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Ultrapure CEDI for Microelectronics Applications: A Cost Effective Alternative to Mixed Bed Polishers

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Abstract

Continuous Electrodeionization (CEDI) technology is now commonly used as a post RO, makeup demineralization process in a variety of applications, such as microelectronics, power, biotechnology, pharmaceutical, and food and beverage. Some efforts have been made in the past to develop CEDI technology as a final polishing step and as a replacement to mixed beds for microelectronics applications. These efforts have met limited success and have not been cost effective. Advances in the understanding of CEDI technology coupled with process optimization and innovative design concepts have resulted in new CEDI products that are suitable and desirable for polishing applications in microelectronics plants. This paper discusses an innovative CEDI process combined with a very cost effective system design (Ionpure VNX) for producing ultrapure water for microelectronics applications. Data will be presented from multiple tests at a variety of sites and under a variety of feed water conditions consistently showing that the product water quality from these CEDI products is consistently maintained above 18 MΩ-cm with over 99.9% silica and boron removal. A cost comparison of mixed bed DI devices vs. ultrapure CEDI will be presented along with advantages and disadvantages of each process.

Introduction

Continuous Electrodeionization (CEDI) technology is now commonly used as a post RO, makeup demineralization process in a variety of applications, such as microelectronics, steam generation, biotechnology, pharmaceutical, and food and beverage. Some efforts have been made in the past to develop CEDI technology as a final polishing step and as a replacement to mixed beds for microelectronics applications. These efforts have met limited success and have not been cost effective.

The latest innovations in the CEDI process combined with low cost CEDI module and system designs (Ionpure VNX) have resulted in a cost effective alternative to mixed bed DI. Operating data from multiple tests at a variety of sites and under various feed water conditions consistently show that the product water quality of these CEDI devices is continuously maintained above 18 MΩ-cm with over 99.9% silica and boron removal. A cost comparison between mixed bed DI and the latest CEDI systems indicate that CEDI will be the technology of choice for all future microelectronics pure water applications.

Ultrapure (UP) CEDI technology

CEDI devices are comprised of cation- and anion-permeable membranes alternating in a module with spaces in between configured to create liquid flow compartments with inlets and outlets. The diluting compartments are bound by an anion exchange membrane (AEM) facing the positively charged anode, and a cation exchange membrane (CEM) facing the negatively charged cathode. The concentrating compartments are bound by an AEM facing the cathode and a CEM facing the anode. 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 bounds of the membranes and compartments. When the electric field is applied, ions in the liquid are attracted to their respective counter-electrodes. The result is that the diluting compartments are depleted of ions and the concentrating compartments are concentrated with ions. The CEDI process has been discussed in variety of publications for several years. A representation of the process is shown in Figure 1.

The Ionpure UP technology is an innovative variation of standard CEDI technology. The aim is to remove weakly ionized species such as boron and silica from the feed water, typically RO permeate, along with attaining very high purity (18 MΩ-cm) in the product water. This task is even more difficult for feed waters from single pass RO containing other competing species such as carbon dioxide.

Layered bed thick cell CEDI

Layered bed CEDI devices such as the Ionpure LX and VNX have the advantage of being able to configure the ion exchange layers within the device to optimize the removal of specific contaminants. Over the last few years there has been a shift towards thicker diluting cells and modular system approaches, both of which have lowered costs. Thicker diluting cells reduce the amount of ion exchange membrane area necessary to treat a given amount of water, thereby reducing the overall cost of the modules. This required a change in the ion exchange filler inside the cells. Thin cell CEDI, the first commercial iteration of the technology and the only available through the mid 1990's, uses a mixed resin bed in the diluting compartments. Because of the short distance across the cell, typically 2-3 mm, there is high likelihood of a continuous path of like ion exchange material between the membranes, something necessary for efficient ion transport. As the cell width increases (current thick cell CEDI devices have a dilute cell thickness of 8-11 mm) the chances of obtaining a continuous path in a mixed bed decreases dramatically. This has led to the use of layers of resin where the layers are comprised of either one type of ion exchange material, i.e. 100% cation or 100% anion, or are a combination of straight layers with mixed bed layers (1).

With layered CEDI technology, the goal of the individual layers is to remove their respective counter ions, i.e. the anion layers remove anions and the cation layers remove cations. To obtain 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 hydrogen ion, H^+. A similar process happens in the anion layer at the cation membrane providing OH^- to replace removed anions. For this process to happen efficiently, the resin layers must be enhanced to promote the water splitting reaction (2). This process is shown in Figure 2.

In the appropriately enhanced layers, the acid or base created through water splitting can regenerate 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 ionized at neutral or slightly acidic conditions, typical of CEDI feedwaters. Silicic and boric acids have pKa values between 9-10. This means the pH must be increased to this range to achieve effective removal. Dissolved CO_2, the predominant species in most RO permeate waters, is also effectively converted to the ionized forms at this pH range. Figure 3 shows the theoretical pH increase in an enhanced anion layer assuming the feed water TDS is due to varying NaCl (3). It also shows how the pH is buffered at higher CO_2 concentrations.

This figure shows that for a typical RO permeate water with a TDS of 2 ppm and containing 2.5 ppm CO_2, for example, the pH in the enhanced anion layer will increase about 3.5 units. Shown in Table A is actual data from one such layer with a similar feed water makeup. The pH in this case increased about 3 units. Notice how quickly the silica is removed once the pH is elevated.
After the pH is elevated in the enhanced layer and weakly ionized species are removed, it is still necessary to pass the liquid through different layers to reduce or neutralize the pH and produce high quality water. This can be accomplished by cation and/or mixed bed layers. The problem is that the electrical resistance of the different layers can be much different. In addition, the resistance of each layer can change due to the form of the resin or the bulk pH.

