Appendix 7.1.2-1

Lecture on Analysis of Fouled Membrane

KINGDOM OF SAUDI ARABIA
SALINE WATER CONVERSION CORPORATION
AL-JUBAIL PLANT

المملكة العربية السعودية
المؤسسة العامة لتحلية المياه المالحة
مركز تطوير الأبحاث والتدريب

الرقم _____
التاريخ _____
المشفوعات _____

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To : Mr. Kitagawa/JICA Team, Al Jubail
From : Abdulrahman Abanmy/Manager RDC (A)

Sub : Lecture on Analysis of Fouled Membranes by Prof. Taniguchi

SWCC R&D welcomes the idea and will be happy to arrange for the lecture at RDC, Al-Jubail. Emphasis is to be on sample preparation and analytical procedure. Also, SWCC would like Prof. Taniguchi to participate in autopsy and analysis of fouled membrane to be performed at the RDC, Al-Jubail. Samples of fouled membranes will be provided by SWCC.

Advanced instruments necessary for fouled membrane autopsy and necessary tests to be performed are outlined in Appendix-1. All instruments are now available at the RDC.

For your information, SWCC R&D has been working on this subject for the last three years. Topic has been discussed in detail at the Center as well as with various SWCC staff engaged in SWRO work. Consultation & assistance has been provided by RDC to other Saudi Organization engaged in RO work. Moreover, several SWCC staff have participated in the autopsy and analysis of fouled membranes in U.S.A. and Japan.

Looking forward to Prof. Taniguchi presentation.

Regards,

(Abdulrahman Abanmy)
Manager RDC (A)

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APPENDIX 1

TESTING AND AUTOPSY OF FOULED MEMBRANES

To establish the reasons for the decline in the performance of fouled membranes, spiral wound or hollow fine fiber the following analytical and autopsy tests are to be performed by our laboratory on fouled membranes obtained from RO plants:

A. Samples and Sample Selection

Membrane elements are to be selected from the:

- Worst performing membranes, and
- Best performing membranes.

In addition, new membranes elements will be included, in this test.

For the case of the worst performing membranes two elements are to be selected from the first inlet and the last outlet elements in the vessel. Selection of the best performing membranes are to be taken again, from the first and last outlet elements in the vessel.

B. Performance Evaluation of Fouled Membranes

Performance evaluation measuring product water

- Flow rate and
- Salt rejection (or product conductivity)

for the above samples are to be determined under standard conditions.
(The performance of the used (fouled) elements is to be compared to that of the new elements and also to their expected performance versus their time in operation).

C. General Appearance of Disassambled RO Elements (Autopsy Test)

In this case **color** of the membranes and **deposit collected on them** are to be examined, photographed and recorded. Also, the element is to be examined for biological fouling, slime, smell, rupture, etc.

D. Determination of Structure and Composition of Deposits

Deposits on the membrane are to be collected and analysed using **Inductively Coupled Plasma** (ICP), or **Atomic Absorption** (AA) for the following elements: **Fe, Ni, Cr, Mo, Cu, Mn, Ca, Mg, Al, Zn, Co,** etc.

(This test is designed to identify the composition of foulant materials collected from the membrane surface. Note both ICP and AA are available at SWCC R&D laboratory).

E. Membrane Surface Analysis

For this type of analysis several analytical techniques can be used

1. Scanning Electron Microscope (SEM)

This technique shows magnified view of deposits on membrane or deposits removed from the membrane. Based on the morphology of the material the SEM* technique can differentiate between **inorganic, organic** and **biological** matter. **Inorganic** matter can be identified by **X-ray microanalyzer** (XMA)*, an accessory attachment to SEM, while the **organic matter** can be identified by **Fourier**

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Transform Infrared spectroscopy (FT-IR)*. (FT-IR)**Membrane surface properties** and the composition of **inorganic matter** can be examined also by the use of **Electron Spectroscopy for Chemical Analysis** (ESCA).

