

Electrodialysis Treatment of Surface and Waste Waters

Authors: Robert P. Allison, Senior Process Engineer

Introduction

Electrodialysis (ED) is a membrane desalination process that was initially developed in the 1950s. The process uses direct current power to remove salts and other ionized species through cation and anion ion selective membranes to a concentrate collecting stream as shown in the first diagram in Figure 1. The membranes are ion exchange resins cast in sheet form. The selectivity for cations or anions is created by the negative or positive charge given to the ion exchange sites in the resin. In the early 1970s Electrodialysis Reversal (EDR) was developed. EDR is a mechanical enhancement of the ED process where the polarity of the applied DC power is periodically reversed. The reversal process alternately exposes the membrane surfaces and flow compartments to the concentrate and the desalting streams, as shown in the two diagrams of Figure 1. It quickly became the predominant form of electrodialysis used, because water recovery capability was enhanced and continuous chemical addition to the concentrate stream for scaling control is not needed for most systems. The current International Desalting Association World Desalting Plants Inventory show that 13.7% of the brackish water desalting capacity in the world is ED and EDR¹. The number of plants with capacities of 25,000 gpd (95 m³) and higher exceeds 1,500. The largest EDR plant has a capacity of 12 million gallons per day (mgd) (45,000 m³/day) and is owned and operated by the County of Sarasota, Florida.

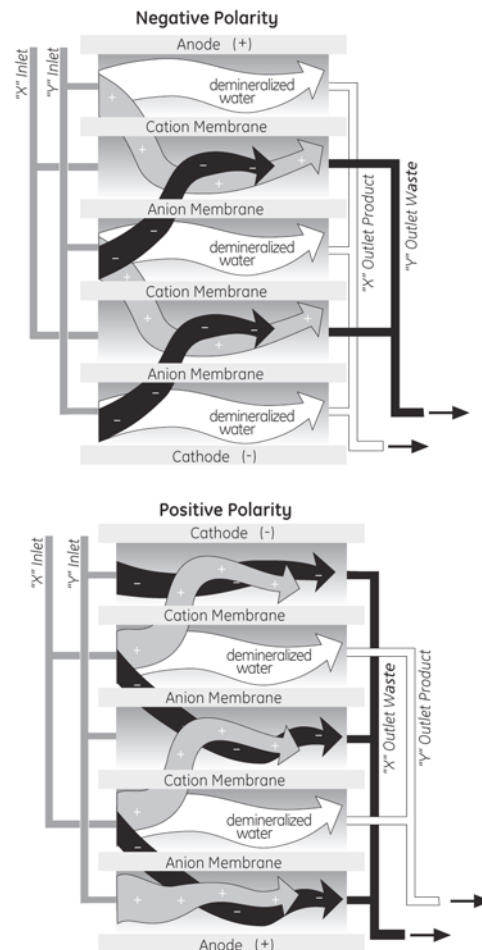


Figure 1: EDR Operation in Negative and Positive Polarities

Prior to 1981 ED and EDR were nearly exclusively used to treat well waters in the Middle East. The anion exchange membranes available before 1981 were subject to irreversible fouling by natural organic material in surface waters. While much of this fouling could be removed, there was an irreversible component which would build up over time



Find a contact near you by
visiting gewater.com or
e-mailing custhelp@ge.com.

Global Headquarters
Trevose, PA
+1-215-355-3300

Americas
Watertown, MA
+1-617-926-2500

Europe/Middle East/Africa
Heverlee, Belgium
+32-16-40-20-00

Asia/Pacific
Shanghai, China
+86-21-5298-4573

©2005, General Electric Company. All rights reserved.

*Trademark of General Electric Company; may be registered in one or more countries.

TP1032EN 0601

limiting useful anion membrane life. In 1981 a new anion exchange resin chemistry membrane was introduced to commercial service after several years of field testing. The membrane was developed with the goal of reducing manufacturing costs and lowering the power required by the process. The membrane achieved these goals but also proved to have properties that finally made EDR desalination of surface and waste waters economical and practical.

Surface and waste waters present challenges that are not normally encountered with well water sources. The first is anion exchange membrane resin fouling by dissolved organic compounds. The second is dealing with biological fouling. The third is fouling by colloidal material and the fourth is how to recover the plant performance if a fouling event happens.

