Desalination and Water Treatment
www.deswater.com

3 (2009) 99–110

Production of high-purity water by membrane processes

Rajindar Singh

Siemens Water Technologies Corp., Colorado Springs, CO, USA
*Tel. +1 719 265 6213; email: rsinghiwt@hotmail.com**

Received 7 July 2008; Accepted 18 February 2009

ABSTRACT

Membrane processes, especially reverse osmosis, have played a major role since the early 1990s in the production of high-purity water for power, pharmaceutical, beverage and semi-conductor industries, and will continue to play a critical role in the growth of this water sector to meet ever-increasing demands of water purity, especially in microelectronics applications. Power plants are the single largest user of high-purity water. Membrane processes are also being increasingly used in the reduction of wastewater, water reclamation, recycle and conservation, and environmental pollution control. The production of high-purity water and ultra-pure water for the above-mentioned industries is described in detail. Recent advances, new processes and membrane development such as high performance systems, hot water sanitisation and shrinking line width in microelectronics devices to meet critical requirements are discussed.

Keywords: RO; Ion exchange; EDI; Power; Microelectronics; USP water; HERO™

1. Introduction

High-purity water (HPW) includes ultra-pure water (UPW) and pure water. The definition of UPW differs from pure water or deionised water. Generally speaking, pure water refers to water that meets the specific needs of a given process or product, for example, in pharmaceutical applications removal of organisms or pyrogenic substances is of utmost importance, whereas in textile washing removal of hardness, iron and manganese is essential. UPW refers to water that is free of "all" impurities. Power plants are the single largest user of high purity water used for steam generation. High-purity water is required to protect the boiler tubes and turbines from corrosion, scale formation and structural defects [1]. Other industrial users of high- purity water include microelectronic, pharmaceutical, beverage and research laboratories. The microelectronics UPW requirements (resistivity >18.2 MΩ-cm) are the most stringent of all the water production requirements in the general industry. HPW (resistivity 1–10 MΩ-cm) is also used in the metals finishing industry to rinse the metal surface clean of any dirt or chemicals prior to the plating operation.

The water source of most HPW plants is city water or municipal water that has undergone pre-treatment. The raw water source may be well water, ground water, or surface water with total dissolved solids (TDS) content in the range of 100–1000 mg/L. A typical HPW plant consisting of various unit operations is shown in Fig. 1. The plant is designed to supply up to 80 m^3/h deionised (DI) water to the point-of-use (POU) with resistivity >16.0 MΩ-cm. The reverse osmosis (RO) unit is the pivotal process virtually in all HPW plants. RO processes may be a single-pass or double-pass as shown in Fig. 2, depending on the product water quality requirements. In the last 15 years, RO has virtually replaced demineralisation by two-bed (cation–anion) ion exchange prior to mixed-bed ion exchange (MBIX) polishing because of higher operating costs of IX systems and disposal of chemical wastewater, and increased reliability and performance of

---

*Present address.

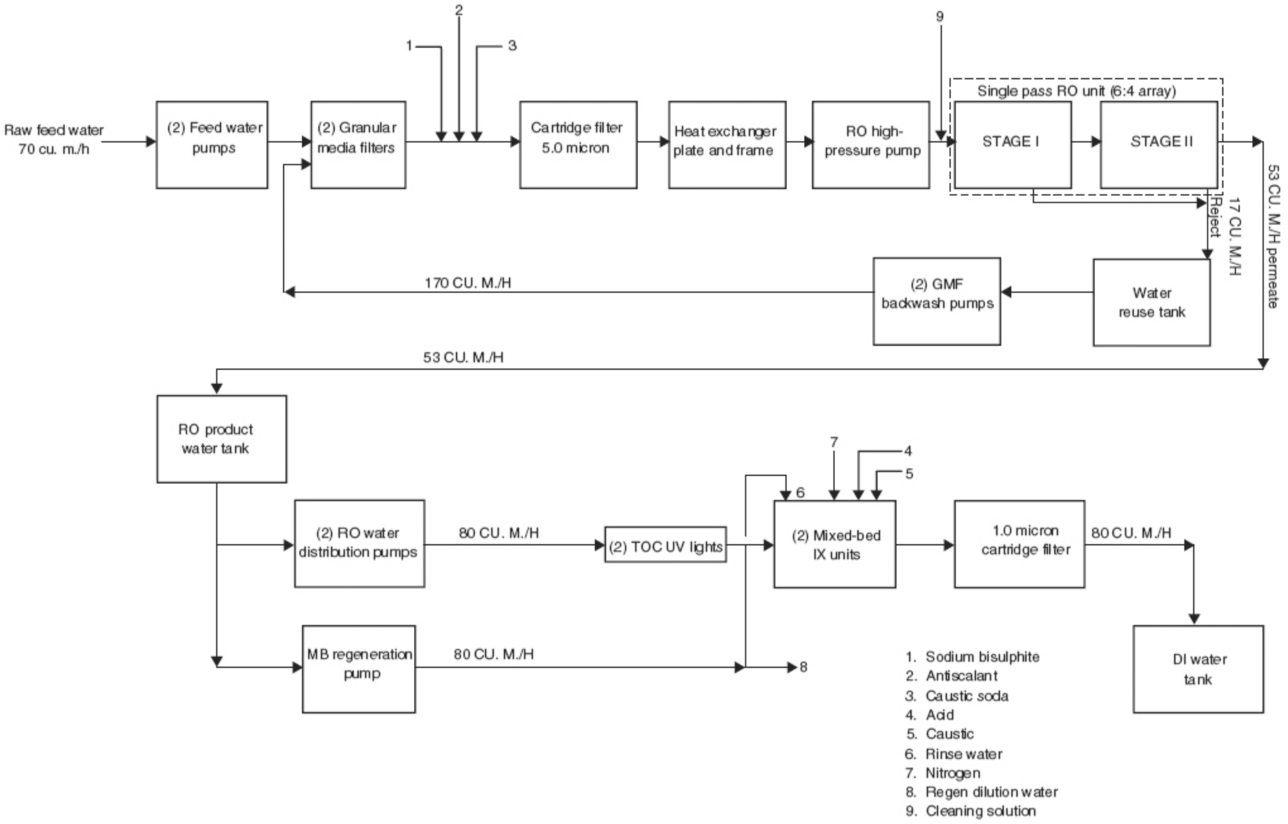

Fig. 1. Process flow diagram of a typical high-purity water plant consisting of pretreatment, RO and on-site regenerable MBIX systems. RO reject water is used to backwash the media filters. RO product water tank receives RO permeate and high-purity water back from the POU distribution loop (not shown).

