

11 July 2006

Technical Memorandum No. 11

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Subject: SWRO Membrane Autopsy Results
MMWD Seawater Desalination Pilot Plant Program
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BACKGROUND

This technical memorandum summarizes the results of autopsy analysis of selected seawater reverse osmosis (SWRO) membrane elements from the MMWD Seawater Desalination Pilot Plant Program pilot units. The physical dissection and autopsy of a RO membrane, followed by characterization of membrane foulant, can be a useful tool in investigating and trouble-shooting the performance of a RO system¹. The information from the autopsy can help the project team to understand changes in membrane element productivity, salt rejection and pressure drop, the amount of foulant, and to identify foulant characteristics (mix of inorganic, organic and microbial material). The information from the autopsy may also help to highlight possible differences in the performance of the pretreatment systems in controlling RO membrane fouling and provide insight into operational strategies for minimizing fouling in a full scale facility.

SWRO MEMBRANE ELEMENT FOULING

The nature and rapidity of fouling experienced by RO systems operated on sea or estuarine waters depends on many factors, most notably source water quality and the type of treatment the source water is provided (pretreatment) prior to RO processing. RO membrane fouling is a function of four primary factors:

1. Scaling and depositions - precipitation of sparingly soluble salts.
2. Particulate fouling - accumulation of particulate inorganic and particulate organic matter.
3. Bio-fouling - attachment and growth of microbes, microorganisms and/or marine life.
4. Organic fouling - deposition of colloidal and dissolved organics.

¹ For purposes of this memorandum, all three of these procedures are referred to simply as autopsy.

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In the MMWD pilot study, MF/UF and conventional pretreatment systems were employed to control fouling caused by accumulation of inorganic/organic matter (factor #2) while scale inhibitor (and if needed, acid) was used to control scaling (factor #1). Biofouling (factor #3) was managed through periodic shock chlorination of intake and pretreatment systems, including filtrate storage tanks and piping, as well as reduction in bacterial concentrations through coagulation and/or filtration. In the case of conventional pretreatment, coagulation also reduced natural organic matter (NOM) concentrations, reducing the nutrient level in the RO feed. Based on the SDI values of the filtrates produced from the two pretreatments, fouling by inorganic and organic particulate matter should be adequately controlled. The use of antiscalant, combined with the low scaling potential of the Bay water at the moderate feedwater recoveries employed in the study, should effectively prevent scaling. Consequently, biofouling control was considered to be the primary challenge.

The primary foulants present in the feedwater to the SWRO pilot units are soluble organics and marine organisms including bacteria and associated nutrients. The fouling potential of these feedwater constituents is also impacted by water temperature, with bio-fouling potential increasing at higher temperatures. Clean-in-place (CIP) cleanings were conducted periodically to remove these materials from the membrane surface and element feed spacer using two general chemical regimes: a low pH (citric acid) solution, intended to solubilize precipitated salts and chelate metals, and a high pH solution, formulated to remove inert inorganic material as well as organic and biological matter.

Technical Memorandum No.10 provides a detailed discussion on the performance and fouling of the SWRO pilot systems.

SWRO MEMBRANE AUTOPSY AND FOULANT ANALYSIS PLAN

On shutdown of the MMWD pilot plant, selected SWRO elements were flushed with feed water, drained thoroughly, sealed in plastic bags and immediately refrigerated. Some of the stored elements were sent to two of the three membrane manufacturers (Dow FilmTec and Hydranautics) for wet testing, physical inspection and limited foulant characterization. These procedures are termed "industry-standard" analysis. A second group of elements were shipped to the Orange County Water District (OCWD) for more "specialized" analysis. The procedures performed by OCWD are not available through the element manufacturers or commercial third party autopsy firms, but were deemed to provide additional, valuable insight into the type of fouling experienced during the pilot, particularly with respect to bio-fouling.

