ADVANCES IN CEDI MODULE CONSTRUCTION AND PERFORMANCE

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ABSTRACT

The advancement in continuous electrodeionization (CEDI) module construction has focused on three design objectives: improving module performance, increasing module reliability and lowering the overall cost of CEDI systems. All three objectives are driven by the goal of making CEDI more competitive with conventional mixed-bed deionization.

Improvement in module performance has been achieved by optimization of resin layering and the use of a series-path design. Module reliability was improved by implementation of O-ring type seals and cylindrical FRP housings. System assembly costs have been reduced via an innovative building block approach to system assembly, based on multiple modules connected in-line like RO elements. The paper will describe the module and system design and present some operating data and cost estimates comparing the new CEDI technology to regenerable mixed-beds

INTRODUCTION

Continuous Electrodeionization (CEDI) is the process of removing ionized or ionizable substances from water using ion exchange membranes, electrically active media (typically ion exchange resin), and a DC electric potential. Since commercial inception in the late 80's, the process has been continuously improved in order to lower the cost and at the same time increase the degree of deionization. The purpose of this paper is to review advances in CEDI module construction with design objectives of improving module performance, increasing module reliability and lowering overall cost of CEDI systems. These objectives are focused on making CEDI competitive with conventional mixed bed deionization. These objectives are especially important in semiconductor pure water applications where the use of conventional mixed bed deionization is undesirable due to periodic fluctuation in product quality caused by exhaustion and regeneration of ion exchange beds.

CEDI TECHNOLOGY

Most commercial CEDI devices comprise 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 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. Explanation of the CEDI process can be found in previous papers (1-4). A representation of the process is shown in Figure 1.

IMPROVING CEDI MODULE PERFORMANCE

CEDI in Microelectronics

Product water specifications for current CEDI technologies are typically in the range of 10-16 megohm-cm with removal of weakly dissociated species such as silica and boron in the 90-98% range. This is sufficient for many industrial uses, such as water production in the pharmaceutical and power generation markets. However, this quality is not sufficient for use in the microelectronics industry where quality requirements are very stringent - requiring greater than 18 megohm-cm with most species non detectable. In this case, and in many power applications where there is a stringent silica requirement, CEDI is followed by ion exchange polishing. While this approach can greatly extend the ion exchange service cycle and reduce operating costs, there are still issues such as regeneration and breakthrough of the ion exchange resin that must be dealt with. The ideal solution would be for the CEDI to produce water directly of a quality acceptable to the microelectronics manufacturing process, i.e. greater than 18 megohm-cm with trace levels of silica, boron and other dissolved species. This is illustrated in Figure 2.

CEDI Trends

Over the last few years there has been a shift towards thicker diluting cells (1) 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 has led to the use of layers of resin where the layers can be primarily cationic, primarily anionic material, mixed bed, etc (5).

Layered Beds and pH Shifting

With layered CEDI technology, obviously the goal of the individual layers is to remove their respective counter ions, i.e. the anion resin layers remove anions and the cation resin layers remove 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 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, layers must be enhanced to promote the water splitting reaction (6).

In these 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 feed waters. Silicic and boric acid have pK_a 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 permeates, is also effectively converted to the ionized forms at this pH range.

Shown in Figure 3 is actual data from an enhanced anion resin layer (7). The pH in this case increased about 3 units. The X-axis in this figure is the fractional length. Notice how quickly the silica is removed once the pH is elevated.

Two-Pass CEDI

Just as the pH is elevated in the enhanced anion layer, the pH can be reduced or neutralized 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 be different, potentially allowing for preferential current flow. In addition, 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 equalize resistance (5). However, for a module to produce very high quality water over a range of feed waters, specific types of layers must be used which have significantly different electrical 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 (8). 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 can be 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. For example, Figure 5 shows three modules feeding two. For higher total flow, this could also represent three first pass systems feeding two 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.

Performance

Six 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 controlled to 10°C. All modules provided stable product quality between 18.1-18.2 megohm-cm. The average silica removal was 99.9%, boron removal was 99.0%, and sodium removal was 99.99%.

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 the 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 the six months of operation, the CEDI unit consistently produced greater than 18 megohm-cm water with silica below the detection limit of 0.5 ppb. The CEDI boron removal proved to be better than the overall mixed bed removal as shown in Table 1. This boron profile shows the boron feed to each RO pass as well as the RO permeate and the effluent from each mixed bed and the test CEDI system. As you can see, the boron from each mixed bed varied significantly. This is believed to be due to different times since regeneration. This caused the composite mixed bed boron to be much higher than the CEDI boron.

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). Figures 6 and 7 show results for the first two months of operation.

INCREASING CEDI MODULE RELIABILITY

Since the mid-1990's the trend in CEDI module design has been toward:

- Modularity, with flow rates of 12.5-17 gpm (2.8-3.9 m^3/hr) per module. Multiple modules are piped in parallel to form systems with higher flow rates.
- Increased robustness, with maximum feed water pressure of 100 psig (7 bar) and temperature of 45°C.
- Increased reliability, with zero leakage.
- Lower cost, with thick-cell construction that reduces the number of spacers and the area of membranes required per unit flow rate.

The CDI-LX™ module commercialized in 2001, for example, achieves these objectives with a combination of:

- Strength of spacer material. Both the dilute and concentrate spacers are molded of strong engineering plastics such as polysulfone.
- O-ring seals between the spacers and the membranes. The thickness of the dilute spacers can accommodate grooves for O-rings that are inserted prior to module assembly.
- Shorter channel length (about 14" vs. 26" for a typical thin-cell module), which reduces the deflection of the sidewalls of the spacers.

In addition to elimination of external leakage by using stronger spacers and O-ring seals, there were other key design changes focused on improving the reliability of both the modules and systems:

- Improvement in the insulation of metallic components to eliminate the possibility of electrical arcing.
- Use of resin-filled concentrate and electrode compartments to avoid the need for concentrate brine injection.
- Elimination of the need for concentrate recirculation, to reduce system complexity and lower the possibility of concentrate biofouling.

