

Continuous Electrodeionization

Production of High-Purity Water without Regeneration Chemicals

by Felice DiMascio, Jonathan Wood, and James M. Fenton

Electrochemical deionization (EDI), also called electrodeionization, is a process that removes ionizable species from liquids using ionically active media and an electrical potential to influence ionic transport. Electrodeionization processes can be batch or continuous. Continuous Electrodeionization (CEDI) is an electrodeionization process where the ion transport properties of the active media are the primary scale-up parameters. There are also batch electrodeionization processes, such as capacitive deionization,¹ where the ion capacity properties of the active media are the primary sizing parameters.

CEDI devices combine the use of ion exchange resins, ion exchange membranes and electrodes without the need for regeneration chemicals. The CEDI cell combines the benefits of ion exchange and electro dialysis while minimizing the problems associated with each of these separate technologies. The CEDI cell uses the ion exchange resin to provide high ionic conductivity to the normally high resistance found in the dilute compartments of an electro dialysis cell. The resin's high ionic capacity increases the residence time of the ionic contaminants inside the cell allowing more time for the transport of these ions into the appropriate compartments. The electrodes generate a potential gradient for ionic movement within the cell. At cation/anion (resin/resin and resin/membrane) interfaces water is dissociated into its constituent ions, H⁺ and OH⁻, which regenerate the resins on-line, so there is no down time or need for regenerative chemicals as in ion exchange.

Electrodeionization Background

The concept of electrodeionization has been extensively investigated since the mid-1950s for various purposes. Walters et al.² investigated a batch electrodeionization process for the concentration of radioactive aqueous wastes, based on electrolytic regeneration of ion exchange resins.

In the late 1950s and early 1960s, the theory, design, and operating conditions of the CEDI process were investigated by Glueckauf.³ He proposed a theoretical model based on a two-stage removal of ions: the diffusive transfer of ions from flowing solution to ion exchange resin beads and the transfer of ions along the chain of ion exchange beads. Sammons and Watts⁴ studied the deionization of sodium salt solutions using multi-cell electrodeionization modules, quantifying the relationships between solution concentration, flow rate, and applied current. They experimentally demonstrated CEDI, but they did not define in great detail the effects of parameters such as liquid flow velocity, cell width, resin particle size, and type of resin filling.

A Dutch company applied for the first patent for an electrodeionization device in 1953. They described an apparatus for the deionization of salt-containing liquids using alternating layers of anion and cation resins. The patent was granted in 1957.⁵ A patent was also granted to Kollman in 1957,⁶ describing a CEDI apparatus for the purification of acetone. In this time period and in the 1960s, numerous patents were granted for various types of electrodeionization devices.⁷⁻¹⁰

Matejka¹¹ and Shaposhnik¹² extended the investigation into the operating conditions and performance

of the CEDI process in the 1970s and 1980s. Matejka investigated CEDI for the deionization of brackish or tap water to produce high-purity water. Several researchers in Israel were also very actively studying electrodeionization.¹³⁻¹⁵ During this time, new devices were being proposed and patents being granted to a number of others.¹⁶⁻¹⁹

The first commercially available continuous electrodeionization modules and systems were introduced in 1987 under the trade name Ionpure, now sold by U.S. Filter Corporation ("U.S. Filter"). A more comprehensive review of the technical literature on electrodeionization is given by Ganzi et al.²⁰ A recent review of CEDI technology was provided by Henley.²¹ It is believed that there are more than 1300 industrial size CEDI installations worldwide, about 95% of which have been supplied by U.S. Filter. Applications have included pharmaceutical, electronics, power generation, food and beverage, and laboratory.

Continuous Electrodeionization Process

The continuous electrodeionization process employs anion and cation permeable ion exchange membranes, with ion exchange resins packed between them. Figure 1 is a typical schematic diagram of the process showing the separate diluting and concentrating compartments and the direction of ion flow. Applying a DC electric potential causes ions to move from one compartment to another, affecting a separation. Since the concentration of ions is reduced in one compartment and increased in the other, the process can be used for either purification or concentration.