Two-pass CEDI

Because in a typical single pass CEDI module the layers are all exposed to the same electric field, i.e. they are electrically in parallel, there is the potential for current to preferentially flow through the layers with lowest resistance. This was overcome by doping certain layers to equalize resistance (4). However, for the UP technology, with the goal of producing 18 MΩ-cm water with almost complete removal of weakly ionized species such as silica and boron, specific types of layers must be used which have significantly different resistances, much more so than in standard modules.

The solution then is to use a two-pass approach by either operating two modules in series or putting the layers electrically in series in a single module. Figure 4 shows how the

layers can be put electrically in series using a folded path design (5). Here the feed water passes through two different beds in series in the same module using one set of electrodes. The two beds are hydraulically and electrically in series. Although the voltage drop through each bed may be different, the current through each is the same because they are in series.
In a two-pass design the number of cells in the second pass is less than that in the first. This is because the first pass is where the pH shifting and removal of weak ions occurs. This can be a slow process requiring several steps and longer residence time. The second pass is primarily for polishing of ions that weren't effectively removed at the pH extremes in the first pass. This is a relatively fast process and requires less residence time.

The other option for operating the two beds in series is to use completely separate modules each run on a different power source or connected in series on the same power source. Again, because the second pass can be operated at higher flow per cell, system designs could use this to reduce the total number of modules or systems. Figure 5 shows eight modules feeding six for example. For higher total flow, this could also represent eight systems feeding six polishing systems.

Using a single, folded path module may be more economical in some instances, but using series modules or systems may offer some added flexibility, especially when using separate power sources. Either method will produce high purity water (18 MΩ-cm) and ultra low or undetectable levels of boron and silica.

CEDI UP performance data

Several folded path modules were assembled and tested for reproducibility. The feed water was RO permeate at 10 μS/cm (primarily Na, Cl, HCO_3), with 4-5 ppm CO_2 and 300-500 ppb of silica. Water temperature was typically 10°C. Data from four of these modules is shown in Table B as modules A, B, C, and D. All modules provided stable product quality greater than 18 MΩ-cm. Silica removal was 99.8-99.9% and boron removal was 98-99%. More recently, a slightly different resin layering was incorporated to further improve removal of all species. Data from a module with the new resin is shown as module E in the table. This module showed improved silica and boron removal with removal rates of 99.98% and 99.44% respectively.

A test system was operated at a major microchip manufacturer in the US for six months. It was installed after 2-pass RO in parallel with four existing chemically regenerated mixed beds. At this site, the mixed beds were regenerated frequently (as often as once per week) due to boron breakthrough. Over six months of operation, the CEDI unit consistently produced greater than 18 MΩ-cm water with silica below the detection limit of 0.5 ppb. Data is shown in Table B as Pilot 1. In addition, the boron removal was excellent and remained below the composite of the mixed beds throughout the testing. Although some of the mixed bed units produced lower boron levels at times, they were regenerated at different times, so the composite (200-600 ppt) was never as low as the CEDI (35-40 ppt).

Another pilot system was run in Asia for several months. Feed water was from a single pass RO with no softening upstream. The total hardness feeding the CEDI unit was about 0.1 ppm as $CaCO_3$. The feed water was about 7 µS/cm with 5 ppm CO_2. The CEDI unit consistently produced 18.2 megohm-cm water with non-detectable silica (less than 0.1 ppb as SiO_2). Data is shown in Table B as Pilot 2.

Cost effective CEDI module and system design

The plate and frame configuration CEDI module is now a widely accepted design as it provides the most even distribution of water flow and DC current flow. However, the issues related to leaking, electrical shorting and cost of CEDI systems have limited the penetration of CEDI technology in many applications. In 2001 the problems of leaking and shorting were eliminated through the introduction of CDI LX modules using double o-ring seals and superior electrical insulation. The costs of systems with multiple CDI LX modules on a rack with all the desired valves and piping was lower than other CEDI modular systems available on the market due to a simplified process design, including the avoidance of concentrate recirculation and brine injection. However, to compete cost effectively with mixed bed deionization, further innovations in the module and system designs were necessary.

In 2003, an alternate plate and frame module design was introduced, utilizing all the earlier design innovations of the CDI LX module and combining them into a stackable housing. The VNX module (Figure 6) comprises a cylindrical FRP housing containing round plate and frame spacers (Figure 7) in a "stacked disk" configuration, with multiple o-ring seals and superb electrical insulation to eliminate any possibility of shorting. Perhaps the most important innovation of the VNX module is the ability to directly connect additional modules in a row (Figure 8) with simple connectors, similar to the interconnectors used in RO modules. The connectability and stackability of the VNX modules (Figure 9) reduces the amount of piping, valves and other components commonly found in standard modular CEDI systems. The 300 gpm preassembled VNX modular system shown in Figure 9 occupies less than half the space of a comparable flow rate CEDI system presently available. In addition, the cost of a VNX based system is 30-40% less than the standard modular CEDI systems available today. We believe that the innovative VNX module design and the modular VNX based system design will become the standards for all CEDI products in the future.

Advantages of new CEDI design

For a variety of reasons the use of mixed bed DI as a polishing treatment to RO has continued despite the significant progress made by CEDI technology in the last 16 years.

Process issues such as the use of brine injection in some CEDI devices and design issues such as leaking and shorting have cast a negative light on the application of CEDI technology. However, as explained above, the latest process and design innovations eliminate these concerns. The advantages of these latest CEDI devices can be summed up as follows:

- Capability to produce high quality water (18 MΩ-cm) with ultra low or nondetectable boron and silica.
- Continuous production of high quality water without breakthrough as experienced in mixed beds.
- No brine injection. Truly a non-chemical process.
- Robust design capable of operating continuously at 100 psi (7 bar).
- No leaking or shorting.
- Small footprint.
- Easily expandable modular design.
- Cost competitive with mixed bed DI, especially with the latest VNX modular systems approach.

