DEIONIZATION

PART 1: A REVIEW OF SPIRAL-WOUND ELECTRODEIONIZATION TECHNOLOGY

Water purification by reducing the concentration of ionic impurities has been an area of considerable technical interest. Water treatment technologies have rapidly advanced in recent years to where a myriad of options have been developed for this purpose. The most well-known processes include electrodialysis, electrodeionization (EDI), liquid chromatography, membrane filtration, and ion exchange. Producing pure water without regeneration chemicals is now a practical reality. EDI is a separation process combining electrodialysis and conventional ion exchange (IX); the resulting hybrid process does not entail regenerant chemicals. EDI technology has been reported in the literature since 1950s (1, 2).

The first patent for EDI was granted to a Dutch company in 1957 (3). A patent for the purification of acetone with EDI was also granted to Kollsman (2) in 1957. For fundamentally the same reasons that reverse osmosis (RO) system are cost-effectively replacing cation and anion units, EDI systems can also supplant mixed-bed deionizers (4). The EDI process is preferred in many systems primarily because of the environmental benefit of no required hazardous regenerant chemicals and the inherent superiority of a continuous process over a batch process (5).

It is critically important for regenerable mixed-bed deionizer operation that

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the resins settle properly and the division between them occurs at the middle collector. Furthermore, the particle size range is limited by the separation requirement. The separation occurs because of the difference in the density of the two types of resin. The cation resin, being heavier, settles on the bottom, while the anion resin, being lighter, settles on top of the cation resin. The degree of separation can be determined using the terminal settling velocities (TSV) of the cation and anion resins respectively. The TSV is calculated using Stokes' law (6) as shown in Equation 1.

$$V = \frac{2 \times g \times a^2 \times (d_1 - d_2)}{9 \times \eta}$$ Eq. 1

Where:
V = Resin terminal settling velocity in centimeters per second (cm/s)
g = Gravitational constant (= 981 cm/s^2)
a = Radius of resin bead (cm)
d_1 = Density of resin in grams per cubic centimeters (g/cm^3)
d_2 = Density of water (g/cm^3)
η = Viscosity of water (Poise)

In the case of regenerable mixed beds, it is essential that distinct separation of cation and anion resins occur upon backwashing to assure complete regeneration of the resins and to avoid contamination by the other regenerant. However, the very nature of a regenerable mixed bed requires compromise: the resins must be able to separate for regeneration and to remain intimately

mixed during exhaustion (7). These are obviously contradictory requirements. If cation resin remains in the anion zone, it will absorb sodium from the caustic regenerant. Conversely, anion resin remaining in the cation zone will attract either sulfate or chloride, depending on whether sulfuric or hydrochloric acid regenerant is used for the regeneration of cation resins. When the EDI process is regenerated, the resins remain mixed and have no separation requirement. Consequently, EDI systems provide a technically superior alternative to mixed beds in a cost-effective manner.

One key factor stimulating the EDI market growth is the desire by many endusers to move to a water treatment approach that consumes fewer chemicals. A main benefit of the EDI system is the elimination of the need for on-site bulk storage of concentrated acid and caustic regenerants as well as the exposure to these chemicals by equipment operators. Moreover, no hazardous waste stream is generated by this technology. In combination with RO, EDI may provide a continuous, chemical-free system.

On the other hand, purifying water through regenerated resin beds may lead to organic release into the downstream treatment steps. When newly regenerated resin beds are installed, high total organic carbon (TOC) leakage may occur. It is interesting to note that EDI systems can readily remove charged organics because membranes have the property of being permeable
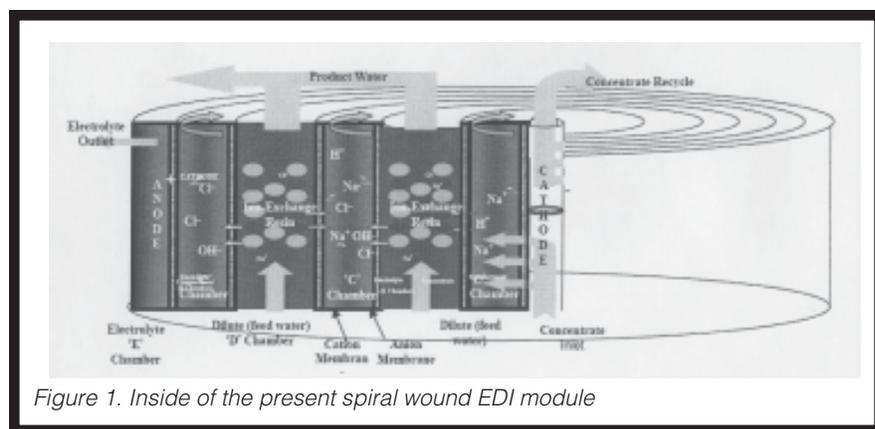

