SEMICONDUCTORS

HOW CAN PREVENTATIVE MAINTENANCE OF FILTERS ENSURE THE HIGHEST QUALITY UPW AT LOWEST COST OF OWNERSHIP?

In today's advanced semiconductor fabs, ultrafiltration (UF) is used as the final filter step in ultrapure water (UPW*) supply plants. It eliminates nanoscale particles, macromolecules and pyrogens. UF has proven to be a highly reliable technology requiring low maintenance and enabling long change-out cycles.

UF even withstands episodic increase of particle numbers in the feed (e.g., caused by conditioning of ion-exchange resins) without negative effects for water quality and service lifetime. Such a particle challenge typically involves high concentrations of ~10-nanometer (nm) particles. On the other hand, current on-line particle counters approach their lower detection limit at about 10 nm. Large numbers of particles nearby and below this limit remain undetected. Hence, the integrity of a UF membrane is essential to keep these small particles under control; it can hardly be evaluated by comparing particle counts upstream and downstream. Therefore, better test methods are needed to identify membrane damages, and to decide on service life and replacement of UF membranes.

UF Technology for UPW

Ultrafiltration is state-of-the-art for final filtration in central UPW supply plants for semiconductor fabs (Figure 1). It typically splits the feed flow into 95% particle-free permeate, and 5% reject flow that carries the vast majority of rejected contamination. The reject is often used as supplement upstream reverse osmosis (RO) as part of the UPW plant.

Ultrafiltration of UPW is performed by means of hollow-fiber membranes bundled in the housings of UF modules[A]. Water flows pressure-driven into the interspace between the hollow fibers. It penetrates the double skinned symmetrical membrane from outside into the interior of the hollow fibers. This filtered water is called *permeate*. It is discharged on both ends of the fiber bundle, leaving the membrane module upwards and downwards. Particles and macromolecules are rejected and accumulated nearby the membrane. They are returned to the core flow in the fiber interspace, and leave the module housing with the remaining water, which is called *reject*.

The main mechanism of the return transport is diffusion driven by radial concentration gradients. Crossflow does not contribute that much to shear-induced fouling layer control, but much more to the discharge of contaminants from the fiber interspace. A long-term equilibrium between mass flow approaching and departing the membrane avoids uncontrolled buildup of fouling layers. This equilibrium is achieved by careful adjustment of transmembrane pressure difference (TMP) and reject rate.

In industrial installations, several UF modules are combined in open module racks or – more advisable – in a closed cabinet[B] (as shown in Figure 3). Combinations of a few units of that kind provide any desired flow capacity. Controlled flow of clean dry air (CDA) prior to and during maintenance creates a clean environment surrounding the UF modules, and reduces contamination of interfaces and piping/ module connections. As an option, the reject may be polished by tight filtration (sub-30 nm) prior to its return to the RO.

UF membranes for UPW are challenged by rather fluctuating numbers of particles in the feedwater. About 10^3 particles > 10 nm per milliliter (mL) is a typical range for smooth periods. Certain events (e.g., replacement of ion-exchange [IX] resins) may result in sudden increase of particle numbers > 10 nm even up to 10^8 1/mL (1).

As long as the UF membranes are intact and free from leaks, this hard challenge does not result in an unacceptably high level of particle numbers in the permeate. A UF module with locally damaged membranes, however, can create a bypass for some of the particles. This fact remains undetected at low-particle concentrations on the one hand as the bypassing stream is sufficiently diluted by permeate provided by the intact membrane area. During high challenge periods, on the other hand, the much higher number of particles is harmful for downstream processes in spite of dilution. Thus, methods are needed to

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ISSN:0747-8291.

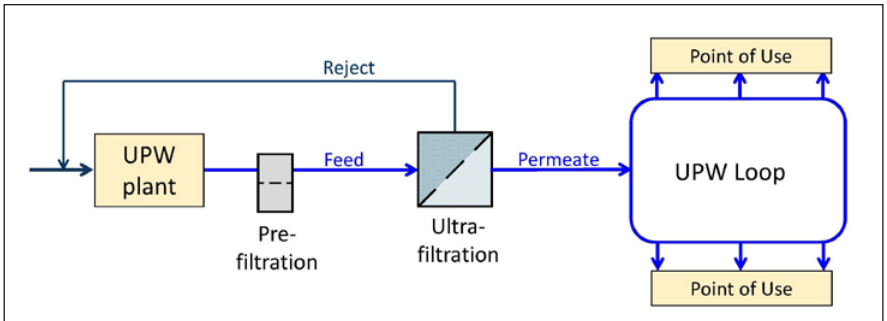

Figure 1. Ultrafiltration in an UPW plant scheme.

