Treatment technology and parts-per-trillion limits

Ultrapure water is used in a range of industries, from computers to pharmaceuticals, and technology increasingly has to deliver at parts-per-trillion limits. **LIS STEDMAN** speaks to some of those who work to provide this technology.

Ultrapure water is a field of expertise that relates to normal water treatment (in as much as many of the treatment technologies are essentially the same) but in the same way that the family Ford car relates to a Formula One racing car. Creating and maintaining such purity requires a dive into pure chemistry and extraordinary requirements for the presence of contaminants of any kind – down to the parts-per-trillion.

The sensitive consumer goods that require these extraordinary levels of purity during the process, usually as a rinsing step, are those that contain such elements as LCD (liquid crystal display) or LED (light emitting diode) backlit screens, silicon chips and thin film transistors – TVs, mobile phones, computers and the like. The countries where ultrapure water is used are, logically, those where these very high-tech industries are located – mainly the US, Japan, South Korea and Taiwan, and increasingly China.

Driving growth of the ultrapure market

Dow ultrapure water specialist Greg Poppe explains that there 'is a fairly well-recognised and continuing demand for ultrapure water for computers, and small electronics. Some elements of the market are reporting a slowdown, but there is continuing to be investment and upgrading in ultrapure water and products, and there are new products in consumer demand such as LCD screens and LED backlit screens.'

Such products require vast quantities of ultrapure water, and there is a further driver for the growth of the ultrapure water market in the continuing miniaturisation of integrated circuit (IC) chips. As these become smaller and more complex, Poppe explains, the purity of the water used in the rinsing of the silicon wafers becomes more stringent to ensure that the products give the optimum yield.

'It is at the point where any small contaminant can contribute an unexpected element to the way the product works and can affect the yield,' he notes. The 'International technology roadmap for semiconductors', which is updated annually, summarises the requirements for ultrapure water as having a resistivity of 18.2 mega-ohms and vanishingly-low levels of individual components dissolved in the water. For instance, levels of metals at less than ten ppt (parts per trillion), sodium at less than 50ppt, and inorganic anions and organic ions at less than 0.2ppb. Total oxidisable carbon has to be below one ppb, ditto silica in either its dissolved or colloidal forms. There is also a specification for the number of particles – less than one per 100ml of water. It's almost impossible to visualise such small numbers, or the types of processes that would require such quality.'

Poppe says that 'even to get it to that level of purity, experience has shown that it can't be accomplished with one single purification step or type of technology.' Newer and upgraded plants, he explains, will use sequences such as two passes of reverse osmosis (RO) in combination with other types of treatment such as ion exchange and electro-deionisation (EDI).

EDI, he explains, is a 'different type of technology where membranes and ion exchange resins work together to produce pure water. It takes as a feed something that has already been purified – it is a polishing step.'

EDIs utilise anion-selective and cation-selective membranes that only allow those particular types of ions to pass through, thus removing them from the feed water. In the Dow system feed water enters from the bottom of the EDI module and is diverted into vertically spiraled cells. The water flows vertically through ion-exchange resins located between the two membranes. The anions and cations will move through the membranes using as their motive force an electrical voltage (DC current) that is applied across the cells (hence the E in EDI). The DC electrical field splits a small percentage of water molecules (H_2O) into hydrogen (H^+) and hydroxyl (OH^-) ions. The H^+ and OH^- ions attach themselves to the cation and anion resin sites, continuously regenerating the resin. 'You almost never need to apply regeneration,' Poppe notes.' And there is a growing interest in using less chemicals.'

Ion exchange resins can be used at the 'roughing' stage – when ordinary potable water is given its first treatments – or at the polishing stage, usually as part of a mixed bed polisher. These one-pass systems do not self-regenerate though, so the interest in EDI is increasing.

If necessary, EDI cationic resins can be regenerated with acid and anionic resins with a caustic solution. 'It's probably the most complicated technology we sell,' Poppe admits. 'As well as ion exchange resins, EDI and RO, another treatment used is UF (ultrafiltration), both for pre-treatment and downstream as a final touch point

Elga's Medica water purification system. Credit: Elga Labwater.

before the water is used in the process. Dow sells all of these technologies so we are uniquely advantaged in being able to provide solutions that are exactly right for each case in terms of what quality is needed and the raw water quality.'

Raw water quality is equally critical, he notes – the approach taken depends on the type of water that is used as a feed. And this initial quality is decreasing. 'Water shortages are becoming more severe in many parts of the world, so the quality of water is becoming degraded and people are looking at more challenging sources that are sometimes the only ones available.'

Meeting the demand

As well as this quality issue there is also one of quantity – the high-tech companies using ultrapure water tend to use vast amounts as well, and reducing the impact of manufacturing on water resources is becoming an increasing focus. 'In general the trend is to being a more green corporate citizen, and this will be continuing,' says Poppe.

Companies are also looking at water reuse – taking their own wastewater, treating it and using it as feed water. 'As they continue to do this, it increases the challenge of the front end of the process,' Poppe notes. 'We've been able to develop new, advanced products that work with these more challenging sources, and more cleanable and higher rejecting membranes, so while these sources are more challenging; they become more manageable.'