2. **Alternative Method for Identification of Inorganic Elements**

   Energy Dispersive X-Ray Spectroscopy (EDS)

   Method allows for the identification of **elements** present on membrane and in **deposits** removed from membrane or other parts of it. It gives semi-quantative results of the major, minor and traces of these elements.

The X-Ray Diffraction* is used to identify **crystalline** patterns of **inorganic** compounds found in the deposit, e.g., scale and corrosion products, while **X-Ray Flouresence Analysis** can be used to identify their (**inorganic material**) structure.

3. **Structure Identification of Organic Matter By Fourier Transform Infra Red** (FT-IR)

The FT-IR spectroscopy is applied in the analysis of **organic** substances adhered to the RO membranes. The same technique can be applied in the determination of the **acetyl group ratio** in the polymer chain. (FT-IR is available at SWCC R&D center).

F. Determination of Physical & Chemical Properties of the Membranes

In this case several test conditions can be applied:

1. **Strength and Elongation** of the membrane using **Instron***

   For a spiral wound membranes the stress/strain (S/S) curve can be established

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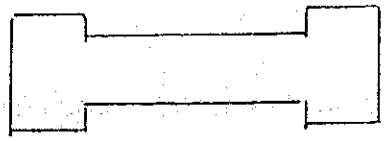
for a thinfilm membrane using a dumb-bell shaped sample



cut by a die from the membrane, while for a hollow fine fiber membrane the S/S curve can be determined by using a fiber sample. Polymer strength and elongation are established from the S/S curve.

2. **Molecular Weight Determination**

The standard process used here is **gel permiation chromatography** (GPC) which gives polymer molecular distribution. This measurement can be determined using **High Performance Liquid Chromatography** (HPLC)* equipped with a **GPC coulmn** (HPLC is available at SWCC R&D center but not the GPC permeation coulmn).

3. **Viscosity Measurement**

Viscosity measurement is used in many cases to determine polymer molecular weight, it also gives an indication of its physical properties.

(These three measurements: F1, F2 & F3 provide an indication of changes in the polymer molecular weight and chain structure).

4. **Degree of Polymer Acetylation**

Either one of two methods may be utilised:

The wet chemical analysis method in which the polymer is hydrolysed in a proper solvent and free acid is measured by neutralisation titration. Alternatively, the **FT-IR method** is used to measure the acetyl group absorption at **1725 cm-1** &

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1230 cm-1.

(The results of this test show whether acetate group hydrolysis occurred or did not take place).

(For experimental procedures for the above tests F1, F2, F3 and F4 the standard methods of analysis are to be employed for the determination of plastic stress/strain, molecular weight by gel permiation chromatography, viscosity measurements and acetyl group determination).

Appendix 7.1.2-2

Analysis of Fouled Material (1)
SEM & EDX Operating Manual for Analysis

Analysis of Fouling Material on the membrane(1)
SEM & EDX Analysis Operating Manual

This method of analysis is applicable to the observation and inorganic analysis of the foulants on fouled membrane surfaces and the surfaces of membrane filters which have captured foulants. The procedures are indicated below.

1. Dry the sample thoroughly. (Natural drying is best. If heat is used, keep it below 40°C)

2. Cut the samples into 7 mm squares and attach to SEM aluminum holders with double sided tape. Use thin tape (for example, Nitto Denko Corporation Tape Product No. 500) and do not make it bigger than the sample.

3. Apply a small quantity of silver-paint with conductivity to the four corners of the mounted sample.

   Note: Carbon type holders and conductive carbon paint may be used. For EDX analysis only the use of carbon is preferred as it avoids the aluminum peak from the holder and the lead peak from the paint.

4. Vapor deposition with ion coater when the paint is dry. For EDX use carbon deposition. For SEM observations use Au or Au-Pd deposition. Make the deposition-thickness about 100 A. The EDX analysis is easier with carbon deposition since it does not produce a Au peak. However, above 4000X the analytical efficiency deteriorates with samples prepared with carbon, so they are not suitable for the detailed structure of foulants or the observation of fine membrane surfaces.

