초청강연 II

ROLE OF MEMBRANE MODULES IN ULTRAPURE WATER SYSTEM FOR THE CURRENT SEMICONDUCTORS INDUSTRIES

* Aromatic polyamide

Hiroshi Iwahori
Nitto Denko Corp, Kusatsu-shi,Shiga Japan

R.O.
– high sel.
– " flux
– chem. resist.
(Cl_2, O_3 ···)

INTRODUCTION

It can be said that the current ULSI technology has been supported and/or accomplished by a major challenge to the clean room environment and the ultrapure water equipment manufacturers as to contamination control. The required improvement in ultrapure water quality, which is shown in Figure 1, would not have been possible without significant improvements in membrane performance and enhancements in analytical capabilities.

The role of membrane modules in ultrapure water systems has changed from a pretreatment throughout the point of use in the entire ultrapure water system. Membrane modules are now used to achieve all the separations listed in Figure 1.
In particular, for total organic carbon (TOC) and submicron particle reduction, the use of membrane separation is the only proven technology capable of achieving the ultrapure water levels required for 16 megabit DRAM production.

I would like to talk how reverse osmosis (RO) and ultrafiltration (UF) application have evolved in the past decade and the specialized membrane products that have resulted. The requirement for each membrane operation will be presented and the performance and characteristics of the RO elements and UF modules will be discussed. Finally, future prospects for ultrapure water applications will be discussed along with the developments in UF and RO membrane technology that will be required to produce ultrapure water for chips with a density of 16 megabit DRAM and beyond.

A generalized flow chart of an ultrapure water system is shown in Figure 2. A dotted line serves to separate two process options that are in common practice.