The latest advance in CEDI module design further improves reliability and reduces cost at both the module and the system level. The module (called the VNX) is housed in a cylindrical housing, with integral mounting brackets at both ends (see Figure 8). The diameter of the cylinder is approximately 18” (46 cm) and the length is 26” (66 cm).

Internally the module is of a thick-cell design. The dilute spacer, shown in Figure 9, is fabricated in a multi-step process. Each spacer consists of two mirror-imaged halves molded in glass-filled polypropylene, which are then clamped together and over-molded 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, endblocks and endplates are sealed inside a fiberglass-reinforced plastic cylinder by O-ring on the periphery of the endblocks (which is analogous to the endcap in an RO vessel). The module is therefore guaranteed to be leak-free at operating pressures of 100 psig (7 bar). Higher pressures may be possible, since the operating pressure is limited only by the effectiveness of the endblock 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. Reduction in both material and labor cost is achieved by using low cost materials for the spacers and by molding O-rings as integral part of the spacers.

LOWERING CEDI SYSTEM COST

The recent trend in CEDI system design follows that of the modules. Multiple CDI-LX modules, for example, are mounted on racks and connected to common feed, product and reject manifolds. The modules do not have independent flow controls, so each system has just one set of flow controls and instrumentation. Modularity reduces the risk of capacity loss in the event of a module failure, but increases the number of piping and electrical connections.

Several design features of the new VNX module will further reduce the complexity and cost of CEDI systems:

- 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 (Figure 10). All the dilute and concentrate compartments in the modules are then operating in parallel, and the connected modules function as a single module. The nominal flow rate per module is 16.7 gpm ($3.8m^3/hr$) so three modules in line for example would form a 50 gpm ($11.4\ m^3/h$) building block. The approach is analogous to a RO system, with the VNX modules equivalent to RO elements and building blocks equivalent to RO vessels housing multiple elements.
- Piping to individual modules or building blocks can be from either end; the inlets and outlets can be on the same or opposite ends. Either flexible hoses or rigid piping can be used.

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. For example, Figure 11 shows a 200-gpm system designed for production of ultrapure water. The modules are arranged in four parallel 50 gpm trains.

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.

The modularity and simplicity of CEDI systems of the new design will reduce the engineering effort required to customize systems for specific applications.

Figure 12 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.

SUMMARY

Performance equal to or better than conventional mixed-bed deionization is now achievable using CEDI technology through enhanced layering and staged CEDI modules. This eliminates the problems caused by fluctuations due to regeneration of the ion exchange polisher used in many semiconductor pure water applications.

Robust module design of VNX CEDI module that utilizes double o-ring seal in a cylindrical housing similar to an RO vessel assures leak-free high pressure operation of the CEDI device.

Integrated system design with multi-modules pre-assembled on a skid significantly reduces the system cost of the CEDI making it cost competitive to regenerable ion exchange polishers.

BIOGRAPHIES

Mr. Anil D. Jha is Vice President of Research and Development at USFilter. 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.

Li-Shiang Liang is the Director of Product Development at USFilter. He has worked on electrodeionization technology since joining the Process Water Division of Millipore, now part of USFilter, in 1988. He was responsible for development of the CDI-LX™ module product line and for the new generation modules described in this paper. He has a Ph.D. from Massachusetts Institute of Technology, Cambridge, MA and has over 27 years of experience in water purification and wastewater treatment, encompassing research, product development and consulting.

Joseph Gifford is a Senior Development Engineer in Applications R&D at USFilter. 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.

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Table1. Boron Profile Through Primary Water Treatment System

Sample	**After 3 Months**		**After 4 Months**	
RO Feed	58900		75900	
First Pass RO Product	43400		55600	
First Pass Removal	26.3%		26.7%	
Second Pass RO Product	25800		28800	
Second Pass Removal	40.6%		48.2%	
	Mixed Beds	**CEDI**	**Mixed Beds**	**CEDI**
1	16	-	23	-
2	14	-	16	-
3	340	-	41	-
4	2170	-	720	-
Combined	**592**	**35**	**242**	**44**
Removal	**97.7%**	**99.9%**	**99.1%**	**99.8%**

*All values in ng/L (ppt)