Anion Exchange Membrane Organic Fouling

In late 1979 a small 100,000 gpd (379 m³/day) industrial EDR system was installed in Texas to desalt municipal water prior to ion exchange demineralization for boiler feed. The municipality uses a surface water source. The original anion exchange membranes irreversibly fouled and failed after 14 months of use. New acrylic based polymer anion exchange membranes had been under field testing for several years at this time, and improved organic fouling resistance was becoming evident. This was an opportunity to put the new membrane to a severe test. The failed membranes were replaced under warranty with the new membranes and were operated for nine years. The new membranes did experience some organic fouling, but it was found the fouling could be fully controlled by circulating a 5% sodium chloride salt solution through the stacks at about four month intervals.

Table 1 shows the analytical results of an acrylic-based resin anion exchange membrane sample taken from an industrial plant in the late 1980s. Samples from the edge gasket area not exposed to the water being treated and the active flow path area are typically analyzed. In the as-received condition, it can be seen that the active flow path area had an electrical resistance 20 times higher than the edge area. The high electrical resistance was seriously impairing the desalting performance.

The procedures for analysis of membranes involve treating the samples in 2N hydrochloric acid and 2N sodium chloride solutions as steps in the process to obtain the rest of the results. The treatments put the resin in the chloride form, and the resistance is lower than in the typical sulfate form the membrane is in when operating. The recovered edge area electrical resistance is 57.1% of the as-received value. This is due to the sample now being in the chloride form. The flow path resistance is only 3.2% of the as-received value and close to the edge area value. During the salt treatment of this sample, the sodium chloride solution color changed from clear to about the appearance of a cup of black coffee indicating extraction of organic foulants. The ion exchange capacity, which gives the membrane its electrical conductivity is nearly equal in the edge and flow path areas after the treatment. The percent water content of both areas is also nearly the same. This plant had operated for a couple of years without any salt solution cleanings being performed and the membranes were extremely fouled with organic material. The analysis showed the membranes could be cleaned easily. The customer did the cleaning and then repeated cleanings about every four months as a routine. As a result, the customer never had to replace the membranes.

Table 1: Analysis of an Acrylic-Based Anion Membrane with Reversible Organic Fouling

Property	Edge Area	Flowpath Area
As Rec'd Resistance (ohm/cm ²)	21.9	435.0
Recovered Resistance (ohm/cm ²)	12.5	14.1
Ion Exchange Capacity (Meq/dry gm)	2.29	2.25
Water Content	47.0%	47.3%

Table 2 shows the same analysis procedure results for a pre-1981 styrene divinyl benzene polymer-based membrane. The flow path as received electrical resistance is high. After the acid and salt solution treatments, the flow path electrical resistance is also still high and the ion exchange capacity is

Table 2: Analysis of a Styrene Divinyl Benzene Anion Membrane with Organic Fouling

Property	Edge Area	Flowpath Area
As Rec'd Resistance (ohm/cm ²)	25.1	97.0
Recovered Resistance (ohm/cm ²)	19.1	72.0
Ion Exchange Capacity (Meq/dry gm)	1.55	0.75
Water Content	44.0%	41.6%

less than one half the edge value. The ion exchange sites are still present in the membrane, but they are occupied by organic anions that inactivate them. Since the organic material is not removed by the salt solution treatment, the inactivation is permanent. The water content is also lower in the flow path. The fouling organic material occupies space in the resin pores and displaces some of the water volume in the membrane. Since the membranes could not be restored with cleaning in this plant, they had to be replaced.

In the 20 years acrylic-based membranes have been used in EDR systems, not one plant has had to replace membranes because organic fouling could not be removed by circulating a 5% sodium chloride solution through the stacks. Many plants experience no organic fouling, as the salt level in the water being treated appears sufficient to keep the membranes clean. In others, the salt solution cleaning is needed at a frequency that is typically one to three times per year.

There is a theory that the natural organic molecules that cause the irreversible fouling have a benzene ring and an ionic site in their structure. Bonding between benzene ring structures of the organic material and in the ion exchange resin polymer adds to the ionic bonding to the ion exchange sites in the resin. The combined bonding is strong enough to make removal impossible. The acrylic-based membranes have no benzene ring structures in the polymer to provide this extra bonding and therefore can be cleaned with a salt solution. The ion exchange industry also makes acrylic polymer ion exchange resins. They are used on waters where styrene divinyl benzene resins experience problems with organic fouling. They are also used to remove color from sugar syrups. The resin does have enough affinity for the organics to remove the color creating material but less affinity than the styrene divinyl benzene resins which allows removal by regeneration.

