

Purer, greener water

Steve Willis charts the benefits of continuous electrodeionisation



FEW production processes now use municipal drinking water, or any water supply, without some form of purification treatment. This is partly because of the variable nature of supply, and partly due to increasing quality demands.

The level of treatment required varies with the application and the quality of the feedwater. In some applications it is enough to filter the water to remove large particles, while in others – such as pharmaceutical production – much more stringent levels of purification are called for. Even apparently simple applications, such as the ‘spot-free rinse’ option in an automatic car wash, require high-quality water. Spot-free rinsing requires deionised water with a conductivity of around 10 $\mu\text{S}/\text{cm}$ or better to ensure that no salt residues can be seen when water droplets dry.

CEDI technology

At the upper limit of water purification, a new generation of continuous electrodeionisation (CEDI) modules is changing the way water is commercially treated. CEDI works by removing ionised or ionisable substances from water using ion exchange membranes, electrically-active media (typically ion exchange resins), and a DC electric potential.

Most commercial CEDI devices have layers comprising alternating cation- and anion-permeable membranes with spaces in between, configured to create liquid flow compartments with inlets and outlets. The compartments bound by an anion membrane facing the positively-charged anode and a cation membrane facing the negatively-charged cathode are diluting compartments. The

compartments bound by an anion membrane facing the cathode and a cation membrane facing the anode are concentrating compartments. To facilitate ion transfer in low ionic strength solutions, the dilute compartments are filled with ion exchange resins.

A transverse DC electrical field is applied by an external power source using electrodes at the boundaries of the membranes and compartments. The electric field attracts ions in the liquid to their respective counter-electrodes, which concentrates the ions in the concentrating compartments (see Figure 1).

The technology is mainly used in the pharmaceuticals, electronics and power industries, because these typically use the highest purities of water. The water qualities typical of these industries are so high that even to touch the water would contaminate it enough to fail the test analysis, or render it unusable. The main impurities present in water can be divided into three categories: organic material, measured as total organic carbon (TOC); ionic material, measured by conductivity or by the level of individual ions and bacteria.

However, even within high purity water specifications there is some variation in the requirements. For example, pharmaceutical systems have to be reproducible, reliable and documentable. Power generation requires very low conductivity and silica levels, while water for electronics manufacture has to be free of any measurable impurities. High purity water systems for semiconductor fabrication now generate a product approaching 100% pure water, with some impurities being measured in parts per trillion (ppt). This industry, in particular, has spurred the development of CEDI technology.

Following pre-treatment (by ultrafiltration, for example) water reaching the purification stage almost invariably undergoes reverse osmosis (RO) before polishing by CEDI. The key technology in most pure water systems for many years, RO membrane technology is very adept at removing a high percentage of all contaminants present. It typically removes

95–99% of ions and 99.99+% of organic and bacterial contaminants.

To achieve the lower conductivity specifications required in many applications it is now very common to treat the RO permeate by CEDI. In the pharmaceutical industry, CEDI with RO has become the standard process for producing purified water or for pre-treating a water for injections (WFI).

As CEDI generates no chemical waste and has low running costs (typically <0.5 kWh/1000 l of product water) it can be a green alternative to mixed bed ion exchange plant.

Conventional mixed-bed deionisation to produce ultrapure water has its drawbacks, mainly because exhaustion and regeneration of ion exchange beds causes fluctuations in produced water quality. As CEDI, by definition, is free from regeneration, it is free from this fluctuation. Designers have focused on making CEDI competitive with conventional mixed bed DI by improving module performance, increasing module reliability and lowering the overall cost of ownership.

earlier limitations

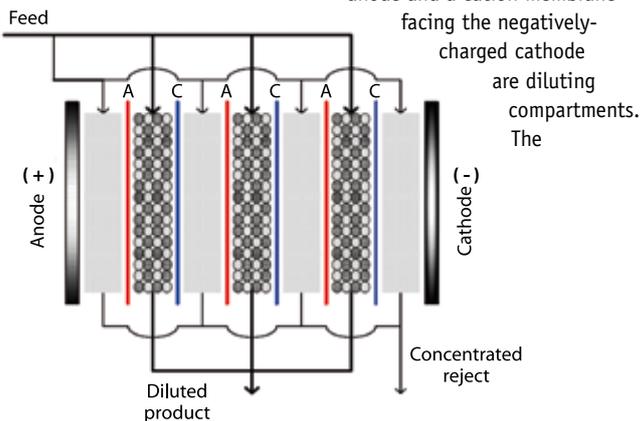
Product water specifications for CEDI technologies in the past were typically in the range 10–16 $\text{M}\Omega/\text{cm}$ with removal of weakly dissociated species, such as silica and boron in the 90–98% range. This is sufficient for many industrial uses but not for the microelectronics industry. Here, and in many power applications where there is a stringent silica requirement, CEDI is followed by ion exchange polishing.

While this approach greatly extended the ion exchange service cycle and reduced operating costs, issues remained with regeneration and ionic breakthrough of the ion exchange resin. The ambition was for the CEDI to produce water directly of a quality acceptable to the microelectronics manufacturing process.

improving performance

In CEDI modules designed by Siemens-Ionpure, the goal of the individual layers is to remove their respective counter ions, ie the anion exchange resin layers remove anions and the cation resin layers remove

Figure 1: Typical plate-and-frame EDI device configuration



cations. To maintain electro-neutrality in a layer where cations are being transferred to the concentrate, water splitting must take place at the anion exchange membrane to provide the hydrogen ion. A similar process happens in the anion layer at the cation membrane, providing the hydroxide ion to replace removed anions. In the layered bed, the acid or base created through water splitting regenerates some of the ion exchange resin. It can also change the bulk pH in that particular layer. This is critical to the removal of species that are very weakly ionised at neutral or slightly acidic conditions, typical of CEDI feed waters. Acids of silica and boron have pKa values between 9–10. This means that the pH must be increased to this range to remove the ions. Dissolved CO₂, the predominant species in most RO permeates, is also effectively converted to ions in this pH range.