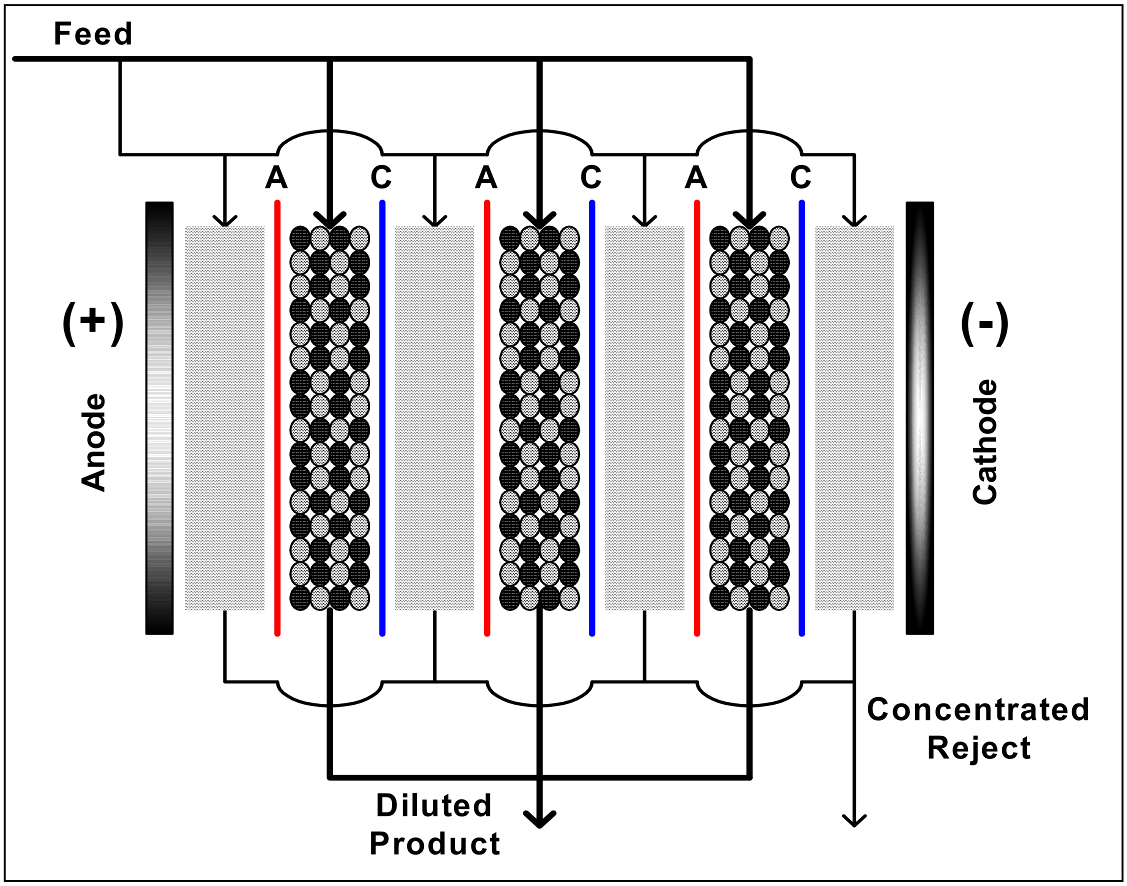

Figure 1. Typical CEDI Device Configuration(1)

