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Technology and Business of Water Treatment

High-Purity Materials

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ULTRAPURE WATER®

Technology and Business of Water Treatment

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FEATURES

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COVER

Inside of Georg Fischer's new clean room welding facility that recently opened in Irvine, CA.
Photo courtesy Georg Fischer Piping Systems

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General Offices:
Media Analytics Ltd.
Suite C, Kingsmead House
Oxpens Road
Oxford OX1 1XX
T: +44 (0)1865 204 208
F: +44 (0)1865 204 209

www.ultrapurewater.com

Christopher Gasson, Publisher
cg@globalwaterintel.com

Mike Henley, Editor
Phone/Fax: 303-745-3890
mike@ultrapurewater.com

Mark Richards, Advertising and Promotions
Phone: 512-716-8532; Fax: 512-551-0108
mark.richards@globalwaterintel.com

Bonnie Eastland, Customer Service
bonnie.eastland@globalwaterintel.com
Phone: 303-731-5618

Layout and Design:
Paul Hasler and Charlotte Massey

For other inquiries:
Jessica Underwood, Executive Director
junderwood@globalwaterintel.com

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ON THE WATERFRONT

DEBUNKING PHARMACEUTICAL WATER TREATMENT MYTHS

Myths. The very word stirs up various connotations. On one side, there is the supposed authority a myth carries.

Under that view, one dare not challenge the common orthodoxy. In the context of high-purity water treatment, the unwillingness to do things differently has been exhibited over the years and is one reason why some observers note that treatment technology changes come "glacially" within the water industry.

Here are two examples:

- The slow adaptation of RO and EDI technologies by some users of ion-exchange (IX) treatment when they were first commercialized.
- Even though now allowed by the USP, the slowness by some users of Water for Injection (WFI) to move toward membrane systems as a way to treat WFI.

Now, on the other hand, the vitality of free markets and the emergence of new industries have played an important role in helping both RO and EDI reach the mainstream and become acceptable members of the water treatment "tool kit." The microelectronics industry is probably the best example. The semiconductor industry was beginning what would be its exponential growth during the same time frame that RO was commercialized.

Builders of the new fabs were willing to try RO, and the rest is history. Consequently, RO gained a track record to prove its usefulness, and now is considered a key component in high-purity and industrial water, and is becoming more widespread at the municipal level. As a result, myths were broken that only traditional treatments (IX, and softening, among others) are capable to meet the needs.

The above explanation provides a backdrop for the upcoming 2015 ULTRAPURE WATER Pharma conference. This year's sessions will be conducted June 2-3 at the DoubleTree Hotel in Bethesda.

We are excited about the theme for the 2015 conference, which will be "Debunking Pharmaceutical Water Treatment Myths." Here are examples of some myths (in the form of questions) that could be addressed in conference sessions:

- Why are Class VI materials required in pharmaceutical water systems?
- Is ozone an added substance?
- Does rapid micro testing have a place in quality control?

There are also many others that could enter the mix.

Of course, our plans call for technical presentations and papers that are technical, educational, and non-commercial. Additionally, the 2015 conference for the first time will include Round Tables and Panels as part of the overall program.

The Round Tables will be hosted by industry experts who will briefly discuss their topic with a table of up to 12 delegates, and then lead a discussion. The tables offer attendees the opportunity to learn and network with other conference delegates. There will be a series of three 20-minute sessions, so attendees will be able to visit three tables during the Round Table session.

Our Panels will focus on specific topics and we plan to invite leading experts to participate.

Visit www.ultrapurewaterpharma.com for information about the program and sponsorship opportunities.

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Lastly, we continue our work to offer the best editorial content on subjects germane to high-purity water treatment. One need we see is to help those new or interested in the water industry to learn more and develop their own knowledge base. Hence, this issue, we are introducing a new feature called "Backgrounder". These articles will take an initial look at important subjects and then offer a listing of several resources from the more than 1,900 technical articles published in *Ultrapure Water* and *Industrial Water Treatment* since 1984. We will also list other pertinent books and articles as well. The goal will be to provide a useful resource to the water industry. We welcome proposals for "Backgrounder" articles.

Mike Henley,
Editor

BUSINESS NEWS

GLV becomes Ovivo

MONTREAL— As reported in the September/October issue of *Ultrapure Water Journal*, GLV Inc. has changed its name to Ovivo Inc. The move came Nov. 14 after company shareholders voted to approve the sale of the company's Pulp & Paper Division and to adopt the Ovivo name.

The name change was to become official at the end of November, and the new Ovivo Inc. will ask the Toronto Stock Exchange for new stock symbols.

The firm's Pulp & Paper Division was sold to 9027173 Canada Inc., a corporation owned by Richard Verreault, the president and CEO of GLV, and Laurent Verreault, the executive chairman of the GLV board.

Marc Barbeau is the new president and CEO of Ovivo. Previously, he led GLV's water treatment business. Brands owned by Ovivo include Christ Water, EIMCO, and Enviroquip. Key water treatment markets for the company include municipal, microelectronics, and energy.

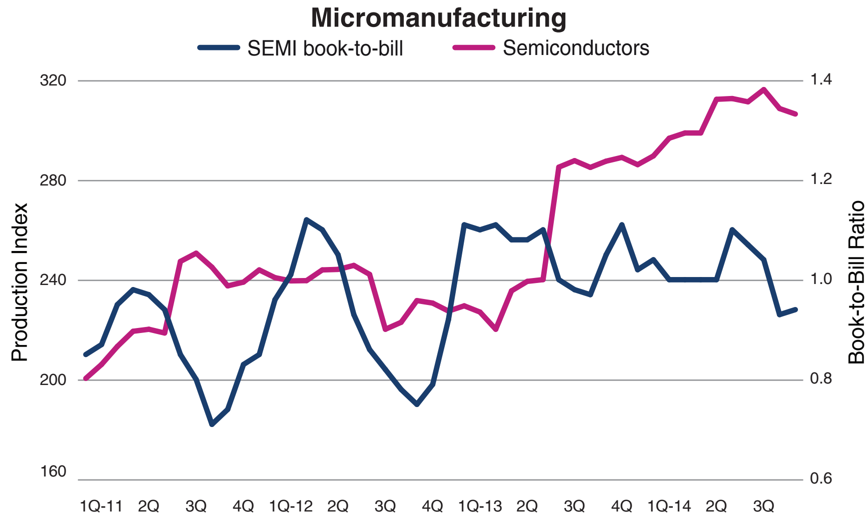
SEMI book-to-bill stays flat

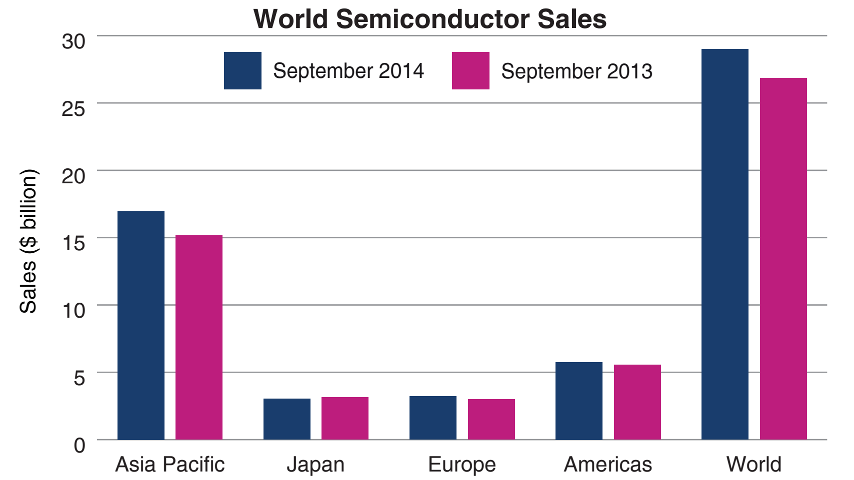
SAN JOSE, Calif.—The book-to-bill ratio kept by the Semiconductor Equipment and Materials International (SEMI) dropped to 0.93 in October. The newest ratio means that $93 in new orders was received for every $100 billed. The September book-to-bill ratio was 0.94.

SEMI reported declines in both bookings and billings from September to October. These numbers are determined by based on 3-month averages. SEMI reported that October billings were $1.18 billion, which was down from $1.25 billion in September. Bookings dropped from $1.18 billion in September to $1.1 billion in October. The top chart on this page follows the SEMI data.

Separately, world semiconductor sales moved higher in September to $29 billion, based on data from the Semiconductor Industry Association (SIA). That is up from slightly from August sales. On a year-to-year comparison, world sales were 8.6% higher from the $28.65 billion posted for September 2013. The bottom chart on this page shows global and regional sales comparisons for July and July 2013.

SEMI and the SIA data provides a picture of industry trends, and microelectronics water business opportunities.





Global sales of semiconductor devices by region for September 2014 and September 2013. The bars on the far right compare world sales for the same months in 2014 and 2013. Source: Semiconductor Industry Association (November 2014).

newterra buys Crane's water treatment business

Brockville, Ontario, Canada—newterra, a designer and maker of modular water treatment systems, recently acquired the business of Crane Water from Crane Co. With the move, newterra, a privately held Canadian company, adds the US-based maker of water treatment equipment to its sales/engineering, and manufacturing facilities in Canada, the United States, and Europe. The acquisition means the firm now employs almost 250 people worldwide.

"We see the acquisition being a catalyst for job growth and efficiency for the operations in Trooper, PA, in Venice, FL, and for newterra as a whole," said company president Robert Kennedy in a press release.

As result of the purchase, the Crane Water name has disappeared. However, the Cochrane and Chicago Heater brands will remain. The acquired business has sales and engineering offices in Trooper, PA, and in Venice, FL, where it also manufactures reverse osmosis (RO) filtration systems. Those locations will continue operations under newterra.

GF Piping opens new facility

IRVINE, Calif.—Georg Fischer LLC and GF Machining Solutions LLC, both units of Switzerland-based Georg Fischer Ltd. have opened a new facility here. The 105,000-square-foot campus includes space for offices, engineering, technical support, training, manufacturing, and warehouse space. George Fischer LLC is part of GF Piping Systems, which is a supplier of high-purity piping and related products.

Mueller reports debt refinancing

ATLANTA—Mueller Water Products, Inc. announced that it has successfully refinanced its long-term debt and reduced its total outstanding debt. As part of the refinancing transactions, Mueller has entered into a new $500 million senior secured term loan. Proceeds from the new loan will be used to fund cash tender offers for any and all of its outstanding senior subordinated notes and all of the outstanding 8.75% senior unsecured notes.

Colo. utilities may eye wastewater as new source of potable water

DENVER—The Colorado Water Conservation Board and other state authorities are working to help develop the first statewide water plan. The effort comes as state water utilities face an expected shortfall of 163 billion gallons, *The Denver Post* reported. The proposed water plan is expected to be released in December and would recognize reuse as an option and give consideration to turning to municipal wastewater as a source for to provide the additional water supplies.

The move here follows the lead of other arid states like Texas that are moving forward with plans to turn to specially treated wastewater as an supplemental source for drinking water.

In practical terms, plans would call for Front Range utilities, where some of the state's largest urban areas (e.g., Metro Denver, Fort Collins, Colorado Springs, and others) are located to push the limits in reusing water, the *Post* said.

One constraint to water reuse in Colorado is the "first-come-first-serve system" for allocating water rights. The *Post* noted this system obligates users who rely on water from rivers to return that water partially cleaned to the rivers. This is to meet the water rights of downriver users.

PEOPLE

Evoqua Water Technologies

Evoqua Water Technologies LLC announced that **Ronald C. Keating** has been named CEO, and will be appointed a member of the board of directors. He comes to the company from Contech Engineered Solutions LLC, where he has been president and CEO. Mr. Keating succeeds **Gary Cappeline**, interim CEO and AEA Investors LP Operating Partner. Evoqua also reported that it has moved headquarters from Alpharetta, GA, to Warrendale, PA.

Excellere Partners

Excellere Partners, a Denver-based private equity firm focused on partnering with middle-market entrepreneurs and management teams, has partnered with **Paul Turgeon** and **Boyd Wainscott**, to pursue opportunities within the water industry. Mr. Turgeon and Mr. Wainscott. In a press release, Excellere principal Patrick O'Keefe said, "Having Paul and Boyd working with us allows Excellere to identify the most attractive segments and investment opportunities, efficiently perform due diligence and provide immediate value to companies following investment."

PATENTS

Particle counter

Inventors: Peter J. Statham and Angus Bewick

Assignee: Oxford Instruments Nanotechnology Tools Limited (Oxon, GB)

Patent No.: U.S. 8,890,065; issued: 11/18/14

Application No.: U.S. 14/350,306; filed: 10/8/12

Summary: The invention is a particle counting instrument used for detecting one or each of the Kikuchi and Kossel diffraction patterns. It consists of the following: 1. An electron column adapted to provide an electron beam directed towards a sample; 2. The electron beam has energy in the range 2 keV to 50 keV; and 3. A particle detector for receiving and counting particles from the sample because of the interaction of the electron beam with the sample. The detector is made up of an array of pixels and has a count rate capability to deal with at least 1,000 particles per second for each pixel. The particle detector is also adapted to provide electronic energy filtering of the received particles in order to count the received particles that are representative of the Kikuchi and Kossel diffraction patterns.

Experiments by the inventors found that the instrument's detection data rate could reach 10,000 events per second, meaning the detector has a count rate capability for each pixel of 1,000 events per second. It can even go higher to 10,000 events per second, and even preferably up to 100,000 events per second.

Reduced RO fouling

Inventors: Francis Boodoo, Fabio De Sousa, James A. Dale, Carmen Mihaela Iesan

Assignee: Purolite Corp. (Bala Cynwyd, PA)

Patent No.: U.S. 8,883,012; issued: 11/11/14

Application No.: U.S. 12/015,429; filed: 1/16/08

Summary: The patent covers a method and pretreatment system that can protect reverse osmosis (RO) or nanofiltration (NF) membranes from fouling, deposits, or chemical precipitation. This pretreatment approach can take on different forms and the patent identifies multiple approaches that involve the use of resins of varying diameters and differing cleaning (regenerating) steps. Brief summaries of two of the methods follow.

In one embodiment, the invention involves the several steps. First, the incoming water passes through a vessel containing a resin component. The macroporous resin has a substantial number of pores with diameters in the range of 1,000 to 500,000 Angstroms, and a crush strength or Chatillon value of at least 24 grams per bead (710 micron bead diameter). Next, this water is taken to the RO or NF membrane.