Figure 10 shows the reduction in capital cost of CEDI systems over the past three years, based on cost for a 120 gpm system designed for general industrial applications with PVC piping. The cost of a mixed bed deionization (DI) system is included for comparison.

Conclusion

A combination of CEDI process and design innovations has resulted in a real alternative to mixed bed DI polishing. The CEDI process is now capable of continuously producing high purity water for microelectronics and other polishing applications. The robust, reliable and cost effective modular systems (Ionpure LX and VNX) are now a product of choice in a new or retrofit application for microelectronics, power and other high flow/high purity applications.

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References

1. Gifford, J. D. and D. Atnoor, "An Innovative Approach to Continuous Electrodeionization Module and System Design for Power Applications", Proceedings of the International Water Conference, Pittsburgh, Pa. (Oct. 23-25, 2000).

2. Ganzi, G. C., et al, U.S. Patent No. 5,868,915 (Feb. 9, 1999).

3. Gifford, J., "A High-Performance High-Purity EDI Module Designed for the Microelectronics and Semiconductor Industries", Ultrapure Water Portland, Presentation at the Executive Forum, Oct. 15, 2003.

4. Dimascio, F., et al, U.S. Patent No. 6,284,124 B1 (Sept. 4, 2001).

5. Giuffrida, A. J., U. S. Patent No. 4,931,160 (Jun. 5, 1990).

Biographies

Mr. Anil D. Jha is Chief Technology Officer at Ionpure Technologies. Mr. Jha has over 30 years of experience in the water treatment industry and is one of the pioneers of commercial continuous electrodeionization (CEDI) technology. He holds multiple patents related to CEDI and other water treatment technologies.

Joseph Gifford is a Senior Applications Engineer at Ionpure Technologies. He has nine years of experience in high purity water treatment, much of which has focused on the development and application of continuous electrodeionization technology. He has a B.S. in Chemical Engineering from Worcester Polytechnic Institute in Worcester, MA, and an M.S. in Chemical Engineering from the University of Massachusetts in Lowell, MA.

Figure 1. CEDI Process (All-filled Configuration)

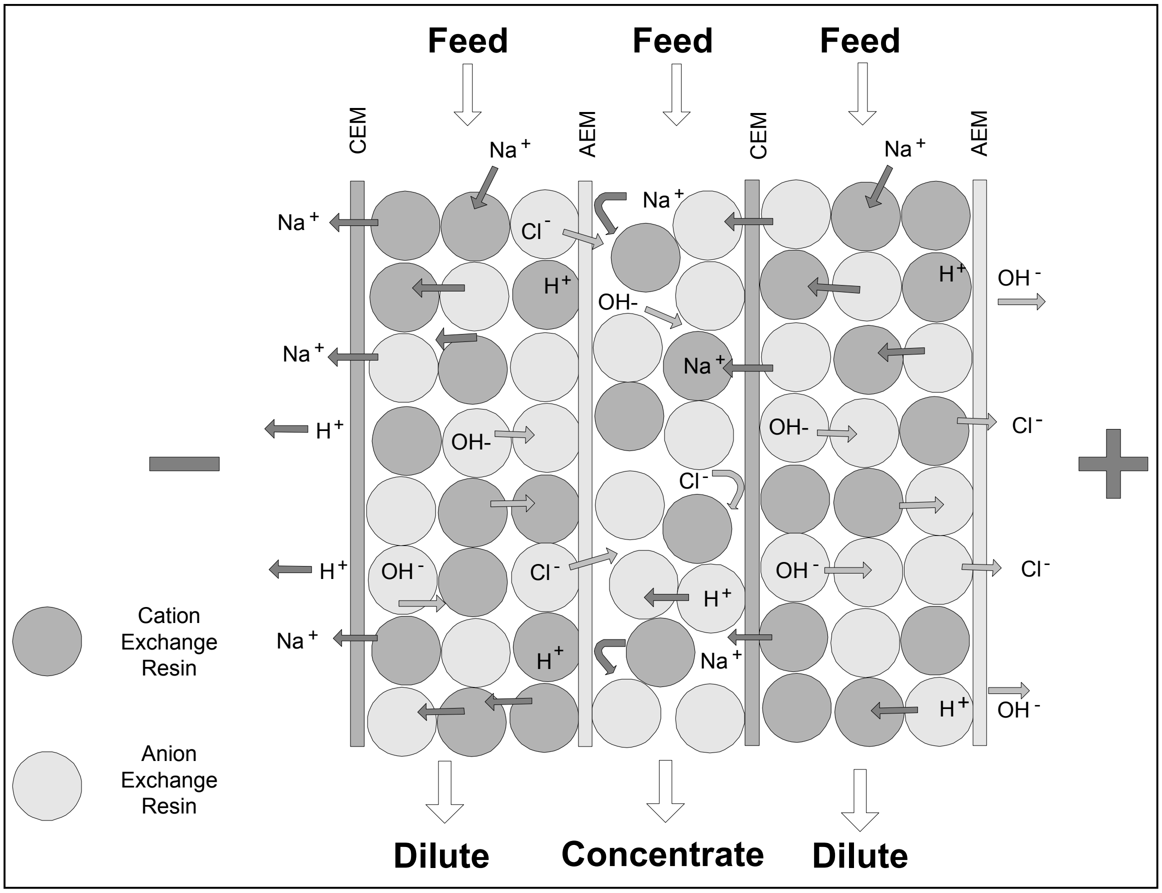

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Figure 2. Water Splitting in Layered CEDI