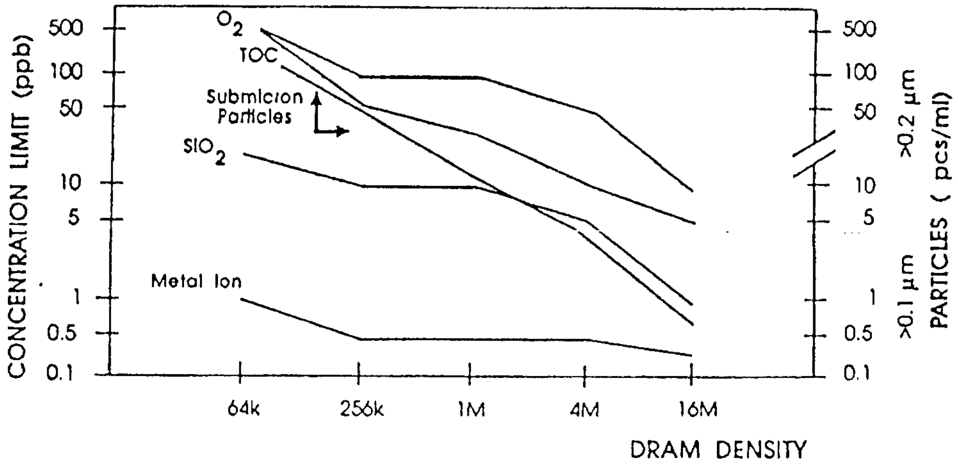


Figure 1: Ultrapure Water Quality Requirements for DRAM Production

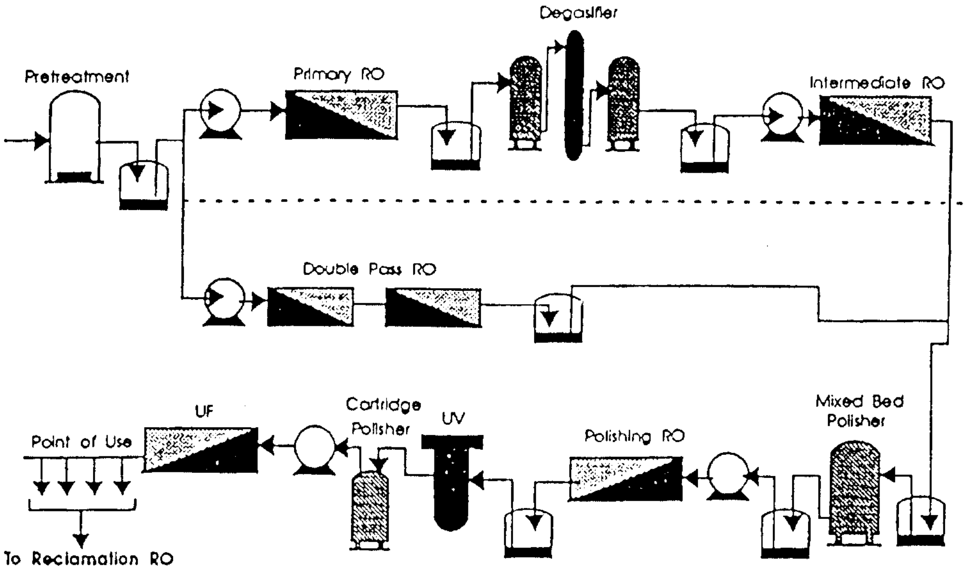


Figure 2: System Example for Ultrapure Water Processing

PRIMARY RO SYSTEM

The development of the composite RO technology during 1980's result in a rapid growth in the number and type of RO membrane available for use in the primary RO position. As shown in Figure 3 the performance of thin-film composite membrane of spiral wound configuration has superior than the traditional asymmetric cellulose acetate (CA) membrane. The composite membranes cover the entire rejection spectrum, ranging from products with significantly higher than CA to products with lower rejection but with a productivity an order of magnitude larger than CA.
Since the major function of the primary RO is ion-removal, the high salt rejection of the aromatic polyamide composite of up to 99.5% makes it the most suitable for primary RO applications.

INTERMEDIATE/SECONDARY RO AND POLISHING RO

As shown in Figure 2, there are two options prior to the polishing loop in ultrapure water system. The first option consists of a primary RO, 2B3T ion exchange process and an intermediate RO. The main function of the intermediate RO is the removal of organic and particulate matter leaching from the ion exchange resins, primarily during regeneration. The other option is a double pass RO (DP-RO) which is becoming increasingly popular. Since the DP-RO has no ion exchange resin, the load of organic and particulate matter, which is possibly leached out from ion exchange resins, can be minimized.

In Figure 3 typical water analysis data of a DP-RO are shown. Thanks to the introduction of current low-pressure type composite RO's, the DP-RO can practically operated by using single pressurizing feed pump, because the first pass RO feed pressure can be kept at rather lower range (below 2 MPa) than the high-pressure type conventional CA membrane.

	Feed Tap Water	1st Stage Permeate	2nd Stage Permeate
pH	8.7	6.1	5.8
Conductivity, µS/cm	128.0	2.1	0.40
Resistivity, mΩ-cm	..	..	2.5
Na^+ (ppm as Ion)	8.6	0.50	0.07
K^+ (ppm as Ion)	1.7	<0.01	<0.01
Ca^{2+} (ppm as Ion)	9.8	<0.01	<0.01
Mg^{2+} (ppm as Ion)	2.1	<0.01	<0.01
Cl^- (ppm as Ion)	14.1	0.22	0.04
NO_3^- (ppm as Ion)	0.4	<0.01	<0.01
HCO_3^- (ppm as Ion)	30.3	1.24	0.29
SO_4^{2-} (ppm as Ion)	11.0	<0.01	<0.01
SiO_2 (ppm as SiO_2)	4.9	0.19	<0.10

OPERATING CONDITIONS
(MEMBRANE
NTR-759HR/HYDRANAUTICS
CPA2)

1st Stage: 2.0 MPa (290 psi)
2nd Stage: 1.0 MPa (145 psi)
Recovery: 80%
Temperature: 25°C

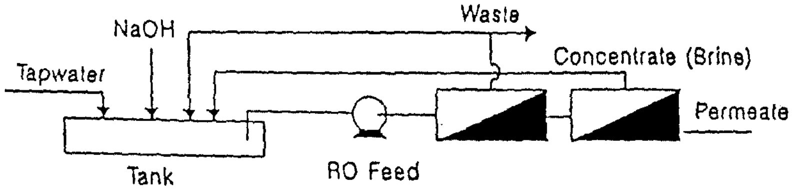


Figure 3: Example of Double Pass RO with Spiral Wound Elements

REJECTION PERFORMANCE WITH VERY LOW LEVELS OF INORGANIC SOLUTES

In Figure 4 performance data of NaCl rejections are shown as to several kinds of RO membranes which is operated with feed water at very low salinity.

As shown in Figure 5 and 6, the ions' rejection irregularly varied with pH range, in particular, between 6 and 9. This phenomenon suggests that the functional groups with positive or negative charge within polymer of membrane play an important role for membrane rejection.

Figure 7 and 8 show RO performance of very low concentration range vs pH with aromatic polyamide composite RO element(NTR-759HR-S4).