Figure 1. Inside of the present spiral wound EDI module

exclusively to charged elements (8). A high degree of TOC removal by spiral-wound EDI devices was earlier reported in the literature (9). Many organic molecules hydrolyze in the electric field. The organics therefore ionize under very high pH gradients developed in the spiral-wound EDI modules. They are then transported like other ions through the membrane and removed (9).

The main consumable in EDI is electricity. The electrical cost of running an EDI system is usually between 0.2 to 3.0 kilowatt hours (kWh) per 1,000 gallons of product water, depending on feedwater quality and product water specifications (10). Recent developments in EDI technology have resulted in significant cost reductions arising from an expandable, modular system approach built upon a base module EDI systems that require minimal expenses to install.

The present EDI modules use a spiral-wound membrane and IX resins, sealed in a high-strength fiber reinforced plastic (FRP) pressure vessel (11). In the present spiral-wound EDI systems, feedwater enters the modules from below and is diverted into vertically spiraled dilute chambers. Concentrate enters the module through the central pipe from below and is diverted into spirally flowing concentrate chambers (Figure 1). The patented cross-flow design of the concentrate stream in the present spiral wound EDI modules is unlike that of the co-flow design used in conventional plate-and-frame devices. This imparts a higher hardness tolerance for the present spiral-wound EDI devices.

The EDI module is composed of flow-directing spacers separated by anion and cation semi-permeable membranes along with IX resin and electrodes. Spacers are provided between alternating cation and anion-exchange membranes to maintain separation of associated membranes and support even distribution of liquid through the chamber. Spacers are usually manufactured from thermoplastic materials. In EDI systems, ions are removed from water by a combination of IX resin, IX membranes, and a DC electric current. Anions migrate towards the positive electrode (anode), and cations towards the negative electrode (cathode).

Permselective and impervious IX membranes that are arranged to form parallel flow chambers limit the migration of ions between anode and cathode. The feedwater entering the EDI apparatus is divided into at least three parts. A small percentage flows over the electrodes, a majority of the feed passes through the diluting chambers, and the remainder passes along the concentrating chambers. Diluting chambers are filled with specially graded IX resins. A conductive path is developed through the resin beads that are much lower in electrical resistance compared to the path through the bulk solution.

The chambers bounded by the anion membrane facing the anode and the cation membrane facing the cathode become exhausted of ions, and are hence called diluting chambers. The chambers bounded by the cathode-facing anion membrane and anode-facing cation membrane are called concentrating chambers. The concentrating chambers will then "trap" ions that have electrically migrated in from the diluting chambers. Consequently, the ionic concentration of the water will decrease in the diluting chamber with a corresponding increase in the ionic concentration of the water in the concentrating chamber. These flow chambers are hydraulically in parallel, but electrically in series.

The current also splits water molecules into hydrogen and hydroxyl ions. The EDI systems operate in two different modes: electrodeionization and electro-regeneration (12). The system is working in the first mode when the feedwater salinity is high (13). On the contrary, the system is working in the second mode when the feedwater salinity is very low because of the passage of strongly ionized species to the concentrating chamber in the upstream flow path. This allows a portion of the resins in the EDI to always be in the fully regenerated state. This will form a highly conductive path through the resin beads. Moreover, a higher degree of regeneration of resin beads will reduce the leakage of all the ionic species, especially weakly ionized species such as boron and silica.