For waters containing dissolved silica, the feedwater passes through the resin vessel. The resin is comprised of an iron-containing media that is an iron oxide attached to an ion exchange resin. This treated water may then be fed into an RO or NF system, a demineralization unit, a cooling tower, or a boiler. When the resin requires regeneration, it is cleaned with an alkali solution, or an alkaline and brine solution. Regeneration can involve one solution of a single chemical, or a mixture of chemicals.

Note: Information for patent summaries is obtained from sources considered reliable such as the U.S. Patent Office. Patent applications can take several years to process, and during that time the applying company may be bought or sold, or change its name. Generally, the listed patent assignee names are based on the company that originated the application. While the assignee name in the issued patent may not be updated, generally the patent rights are transferred to the new company.

EVENTS

2015

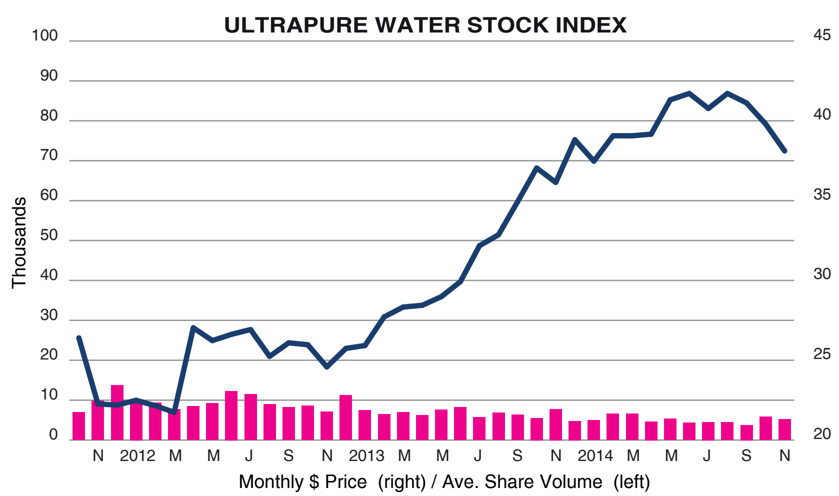
Produced Water Society

When: Jan. 13-15; *Where:* Houston; *Spon-*

ULTRA STOCK QUOTES

Company	Symbol	Nov	12 Month Low	12 Month High	Shares Outstanding (Millions)
American Water Works	AWK/NYSE	52	42	53	174
		554	536	870	
Ashland Oil Inc.	ASH/NYSE	114	91	114	65
		885	538	1345	
Calgon Carbon Corp.	CCC/NYSE	21	19	22	40
		229	212	393	
Danaher Corp	DHR/NYSE	83	74	83	154
		2393	2228	3976	
Ecolab	ECL/NYSE	114	101	117	232
		1175	749	1390	
Energy Recovery	ERII/NASD	5	4	6	50
		238	204	978	
Esco Technologies	ESE/NYSE	36	34	37	11
		53	53	140	
GLV Inc.	GLV.A/Toronto	2	2	4	11
		21	8	52	
H2O Innovations	HEO/TSX	0	0	0	25
		56	15	166	
Nuverra Environ.	NES/NYSE	10	9	20	26
		461	256	609	
IDEX	IEX/NYSE	20	15	35	30
		27	13	34	
Layne Christensen	LAYN/NASD	7	7	18	16
		392	109	482	
MKS Instruments	MKSI/NASDAQ	37	28	37	53
		296	177	315	
Mueller Water Prods.	MWA/NYSE	10	8	10	155
		1244	700	1584	
Pall Corp.	PLL/NYSE	98	81	98	115
		683	440	761	
Pentair	PNR/NYSE	68	67	80	49
		1114	844	2114	
Polypore Intern. Inc.	PPO/NYSE	52	32	52	173
		436	219	1005	
Veolia Environnement	VE/NYSE	1	1	20	405
		0	4	253	
Waters Corp.	WAT/NYSE	116	100	116	30
		496	364	917	
Xylem	XYL/NYSE	39	33	39	185
		901	704	1826	
Water Index		38	26	42	43
		5203	3777	7792	593

Price/Volume Shares (Volume = 1,000 Shares)



Stock quotes courtesy of Gerard Sweeney, Analyst-Water & Infrastructure; Boenning & Scattergood, 610/832-5212.
Notes: Some figures are rounded. NASD= National Association of Securities Dealers. AMEX= American Stock Exchange. NYSE= New York Stock Exchange. TOR= Toronto Stock Exchange. n/a= not available. NM= not meaningful. Stock quotes come from sources we believe to be reliable but are not guaranteed to be all-inclusive or complete. This information is not to be construed as an offer or the solicitation of an offer to buy or sell the listed stocks above. Contributing firms and/or their individual brokers and/or members of their families, may have a position in the securities mentioned and may make purchases and/or sales of these securities from time to time in the open market or otherwise.

sor: Produced Water Society; *Details:* Zac Roesch at 512-961-5693 or zachary.roesch@globalwaterintel.com, or http://www.producedwatersociety.com.

Industrial and Commercial Water Reuse Conference
When: Feb. 1-3; *Where:* Austin, TX; *Sponsor:* WateReuse Association; *Details:* www.watereuse.org.

Cooling Technology Institute
When: Feb. 8-12. *Where:* New Orleans; *Sponsor:* Cooling Technology Institute. *Details:* www.cti.org.

AMTA/AWWA 2015 Membrane Technology Conference
When: March 2-6; *Where:* Orlando; *Sponsors:* American Membrane Technology Association and American Water Works Association; *Details:* http://www.amtaorg.com or http://www.awwa.org.

WQA Aquatech USA
When: April 21-24; *Where:* Las Vegas, Nev.; *Sponsor:* Water Quality Association; *Details:* or http://www.wqa.org/Aquatech.

Global Water Summit 2015
When: April 27-28; *Where:* Athens, Greece; *Sponsor:* Global Water Intelligence; *Details:* +44-(0)1865-204208, or: http://www.watermeetsmoney.com/.

AMTA/SWMOA Technology Transfer Workshop
When: May 19-21. *Where:* Carefree, AZ; *Sponsors:* American Membrane Technology Association and Southwest Membrane Operator Association; *Details:* www.amtaorg.com and www.swmoa.org.

ULTRAPURE WATER Pharma 2015
When: June 2-3; *Where:* Bethesda, MD; *Sponsor:* Ultrapure Water Journal; *Details:* 303-745-3890, 512-961-5693, or http://www.ultrapurewaterpharma.com/.

Electric Utilities Chemistry Workshop
When: June 2-4; *Where:* Champaign, IL; *Sponsor:* University of Illinois at Urbana-Champaign; *Details:* http://www.conferences.uiuc.edu/eucw/.

ACE15 - AWWA Conference & Exposition
When: June 7-10; *Where:* Anaheim, CA; *Sponsor:* American Water Works Association. *Details:* www.awwa.org.

BACKGROUNDER

WHY MATERIALS OF CONSTRUCTION MATTER

Corrosion. Leaching. Safety. These are three of many concerns one might list that will drive decisions when engineers and other decision makers select the materials used for a plant's high-purity water treatment system. The purpose of this short article is to provide initial background as to why materials of construction are important. The nature of this discussion is general, but at the close of the article, we will provide a list of some resources for those wishing to learn more specifics about this important area.

Often materials of construction are primarily associated with piping, valves, and gaskets. However, they extend far beyond the water distribution system and encompass the pumps, filters, pressure vessels, screens, and literally all different areas of the water plant. It should be noted that some materials are critical to ensuring the water purity and that will be the focus of the remainder of this discussion.

Wetted parts. Within the high-purity water world, the choice of materials of construction used in the treatment equipment and piping surfaces is critical. Besides piping and valves, other areas where attention may be given to the use of specialty materials would include pumps, pressure vessels, gaskets, heat exchangers, instrument sensors, ultraviolet sleeves, and filters and membranes, among others.

One concern is that the chosen material not accidentally become the source of a water contaminant. For example, in a semiconductor plant great care is given to ensure that piping systems and pumps not be the source of releasing ionic contaminants back into the water or become a source of particles. It is for those reasons that at least in the microelectronics industries that polyvinidene fluoride (PVDF) is so widely used for valves and distribution systems. PVDF is considered a pure material that will maintain the purity of the treated high-purity water. And it is because of these concerns that stainless steel is not used to distribute the water in semiconductor plants.

However, on the power generation side, metals are the mainstays for piping and boiler tubes. Therefore, power plant operators are concerned that the treatment system piping and the boiler tubes be durable and resist corrosion. Safety is another concern. Facility operators do not want to see a boiler explosion caused by plugged tubes or leaks caused by corrosion.

Facilities using pharmaceutical-grade waters for years have been associated with using stainless steel. One reason is because of the heat sanitization and sterilization practiced in facilities. Another reason has been because of the widespread practice to use distillation to produce Water for Injection. But, in the pharmaceutical industry there are places where fluoropolymers may be used. The key is that any alternative piping and other component materials be able to be sanitized or sterilized. This is because of one critical concern within the industry that the treatment system not be a source of bacteria or viruses.

Closing Thought

This aim of this brief discussion is to start an initial understanding of the important role materials of construction play in water treatment systems. As the treated water touches the piping and other elements, it either retains its purity, or may be recontaminated by the pipes, gaskets, pump surfaces, etc.

In the "For Further Study" section

By **Mike Henley**
(Editor, *Ultrapure Water Journal*)

(Editor's note: This is the first in the series of articles on subjects germane to high-purity water treatment. The goal is to provide a beginning foundation about these subjects for those individuals, who are new to the water treatment area, and those already involved, but who wish to learn more. This series will be an open forum, and we welcome proposals for future articles.)

below is a small listing of technical articles published over the years in *Ultrapure Water Journal* that have "materials of construction" as a key word. These articles have been authored by individuals who have worked in different ways with piping and other high-purity water treatment system materials.

Future Articles

In coming issues, we will examine other topics. The goal of this series will be to provide initial background in that will help those who are new to the industry to have a better understanding. We welcome proposals for "Backgrounder" articles on other subjects by those with expertise in high-purity water treatment. Interested parties should either call or email the author.

For Further Study

Biressi, G.; Haggard, K.; Neubauer, B. "Fluoropolymer Applications in High-Purity Water Distribution Systems", *Ultrapure Water Journal 30(6)*, pp. 15-18 (November/December 2013).

Biressi, G.; Neubauer, B. "Part 2: Ozone Sterilization of PVDF Piping Systems for High-Purity Water Distribution", *Ultrapure Water Journal 29(6)*, pp. 18-22 (November/December 2012).

Biressi, G.; Neubauer, B. "Part 1: Steam Sterilization of PVDF Piping Systems for High-Purity Water Distribution", *Ultrapure Water Journal 29(3)*, pp. 13-16 (May/June 2012).

Hanselka, R.; Williams, R.; Bukay, M. "Materials of Construction for Water Systems Part 1: Physical and Chemical Properties of Plastics", *Ultrapure Water Journal 4(5)*, pp. 46-50 (July/August 1987).

Hanselka, R.; Reinzuch, K.J.; Bukay, M. "Materials of Construction for Water Systems Part 2: Real-life Failure Modes of Plastics", *Ultrapure Water Journal 4(6)*, pp. 50-53 (September 1987).

Hanselka, R.; Williams, R.; Bukay, M. "Materials of Construction for Water Systems Part 3: Proper Selection of Elastomers", *Ultrapure Water Journal 4(8)*, pp. 52-55 (November 1987).

Harfst, W.F. "Piping Materials of Construction", *Ultrapure Water Journal 30(6)*, p. 24 (November/December 2013).

Howell, A.G. "Hydrogen Damage Mitigation by Boiler Chemical Cleaning", *Ultrapure Water Journal 31(3)*, pp. 21-25 (May/June 2014).

Libman, S.; Buesser, D.; Ekberg, B. "Next Generation of UPW Distribution System for the Next Generation of Semiconductor Fabs", *Ultrapure Water Journal 29(1)*, pp. 23-30 (January/February 2012).

Roll, D.L.; Ekstrand, B.J. "Surface Chemistry Improvement on 316L Stainless Steel Weld Zones Using a Gelled Citric Acid-Based Passivation Agent", *Ultrapure Water Journal 25(8)*, pp. 24-28 (November 2008).

Wermelinger, J.; Mueller, H.; Burkhart, M. "New 450-mm PVDF Piping Systems for Conveying High-Purity Water in Semiconductor Plants", *Ultrapure Water Journal 28(7)*, pp. 15-24 (July 2011).

Key words: COPPER, GASKETS, MATERIALS OF CONSTRUCTION, PVDF, STAINLESS STEEL, STEEL

SEMICONDUCTORS

UPW QUALITY AND TECHNOLOGY TO SUPPORT NEEDS IN ADVANCED INDUSTRIES

High-purity water systems and technologies have evolved during recent decades along with and driven by semiconductor technology needs. The development has been mainly driven by the growing purity requirements, infrastructure, challenges, cost opportunities, and operational reliability. Single short-term interruptions to production in the semiconductor industry often result in multimillion dollar impacts.

The semiconductor industry has demonstrated its ability to effectively collaborate professionally across the market, despite often competitive nature of the development. It became apparent in late 1990s that enabling future technology could only be possible via combined effort of defining risks and needs via International Technology Roadmap for Semiconductor (ITRS), which defines requirements to technology suppliers. Based on ITRS information, Semiconductor Equipment and Materials International (SEMI) develops standards for new solutions, thus facilitating the reliability and robustness of those solutions, focusing on the most advanced generation of the semiconductor market (1).

The American Society for Testing and Materials (ASTM) 5127 standard provides a good reference for water quality specifications, as well as historical retrospective on the water quality requirement changes as a function of the technology node. Although there is significant difference between the ultrapure water (UPW*) quality specs of different fabs or even geographic zones, Table A is representative of design criteria of semiconductor UPW systems.

By **Slava Libman, PhD**
(*Air Liquide Electronics U.S. LP—Balazs NanoAnalysis*)

ASTM (2) has been developing and maintaining standards across industries for generations.

"A time to market" driver allowed fast-track development of new solutions, which might not be possible in different industries otherwise. Risk of extremely high cost impact supported capital intense solutions.

