HOW DOES PARTICLE CONCENTRATION AND THE FACE VELOCITY IMPACT THE REMOVAL OF SUB-100-NM PARTICLES FROM HIGH-PURITY WATER?

The critical feature size of state-of-the-art semiconductor devices line widths is < 20 nanometers (nm) and it is expected to decrease to < 10 nm by 2017 (1). Particles on the order of half this feature size in the ultrapure water (UPW*) used during device manufacturing can reduce manufacturing yield and finished device reliability. Concentrations of these small particles in present day UPW systems are believed to be < 1E6/milliliters (mL) for particles >20 nm.

Microfiltration (MF) and ultrafiltration (UF) devices with particle removal ratings below 50 nm are commonly used to reduce particle concentrations in process water used during device manufacturing. The particle retention capability of these devices is frequently measured with challenge concentrations that are significantly higher (orders of magnitude higher) than those in UPW. Also, testing is often performed using filter face velocities that are very different from those used in UPW systems.

This article shows a number of examples which indicate that:

- Particle challenge concentration and face velocity can have a significant effect on particle retention.
- Filter particle retention measured under conditions other than expected operating conditions can be misleading.
- Test conditions used to measure filter retention should mimic actual use conditions as closely as possible in order to accurately predict filter retention characteristics in actual use conditions.

By **Donald C. Grant**
and Gary Van Schooneveld
(CT Associates, Inc.)
and **Uwe Beuscher**
(W.L. Gore and Associates, Inc.)

ISSN:0747-8291. COPYRIGHT (C) Media Analytics Ltd. Reproduction in whole, or in part, including by electronic means, without permission of publisher is prohibited. Those registered with the Copyright Clearance Center (*www.copyright.com*) may photocopy this article for a flat fee per copy.

Test methods. In this study, filter retention was measured as a function of face velocity and challenge concentration. Face velocity is flowrate per unit filter area. The face velocity of a 10-inch (in) cartridge with 10 square feet (ft2) of membrane area operated at a flowrate of 10 liters per minute (L/min) is 1.1 centimeter (cm)/min.

Disc and cartridge filters were tested using three methods. In Method 1, the retention of 50-nm fluorescent polystyrene latex (PSL) beads by 142-millimeter (mm) disc filters was measured. 250 mL of challenge suspension was passed through a 142-mm disc at constant velocity. The filtrate was analyzed in 25 mL aliquots using spectrophotometry. In Method 2, the retention of 50-nm and 70-nm PSL beads by 142-mm disc filters was measured by challenging the filters at constant face velocity and measuring upstream and downstream particle concentrations using an M50 optical particle counter (Particle Measuring Systems, Boulder, CO). In Method 3, filter cartridges were challenged with 12-nm, 18-nm, and 28-nm silica particles at constant face velocity; upstream and downstream particle concentrations were measured using a Liquid Nanoparticle Sizer (LNS) (2). Additional details describing these methods are available in References 3 through 5.

Filters tested. Filters with retention ratings between 10 nm and 50 nm from a number of manufactures were tested. Filter rating methods are manufacturer dependent and are not disclosed in this article. Filter membranes materials were polyethylene, polysulfone, and fluoropolymer. All are commercially available.

The effects of concentration on retention and face velocity were each measured using 4 types of filters. The filters tested in the concentration and velocity tests are labeled A-D and E-H in this article.

Filter loading. When a filter removes particles from a liquid the filter becomes "loaded" with particles and its retention performance can change. Numerous references indicate that as loading increases retention decreases (6-9). The decrease in retention has been attributed to selective clogging of the smaller pores in the filter as the filter is loaded.

The rate at which filters are loaded with particles, defined in this study as particles entering the filter per unit area of filter, increases during a test with increasing challenge concentration and face velocity. However, retention with loading, rather than time, has been shown to be independent of concentration and face velocity in some instances (4).

All retention measurements shown in this article will be presented as a function of loading rather than time using the units of monolayers of coverage. Coverage is one monolayer at the time when the cross-sectional area of the cumulative number of particles that have entered the filter equals the filter surface area.

Concentration Effect on Retention

Figures 1 to 3 present three examples of the effect of particle concentration on retention. Each example presents filter log reduction value (LRV) as a function of loading (Equation 1).

