Membrane Fouling by Marine Algae in Seawater Desalination
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Membrane Fouling by Marine Algae in Seawater Desalination

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FOREWORD

The Water Research Foundation is a nonprofit corporation that is dedicated to the implementation of a research effort to help utilities respond to regulatory requirements and traditional high-priority concerns of the drinking water community.

The Arsenic Water Technology Partnership (AWTP) program is a partnership between Water Research Foundation, Sandia National Laboratories (SNL) and WERC, a Consortium for Environmental Education and Technology Development at New Mexico State University that is funded by DOE and the Water Research Foundation. The goal of the program is to provide drinking water utilities, particularly those serving small and rural communities, with cost-effective solutions for complying with the new 10 ppb arsenic MCL. This goal is being met by accomplishing three tasks: 1) bench-scale research to minimize operating, energy and waste disposal costs; 2) demonstration of technologies in a range of water chemistries, geographic locales, and system sizes; and 3) cost effectiveness evaluations of these technologies and education, training, and technology transfer.

The AWTP program is designed to bring new and innovative technologies developed at the laboratory and bench-scale to full-scale implementation and to provide performance and economic information under actual operating conditions. Technology transfer of research and demonstration results will provide stakeholders with the information necessary to make sound decisions on cost-effective arsenic treatment.

The Foundation participates in the overall management of the program, helps to facilitate the program’s oversight committees, and administer the laboratory/bench-scale studies. SNL conducts the pilot-scale demonstrations and WERC oversees the education, training, economic analysis, and outreach activities associated with this program.

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EXECUTIVE SUMMARY

OBJECTIVES

The overall objective of this project was to discover fundamental knowledge about how marine bloom-forming algae affect membranes used for seawater desalination. Reverse osmosis (RO) membranes were of interest, but also microfiltration (MF) and ultrafiltration (UF) membranes that are gaining popularity for pretreatment ahead of RO.

BACKGROUND

Because of increasing water demand many parts of the world are turning to seawater desalination as an additional means of providing municipal water. One of the challenges facing seawater desalination facilities is membrane fouling caused by a buildup of organic matter or biological growth that impedes water production and increases energy requirements. One occasion when fouling becomes extreme is during an algal bloom event when marine algae rapidly increase in concentration and cause the particulate and total organic matter content of the water to reach abnormally high levels. The most notorious of these events is called “red tide” because the algal-laden waters have a red color that is obvious to the naked eye. What an earthquake is to a building, a red tide is to a seawater desalination plant; it can lead to severe failure of the desalination treatment train. Some full-scale membrane facilities have been challenged by red-tide events and red tides are common in other areas where desalination plants have been proposed; however, little is known about the mechanisms of algal fouling in desalination facilities, nor about the nature of the material derived from algae that would be most responsible for fouling problems. Further, there is no consensus in the industry about how best to remove algae from the water to protect the desalination plant.

APPROACH

This project involved a set of bench-scale experiments aimed at answering basic questions about the nature of algae and their foulant material. A strain of bloom-forming algae was cultured in the laboratory and used to challenge membranes under various conditions. RO membranes were challenged with algal organic matter to measure the decline in performance. Several “membrane autopsy” techniques were used to characterize the fouling quantitatively and qualitatively.

MF and UF membranes were also used in bench-scale tests. Algae were exposed to hydrodynamic shear to determine how algal breakup and organic matter release would affect MF and UF performance. Experiments were performed to determine which size fraction and chemical species of algogenic organic matter (AOM) were most responsible for MF and UF fouling.

Because bacteria are present during algal blooms, the effects of bacteria on filtration were of interest. A simulated algal bloom was created where algal and bacterial numbers were monitored and MF filtration tests were performed over several weeks to determine how fouling changed as the algal bloom composition changed.
Lastly, a potential method for removing algae and enhancing membrane performance was tested: clay flocculation. Kaolin clay was added to algal samples in a variety of MF tests to determine whether clay flocculation might be a viable means of minimizing membrane damage from algal blooms.

RESULTS/CONCLUSIONS

Direct spikes of algae (40,000 cells/ml) in bench-scale RO tests caused about 10% flux decline in 24 hours. This represents a worst-case scenario of algae feeding directly into the RO membranes. When particulates ( > 0.45 µm) were removed the remaining AOM caused very little flux decline (~ 2%). Autopsy revealed that AOM did deposit on the membrane, but because RO membranes are inherently resistive to water passage the AOM did not significantly increase the overall resistance. Fouling patterns show that algae and AOM deposited in dead zones around the feed spacer and in dimples formed in the membrane by the permeate carrier. Proteins were more abundant than carbohydrates, but both were present in the foulant cake layers.

Algae were much more problematic (in terms of flux decline) for MF and UF membranes. The algal cells themselves (about 10 to 15 µm in size) caused rapid flux decline in bench-scale tests, but cell-derived material down to 0.2 µm caused an even more pronounced decline. Hydrodynamic shear applied to the algal cells caused them to break apart and produce an abundance of the highly fouling particulate fraction. Adsorption of dissolved AOM had minimal impact on short-term filtration (using 0.1 µm hydrophilic MF membranes).

Bacteria were an important cause of flux decline during the simulated algal bloom; flux decline was exacerbated as bacterial numbers increased even after algal numbers declined. Bacteria are in the size range (around 1 to 2 µm) that proved most problematic for MF/UF filtration.

Clay flocculation was successful in both aiding removal of algae during jar tests and in decreasing fouling during MF tests. Clay was most effective when coupled with ferric chloride to induce flocculation. The most notable benefit of clay addition was improved flux recovery over multiple filtration cycles compared to ferric-chloride-only flocculation that actually decreased flux recovery.

APPLICATIONS/RECOMMENDATIONS

Reverse Osmosis

It is unlikely that algae in their native form would be capable of passing through pretreatment and entering full-scale RO modules. Thus flux decline due to thick algal cake layers would not be expected. AOM derived from algae is the more probable cause for concern. Algae can generate large quantities of organic matter and release these into the water matrix, especially if they are sheared in intake pumps and plumbing. The AOM itself would not likely cause much flux decline, but it could form a conditioning film on the membrane surface that enables bacterial attachment. AOM could also serve as substrate for biofilm growth inducing a serious biofouling situation.

The best protection for RO membranes would be to remove the algae, AOM, and bacteria during pretreatment. If possible, pretreatment should be done with a low-shear system to minimize AOM release. Fluorescence measurements of raw and filtered (i.e. using a laboratory
syringe filter) are recommended as a means to determine if cell breakup due to shear is occurring during pretreatment.

Next-generation RO modules should be designed with minimal dead zones to reduce the fouling that occurs around the conventional feed spacer pattern. Also, a permeate carrier that produces less roughness (on the mm scale) would aid in minimizing AOM buildup in the modules.

### Microfiltration and Ultrafiltration

This study calls into question whether MF and UF membranes are a good strategy for seawater RO pretreatment when algal blooms are common. Algae and their associated bacteria can severely damage an MF or UF facility. But where MF and UF are employed, preventative measures can be used to minimize algae-related problems.

Hydrodynamic shear should be minimized to reduce algal breakup. Low-shear pumps should be sought during facility design and pumps can be run at lower speeds during a bloom event. Plumbing and valves should also be evaluated to determine where shear can be minimized. This may be difficult, practically speaking, but a reduction in shear may mean significant improvements in the filtration process.

Clay flocculation may be a promising avenue for algal fouling mitigation. Clay can enhance algal removal in coagulation/flocculation/settling, or it can be added directly to the feed to improve flux when no settling basin is available. Facilities that use ferric chloride for flocculation should seriously consider clay amendment, since ferric chloride caused worse flux recovery during bench-scale experiments than untreated algae. The major drawback to clay addition would be increased solids handling, but low concentrations of clay did show beneficial effects and since algal blooms are intermittent, clay would only be needed for short time periods. More work is certainly needed since this study is the first to explore clay amendment for algae, but the proof of concept has been established here.

### PARTICIPANTS

The participants in this project were the Long Beach Water Department, Long Beach, CA, represented by Robert Cheng, and the Marin Municipal Water District, Corte Madera, CA, represented by Bob Castle.
CHAPTER 1: INTRODUCTION

The problem of fouling by algae in integrated membrane systems (RO preceded by MF or UF) requires background in several arenas. It is useful to explore what is known about fouling phenomena in general from textbook presentations after decades of fouling studies and industry experience. Often the phenomena that are seen in the low-pressure regime (where fouling studies have been more extensive) are also applicable to the high-pressure case; both are treated together here. Mechanisms of membrane fouling like pore blocking, adsorption, and cake-enhanced concentration polarization are discussed.

Because of the applied nature of the algal fouling problem it is important to evaluate bench-, pilot-, and full-scale data from studies with natural waters. Most natural-water fouling tests are performed with fresh surface and river waters. Insight from some of those studies is presented here, but the focus is on seawater literature, which is sparser. Also sparse are reports of fouling by algae in seawater desalination systems, since seawater desalination for municipal drinking water is still rarely used (especially in the United States) and algal blooms occur sporadically. There have been enough cases, however, to suggest that algal blooms will become a bigger problem as seawater desalination becomes more widespread. Here we will present case studies of pilot and full-scale facilities that have experienced bloom problems. We will also explore the small body of research papers that have investigated algal fouling in the laboratory.

The body of knowledge from oceanographic and biological research is also useful. Much has been accomplished in the way of characterizing marine algal blooms like the notorious “red-tide” events that plague coastal areas. Information about species types and bloom dynamics from oceanographic research can give clues to the engineering community on how to mitigate fouling problems.

MEMBRANE FOULING

Membrane fouling has been an important issue for as long as membranes have been employed for water treatment. Several textbooks that deal with water treatment and/or membranes contain sections or chapters on fouling and readers are referred there for a big-picture view of the body of fouling knowledge (Mulder 1991; Cheryan 1998; Duranceau 2001; Crittenden et al. 2005). A concise literature review of membrane fouling in water treatment was published recently that discusses advancements in fouling understanding over the past several years (Escobar et al. 2005). A short summary of this “textbook” knowledge about fouling is presented here, with a focus on information that is directly applicable to algal fouling problems.

Fouling is defined as the buildup of material on the membrane surface that causes a reduction in flux. Reversible fouling is flux decline that can be recovered with a backwash of the membrane. Irreversible fouling is longer-term fouling that is not recovered with a backwash. The distinction between reversible and irreversible fouling is relevant mainly for low-pressure membranes, since high-pressure membranes have such low intrinsic permeability that they cannot be backwashed.

Fouling depends heavily on the membrane material, with hydrophobic membranes generally fouling more readily than hydrophilic membranes (Laine et al. 1989; Jucker and Clark 1994; Howe and Clark 2002). Membrane surface morphology is also important; rough surfaces are usually more easily fouled than smoother surfaces (Elimelech et al. 1997; Vrijenhoek et al.
Membrane Fouling by Marine Algae in Seawater Desalination

2001; Li et al. 2007). Low pH and high ionic strength can increase fouling, especially for extracted natural organic matter (NOM) (Jucker and Clark 1994; Braghetta et al. 1998). All material rejected by the membrane (including foulants) build up in the concentration polarization layer (DiGiano et al. 2000). When flux is increased, the balance of forces in the concentration polarization layer favors compaction of the foulant layer and increased concentrations; at some point, a “critical flux” may be reached. Beyond this critical flux, foulants interact more heavily with the membrane, often causing irreversible fouling (Zhu and Elimelech 1997).

Calcium has been shown to be quite important in natural-water fouling. Calcium appears to form a bridge between the membrane surface and the organic foulants (Ahn et al. 2008). Additionally, aluminum and silica have been identified in surface-water foulants (Howe et al. 2002). These results are consistent with previous research claiming that both inorganic and organic foulants should be studied simultaneously (Schafer et al. 2000). Calcium would be expected to be important in seawater studies, since it is abundant; however, the high concentration of other salts may change the impact of calcium on fouling.

Natural waters contain particular size fractions of NOM that have more fouling propensity than the bulk NOM. In one lake water study, only a small fraction of dissolved organic matter (DOM) falling between 3 and 20 nm in size, caused fouling of UF membranes (Howe and Clark 2002). It has been shown that high-molecular-weight NOM consisting of biopolymers may be the main cause of fouling in wastewater treatment (Jarushitthirak and Amy 2006).

Cake-enhanced concentration polarization

One fouling mechanism unique to high-pressure salt-rejecting membranes deserves special attention here: cake-enhanced concentration polarization (CECP). As mentioned above, concentration polarization is the buildup of salts at the membrane surface. Salt buildup is balanced by back-diffusion of salts toward the bulk feed solution and back-diffusion is enhanced by crossflow. Under the CECP model the foulant layer hinders back-diffusion because the solute travel path is more tortuous and because crossflow is diminished (Hoek and Elimelech 2003). A diagram comparing concentration polarization to CECP is shown in Figure 1.1. Note that CECP would not occur in low-pressure membrane systems since salts are not rejected.

The first few studies to investigate the importance of CECP focused on monodisperse 100-nm latex particles as model colloidal foulants (Hoek et al. 2002; Hoek and Elimelech 2003). Flux decline was caused mainly by heightened osmotic pressure rather than by hydraulic resistance in the foulant layer. In natural seawaters, especially under algal bloom conditions, the foulants will not be monodisperse and it is unclear whether hydraulic resistance or CECP would dominate. Fouling by combined colloidal and dissolved materials is different than fouling by either colloidal or dissolved material alone (Li and Elimelech 2006).

Since the introduction of the CECP concept several investigators have applied the model to their membrane fouling studies. In most cases CECP is simply cited as a most-probable fouling mechanism with little effort at finding evidence for whether it was indeed present. Other workers, however, have verified that CECP does occur. Chong et al. (2007) used a novel NaCl tracer test whereby they found that CECP did in fact elevate the NaCl concentration at the membrane surface and cause decreased flux. The test was done in a dead-end mode where CECP would be more prevalent since crossflow was not present to aid back-diffusion. Lee et al. (2005)
found that CECP was not always dominant; for their particular case with NF membranes NOM-calcium complexation that reduced hydraulic permeability was more important.

The CECP concept has been extended to biofouling with what was dubbed “biofilm-enhanced osmotic pressure” (Herzberg and Elimelech 2007). An interesting finding was that CECP was more dominant compared to hydraulic resistance for early biofilms and dead bacterial cells. With living cells in a well-established biofilm hydraulic resistance played a more important role. EPS filling the voids between bacterial cells caused a decrease in hydraulic resistance without greatly changing the level of CECP. This finding was supported with the evidence that salt rejection was the same for the two biofilms while the EPS-filled biofilm showed greater flux decline.

Some investigators have taken a mathematical approach at modeling the CECP phenomenon to determine how various parameters affect it. For a model biofilm CECP was enhanced because extracellular polymeric substances (EPS) retard back-diffusion of salts more than would be seen with hard-spheres particles (Kim et al. 2006). Tortuosity, (which is the reason that back-diffusion of salts is hindered) in a random, irregular structure like a biofilm is more drastic (Kim and Chen 2006).

Ng and Elimelech (2004) showed that CECP caused a decrease in trace-contaminant rejection; intrinsic membrane rejection was constant, but because the contaminants built up in the cake layer a higher concentration was available for permeation.

From the papers on CECP mentioned above, it appears that CECP is an important mechanism for flux decline in high-pressure systems. Hydraulic resistance is often downplayed as a mechanism, perhaps because the paper that introduce CECP emphasized that hydraulic resistance was significantly less important (Hoek and Elimelech 2003); however, hydraulic resistance was important in a few of the cases above, specifically for colloids coated with NOM and for biofilms with EPS. One of the challenges remaining in high-pressure fouling studied is to find ways to measure the relative contributions of CECP and hydraulic resistance to overall flux decline, especially in natural-water systems where the foulants are not well-characterized.

**ALGAL BLOOMS AND MEMBRANE FOULING**

**Marine algal blooms**

One potentially severe membrane foulant for seawater desalination is algae introduced to the feed water during a bloom. Marine algal blooms are caused by a few classes of phytoplankton, dinoflagellates being the most common. The dinoflagellate species *Lingulodinium polyedrum* has been the cause of massive red tide events in coastal California (Kahru and Mitchell 1998; Moorthy et al. 2006). In the Gulf of California, *Dinophysis caudate* and *Alexandrium catenella* have been identified (Lechuga-Deveze and Morquecho-Escamilla 1998). *Karenia brevis* (previously known as *Gymnodinium breve* and *Ptychodiscus brevis*) is a dinoflagellate causing toxic red-tide blooms in coastal Florida (Kirkpatrick et al. 2004; Kirkpatrick et al. 2006). *Heterocapsa pygmaea, Prorocentrum minimum*, and many others, have been identified (Johnsen et al. 1997; Trigueros and Orive 2000; Heil et al. 2005; Maso and Garces 2006). Even in waters where blooms are rarely seen, like the San Francisco Bay, dinoflagellate species can sometimes find just the right water quality and weather conditions to make a cameo appearance (Cloern et al. 2005).
Membrane Fouling by Marine Algae in Seawater Desalination

Blooming dinoflagellates are in a size range (10 to 50 µm) that would easily pass through inlet screens. Their neutral buoyancy and ability to swim also make settling chamber removal impractical, though certain types of coagulation/flocculation or floatation-based methods may be worth considering (Edzwald 1993; Sengco et al. 2001; Pierce et al. 2004; Sengco and Anderson 2004). Dinoflagellates are easily rejected by microfiltration (MF) and ultrafiltration (UF) membranes, but a bloom with high cell concentration (on the order of $10^5$ cells per ml) will quickly form a thick cake layer and impede water passage. If cells are damaged, either through natural death cycles, or through shear in the pumping system, they may release organic matter that passes through the pretreatment system to the RO membranes. Organic matter can directly foul the RO membrane and/or serve as substrate for bacterial species in biofouling.

As an algal bloom life cycle peaks and decays, a significant amount of organic material is released upon cell death (Whipple et al. 2005). Bacteria feed on the decaying material and release their own extracellular polymeric substance (EPS) that has the potential to foul pretreatment and RO membranes (Asatekin et al. 2006; Rosenberger et al. 2006). It is possible that the material from decomposition could have more of an impact on membrane fouling than the algal cells themselves.

Industry experience with algal fouling

Fouling by algae in full-scale membrane systems is a topic that has recently come to the forefront of the discussion among industry personnel working on seawater desalination. Much of the available knowledge is found in conference proceedings, news reports, and personal communications. These are presented here with a recognition that such sources are probably less reliable than peer-reviewed papers, but they give us a feel for the breadth of the problem and the mitigation strategies that are currently being employed.

MF and UF pretreatment systems are often effective for mitigation of fouling in seawater RO (Wilf and Klinko 1998; Drioli et al. 1999; Brehant et al. 2003; Teng et al. 2003). UF membranes, especially, are able to remove many organic constituents released by phytoplanktonic organisms; however, in one study even UF pretreatment did not prevent RO fouling at high flux (Glucina et al. 2000). It was assumed that the foulant was organic material small enough to pass through the UF membrane. From oceanographic studies, it is known that there exists a large fraction of seawater DOC smaller than the molecular-weight cutoffs of UF membranes (Aluwihare et al. 1997).

The authors’ first knowledge about algal bloom problems experienced in seawater desalination came through discussions with representatives at the US Navy’s Port Hueneme, CA, desalination test facility and with their collaborator at the Orange County Water District, CA (Ishida 2006). They experienced a red tide event during testing of an integrated membrane system (MF followed by RO). The worst damage occurred on the MF membranes, which were subsequently taken offline for extensive cleaning. The membranes were coated with an orange-yellow fouling layer and infrared absorption analysis revealed peaks for carbohydrates and proteins. It was suspected that large macromolecules, as opposed to the whole algal cells themselves, were the main fouling culprit.

The French water company Degrémont has been active in designing desalination plants and have published their ideas of combating algal blooms and low-quality water sources, in general. A pilot test for a proposed plant in Chile experienced algal bloom problems early in the testing phase (Petry et al. 2007). Dual-media filtration (DMF) was insufficient in removing
algae. Dissolved air flotation (DAF) was added before the filtration step, but performance was still inadequate. The final design called for DAF followed by two stages of DMF in order to achieve sufficient water quality during algal blooms. With such aggressive pretreatment RO membrane fouling was not observed.

Degrémont representatives more recently reported their cost analysis of using MF or UF for RO pretreatment (Bonnélye et al. 2008). A conventional treatment train using DMF was more cost effective when the seawater quality was good, since DMF capital and operating costs were lower than MF/UF. For poor water quality as found during an algal bloom, however, MF/UF became economically viable because it was better at removing foulants and protecting the downstream RO elements.