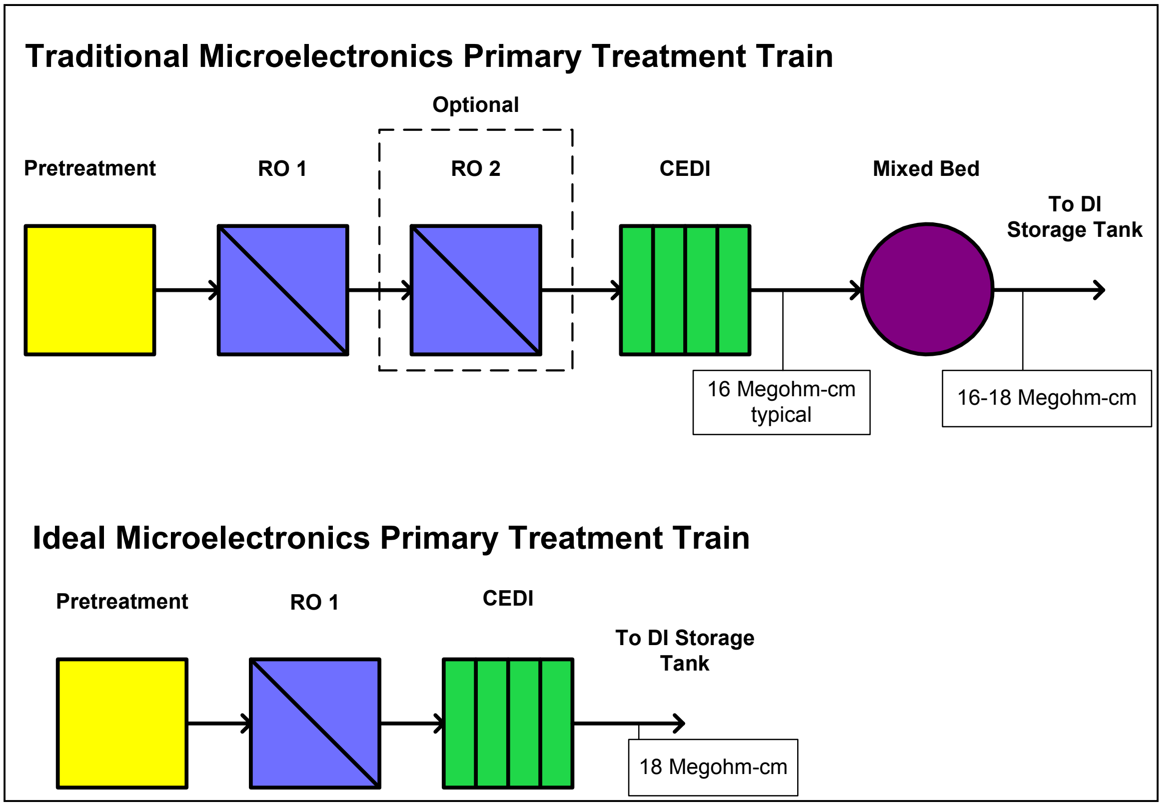

Figure 2. Microelectronics Primary Water Treatment Process

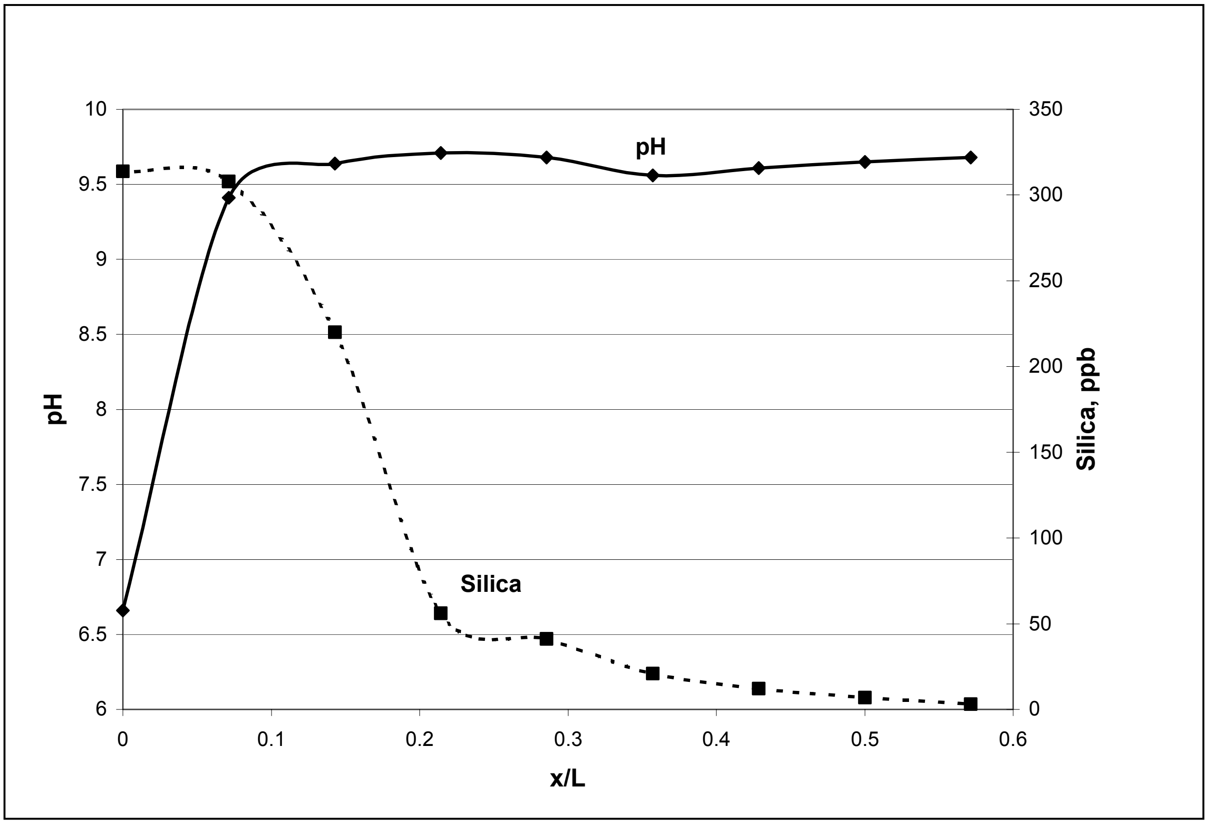

Figure 3. pH Change and Silica Removal in Enhanced Anion Layer