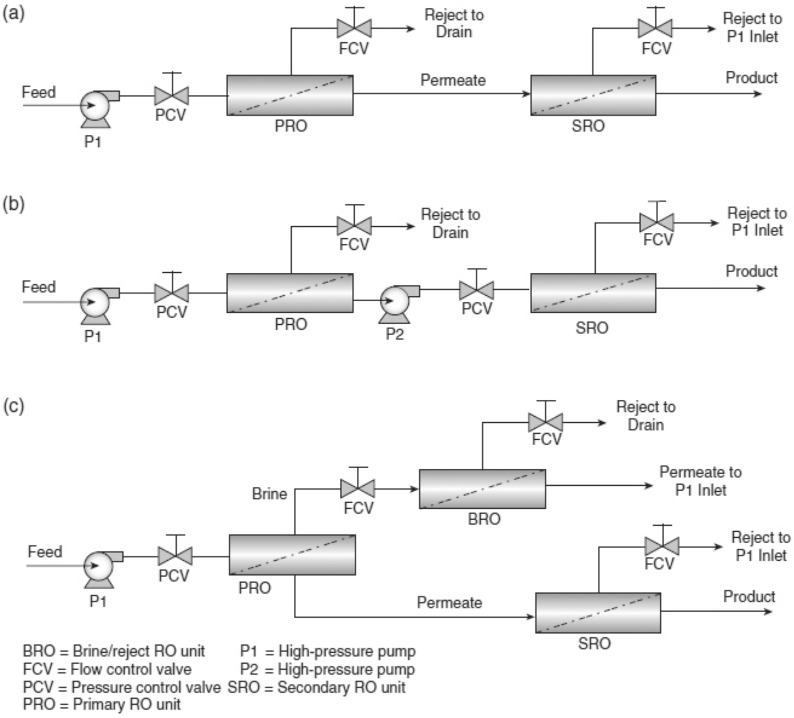

Fig. 2. RO system process flow schematics: (a) two-pass RO with-out inter-stage pressure boosting; (b) two-pass RO with inter-stage pressure boosting; and (c) two-pass RO with RO reject recovery.

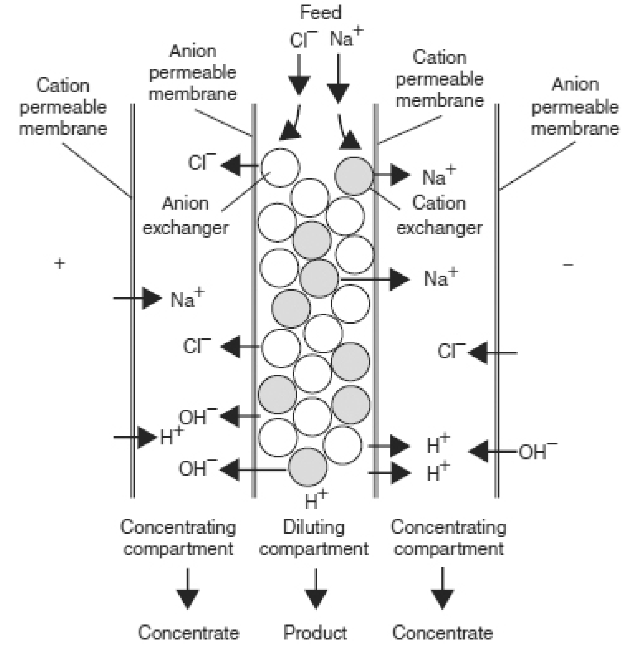

Fig. 3. Schematic diagram of an EDI cell showing cation resin and anion resin beads.

RO systems. RO treatment is more cost effective than ion exchange especially when the feed water TDS is greater than 350 mg/L since the cost of ion exchange is directly proportional to the concentration of ions in feed water [2].

Increasingly, electrodeionisation (EDI) is either complementing or replacing mixed-bed ion exchange (MBIX) deionisers depending on the quality of product water required [3,4]. A schematic diagram of an EDI cell is shown in Fig. 3. As in the case of electrodialysis, direct current (DC) is the driving force for removing ions from the feed stream. In addition, EDI incorporates continuous regeneration of the cation and anion ion exchange resins. This process produces water of consistent quality without the problems and costs of regenerating IX resins and waste neutralisation. Hybrid RO+EDI systems use 95% less chemicals than ion exchange. HPW of up to 18.0 MΩ-cm resistivity can be produced with an EDI system using RO permeate of conductivity <1.0 μS/cm as feed water with product water recoveries in the 90–95% range [%Recovery = (Product flow rate/feed flow rate) × 100]. Further, EDI is more effective than MBIX for removing weakly ionised ions boron and silica. Typical feed water specifications for EDI modules are given in Table 1 [3].

Several operational parameters can help maximise the recovery of EDI units:

- Use softeners instead of anti-scalant for RO pretreatment — lower hardness leakage through the RO and less chance for upsets allows operation at higher recovery;
- Lower the alkalinity and CO_2 loading to the EDI by operating the RO at high pH. This generally requires softened RO feed water;
- CO_2 is transferred to the EDI reject. When the reject is recycled to the RO inlet, raising the pH of RO feed water is required when the CO_2 level is high.

Various HPW systems and processes as well as recent developments are discussed in this paper.

Table 1
Typical feed water specifications for EDI units

Parameter	Value
Hardness, ppm, as $CaCO_3$	<1
Silica, ppm, as SiO_2	1
Heavy metals, ppb	<10
Chlorine, ppb as Cl_2	<20[a]
TOC, ppb as C	<500
Temperature, °C	5–45

[a] Non-detectable.

2. Boiler water treatment

Power plants require high-purity make-up water for producing steam to drive turbines and generate electricity. In thermoelectric power plants steam is generated at a pressure of 40 to 200 bar g with the power generation efficiency increasing with steam temperature and pressure. HPW needs to be devoid of contaminants such as sodium, chloride, or silica in the steam [1] since increased volatility of salts and silica at high temperatures and pressures, results in, for example, silica carryover into the steam phase. When the steam pressure is reduced in low-pressure turbines, silica precipitates on the turbine blades resulting in corrosion that can weaken and damage the turbines. Organic impurities decompose in the steam-water circuit to produce carbon dioxide and organic acids including acetic, formic, glycolic that can cause corrosion [4]. The make-up water quality requirements vary, depending on the type of boiler system, and are published by many authorities such as the American Society of Mechanical Engineers (ASME, 1994). The typical make-up water specifications for high pressure boilers are given in Table 2.

Steam generation in chemical process plants such as oil refineries, pulp and paper production, and food processing, on the other hand, does not require water of the same purity since steam is used for process heating. Instead, low pH corrosion of the condensate return lines is a problem. This is resolved by removing bicarbonate and carbonate alkalinity from the feed that prevents the formation of carbon dioxide and its passage to the condensate lines [1]. Water usage in non-conventional

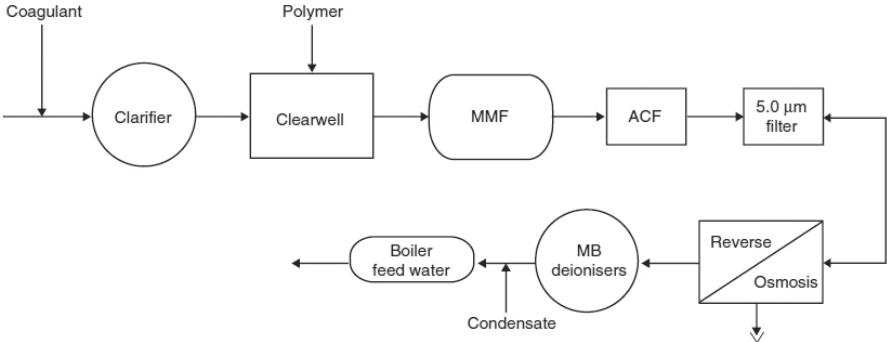

Fig. 4. Typical boiler feed make-up water treatment process flow schematic consisting of the pretreatment section, RO system and MBIX deionisers (or EDI units). Condensate return line is also shown.

