



## WATER PROCESSES AND PRODUCTION

# HIGH AND ULTRA-HIGH PURITY WATER

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**There are various filtration techniques available to produce the different grades of pure and ultrapure water required in industry. What are the differences between these process solutions and the type of water that they produce?**

**P**ure water can be defined in terms of various parameters, including resistivity, microorganism content, pyrogen (endotoxins) levels, reactive silica levels and total organic carbon (TOC) levels. We have determined that at least five grades of pure water are available as defined by various standards and conventions, which are summarised in Table 1.

Each grade of pure water is used in a number of applications that include:

- Deionised Water – medium pressure boiler feed, renal dialysis make-up, battery top-up;
- Purified Water – pharmaceuticals, cosmetics, chemical manufacturing;
- Apyrogenic Water – vial washing, tissue culture, water for injections;
- High Purity Water – high pressure boilers, combined heat and power systems, laboratories;
- Ultrapure water – micro electronics, supercritical boilers.

It is important to be quite specific about the definition of ‘high purity’ water as often the term is used to describe the range of pure water specifications defined in Table 1. Deionised water is defined in terms of resistivity, which should be a minimum of 0.05 Megohm.cm. Resistivity is the inverse of conductivity. Hence, 0.05 Megohm.cm is equivalent to 20  $\mu$ S/cm. Purified water has a microorganisms requirement of less than 100 CFU/ml as well as <0.5 mg/l as C – TOC. Apyrogenic water is purer still at 0.8 Megohm.cm but a maximum level of 0.35 EU/ml pyrogens (endotoxins) is the main determinant specification for

that grade of water.

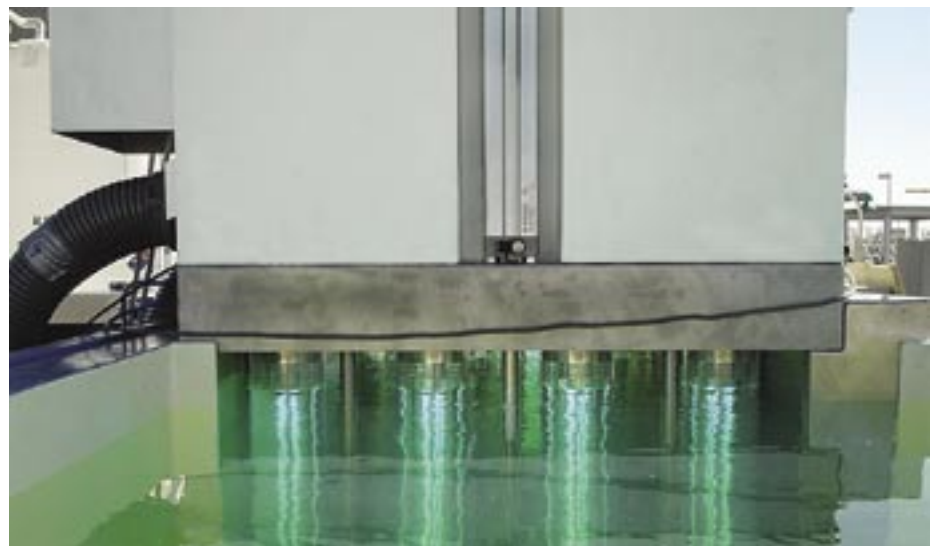
High purity water has a resistivity of at least 10 Megohm.cm but does not have a TOC specification. Ultrapure water typically has a TOC limit of 0.05 mg/l as C but a resistivity of 18 Megohm.cm.

