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Surface and Wastewater Desalination by Electrodialysis Reversal

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Introduction

In the past ten years Electrodialysis Reversal (EDR) has earned a reputation as a membrane desalination process that works economically and reliably on surface and wastewaters. EDR systems are routinely desalting river and lake waters in industrial and municipal applications. They are also operating on cooling tower blowdowns, industrial wastes and municipal wastewaters, in a variety of reuse and zero waste discharge programs.

The reason EDR is successful in these applications is a combination of equipment design and membrane properties. Equipment design permits routine operation at higher levels of turbidity and silt density index (SDI) than other membrane desalination equipment. The design also allows disassembly and manual cleaning if particulate fouling should occur. The membranes have substantial resistance to oxidizing disinfectants, are not affected by exposure to pH values of 0 to 10, and have extreme resistance to irreversible fouling by organics. This combination allows EDR to operate on these waters with economical pretreatment and survive when pretreatment systems do not operate as intended.

Physical Design and Colloidal Fouling

Deposition and Removal Forces

Membrane desalination equipment generally produces 10 to 25 gallons per day of product water per square foot of active membrane area. If the equipment size and capital cost is to be kept at a practical minimum, then the water must be desalted in small passages manufactured at low cost. Typically the passage thickness ranges from .015 to .040 inches.

Membrane processes, by their nature, have driving forces that tend to deposit colloidal material on the membrane surface. In reverse osmosis this is a flow of water perpendicular to the membrane in the boundary layer as it approaches the membrane to pass through. When the particles reach the membrane surface the water flows through the membrane and other forces tend to hold the deposit in place.[1]

Colloidal particulates interact with water to form an effective charge at the surface of their bound water layer. This charge is negative in natural and most wastewaters. The DC electric power field applied to electrodialysis stacks is a driving force that moves colloids toward the anion membrane. When the particles reach the membrane surface, the electric field and electrostatic attraction to ion exchange sites in the anion exchange membrane tend to hold the deposit in place as shown in Figure 1.

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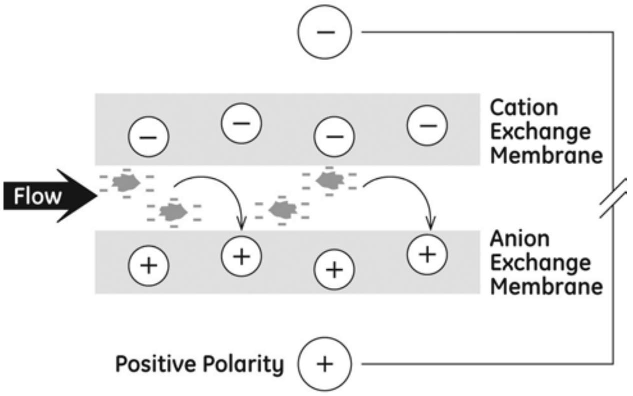

Figure 1: Colloidal Deposition Force in EDR

EDR employs periodic reversal of the DC electric field. Typical field reversal frequencies range from 15 to 30 minutes. When the field is reversed, the electric driving force is reversed, which tends to remove deposited colloids into the brine stream as shown in Figure 2.

