Roles of RO Membranes in Ultra Pure Water Production

Yasushi Maeda and Hideki Miyamoto
Dow Chemical Japan Limited, Gotemba Laboratory
92-2 Ogurano, Gotemba-shi, Shizuoka, 412-0013, Japan

Introduction

Ultra pure water (UPW) is essential to properly fabricate today's LSI/LCD products. It is the primary cleaning solvent used to rinse all contaminants and remnants of silicon etched away during the production process. The geometry of today's integrated circuits is so minute and complex that even the smallest contaminant can prevent a circuit from functioning properly. These contaminants decrease the production yield of usable circuits. UPW quality requirements have steadily become more and more stringent. The following additional requirements have emerged recently in UPW production and its process from the standpoint of overall cost reduction and environmental protection [1].

- ✧ Reduction of initial (i.e., capital) costs
- ✧ Reduction of operating and O&M costs
- ✧ Reduction of space or footprint
- ✧ Reduction of waste and wastewater reuse

To address these issues, original equipment manufacturers (OEMs) and end use customers in the semiconductor industry have been continuously developing innovative water treatment technologies that include low energy and/or less fouling reverse osmosis (RO) elements, electrodeionization, membrane deaerator, and ion exchange and chelating membrane filters [2]. Within the entire UPW process, RO has been playing an important role. In this symposium, the roles of RO and some advancements are reviewed in more detail.

Producing Ultra Pure Water

As the degree of integration becomes increasingly more complex, the semiconductor industry requires higher levels of water purity. Last year the standard guide for UPW used in the electronics and semiconductor industry (ASTM D 5127-99) was revised in which

Table 1 ASTM Standard Guide for UPW Used in the Electronics and Semiconductor Industry

Parameter		Type					
		E-1	E-1.1	E-1.2	E-2	E-3	E-4
Linewidth	µm	1.0-0.5	0.5-0.25	0.25-0.18	5.0-1.0	>5.0	–
Resistivity, 25°C	MΩ·cm	18.2	18.2	18.2	17.5	12	0.5
Endotoxin	EU/ml	0.03	0.03	0.03	0.25	–	–
TOC	ppb	5	2	1	50	300	1000
Dissolved oxygen	ppb	1	1	1	–	–	–
Residue after evapo.	ppb	1	0.5	0.1	–	–	–
SEM particles							
0.1 - 0.2 µm	counts/L	1000	1000	200	–	–	–
0.2 - 0.5 µm	counts/L	500	500	100	3000	–	–
0.5 - 1.0 µm	counts/L	50	50	1	–	10000	–
10 µm	counts/L	–	–	–	–	–	100000
Bacteria							
100 mL Sample		1	1	1	–	–	–
1 L Sample		1	1	0.1	10	10000	100000
Silica - total	ppb	3	0.5	0.5	10	50	1000
Silica - dissolved	ppb	1	0.1	0.05	–	–	–

the water qualities are classified according to the line width of semiconductor devices. As can be seen in Table 1, the most stringent UPW, designated as E-1.2 corresponding to a line width of 0.25-0.18 μm, requires a resistivity of 18.2 MΩ·cm (0.055 μS/cm) at 25°C, 0.05 ppb of dissolved silica, and 1 ppb of TOC. The amount of ions and metals is approaching ppt levels. These water quality guidelines are consistent with target values in Japan as shown in Table 2 [3]. Japanese targets, however, look more challenging in terms of TOC and particles. To meet those very strict UPW quality requirements, complicated and highly integrated water treatment systems are imperative. Furthermore, UPW treatment systems vary depending on the source of the water to be processed and the ultimate purity influenced by the complexity of the semiconductor device.

Table 2 Ultrapure Water Quality Target Values for Semiconductor Manufacturing in Japan

Items	Integration Scale	256 Kbit	1 Mbit	4 Mbit	16 Mbit	64 Mbit	256 Mbit
Line width	μm			0.8	0.5	0.35	0.25
Resistivity	MΩ·cm	17 - 18	17.5 - 18	> 18	> 18.1	> 18.2	> 18.2
Particle (number/ml)	0.1 μm	50 - 150	10 - 20	< 5			
	0.05 μm			< 10	< 5	< 1	
	0.03 μm					< 10	< 5
Bacteria	num./l	50 - 200	10 - 50	< 10	< 1	< 0.1	< 0.1
TOC	ppb	50 - 100	30 - 50	< 10	< 2	< 1	< 0.5
O_2	ppb	50 - 100	30 - 50	< 50	< 10	< 5	< 1
SiO_2	ppb	10	5	< 1	< 1	< 0.5	< 0.1
Metal, Ion	ppt	- 1000	100 - 500	< 100	10 - 50	< 5	< 1