### Technologies

#### Membranes

Membrane technology has a significant part to play in the production of all grades of pure water. Depending on the feed water available, additional membrane technologies may be incorporated as pretreatment technologies. Ultra filtration (UF) or microfiltration (MF) technology can be effectively used as a pre-treatment for reverse osmosis (RO) depending on the nature and vari-

ability of the feed supply to the water treatment system. With a resistivity of 0.05 Megohm.cm (conductivity 20  $\mu$ S/cm), deionised water can be easily produced using single pass RO systems as the final process step. These would be fitted with high rejection (HR) membranes. RO is a cross-flow membrane separation process providing a level of filtration down to ionic levels for removal of dissolved salts. Permeate is produced from the membrane with the majority of the dissolved content of the feed transferred to the waste concentrate stream. Depending on the quality of the feed water supply, RO membranes can be configured in an array system to give an overall concentrate stream flow as low as 10% of the feed supply, equating



*A typical UV system. Severn Trent Services' MicroDynamics microwave UV unit. Image courtesy of Severn Trent Services.*

**Table 1: Pure water quality classification**

Pure Water Type	Resistivity Megohm.cm at 25°C	Maximum Micro Organisms CFU/ml	Maximum Total Dissolved Solids (TDS) mg/l	Pyrogens (Endotoxins) EU/ml	Reactive Silica µg/l as SiO <sub>2</sub>	Total Organic Carbon (TOC) mg/l as C
Deionised	0.05	not specified	10	not specified	500	not specified
Purified	0.2	100	1	not specified	100	<0.5
Apyrogenic	0.8	0.1	1	0.25	100	0.05–0.07
High Purity	10	1	0.5	not specified	20	not specified
Ultrapure	18	1	0.005	not specified	2	0.05

to an overall system recovery of up to 90%. The salts present in the feed supply are then concentrated in the rejected concentrate stream, which must then be treated by subsequent processes on-site or discharged to the sewerage system for further treatment by the local wastewater treatment company. Individual RO membranes typically reject 95 – 98 % of the total dissolved solids (TDS) in the feed supply, thereby reducing the ionic loading onto downstream processes. HR membranes reject at the higher end of this range. UF and MF technology can also be used for final polishing of pure water and removal of bacterial endotoxins, bacteria and particles in pharmaceutical apyrogenic and semiconductor applications. In addition to the waste stream from membrane applications, it is important to note that membrane systems require periodic cleaning-in-place (CIP) using a combination of acid and alkaline-based cleaning agents to remove organic and inorganic contaminants that build up within the membrane modules. Consideration within process designs is required so that waste from CIP processes can be handled and treated appropriately.

**UV emission**

The use of ultraviolet (UV) emission technology is widespread in pure water production, especially where there is a requirement for low total organic carbon (TOC) levels, such as in purified, apyrogenic and ultrapure water applications. Research and development over recent years has shown that short wavelengths (190 – 195 nm) are highly effective at breaking down organic molecules present in pure water, especially low molecular weight contaminants. For example, HANOVIA's

(www.hanovia.com) SuperTOC lamp uses these short wavelengths to oxidise organic molecules present in water. In addition to oxidation of organics by OH<sup>-</sup> radicals from the photolysis of water, direct photolysis also occurs, a process where the chemical bonds within a molecule are destroyed. By concentrating on the wavelength generated these short-wavelength arc-tubes operate at a lower temperature than their predecessors, thereby increasing expected lifespan. UV systems are also used for disinfection, dechlorination and de-ozonation within pure water treatment processes. Several of the process stages in the manufacture of pharmaceutical products can cause downstream microbial contamination and UV can be used as an effective barrier to ensure that separate process stages do not compromise overall quality requirements. Installation or retrofitting of UV units into existing systems is relatively straightforward, requiring minimum disruption and site preparation. Depending on the level of use, maintenance only generally necessitates changing the arc-tubes annually. This is a simple procedure that can be carried out on-site.

**Ion exchange**

Either electro deionisation (EDI) or ion exchange (IX) technologies are required for producing high purity water; both technologies utilise ion exchange resins. These are an insoluble matrix made up normally from small beads, approximately 1-2 mm in diameter, fabricated from an organic polymer substrate. The 'trapping' of ions takes place with a simultaneous release of other ions, hence the term ion exchange. Most typical ion exchange resins are based on cross linked polystyrene. There are

4 general types of ion exchange resin which differ in their functional groups:

- Strongly acidic - sulfonic acid groups
- Weakly acidic - carboxylic acid groups
- Strongly basic - trimethylammonium groups
- Weakly basic - amino groups

'Strong' resins have a greater affinity for all ionised constituents in water and are capable of removing even weakly ionised constituents such as silica. 'Weak' resins are ineffective at removing weakly ionised constituents but their exchange capacities are two or three times that of strong resins and they can be regenerated more efficiently. Ion exchange resins have a higher affinity for polyvalent ions so divalent ions are removed first as water passes through a resin bed.

