also, the figures describe flux vs. measurement number within each experiment instead of flux vs. time. This was necessary to allow flux data for the three copolymers to be presented on the same graph since the time required to produce 150ml of permeate was highly variable between the different copolymers. Therefore, when interpreting the data in the figures presented below, it should be noted that a flux measurement was performed for every 150ml volume of permeate produced during the experiment. Lower flux is a reflection of increased time between flux measurements.

5.4 Flux of Different EO/PO Polyglycols

This section describes the relationship of microfiltration flux to hydrophobic/hydrophilic balance. Section 5.4.1 provides flux data for the three different EO/PO ratio copolymers as a function of pH and ionic strength. Section 5.4.2 discusses the relationship between the flux data and EO/PO chemical characteristics.

5.4.1 Flux Data for EO/PO Copolymers

Figure 5.1 illustrates the flux of the three 0.25% solutions of polyglycol at pH=5.5. It is observed that increasing the PO proportion in the copolymer reduces flux. For the 1:1 copolymers, the larger molecular weight and anionic-modification lead to lower flux and an increased time required to approach equilibrium. Figure 5.1 shows that initial differences that exist between the flux of the 3:1 and 1:1 nonionic copolymers do not change significantly with increased ionic strength. For the anionic, sodium sulfate is observed to temporarily have a positive impact on flux.

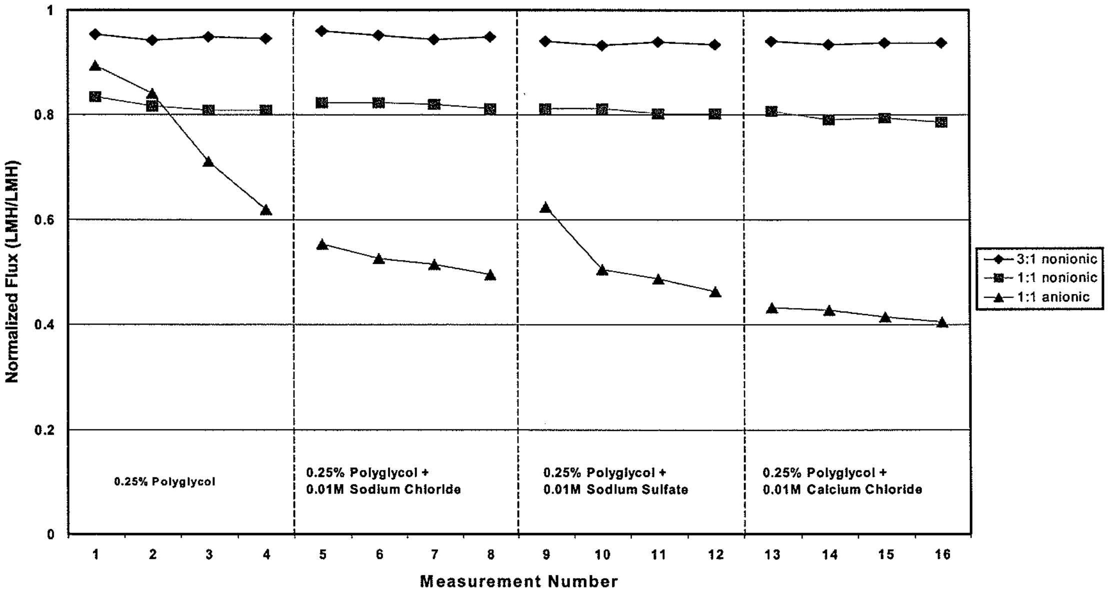


Figure 5.1. Normalized flux of ethylene oxide/propylene oxide block copolymers in 0.25% solution (pH=5.5). Various salts added to copolymers after fourth measurement.

