AUTOPSY OF MEMBRANES

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ABSTRACT

Desalination membranes such as NF and RO membranes tend to undergo performance deterioration with time, which depends on the efficiency of the pretreatment. The decline in performance due to fouling or scaling of the membrane, in many cases, can be restored to some extent by means of chemical cleaning. However, the performance decline due to irreversible damage to membrane polymer cannot be restored. In order to find out the actual reason for the irreversible decline in membrane performance, autopsy becomes very essential, in addition to the investigation of the operation history of the membrane. Membrane autopsy procedure involves dissection of membranes, visual inspection of the surface of the membranes as well as other components of module to discover any physical damage. Furthermore, the foulants and the membrane itself are analyzed by various analytical procedures. A wet chemical analysis of the foulants deposited on the membrane is carried out to identify the chemical composition of the foulant, which is also supplemented by EDAX analysis. The SEM analysis gives detail micrographic view of the membrane surface, which shall help in establishing nature of deposits. Biological analyses are conducted to study the possibility of biofouling. Tensile testing and intrinsic viscosity measurements are used to determine membrane polymer degradation, if any. This paper describes a few cases of membranes autopsy carried out at RDC to find out the reason for membrane poor performance. Cases studied include both NF and RO spiral wound membranes and hollow fine fiber RO membranes made of both polyamide as well as cellulose triacetate polymers.

Keywords: *Autopsy, Scaling, Fouling, Membranes, Spiral Wound and Hollow Fine Fiber.*

الملخص

إن تحلية المياه المالحة باستخدام أغشية التناضح العكسي أو باستخدام النظام المزدوج من نظام النانو والتناضح العكسي ولمدة أكثر من سنة قد يعرض هذه الأغشية إلى هبوط في أدائها عندما لاتكون المعالجة الأولية بالكفاءة المطلوب علمـاً بأن هبوط أداء هذه الأغشية يعزى إلى التكلس (تكون القشور) أو الترسبات الملحية (Scaling) ، وذلك لوجود نسـبة عاليـة من عناصـر العسر بمياه البحر أو تلوث معدات التحلية الناتج من وجود المواد العالقة والبكتيريا بمـاء البحـر (Fouling). وفي كثير من الحالات يمكن رفع كفاءة أداء الأغشية بعد تدهور أدائها بالغسيل الكيميائي , وفي بعـض الحالات الأخرى لا يمكن استعادة أداء الأغشية عندما تتعرض الأغشية ذاتها إلى تكسر روابطها (عمليات الأكسدة على

سبيل المثال). ولمعرفة الأسباب التي تؤدي إلى تدهور أداء هذه الأغشية يلزم تشريحها ويشمل ذلك التشـريح الفحـص العيني لأسطح الأغشية وحاوية الضغط ومكوناتها الداخلية للتعرف على وضع الأغشية المتدهورة ، وبالإضافة إلى ذلك يتم فحص المواد الملوثة وتحليلها بالطرق التحليلية ، وكذلك يتم عمل التحليل الكيميائي للملوثات المترسبة على أسـطح الأغشية للتعرف على التركيب الكيميائي مدعماً بتحليل ماسح الطيف الألكتروني EDX ، ويستخدم الماسح المجهـري SEM للتعرف على طبيعة الرواسب الموجودة على أسطح الأغشية ، ويستخدم التحليل البيولوجي للتعرف على مـدى وجود أثر للتلوث الحيوي ، وكذلك يستخدم اختبار قياس قوة الشد واللزوجة الجوهرية للتعرف على مدى تكسر روابط البوليمر المكون للأغشية ٠ وهذا البحث يعرض بعض حالات تدهور الأغشية التي تم تشريحها بمركز الأبحاث والتطوير للتعرف على الأسباب التي أدت إلى تدهور هذه الأغشية وتشمل كل من أغشية النانو والتناضح العكسي .

1. INTRODUCTION

One serious problem faced in the seawater reverse osmosis (SWRO) desalination process is the "fouling" of the membranes. Membrane fouling is an extremely complex phenomenon that has not been defined precisely but in general the term is used to describe the undesirable formation of deposits on membrane surfaces. Fouling occurs when rejected solids are not transported from the surface of the membrane back to the bulk stream. Fouling can be classified mainly into (1) inorganic fouling due to deposition on membrane surface of inorganic scales or colloidal matter and (2) biofouling due to microbial attachment to membrane surface followed thereafter by their growth and multiplication in presence of adequate supply of nutrients in the pretreated feed. To a great extent fouling can be prevented by the proper plant design, including an efficient pretreatment system and also by good plant operation and maintenance. However, if the feed pretreatment is inadequate and is unable to remove all the potential membrane foulant matter from it, membrane fouling becomes almost inevitable, and it takes place sooner or later. Membrane fouling leads to reduction not only in product water quantity and quality but also it is detrimental to membrane service life. SWRO, brackish water reverse osmosis (BWRO) and nanofiltration (NF) membranes of different configurations, hollow fine fiber (HFF) as well as spiral wound (SW), are either made of aromatic polyamide or cellulose acetate base polymers.

Cellulose acetate (CA) membranes are widely used in RO desalination industries because of the overall advantages of their properties, cost and ease of use. A major cause for the chemical degradation of CA is oxidation. Oxidation is accelerated at high concentration of oxidizing agents such as chlorine (Cl_2), which is used in RO process as disinfectant [ASTM 1989]. Studies [ASTM 1983] indicated that chlorine in presence of heavy metals lead to oxidation as well as some times to hydrolysis of CA membranes. Cobalt and copper have a remarkable effect on the deterioration of the CA membranes while iron, manganese and nickel affect membrane performance but to a lesser extent. Also, temperature, pH and chlorine concentration have an influence on CA membrane performance. The effect of oxidation is mainly through the scission of membrane polymer chain, thus reducing both its molecular weight as well as mechanical strength, resulting in a decline in salt rejection and to an increase

in permeates flux of RO membrane. The oxidation can be detected by either mechanical strength measurement and/or by molecular weight determination. Several methods are used in determination of molecular weight of polymer including intrinsic viscosity, which is directly proportional to the polymer molecular weight. In this study degree of acetylation, intrinsic viscosity and tensile strength measurements, were used for identifying the causes of the poor performance of two cellulose triacetate hollow fine fiber membranes obtained from a commercial SWRO plant after being in operation for five and two years, respectively.

Aromatic polyamide membrane (B-9) also is widely used in BWRO systems. A major cause for the chemical degradation of aromatic polyamide is oxidation by chlorine (Cl_2). Two B-9 membranes with good performance and poor performance were analyzed at RDC. Autopsy was conducted on two B-9 membranes after their performance evaluation using NaCl solution as feed.

SWRO pretreatment using NF membranes lead to a significant improvement in the seawater desalination processes. Two NF membranes out of 10 NF membrane used in a NF pilot plant which were operated continuously for more than 10,000 hours was subjected to autopsy, which includes biological, chemical and physical analyses of membranes and foulant deposits on its surfaces.

Five different SWRO membranes of different configuration of HFF as well as SW were evaluated using feed water pretreated by conventional coagulation-filtration using $FeCl_3$. After2 ½ years in operation an autopsy was performed on these membranes which includes biological, chemical and physical analyses as well as SEM &EDX of membranes and foulant deposits on its surfaces.

The objective of this paper is to describe various method used for identifying the foulants and causes of the membrane degradation for different types and configuration of membranes by means of autopsy.

2. EXPERIMENTAL

2.1 Membranes

The two different configurations of HFF and SW membranes are used in SWRO, NF and BWRO processes. HFF membranes are made from cellulose triacetate and aromatic polyamide while SW is made from thin film composite polyamide. Both the commercial membranes (HFF & SW) were autopsied and samples were collected from inner, middle and outer portions in case of HFF and feed side, brine side and middle side portion in case of SW for detailed analyses.

