Editor’s Note: When new technologies arrive on the scene, various companies and researchers publish their own particular view of their use and value. After a few years, some, like capacitive deionization, achieve a toehold in the industry and are deserving of the more considered look these authors have given them.

CAPACITIVE DEIONIZATION (CDI), often called capacitive desalination, electrochemical desalination or flow-through capacitor, is a fairly new desalination method. Over the past couple of decades, CDI has been promoted as a cheap, low-energy, high-yield competitor to reverse osmosis (RO) and electrodialysis (ED), with applications ranging from water softening to seawater desalination.

CDI electrochemically removes ions from salty water. A saltwater process stream flows between two electrodes held at a potential difference of around 1.2-1.5 V. Ions in the solution are attracted to the oppositely charged electrodes.

The ions are electrosorbed onto the electrodes, removing them from the process stream, and the deionization cycle continues until the electrodes are saturated with ions. Then, during the regeneration cycle, the two electrodes are discharged or the polarity of the electrodes is reversed. This releases the ions into a waste stream, which has a much higher salt concentration than the process stream.

The major market advantage that CDI currently has over competing technologies is its ability to remove a wide range of ionic contaminants with high recovery rates. CDI can remove nearly all ionic contaminants – sulphates, nitrates, iron, arsenic and fluorides, along with sodium, calcium and magnesium salts.

RO, which forces salty water through a nanoporous membrane, removes water from salt. By contrast, CDI removes salt from water.

CDI has a much higher water recovery (up to 90% or more) than RO, which normally has a recovery rate of 50% or less. While CDI’s high recovery rate is advantageous, it can also cause brine disposal issues.

Brine injection back to source water can gradually increase total dissolved solids (TDS) in underground water, causing long-term environmental damage, which is a growing concern in developing countries such as India and Bangladesh. Meanwhile, CDI-based water softeners are being developed to compete with conventional resin technology, which, in contrast to CDI, requires the use and disposal of large amount of salty water, which can be environmentally unfriendly.

Unlike many, we believe that, at least in the short term, CDI will be used for low TDS applications (<5,000 ppm) and not for seawater desalination, due to high CDI unit costs, as discussed below, and the acceptability of low water-recovery in seawater desalination.

ENERGY USE
During CDI’s initial development, the potential for very high energy efficiency was seen as a major selling point. The more optimistic energy-use projections, however, require recovering energy during the regeneration cycle of operation; this requires a slow discharge to minimize losses due to polarization, and the electronics needed increase the cost and complexity of a CDI unit.

Because fewer charge/discharge cycles can take place in a given time with energy recovery than without, the unit cost increases when using energy recovery.

No currently commercially available CDI system uses energy recovery. In fact, most CDI systems reverse polarity during the regeneration cycle, speeding up kinetics and increasing throughput while consuming additional energy.

COST CHALLENGE
The major challenge for CDI is its cost – both capital and operational costs are concerns. An RO system capable of treating 1,000 L/h costs between US$ 3,000 and US$ 4,000, whereas a similar capacity CDI system costs about US$ 10,000.

It is possible for CDI units to be sold at a premium price over RO, primarily because of CDI’s low life-cycle cost and its ability to remove a wide range of ionic contaminants with substantially higher water-recovery than RO.

In the future, CDI may become more cost competitive. No components in CDI (apart from membranes) are expensive; today’s high costs are due to
low manufacturing volumes and immature manufacturing processes.

**SCALING ISSUE**

Electrode scaling is one of the biggest issues encountered in CDI. Virtually all source waters contain calcium and magnesium ions, which are innocuous in concentrations normally seen but can create precipitates at high concentration.

During operation, the negative electrode electroosorbs positive ions indiscriminately, including calcium and magnesium ions. When the unit is discharged, a buildup of magnesium and calcium compounds can form when high concentrations of magnesium and calcium are released.

To date, mild acids (such as citric acid) have been the preferred descaling method; however, process monitoring to determine when to descale the unit adds to complexity. According to Idropan’s CEO, Mariella Servida, CDI unit cleaning is a major technical challenge.

Idropan claims to have solved this problem using a patent-pending microinjection system that injects a citric acid-based solution on a daily basis. Other companies including AquaEWP and Enpar also have product literature and/or patent applications noting the use of citric acid to clean CDI units.

**CDI AND MEMBRANES**

Historically, CDI has been touted as a membrane-free technology, and hence free from the issues facing membrane-bound processes such as RO and ED. Nonetheless, overcoming inefficiency and kinetic issues has generally required the use of membranes in practice.