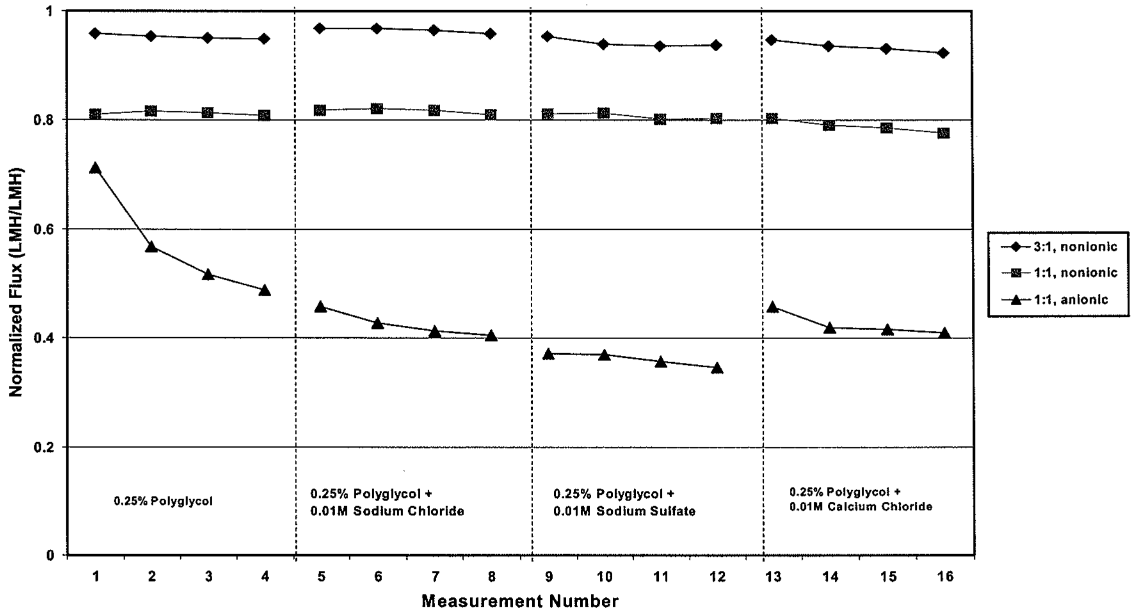


Figure 5.2. Normalized flux of ethylene oxide/propylene oxide block copolymers in 0.25% solution (pH=10.5). Various salts added after fourth flux measurement.

The conditions of Figure 5.1 were also replicated at pH=10.5. The data are provided in Figure 5.2. Similar to pH=5.5, the 1:1 copolymers exhibited more flux decline than the 3:1 copolymers, with the anionic copolymer exhibiting the most flux-decline. The fluxes for the nonionics were observed to be approximately the same at both pH levels, and flux differences between the 1:1 and 3:1 were not observed to change by added ionic strength. For the anionic, calcium chloride was found to increase flux. Sodium sulfate did not increase flux.

5.4.2 Discussion of EO/PO Copolymer Flux Decline

Copolymer adsorption to solid interfaces has been the topic of a considerable amount of surface chemistry research (Marques et al., 1988; Adamson and Gast 1997; Webber et al., 1990). It has been shown previously that EO/PO copolymer adsorption to surfaces such as carbon, silica, and nylon depends the affinity of the copolymer for the surface, the affinity of the copolymer for the solvent, and the affinity of the solvent for the surface (Howard and McConnel, 1967a,b,c; Lipatov and Sergeeva, 1974). Thus, when comparing different EO/PO copolymers in aqueous solution for their flux through aluminum oxide membranes, the degree of solubility imposed by the overall molecular weight and hydrophobic/hydrophilic balance should be considered.

Contrary to previous observations in the literature for low MWCO ultrafiltration, flux is observed to be related to EO/PO ratio during microfiltration

(Mahdi and Sköld, 1990). In Section 4.1, it was observed that the 1:1 nonionic copolymer exhibited lower flux than the 3:1 nonionic copolymer. As seen in Table 1, this was due to the increase in propylene oxide mass relative to ethylene oxide mass per molecule. Also observed in Table 1 is that the molarity of the 1:1 solution was approximately 40% lower than the molarity of the 3:1 solution. This means that per liter, the 1:1 copolymer had 40% fewer copolymers available to interact with the membrane surface. However, since propylene oxide is less soluble in water than ethylene oxide, increasing the mass of propylene oxide relative to ethylene oxide increased the level of surface interaction and helped to lower the flux of the 1:1 nonionic copolymer relative to the 3:1 nonionic copolymer. This effect was not observed to be strongly influenced by moderate changes in pH or ionic strength.

The driving force for the interaction between the nonionic copolymers and the membrane is the hydrophobic effect (McKenzie et al., 1994). Hydrophobic interactions are a consequence of free energy considerations and are observed when two molecules exhibit a stronger attraction in a polar solvent such as water than they would in free space. It follows that 1) the hydrophobic portion of the copolymer will adsorb to the surface with the attached hydrophilic polymer extending into the solution, and 2) increasing the hydrophobic content of the copolymer increases the driving force for adsorption (Munch and Gast, 1988).

The anionic polyglycol exhibited a lower flux through the membranes than the nonionics. This is in part due to the increased molecular weight of the anionic copolymer as described previously (Webber et al., 1990). The increased molecular weight means that there is a longer hydrophilic portion of the copolymer extending away from the wall. This will exert a larger amount of hydrodynamic drag on the permeating solution per copolymer adsorbed to the surface. Thus, it is expected that the increased resistance to flow by the larger molecular weight anionic copolymer accounts for part of the lower flux observed.

5.5 Residual Effects of Anionic Polyglycols

This section describes the mechanism by which anionic modification of EO/PO polyglycols can lead to reduced flux. The anionic contribution to flux decline is revealed by observing the flux-decline caused by water and other non-fouling solutions when permeating through membranes known to contain adsorbed anionic polyglycol copolymer at the membrane surface.