"Industry-Standard" Analysis of Hydranautics and Dow FilmTec Elements

The elements selected for "industry-standard" (or standard) analysis by the membrane manufacturers are shown in Table 1. The project team selected the Dow and Hydranautics elements for standard analysis since both were operated in SWRO Unit #1 and SWRO Unit #2 and accumulated the longest operating history of the four element types tested. The second

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element from the lead vessel of both units was selected for standard analysis because the first two elements in the lead vessel would most likely have experienced the greatest amount of particulate and bio-fouling. (The first element was reserved for special analysis.) In each instance, the same brand element (location wise) from each of the two RO units was autopsied and analyzed by the respective manufacturer.

Table 1: “Standard” Autopsy Analysis Plan

Membrane Element Brand	SWRO Membrane Element Serial Number	SWRO Unit (#1 = MF/UF) (#2 = Conventional)	Position of the element within SWRO Vessel
Dow FilmTec	A9941826	#1	#2
Dow FilmTec	A9906540	#2	#2
Hydranautics	S4X90124	#1	#2
Hydranautics	S4X90204	#2	#2

The standard analyses comprised the following:

- **Element Wet Test** – Flow, pressure and salt rejection are measured, normalized and compared to element performance prior to operation.
- **Internal Visual Inspection** – The elements are dissected, glue lines are inspected and areas with foulants are noted for further analysis.
- **Dye Test** – Visual indication of membrane uptake of chlorine.
- **Energy Dispersive X-Ray (EDX) and Scanning Electron Microscope (SEM)** – identifies inorganic foulants semi-quantitatively.
- **FTIR Spectroscopy** – identifies the presence of certain organic compounds (foulants) and changes in polyamide structure that might indicate oxidation.
- **Loss on Ignition (LOI)** – used to obtain relative quantity of organic vs. inorganic foulant.

The standard analysis described above will allow a determination of the extent of fouling, what percentage of fouling is organic versus inorganic, what the major inorganic (elemental) foulants are, and whether the polyamide film was exposed to chlorine and if the polyamide structure was modified by such exposure. Parallel and identical analysis of elements from SWRO #1 and #2 will provide insight into differences between the two pretreatment systems with respect to degree and type of membrane foulant.

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“Specialized” Autopsy and Foulant Characterization of Dow FilmTec Elements

To respond to MMWD’s concern about fouling of the SWRO elements in general and potential bio-fouling in particular, Kennedy/Jenks-CH2M HILL contracted with OCWD to conduct more specialized RO membrane autopsy and foulant characterization procedures, some of which are not available through the element manufacturers or commercial third party autopsy firms. The specialized autopsy analysis can be used to evaluate the degree and type of microbial derived foulant on the membrane surface. The elements shown in Table 2 were sent to OCWD for “specialized” analyses.

Table 2: “Specialized” Autopsy Analysis Plan

Membrane Element Brand	SWRO Membrane Element Serial Number	SWRO Unit (#1 = MF/UF) (#2 = Conventional)	Position of the element within SWRO Vessel
Dow FilmTec	A9906551	#1	#1
Dow FilmTec	A9941802	#2	#1

The project team selected the Dow FilmTec elements (rather than the Hydranautics elements) for specialized analysis because they were installed after the initial “bio-fouling event”, which was not considered representative of proper full-scale plant pretreatment system operation. The lead elements from the lead vessels of both SWRO units were analyzed as they are the most likely to exhibit biofouling.

The “specialized” analyses and testing comprised the following once element dissection was completed:

- **Visual Examination and Light Microscopy** – visual and photographic examination of the microbial foulants on the membrane surface.
- **ATR/FTIR Spectroscopy** – used to identify the nature of organic and inorganic foulants.
- **Protein and Carbohydrate Content Analysis** – used to evaluate biomass deposition and may indicate the significance of any biological fouling.
- **Total Bacterial Count** – epifluorescent microscopy count of foulant removed from pre-determined area of membrane leaf to evaluate the number of organisms per unit membrane area.