Higher conductivity in the concentrate stream is accomplished by concentrate recirculation and occasional brine injection in the concentrate stream. This design facilitates the transfer of current. Back-diffusion can limit effluent quality. Consequently, a certain percentage of the concentrate flow must go to the drain. The increase in the electric current flow because of higher electrical conductivity of the concentrate water lowers the power consumption of the device because of decreases in the EDI module resistance and applied voltage.

Further improvement in the power economy was accomplished by passing the current through a series of cell pairs with electrodes only at the terminal points of the series. A cell pair consists of a cation membrane, spacing material through which the feed and the treated water flows in the diluting chamber, an anion membrane, and the spacing material through which the concentrate water flows. Consequently, the loss of energy at the electrodes per equivalent of salt removal from the RO permeate water will reduce to a minimum.

In today's demanding business climate, research and development is crucial to the survival and success of water treatment enterprises. The present spiral-wound EDI manufacturer has a patent pending for an improved resin-containing design. This illustrates the type of commitment needed by water treatment equipment companies toward research and development, and for the continuous improvement of their products.

EDI Module Construction
Industrial-scale EDI devices are available in two major configurations: plate-and-frame, or spiral-wound. While the majority of these systems employ first generation plate-and-frame designs, the spiral-wound version is becoming a fast growing technology in the EDI field. The reliability of the present spiral-wound EDI modules in the high-purity water generation application is substantiated by more than 40,000 gallons per minute (gpm) of installed capacity within the last 3 years.

The plate-and-frame type EDI devices are similar in construction to a plate heat exchanger, with multiple fluid chambers sandwiched between a set of end-plates (and electrodes) that are held in compression by bolts or threaded rods. Plate-and-frame devices are commercially available in two main configurations. These are thin cell and thick cell, designated as such based on the thickness of the diluting chambers. Plate-and-frame devices are large in size and characteristically suffer from leaks because of the difficulty of sealing large vessels. Moreover, the units often are oversized because of inflexibility in designing for capacity, necessitating undesirably high capital and operating costs (14). The spiral-wound membrane design incorporates a non-metallic pressure vessel more similar to RO mem-
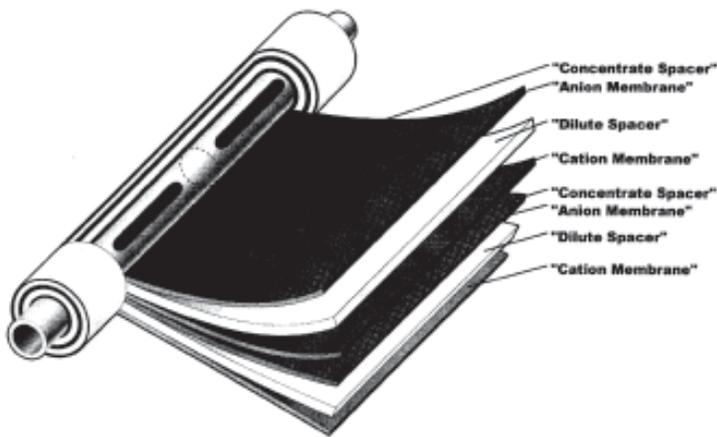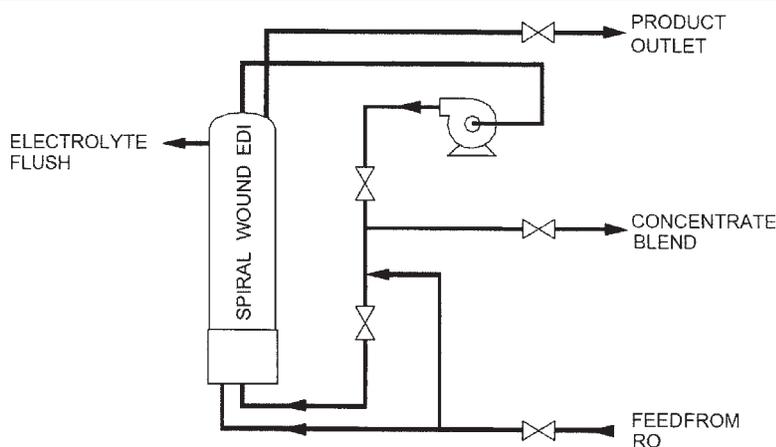
Figure 2. Spiral-wound EDI membranes.

