

# AN INNOVATIVE APPROACH TO CONTINUOUS ELECTRODEIONIZATION MODULE AND SYSTEM DESIGN FOR POWER APPLICATIONS

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Summary: This report takes a brief look at the evolution of continuous electrodeionization comparing thin and thick cell technologies. A new, innovative approach is presented which demonstrates removal efficiency comparable to chemically regenerated mixed bed ion exchange.

## 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 some of the progress made over the last 13 years and introduce a new approach that combines years of experience with technical innovation to further this goal.

## 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. A representation of the process is shown in Figure 1. Here the anion exchange membranes are denoted as A and the cation exchange membranes are denoted as C. This diagram also shows a concentrate recirculation

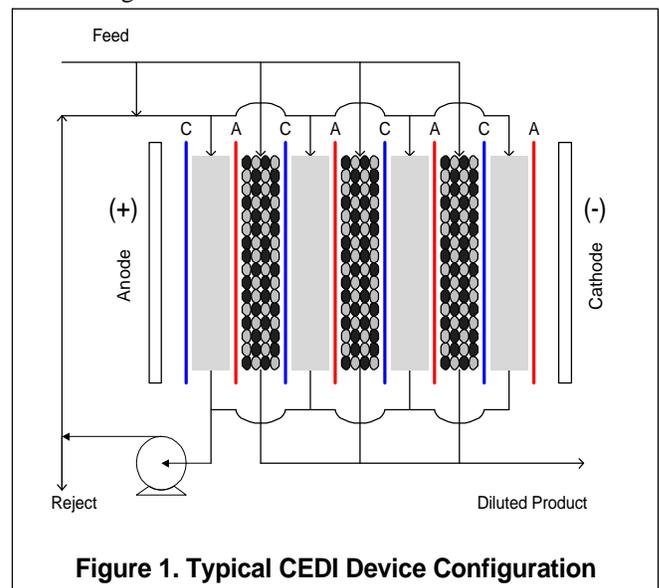


Figure 1. Typical CEDI Device Configuration pump, typical of commercial CEDI devices.

There are various types of CEDI devices. Due to the nature of the process however, i.e. alternating diluting and concentrating cells between ion exchange membranes with a transverse DC field, manufacturers to date have taken only two design approaches. These are plate and

frame and spiral wound. The plate and frame design was the first to emerge and is similar to a plate and frame filter press or heat exchanger in construction. Alternating diluting and concentrating cells are stacked between the electrodes and sandwiched together with some type of closing mechanism. Increasing the number of cell pairs (one dilute and one concentrate cell) increases the capacity of the unit. The main advantage of this type of construction is the ease of assembly.