Section 5.5.1 demonstrates that anionic polyglycol can remain adsorbed to the membrane after cleaning and can impact the flux of non-fouling solutions in subsequent experiments. Section 5.5.2 describes cleaning conditions that can remove anionic

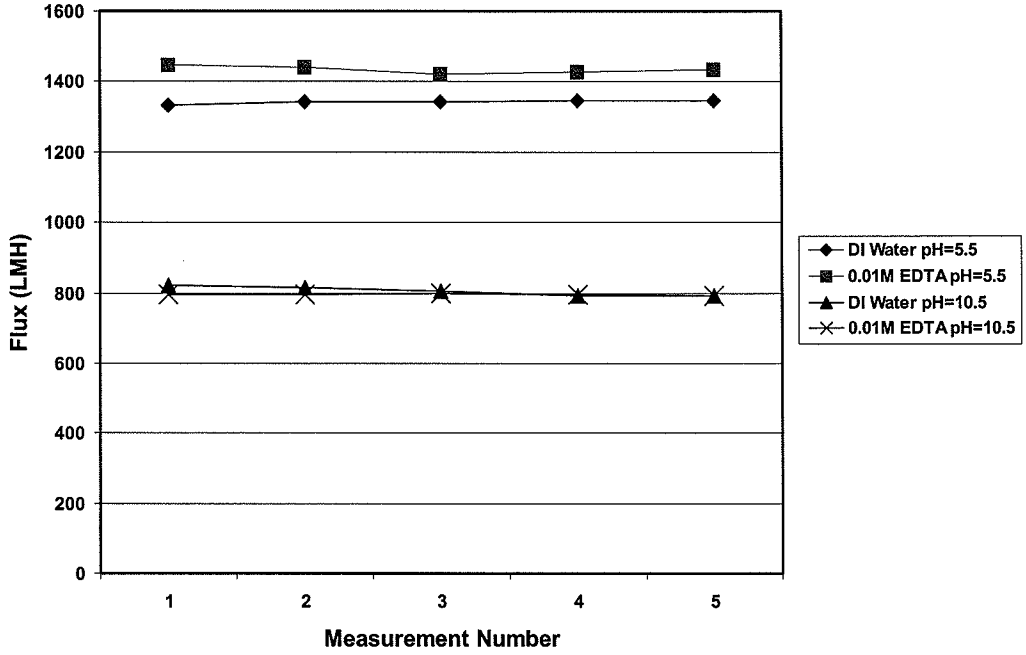


Figure 5.3. Flux of tetrasodium EDTA (10^{-2} M) and deionized water at pH of 5.5 and 10.5 after membrane exposure to anionic polyglycol, cleaning at 45°C, and rinsing with deionized water.

copolymer from the membrane surface. Section 5.5.3 compares flux data for different salt solutions through membranes known to contain adsorbed anionic copolymer at the membrane surface. Section 5.5.4 uses these data to elucidate the mechanism by which anionic modification can lead to flux decline.

5.5.1 Residual Effects after Copolymer Exposure

A 45°C aqueous mixture of KochKleen detergent (Koch Membrane Systems, Wilmington, MA) at 1% and Ultrasil 11 (Klenzade, St.Paul, MN) added to reach pH=12 was investigated for its effectiveness in restoring membrane water flux after exposure to the three EO/PO polyglycols. The three membranes used in Figure 5.2 were soaked in this cleaning solution for a period of one hour. After rinsing the membranes, it was found that water flux (pH=5.5) was restored by this procedure for all membranes.

To test if residual effects remained on the membrane surfaces, a 10^{-2} M solution of tetrasodium ethylenediamine tetraacetate (tetrasodium EDTA, a commonly used chelating agent found in MWFs) was filtered through all three membranes at pH=5.5 and pH=10.5. For the two membranes previously exposed to nonionic polyglycol, EDTA flux was observed to be approximately the same at pH=5.5 and pH=10.5 as it was in a new membrane. It was thus concluded that the two membranes exposed to nonionic copolymer had no residual effects remaining after cleaning.

As shown in Figure 5.3, for the membrane previously exposed to anionic polyglycol, EDTA flux was observed to be approximately the same as water at pH=5.5. However, at pH=10.5, the flux of both EDTA and deionized water fell approximately 40% below their levels observed at pH=5.5. In a new membrane, neither EDTA nor deionized water exhibited this flux decline upon raising the pH from 5.5 to 10.5. Thus, it was concluded that previous membrane exposure to anionic copolymer caused pH-dependent flux of otherwise non-fouling solutions in subsequent experiments. Figure 5.3 shows that the magnitude of pH-dependence after membrane exposure to anionic copolymer is approximately the same for EDTA and deionized water.

Figure 5.4a provides a Field Emission Environmental Scanning Electron Microscope (FE-ESEM) image of a membrane surface after exposing the membrane to anionic polyglycol, performing the cleaning procedure described above (45°C, pH=12), and rinsing with deionized water at pH=5.5. Figure 4b provides an image of a membrane that was subjected to the same procedure, but that subsequently was rinsed with deionized water adjusted to pH=10.5. The comparison reveals that after cleaning, the anionic copolymer can remain adsorbed to the membrane surface and exhibit swelling that is a strong function of the pH. The swelling serves to reduce the available void-space for permeation and is responsible for the pH-dependent flux observations above.

