

Application of Electrodeionization in Ultrapure Water Production: Performance and Theory

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Note: GE Water & Process Technologies purchased Ionics in 2005.

Introduction

Ultrapure water is critical in a number of industrial applications, such as power generation, semiconductor manufacturing, and pharmaceutical formulation. Traditionally, ion exchange has been used to provide ultrapure water in these industries but membrane processes are becoming increasingly popular as pretreatment steps or as replacements for ion-exchange systems altogether. Membrane processes can provide very high levels of demineralization and offer the advantage of continuous operation. Moreover, membrane processes are not as mechanically complex as ion-exchange systems, and they require no acid and caustic regeneration, nor waste neutralization.

In semiconductor fabrication, the use of reverse osmosis (RO) is considered essential to achieve the purity levels necessary for wafer production. In power plants, increased recognition of the effect of ultrapure water quality on system component life has resulted in demand for membrane systems which can render an even higher purity of water than mixed-bed deionization systems alone can achieve (e.g. lower TOC, particles, etc.). Such high levels of demineralization can be obtained using electrodeionization (EDI). EDI combines ion-exchange resins, ion-exchange membranes, and a direct (DC) electric field. Basically, EDI is an electrodialysis (ED) process modified by the addition of

ion-exchange resin. When EDI is used for the production of high purity water, the ion-exchange resin beads enhance mass transfer, facilitate water splitting, and reduce stack resistance. The ion-exchange resin exchanges ions with the incoming feed stream. The DC electrical field splits water into hydrogen and hydroxyl ions, which, in turn, continuously regenerate the ion-exchange resins. The exchanged ions are transferred through the membranes to the brine stream and flushed from the system.^{1,2} Compared to conventional ion exchange, EDI has the advantage of being a continuous process with constant stable product quality, which is able to produce ultra high purity water without the need for acid or caustic regeneration.

This paper presents data from five commercial scale EDI installations now in operation. Four of these EDI installations are located at electric generation plants. The fifth EDI system is part of a silicon wafer manufacturing facility located in the Midwest (Si FAB). The electric power plants are Grand Gulf Nuclear Station (GGNS), Arkansas Nuclear One (ANO), Florida Power & Light Turkey Point Power Station (TPPS), and the Riverbend Nuclear Station (RBNS). In the power plants, the ultrapure water is used for makeup to high-pressure boilers and for plant usage. In the semiconductor plant, ultrapure water is used for wafer rinsing.

In each of the five installations discussed in this paper, the EDI units are integral parts of multi-step purification systems that supply high purity water. The EDI process pretreatment includes filtration and partial demineralization by reverse osmosis (RO). RO removes many of the contaminants which could harm an EDI system, such as organics, which can foul anion and cation ion-exchange resins, and particulate matter, which would be difficult to remove from an EDI unit. Scaling ions, such as



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magnesium and calcium which, at high enough concentrations, could necessitate the use of continuous acid addition to the EDI, are removed at least 95 percent by an RO system. The combination of reverse osmosis and EDI allows the EDI to perform at its optimum level. In a process train in which RO is followed by EDI, water can be produced that is comparable to mixed-bed ion-exchange treated water.³

Performance

In the installations reported in this paper, EDI is part of water treatment processes that deal with quite different feedwater conditions. The processes vary in feedwater sources, composition, and pre-treatment equipment upstream of the RO unit. In all cases, the water treatment systems also have to handle feed water quality variations, such as seasonal changes in the ionic load, temperature, organics and pH. Such changes, as well as the process conditions, affect the performance of the EDI demineralizers. Table 1 lists the unit processes that are used in each installation and summarizes key variables describing the feedwater.