In a Korean pilot study sand filtration was inadequate to remove red-tide algae so MF was installed (Kim et al. 2007). The MF membranes were able to effectively remove the algae and RO membranes performed well; however, the authors did not describe whether MF performance was affected by algae.

The most recent report found of a seawater desalination plant being affected by an algal bloom was a facility in Fujairah, United Arab Emirates (Sambidge 2008). DMF filters were overloaded with solids (algal biomass) during the event and the facility had to be shut down until the bloom subsided. The algal species in that case was a golden-brown Heterosigma species at a concentration of 1,800 to 2,400 cells/ml (Marquis and Trick 2008). Heterosigma is of the raphidophyte class which is similar to dinoflagellates in that it is unicellular and motile.

In several of the cases mentioned above DMF was not effective for algal removal, but in a Gibraltar seawater desalination plant chlorophyll a and its breakdown product pheophytin were removed through a single-stage DMF. It is expected that the difference was due to foulant concentration. The Gibraltar plant did not experience bloom conditions so the low levels of algae present could be removed. It is important to recognize this dependence on concentration when considering the removal efficiencies reported for different systems.

An integrated membrane treatment plant using UF and RO for surface-water treatment in the Netherlands experienced increased biofouling of UF membranes when algal blooms were present (Kamp et al. 2000). Membranes were cleaned with a more alkaline solution to improve flux after the fouling event. Biofouling of the RO elements was also reported. Cell fragments (assumed to be bacterial/biofilm cells in this case) passing the UF system contributed to the RO-element biofilm growth.

The reports and case studies mentioned here are sufficient to conclude that algal fouling of integrated membrane systems is a problem in seawater desalination. RO membranes can be protected by MF and UF membranes, which are better at removing cells than conventional media filtration; however, the MF/UF membranes are then themselves fouled.

Algal fouling laboratory studies

A few investigations of membrane fouling by algae have been performed in the laboratory. Her et al. (2004) used blue-green algae (cyanobacteria) for NF fouling. They determined that AOM was more detrimental to the membranes than Suwannee River humic acid (SRHA). The AOM molecular weight was highly heterogeneous (high polydispersivity) and had a high hydrophilic fraction (57%) compared to SRHA. The authors concluded that the heterogeneously-sized hydrophilic material was responsible for the exacerbated fouling by AOM. The AOM was comprised of 68% protein, 22% carbohydrate, 5% lipid, and 3%
chlorophyll \( a \) (according to the supplier); both proteins and carbohydrates were found in the foulant layer.

Fouling of UF membranes by the fresh-water cyanobacterial species *Microcystis aeruginosa* was studied to determine how cells interacted with NOM in the foulant layer (Kwon et al. 2005). Cells and NOM had a synergistic effect on fouling; the combined flux decline was greater than the sum of each component’s flux decline. It should be noted that though cyanobacteria are called blue-green algae, they are a bacterial species and their cell size (~3 \( \mu m \)) is smaller than most bloom-forming marine algae (10 to 50 \( \mu m \)). Still, it is possible that a synergistic effect between cells and organic matter occurs in any algal fouling event.

In an effort to optimize MF for removal of red-tide algae one team reported that crossflow filtration was more effective than dead-end, which would be expected for a high-biomass sample (Kim and Yoon 2005). Two algal species were used and different fouling propensity was observed; the dinoflagellate species *Prorocentrum micans* produced a larger amount of soluble microbial products (SMP) and caused more fouling than the diatom *Thalassiosira* sp. even though *P. micans* was larger (35-70 \( \mu m \)) than *Thalassiosira* (10-50 \( \mu m \)). The authors hypothesized that SMP penetrated into the membrane matrix and blocked pores more dramatically than the whole algal cells on the membrane surface. Interestingly, however, the membrane used here was reported to have a pore size of 2 to 3 \( \mu m \), which is quite large for microfiltration. SMP was detected by carbohydrate measurements alone and the size distribution was not determined. It is possible that the measured SMP contained particles in the 2 to 3 \( \mu m \) range that were not actually soluble, but that did enhance fouling.

**Effects of shear on algal fouling**

One concern that has been lightly addressed in algal fouling studies is the release of internal organic material when cells are broken by hydrodynamic shear forces. Shear is important in the release of toxins from some algal types (Himberg et al. 1989) and the release of taste-and-odor-causing compounds from others (Jenkins et al. 1967). Cells can withstand various levels of shear based on their cell wall structure (Joshi et al. 1996) which varies among different species. Some have a strong cell wall and thecal plates that constitute a type of “armor.” Others, like the Gulf of Mexico red tide culprit *Karenia brevis* are unarmored and fragile enough to be broken apart by wave action (Kirkpatrick et al. 2004). Efforts have been made to quantify the shear forces experienced by algae for different pump and valve configurations (Jaouen et al. 1999; Vandanjon et al. 1999) and to determine the individual species’ shear threshold.

Small particles and colloidal material released from algae could be more detrimental to filtration than the whole algal cells. Small particles and colloids are likely to produce greater flux decline because of enhanced pore blocking and a less porous cake layer. Such a phenomenon has been seen in membrane fouling studies using bacterial organic matter (Shimizu et al. 1994). Similarly, studies have shown that coagulants forming more compact bacterial floc structures result in more dramatic cake-layer resistance than less-dense floc formations (Wang et al. 2008). Fouling could also be exacerbated with shear due to increased availability of dissolved and colloidal organic material that fouls by an adsorption mechanism. In MF and UF filtration of fresh surface waters it has been shown that the small dissolved colloidal fraction is the most important foulant due to its specific adsorptive interaction (Howe and Clark 2002). Some size fraction of algal organic matter could also have a specific interaction with membranes and be the principal foulant.
CLAY FLOCCULATION FOR ALGAL REMOVAL

Several articles in oceanographic literature describe the use of clay for mitigating the effects of harmful algal blooms (Sengco et al. 2001; Pierce et al. 2004; Sengco and Anderson 2004). Montmorillonite, kaolinite, and yellow loess clays have been spread over affected ocean areas to help aggregate and settle algal cells in an effort to protect the aquatic environment and minimize negative effects on tourism and fishing. The mineral particles flocculate with algal cells and the large aggregates rapidly settle.

The inverse application has also been explored; the cyanobacterial species *Phormidium parchydematicum* was recently touted as an “environment-friendly” (more so than FeCl₃ and Al₂(SO₄)₃) coagulant for decreasing turbidity caused by clay (Kim et al. 2010). The fundamental principles here are the same as in the bloom-mitigating studies: algae and clay interact with each other to flocculate and enhance sedimentation.

It is reasonable to assume that if such an approach is effective at large-scale—great quantities of clay applied to wide areas of open ocean—it could be feasible in the smaller-scale, well-controlled environment of a treatment plant. This method would not need to be used continuously, but only during a bloom. The low cost of clay minerals makes the approach worth investigating.

PROJECT HYPOTHESES

Based on the literature review and introduction given above, several project hypotheses were developed:

**Hypotheses regarding high-pressure RO fouling**

1) Dissolved AOM will cause significant RO fouling because of the high concentrations of colloidal and organic material available for membrane deposition.
2) A coarse permeate carrier will cause more exacerbated fouling than a fine permeate carrier because foulants can more easily deposit on the rougher membrane surface caused by the coarse permeate carrier.
3) Cake-enhanced concentration polarization (CECP) will be more important than cake hydraulic resistance as an RO fouling mechanism.

**Hypotheses regarding low-pressure MF and UF fouling**

1) MF fouling will exhibit a pore blocking mechanism and UF fouling will exhibit a cake filtration mechanism.
2) Shear stress applied to an algal sample will exacerbate fouling through the release of AOM. A certain size fraction of the AOM will be the most damaging foulants.
3) Shear stress will cause reduced organic-matter rejection.
4) Bacteria will be an important factor in low-pressure fouling during an algal bloom.
5) Clay amendment will improve algal removal in flocculation and sedimentation thereby improving membrane performance.
Figure 1.1. (a) Concentration polarization in operation of salt-rejecting membranes. $C_b$ is the bulk salt concentration and $C_m$ is the concentration at the membrane wall, which is always higher than $C_b$. Salt diffuses away from the membrane according to the bulk diffusion coefficient $D_\infty$. $C_p$ is the permeate salt concentration. (b) The cake-enhanced concentration (CECP) model predicts that salt diffusion is hindered when fouling occurs resulting in a lower diffusion coefficient $D^*$. Both $C_m$ and $C_p$ are elevated compared to the non-fouled case.
CHAPTER 2: METHODS AND MATERIALS

SEAWATER

Seawater from San Diego Bay was collected by project consultants at MWH (Pasadena, California). Four 200-liter, low-density polyethylene (LDPE) barrels were collected and shipped via refrigerated carrier. The barrels were stored in a walk-in refrigerator at 4°C. The seawater composition was measured by project consultants at MWH; these data are reported in Table 2.1. Other, smaller samples were collected from the Long Beach Water District desalination test facility. These were shipped over night in 20-liter LDPE collapsible containers in ice chests with cold packs. These were also stored in the walk-in refrigerator until use.

Synthetic seawater was used for some experiments as an organic-free control or because of limited natural seawater availability. It was made by adding the major inorganic seawater species to deionized water in the following concentrations: 23.9 g/l NaCl, 4 g/l Na₂SO₄, 0.7 g/l KCl, 0.2 g/l NaHCO₃, 0.1 g/l KBr, 10.8 g/l MgCl₂·6H₂O, and 1.5 g/l CaCl₂·2H₂O. The recipe was suggested by previous workers who were mimicking the composition of “standard seawater” defined to have a salinity of 35x10⁻³ (Grasshoff et al. 1983).

ALGAL CULTURE

The algal species used throughout this project was Heterocapsa pygmaea, designated CCMP1132, purchased from the Provasoli-Guillard National Center for Culture of Marine Phytoplankton (West Boothbay Harbor, ME). The initial sample was spiked into several culture tubes containing f/2 medium (Andersen 2005) prepared with 0.45-µm-filtered and autoclaved (121°C) San Diego seawater. Cultures were grown in glass bottles and Erlenmeyer flasks in volumes of 200 to 900 ml. They were exposed to a constant mercury-florescent light source (Sylvania Premium Cool White, 40W, 4100K) at a distance of approximately 30 cm. The light was attenuated with a plastic covering to yield an average intensity of 19 µmol photons m⁻² s⁻¹. Growth was monitored weekly with a SpectraMax Gemini fluorescence microplate reader (Molecular Devices, Sunnyvale, CA). Cell concentrations were periodically verified with a hemacytometer and visible-light microscopy. A batch culture rotation was carried out by waiting two to four weeks for algae to reach a cell concentration of roughly 100,000 to 300,000 cells/ml then spiking a small volume of that culture into a fresh bottle of f/2 media at a dilution of 6:100 (i.e. 30 ml of algal culture into 500 ml of f/2 media). The batch culture rotation process was repeated throughout the project duration.

REVERSE OSMOSIS

Bench-scale RO testing apparatus

The bench-scale reverse osmosis (RO) testing apparatus was designed according to the diagram diagram in Figure 2.1. The key components were the membrane test cell, pump, motor, pressure gauges, temperature control unit, valve, balance, and data acquisition equipment. Specifications for these components are given in Table 2.2.
The membrane test cell (SEPA II, GE Osmonics, Minnetonka, MN) is a commonly-used apparatus designed to simulate spiral-wound modules in industrial RO applications. Wetted parts of the cell were 316 stainless steel, as were the tubing and wetted parts of the high-pressure pump. This grade of steel was necessary because of the high corrosion propensity of seawater. The only components not comprised of 316 stainless steel were two Tygon tubes used for the inlet to the pump and the outlet of the temperature control heat exchanger. The pump motor was a 2-horse power variable frequency drive motor capable of 20:1 turndown at constant torque. It was an inverter-duty motor, meaning the insulation was sufficient to prevent failure as the motor temperature rose under low-frequency conditions. For varying motor speed a phase inverter was used that was controlled by a 0-10 volt signal from the computer. A metering valve designed for low flow rates (around 800 ml/min) was installed in the concentrate line immediately after the membrane cell to provide pressure control.

Permeate flow rate was measured with a flow meter with a voltage signal output. The flow meter proved to be somewhat unreliable, however, because of interference from bubbles and drift over time. To ensure proper flux measurement the permeate was also fed into a collection vessel held by a balance. Balance measurements were sent to the computer through an RS232 signal. For continuous balance measurements, a self-emptying collection vessel was used, as depicted in Figure 2.1. Temperature control was provided by a heat exchanger made in the laboratory. Three meters of stainless steel tubing was coiled and connected to the concentrate outlet of the membrane cell. The coil was immersed in a water bath, with cooling water circulated through a temperature control unit. To ensure adequate cooling, pump feed temperature was recorded manually or via a voltage signal from a thermocouple and transmitter.

Data acquisition and control was achieved with a personal computer running Labview software. The controller program featured continuous monitoring of feed conductivity, pressure, and temperature, as well as permeate flow rate from the flow meter and permeate mass measurements from the balance. Automated speed control was implemented to maintain the target pressure in the event of pressure spikes. Data were recorded in ten-second intervals. Post-processing was performed with programs written in Matlab (Mathworks, Natick, MA).

RO Membranes

Reverse osmosis membranes were obtained from two manufacturers: SW30HR from Filmtec a wholly owned subsidiary of the Dow Chemical Company (Midland, Michigan), and SWC4 from Hydranautics a Nitto-Denko company (Oceanside, California). These are both polyamide thin-film composite membranes commonly used in seawater desalination applications. Membranes were received as flat sheets and were stored dry in sealed plastic bags protected from light. Coupons for experiments were cut and placed in DI water, then stored at 4°C with DI water replaced regularly.

Algal fouling experiments

In order to test fouling by algae and their associated organic matter, a series of experiments was performed where RO membranes were challenged with a direct spike of algal-laden seawater. During the tests AOM was released as cells were sheared in the pump and valve. After the direct-spike test the water was filtered through an MF membrane (0.45-um mixed cellulose ester, Millipore, Billerica, MA). Filtration was performed on a flat-sheet cell (Amicon)
in dead-end mode at 30 psi. Algal material caused a significant flux decline, so several runs were performed to filter all of the water sample. The microfiltered AOM sample was then re-run on the bench-scale RO unit with a fresh membrane coupon to determine the effects of dissolved AOM. Further details of these tests including flow rates, pressures, etc., are described in the results and discussion section.

MICROFILTRATION AND ULTRAFILTRATION

Dead-end cell setup

MF and UF flux tests were performed at room temperature (21 ± 1°C) using circular membrane coupons in an unstirred dead-end cell. Two cell sizes were used, depending on the volume of feed to be processed. The larger cell (Amicon model 8050, Millipore) had a 50-ml fluid capacity and 11.9 cm² active membrane area. The smaller cell (Amicon model 8010, Millipore) had a 10-ml fluid capacity and 3.6 cm² active membrane area. Pressure varied according to the experiment, but 69 kPa (10 psi) for MF and 207 kPa (30 psi) for UF were typical (actual pressures used are given in the discussion of each experiment). Membrane coupons were soaked at least overnight in deionized water to remove soluble processing chemicals. To provide extra support and resistance against membrane deformation a mesh screen was placed under the coupon. The screen was cut from the permeate carrier of a spiral-wound nanofiltration module (ESNA-1 LF, Hydranautics, Oceanside, CA). The membrane cell was fed by a one- or four-liter feed tank pressurized with a nitrogen cylinder. Membrane flux was determined by recording the mass of permeate collected over time on a top-loading balance (Model PB3002-S, Mettler-Toledo, Inc., Columbus, OH) using data acquisition software (Winwedge Standard, TAL Technologies, Inc., Philadelphia, PA) and a macro written into Microsoft Excel.

A clean-water flux run preceded each MF or UF filtration. The clean-water flux was tested by filtering ultrapure (18 MΩ-cm) water purified through a system of ion exchange and carbon adsorption cartridges (NANOpure, Barnstead-Thermolyne, Dubuque, IA). Clean-water flux was measured after accumulation of two liters of permeate (for 0.45-μm and 0.22-μm membranes) or after 30 minutes (for 0.1-μm, 100-kDa, and 30-kDa membranes). The clean-water flux run served as a control for the experimental setup; an abnormally high clean-water flux indicated an integrity breach and flux decline indicated contamination. Thus, if more than 5% variation in flux was seen over the last two-thirds of the clean-water run, the membrane was replaced. Experiments were performed at room temperature (typically 21 ± 1°C). Sample temperature for both clean water and fractionated samples was monitored to ensure it was within that range.

For clay flocculation experiments, artificial seawater was used to dilute the algal concentration to the targeted concentration before MF tests. Some tests used several filtration steps in series to determine the extent of irreversible fouling. Flux decline tests were performed normally but after the flux declined the membrane was rinsed with prefiltered (0.1 μm) artificial seawater by vigorously spraying with a squeeze bottle. Artificial seawater was used instead of tap or deionized water in order to prevent osmotic gradients that could burst algal cells. Five filtrations were typically performed with a rinse between each.
MF and UF Membranes

A set of four membranes, two MF and two UF, constituted the majority of low-pressure membranes used during this research. MF membranes had pore sizes of 0.45 µm (cellulose acetate, Millipore) and 0.22 µm (cellulose acetate, GE Water & Process Technologies, Minnetonka, MN). UF membranes had molecular-weight-cutoffs of 100 and 30 kilo-Dalton (kDa) (both were regenerated cellulose, Ultragel PLC, Millipore). These cellulose acetate and regenerated cellulose membranes are designated by the manufacturers as low protein binding membranes suited for filtration of biological samples. These low-fouling membranes were chosen for experiments where low adsorption was desired, like when pore blocking was studied and when organic-matter fractionation was performed.

Another membrane used had a 0.1-µm pore size and was made of material described as “hydrophilic PVDF” (Millipore VVLP). These membranes are similar in pore size and material to hollow-fiber membranes used in full-scale applications. The PVDF material is not itself hydrophilic but was modified to increase the hydrophilicity. The exact modification procedure used is proprietary, but is likely graft-polymerization of a polymerizable monomer such as hydroxyalkyl acrylate or methacrylate (Steuck 1984; Momtaz et al. 2005).

The final membrane was a 0.45-µm membrane made of mixed cellulose esters (Millipore MCE). This was used for removal of particulate material in natural seawater samples and for other routine lab filtration.

HYDRODYNAMIC SHEAR

Algal cells were exposed to hydrodynamic shear by pumping samples through the needle valve (SS-2MG4, Swagelok, Solon, OH) of the RO system using the plunger pump (model 231, Cat Pumps, Minneapolis, MN). The pump design was such that water could not be completely removed from the manifold, so the system was flushed with 0.45-µm-filtered seawater to ensure that new samples would not experience a salinity gradient. A two-liter algal sample was added to the system and mixed at low pressure (10 kPa; 23 psi) for five minutes. Algal concentration after mixing was approximately 100,000 cells/ml as measured by hemacytometry. After the five-minute mixing period, one liter was withdrawn for two “non-sheared” MF and UF filtrations of 500 ml each. High shear was subsequently created by increasing the pressure and flow rate to 6,900 kPa and 800 ml/min, respectively. The system ran in recycle mode with the remaining 2.3-liter sample for 150 minutes, or approximately 50 passes through the valve. A second one-liter sample of “sheared” material was then withdrawn for duplicate MF and UF filtrations.

To quantify the level of shear in the valve, the power density $\Phi_m$ was calculated. Power density is a useful parameter for characterizing drop breakup in homogenization (Karbstein and Schubert 1995) and can be determined by

$$\Phi_m = \frac{E_v}{\tilde{t}_{res}}$$

where $E_v$ is the energy density and $\tilde{t}_{res}$ is the residence time over which the liquid experiences the pressure drop. Energy density $E_v$ for the valve was equal to the pressure drop over the valve, $6.4 \times 10^6$ J/m³ (inlet pressure was 6,900 kPa and outlet pressure was 500 kPa). Residence time $\tilde{t}_{res}$ was estimated at $1.5 \times 10^{-4}$ s using an active valve volume of 2 mm³ determined from
manufacturer drawings and the measured flow rate of 800 ml/min. Hence, power density was 4 x 10^{10} \text{ W/m}^3.