5.5.2 Cleaning Considerations for Anionic Copolymers

It was found that the residual anionic copolymer remaining at the membrane surface after cleaning could be removed if the temperature of the cleaning solution (pH=12) was raised to 80-90°C. The increase in cleaning temperature returned the flux of water and EDTA to their levels observed in a new membrane at pH=10.5. In other words, solution pH no longer had a major impact on the flux of water or EDTA after the temperature-modified cleaning procedure was performed. In contrast, performing the temperature-modified procedure did not remove the anionic copolymer from the membrane if the pH of the cleaning solution was set to 10 instead of 12. If the pH of the cleaning solution was set to 10, both EDTA and water exhibited pH-dependent flux characteristics even if the temperature of the cleaning solution was set to 90°C. Therefore, it was concluded that both elevated pH and temperature can assist in removing the anionic copolymer from the membrane during cleaning.

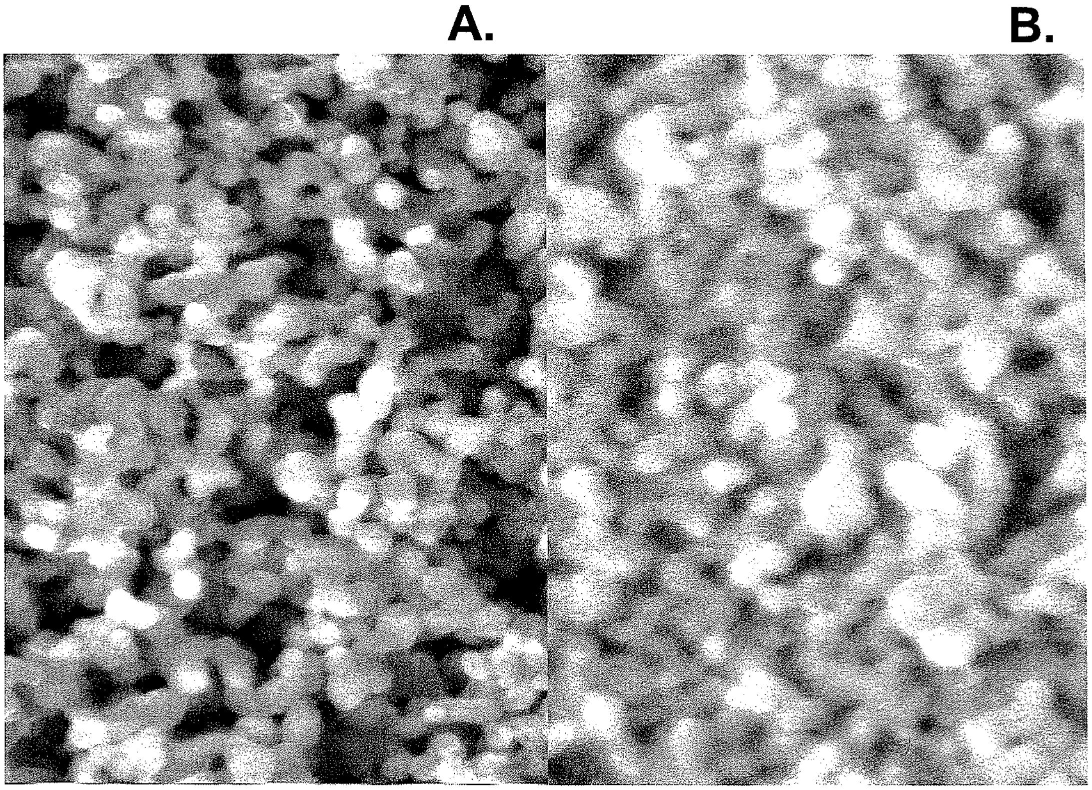


Figure 5.4. FE-ESEM image of membrane surface with anionic residual. (a) at low pH. (b) at elevated pH. Imaging conditions were identical with respect to working distance, magnification, beam voltage and size, and vacuum level.

The role of elevated pH in assisting anionic copolymer removal from the surface of the membrane is derived from the amphoteric nature of aluminum oxide surfaces. Amphoteric surfaces exhibit the properties of both an acid and a base. Thus, the state of charge on the membrane surface can be described by the following equation,

$$AlOH_2^{+} \xleftarrow{H+} AlOH \xrightarrow{OH-} AlO^{-} + H_2O . \qquad (5.3)$$

Equation 5.3 indicates that the sign and magnitude of charge on aluminum oxide surfaces are a function of the solution pH (Hankins et al., 1996). Therefore, the electrostatic attraction or repulsion between the anionic copolymer and the surface will depend strongly on the pH of the solution, which also determines state of ionization of the carboxylic acid on the copolymer (see Equation 5.2).