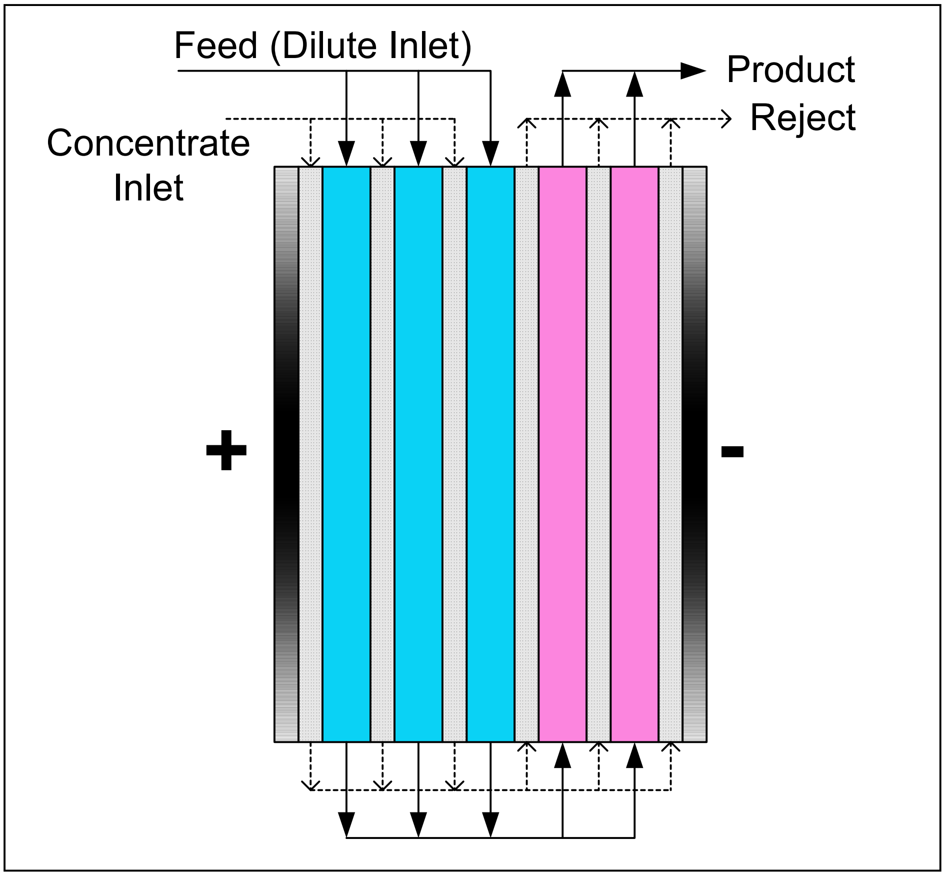

Figure 4. Folded Path Module Design

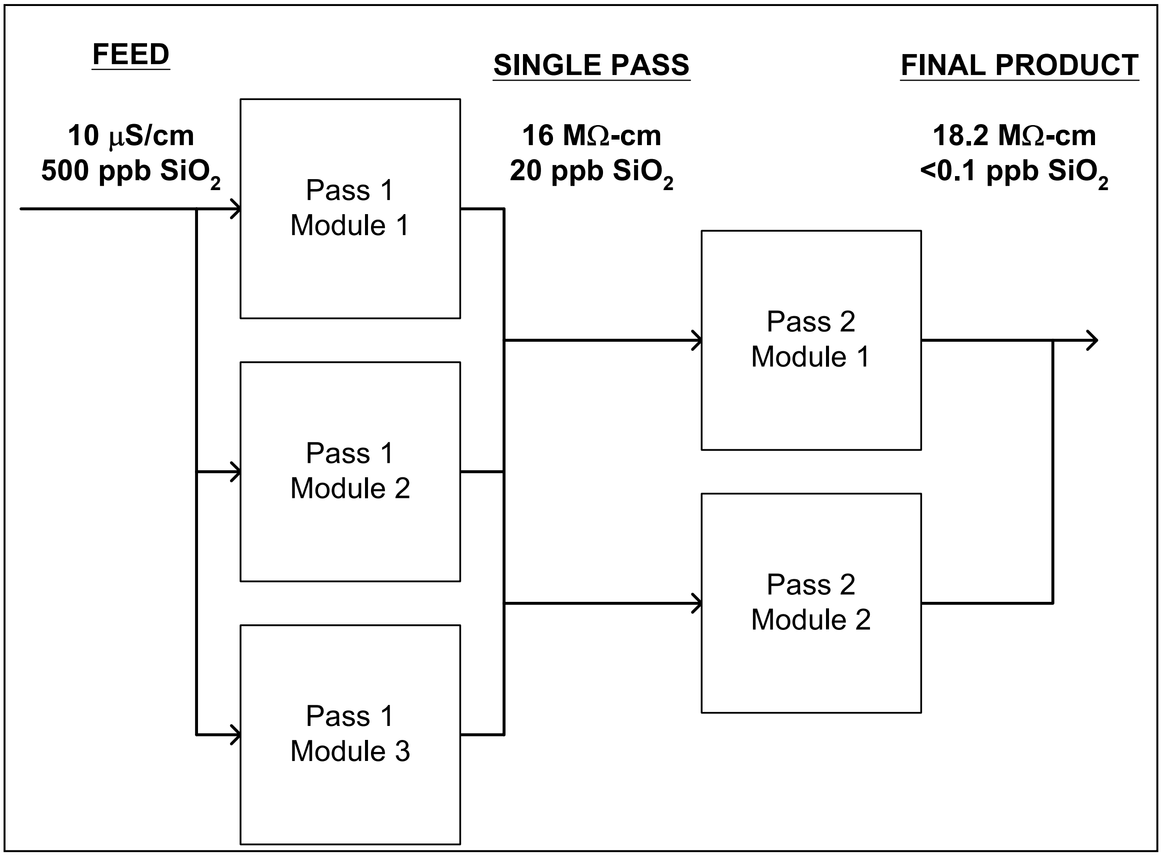

Figure 5. Two Pass CEDI Using Series Modules or Systems