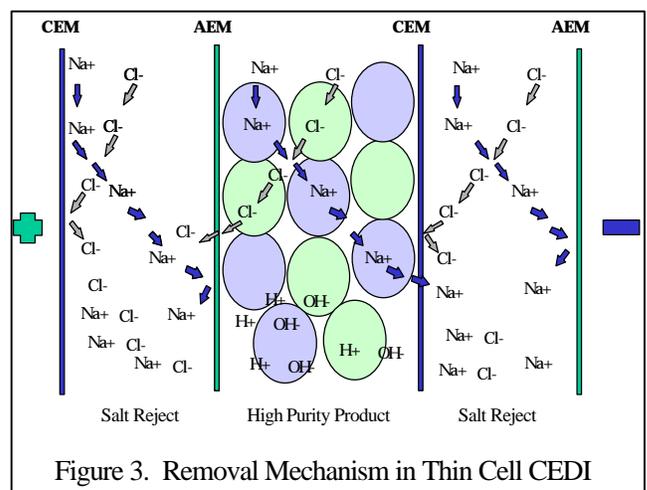
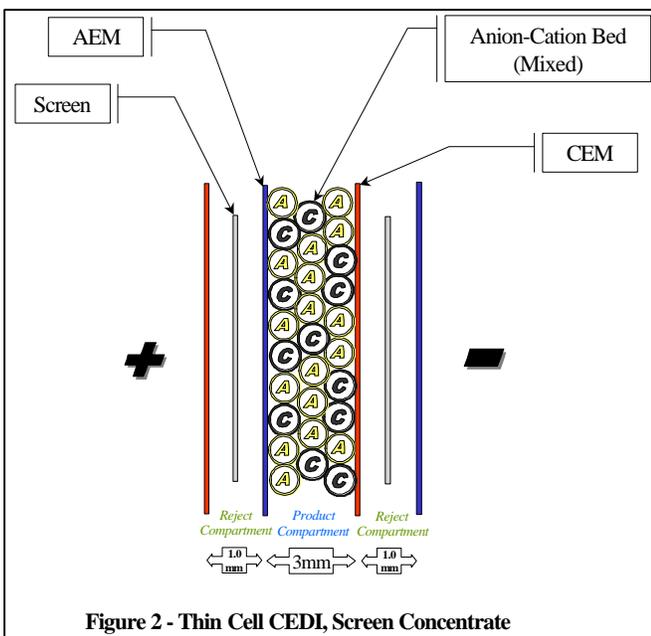
Given that the majority of commercial applications incorporate plate and frame devices, we will limit our discussion to them. Plate and frame devices can be broken down into two major subsets. These are thin cell and thick cell, designated as such based on the thickness of the diluting compartments. For the purposes of this paper, thin cell will encompass devices with a diluting cell thickness of 2-3 mm and thick cell will encompass 8-10 mm.

**THIN CELL CEDI**

First commercialized in 1987 by the Process Water Division of Millipore [1], which is now part of US Filter/Vivendi, thin cell mixed bed CEDI, or CEDI-MB, has proven to be an extremely effective, reliable process. These devices use mixed bed ion exchange resin in a relatively thin diluting compartment (~3 mm) and an inert screen in a thinner (~1.0 mm) concentrating compartment. Figure 2 shows one diluting and two concentrating cells of this configuration. Here, the anion exchange membranes are labeled AEM and the cation membranes are labeled CEM. In practice, a module would consist of multiple diluting and concentrating cells between one set of electrodes as shown in Figure 1.

This technology has been incorrectly referred to in the literature [2] as “low-flux” CEDI due to a typical product flow rate of about 150 gallons per minute per square foot of active membrane area per day (gfd). To put this into perspective, the typical flux for a reverse osmosis system is about 20-30 gfd. In RO, however, the water actually flows through the membrane, and membrane flux is an appropriate term. In CEDI, the product water flows through the resin bed. Only salts, in the form of ions, transfer through the membrane. Perhaps residence time is a more defining term for CEDI devices. In that respect, current thin cell and thick cell technology are in the same range.

In thin cell, mixed bed CEDI, two distinct zones are created inside the diluting compartments. Strongly ionized substances are removed first and then weakly ionized substances are removed as the water continues down through the flow path. We refer to these zones as enhanced transport and electroregeneration respectively. In the production of ultrapure water, the feed to a CEDI device is pretreated with reverse osmosis. This water contains low amounts of dissolved, ionized solids (in the range of 10 ppm as CaCO<sub>3</sub> or less) and some weakly ionized substances such as carbon dioxide, silica, boron, and slightly polar organics. Because of the low load, the device is able to remove most of the strongly ionized substances in the top portion of the bed or the enhanced transport zone. Here, the ion exchange resin simply acts as a conductor to speed the passage of ions from the dilute compartment through the respective membrane, and into the concentrating compartment. This is because the ion exchange resin is several orders of magnitude more conductive than the water. This is shown in the top portion of the resin bed in Figure 3.



After the strongly ionized substances have been removed at the top of the cell in the enhanced transfer

regime, conductance of the diluting cell is maintained by the ion exchange resins. At locations where the minimum thermodynamic overvoltage for water splitting is applied, the concentrations of hydrogen ( $H^+$ ) and hydroxyl ( $OH^-$ ) ions are increased [3]. This is shown in the lower portion of the bed and is referred to as the electroregeneration regime. The decomposition reaction is catalyzed by conditions at the resin/resin or membrane/resin interfaces of dissimilar polarities, i.e. the cation and anion resin bead interface. Here, liberated  $H^+$  and  $OH^-$  ions convert the resins into the regenerated state where weakly ionized substances can react, become ionized and be moved into the concentrating stream.