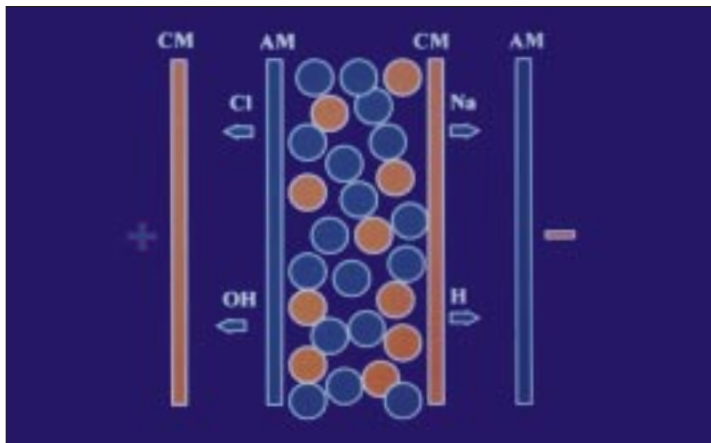


Fig. 1. Schematic of CEDI process.

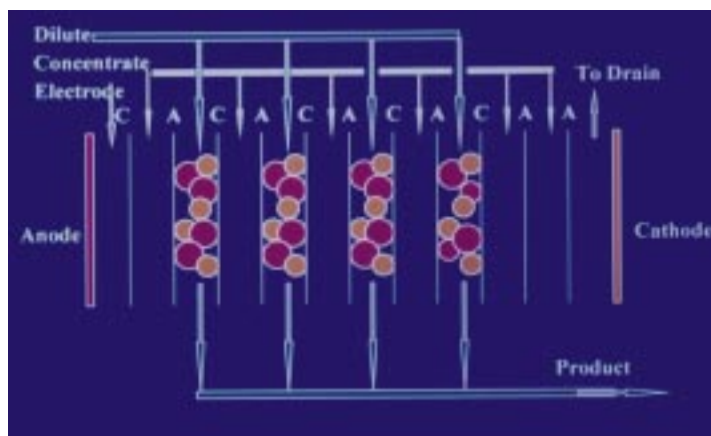


Fig. 2. CEDI process flow schematic.

Under the influence of the electric field, cations will migrate in the direction of the negatively charged cathode, through the cation-exchange resin, cation-permeable membrane and into the concentrating stream. An anion permeable membrane on the opposite side of that stream prevents further migration, effectively trapping the cations in the concentrating stream. The process for anion removal is analogous, but in the opposite direction, toward the positively charged anode.

In continuous electrodeionization for the preparation of deionized water, the process operates in two regimes.²² In the first regime, at higher salinity or at the inlet portion of the resin bed, the resins in the diluting streams remain in the salt forms, and efficiencies are derived from the resin-enhanced electrical conductivity of the ion-depleting compartments.

In the second regime, at low salinity or at the outlet portion of the resin bed, the DC electric potential causes water to dissociate into its constituent ions, H⁺ and OH⁻, electrochemically converting the resins to the hydrogen and hydroxide forms. This phenomenon, known as electroregen-

eration, accounts for the ability of CEDI systems to produce multi-megohm water, much like a continuously regenerated mixed bed ion-exchange column.

Most commercially available CEDI modules are plate and frame devices with multiple arrangements of alternating diluting and concentrating compartments, hydraulically in parallel and electrically in series, as shown schematically in Fig. 2. There are presently two sizes of CEDI modules available from U.S. Filter. So-called "industrial" modules can have 30–240 diluting compartments and are capable of flow rates of 2.0–64.0 gpm (0.45–14.5 m³/h). The smaller version, "compact" CEDI modules, typically have 10–40 diluting compartments and are capable of flow rates of 0.5–4.0 gpm (0.1–0.9 m³/h).