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Three swatches, taken from feed, middle and concentrate locations within the element, were analyzed to provide results that have statistical relevance.

AUTOPSY AND ANALYSIS RESULTS

Dow FilmTec Elements

The results from the standard and specialized analyses of the Dow FilmTec elements are summarized in this technical memorandum. The detailed autopsy reports are attached as Appendix A and B. The report for the standard autopsy of the Hydranautics elements will be provided as Appendix C when it is available.

It is important to note that the results presented herein represent the condition of, and foulants present on, the specific element autopsied and may not fully represent condition of and foulants present on other elements in the SWRO units. These data must also be evaluated in conjunction with the performance (normalized) data of the SWRO units. The performance data will show fouling trends for the performance of each manufacturer’s elements as a whole, operating in a single array. Technical Memorandum No.10 provides a detailed discussion on the performance and fouling of the SWRO membrane pilot systems.

Organic and Bio-Fouling Analysis

Table 1 presents a summary of the results of the specialized analysis for the Dow FilmTec elements. As noted previously, the specialized analysis was focused primarily on membrane/element organic and bio-fouling.

Table 1: “Specialized” Autopsy Results on Dow Elements (Lead Element in Vessel)

Autopsy Test	Purpose of Test	SWRO #1 (MF/UF Pretreatment) Results	SWRO #2 (Conventional Pretreatment) Results
Visual Inspection	General observation and inspection	Slight discoloration; little to no foulants; slightly more fouling at feed end	Yellow-orange discoloration; Noticeable foulant; increase in foulant toward the feed end
Membrane Surface Microscopic Analysis	Microscopic inspection at 10 to 1,000 microns	Lightly coated with material; no discernable particles	Brown coating of material; observed particles < 10 micron
Membrane and Feed Spacer False Color Analysis	False color observation of foulant deposition	Slight feed spacer fouling with more on feed end and less on concentrate end	Heavier surface and feed spacer fouling with more on feed end and less on concentrate end

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Autopsy Test	Purpose of Test	SWRO #1 (MF/UF Pretreatment) Results	SWRO #2 (Conventional Pretreatment) Results
Permeate Carrier Analysis	Microscopic inspection at 10 to 1,000 microns	No material present. See pictures below	Brown staining; observed particles < 10 micron possible chemical precipitate
ATR-FTIR Analysis	Identify the presence and type of organic and inorganic foulants	Proteins, carbohydrate and polysaccharides present, indicative of bacterial fouling; greater deposition at feed end	Aluminum silicate (clay) dominant fouling; foulant layer >1 um thick. Proteins, carbohydrate and polysaccharides present indicative of bacterial fouling; greater deposition at feed end, heavier fouling than SWRO#1
Protein/ Carbohydrate Analysis	Identify amount organic matter on the membrane surface related to bio-fouling	Low levels of microbially-derived organic matter: P ¹ – 13 ug/cm ² CH ² – 32 ug/cm ² CH/P – 2.5	Higher levels of microbially-derived organic matter: P – 42 ug/cm ² CH – 46 ug/cm ² CH/P – 1.1
Bacterial Count	Identify amount of micro-organisms on the membranes	Avg – 1.62E+8 /cm ² more in middle; monoculture	Avg – 1.15E+8 /cm ² more on feed end; heterogeneous
¹ P = proteins ² CH = carbohydrates			

The specialized protein/carbohydrate and bacterial count analysis of the lead Dow elements provides the following observations:

- The element with conventional pretreatment exhibited greater overall protein and carbohydrate fouling than did the element with MF/UF pretreatment.
- Carbohydrate deposition was proportional to protein deposition from feed to concentrate end of element with conventional pretreatment; however, in the MF/UF pretreated element, carbohydrate concentration increased from the feed to concentrate end, while protein deposition decreased. The carbohydrate/protein ratio was constant in the conventionally pretreated element; however, the carbohydrate/protein ratio increased from the feed to the concentrate end in the MFUF pretreated element. This increase was caused both by decrease in protein and increase in carbohydrate. Such a shift may indicate a change in the physiological state of the organisms on the membrane surface (increase in exopolymers [carbohydrate based polysaccharides] related to adhesion from feed to concentrate end).
- The changing chemistry of the feed water along the element could be causing differences in organisms from one end to the other.