**CELL BREAKUP CHARACTERIZATION**

Cell breakup was monitored using hemacytometry, flow cytometry, and bulk fluorescence measurements. Breakup was modeled with a first-order equation (2) used previously for characterization of protein release during yeast breakup in industrial homogenization (Follows et al. 1971; Moore et al. 1990).

\[
\frac{dc}{dt} = -kC \tag{2}
\]

Here $C$ is the algal concentration in cells per ml, $t$ is time, and $k$ is the rate constant. The rate constant is expanded to

\[
k = \frac{1}{\kappa \tau} \tag{3}
\]

where $\kappa$ is a strength parameter and $\tau$ is the time constant. The time constant is determined by $\tau = V_s/Q_s$ where $V_s$ is the volume of the recirculated fluid and $Q_s$ is the flow rate of recirculation. Note that $t/\tau$ is the average number of passes through the valve. The cell breakup model formulation is most appropriate if all algal cells have the same structural strength ($\kappa$). However, it is possible that there exists a distribution of cell strength with some cells being stronger than others. For a case where two cell classes exist the total cell concentration can be expressed as

\[
C = C_s + C_w \tag{4}
\]

where the subscripts $s$ and $w$ denote the strong and weak fractions. The breakup model (Equation 2) can then be written

\[
\frac{dc}{dt} = \frac{dc_s}{dt} + \frac{dc_w}{dt} = -k_s C_s - k_w C_w \tag{5}
\]

The two cell classes are independent of one another (breakup of weak cells does not depend on the number of strong cells); hence, the solution to the breakup model can be found for each class

\[
C_s = C_{so} e^{-k_s t} \quad \text{and} \quad C_w = C_{wo} e^{-k_w t} \tag{6}
\]

Taking Equations 4 and 6 together, we find the total algal cell concentration with respect to time:

\[
C = C_{so} e^{-k_s t} + C_{wo} e^{-k_w t} \tag{7}
\]

The sum of $C_{so}$ and $C_{wo}$ must equal the initial cell concentration $C_o$ so we can write

\[
\frac{c}{c_o} = \frac{C_{so}}{C_o} e^{-k_s t} + \left(1 - \frac{C_{so}}{C_o}\right) e^{-k_w t} \tag{8}
\]
The rate constants associated with the first-order breakup model (Equation 2) and the two-term model (Equation 8) were found by fitting the breakup data from hemacytometry and flow cytometry using a nonlinear least squares method in the curve fitting tool of Matlab (Mathworks, Natick, MA).

SIZE FRACTIONATION

Sheared and non-sheared algal culture samples were size fractionated to determine the effects of different organic-matter size classes on fouling. Algae were collected from culture and diluted to a concentration of 100,000 cells/ml in 0.1-µm-filtered seawater. The non-sheared sample was used directly in the fractionation procedure that follows. The sheared sample was prepared by passing algae through the pump and valve apparatus as described in the Hydrodynamic Shear section above, except that the volume was higher (3.8 liters) and 300 minutes were required to achieve the desired 60% cell breakup.

Seven sub-samples of each (sheared and non-sheared) batch were used for subsequent fractionation as shown in Figure 2.2. One sub-sample was not fractionated. The second sub-sample was centrifuged (5000 G, 5 minutes; designed to selectively remove algal cells) and the supernatant was collected. The third sub-sample was filtered with a glass-fiber filter (Millipore AP-40) to remove particulate matter including algal cells, bacteria, and any other debris rejected by the nominal 0.7-µm pore size. The fourth through seventh sub-samples were also glass-fiber filtered then were filtered through either 0.45-µm cellulose acetate (GE-Osmotics), 0.22-µm cellulose acetate (GE-Osmotics), 100-kDa regenerated cellulose (Millipore), or 30-kDa regenerated cellulose (Millipore) membranes. These were the same cellulose acetate and regenerated cellulose membranes used in previous experiments and are desirable here, as before, because of their low adsorptive fouling potential.

Glass-fiber filtration was done with roughly 2 kPa vacuum using a flask and filter holder. The first 50-ml was discarded to minimize any effects of organic matter leaching from or binding to the filter. A cleaned and baked (300°C, four hours) vacuum flask collected the remainder of the sample. The filter was replaced after passing 500 ml of solution so that the filtration properties would not change drastically as a cake layer formed. All glass-fiber filtered samples were combined in a single container to ensure sample homogeneity for subsequent fractionation steps. Fractionation filtrations were performed in the same dead-end cell used for previous experiments at a pressure of 69 kPa (10 psi) for MF (0.22 and 0.45 µm), 207 kPa (30 psi) for 100 kDa-UF, and 276 kPa (40 psi) for 30-kDa UF.

The fouling propensities of each fractionated sub-sample were determined by measuring flux decline on 0.1-µm PVDF membranes. Filtrations were performed in the same manner as the fractionation filtrations above, but with the smaller dead-end cell (Amicon model 8010, 10-ml fluid capacity, 3.63 cm² active surface area).

JAR TESTS AND CLAY AMMENDMENT EXPERIMENTS

Jar tests were performed in a conventional jar-testing apparatus that provided equal mixing to all jars and variable mixing speed (Phipps and Bird). Three types of jar tests were used, all with two liters per jar and coagulant addition immediately before rapid mixing. 1) Rapid-mix/slow-mix/settling tests had 30-s rapid mixing at 280 rpm, slow mixing for 30 min at 25 rpm, and settling for one hour. The sample was siphoned off the top for evaluating algal
Chapter 2: Methods and Materials

removal and for subsequent membrane filtration experiments. 2) Rapid-mix/slow-mix tests had 30-s rapid mixing at 280 rpm then slow mixing for 15 min at 25 rpm. Samples were immediately siphoned off the top for subsequent analysis. 3) Rapid-mix-only tests had 30-s rapid mixing at 280 rpm then the sample was poured out for analysis with no allowance for removal by settling. The three tests just described represent (1) a treatment process with significant settling basin volume and retention time, (2) a treatment process with some settling basin removal, but little retention time, and (3) a treatment process where coagulants can be added and mixed, but no settling basin exists for solids removal.

Clay and ferric chloride were tested as coagulants/coagulant aids. The clay was kaolinite purchased from Sigma-Aldrich and used as received. Ferric chloride (Sigma-Aldrich) stock solutions were prepared from anhydrous FeCl₃ and doses reported here are in units of mg/l as FeCl₃.

ANALYTICAL METHODS

Algal and bacterial enumeration

Algal cells were counted manually via hemacytometry. Approximate 10 µl samples were placed on side-by-side grids (0.9 mm² volume per grid) of the hemacytometer (Hauser Scientific, Horsham, PA). Counts were performed with a visible-light microscope (Zeiss Jena Laboval, Maple Grove, MN) using a 10x objective and 10x eyepiece for a total of 100x magnification. Only whole, clearly-identifiable cells were counted even when material was present that appeared to be derived from cells.

Fluorescence microscopy was used to directly count and compare algal and bacterial cell concentrations. Preparation of slides began by filtering a small volume (150 to 2000 µl) of algal culture onto a 0.2-µm pore size, track-etched black polycarbonate membrane (Isopore, Whatman, Florham Park, NJ). A backing filter cut from a 0.45-µm membrane of mixed cellulose esters (type HAWP, Millipore) provided extra support. Filtration was performed using vacuum suction at about 2 kPa. After filtration 400 µl (enough to cover the 1.9 cm² active membrane surface) of a DAPI staining solution (1 mg/l of 4',6-diamidino-2-phenylindole in phosphate buffered saline) was applied for three minutes. The staining solution was then filtered through and the membrane was immediately placed on a microscope slide cleaned with 70% ethanol. Several drops of anti-fade solution (type AF1, Citifluor, London, United Kingdom) were placed on the membrane and a cover slip (also cleaned with 70% ethanol) was applied. The anti-fade solution adhered the cover slip to the slide with the membrane between. In some cases the slide was sealed with fingernail polish on two sides to prevent movement of the specimen, but later this was shown to be unnecessary.

Immediately after preparation of slides, algal cells were observed under the microscope (Zeiss Axioscope, Carl Zeiss AG, Maple Grove, MN). An X-Cite 120 fluorescent bulb (EXFO, Mississauga, Canada) was used for illumination. The filter set for algal detection (autofluorescence) was a Chroma 41001 (Rockingham, VT). In the set was an excitation filter with 480-nm center wavelength and 40-nm bandwidth, a beamsplitter with 505-nm longpass cutoff, and an emission filter centered at 535 nm with a 50-nm bandwidth. Images were captured using an Axiocam MRm digital camera (Carl Zeiss AG, Maple Grove, MN). Twenty-one images were collected for each slide using 100x magnification. Observation began at one edge of the
active filter area and images were collected along a transect until reaching the other edge. Twenty-two images were typically collected along the transect.

After algal counts, bacteria were observed on the same slide. Magnification was switched to 1000x and immersion oil (Immersol 518 F, Zeiss) was placed between the objective and the slide. The filter set was switched to one optimal for DAPI stain detection (Chroma 31000). The set included an excitation filter with a 360-nm center and 40-nm bandwidth, a beamsplitter with 400-nm longpass cutoff, and an emission filter centered at 460 nm with 50-nm bandwidth. At least fifteen images were collected at random locations on the slide.

The number of cells on the membrane in most cases was counted by the operator. In some cases an image processing program written in Matlab was used. The program detected all pixel values above a certain threshold (set by the user) and found the total intensity of those pixels. Typically five images per slide were counted manually for use as a calibration. The user counted the number of cells present and entered the value. Then, the other images were automatically counted with the program using the calibration information. After the number of objects per image was determined, the data were adjusted to cell concentration using the known volume filtered and area per membrane. Several images were chosen at random and counted manually after analysis to verify the accuracy of automated counts. The variability associated with automated counting was always lower than the variability caused by random and non-uniform cell dispersion.

In some cases fluorescence microscopy was used simply to examine cells and capture images and the same procedure was used. Images were captured in grayscale mode and false color was added with a script written in Matlab.

**Flow cytometry**

Flow cytometry was used to count algae and broken particles. Light scattering measurements were indicative of particle size and morphology. A BD LSR II flow cytometer (BD Biosciences, San Jose, CA) was used with two illumination channels; a 488-nm argon-ion, air-cooled laser (Coherent, Santa Clara, CA) with a 530/30 bandpass filter was used for algal cell excitation, and a 633-nm, red He Ne Uniphase™ Laser (JPS, Milpitas, CA) with a 735-nm longpass and 660/20 bandpass filter was used for detecting fluorescent calibration beads. The fluorescence data were analyzed using FCS Express flow analysis software (De Novo, Los Angeles, CA). Samples were prepared by adding 450 µl to 50 µl of 10-µm Flow-Check™ Fluorosphere calibration beads (Beckman Coulter, Fullerton, CA) at a concentration of 1.35 x 10⁶ beads/ml. The flow rate of the machine was measured by counting the number of bead events recorded in a given time period and calculating the volume processed using the bead concentration. Sample tubes were vortexed prior to analysis to ensure homogeneity.

Algal cells were identified in flow-cytometry data by their light-scatter and fluorescence properties. Cells had forward scatter greater than 200, side scatter between 250 and 500, 633-nm fluorescence greater than 300, and 488-nm fluorescence greater than 300; the numbers are unitless measures of the peak area for each cell signal. Separation between the algae and background particulate material occurred most dramatically on the 488-nm channel while separation between algae and calibration beads was best observed on the 633-nm channel. Based on the scatter and fluorescence signals, particles were gated and labeled accordingly. Hemacytometry was used to calibrate the flow cytometry counts and ensure that whole algal cells were properly distinguished from other material.
**Bulk fluorescence**

A fluorescence microplate reader (Molecular Devices, Sunnyvale, CA) was used for measurement of bulk sample fluorescence. Samples were measured in triplicate (300 µl each) in a 96-well plate. Excitation was set at 450 nm and emission was set at 680 nm with a longpass cutoff of 665 nm.

**Ultraviolet absorbance**

UV absorbance at 254 nm was measured on a UV-vis spectrophotometer (UV-2450, Shimadzu, Kyoto, Japan). Samples were measured in a 1-cm path-length quartz cell (QS 284, Fisher) and an identical cell with ultrapure water was used as a reference.

**Total organic carbon**

Total organic carbon (TOC) was measured with an analyzer using an oxidative combustion-infrared method (Shimadzu TOC-VCPN, Kyoto, Japan). A known volume of sample was injected into a combustion tube maintained at 680°C. Ultrapure air carried the sample through the combustion tube and past a platinum catalyst where the sample was oxidized to carbon dioxide. The carbon dioxide was measured by an infrared detector. A calibration curve made from potassium hydrogen phthalate TOC standards was used to determine sample concentrations.

**Carbohydrates**

Organic matter was also characterized as to its carbohydrate composition. Both monosaccharides and polysaccharides were measured using a procedure slightly modified from that of Myklestad et al. (1997). Three reagents were prepared for the analysis, all with ACS-grade stock chemicals. Reagent A was 0.7 mM potassium ferricyanide (Fisher Scientific, Pittsburgh, PA) in 10-mM sodium hydroxide (Fisher) and 0.19-M sodium carbonate (Fisher). Reagent A was stable, so one solution was used throughout the experiments. Reagent B was made in two parts. The first part was 5-M acetic acid (J.T. Baker, Phillipsburgh, NJ), 1.2-M sodium acetate (Fisher), and 0.2-M citric acid (Fisher). This solution was stable and only remade when depleted. The second part of reagent B was 2-mM ferric chloride (anhydrous, Fisher), which was prepared daily. Reagent C was 2.5 mM TPTZ (2,4,6-Tripyridyl-s-triazine, Sigma-Aldrich, St. Louis, MO) in 3-M acetic acid. This was also prepared daily. For monosaccharide measurement, one ml of sample was placed in a glass digestion vial (Hach, Loveland, CO) followed by one ml of Reagent A. The vial was capped and placed in a 105°C oven for 20 minutes. One ml of Reagent B was then added, followed by two ml of Reagent C. After 20 minutes of incubation in the dark at room temperature, the 595-nm absorbance was measured with a spectrophotometer (DR/4000U, Hach, Loveland, CO) blanked against deionized water. Standards of 0.25, 0.5, 1, and 2 mg/l glucose were prepared by serial dilution of a glucose stock solution (Ricca Chemical Co., Arlington, TX). To determine polysaccharide concentration, samples were hydrolyzed before measurement. A 0.9-ml sample was placed in a digestion vial followed by 0.1 ml of 1-M HCl. Vials were capped and incubated at 105°C for 24 hours, then
neutralized by addition of 0.1 ml of 1-M NaOH. Measurement then proceeded as for monosaccharides. Glucose standards were treated alongside the samples.

**Proteins**

Protein concentration was measured with the bicinchoninic acid protein assay (Smith et al. 1985) using a prepared kit (Thermo Scientific). The protein concentration in bulk water samples was below the method detection limit of 5 mg/l, so bulk measurements could not be made. However, it was possible to measure proteins either by desorbing them with 0.01-M NaOH or by adding the reagents directly to a small membrane sample. A similar direct-measurement procedure was performed previously for seawater conditioning films on glass slides (Garg et al., 2009). Two 0.8-cm² membrane samples were cut from each coupon of interest and placed in replicate digestion vials with 150 μl of ultrapure water (to bring the total reagent volume up to that of the standards). Smaller samples, 0.1 cm², were used when glass-fiber filters were measured since the concentration was higher. For each membrane type, two replicates of a clean membrane were also measured to control for reactions between reagent and membrane polymers. Three milliliters of the bicinchoninic acid working solution was added to each vial and the samples were incubated for 30 minutes in a 60°C water bath. Samples were then cooled in a room-temperature bath and their 562-nm absorbance was measured in a Shimadzu UV-vis spectrophotometer (Shimadzu X250) with 1-cm path length quartz cuvettes. Standards were prepared with bovine serum albumin (BSA; Sigma). Different proteins have variable reactivity so the concentrations reported here are “as BSA.”

**Size-exclusion chromatography**

Size exclusion chromatography (SEC) was used to determine the size distribution of dissolved organic matter in samples. SEC was performed on a Shimadzu VP instrument. The column had a molecular weight separation range of 2 to 80 kDa (Protein-Pak 125, Waters, Milford, MA). Size calibration standards were polystyrene sulfonate (Polysciences, Inc, Warrington, PA). Detection was by ultraviolet absorbance in the range of 200 to 300 nm, with a resolution of 1 nm using a photodiode array.

**Visual image analysis of fouled membranes**

Visual image analysis was used to determine the spatial distribution of visible membrane foulants on a size range between about 0.1 to several millimeters. This aided in determining the influence of feed spacers on deposition patterns. Membrane coupons were dried and scanned on a desktop scanner to obtain a digital image. A resolution of 600 dots per inch was used. Color images were comprised of red, green, and blue channels. The blue channel proved to be the best indicator of fouling. Horizontal transects (in the direction of flow) of the blue-channel image data were converted into the frequency domain using a Fourier transform with scripts written in Matlab. The transformation resulted in a power spectrum for that transect. Power spectra of all of the transects were averaged to minimize noise and the averages were reported.
Laser-scanning cytometry

Laser-scanning cytometry (LSC) is a method for surface scanning to detect particles and cells. An LSC instrument was previously built in our laboratory for use as a particle detector for low-pressure membrane integrity tests and was calibrated with fluorescent microspheres (Ladner et al. 2007). Because algal cells show strong fluorescence, LSC was evaluated for its usefulness as an algal foulant detection device. Strictly speaking, the method is not “cytometry” as this term indicates single-cell counting or analysis, but we retain the LSC designation for consistency.

For LSC analysis a small (2.5-cm square) section of membrane was cut out of the coupon and mounted on a microscope coverslip with double-sided tape. The specimen was placed on a movable stage onto which laser light (635 nm) was directed. Scanning proceeded in a helical path similar to a compact disk or DVD. Fluoresced light was detected with a photomultiplier tube (PMT). A cutoff filter in front of the PMT ensured that most of the detected light was indeed fluoresced and not reflected. Data were processed with Matlab to generate a histogram of raw PMT readings as well as an image with spatial information.

Infrared spectroscopy

Attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR) was used to evaluate organic foulants accumulated on the membranes after seawater experiments, as has been done in other membrane fouling studies (Kim et al. 1997; Zhu and Nystrom 1998; Howe et al. 2002). Infrared measurements were performed with a Nexus 670 instrument from Thermo Nicolet supplemented with a Smart Golden Gate ATR accessory with a diamond crystal and zinc-selenium focusing element (Waltham, MA). The crystal was washed with 100% ethanol and rinsed with distilled water prior to each measurement. Membrane samples were pressed against the diamond crystal and 32 scans were recorded and averaged with a resolution of 4 cm⁻¹. This was repeated on at least five separate locations in the fouled portion of the membranes. Clean membranes or the clean edge of fouled membranes (protected from foulants by o-rings) were used for obtaining the background membrane spectra.

Scanning electron microscopy

Scanning electron microscopy (SEM) was used to visualize foulants on a scale of about 100 nm to ten microns. For SEM membrane samples stored in a dessicator were sectioned into small (about 2-mm by 6-mm) strips and mounted with carbon tape on an SEM stage. Sputter coating was performed for 30 seconds with gold palladium. A JEOL 6060 SEM was employed in high vacuum mode at a voltage of 20 kV and images were taken at 10,000 times magnification.