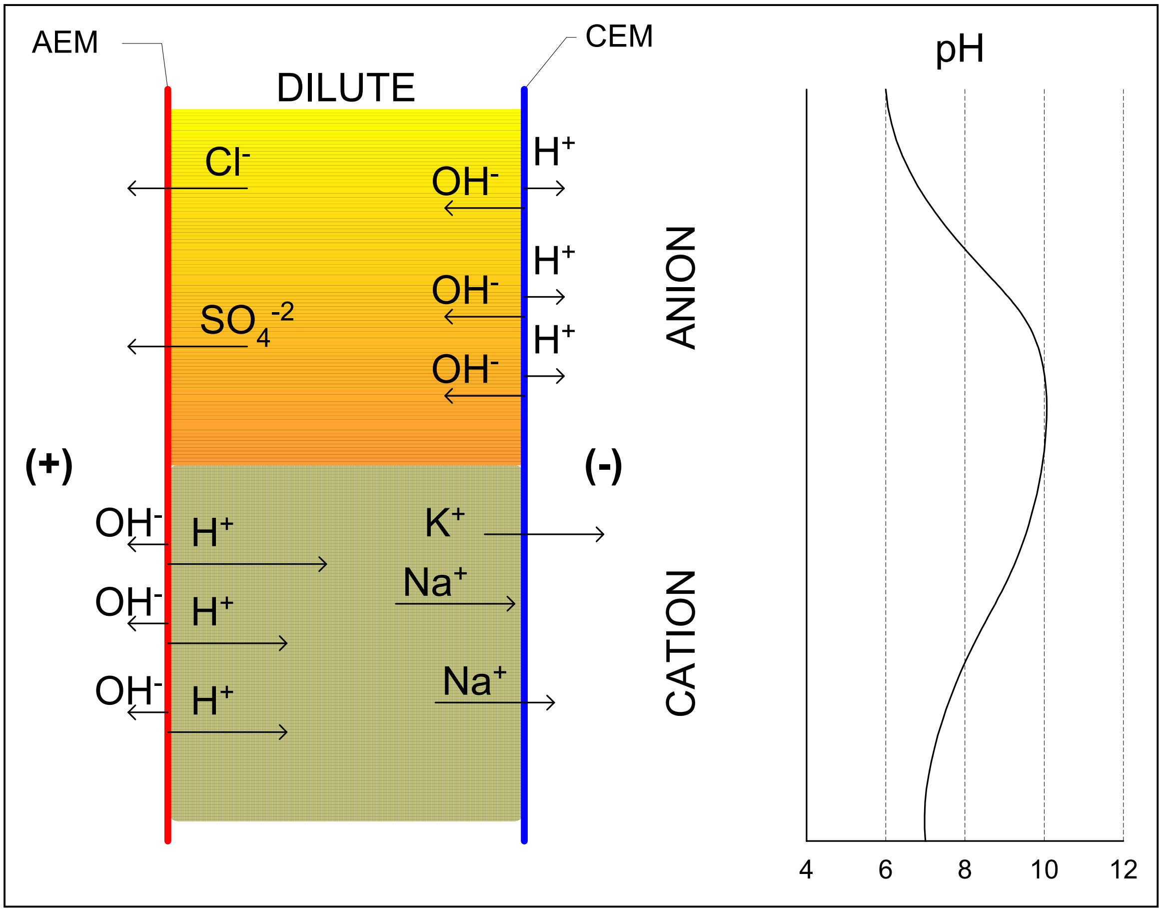

Figure 3. Theoretical Maximum Bulk pH Increase in an Enhanced Anion Layer

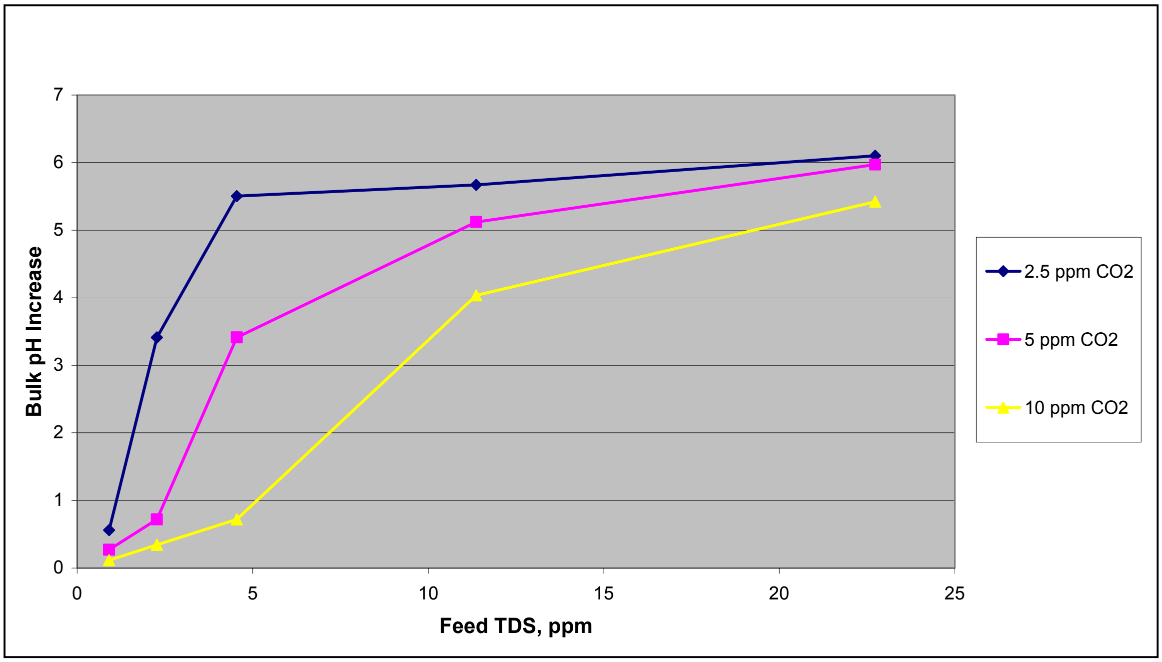

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Figure 4. Two Pass CEDI in a Single Module Using a Folded Path Design