At pH=12, the interaction force should be more repulsive than attractive (Hirata et al., 1992). This is because the isoelectric point of alumina (i.e., the pH where net surface charge is zero) is approximately 9 and the carboxylic acid group on the anionic copolymer is ionized at this pH (Lee et al., 1996; Hidber et al., 1996). In light of this, increasing the pH to 12 in the presence of surfactants during cleaning should assist in removing the copolymer from the membrane surface.

It was observed above that high pH was required to remove the anionic copolymer residual from the membrane surface. However, it was also found that temperature was an important factor. It is believed that the temperature increase during cleaning assisted by increasing convection of the cleaning solution through the membrane since the cleaning solution was not forced through the membrane under pressure. Permeation of the cleaning solution under pressure was later found to permit cleaning at lower temperature (e.g., 50°C), as long as the pH remained equal to 12.

5.5.3 Flux of Selected Salts After Membrane Exposure to Anionic Polyglycol

Figure 5.5 provides flux data for various salts using membranes known to contain residual anionic copolymer. Unlike EDTA, these salts are not found in MWF formulations. However, by measuring the flux of these salts in the absence of anionic copolymer in solution, the role of anionic modification in contributing to flux-decline can be assessed.

The anionic copolymer residual was established in five clean membranes by filtering a 0.25% solution of anionic copolymer for a period of one hour. After filtration, the membranes were cleaned using the original cleaning procedure (45°C) and rinsed with deionized water to maintain residual effects. The five membranes were then filtered with 10^{-2} M solutions of sodium chloride, sodium sulfate, calcium chloride, and a 0.50 v/v% solution of cationic surfactant. All solutions were adjusted to pH=10.5. The flux data are provided in Figure 5.5 along with the data for EDTA from Section 5.1. The flux data are normalized to deionized water flux at pH=10.5 measured immediately before the flux of the salt solutions.

Flux increases were observed for the cationic surfactant and calcium chloride relative to deionized water flux at pH=10.5. The fluxes of sodium sulfate, sodium chloride, and EDTA were similar to deionized water at pH=10.5. The data show that altering the ionic characteristics of the solution can have a significant impact on the magnitude of copolymer swelling at elevated pH. The relationship between anionic modification, salt flux, and the mechanism of pH-dependent swelling is described in the next section.

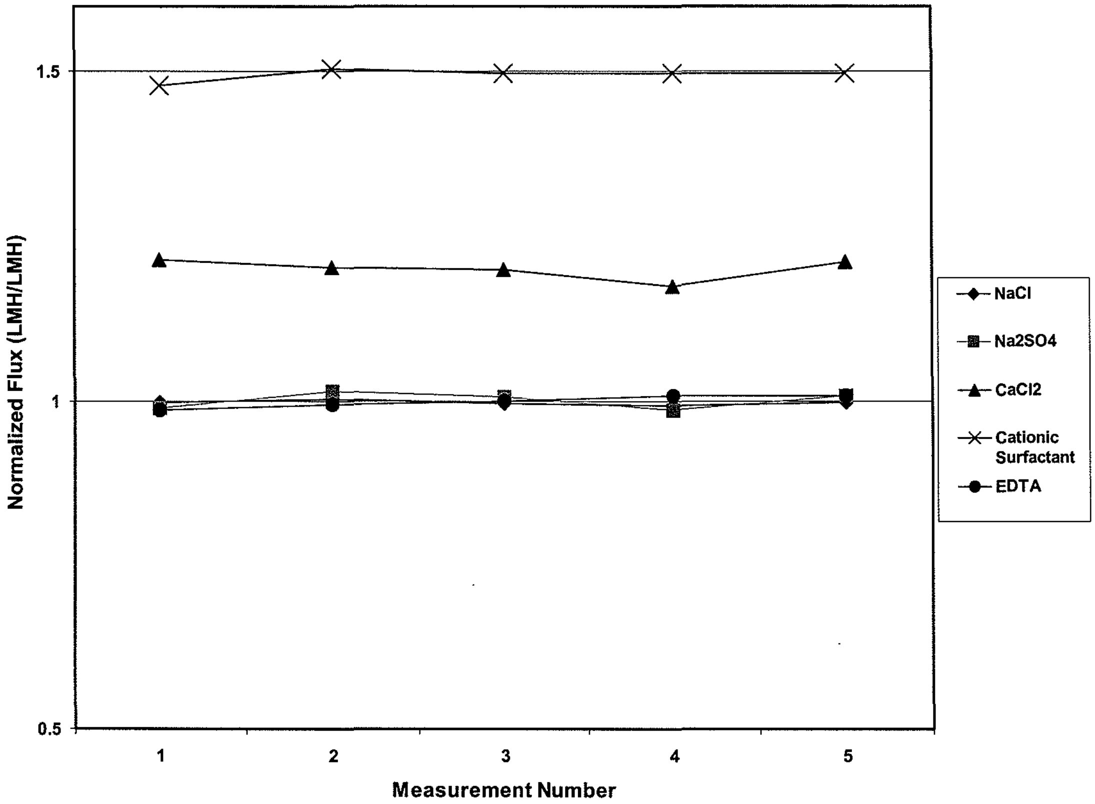
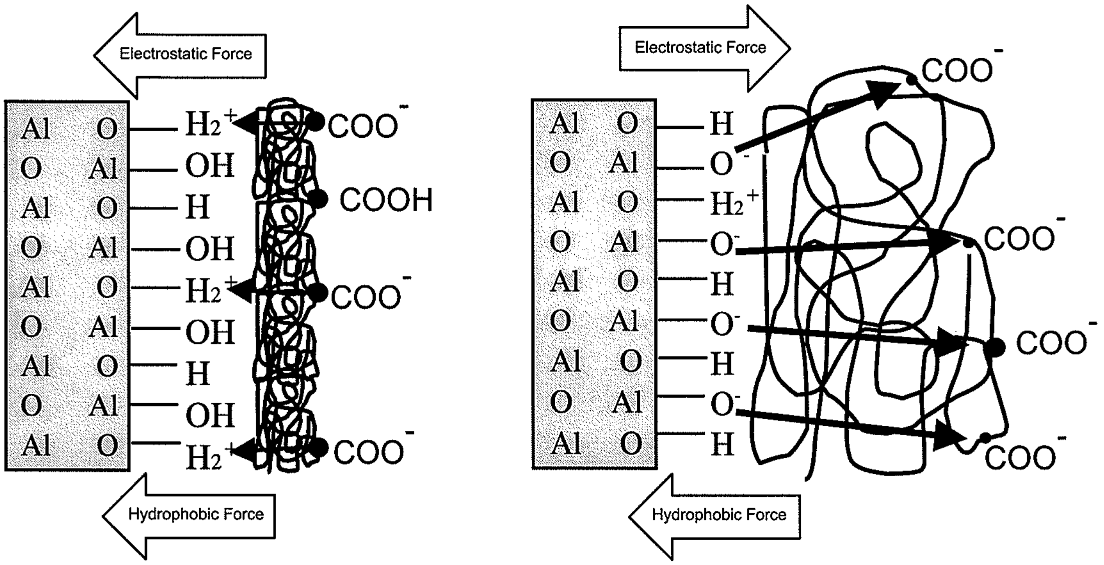