Y. Motomura, Kurita Water Industries Ltd., Membrane Journal (Korea), 6, No 3, 141 - 158 (1996)

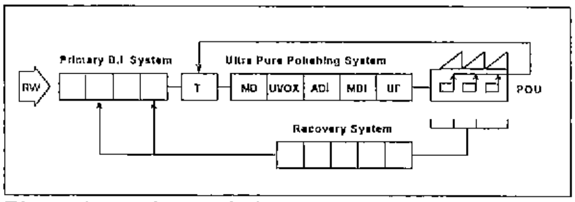


Figure 1 Advanced ultra pure water system

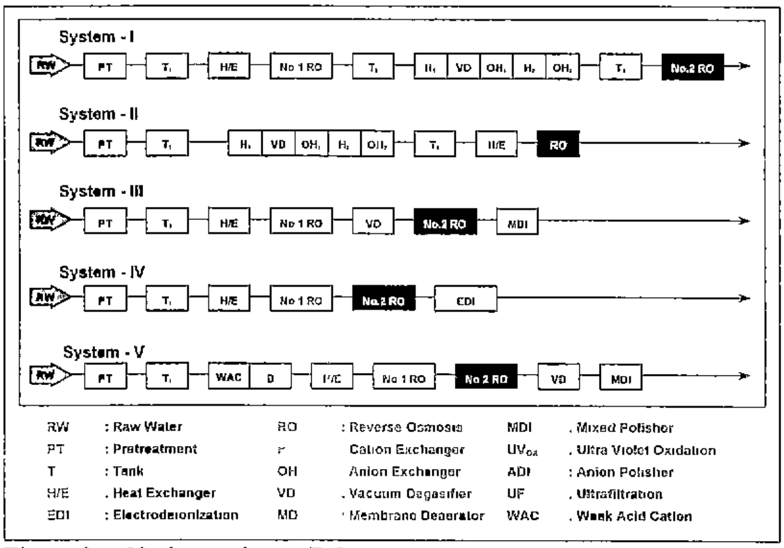


Figure 2 Various primary D.I. systems

A UPW system generally consists of three parts: primary deionization (D.I.) system, polishing system and recovery system (Figure 1) [4]. For the primary D.I. system, a variety of system configurations have been proposed as shown in Figure 2. In the D.I. system, RO plays key roles in No.1 and No.2 positions. A main role of No.1 position RO is to remove TDS and natural organic matter (NOM), whereas that for No.2 RO is to further remove a trace amount of TOC and particles.

As mentioned before, the semiconductor industry is seeking UPW systems that are more friendly to the environment and conserve water. To address these issues, the following two processes have been implemented: electrodeionization (EDI) or continuous deionization (CDI) – System-IV [5,6] and the high efficiency RO – System-V [7-9]. EDI is an electrically driven demineralization process combining ion exchange resin and ion exchange membranes. Recently, the EDI process has gained attention due to continuous operation and the elimination of hazardous regeneration chemicals. A newspaper reported recently that one of the largest semiconductor manufacturers in Japan had decided to adopt the EDI process [10].

One of the major obstacles of RO is that recovery cannot be increased where feed silica concentration is high (e.g., more than 20 – 30 mg/L). In the System-V, hardness and residual alkalinity is completely removed by weak acid cation (WAC) resin and a degasifier. After this pretreatment, feed pH can be increased up to 10 – 11 where silica solubility is dramatically increased. A recent paper reported that RO can recover 90 – 95% of feed water containing 80 mg/L of silica (9). In both cases, high rejection and high pH tolerance RO elements are critical.

RO Elements for UPW production

FilmTec, a wholly owned subsidiary of The Dow Chemical Company, has continued to extend its high precision manufacturing technology to a wide variety of RO and nanofiltration (NF) products. A product range of RO/NF and brackish water (BW) RO element specifications relevant to UPW production are illustrated in Figure 3 and Table 3. The BW30-365FR (fouling resistant) and SG30LE-430 (semiconductor grade) are newly developed 8 inch diameter RO elements. To better understand the applicability of these elements, those best suited to the UPW process are illustrated in Figure 4 which represents one of the typical UPW systems designated as System-I in Figure 2. In the following sections, the features and benefits of these RO elements will be reviewed briefly.

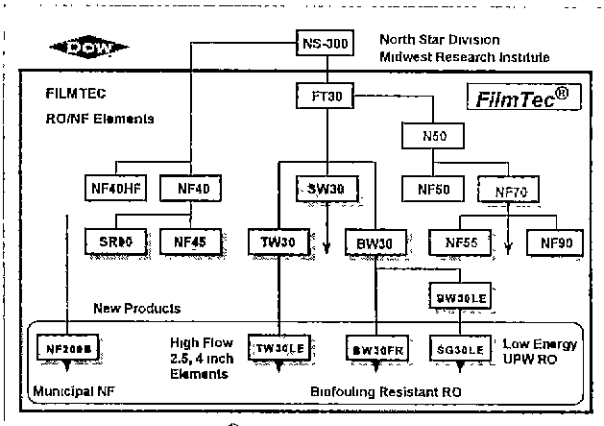


Figure 3 FILMTEC® RO/NF Elements

Table 3 High surface area low-energy 8 inch BW elements

MODEL NUMBER		BW30-365	BW30-365FR1 BW30-365FR2	BW30-400	BW30LE-440	SG30LE-430
Product Water Flow Rate	m^3/D	36	36	40	44	38
Min Salt Rejection	%	98	98	98		–
Typical Field Salt Rejection	%	99.5	99.5	99.5	99.0	–
Test Conditions at 25°C						
Feed Concentration	mg/l	2,000 (NaCl)	2,000 (NaCl)	2,000 (NaCl)	2,000 (NaCl)	Pure Water
Feed Pressure	bar	15.5	15.5	15.5	10.3	7.4
Recovery	%	15	15	15	15	15
Operating Limits						
Max. Operating Pressure	bar	41	41	41	41	41
Max. Oper. Temperature	°C	45	45	45	45	45
Max. Feed Turbidity	NTU	1	1	1	1	1
Max. Feed SDI		SDI 5	SDI 5	SDI 5	SDI 5	SDI 5
Free Chlorine Tolerance	mg/l	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1
pH range, Continuous Operation		2-11	2-11	2-11	2-11	2-11
Maximum Feed Flow	l/min	265	265	265	321	321