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- The mass and pattern of deposition of bacteria differed between the two membranes; conventional pretreatment showed more bacteria at the feed end of the element while MF/UF showed less at the feed end and more in the middle to brine end. Moreover, the pattern of distribution did not correlate well with the patterns of distribution of protein and carbohydrate for either pretreatment.
- The lack of good correlation between patterns of protein, carbohydrate and bacterial distribution may indicate that much of the adsorbed protein and carbohydrate does not come from fouling by whole cells. Deposition of dissolved material and nanoscopic microbial debris may account for much of this material.
- The differences in bacteria on the membrane surface of elements receiving the two types of pretreated feedwater could be caused by differences in feedwater chemistry. Conventional treatment produces a feedwater with lower pH, residual coagulant and presumably less assimilable organic carbon (AOC).
- The more well defined mono-culture of bacteria in the MF/UF elements suggests that bacteria are growing downstream of MF/UF, most likely in the filtrate tank and piping. The bacteria in the conventional elements were more heterogeneous, smaller and dispersed among other foulants.

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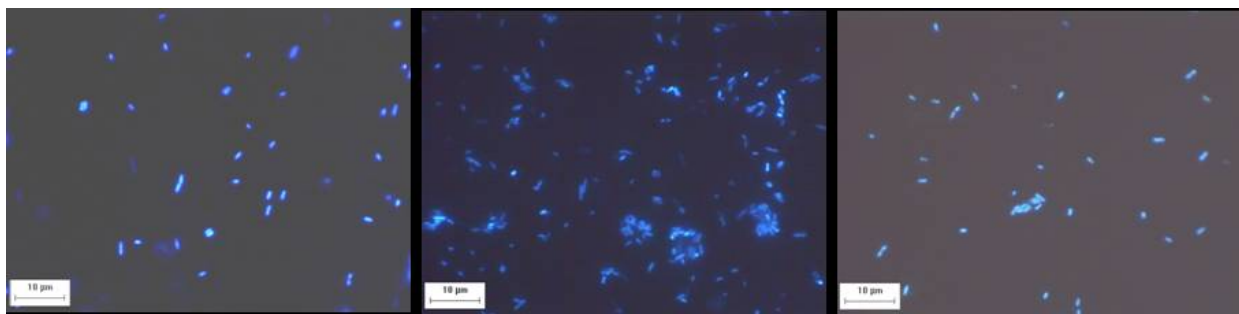
Photos below show images of bacteria taken from different places on each element and made visible through epifluorescent microscopy.