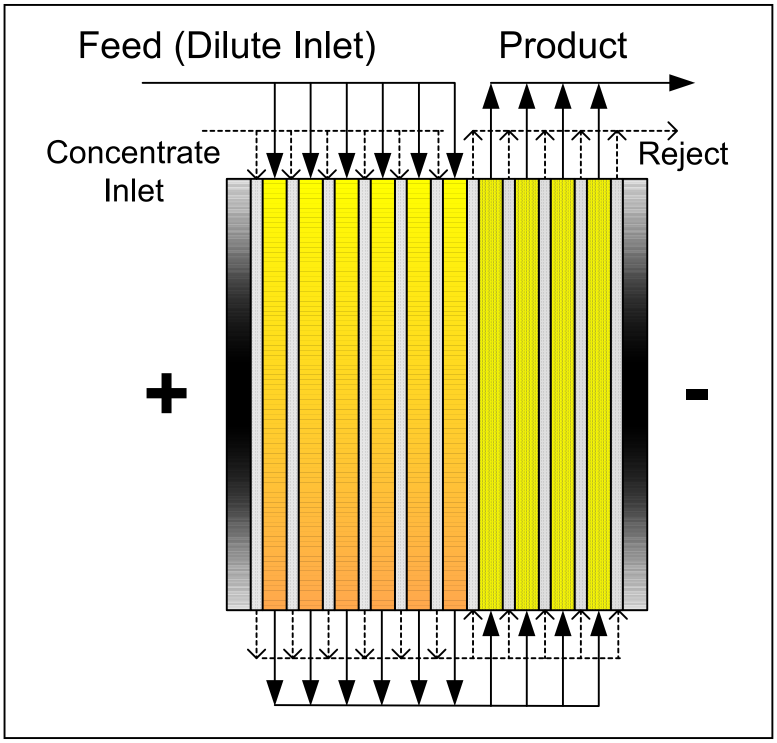

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Figure 5. Two Pass CEDI Using Multiple Modules or Systems