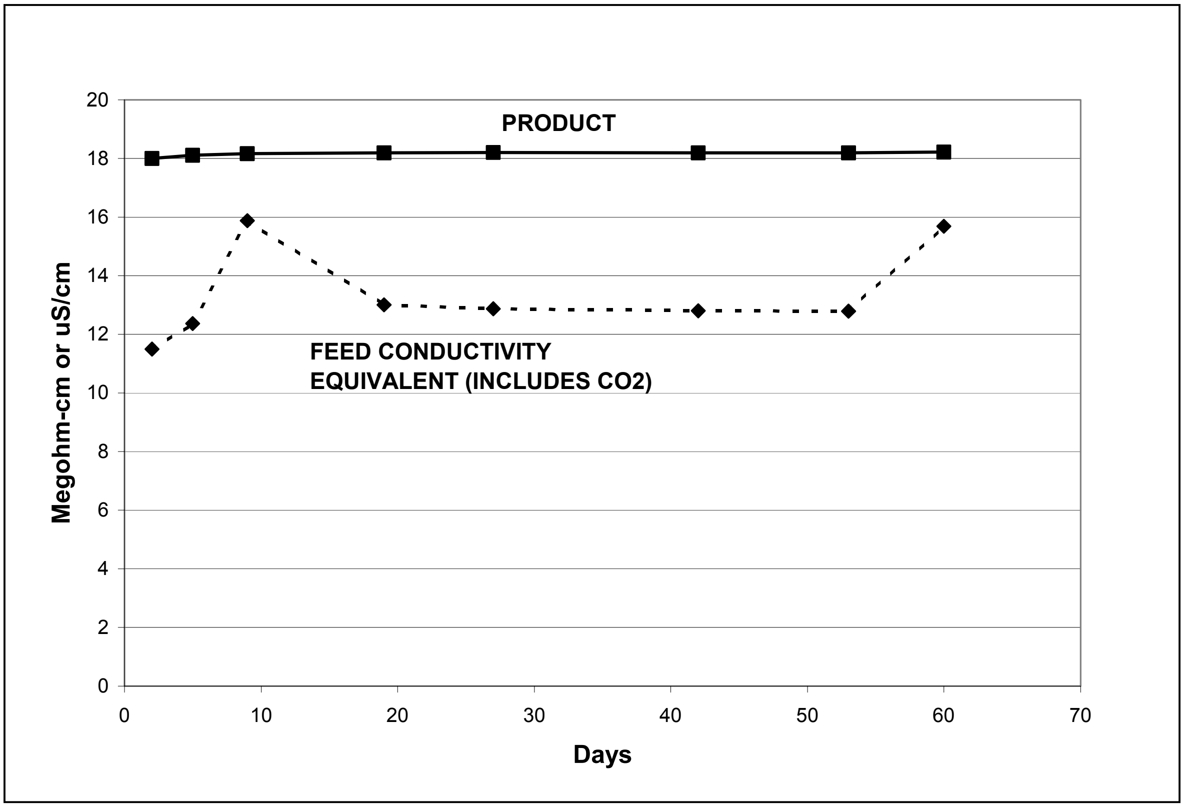

Figure 6. Pilot System with Single Pass RO Feed – Feed and Product Quality

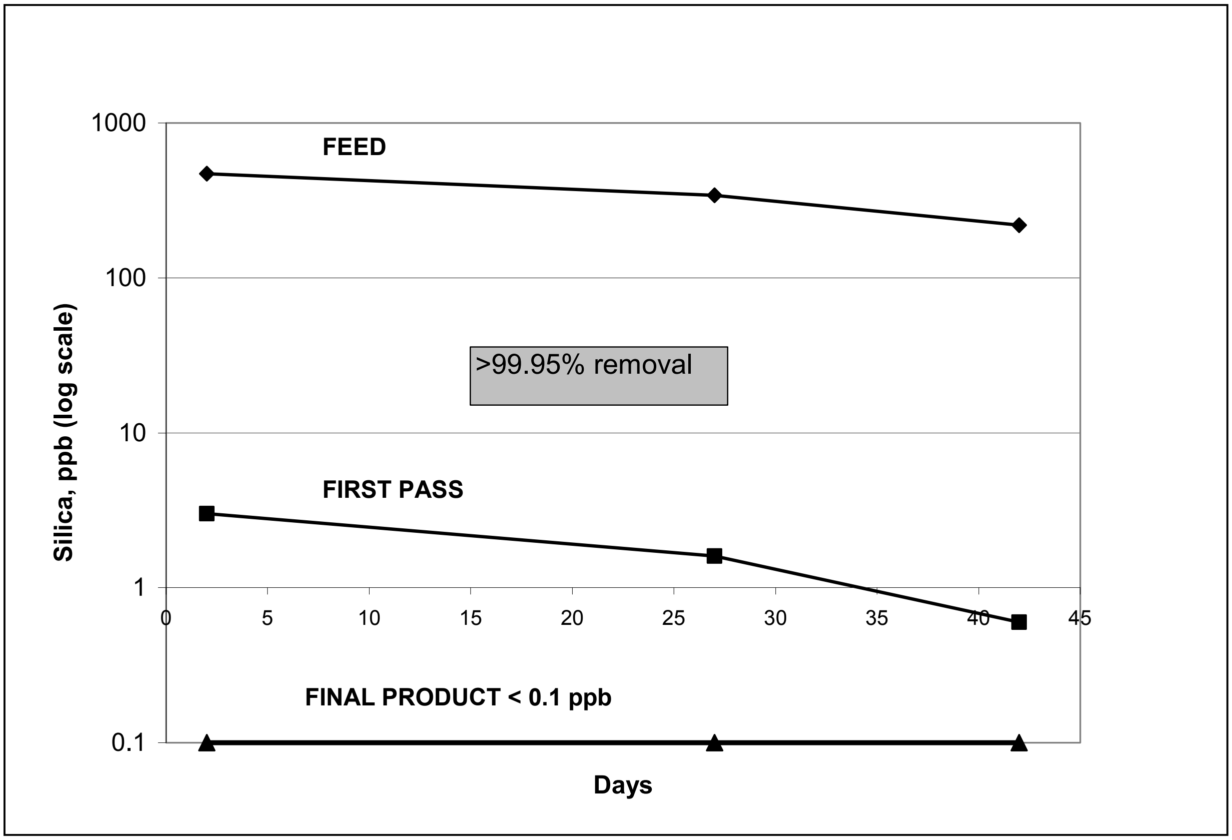

Figure 7. Pilot System Silica Removal