This evolution resulted in new technologies and applications. Examples include the following:

- Membrane technologies/applications: High Efficiency RO, electrodeionization (EDI), membrane vacuum degasification (MVD), microfiltration, and ultrafiltration (UF) for fine particle control.
- Advanced oxidation processes (AOP), based on ozone, persulfate, hypobromide, and other chemistries.
- Metrology and analytical techniques for measuring ultralow levels of particles, silica, metals, ions, organics, and gases.
- New materials: polyvinylidene fluoride (PVDF) piping, perfluoroalkoxy (PFA) tubing, high-purity elastomers, polytetrafluoroethylene (PTFE) components, ethylene-tetrafluoroethylene (EFTE), and ethylene-chlorotrifluoroethylene (ECTFE) coating, clean polypropylene, clean polyvinylchloride (PVC), and others.
- As a result, technologies developed, validated, and commercialized for semiconductor industry became available for the less capital intense industries.

Design Considerations

A UPW system consists of two main parts: UPW make-up, providing treated UPW at purities almost down to the final qualifying purity levels, and UPW polish, providing final treatment and maintenance of the water quality at the target level.

Make-up system. Starting from mainly ion exchange (IX)-based deionization processes in the 1970s and 1980s, UPW technology transformed into reverse osmosis (RO)-based treatment. Depending on the limitations, the following three concepts of integration of the RO followed by IX deionization (DI) are the most common in the industry: 1. double-pass RO; 2. high efficiency RO (known as HERO™); and 3. DI in RO pretreatment. Table B provides the main pros and cons of these approaches.

The main focus of the make-up plant is delivering cost-effective dissolved and suspended solids removal. RO removes ~99% of total organic carbon, leaving mainly low molecular weight neutral organics. Although RO has defects in the membranes, a significant majority of particulates, including silts, particles of various sizes and types, bacteria, and viruses are removed.

The DI process, following an RO, removes nearly all ions. This deionization is typically based on the use of mixed IX resin, achieving resistivity of >18.1 megohm-cm. Due to the high cost of regenerating primary mixed beds (MB), anion exchange beds, or electrodeionization (EDI) are used upstream of the MBs to remove boron, silica, carbonic acids, and organic acids. The efforts of using EDI to replace primary MBs did not find wide use in the industry, despite significant progress in the development of EDI technology. This is because of limited removal efficiency of EDI, compared to the MB and due to its high energy consumption.

The UPW polish system design has been streamlined and is relatively consistent

TABLE A
Partial List of Typical UPW Requirements for Semiconductor-Based on ASTM and SEMI Standards

	Linewidth, micron						
	Type E-4	*Type E-3*	*Type E-2*	*Type E-1*	*Type E-1.1*	*Type E-1.2*	*SEMI F063*
Test Parameter	*Plating*	*>5.0*	*5.0–1.0*	*1.0–0.5*	*0.5–0.25*	*0.18–0.09*	*<0.065*
Resistivity, 25°C (on-line)	0.5	12	16.5	18.1	18.2	18.2	>18.18
TOC (ug/L) (on-line for <10 ppb)	1,000	300	50	5	2	1	<1
On-line dissolved oxygen (ug/L)	–	–	–	25	10	10	10
On-line residue after evaporation (ug/L)	–	–	–	1	0.5	0.1	0.1
On-line particles/L (micron range)							
>0.05	–	–	–	–	<1,500	<600	<200
SEM particles/L (micron range)							
0.1 – 0.2	–	–	–	1,000	1,000	<500	–
0.2 – 0.5	–	–	3,000	500	400	<100	–
0.5 – 1.0	–	10,000	–	100	50	<30	–
>1.0	100,000	–	–	<50	<30	<10	–
Silica – total (ug/L)	1,000	50	10	5	3	1	0.5
Silica – dissolved (ug/L)	–	–	–	3	1	0.5	0.5
Bacteria in CFU/Volume							
100 mL	100	50	10	5	3	1	1
Metals/Boron by ICP/MS (ug/L)							
19–22 Most common metals **; range for different metals	<500–1,000*	<2–5*	<1	<0.05	<0.02	<0.001–0.005	<0.001–0.01
Boron	–	–	0.05	0.3	0.1	0.05	0.05
Ions by IC (ug/L)							
Ammonium (ug/L)	–	–	–	0.1	0.1	0.05	0.05
7 Major Anions	<500–1,000*	<5–10*	<1–2*	0.1	0.05	0.05	0.05

** partial list of parameters*
*** ASTM5127 considers 19 metals, SEMI063 22, and ITRS all commercially available*

in newer facilities. Although the polish system involves less treatment steps, it is often more expensive than make-up because of higher capacity (consumption + recirculation), extensive use of high-purity materials, and expensive analytical instruments. The focus of the polish system is to provide the following: oxygen control, TOC polishing, particle removal, bacteria control, final quality monitoring, and pressure and flow control in the distribution.

A typical UPW polish system begins at the high-purity water tank equipped with a nitrogen blanket. Some systems provide ozone addition in the tank or piping, feeding the tank or leaving the tank. Ultraviolet (UV) treatment provides additional TOC control and ozone decomposition, when applicable. Membrane or tower degasification provides oxygen and nitrogen control, as well as removal of volatile organics. Polish mixed beds (typically non-regenerable) remove traces of contamination coming from the pretreatment or from the return. They also remove by-products of ozone and UV oxidation. The last step of polish treatment is final filtration for removal of fine particles of 10-nanometer (nm) size and larger. Most of the advanced facilities use cross flow ultrafilters with or without cartridge pre-filters.

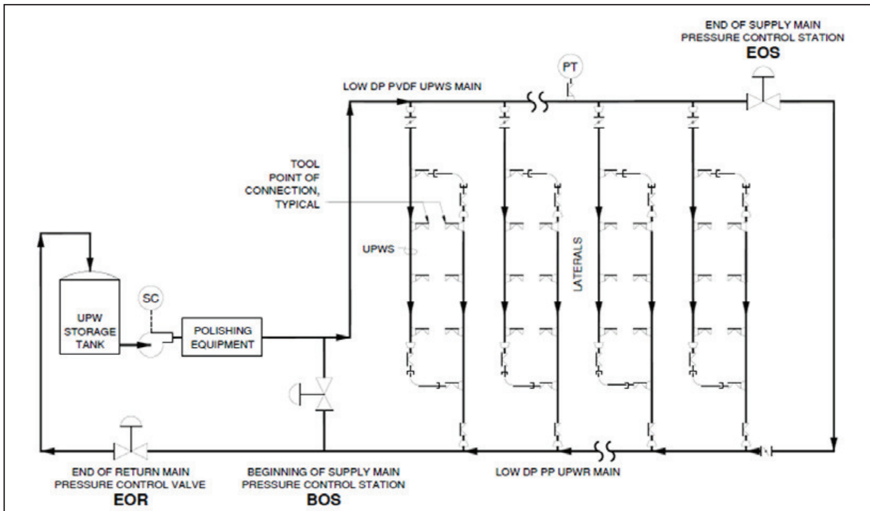


Figure 1. Schematic diagram of different typical locations of the pressure control valves in the distribution system.

Advanced metrology allows for tight control of dissolved oxygen, silica, boron, TOC, sodium, non-volatile residue, and particles.

Distribution system. One of the important factors determining UPW quality is

TABLE B
Advantages and Disadvantage of the Typical Configurations

Configuration	*Key Features*	*Pros*	*Cons*
Double-pass RO	Chemical pretreatment; RO recovery 65% to 80%.	Low chemical usage, no concentrated waste for disposal, less OPS involvement.	Lower rejection, high cost, organic /biofouling may cause OPS problems.
HERO	Complete hardness removal, CO^2 decarb, pH = 10.5-11. RO recovery 95%–99.5%	High rejection of organics, boron, silica. Relatively low cost. High efficiency of water use. Less OPS involvement downstream RO.	Limited number of suppliers. High chemical consumption. Concentrated waste. Needs tight hardness control.
DI-RO	SAC-Decarb-SBA IX, RO recovery 95%	Boron and silica removed in pretreatment. High efficiency of water use. Less OPS involvement downstream RO.	High chemical consumption. Concentrated waste.

the flowrate at the end of the pipes, at points where the flowrate is lowest and therefore the possibility of contamination is the highest (i.e., bacteria and pipe leach-outs, among others). Initial UPW systems had piping materials of construction made of lower purity materials (i.e., polyvinyl chloride [PVC]) that required maintaining high minimum velocity criteria of 1 foot per second (fps) or even higher. As technology evolved, piping purity changed to high-purity materials (i.e., PVDF and PFA) that allowed reducing minimum flow velocity down to 0.5 feet per second (fps). Since this criterion determined the significant portion of the system cost, further investigations and industry learning allowed for further tightening the criteria (3). A Reynolds number of 3,000 to 4,000 became popular, allowing a minimum flow criteria based on the turbulence factor. More sophisticated designs of UPW distribution and pressure control systems allowed for additional reduction in the recirculation to consumption ratio.

Figure 1 (4) shows a schematic diagram of different typical locations of the distribution system pressure control valves.

The right choice of lateral design, direct return versus reverse return (see Figure 2) permitted proper pressure control at a time when distribution design factors were shrinking (4).

Challenges in the Semiconductor Industry

UPW quality. The advanced semiconductor technology nodes of the future will require the most demanding high-purity water specifications.

Particles. The biggest challenge for UPW is particle control. This is due to the inability to detect "killer" particles and the concern that the final filters may be unable to remove those particles efficiently.

The size of "killer" particles is determined by half of the size of the node of semiconductor manufacturing. Table C indicates the size of the node and critical particle size as defined by ITRS, while Table D summarizes particle requirements as defined by the UPW ITRS (at www.itrs.net, "Yield Enhancement", Table 4).

In addition to the critical particle size, a new category of electrically active particles has been added, indicating that potentially even smaller than ½ node size particles will be detrimental to production (1). It can be noted that the concentration of the allowed particle level in UPW does not change, though the size of the particles goes down with decreasing node size. This is because of the assumption that particle deposition does not depend on the size of the particles, while the allowed level of defects is relatively constant throughout the technology generations. These assumptions and criteria are reviewed and updated every two years.

A benchmarking study using SEM (scanning electron microscope) analyses and nano-particle concentrating device

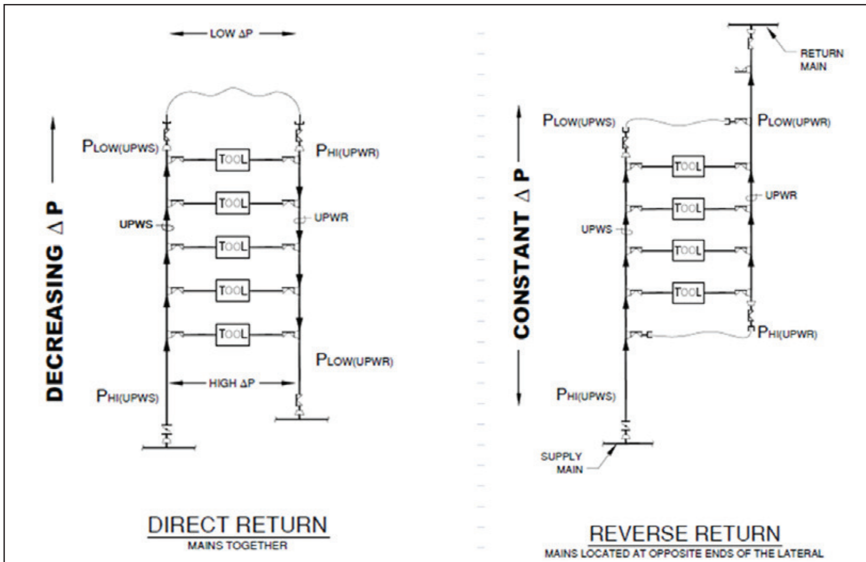


Figure 2. Typical "direct" and "reverse" return lateral configuration.

TABLE C
Critical Particle Size in UPW

Year of production	*2013*	*2014*	*2015*	*2016*	*2017*	*2018*	*2019*
Flash ½ Pitch (nm) (un-contacted Poly) (f)	23	20	18	15.9	14.2	12.6	11.3
DRAM ½ Pitch (nm) (contacted)	32	28	25	22.5	20.0	17.9	15.9
MPU/ASIC Metal 1 (M1) ½ Pitch (nm)	27	24	21	18.9	16.9	15.0	13.4
MPU Printed Gate Length (nm) ††	28	25	22	19.8	17.7	15.7	14.0
MPU Physical Gate Length (nm)	20	18	17	15.3	14.0	12.8	11.7
Water Environment Control such as Cleanroom, SMIF POD, FOUP, etc... not necessarily the cleanroom itself but water environment.							
Critical particle size (nm) [1]	20	17.9	15.9	14.2	12.6	11.3	10

TABLE D
Particles Spec Roadmap

Year of production	*2013*	*2014*	*2015*	*2016*	*2017*	*2018*	*2019*
Colloidal Silica (ppb) as SiO_2 [26.2]	TBD	TBD	TBD	TBD	TBD	TBD	TBD
Number of particles >critical particle size (see above) (#/L) [26]	1,000	1,000	1,000	1,000	1,000	1,000	1,000
Number of particles for EUV mask production >critical particle size (see above) (#/L) [26.3]	100	100	100	100	100	100	100
Electrically Active Particles >critical particle size (#/L) [26.4]	TBD	TBD	TBD	TBD	TBD	TBD	TBD

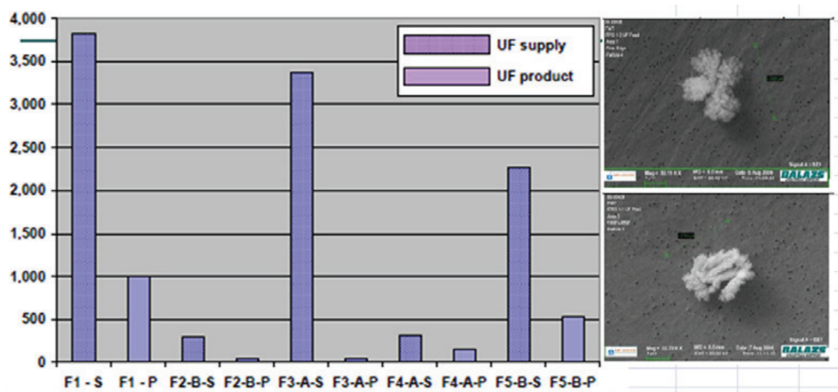


Figure 3. Particles counted using SEM in the samples pre-concentrated by nPCD (presented in relative number of counts for 5 different locations).