Labels in figure: "Concentrate Spacer", "Anion Membrane", "Dilute Spacer", "Cation Membrane", "Concentrate Spacer", "Anion Membrane", "Dilute Spacer", "Cation Membrane"

Figure 3. Spiral-wound EDI process flow diagram.

Labels in figure: PRODUCT OUTLET, ELECTROLYTE FLUSH, SPIRAL WOUND EDI, CONCENTRATE BLEND, FEED FROM RO

branes (15). Spiral-wound EDI devices are commercially available in two main configurations: cathode at the center or anode at the center. The spiral-wound EDI modules discussed in this article use central cathodes.

The present spiral-wound EDI membranes are similar to that of RO membranes in that the membranes and spacers are rolled to form a cylindrical element (Figure 2). The EDI element is manufactured by placing a stainless steel concentrate pipe on a rolling machine and winding the membrane and spacers around the pipe. The element is then placed into a fiberglass pressure vessel and dilute chamber spacers are filled with resin. The unit is sealed inside the pressure vessel. The central stainless steel pipe acts as the concentrate distributor/collector and the cathode. A titanium anode lines the inside of the fiberglass pressure vessel and becomes the anode (15).

Spiral-Wound EDI System
When multiple EDI modules are present in one system, the feed flow enters the system through a header and is distributed to all modules. The treated water exits the diluting chambers while the water from the concentrating chambers is recirculated, promoting mixing. The product flow is collected on the outlet of the modules and exits the system through another header. It is commonly known that the high flowrate of the concentrate stream is achieved by employing recirculation of concentrate stream inhibits scales from forming.

To prevent ion concentration from reaching the point of precipitation, a small stream is bled from the concentrated stream loop. By employing the recirculation of concentrate stream, the ion concentration within the concentrate water increases and this in turn leads to higher electrical conductivity of the concentrate water. If necessary, the manufacturer of the present spiral-

wound EDI device recommends injecting food-grade brine that is low in metallic impurities in the concentrate loop of their modules to maintain the conductivity of the concentrate stream between 250 and 600 microsiemens per centimeter (μS/cm) at 25°C. A small portion of concentrated stream is also used to flush the electrodes to eliminate any build-up of gases. Electrolyte chambers are provided so that reaction products from the electrodes can be separated from the other flow chambers.

The present spiral-wound EDI modules incorporate two terminal electrode chambers containing an anode and a cathode respectively, which are used to pass DC current transversely through the module. A small make-up stream from the feedwater balances the flow lost through concentrate bleed and electrode flush. Figure 3 illustrates a typical process flow diagram. It is imperative to note that EDI systems are typically available with plastic piping because of the danger of accelerated corrosion from stray currents (16). Stainless steel piping can be used if proper grounding techniques are adopted.

The manufacturer of the present spiral-wound EDI modules adopts a modular system approach for the deionization of RO permeate water, which is comprised of a skid-mounted plurality of EDI modules, a patent-pending DC rectifier, a concentrate recirculation pump, a brine dosing system, instrumentation, a programmable logic controller (PLC)-based control system, and interconnecting polyvinyl chloride (PVC) piping and fittings. The manufacturer of the present spiral-wound EDI modules offers skid-mounted systems that considerably reduce the footprint.

The footprint of a complete system is largely dependent upon the aesthetics of the layout. In pre-engineered systems, the manufacturer of the present spiral-wound EDI modules designs the systems using the user-friendly features. For example, all spiral wound EDI modules are accessible from the ground level and module layout is designed for customer convenience with a walkway in the middle for easy access to the entire system. Module isolation valves and sample ports are included for every module, allowing for easy troubleshooting and reliable system operation.