No.1 (roughing stage) RO Elements

For No.1 RO (roughing stage), BW30-400 and BW30LE-440 can be considered as standard elements due to their reliable and robust performance. The FILMTEC® BW30LE-440 element has a nominal active membrane area of 440 ft^2 (40.9 m^2) and an average permeate flow of 11,500 gpd (44 m^3/d) at 150 psi (10.3 bar) under standard conditions. Optimizing membrane chemistry results in a lower pressure operation than when the FILMTEC BW30-400 element is used, which means system operating economy is enhanced. The high surface area of the FILMTEC BW30LE-440 element permits designs of new RO systems that meet productivity targets with fewer elements than standard 8 inch elements resulting in lower installed system cost by reducing the number of system components.

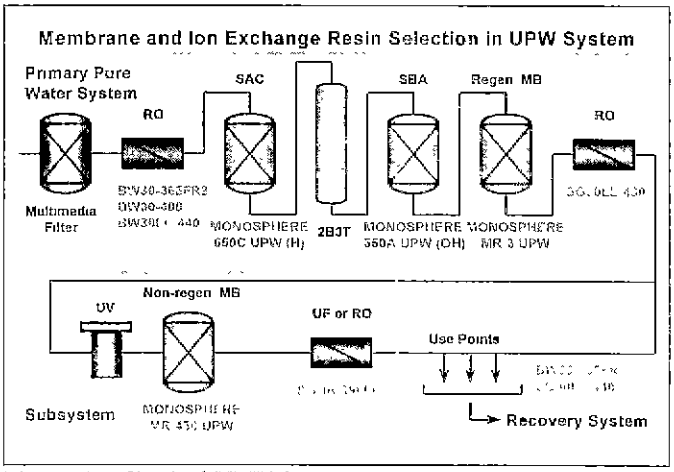
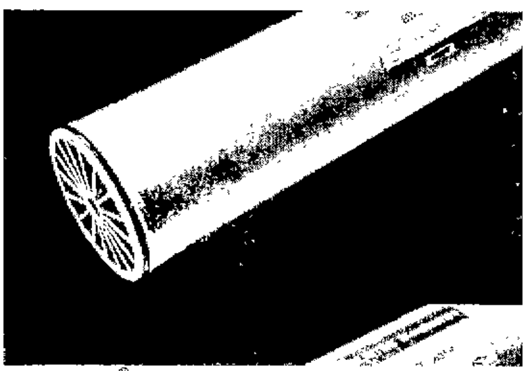


Figure 4 Typical UPW System

One of the problems associated with a steady state UPW RO operation can be attributed to biofouling, especially for surface water supply and warm, highly bacteria-active water. To improve the performance of RO elements operating under those conditions, Dow has developed a series of fouling resistant (FR) RO elements using proprietary surface modifications of the FT30 membrane chemistry. The FILMTEC BW30-365 FR1 element is suitable for use in potable water applications, whereas the FILMTEC BW30-365 FR2 element is recommended for use in non-potable water applications. Both RO elements use FilmTec's unique element construction utilizing more, but shorter, membrane leafs that yield an unsurpassed element efficiency not only in productivity but also in cleanability. The FILMTEC BW30-365 FR1 and FILMTEC BW30-365 FR2 elements have a nominal active membrane area of 365 ft^2 (33.9 m^2) and an average permeate flow of 9,500 gpd (36 m^3/d) under standard test conditions. The high surface area of these FR elements permits designs of new RO systems that meet productivity targets with fewer elements. This, in turn, means more compact systems resulting in significantly less system components and lower installation expenses. The productivity advantages of the FR elements can also be employed in the design of new systems that can produce the desired flow while operating at lower feed pressures. Also, since the FILMTEC BW30-365 FR1 and FILMTEC BW30-365 FR2 elements have the same high flow and high rejection properties as the FILMTEC BW30-365 element, they can easily be used in retrofit applications to obtain lower membrane fouling, reduce average system operating pressure, and extended membrane service life.


FILMTEC® BW30-365FR Element

In the following figures, actual performance data is reviewed for a water treatment system with conventional pretreatment at a large oil refinery consisting of multiple RO trains which experienced biofouling that necessitated in situ chemical cleaning once every 4 weeks. Cleaning was done when the differential pressure reached 60 psig per stage. A useful life of 3 years was projected for the RO elements under this operating discipline. Figure 5 shows the differential pressure over 41 days of operation with conventional RO elements and a chemical cleaning done after 34 days. FILMTEC

BW30-365 FR1 elements were installed in April, 1997 and have been in service since, having being cleaned only twice through early August, 1998. Figure 6 shows the differential pressure in the first stage of one of the trains in this field trial. Other trains show similar performance. This large oil refinery has chosen to install FILMTEC BW30-365 FR1 elements in all the RO trains of this greater than 1500 gpm (340 m^3/hr) water treatment system. To maximize time between chemical cleanings, the RO system is sanitized periodically with a non-oxidizing biocide (DBNPA).