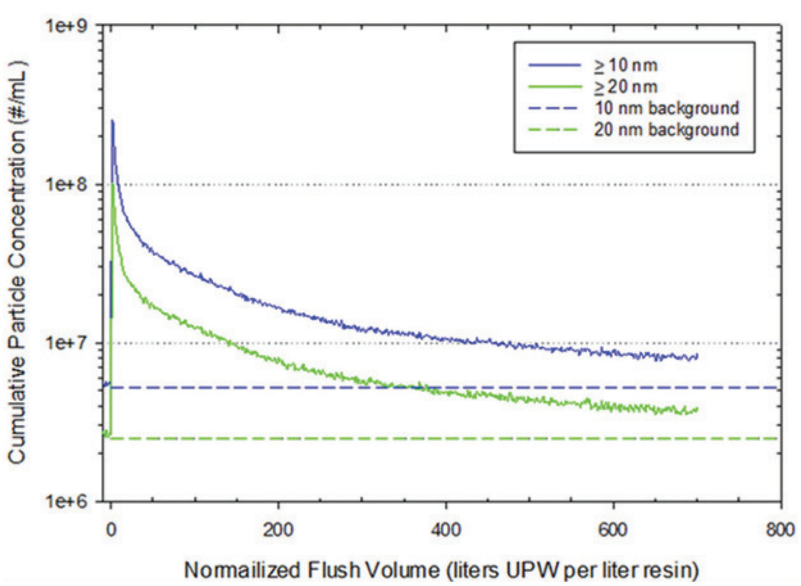


Figure 4. Particles concentration measured by LNS (liquid nano-particle size) for virgin resin provided by one of the major suppliers of high-purity IX resins.

(nPCD) (5) suggested that metal particles exist downstream of ultrafilters. Figure 3 indicates that metallic particles identified and counted by SEM were only partial removed (each pair of bars references feed and product sides of the ultrafilters). SEM images indicate flake structure of well visible particles made of very small particles, which would not have been seen without agglomeration using nPCD.

Scanning electron microscopy-energy-dispersive spectroscopy (SEM-EDS) also confirmed that those particles were made of stainless steel. The stainless steel particles are known to be produced by the distribution pumps.

Another particle source is associated with new IX resin. Loading virgin resin will generate a very high concentration of the particles, which may take awhile to rinse down (6). Figure 4 indicates that for some of the resin sources tested, even after hundreds of bed volumes of rinsing, the cumulative particle concentration in the critical size range (10 nm and larger) is still higher than 10^6-10^7/milliliter (mL) range. Given the information (7) that UFs do not fully remove particles of 10-nm size, having this high presence of particles leached off of the IX resin represents significant concern to production.

Colloidal silica is defined as a separate category of particle for the following reasons:

- Retention as organic and metal particles by final filters is not as good (8).
- Adsorption of metal ions and as such concentrating and carrying metals, affecting the process (9).
- Detection by laser particle counters is difficult because of its optical properties.

Organics. The presence of dissolved organics in UPW has presented a significant challenge to semiconductor facilities over the last decade. Since TOC measurement techniques have improved, more organic compounds have become detectable in UPW. Urea is one of more common sources of TOC and is difficult to remove due to its low molecular weight and neutral (no/low charge) nature. Depending on conditions, RO typically removes between 20% and 50% of urea. Rydzewski (10) indicated that urea may cause a T-topping effect on exposed chemically amplified resist. State-of-the-art immersion lithography became a driver of a 1-part per billion (ppb) total organic carbon (TOC) specification in UPW. For most surface water sources, urea is always present. TOC can be extremely difficult to control during seasonal urea excursions. Urea concentrations can rise as high as 100 ppb during seasonal excursions. A benchmarking study for organic speciation, involving 10 semiconductor-grade UPW systems demonstrated that for all sites fed with surface water, urea concentration varied between 0.6 and 6 ppb (11).

An overview of the different methods of organic speciation has been described by Gotts and Libman (12). Figure 5 represents typical LC-OCD results for UPW organic speciation. Huber, et al. (13) provides additional details about LC-OCD characteristics and capability. Using pre-concentration, this technique allows for speciation of the organics at a level lower than 1 ppb as TOC. As shown in Figure 5, the most common UPW organics are urea and low-molecular weight acids. The acids can be by-products of UV oxidation and may not be 100% removed by polishing MBs. In some cases, organic acids may be due to environmental sample contamination. An ITRS benchmarking study indicated that long life time of the resin in the polishing MB may result in biogrowth, producing biopolymers (14). In addition, new IX resin may also produce TMA and other organic compounds that may be difficult to treat, once again emphasizing the importance of selection of high-purity IX resin.

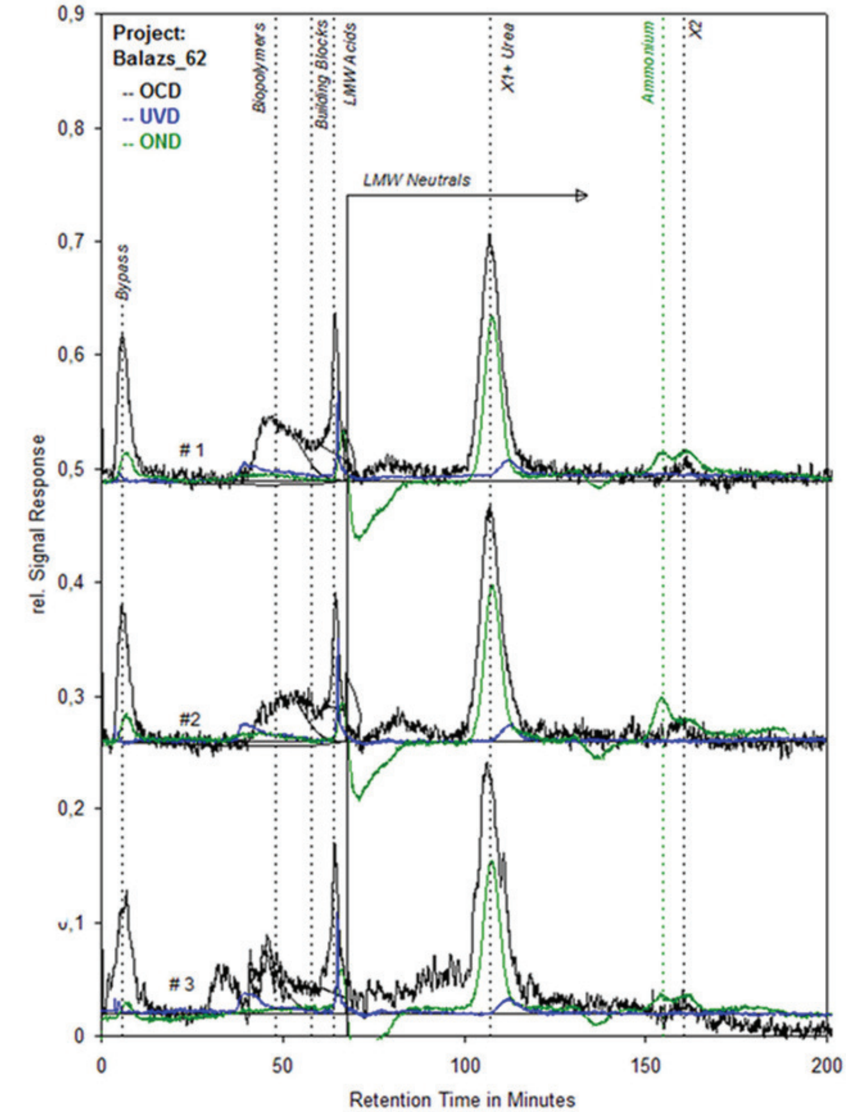


Figure 5. Triplicate result of organic speciation using LC-OCD

However, not all organic compounds are considered critical. UPW ITRS has defined only volatile organics with a boiling point higher than 200°C detrimental to the process. This is driven by the requirement to not exceed 1E+12 atoms per square centimeter (cm^2) concentration of carbon atoms on the surface of wafers. Although it is difficult to completely remove trihalomethanes (THM), it is an example of UPW non-critical organics. If the critical organics allowed level is 1 ppb, the non-critical level can be as high as 3 ppb (1). Independent of the definition of critical organics in UPW, immersion lithography may still continue to require 1 ppb TOC spec, which may still need to be addressed in POU applications.

Metals. Although the presence of metals in UPW is very low (at single digit parts per trillion or less) and modern high-purity water treatment systems are very reliable, keeping metallic contamination under control has been an important factor in UPW quality considerations and system design.

The key concerns and considerations include the following:

- High-purity piping materials used in

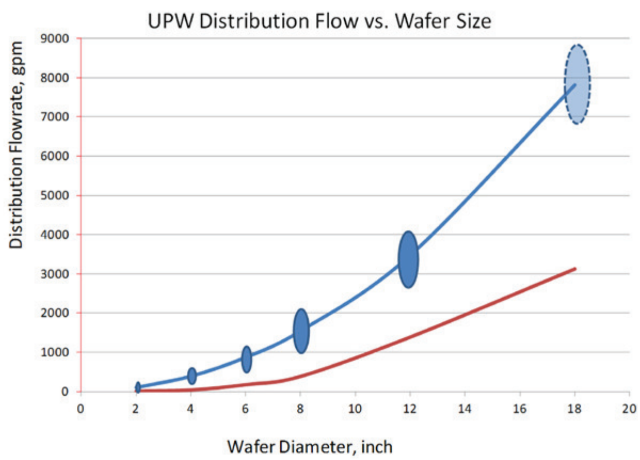


Figure 6. Growth of water consumption with increased wafer size.

UPW will leach out metals (calcium and iron, among others), originating from the raw material and manufacturing processes. Similar contamination may be introduced via the construction environment and handling. Schedule pressures of fast-track projects may result in relatively high residual contamination in the range of 10 to 20 parts per trillion (ppt) to be present in water;

- High pH of SC1 cleaning may precipitate metals on the wafer that may be difficult to remove.
- Trace levels of sodium may result from IX regeneration (bigger concerns if regenerable resin is used in polishers).
- Stainless steel components downstream from IX beds may leach metals;
- Improperly chosen elastomers and other components may add metal contamination.
- Heat exchangers may have internal leaks.

Current analytical techniques can provide metal detection down to the 0.2 ppt level (200 parts per quadrillion [ppq]). However such tests can only be done in a grab sample mode and require very clean sampling methods. It is important that trace metals contamination is addressed at the stage of system design and project planning.

Capacity challenges. Despite significant efforts to minimize UPW and site water consumption in the semiconductor industry, UPW usage grew exponentially with the technology nodes. The diameter of the main UPW distribution piping coincidently matched the size of the wafer manufactured by the facility. Figure 6 illustrates that increasing UPW consumption (lower line) drove increases in polish system capacity (flowrate of the recirculation – upper line), which determined the diameter of the largest UPW "main" line.

Significant growth in UPW consumption forced the industry to reconsider UPW system capacity sizing criteria. This means that any excess of the UPW polish system capacity needed to control cleanliness and pressure became extremely expensive. For example, with 200- millimeter (mm) wafer usage and smaller, the system capacity could be as high as 5 times the average consumption. Converting to 300-mm production would result in very expensive and sometimes not feasible configurations because of space constraints. The transition from flow velocity to Reynolds number criteria and more sophisticated distribution design provided partial solutions to the distribution capacity issue.

UPW consumption reduction efforts resulted in optimized tool and recipe design. However, increasing sensitivity to wafer contamination required increased UPW consumption, steadily growing from generation to generation of the semiconductor processes (15). UPW consumption is expected to continue increasing, posing challenges to the local infrastructure. The only solution to this usage is going to be extensive water reclamation and reuse.

Another source of water loss and capacity challenge is losses in UPW production. Some facilities lose 20% to 50% of raw water, depending on system configuration and incoming water quality. The focus on reduction in water consumption on the facility side is currently around increasing water efficiency of UPW system (i.e., higher RO recovery) and reclamation/recycling. This includes installation of IX processes in front of the RO or reclaiming wastewater from the UPW system.

Next generation factories are expected to consume 4 million to 5 million gallons of water per day, most of which is high purity. It is important to note that such mega-fabs are typically added to already existing giant semiconductor manufacturing sites. It is expected to be extremely challenging to support such development from infrastructure, environmental, and purity points of view.

Additional non-UPW water consumption challenges driven by the evolution of semiconductor manufacturing are related to air pollution control and energy usage. Increasing requirements for air emissions require a growing number of highly efficient abatement systems, using water for absorption of the toxic gases and their decomposition bi-products. Smaller features of semiconductor wafers will require a new generation of lithography tools. Next generation of EUV (extreme ultraviolet lithography) will significantly increase fab energy consumption, and as a result, the cooling load. This will drive higher cooling tower evaporation. Increased evaporation will not only require higher water consumption, together with reclamation efforts, it will significantly concentrate salts and organics in the site effluent, posing environmental compliance issues. This will require additional technology solutions for wastewater treatment. This is described in Currier, et al. (16).

Potential Solutions

Solutions for the above challenges are based on already existing technologies and applications.

- UPW systems will likely require more extensive use of IX in the pretreatment to the RO to maximize efficiency of the RO for those locations where handling concentrated regeneration waste is cost effective. In other areas, RO reject will be reclaimed for cooling towers or for UPW production.
- UPW Polish system design will minimize use of stainless steel to reduce the risk of metal ions or ultra-fine metallic particles.
- Polishing IX resin will be tightly monitored and controlled for organics, particles, and other contamination.
- Organics control will continue to evolve with more efficient

advance oxidation systems.

- A lot of effort will be put in the ultrafine particles control by higher efficiency of filtration and using multiple filtration barriers.
- UPW distribution capacity management will be further optimized, using more sophisticated concepts.
- Advanced metrology and analytical techniques will continue to evolve and provide solutions for the growing water quality challenges.

Water technology and management challenges will require better integrated and more sophisticated solutions. The role of water technology in the coming generations of semiconductor manufacturing will continue to grow. Tighter collaboration between semiconductor and facility technologies will be required.

Lastly, the knowledge gained from the semiconductor industry, as well as new technological solutions, will be available for application in other advanced industries.

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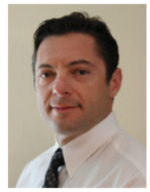
Endnote

*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 Slava Libman, Ph.D., is the director of advanced water analysis at Air Liquide-Balazs NanoAnalysis in Fremont, Calif. He has more than 18 years of experience in water and wastewater treatment, desalination, and water reuse in municipal and industrial applications. Dr. Libman earned his doctorate in environmental engineering from the Technion, Israel Institute of Technology (Haifa, Israel). Dr. Libman’s contributions include more than 30 publications. He is a co-chair of the UPW ITRS, and coordinates a number of task forces within SEMI addressing UPW technology needs.