The removal of the spiral-wound EDI modules do not usually require a crane or other special equipment. Each comparable square plate-and-frame stack

weighs 200 to 220 pounds (lb), according to published literature (17), while each round plate-and-frame stack weighs 610 lb (18). The present spiral-wound EDI module weighs only 60 to 70 lb. The manufacturer of the spiral-wound EDI modules highlighted in this article can also provide custom engineer systems to fit in a given space requirement. The spiral-wound EDI does not use a multi-port design, which is known to suffer from reduced flow in the latter vessels in RO systems.

Industrial Applications

The requirements for high-purity water in various industrial uses are immense. The purification of aqueous streams using EDI has become of increasing interest in many industries. EDI is the answer in demanding applications that require reliable and economical removal of ionic contaminants from aqueous streams without the application of hazardous chemicals. EDI has been extensively used in electronics, pharmaceutical, and power industries for high-purity water production. Production of high-purity water in a cost-effective manner is becoming more and more important in these industries. To be competitive in the deregulated power market, authorities are looking for ways to reduce operating costs while maintaining an unfailing supply (16). Effective application of EDI systems can in many cases provide a critical competitive edge.

Water Recovery and Scaling

Scaling in an EDI device takes place when sparingly soluble impurities are concentrated in the concentrating chambers beyond their solubility limit. The scaling occurs in the concentrating chambers under conditions of high water recovery. For example, if an EDI system is operated at 90% recovery, the concentrations of various impurities in the concentrate chambers will be 10 times the concentrations in the EDI feed stream. Scaling potential increases with the increase in the water recovery.

The concentrate stream accepts ions removed from the dilute stream and provides necessary pressure balance with the dilute stream to control salt transfer. Unfortunately, scaling predominantly occurs because the concentrate stream becomes rich in hardness or heavy metals: the ions that scale. Consequently, the recovery rate is decided by EDI feedwater hardness. The follow-
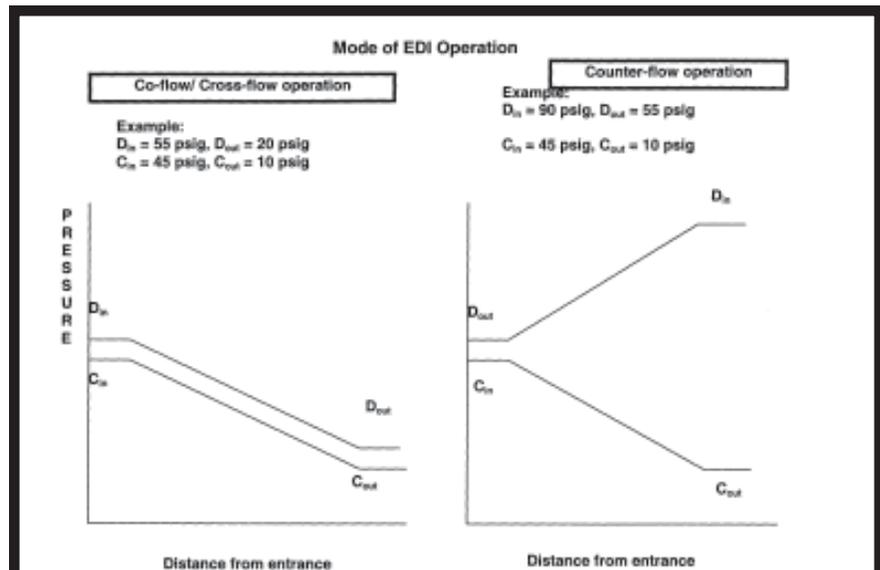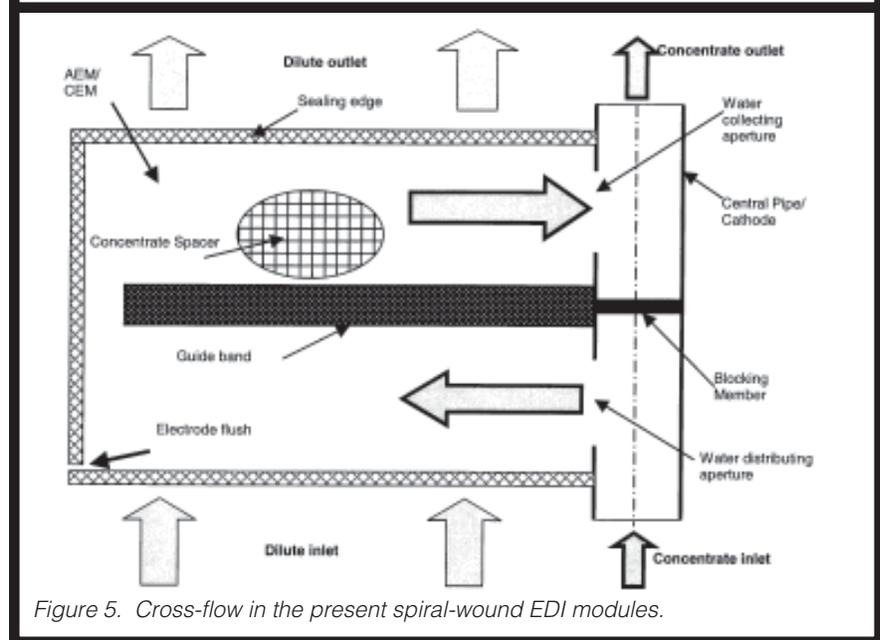