Epifluorescent Microscopy

Feed End

Middle of element

Brine End

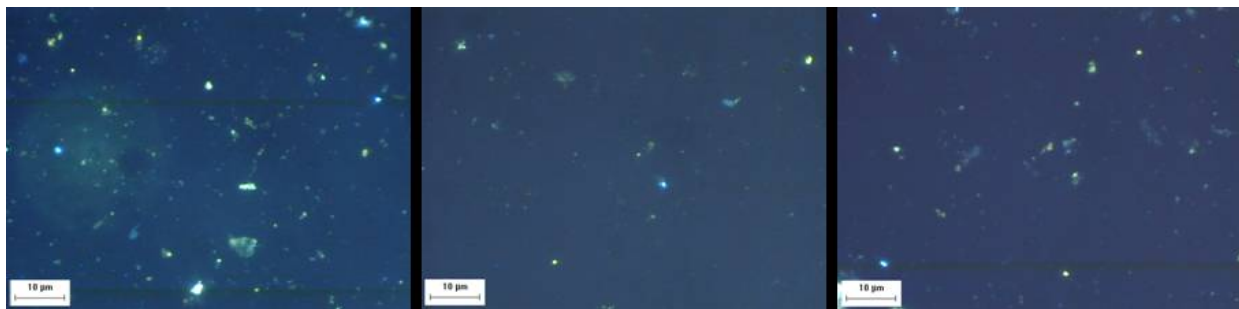


Epifluorescent Microscopy Images of Dow FilmTec Membrane (MF/MF pretreatment)

Feed End

Middle of element

Brine End



Epifluorescent Microscopy Images of Dow FilmTec Membrane (conventional pretreatment)

Particulate Fouling Analysis

Table 2 presents a summary of results from the “standard” analysis performed on the second position Dow FilmTec from each SWRO pilot unit. The standard analysis focused more on particulate and inorganic fouling, with less focus on organic and bio-fouling.

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Table 2: “Standard” Autopsy Results on Dow Elements (Second Element in Vessel)

Autopsy Test	Purpose of Test	SWRO #1 (MF/UF Pretreatment) Results	SWRO #2 (Conventional Pretreatment) Results
Permeate Flow	Flow performance relative to new element	Essentially same as new	Essentially same as new
Salt Rejection	Salt rejection performance relative to new element	Essentially same as new	Essentially same as new
Visual Inspection	General observation and inspection	Slight discoloration; little to no foulants; no glue-line damage	Noticeable foulant; slimy to touch; no glue-line damage
Oxidative Testing	Determine if an oxidant (chlorine) damaged the RO elements	No oxidant damage to membrane	No oxidant damage to membrane
ICP Spectroscopy	Identify type and amount of metals on the membrane surface	Low levels of metals: Na – 16.2 mg/m ² Fe – 3.5 mg/m ² Si – 2.7 mg/m ²	Higher levels of metals: Na – 260.4 mg/m ² Fe – 189.9 mg/m ² Si – 178.2 mg/m ²
LOI Testing	Identify amount and nature of foulant	Not enough foulant to perform test	7.8 g/m ² ; 33% inorganic; 67% organic
Cleaning Test	Ability of chemical cleaner to remove foulants	N/A	Caustic appeared to remove foulant

The following observations can be made from the standard analysis results:

- The element receiving conventional pretreated feedwater exhibited greater overall particulate fouling than did the element receiving MF/UF pretreated feedwater. The MF/UF pretreated element did not have sufficient foulant to enable an loss of ignition analysis. Particulate fouling included organic matter, clay and silt particles as well as iron from the conventional pretreatment coagulation chemicals. The conventionally-pretreated element was slimy to the touch and had foulant attached to the feed-brine spacer
- The greater levels of fouling on the conventional pretreated element did not significantly impact the element wet test permeate flow or salt rejection. Wet testing of both elements prior to autopsy showed product flow, NaCl rejection and differential pressure to be within specifications. (See TM 10 for a discussion on overall system performance and normalized differential pressure impacts.)