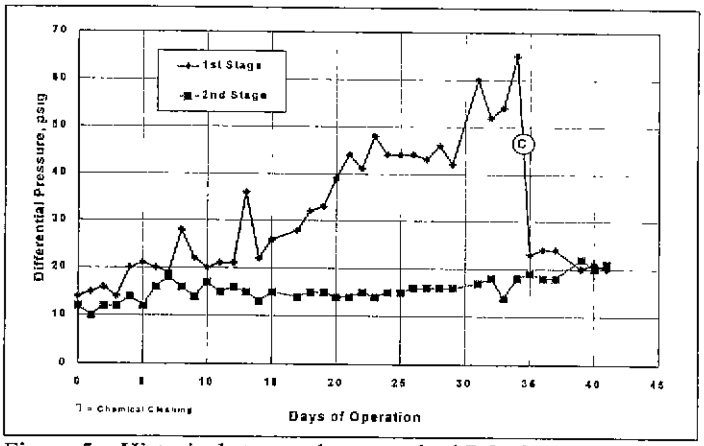


Figure 5 Historical startup data, standard RO elements differential pressure

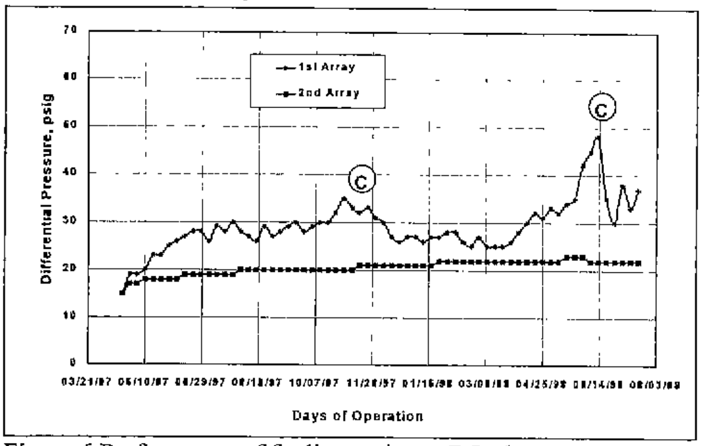


Figure 6 Performance of fouling resistant RO elements, differential pressure

No.2 (secondary stage) RO Element

The SG30LE-430 RO element was specifically developed to meet the requirements for the No.2 RO having higher rejection of lower molecular weight organic compounds and silica, and an accelerated total organic carbon (TOC) rinse down profile. Other distinguishing features/benefits of this product are:

a) TOC and salt rejections of the SG30LE membrane have been improved while maintaining high flow. Permeate flow rates of the SG30LE-430 element are shown in Figure 7 and compared with standard 8 inch elements. At the same time, the SG30LE-430 element has higher NaCl rejection at 150 psi and 2,000 ppm than the BW30LE-440 high flow element; thus, UPW systems can run with lower operating pressure while maintaining high TOC rejection.

b) FilmTec's advanced element fabrication process enables production of cleaner elements, resulting in faster TOC and resistivity rinse times.

c) Completely automated element

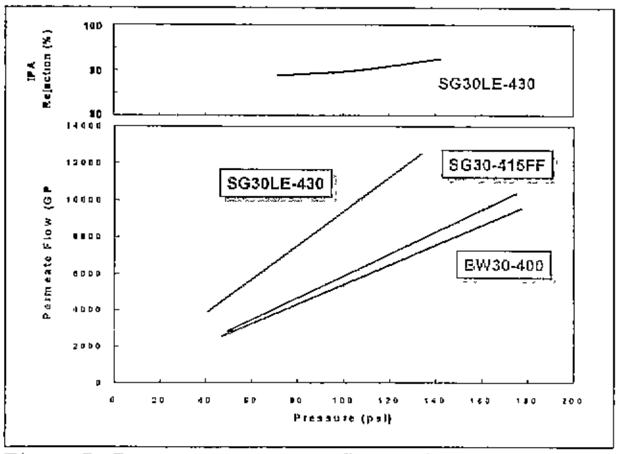
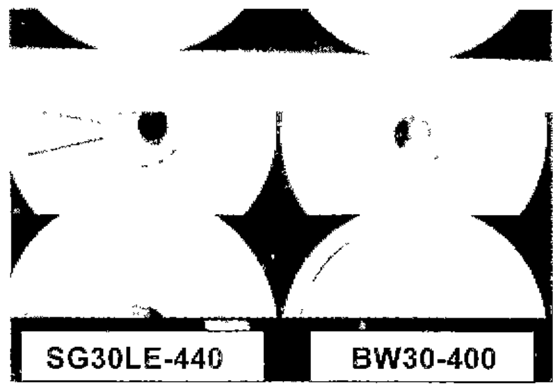


Figure 7 Pure water permeate flow and IPA rejection of the SG30LE-430

fabrication results in consistently high quality elements. This capability allows optimization of leaf length and number of leaves plus precise placement of spacer materials and glue lines. In higher flux or lower applied pressure applications, this element has an improved permeate carrier efficiency that results in a higher net driving pressure.

d) To further reduce permeate pressure loss and to ensure high flow operation in UPW applications, the product water tube internal diameter (I.D.) was increased from 1.125 to 1.5 inches. This is especially beneficial with the higher flow SG30LE-430 element, having 430 square feet of active membrane area.