Figure 4. Mode of EDI operation.

Figure 5. Cross-flow in the present spiral-wound EDI modules.

ing guidelines for the water recovery based on the feedwater total hardness are established for the present spiral-wound EDI modules (Table A).

Scaling has been found to take place in localized regions of EDI devices, and mainly in those where high pH is characteristically present (19). The Langelier Solubility Index (LSI) in the concentrate stream is commonly negative during the operation of the commercial EDI devices that accept feedwater according to the recommendation of the EDI manufacturers. Thus, on the basis of consideration of LSI alone, one would not expect the precipitation of calcium carbonate ($CaCO_3$) scale that occurs within concentrating chambers. This phenomenon is instead explained by the existence of high-pH regions on the surface of the concentrate chamber side of anion-exchange membranes (20). It is believed that the pH at the concentrate chamber side of an anion-exchange membrane boundary layer augments with applied current. Therefore, the current needs to be optimized, based on the desired product water quality and the incidence of scaling.

In the same way, scaling occurs in the alkaline environment of the cathode chamber. Because of high pH levels, scaling problems are expected at the cathode chamber. The following reaction takes place at the cathode as shown in Equation 2.

$$2 H_2O + 2 e^- \rightarrow 2 OH^- + H_2 \quad \text{Eq. 2}$$

TABLE A
Water Recovery versus Present Spiral-Wound EDI Feedwater Hardness

EDI Feedwater Total Hardness (ppm as $CaCO_3$)	Water Recovery (%)
0.0 – 0.5	95
0.5 – 1.0	90
1.0 – 1.5	85
1.5 – 2.0	80

Carbonate (CO_3^{2-}), bicarbonate (HCO_3^-), and hydroxide (OH^-) ions that migrate through the anion-exchange membrane from the diluting chambers are concentrated near the concentrate chamber side of anion-exchange membranes. In addition, hardness, contributing polyvalent cations in water in the concentrating chambers is drawn, or driven to the anion-exchange membrane, so that CO_3^{2-}, HCO_3^-, and OH^- react with Ca^{2+} to form scales of calcium carbonate on the surface of the concentrate chamber side of anion-exchange membranes (21). Such scale formation results in higher electrical resistance and less electric current flow at that section (22). At the extreme condition, enough current to achieve the desired product water specification cannot be applied within the maximum voltage of the device, and the quality of the treated water declines.

Cross-Flow Designs
Co-flow is the term given to the mode of EDI operation where the direction of flow in the concentrate chambers is the same as in the diluting chambers. Hardness-contributing polyvalent cations are readily removed from the diluting chambers flow path to the concentrate water flowing in the concentrate chambers. Such polyvalent cations continue to move further towards the cathode and reach the concentrate chamber side of anion-exchange membranes near the concentrate chamber outlet. A high average rate of water splitting is normally achieved by applying a high voltage drop across the diluting chambers. A substantial amount of OH^- ions migrate from diluting chambers to the concentrate water flowing in the concentrate chambers in the downstream section of the modules. The pH of the solution on the concentrate chamber side of the anion-exchange membranes near the concentrate chamber outlet becomes very high and triggers the hardness-scaling phenomenon. The majority of commercially available EDI devices use a co-flow deign.