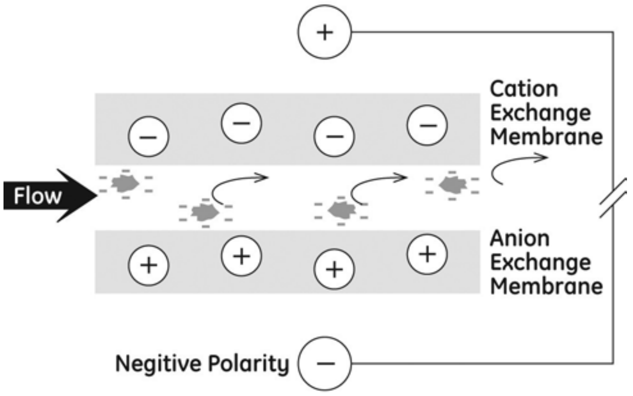

Figure 2: Colloidal Removal Force in EDR

EDR Feedwater Colloid Limits

Because the mechanisms for depositing and holding colloids on the membrane surface in EDR equipment depend on the degree of charge on the particles, precise limits for turbidity or SDI cannot be defined for EDR as a general limit. Colloidal fouling has never been experienced below a feedwater five minute SDI of 12, while fouling is likely if the five-minute SDI is above 16. These values generally correspond to turbidities of 0.25 to 0.50 NTU. Exceptions do occur; a few EDR plants have operated for sustained periods of several months with feedwater five-minute SDI values in excess of 19 without problems.

Colloids and Spacer Design

The spacer design also helps reduce colloidal fouling. Many desalination membranes are very thin and require considerable supporting structure. Most manufacturers use plastic screens to provide this support and form the flow channel. The screen structure helps hold deposited colloids in place.

EDR membranes are three times thicker than most membranes and are quite rigid. This allows the use of tortuous flow path spacers that are manufactured from polyethylene sheet stock and have no membrane support structure in the flow paths. These spacers have cross straps, which are needed to give the spacer physical integrity and are, positioned to optimally promote turbulence which helps minimize colloidal deposition. The .040-inch thickness of EDR spacers is greater than the typical spiral wound reverse osmosis thickness of .030 inches and the thickness of some electrodialysis spacers that are as thin as .015 inches. The overall result is a spacer design that provides uniform turbulent flows essential to optimum operation that minimizes the effects of deposits on system pressure drop and the potential for solids entrapment.

Removal of Colloidal Deposits

EDR systems are assembled in "stacks" which can be disassembled for inspection, repair or cleaning. Some surface and wastewater plants have had events of severe colloidal fouling. Tests were conducted, with before and after stack inspections, on a variety of generic and proprietary cleaners for removing colloidal deposits. These tests appeared effective as the cleaning solutions became turbid and colored. Equipment performance also improved, but only temporarily for periods of a few days to a week or more. Stack inspections revealed that little deposit was actually removed by these cleaners.

Some of this experimentation was performed on a 300,000 gpd plant located overseas. This plant was installed in 1984 to demineralize municipal water supplied from reservoirs in a boiler feed application. On site pretreatment was single media sand filtration with no chemical feed. The plant severely fouled after 2000 hours of operation with colloidal clay deposits. Investigation determined that the five-minute SDI was over 19 after the sand filter. The filtration was not removing the colloidal particles that ranged in size from 0.2 to 5 microns in size.

The problem was solved in three days by manually cleaning the membranes and converting to contact filtration using 0.27 mg/l of a cationic polymer dosed before the filter. The customer reported in 1990 that the cleaning procedure never had to be repeated.

Manual cleaning of EDR stacks can be performed by unskilled labor at a small fraction of the cost of replacing membranes in systems that do not have this cleaning option. In the 300,000 gpd example above, 96 man hours were required to complete the cleaning. At $10 per hour, this amounts to a cost of $960.

Membrane Properties

Acid Resistance

The membranes also have important properties that contribute to the success of EDR plants treating surface and wastewaters. EDR membranes are unaffected by pH exposures of pH 0-10. This allows the use of strong acid solutions to remove scales and metal hydroxide deposits. A 5% hydrochloric acid solution is a standard cleaning solution for EDR systems.

Recently a major EDR plant had a problem with a pretreatment upset from overdosed alum in the clarifier. The floc was weak and broke through the media filters entering the EDR system. The floc fouled the system increasing pressure drop through the stacks and reducing the desalting performance. A short 1/2 hour flush with a 3% hydrochloric acid solution removed the deposit and fully restored performance.

Anion exchange membranes used in electrodialysis equipment were based on styrene divinyl-benzene chemistry developed originally by the ion exchange industry. Membranes based on this chemistry have two major problems when used in equipment treating surface and wastewaters. The first problem is poor resistance to chlorine. Secondly, they become irreversibly fouled by organic materials. In 1981 acrylic based anion exchange membranes, which overcome these problems and have superior performance, were introduced to EDR service.