REJECTION PERFORMANCE WITH VERY LOW LEVELS OF ORGANIC SOLUTES

Along with the improvement of the quality levels of ultrapure water, they also paid attention to lower levels of organics which originate from various sources, for examples naturally existing organics, ion exchange resins, piping, tanks and pumps in the polishing loop subsystem. Accordingly a RO module with a higher rejection performance of TOC is necessitated. Since Isopropanol (IPA) is a standard TOC solute of a low molecular weight organic for JIS testing procedure of RO membrane, TOC rejection performance measured with low feed concentrations below 1000 ppb by using production RO elements; NTR-759HR and NTR-759UP are shown in Figure 9. TOC rejection performance with ultrapure feed water by using several kinds of production RO elements are shown in Figure 10.

TYPICAL EXAMPLE OF POLISHING RO PERFORMANCE

In order to reduce the down time of the entire pure water system, polishing RO performance has to become stable immediately after start-up. That is of particular importance for the operation of ultrapure water system when element replacement becomes necessary. Figure 11 illustrates that the resistivity and TOC of the product stabilizes within hours after start-up. The importance of an RO system in polishing loop becomes clear in Figure 12. The RO is able to act as a buffer and control the TOC within reasonable limits after a sudden increase occurs in feed TOC due to mixed bed regeneration.

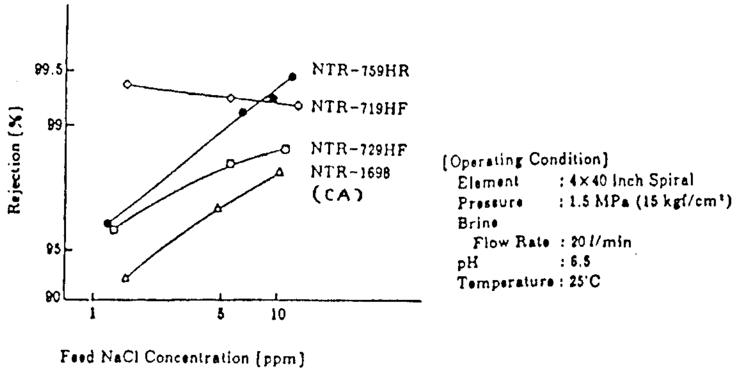
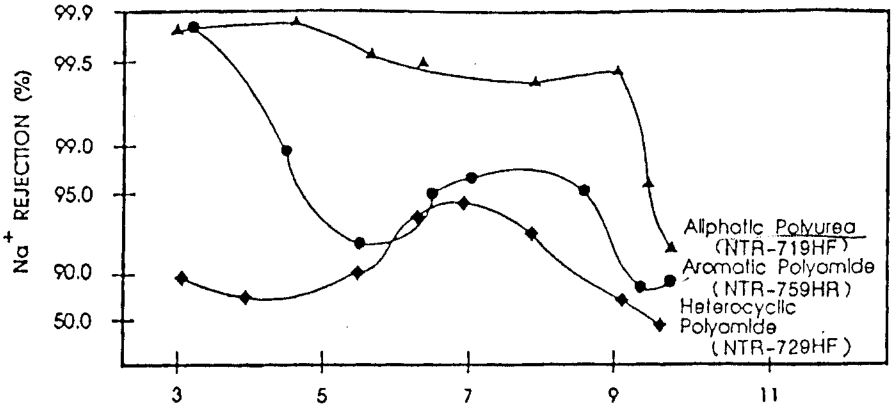


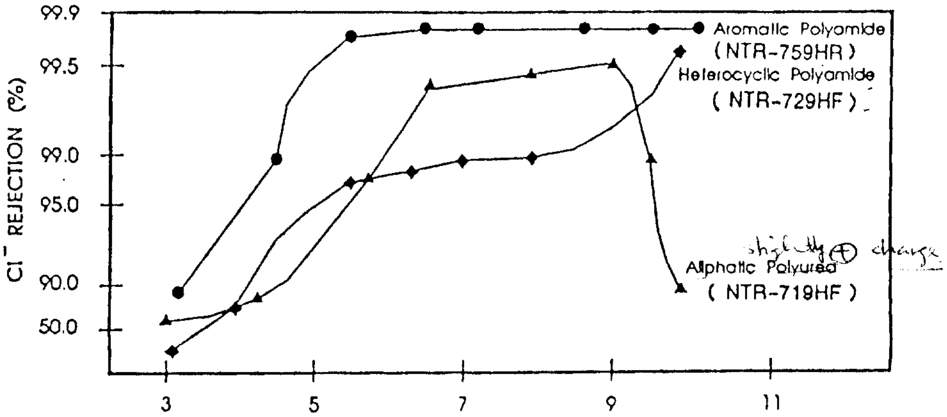
Figure 4: NaCl Rejection Performance at Low Concentration Range