Counter-flow is the term given to the mode of EDI operation where the direction of flow in the concentrate chambers is opposite to that in the diluting chambers. Assuming the flow in the diluting chambers to be downward, the flow in the concentrate chambers is introduced at the bottom of the module in a counter-flow operation. Counter-flow operation is intrinsically more efficient compared to the co-flow operation to avoid scaling.

In this flow configuration, once the polyvalent cations migrate from the diluting chambers to the concentrate water flowing in the concentrate chambers, they exit the module immediately before reaching the surface of the anion-exchange membranes. Consequently, the scaling potential reduces significantly in this mode of operation. However, it is imperative to operate the system with the concentrate inlet pressure be 5 to 10 pounds per square inch gauge (psig) less than the dilute outlet pressure in this flow configuration.

To satisfy this criterion, this flow configuration necessitates a very high feed pressure for the operation of the EDI system. For instance, the minimum feed pressure should be at least 90 psig to provide 10 psig for the ΔP ($D_{out} - C_{in}$) when the concentrate inlet pressure and feed to product pressure drop are respectively 45 and 35 psig (Figure 4). Such a high feed pressure augments the power consumption drastically and interferes with the sealing efficiency of the modules. Additionally, variation in ΔP across the membranes in counter-flow operation also undesirably stretches them. At this point, it is important to recognize that the feed-to-product pressure drop increases significantly at higher flowrates and lower operating temperatures. Pressure drop also increases with fouling of the IX beads in the diluting chamber and agglomeration of organic contaminants in the concentrate spacers.

Consequently, the feed pressure requirement may exceed the maximum allowable pressure of 100 psig in the counter-flow mode when the modules are operated on water streams with high organic impurity levels at high flowrates during the winter months. On the contrary, the minimum feed pressure is only 55 psig in conventional co-flow mode to provide 10 psig for the ΔP ($D_{in} - C_{in}$) when the concentrate inlet pressure and feed to product pressure drop are respectively 45 and 35 psig (Figure 4).

Cross-flow is the term given to the mode of EDI operation where the direction of flow in the concentrate chambers is perpendicular to that in the diluting chambers. The present spiral-wound EDI modules operate on a cross-flow mode (Figure 5). This patented concentrate flow design of the present spiral-wound EDI modules is unlike that of the co-flow design employed in conventional plate-and-frame EDI devices (11). The concentrate chamber is separated into two compartments: lower and upper.

Spiral flow in the lower compartment is away from the central cathode, while the flow direction in the upper compartment is towards the central cathode. Migration of strongly ionized polyvalent cations always occurs in the lower compartment of such concentrate chambers. Reversal of flow direction in the concentrate chambers in these spiral-wound EDI modules can be described as a two-pass design. Such a two-pass flow in the concentrate chambers promotes turbulence and lowers the scaling potential as the thickness of the localized alkaline boundary layers on the concentrate chamber side of the anion-exchange membranes is greatly reduced.

The use of multiple flow paths connected in series provides a tortuous path and good fluid distribution within the concentrate chamber. However, the hardness contributing polyvalent cations continue to move further towards the cathode at the center of the EDI modules and may reach the concentrate chamber side of the anion-exchange membranes. In the cross-flow configuration, concentrate water flows spirally in a direction perpendicular to the upward flow path in the diluting chambers and the transverse DC electric field drives the various cations in a direction perpendicular to that of the spiraled concentrate flow.