Table 1: Unit Processes and Feedwater Variables for Each EDI Installation

Location	Feed Source	Feed TDS gpm (m ³ /h)	Temp F° (C°)	Flowrate gpm (m ³ /h)	System Flowsheet
GGNS	Surface	400 (1.5)	55-82 (13-28)	50 (0.2)	MMF/ACF/UF/EDR/RO/EDI
ANO	Surface	100 (0.4)	50-86 (10-30)	200 (0.8)	MMF/ACF/UF/EDR/RO/EDI
Turkey Point	Well	475 (1.8)	77-82 (25-28)	200 (0.8)	MMF/DEGAS/UF/RO/EDI
Riverbend	Well	230 (0.9)	82-88 (28-31)	50 (0.2)	CF/RO/EDI
Silicon Fab	Well	900 (3.4)	66-72 (19-22)	100 (0.4)	MMF/DEGAS/UF/RO/EDI

(MMF= multimedia filtration, ACF=activated carbon filtration, UF=ultrafiltration, EDR=electrodialysis reversal, DEGAS=forced draft deaerator, CF=cartridge filtration)

In all of the above cases the EDI product water is further polished using portable ion exchange beds. Portable ion-exchange beds are economical to use in these cases since the EDI product water has a very low ionic load which translates into long bed life, usually several months in length. Portable ion-exchange beds also offer higher water quality than is normally achieved in conventional in-situ ion-exchange systems, since resin regenerations are conducted in small volumes at one dedicated facil-

ity where regeneration of resins can be tightly monitored and controlled.

Conductivity Removal

The performance of EDI can be determined in a number of different ways. One simple method is to measure the change in conductivity, which is directly related to total dissolved solid (TDS), across the EDI unit. Figures 1-4 show time averaged conductivity removal accomplished by the EDI units at GGNS, ANO, TPPS, and RBNS. Conductivity data was obtained using on-line Thornton Dot Two series and 770 series conductivity instruments. In the figures, 100% removal corresponds to reaching the lowest possible conductivity, which stems from water dissociation.

EDI has been operating at GGNS since September 1991 and was the subject of previous papers.^{3,4,5,6} The data shown in Figure 1 covers the operation of an upgraded EDI stack in operation since July 1993. This stack has shown conductivity removal in the range of 99.5%+ since its installation.

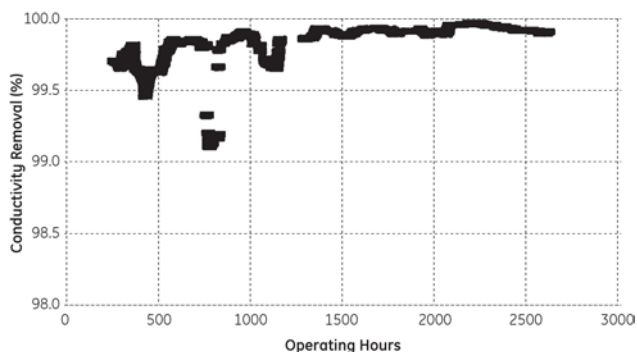


Figure 1: Electrodeionization Conductivity Removal, GGNS

Figure 2 shows conductivity removal for one 100 gpm unit of a 200 gpm (0.8 m³/h) EDI system located at ANO. This unit was also discussed in detail previously.⁴ This unit has been in operation since April 1993 (i.e. over 5000 operating hours). Since its operation was optimized (after around 1200 hours of operation), the conductivity removal has been above 99 percent.

Figure 3 shows the conductivity removal over time for one 100 gpm (0.2 m³/h) unit of a 200 gpm (0.4 m³/h) EDI system located at Turkey Point Power Station (Fossil). The unit has been in operation since September 1993. The system at Turkey Point is unique in that it is the first installation by Ionics (now GE) of EDI without the use of EDR upstream of the RO unit. The unit has performed very

well over the first year of operation with conductivity removal in the 98% to 99% range.