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Key words: CONSERVATION, GUIDELINES, ITRS, MONITORING, PARTICLES, REUSE, SEMICONDUCTORS

BRIEFING

REVIEW OF THERMOPLASTIC FLUOROPOLYMERS USED IN HIGH-PURITY WATER APPLICATIONS

A fluoropolymer by definition is any polymer with a fluorine atom in the molecular structure. Thermoplastic fluoropolymers are one of the many niche families of specialty polymers that can be used in molding, extrusion, coating, solvent casting or foaming to make final components for handling chemicals, including various qualities of water. The range of this discussion will be oriented to present data and documented uses on the most common melt processable fluoropolymers that make up more than 95% of the commercial market (1).

For the purposes of setting limits related to polymer discussion, polytetrafluoroethylene (PTFE) will not be included. While melt-processable versions of PTFE are being developed, they are not yet used in chemical handling equipment at the volumes of the other melt processable fluoropolymers like polyvinylidene fluoride (PVDF), polyvinylidene fluoride copolymer (VF2/HFP), fluorinated ethylene-propylene copolymer (FEP), perfluoroalkoxy copolymer (PFA and MFA), poly ethylene-tetrafluoroethylene (ETFE), and poly ethylene chlorotrifluoroethylene (ECTFE).

Additionally, for the purposes of setting limits to the discussion, the fluoropolymers described here will be those that are typically sold at prices below $65 per kilogram (/kg) to the manufacturers that make the original processed components (2).

By **David A. Seiler, Sr.,**
Sean M. Stabler,
and **Dwana Gresham**
(*Arkema Inc.*)

Fluoropolymers used in Water Systems

In most comparisons of polymer families, fluoropolymers are considered to be on the high end of the engineering family of polymers. For ease of understanding the performance ranges of fluoropolymers they are often categorized as "soft" or "hard". While there are exceptions, soft fluoropolymers tend to be made up mostly of carbon and fluorine and hard fluoropolymers have significant amounts of carbon and fluorine, but also hydrogen in the polymer backbone. Soft fluoropolymers tend to have very high melting points and hard fluoropolymers tend to have higher tensile strength values up to 140°C.

Here is a list of the most commonly used fluoropolymers:

Soft fluoropolymers: FEP, MFA, PFA
Hard fluoropolymers: ECTFE, ETFE, PVDF, VF2/HFP

Fluoropolymers become attractive in the high-purity water process because they can possess many properties not found in alternative materials of construction. Each fluoropolymer has important properties that vary compared to others in this family, but selected properly, fluoropolymers can give excellent performance that cannot always be achieved by other polymer types or metals.

Advantages

Depending on the choice of soft or hard fluoropolymers, these materials can offer the following advantages:

- No rusting or rouging throughout the life of the system in contact with water.
- Limited extraction of ionic or organic species.
- High resistance to cleaning agents of all sorts (bleach, acid, ozone, and peroxide, among others).
- The ability to autoclave and no loss of performance after steam cleaning (3).
- Very smooth inner surface of process components.
- Low friction surface.
- High impact resistance at ambient and colder temperatures.
- High resistance to burning (FM 4910 compliance; ASTM E84 25/50 rating).
- Improved resistance to biofilm buildup (4).
- Low permeation to water and oxygen (5).
- Easily thermoformed, welded or machined.
- High abrasion resistance (specific to hard fluoropolymers).
- Regulatory listings and/or compliance (FDA, USP Class 6, NSF—dependent on manufacturer).
- Powder or liquid coating versions available for application to metal.
- Soluble in common solvents for casting of micro-porous membranes (specific to hard fluoropolymers).
- Extrudable into fine fibers for nonwoven filtration products (specific to hard fluoropolymers).

In comparing the common thermoplastic fluoropolymers, it may be best to point out some comments followed by a description of the most popular uses of these materials in the high-purity water handling applications such as the semiconductor and biopharma industries.

Characteristics

From the engineering cost performance standpoint, it is well known that PVDF is the least expensive fluoropolymer based on density and price per pound (2).

TABLE A
Physical, Thermal, and Mechanical Properties of Fluoropolymers

Property	*Test Method and (Units)*	*FEP*	*PFA*	*ECTFE*	*ETFE*	*PVDF*	*VF2/HFP Copolymer Range**
Melting Point	ASTM D3418 – (°C)	260	305	240	245	168	95-167
Specific Gravity		2.15	2.15	1.69	1.70	1.76	1.77 – 1.81
Tensile Yield	ASTM D638 – (MPa)	17	17	34	34	52	6 - 41
Hardness	ASTM D2240 – (Shore D)	55	60	75	75	78	45 - 75
Flexural Modulus	ASTM D790 – (MPa)	600	600	1660	1200	2070	69 - 1240
Tabor Abrasion	CS-17 1000g – (mg/1,000 cycles)	75	25	7	60	7	6 - 70
Limiting Oxygen Index (LOI)	ASTM D2868 – (%)	95	95	64	30	42 - 65	42

**This is a series of resins that can exhibit the ranges given and can be specifically selected to meet a requirement at either end of the data listed.*

This lower cost makes PVDF often the first fluoropolymer considered in design when the high performance is needed. PVDF is also able to be processed on standard molding and extrusion equipment without exotic design because of its lower melting point and processing temperatures. PVDF homopolymer has the highest heat deflection temperature as well as the highest abrasion resistance, which is about the same low material loss as ECTFE and some forms of VF2/HFP copolymer. Finally, PVDF homopolymer grades that have been subjected to a rigorous 20,000 hour test are given a UL® RTI rating of 150°C.

PVDF copolymer (VF2/HFP) covers a very broad set of properties, depending on the level of HFP in the molecular structure. In general, this copolymer is more flexible and impact resistant than PVDF homopolymer. PVDF copolymer broadens the range of PVDF by essentially having the opposite properties when it comes to flexibility. Also, PVDF copolymer is able to be blended with PVDF homopolymer to tailor make products or, to make welded structures that require both a rigid and a flexible product in the same design.

ECTFE and ETFE round out the common hard fluoropolymers. These fluoropolymers have higher melt points than PVDF but lower deflection temperatures (6), so care must be taken to understand any actual advantages. Under low pressure, these materials have useful properties above 160°C. They can be post welded and fabricated in similar manners to PVDF or PVDF copolymer.

FEP is well known as a fluoropolymer with adequate flexibility for tubing, and a high melting point. It has almost universal chemical resistance, but because of it being soft, it is not often used as a self-supporting structural material. In the high-purity industry, FEP is often over-shadowed by PFA, which is more expensive, but has a higher temperature rating and is more universal for very high-end performance needs (7). FEP, PFA, or MFA would be considered for tubing or bonded structures where very high temperatures or extremely aggressive cleaning agents are involved in pure water processing. Figure 1 shows pipes, fittings, wetted pump components, and composite tank structures used for high purity water.

While there are more than one manufacturer of each version of fluoropolymer, Table A makes an effort to compare "general" properties of each of the fluoropolymers mentioned. It is highly recommended that a design professional do a more involved search of each manufacturer's typical property ranges before making a decision on a fluoropolymer type (especially for the soft fluoropolymers that show the greatest variation in literature).

Based on the chemical resistance and the physical, thermal, and mechanical properties, the manufacturers of the fluoropolymers list the following general applications in the high-purity water industry (shown in Table B) (8).

Final Thought

Thermoplastic Fluoropolymers have

Figure 1. Examples of molded, extruded, and formed fluoropolymer parts.

Figure 2. Fluoropolymer composite tubing designed for high flexibility in biotech applications.
Photo courtesy of Eldon James, Denver, CO.

Figure 3. Hard fluoropolymers such as found in hollow fiber membranes.

TABLE B
Common Fluid Handling Components Made with Thermoplastic Fluoropolymers

Fluoropolymer	*Applications*
FEP (TFE/HFP)	Tubing, Sheets, Rods & Blocks, Film, Vessel lining, Pipe Lining
ECTFE	Solid & Lined Pipe, Pumps, Valves, Tanks, Vessel Lining, Housings, Fabrics, Coatings, Sheets, Rods & Blocks, Fittings, Films
ETFE	Tanks, Pumps, Valve & Pipe Linings, Coatings, Fittings, Sheets, Rods & Blocks, Films, Tower Packing, Vessel Lining, Rotomolding
PFA	Tubing, Piping, Wafer Carriers, Vessel Linings, Tanks, Sheets, Rods & Blocks, Pumps, Filter Housings, Tower Packing, Seals, Films, Filtration Systems, Fittings, Valves, Rotomolding
PVDF	Piping, Pumps, Tanks, Sheets, Rods & Blocks, Nozzles, Instrumentation, Tubing, Tower Packing, Filtration Systems, Membranes, Vessel Linings, Tanks, Pipe Lining, Films, Fittings, Valves, Housings, Fabrics, Coatings, ASTM E84 25/50 components
PVDF Copolymer	Piping, Pumps, Tanks, Sheets, Rods & Blocks, Nozzles, Instrumentation, Tubing, Filtration Systems, Membranes, Vessel Linings, Tanks, Pipe Lining, Films, Fittings, Valves, Housings, Fabrics, Coatings, Composite Tubing Structures, Rotomolding

been a highly developing field of polymers over the last 10 years and for the next 3 years are projected to grow at about 5% globally across all markets (9). Some of the new things to look for that are becoming available are:

1. PVDF resins composites with tensile yield properties of 70 megapascal (MPa) for structural applications.
2. PVDF copolymer/polyurethane composite tubing for biotech applications that combine the purity and chemical resistance of PVDF with the high flexibility of polyurethane. Figure 2 shows an example of a highly flexible two-layer polymer tube with an inner layer of PVDF copolymer used for food processing and pharmaceutical pure water.
3. PVDF homopolymer fibers of very low diameter for filtration fabrics. Figure 3 shows hard fluoropolymers such as found used in hollow-fiber membranes.

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Author David A. Seiler received his BS in chemical engineering from Penn State University in 1983. He is employed for Arkema Inc. as the Americas Business Manager Industrial/Global Technical Advisor Fluoropolymers, and has worked in the area of Fluoropolymers for 31 years. Mr. Seiler is currently a voting committee member on ASME-BPE sub-committee on polymers, and an active member of ASTM (D, E, F), ICC, NFPA, and SEMI.

Coauthor Sean M. Stabler is a business development engineer in the Fluoropolymers Business Group at Arkema and is responsible for foams, fibers, membrane and industrial water markets. Mr. Stabler holds a BS in plastic and polymer engineering technology from the Pennsylvania College of Technology, and he received his MS in materials science and engineering from Drexel University in Philadelphia, PA.

Coauthor Dwana Gresham is marketing coordinator and inside sales for Arkema Fluoropolymers. Ms. Gresham holds a BS in business management from Rosemont College. She has worked in fluoropolymers for 15 years.

Key words: MATERIALS OF CONSTRUCTION, PHARMACEUTICALS, PIPING, PVDF, SEMICONDUCTORS

LAB WATER

ADVANTAGES OF RECIRCULATING FAUCETS TO CONTROL POU MICROBIAL CONTAMINATION

Laboratory faucets, sometimes referred to as gooseneck faucets, abound in environments where a small amount of Purified Water (PW*) or deionized (DI) water is needed for biological or laboratory tests, reagent or standards preparation, and glassware or instrument cleanup, just to name a few processes. There are a variety of these faucets available from a number of suppliers in today's market.

The majority of these laboratory faucets are usually chosen for installation based on their inexpensive cost or aesthetically conforming design with little or no concern given to overall quality of water delivered through those direct-flow fixtures, which allows for biofilm buildup in the static flow stream within the faucet and upstream piping during no-flow conditions. Often overlooked by laboratory design professionals is the installation of the recirculating laboratory faucet (RLF), where the flow is constantly circulating through the head of the faucet in close proximity to the valve and outlet.

Stagnant areas in a laboratory PW faucet can negatively influence the outcome of an experiment via unwanted biofilm contamination. Good piping design practices dictate that a dead leg in a hot water system, as defined by Genova (1), should not exceed a length greater than six pipe diameters; in a cold system, it is any static area, although a rule of thumb numbers of three or four pipe diameters is commonly used. Proper use of RLFs in a laboratory setting will have a profound effect over reducing, or eliminating the propagation of colony forming units (cfu) when compared to non-RLF type goosenecks.

The authors of this article seek to show the microbial performance difference in RLFs versus non-RLFs in a controlled study conducted at a lab specializing in ultra-trace contaminant analysis.

By **John Wammes, CPIP,**
(*Water Works Inc.*)
Tom Sixsmith,
Paul Galvin,
(*Georg Fischer Piping Systems*)
and **Marty Burkhart**
(*Hi PureTech, Inc.*)

Maintaining Quality—A Significant Investment

According to Good Engineering Practice (GEP) principles, "equipment should be fit for purpose, appropriate, reliable and cost effective". This should also include the cost of maintaining water quality. To maintain PW quality, a totally recirculating distribution loop will include a significant investment in various purification technologies, including the ongoing costs for operation and maintenance. The range of equipment used to purify water and the architecture of distribution systems can vary widely from facility to facility. But in general, a central water system in a facility is a key component for any life science organization. In some applications, the system is also subject to qualification under validation protocols if used in a current Good Manufacturing Practice (cGMP) process. Per cGMP guidelines, quality should be built into the design of a system, since it is more difficult and expensive to apply quality later. This philosophy is also valuable to non-GMP system designs.

Once made, PW is typically distributed to the points of use (POU) through a recirculating distribution loop. The continuous flow of the recirculating loop is used to ensure that the water remains in motion since stagnant water is prone to absorbing contaminants and fostering microbial growth. Numerous studies have been conducted trying to identify the optimal velocity or rate of recirculation. Although consensus to which parameters are best has never been reached, recirculation versus stagnation is a key, universally accepted principal to maintaining microbial quality for all systems. This principal is also critical to the life and quality of natural waters as seen in the drastic differences in slow or stagnant water versus flowing rivers and streams.

PW is often recirculated through steps such as ultraviolet (UV), deionization, sub-micron filtration, or heat exchangers, which are needed to continuously polish and passively sterilize the water to maintain quality and ready-for-use condition. For this reason, it makes sense to consider the purification equipment, the distribution loop, and the POU as mutually dependent in forming a complete, cohesive system.

Maintaining the PW system typically includes some form of system sanitization. Unlike municipal water systems that retain an added, residual chemical oxidant such as chlorine for continuous control of microbial contaminants, PW systems are devoid of these residual chemical controls because the addition of these chemicals would be contrary to the purification process. Without the added chemical control, PW piping systems are subject to microbial growth. To mitigate this microbial growth, many systems employ scheduled sanitization procedures that can include chemical or heat sanitization. Low-flow, or stagnant conditions hinder the sanitization process, increasing the time and expense of this service.