Autopsy and analysis were conducted on all membranes using the standard procedure adopted for SWRO, BWRO and NF [Avlonitis et al. 1992]. It involved cutting open the membrane, visual inspection of surface, estimation of amount of deposits on the membrane surface after drying, chemical analyses of deposits using Atomic Absorption Spectroscopy (AAS) and Inductively Coupled Plasma (ICP) and bacterial enumeration on membrane surface. After removing the samples for bacterial enumeration, foulant deposits were scrapped off from the surface and thoroughly dried before analyzing for various inorganic elements using AAS and ICP. Also, Scanning Electron Microscopy (SEM) and Energy Dispersive X-ray (EDX) analyses were conducted on representative samples cut from the membranes which were thoroughly dried and were used without any cleaning. In addition to abovementioned analyses HFF membranes were also subjected to stress strain measurement and intrinsic viscosity measurement. Moreover, degree of acetylation also was determined for HFF-CA membranes.

2.2 Performance Evaluation

Performance of membranes is evaluated using seawater or NaCl solution at different feed pressure as well as feed flow at ambient temperature. The results obtained are then normalized using standard ASTM procedure [Baker & Dudley, 1998].

2.3 Biological Analysis

Samples are aseptically collected from membranes and are analyzed for both bacteria and fungi according to standard protocol [5]. Bacteria and Fungi attached to membrane surfaces are counted using a pour plat technique and numbers are expressed per cm^2.

2.4 SEM and EDAX

Samples as well as reemay samples were collected from membranes and dried thoroughly before analyzing the deposits on the membrane surfaces using SEM & EDAX.

2.5 ICP & AAS

After removing the samples for bacterial enumeration, foulant deposits were scrapped off from the surface and thoroughly dried before analyzing for various inorganic elements using AAS and ICP.

2.6 Degree of Acetylation

Acetylation degree of membranes, which is normally expressed as percent of acetyl group in the polymer, was determined using standard ASTM procedure with slight modification [6]. In this method, a known amount of membrane sample (0.7 g) was first added to 70 ml of acetone in an Erlenmeyer flask and kept stirring using a magnetic stirrer, for 1 hour followed by addition of 5 ml of methanol. After 30 minutes of additional stirring, 1N NaOH was added in excess (15 ml), to the highly swollen (not completely soluble) membrane sample solution and kept stirring for another 1 hour. After adding hot (60^oC) distilled water for washing down the

sides of the flask and continuing stirring for another 10 minutes, the unreacted excess amount of NaOH was titrated against standard sulfuric acid (0.5 N) using phenolphthalein indicator. When the pink color disappeared completely, an excess (0.2 - 0.3ml) of sulfuric acid was added and re-titrated with 0.1 N NaOH. For each sample, a duplicate was also carried out as well as two blank analyses. The acetylation degree was then calculated as the percentage weight of combined acetic acid formed to the total weight of membrane polymer during hydrolysis by the excess NaOH.

2.7 Stress Strain Measurements

Instron Series IX automated Materials Testing System, Series 4200 Interface, was used to measure the tensile properties. Hollow fine fibers samples of length 7 to 8 cm were soaked in distilled water prior to the tensile measurement. To prevent the fibers from drying, distilled water was sprayed on to the fiber while running the test. The test conditions were as follows:

Number of test specimens	10
Sample length between the grips	2 cm
Cross head speed	2 cm/min.

Percentage elongation and tensile strength at break were automatically calculated by the computerized Instron for each of the fibers.

2.8 Intrinsic viscosity measurement

The intrinsic viscosity **$[\eta]$,** which is related to the polymer molecular weight, was determined following the standard procedure [Flemming, 1993]. Ubbelohde type capillary viscometer was used at constant temperature of 30 ± 1°C. After determining the efflux time (t_o) for the solvent DMSO or methylene chloride/ methanol (9/1) mixture, the same (t_i) was determined for the known concentration of the sample. For each concentration of sample, five measurements were made and average of three measurements were taken after discarding both the lowest and highest readings. The measurements were made at different concentrations for each sample by successive dilution using the above solvent. The intrinsic viscosity $[\eta]$ was then obtained as intercept of the plot of η_{sp} / c against c, where c is concentration (g/dl) of membrane sample and η_{sp} is specific viscosity. The specific viscosity can be obtained from relative viscosity (η_{rel}) as $\eta_{rel} - 1$. The η_{rel} can be determined from the efflux time of solvent t_o and sample t_i as $\eta_{rel} = t_i / t_o$.

3. RESULTS & DISCUSSION

NF, SWRO and BWRO of different configuration such as HFF and SW membranes are discussed separately.

3.1 NF membranes (SW Thin Film Composite -TFC)

At the end of the 10,000 h operation of NF membranes in the aforementioned arrangement, the total normalized product flow of NF membranes were decreased from a value of about 16 l/min to about 11.2 ml/min amounting to a 30% decline. Before performing autopsy, the performance of each of the five modules (contains two NF elements) were determined and the obtained normalized product flow are tabulated in Table 1. It can be observed that the modules containing lead elements (V5 & V6) are having the least performance. The performance of remaining elements was better as we progressively move to the last element as can be seen from the same table. Only one of the lead element was autopsied along with last element for comparison.

The visual inspection of the lead element which had lowest product flow was found to be completely covered with reddish brown colored slimy deposits throughout the membrane leaves (see Figure 1) which can be easily scrapped and dry weight of these deposits amount to about 1.55 mg/cm^2 of membrane area. Whereas, the last element which had the highest permeate flux, was relatively clean and only a thin reddish brown coating of the same kind of deposits found on the lead element were observed on its surface (see Figure 2) and dry weight of this thin deposit is only about 0.3 mg/cm^2 of the membrane area as can be seen from the Table 2. This indicates that most of the foulant deposits are accumulated on the surface of the lead element, and these deposits are mainly responsible for about 35% of flux decline of the lead element compared to the last elements.

The detailed chemical analyses of the foulant deposits scrapped off from the surface of the membranes reveal that other than the primary organic matter, the iron (Fe) constitutes the major inorganic chemical component in these deposits for both lead and last element. Fe forms about 25% and 12.5% in lead and last element, respectively and must have deposited on the membrane surface as a result of corrosion of the stainless steel piping. This assumption is supported by the presence of about 5.1% and 2.8% of Cr respectively in the lead and last element respectively. However, presence of large amount Fe prompted us to examine other source of iron deposition. Since, during the entire experiment, coagulant based on iron (such as $FeCl_3$) or other chemicals were not used, possibility of iron from these sources can be ruled out. Nevertheless, the present NF unit was using the same pretreatment unit, which was used for evaluating SWRO membrane in earlier studies, where $FeCl_3$ was used as coagulant and also the kind reddish brown deposits found on membranes were also found on those SWRO membranes. This made us to open up and inspect the media filters to find out any residual Fe trapped between the media. It was observed that lumps of Fe deposits were trapped in between the media. These trapped Fe could have possibly escaped slowly during the long term non coagulant dosing operation of NF unit and got deposited on the membrane surface. It is also observed that the amount of both Fe and Cr reduced to 50% in the last element compared to the lead element (Table 2).

Rest of the chemical constituents in the foulant deposits are very little in quantity except the chloride and sulfur, both of which could be expected because of the seawater feed itself. It is interesting to note that scale forming hardness ions such as calcium and magnesium are not found in significant quantities in these foulant deposits, despite NF unit was in operation most of the time without dosing any antiscalant chemicals or acid. This was also true for the last element, which is exposed highly concentrated feed containing high concentration of hardness ions. The absence of scale ions may be related to the relatively low permeate recovery of less than 50%.

The losses on ignition, which is the indication of the primary organic matter, were about 46.5% and 61.2% respectively, for both the lead and last elements. These values suggest that the membranes possibly may not have biofouled, if so the value could have been more than 70% as reported by Flemming [Fujiwara et al. 1994] and more than 50% as reported by Baker and Dudley [Farooque, 1997]. Moreover, the bacteriological analyses supports the absence of biofouling on these NF membranes as can be seen from the bacteria count analysis which are given in Table 3. Here, the colony forming unit (CFU) count for both the membranes at their respective feed and brine side end of the element were well below the value of 10^5 CFU/cm^2 according to Flemming [Fujiwara et al. 1994] and as well as 10^6 CFU/cm^2 according to Baker and Dudley [Farooque, 1997] which are lower limit values of biofouled membranes. Hence, it can be clearly stated that even though no chlorination or disinfection methods were used during the long term NF operation, the membranes were not biofouled.

However, the SEM and EDX studies of these membranes reveal some interesting results. The study indicates presence of very few diatoms on the membrane surface as can be seen from Figure 3. EDX spectrum of the same show predominant Si peak and which confirms it to be a diatom. However, these diatoms cannot survive and thrive on membrane surface on account that they are autotrophic in nature and they cannot get required sunlight which is essential for its food preparation by photosynthesis.