Atomic force microscopy

Membrane surface roughness was determined by atomic force microscopy (AFM). Tapping mode AFM measurements were made using an etched silicon probe on an MFP-3D instrument (Asylum Research, Santa Barbara, CA). Clean membrane coupons were allowed to dry for 24 hours in a desiccator before AFM scans were performed. The RMS roughness is given by the standard deviation of the individual height measurements for three replicates.
## Tables

**Table 2.1**

Composition of San Diego Bay seawater

<table>
<thead>
<tr>
<th>Analyte</th>
<th>Units</th>
<th>Value</th>
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<tbody>
<tr>
<td>Alkalinity in CaCO₃ units</td>
<td>mg/l</td>
<td>110</td>
</tr>
<tr>
<td>Bicarb. Alkalinity as</td>
<td></td>
<td></td>
</tr>
<tr>
<td>HCO₃</td>
<td>mg/l</td>
<td>130</td>
</tr>
<tr>
<td>pH</td>
<td>pH Units</td>
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</tr>
<tr>
<td>(SDI)₁₅</td>
<td>-</td>
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<td>TDS</td>
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<td>Boron</td>
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<tr>
<td>Barium</td>
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<td>Bromide</td>
<td>ug/l</td>
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<tr>
<td>Strontium</td>
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<tr>
<td>Total Coliform Bacteria</td>
<td>MPNM</td>
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</tr>
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</table>

**ND**: Not detected  
**NA**: Not available
### Table 2.2
Components of bench-scale RO testing unit

<table>
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<tr>
<th>Description</th>
<th>Manufacturer</th>
<th>Model/Catalog #</th>
</tr>
</thead>
<tbody>
<tr>
<td>Membrane test cell</td>
<td>GE Osmonics, Minnetonka, MN</td>
<td>SEPA II</td>
</tr>
<tr>
<td>Hydraulic hand pump</td>
<td>Brand Hydraulics, Champaign, IL</td>
<td>HP-121DA50</td>
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<td>Pump</td>
<td>Cat Pumps, Minneapolis, MN</td>
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<td>Motor</td>
<td>Marathon Electric, Wausau, WI</td>
<td>MicroMAX 145THFR5329/Y368</td>
</tr>
<tr>
<td>Phase inverter</td>
<td>Toshiba, New York, NY</td>
<td>S-11</td>
</tr>
<tr>
<td>Pressure transducer (P&lt;sub&gt;3&lt;/sub&gt;)</td>
<td>Cole Parmer, Vernon Hills, IL</td>
<td>68072-14</td>
</tr>
<tr>
<td>Stainless steel tubing</td>
<td>Swagelok, Solon, OH</td>
<td>SS-T6-S-035-20</td>
</tr>
<tr>
<td>Elbows, Ts, Couples</td>
<td>Swagelok, Solon, OH</td>
<td>SS-600 series</td>
</tr>
<tr>
<td>Regulating needle valve</td>
<td>Swagelok, Solon, OH</td>
<td>SS-1RS6</td>
</tr>
<tr>
<td>Pressure relief valve</td>
<td>Swagelok, Solon, OH</td>
<td>SS-4R3A5; spring kit 177-R3A-K1-C</td>
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<td>Alicat Scientific, Tucson, AZ</td>
<td>L-10CCM-D</td>
</tr>
<tr>
<td>Balance</td>
<td>Mettler Toledo, Columbus, OH</td>
<td>PB3002-S</td>
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<tr>
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<td>EW-12101-00</td>
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<tr>
<td>Shielded I/O Connector Block</td>
<td>National Instruments, Austin, TX</td>
<td>SCB-68</td>
</tr>
<tr>
<td>Programming software</td>
<td>National Instruments, Austin, TX</td>
<td>Labview 7.0</td>
</tr>
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</table>

Figure 2.1. Diagram of the bench-scale SWRO membrane testing unit. Diamond symbols indicate electronic interface between the computer and components. Automated data acquisition locations are shown for feed conductivity (Cf), feed pressure (Pf), permeate flow rate (Qp), and permeate mass (Mp). Automated control of the high-pressure pump, and thereby the feed flow rate (Qf), is also indicated.
Figure 2.2. Schematic of the fractionation procedure. The procedure was repeated twice; once for a non-sheared algal culture sample and once for a sheared sample. CA = cellulose acetate. RC = regenerated cellulose. PVDF = polyvinylidene fluoride. Source: Ladner, D. A., D. R. Vardon and M. M. Clark (2010). "Effects of shear on microfiltration and ultrafiltration fouling by marine bloom-forming algae." Journal of Membrane Science 356(1-2): 33-43. Reproduced with permission from Elsevier.
CHAPTER 3: RESULTS AND DISCUSSION

REVERSE OSMOSIS FOULING BY MARINE ALGAE

As noted in the literature review, fouling by marine algae and AOM is a cause of concern for desalination facilities. Red-tide events have severely damaged pilot MF/RO systems (Ishida 2006) and full-scale RO systems with dual media filtration pretreatment (Petry et al. 2007; Kim et al. 2007; Sambidge 2008). In these reports little information was collected as to the extent to which AOM fouling occurred. The laboratory experiments described here elucidate the magnitude of fouling by AOM on RO membranes.

The main hypothesis of this research direction was that dissolved AOM would cause significant RO fouling. This was expected because several literature reports discuss fouling by colloids and natural organic matter on RO membranes (i.e. Zhu and Elimelech 1997; Kumar et al. 2006; Chong et al. 2007) and high concentrations of colloids and organic matter are present in an algal bloom scenario. Dissolved AOM is the material most relevant to a full-scale RO process because it can pass through many pretreatment processes. Experiments were performed to determine the extent of dissolved AOM fouling compared to fouling by bulk algal material (comprised with a combination of cells, cell-derived particles, and dissolved AOM).

The second hypothesis was that a coarse permeate carrier would cause more exacerbated fouling than a fine permeate carrier. The coarse permeate carrier had a wider gap between fibers that allowed a greater degree of membrane deformation. Foultants were expected to more easily deposit in the relatively deep valleys caused by the coarse permeate carrier. Membrane autopsy was performed after fouling runs to determine the extent of foulant deposition.

The third hypothesis evaluated in this effort dealt with fouling mechanism. It was expected that cake-enhanced concentration polarization (CECP) would be more important than cake hydraulic resistance. CECP has been previously reported as the main fouling mechanism for salt-rejection membranes (Hoek and Elimelech 2003). Flux data were modeled to elucidate the interplay between CECP and hydraulic resistance fouling mechanisms.

Design of experiments

*H. pygmaea* culture and AOM were spiked into the RO unit feed and flux was measured over time at constant pressure. The RO unit configuration was shown in Figure 2.1. Experiments were performed with two commercial membranes: SW30HR and SWC4. Two types of permeate spacer were also tested, one having a finer mesh spacing than the other. The coarse permeate spacer was provided by GE Osmonics with the SEPA II crossflow testing apparatus. The fine permeate spacer was cut from the permeate carrier of a commercial spiral-wound nanofiltration module (ESNA-1 LF, Hydranautics, Oceanside, CA; this was the same spacer used for extra support in the dead-end low-pressure experiments). The two permeate carriers are shown in Figure 3.1.

Two experiment types were performed: a direct algal spike and a spike of microfiltered AOM. Direct algal spikes proceeded by adding algal culture to prefiltered (0.45 μm) San Diego seawater to make a 20-liter batch of algae at 40,000 cells/ml. Cells were harvested during their active growth phase and were observed to be swimming vigorously in the seawater matrix. The spiked seawater sample was run on the bench-scale reverse osmosis unit in full recycle mode
Membrane Fouling by Marine Algae in Seawater Desalination

(permeate and concentrate fed back to the feed tank), at 6,900 kPa pressure and a flow rate of 800 ml/min (which translates roughly to a crossflow velocity of 0.47 m/s and Reynolds number of 270). Temperature was held at 20 ± 1°C. Before each run, the membrane was compacted and greater than 98% salt rejection was verified using a 32 g/l NaCl solution.

After performing the direct algal spike experiment the sample was removed and filtered through 0.45-μm membranes (Millipore MCE) in the dead-end low-pressure filtration apparatus. The resulting sample was then used for the microfiltered AOM experiment with the same operating conditions as the direct algal spike.

Algae were counted and fluorescence was measured over the course of the experiments to determine changes in feed-water composition. Fouled membranes were removed and examined using visual imaging, laser-scanning cytometry (LSC), scanning electron microscopy, and infrared spectroscopy to determine the extent and spatial patterns of fouling.

A fouling model was applied to help elucidate flux decline mechanisms. The flux decline contributions of hydraulic cake resistance and cake-enhanced concentration polarization (CECP) were determined.

Flux decline caused by algae

Direct algal spikes caused greater flux decline than microfiltered AOM for all three membrane/permeate carrier combinations (Figure 3.2). This was expected, since the direct spikes contained algal cells and higher concentrations of AOM. Microfiltered AOM caused slightly more flux decline (five percent) on the coarse permeate carrier than it did on the fine permeate carriers (two to three percent).

No significant difference in fouling was apparent between the two membranes tested; both the direct algal spikes and the microfiltered AOM experiments resulted in similar flux decline for each membrane type. This is interesting since roughness values measured by AFM were quite different between the two membranes; 78.3 ± 7.8 and 150.5 ± 5.4 nm for SW30HR and SWC4 membranes, respectively. It seems that macroscale roughness (on the order of millimeters) caused by the shape of the permeate carrier membrane was more important than nanoscale roughness.

AOM characterization

During the direct algal spike into the RO system a dramatic drop in cell number was observed. Cells first showed signs of damage in that they ceased swimming. As the run continued, cell number decreased until only a few intact cells could be observed in each microscope sample collected. Subsequent experiments showed that the cells were broken apart as they passed through the concentrate valve. Pressure drop over the valve was high (about 6,400 kPa) and the hydraulic residence time in the valve was quite small (about 2x10^{-3} seconds) so the hydrodynamic shear was quite high, causing the observed algal breakup. These initial results on cell breakup led to a more detailed investigation into the effects of shear on algal cells and on their subsequent fouling in microfiltration and ultrafiltration. The results of that investigation are given later.

Figure 3.3 shows the change in cell concentration during one of the direct algal spike runs; results were similar for all of the direct algal spike experiments. Approximately half of the cells were broken apart in the first hour then the cell breakup rate flattened as the run progressed.
In the later section on shear the hypothesis is presented that the algal cells removed in the early period were the weaker cells in the population. The algal cells that remained for a longer time (and thus a higher number of passes through the valve) were the structurally stronger cells.

Internal organelles, biopolymers, and dissolved AOM were released as algal cells broke apart. Much of the released organic matter was fluorescent material that caused an increase in bulk fluorescence of the sample (Figure 3.3). The bulk fluorescence increase was likely due to the release of light-harvesting pigments peridinin and chlorophyll \( a \). The total concentration of pigment did not increase, but before shear self-shading in algal cells resulted in lower fluorescence; this self-shading is called the “package effect” (Kirk 1994). As the cells were broken apart the pigments were released and the package effect was minimized. Most of the released fluorescent material was dissolved as confirmed by the fluorescence readings of 0.45-μm filtered samples shown in Figure 3.3. Filtered fluorescence was negligible at the beginning of the run, but as cells were sheared the filtered fluorescence and bulk fluorescence increased and decreased at similar rates.

Fluorescence peaked and began to decay at about four hours for the unfiltered sample and seven hours for the filtered sample. This decrease in fluorescence with time could be due to adsorption of fluorescent material on the membrane during the run. Alternatively, bacteria may have been actively metabolizing the fluorescent pigments. During one of the runs bacteria levels were measured. Bacteria more than doubled during the run, from \( 5 \times 10^5 \) to \( 1.2 \times 10^6 \) cells per ml confirming that biological activity was occurring. The extent to which pigments were degraded biologically, however, is unknown.

**Fouled membrane autopsy**

**Visual and fluorescence image analysis**

A distinct brown coloration was observed in scanned images of RO membranes fouled by a direct algal spike in Figure 3.4 (column 1, a-c). When the coarse permeate carrier was used (a), foulants preferentially deposited in a pattern caused by the feed spacer. With the fine permeate carrier the SW30HR membrane (b) showed a slight pattern in the visual image and a more apparent pattern in the LSC fluorescence image (column 2). No discernable feed spacer pattern was seen in the SWC4 fine permeate carrier case (c). Microfiltered AOM caused a distinct foulant pattern in the coarse permeate carrier case (d), but no obvious pattern could be seen in either of the fine permeate carrier samples (e, f).

Fluorescence histograms (Figure 3.4 column 3) show that the mean fluorescence readings were higher and the foulants were more evenly distributed (histograms were more Gaussian-shaped) for direct algal spikes when the fine permeate carrier was used (b, c). With the coarse permeate carrier (a) the distribution showed a strong tail toward higher fluorescence readings. This tail represents the locally high fluorescence data points, while the overall fluorescence (mean) was lowered because some regions had lower foulant accumulation and lower fluorescence.

With microfiltered AOM the fluorescence histogram for the coarse permeate carrier (d) had a tail toward high fluorescence from the locally elevated patches of foulant. With the fine permeate carrier (e, f), however, the fluorescence histograms were sharp and narrow. A control scan of a membrane used to filter an organic-free sodium chloride solution gave an almost identical histogram as those in Figure 3.4 e3 and f3 indicating that the mean fluorescence of 660
was the background fluorescence reading for a non-fouled membrane. Thus it was concluded that no measurable foulants were detected by LSC when a fine permeate carrier membrane was used with microfiltered AOM. There was little to no deposition of fluorescent material.

The fact that LSC was able to detect AOM foulants lends insight into the nature of the organic matter. Strict carbohydrates (starches, dextrans, or other polymers containing only sugar monomers) would not be expected to display significant fluorescence. Aminosugars or proteins, however, could potentially exhibit fluorescence and chlorophyll and peridinin would yield a positive response.

Fouled membrane images were analyzed by Fourier transform analysis. Power spectra of horizontal transects (in the direction of feed-water flow) were obtained. Figure 3.5 shows spectra for the six fouled membranes of interest and two control samples (coarse and fine permeate carriers run with non-fouling water). The direct algal spike with the coarse permeate carrier (a) resulted in strong peaks at 1.94, 3.87, and 10.38 wavenumbers (cm$^{-1}$). Wavenumbers are the frequency of a repeating feature on the images. Reciprocal wavenumbers give the length (i.e. wavelength) of those features. Thus the peak at 1.94 resulted from the foulant pattern caused by the 0.5-cm mesh feed spacer. The 3.87 cm$^{-1}$ peak was a harmonic of the foulant pattern peak; harmonics are usually found in power spectra at halves and multiples of a strong peak (Smith 1999). A second harmonic was evident at 5.81 cm$^{-1}$ in the coarse permeate carrier direct algal spike spectrum. The other strong peak of interest at 10.38 cm$^{-1}$ was caused by dimples in the membrane where it deformed into the permeate carrier. The reciprocal indicates that the coarse carrier had a repeating length scale of about 0.09 cm. This peak was stronger than that found for a control sample run with sodium chloride only (g) because foulants had preferentially deposited in the dimples giving them a darker color and stronger power spectrum signal.

Foulant patterns caused by the feed spacer were markedly reduced in the fine-permeate carrier direct spike power spectra (Figure 3.5b and c). Peaks in the 1.9 cm$^{-1}$ region were slightly evident but were much less intense than in the coarse feed spacer sample. This was due to the foulant material being more evenly distributed across the membrane surface instead of preferentially depositing around the feed spacer. The fine permeate carrier caused a characteristic peak at 17.1 cm$^{-1}$ indicating that the fine permeate carrier dimples had a length scale of 0.06 cm, which was 2/3 the mesh size of the coarse permeate carrier. The fine permeate carrier peaks were small in the direct algal spike case because foulants had covered the dimples.

Microfiltered AOM on a coarse permeate carrier (d) resulted in similar peak locations as those for the direct algal spike (a). The 2.01, 3.80, and 5.65 cm$^{-1}$ peaks were smaller in magnitude because the feed spacer pattern was not as prominent. The 10.92 cm$^{-1}$ peak was about as high as in the direct spike, indicating that the permeate carrier pattern was just as strong. The peak was stronger than the control case (g) indicating that foulants had preferentially accumulated in the dimples and made the pattern more obvious.

Microfiltered AOM run on the fine feed spacer (e, f) resulted in prominent peaks at 17.1 and 8.55 cm$^{-1}$ which can be compared with the fine carrier control sample (h) to show that they arose from the dimple pattern. The SW30HR membrane (e) also showed a small peak at 2.0 cm$^{-1}$ indicating that some foulant material had deposited in the feed-spacer pattern. The SWC4 membrane did not show that peak so feed-spacer-pattern fouling was not evident.

In short, image analysis clearly distinguished between the coarse and fine permeate carrier membranes based on their dimple pattern. More importantly, the coarse permeate carrier caused foulants to deposit according to the feed spacer pattern. This suggests that the shape of the permeate carrier is important in determining how foulants accumulate around the feed spacer.
Both the permeate carrier and feed spacer were important in defining the crossflow hydrodynamics and foulant deposition.

**Scanning electron microscopy**

SEM images (Figure 3.6) reveal foulant accumulation at the micron scale. Letters $a$ through $f$ in Figure 3.6 designate the same samples as $a$ through $f$ in Figure 3.4. Letters $g$ and $h$ show new, clean SW30HR and SWC4 membranes, respectively. In the direct algal spike fouled membranes ($a$, $b$, $c$) foulant material completely covered the membrane surface. The SEM images were taken at locations where a crack was present in the dried sample in order to provide a qualitative picture of the depth and thickness of the foulant layer; the membrane surface could not be seen in any of the images. The smooth foulant surfaces around the cracks show what was found over the majority of the sample coupon surface. Foulant material created a relatively smooth, thick layer. No algal cells were identified in any of the samples examined suggesting that whole-cell deposition was less important than colloidal and dissolved organic matter deposition; however, it is unclear whether whole cells would be identifiable by this technique, since the samples were not prepared in a way in which whole cells would be preserved.

For the microfiltered AOM experiments ($d$, $e$, $f$) SEM images showed some organic-matter accumulation on the membrane surfaces in all three cases. Fouling was not spatially homogeneous, but Figure 3.6 $d$, $e$, and $f$ give typical observations. By comparison with clean membranes ($g$ and $h$) it can be surmised that the microfiltered AOM foulant was not thick enough to completely mask the underlying membrane features. All three microfiltered AOM cases had qualitatively similar amounts of foulant material. The coarse permeate carrier ($d$) seemed to result in slightly more organic matter accumulation, but the effect was not quantifiable. Foulants accumulated in patches, with clumps of material found next to clean membrane surfaces. This suggests a nucleation phenomenon where incoming foulants had a higher affinity for pre-adsorbed foulant regions as opposed to the clean membrane; foulants may adhere better to other foulants than they do to the membrane.

**Infrared spectroscopy**

ATR-FTIR spectra give information about the chemical character of foulants. In Figure 3.7 three regions of interest are plotted and two clean-membrane spectra are given for comparison. All the curves here are averages of at least three and usually five locations on the membrane. The large peak between 3,000 and 3,600 cm$^{-1}$ is in an area sensitive to N-H stretching of proteins or O-H stretching of polysaccharides and adsorbed water (Mayo et al. 2004). The direct algal spikes had the highest absorbance in this region due to the high concentration of mass deposited. The coarse membrane was highest of all indicating a greater foulant concentration than the others, which is perhaps inconsistent with the visual and LSC fluorescence observations; the coarse permeate carrier had more patchy foulant and the underlying membrane was visible so one would expect that some measurements would be taken from cleaner areas than others and the average absorbance would be decreased. Microfiltered AOM ($d$, $e$, $f$) showed intermediate absorbance indicating that a significant amount of foulant material had deposited and was detectable by infrared spectroscopy. Note, however, that the spectra are only semi-quantitative; the evanescent infrared wave passing through the ATR
apparatus is most sensitive to material pressed directly on the crystal and material stacked above is blocked. Thus, thick cake layers would not be completely detected.

The FTIR region between 1,800 and 1,300 cm\(^{-1}\) is an area where proteins absorb in a characteristic pattern. Proteins are indicated by strong absorbance at the 1,650 cm\(^{-1}\) amide I peak, the 1,550 cm\(^{-1}\) amide II peak, and the 1,350 to 1,450 cm\(^{-1}\) amide III region (Nelson 1991; Mayo et al. 2004). Here the two fine-permeate carrier samples had higher absorbance than the coarse permeate carrier samples for direct algal spikes. This is more in line with visual and LSC fluorescence observations, since the membranes were completely covered with foulants when fine permeate carriers were used. With microfiltered AOM the protein peaks were greater for the coarse permeate carrier, which is consistent with its greater flux decline and its greater visible and fluorescence activity than the microfiltered AOM samples on the fine permeate carrier. Protein measurements from the wet-chemical BCA assay performed with desorbed foulant material (Figure 3.8) corroborate the results of the FTIR data just described. The fine permeate carrier experiments had roughly twice as much protein as the coarse permeate carrier for direct algal spike experiments. For microfiltered AOM the coarse permeate carrier resulted in slightly higher protein numbers, but these were in the low range of the protein assay and not as trustworthy; the control coupon run with only NaCl (Figure 3.8g) gave a similar protein measurement as the microfiltered AOM runs.

Carbohydrates are indicated in FTIR data by the C-O stretching region from about 900 to 1,100 cm\(^{-1}\) (Mayo et al. 2004). As was the case for proteins, the direct algal spikes with fine permeate carriers showed higher absorbance than the coarse permeate carrier sample in the carbohydrate region. Microfiltered AOM showed less absorbance in this region. Though all the fouled samples were higher than the clean-membrane samples, they had very similar absorbance. Thus carbohydrates were evident in microfiltered AOM, but they were only slightly above background.