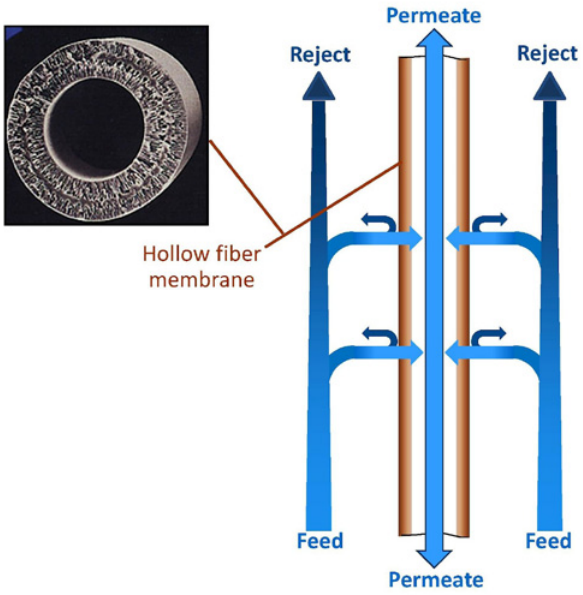

Figure 2. Ultrafiltration process scheme.

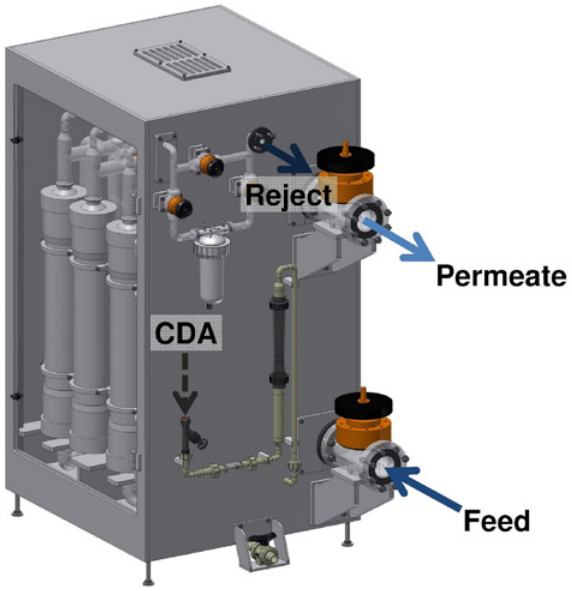

Figure 3. Ultrafiltration unit with reject polishing, 50 m³/hr nominal UPW capacity.

keep the balance between cost and reliability (i.e., methods).

- To detect membrane damages in time independently on the particle challenge level
- To replace membrane modules early enough, but not too early.

UF modules quality monitoring

UF modules need to be replaced in the following situations when:

- Their permeability has decreased below limits
- Parts of the membrane area have lost their integrity
- Accumulated contamination not removed by the reject mechanism must be discarded
- Mechanical properties of the fibers reach critical limit

Typical residues of membrane surfaces are caused by IX resins (Figure 4) or other contaminants (Figure 5), and normal aging of the polymeric membrane material, combined with mechanical stress. For the user, this deterioration becomes visible by an irregular increase of the transmembrane pressure difference and possible leaking of metal ions level into the UF permeate and— at high challenge situations— by increasing particle counts.

Aging of membranes is indicated by reduced elasticity of the hollow fibers (elongation at break). The number of fiber breaks dramatically increases at remaining elongation properties (elongation retention) below 50% of initial figures as Figure 6 illustrates. This result, combined with long-term field experience, justifies 4 to 6 years recommended service life for the UF modulesA at ambient UPW temperatures.

Close to the 50% level of remaining elongation, the risk for a complete or partial breakage of hollow-fiber membranes increases rapidly. Typical locations of fiber breakage are close to the potting material as there is the region with highest static and dynamic bending stress. Figure 6 illustrates degradation of hollow-fiber membrane material over service time.