Figure 8. VNX module

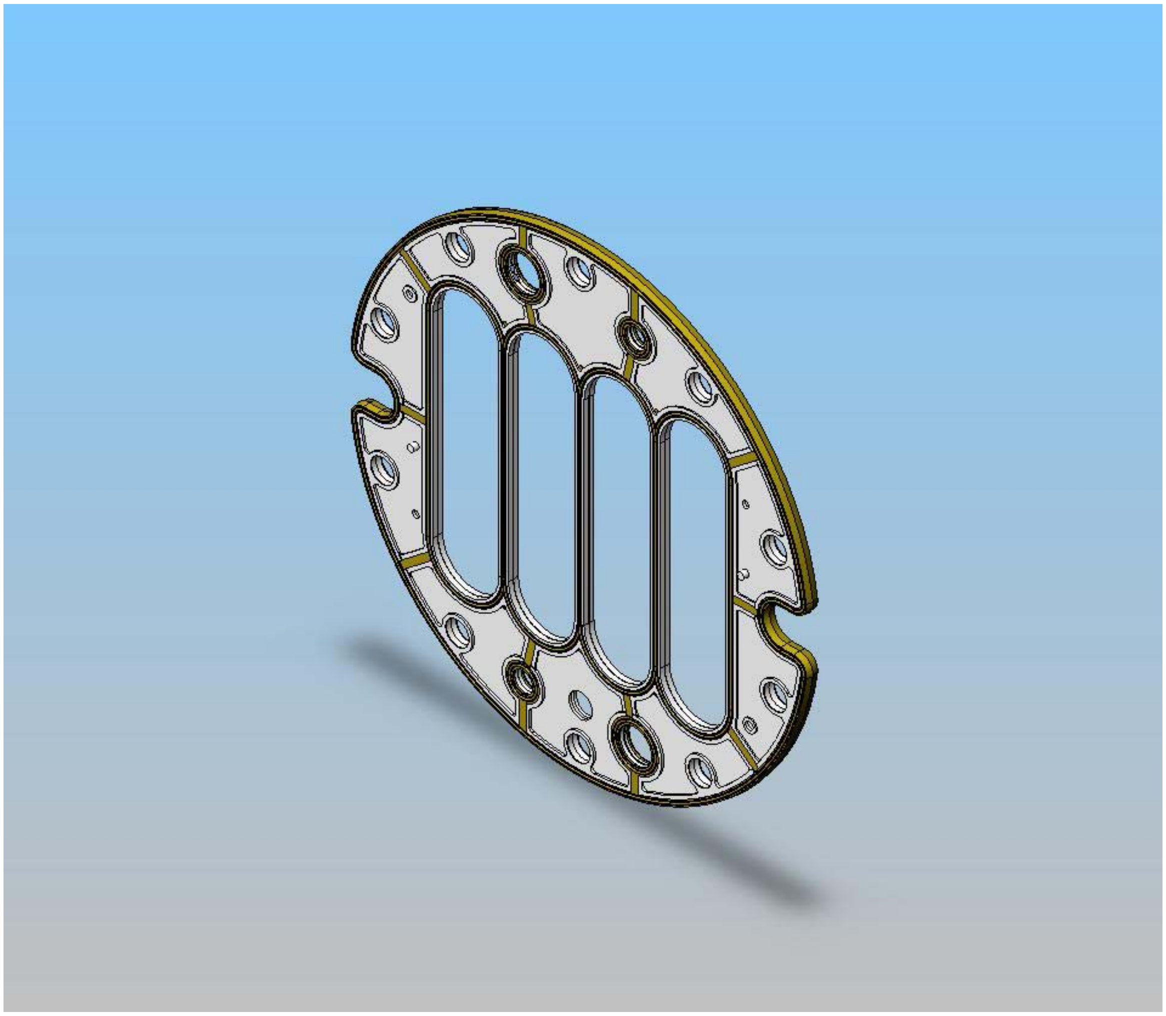

Figure 9. Dilute spacer in VNX module

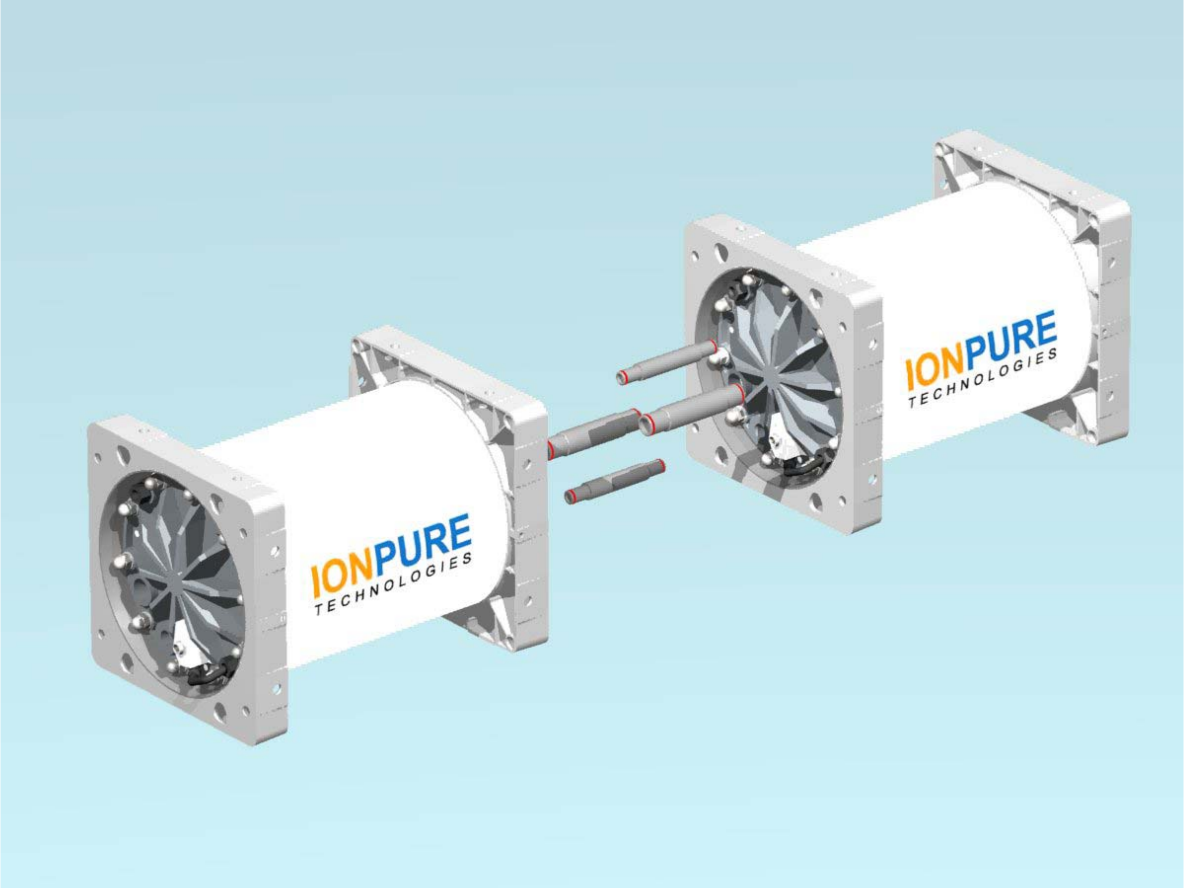

Figure 10. Multiple module connected in-line using interconnect tubes