The removal of some weakly ionized materials, such as silica, is controlled by particle diffusion. Therefore, the resin and membrane materials are critical. The use of low crosslinked, high water content ion exchange resins and membranes can dramatically improve silica removal by increasing the intra-particle diffusion rate. This has been in practice for thin cell CEDI devices for several years [4].

Water splitting is critical for the removal of weakly ionized species like silica, carbon dioxide, and boron. For a given feed water concentration, this translates to higher the current. From Faraday's law, current is a direct indication of ionic transport through the membrane. Therefore, the amount of current above that needed for ionic transport is indicative of the amount of water splitting (neglecting other inefficiencies).

Increasing the current requires increasing the voltage and/or lowering the module electrical resistance. Increasing the voltage imparts several drawbacks including increased safety risks and decreased reliability. It was shown that using strongly acidic and strongly basic ion exchange membranes can catalyze the water splitting reaction [5], therefore reducing the module resistance and improving weak ion removal.

Another way to reduce the overall module electrical resistance is to reduce the resistance of the concentrating stream. With ion exchange resin in the diluting cell, the concentrating stream is really the limiting resistance in a module. Reducing the resistance of the concentrating stream can be done by increasing the water conductivity.

The first process modification to increase the conductivity of the concentrate was reject recirculation, turning the concentrating stream into a feed and bleed configuration. In this way the overall recovery is increased, the concentrate stream conductivity increases, and the module electrical resistance is reduced. In addition, by increasing the velocity of the stream,

boundary layer film thickness is reduced on the concentrate side of the ion exchange membranes, especially important when treating high salinity feed waters. This process of concentrate stream recycling is now commonplace in large-scale commercial CEDI equipment.

There are also several disadvantages to using concentrate recirculation. Concentrate recirculation requires the use of a pump and additional ancillary equipment for control such as motor starters and throttling valves. This adds complexity to the system design and increases overall cost. In systems with fluctuating operating conditions, operation or adjustment of the pump can make the process more labor intensive. The power required to operate the pump can be a significant portion of the total power consumption of the system. In a typical scenario, an industrial thin-cell CEDI system would consume about 1 kilowatt-hour per thousand gallons of product water (KWh/kgal), where two-thirds of that is for the recirculation pump.

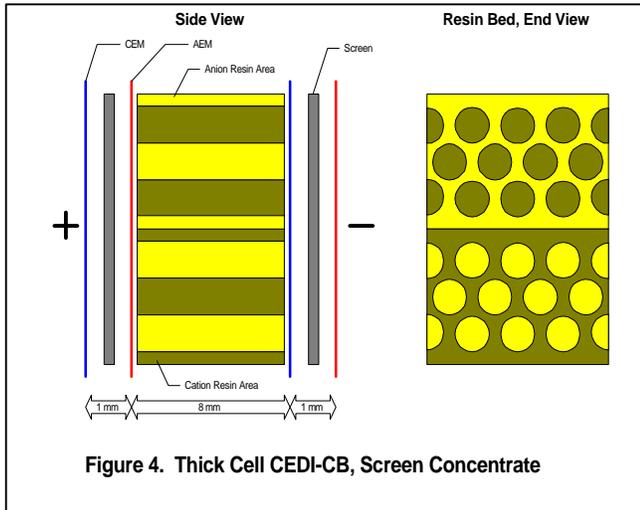
Another innovative development in thin cell CEDI technology was the addition of ion exchange resin to the concentrate compartment [6]. This change nearly halved module resistance and allowed a doubling of throughput at the same level of deionization. Addition of resin not only improved the overall electrical resistance but also reduced boundary layer film thickness by providing a path for transport away from the concentrate side of the membrane. Many commercial systems today incorporate a combination of concentrate recirculation and concentrate resin filling.