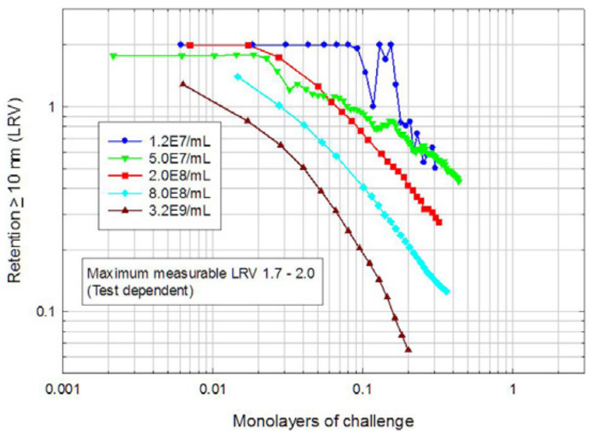

Figure 1. Retention of 12-nm silica particles by Filter A at 0.95 cm/min.

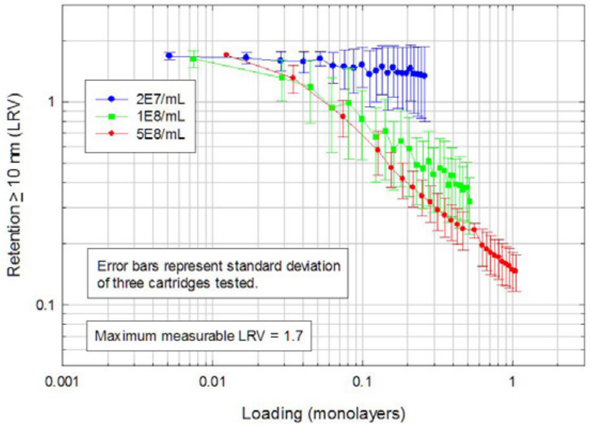

Figure 2. Retention of 10- to 30-nm silica particles by Filter B at 0.95 cm/min.

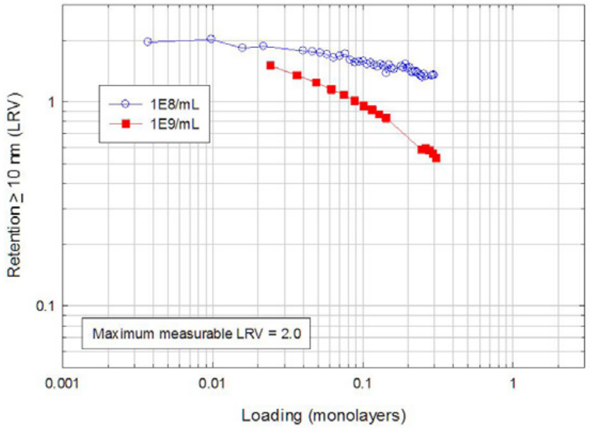

Figure 3. Retention of 30-nm silica particles by two Type C Filters at 1.5 cm/min.

$$LRV = \log_{10}(C_C/C_F) \qquad \textit{Eq. 1}$$

Where:
C_F = filtrate concentration
C_C = challenge concentration

Figure 1 shows retention of 12-nm silica particles by five Type A filters at five different challenge concentrations. Retention was seen to decrease with loading in all cases. The rate of decrease increased with increasing concentration. Similar losses in retention with increased concentration are seen for Filter B with 10- to 30-nm silica particles (Figure 2) and Filter C with 30-nm silica particles (Figure 3.

Figure 4 presents two examples depicting the effect of challenge concentration on the retention of PSL particles by Filter D. The graphs show retention as a function of concentration at fixed loadings. Retention is seen to decrease with loading without (Figure 4a) and with (Figure 4b) surfactant present.

Face Velocity Effect on Retention

Figure 5 presents four graphs showing the effect of face velocity on retention. All present retention as a function of loading at different face velocities. Examples 3a and 3b depict retention of silica particles by two types of filters, while Examples 3c and 3d are for retention of PSL particles by two types of filters. All experimental data show that retention decreased with increasing face velocity.

Implications for UPW Filter Testing Conditions

The results shown in Figures 1 through 3 indicate that particle retention by filters can be strongly influenced by both the incoming particle concentration and the filter face velocity. In the examples shown, retention decreased with increasing concentration and face velocity; sometimes substantially. Hence, filter performance should be measured under conditions that closely mimic actual use conditions.

The concentrations of 10- to 30-nm particles in UPW are unknown at present as instrumentation to measure these small particles has only recently become commercially available. The concentrations of particles >10 nm are estimated to be in the range of 1E3 to 1E6/mL, based on an extrapolation from measureable particle concentrations using a 3rd order size functionality on the cumulative size distribution function.