CEDI Performance Improvements

Although about thirty years passed between the invention of electrodeionization and the commercialization of the continuous electrodeionization process, the rate of advancement of the U.S. Filter CEDI process has been com-

paratively rapid, as shown in Table I.²³

CEDI[®] Modules and Systems refer to commercial continuous electrodeionization devices developed and sold by U.S. Filter. U. S. Filter is the dominant manufacturer of industrial size CEDI. Millipore Corporation manufactures low-flow CEDI devices, under the trade name Elix, for laboratory water purification applications. Recently other companies (Christ Ltd., Electropure Inc., Elga Ltd., Glegg Water Conditioning, and Ionics Inc.) have begun to offer CEDI units, but presently together represent less than an estimated 3% of the total number of installed CEDI systems.

Advantages of CEDI

When compared with conventional resin-based, chemically regenerated deionization equipment, CEDI systems offer a variety of benefits. Most obvious is the elimination of the regeneration process and its associated hazardous regeneration chemicals, acid and caustic. Since CEDI operates through a combination of ion transfer across the resins and membranes, as well as electrochemical regeneration of the outlet portion of the bed, the resins and membranes are never fully exhausted.

In addition, the CEDI system product water quality stays constant over time, whereas in regenerable deionization, product water quality degrades as the resins approach exhaustion. For those processes requiring deionized (DI) water on a continuous basis, conventional systems must be duplexed, so that one system can provide water while the other is regenerated. Duplexing adds cost, complexity, and size to conventional DI systems. Since CEDI is continuous, and not a batch process, duplexing is not necessary. As a result, CEDI system footprints are often one half of the size of their conventional counterparts.

There are significant tangible cost benefits associated with the elimination of regeneration. The costs of regeneration labor and chemicals are replaced with a small amount of electrical consumption. A typical CEDI system will use approximately 1 kW-hr of electricity to deionize 1,000 gallons from a feed conductivity of 50 μ S/cm to 10 M Ω -cm resistivity. Since the waste stream contains only the feed water contaminants at 5–20 times higher concentration, it can be discharged without treatment. Thus, facilities costs can also be reduced

since waste neutralization equipment and ventilation for hazardous fumes are not necessary.

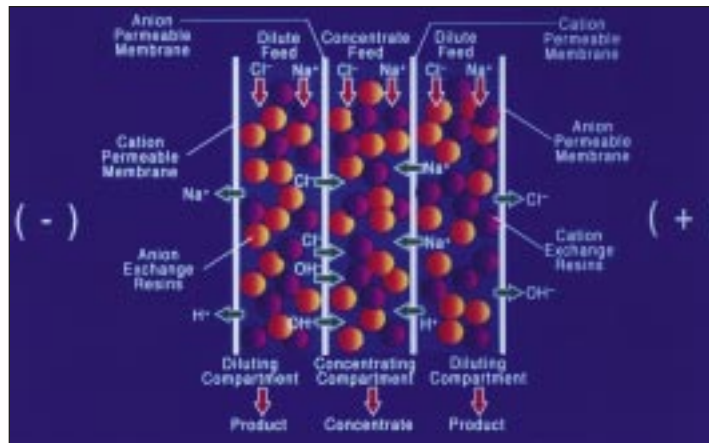
There are also less tangible cost reductions, which are harder to quantify, but clearly favor the use of CEDI systems. By eliminating hazardous chemicals wherever possible, workplace health and safety conditions can be improved. With today's increasing regulatory influence on the workplace, the storage, use, neutralization, and disposal of hazardous chemicals result in hidden costs associated with monitoring and paperwork to conform with EPA and OSHA requirements as well as the "Right To Know" laws. In addition, the fumes, particularly from acid, often cause corrosive structural damage to facilities and equipment.

Applications in Water Purification

The principal use of CEDI systems has been in the production of pure or ultrapure water for industrial process use since the first commercial device was introduced in early 1987. U.S. Filter has installed over 1300 CDI systems worldwide. These range in flowrate from 1 to 960 gpm. In addition, Millipore Corp. has sold over 2000 units for low flow rate laboratory applications, less than 100 lph.