To be effective, the sanitization chemical or heat treatment must reach all of the areas within the distribution system. The best way to do this is through complete recirculation to achieve the recommended working concentration or temperature

Figure 1. Parallel DI loop valves and instrumentation with 1-in branch piping connected to a 3-in main loop.

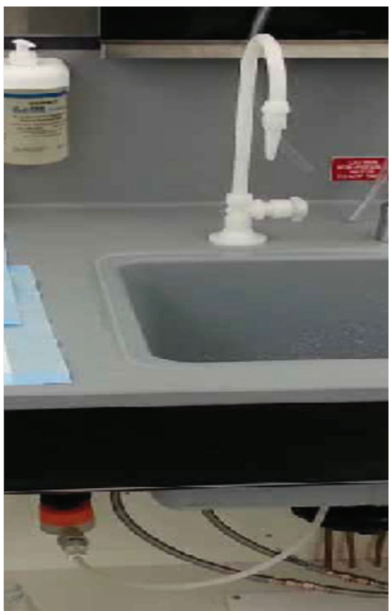

Figure 2. Non-RLF point-of-use valve and tubing.

Figure 3. An RLF faucet with supply and return tubing.

of the sanitization procedure. The system must be rinsed or cooled after sanitization. Stagnant sections within the distribution system can harbor residual sanitization chemical that would affect enduser experiments and possibly safety. Again, the best and most economical way to accomplish post-sanitization rinse-up is through complete recirculation.

Distribution to POU

PW distributed through a recirculating loop can be fed to a POU valve that is connected to a piece of equipment or, more often, it is connected to a lab faucet. In most research facilities, lab faucets account for 60% to 80% of the POU, whereas, equipment accounts for about 20% to 40% of the POU. It is best practice to evaluate each POU on a distribution system to ensure it meets the requirements for minimal dead leg length.

The most common type of distribution system is a serpentine loop that snakes through the facility with a single dedicated supply and return line. This architecture allows full design flow throughout the facility, maximizing the recirculating purification efforts.

Less common is the parallel loop design that can have multiple supply and return lines going back to a common loop supply and return header. This architecture applies full design flow to only the main supply and return header with restricted flow to the smaller branch loops. The perceived economic advantage of this design is that smaller diameter piping can be used on the various branch loops.

However, as shown in Figure 1, additional valves and instrumentation is typically required to force water flow from the full size header through the restricted branch loops to achieve sufficient flow. It can be difficult to correctly engineer, commission, and balance this type of loop to optimize flow to each POU on the branch. If left unbalanced, low flow or stagnant conditions within the branch loops can give rise to or enhance biofilm growth. If there is not complete recirculation, the entire system may be compromised.

Non-RLF Installations

Many systems employ non-recirculating type faucets that are connected to the loop with a piece of small diameter tubing (3/8 inch [in] to ½ in) that can range in length but is typically a few feet long. The dead leg tubing shown in Figure 2 is typical for non-RLF type faucets. The isolation valve is optional but often used on most installations. If the loop size is 2 in, for example, a 2-in by ½-in tee connection with a short dead leg pipe section will be installed that is often terminated with an isolation valve like the one shown in Figure 2. Flexible tubing of polyethylene, polypropylene, or polyvinylidene fluoride (PVDF) is normally used to connect to the faucet.

Static water contained within the dead leg tubing of non-RLFs is an ideal breeding ground for bacterial contaminants. Microbial contaminated water can be a threat to life science operations in several ways. Contaminant microbes can compete with biotech processes or experiments that use living organisms, consuming nutrients needed for the experiment, and reducing cell culture yield and viability. Contaminant microbes can also possess higher concentrations of ions, organic contaminants, and cellular debris that are released when the cell dies, contaminating the experiment or process that requires PW. Water quality that fails to meet the enduser's requirements is typically non-usable and must be re-purified or replaced.

Other Strategies

To help minimize the impact of microbial contaminants emanating from non-RLFs, endusers will sometimes implement other strategies such as flushing protocols and/or POU filtration. Although these strategies can provide a temporary or expedient remedy, it does not address the main problem of microbial growth within the system. Biofilm growth within stagnant sections (dead legs) of the system can be prolific, forming deeply embedded colonies that will often slough into the main recirculating flow and traveling to and establishing in other sections of the system.

Flushing. A temporary control strategy for non-RLFs that is often used involves flushing of the POU to dislodge and rinse microbial contaminants, growing within the dead leg tubing, to drain. Example 1 is from a life science lab location where the system recirculates with a water quality of 17.8 to 18 megohm-cm resistivity, < 100 cfu per milliliter (cfu/mL) bacteria and 3 to 5 parts per billion (ppb) of total organic carbon (TOC). This lab has a documented protocol to flush each POU once per week for 2 minutes. They have four labs, or a total of approximately 50 faucets throughout the campus that get rinsed at a rate of 4 liters per minute (L/min). A total annual volume of nearly 21,000 L of expensive DI rinse water is wasted to drain in this flushing protocol, imposing avoidable expense, environmental waste, and additional lab time.

POU filtration. Other strategies may include POU purification or filtration in a single-pass process. This remedy of using a 0.2-micron (µm)filter at the end of the dead leg tubing does nothing for TOC or endotoxin control. As live bacterial cells get trapped in the pores of the filter membrane, there is the possibility of bacterial grow through, resulting in bacteria on the clean side of the membrane filter.

Recently, POU filters were added to the goosenecks at a facility in order to meet a < 10 cfu/100 mL bacteria requirement that could not be continuously met with the stagnant dead leg tubing at the non-RLFs. There are 25 faucets at an approximate cost of $100 per filter installed. These filters are replaced every 6 months for a total annual maintenance cost of approximately $5,000 per year to implement and maintain this strategy.

RLF installations. Recirculating lab faucets (Figure 3) use the key universal principal of flowing or non-stagnant conditions to reduce or eliminate the colony forming units when compared to non-RLF type goosenecks. RLFs have water passing continuously by the nozzle, just behind the faucet valve via a U-bend loop configuration within the faucet body. To accommodate the reduction in pipe size required to connect to a RLF, smaller branch supply and return piping or tubing is typically needed.

Buesser (2) states that differential pressure in a high-purity water loop is the force that drives water from supply to return and is analogous to voltage across a circuit. Flowing water will normally take the path of least resistance, so to force flow through the smaller branch piping a valve or an engineered orifice type device is needed at each RLF. If a valve is used, a flow meter and pressure gauge may be required to adjust and optimize the flow to each point of use, similar to parallel loop architecture.

Experimental Overview

To demonstrate the impact that a recirculating faucet has on the overall health of a PW system, two types of faucets were tested. A popular and often-specified, non-recirculating faucet, and a popular recirculating lab faucet were tested over an 11-week period. All materials were new and commercially purchased from standard sources. Tubing and materials were high-quality PVDF with very low extractable contaminants.

The test stand shown in Figure 4 used the house high-purity PVDF water system from the test lab to feed high-purity water through a standard 25-millimeter (mm) serpentine loop design to both faucets. The house DI water system is designed and maintained to produce high-purity water for semiconductor analysis with very low contaminant levels. The test stand was fitted at the end of the lab's DI system return line just before returning to the storage tank.

The non-recirculating lab faucet was installed using a PVDF tee fitting and 6 ft. of dead leg PVDF tubing to the faucet. The recirculating lab faucet was installed using 6 ft. of supply and return PVDF tubing with an inline flow diverter to route a small portion of the recirculating loop water through the faucet.

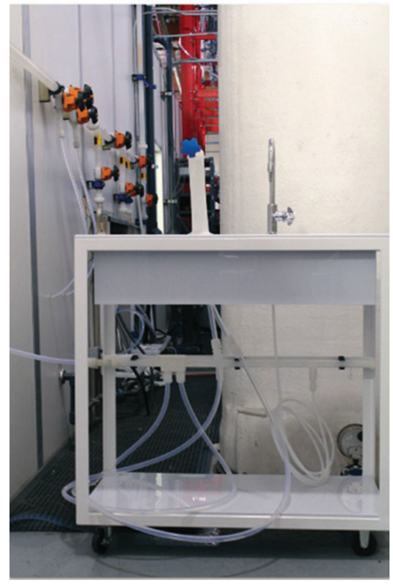

Figure 4. Test stand with non-RLF and RLF goosenecks.

Inline Flow Diverter for RLF

The simple basics of the in-line flow diverter (IFD) is shown in figure 5. The IFD is engineered to produce a small pressure differential that forces a portion of the recirculating loop flow through the faucet. According to Georg Fischer manufacturing literature, the laboratory system's 9 gallons per minute (gpm) flowrate equated to approximately 1.2 gpm through the AquaTap RLF, and a 0.6 pounds per square inch gauge (psig) pressure loss (3).

One note on the economics of the RLF faucet that uses the in-line flow diverter: Incorporation of the IFD device into

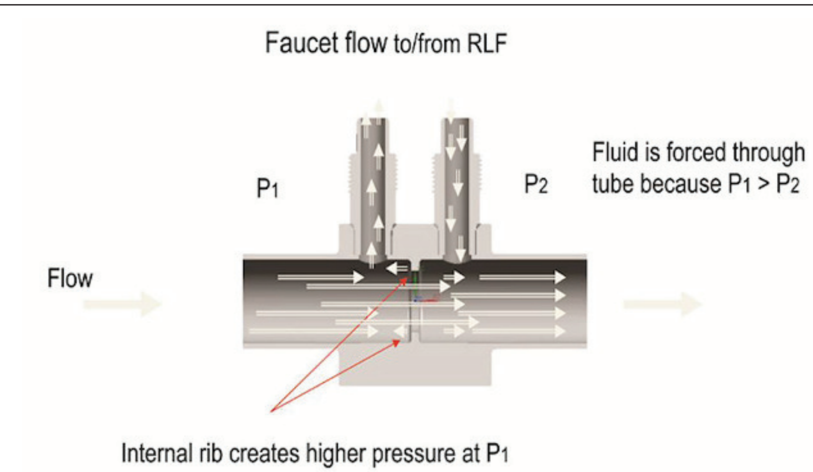

Figure 5. In-line flow diverter for RLF design.

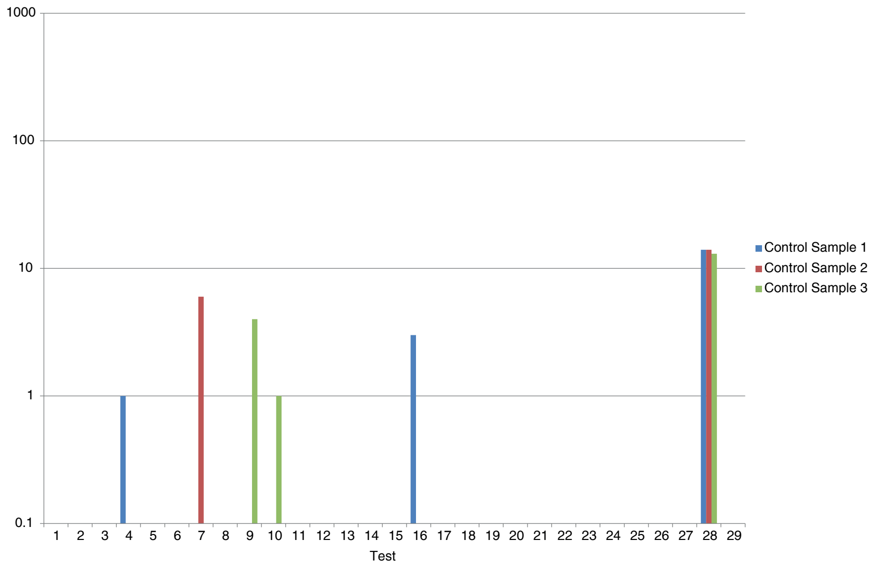

Figure 6. Colony forming units incubated from control samples (note log scale).

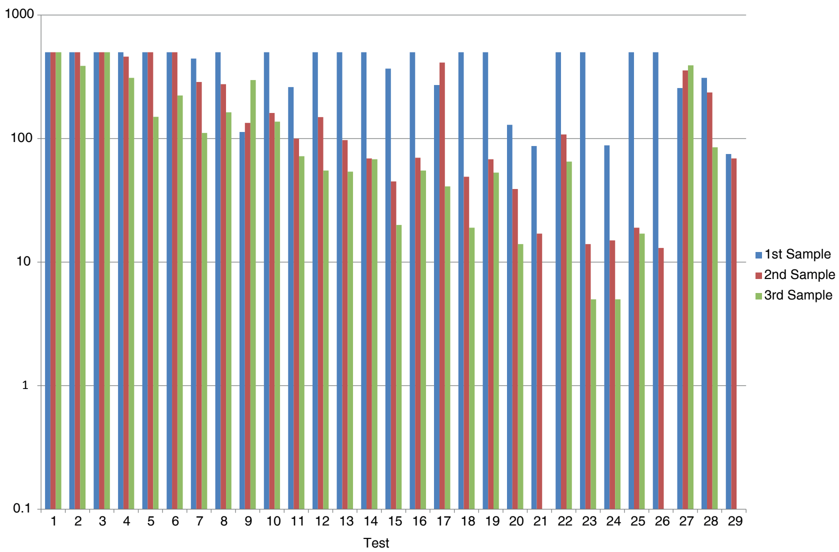

Figure 7. Colony forming units incubated from non-RLF faucet (note log scale).

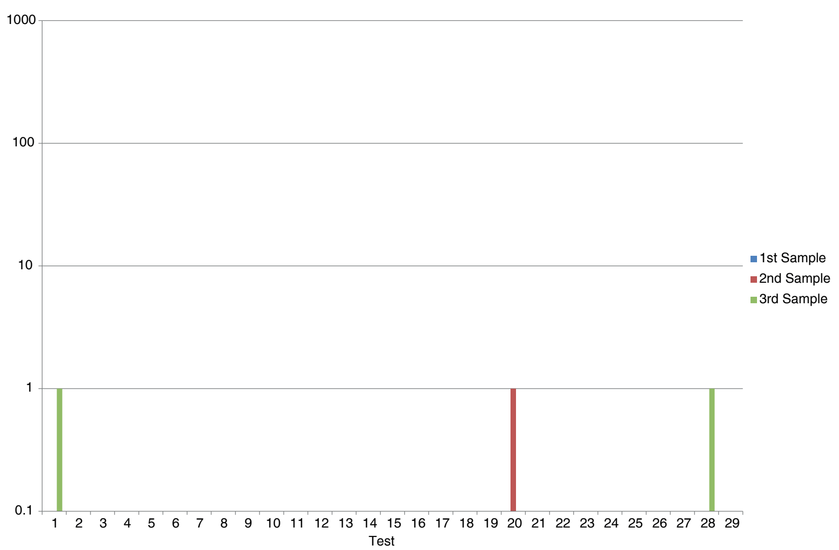

Figure 8. Colony forming units incubated from RLF AquaTap faucet (note log scale).

the system design provides the smaller piping characteristic and economic benefits of the parallel loop design but without the associated extra valves and instrumentation needed for the parallel loop design. Flow characteristics of the IFD are engineered based upon the loop pipe size, reducing the chance of engineering or installation error. We found installation of the IFD and associated supply and return tubing to be simple and straightforward. Given the smaller diameter and flexibility of the RLF installation protocol, it may be an ideal solution for installation in existing locations without the need for wall or lab bench removal.