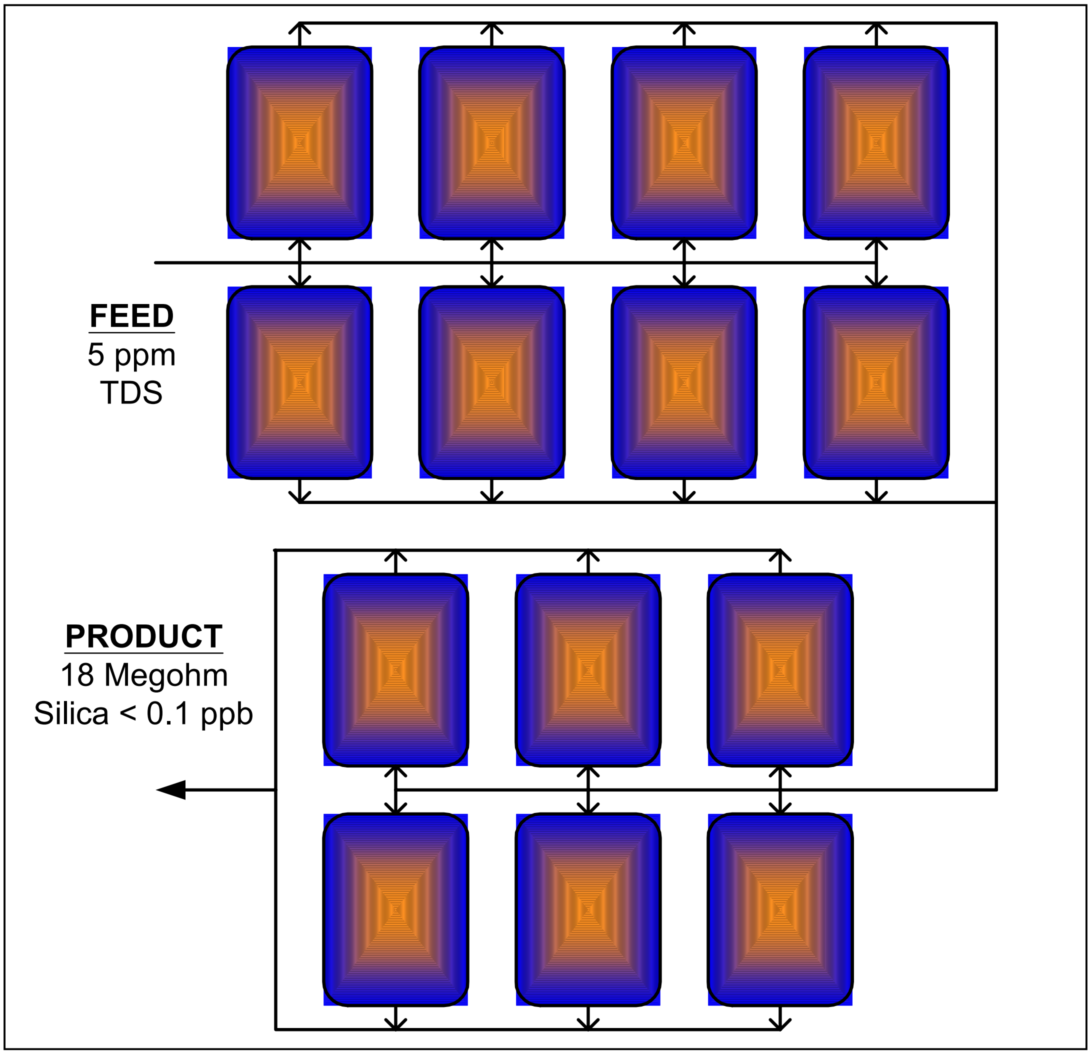

Figure 6. Ionpure VNX Module

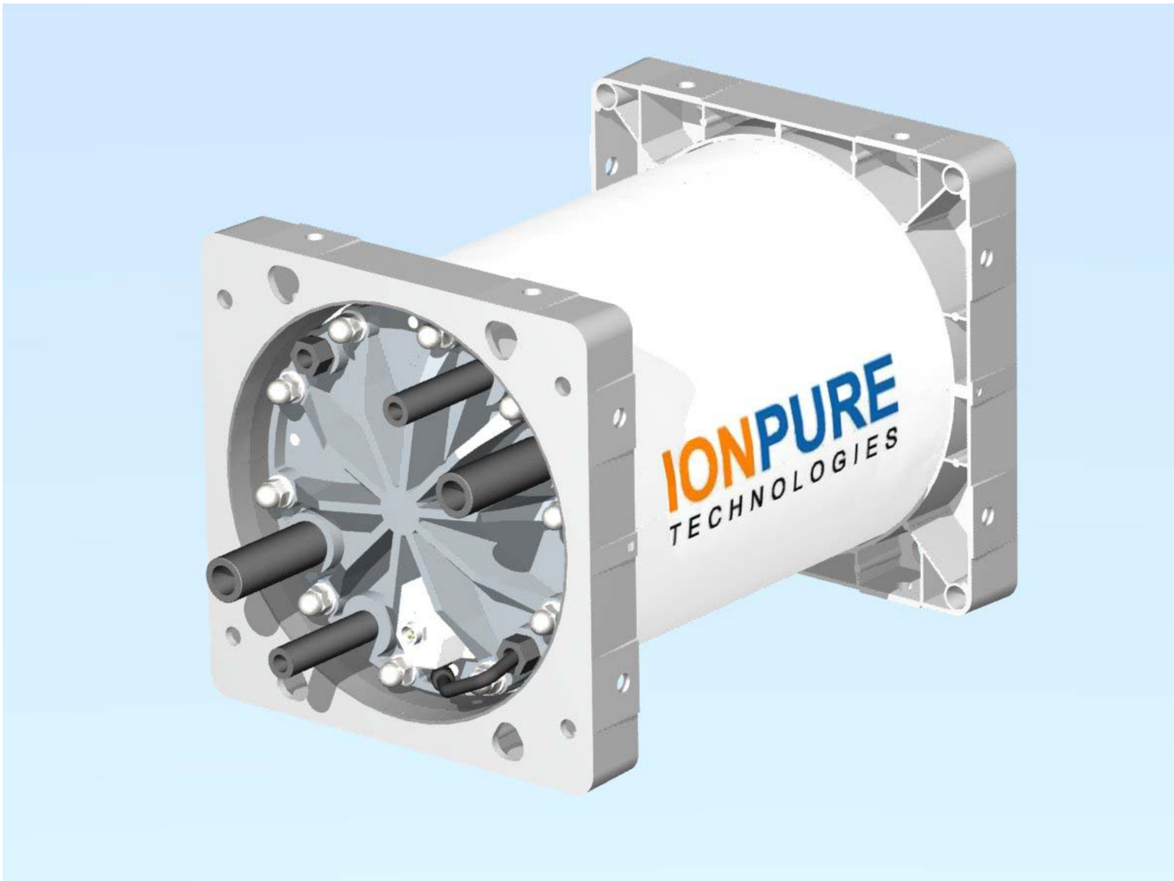

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Figure 7. VNX Dilute Spacer

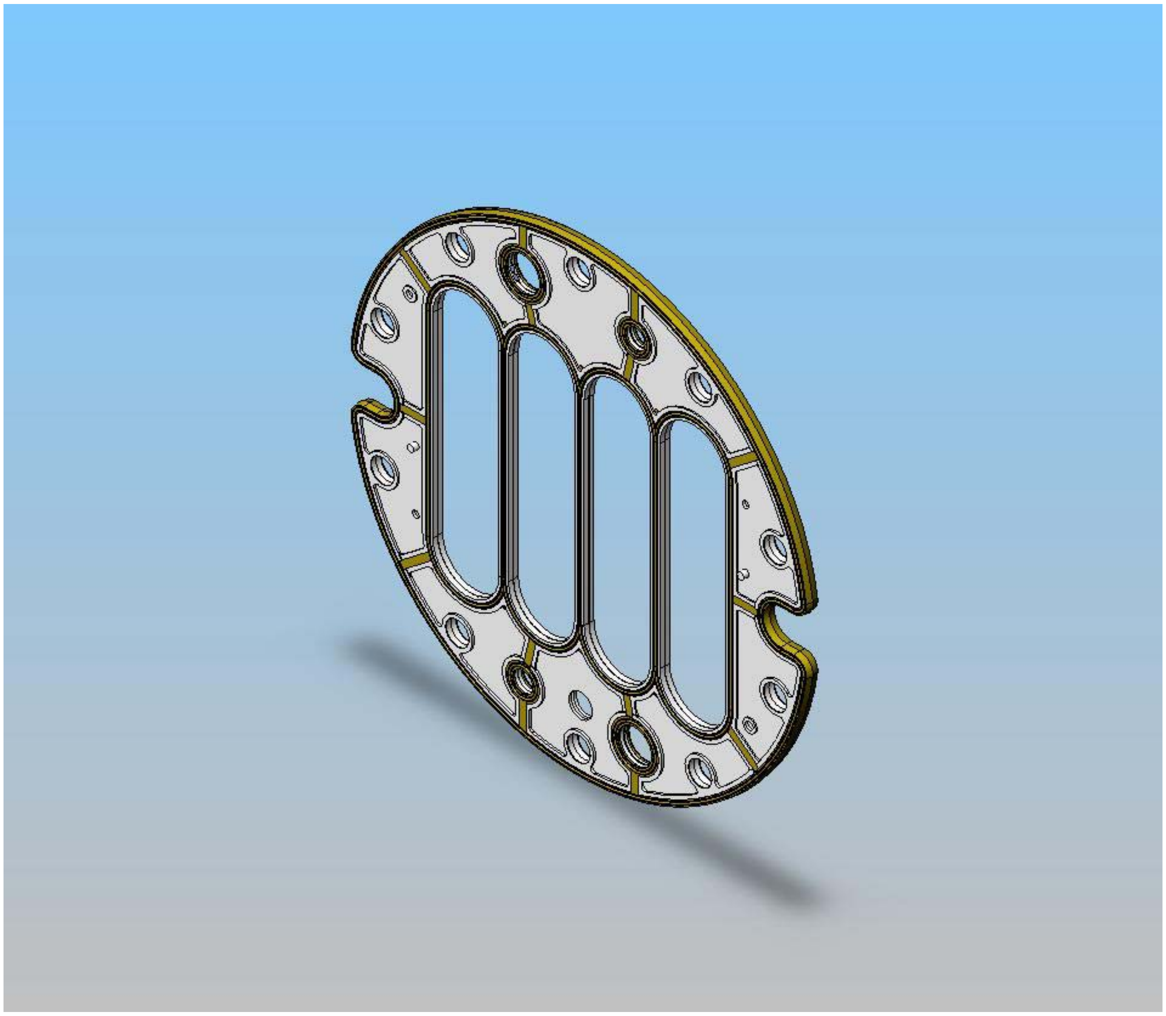