Just as the pH is elevated in the enhanced anion layer, the pH can be reduced or neutralised in an enhanced cation or mixed bed layer. So it is necessary to pass through different types of layers to produce high quality water. The problem is that the electrical resistance of the different layers can vary, potentially allowing preferential current flow. Also the resistance of each layer can change due to the form of the resin or the bulk pH. This issue was overcome in standard single pass modules by doping certain layers to equalise resistance.

advanced construction

The latest innovation in CEDI module design improves reliability and reduces cost at both the module and the system level. The VNX-type module has a cylindrical housing, with integral mounting brackets at both ends. The diameter of the cylinder is approximately 46 cm and the length is 66 cm. Internally, the module is of a thick-cell design, which reduces the amount of ion exchange membrane area necessary to treat a given amount of water. The dilute spacer is fabricated in a multi-step process and consists of two mirror-imaged halves moulded in glass-filled polypropylene, which are then clamped together and over-moulded with thermoplastic elastomer (TPE). The TPE thermally bonds the two halves together and forms integral O-rings that seal the membranes to the spacers and the spacers to each other.

The stack of spacers, end-blocks and endplates are sealed inside a fibreglass-reinforced plastic cylinder by O-rings on the periphery of the end-blocks (analogous to the end-caps in an RO vessel). The module is therefore guaranteed to be leak-free at an operating pressure of 7 bar.

Higher pressures may be possible, since the operating pressure is limited only by the effectiveness of the end-block, O-rings and the pressure rating of the cylinder and the endplates. The new module combines the superior flow distribution of a plate-and-frame design with the benefits of a cylindrical housing.

A building block approach to system assembly, based on multiple modules connected in-line (much like RO elements) reduces costs. With VNX, mounting holes in the end brackets allow the modules to be bolted together end to end, side by side, or stacked vertically, thereby reducing the amount of framing and structural support necessary.

Multiple modules can be connected in line using sections of pipes with O-rings at both ends, similar to the product interconnect tubes in RO vessels. This multi-module building block approach provides the system designer with the flexibility of modular design without increasing the complexity of mechanical

mounting, piping and electrical connections.

A basic system, consisting of modules arrayed on a skid, can form the basis for system integrators to construct systems for specific applications by adding the required piping, instrumentation, controls and power supply. Direct shipment of the basic system from the factory to site is possible, with final assembly on site.

conclusion

Modern water systems using the appropriate combination of technologies can reliably achieve very high levels of water quality. In microelectronics water systems, the level of purity is limited only by the accuracy of the monitoring devices available. For pharmaceutical water treatment, standard skid-mounted systems are now available that can be fully factory tested and most of the validation work completed prior to arriving at site. This makes them quick and easy to connect and commission on site. **tce**

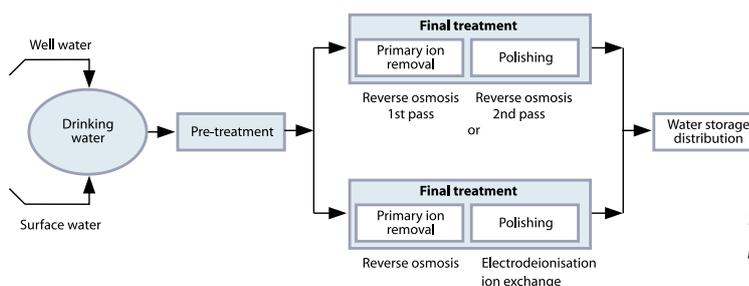


Figure 2: CEDI process schematic

Memory size	256M	1G	2G	4G	16G	64G
Geometry design rules (µm)	0.25	0.18	0.15	0.13	0.10	0.07
Manufacturing date	1997	1999	2001	2003	2006	2009?
TOC (ppb)	<1	<1-<0.5	<1-<0.5	<1-<0.5	<1-<0.5	<0.5?
Particle counts L $\leq 0.3 \mu\text{m}$	-	<500?	<300>			
Particle counts L $\leq 0.5 \mu\text{m}$	<500	<300	<300	<300	<100	<100?
Boron (ppt)	<100	<50	<50	<50	10-50	10-50?
Na ⁺ (ppt)	<7	<5	<5	<2	<2	<1?
K ⁺ (ppt)	10	<5	<5	<2	<2	<1?
F ⁻ (ppt)	30	30	30	<10	<10	<5?
Cl ⁻ (ppt)	<20	<20	<20	<10	<5	<5?
Chromium (Cr) (ppt)	4	2	2	2	2	<1?

Table 1: Examples of pharmaceutical and typical electronics water specifications

Test	USP	Ph. Eur
Conductivity: at operating temperature at 25°C at 20°C after saturation with KCl	Compare with tables <math>< 1.3 \mu\text{S}/\text{cm}</math>	--- --- <math>< 4.3 \mu\text{S}/\text{cm}</math> ---
TOC	<math>< 500 \text{ ppb}</math>	<math>< 500 \text{ ppb}</math> or oxidisable substances test
Nitrates	N/A	NMT 0.2 ppm
Heavy metals	N/A	NMT 0.1 ppm
Aluminium	N/A	NMT 0.1 ppb*
Endotoxin	N/A	<math>< 0.25 \text{ IU}/\text{mL}</math>* (*only for bulk water for dialysis)
TVC	<math>< 100 \text{ cfu}/\text{mL}</math>	<math>< 100 \text{ cfu}/\text{mL}</math>

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