### **THICK-CELL CEDI**

Thick cell CEDI devices arrived commercially in 1996 when the first pilot units were installed [7]. These are of the clustered-bed configuration, or CEDI-CB, shown in Figure 4 and described in more detail later in this report. These devices incorporate separate patches of cation and anion resin types within a diluting cell to maintain a continuous path of like resin between membranes. Other variations have since become available which use completely separate beds of cation and anion resins, or CEDI-SB [8].

Thick diluting channels can be a detriment to performance using mixed bed resin filler due to a lower chance of obtaining a continuous path between membranes. Water splitting can still occur at dissimilar resin/resin and resin/membrane interfaces but much of the split  $H^+$  and  $OH^-$  ions will recombine when they encounter the counter ions travelling in the opposite direction. In one study, the performance of one thick cell mixed bed device was found to be inferior to two thick

cell separate bed devices [9]. However, it appears the performance of these thick cell, separate bed devices is still inferior to the performance of thin cell mixed bed CEDI [10].



Commercially, thick cell CEDI has been limited to the use of separated resins in the diluting cells as opposed to mixed bed. The basis for ion removal is different in these devices. Because a single type of resin is present at any given point between membranes, the transfer of co-ions is not possible. Therefore, water must decompose to provide  $H^+$  or  $OH^-$  ions for transfer to take place while maintaining electrical neutrality. Therefore, current passage and water splitting are critical for both weak *and* strong ion removal.

### CEDI-CB

To date, the most commercially prevalent thick cell technology has been the clustered-bed or CEDI-CB device. As thin cell technology has been mislabeled “low-flux”, CEDI-CB technology has been mislabeled “high-flux” CEDI due to typical operation at a product flow rate of 550 gfd. These devices produce more product water per unit active membrane area, but the residence time (empty bed contact time) is comparable to thin cell devices.

The construction of the CEDI-CB is shown from two different views in Figure 4. The figure to the left represents one dilute cell and two concentrate cells shown from the side. The figure on the right is a front view of the resin bed showing the resin clusters [11].

This design has several drawbacks. In order to fill the cell with the clusters, an inert binder must be used to hold the resin in place. This inert filler can block fluid flow and current passage increasing the pressure drop and

electrical resistance through the bed. In addition, the concentrate cells are filled with open screens that allow the concentration of the water in the cell to control the module electrical resistance. Because of this, the DC voltage on the stack commonly reaches 600 VDC to obtain the recommended 3.0-4.5 amps.

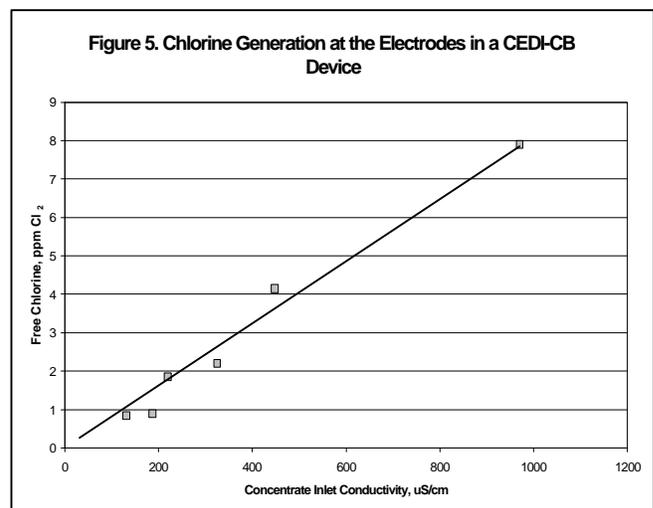
To lower the resistance, continuous injection of sodium chloride into the concentrate stream is a common practice in the application of this design. This in turn creates several problems. Increasing the salt concentration in the CEDI reject:

- Limits the ability to recover that stream,
- Increases the concentration gradient between the diluting and concentrating cells facilitating co-ion back diffusion if the membranes are not ideally permselective, and
- Increases the possibility of salt bridging and electrical shorting.