Figure 8. Multiple VNX Modules Connected Inline with Interconnect Tubes

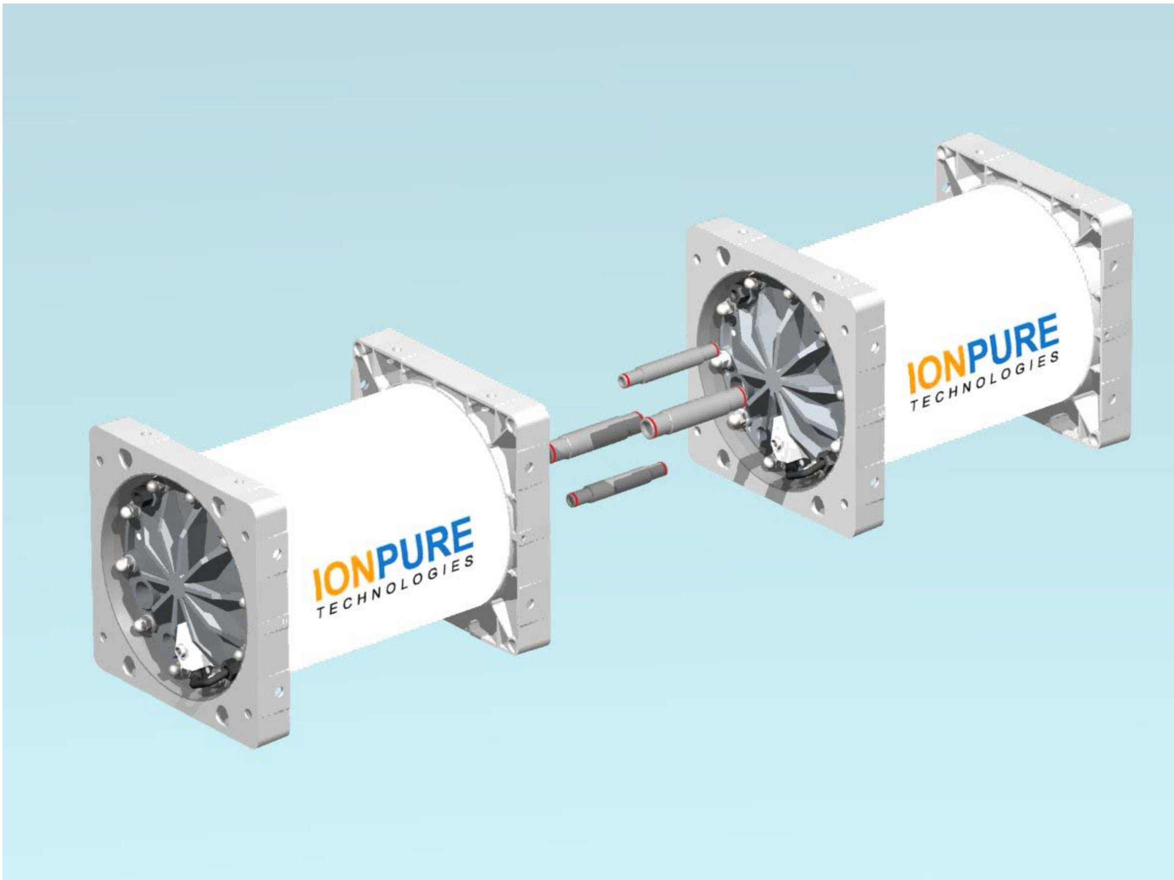

Figure 9. 300 GPM (70 m^3/hr) VNX System (Approximately 3.5m long, 1.2m wide, and 1.75m high)