Table 2
Typical make-up water specifications for high pressure boilers

Parameter	Value
Conductivity, μS/cm at 25°C	<0.1
Silica, ppb	5–10
Sodium, ppb	2–5
Chloride, ppb	2–5
Sulphate, ppb	2–5
TOC, ppb	<100

power plants such as fuel cells is also markedly different as DI water is required for producing hydrogen. Hence, water of conductivity ~1.0 μS/cm is adequate [5].

A typical make-up water process flow schematic diagram for producing HPW for steam generators is shown in Fig. 4. In order to minimise the overall water consumption, the make-up is combined with purified condensate steam as shown in the figure to provide boiler feed water. In the case of utility boilers, most of the steam is usually returned as condensate, and less than 5% make-up water is required. However, for some industrial cycles there is little or no return condensate, so up to 100% make-up is necessary. Since condensate has been purified by prior evaporation, in many cases it can be directly mixed with the make-up water to supply it to the boiler as shown in the figure. Most high-pressure boilers (>60 bar g) deploy a condensate polishing system to remove the dissolved impurities and filter out the suspended solids such as corrosion products of iron and copper, and occasionally organic material [6]. Sodium cycle strong cation ion exchange or MBIX are generally used to remove these contaminants depending on the level of purity required.

The contaminants in the feed water get concentrated in the boiler. Hence, a small portion (<5%) of the water in the boiler is drained (blowdown) to maintain the water quality. High-purity make-up water is fed to the boiler to make-up for losses due to blowdown, evaporation and system leaks.

Case study. It takes about 2 m^3 of HPW to produce 1 MWh of electricity. With increasing focus on water conservation, and tighter pollution control regulations, power plants have to rely on reclaimed water in many cases. Reclaimed water generally means treated effluent from municipal wastewater treatment plants. The process flow schematic of one such water treatment plant producing HPW from reclaimed water at a 550-MW combined cycle power plant in New Jersey, USA, is illustrated in Fig. 5 [5]. Waste treatment effluent is filtered and most of it flows to the cooling towers. A small portion of the filtered water flows to the multimedia filters @ 114 m^3/h. The media filter effluent is pumped through the first-pass RO unit. More than 98% of dissolved ions are removed. The RO permeate flows through a bank of membrane degasifiers, which remove dissolved carbon dioxide to reduce the ionic load on anion resins of MBIX polishers downstream. Dissolved oxygen is also removed since oxygen in boiler water having traces of chlorides or solids can cause pitting corrosion of metal surfaces [4].

The second-pass RO unit reduces the TDS of water to 1 mg/L, and is polished by MBIX to produce deionised water required for the boiler. The membrane system supplies 70 m^3/h HPW to the steam generator with conductivity <0.2 μS/cm and silica <20 μg/L. Reusing reclaimed water reduced the power plant's dependence on potable water with savings of nearly 2200 m^3/day of city water to the local community.

3. Microelectronics rinse water

UPW is used in the microelectronics industry for applications such as rinsing and washing wafer surfaces between chemical etching steps and immersion lithography [1,7,8]. Why is water of extremely high quality required in the washing process of the semi-conductor industry? A simple explanation is that unless UPW is used, short-circuiting is a real risk, resulting in lower yields of the wafers. In 1984 the level of water purity was based on microcircuits with 2.0 μm line spacings. By 1995,

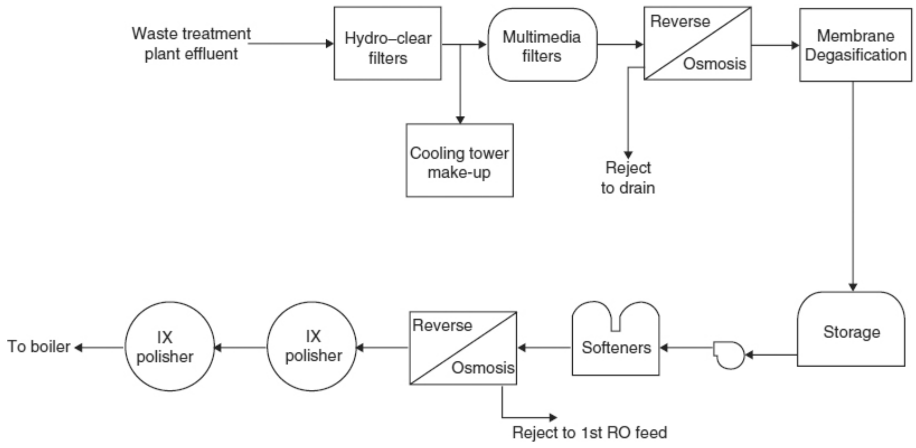

Fig. 5. Process flow schematic for power plant boiler water production from a municipal wastewater effluent plant. System consists of a wastewater filtration system, double-pass RO system, membrane degasifiers, IX softeners and MBIX polishers.

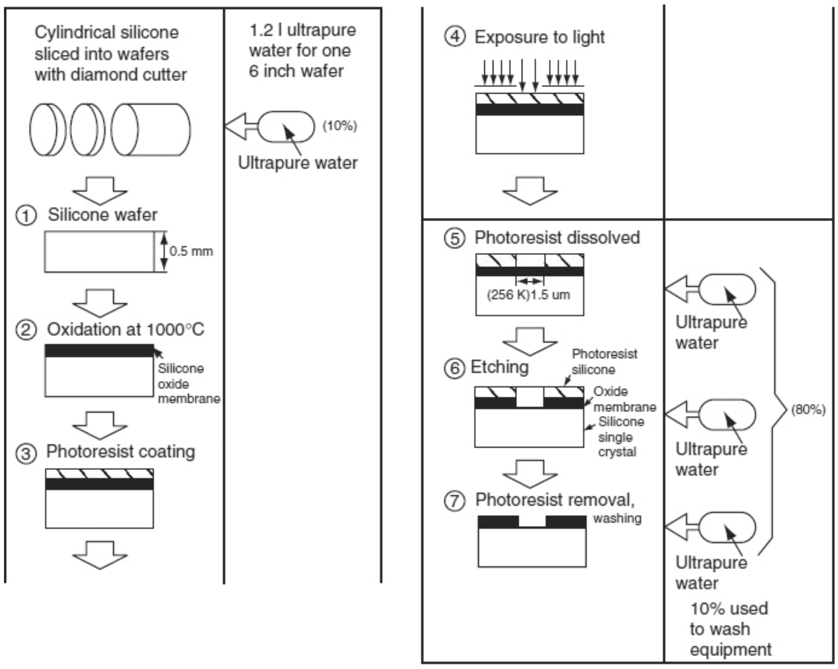

Fig. 6. Ultrapure water applications during manufacture of a very large semiconductor integrated (VLSI) wafer.

the spacing had decreased to 0.3 μm. A new requirement for line width size is 0.03 μm for certain uses [8]. The amount of UPW required to produce one 150-mm wafer is about 4–5 m^3. A large semi-conductor fabrication facility typically uses 160 m^3/h of UPW. A method of manufacturing a VLSI wafer is shown in Fig. 6 [5] with four steps required for rinsing with UPW. Current UPW requirements for 300-mm wafer producing fabs are typically as follows: resistivity >18.2 MΩ-cm, TOC <0.5 ppb, silica <0.1 ppb, boron 10–50 ppt and particle count (0.05 μm) <200/L.