Test Protocol

The test protocol was conducted at a well-known, trace analytical lab. Samples were checked for cfu according to American Society for Testing and Materials International (ASTM) methods at a detection limit of 1 cfu/100 mL. Both faucets were allowed to go stagnant at the nozzle for several days prior to testing. The sample size was 100 mL collected in bacterial sampling containers. 100 mL water samples were taken from each faucet in triplicate.

Samples were taken at 2 specific test intervals. The first interval included Samples 1 through 12, which were allowed to go stagnant for 3 days and then samples were drawn following a 5-second flush of each faucet.

The second interval included Samples 13 to 26, which were also allowed to go stagnant for 3 days, but the samples were drawn immediately upon opening the faucet, without the benefit of an initial 5-second flush cycle.

Lastly, Samples 27 to 29 were allowed to go stagnant for 1 week and samples were drawn for bacteria testing.

Test Results

Control samples. The labs house high-purity water was used as a control. Control samples were taken in triplicate resulting in 87 total control samples drawn. As shown in Figure 6, results for most of the controls were non-detectable or at the detection limit of 1 cfu/100 mL with 4 of the 87 control samples in the range of 5 to 15 cfu/100 mL.

TABLE A
CFU Summary for RLF and Non-RLF Faucets

Sample Description	*Number of Times cfu's Exceeded Detection Limits of 1*	*Number of Times cfu's Exceeded TNTC*
AquaTap recirculating faucet	3 (out of 87 samples)	0 (out of 87 samples)
Non-recirculating faucet	84 (out of 87 samples)	25 (out of 87 samples)

Sample Description	*% of Times cfu's Exceeded Detection Limit of 1*	*% Times cfu's Exceeded TNTC*
AquaTap recirculating faucet	3%	0%
Non-recirculating faucet	97%	29%

TNTC = too numerous to count

Non-RLF samples. Figure 7 illustrates data for the non-recirculating faucet. 500 cfu/100 mL was used as the high limit of TNTC (too numerous to count).

Again, Samples 1 through 12 were taken after a 5-second flush and Samples 13 through 26 were taken immediately upon opening the faucet following 3 days of stagnation at the nozzle. Samples 27, 28, and 29 were taken after a week of stagnation.

RLF samples. Figure 8 illustrates data for the recirculating lab faucet with the IFD. Test results for the RLF samples showed only 3 out of 87 samples as positive microbial counts at the limit of detection = 1 cfu/100 mL. Of the 3 positive samples, 1 was taken from second draw of a faucet and 2 were taken from the third draw of the triplicate samples taken from these 3 faucets.

Case Summary

Table A provides a summary of the bacterial counts (cfu) for both faucets. For the non-RFL, the first sample draw (blue line) of the triplicate normally resulted in higher counts with subsequent second and third sample draws of the triplicate containing slightly lower counts.

This is likely due to the flushing effects of the 1st 100-mL draw. This effect was less pronounced when preceded by the 5-second initial flush as seen in Samples 1 through 12. When samples were drawn immediately upon opening the faucet, the flushing effect appeared to be more pronounced on the second sample drawn, resulting in lower cfu counts for the second sample drawn. This could be due to a more consistent, lower velocity flow pattern associated with sample draw that would be less likely to disturb biofilm layers versus the high-velocity flow pattern associated with the initial 5-second flush, which could induce additional sloughing of biofilm layers prior to sampling.

Of particular note was Sample 28 which had slightly abnormal data points for the control samples, the non-RLF samples, and the RLF samples. Data for Sample 28 was retained despite the abnormalities.

Conclusion

The RLF, with water passing continuously by the nozzle, just behind the faucet valve via the u-bend loop configuration within the faucet body, had vastly fewer cfu than the non-RLF type gooseneck where the water was trapped within the single feed tubing run. The excessive dead-leg lengths associated with the non-RLF faucet promoted bacteria growth as indicated in large numbers of CFUs being detected.

Laboratory personnel and system designers, architects and engineers should understand that installing a continuous piping loop for their PW without ensuring that all fixture feeds are part of this flow stream are defeating the purpose of continuous flow design. Recirculating lab faucets add significant performance value to the overall design of the system, whereas non-recirculating lab faucets with excessive dead-legs worsen the overall performance of the system. Quantifying this issue helps to bridge the gap between inexpensive dead leg, non-recirculating faucets, and the investment in recirculating lab faucets.

Although many labs have adopted procedures or temporary remedies to mitigate microbial contaminants at their lab faucets such as flushing or POU filters, it is very apparent that a recirculating lab faucet provides the necessary bacterial mitigation without additional equipment or waste of DI water and time, providing better overall value for the end-user.

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Author John Wammes is a co-founder, president, and CEO of Water Works, Inc. His expertise stems from over 20 years of engineering and implementing water purification solutions for the life science industry. Prior to founding Water Works in 2007, John developed industrial and large scale municipal RO processes as an applications engineer at Hydranautics and GE/Ionics. Mr. Wammes earned *a BA degree in business and economics from Hope College, Holland, MI, and is ISPE-certified as Pharmaceutical Industry Professional (CPIP).*

Coauthor Thomas Sixsmith is the senior technical director for Georg Fischer LLC. He coauthored the book, "Handbook of Thermoplastic Piping System Design" and numerous professional papers in the field of engineering, semiconductor pure water usage and chemical processing and holds several U.S. patents. Mr. Sixsmith holds a BS in chemical engineering from the University of Pittsburgh.

Coauthor Paul G. Galvin is the business development manager, Life Science/Institutional for GF Piping Systems LLC. He has been involved with design and installation of Special Waste Piping, Special Waste Neutralization, and Process Water Piping Systems for more than 35 years. Mr. Galvin has been a full-time member of the GF Piping Systems team since 2000. He currently is secretary of the "Sub-Committee on Polymers and Elastomers" for the ASME Bio-Processing Equipment Standard.

The late Marty Burkhart acted as a coauthor of this paper, providing his knowledge and insights to the other authors. Prior to his passing, he was a consultant to Georg Fischer Piping Systems, providing technical support for high-purity products. Between 1992 and 1996, he was employed by Georg Fischer as the technical marketing manager for high-purity products in Switzerland. He also worked 13 years with Texas Instruments in Dallas, TX, and was very active in SEMI's standards method development program.

Endnote

*Purified Water or PW refers to a certain quality of water treated to meet the specifications of the United States Pharmacopeia, or other pharmacopeias (of which the Japanese Pharmacopeia or European Pharmacopeia are examples). PW is used in pharmaceutical plants, as well as in applications required to use pharmaceutical-grade water in their processes.

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Key words: BACTERIA, LABORATORY WATER, MICROBIALS, PURIFIED WATER

MEMBRANES

A NOVEL APPROACH TO CONTROL MICROBIAL FOULING OF REVERSE OSMOSIS ELEMENTS

Microbial fouling of reverse osmosis (RO) membranes is associated with loss of product water flow, increase in feedwater pressure, and increase in product water microbial levels. Membrane fouling can be reduced by reducing the total viable bacteria level in the RO system feedwater. In-line ultraviolet (UV) treatment of feedwater, positioned downstream of RO unit waste recycle, can significantly reduce total viable bacteria to levels that are not detectable in a 100 milliliter (mL) sample. UV radiation at a wave length of 184.9 nanometers (nm) produces both highly oxidative ozone and the hydroxyl radical, capable of rapid inactivation of bacteria. The 184.9-nm wave length technology can be "mixed" with classical 253.7-nm wave length technology to protect thin-film composite membranes from oxidation. Pilot and operating data are provided in this article to demonstrate the effectiveness of the technology.

Bacteria Sources in RO Feedwater

Raw water supplies to RO unit pretreatment components will generally meet the U.S. Environmental Protection Agency's (EPA) National Primary Drinking Water Regulations (NPDWR) (1) or equivalent regulations such as defined by the World Health Organization (2). The following microorganisms are listed in the NPDWR: *Cryptosporidium, Giardia lamblia, Heterotrophic* Plate Count (HPC), *Legionella*, Total *Coliforms*, and viruses (enteric).

The EPA's Surface Water Treatment Rule (SWTR) requires that source water from a surface supply or groundwater supply under the direct influence of a surface source be treated with a disinfecting agent and filtered to meet specific criteria (3, 4). HPC is an analytical method used to measure the variety of bacteria in water (5). An acceptable HPC level is ≤ 500 colony forming units per milliliter (500 cfu/mL). Raw water supplies *will* exhibit the presence of bacteria even though residual disinfecting agent is also present.

Raw water supplies, primarily from sources defined by the SWTR will exhibit the presence of naturally occurring organic material (NOM) from sources such as rotting vegetation, and leaves, among others, entering the surface source through "runoff". Total organic carbon levels (TOC) associated with NOM will generally vary between 2 to 10 milligrams per liter (mg/L), depending upon source water geographical, climatic, and seasonal influences. The TOC level in RO feedwater influences the rate of microbial fouling since it provides a nutrient for microbial growth on the surface of an RO membrane.

RO pretreatment unit operations may include particulate removal, water softening, and activated carbon (or alternative method for removal of disinfecting agent). Pretreatment techniques increase bacteria levels in RO feedwater. RO Pretreatment techniques discussed in this article are for non-disinfecting agent tolerant membranes such as thin-film composite polyamide type.

Particulate removal can be achieved by several techniques, including cartridge filtration, surface filtration, and depth filtration. Cartridge filtration can provide a surface for bacteria to accumulate and replicate. This is often noted by the physical observation of a "slime-like" material on the surface of filters (6). Both sand filtration and multimedia filtration units are backwashed, which provides effective removal of entrapped microorganisms. Ripened multimedia filtration units may reduce the concentration of heavy molecular weight organic material and/or colloidal material in a complex with heavy molecular weight organic material (7). However, since the feedwater to particulate removal filters generally contains residual disinfecting agent, bacteria are not significantly increased.

Water softening removes multivalent cations from feedwater significantly, reducing scale formation on RO membranes. If water softening is performed prior to removal of a disinfecting agent, minimal increase in bacteria is noted. Water softening unit operation and regeneration does not provide effective removal of bacteria and may in fact introduce microorganisms from a "wet" brine storage system (8). Cation resin in water softening units will not remove/reduce NOM in filtered water.

Removal of raw water disinfecting agent by activated carbon. When properly designed, operated, and maintained, activated carbon provides an excellent method of completely removing raw disinfecting agents such as chlorine (hypochlorite ion and hypochlorous acid) and monochloramine (9). Further, activated carbon reduces the concentration of NOM by an estimated 30% to 70%, depending upon the type and nature of the humic and fulvic acid components contributing to NOM. The literature suggest that a greater reduction of NOM can be achieved by positioning the activated carbon unit prior to water softening, allowing multivalent cations to "coil" long,

By **William V. Collentro**
(*Pharmaceutical Water Specialists, LLC*)

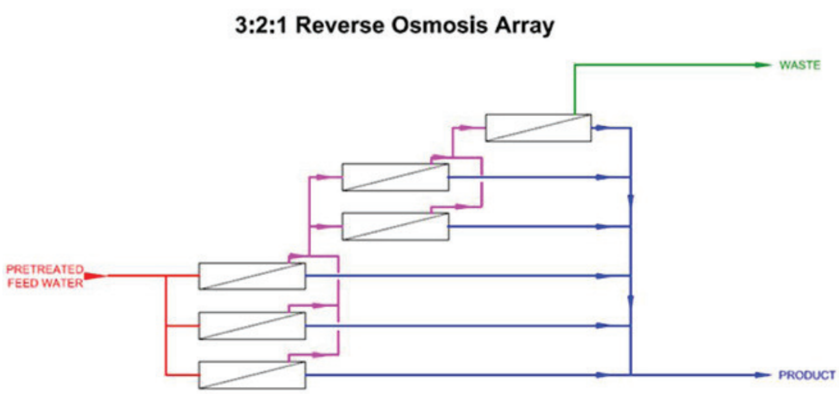

Figure 1. A 3:2:1 RO array. Feedwater first flows to the three pressure vessels. From there, the waste stream flows to the two pressure vessels, and then the waste flows to the single pressure vessel.

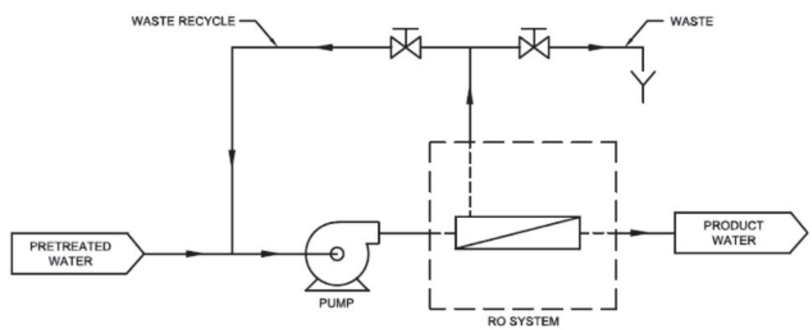

Figure 2. Final wastewater from the last array is directed back to the feedwater piping upstream of the RO high-pressure feedwater pump.

"straight chain" NOM molecules (10).

Unfortunately, while activated carbon provides two critical pretreatment functions, bacteria will grow in the lower portion of the bed because of the warm, wet, carbonaceous rich environment. While periodic ambient backwash can reduce the increase in bacteria through an activated carbon unit, periodic hot water sanitization may be considered. Frequently, activated carbon unit product water total viable bacteria levels are "Too Numerous to Count" (TNTC), > 5700 cfu/mL.

Removal of raw water disinfecting agent by injection of a reducing agent. Reducing agents such as sodium bisulfite may be used to remove raw water disinfecting agents. Reducing agents, unlike activated carbon, will not reduce the concentration of NOM. Further, bacteria levels in RO feedwater for a system using reducing agents in lieu of activated carbon do not appear to be appreciably lower (4).