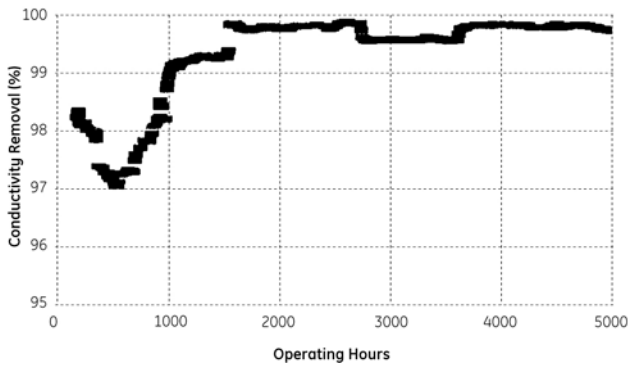


Figure 2: Electrodeionization conductivity Removal, ANO

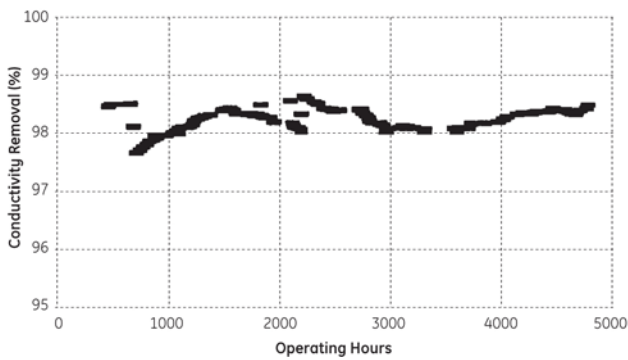


Figure 3: Electrodeionization Conductivity Removal, TPPS

Figure 4 shows conductivity removal over time for a relatively new installation at Riverbend Nuclear Station. The feedwater to this plant is a low TDS, low organic, well water which allows this plant

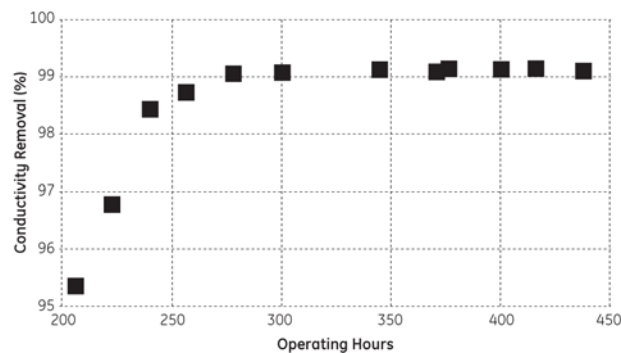


Figure 4: Electrodeionization Conductivity Removal, RBNS

to operate with just a cartridge filter upstream of the RO unit. After about 250 hours of operation, this EDI unit reached conductivity removal performance of above 99%.

Specific Ion Removal

A more informative measure of EDI performance is the specific ion removal across the unit. Table 2 summarizes results of EDI feed and product water analyses of samples from the five EDI sites. These samples were analyzed by capillary electrophoresis for their sodium, calcium, magnesium, chloride, and sulfate contents. Table 3 presents the corresponding specific ion in terms of percentages.

The percent rejection of specifications is consistent from site to site. At each site the EDI reduces specifications to low ppb levels with most ions removed down to the detection level of the analytical method. The specific ion levels produced by the EDI units at GGNS, ANO and RBNS are comparable to the level achieved by using mixed-bed ion-exchange resin alone.

Silica and Carbon Dioxide Removal

Silica removal is very important in power plants since silica deposition on the turbines can result in low efficiencies of power generation and eventually in downtime necessary to remove silica deposits. In the semiconductor industry, low silica content in the water is also critical because silica deposits on the wafers, which can cause costly defects.

Removal of CO₂ is another important aspect in ion-exchange demineralization. Often, CO₂ is the predominant anion present in the feedstream to the ion-exchange bed, especially when RO is used upstream. Since CO₂ competes with silica ions for exchange sites, the amount of CO₂ in a feedstream affects bed life and silica removal efficiency in the ion-exchange bed. CO₂ is weakly ionized, which makes it difficult to remove from water. Conventional means (e.g. forced draft decarbonator) can bring CO₂ levels to the low ppm range whereas membrane demineralization processes, including RO, ED and EDR, usually do not remove CO₂ to any significant degree.^{3,7,8} Data show that EDI, however, routinely reduces CO₂ levels by at least 98 percent in most installations.

Tables 4 and 5 present a summary of silica and carbon dioxide feed levels and the corresponding removals achieved with EDI at the five sites mentioned above.