Figure 5.5. Normalized flux of selected salts at 10^{-2} M adjusted to pH of 10.5 after membrane exposure to anionic polyglycol, cleaning, and rinsing. Data are normalized to water flux adjusted to pH=10.5.

5.5.4 Mechanism of pH-Dependent Swelling of Anionic Polyglycols

The magnitude of flux decline caused by pH-dependent swelling is determined by: 1) the distance the adsorbed polymer extends into solution to constrict pores, and 2) the permeability of the pore-constricting layer. Figure 5.6 illustrates the effect of adsorbed copolymer extension on membrane pore-constriction and flux-decline.

Figure 5.6 offers mechanistic insight into the pH-dependent flux-erosion behavior of the anionic copolymer residual. When cleaning procedures were insufficient to remove the copolymer from the membrane, normal flux was observed at the pH of deinoized water (pH=5.5) because the copolymers assumed a non-pore constricting conformation. This was possible due to low levels of repulsive interaction among the copolymers and between the copolymers and the alumina surface. However, increasing the pH of the permeating solution simultaneously ionized the carboxylic acid groups of the anionic copolymer and shifted Equation 5.3 strongly to the right. The repulsive interactions increased the mean distance between the copolymer and the surface and the



Moderately Low Solution pH

High Solution pH

Figure 5.6. Conceptual illustration of copolymer swelling at elevated pH.

mean distance between copolymer chains. The end-effect was a dramatic swelling of the copolymers adsorbed to the membrane surface that was observed in Figure 5.4 and which presented a strong barrier to permeation that was detected by flux observations.

The configuration of adsorbed copolymer in the membrane can change in the presence of salts. For instance, it was observed in Figures 5.1 and 5.2 that flux of the anionic polyglycol increased when a salt with divalent ion of sign opposite the prevailing charge on the membrane surface (divalent counterion) was added to the solution. The divalent counterions were capable of interfering with membrane-copolymer and copolymer-copolymer repulsions such that the copolymer swelling decreased. The pH of the solution relative to the isoelectric point of the surface determined whether positive or negative ions impacted the degree of flux-erosion caused by the anionic copolymer.

Figure 5.5 also suggests that counterion valence impacts the degree of flux-erosion. The effect of ion valence (z) on intermolecular forces has been approximated by the Shulz-Hardy rule which states that repulsive forces between particles decrease with added ionic strength by z^6, where z is the relevant ion valence (Adamson and Gast, 1997). In Figure 5, increasing cation valences between NaCl ($z_+ = 1$), $CaCl_2$ ($z_+ = 2$), and the cationic surfactant ($z_+ >> 2$) had a significant impact on flux. In fact, the addition of the cationic surfactant reversed the impact of pH-dependent swelling and returned flux to levels observed at lower pH.