Carbohydrates were measured with the wet-chemical phenol-sulfuric acid method for several of the fouled RO membranes (Figure 3.9). In all cases, carbohydrate concentrations were at least 60% lower than protein concentrations.

**Fouling Mechanisms**

Flux decline in RO should not occur by a pore blocking mechanism since water passage is diffusional and the “pores” are too small for foulants to penetrate. Foulant cake-layer hydraulic resistance is a more probable mechanism, since foulants are located on the membrane surface. Another mechanism for flux decline is cake-enhanced concentration polarization (CECP) which occurs because back-diffusion of ions is hindered by the tortuous foulant cake. The cake also reduces crossflow velocity at the membrane surface so salts are not as easily swept away. It is difficult to determine whether hydraulic resistance or CECP is the major foulant mechanism because the resultant flux decline is similar; in fact, it is likely that both mechanisms operate simultaneously. Here the theory behind the two mechanisms is explored to help determine which was dominant in these experiments.

An approach for determining the relative contributions of hydraulic resistance and CECP is presented here, building on work by Hoek and Elimelech (2003). Hydraulic resistance is modeled using the Carman-Kozeny equation written as
\[ \Delta P_c = \frac{180 \nu \mu (1 - \varepsilon)^2}{d_p^2 \varepsilon^3} \delta_c \]  

Here \( \Delta P_c \) is the pressure drop (kPa) due to hydraulic resistance, \( \nu \) is the flux (m/s), \( \mu \) is viscosity of water \( (1.00 \times 10^{-6} \text{ kPa} \cdot \text{s at } 20^\circ \text{C}) \), \( \varepsilon \) is the porosity (unitless), \( d_p \) is the particle size (m) and \( \delta_c \) is the cake thickness (m).

CECP results in a reduced, or hindered diffusion coefficient \( D^* \) that arises because solute molecules must travel a longer, more tortuous path to diffuse away from the membrane. \( D^* \) is related to the bulk diffusion coefficient, \( D_\infty \), by

\[ D^* = \frac{\varepsilon D_\infty}{\theta^2} \]  

where \( \theta \) is the tortuosity and \( \theta^2 \) is called the tortuosity factor. Note that Hoek and Elimelech (2003) defined \( \theta^2 \) as the tortuosity, but here we use the nomenclature as set forth in previous work (Boudreau 1996). It is important to recognize that tortuosity is not strictly defined by pore geometry. The term arises from a modification of Fick’s First Law given in unidimensional form as

\[ F = -\frac{\varepsilon D_\infty \partial C}{\partial x} - \frac{1}{\theta^2} \]  

where \( F \) is the solute flux at a concentration \( C \) and location \( x \). Thus the tortuosity factor is a term that acts on the diffusion coefficient to account for hindrances and it must be evaluated experimentally. The tortuosity factor should, of course, be related to pore geometry and one relationship that fits many data sets is (Boudreau 1996)

\[ \theta^2 = 1 - \ln(\varepsilon^2) \]  

The tortuosity factor defined here is related only to the porosity, but in reality the tortuosity will vary according to other geometrical properties like grain shape and pore-size heterogeneity. Hindered diffusion and crossflow velocity in the cake layer result in a diminished mass transfer coefficient, \( k^* \).

\[ k^* = \left[ \delta_c \left( \frac{1}{D^*} - \frac{1}{D_\infty} \right) + \frac{1}{k} \right]^{-1} \]  

Here \( k \) is the mass transfer coefficient obtained when no foulant cake is present. Using \( k^* \) the concentration polarization factor \( f_{cp} \) can be determined by

\[ f_{cp} = \frac{C_m}{C_b} = \left( 1 - R_i + R_i \exp \left( -\frac{\nu}{k^*} \right) \right)^{-1} \]
The CECP model predicts that the salt concentration at the membrane surface $C_m$ will be elevated compared to the bulk salt concentration $C_b$ when a cake is present so the observed salt rejection $R_o$ should be diminished according to

$$R_o = 1 - \frac{C_m - R_i C_m}{C_b}$$  \hspace{1cm} (7)$$

where $R_i$ is the intrinsic membrane salt rejection.

The pressure drop $\Delta \pi^*$ caused by CECP is given by

$$\Delta \pi_m^* = f_{os} C_o R_o \exp \left( \frac{V}{k^*} \right)$$  \hspace{1cm} (8)$$

where $f_{os}$ is a factor relating salt concentration to osmotic pressure. An empirical relationship for $f_{os}$ was used here. Salt concentrations were determined from conductivity measurements.

The sum of cake-resistance pressure drop, CECP pressure drop, and intrinsic membrane pressure drop must be equal to the applied pressure $\Delta P$, so

$$\Delta P = \Delta P_c + \Delta \pi_m^* + \Delta P_m$$  \hspace{1cm} (9)$$

where $\Delta P_m = \nu \mu R_m$ with $R_m$ being the intrinsic membrane resistance. Note that $\Delta \pi_m^*$, the result of CECP, is elevated compared to the osmotic pressure from concentration polarization without a cake layer, $\Delta \pi_m$. To quantify the degree of additional pressure drop $\Delta \pi_a$ caused by CECP we will here use

$$\Delta \pi_a = \Delta \pi_m^* - \Delta \pi_m$$  \hspace{1cm} (10)$$

The AOM in our studies was not well characterized and we are left without accurate knowledge of particle size, porosity, or cake layer thickness. Further, the relationship between tortuosity and porosity may not be the same as Equation 4. Because of these uncertainties we cannot strictly determine whether cake layer resistance or CECP was most important in the observed flux decline. We can, however, ask the model to tell us which mechanism would be more important over a range of possible particle sizes, porosities, and tortuosities. To do this we used an iterative equation solver script written in Matlab. An initial guess at cake thickness was made followed by calculation of pressure drop from hydraulic resistance $\Delta P_c$ using Equation 1. At the same time the hindered mass transfer coefficient $k^*$ was calculated with Equation 5 and $f_{cp}$ was determined with Equation 6. The new membrane wall concentration ($C_m = f_{cp} C_b$) was fed to Equation 7 for determining the observed salt rejection $R_o$ and the cake-enhanced osmotic pressure $\Delta \pi^*$ was found with Equation 8. These steps were repeated with varying cake layer thickness until the sum of hydraulic resistance pressure drop, CECP pressure drop, and intrinsic membrane pressure drop was equal to the applied pressure.

With the above modeling procedure we found the pressure drops associated with hydraulic resistance and CECP for the direct algal spike on the SWC4 membrane with a fine permeate spacer. Measured operating conditions at the end of the run (when flux had declined to its lowest level) were input to the model. Flux decline was ten percent (27.1 lmh initial, 24.4 lmh final), pressure was 6,880 kPa, and intrinsic membrane salt rejection was 99%. The pre-fouling
mass transfer coefficient \((k)\) was calculated using a rearrangement of Equation 6 with \(f_{CP}\) equal to 1.32 as determined during the clean-water flux run with procedures from Chapter 4. Intrinsic membrane resistance \(R_m\) was also determined during the clean-water flux run. Other parameters were \(D_\infty = 1.61 \times 10^{-9} \text{ m}^2/\text{s}\), \(\mu = 1.00 \times 10^{-6} \text{ kPa-s} (\text{at } 20^\circ\text{C})\), and bulk conductivity \(\sigma_b = 50.0 \text{ mS/cm}\).

Figure 3.10 shows the modeling results for varying particle size, porosity, and tortuosity. Similar results would be obtained for the other fouled membrane cases except that the cake thickness and total pressure drop would change with the level of fouling. The first interesting finding is that for a given porosity and tortuosity there exists a maximum cake thickness obtained when particle size is large and CECP dominates (see Figure 3.10a). This maximum exists because any thicker cake (with the same porosity and tortuosity) would cause more CECP resistance than was found in the experiment. The cake can only be thicker if the porosity is higher (Figure 3.10b) making the hindered diffusion coefficient \((D^*)\) greater, as is described in Equation 2. Coupled with that effect, a high porosity means a lower hydraulic resistance, as described in Equation 1; thus very porous cakes are much more likely to cause CECP resistance than hydraulic resistance. If the tortuosity is high the cake thickness must be smaller (Figure 3.10c). Tortuosity has an inverse effect on cake thickness because higher tortuosity gives a lower \(D^*\). Pressure drop does not vary as much with tortuosity changes as it does with particle size or porosity changes, so pressure drop seems less sensitive to tortuosity.

In general Figure 3.10 shows that hydraulic resistance is the dominant mechanism at low particle size, porosity, or tortuosity. As any of these increase CECP becomes dominant. A crossover point exists where hydraulic resistance and CECP contribute equally to the pressure drop. For the analyses in Figure 3.10 the crossover point was at \(d_p = 10 \text{ nm}, \varepsilon = 0.39\), and \(\theta^2 = 2.5\); however, these values are only valid for the conditions of the modeling (described in the caption). To see how the crossover point changes as conditions vary, further modeling was performed.

For a given flux decline measurement there exists only one particle size and cake thickness combination that fits the model at the crossover point for each porosity and tortuosity value. Plots of cake thickness and particle size versus porosity at the crossover points for several values of tortuosity are shown in Figure 3.11; these are here called crossover point curves. The curves give information about the relative importance of hydraulic resistance and CECP for cakes with different properties. For example, a cake that is 20 \(\mu\text{m}\) thick and has a tortuosity factor \((\theta^2)\) of 2 will have equal pressure drops from hydraulic resistance and CECP when the porosity is about 0.9. If the porosity or tortuosity were lower, hydraulic resistance would dominate (as we know from Figure 3.10). A cake made up of 20-nm particles with a porosity of 0.4 would be at its crossover point if the tortuosity were one. If the tortuosity is higher than one, CECP will dominate.

From the crossover point curves a few suppositions can be made about the importance of hydraulic resistance compared to CECP for this experimental run (and the other fouled-membrane tests performed here under similar conditions). First if we assume a set of reasonable cake parameters such as a cake porosity of 0.4 (what would be found in a random assemblage of spherical particles) and a tortuosity factor of 2.83 (found from the \(\theta^2 = 1-\ln(\varepsilon^2)\) relationship given by Boudreau (1996)) then hydraulic resistance would only dominate if the particle size were less than about 15 nm. The cake thickness in that case would be limited to about six \(\mu\text{m}\). It is certainly possible that such a thin, densely packed cake could form at the membrane surface. SEM images (Figure 3.6) of dried foulants show a homogeneous layer with no large particles
present. However, there is much more room for possibility on the other side of the crossover point. The flux in these experiments, though high for RO, was much lower than the crossflow velocity and would likely yield a loosely packed cake. Indeed much of the wet foulant material immediately after the experiment could be rinsed away easily so it appeared to have only a loose attachment (the apparently tight, homogeneous cake in SEM images may have formed upon drying). This would mean a higher porosity and much more likelihood that CECP would dominate as a resistance mechanism.

One significant piece of evidence to shed light on the fouling mechanism is the salt rejection data. The model presented here suggests a 1% decrease in salt rejection if CECP dominates while if hydraulic resistance is dominant no change in rejection would be expected. Observed salt rejections for our experiments are plotted in Figure 3.12; observed rejection increased in all cases. The increase was similar for all six experiments, whether flux decline was observed or not. The coarse permeate carrier resulted in slightly lower rejection than the fine permeate carrier, perhaps because the membrane deformed to a greater extent and structural stability was not maintained; however, greater than 99.5% rejection was achieved by the end of the experiments, which was still very good for bench-scale tests.

Non-decreasing salt rejection data support the hydraulic resistance model and suggest that CECP did not dominate; however, it is possible that CECP did occur, but the membranes were still able to reject the salts and hide its effect. In Hoek and Elimelech’s study (2003) a nanofiltration membrane with 70-80% salt rejection showed the biggest decrease in observed salt rejection and the greatest evidence for cake-enhanced concentration polarization. The RO membranes had 94 to 98% salt rejection and the observed salt rejection decreased very little so the evidence for CECP was not as strong, though they cited another of their studies where rejection was observed to decrease more significantly over a longer time period with the same membranes and similar colloidal foulants (Hoek et al. 2002). In our study the observed rejections were between 98.8 and 99.9% and always increased even as flux declined. Perhaps our highly rejecting membranes did not allow observation of the cake-enhanced concentration polarization phenomenon. Another possibility is that the increasing rejection due to membrane compaction masked the decrease in rejection that would have been observed with elevated feed salt concentration. Even though the membranes were compacted before the fouling runs it is possible that some degree of compaction was still occurring and the membrane rejection tightened over time.

In summary, though we cannot strictly conclude whether hydraulic resistance or CECP was the dominant fouling mechanism in our experiments, we were able to model the way in which varying cake properties would determine the relative importance of each mechanism. Hoek and Elimelech (2003) assert that CECP will dominate for salt-rejecting membranes and in their study with 100-nm spherical particles CECP certainly did dominate. We used their data in our model and showed that for 100-nm particles CECP dominates for any porosity (0.1 to 1) and tortuosity (1 to 5). For the AOM in our experiments, however, there was a wide range of particle size, from dissolved up to the size of the algal cells themselves (10 to 15 μm). Such material could form dense cakes with low porosity; hydraulic resistance would then be more important than CECP.
Figures

Figure 3.1. (a) Coarse permeate carrier. (b) Fine permeate carrier. Scale bar is 2 mm.
Figure 3.2. Normalized RO specific flux for microfiltered AOM and direct algal spikes (40,000 cells/ml) on (a) coarse permeate carrier with SW30HR membranes (b) fine permeate carrier with SW30HR membranes, and (c) fine permeate carrier with SWC4 membranes.
Figure 3.3. Cell concentration determined by hemacytometer during a direct-spike algal fouling experiment along with fluorescence of filtered (0.45 μm) and unfiltered samples.
Figure 3.4. (Column 1) Visual images, (Column 2) LSC fluorescence images, and (Column 3) fluorescence histograms of RO membranes fouled by algogenic organic matter. (a) Direct algal spike, SW30HR, coarse permeate carrier. (b) Direct algal spike, SW30HR, fine permeate carrier. (c) Direct algal spike, SWC4, fine permeate carrier. (d) Microfiltered AOM, SW30HR, coarse permeate carrier. (e) Microfiltered AOM, SW30HR, fine permeate carrier. (f) Microfiltered AOM, SWC4, fine permeate carrier. In LSC images (2) contrast was adjusted to highlight notable features so grey levels are not comparable among images. Histogram heights in (3) were normalized to the maximum peak heights.
Figure 3.5. Power spectra from image analysis of fouled membranes. (a-f) Samples as designated in Figure 3.4. (g) Non-fouled control from a coarse permeate carrier run. (h) Non-fouled control from a fine permeate carrier run. Intensity is in arbitrary units and spectra are offset on the vertical axis for clarity.
Figure 3.6. SEM images of fouled RO membranes. Letters (a-f) designate the samples listed in Figure 3.4. (g) Clean SW30HR. (h) Clean SWC4. Images were taken at 20 kV in secondary electron imaging mode with 20 kV acceleration voltage. White scale bar spans five μm.
Figure 3.7. Infrared absorbance spectra of fouled and clean RO membranes in the wavenumber regions 3700 to 2600 cm\(^{-1}\), 1800 to 1300 cm\(^{-1}\), and 1200 to 800 cm\(^{-1}\). Letters (a-f) designate the samples listed in Figure 3.4. (g) Clean SW30HR. (h) Clean SWC4.
Figure 3.8. Surface protein concentrations of fouled RO membranes. Letters (a-f) designate the samples listed in Figure 3.4. (g) Non-fouled control from a fine permeate carrier run. Error bars span standard error of triplicate measurements.
Figure 3.9. Algal biopolymer concentrations on fouled SW30HR and SWC4 membranes. Both bulk algal samples (direct algal spikes) and cell-free (microfiltered AOM) biopolymer samples were tested.
Figure 3.10. Top row: modeled cake thickness compared to other cake properties for a direct-spike fouling test (SWC4 fine permeate carrier). Bottom row: contributions of hydraulic resistance (broken line) and CECP (solid line) to the foulant-layer pressure drop from the model for the same fouling test. (a) Varying particle size \( d_p \) with constant porosity \( \varepsilon = 0.4 \) and tortuosity \( \theta^2 = 1-\ln(\varepsilon^2) = 2.83 \). (b) Varying porosity with constant particle size \( d_p = 10 \text{ nm} \) and tortuosity \( \theta^2 = 2.83 \). (c) Varying tortuosity with constant particle size \( d_p = 10 \text{ nm} \) and porosity \( \varepsilon = 0.4 \).
Figure 3.11. Crossover point curves (where CECP and hydraulic resistance yield equal pressure drops) for a direct-spike fouling test (SWC4 fine permeate carrier). (a) Cake thickness and (b) particle size are given for varying porosity and tortuosity.
Figure 3.12. Salt rejection data for direct algal spikes and microfiltered AOM on coarse and fine permeate carriers for two RO membrane types. Letters indicate samples as designated in Figure 3.4.
FOULING BY DIRECT ALGAL FILTRATION ON MF AND UF

As reported in the previous section, high-pressure RO bench-scale tests resulted in minimal flux decline due to algae. The situation was different for low-pressure filtration; algae caused quick and dramatic flux decline. This section investigates the mechanisms of flux decline by algae on microfiltration and ultrafiltration membranes. Experiments were performed in the 50-ml dead-end cell at a constant pressure of 200 kPa (30 psi). Two membranes were used: 0.45-μm MF membranes made of mixed cellulose esters (Millipore) and 100-kDa UF membranes made of regenerated cellulose (Millipore). Algae were fed at a concentration of 70,000 cells/ml. After flux declined the membranes were rinsed with deionized water and another flux decline test was performed. This was repeated five times for the MF membrane and three times for UF.

Flux verses time plots for direct algal filtrations on the MF membranes are shown in Figure 3.13 where it is clear that algae caused rapid flux decline. After the first rinse only about half (53%) of the clean-water flux was recovered, so 47% of the flux decline was reversible. In subsequent stages irreversible flux decline continued; flux recovered to 30, 26, and 20 percent of the clean-water flux with subsequent backwashes. Note, however, that irreversible flux decline becomes less important with each subsequent stage. Stage b recovered 59% of the flux in stage a, stage c recovered 57% of stage b, stage d recovered 87% of stage c, and stage e recovered 77% of stage d. This is consistent with a fouling model where some pores were irreversibly blocked in the early stages of filtration then in later stages many of the remaining active pores were small enough or had a suitable geometry so that foulants were not lodged in the pores and could be rinsed away.

An often-used method of characterizing porous membrane fouling is the approach of Hermia (1982) who considered four conceptual blocking filtration models: cake filtration, intermediate blocking, standard blocking (pore constriction), and complete blocking. The four models can be presented in a characteristic form given by Equation 11.

$$\frac{d^2t}{dV^2} = k \left(\frac{dt}{dV}\right)^n \quad (11)$$

Here $V$ is the permeate volume, $t$ is time, and the exponent $n$ depends on the model; $n = 0$ for cake filtration, $n = 1$ for intermediate blocking, $n = 3/2$ for standard blocking, and $n = 2$ for complete blocking. Values of $n$ falling between these levels suggest a combination of mechanisms. The units of the constant $k$ also vary depending on the model.

Equation 11 can be written in linear form by taking the logarithm of both sides

$$\ln\left(\frac{d^2t}{dV^2}\right) = n \ln\left(\frac{dt}{dV}\right) + \ln(k) \quad (12)$$

Plotting $\ln(d^2t/dV^2)$ versus $\ln(dt/dV)$ and finding the slope gives evidence for the mechanism at play in the fouling process (Crittenden et al. 2005). Equation 12 was used to analyze MF flux decline data; resulting plots are shown in Figure 3.14. Solid lines indicate the best linear fit of the data with the exponent $n$ reported at the side. In the first filtration, $n$ was 1.4, which was close to the standard blocking (pore constriction) model. Subsequent filtrations gave a decreasing trend with $n$ equal to 1.3, 1.0, 0.8, and 0.7. This supports the idea presented above that pore blocking (higher $n$) was more dominant at the beginning and cake filtration (lower $n$) was more dominant.
as fouling progressed. In fact, the first filtration appears to have two segments, as shown by the broken lines in Figure 3.14a. Segment a followed the complete blocking model \((n = 2)\) and the later segment followed the intermediate blocking model \((n = 3/2)\). It seems that the pores blocked during the first segment were not cleared with rinsing, since subsequent filtrations did not show the early pore blocking segment.