Side View of BW30-400 and SG30LE-430

Rejection data for inorganic and organic species are tabulated below.

Table 4 Typical Organic Compounds Rejection

Organic Compound	MW	Rejection (%)
Methanol	32	23
Ethanol	46	40
Acetone	58	48
Isopropanol	60	92

Test conditions: feed concentration 10 ppm, 0.74 MPa (107 psi), 25 °C, pH 7, and 15% recovery

Table 5 Typical Inorganic Compounds Rejection

Feedwater Composition		SG30LE-430 PERCENT REJECTION		
Inorganic Compound	Concentration (ppm)	0.49 MPa (5.0 Kg/cm^2) (72 psi)	0.74 MPa (7.5 Kg/cm^2) (107 psi)	0.98 MPa (10 Kg/cm^2) (145 psi)
Silica	1	97.6	97.0	97.9
	10	98.3	98.7	98.9
NaCl	100			
as Na^+		99.5	99.6	99.7
as Cl^-		99.7	99.8	99.9
$MgCl_2$	100			
as Mg^{2+}		99.8	99.9	99.9
as Cl^-		99.3	99.4	99.4

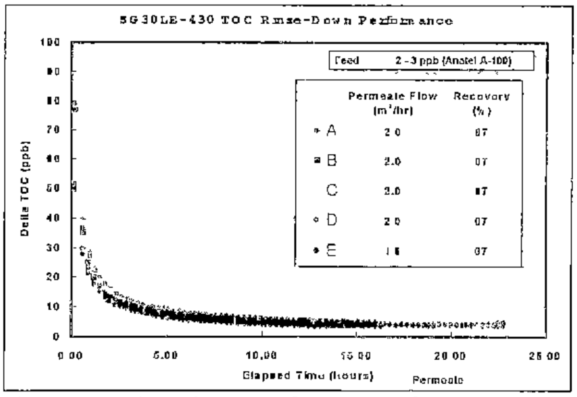


Figure 8　Rinse down performance of SG30LE-430

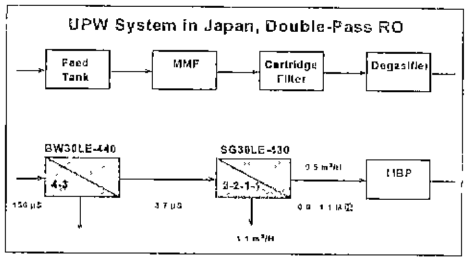


Figure 9　Double pass RO system

Figure 8 shown above illustrates the TOC rinse down properties over the first 24 hours for the SG30LE-430 element. The feedwater rinse conditions were permeate flow of 2.0 m^3/hr (12,680 gpd), temperature 25°C, 2-3 ppb TOC and 17-18 MΩ·cm resistivity. The actual performance of the SG30LE-430 element is demonstrated in the following case studies. Firstly, the SG30LE-430 was adopted in the second position of the double-pass RO system (Figure 9). In this system, to take advantage of the lower operating pressure and electric consumption, two types of low energy 8 inch RO elements were used simultaneously (i.e., the BW30LE-440 in the first pass and the SG30LE-430 in the second pass). Figure 10 shows the several performance indicators of the system. Silica concentration was lineally (logarithmically) decreased from 35 ppm to 16 ppb and the conductivity dropped to 1 μS/cm. Secondly, the SG30LE-430 was placed at the No.2 position as shown in System-I. A schematic flow diagram is shown in Figure 11. Figure 12 shows the normalized single element flow over 400 days of operation. Permeate flow is constant and maintained its initial performance. No prominent membrane fouling or performance deterioration was observed. Figure 13 shows the TOC profiles of feed and permeate. SG30LE-430 kept the permeate TOC level at 1.5 ppb even during some TOC spikes.