Table 2: EDI Feed and Product Ion Levels (typical ppb)

Ion	GGNS		ANO		TPPS		RBNS		SIFAB	
	Feed	Prod	Feed	Prod	Feed	Prod	Feed	Prod	Feed	Prod
Sodium	1,560	2	871	3	5,540	23	1,370	3	2,880	33
Calcium	10	< 0.5	42	0.7	575	1.7	20	1	527	6.4
Magnesium	4	< 0.5	7	< 0.5	21	< 0.5	5	0.5	259	2.2
Chloride	58	< 2	594	< 2	1,200	6	51	< 2	3,890	9
Sulfate	70	< 4	88	< 4	785	< 4	18	< 4	2,240	3

Table 3: Summary of Specific Ion Removals by Site

Ion	GGNS	ANO	TPPS	RBNS	SIFAB
Sodium	99.9	99.7	99.6	99.9	98.9
Calcium	> 95.0	98.3	99.7	95.0	98.8
Magnesium	> 87.5	> 92.9	> 97.5	> 90.0	99.2
Chloride	> 96.5	> 99.7	99.5	> 96.1	99.8
Sulfate	> 94.3	> 95.5	> 99.5	> 78.8	99.9

Table 4: Silica Levels and Removal by Location

	GGNS	ANO	TPPS	RBNS	SIFAB
Feed SiO ₂	640	3830	170	380	116
Product SiO ₂	3	140	8	10	10
% Cut SiO ₂	> 99.53	96.4	95.2	97.4	91.4

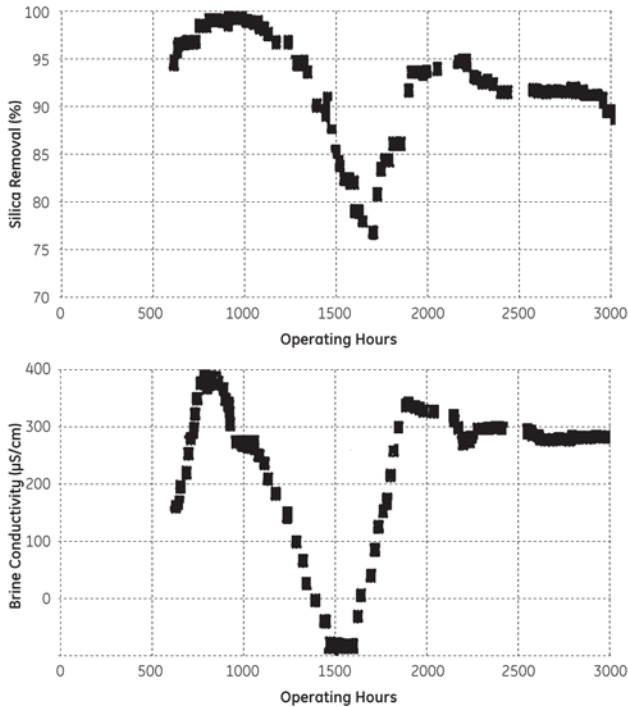
Table 5: CO₂ Levels (PPB) and Removal by Location

	GGNS	ANO	TPPS	RBNS	SIFAB
Feed HCO ₃	300	800	9,500	3,540	1,500
Feed Free CO ₂	2,700	4,200	700	8,000	6,000
Feed Total CO ₂	2,920	4,780	7,550	10,550	7,080
Product Total CO ₂	17	8	100	27	70
% Cut Total CO ₂	99.4	99.8	98.7	99.7	99

Feed and product silica levels were monitored on-line with a Hach series 5000 analyzer. Silica removal varies with feed composition (e.g. feed conductivity) and operating parameters (e.g. temperature, voltage), but some general conclusions are possible as far as suitable operating conditions are concerned. For example, high brine conductivity is important, since it decreases the resistance of the brine stream and thus redistributes the voltage drop to the dilute stream which, in turn, enhances water splitting. Water splitting, in turn, regenerates the anion resin, which is essential for high silica removal. The effect of brine conductivity on silica cut is shown in Figures 5a and 5b.