The SEM and EDX results obtained from both membranes are shown in Figures 4 & 5 Lead element (Figure 4) show that its surface is thickly covered with deposits, whereas last element (Figure 5) surface is relatively clean. Moreover, EDX spectra of both elements show that, the elemental compositions are similar for both the membranes and it supports the chemical analysis results of the deposits. Here, predominant peaks are of O, Fe, Cl, Na, S, Cr etc. most of which were also found during the chemical analysis of the foulant deposits. The major peak of course is due to Fe which forms the major inorganic foulant as was confirmed by the chemical analyses results. Other chemical constituents are of minor in nature. The peaks due to sulfur could be both from the sulfate deposited on the membrane surface as well as the from the polysulfone support of the TFC membrane.

3.2 SWRO Membranes (SW TFC & HFF PA)

The autopsy was carried out for all the membranes 8 months after their last chemical cleaning. Visual inspection of all the five membranes showed no physical damages. However, thick reddish brown deposits were present on the entire surface of the each membrane indicating that the membranes are fouled. Unlike the biofilms which are very adherent to the membrane surface, the deposits were of the type which can be easily scrapped off from the surface.

The results of the chemical and EDX analyses of all the five membranes are shown in Table 4. The results of the chemical analysis and EDX are in agreement indicating the uniformity of foulant deposits on the membrane surface. It is known that the EDX mainly analyze the surface composition of the deposits. It was also found that all the membranes deposits were similar in composition and obviously is due to their common feed. As was observed in the cleaning solution, Fe constituted the major foulant. Most of the Fe originated from the $FeCl_3$ which is used as coagulant in the pretreatment to remove the suspended particles and which escaped the media filtration system. However, a part could have originated from the corrosion products of stainless steel piping of high pressure part of RO as is substantiated by the presence of high amount of Cr (about 5%) which forms a major part of the stainless steel composition. However, the amount of Ni which is also a part of the stainless steel is found to be low is due to the fact that Cr forms a protective oxide layer on the surface of stainless steel and is attacked first during corrosion process. The presence of oxygen is understandable and it could be existing in different form either organic or inorganic nature. The elements Na, Cl, Ca, Mg, Al, K, Si and S which were present in the deposit originate from the feed seawater. Dosing of sulfuric acid as well as SBS which was dosed during the short period when chlorine was used in the pretreatment for disinfection experiment could also contribute to the presence of S. The amount of foulant per unit area of the membrane surface were in the range of 1.44 to 3.99 mg/cm^2.

The loss on ignition at 550 ^oC which is taken as measure of primary organic matter is about 28% for all the membranes indicating absence of any major biofouling of the membranes. This is in spite of no disinfectant was employed in the feed pretreatment. Usually biofouled membrane on which the biofilm is formed on their surface tend to contain above 70% of organic matter [Fujiwara et al. 1994]. This also have been supported by the low bacterial count which was observed on all the membranes in the range of 2.4×10^3 to 2.2×10^4 cfu/cm^2. This number is also low compared to the biofouled membranes of more than 10^5 [Fujiwara et al. 1994]. The bacterial count obtained were similar in range to that reported earlier in the feed to the membrane.

Figures 6 & 7 show typical SEM micrographs of one of the SW membranes and HFF membrane and their corresponding EDX spectrum. The SEM results show presence of very thick deposits on the surface of all the membranes. No other significant features were

observed on the surface of the membranes. Performance evaluation of membranes cut from the feed and brine side end areas of membrane were carried out and it was found that it had similar performance regardless of the area from which it were cut.

3.3 SWRO Membranes (HFF CA)

3.3.1 Degree of Acetylation

The degree of acetylation for the tested CA membranes sample, i.e., virgin, oxidized hydrolyzed, and two commercial samples (Cellulose Triacetate, Mem #1 and Mem # 2) with poor performance, are shown in Figure 8. For all the membrane samples analyzed, the difference between different portions (i.e., inner, middle and outer) of membrane was found to be not significant as can be seen from the figure. It is very clear from the figure that the hydrolyzed membrane is definitely having lower degree of acetylation (acetyl content) than that of the virgin or the oxidized membranes, where no hydrolysis is supposed to take place. The commercial membrane (Mem#1) which was in operation for nearly 5 years showed only a slight loss (about 1.4%) in degree of acetylation, whereas the Mem#2, which was in operation for about 2 years, showed a remarkable loss in degree of acetylation (about 5%), indicating a severe degree of the membrane polymer hydrolysis. So, it can be said that the hydrolysis was the main reason for the poor performance of Mem#2 and the observed slight hydrolysis of Mem#1 have contributed somewhat to its poor performance.

3.3.2 Tensile Strength

The membranes tensile strength and percentage elongation at break are shown in Figures 9 & 10. Both the percentage elongation and tensile strength show the same trend in that a reduction in the membrane polymer molecular weight, resulting from polymer chain scission by oxidation is noticed for the Mem#1 and Mem#2 samples but not for the virgin or hydrolyzed membrane fibers. The tensile strength of the oxidized fibers could not be evaluated, as the fibers were too brittle for the measurement, indicating that the membrane polymer is highly oxidized. A maximum value of tensile strength and percent elongation at break are noticed, as expected, for the virgin membrane fibers, and with comparable values for the hydrolyzed membrane. Thus proves that the latter membrane did not undergo any sort of oxidation leading to membrane polymer scission. Hydrolysis removes the pendant acetyl group and is not expected to affect the chain backbone which is responsible for the polymer strength. By comparison to virgin membrane, the tensile strength and percent elongation of Mem#2 were 48% and 60%, respectively, of that for the virgin fibers, indicating membrane polymer oxidation. Whereas the tensile strength and percent elongation of Mem#1 were found to be too much lower than those of Mem#2, i.e., only 24% and 10% respectively of that of the virgin fibers (see Figures 9 & 10). So, it can be said that both the commercial membranes have undergone oxidation, and the Mem#1 which was in operation for nearly 5 years was highly oxidized and more so than Mem#2.

3.3.3 Intrinsic Viscosity

Intrinsic viscosity measurement results support the tensile strength (see Figure. 11). As expected, virgin membrane was found to have the maximum value of intrinsic viscosity (1.24 dl/g) and the oxidized membrane had the lowest value (0.30 dl/g). For hydrolyzed membrane, the intrinsic viscosity was found to be about 1.24 dl/g indicating that the membrane did no undergo any oxidation, thus confirming the results obtained by tensile measurement. Intrinsic viscosity of Mem#2 could not be measured because the fibers were not soluble in the solvent (methylene chloride/methanol mixture). This was obvious, because it is known that the solubility of cellulose acetate polymers in a particular solvent is strongly influenced by the degree of acetylation [Motomura and Taniguchi, 1981]. Degree of acetylation measurement results indicated that Mem#2 had lower degree of acetylation compared to all the other membranes analyzed, thus making it insoluble in the solvent by altering the solubility property of the polymer. The Mem#1 sample showed a remarkable reduction in intrinsic viscosity (0.72 dl/g) indicating that membrane polymer molecular weight was decreased by polymer chain scission due oxidation, thus supporting the tensile study that the membrane was oxidized.

3.4 BWRO Membranes (HFF PA)

The normalized product flow and salt passage for both membranes are given in Table 5. It is evident from the results that Mem#2 has higher product flow (2.81 m^3/h) as well as salt passage (78.52%) compared to Mem#1 (1.72m^3/h and 18.63%, respectively) indicating a possible damage to Mem#2. This has confirmed by the viscosity data, where Mem#2 is found to have lower intrinsic viscosity (0.4033 dl/g) compared to Mem#1 (0.4924 dl/g), indicating a decrease in molecular weight of membrane polymer of Mem#2. The decrease in molecular weight occurs due to polymer chain scission, as a result of oxidation reaction. Usually this happens to an aromatic polyamide membrane when exposed to Cl_2 or similar strong oxidizing agents. As Riyadh Waste Water Authority (RWWA) claims that the membranes are operated in non-chlorinated environment, it is surprising to see such type of oxidation in the membrane, which occurred after preservation of the same in sodium bisulphate (SBS). It seems that the membrane is some how exposed to some strong oxidizing agent, which resulted in chain scission of membrane polymer thus leading to higher salt passage as well as product flow for Mem #2.