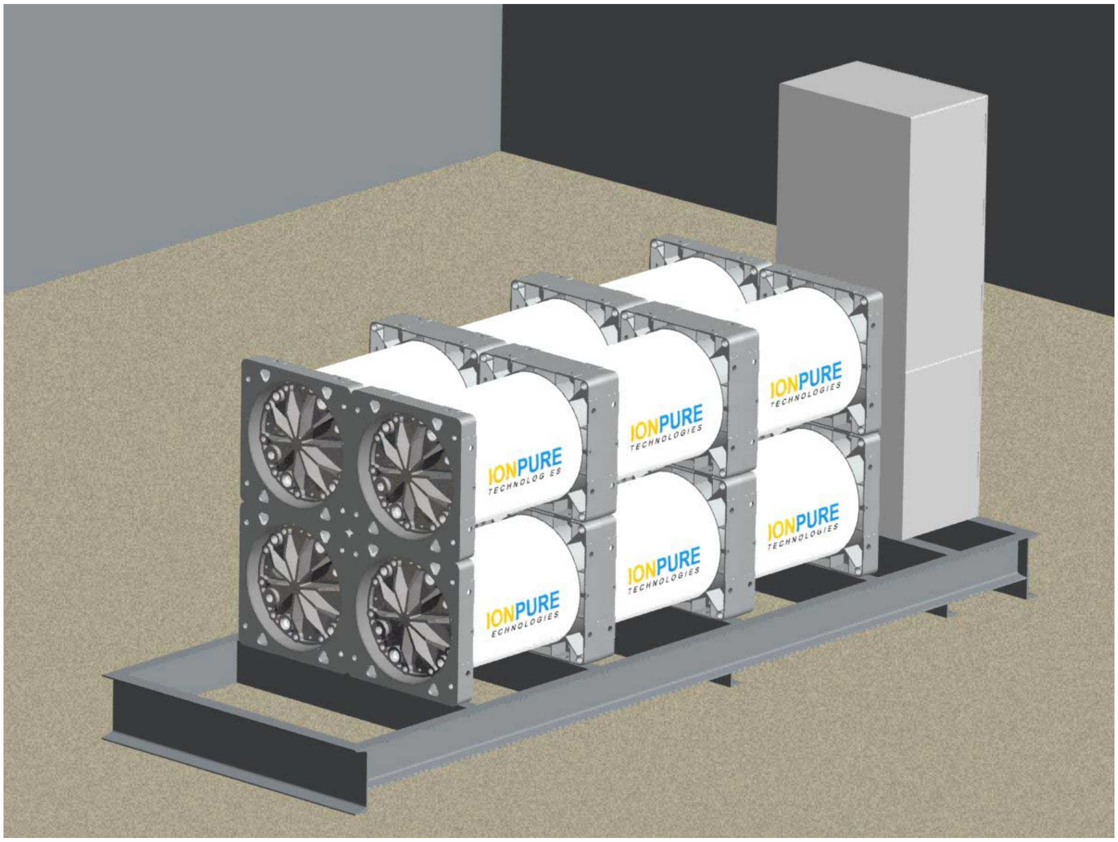

Figure 11. 200-gpm VNX system

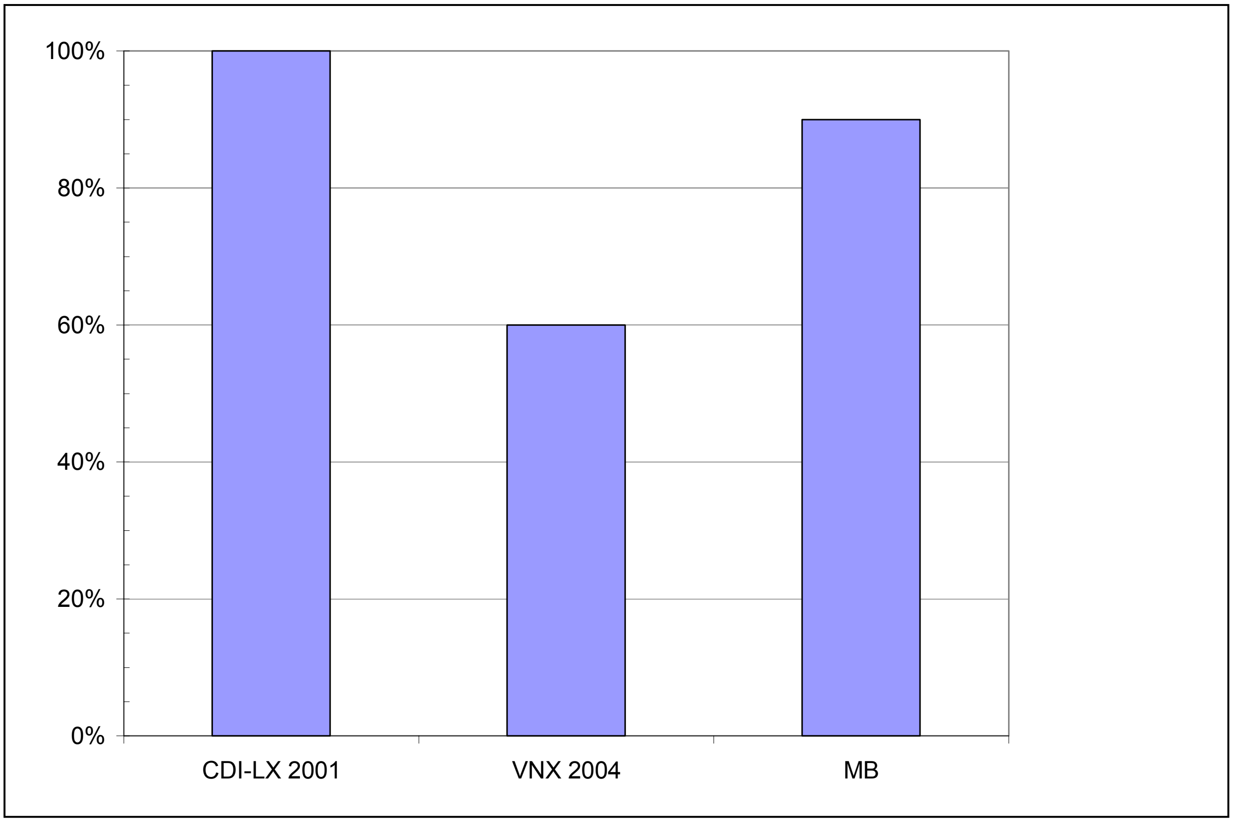

Figure 12. Reduction in capital cost of CEDI systems