Some plants desalting municipal waste water have experienced faster organic fouling than indicated above. One plant has needed the salt solution cleanings as frequently as once per month at times. It has been in operation for over three years. Another plant that has been in operation for ten years still is equipped with original membranes.

Oxidizing Disinfectant Tolerance

Prior to the introduction of the acrylic-based anion exchange membranes, it was standard practice to dechlorinate before ED and EDR systems because the anion exchange membranes had very little chlorine tolerance. The acrylic membranes do have chlorine tolerance, and it is now common practice to maintain a disinfectant level through ED and EDR systems when they are treating biologically active waters. Free residual chlorine in the range of 0.1 to 0.5 mg/l as well as chloramines to 2-mg/l and chlorine dioxide at low residuals around 0.1 mg/l are being used on a continuous residual basis. While some pilot testing has been done with an ozone residual in the water, operation with a residual is not recommended due to insufficient testing.

Foss, a 3-mgd (11,000 m³/day) municipal water ED plant, was commissioned in 1974. It treats surface water in western Oklahoma. Pretreatment is lime softening followed by dual media filtration. The original top media was activated carbon for dechlorination as the anion membranes were not chlorine tolerant. In 1985, the plant was converted to the acrylic-based anion exchange membranes because the original membranes were fouled with organics. Table 2 is an analysis of an original membrane from this plant. The activated carbon was replaced with anthracite to allow a chlorine residual to pass to the EDR. The plant chemical cleaning frequency dropped from about once per 800 operating hours to once every 1,500 operating hours, with the presence of 0.3 mg/l free residual chlorine in the water being desalted. The replacement anion exchange membranes did stay cleaner with the residual present, and are still in service now 16 years later. In the past few years, the customer has been looking at options to modernize and increase the capacity of the plant. One option that was piloted for over two years was nanofiltration. Nanofiltration achieves high salt rejection on the high calcium sulfate water at this plant. Chlorine was removed before the test unit by adding sodium sulfite. Biological fouling did occur and became a severe problem that required disinfecting treatments twice per week in the summer and less frequently during colder seasons to control effectively. The chemicals used were generic and inexpensive, but did take operator time and required the unit to be out of service. The ED plant has never had any significant biological fouling

problems even before operation with residual chlorine in the feed was started.

The Foss experience indicates that ED and EDR systems even without disinfectant residual are more resistant to biological fouling than RO, but ED and EDR can experience severe biological fouling. Experience is mainly from plants operating on contaminated well sources before the membranes with oxidizing disinfectant tolerance were available.

In 1985, another benefit of free chlorine exposure tolerance was discovered. On the first day of operation of a new municipal 300,000 gpd (1100 m³/day) EDR plant in Texas, cationic polymer was inadvertently dosed to the pretreatment clarifier at about 200 mg/l. The polymer fouled the EDR unit and had a severe effect on performance. Normal hydrochloric acid and sodium chloride cleanings only partially restored performance. We then tried a cleaning with a sodium chloride salt solution maintained at a free chlorine residual of 25 mg/l for an hour. This fully restored the plant performance. Analysis of the membranes after the event proved there was no damage to the membranes and the plant still has most of the original membranes in use. A similar event happened at a power station with two 300,000 gpd units in 1995. A polymer salesman told them to use 20 mg/l in their pretreatment. When they called for help, we advised them to perform the salt chlorine solution cleaning and they reported the plants were working fine two days later. The plants are still operating today and the membranes have not been replaced.

Turbidity and Silt Density Index

EDR systems have higher limits for colloidal particulate material in the system feed than spiral wound RO systems. The guideline is a maximum turbidity of 0.5 NTU. Because of this higher tolerance, pretreatment equipment is typically dual or multi media filtration and clarification ahead of the filters if the turbidity requires reduction prior to filtration. Cationic and anionic polymers are used as well as ferric and aluminum-based coagulants. The only guideline we have is that aluminum based coagulant should not be used in a lime softening clarifier. This is because aluminum is more soluble at the high pH in the clarifier and can precipitate after the pH is lowered. Foss was operated with alum when initially started. This problem did occur

in the ED system and was corrected by switching to ferric coagulant.