Biological analysis is done at RDC after carrying out performance evaluation of membrane using standard NaCl solution (3.5%), which could alter biological nature of membranes and may not reflect real biological status of the membrane. Nevertheless by assuming that not much change has taken place, the analyses are conducted. Bio-analyses showed that both average bacterial and fungal population on the membrane surface of Mem#2 (4.91×10^4 cell/cm^2) is higher than that of Mem#1 (2.62×10^3 cell/cm^2). However, even the higher value for Mem#2 is less than the lower limit termed for a biofouled membrane of $10^5/cm^2$ according

to Flemming et al [Fujiwara et al. 1994] and $10^6/cm^2$ according to Baker et al [Farooque, 1997]. Hence, it can be said that both the membranes are not biofouled.

Relatively cleaner membranes, which are observed (Fig 12 & 13) during visual inspection, indicate that the pretreatment is efficient. The SEM micrographs for both membranes also show that they are relatively clean and very little deposits are seen on the fibers especially on the inner fibers, which are closer to the feed tube (Fig 14 & 15), more on Mem#2 than Mem#1. EDAX analyses of both membranes showed similar composition in their foulant deposit and mainly consists of Fe, Mg, S, Ca, Zn, Si, Co, Na, Cr and O, which have to be removed by proper chemical cleaning in order for an effective PT-A and PT-B treatment to take place. Fe and Cr, which could have originated as a result of corrosion of stainless steel parts are found to be more in Mem#2 than on Mem #1. The presence of heavy metals could enhance oxidation in presence of oxidation agent, which is reported in the case of CTA membrane [ASTM 1983].

4. CONCLUSION

The autopsies of different types of commercial membranes of both SW and HFF, which receive a different feed, reveal that the composition of foulant deposited on surface of all membranes is similar regardless of the feed type as well as type of membrane. Corrosion products and other trace elements also were found on all membranes surfaces in different ratio. Membrane that received feed using conventional coagulation filtration system, was found to contain foulants consisting mainly of oxides of Fe, which is due to the usage of the coagulant $FeCl_3$ that could not be completely removed by the media filtration.

The presence of low primary organic matter as well as bacterial count suggests that the membranes were not biologically fouled in spite of feed disinfection or no feed disinfection. It was established that same CTA HFF membrane exposure to high concentration of chlorine and to high pH induced decreases in polymer chain molecular weight and in degree of acetylation. Also, it was established that polyamide aromatic B-9 BWRO membranes have poor performance due to oxidative degradation of membrane.

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Table 1. Individual module (2 elements/vessel) performance at the end of NF operation

Vessel number	Normalized Flow (liter/minute)
V5	1.8
V7	2.0
V6	1.8
V8	2.9
V9	2.7

Table 2 : Foulant deposit analyses results on NF membranes

Parameter (%)	Membrane	
	Lead Element	**Last Element**
Ca	0.41	0.42
Fe	24	12.5
Cr	5.1	2.8
Cu	0.05	0.03
Mg	0.24	0.49
Ni	0.01	ND
Si	0.08	0.09
Cl	2.9	7.2
S	5.5	3.4
Loss on ignition at 550 ^{o}C	46.5	61.2
Foulant per unit area (mg/cm^2)	1.55	0.30

ND = Not detected

Table 3: Bacteria count on the membrane surface

Membrane	No. of Bacteria (CFU/cm^2)	
	Lead Element	Last Element
Feed Side	1.34×10^4	5.88×10^3
Brine Side	2.45×10^4	7.32×10^3

Table 4. Autopsy and foulant analyses results of all five membranes

Parameter (%)	Membrane									
	No. 1		No. 3		No. 4		No. 5		No. 6	
	Chemical analysis	EDX	Chemical analysis	EDX	Chemical analysis	EDX	Chemical analysis	EDX	Chemical analysis	EDX
Ca	0.96	1.02	0.88	0.72	0.83	0.71	0.81	0.53	NA	0.67
K	0.52	0.28	0.21	0.26	< 0.01	0.35	< 0.01	0.33	NA	0.42
Al	0.40	1.14	0.42	1.22	0.55	1.02	0.63	1.94	NA	1.55
Fe	22.74	34.7	22.44	31.2	27.31	36.1	28.99	33.8	NA	14.8
Cr	4.48	7.42	4.17	5.93	3.51	5.62	3.24	3.66	NA	1.46
Cu	< 0.01	ND	< 0.01	ND	0.17	ND	0.20	ND	NA	ND
Na	11.92	10.85	11.1	13.7	10.09	9.98	10.22	5.33	NA	14.75
Mg	1.62	1.95	1.54	2.37	1.38	2.23	1.37	3.08	NA	3.16
Ni	0.03	ND	0.02	ND	0.10	ND	0.13	ND	NA	ND
O	NA	34.45	NA	34.4	NA	35.8	NA	48.85	NA	51.4
Si	0.18	0.79	0.15	1.06	0.22	0.58	0.24	0.90	NA	0.83
Cl	NA	6.82	NA	7.95	NA	6.83	NA	5.88	NA	8.94
S	0.99	ND	1.04	1.16	0.98	1.12	0.83	4..59	NA	2.05
Loss on ignition at 550 ^{o}C	28.46		27.85		28.07		26.06		NA	
Foulant per unit area (mg/cm^2)	3.99		2.13		2.28		1.44		NA	
Bacterial Count (cfu/cm^2)	9.5×10^3		NA		4.5×10^3		2.4×10^3		2.2×10^4	

ND = not detected ; NA = not analyzed.

Table 5. Results of Various Analyses Performed on B-9 Membranes

Analyses		**Mem#1**	**Mem#2**
Performance Evaluation	Normalized Product Flow (m^3/h)	1.72	2.81
	Normalized Salt Passage (%)	18.63	78.52
Biological Analysis	Bacteria (cell / cm^2)	1.17×10^3	4.60×10^4
	Fungi (cell / cm^2)	1.45×10^3	3.04×10^3
Intrinsic Viscosity (dl/g)		0.4924	0.4033