Marc Andelman of Biosource Inc first developed membrane CDI technology, and today most CDI units have ion-exchange (IX) membranes against their activated carbon electrodes to improve performance, while increasing cost. The IX membranes allow only positive ions to pass through to the negatively charged electrode, and only negative ions to pass through to the positively charged electrode.

This solves two major problems: slow kinetics, and inefficiency due to counterion desorption with increased cost and decreased reliability.

Counterion desorption refers to the expulsion of ions with the same sign as the electrode. When the electrodes are at the same potential, they have ions of both charges (positive and negative) adsorbed on their surface. Upon charging they expel same-charged ions (counterions) and attract oppositely charged ions.

For instance, the positive electrode expels positive ions and attracts negative ions. This causes a net transfer of positive ions to the negative electrode, and negative ions to the positive electrode, independent of the deionization, reducing efficiency.

With membranes in place, the need to maintain electroneutrality necessitates that ions from solution cross the membrane to balance out the counterions, so that counterion desorption no longer causes inefficiency.

Charge transfer membranes also dramatically improve device kinetics. When a CDI unit goes in the regeneration cycle without a membrane, it takes a relatively long time for the ions to diffuse out into the waste stream. With a membrane, the need to maintain electroneutrality at each electrode forces the ions to travel through the membrane quickly during the regeneration cycle, improving device throughput.

Despite the advantages of adding membranes, they are prone to fouling and degradation, and are expensive. While the continual charge transfer across the membrane is believed to help maintain the surface, prefiltration before the water reaches the CDI unit is necessary.

Historically, ED units, which use ion-exchange membranes like those used for CDI, have had device lifetimes limited by membrane longevity. However, electrodialysis reversal (EDR), where the polarity of an ED system is periodically reversed, has shown improved longevity. Since in CDI the polarity is reversed every cycle, this lends credibility to the idea that the membrane will be more robust than in ED.

CDI units appear to decrease in water recovery over time due to engineering/design and membrane issues. It is believed that the space between electrodes increases with time, decreasing the flow resistance of water between the electrodes. This may be from the membrane wearing away during the repetitive charge and discharge cycling, pointing to the need for further membrane development work and improved device engineering.

There are very few companies that manufacture membranes specifically for CDI, one notable company is Fujifilm’s Netherlands operation. Little published research has focused on characterizing and improving membranes for CDI. CDI’s reliability problems are design-related, and therefore can be solved as the technology matures.

**NOVEL MATERIALS**

While membrane development for CDI has seen little attention, much fundamental research has focused on novel carbon materials for use in CDI. Materials such as nanotubes, graphene and aerogel have been tested for use in CDI electrodes; the interest in novel carbon materials for CDI has been so high that Oak Ridge National Laboratories won an R&D 100 Award in 2011 for creating an ordered mesoporous carbon for CDI.

However, activated carbon, at only US$ 4/kg for commodity carbon and US$ 15/kg for highly purified, specially selected supercapacitor carbon, remains much cheaper than the alternatives, which cost US$ 50/kg or more. Larger activated carbon electrodes are much cheaper than relatively small exotic carbon electrodes, and can remove just as much salt for a given current.

The performance increase from novel carbons is insufficient to motivate their use at this point, especially since virtually all CDI applications under serious near-term
CDI used as a point-of-entry system for treating incoming water for residential homes. (Image courtesy: Idropan, Location: Chennai, India)

consideration are stationary applications, where unit size is a relatively minor consideration.

Unlike RO and ED, which took several decades and several billion dollars to reach their current state, total CDI investment to date is below US$ 100 million (excluding substantial internal research & development expenses incurred by General Electric (GE), but including government-sponsored grants and contracts). CDI was initially developed in the late 1960s but became widely known following work by Lawrence Livermore National Laboratory’s Farmer and colleagues.

The first company to attempt to commercialize CDI technology was Capacitive Deionization Technology Systems Inc, which was founded in 1996 based on work done at Lawrence Livermore National Laboratory. They voluntarily filed for bankruptcy in 2008. Other CDI developers have come and gone. GE invested substantially in CDI, leading to over 9 US patent applications between 2005 and 2009. However, they have remained dormant for the past 3 years or so, for unknown reasons.

Several other companies including Materials Method, Sanabelle Water, and WL Gore & Associates, which were once active in this field are no longer active in research or have made a decision to leave the market. This may be due to lack of an initial market identification, technical challenges or both.