Test methods designed to measure filter particle retention must be performed under conditions that allow measurement of the particle concentrations entering and exiting the filter. The lowest concentration of 10- to 30-nm particles that present day instrumentation can measure is approximately 1E6/mL. Also, it is desired that filters be loaded to 0.1 to 1.0 monolayers in a reasonably short test; for example < 48 hours. For these reasons, filter testing is often performed using challenge concentrations of > 1E9/mL; concentrations much higher than the concentrations of particles present in UPW.

Testing filters at these high concentrations can potentially lead to very misleading results. An example of how misleading test results can be is shown in Figure 4, which shows retention of 12-nm silica particles by Filter H at 0.2 monolayers coverage as a function of challenge concentration at two different face velocities. The lines in Figure 4 represent linear regressions of the data and indicate a strong relationship between concentration and retention.

Figure 4 indicates that when Filter H was tested at a face velocity of 4 cm/min with a challenge concentration of 1E9/mL, the filter showed an LRV of only 0.15 (30% retention). However, if the filter were to be operated at a face velocity of 1 cm/min with a challenge concentration of 1E4/mL, the LRV

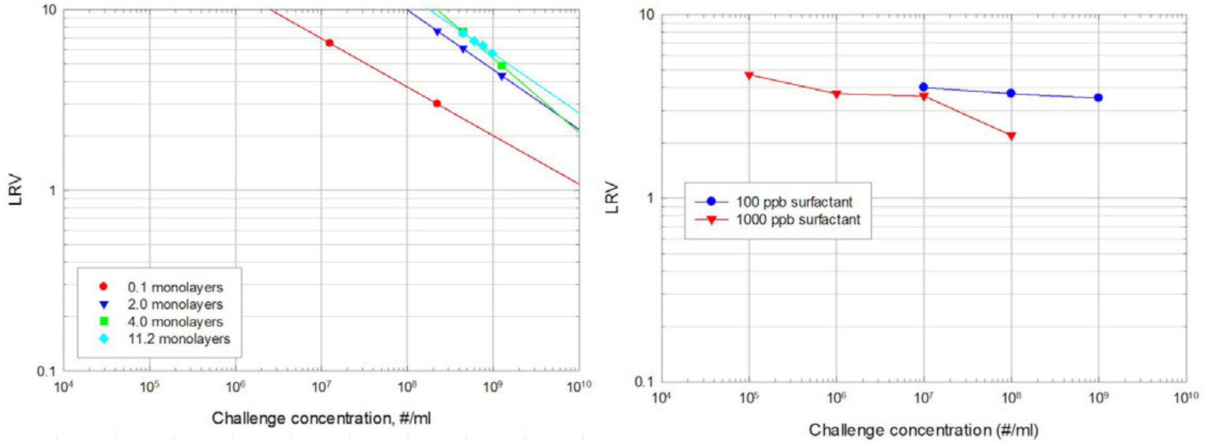

Figure 4. The effect of challenge concentration on PSL particle retention. 4a (left) shows the retention of 70-nm PSL particles by Filter D without surfactant present, 1.0 cm/min. Figure 4b provides data on retention of 70-nm PSL particles by Filter D with surfactant present, 1.0 cm/min.