Another way to visualize the fouling mechanism at play is to compare flux vs. time plots against the four model fits. Each model was expressed in a form where permeate flow (which is directly proportional to flux) was given as a function of time. Model parameters were lumped into a single term for data fitting. The cake filtration model was given by

\[
Q = \frac{Q_0}{(1 + K_{cf}t)^{n/2}}
\]  

(13)

where \(Q\) is the permeate flow rate, \(Q_0\) is the initial flow rate, and \(K_{cf}\) is the lumped fitting parameter for cake filtration. The intermediate blocking model was given by

\[
Q = \frac{Q_0}{1 + K_{ib}t}
\]  

(14)

where \(K_{ib}\) is the fitting parameter for intermediate blocking. Standard blocking was given by

\[
Q = \frac{Q_0}{(1 + K_{sb}t)^{2}}
\]  

(15)

where \(K_{sb}\) is the standard blocking fitting parameter. Finally, the complete blocking model took the form

\[
Q = Q_0 \exp(-K_{cb}t)
\]  

(16)

where \(K_{cb}\) is the fitting parameter for complete blocking.

The four fouling models were fitted to flux data using a script written in Matlab. First the data were normalized to the initial flow rate \((Q_0)\) then an iterative solver function found the \(K\) parameter that minimized the sum of squares error for each model. The results are plotted in Figure 3.15. By comparing the data to the closest fitting model it was confirmed that a combination of complete blocking and standard blocking best represented flux curve a. Curve b was represented well by standard blocking. Curves c, d, and e were well represented by the intermediate blocking model.

UF flux data versus volume filtered are plotted in Figure 3.16. Similar to MF, algae caused rapid flux decline in UF; however, more of the flux was recoverable. Stage b recovered 70% of the stage-a flux and stage c recovered 97% of the stage-b flux. This suggests that much of the flux decline was due to cake-layer formation and pore blocking by material that did not penetrate or adsorb within the UF membrane pores; the foulants were mainly larger than the pores (100-kDa). Also noteworthy is that the irreversible portion of fouling (30% of the overall flux decline) occurred mainly in the first stage (a). With stage b only 3% was irreversible fouling.
Fouling mechanism analysis plots for UF filtrations are shown in Figure 3.17. The characteristic blocking law terms, \( n \), for UF were 2.3, 2.8, and 1.9. These would suggest that pore blocking \((n = 2)\) was the principal mechanism at play during the fouling process; however, this result is counterintuitive since algal cells (10 to 15 \( \mu \)m in size) were much larger than the pores and much of the fouling was reversible. Cake filtration was expected as the dominant mechanism. When the flux versus time plots were compared to the predictions of the four blocking models (Figure 3.18) cake filtration did give the best fit in all cases. It is felt that the \( \ln(d^2t/dV^2) \) vs. \( \ln(dV/dt) \) plots (Figure 3.17) was less reliable than the flux versus time plots (Figure 3.18) in this case, since the former had significant scatter and \( \ln(dV/dt) \) did not vary over a wide enough extent to make the analysis meaningful. Cake filtration was the more likely flux decline mechanism for UF.
Figures

Figure 3.13. Normalized flux for filtration of an algal-laden sample (70,000 cells/ml) on a 0.45-μm MF membrane. The five stages (a, b, c, d, e) are separated by breaks where the membrane was rinsed. Clean-water flux ($J_0$) was 22,400 lmh.

Figure 3.14. Fouling mechanism analysis plots for the five MF algal filtration flux curves (a, b, c, d, e) presented in Figure 3.13. Solid lines show the linear fit, the slope of which ($n$) is also given. Curve $a$ has two additional fits indicated by broken lines; $n = 2$ for the first segment and $n = 1$ for the second segment.
Figure 3.15. Flux versus time plots for the five regions (a-e) shown in Figure 3.13. Data are indicated by circles and data fits for four fouling models are also shown.
Figure 3.16. Normalized flux for filtration of an algal-laden sample (70,000 cells/ml) on a 100-kDa UF membrane. The three curves (a, b, c) are separated by breaks where the membrane was rinsed. Clean-water flux \( J_0 \) was 520 l/mh.

Figure 3.17. Fouling mechanism analysis plots for the three UF algal filtration flux curves (a, b, c) presented in Figure 3.16. Solid lines show the linear fit, the slope of which \( n \) is also given.
Figure 3.18. Flux versus time plots for the three UF filtration regions (a-c) shown in Figure 3.16. Data are indicated by circles and data fits for four fouling models are also shown.
SHEAR AND ITS EFFECTS ON MF AND UF

Effects of shear on algal cells

Shear forces in the valve caused cell lysis and release of internal organelles and organic matter. The internal material was scattered and was difficult to detect with visible-light microscopy, but Figure 3.19 shows an intact cell and a cell that was crushed under the microscope slide to demonstrate release of AOM. Figure 3.20 displays flow cytometry data for one experiment before and after 150 minutes of shear with a valve pressure drop of 6,400 kPa. Light-scatter parameters are indicative of particle size. A particle was confirmed to be a cell by its 488-nm fluorescence. Cell numbers dropped significantly after shear while the number of “background” data points (having low forward-scatter and side-scatter) increased significantly. There was clear separation between the whole-cell and background data clouds indicating that cells did not break into mid-size pieces (between 5 and 8 µm), but dissociated into smaller fragments upon breakup. Bulk sample fluorescence increased over time with shear as cells broke apart and less self-shading occurred. Self-shading is known to be a factor in fluorescence measurements; fluorescence is always lower in a whole-cell suspension than in a solution of pigments with the same total pigment concentration due to the package effect (Kirk 1994; Johnsen et al. 1997).

For one run a time series of flow cytometry sub-samples was taken (Figure 3.21). At each time step the number of points in the “whole cell” data cloud and the “background” data cloud were counted. The same sub-samples were examined with hemacytometry, which confirmed that flow cytometry was appropriately identifying whole cells. Cell numbers declined and background material increased over the course of the shearing run. The number of background particles measured by flow cytometry did not rise very far above the initial algal cell concentration even though it was suspected that cells ruptured into multiple parts. This was most likely due to the broken segments and released organic matter being smaller than the lower size detection threshold of the flow cytometer, about 0.5 µm.

Breakup kinetics were first characterized using the first-order model given in Equation 2. Data were normalized to the initial concentration before analysis so $C_o$ was set to unity. This resulted in a fitted breakup constant ($k$) of 0.016 min$^{-1}$ and a cell strength ($\kappa$) of 15 ($\tau$ was 4.26 min$^{-1}$). However, the data fit (not shown) overestimated cell number in the early stages and underestimated cell number in the later stage of the experiment. A better data fit was obtained with the two-term first-order model (Equation 5) plotted in Figure 3.21. It was not surprising that a model with more terms would yield a better fit, but there is physical meaning in the extra parameters. It is suggested here that there exists a distribution of cell structural strength with some cells being stronger than others. The two-term model describes a dichotomy of cell class: a structurally strong fraction and a structurally weak fraction. $C_{so}$ was 0.56 suggesting that about half the cells were of the strong class. $C_{wo}$ (constrained by the model to be 1-$C_{so}$) was 0.44 and represented the weaker cell fraction. The cell strength $\kappa_s$ for the strong-cell class was 29 and the weak-cell strength $\kappa_w$ was 3.1, suggesting an order-of-magnitude difference in strength between the two cell classes. These strength parameters are applicable only for the power density used in our system and only for the H. pygmaea algal species, which is small and armored making it structurally stronger than larger, unarmored species. An interesting future research direction would be to determine how cell breakup varies with power density and how cell breakup...
compares among different algae, especially larger, unarmored species like *Karenia Brevis* in Gulf of Mexico Red Tide events.

The power density chosen for our study was a fairly high value in order to deliver sufficiently rapid breakup of our armored cells. For comparison, we calculated power densities using information from the literature for other systems. Our valve $\Phi_m$ ($4 \times 10^{10}$ W/m$^3$) fell between the $\Phi_m$ for open, low-shear valves of an algal photobioreactor ($2 \times 10^7$ W/m$^3$; (Vandanjon et al. 1999)) and the high shear that is typical for an industrial milk homogenizer ($8 \times 10^{12}$ W/m$^3$; (Thiebaud et al. 2003)). It is difficult to predict the power densities expected for full-scale desalination facilities because shear has not been a main concern in previous studies and power densities are not reported. Power density measurements for actual pumps and valves, coupled with species-specific breakup data, would enable better understanding of the full-scale effects of shear on marine algae.

**Effects of shear on flux**

Flux data for the four sets of algal-laden membrane fouling experiments (one set for each membrane pore size) are presented in Figure 3.22. Flux ($J$) was normalized to the initial clean-water flux ($J_0$). In all cases flux decline was more drastic after shear than before shear. The difference was dramatic for 0.45-µm membranes (Figure 3.22a). There was less difference before and after shear for the 0.22-µm membrane (Figure 3.22b). In the 100-kDa UF experiment (Figure 3.22c), the curves had an almost linear region toward the middle of the run before shear. After shear, however, flux decline was more decaying-exponential in nature. In the 30-kDa UF experiment (Figure 3.22d) the before-shear fouling rate increased with mass filtered (i.e. the curve dropped downward instead of leveling out). This could have occurred due to changes in cake morphology as have been observed elsewhere (Belfort et al. 1994; Chellam and Xu 2006; Kovalsky et al. 2007). The algal cells may have gently collected on the membrane surface in a loose arrangement during initial deposition, but over time the cells reoriented themselves by filling in voids to form a less porous cake. The effect was seen most prominently in the 30 kDa case because the 30 kDa membrane was the most resistive and the actual flux was lowest leading to gentle, loose deposition. The 100 kDa membrane was the next most resistive and a cake settling event may have also occurred. The effect was not seen in the 0.45 and 0.22 µm membranes because their high flux caused a tightly packed initial cake deposit. After shear cake settling was not observed for any of the membrane types because the wide range of particle sizes led to densely packed cakes from the outset.

**Effects of shear on organic-matter rejection**

Organic-matter rejection was determined for one set (one rep for each membrane type) of filtration experiments. Total carbohydrates, monosaccharides, UV absorbance, and fluorescence for feed samples are presented in Table 3.1 along with rejection values calculated by $R = 1 - C_p/C_f$ where $R$ is the rejection, $C_p$ is the permeate concentration (or measurement) and $C_f$ is the feed concentration (or measurement).

Though there was significant scatter in total carbohydrate and monosaccharide measurements (e.g. the drop in feed concentrations after shear and the 0.06 monosaccharide rejection by 0.22-µm membranes seem anomalous), rejection of total carbohydrates and monosaccharides decreased with shear in all cases. The majority of carbohydrate material
passing through the membranes after shear was smaller than 30 kDa, as indicated by the fact that the 30 kDa permeate concentration was similar to the permeate concentrations of the other membranes.

Rejection of UV absorbance changed very little after shear. Even though the permeate UV absorbance values were elevated with shear, the feed concentrations were also elevated so that the calculated rejection values were similar with or without shear. Shear caused an increase in UV absorbance because intracellular material was released and the package effect was decreased.

Fluorescence was a very good indicator of shear since before shear it was almost perfectly rejected by all membrane types, but after shear fluorescent material could permeate the membranes. Algal cells did not release much dissolved fluorescent material into the water matrix during culture. After shear, however, the total fluorescence increased by 3.3 times, from 150 to 499 (arbitrary units). Similar to carbohydrates, much of the released material was smaller than 30 kDa.

Fractionation Flux Results

Flux data for fouling of 0.1-μm PVDF membranes by different size fractions of algogenic organic matter are presented in Figure 3.23. In order to make quantitative comparisons in the discussion of these results, we will consider the percentage fouling caused by each fraction. We will make the comparisons at 200 L/m² specific volume filtered since all samples were run at least up to that point. The non-fractionated algal culture was comprised of all possible foulant material and thus is defined as 100% fouling. The centrifuged sample caused 71% of the fouling in the non-sheared case and 91% of fouling after shear. The glass-fiber filtered sample caused 59% of fouling before shear and 76% after. The majority of foulant material was not removable by either centrifugation or glass-fiber filtration and shear caused an increase in the relative importance of these fractions.

Material smaller than 100-kDa and 30-kDa caused no discernable flux decline either before or after shear. From this and the organic analyses it appears that fouling of 0.1-μm PVDF membranes did not occur by adsorption of dissolved material. Only the fractions larger than the membrane pore size were capable of causing flux decline.

Fractionation Analytical Results

Measurements of TOC, carbohydrates, UV absorbance, and fluorescence, for the seven size fractions of non-sheared and sheared algal samples were used to produce the organic matter size distributions in Figure 3.24. Moving from left to right in the plots, one can visualize the amount of material removed by each fractionation step. For example, in the non-sheared case, 58% of the TOC was large enough to be removed with centrifugation and about 37% was small enough that it passed through all the fractionation steps. Only 5% of the TOC was removable by the intermediate fractionation steps before shear. In the sheared sample, however, centrifugation removed only 28% of the TOC and there was now 51% that was small enough to pass through all fractionation steps. There was now 12, 5, 1, 2, and 2 percent TOC retained by glass-fiber, 0.45-μm, 0.22-μm, 100-kDa, and 30-kDa filtration, respectively. Thus, the overall result of shear was to break the algal samples into a more heterogeneously sized mixture. The amount of dissolved material increased and the amount of intermediate-sized material also increased.
A similar change in size distribution was seen in the carbohydrate data of Figure 3.24. Carbohydrates were 80% contained within the algal cells in the non-sheared sample and only 6% was smaller than 30-kDa. The algae did not release many dissolved or colloidal carbohydrates during culture. With shear, however, carbohydrates were released and dissolved and intermediate-sized material comprised a larger fraction of the total.

Carbohydrate and TOC measurements can be compared directly to evaluate the chemical makeup of each size fraction. Carbohydrates accounted for 34% and 31% of the TOC for the raw non-sheared and sheared samples, respectively. After centrifugation, the carbohydrate content dropped to 18% and 21%. Glass fiber filtration gave similar results, 19 and 19%, respectively. Further fractionation left the ratio at 12 and 13% for the 0.45-µm fraction, 14 and 15% for 0.22-µm, 14 and 17% for 100-kDa, and 5 and 14% for 30-kDa fractions. In general, then, shear did not change the carbohydrate:TOC ratio in each size fraction, it only increased the total mass of the smaller fractions. Also, carbohydrates were enriched in the larger size fractions and were less important in the smaller fractions.

The UV absorbance size distribution of Figure 3.24 was distinct from TOC and carbohydrates in that the sub-30-kDa fraction changed very little and actually decreased after shear. Note, however, that the initial TOC concentrations of non-sheared and sheared samples were the same (7.3 mg/l) while the initial UV absorbance values for non-sheared and sheared samples were quite different, 0.055 and 0.097, respectively. The size distributions were normalized to those initial values, so it is not readily apparent that the sub-30-kDa fraction had a higher absorbance after shear (0.034) than it did before shear (0.022). Thus, dissolved material did increase in quantity even though its relative importance in the overall UV measurements decreased. The intermediate-sized fractions increased in magnitude and in importance, consistent with TOC and carbohydrate measurements.

Fluorescence data were unique compared to other analytical techniques in that the difference in apparent size distribution between sheared and non-sheared samples was extreme. As noted previously, before shear almost all the fluorescent material was within the algal cells. With shear it was released and spread over the entire size distribution. Fluorescence is specifically an indicator of the light-harvesting pigments chlorophyll and peridinin. Chlorophyll and peridinin were associated with all of the size classes after shear.

The protein content of bulk water samples was too low to be quantified, but proteins were measurable directly on the fractionation membranes and the concentration in bulk samples was determined. The tightest membrane (30 kDa) collected the most material, indicating the upper limit of the verifiable protein concentration in the highly-fouling fraction (material that passed through the glass-fiber filter). The non-sheared sample had roughly 0.35 mg/l of protein and the sheared sample had 0.85 mg/l, which shows that shear released proteins. Proteins large enough to be collected on the 30-kDa membrane represented 13 and 19% of the non-sheared and sheared TOC, respectively, which was in the same range as found for carbohydrates (19 and 19%). Even though the total organic carbon concentrations were different for non-sheared and sheared samples (2.7 and 4.4 mg/l, respectively) the carbohydrate and protein ratios were quite similar. This suggests that the highly fouling particulate fraction is composed of similar material whether it be released naturally or through engineered shear.

The effect of dissolved biopolymers and colloidal material on flux is elucidated with the size-exclusion chromatograms in Figure 3.25. High-molecular weight dissolved and colloidal material (the peak between 6 and 7 minutes) was very similar in concentration for all the size fractions larger than 100 kDa, yet fouling was very different. Also, the 100 kDa and 30 kDa
sheared fractions had more high-molecular-weight material than all of the non-sheared fractions, yet no flux decline was seen for these samples. Though this material was in high abundance and increased with shear, it apparently passed through the microfiltration membranes without causing flux decline. This does not rule out the possibility that the dissolved material could interact with the particulates to have a synergistic effect; such a phenomenon has been seen in other fouling studies (Li and Elimelech 2006). However, without particulate matter present the high-molecular weight dissolved material was not able to cause fouling in these short-term tests. This is contradictory to other studies where adsorptive fouling was found to play an important role (Howe and Clark 2002; Koh et al. 2005; Howe et al. 2006). Those studies were performed with fresh waters whose humic materials may have a stronger affinity for adsorption than our AOM. Also, here we used a hydrophilic PVDF membrane while previous work was done with polypropylene which is hydrophobic and polyethersulfone which is moderately hydrophobic (Cheryan 1998). Membrane manufacturers are turning more and more toward hydrophilic membranes, like the modified PVDF used in this study. Thus, adsorptive fouling is expected to be a less important mechanism at full scale. A gradual process where adsorptive fouling would occur over several backwashes in a full-scale facility could still be important; longer-term experiments would be needed to assess that possibility.

The distributions of organic matter shown in Figure 3.24 help to determine the quantity of foulant material present. Centrifuged and glass-fiber-filtered fractions together made up only seven percent of the total organic matter and 10% of the carbohydrates before shear. Despite these low mass percentages, these fractions contributed most of the flux decline. After shear, the mass percentages increased to 13% of TOC and 23% of carbohydrates. Along with this increase in mass percentage, the flux decline was exacerbated. This supports the hypothesis that this size fraction was the principal foulant. Further, it suggests that the majority of the organic matter (that which is larger or smaller than this size fraction) is not heavily responsible for flux decline.

Some hypotheses can be drawn here about the cellular components of *H. pygmaea* that were scattered upon cell breakup and caused the exacerbated flux decline. Hemacytometry data indicated that the cells broke into pieces that were smaller than roughly two or three microns. *H. pygmaea* has a theca (covering) of plates that give rigidity and protection (Figure 3.26a). There are 35 thecal plates in a typical cell and their average width is roughly two microns (Loeblich et al. 1981). When the cell is disrupted these plates could separate and remain in solution as three-micron particles made up principally of carbohydrates (cellulose). Chloroplasts, pyrenoids, and mitochondria are roughly one to three microns in size (Figure 3.26b) (Bullman and Roberts 1986). The pyrenoids are locations of starch production/collection. If they remain intact, they would be pore-blocking particles and if they are broken apart they could be a source of dissolved or colloidal carbohydrates. Fibers run throughout the cells and provide structural strength and thecal plate alignment (Roberts et al. 1987). Flagella are also made of fibrous material (Figure 3.26c) that could form small particles with cell breakup.

Chloroplasts have several levels of structure. Chromoprotein complexes containing light-harvesting pigments have molecular weights between 17 and 32 kDa (Jovine et al. 1995). The most abundant structure of this class is the Peridinin-Chl *α*-Protein complex (PCP) that gives the algae their brick-red color (Jovine et al. 1992). These are located in the thylakoids which are arranged in grana stacks that are 0.1 to 0.5 microns. Thus when chloroplasts are released from the cells they could be broken down into smaller units of grana, thylakoids, and/or protein complexes. It has been shown that cell disruption and thylakoid release results in the creation of thylakoid micelles that retain intact chromoprotein complexes (Johnsen et al. 1997). It is possible
that cell breakup creates chloroplast fragments of varying size because of different degrees of damage. This could account for the wide distribution of size classes detected by fluorescence measurements.
Tables

Table 3.1
Feed concentrations and rejections calculated for total carbohydrates, monosaccharides, UV, and fluorescence for four membrane pore sizes. ± indicates standard error of triplicate measurements.