Despite the failure of Capacitive Deionization Technology Systems Inc, and decisions by GE and others to abandon the market, several companies worldwide are now developing CDI-related products. The leading companies active in CDI are Voltea (Netherlands), AquaEWP (USA), Atlantis (USA), Idropan Inc (Italy), LT Green Energy (Australia) and Enpar (Canada).

Several relations exist or existed between CDI manufacturers. For example, AquaEWP was a subcontractor to Biosource on a US Defence Advance Research Projects Agency contract that resulted in the development of membrane-based CDI. Biosource was acquired by Voltea in 2008, and thus owns Biosource’s membrane-related intellectual properties.

AquaEWP also had licensing agreements with Idropan and LT Green Energy. While there are currently several companies active in the CDI area, the number of companies will likely increase in years to come. CDI is one of the technologies that originated in USA but will likely benefit developing countries primarily, since their water problems are more severe than in the developed world.

It is expected that there will be an increase in funding for CDI technology by governmental organizations in the United States and worldwide. Equity investments in CDI are also expected to increase.

The largest equity investment so far has gone to Voltea, which raised over US$ 10 million in two rounds of investments where firms such as Pentair, Rabo Ventures and Unilever Ventures participated. Enpar is a publicly traded company listed in the Canadian stock exchange, with yearly operational expenses of about Can$ 1-2 million (US$ 0.96-1.92 million) and 2012 revenue of about Can$ 192,000 or less.

As most other companies in CDI are privately held, their revenue numbers are unknown. The total annual sale of CDI units is likely below US$ 5 million.

Pentair is currently launching a CDI-based product (Hybrid-DI) for water softening. This product was developed jointly by Voltea and Pentair, and is expected to reach market in the near term. No pricing information is available yet.

The Hybrid DI is expected to come in four variations, which can treat up to a maximum of 6 GPM (2.8 L/s). The main advantage that this CDI unit will
provide over resin-based water softeners is the elimination of the need for salt for recharging.

CDI-based water softeners can be viable in many US states, such as California, which have strict brine-disposal regulations associated with operation of resin-based water softeners. CDI is also attractive for many other low TDS applications such as treating input water for cooling towers, point-of-entry related water treatment, and treating produced water from oil, gas and mining.

CDI, which once promised to offer low-cost seawater desalination in the 1990s, is yet to be fully commercialized, though the technology has matured over the past several years. The applications where CDI can be beneficial at an early stage of technological maturity are becoming well-defined, which is a positive sign for the low relative investment it has received.

Most CDI companies are becoming realistic about its potential and the challenges being seen. There is, however, a large gap in the understanding of the challenges and opportunities between the academic researchers and CDI manufacturers.

It is unclear what market will become the major initial market for CDI. Groundwater decontamination in the developing world is a large market with unmet needs and, if CDI succeeds, it may very well represent the major market for the technology. However, resin-based water-softener replacement or water treatment for cooling towers may also be attractive applications.

We envision large investments in CDI technology, and many startups will enter and succeed as the market becomes better defined and very specific niches become clearer. Despite the challenges, it is very possible that CDI will play a significant role in the water industry, while its short-term impact may be much less than what was once hoped.

ACKNOWLEDGMENTS
The authors would like to thank Bart van-Limpt (Voltea – Netherlands), Mariella Servida (Idropan – Italy), Narender Ahuja (HEW Water – India), and Stephen Jaffe (Material Methods, LLC – USA), for helpful discussions about CDI.

ABOUT THE AUTHORS
Lawrence Weinstein is an electrochemical and materials science professional. He earned his MS in Materials Science & Engineering from Rutgers University in 2008. From 2008 to 2011, he worked on supercapacitor carbons, carbon electrodes and CDI at Y-Carbon Inc. He contributed to several technical proposals on CDI, and developed electrode-making processes and prototype deionization units. Since 2011, he has been working on developing specialty batteries at FlexEl LLC. He can be reached at Lawrence.E.Weinstein@GMail.com.

Ranjan Dash is a techno-commercial professional with over 10 years of experience in the development and management of materials science related technologies. Most recently, he served as CEO of Y-Carbon Inc, a Drexel University spinoff involved in development and manufacturing of electrodes for CDI. Ranjan has a PhD in Materials Science and Engineering, and an MBA in Organization Management from Drexel University, and BE (BS equivalent) in Ceramics Engineering from National Institute of Technology, Rourkela (India). Ranjan is Principal at Dash and Associates, LLC. He can be reached at RanjanKumarDash@GMail.com.