Many different industries require deionized water, and each has its own specific requirements for the quantity and quality of water used. CDI systems are now operating in a variety of industries, from process feed water in pharmaceutical, biotechnology and food and beverage applications to high-quality rinsing water for electronics, surface finishing and optical glass applications. More recently, increases in flowrate capability and improved silica

FIG. 3. All filled configuration CDI process.



removal have made the CDI process a viable alternative for boiler makeup in power and cogeneration, as well as for semiconductor manufacturing. CDI systems have also been installed at institutions such as hospitals, universities and dialysis centers.

Most of the early CDI systems operated on pretreated tap water and gave water quality similar to that produced by separate-bed deionizers. The current trend is to combine CEDI with reverse osmosis (RO) to produce ultrapure, mixed-bed quality water. Presently, the largest user is the pharmaceutical industry. One of the reasons for this is that when operated properly, CEDI modules do not cause proliferation of bacteria, and have even in some cases shown to be bacteriostatic.²⁴ The number of installations is more evenly spread out among the other market segments.

Water of the highest possible purity is also used in the electronics industry for critical rinsing steps in the fabrication of semiconductor wafers. Of particular importance to the electronics industry is the demonstrated ability of the CEDI system to provide a contin-

uous reduction in total organic carbon (TOC).²⁵ The pretreatment scheme is similar to that used in the pharmaceutical industry, as are the placement of the RO and CEDI systems. The storage, distribution, and polishing differ considerably from pharmaceutical systems however, with storage tanks commonly blanketed with nitrogen gas and sparged continuously with ozone for microbial control. The polishing step includes 185 nm UV light for organic oxidation, followed by polishing mixed-bed deionization, 254 nm UV light, 0.5 micron cartridge filtration, and finally 0.1 micron cartridge filtration. This ultrapure water is distributed to the points of use, with a recirculation loop returning unused water to the storage tank. RO/CDI based systems have been installed for semiconductor wafer and other rinsing applications at both manufacturing and research facilities for many Fortune 500 companies. The systems typically meet ASTM specifications for "Electronics Grade Water."

CDI systems have also been used for general industrial applications requiring

TABLE I. CEDI® System Technological Milestones

1987First commercial product5 gpm and 10 gpm modules
1989Uniform particle-size ionCO ₂ removal without chemical feed exchange resins
1991Improved ion exchange membranesDissolved SiO ₂ removal Improved salt removal
1992240-compartment moduleUp to 64 gpm product flow
1993"Compact" moduleResin-filled concentrate compartments Improved performance
1994Improved ion exchange membranes: polyethyleneBetter chemical & electrical resistance Heat-weldable
1998All-filled "industrial" module (FIG. 3)Resin-filled concentrate compartments Twice the flow per cell Capable of polarity reversal



FIG. 4.
80 gpm CDI
system.

low to medium quality deionized water. In these cases, the use of RO is not necessary, as CEDI can remove from 95-99% of the dissolved ions from pretreated tap water. The pretreatment is quite similar to that of a RO system, except that an organic scavenger is sometimes required to prevent fouling of the CEDI by humic and fulvic acids found in many surface water sources. Systems have been installed for such applications as electrocoat painting, chemical manufacturing, electroplating, bottle washing, humidification, and optics manufacturing.

The Future of CEDI Technology

The CEDI process has become a viable alternative to conventional,

regenerable resin-based deionization systems. Since the initial commercialization in 1987, CDI systems have found worldwide application in industries with the most demanding high purity water requirements such as in the manufacture of pharmaceuticals, semiconductors, and high quality optics, in surface finishing of electronic components and durable goods, and in the generation of electric power. Typical of any high technology product of this age, CEDI is constantly evolving, with improvements in deionization performance and increases in single module flow rate capability arising with each new generation, such as the 80 gpm "all-filled" industrial CDI module shown in FIG. 4. Future improvements will likely achieve more

efficient deionization and even higher flow rates.

To date, the CEDI process has been mainly applied to water purification. While some systems have been installed for wastewater treatment,²⁶ there may also be nonaqueous applications for CEDI in such areas as food and beverage manufacturing and chemical processing. Some of these applications are presently under investigation, and CEDI equipment is already in use for fruit juice deionization.²⁷ Millipore Corporation has continued to apply electrodeionization to specialty separations in the pharmaceutical industry.²⁸⁻²⁹ ■

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