There are numerous methods to monitor the membrane conditions. They are listed in Table A. A distinction is drawn between destructive tests and non-destructive ones; only the latter are applicable for routine field tests.

Unfortunately, particle counting as well as monitoring the permeate referring to specific conductivity and flux/TMP provides limited information because of the reasons mentioned above. During low-challenge periods, the disadvantageous effects of deteriorated membrane sectors are widely covered by the high permeate quality and volume generated by intact membrane areas. A test method that provides information on membrane integrity independently on a certain particle challenge is imperative to save the user from expensive surprises in high-challenge periods.

The Non-Destructive Membrane Integrity Test

The Pressure Decay Test meets these requirements. This method, also known as pressure decay test, is a variation of the diffusion test or forward-flow test (2). It is based on the facts (Figure 7) that in a wetted membrane under a differential pressure.

- Liquid is held in the pores by surface tension and capillary forces—Scenario A.
- This liquid is forced out of larger pores at lower pressure than in case of smaller pores.
- Diffusional gas flow through a pore filled with liquid is much lower than convectional gas flow through a pore filled with gas.

The critical differential pressure Δpc at which liquid is driven out of the largest pore is called bubble point. It may be calculated for a cylindrical pore with a diameter, D, as shown in Equation 1.

$$\Delta p_c = \frac{4 \cdot \sigma \cdot \cos\theta}{D} \qquad Eq.1$$

More complicated pore geometries are summed up by shape correction factors. Equation 1 illustrates the influence of the surface tension, σ, the contact angle, θ, and the pore diameter, D.

In the pressure-hold test, first a gas pressure well below the bubble point pressure Δp_c is applied and stabilized in the shell space between UF module housing and upstream membrane surface. Clean dry air (CDA), or nitrogen gas (N_2) are applied. After pressure stabilization, gas feeding is stopped, and the compressed gas volume is isolated. The gas pressure slowly drops because of the loss of gas by diffusive transport through wetted pores, or faster— in the worst case— because of large convective extra flow through big emptied pores or leaks. Measuring the pressure drop over a time period provides a criterion for the integrity of the pore system.

Fortunately, the test results are highly reproducible and sensitive to fiber breakage. Figure 8 shows the pressure decay repeatedly measured on 11 UF membrane modules. The repeated measurements on intact modules provide reproducible results in a narrow band of pressure decay fairly below 100 mbar in 120 seconds. The decay figures of failed tests indicate considerably higher gas flow, suggesting convective gas flow.

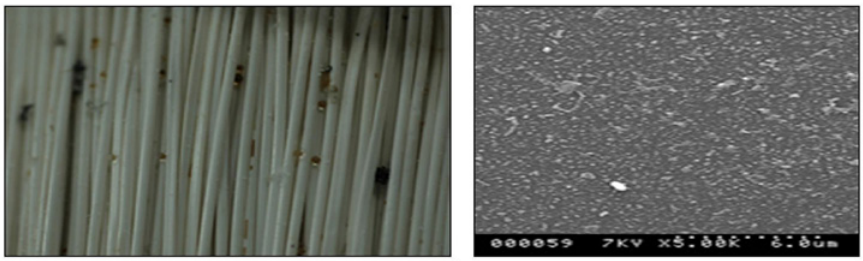

Figure 4. Membrane contamination by IX resins. Module: Microza OLT-6036Ha after 7 years of service (20% relative permeability). Left: Fiber membrane bundle; right: outer surface, 5.000 X. Courtesy of Asahi Kasei (2015).

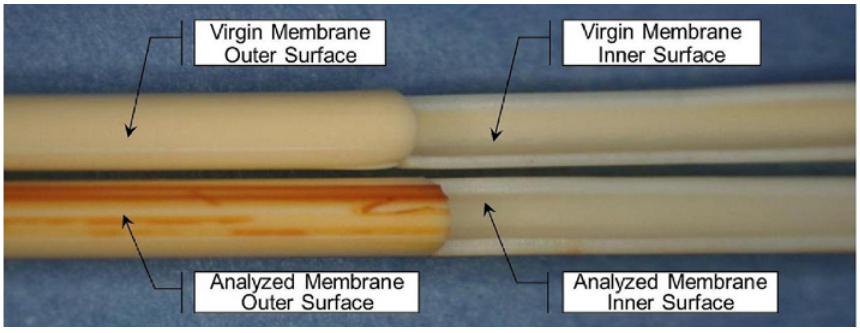

Figure 5. Contamination of an outer membrane surface by a positively charged substance, visualized by a staining test using acidic dye that turns the stained membrane orange. Courtesy of Asahi Kasei (2015).