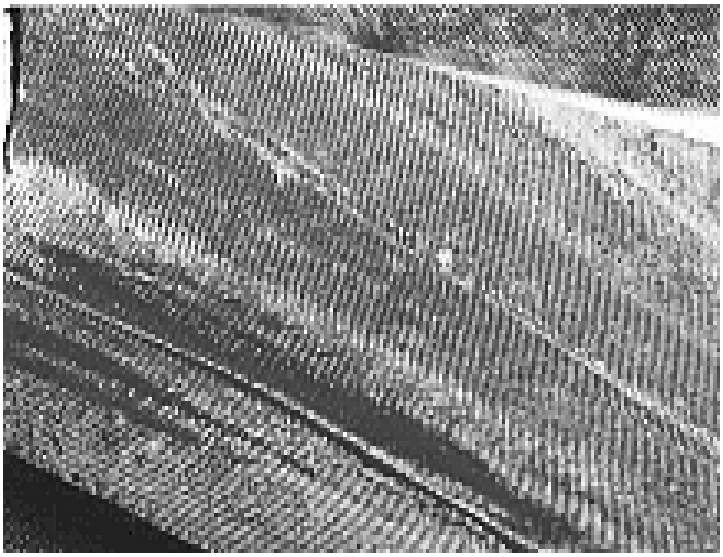


Figure 1 : Photograph of lead element NF membrane surface

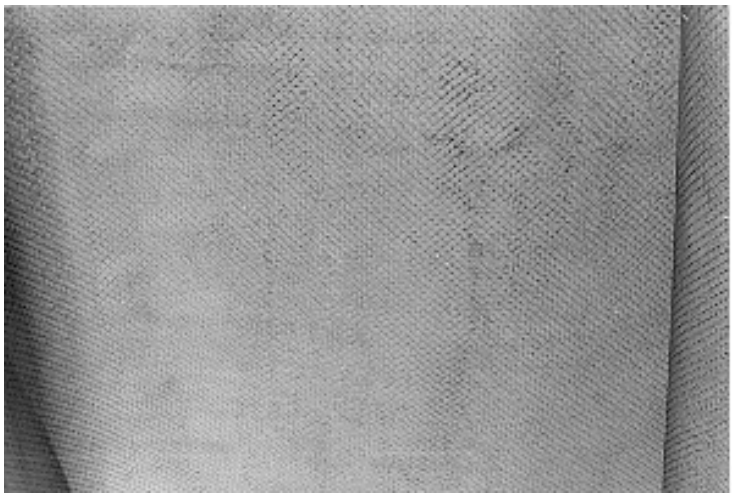


Figure 2. Photograph of last element NF membrane surface

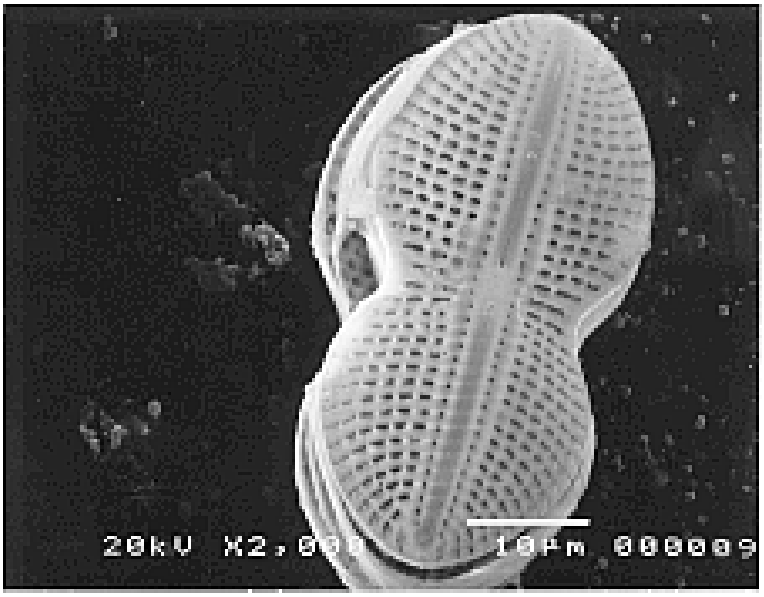
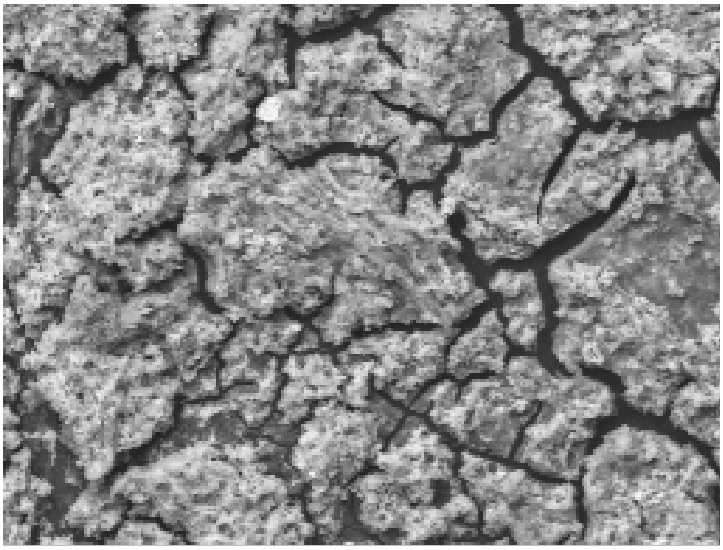


Figure 3. SEM Micrograph of one of the diatoms found on the NF membrane surface

Top



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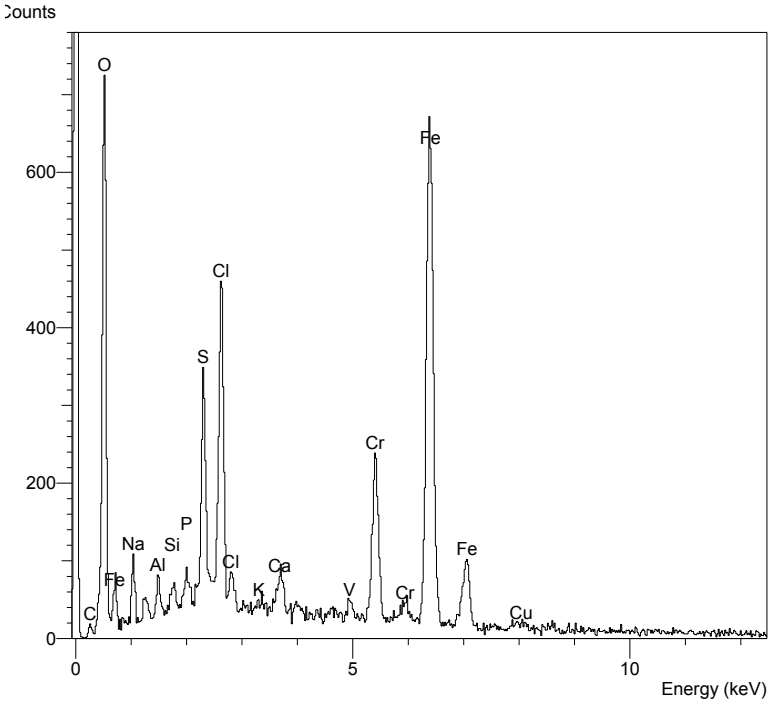
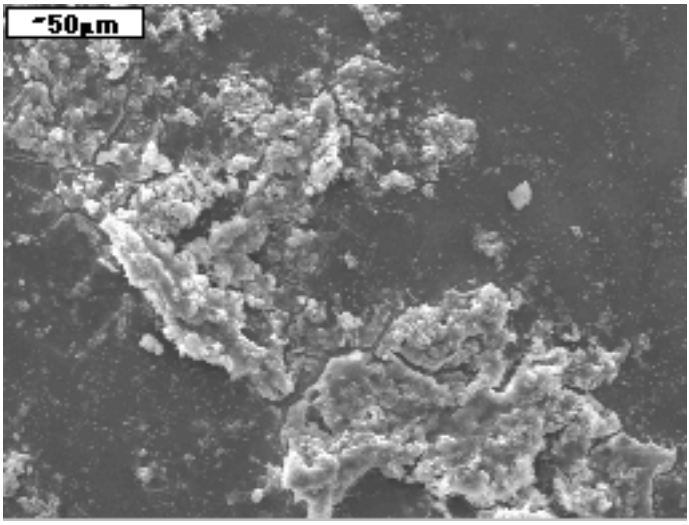


Figure 4. SEM micrograph and EDX spectra of lead element



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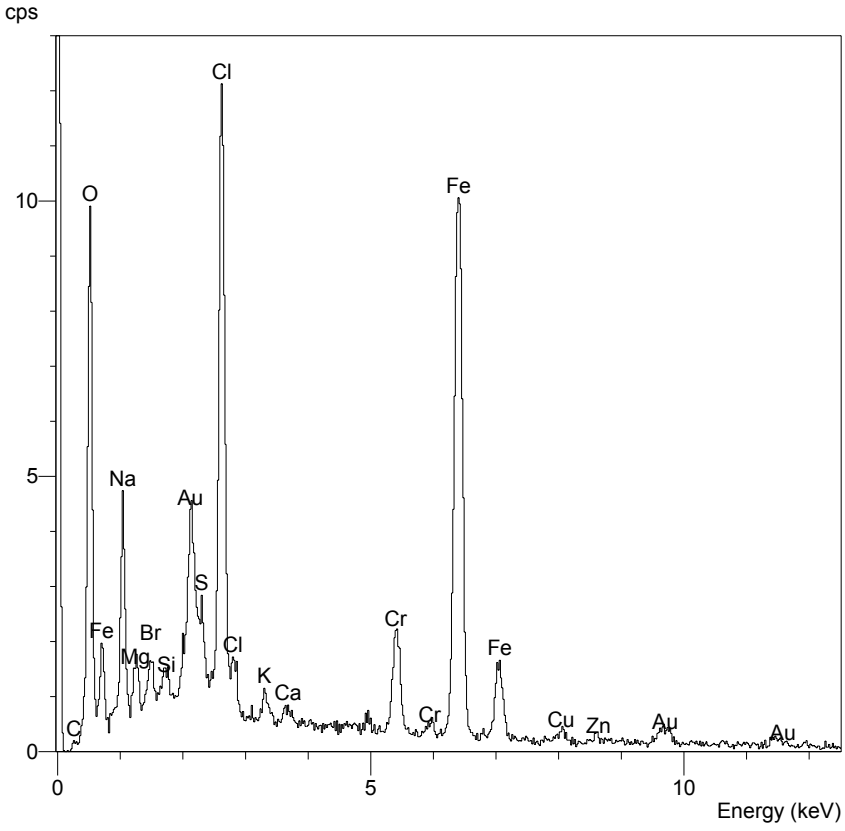