He notes that as well as LCD screens, silicon chips and the like, ultrapure water is also used in the manufacture of photovoltaic cells 'which like flat screen monitors require a very clean rinsing step'. The search for renewable energy is making solar cells an increasingly popular option that again is driving greater use of ultrapure water.

There are very different aspects and applications for ultrapure water, though, as Elga Labwater's managing director Nora Ikene explains. The Veolia company focuses on process water in two categories, pure and ultrapure water. She notes that clients include hospital medical centres, healthcare laboratories, the dental, clinical and diagnostic markets, and academic research bodies. 'Everywhere you have a lab there is a need for ultrapure water,' she explains.

Elga Labwater's main markets are Europe, Latin America, Asia, India and the US. Elga produces ultrapure water for companies such as Roche and Dechmann, major manufacturing companies that produce analysers – the ultrapure water is used to secure samples as well as in analysis procedures. Another client is cosmetics giant L'Oreal. Cosmetic creams and powders are produced under the most stringent possible standards, so ultra-pure water is seen as a necessity – indeed a component of the product.

The company produces ultrapure water to the set standard of 18.2 megaohms, or tailored to client needs. 'The pharmaceutical sector, cosmetics and microelectronics use the same level. In microelectronics, ultrapure water is used to rinse the chips for credit cards, mobile phones and TVs – they need a sterile environment to secure the quality.'

Broadly, Elga Labwater addresses all of the markets where ultrapure water is found, the difference between it and parent Veolia Water being in the volumes produced – Elga Labwater focuses on smaller systems and Veolia Water on systems that require high throughputs. 'You can't put a big machine on a bench,' Ms Ikene notes. 'We design, manufacture and sell small systems comparable in size to a fridge.'

The technologies that the company uses to produce ultrapure water include conventional ion exchange

Elga's Purelab Option water purification system. Credit: Elga Labwater.

resin systems, reverse osmosis (RO), UV, photooxidation, activated carbon and EDI. 'All of the technologies are existing ones,' she adds. 'Veolia has the largest portfolio of solutions, so we are able to address all our clients' water treatment issues in this unique market-place. We are not reinventing the wheel, the strength of Elga Labwater and Veolia Water is their capacity to combine these technologies together – it is the key to our expertise.'

For ultrapure water in particular this often means, as outlined above, that combinations of treatments are used – RO and EDI, for instance, or EDI and UV. The skill is in choosing the right one for the particular application, Ms Ikene explains. 'It's not easy – that's why we've got the biggest range of any water company in the world.' The company has had five people working on R&D relating to this issue for 30 years, so its expertise is significant.

She adds: 'Clients are asking for more compactness, cost effectiveness, there are long term environmental considerations which was not the case ten years ago – this is why we are working now with very specific combinations of technologies to address the market trends. For instance, recycling creates less water use, but it is not something you can set up easily if you can't control all of the technologies and combinations of technologies and apply them to address the client's needs.'

She notes that as the ultrapure water is such a critical element of the products involved, setting up the correct product and solutions that perform as required is critical. 'If we can't produce these, they can't work. Even if we are addressing the market for small systems, we need also to satisfy our clients with the right level of service, developed locally. We have a strong technician network.' For a client such as Roche, she explains, the Elga machine is connected directly to its own systems so if the Elga system goes down, so does the Roche one, something that simply cannot happen. 'The service is highly demanding, but we are number one. Elga is able to set up the right service. When clients ask for laboratory water systems, they want this quality of water on a daily basis, when they want it.'

It is also extremely important that the client staff are trained in using the machines, she stresses. 'Our systems are robust, but I wouldn't want to compare them to a coffee machine. You need people who are trained – it is the same for all water treatment installations.' The company's great strength, she stresses, is that 'we are controlling everything – controlling the business from the first idea to the final product. We don't design our products just for pleasure, we work with our client – we are following the market. No product leaves our premises without being approved by the client.'

Stringent controls

In the US, the ultrapure water market and requirements echo those of other user countries. CDM Associate Bob Kimball says: 'The biggest user of ultrapure water is the semiconductor industry, which uses it for cleaning and etching of wafers. The next largest user is the pharmaceutical industry, which uses ultrapure water in the process but also as an ingredient in its products. In that industry, because the water becomes part of the product, to design an ultrapure water system for them they require you to get FDA (Food and Drugs Administration) approval.'

There are many other industries using ultrapure water, he notes, such as clean rooms' laundry facilities, because it is extremely important that clothing used in a clean room has as few contaminants attached as possible. 'The fastest-growing sector is manufacturers of flat screen displays. Biotech is using ultrapure water more and more, as is power generation, mainly for the production of high pressure steam.'

The latter requires stringent contaminant control because elements like silica can cause fouling of turbines that the steam passes over, as well as the heat exchanger tubes in the high-pressure boilers, which could become coated with this and other contaminants were they not removed. 'Any minor constituents can coat out on the heat transfer surfaces,' Kimball notes.