Because these CEDI devices feed the reject water to the electrode chambers, salt injection increases the chloride concentration at the electrode. As shown below in Eq. (1), chloride at the anode can be converted to chlorine, damaging ion exchange membranes and creating a safety risk for those near the device.

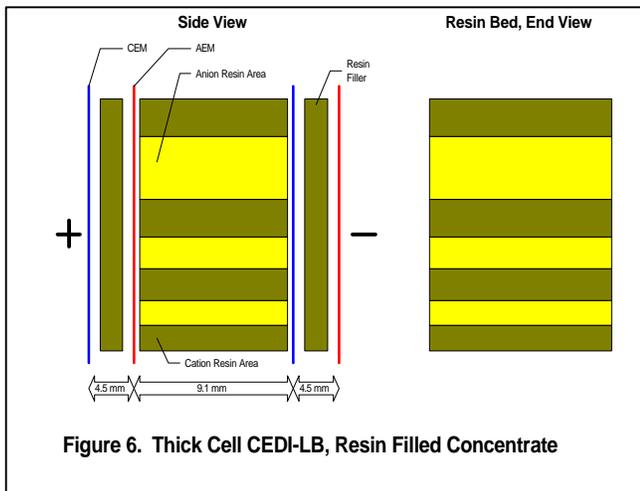


To investigate the extent of chlorine formation, a CEDI-CB device was operated at 3.0 amps of current and the concentration of sodium chloride was varied at the inlet of the concentrate cells. Free chlorine was measured in the electrode product water. As shown in Figure 5, a significant amount of free chlorine was detected. There was also a large off gassing of chlorine evidenced by the odor near the device.



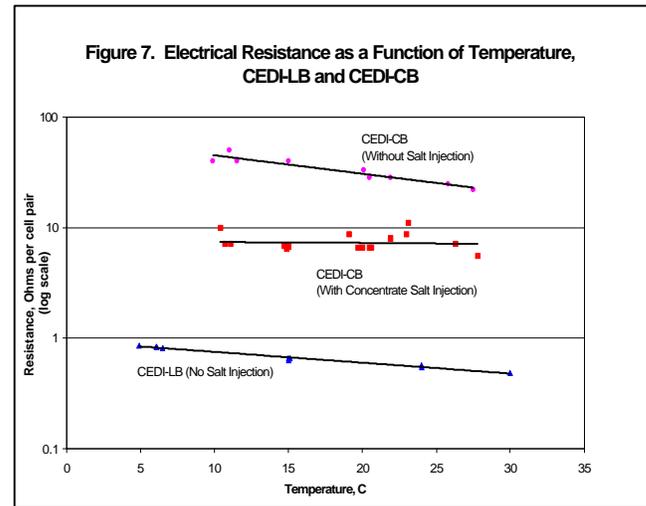
## CEDI-LB (AN INNOVATIVE THICK CELL DEVICE)

Thirteen years of experience and a refined market demand have spurred the creation of a new technology. The thick cell layered bed or CEDI-LB device incorporates all the benefits of the thick cell devices with the innovations realized during the development of thin cell mixed bed, CEDI-MB. A representation of the basic design is shown in Figure 6. The diluting cells incorporate layers of separate ion exchange resins while the concentrate cells also incorporate resin filler. Differentiated from the CEDI-CB, the layers here extend across the entire bed.



### LOW ELECTRICAL RESISTANCE

The basic principles guiding ion removal are similar to those of the other thick cell devices. However, the layering in the CEDI-LB does not necessitate binder material to hold the ion exchange resin in place as does the CEDI-CB. This, coupled with resin filling in the concentrate has reduced the voltage drop by an order of magnitude. Shown in Figure 7 is the voltage drop per cell pair for the CEDI-LB as a function of temperature. Also shown is data for a CEDI-CB device with and without salt injection into the concentrate to lower the module resistance. Given that the standard CEDI-LB unit has 24 cell pairs, this shows an operating voltage of 38 VDC to obtain 3 amps at 25°C. This is about 6% of the operating voltage (600 VDC) and hence the power consumption of the CEDI-CB with salt injection.