<table>
<thead>
<tr>
<th>Feed</th>
<th>Non-sheared</th>
<th>Sheared</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.45 μm</td>
<td>5.84 ± .1</td>
<td>3.67 ± .3</td>
</tr>
<tr>
<td>0.22 μm</td>
<td>1.14 ± 0.02</td>
<td>1.07 ± 0.03</td>
</tr>
<tr>
<td>100 kDa</td>
<td>0.87 ± .03</td>
<td>0.74 ± .08</td>
</tr>
<tr>
<td>30 kDa</td>
<td>0.82 ± .02</td>
<td>0.43 ± .07</td>
</tr>
<tr>
<td>0.94 ± .09</td>
<td>0.43 ± .07</td>
<td></td>
</tr>
<tr>
<td>0.94 ± .09</td>
<td>0.43 ± .07</td>
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</tr>
<tr>
<td>0.94 ± .09</td>
<td>0.43 ± .07</td>
<td></td>
</tr>
</tbody>
</table>

Calculated Rejection

<table>
<thead>
<tr>
<th>Feed</th>
<th>Non-sheared</th>
<th>Sheared</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.45 μm</td>
<td>0.87 ± .03</td>
<td>0.74 ± .08</td>
</tr>
<tr>
<td>0.22 μm</td>
<td>0.50 ± .05</td>
<td>0.43 ± .07</td>
</tr>
<tr>
<td>100 kDa</td>
<td>0.55</td>
<td>0.56</td>
</tr>
<tr>
<td>30 kDa</td>
<td>0.55</td>
<td>0.56</td>
</tr>
</tbody>
</table>

Figure 3.20. Flow cytometry scatter plots for non-sheared and sheared (150 minutes at 6,400 kPa pressure drop) algal samples. Light scatter and fluorescence parameters were measured to determine sample composition. Cell concentration (labeled as algal cells in the figure) significantly decreased during shear as background particle detection increased proportionately. Source: Ladner, D. A., D. R. Vardon and M. M. Clark (2010). "Effects of shear on microfiltration and ultrafiltration fouling by marine bloom-forming algae." Journal of Membrane Science 356(1-2): 33-43. Reproduced with permission from Elsevier.
Figure 3.21. Algal counts by hemacytometry and flow cytometry during shear. The model is the best fit to the combined data set, with $C_{so} = 0.56$, $C_{wo} = 0.44$, $\kappa_s = 29$, and $\kappa_w = 3.1$. Background particulate material was enumerated by flow cytometry. $C_o$ for background material was normalized to the initial flow cytometry algal count in order to make a direct comparison with algal concentrations. Source: Ladner, D. A., D. R. Vardon and M. M. Clark (2010). "Effects of shear on microfiltration and ultrafiltration fouling by marine bloom-forming algae." Journal of Membrane Science 356(1-2): 33-43. Reproduced with permission from Elsevier.
Figure 3.22. Flux curves for (a) 0.45 µm, (b) 0.22 µm, (c) 100 kDa, and (d) 30 kDa experiments. Two runs were performed with non-sheared samples (squares) and two runs were performed with sheared samples (circles) for each membrane type. Source: Ladner, D. A., D. R. Vardon and M. M. Clark (2010). "Effects of shear on microfiltration and ultrafiltration fouling by marine bloom-forming algae." Journal of Membrane Science 356(1-2): 33-43. Reproduced with permission from Elsevier.
Figure 3.23. Flux results for various size fractions of (a) non-sheared algal culture and (b) sheared algal culture filtered on a 0.1-µm PVDF membrane. Source: Ladner, D. A., D. R. Vardon and M. M. Clark (2010). "Effects of shear on microfiltration and ultrafiltration fouling by marine bloom-forming algae." Journal of Membrane Science 356(1-2): 33-43. Reproduced with permission from Elsevier.
Figure 3.24. Organic matter size distributions for non-sheared and sheared algal samples based on four analytical methods. The data are normalized to the concentration measured in the unfractionated sample. The lowest (light color) bar represents the smallest-sized material that was able to pass through all six fractionation steps. The top bar (dark color) represents the largest-sized material that was removed by centrifugation. Intermediate bars represent material that permeated some fractionation step but was retained in subsequent steps. Bar widths indicate the weight of the given size class; i.e. 37% of TOC passed through all fractionation levels without shear and 50% passed through after shear. Overlapping bars result from measurement uncertainty. Source: Ladner, D. A., D. R. Vardon and M. M. Clark (2010). "Effects of shear on microfiltration and ultrafiltration fouling by marine bloom-forming algae." Journal of Membrane Science 356(1-2): 33-43. Reproduced with permission from Elsevier.
Figure 3.25. Size exclusion chromatograms for fractionated algae. The full range is presented in the top two plots and a narrower range (magnified view) in the lower plots. Both non-sheared and sheared algal samples were fractionated into various size classes: unfractionated (a), centrifuged (b), glass-fiber filtered (c), 0.45 μm (d), 0.22 μm (e), 100 kDa (f), and 30 kDa (g). Source: Ladner, D. A., D. R. Vardon and M. M. Clark (2010). "Effects of shear on microfiltration and ultrafiltration fouling by marine bloom-forming algae." Journal of Membrane Science 356(1-2): 33-43. Reproduced with permission from Elsevier.
Figure 3.26. Structural features of *H. pygmaea*. (a) Thecal plates and their designations (according to Loeblich et al. (1981)). (b) Cross-sectional view of internal organelles as interpreted from TEM images (Bullman and Roberts 1986). (c) Typical morphology and orientation of flagella as interpreted from SEM images (Roberts et al. 1987). Scale bar is five microns. Source: Ladner, D. A., D. R. Vardon and M. M. Clark (2010). "Effects of shear on microfiltration and ultrafiltration fouling by marine bloom-forming algae." *Journal of Membrane Science* 356(1-2): 33-43. Reproduced with permission from Elsevier.
THE IMPORTANCE OF BACTERIA IN MF AND UF

The life cycle of an algal bloom involves a lag phase, a rapid increase in phytoplankton cell number, and a subsequent rapid increase in bacterial cell number. The seawater organic matter composition changes drastically from pre-bloom background material to algal cells and AOM to bacterial cells and bacterial organic matter. This makes for a particularly challenging situation when pre-treatment strategies are being considered for seawater desalination facilities; operators must deal with feed water that changes greatly from day to day in terms of organic matter and microbiological concentration and composition.

To provide some insight into how the varying concentration and composition of organic matter may affect pretreatment membranes, a simulated algal bloom was created in the laboratory and filtration performance was measured during the various stages of bloom development. Water quality was monitored over time and compared to the flux decline experiments to determine which factors would be of greatest concern to membrane filtration plant operators. The importance of bacteria during this bloom life cycle was investigated.

Simulated algal bloom

Algae were cultured as described in the Methods and Materials chapter. Ten bottles with a volume of 500 ml each were spiked on the same day and grown side-by-side for seven weeks. The seven-week period encompassed the simulated algal bloom; it began with a small algal concentration then algal numbers peaked and decayed. Three times each week two bottles were measured via hemacytometry and fluorescence microscopy to determine algal cell concentration. Fluorescence microscopy was also used for bacterial counts. Additionally, ultraviolet (UV) absorption and bulk fluorescence were measured three times per week. Approximately each week (sometimes twice per week) a culture bottle was removed and used for membrane performance experiments.

Membrane Filtration Tests

Membrane filtration tests during the algal bloom life cycle experiment were performed using two 25-mm diameter dead-end test cells for side-by-side replication. Membranes were 0.1-μm hydrophilic PVDF (Millipore type VVLP) that represent full-scale hollow-fiber filtration. A new membrane coupon was used for each test. The standard filtration protocol was used with the following modifications. After the clean-water flux test, the feed was switched from ultrapure water to a one-liter pressure vessel containing 200-ml of algal culture. The culture was collected by siphoning from the top of the culture bottle to avoid collecting settled material. Forty milliliters of feed were saved for analysis. A magnetic stir bar was used in the pressure vessel to ensure entrainment of algal cells. Filtration was performed at 69 kPa (10 psi). The sample was filtered until exhausted or until flux dropped below 100 liters per meter squared per hour (lmh).

After filtration of the algal culture, the membrane was rinsed by adding about 25 ml of 0.1-μm filtered and autoclaved seawater (clean seawater) to the vessel, shaking for ten seconds and discarding. Rinsing was performed three times. The membrane was then inverted and placed back in the filtration cell. The support screen was helpful in facilitating membrane inversion; without a support screen the membrane deformed more and was harder to remove from the cell without damage. Membrane backwash was done with 100-ml of clean seawater. The membrane
Membrane Fouling by Marine Algae in Seawater Desalination

was then inverted again and another 100-ml of clean seawater was filtered to measure the flux recovery. The reason clean seawater was used instead of nanopure water for rinsing, backwashing, and flux recovery is that nanopure water could break algal cells due to osmotic shock. All flux experiments were done at room temperature (22 ± 2°C). Each test was performed twice using the dual-filtration-cell setup.

**Algal bloom life cycle results**

Algal concentration during the simulated algal bloom followed a fairly classic pattern of lag phase and exponential growth. This was evident in both the hemacytometry and fluorescence microscopy data given in Figure 3.27. The expected stationary and decline phases were difficult to determine due to scatter in the data. The latter data seemed to be a combination of stationary and declining phases; though the algal numbers had dropped from their peak, they experienced a slow decline instead of remaining steady or dropping completely.

Bacterial measurements (Figure 3.28) showed a lag phase for ten to fourteen days then cell numbers began to increase dramatically. Bacteria continued to increase in number up to the 46-day end of the experiment, though in later stages the growth rate appeared to taper. These data are consistent with the idea of a bacterial bloom following the algal bloom. Algal numbers started increasing dramatically at about eight days. Organic matter from the algal bloom was then available for the bacterial bloom that began about one week later. As the algal bloom peaked and cell numbers started declining, bacteria fed on the algal remains. There was sufficient organic matter for the bacteria to continue feeding through the end of the experiment, but since algal numbers had dropped, bacterial growth rates also declined. It is presumed that had the experiment continued, bacterial numbers would have reached a peak and also begun to decline.

In enumerating algal and bacterial cells it is important to note their morphology. The fluorescence microscope images in Figure 3.29 show the way bacteria and algae interact in culture. Bacteria often attach to an algal cell and form a globular biofilm as in Figure 3.29a. Alternatively, bacteria can enter into an algal cell and feed off organic matter from within (Figure 3.29b). When bacteria were enumerated, these globular biofilms and invaded algal cells were not considered; only planktonic bacteria were enumerated, keeping floc-associated biofilms separate. Thus, the actual biomass in a sample was underestimated, since it did not include floc-associated bacteria.

The simulated algal bloom was also tracked using optical techniques. UV absorbance at 254 nm (Figure 3.30) showed a slight decrease during the first seven days of the experiment. The reason for the decrease is unknown, since algal and bacterial numbers were both rising (though slowly) during that time period, but UV-absorbing vitamins in the nutrient medium may have been utilized by algae or consumed by bacteria in the early stage.

After the initial decrease, UV absorbance increased in a linear fashion as time progressed. This was the case for both unfiltered and filtered (0.22 µm) samples. The trend followed the bacterial growth pattern. Since algal numbers showed a different pattern (they decreased after 20 days) UV absorbance was more correlated to bacteria than it was to algae. There was a linear relationship between unfiltered and filtered UV absorbance. Assuming that the difference between unfiltered and filtered samples was due to the presence or absence of cells (bacterial or algal), it appears that cells released UV-absorbing extracellular material at a constant rate throughout the experiment.
Fluorescence data shed further light on the nature of organic matter present during the algal bloom simulation. Fluorescence of bulk (non-filtered) samples (Figure 3.31) followed the algal cell numbers for the first thirty days of the experiment; the increase in algal cell numbers starting around day eight is evident in the non-filtered fluorescence plot. Further, the peak in algal numbers at about day 20 is also evident via fluorescence. The pattern broke down, however, after day 34 when unfiltered fluorescence was dramatically higher than any other day of the experiment, even though algal numbers were on the decline.

In order to better understand the fluorescence information the data were plotted according to the bottle measured. As noted previously, during the experiment culture bottles were removed for membrane tests. Thus, on days two to ten bottle a was measured, but after the first membrane test on day 11, bottle b was used. This pattern continued through the experiment and in Figure 3.31 the bottle measured is indicated. It turns out that the anomalously high fluorescence data occurred in bottles g and h. It is presumed that in those bottles the bacterial bloom involved a strain with extremely fluorescent cellular components; for example, a strain that produced large quantities of fluorescent proteins similar to the green fluorescent protein found in jellyfish. Even though the culture bottles were all spiked at the same time and with the same mixture of algae and bacteria, the bacterial population was heterogeneous and the population dynamics among bacterial species was random so that different strains could take over the culture. In fact, it appears that the fluorescent bacteria in culture bottle g bloomed and decayed over the eight days it was monitored, while fluorescence in bottle h was slightly increasing.

Fluorescence data for filtered samples shed further light on the organic-matter composition in culture bottles. Figure 3.32 shows that filtered fluorescence intensity was quite low for the first ten days, then began increasing after day 16. This followed the bacterial trend much more closely than the algal trend, indicating that dissolved-matter fluorescence was correlated with bacterial abundance. Even though the algae were quite fluorescent, they did not appear to release their fluorescent material when they were in growth stage. For the culture bottles that had very high unfiltered fluorescence, the filtered fluorescence also spiked. In fact, the increase was so intense that the data had to be plotted on a broken y axis in Figure 3.32. The trends in filtered fluorescence for bottles g and h followed the trend for non-filtered fluorescence indicating that dissolved fluorescent material was the reason for elevated bulk fluorescence. For bottle g the filtered fluorescence was as much as 90 percent of the unfiltered fluorescence (on days 37 and 39) and for bottle h filtered fluorescence reached 71 percent of the unfiltered fluorescence (day 46). One hypothesis is that the bacterial cells in those bottles released a fluorescent extracellular product. An alternative hypothesis is that culture vessels g and h contained bacteria that had a propensity to lyse and release material from algal cells. It was seen during shear experiments that fluorescence increased with shear as the cells broke apart. If bacteria were able to lyse the cells, this could have been a mechanism for release of algal fluorescent organic matter.

Flux measurements along the life cycle of the algal bloom (Figure 3.33) showed an expected trend; flux decline was more rapid with each successive experiment. As algal numbers increased, flux decline also increased. However, as the algal population peaked and decayed, flux decline continued to increase. It appears that bacteria were the culprits in this continued exacerbation of fouling. Flux recovery did not follow the same trend; the lowest recoveries were found in the first 20 days of the simulated algal bloom (Figure 3.34). Here the recovery was calculated by dividing the clean-water flux after backwash by the clean-water flux before the test. It is remarkable that when flux decline was at its worst, flux recovery was at its best.
suggests that the bacteria and associated organic matter in late stages had lower adsorptive affinity with the membrane than the algae and AOM in the early stages.
Figure 3.27. Algal concentration as measured with hemacytometry and fluorescence microscopy over the course of the simulated algal bloom.
Figure 3.28. Bacterial concentration as measured by fluorescence microscopy during the simulated algal bloom.
Figure 3.29. Fluorescence microscope images of bacteria interacting with algae. Bacteria are visible by DAPI staining and have been colored purple in these pseudo-color images. Algae are autofluorescent and have been colored green. a) Globular biofilm surrounding an algal cell. b) An algal cell into which bacteria have entered. The outline of the cell is not readily apparent; only a few chloroplasts remain intact and are fluorescing. White bars represent ten micrometers.
Figure 3.30. UV absorbance of raw (unfiltered) and filtered (0.22 µm) samples drawn from culture vessels over the time period of the simulated algal bloom.
Figure 3.31. Fluorescence data for bulk (non-filtered) samples during the simulated algal bloom. Letters a-i are the bottle labels.
Figure 3.32. Fluorescence data for filtered samples during the simulated algal bloom. Letters a-i are the bottle labels.
Figure 3.33. Flux data for filtrations performed during the simulated algal bloom.
Figure 3.34. Flux recovery measured after the filtrations shown in Figure 3.33 (including replicate filtrations not shown in Figure 3.33).
CLAY FLOCCULATION FOR ALGAL REMOVAL AND FLUX IMPROVEMENT

Clay addition enhanced algal removal in rapid-mix/slow-mix/settling jar tests using 50,000 cells/ml algal concentration (Figure 3.35). As much as 31% algal removal was achieved with one g/l clay addition. Ferric chloride removed 76% of algae with the lowest dose (5 mg/L) and 98% removal was achieved with the highest dose (100 mg/L) (Figure 3.35). Turbidity spiked immediately after both clay and ferric chloride addition (Figure 3.36). In clay-addition tests the turbidity remained elevated even after settling and the highest turbidity values were found with the highest clay doses. For ferric chloride tests the turbidity dropped by the end of settling and all doses (5 to 100 mg/l) resulted in much lower turbidity than the non-dosed algal sample. These data show that ferric chloride was a much better coagulant than clay, as would be expected. Fe$^{3+}$ ions can neutralize the negative surface charges of algal cells to induce coagulation and settling. Clay is itself negatively charged and would not be expected to flocculate algae by a charge-neutralization mechanism. Instead, it is more likely that clay addition simply increased the total amount of material present and thus increased the probability for contact and flocculation. Clay may have entrained algal cells as it settled.

Flux data for samples produced by the jar tests just described show that fouling was mitigated as algae were removed both by clay and ferric chloride; samples that had higher algal removal due to higher clay and ferric chloride doses also had higher overall flux (Figure 3.37). Even the lowest ferric chloride dose (5 mg/l) resulted in higher flux than the highest clay dose (1 g/l). Flux decline with ferric chloride was more linear than with clay, suggesting a cake buildup mechanism for ferric chloride instead of a pore blocking or intermediate filtration mechanism for clay. This could suggest that the clay-addition samples contained small pore-plugging/adsorbing material while ferric chloride succeeded in flocculating such material so that it could not as easily enter the pores.

It should be noted that tests were also performed with clay added to clean seawater and the flux decreased with clay addition, as would be expected (data not shown). When algae were present, however, clay addition increased the flux (Figure 3.37a). Even though clay was not as effective as ferric chloride, it is demonstrated here that its addition to an algal sample did have a positive effect on filtration.

Rapid-mix/slow-mix jar tests were performed with combinations of ferric chloride and clay to investigate the possibility for synergistic effects. Two ferric chloride doses were used (5 and 10 mg/l) with and without 0.25 g/l clay addition. Clay improved flux for both ferric chloride doses (Figure 3.38). Flux correlated well with algal removal; the highest-flux case had the most algal removal and flux was similar for the two cases where algal removal was similar (Figure 3.38 caption). The two similar cases were 5 mg/l FeCl$_3$ + 0.25 g/l clay and 10 mg/l FeCl$_3$ + 0 g/l clay. This suggests that clay addition could reduce the ferric chloride dose required to remove algae and decrease fouling.

In many full-scale applications no settling is possible before membrane filtration. To determine if clay would be feasible in those applications, rapid-mix-only jar tests were performed with 5 mg/l FeCl$_3$ and varying clay dose. There was no algal removal since no settling occurred; even so, flux improved when clay was present (Figure 3.39). This suggests that the presence of clay changed the floc structure in such a way that pore blocking was reduced (by entraining more dissolved material in the flocs) and/or the foulant cake structure was more open and had less hydraulic resistance (from the presence of larger particles with more void volume).
Longer-term experiments were also performed, preceded by rapid-mix-only jar tests. Five filtration cycles were run with a membrane rinse between cycles to remove loose cake layers. This enabled a measurement of irreversible fouling. In experiments with FeCl₃ alone (no clay amendment) very little (less than five percent) of the flux was recoverable (Figure 3.40). FeCl₃ was so effective at charge neutralization and flocculation that the algal foulants readily adsorbed or adhered to the membrane surface and were not easily rinsed away. When clay was present in doses of either 250 mg/l or as low as 10 mg/l, flux recovery was over 50% with each cycle (Figure 3.40). A few mechanisms for clay’s effect could be occurring. Clay may have caused the foulant cake layer to assume a looser arrangement than when only algae and organic matter were present. Clay-algae attractive surface forces may have been weaker than algae-algae surface forces after charge neutralization by FeCl₃. Also, clay-membrane interactions may have been weaker than algae-membrane interactions making clay particles easier to remove than algal particles; thus clay may have served as a protective, reversible coating for the membrane.