Because the manufacture of ultrapure water requires removal of so many different substances, from particles to dissolved ions, dissolved gases and organics, the range of products used for removal spans the entire water treatment gamut. He points to primary RO, ion exchange, UF and degasification technologies as the most common, often teamed with UV for sterilisation.

'In most cases all of the technologies are required, however the specific configuration and degree to which they are used depend on two things – the feed water quality available and the end use requirements of the industry. The real trick is to find the right sequence and combination of technologies to achieve their water quality requirements for that particular application,' Kimball adds.

As technology improves and chips shrink, the water quality requirements become more stringent, he notes. 'In the US one of the challenges they have, as water quality requirements become more stringent as the chips become smaller and smaller, is that there is a real shortage of feedwater supplies especially in the south west, where a lot of these industries are located. Many companies are trying to recycle as much wastewater as possible to the front of the process for reuse. This is becoming a real market and is driving the technologies in some areas.'

Reduction of energy consumption and increased removal of contaminants are key targets. 'We are also seeing nanotechnology as an up-and-coming technology across all industry sectors. It is currently being used to develop more efficient RO membranes that operate at much lower pressures to save energy. Nanotechnology devices are being used to monitor contaminants in ultrapure water in real time – nanotechnology has led to the development of monitoring devices that see nanoscale particles and pathogens in water.' As the specifications require lower and lower levels of contaminants, there is a parallel need to be able to measure exactly what is left in the water, he explains. 'The developments in the nanotechnology market are astounding.'

The total ultrapure water market is estimated as being in the $5 billion range next year, he adds. 'It is about 25% greater than three years ago.' There is also a collateral benefit for the manufacturers of associated systems such as control and instrumentation, and pipe and valve materials. 'A lot goes into sterilisation – ensuring the manufacturing materials don't leach contaminants into the water, as well as other components such as piping and valves. The cleaner the water is, the more aggressive it is towards leaching contaminants.'

Asia has slightly over half of the ultrapure water market, he adds, followed by the US and Europe. These represent the major markets, with any others being of much smaller size. 'I think the use will probably increase as the technology age continues to take off, and as we want to eliminate discharges,' Kimball predicts. However, ultrapure water will remain the preserve of those industries that really require it because the costs of such extraordinary levels of purification are so high. 'It's amazing it's even possible to improve on it,' he concludes.

Amazing indeed. And, from the direction that advanced IT is moving, things are likely to become even more amazing in future as the relentless drive towards ever-more minute and delicate technology requires water of a quality that is would have been unimaginable just a few years ago. ●

Progress for the microelectronics sector

Dow's iLEC technology provides face-to-face contact between membrane permeate tubes. It is a compression fit with no wear and no possibility of leakage or abrasion products. The older o-ring system creates a significant pressure drop (back pressure) that means pumping increases. According to Dow, with iLEC this does not occur, which enables a small but significant reduction in costs.

The system has been installed at Texas Instruments headquarters in Freising, Germay, where there is an advanced BiCMOS/CMOS wafer fabrication operation. Sliding membrane interconnectors, currently an industry-wide feature of spiral-wound membrane elements, must be lubricated to maximise sealing performance and to ensure longevity. Because the water at the site is intended for use in semiconductor processing, o-ring lubricants are not permitted. The lack of lubricants shortens seal life and raises the likelihood of leakage from worn and abraded o-rings. Such leakage impairs permeate quality, while the associated o-ring abrasion is a source of particulate contamination.

Filmtec semiconductor grade (SG) elements with iLEC were installed in one pressure vessel in the second stage of the RO system. The aim was to stop the o-ring leakage and document improved permeate quality and reduced energy consumption. This was also an opportunity to demonstrate the benefits of the Filmtec SG elements, which are formulated to provide low levels of TOC (total organic carbon) on start-up and lower operating costs by reducing TOC rinse-out time. The end result of the before-and-after comparison showed that the iLEC element addressed the leakage problems associated with the sliding couplers, and the permeate quality improved dramatically.

Meanwhile, the Fab 30 plant in Dresden, Germany, is AMD's main microprocessor plant and the largest microprocessor plant in Europe. The move to sub-micron devices has posed additional challenges to the already-stringent water quality demands as research has show that boron in process water can affect the production yield of these devices. Boron is difficult to remove with conventional water-treatment systems, and boron compounds can have negative effects on the water-treatment system itself.

At the plant, a conventional ultrapure water (UPW) treatment plant purifies water with a two-pass reverse osmosis (RO) system followed by a two-pass mixed-bed ion exchange (IX) system. Typically, silica breakthrough signals exhaustion of the IX beds and prompts regeneration. However, a study at AMD's Submicron Development Center showed that boron breaks through earlier than silica, making boron the most critical parameter for determining exhaustion of IX beds in a boron-sensitive UPW system.

Dow's Upcore system was installed as a first-pass treatment instead of a conventional RO-IX mixed-bed design. The Upcore system is based on counter-current ion exchange technology, a packed bed design, an upflow regeneration / downflow service and a uniform particle size (UPS) resin technology. This vessel is followed by an RO system and primary and polishing mixed-bed IX systems. The RO system includes equipment to enhance the pH in the RO feed to achieve a higher boron rejection. The complex system reduced levels of boron to below detection limits.