Removal of raw water disinfecting agent using 184.9-nm UV radiation. The use of 184.9-nm UV radiation for removal of disinfecting agent and reduction of organic material is discussed further in this article. The technology may be used with, or without activated carbon or a reducing agent. Complete removal of monochloramine by 184.9 nanometer ultraviolet radiation requires conservative design considerations. As discussed later in this article, the technology can significantly reduce RO feedwater bacteria levels. Further, the technology can reduce the concentration of RO membrane fouling organic material.

RO Design and Operation

Background. RO unit design is developed using computerized "projection" that require feedwater impurity data. Parameters such as RO feedwater, product water and wastewater flowrates, pressure, and temperature, as well as the percent recovery of feedwater as product water are established. The number of RO membranes and membrane arrays are determined. All parameters must meet RO membrane manufacturer's guidelines. The RO computerized projection will provide a "warning" if required membrane parameters, such as excess percent recovery or low membrane flowrate are determined. While there are several items that determine microbial fouling of RO membranes, there are two important items that should be considered; waste recycle and impurity "layering".

Waste recycle. As feedwater passes through RO membranes, water is removed as product. The waste from a membrane becomes the feedwater to the next membrane (in series). Since the flowrate of water decreases after each membrane and the concentration of impurities increases, membranes are positioned in pressure vessels and configured into an "array". The array provides a "tapering" mechanism to maintain water velocity, minimizing precipitation of concentrated impurities. As an example, a 3:2:1 array, shown in Figure 1, indicates that feedwater flows to three pressure vessels configured in parallel. Each pressure vessel may contain one or more membranes. The waste from the three pressure vessels flows to two pressure vessels configured in parallel. Finally, the waste from the two pressure vessels would feed a single pressure vessel.

While the membrane array attempts to maintain feedwater/waste flowrate, "waste recycle" is used to increase the flowrate of feedwater. As shown in Figure 2, a portion of the final wastewater from the final array is directed back to the feedwater piping upstream of the RO high-pressure feedwater pump. Unfortunately, bacteria levels in the waste recycle stream are generally TNTC. Subsequently, control of bacteria in raw feedwater and within pretreatment components is offset by significant introduction of bacteria in the actual RO feedwater as a result of waste recycle.

Layering of impurities on RO membranes. A second item of concern related to microbial fouling of RO membranes is "layering". The literature (11, 12) states that impurities deposit on RO membranes surfaces in distinct layers as shown in Figure 3.

Field experience and RO membrane manufacturer's cleaning procedures support the layering concept. The sequence for RO membrane cleaning includes a low-pH cleaner to remove scalants followed by a high pH cleaner to remove foulants, and final chemical sanitization. Bacteria and bacterial endotoxins exist on the membrane surface. Bacteria will proliferate with increasing rate as organic foulants provide nutrient to support growth. Further, operations such as hot water sanitization may destroy bacteria in the biofilm but do not remove the biofilm. As a result, bacteria in RO feedwater will rapidly appear in the biofilm subsequent to hot water sanitization decreasing the long-term effectiveness of the sanitization operation and resulting RO product water flowrate.

Control of RO System Feedwater Bacteria and Organic Foulants

Based on classical pretreatment and RO unit waste recycle, the total viable bacteria levels in RO feedwater are high, often too numerous to count. Since the RO waste recycle introduction location is generally directly upstream of the RO high-pressure feedwater pump, sampling is not practical because of pump feedwater line "vacuum" conditions. Subsequently, the "real" RO unit feedwater total viable bacteria levels are generally unknown. In-line UV radiation, at a wave length of 184.9 nm, installed downstream of RO waste recycle can significantly reduce total viable bacteria levels in feedwater and subsequently microbial fouling of RO membranes. Further, the technology reduces the concentration of organic material.

General design considerations.

Oxidizing UV radiation basic theory. UV radiation at a wave length of 253.7 nm has historically been used in several water purification applications for bacteria control (sanitization) (13). However, "sanitization" UV radiation at a wave length of 253.7 nm does not *destroy* bacteria but merely inhibits replication by modifying deoxyribonucleic acid (DNA) and ribonucleic acid (RNA) (14, 15). Some researchers suggest that photoreactivation of inactivated bacteria may occur (16).

In practice, a 1 to 2 log reduction in total viable bacteria may be observed (17), particularly in high-purity water with low levels of impurities. On the other hand, oxidizing UV radiation at a wave length of 184.9 nm destroys bacteria by production of ozone and the hydroxyl radical, both extremely powerful oxidizing agents (18, 19). Further, the highly oxidative environment results in the partial or complete oxidation of RO membrane fouling organic material. Finally, effective removal of disinfecting chlorine (hypochlorous acid and/or hypochlorite ion) may be achieved.

Chemical reactions. Ultraviolet oxidation at 184.9 nm involves several different chemical reactions. The reactions include the following:

1. Reaction with dissolved oxygen in water to produce ozone. Subsequently, there is oxidation of organic material and destruction of bacteria by ozone.
2. Generation of the hydroxyl radical by "splitting" of the water molecule. Other features are rapid oxidation of organic material and destruction of bacteria by the hydroxyl radical.
3. Production of hydrogen peroxide by reaction with water and dissolved ozone. There is additional production of the hydroxyl radical by the reaction of hydrogen peroxide with 253.7-nm UV radiation, a portion of the UV spectrum.
4. Numerous parallel reactions involving RO feedwater inorganic, organic, and colloidal impurities.

The hydroxyl radical, while an extremely powerful oxidizing agent with significant absorption rate to target compounds and bacteria has a very short life, less than a second. Subsequently, oxidation associated with the hydroxyl radical is essentially limited to the stainless steel chamber of the in-line UV unit. On the other hand, dissolved ozone will be present in UV system product water and continue to oxidize material, including bacteria. Ozone decomposes to oxygen with a half-life as long as 20 to 165 minutes in ultra-high-purity water. In RO feedwater with inorganic, organic, colloidal, and microorganisms, the actual half-life of ozone is reduced. System design must carefully consider the desire to destroy bacteria while avoiding oxidation of RO membranes. Proper system sizing is a function of several variables discussed in the next part of this article.

Technology Application

Raw water source. The source of raw water must be considered. Raw water from a surface source will generally exhibit lower hardness and alkalinity levels but higher NOM concentration. An increasing percentage of municipal raw water supplies from a surface source will use monochloramine as a secondary disinfecting agent. Monochloramine removal by 184.9-nm UV may be achieved. However, this competing reaction for 184.9-nm UV radiation, even at increased UV intensity, limits both bacteria destruction and oxida-

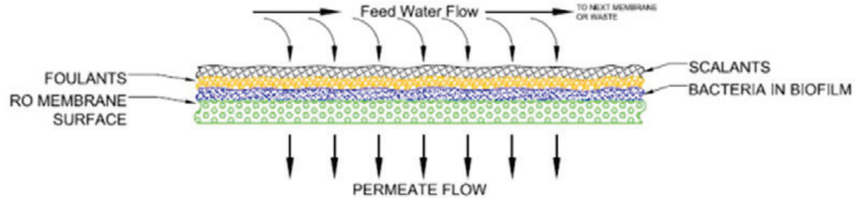

Figure 3. Example of how impurities form layers on a membrane surface.

tion of organic material. As a result, pretreatment system design may require classical activated carbon adsorption for removal of monochloramine and reduction of NOM prior to the 184.9-nm UV system.

Raw water from a groundwater source influenced by a surface water source may contain increased hardness and alkalinity concentration. Both iron and manganese may be present in raw water. The municipality may inject a sequestering agent such as a polyphosphate or orthophosphate to minimize iron staining of domestic fixtures. The sequestering agents often produce a colloid if not removed by upstream pretreatment system particulate removal filters or water softening. The highly oxidative condition within the 184.9-nm UV will attack the sequestered material, producing particulate iron and manganese. System design will require filtration downstream of the 184.9-nm UV system, prior to the RO high-pressure pump.

Raw water from a groundwater source will generally exhibit higher total hardness and total alkalinity values. While municipal primary and secondary disinfection may use chlorine, monochloramine may be present in delivered water because of the presence of naturally occurring ammonia (20). If monochloramine is not present, activated carbon may be omitted from the pretreatment process with chlorine removal and bacteria destruction provided by the 184.9-nm UV. Sequestered iron and manganese, discussed earlier, may require post-UV particulate removal.

Radiation intensity. The UV radiation intensity required for effective oxidation is a function of the chemical composition and nature of the pretreated water. The UV intensity may be 5 to 20 times the 30,000 millijoules (mJ/cm^2) value employed for disinfecting UV units at 253.7 nm.

Other design considerations. The following is a list of other areas that can impact a successful design.

1. Low-pressure mercury vapor lamps emit UV radiation with defined "peaks" at 253.7 and 184.9 nm, ideal for achieving the desired oxidation wave length. The literature suggests that medium pressure lamps require greater electrical input resulting in a "continuous" UV spectrum with broadened and partly "self-adsorbed" resonance lines (21).
2. Lamp sleeve material should not adsorb the 184.9-nm UV radiation. Quartz material, without "additives" is preferred.
3. Lower feedwater temperature increases the solubility and half-life of ozone.
4. Multiple lamp UV units should use a lamp arrangement that eliminates, or minimizes "shadowing," which provides "blind spots" within the chamber.
5. Lamp and sleeve replacement should be considered every 6 months to maximize 184.9-nm UV intensity.
6. The 184.9-nm UV radiation penetration length through water, particularly pretreated feedwater to an RO system, is much less than sanitizing 253.7-nm UV radiation. A longer oxidizing chamber with narrower diameter, or multiple chambers, is preferred.
7. The inner wall of the oxidizing chamber should be electropolished 316L stainless steel to increase reflection of UV radiation.
8. Both the hydroxyl radical and ozone may produce fragmented organic compounds that have not been fully oxidized to carbon dioxide. An "organic scan" of both 184.9-nm UV system product water and RO product water should be performed to verify that undesirable light molecular weight fragmented compounds are not present in RO product.
9. All samples for total viable bacteria should be collected in a sterile container containing sodium thiosulfate (22). This eliminates suppressed total viable bacteria results associated with oxidation of culture media during enumeration.

Case History

Historical information. The feedwater to a facility with a high-purity water system is from a municipal supply. The source water to the municipal treatment facility is from a groundwater supply influenced by a surface water supply. Municipal treatment includes chlorination, pH adjustment, and injection of an iron-sequestering polyphosphate. RO pretreatment includes multimedia filtration, water softening, activated carbon adsorption, and cartridge filtration. The RO membranes exhibited significant bacteria fouling with significant odor and fouling with colloidal iron. RO membranes were replaced about once every 3 months.

Analytical data. The following is a summary of the raw water and RO feedwater quality prior to the pump.

Raw water:
Conductivity = 400-550 microsiemens per centimeter (µS/cm)
TOC = 1.1–1.7 milligrams per liter (mg/L)
Total hardness = 70-92 mg/L as calcium carbonate ($CaCO_3$)
Total alkalinity = 55-72 mg/L as $CaCO_3$
Total viable bacteria = 26–298 cfu/mL
Total iron by inductively coupled plasma-mass spectrometry (ICP-MS) = 0.22–0.26 mg/L
Free chlorine = 0.2–0.6 mg/L
Total chlorine = 0.2–0.8 mg/L

RO Feedwater prior to pump:
Conductivity = 387-720 µS/cm
TOC = 0.65-0.98 mg/L
Total hardness = < 1 mg/L as $CaCO_3$
Total alkalinity = 48-82 mg/L as $CaCO_3$
Total viable bacteria = ~ 1,600 - >5,700 cfu/mL
Total iron by ICP-MS = 0.20–0.29 mg/L
Free chlorine = < 0.01 mg/L
Total chlorine = <0.01–0.05 mg/L

UV installation. A 184.9-nm in-line UV system was installed prior to the RO feedwater pump. The RO unit's 5-micron (µm) cartridge prefiltration system was repositioned to a point downstream of the UV system. An in-line pump was positioned upstream of the UV unit. RO waste recycle was introduced prior to the new pump.

Post-UV installation results. Initial operation after system modification indicated significant iron particulate accumulation on the RO prefilters. Inspection of the RO membranes also indicated the presence of particulate iron. RO prefilter cartridges with a 1-µm rating were installed. Ultimately, 0.45-µm "nominal" RO prefilter cartridges were used to remove iron.

Once the iron issue was resolved, analytical data from analyses of RO feedwater to the high-pressure pump indicated the following:

Conductivity = 370-750 µS/cm
TOC = 0.27–0.44 mg/L
Total hardness = < 1 mg/L as $CaCO_3$
Total alkalinity = 34-68 mg/L as $CaCO_3$
Total viable bacteria = <1–4 cfu/100 mL
Total iron by ICP-MS = 0.03–0.05 mg/L
Free chlorine = < 0.01 mg/L
Total chlorine = <0.01 mg/L

The RO membranes were removed after 3 months of operation and replaced with new membranes. The removed membranes were sent to an RO membrane cleaning facility with extensive membrane analytical capability. The cleaned RO membranes indicated the absence of oxidation, essentially no loss in ion rejection, and no loss in flux. The cleaned RO membranes were treated with a preservative and returned to the facility. The "second" set of RO membranes were removed after 6 months of operation and replaced with the cleaned membranes. The second set of membranes exhibited excellent performance characteristics and an absence of oxidation before cleaning.

Conclusions

In-line ultraviolet systems using 184.9-nm lamps can enhance RO system operation by eliminating microbial fouling and reducing the concentration of organic material. However, proper selection, design, and operation of 184.9-nm UV units are critical to avoid RO membrane oxidation and subsequent loss of integrity. Further, additional treatment techniques for removal of certain oxidizable raw water impurities such as colloidal iron must be considered as part of system design.

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Author William V. Collentro, MS, ChE, has spent nearly 45 years of his career working in the water purification and related areas. He received his BS and MS in chemical engineering from Worcester Polytechnic Institute. Currently, Mr. Collentro is a senior consultant at Pharmaceutical Water Specialists, LLC. His academic associations include adjunct professor at Stevens Institute, faculty member at PDA's Training and Research Institute (TRI), and adjunct instructor at Temple University's Quality Assurance/Regulatory Affairs program. In 1998, he received the PDA-TRI James P. Agallogo Award for excellence in teaching. Recently, Mr. Collentro received IVT's Kenneth G. Chapman Lifetime Achievement Award for excellence in the field of validation and compliance.

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