EDI is a continuous compact process that eliminates the requirement for regeneration chemicals and waste neutralisation that are synonymous with conventional ion exchange systems. However, the process uses electricity, with the associated cost, to further demineralise deionised water by removing CO<sub>2</sub>, remaining TDS and sometimes reducing TOC, particularly in combination with short wavelength UV. EDI is mainly used for deionisation downstream of RO for polishing and removal of silica and other ions. When processing RO permeate, EDI systems typically achieve better than 99.5% salt rejection and they can produce up to 18 Megohm.cm resistivity.

Feedwater entering an EDI system flows through membrane compartments containing ion exchange resin. An electric potential drives the passage of cations through cation-permeable membranes and anions through anion-permeable membranes into a waste stream. Pure water remains in the compartment and leaves the system as the treated water stream.

In contrast, ion exchange processes operate in vessels containing a combination of cation and anion exchanging resin. The cation resin has H<sup>+</sup> ions attached that are readily exchanged for cations such as calcium and magnesium in the feed supply. The anion resin has OH<sup>-</sup> ions attached, to be exchanged for anions such as sulfate and chloride.

The resulting H<sup>+</sup> and OH<sup>-</sup> ions released from the resin combine to form water. Recent developments to minimise chemical consumption, reduce running costs and maximise water usage have been made possible by incorporating the latest versions of anion and cation resins. For example, Veolia's (www.veoliawater.com) short cycle RAPIDE Strata system incorporates a stratified anion bed. This has both weak base anion resin (for organic removal) and strong base anion resin (for anion removal). Chemical 'pulses' rather than continuous injection of regenerants are claimed to give better cleaning and regeneration. A twin bed short cycle system can typically achieve around 5 µS/cm conductivity while with the inclusion of a second cation polishing

bed, 18 Megohm.cm can be achieved. However, MBIX technology provides a reliable and proven method of consistently producing up to 18 Megohm.cm resistivity. In comparison to EDI, MBIX uses minimal electricity but consumes chemicals to regenerate the resins as well as producing volumes of acid and alkalibased waste to treat. Also, the performance of MBIX systems reduces between regenerations. Resistivity deteriorates as H<sup>+</sup> and OH<sup>-</sup> ions are removed and the mixed resin becomes 'exhausted'. The plant is then regenerated by firstly backwashing with treated water to fluidise the resin and separate the heavier cation resin from the lighter anion resin. Diluted alkali is passed downwards through the anion resin whilst diluted acid is simultane-

ously passed upwards through the cation resin. The combined flow exits at the central cation/anion resin interface and is transferred to waste. Sodium hydroxide is generally used as the alkali and it regenerates the anion resin with OH<sup>-</sup> ions. Hydrochloric or sulphuric acid is used to regenerate the cation resin. Displaced ions are transferred to the waste stream and the resins are then re-mixed using low-pressure air. MBIX can be cheaper than EDI where regenerant chemicals are already available on site, large throughputs are required and electricity is expensive. The current trend upwards in utility costs may thus render EDI uncompetitive. On the other hand, EDI can be more effective where compact systems are required and electricity is less expensive. This could be in the situation where CHP systems generate electricity on site, or where renewable energy projects can be combined with water purification technology.

**Purified water in pharmaceuticals**

Production of pharmaceutical water is a demanding application because of legislative requirements and practices, which are detailed in pharmacopoeias. See Table 2. These standards have been in place for over 20 years, with many of the manufacturing processes and technologies used remaining unchanged. Ion exchange technology has been an integral part of these treatment processes. RO combined with other technologies, is now the preferred main treatment option in Purified Water production. This is due to a combination of reasons including the security of meeting the TOC limit, handling chemicals and effluent, and microbiological quality.