Special features of the pressure decay test are as follows:

1. Single modules can get isolated and remain in the skid while tested. Full racks can be tested, too, allowing a rapid screening of multiple module installations.

2. Pre-filtered dry CDA or N_2 is applied at a gas pressure fairly below the critical differential pressure (bubble point). Hence, there is no convective

Table A
Selected Methods to Monitor Membrane Module Conditions

Method	*Details*	*Type*	*Comments*
A) Appearance check	Visual observation of over-all appearance and potting surface of feed and permeate section	Non-destructive	Off-line, limited information
B) Integrity test	Leak check of membrane and potting using CDA or N2 in a pressure decay test	Non-destructive	Periodic in-situ test, high resolution → combination with C
C) Particle monitoring	Particle counting in UF permeate	Non-destructive	Long-term trend test, on-line, limited resolution → combination with B
D) Flux measurement	Measuring permeate flux and/or TMP to compare with initial figures	Non-destructive	Long-term trend test, on-line, limited resolution
E) Specific resistivity	Checking the specific resistivity and ion contamination in permeate	Non-destructive	
F) Physical property check	Checking tensile elongation and strength of sampled hollow fibers to compare with initial figures	Destructive	Off-line; to investigate failed modules and identify failure causes
G) Molecular weight cut-off	Measuring molecular weight cut-off using dextran retention test to compare with initial figures	Non-destructive	
H) SEM observation	Observation of inner/ outer sur-faces of a membrane by SEM, examina¬tion of contaminations on membrane	Destructive	

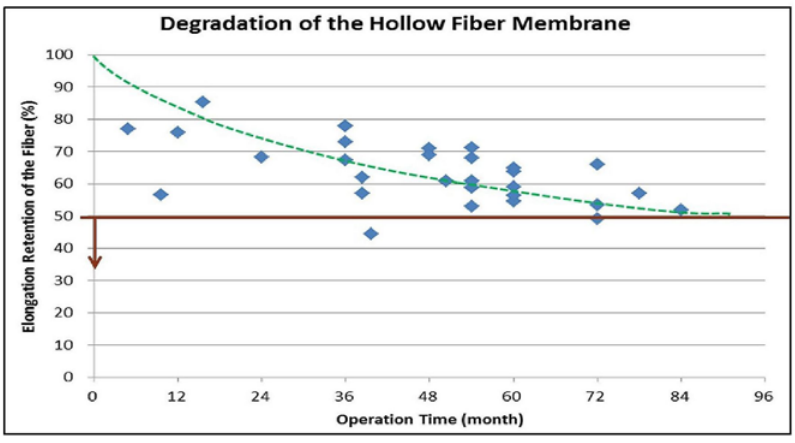

Figure 6. Degradation of hollow-fiber membrane material over service time, indicated by retention of elongation at break. Courtesy of Asahi Kasei (2015).

flow through intact pores, and therefore, no drying of the membrane as long as it is intact.

3. Even single fiber pinholes, ruptures or membrane cracks are reproducibly detected.

Takeaways

Here are some conclusions from our report:

1. Continuous particle monitoring cannot reliably detect small breaches of integrity of UF membranes in industrial-scale installations. Continuous particle monitoring, however, is helpful as a trend monitoring procedure to observe the overall status of UPW installations.

2. A non-destructive test of UF modules by pressure decay measurements is a necessary addition to quality monitoring of UPW plants. Long-term test recordings prove the theoretical background. The advantages referring to economy and reliability clearly overrule the impact of interruptions of production cycles.

3. Regular inspection of UF membrane modules, starting with the baseline obtained at start-up provides a valuable insight into the conditions of the modules during service life.

4. Initial testing and documentation by qualified personnel will provide additional quality documents (excluding installation of faulty modules due to logistic damages).