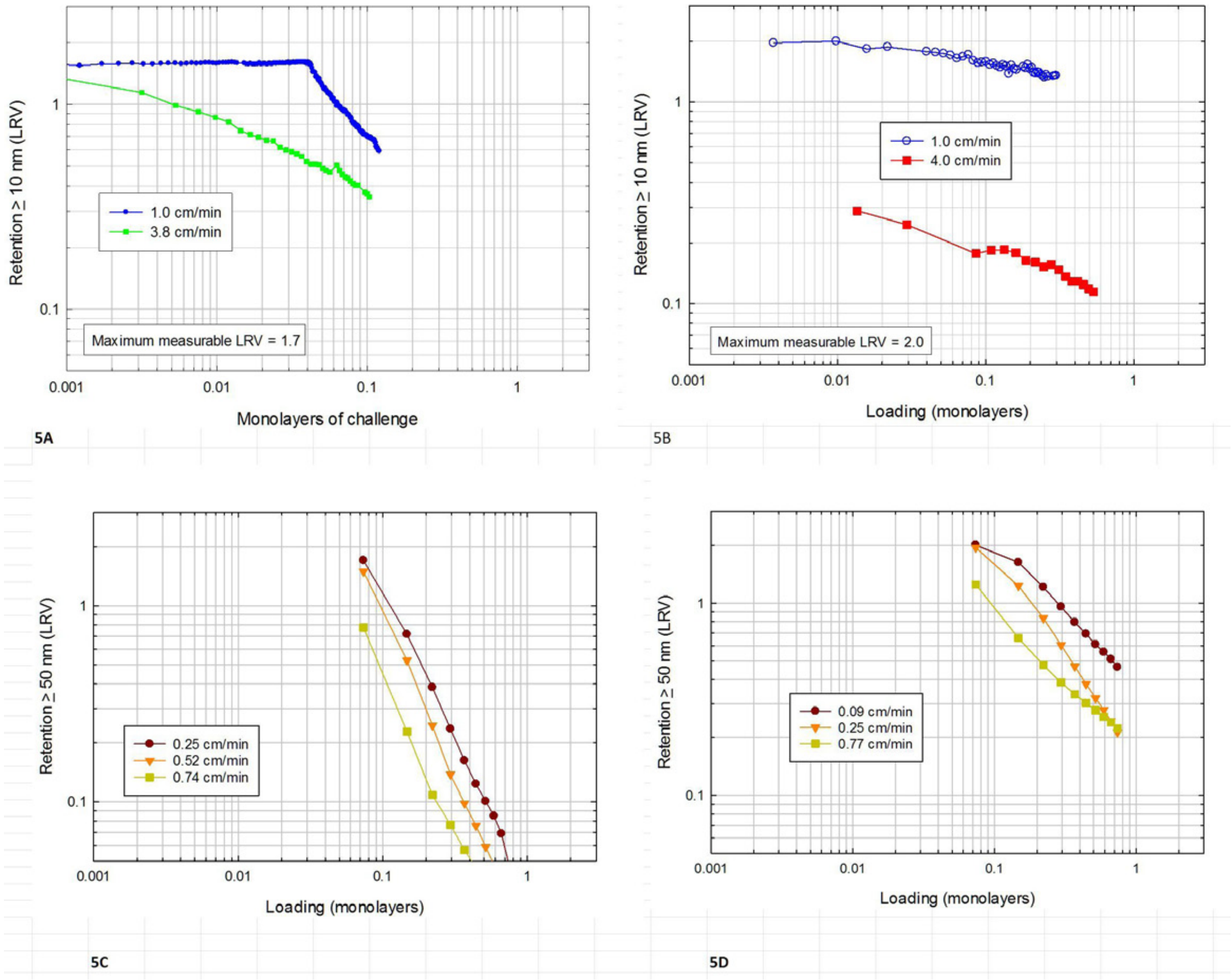

Figure 5. The effect of face velocity on particle retention. Figure 5a (top left) shows the retention of 12-nm silica particles by Filter E, challenge concentration = 1E8/mL. Figure 5b, top right) shows retention of 30-nm silica particles by Filter F. Challenge concentration = 1E8/mL Figure 5c (bottom left) shows retention of 50-nm PSL particles by Filter F, challenge concentration = 1.5E10/mL. Figure 5d (lower right) illustrates retention of 50-nm PSL particles by Filter G, challenge concentration = 1.5E10/mL.

at the same loading is projected to be >10 (>99.99999999% retention).

If UPW contains 30-nm particles at a concentration of 1E4/mL and Filter H is operated at a face velocity of 1 cm/min, the filter loading rate would be 0.04 monolayers/year. Hence, the filter is predicted to retain >99.99999999% of the particles after 5 years of operation rather than the much lower retentions seen in high concentration/high face velocity tests.

The above example relies of extensive extrapolation of measured filter retentions to predict retentions in actual use

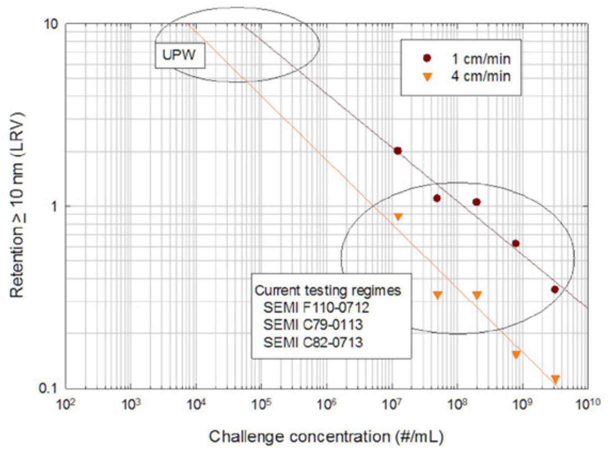

Figure 6. Retention of 12-nm silica particles by Filter H at 0.2 monolayer coverage.

conditions. It is possible that particle retention by Filter H would be substantially lower than the >10 LRV predicted. However, it is evident that the filter would be expected to have significantly higher retention than that measured in high challenge concentration tests. Hence, testing under conditions that closely mimic filter operating conditions in UPW is highly desirable.