Figure 5. SEM micrograph and EDX spectra of end element

Top

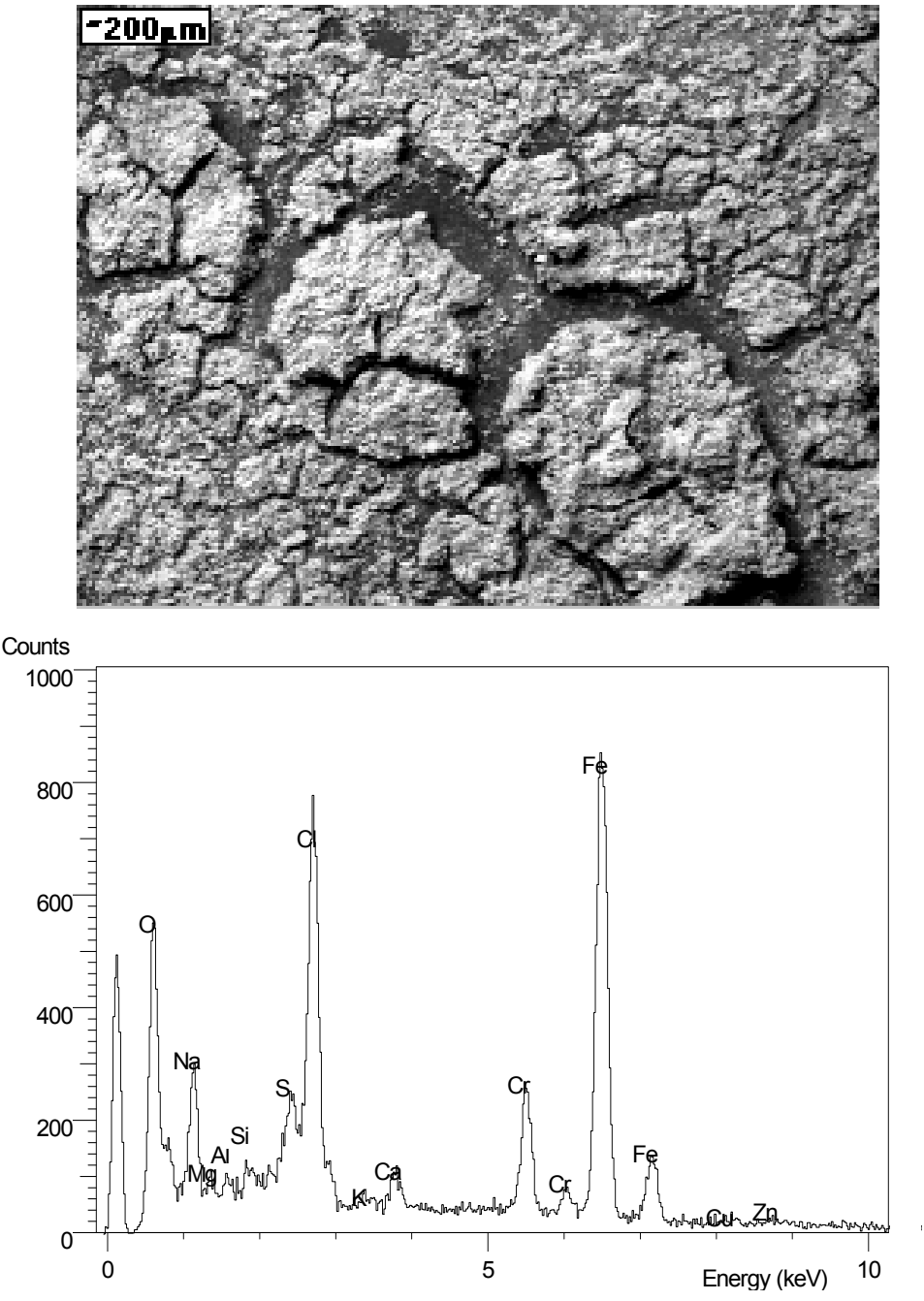
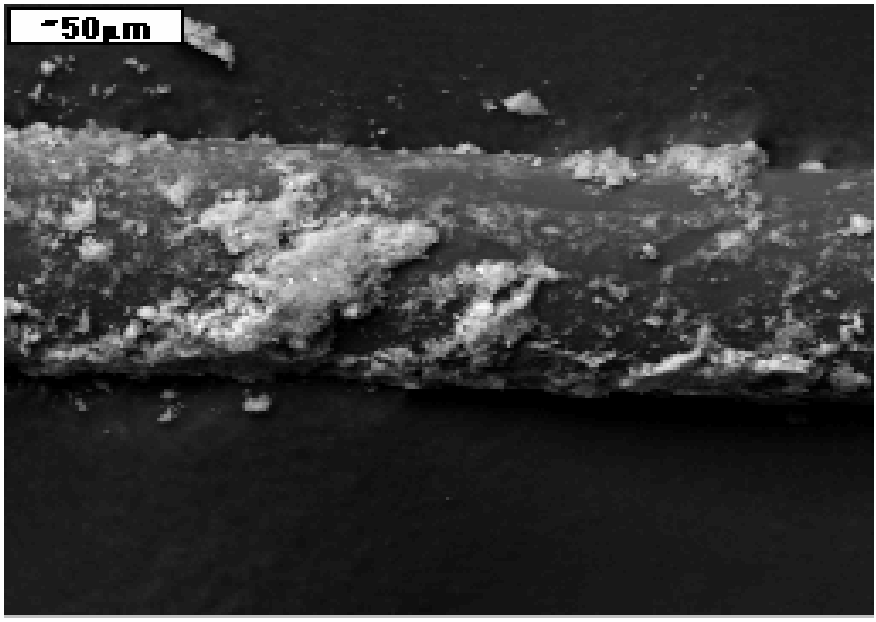


Figure 6. SEM micrograph and its corresponding EDX spectrum of one of the spiral wound membrane.

Top



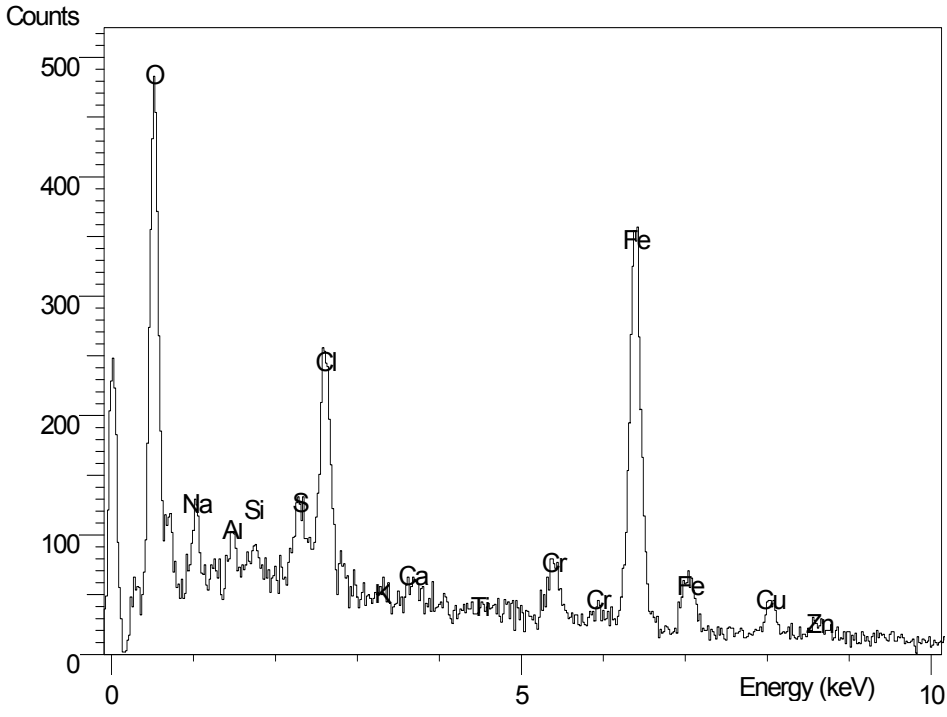


Figure 7. SEM micrograph and its corresponding EDX spectrum of hollow fine fiber membrane