Test Conditions :

Element: 4 x 40 in. spiral Feed Flow: 20 L/min
Pressure: 215 psi (1.5 MPa) Temperature: 25 °C

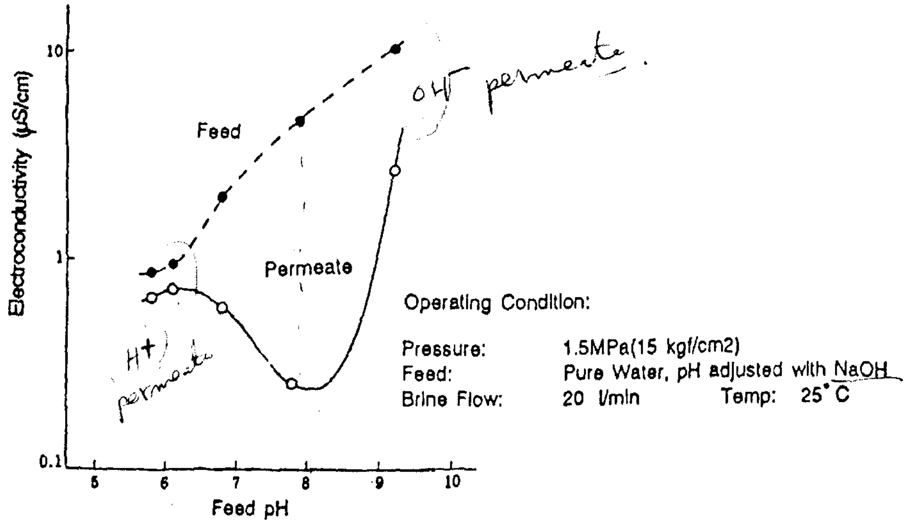
Figure 5: Sodium Ion Rejection vs. pH at 1ppm NaCl



Test Conditions :

Element: 4 x 40 in. spiral Feed Flow: 20 L/min
Pressure: 215 psi (1.5 MPa) Temperature: 25 °C

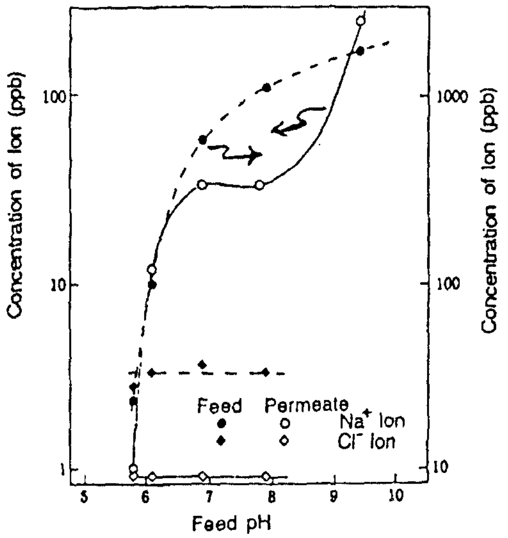
Figure 6: Chloride Ion Rejection vs. pH at 1ppm NaCl



Operating Condition:

Pressure: 1.5MPa(15 kgf/cm2)
Feed: Pure Water, pH adjusted with NaOH
Brine Flow: 20 l/min Temp: 25°C

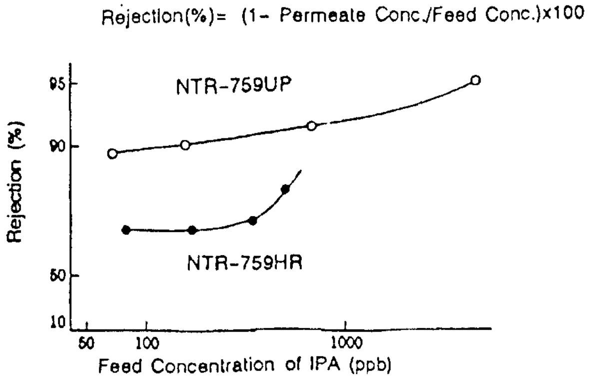
Figure 7: RO Performance as Electric-conductivity Removal vs. pH with NTR-759HR 4" Element



Operating Condition:

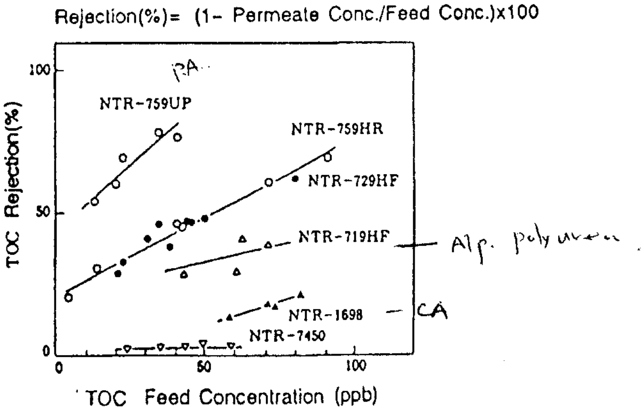
Pressure: 1.5MPa(15 kgf/cm2)
Feed: Pure Water, pH adjusted with NaOH
Brine Flow: 20 l/min Temp: 25°C

Figure 8: RO Performance as Sodium and Chloride Ion's Removal vs. pH with NTR-759HR 4" Element


Rejection(%)= (1- Permeate Conc./Feed Conc.)x100

Pressure: 1MPa(10 kgf/cm2)
Recovery: 30%

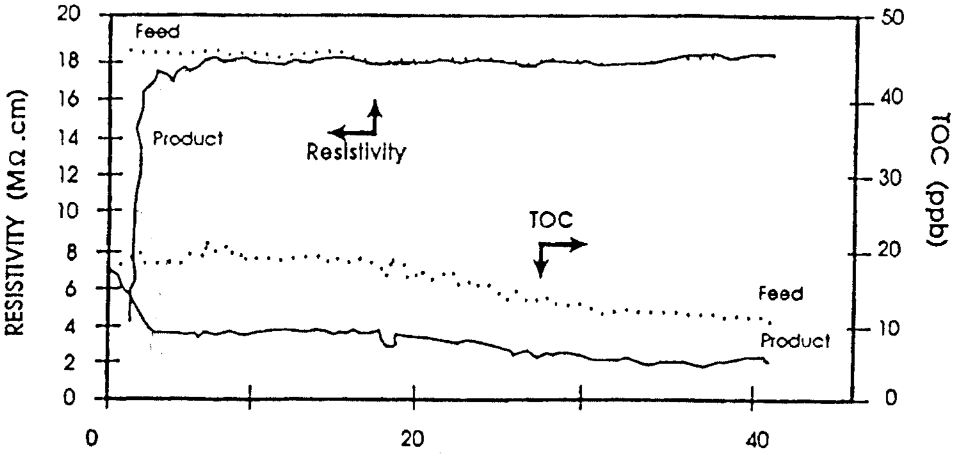
Figure 9: IPA Rejection with NTR-759HR or UP grade Membrane Elements


Rejection(%)= (1- Permeate Conc./Feed Conc.)x100

UV ±10 ppb

Operating Condition:
4x40 Inch Element, Feed: Ultrapure Water (18 M-ohm.cm), TOC Analysis by ANATEL A-100
Pressure: 1MPa(10 kgf/cm2), Recovery: 80%, Temp.: 19 - 20°C

Figure 10: TOC Rejection Performance at Low Concentration Range 3)

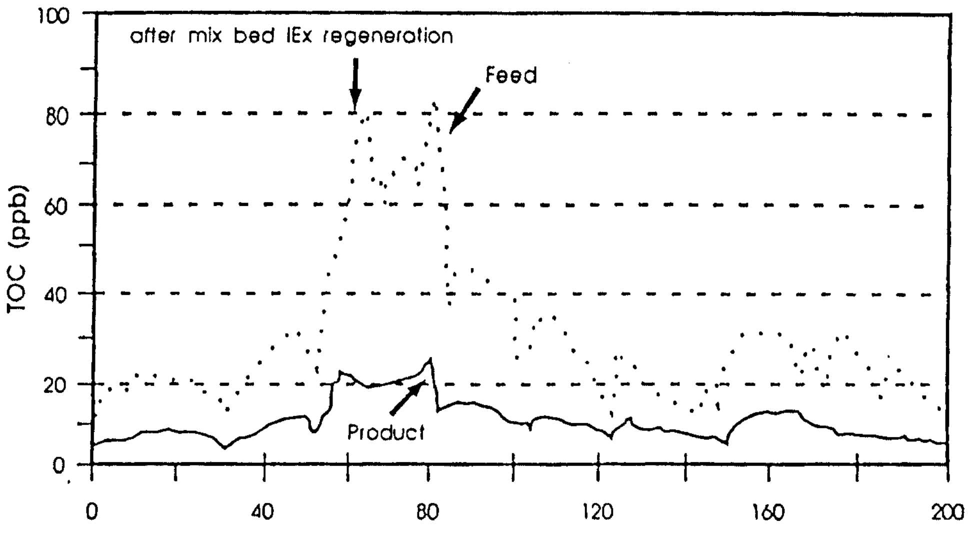


Operating Conditions:

Element: 4 x 40 in spiral, aromatic polyamide, UPW Grade

Pressure: 215 psi (1.5 MPa) Recovery: 30%

Figure 11: Start-up Resistivity and TOC



Operating Conditions:

Element: 4 x 40 in spiral, aromatic polyamide, UPW Grade

Pressure: 215 psi (1.5 MPa) Recovery: 30%

Figure 12: TOC After Mix-bed Ion Exchange Regeneration 1)

TOC conc. by concentration

POLISHING UF 2)

Nowadays in Japan, it is generally recognized that ultrafiltration membranes perform better in polishing units than the traditional cartridge microfiltration membranes in regards to removal of submicron particles and stability of performance. The capillary configuration of the UF membrane has been shown to give better performance than the spiral wound configuration. The advantage of capillary type modules include fewer wetted components on the permeate side, a structure that completely eliminates dead spaces and an extremely quick start-up performance. The capillary modules are typically installed downstream of the polishing RO, immediately before the actual point of use. The primary function of the capillary modules is the rejection of submicron particles and pyrogen generated on the permeate side of the polishing RO and in the equipment or piping downstream of the polishing RO.

The original design of the capillary modules was the so called inside/out design, internally pressurizing type shown in Figure 13. The feed water flows through the center of the membrane fibers, the product water flows through the membrane and is collected on the outside of the fibers. Operation of these modules without interruptions produces a very low particle count in the permeate. However, a change in operation due to , for instance the opening or closing of a valve, would cause a small vibration in the module and generate a sharp, short term increase in the number of particles in the permeate.
The outside/in design, externally pressurizing type was recently developed to reduce particle generation in systems that require frequent changes in operation. As shown in Figure 13, the feed water flows around the membrane fibers and the permeate is collected on the inside of the fibers. In both designs the membrane fibers have asymmetric double skin layers with a tight UF layer on the inside of the fiber. That construction optimizes membrane flux and mechanical strength of the fibers. The outside/in design has several advantages. The tight surface on the inside of the fibers prevents particle shedding of membrane material into the permeate. Particle contamination of the module during manufacturing would occur mainly on the outside of the fibers. In the outside/in design these particles cannot permeate the membrane and therefore cannot end up in the permeate. Finally, the total wet contact area on the permeate side of the outside/in module is reduced in comparison with the inside/out design.

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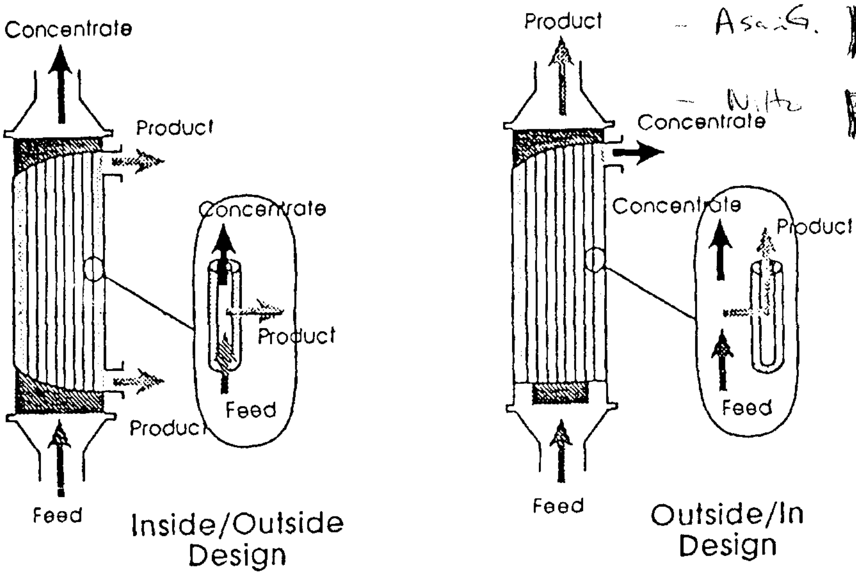
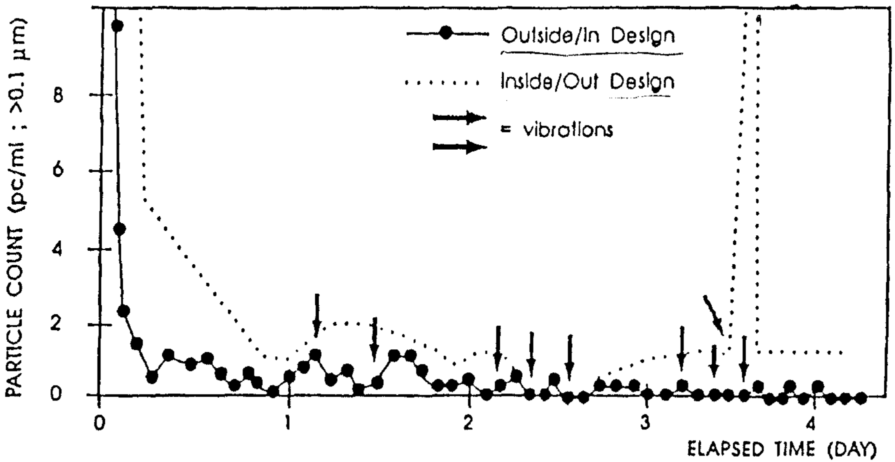