In contrast, increasing anion valences going from NaCl ($z_- = 1$), to Na_2SO_4 ($z_- = 2$), and tetrasodium EDTA ($z_- = 4$) had no significant impact on flux. The flux of these salt solutions was approximately the same as water flux at elevated pH. Increasing anion valence had no significant impact on flux because the swelling results from repulsive forces between negative charges on the membrane and the negatively charged anionic copolymers. Only positive charges can disrupt these repulsive forces, and consequently, only positive charges can reduce the swelling of the adsorbed anionic copolymer that leads to reduced flux at elevated pH. The results provided here show that the valence of cations in solution has a significant influence on this process.

5.6. Conclusions

During the microfiltration of uncontaminated synthetic MWFs using aluminum oxide membranes, the interaction of relatively low concentration specialty additives with the membrane surface has a significant effect on the overall productivity. For the case of polyglycol copolymers used as hydrodynamic lubricity additives, adsorption leading to pore-constriction and increased resistance to flow is the dominant mode of flux-decline. The concentration of these additives has a significant effect on the maximum achievable filtration rate of the process. In particular, the paper has shown that:

1. Both nonionic and anionic diblock copolymers can adsorb to α-alumina membranes to reduce flux. Increasing the mass of propylene oxide relative to ethylene oxide can increase the magnitude of flux decline. Anionic modification can also lead to flux-decline and requires special attention during cleaning.

2. Anionic copolymers adsorbing to aluminum oxide surfaces can assume variable pore-constricting configurations as a function of pH. Divalent cations and cationic surfactants in solution can improve permeability at pH above the isoelectric point of alumina, but they only have a minimal impact when the anionic polyglycol is present in the permeating solution.

3. Interactions between anionic copolymers and the membrane surface can be removed through the application of high temperature/high pH cleaning solutions. Increased convection of the cleaning solutions through the membrane assists this process. However, deionized water flux alone at typical pH (e.g., pH=5.5) will not detect residual anionic polymer remaining after cleaning. A supplemental indicator fluid at elevated pH must be used to assure the residual polymer has been removed.

4. Aluminum oxide microfilters offer several advantages in the synthetic MWF recycling application. These include chemical and biological stability, ability to withstand harsh cleaning procedures, and resistance to mechanical damage by machining particulates. However, the results presented here show that the use of aluminum oxide membranes poses special challenges in certain applications, such as during the recycling of anionic copolymers used as hydrodynamic lubricity additives in metalworking fluids. When anionic copolymers are required for a given operation, they should be used at the minimum concentration required by the metalworking process.

Chapter 6

Conclusions and Recommendations

6.1. Conclusions

The state-of-the-art application of metalworking fluids (MWFs) in the machine tool industry has four critical issues that require attention.

1. Particulate, tramp oils, and bacteria are known to reduce the quality of metalworking operations.
2. These contaminants lead to premature disposal of the MWF and thus reduce the profitability of metalworking operations.
3. The disposal of MWF places a significant burden on the environment.
4. Bacteria and the biocides used to control their growth in MWFs can be a significant health hazard.

The process of membrane filtration has the potential to alleviate all four of these critical issues by removing particulate, tramp oils, and bacteria from MWFs and permitting the reuse of MWF at the machine tool. To facilitate and better understand that process, this research had three objectives:

- Experimentally isolate MWF ingredients that cause productivity loss during membrane filtration recycling;
- Study the mechanisms of productivity loss during the membrane filtration recycling of MWFs;

These objectives were fulfilled in the context of uncontaminated synthetic MWF microfiltration using aluminum oxide membranes. The following describes the specific conclusions corresponding to each objective.

Experimentally isolate MWF ingredients that cause productivity loss during membrane filtration recycling. Controlled experimentation with aluminum oxide membranes revealed that uncontaminated synthetic MWFs can cause significant productivity loss compared to water. In the process of studying synthetic MWF ingredients that can cause productivity loss, the following conclusions were reached:

- Base fluid constituents comprising greater than 99% of the formulation investigated and common to synthetic MWF chemistries do not cause productivityerosion independent of previous membrane exposure to specialty additives.

- Productivity decline in uncontaminated synthetic MWFs results from low concentration specialty additives such as lubricant additives, biocides, and defoamers.

- Specialty additives can impart changes to the surface behavior of aluminum oxide membranes that remain after cleaning and are undetectable with water flux measurements. These residual effects reduce the subsequent productivity of base fluid ingredients in subsequent experiments with the membrane.

- Due to the sensitivity of membrane filtration productivity to low concentration specialty additives, specialty additives require particular attention with respect to their chemistry and use concentration when optimizing MWF formulations with respect to membrane filtration recycling.