Top

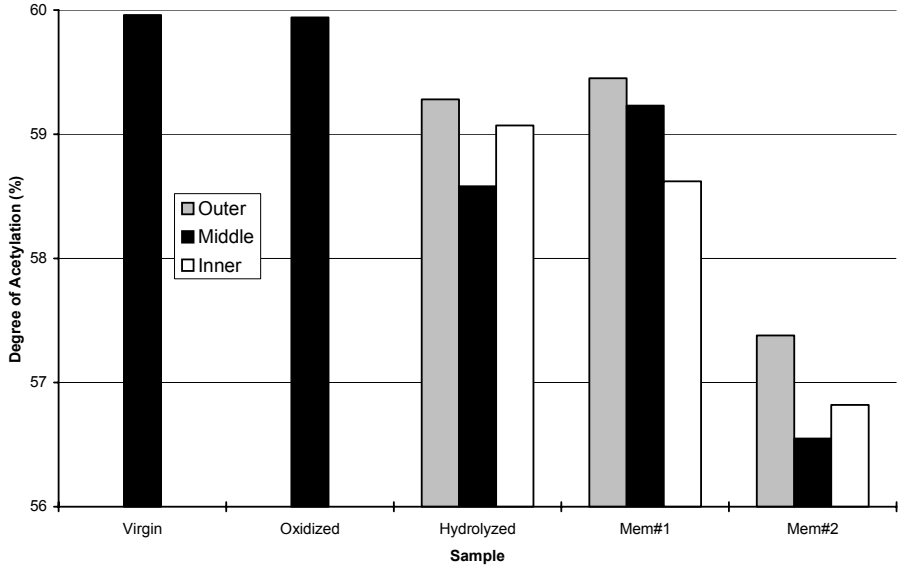


Figure 8. Degree of Acetylation of Various Membrane Samples

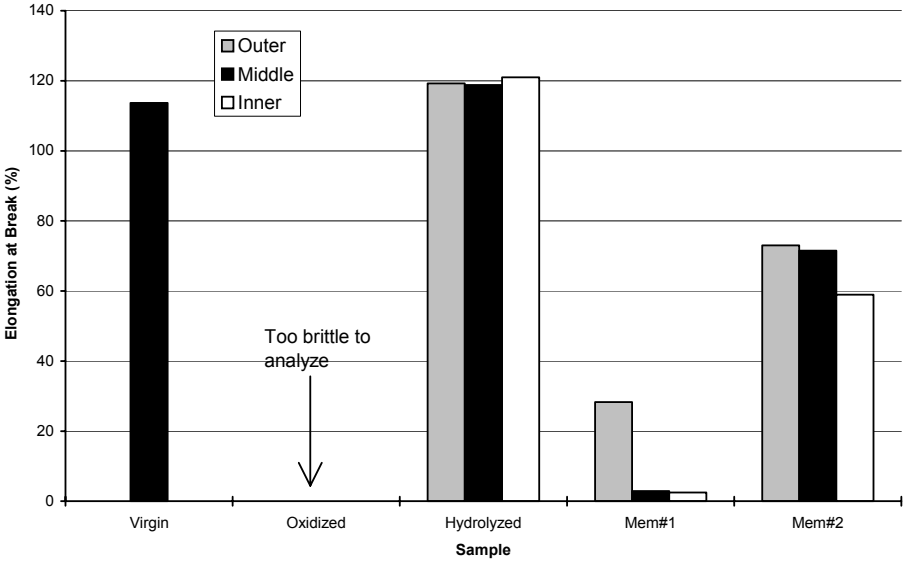


Figure 9. Percentage Elongation at Break for Various Membrane Samples

Top

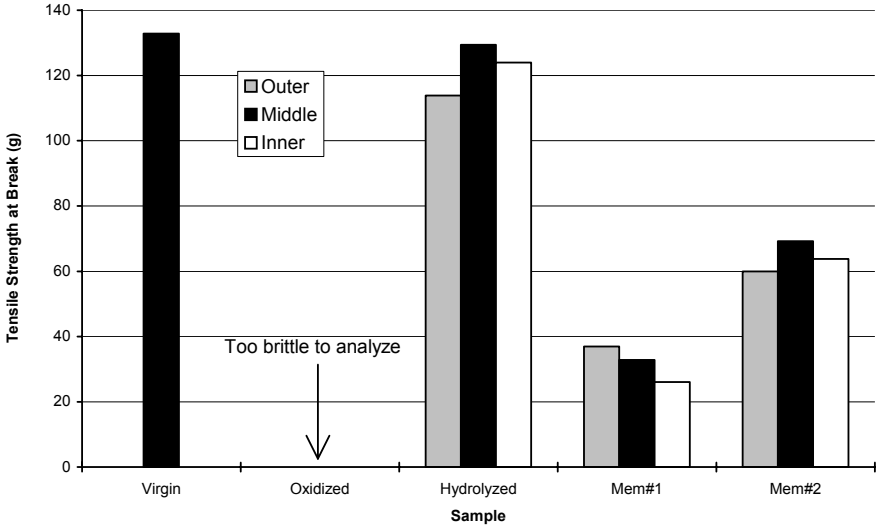


Figure 10. Tensile Strength at Break of Various Membrane Samples

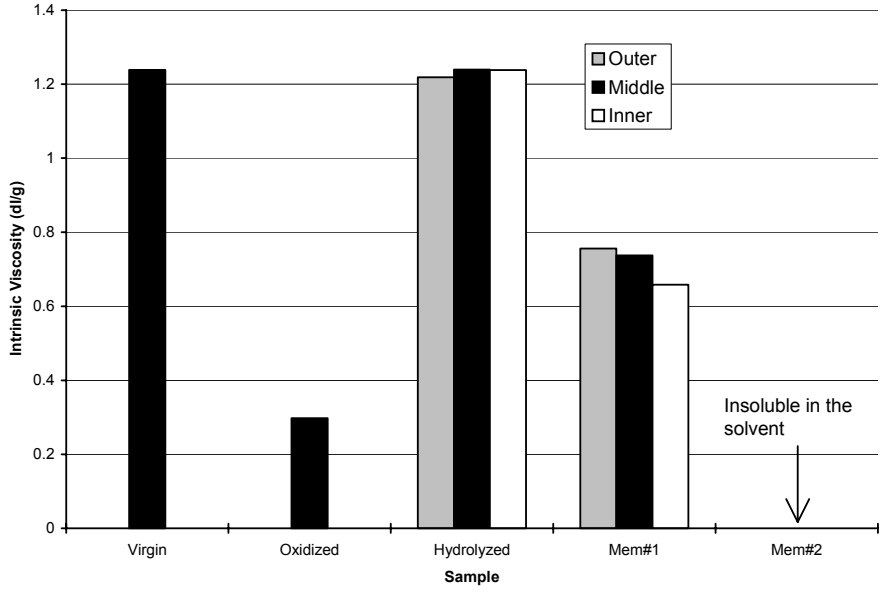


Figure 11. Intrinsic Viscosity of Various Membrane Samples