Case study. The hybrid membrane plant described in this case study provides 15 m^3/h UPW to a fab manufacturing facility. The UPW plant consists of a pretreatment section, a double-pass RO system, and a post-treatment section similar to the one shown in Fig. 7 [5]. The water requirements are given in Table 3. Raw (city) feed water is surface water with TDS = 492 mg/L consisting of the following major constituents: bicarbonate, 183 mg/L; chloride, 61 mg/L; sulphate, 83 mg/L; silica, 14 mg/L; potassium, 3 mg/L; sodium, 147 mg/L.

City water is pumped to the carbon filter at 13 m^3/h and 5 bar G. Activated carbon media remove organic compounds and free chlorine from water. The dechlorinated filtered water flows to the IX softener at 13 m^3/h. The softener containing strong acid cation IX resins reduces the total hardness to <2 mg/L by removing calcium, magnesium, barium and strontium ions, thereby,

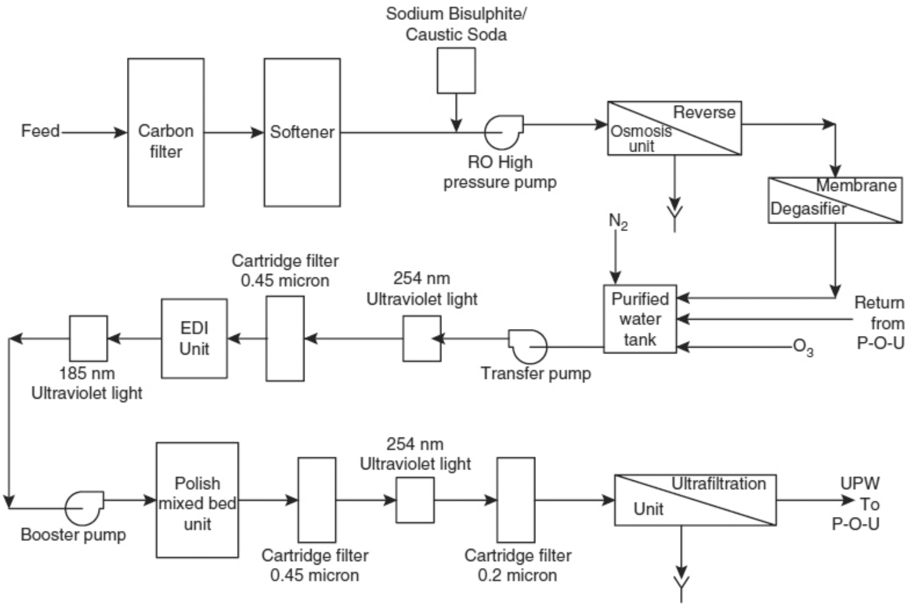

Fig. 7. Process flow schematic of a typical water treatment system for producing UPW used in microelectronics manufacturing. A portion of the UPW recycles from the POU to the purified water tank to ensure there is no stagnant water in the distribution loop.

Table 3
Typical HPW specifications for microelectronics manufacturing

Parameter	Value
Resistivity, MΩ-cm	≥18.2
Particles, count/L	
>0.2 μm	<10
>0.5 μm	<1
Bacteria, cfu/100 mL	<1
Total organic carbon (TOC), μg/L	<2
Dissolved oxygen, mg/L	≤2
Calcium, μg/L	<2
Cations (each), μg/L	<0.2
Chloride, μg/L	<0.1
Anions (each), μg/L	<0.2
Silica (dissolved), μg/L	<3

preventing scaling of RO membranes by sparingly soluble salts, e.g. calcium carbonate.

Softened water flows to the RO pre-filter at 13 m^3/h. The RO pre-filter contains 5.0 μm (nominal pore size) polypropylene dead-end cartridges for removing resin fines, particles and complexed colloids, thereby, protecting the RO membranes from particulate fouling. The pretreated water is transferred by the high-pressure RO pump to the first-pass RO membrane unit at 16 m^3/h (13 m^3/h make-up + 3 m^3/h second-pass reject recycle) and 35 bar g (see, for example, Fig. 2b). The first-pass RO unit is a three-stage (2:1:1) array producing 12 m^3/h permeate at 75% recovery (12 m^3/h product ÷ 16 m^3/h feed). A schematic of a typical three-stage array is shown in Fig. 8.

The permeate flows to the second-pass RO unit at 12 m^3/h, and the reject flows to the drain at 4 m^3/h. In order to conserve water, 50–80% of the reject water can be recovered using a brine recovery RO and/or nanofiltration (NF) unit similar to the one shown in Fig. 2c [9].

The thin film composite (TFC) polyamide RO membranes (20 cm diameter × 100 cm long spiral-wound elements) reduce the total dissolved solids (TDS) from 492 mg/L in feed water to less than 3 mg/L in product water at an average rejection of 99% where %Rejection = [(feed concen.−permeate concen.)/feed concen.]×100. The second-pass RO unit is a two-stage (1:1) array designed to produce 9 m^3/h permeate at a recovery of 75% (9 m^3/h product ÷ 12 m^3/h feed). The reject flows back to the first-pass RO pump inlet at 3 m^3/h. The second-pass TFC membranes produce water with conductivity less than 1.0 μS/cm.

The double-pass RO system produces 9 m^3/h permeate at an overall product water recovery of ~69% (9 m^3/h product ÷ 13 m^3/h make-up feed). A caustic soda solution is injected into the second-pass feed water line (first-pass permeate) to raise the pH from 5.4 to 8.0. At alkaline pH, free CO_2 gas in water is converted to bicarbonate ions, which are easily rejected by the RO membrane.

RO product water flows through a 185-nm rated ultraviolet (UV) unit at 9 m^3/h and is degasified in