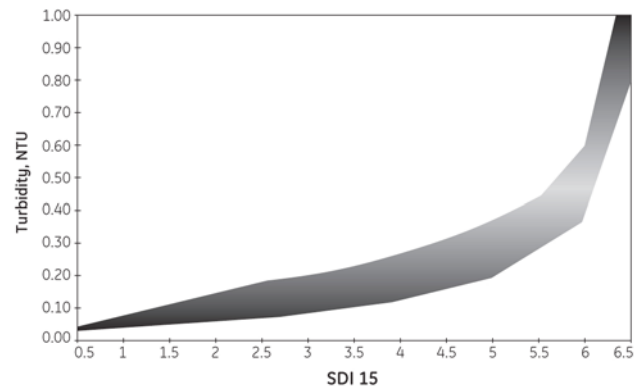


Figure 2: Correlation of Turbidity and SDI 15

Turbidity is a term well known and understood in the municipal water treatment industry. Silt Density Index is an alternative measurement that was adopted by the RO industry many years ago due to the difficulty of measuring low turbidity accurately.² It is a measurement of how fast a 0.45 micron membrane filter test pad plugs with particulate material when operated at a 30 psi pressure drop for a specific time period. Generally the time period is 15 minutes, but it can be less. Figure 3 shows a general relationship of turbidity vs. 15 minute SDI values. The data used to generate this figure is from well waters, pretreated surface waters and tertiary waste waters. It shows there is a general but not precise correlation between SDI and turbidity. The EDR 0.5 NTU guideline for maximum turbidity corresponds to a 15 minute SDI of about 6.0. This is actually a value too high to be considered accurate, and for EDR applications a 5-minute SDI test is more appropriate. The 5 minute SDI value roughly corresponding to a turbidity of 0.5 NTU is 15. RO membrane manufacturer guidelines are generally SDI 15 = 4 to 5 maximum and a well known additional guideline is that cleaning frequency increases if the SDI 15 is over 3.

The driving force for colloidal deposit formation on an RO membrane is the water flow towards and through the membrane. The water flow carries the colloids to the surface where they are blocked and deposited. In an EDR system, species that carry an electrical charge are carried towards the membranes. Species such as dissolved salts and small organic ions with molecular weights below about 200 pass freely through the membrane to the concentrate. Particles in water also have an electrical charge and the charge is nearly always negative.

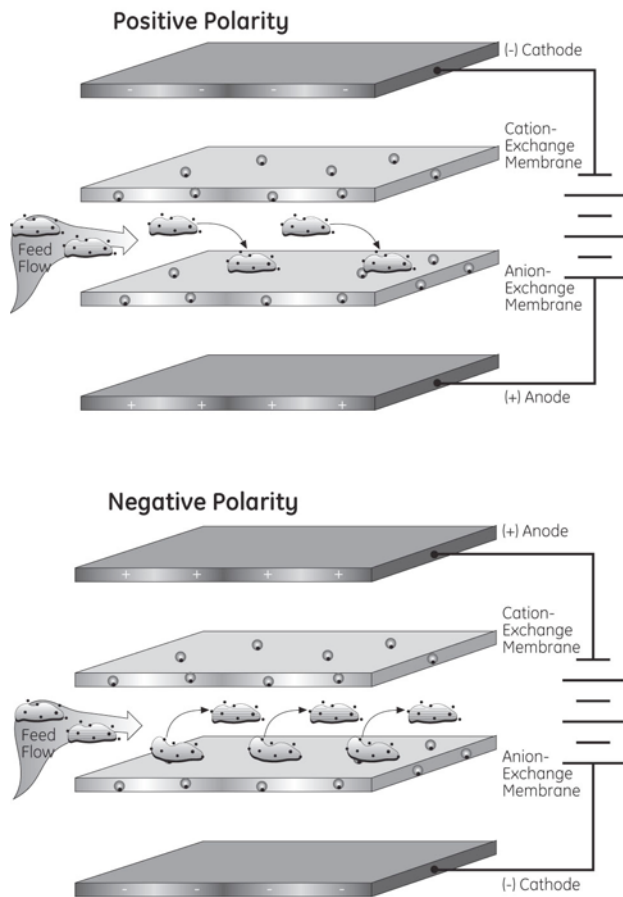


Figure 3: Colloid Deposition and Removal Forces in EDR

In an ED or EDR system the applied DC power is the driving force that moves the particles towards the anion exchange membrane where a deposit can form. Figure 3 shows the deposition force and how in EDR the periodic reversal of the applied DC power reverses the driving force for deposition into a driving force for deposit removal.