The CO₂ level in the EDI feed was determined by analyzing field samples off-line using a Total Inorganic Carbon/Total Organic Carbon (TIC/TOC) analyzer. Due to the significant effect of atmospheric CO₂ at low CO₂ levels (few ppb), the CO₂ content of the EDI product, was calculated from specific ion analyses (i.e. capillary electrophoresis) and on-line product resistivity data. As seen in Table 5, a significant amount of the total carbon dioxide in the EDI feed is present as free CO₂ (e.g. 8 ppm free CO₂ at RBNS), yet the level of total CO₂ rejection is far better than one can expect for any other membrane process without the use of caustic injection.

The excellent CO₂ rejection observed at the commercial EDI installations was confirmed in laboratory studies using a TIC/TOC Analyzer. This instrument, highly accurate in the ppb range of TIC, was used to monitor on-line the CO₂ rejection of a 20 gpm (0.1m³/h) EDI unit in the GE laboratory. The pH of the EDI feed to this unit was 5.5, which means that most (i.e. 85%) of the total carbon dioxide in the feedstream is present as free CO₂. A graph of the inlet and outlet TIC levels as a function of time is shown in Figure 6.



Figures 5a and 5b: Effects of Brine Conductivity on Silica Removal, ANO a. Silica Removal vs. Operating Hours, ANO b. Brine Conductivity vs. Operating Hours, ANO

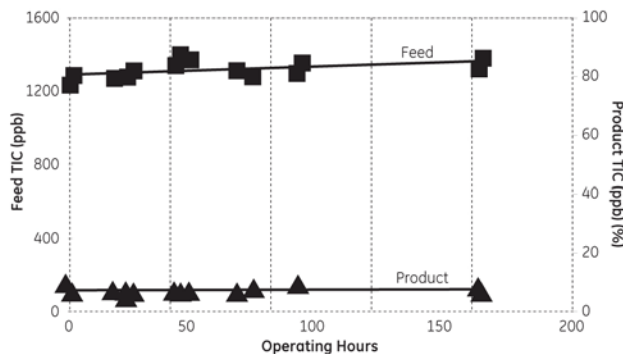


Figure 6: TIC Rejection in 20 gpm Laboratory EDI Unit

EDI and Resin pH

EDI can accomplish very high levels of demineralization because it combines a number of different ion removal mechanisms. In an EDI stack, strong and weak ions are removed at different points along the flowpath. Initially, the dilute stream is relatively rich in ionic constituents (compared to the final product). The stack current is carried by the ions in the feed-stream, with significant transfer of monovalent and divalent ions from the dilute stream to the concentrate stream. Once most of the strongly ionized species are removed, polarization and water splitting take place. Removal of weakly ionized components, such as silica and CO₂, is related to water splitting. Water splitting continuously regenerates a portion of the resin in the stack. It also creates areas of high and low pH, especially in the ion exchange resin and membranes. High pH in the anion resin/membrane is necessary for species such as CO₂ (pK₁ 6.4) and silica (pK₁ 9.8) to ionize and thus transfer from the dilute to the concentrate stream.

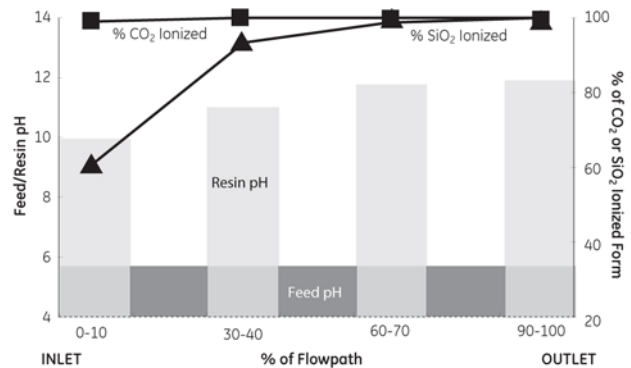


Figure 7: Effect of Resin pH on the Ionization of Silica and Carbon Dioxide

Evidence that the commercial scale EDI stacks do indeed rely on such removal mechanisms was obtained by disassembling and analyzing a stack that had been in operation at GGNS for approximately 7000 operating hours. Typical EDI feed composition at this site is given in Table 2; the performance of this 50 gpm stack is described elsewhere.⁶ Anion resin was of strong base type whereas cation resin was of strong acid type. Membranes were patented ion-selective membranes, chosen to operate in the local pH extremes typical of EDI in ultrapure water applications. The stack components (i.e. resin and membranes), sampled at four different locations along the dilute side flow paths of several cell pairs, were analyzed