Study the mechanisms of productivity loss during the membrane filtration recycling of MWFs. A comparison between flux data for MWF specialty additives and known characteristic flux data described in the literature for various fouling mechanisms suggested that adsorption of MWF ingredients to aluminum oxide membranes is the dominant source of flux decline for the specialty additives. This was confirmed using Field Emission Environmental Scanning Electron Microscopy (FE-ESEM). In addition, general chemical characteristics that lead to adsorption and flux decline were revealed for a common class of lubricant additives found in water-soluble MWFs. Specifically, it was revealed that:

- Adsorption of synthetic MWF specialty additives leads to a reduction of pore diameter (pore constriction) that serves to reduce productivity.

- The bulk of the pore constriction and productivity decline caused by the full synthetic MWF investigated in this research is accounted for by a single diblock copolymer used as a hydrodynamic lubricant additive.

- Organosiloxane defoamer dispersions in water cause flux decline by cake layer formation at the membrane surface.

- A mixture of defoamer and synthetic MWF does not cause the formation of a cake layer, but the defoamer still adsorbs to the membrane surface resulting in increased foaming tendency for the MWF.

- Various types of diblock copolymers are commonly used as hydrodynamic lubricant additives in water-soluble MWF formulations. Both nonionic and anionic diblock copolymers found in MWFs can adsorb to α-alumina membranes to reduce productivity. Increasing the hydrophilic to hyrdrophobic ratio in the copolymers can increase the magnitude of productivity decline. Anionic modification can also lead to productivity-decline and requires special attention during cleaning.

- Anionic diblock copolymers adsorbed to aluminum oxide surfaces can assume variable pore-constricting configurations as a function of pH. Divalent cations and cationic surfactants in solution can improve permeability at elevated pH, but they only have a minimal impact when the anionic polyglycol is present in the permeating solution.

- Adsorption of the anionic copolymers to the membrane surface can be eliminated through the application of high temperature/high pH cleaning solutions. However, a supplemental indicator fluid at elevated pH must be used after cleaning to assure the residual copolymer has been removed from the membrane.

- Aluminum oxide microfilters offer several advantages in the synthetic MWF recycling application. These include chemical and biological stability, ability to withstand harsh cleaning procedures, and resistance to mechanical damage by machining particulates. However, the results presented here show that the amphoteric nature of aluminum oxide membranes poses special challenges during the recycling of anionic copolymers.

6.2. Recommendations for Future Research

Investigate the compatibility of mineral oil-containing MWFs with membrane filtration recycling. Some MWFs that are mineral oil emulsions (i.e., semi-synthetics and soluble oils) contain the same lubricant additives and defoamers investigated in this research. They also contain emulsion droplets that further complicate MWF transport through the membrane and present an additional opportunity for membrane fouling. Also, surfactants present in semi-synthetic and soluble oil formulations may emulsify contaminant oils from the machine tool and increase the effective particle size of the fluid. This can lead to subsequent retention of the MWF that may have been initially absent. The academic study of semi-synthetic and soluble oil compatibility with membrane filtration has yet to be performed.

Determine the impact of contaminants on the productivity of membrane filtration processes. Previous academic research of ceramic grinding chip removal should be extended to other contaminants such as oils, microorganisms, and the wider assortment of chip morphologies and materials that may be encountered in used MWF. This research should be conducted in the presence of MWF ingredients and formulations commonly used in the machine tool industry.

Investigate alternative membrane materials and pore-size distributions. Aluminum oxide membranes are robust to industrial manufacturing conditions and have a long service life but are several times more costly than polymeric membranes currently available. Although the higher cost of ceramic membranes will not preclude their use in industrial applications, in some applications where they are applicable, polymer membranes might increase the profitability of the recycling process.

Pore-size distribution can have a major impact on the passage and productivity observed for a given membrane. For instance, polyglycol lubricant additives that are retained by ultrafiltration (10,000 MWCO) membranes are not significantly retained by microfiltration membranes (0.2μm). Similarly, preliminary research with semi-synthetic MWFs has revealed that semi-synthetic emulsions that do not permeate through 0.2μm membranes can permeate through 0.5μm or 1.3μm membranes. A better understanding of the role of pore-size distributions in productivity and retention characteristics of MWFs is a prerequisite to optimizing membrane filtration for the gamut of chemistries currently available in the machine tool industry.

Develop process-models for metalworking operations in the presence of cutting fluid. Process models to relate MWF chemistry to process performance are not currently available. Such models are required for optimization of the recycling process since the MWF chemistry has a significant bearing on metalworking performance as well as membrane filtration productivity. MWF formulations that have higher productivity during membrane filtration should not be allowed to compromise MWF performance, and conversely, elevated concentrations of ingredients that are not required by the metalworking process should not be used with membrane filtration.

Investigate the reduction of MWF volumes used in machining applications. Lower MWF volumes are more amenable to contaminant control and naturally lower acquisition and disposal costs. Current research has shown that in some applications MWF application volumes can be reduced by an order of magnitude without impacting manufacturing performance. Minimal MWF volumes should be used where possible.

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