Figure 13: Capillary UF for Polishing Loop Applications



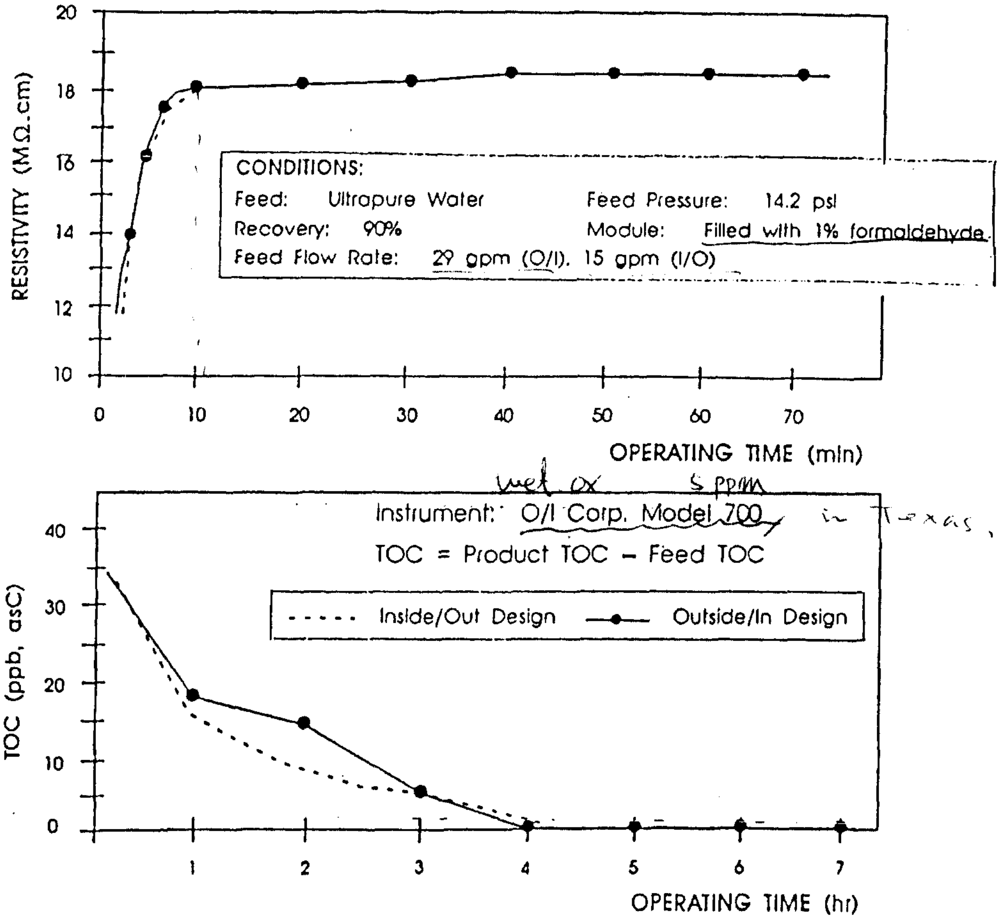
CONDITIONS:

Feed: Ultrapure Water (ambient) · Feed Pressure: 14.2 psi

Feed Flow Rate: 29 gpm (O/I), 15 gpm (I/O) Recovery: 90%

Measuring Instrument: Particle counter (Horiba PLCA-310 type)