5. Mount in SEM.

If analysis is possible, analysis and observation are normally carried out under the following conditions. However, since capacity and operation differ with some SEMs, please refer to the operating manual for details. SEM observation is suitable since the lower the acceleration voltage, the easier it is to obtain surface data and there is less damage to membrane surfaces and foulants.

	Acceleration voltage (KV)	Working distance (mm)
SEM observation	<10	2 - 5
EDX analysis	20	20

6. SEM and EDX Observations

For SEM, scan the entire sample under low magnification. Then observe and analyze typical portions of the sample under medium magnification (800X) and high magnification (4000X). EDX over the whole surface at medium power and spot analyses at high power should give a clear grasp of the surface conditions.
The selection of 4000X as the high magnification enables bacteria to be identified, facilitates the ready detection of bacterial fouling and gives adequate resolution even with EDX.

Notes:

- With EDX, fouling conditions can be readily understood with line analyses or surface analyses, depending on the circumstances of the fouling, but adequate signals can not be obtained if peak counts are less than 1000.
- Depending on the type of accumulation, observations across a cross section are also significant. To prepare the cross section, the sample is broken down in liquid nitrogen, stood in the holder and coated by vapor deposition.
- Photography is best done with negatives films but developing and printing takes time and exposure conditions need to be confirmed later. For quick results, use a Polaroid or video printer.

7. Sample storage

After analysis, samples should be placed in a schale and kept until the results have been completed. When the results are completed, remove the sample from the holder and wipe off the conductive paint with ethanol. The holder can be used for the next sample.

Appendix 7.1.2-3

Analysis of Fouled Material (2)
FT-IR Operating Manual for Analysis

Analysis of Fouling Material on the Membrane(2)
FT-IR Analysis Operating Manual

1. ATR Membrane Analysis

This method of analysis is applicable to the analysis of organic and inorganic foulants on fouled membrane surfaces and membrane filters which have collected foulants.

1-1. Dry the sample naturally but thoroughly. If heat is used, keep it around 40°C.

1-2. Cut the sample into pieces which will fit into the FT-IR ATR holder. When cutting the sample, use forceps to hold the sample and avoid touching the surface to be analyzed with the fingers.
Cut each sample to roughly uniform sizes at each time.

1-3. Use KRS-5 for the ATR reflector plate. This enables adsorption over a wide range of wave numbers (400-4000 cm-1). The reflector plate angle is 45 .

1-4. Attach the sample firmly and evenly to the reflector plate.

1-5. Integrate to a level where noise can be ignored. A resolution of 8 cm-1 is adequate.
Note: Since integration counts differ with the performance and mechanism of the FT-IR, please refer to the operating instructions for each container.

1-6. Take a differential spectrum from a new membrane. When taking this spectrum, adjust so that the strong

adsorption of the new membrane can be reduced to the base line.

1-7. Compare the standard spectrum collected with the standard spectrum file and identify the foulants.

2. Foulant Analysis with KBr

This method of analysis is applicable to inorganic and organic analysis of the actual foulants as well as materials in solution in the water. Collect a quantity of foulant from the membrane surface or, in the case of a water sample, evaporate completely, mash with KBr and take an absorption spectrum as a pellet.

2-1. Dry the sample thoroughly. For complete drying, it is best to dry for 2 hours at 110°C.

2-2. After drying, place a suitable quantity in an agate mortar together with a little KBr and mix well. To avoid the absorption of moisture, the mixing should be done quickly in an air conditioned room.

2-3. Make the pellets in a pelleting jig. Some handy jigs which can be used for this purpose have recently become available.

2-4. Take an absorption spectrum in the same way as ATR. Depending on the quantity, the absorption strength may be small or large. In this case, adjust by changing the proportions of KBr and sample to obtain the most suitable spectrum.