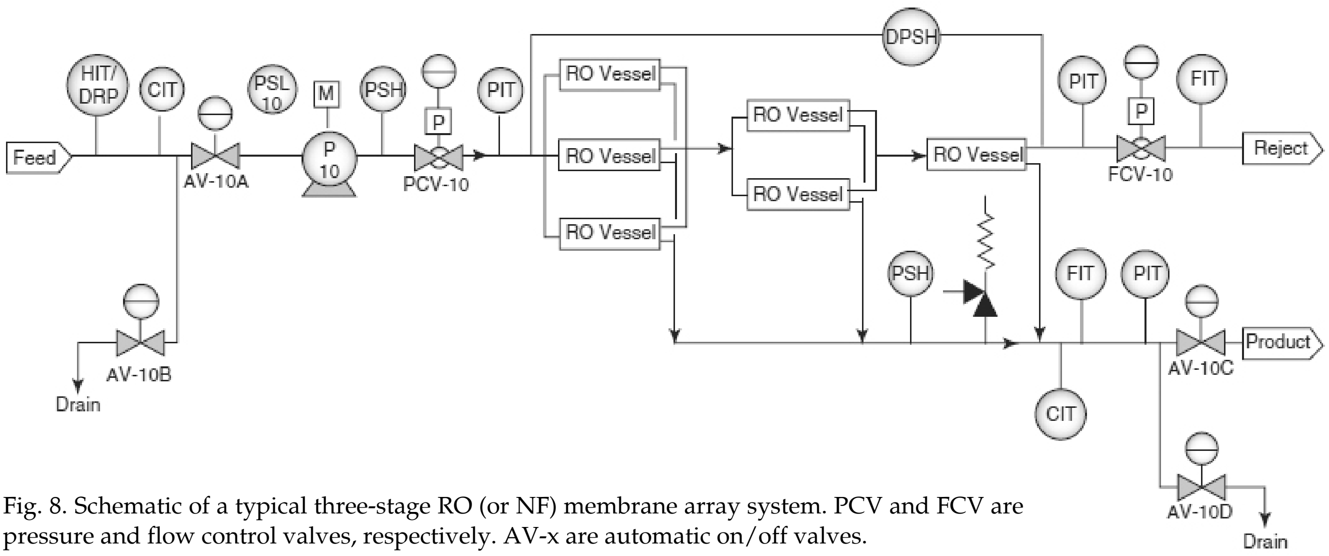

Fig. 8. Schematic of a typical three-stage RO (or NF) membrane array system. PCV and FCV are pressure and flow control valves, respectively. AV-x are automatic on/off valves.

membrane contactors (MC). The UV light reduces the total organic carbon (TOC) in water as discussed later in this section. The three MC units operate in series as shown in Fig. 9, and remove dissolved gases from water with nitrogen flowing in the permeate side as sweep gas. Degassed water flows at 9 m^3/h to the primary and polishing MBIX deionisers operating in series. The deionised (DI) product water resistivity should be >16.0 MΩ-cm.

Irradiation with 185 nm UV light is very effective in destroying residual organic matter (TOC) that is not removed by RO membranes, and thus reduces the organic load on anion resins in the MBIX deionizers downstream. The UV units also render more than 90% bacteria ineffective. This is especially important since the MB units operate at neutral pH; they are capable of supporting bacteria proliferation.

The DI water flows through a 1.0-μm (absolute pore size) microfilter. The polysulfone dead-end cartridges trap IX resin fines before the purified water flows to the DI water storage tank. The DI tank also receives water back from the distribution loop at 8 m^3/h (max.). The DI tank is provided with a high efficiency particulate air filter and a nitrogen blanket to prevent atmospheric contamination and increase in conductivity due to absorption of CO_2.

The DI water is further polished to meet the specifications given in Table 3. Water is transferred from the DI water storage tank to a TOC destruct 185 nm UV unit at 17 m^3/h used for oxidation of organic matter to a carboxylic acid or CO_2. Other oxidation processes include hydrogen peroxide and ozone. Direct feed of ozone (see Fig. 7) followed by irradiation with 254 nm UV light is very effective in reducing TOC levels to <5 ppb [1].

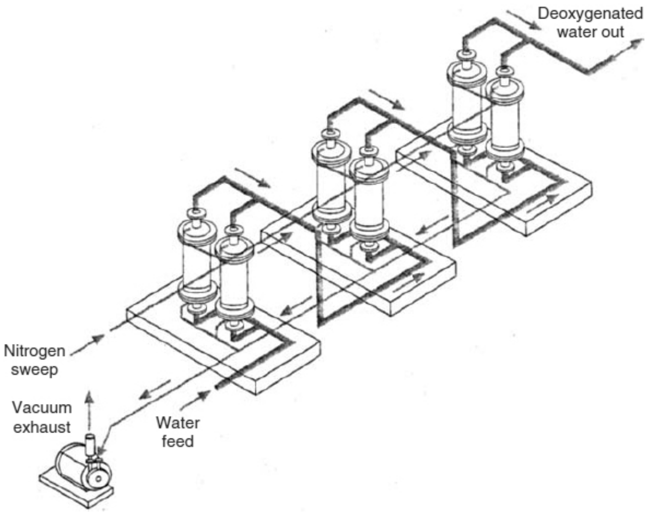

Fig. 9. Membrane contactor (MC) system for degasification. Typical operating conditions: water flow rate, 55 m^3/h at 25°C; feed and outlet O_2 concentration, 5 ppm and <10 ppb; MC, 25 cm diameter × 70 cm long; 3 series × 2 parallel array; vacuum, 700 mm Hg; N_2 sweep flow rate, 1900 cm^2/min.

Decomposition of organic carbon by TOC UV light results in a drop in resistivity of pure water. The UV effluent is, therefore, further polished; water flows through a bank of five parallel MB ion exchange polishers producing UPW with resistivity = 18.2 MΩ-cm. The MBIX product water flows through a bacteria reducing 254 nm UV unit to deactivate bacteria and destroy any traces of organic matter. The irradiated water flows through four parallel UF elements. The polysulfone UF membranes (MWCO of 10,000 Dalton) act as final barrier for reducing the particle count.

The UPW is monitored continuously for silica, dissolved oxygen, particle count, TOC and resistivity before it flows to the POU at 15 m^3/h. Up to 8 m^3/h of the POU supply water recycles to the DI water tank to ensure there is no stagnant water in the distribution loop. All piping used in the polishing loop is polyvinylidene fluoride (PVDF), which has a lower coefficient of friction than stainless steel. Low friction and high flow velocities of 3–5 m/s in the UPW distribution loop prevent microorganisms (bacterial and fungi) from growing and adhering to the pipe walls.

4. USP grade water

The United States Pharmacopoeia (USP) has three general specifications for water quality that are applicable to medical and pharmaceutical uses, namely, USP water for injection" (WFI), USP purified water" and "drinking water" [10]. Sterile WFI is the most demanding and expensive to produce. It is used for the final purification steps of parenteral products or when it is cost effective. Standard USP PW (sterile purified water) water specifications for pharmaceuticals manufacturing are: conductivity <1.3 μSiemens/cm at 25°C; pH 5.0–7.0, TOC level <500 ppb, and bacteria count <10 cfu/100 mL. USP WFI also requires that the endotoxin level is <0.25 EU/mL. The types of water recommended for various pharmaceutical applications and operations are given in Table 4 [11]. WFI water is not recommended for laboratories since WFI water can contain metals leached from stainless steel piping resulting in higher conductivity even though it is generally within the USP requirements.

Traditionally, pharmaceutical plants used evaporation stills to obtain water free of organisms and pyrogens. Currently when large amounts of USP purified water but only small amounts of WFI are required, RO+EDI system is used for the production of the USP purified water, and a small distiller for the production of the WFI as shown in Fig. 10 [12]. The European Agency for the Evaluation of Medicinal Products has designated a new grade of water called "Highly Purified Water", to be used "for the preparation of products where water of high biological quality is needed except where WFI is required" [11]. This type of water is generally produced using a double-pass RO followed by deionisation and MF or UF filtration.