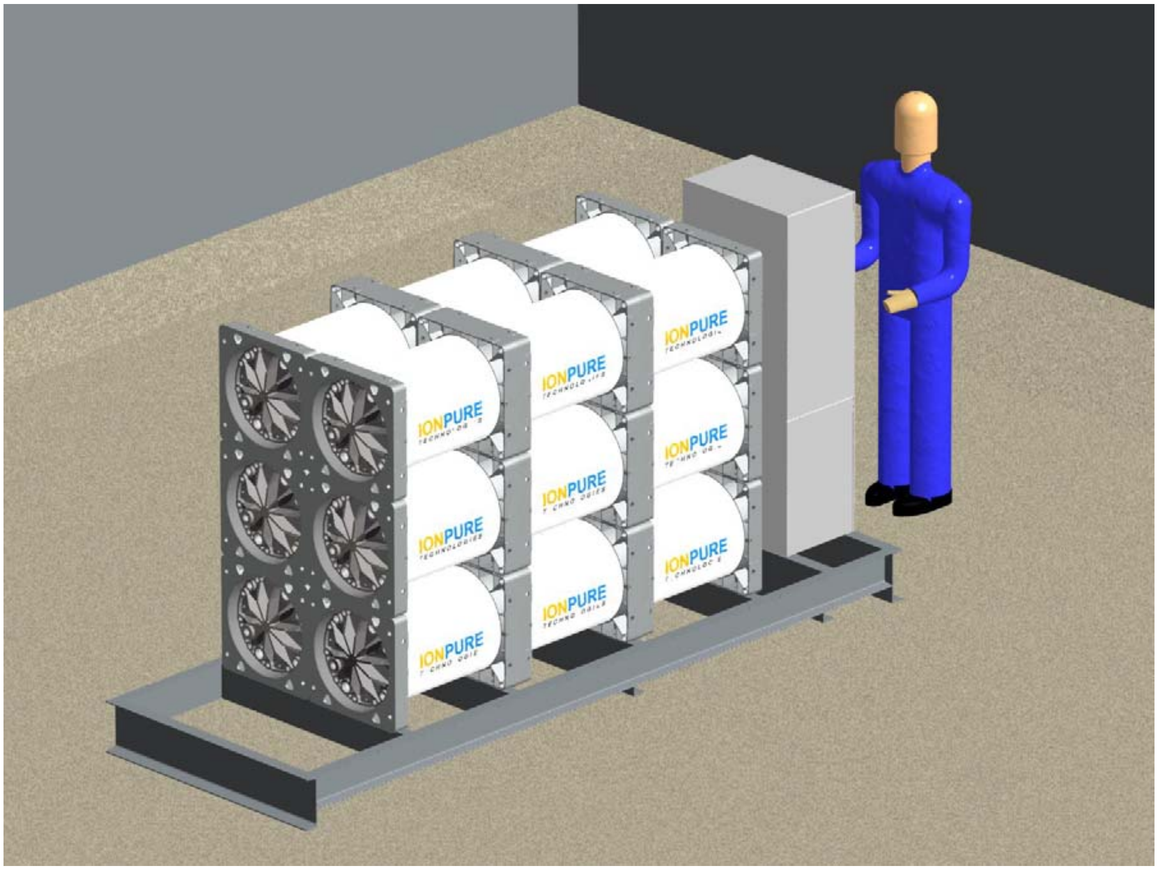

Figure 10. Reduction in Capital Cost for CEDI Systems Compared to Mixed Bed Deionizers

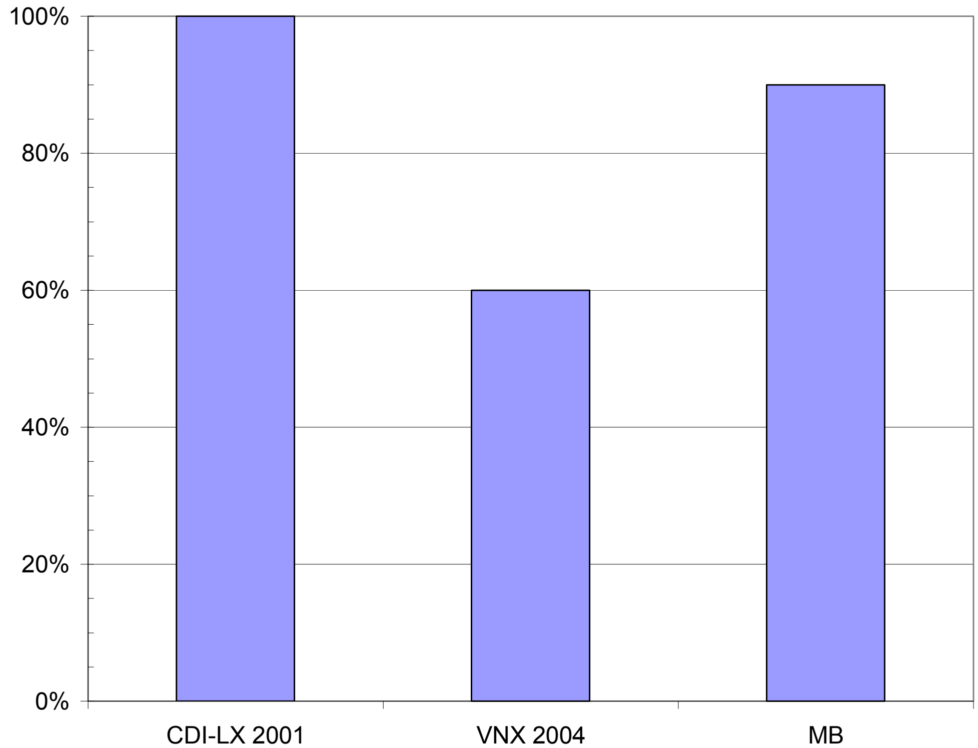

Table A. pH Increase and Silica Removal in an Enhanced Anion Layer

Percent of Bed Depth	pH	Silica ppb
0	6.66	314
7	9.41	308
14	9.64	220
21	9.71	56
29	9.68	41
36	9.56	21
43	9.61	12
50	9.65	7
57	9.68	3

Table B. CEDI UP Performance Data

Module	Product MΩ-cm	Species	Feed, ppb	Product, ppb	Removal, %
A	18.06	**Silica**	460	0.4	99.91
		Boron	0.8	< 0.01	> 98.75
B	18.04	**Silica**	430	1.0	99.8
		Boron	70	1.0	98.6
C	18.05	**Silica**	500	1.0	99.8
		Boron	0.7	0.011	98.4
D	18.2	**Silica**	470	0.8	99.83
		Boron	1.7	0.015	99.12
E	18.2	**Silica**	480	0.1	99.98
		Boron	5.0	0.028	99.44
PILOT1	> 18	**Silica**	6-7	< 0.5	> 92.9
		Boron	25-30	0.03-0.04	99.9
PILOT2	> 18	**Silica**	200-500	< 0.1	> 99.98