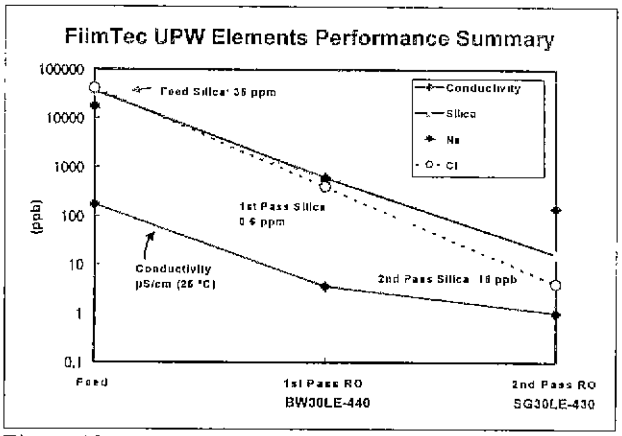


Figure 10

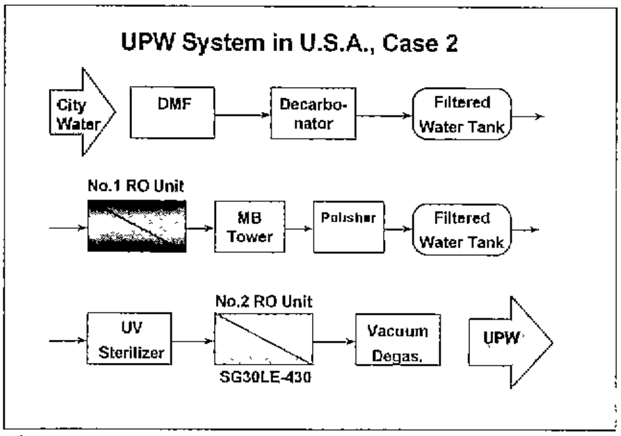


Figure 11　UPW system in the U.S.

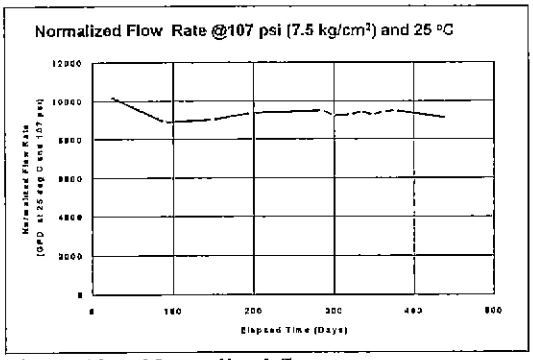


Figure 12 Normalized flow

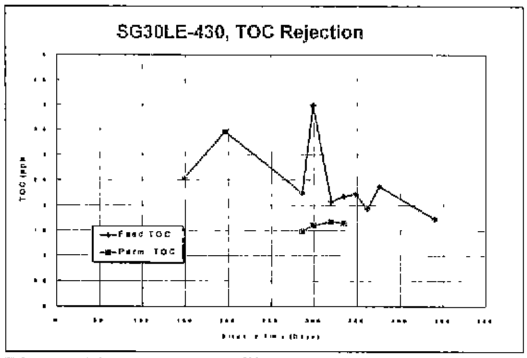


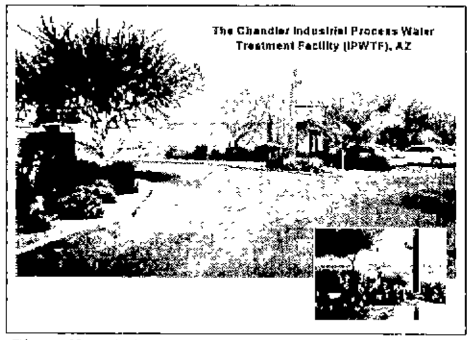
Figure 13 TOC profiles

RO Elements for the Recovery System

Due to environmental concerns (ISO 14000 series), regulations, and water shortages, the semiconductor industry has begun to recover or reclaim wastewater streams from various wet processes and reuse it as a source of UPW. In general, Japanese manufacturers and OEMs have been eager to recover the wastewater as seen in many published papers and patents:

- Organic waste: DMSO and TMAH [11-13].
- Chemical Mechanical Polishing (CMP) Slurry [14,15]
- Inorganic: HF
- Others: RO concentrate, end of pipe treatment [16]

Wastewater reclamation, however, has been paid little attention until recently in the U.S. [17]. To achieve effective wastewater reclamation, a variety of technologies such as the advanced oxidation process (AOP), biological treatment (membrane bioreactor and biofilter), and several types of membranes (MF, UF, NF, RO, ED) need to be combined. A role of RO in this application is to polish pre-treated wastewater so that the permeate can be used as a feed source for the UPW process. Here, two cases will be briefly introduced.



Chandler IPWTF

Firstly, the City of Chandler, Arizona, built a water reuse plant to attract one of the world's largest semiconductor manufactures and protect precious ground water resources[18-19]. The Chandler Industrial Process Water Treatment Facility (IPWTF) recharges the local aquifer with high-quality reclaimed water to improve the area's overall water balance and, at the same time, reduce the volume of wastewater treated at the city's conventional wastewater treatment plant. The IPWTF began operating in July 1996 with nominal