Figure 12. View of Feed tube of Mem#1

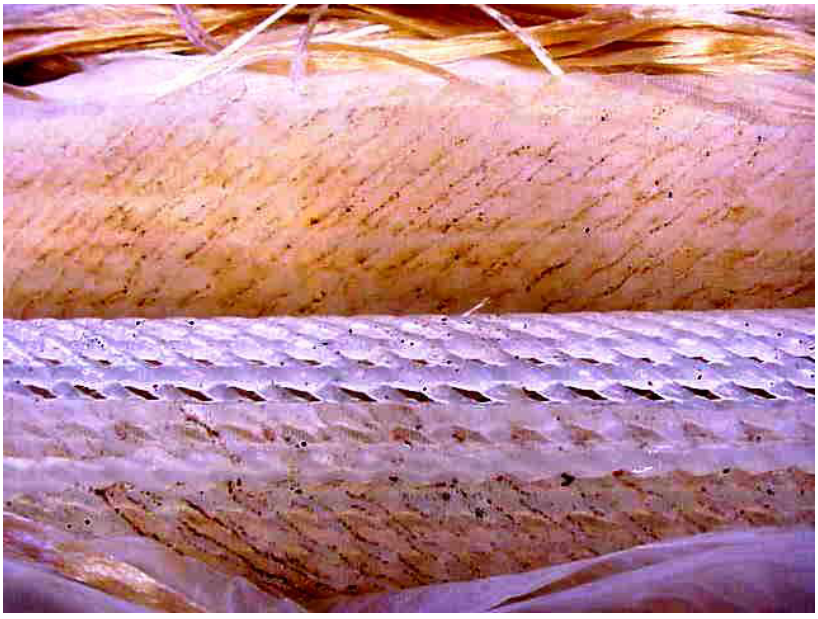
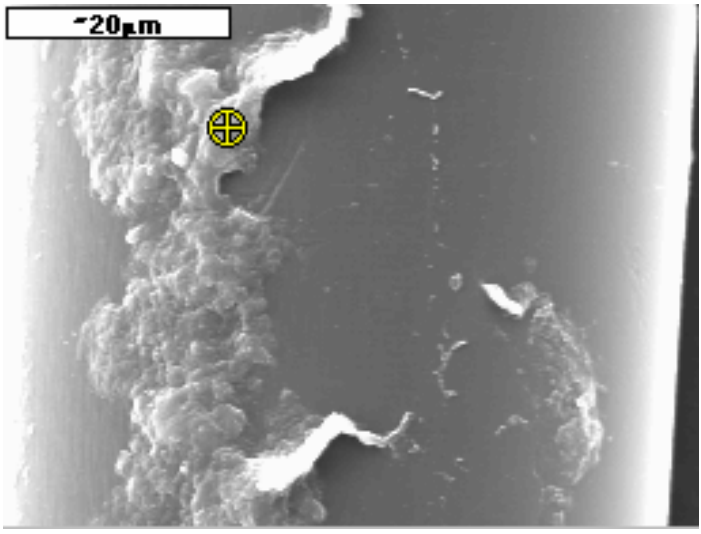


Figure 13. View of Feed tube of Mem#2



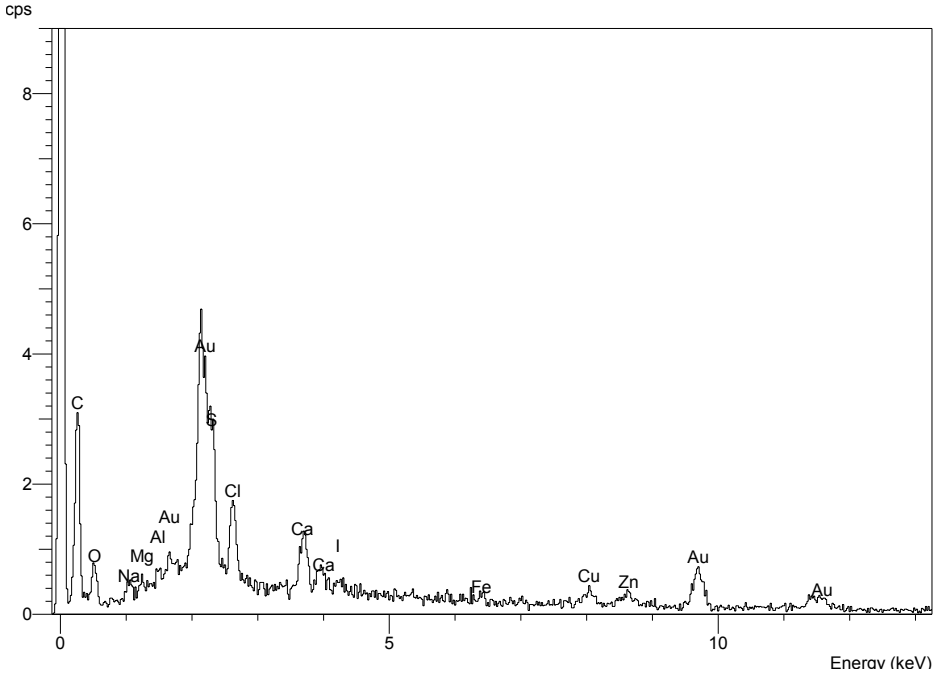


Figure 14. SEM Micrograph and EDAX of a Membrane Fiber from Mem#1

Top

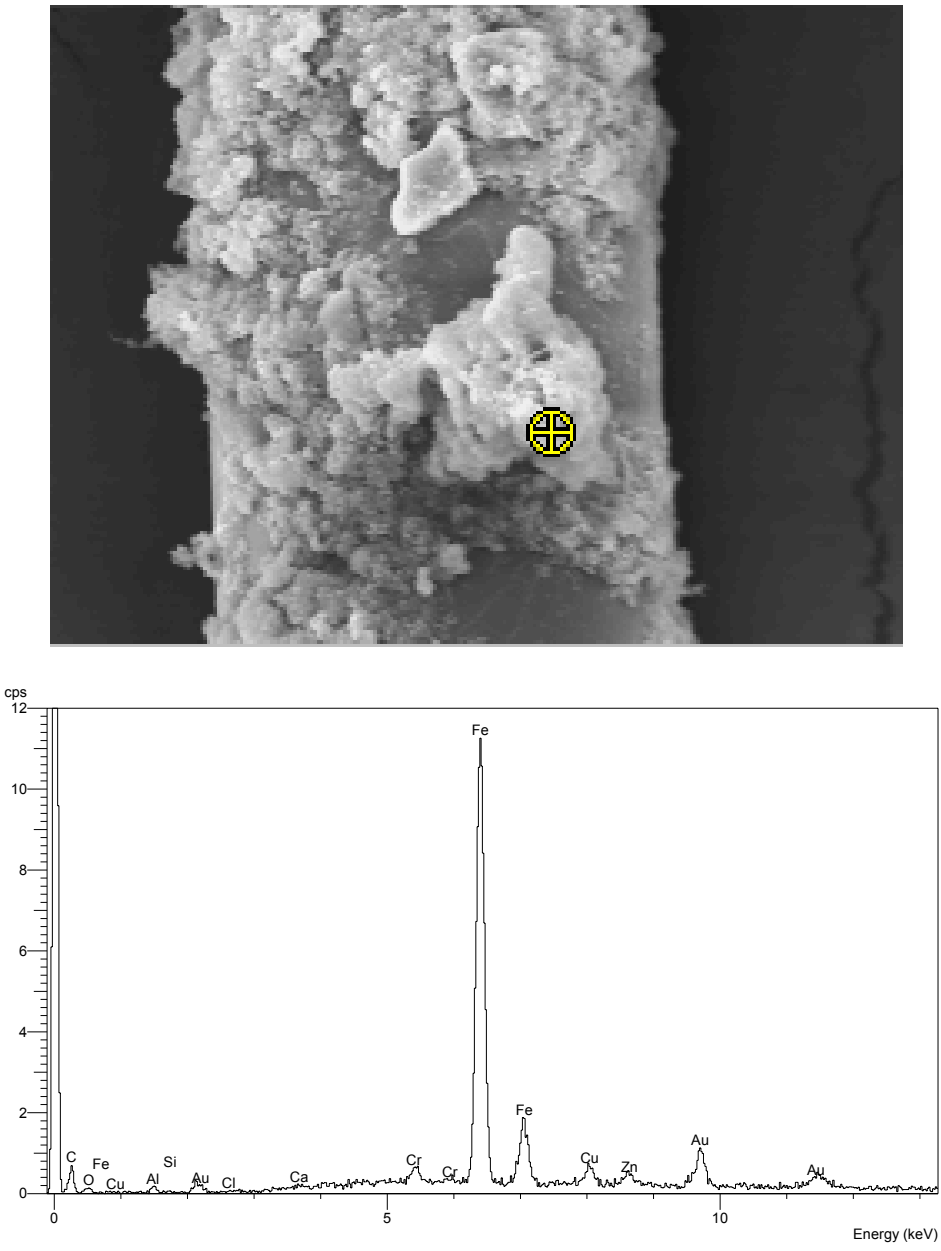


Figure 15. SEM Micrograph and EDAX of a Membrane Fiber from Mem#2

Top