The main reason for the reduced usage of ion exchange technologies has been the development of EDI. RO and EDI are complementary technologies. Both require electricity and both are provided in similar modularised systems, compact and easy to skid mount or containerise. This allows for more comprehensive factory acceptance testing and minimisation of installation and commissioning times. CHRIST (www.christwater.com) has introduced the Septron Bio-Safe to assist in the production of Purified Water where a typical design configuration is to use RO and EDI followed by a second membrane stage to ensure the endotoxin

**Table 2: Purified water specification**

Parameter	Units	US Pharmacopeia	European Pharmacopeia
TOC	mg/l as C	0.50	<0.5 (Optional)
Oxidisable substances	n/a	Optional	Optional faint pink color remains
Conductivity	µS/cm @ 25°C	<1.3 (Stage 1 test)	<5.1
Nitrate (NO <sub>3</sub> )	mg/l	n/a	<0.2
Heavy metals	mg/l as Pb	n/a	<0.1
Aerobic bacteria	CFU/ml	<100 (Action level) minimum sample – 1.0 ml for pour plate method	<100 (Action Limit) sample size based on expected result



*Christ's Loopo, which is a packaged ring main distribution and disinfection system. This installation destroys ozone using a UV irradiator.*

specification of Highly Purified Water is always met.

Although EDI technology has been in use for 25 years, probably the most significant improvements in the technology have happened in the last 5 years. These have overcome initial problems such as leakage from the modules by using new sealing methods, and the use of hot water sanitisable modules, making it possible to sanitise the entire Purified Water generation system.

The water quality produced can be as good as 18 Megohm.cm resistivity, < 10 mg/l as C – TOC, < 10 cfu/100 ml and < 0.25 EU/ml. This improved water quality is arguably a less important benefit to the patient and to manufacturers. It could be regarded as a 'by-product' of the improved consistency and reliability that the new generation of systems provides.

### Ultrapure water applications

Ultrapure water is required for two main industrial applications – semi-conductor rinsewater and supercritical boiler feed. It has a TOC limit of 0.05 mg/l as C as well as a consistent resistivity of 18 Megohm.cm.

At 25° C, 18 Megohm.cm is the maximum resistivity that is practically achievable and measurable under industrial conditions. Only marginally higher levels can be achieved in the laboratory. At such high resistivity (low conductivity) the accuracy of process instrumentation becomes critical and specialised materials are required where process equipment comes into contact with water to ensure no contaminants are released into the product water.

Hence, to make the jump from high

purity at 10 Megohm.cm to a guaranteed and continuous ultrapure production at 18 Megohm.cm, significant additional investment in capital equipment can be required, both in terms of process plant but also with regards to the use of more expensive materials and more sophisticated process instrumentation and control systems.

In supercritical boilers, potential corrosion problems, such as the presence of iron oxide, can be eliminated by using ultrapure water. These risks are elevated at the high temperature and pressure characteristics of this type of boiler. Ultrapure water is regarded as the cleanest possible material available to the semiconductor industry, after the basic silicon, and hence it is a valuable resource. It is extensively used for all final washing processes throughout the manufacturing operation both in semiconductor wafer fabrication and in final assembly into finished component packages.

As wafer geometries have become smaller, purity requirements have become more stringent. Current geometries are less than 1 micron distance between adjacent connecting lines on a microchip; hence, any impurities in the rinse water would lead to damage of the microchips due to electrical short circuiting.

The current focus is on the TOC level as the final discriminator to define ultrapure water quality. This must be less than 0.05 mg/l as C and can be achieved with the use of UV emission technology as described above. However, suitable pre-treatment utilising membranes and subsequent use of ion exchange resins (whether EDI or MBIX)



is required before the final process step of removing TOC is undertaken.

### Conclusions

There are a number of complexities involved in the production, storage, transport and utilisation of pure water to avoid contamination at any point in the process. A detailed investigation of the feed water variability, site constraints and product water requirements is required before the most suitable process solution can be implemented. Also, taking into account the costs of operating, managing, monitoring and testing a high purity or ultrapure water system, it is important to note that the actual cost of the water treatment system is often a small component of the total cost across a typical system lifespan. Hence, it would often be sensible to increase capital budgets to make sure that best available technology is implemented. This more forward-looking approach will ensure consistent pure water supply, minimise maintenance requirements and maximise operational integrity. <<



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