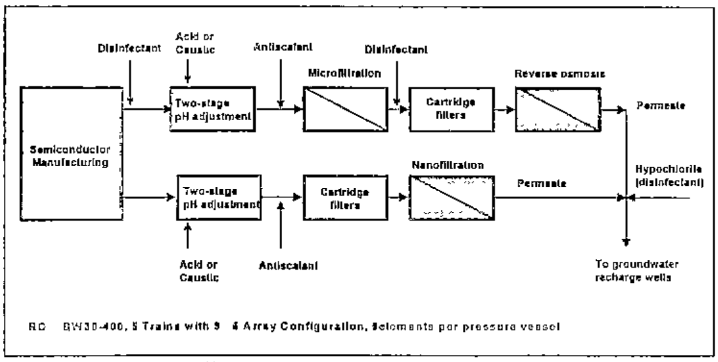


Figure 14 Chandler IPWTF process flow diagram

capacity of 8,700 m^3/d (2.3×10^6 gpd). The IPWTF features three membrane types. A nanofiltration (NF) system reclaims water from the semiconductor plant's RO reject streams. An RO system equipped with the BW30-400 element reclaims water from a mixture of process wastewater streams. An MF system, added in January 1999, pretreats water heading to the RO unit. A schematic flow diagram is shown in Figure 14. The RO process equipment includes five trains, each arranged in a two stage 9 × 5 configuration of six-element pressure vessels (PVs). The membrane based processes consistently have produced a high quality finished water that exceeds the requirements of the aquifer protection permit. The city monitors the quality of the injected treated water (a blend of RO and NF) and water from monitoring wells. Injected water concentrations are less than or about equal to those from the monitoring wells (Table 6). For a design of the Chandler IPWTF, Black & Veatch, Phoenix, Arizona, received the Superior Achievement for Excellence in Environmental Engineering award from the American Academy of Environmental Engineers in 1997 [20].

Table 6 Chandler IPWTF recharge water quality comparision

Parameter		Injected	MW-5	MW 8	Is injected less than or equal to MW?
Physical					
Conductivity	μS/cm	707	743	713	Yes
TDS	mg/L	323	401	413	Yes
Inorganic					
Sodium	mg/L	114	110	74	About same
Potassium	mg/L	<2	2.3	4	Yes
Boron	mg/L	0.26	0.28	0.21	About same
Calcium	mg/L	7	18	41	Yes
Magnesium	mg/L	1.3	3.3	8.3	Yes
Total Hardness	mg/L	23	58	137	Yes
Alkalinity, total	mg/L	78	89	101	Yes
Chloride	mg/L	130	140	126	About same
Sulfate	mg/L	33	47	53	Yes
Silica	mg/L	3.5	4.2	12.7	Yes
Nitrate as N	mg/L	0.3	1.0	1.2	Yes
Nitrite as N	mg/L	<0.1	<0.1	<0.1	Yes
Organic					
TOC	mg/L	<0.3	<0.2	<0.2	Yes (given sensitivity)

Secondly, field trial results of a FilmTec 4 inch FR Element (TW30-4040FR) will be demonstrated. At this electronic device manufacturing site, an organic waste stream is currently treated with biological treatment, continuous microfiltration and reverse osmosis as shown in Figure 15. Treated water is reused at the site. Major contaminants causing RO membrane fouling are bacteria and residual organic solvents used at this specific site. During the course of evaluating various process, an OEM tested several types of RO elements under the following conditions:

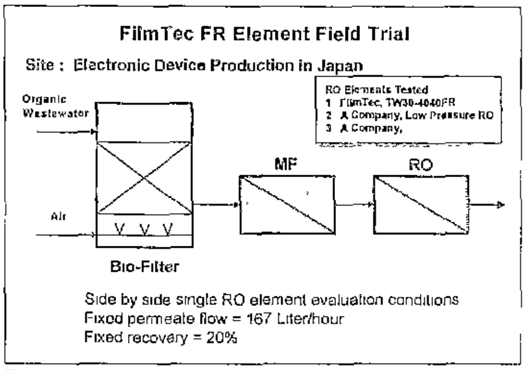


Figure 15 Wastewater reclamation

- Element Evaluated :
  FilmTec TW30-4040FR
  Company A Element A, Ultra Low Pressure Type
  Company A Element B
- Permeate flow rate was set to 167 l/min (44 gpm) for each element
- Element recovery was set to 20 %
- Temperature was ambient ranging 22 - 25 °C
- Cleaning solution is NaOH. pH of cleaning solution was controlled at pH 11-12. Cleaning temperature was set to about 40 °C. Alkaline cleaning was conducted 8 times during the trial

Feed water was taken via a branch pipe from the existing RO unit. Consequently, the cleaning solution came through the trial elements when the existing RO plant required cleaning. Three PVs were placed in parallel adjacent to the existing RO unit. The trial started on Feb 13, 1998 and ended on Sep 29, 1998. (7 months). The trial was carried out at fixed permeate flow and fixed element recovery. Main parameters measured were feed pressure, differential pressure (delta P) and salt rejection. Salt rejection presented here is based on conductivity of the feed and permeate. Figure 16 and 17 show the profile of feed pressure, delta P and salt rejection throughout the entire trial runs. An increase in delta P was considered to be mainly due to biological fouling. The TW30-4040FR element showed the best performance for minimal delta P increase (i.e., the delta P of the FR element stayed the lowest throughout the trial). The delta P increase rate was the lowest for the FR element even when all three elements experienced severe increases during March-April timeframe. An increase in feed pressure was attributed to biological and organic fouling. Major organic contaminants are organic solvents and surfactants coming from the process. The highest feed pressure increment among the tested elements was observed for the low pressure type RO element A. In the case of biofouling, the operating pressure of these elements was more or less the same. In terms of salt rejection, there was no significant difference observed for all the tested elements. Salt rejection at start-up was 99.0 – 99.2%, whereas at the end of the test, salt rejection was still 99.1 %.