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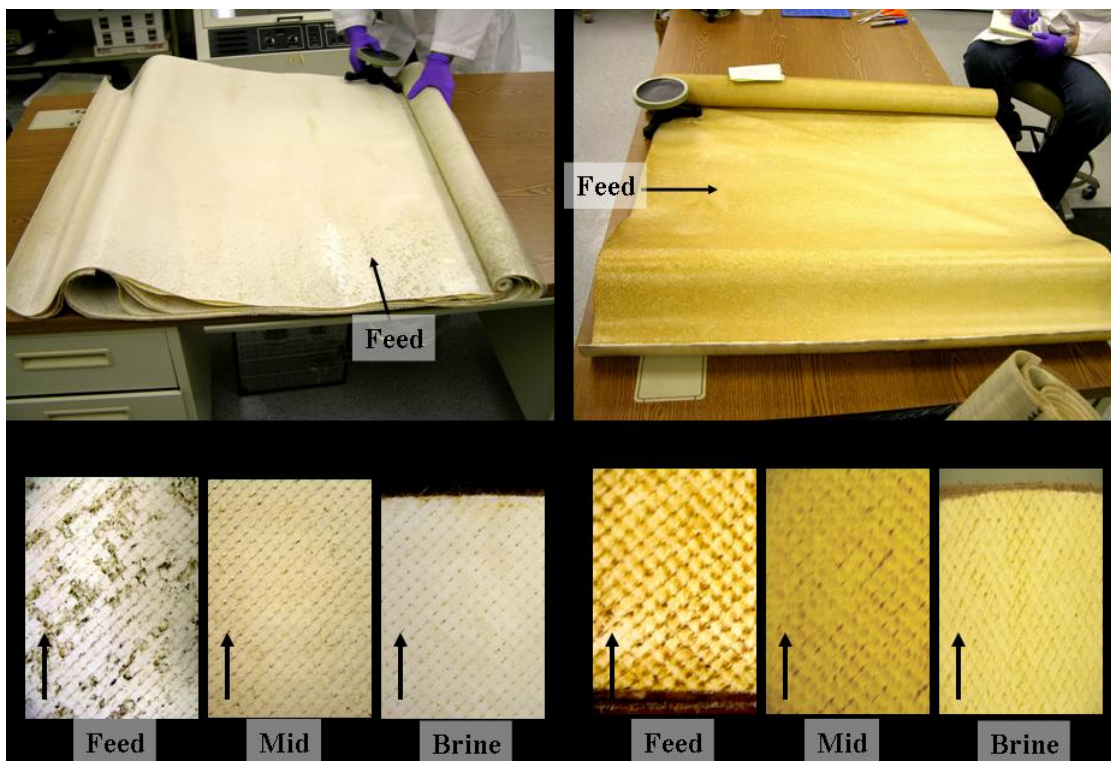
- The sodium bisulfite feed prevented any chlorine carry-over (from the daily maintenance washing of the MF/UF pretreatment system and periodic shock chlorinations) from damaging the SWRO membranes.
- Black debris was noted at the concentrate end of the MF/UF and conventional pretreated elements. These particles were small plastic shavings from the impellers of the SWRO high pressure pumps.
- Dow recommends cleaning first with a caustic (high pH) solution to remove organic fouling and then cleaning with an acid (low pH) solution for inorganic scale removal. This is opposite from what is typically recommended since there is a higher percentage of organic foulants and the organics could be “hardened” with an initial acid cleaning and made more difficult to remove.

Photos on the following pages highlight particulate fouling of the two membrane elements.