The resulting movements of the polyvalent cations under the presence of the boundary layer of the anion-exchange membranes are in a plane perpendicular to the plane in which dilute stream is flowing. This flow pattern ensures a low concentration of such cations on the anion membrane side of the concentrate stream near the outlet of the dilute flow where the alkaline environment mainly exists. This phenomenon greatly reduces the scaling potential in such cross-flow EDI operation. The unique cross-flow design of the present spiral-wound EDI modules results in higher feedwater hardness tolerance compared to the conventional plate-and-frame devices. Vendors of plate-and-frame EDI devices suggest that the maximum total hardness in the feed to the EDI be limited to 0.5 to 1 parts per million (ppm) as $CaCO_3$ whereas the present spiral-wound EDI modules can accept a maximum total hardness of 2 ppm as $CaCO_3$ in the feed to the EDI. It frequently translates to a reduction in capital expenditures for water treatment systems by eliminating the need for a softeners and/or double-pass RO ahead of the EDI systems. Furthermore, even higher feed hardness levels are possible with increased frequency of cleaning.

The cross-flow mode enjoys fundamentally a similar pressure profile with co-flow mode. The minimum feed pressure is only 55 psig in cross-flow mode spiral-wound EDI to provide 10 psig for the ΔP ($D_{in} - C_{in}$) when the concentrate inlet pressure and feed-to-product pressure drop are respectively 45 and 35 psig. Consequently, this unique cross-flow mode allows higher feedwater hardness without augmenting the power consumption compared to conventional plate-and-frame design operating in a co-flow mode. It is worthy to note that the maximum allowable inlet pressure is 100 psig, which allows product water pressure up to 70 psig.

At the particular moment of flow reversal (Figure 5), there is a sudden increase in the turbulent conditions of flow. The boundary layer separates from the guide band immediately past the shoulder, creating a large wake behind. The formation of a standing eddy behind the guide band, caused by accumulation of vorticity can be explained using introductory fluid dynamic publications (23). The ratio between the average flow velocity and the maximum flow velocity in the concentrate chamber increases with the increasing turbulence in the chamber. This will ensure a more uniform flow distribution throughout the concentrate chamber. To the contrary, plug flow conditions exist in plate-and-frame modules. Because of a lack of turbulence in this configuration, the flow is strongly influenced by the presence of a thicker boundary layer, which accelerates scaling in the alkaline environment that exists on the concentrate chamber side of the anion-exchange membrane.

A closer look at the Figure 5 will reveal that the concentrate stream has a side entry and exit to and from the spiraled concentrate chamber. In case of plate-and-frame devices, the entrance and exit are located at the bottom and top section of the module. Consequently, full plate-and-frame concentrate flow will exit the module where an alkaline environment exists in the concentrate chamber side of the anion-exchange membrane and promote scaling. In the present spiral-wound EDI module, only a part of the total concentrate flow will come in contact with the localized alkaline environment in the concentrate chamber side of the anion-exchange membrane that corresponds to the polishing section of the diluting chamber where high degree of electro-regeneration occurs. One should realize the advantage of a side exit when compared to the top/bottom exit in the conventional plate-and-frame devices. The present spiral-wound EDI modules alleviate the scaling potential because of the following phenomenon.

1. Turbulence in the concentrate chambers equalizes the concentration of polyvalent cations in the concentrating chambers. Equalization of polyvalent cation concentration in the concentrate chamber reduces their concentration in the alkaline boundary layer next to the concentrate chambers side of anion-exchange membranes. This phenomenon will greatly reduce scaling potential.

2. Only a part of the total concentrate flow with a low equalized polyvalent cation concentration will be exposed to highly alkaline environment that exist in the concentrate chamber side of the anion-exchange membrane because of the side exit. Consequently, a small fraction of the total polyvalent cations present in the concentrate chambers can possibly take part in the scale formation.

3. Super-saturation of salts leads to nucleation and until they achieve a critical size, the nuclei may re-dissolve. Turbulent flow conditions that exist in the concentrate chambers of the spiral-wound EDI modules inhibit salt crystal growth and prevent precipitation.

Coming in Part 2
In Part 2 of this article series, we will examine serviceability and EDI module life of the spiral-wound design. Other topics to be addressed will include IX resin, feedwater requirements, power consumption, the pairing of spiral-wound EDI modules, and performance data.∎

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Endnote

The spiral wound EDI equipment referred to in this article is made by Omexell Inc., based in Houston, Texas.

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