Case study. The water treatment plant supplies 9 m^3/h of USP purified water to a drug manufacturing facility where it is used in the preparation of topical and oral medications. The plant, similar to the one shown in Fig. 10, consists of a pre-treatment section, a double-pass RO system with an inter-pass pressure booster pump, and a post-treatment section. Raw (city) feed water is surface water at pH 7.6 and TDS = 140 mg/L consisting of the following major constituents: bicarbonate, 19 mg/L; chloride, 19 mg/L; sulphate, 47 mg/L; silica, 7 mg/L; calcium, 9 mg/L; magnesium, 4 mg/L; sodium, 30 mg/L.

Table 4
Recommended USP water quality by application

Application/operation	Water quality
Media preparation	USP purified
Seed and production bioreactor batching	USP purified
Cell or mycelia separation	USP purified
Cell or mycelia washing	USP purified
Buffer preparation	USP purified
Diafiltration	USP purified
Column chromatography (pre-columns)	USP purified
Column chromatography (final column)	WFI
Viral clearance	USP purified
Final filtration	WFI
Lyophilisation	WFI
Cleaning-in-place (initial)	Non-compendial or previous final rinse
Cleaning-in-place (final)	USP purified
Glassware and equipment washer (initial)	Non-compendial or previous final rinse
Glassware and equipment washer (final)	USP purified
WFI still	USP purified or softened RO reject
Clean steam generation	USP purified
Housekeeping	Non-compendial

City water flows to multimedia filters operating in parallel at 18 m^3/h and 3–4 bar g. Multimedia filtration improves clarity by removing particles from coarse sediment down to 10.0 μm, and reduces turbidity to <1.0 NTU, thereby protecting the equipment downstream from particulate fouling. The filtered water flows to duplex IX softeners at 18 m^3/h. Water softening by ion exchange is required to remove hardness ions and protect the RO membranes from scaling by sparingly soluble salts. Antiscalants are not recommended in USP water production plants. The softeners operate in series with the primary unit removing most of the hardness ions and the polishing unit removing the remaining hardness ions. The softeners produce water with hardness <1 mg/L. The softeners shown in Fig. 10 are two units operating in parallel.

Softened water flows to a holding tank at 18 m^3/h. The tank also receives up to 9 m^3/h EDI polished product water when the RO/EDI system is in re-circulation mode as discussed below. The tank provides storage for pretreated water and for recycled water thereby preventing various upstream and downstream equipment from cycling on/off frequently. Thus, the tank allows the RO/EDI/UV system to operate in a continuous mode during periods when the purified water storage tank is full. The tank is provided with 0.2 μm hydrophobic vent

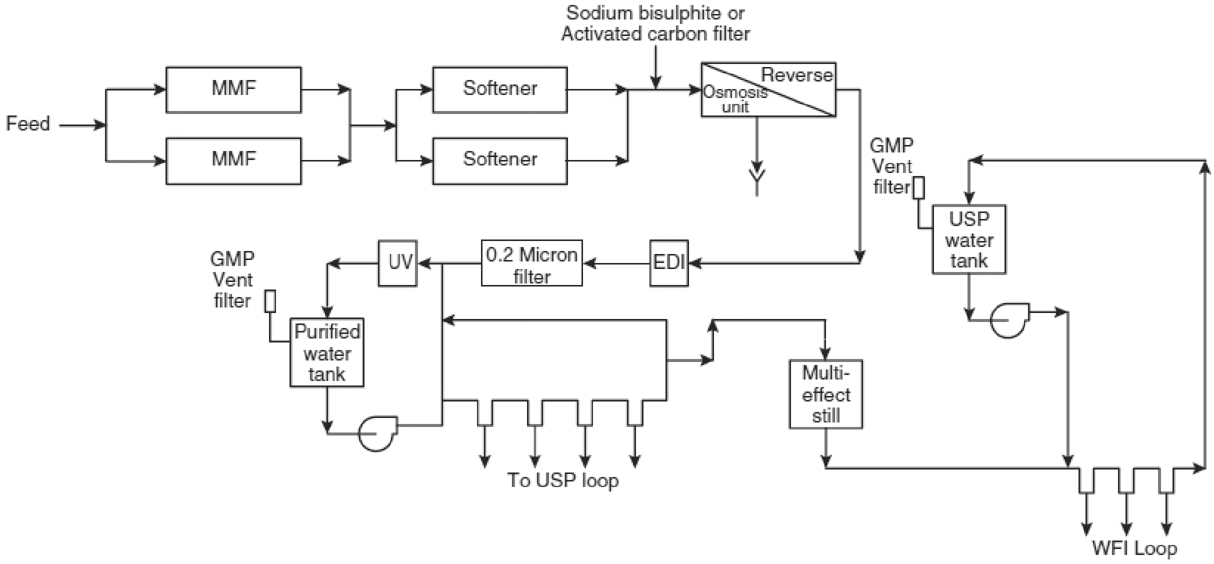

Fig. 10. Process flow schematic of a typical HPS system for producing USP water and WFI in pharmaceuticals manufacturing. The product water from the EDI unit typically re-circulates to a break tank (not shown) upstream of the RO unit when the purified water tank is full. A multi-effect still is provided only when WFI is required.

filters that prevent water from getting contaminated by particles from the atmosphere.

Water is transferred from the holding tank to the carbon filter by booster pumps at 15 m^3/h and 3 bar g. The pump motors are provided with variable frequency drives to maintain constant pressure. Activated carbon media remove organic compounds and free chlorine from water. Since the polyamide TFC RO membranes are damaged by oxidants such as chlorine, dechlorination of RO feed water is mandatory. The carbon filter effluent flows through a steam heat exchanger before it flows to the RO skid. The heat exchanger maintains the RO feed water temperature at 25°C during the normal service run. It is also used to heat water to 80°C during the hot water sanitisation cycle. A rule of thumb is that the RO product water (permeate) flow rate increases 3% per °C rise in water temperature due to lower viscosity based on the general relationship between flux and temperature:

$$J_M = J_S \times 1.024 \exp\,(T_M - 20)$$

Constant water temperature is, therefore, required to compare RO flux data. Flux data are normalised using the following equation [5]:

$$J_S = J_M\,(\Delta P_S/\Delta P_M) \times (1.024) \exp\,(T_S - T_M)$$

where J_S and J_M are permeate flux at standard and measured conditions; ΔP_S and ΔP_M are net differential pressure across the feed inlet and reject outlet at standard and measured conditions; and T_S and T_M are fluid temperature at standard and measured conditions, respectively.

RO feed water flows through two parallel 5.0 μm pore size (nominal) cartridge filters at 15 m^3/h. The microfilters remove carbon fines and particles, thereby protecting the RO membranes from particulate fouling. The RO prefilters effluent flows through a 254 nm UV light. The UV lamps destroy organic matter and renders biological organisms inactive, thus protecting the RO membranes from biological fouling, which is often irreversible.

The pre-treated water is pumped by the first-pass RO high-pressure pump to the RO membrane array at 20 m^3/h (15 m^3/h feed + 5 m^3/h reject recycle) and 8 bar g. The RO system is designed to run continuously and supply water to the EDI unit. The first-pass RO unit is a three-stage (2:1:1) array designed to produce 12 m^3/h of purified water at an overall recovery of 80% (12 m^3/h product ÷ 15 m^3/h make-up feed). A portion of the reject flows to drain at 3 m^3/h, and the remaining reject recycles to the RO pump inlet at 5 m^3/h.