Conclusions

The effects of challenge concentration and face velocity on retention of sub-100-nm particles by multiple filter types were measured. Testing was performed with both colloidal silica and PSL particles. Many examples in which filter particle retention decreased with challenge concentration and face velocity were shown. Decreases occurred with both particle types and multiple filter types.

Filter testing is often performed at challenge concentrations and face velocities that are very different from actual usage conditions. One example was shown in which laboratory testing indicated particle retention of only 30%, while projections indicate that the filter would retain >99.99999999% of the particles in a UPW system.

These observations indicate that filter particle retention test methods should closely mimic actual usage conditions in order to measure representative filter particle retention efficiencies.

References

1. *International Technology Roadmap for Semiconductors*, 2013 edition, International Technology Roadmap for Semiconductors www.itrs.net (2013).
2. Grant, D.; Beuscher, U. "Measurement of Sub-50 nm Particle Retention by UPW Filters", *Ultrapure Water Journal 26(11)*, pp. 34-40 (November 2009).
3. Grant, D.; Chilcote, D.; Beuscher, U. "Removal of 12 nm Particles from UPW by a Combination of Ultrafiltration Modules and Microfiltration Cartridges", *Ultrapure Water Journal, 29(3)*, pp. 17-23 (May/June 2012).
4. Grant, D.; Van Schooneveld, G.; Beuscher, U. "The Effect of Particle Concentration and Face Velocity on the Removal of Sub-100-nm Particles from Ultrapure Water", *Proceedings of Ultrapure Water Micro 2013*, Portland, OR (November 12-13, 2013).
5. Beuscher, U., "Modeling Sieving Filtration using Multiple Layers of Parallel Pores", *Chemical Engineering and Technology*, 33:1-6 (2010).
6. Grant, D.; Liu, B. Particle & Particle Systems Characterization, 8:142-150 (1991).
7. Grant, D.; Chilcote, D.; Beuscher, U. "Removal of 12-nm Particles from UPW by a Combination of Ultrafiltration Modules and Microfiltration Cartridges", *Proceedings of Ultrapure Water Micro 2012*, Phoenix, AZ (Nov. 13-14, 2012).
8. Zahka, J.G.; Grant, D.C. "Predicting the Performance Efficiency of Membrane Filters in Process Liquids Based on their Pore-Ratings", *Microcontamination*, pp. 23-29 (December 1991).
9. Lee, J.-K.; Liu, B.Y.H.; Rubow, K.L. "Latex Sphere Retention by Microporous Membranes in Liquid Filtration", *Journal of the IES*, pp. 26-36 (January 1993).

Endnote

*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).

Author Gary Van Schooneveld is president of CT Associates, Inc., which has performed contract research, development and testing services related to contamination control, particle measurement and control, filtration, permeation, and chemical engineering since 1991. He has more than 23 years of experience with high-purity chemical delivery and ultrapure water systems and testing of associated materials and components. Mr. Van Schooneveld was the founder of Precision Purity, a high-purity component testing company that merged with CT Associates in 1999. He has BS and MS degrees in materials engineering from Rensselaer Polytechnic Institute (Troy, NY), and an MBA from the University of Texas (Arlington, TX).

Author Don Grant is a staff technologist at CT Associates, Inc. He has more than 40 years of experience in analysis and purification of fluids and is the author or co-author of more than 170 publications and presentations. He received an MS in mechanical engineering from the Particle Technology Laboratory at the University of Minnesota, and a BS in chemical engineering from Case Western Reserve University.

Author Uwe Beuscher is a senior filtration technologist for W.L. Gore & Associates, Inc. He has more than 20 years of experience exploring separations and mass transport problems for a variety of high performance applications using unique experimental approaches and numerical simulation. He has authored or co-authored more than 30 technical papers, book chapters, and presentations. Dr. Beuscher earned a diplom-engineer degree in mechanical engineering from RWTH Aachen University, and holds a PhD in chemical engineering from Clemson University. He has served on the SEMI standard committees and as the president of the North American Membrane Society (NAMS).

Key words: MEASUREMENT, MONITORING, PARTICLES, SEMICONDUCTORS