Figure 14: Performance of Capillary Modules with Periodic Vibrations by Hammering



CONDITIONS:

Feed: Ultrapure Water Feed Pressure: 14.2 psi

Recovery: 90% Module: Filled with 1% formaldehyde

Feed Flow Rate: 29 gpm (O/I), 15 gpm (I/O)

wet ox 5 ppm

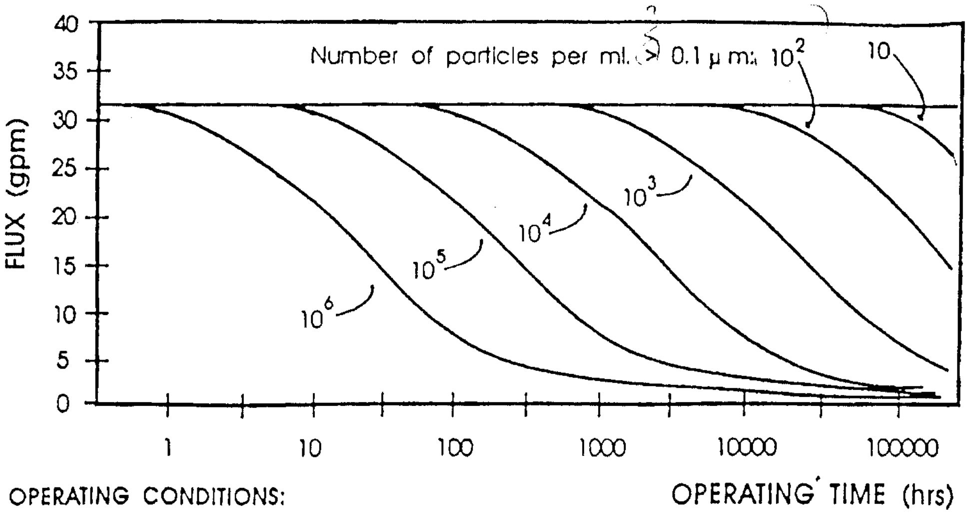
Instrument: O/I Corp. Model 700 in Texas,

TOC = Product TOC − Feed TOC

Figure 15: Start-up Performance of Capillary Modules

The results of operation in the polishing loop of both types of capillary modules are shown in Figure 14. It is quite obvious that frequent vibrations of the module have no influence on the permeate water quality in the outside/in design. However, in the inside/out design a sharp increase in particle numbers was observed during vibration.

The rinse down characteristics of the capillary modules is shown in Figure 15. The resistivity stabilizes after just 10 minutes of operation and the permeate TOC is equal to the feed TOC after 4 hours.
The reduction in flux, as a result of particle fouling, can be estimated with the cake filtration theory. Figure 16 shows the flux decline versus operating time for various particle levels in the feed water. The maximum recommended amount of particles in the feed water to the outside/in capillary module is 100 pcs/ml, with a particle diameter larger than 0.1 um, measured by a particle counter.



OPERATING CONDITIONS:

Feed: Ultrapure Water and Particles

Feed Pressure: 14.2 psi Recovery: 90%

Figure 16: Flux Decline in Outside/in Capillary Module (NTU-3306-K4R) Versus Feed Water Quality

CONCLUSIONS

The performance of RO membrane at low salinity levels cannot easily be predicted from the brackish data. The rejection at low concentration is dependant on the pH of the feed solution and the membrane charge. These effects do not play a role in the rejection of organic solutes. The organics rejection at low concentration is similar to the rejection at higher concentrations.

Ultrapure water grade polishing RO modules are capable of producing water with TOC below 5 ppb. Furthermore, they are excellent for reducing or eliminating TOC upsets in ultrapure water system operation.

Externally pressurizing type capillary UF modules are very effective in the removal of particles and pyrogen. They are recommended to be used as a final step in the polishing system.

REFERENCE

1) Ary, S., Lesan, R., Kamiyama, Y. and Kawada, I.:"MEMBRANE MODULE FOR ULTRAPURE APPLICATION", ICOM '90, 392, (1990)
2) Gerard R., Lesan, R., Kawada I. and Tasaka, K.: "ROLE OF MEMBRANE EQUIPMENT IN STATE-OF-THE-ART ULTRAPURE WATER SYSTEM", the 10th Annual Semiconductor Pure Water Conference(1991)
3) Ikeda Kenichi: "DEVELOPMENT AND PRACTICAL USES OF LOW PRESSURE TYPE REVERSE OSMOSIS MEMBRANE", MEMBRANE Vol.16:No.4, 223-232(1991)