The first-pass RO permeate flows to the second-pass RO high-pressure pump at 12 m^3/h. The second-pass RO pump transfers water to the second-pass RO membrane array at 20 m^3/h (12 m^3/hr first-pass permeate + 8 m^3/h second-pass reject recycle) and 8 bar g. The second-pass RO unit is a two-stage (2:1) array designed to produce 10 m^3/h of purified water at an overall recovery of 83% (10 m^3/h product ÷ 12 m^3/h feed). The reject recycles to the second-pass RO pump inlet at 8 m^3/h. The TFC membranes (20 cm diameter × 100 cm long spiral-wound elements) reduce the TDS from 144 mg/L in softened feed water to 3 mg/L in final RO permeate at an average rejection of 98%.

The RO system product water flows to the EDI skid at 10 m^3/h through a TOC reduction 185 nm rated UV unit. The EDI skid houses four EDI modules (24 cell pairs/module) all operating in parallel. The EDI system performance specifications are: product water recovery, 95% (9 m^3/h product ÷ 10 m^3/h feed); rejection, >99%; product water resistivity, 5.0 MΩ-cm (conductivity, 0.2 μS/cm). The product water flows to the purified water storage tank at 9 m^3/h.

The RO and EDI systems are sanitized with hot water at 80°C typically periodically as required. The hot water sanitisation cycle is described in the next section. Often the carbon filter is sanitized first before the RO/EDI loop is sanitized.

5. Advanced technologies and recent developments

5.1. Hot water sanitisation (HWS)

HWS, or pasteurization, is commonly used to kill microorganisms. RO membranes reject bacteria and other microbes. However, due to defects in the membrane surface, the rejection is not 100% so that microorganisms can pass through the membrane into the permeate side of the membrane where they can multiply. Hence, sanitization of a membrane system is essential for the production of USP water and for WFI to meet the very low bacterial limits [13,14].

HWS of RO membrane (and EDI) systems is a relatively recent development made possible by the development of TFC membranes and membrane equipment capable of handling hot water as high as 85°C for brief periods of time; hot water sanitizable membrane elements are manufactured with special adhesives, permeate tubes and connectors to withstand elevated temperatures. These membranes also make it possible to sanitize and protect the RO membranes from biofouling, especially when the use of biocides is not acceptable.

Membrane manufacturers recommended procedures for hot water sanitizable TFC membranes are given in Table 5 [5]. The HWS equipment includes a CIP skid with a tank, heat exchanger and a pump to circulate hot water through the membrane system loop and provide cooling during the cool-down period. HWS is comprised of the following steps:

1. Clean the membranes with a low-pH cleaner to remove mineral scale and foulants.
2. Heat the water to 80°C at 3–5°C/ min at a low flow rate (<10 m^3/h) and pressure (<3 bar g).
3. Circulate the water in the CIP–RO(/EDI) skid loop at 80°C for up to 1 h. Maintain a cross-flow velocity so that the pressure drop is <0.15 bar per membrane element.
4. At the end of the re-circulating period, cool the membrane system to <30°C, preferably at 3–5°C/min.

Table 5
Membrane manufacturers' recommended conditions and procedures for HWS of TFC polyamide RO membranes[a]

Item	Specification
Membrane element size, cm	20 dia. x 100 long
Membrane element configuration	Full-fit
Membrane surface area, m^2	36
Rejection @ standard conditions[a], %	96–98
Membrane flow rate, m^3/day	22–29
Recovery per element, %	15
Feed temperature (service), °C	≤45
Feed pressure (service), bar g	≤40
Feed SDI rating	≤5
Feed turbidity, NTU	≤1
Feed free chlorine, mg/L	<0.1 mg/L
Feed pH (continuous)	2–11
Feed pH (cleaning, 30 min)	1–12
Sanitisation temp. (max.), °C	≤80
Sanitisation feed pressure (max.), bar g	3
Sanitisation duration, min	60
Sanitisation cycles	≤150
Sanitisation feed flow rate (max.), m^3/h	10
Sanitisation permeate flow rate, m^3/h	0.2 per element
Transmembrane pressure (max.), bar	1.7

[a]Standard conditions: 2000 mg/L NaCl, 16 bar g, 25°C, pH 8, and 15% recovery.

HWS is a superior process to chemical sanitisation because it does not require prolonged rinsing as in the case of biocide sanitisation and generates minimum wastewater. However, two points need to be noted. First, HWS is performed more frequently than biocide/chemical sanitisation. Second, high temperature reorients the polymer chains permanently; at high temperatures, the membrane structure becomes tighter due to changes in the membrane morphology as a result of changes in the glass transition temperature [15]. The first shrinkage results in almost a 50% reduction in flux during the normal operating cycle, but after the initial shrinkage subsequent HWS cycles are unaffected. To compensate for the anticipated loss, HWS systems are designed with more surface area then ambient temperature membrane elements [13].

5.2. Immersion lithography

Advanced wet cleaning processes are evolving to meet the challenges of manufacturing semi-conductor devices with smaller geometries and higher performance. New materials and manufacturing processes, larger wafer size, line width shrinkage to 0.03 μm and environmental concerns are the driving forces behind new cleaning/rinsing methods [7,8]. Very fine filtration with hydrophobic membrane filters with high efficiency for bubbles removal and particle retention is critical for removing particles down to 0.03 μm. Dissolved gases in UPW can create bubbles as in the case of gases/bubbles generated by the UV oxidation process. The dissolved gases must be removed to ppb levels. The role of UPW is, therefore, expanding from conventional wafer rinsing to advanced applications such as [8]:

- immersion optical lithography
- gasified UPW for wafer cleaning
- humidification with UPW of ultra-clean air in lithography environments where control of organics in the air is critical
- new specialty chemical formulations for wet etch and cleans.

The microelectronics industry is developing 65 nm circuits by switching from dry lithography to wet immersion lithography using UPW between the imaging lens and resist surface. This requires that the purified water quality must be maintained at the highest level of clarity (i.e. low absorbance) and purity (i.e. parts per trillion or ppt levels contaminants) to ensure high transmission of imaging radiation through water [7]. Newer UPW systems must, therefore, be able to efficiently remove dissolved gases and bubbles, particles, TOC, non-volatile residue as well as ionic and organic extractables from process equipment to prevent imaging defects. Refractive index of water is a critical parameter that can be influenced by these contaminants. Organic contaminants are undesirable as they can absorb deep UV energy and cause defects. Hence, TOC needs to be reduced from ppb levels to ppt levels. A UV-IX process has been developed that achieves ppt levels of TOC by breaking down most organic molecules into carbon dioxide and water [7].

Further, removal of ions in the immersion system is accomplished with the aid of MBIX polishers operating in series with silica and boron purifiers. These systems use strong IX resins for removing most metals and weakly dissociated silica and boron. Silica in HPW typically exists in the dissolved form and colloidal form. The IX purifier is effective in removing anionic silica and boron.