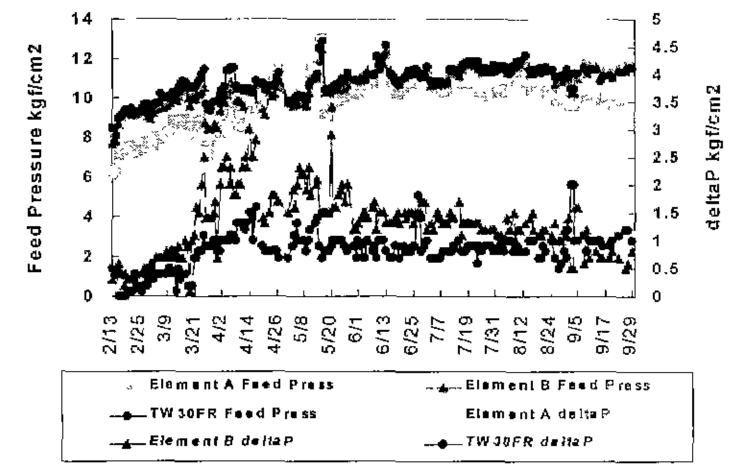


Figure 16 Feed pressure and delta P, Feb-Sep, 1998

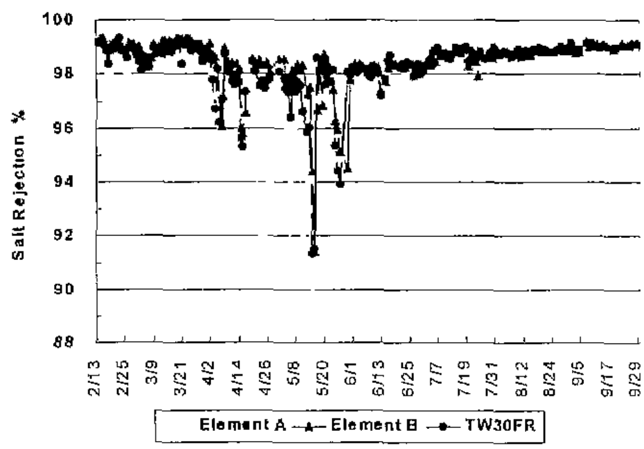


Figure 17 Salt rejection, Feb-Sep, 1998

Conclusion

In this paper, some advancements in RO technologies for UPW production and wastewater reclamation have been described. It is anticipated that membranes in general, and RO in particular, will continue to play important roles and provide effective and highly optimized solutions to purify and recovery water while minimizing UPW production costs when integrated with other advanced technologies such as AOP, membrane bioreactor, ion exchange, EDI, and so on.

Acknowledgements

The authors would like to express our appreciation to Rick Mulligan, Dow Chemical Canada Inc., for his review and assistance in preparing the manuscript.

References

1. R. Ikegami, Clean Technology, 1995 No.9, 50 (1995)
2. Ultra Clean Technology 9, Supplement 1, IV-2 (1999)
3. Y. Motomura, Membrane Journal (Korea), 6(3), 141 (1996)
4. Cho Junsui no Kagaku, Realize Inc., K. Yabe, pp. 141 (1990)
5. P. Rychen and J. Leet, ULTRAPURE WATER, Feb., 36 (2000)
6. L. Fleming, T. Prato, L. Zhang, and B. Hernon, IWC-99-28 (1999)
7. D. McBride and D. Mukhopadhyay, ULTRAPURE WATER, May/June, 24 (1997)
8. D. Mukhopadhyay and S. Whipple, ULTRAPURE WATER, October, 21 (1997)
9. S. Chino, I. Sugiyama, J. Holloway, and D. Mukhopadhyay, IWC-99-66 (1999)
10. Handotai Sangyo Shinbun, February 23 (2000)
11. FilmTec Brochure, 609-00261, FILMTEC Fouling Resistant Membrane Elements - Winning The Battle Against Biofilm Formation
12. T. Muratani, Sharp Giho, No.73, 22 (1999)
13. M. Tokuyasu, T. Jizaimaru, and M. Sato, Ultra Clean Technology, 11(2), 94 (199)
14. S. Kiryu, Clean Technology, 9(2), 18 (1999)
15. R. W. Junnier, S.K. Dentel, A. Ramana, and D. Thuresson, Proc. Mid-Atl Ind. Hazard Waste Conference, vol.30, pp.369 (1998)
16. Irv B. Morrow and D.F. Turner, ULTRAPURE WATER, March, 33 (1999)
17. D. Lopez and T. Iraclidis, Proc. 1999 Semiconductor Pure Water and Chemicals Conference, pp.197 (1999)
18. A.R. Shah and J.H. Ploeser, J. AWWA 91(8), 58 (1999)
19. S. Freeman and G. Harvey, Industrial Wastewater, Sept/Oct, 30 (1999)
20. S. Freeman and G. Harvey, WEFTEC'98, Industrial Issues and Treatment Technology Symposium: Industrial Application of Membrane Technologies, Session 74, pp.611 (1998)
21. http://www.enviro-engrs.org/award97.htm