### HIGHER PRESSURE AND TEMPERATURE

There are benefits to the thick cell design. Thick spacers allow for certain designs not possible with thin spacers. The CEDI-LB device incorporates o-rings in the dilute spacers to create positive seals against the concentrate spacers. This is a tremendous improvement over previous sealing methods that has allowed the unit to operate above 100 psi at temperatures above 45°C without leaks. Most other devices described here rely on the gasketing effect of the concentrate spacers to seal the unit and prevent external and internal leaks.

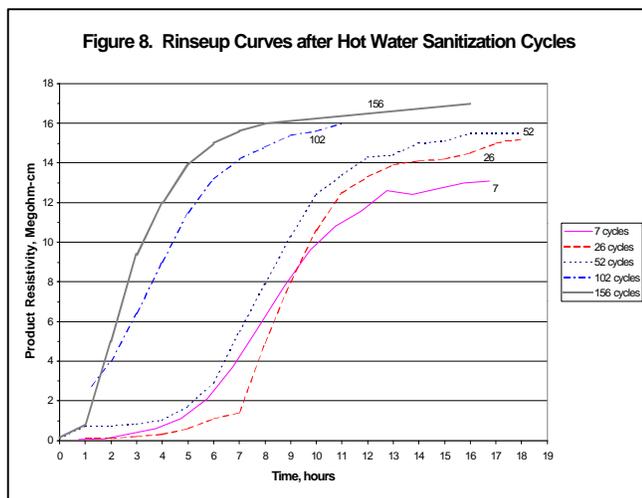
### HIGH RECOVERY, NO RECIRCULATION PUMP

Another innovation in the CEDI-LB is the use of thinner concentrate spacers. Along with the resin filling this alleviates the need for a concentrate recirculation pump, reducing the system design complexity, cost, and power consumption significantly. In addition, salt injection into the concentrate will never be necessary because the ion exchange resin and not the conductivity of the solution control the concentrate electrical resistance. In several applications the electrode streams were measured for free chlorine and found to be below detection (<0.01 ppm as Cl<sub>2</sub>). This has allowed, through reject and electrode recirculation, 100% CEDI water recovery in some applications.

### HOT WATER SANITIZATION

In addition to the o-ring seals, a special spacer material is used to impart significant thermal stability. This allows for continuous operation at extremes of below 5°C up to 45°C and periodic heat sanitizations to 80°C for bacteria control. Because the spacer materials are rated at

temperatures far in excess of 80°C, the only material that might not be suitable for high temperature sanitization is the ion exchange resin. A test was carried out to determine if sanitization would degrade the module performance. One system was sanitized with hot water at 80°C 156 times corresponding to one cycle every week for 3 years. Each cycle consisted of a ramp from 27°C to 80°C in one hour, a one hour hold at 80°C, and a 30 minute ramp back down. Figure 8 shows the rinseup curves generated after 7, 26, 52, 102, and 156 cycles by running the unit with RO water feed until the product quality was above 10 MΩ-cm. Although not necessarily indicative of steady-state performance, these curves are used as a relatively quick measurement of the functionality of the unit.



No detriment to performance was observed. In fact, there was a slight improvement in performance over the cycles, possibly due to the increasing water temperature through the duration of the testing.

### FLEXIBLE FILLING

The lack of dilute resin binder also allows for flexibility in filling. This leads to application-specific products that can target certain ionic species for removal. In the power and microelectronics markets this would mean high silica and/or boron removal.

One CEDI-LB device running at a product flow of 350 gfd was able to achieve the steady-state performance shown in Table 1. The feedwater was softened and treated by reverse osmosis. The conductivity was about 7 μS/cm with 2.5 ppm of carbon dioxide. Samples of the RO permeate, the CEDI-LB product, and the product water from a mixed bed deionizer were submitted at the same time for comparison. The MB deionizer sample was from a high-

purity polishing cartridge containing specially treated resins and inert plastics; pretreatment for the cartridge consisted of softening, reverse osmosis and chemically regenerated mixed bed ion exchange. Unfortunately, the CEDI-LB system (piping, valves, etc.) was not high purity but made up mostly of PVC material.