5.3. *High efficiency reverse osmosis (HERO) process*

The HERO™ process was patented a decade ago for UPW production at semi-conductor plants or other HPW plants where post-RO ion exchange polishers are regenerated based on sodium and especially, silica and boron breakthrough [16]. The main objective was to produce RO permeate with minimal silica and boron, thereby reducing the load on MBIX polisher resins. Since the regeneration of these polisher resins is the most expensive single unit operation in HPW treatment systems, increasing service throughput is an important consideration.

The HERO technology consists of three basic processes operating in series:

- weak acid cation (WAC) ion exchange for removing hardness associated with alkalinity;
- degasification for removing carbon dioxide resulting from alkalinity removal as a result of acid addition to lower the pH;
- single-pass RO unit operating at high pH (>10.0).

The process is capable of high rejection of silica, TOC and boron without the second-pass RO unit. Weak acids and undissociated compounds such as silica and boron are poorly rejected by RO membranes at pH <8, e.g. boron exists as a weakly dissociated boric acid, H_3BO_3 at pH <8.2. Silica dissolves in water forming weakly ionised silicic acid, which in alkaline conditions, dissociates to form silicates:

$$SiO_2 + H_2O \Leftrightarrow H_2SiO_3 \Leftrightarrow H^+ + HSiO_3 \Leftrightarrow 2H^+ + SiO_3^-$$

At pH >9 silica and boron get ionised with substantial increase in solubility resulting in their high rejection by RO membranes. At high pH values silica rejection also increases due to the molecule structure changing from silicic acid to orthosilicate associated with six water molecules making a larger molecule resulting in higher rejection. Boron rejection levels are enhanced at the elevated pH levels when the boron changes from boric acid to its salt; %rejection changes from approximately <30% to >90%. When a double-pass RO system is used, silica can be reduced from 10 ppm to <1 ppb, boron from 12 ppb to <100 ppt and TOC from 2 ppm to <5 ppb [17].

5.4. *USP plant operation*

Current HPW production methods are based on certain well-established rules such as RO product water recovery of 70–80%, high fluid velocities in the HPW loop, hot water sanitisation of USP water systems, and use of stainless steel piping in USP water systems. Some modifications to these design guidelines given below have been recently suggested [11]:

- Operate the RO units systems at 50% recovery instead of 70–80%. This reduces the frequency of membrane cleanings substantially, increases reliability, and results in consistent product water quality. In addition, the reject water is better suited for reuse applications such as for cooling tower make-up. It can also be used as feed for vapour compression stills and clean steam-generators provided the silica content is less than 15 mg/L.
- It is not necessary to operate the RO/EDI system in a

USP water plant continuously. This wastes water and there is no benefit in microbiological control. Similarly, hot water sanitizable RO and EDI systems are not necessarily better at controlling bacteria.

- Frequent backwashing of carbon media filters is more effective than hot water or steam sanitisation since the microbial load reduction by sanitisation is temporary due to the rapid recolonisation of the sanitized biofilm in the carbon bed.
- Minimum fluid velocities in the HPW recirculating loops are 2–3 m/s. Apparently, there is no single velocity based on which a loop system can be designed or operated to control the formation of biofilms.
- WFI operation is just as effective at 60°C as it is at 80°C. If this is true, perhaps hot water sanitisation of the RO/EDI systems should also be done at 60°C instead of 80°C.
- As in the case of semi-conductor UPW plants, PVDF piping should be used in the high purity loops in USP plants. It is 30–35% cheaper than 316L SS, and reduces steps such as cleaning and passivation of SS components.

6. Conclusions

The current world market for HPW exceeds $1B, divided approximately equally between power, pharmaceuticals, beverages and microelectronics. HPW plays a critical role in the manufacture and use of advanced materials such as biotechnology, quenching of turbine forgings, final rinsing of fluorinated polymer films, manufacture of new glass laminates, and the use of UPW (resistivity >18.2 MΩ-cm) in the production of semiconductors and graphite fibres. Power plants are the single largest user of HPW required for high pressure boilers for generating steam.

Membrane processes — RO, NF, UF, MF and EDI — have played a major part in the last 15–20 years in the production of HPW, and will continue to play a critical role in the growth of this water sector to meet ever-increasing demands of water purity, especially in semiconductor applications. Membrane processes are also being increasingly used in the reduction of wastewater, water reclamation, recycle and conservation, and environmental pollution control at HPW plants, e.g. application of brine recovery RO/NF processes to increase the recovery at RO plants to 90–95% and reduce brine disposal costs [9,18].

References

[1] G.A. Pittner, High purity water production using reverse osmosis, in: Reverse Osmosis, Z. Amjad, ed., Van Nostrand Reinhold, New York, 1993, pp. 334–363.
[2] G.A. Pittner, The economics of desalination processes, in: Reverse Osmosis, Z. Amjad, ed., Van Nostrand Reinhold, New York, 1993, pp. 76–103.
[3] J. Wood, Continuous electrodeionisation for power plants, Filtr. Sep., 45(5) (2008) 17–19.
[4] A. Dey, Ultrapure water membranes, in: Advanced Membrane Technology and Applications, N.N. Li, A.G. Fane, W.S.W. Ho and T. Matsuura, eds., Wiley, Hoboken, NJ, 2008.
[5] R. Singh, Hybrid Membrane Systems for Water Purification: Technology, Systems Design and Operation, Elsevier, Oxford, UK, 2006.
[6] S.D. Strauss, Water treatment, Power, June (1993) 1–52.
[7] B. Parekh, A. Xia, M.E. Clarke and J. Smith, Process to purify water for immersion lithography, Ultrapure Water, 24(7) (2007) 31–36.
[8] B. Parekh, Emerging applications of high purity water: meeting challenges of advanced semiconductor manufacturing, Ultrapure Water, 25(4) (2008) 38–43.
[9] R. Singh, Brine recovery at industrial RO plants — Conceptual process design studies, 2nd Oxford and Membranes Research Event, Oxford, UK, 2008.
[10] W.V. Collentro, Pharmaceutical Water, CRC Press, Boca Raton, FL, 1999.
[11] H. Moes and R.C. Livingston, Producing affordable high-purity water, BioPharm Internat., 17(8) (2004) 28–40.
[12] G. Gsell, Water systems utilising multiple-effect and vapour compression technologies compared, Pharma. Eng., March/April (2004) 48.
[13] B. Wise, Hot water sanitization membranes tackle microbes in RO permeate water, Chem. Process., accessed on-line, 2002.
[14] W.V. Collentro, Hot water sanitization of RO and double-pass RO/EDI systems, Ultra Pure Water Journal's Expo, Philadelphia, 2003.
[15] M. Mantarri, A. Pihlajamaki, E. Kaipainen and M. Nystrom, Effect of temperature and membrane pre-treatment by pressure on the filtration properties of nanofiltration membranes, Desalination, 145 (2002) 81–86.
[16] D. Mukhopadhyay and S. Whipple, RO system that reduces membrane scaling and fouling tendencies, Ultrapure Water, 14(7) (1997) 21–27.
[17] The HERO™ Process, Desalination Water Reuse, 18(1) (2008) 43–44.
[18] R. Singh, Analysis of high recovery brackish water desalination processes using fuel cells, Sep. Sci. Tech., 44 (2009) 585–598.