for their ionic form. The results, consistent for all cell pairs and flow paths, indicate that a significant portion of the resin along the flow path is indeed in regenerated form. The internal pH of the anion resin is calculated based on resin-sample analysis. More specifically, the pH was calculated based on the percent of anion resin capacity being in carbonate, bicarbonate, and hydroxide form.** As shown in Figure 7, the internal anion resin pH is significantly higher than the bulk pH of the EDI feed. Also, the internal anion resin pH increases from the inlet to the outlet of the flowpath. At the higher pH values, most of the silica and all of the carbon dioxide are ionized and thus transported from the dilute to the brine side via the anion resin and membrane.

**equilibrium constants in the resin were taken to be the same as in solution

Conclusions

The performance of EDI at the various sites has been excellent. EDI continues to produce consistently high purity water over time. Additionally, the rejection performance of conductivity and specific ions is exceptionally high, predictable and stable over time. The EDI units are also able to consistently and predictably remove weakly ionized species such as carbon dioxide and silica. This ability to consistently and predictably remove dissolved ionic species as well as weakly ionized species, without the need for chemical addition into the feed stream, sets EDI apart from other large scale commercial membrane processes. The combined operating capacity of the five locations discussed is 600 gpm. Each one of the EDI units is a critical component in the production of ultrapure water for either electric power production or silicon wafer fabrication. The operating success of these units demonstrates the commercial viability of the EDI process for large scale ultrapure water production plants.

The water quality that is produced by EDI, especially in combination with RO, is exceptional. The level of purity achieved is generally at or near the standard definition of high purity water. When EDI is compared to conventional ion-exchange systems, the advantages are very strong: EDI obviates the need for on-site storage, use and ultimate disposal of large quantities of acid and caustic regenerating chemicals, eliminating associated safety, regulatory and environmental concerns; EDI by operating in a continuous mode is inherently more stable and less prone to upsets caused by batch operations.

Ionics' (now GE) EDI now operate at multiple installations around the world in the production of ultrapure water for the microelectronics, power and pharmaceutical industries. The use of EDI in the production of ultrapure water is expected to continue to grow significantly over the next few years.

References

1. Katz, W.E. et. al. U.S. Patent, 5,026,465, 6/25/91.
2. Parsi, E.J. et. al. U.S. Patent, 5,066,375, 11/19/91.
3. Hernon, B.P.; Zanolalidou, R.H.; Zhang, L.; Sims, K.J.; Siwak, L.R., "Electrodeionization in Power Plant Application," *Ultrapure Water*, July/August 1994, p. 33.4.
4. Smith, G.E.; Wilson, K.S., "Makeup Water Treatment Utilizing Triple Membrane Demineralizers at Entergy Operations, Inc.'s Grand Gulf Nuclear Station," *Ultrapure Water Expo '90 West, Conference on High Purity Water*, San Jose, CA, November 28-29, 1990.
5. Valcour, H.C., "Triple Membrane Water Treatment at Four Nuclear Power Plants," *International Water Conference*, Pittsburgh, PA, October 21-23, 1991.
6. Coker, et al., "Makeup Water Treatment Incorporating Electrodeionization Along with Triple Membrane Treatment at Grand Gulf Nuclear Station," *International Water Conference*, Pittsburgh, PA, October 9-21, 1992.
7. Comb, L., Schneekloth, P., "High Purity Water Using Two-Pass Reverse Osmosis," *Ultrapure Water*, April 1990, p. 49.
8. Pittner, G.A. et. al., "Unique Double Pass Reverse Osmosis System Eliminates the Need for Many Deionization Applications," *Ultrapure Water*, September/October 1986, p. 23.