5. Using expired modules for destructive analysis creates options for in-depth contamination monitoring below detection limits of on-line instruments.

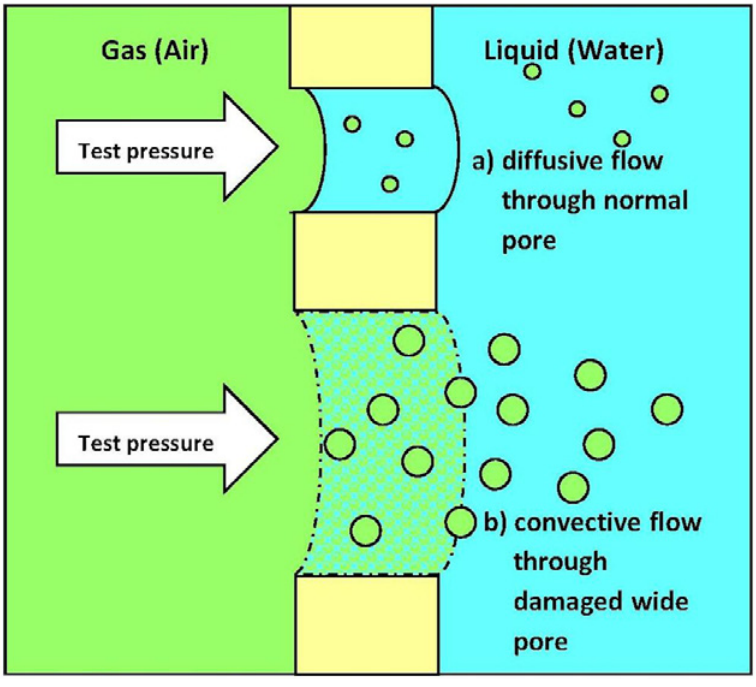

Figure 7. Pressure hold test basics.

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Endnotes

*In the text, the term UPW refers to semiconductor-grade water produced in microelectronics facilities. Its quality parameters are defined under the International Technology Roadmap for Semiconductors (ITRS).

[A]The UF modules referred to in the text at Microza Ultrafiltration Modules OLT Series, which are offered by Pall Corp. Microza is a trademark of Asahi Kasai Chemical Corp.

[B]UPW ultrafiltration unit, Pall Corp. (2015).

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This paper was presented at the 2015 ULTRAPURE WATER Micro, which was conducted Oct. 27-28, 2015, in Portland, OR, at the Jantzen Beach Red Lion Hotel.

Key words: FILTERS, ION EXCHANGE, MAINTENANCE, MONITORING, OPERATIONS, PARTICLES, SEMICONDUCTORS, TROUBLESHOOTING, ULTRAFILTRATION

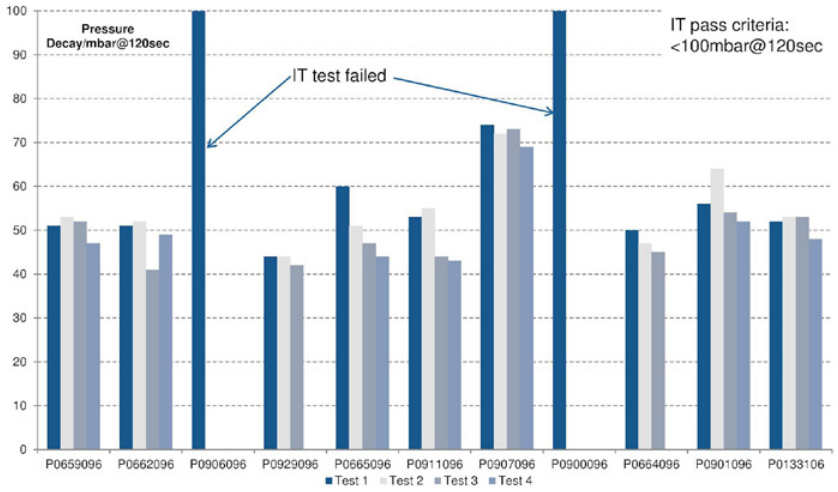

Figure 8. Repeated measurement of pressure decay on 11 UF membrane modules (Pall GmbH 2014).