It is interesting to note that when no FeCl₃ was used for cyclical filtrations of 30,000 algal cells/ml flux recovery (~ 85%) was much better than with 5 mg/l FeCl₃ (~ 5% or less) (Figure 3.41). Again it appears that FeCl₃ increased algal surface interactions with the membrane. The combination of FeCl₃ with clay, however, resulted in higher average fluxes (Figure 3.41). The addition of clay without FeCl₃ gave better flux recovery than algae alone (compare Figure 3.41 and Figure 3.42) and higher clay doses resulted in slower flux decline for each filtration cycle (Figure 3.42). In these experiments approximately the same filtration time was used so even if the difference in slope on the flux decline curves seems minimal, one can readily see that a higher total water volume was filtered with the higher clay dose (Figure 3.42).

Control experiments with no algae present gave additional insight into the interactions of coagulant and clay with the membrane. When clay alone was filtered in artificial seawater on these 0.1 µm PVDF membranes almost 100% flux recovery was achieved with each cycle (Figure 3.43). When 5 mg/l of FeCl₃ was used, recovery diminished with each cycle to only around 20% by the end. With a combination of clay and FeCl₃ flux recovery was near 90% and seemed to diminish only slightly over time. It appears that adsorption of Fe³⁺ ions may have changed the membrane surface chemistry to make it less permeable to water. If this occurred, there was a kinetic effect, since flux diminished over time. Another possible explanation is that FeCl₃ caused precipitation of some of the salts in the artificial seawater. Whatever the case, it is clear that clay alone did not cause similar problems. Clay did result in flux decline, but its interactions with the membrane were weak and flux was recoverable. Clay also reduced whatever effect FeCl₃ had on the membrane or water matrix. Clay may have served as an Fe³⁺ adsorbant making it less available to interact with the membrane. Clay, then, was not only useful for its effect on algae, but was also useful because of its effect on the coagulant itself.
Figures

![Graph showing algal removal as a function of clay and FeCl₃ doses.](image)

Figure 3.35. Algal removal in jar tests (30-s rapid mix, 30-min slow mix, 1-hr settling) for various clay and FeCl₃ doses. Initial algal concentration was 50,000 cells/ml.
Figure 3.36. Turbidity versus time during jar tests (30-s rapid mix, 30-min slow mix, 1-hr settling; i.e. on these plots, settling commenced at 30 minutes). (a) Dosed with clay, units in legend are g/L. (b) Dosed with FeCl₃, units in legend are mg/L as FeCl₃.
Figure 3.37. Membrane flux for various clay and FeCl₃ doses. (a) Varying clay dose (g/l). (b) Varying FeCl₃ dose (mg/l).
Figure 3.38. Flux results for combinations of clay and FeCl₃ dosed to an algal concentration of 50,000 cells/ml in jar tests with 30-s rapid mix (280 rpm) and 15-min slow mix (25 rpm). Algal removal in the jar tests was 69, 58, 59, and 43% (top to bottom in the legend).
Figure 3.39. Flux results for 30,000 cells/ml algal concentration with 5mg/l FeCl₃ and varying clay doses in rapid-mix-only filtration experiments.
Figure 3.40. Normalized flux for 30,000 cells/ml *H. pygmaea* run for five cycles with membrane rinse between cycles. (a) 5 mg/l FeCl$_3$ with and without 250 mg/l clay. (b) 5 mg/l FeCl$_3$ with and without 10 mg/l clay.
Figure 3.41. Flux data for five cycles of 30,000 cells/ml algae comparing FeCl₃ and clay amendment to algae only (no FeCl₃ and no clay).
Figure 3.42. Normalized flux for 30,000 cells/ml *H. pygmaea* with no FeCl₃ and varying clay dose.
Figure 3.43. Control experiments performed with no algae added to artificial seawater.
CHAPTER 4: CONCLUSIONS AND FUTURE RESEARCH

REVERSE OSMOSIS MEMBRANE FOULING BY MARINE ALGAE

Conclusions

It was hypothesized that dissolved AOM would cause significant fouling of RO membranes during seawater desalination. Dissolved AOM is the material that would be most likely to pass through pretreatment and reach the RO membranes in a full-scale system. The hypothesis did not hold here because dissolved AOM did not cause severe flux decline in this bench-scale study. Only when algal-derived particulate material (greater than 0.45 μm) was present did flux decline occur. A significant amount of material was deposited before flux decline was noted. The intrinsic resistance of RO membranes is substantial and the flux is low (relative to other membrane processes) so foulant layers must be significant in order to add measurably to the resistance.

Another hypothesis was that permeate carrier morphology would affect foulant deposition; a coarse permeate carrier would lead to exacerbated foulant deposition compared to a fine permeate carrier because of the larger peaks and valleys created as the membrane was pressed on the permeate carrier. This hypothesis was confirmed in the dissolved AOM case. More material deposited and flux declined to a greater extent when a coarse permeate carrier was used. In the direct-algal-spike case, when particulate material was present, both permeate carriers caused similar flux decline, but the deposition pattern was different. The coarse permeate carrier caused foulants to deposit in a pattern that matched the feed-spacer morphology while the fine permeate carrier resulted in more homogeneous, less patterned deposition. The significant result here is that both the permeate carrier and the feed spacer morphologies are important for foulant deposition.

The final hypothesis regarding AOM fouling of RO membranes was that CECP would be the dominant fouling mechanism instead of hydraulic resistance since CECP has been reported to dominate for salt-rejecting membranes. However, the heterogeneous nature of particulate and dissolved AOM results in cake layers with low porosity and particle size. With such cake layers hydraulic resistance can be just as important as CECP. The concept of the “crossover point” was presented; for any given combination of flux decline and particle size there exists a single crossover point where hydraulic resistance and CECP give equal resistance. At that point cake thickness, porosity, and tortuosity are defined. This sets the stage for applying future experimental data to verify that the equations and assumptions used in the modeling (which is the same model used by previous workers) are accurate.

Future research

It has been reported in pilot studies that algal fouling is detrimental to the system, but over longer time periods (several days) than tested here. It is possible that AOM cake layers build up over time to cause more significant resistance. More likely, bacterial growth enhanced by AOM may be the principal fouling mechanism. In the experiments performed here, only colloidal or organic fouling was of interest so experiments were not allowed to run long enough
to allow biofouling by actively growing bacteria. Examining the interplay between adsorbed AOM and biofouling would be a useful area of future research.

Since AOM does adsorb to the membrane and form a conditioning film, an important question is whether there exists a highly-fouling fraction of AOM on RO membranes (analogous to the highly-fouling AOM material observed in low-pressure membranes). It is possible that some class of protein, carbohydrate, or lipid material is the highly-fouling fraction and selectively adsorbs to the membrane surface. The PCP protein complex would be a good candidate for initial examination since it is well-characterized and we have already observed that it deposits on the membrane surface. LSC could be used to help determine PCP deposition since PCP fluorescence is detectable by LSC.

Further development of the LSC technique for foulant characterization could also be useful. The LSC technique could supplement visual image analysis by providing a measure of fluorescent material. It could be used in full-scale autopsy to determine whether algal pigments are present in the foulant layer. The method could be expanded by including additional fluorescence channels indicative of other components, like humic acid. Further, foulant layers could be stained with chemical-specific dyes and the LSC could measure their spatial distribution. A live-dead stain for bacterial activity or a 16S-rRNA stain for species specificity could be envisioned.

Another future need is improvement in RO module hydrodynamics. Full-scale modules should be designed with feed spacers that minimize foulant deposition. Spacers should also be designed to decrease concentration polarization. A module with high crossflow velocity achieved by lengthening the flow path could be effective. The permeate carrier morphology should be taken into consideration to minimize foulant deposition in this next-generation module design.

LOW-PRESSURE MEMBRANE FOULING BY MARINE ALGAE

Conclusions

The first hypothesis with regard to low-pressure fouling was that MF fouling would exhibit a pore blocking mechanism and UF fouling would exhibit a cake filtration mechanism. The hypothesis was confirmed except that MF fouling changed from pore blocking to intermediate blocking over several filtration cycles. The model suggests that MF pores were irreversibly plugged over time so that the remaining pores were smaller and foulants accumulated on the surface.

The second hypothesis was that shear stress applied to an algal sample would exacerbate fouling through the release of AOM. Shear stress did exacerbate fouling by increased pore blocking and tighter-porosity cake deposits. The most highly fouling size fraction was material not removed with centrifugation or glass-fiber filtration, but largely removed with 0.22-µm filtration. This included algal cell fragments and colloidal/particulate AOM. The whole algal cells did not fall into this size class, nor did dissolved biopolymers. The highly-fouling material had very similar protein and carbohydrate composition before and after shear; 13% protein and 19% carbohydrate before shear, 19% protein and 19% carbohydrate after shear. This suggests that the highly fouling fraction is the same with or without shear, but after shear there is more highly fouling material available. Adsorption of dissolved organic matter was not a significant fouling mechanism in these short-term tests.
Along with effects of shear on flux, we hypothesized that shear would cause reduced organic-matter rejection. This was confirmed since TOC, carbohydrates, UV absorbance, and fluorescence were all elevated in permeate samples after shear. This was due to the release of dissolved organic matter that was small enough to pass through all of the membranes. Fluorescence was the best indicator of shear since almost no fluorescent material permeated the membranes before shear, but fluorescence was greatly elevated after shear.

As part of the effort to test shear effects, algal cell breakup kinetics were evaluated. A steep decline in cell number was observed at the beginning of the shear exposure, with breakup rate tailing off over time. Breakup data could be modeled by considering two cell classes: a structurally strong class and a structurally weak class. Thus, members of the same algal cell population have different structural strengths.

Another hypothesis tested here was that bacteria would be an important factor in low-pressure fouling during an algal bloom. The hypothesis was confirmed because bacteria were found to be in the highly-fouling size class. Further confirmation was obtained because fouling increased along with bacterial numbers even as algal numbers decreased.

A final conclusion that was indirectly tested during this project is that low-pressure membranes are much more dramatically fouled by algae than high-pressure membranes in the first several hours or days of filtration. Productivity of the RO membranes never declined below 90% even after 24 hours, but MF and UF membrane performance was drastically diminished in a matter of minutes. In an integrated membrane system the pretreatment membranes would be expected to fail first during an algal bloom.

These results on fouling by algae and algogenic organic matter have implications for full-scale application of MF and UF as pretreatment to RO for seawater desalination. Algal cells could potentially experience sufficient shear for cell lysis in intake and pumping systems so that membrane fouling is exacerbated. The membrane elements themselves may also have hydrodynamic regimes where shear could be problematic. Perhaps dead-end, open tank membrane configurations similar to those used for membrane bioreactors would be more appropriate than crossflow modules. Studies of local shear stresses in different systems would be needed to determine which configurations were indeed optimal.

**Future research**

Though the highly-fouling fraction of AOM was identified here as material larger than 0.22 μm and adsorption of biopolymers was not indicated as a fouling mechanism, it is recognized that these short-term experiments may not be representative of the longer-term case. Future work should be performed to determine if adsorption of biopolymers and colloids causes fouling over many backwash cycles as full-scale plants are operated.

Several future research projects could be performed regarding the effects of shear on algae. On one hand, the structural strength of different algal species should be determined, since the *H. pygmaea* cells used here have different morphology than many found in nature. On the other hand, the full-scale treatment train should be evaluated to determine the magnitude of shear in the intake systems, pumps, valves, and membrane modules. These studies will help to determine how much cell breakup—and thus release of highly-fouling organic matter—is occurring at full scale. During such tests, fluorescence measurements can be used as an effective indicator of shear.
Lastly, because algae rapidly foul low-pressure membranes, alternative removal strategies should be sought. Coagulation before filtration may be an effective strategy since large flocs should have lower fouling potential. Dissolved air floatation is another possibility, since cells do not settle well. Whatever the case, the algal-removal strategy should be designed to minimize shear and cell breakup.

CLAY FLOCCULATION AS AN ALGAL-BLOOM MITIGATING STRATEGY

Conclusions

It was hypothesized that clay amendment would help reduce flux decline by algae in low-pressure systems. Clay alone was not as effective as ferric chloride for algal removal in a coagulation/flocculation/settling scheme. However, clay addition did improve membrane flux, especially in concert with ferric chloride. Clay could be a useful additive when seawater desalination plants face algal blooms. Clay is inexpensive and environmentally benign. It could be helpful for reducing the cost of ferric chloride and may result in lower iron concentrations in the RO feed and concentrate. Clay is well removed by the pretreatment membranes, unlike dissolved iron.

There would be disadvantages to clay addition. Sludge production could be unwieldy, especially for some of the high doses used here, and the mechanics of clay addition could present a challenge if no mechanism for mixing is present. However, these disadvantages should be weighed against the algal-bloom situation that would already cause severe problems for the treatment facility. Lower clay doses (down to 10 mg/L) were shown to be effective here and even with high doses and sludge handling problems, if both the pretreatment and downstream RO membranes are protected, clay addition could be worth its difficulties.

Future Research

Several unanswered questions remain with regard to clay flocculation. No effort was made here to size fractionate the clay material to determine what size was most effective for flocculation. Nano-sized clay (between 1 and 100 nm) may prove to be useful because it could coat algal surfaces with a minimum of total clay mass addition. Also, only one clay mineral, kaolinite, was used; other clays may have varying properties (i.e. surface charge, primary particle size, adsorption capacity) that make them more applicable. Thirdly, flat-sheet membrane coupons were used in these bench-scale tests while hollow-fiber membranes are typically used at full scale. Foulants likely deposit differently in hollow-fiber modules changing the way clay affects the cake layer (if a clay cake layer forms at all). All of these would be important areas of future research on the topic of clay flocculation.
CHAPTER 5: RECOMMENDATIONS TO UTILITIES

This study is somewhat anticipatory; the problem it addresses is currently applicable to a relatively small number of water treatment plants around the world, considering that seawater desalination makes up a very small percentage of total municipal water demand. But as the number of seawater desalination plants increases and as algal blooms may become more prevalent due to climate change, the problem will need to be addressed more fully.

MITIGATING ALGAL-BLOOM PROBLEMS IN REVERSE OSMOSIS

It is unlikely that algae in their native form would be capable of passing through pretreatment and entering full-scale RO modules. Thus flux decline due to thick algal cake layers would not be expected. AOM derived from algae is the more probable cause for concern. Algae can generate large quantities of organic matter and release these into the water matrix, especially if they are sheared in intake pumps and plumbing. The AOM itself would not likely cause much flux decline, but it could form a conditioning film on the membrane surface that enables bacterial attachment. AOM could also serve as substrate for biofilm growth inducing a serious biofouling situation.

The best protection for RO membranes would be to remove the algae, AOM, and bacteria during pretreatment. If possible, pretreatment should be done with a low-shear system to minimize AOM release. Fluorescence measurements of raw and filtered (i.e. using a laboratory syringe filter) samples are recommended as a means to determine if cell breakup due to shear is occurring during pretreatment.

Next-generation RO modules should be designed with minimal dead zones to reduce the fouling that occurs around the conventional feed spacer pattern. Also, a permeate carrier that produces less roughness (on the mm scale) would aid in minimizing AOM buildup in the modules.

In planning for and testing different algal removal techniques, bench-scale testing and membrane autopsy can be employed. Novel autopsy methods presented here will help to examine fouling behavior to make accurate determination of the best pretreatment techniques and operating conditions. These tools and the knowledge gained here could aid in enabling sustainable application of seawater desalination even in the event of algal blooms.

MITIGATING ALGAL-BLOOM PROBLEMS IN MF AND UF

This study calls into question whether MF and UF membranes are a good strategy for seawater RO pretreatment when algal blooms are common. Algae and their associated bacteria can severely damage an MF or UF facility. But where MF and UF are employed, preventative measures can be used to minimize algae-related problems.

Hydrodynamic shear should be minimized to reduce algal breakup. Low-shear pumps should be sought during facility design and pumps can be run at lower speeds during a bloom event. Plumbing and valves should also be evaluated to determine where shear can be minimized. This may be difficult, practically speaking, but a reduction in shear may mean significant improvements in the filtration process.
Bacterial cells are included in the size range that was most responsible for fouling. During our simulated algal bloom the bacterial numbers increased steadily even as algal numbers declined and membrane flux continued to deteriorate. Bacteria, then, may be more detrimental to membrane flux than the algal cells in an actual bloom. Algae are fairly easy to detect and count because of their large size and fluorescent pigments; however, it behooves operators to take their detection strategies to the next level and use methods that will allow them to also measure the bacterial populations during an algal bloom.

Some engineers have considered additional steps for algal removal before (or instead of) MF or UF membranes. Dissolved air floatation (DAF) has been put forward as one possible solution. Coagulation and flocculation could be another alternative. In these or other approaches it will be important that the systems not only remove the algal cells, but that they do it in a manner which minimizes cell lysis. For maximum effectiveness, the pretreatment approach should be able to remove algal cells as well as the smaller particulate and bacterial matter that accompanies the algal bloom.

Clay flocculation may be a promising avenue for algal fouling mitigation. Clay can enhance algal removal in coagulation/flocculation/settling, or it can be added directly to the feed to improve flux when no settling basin is available. Facilities that use ferric chloride for flocculation should seriously consider clay amendment, since ferric chloride causes worse flux recovery than untreated algae. The major drawback to clay addition would be increased solids handling. But low concentrations of clay do show beneficial effects and since algal blooms are intermittent, clay would only be needed for short time periods. More work is certainly needed since this is the first study to explore clay amendment for algal removal in a seawater desalination treatment train, but the proof of concept has been established here.
REFERENCES


ABBREVIATIONS

AFM  atomic force microscopy
AOM  algogenic organic matter
ATR-FTIR  attenuated total reflectance Fourier transform infrared spectroscopy

BSA  bovine serum albumin

CA  California
CECP  cake-enhanced concentration polarization

DAF  dissolved air floatation
DAPI  4',6-diamidino-2-phenylindole (a fluorescent DNA stain)
DMF  dual-media filtration
DVD  digital video disk

EPS  extracellular polymeric substance

LSC  laser-scanning cytometry

MF  microfiltration

NOM  natural organic matter

PMT  photomultiplier tube

RMS  root mean squared

RO  reverse osmosis

SEM  scanning electron microscopy

SMP  soluble microbial products

SW30HR  (model designation for one type of Dow-Filmtec RO membranes)
SWC4  (model designation for one type of Hydranautics RO membranes)

TOC  total organic carbon

UF  ultrafiltration

UV  ultraviolet

Mathematical Variables

$C$  algal concentration or solute concentration
$C_b$  concentrate-side bulk solute concentration
$C_m$  solute concentration at the membrane surface
$C_o$  initial concentration of algal cells
$C_p$  permeate-side solute concentration
<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
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<tbody>
<tr>
<td>$C_s$</td>
<td>concentration of strong algal cells</td>
</tr>
<tr>
<td>$C_{so}$</td>
<td>initial concentration of strong algal cells</td>
</tr>
<tr>
<td>$C_w$</td>
<td>concentration of weak algal cells</td>
</tr>
<tr>
<td>$C_{wo}$</td>
<td>initial concentration of weak algal cells</td>
</tr>
<tr>
<td>$D_x$</td>
<td>bulk diffusion coefficient</td>
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<tr>
<td>$D^*$</td>
<td>cake-retarded diffusion coefficient</td>
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<td>$E_v$</td>
<td>energy density in a valve inducing pressure drop and shear</td>
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<td>$K_{cb}$</td>
<td>Lumped fitting parameter for complete blocking in Hermia flux decline models</td>
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<td>$K_{ib}$</td>
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<td>$R_i$</td>
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<td>$V$</td>
<td>volume passed through MF or UF membrane in flux decline models</td>
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<td>volume of the recirculated fluid in cell breakup experiments</td>
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<td>permeate flow rate in Hermia flux decline models</td>
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<td>$d_p$</td>
<td>diameter of particles in a model foulant cake</td>
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<td>$f_{cp}$</td>
<td>concentration polarization factor</td>
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<td>$f_{os}$</td>
<td>factor relating salt concentration to osmotic pressure</td>
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<td>rate constant for cell breakup</td>
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<td>mass transfer coefficient for non-fouled RO membrane</td>
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<td>rate constant for breakup of strong cells</td>
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<td>$k_w$</td>
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<tr>
<td>$\Delta P_m$</td>
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<td>$\Delta \pi_a$</td>
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<tr>
<td>$\Delta \pi_m$</td>
<td>transmembrane osmotic pressure</td>
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<tr>
<td>$\Delta \pi_m*$</td>
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<td>$\Phi_m$</td>
<td>power density</td>
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<td>porosity in foulant cake</td>
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<td>( \kappa )</td>
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<tr>
<td>( \mu )</td>
<td>viscosity of water</td>
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<td>( \tau )</td>
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