An outside lab completed the analysis for over 80 different elements and ions. Only those detected are presented in the table. It is very interesting to note the concentration of boron in the mixed bed product, 190 ppt, whereas it was below the detection limit (DL) (<50 ppt) in the CEDI-LB product water. The boron removal for the CEDI-LB was greater than 99.6% and the silicon (silica) removal was greater than 99.5%.

**Table 1. Water Analysis for the CEDI-LB**  
(All values given in ppb)

Component	RO	CEDI	Removal %	MB	DL
<b>Anions by IC</b>					
Chloride	750	*	>99.99	*	0.02
Nitrate	58	*	>99.96	*	0.02
Phosphate	27	*	>99.92	*	0.02
Sulfate	210	*	>99.97	*	0.05
<b>Cations by IC</b>					
Sodium	1100	0.24	>99.97	*	0.01
Ammonium	7	*	>99.28	*	0.05
Potassium	26	*	>99.92	*	0.02
Calcium	6	*	>99.66	*	0.02
<b>Trace Metals by ICP-MS</b>					
Aluminum	0.22	*	>98.63	*	0.003
Boron	13	*	>99.61	0.19	0.05
Lithium	0.05	*	>96.00	*	0.002
Manganese	0.03	*	>93.33	*	0.002
Potassium	23	*	>99.56	*	0.1
Rubidium	0.04	*	>97.50	*	0.001
Silicon	110	*	>99.54	*	0.5
Sodium	1300	0.26	>99.98	*	0.007
Zinc	0.09	*	>94.44	*	0.005

\* below detection limit

Another CEDI-LB device of a different configuration running at a product flow of about 700 gfd was able to achieve a product quality greater than 17 MΩ-cm and 98% silica removal from the feed water described above. This configuration would prove suitable for other applications where the removal of silica and boron may or may not be critical but where higher throughput and hence lower cost is the goal.

The simplicity of the system design for the CEDI-LB and the high pressure rating allow for the use of this technology in polishing loops. With a reduced feed

water load due to product water recirculation, one 50 gpm pilot system was able to polish feed water of 2  $\mu\text{S}/\text{cm}$  and about 2 ppm  $\text{CO}_2$  to 17.5  $\text{M}\Omega\text{-cm}$ . The unit was taking a feed silica concentration of 56.5 ppb down to 2.5 ppb, a removal of 95.6%. What's interesting about this case is that the system flow rate was extremely high at 977 gfd, almost double the current "high-flux" CEDI-CB.

So far, the bulk of the pilot systems have been small scale, 5-10 gpm total product flow. These systems have operated reliably, consistently meeting demand in various applications for almost two years. Larger-scale, 50-100 gpm systems are currently starting up. Future reports will detail these as case studies.

### CONCLUSIONS

Continuous Electrodeionization technology has come a long way since it's commercial inception in 1987. Drawing on experience from the past 13 years and technological innovation, CEDI is drawing nearer to the performance of mixed bed ion exchange.

The next step in the progress of this evolving technology is the layered bed design, CEDI-LB. It has the benefits of thick diluting cells without the drawbacks of binder material and it has resin filled concentrate cells. This product offers many benefits to the power, microelectronics, and pharmaceutical industries:

1. The modules can tolerate high operating pressure and temperature. The o-rings seals create a positive, leak-free seal both externally and internally.
2. They can be hot water sanitized at up to 80°C.
3. The system does not require a recirculation pump or salt injection, simplifying system operation and leading to use in new applications such as polishing loops.
4. There is no chlorine generation at the electrodes leading to safer operation, a longer module life, and 100% CEDI system water recovery.
5. The electrical resistance is significantly lower than any other commercial device, lowering power consumption and increasing safety.
6. The resin bed is configurable to target specific applications. In fact, one configuration has demonstrated over 99.5% silica and 99.6% boron removal consistently producing over 18  $\text{M}\Omega\text{-cm}$ .

### ACKNOWLEDGEMENTS

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