Photos of SWRO Membrane Visual Analysis

SWRO Element with MF/MF Pretreatment

SWRO Element with Conventional Pretreatment



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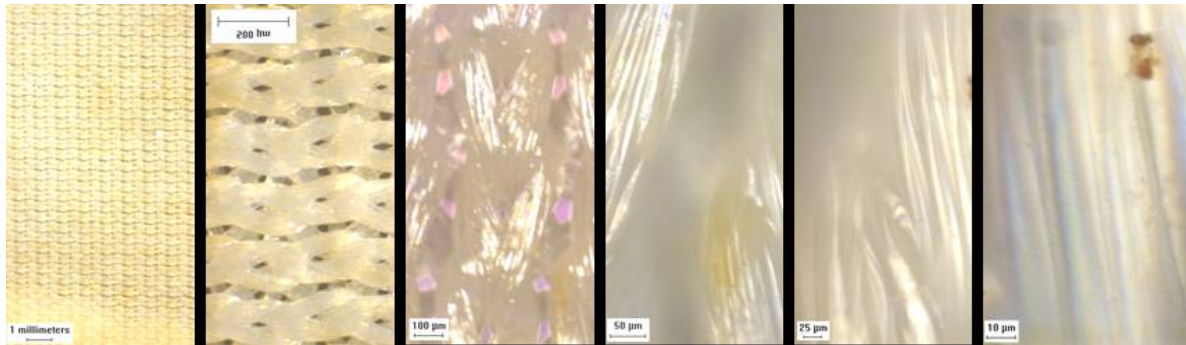
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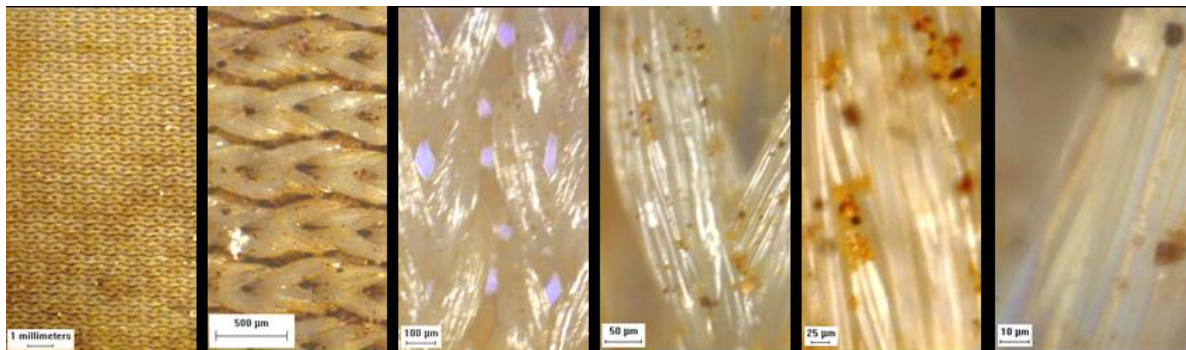
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Photos of SWRO Membrane Permeate Spacer Microscopic Analysis

Photos go from 1 mm to 10 micron resolution.



SWRO element with MF/MF pretreatment



SWRO element with conventional pretreatment

SUMMARY AND CONCLUSIONS FROM SPECIALIZED AND STANDARD ANALYSIS OF DOW FILMTEC ELEMENTS

1. MF/UF pretreatment was more effective in limiting the amount foulant deposited with the RO elements. Conventional pretreatment allowed more particulate material to accumulate with the element and at the membrane surface, particularly inorganic material. The foulant present in the elements pretreated by conventional treatment contained iron, most likely carryover from ferric coagulation, as well as clay particles, presumably from the source water. The clay particles (aluminum silicates) were significant and constituted the majority of the inorganic portion of the foulant, along with iron.

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2. There were iron oxide particles in the permeate carrier of the element pretreated by conventional treatment. These particles suggest post-precipitation of iron added during coagulation, indicating that the coagulation process may not have proceeded to completion prior to reverse osmosis. The coagulation process is known to take more time in high salinity waters such as seawater than in low TDS waters. For wet season high coagulant doses, additional coagulation residence time should be provided for the conventional pretreatment process.
3. The presence of both proteins and carbohydrates in the foulant indicate that bacterial fouling occurred with both types of RO feedwater pretreatment. The amount of biological material was greater in the foulant removed from the conventionally-pretreated element. The spatial pattern of P/CH deposition from feed to concentrate end as well as the P/CH ratio differed for each pretreatment. These differences may indicate a shift in the physiological state of the bacteria and the state of activity (exopolymeric substance secretion versus active growth phase).
4. Despite the presence of foulants and the noted differences, the performance of elements receiving the two types of pretreated feedwaters was within manufacturer's specifications.
5. No chlorine uptake or damage was observed by the qualitative methods employed. This is consistent with wet test results, which indicated salt rejection in compliance with specifications.

cc: Joel Faller
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