Until the middle 1990s, EDR systems employed “tortuous flow path” spacers. The .040-inch thickness, open flow path design and flow velocity of about three times that in RO systems was thought to be a significant contributor to the higher suspended solids tolerance than spiral wound RO. In the mid 90s, a new 0.030-inch thick sheet flow spacer was developed for EDR.³ This spacer employs a plastic screen similar to that used as a feed spacer in spiral wound RO elements. The flow velocity through the spacer is also similar to that in a RO element. There are currently 31 plants with a combined capacity of 22.4 mgd (85,000 m³/day) using these new spacers. Over 16 mgd (61,000 m³/day) of this capacity is treating surface and

waste waters. The tolerance of the systems using these spacers for turbidity in the feed is proving to be equal to the older tortuous spacer design.

With over 1,500 ED and EDR plants installed around the world, it is inevitable that a few have been operated with feed turbidities over 0.5 NTU. EDR plants will survive short term operation at higher turbidities, but will foul if operated for extended time over this limit. As with RO systems, severe deposits are very difficult to impossible to remove with a chemical solution cleaning. EDR stacks are made to be disassembled for maintenance if needed. It takes two people about 8 hours to disassemble, hand clean the components and reassemble a full size EDR stack. This is a job that can be done by unskilled workers. The largest EDR plant that has required manual cleaning is a 3-mgd plant with 72 stacks, that became fouled about 10 years ago due to clarifier problems. The plant was cleaned in 14 days with 10 hired manpower people and one supervising field engineer. The plant availability was kept at 75% during the day shift when the work was being done and at 100% when work was not being performed. The cost for this cleaning effort was about \$20,000.

Cation Exchange Membranes

The cation exchange membranes used in EDR were based on styrene divinyl benzene chemistry up to 1991, when acrylic-based cation exchange membranes were introduced to service. Both types of cation exchange membranes are tolerant to chlorine residuals in the feed water. Free chlorine in water has two forms. These are unionized hypochlorous acid and hypochlorite anion. As there is no cationic form of chlorine in water, the chlorine does not get into cation membranes to chemically attack the resin.

We have not seen organic fouling in either type cation membrane when operated on surface waters or municipal waster waters. Prior to 1991, we did use a cationic dye with benzene rings in it's structure to permanently mark cation membranes. The dye washed out of the newer acrylic membranes within one hour when placed in water. We had to develop a new marking system.

It is typical for cation membranes to have very long life in EDR plants. Failures, when they happen, are

due to physical damage from rough handling and scaling events. Most of the cation membranes in the Foss plant for example, are original after 27 years of operation. An analysis in 1999 showed the membrane properties still met original QC specifications.

Conclusion

EDR has been successfully desalting surface and waste waters for four basic reasons. The process is tolerant to the turbidity values that can be routinely achieved using clarification and media filtration processes. The membranes have tolerance for continuous exposure to effective levels of oxidizing disinfectants to assure biological fouling will not be a problem. The membranes are extremely resistant to irreversible fouling by dissolved organic material found in surface and waste waters and there are effective methods to recover the systems from physical and chemical fouling problems should they occur. These capabilities have been proven in plants for the past 20 years, and continue to be proven by the many plants that continue in operation.

References

1. Wangnick, K., "2000 IDA Worldwide Desalting Plants Inventory Report," No. 16; Int'l Desalting Association, Dec. 31,1999.
2. Standard Test Method for "Silt Density Index (SDI) of Water", D 4189-95, American Society for Testing and Materials, Vol. 11.01 Water, 2000, pp. 395 - 397.
3. von Gottberg, A., "New High Performance Spacers in Electrodialysis Reversal (EDR) Systems," Proceedings, American Water Works Assoc. Annual Conf., Dallas TX, 1998.