Oxidizing Disinfectant Tolerance

Membrane desalination systems, with their small passages, are likely to have problems with bacterial growths when treating these waters if a disinfectant residual is not maintained. The acrylic based anion exchange membranes have substantial resistance to chlorine. Figure 3 shows ion exchange capacity data from a comparative test where both membrane types were operated with 10 mg/l of free residual chlorine in the feedwater. After 1,000 hours the styrene divinyl-benzene based membrane was seriously degraded. Systems using these membranes need residuals below 0.1 mg/l for long life. The acrylic based membrane shows only relatively minor capacity loss after 4,000 hours of operation. With this chlorine tolerance, EDR systems are operated with an average of 0.3 to 0.5 mg/l of free chlorine residual in the feedwater, which has proven to be very effective for controlling bacterial growth. Much higher residuals can be used for shorter periods for sterilization and other purposes.

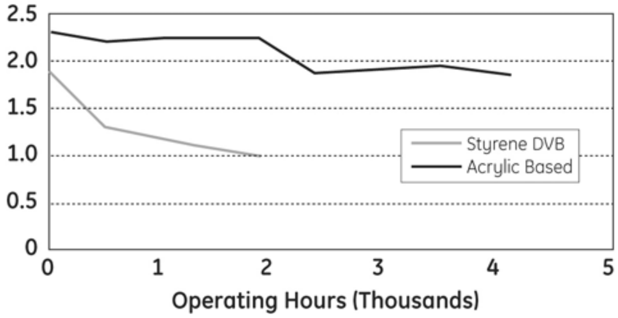

Figure 3: Ion Exchange Capacity vs. Operating Hours at 10 mg/l of Free Chlorine

In 1985 a new 300,000 gpd plant was fouled with a poly (DADMAC) cationic polymer when approximately 200 mg/l was dosed to the clarifier on the first day of operation. Salt removal was reduced from 75% to 30% within a few hours. While this polymer has good chlorine tolerance, circulation of a water solution maintained at 25 mg/l free residual chlorine for a couple of hours, fully restored performance to design levels. Subsequent analysis of the membranes showed no degradation and they are still in service.

The reactions of chlorine with organics to form trihalomethanes (THMS) and organic halides (TOX) have created a lot of interest in alternate disinfectants. Chloramines do not harm the acrylic-based membranes. In some wastewater applications, levels of total residual chlorine have been measured repeatedly at levels of 10 to 20 mg/1.

Ozone has not been tested on membranes directly, but is likely to cause damage. A 600,000 gpd EDR plant has been operating for 7 years on water pretreated with ozone. There is no treatment to remove the ozone, but there is no measurable residual when the water reaches the equipment. The membranes have never been replaced.

Hydrogen peroxide has been used routinely in one plant as a cleaner for about 15 years. It does not harm styrene divinyl-benzene or acrylic-based membranes. Potassium permanganate also does not harm membranes but can cause manganese dioxide deposits on the membranes and electrodes. Manganese dioxide can be dissolved by hydrochloric acid, but the concentration needs to be at lease 15% to be effective. While it is possible to flush an EDR system with this concentration of acid the procedure has never actually been used. Chlorine dioxide is not currently used in any EDR facility. Tests show cation and acrylic-based anion exchange membranes are unaffected by exposure to 100,000 ppm hours.

Organic Fouling

Irreversible organic fouling of styrene divinyl-benzene based anion exchange membranes limits useful membrane life to one to five years on surface waters and possibly much less on some wastewaters. The high affinity these resins have for organics prevents full removal by any known means. The acrylic-based anion exchange membranes have a lower affinity for organics. Flushing these membranes with a 3 to 5% sodium chloride brine effectively removes fouling.

Figure 4 shows acrylic-based anion exchange membrane data from a plant operating on Mississippi River water in Louisiana. The “as received” electrical resistance of the membrane in the active flow area is nearly twenty times that of the unexposed and unfouled edge area. The membrane sample was then treated in 2 n hydrochloric acid and 2 n sodium chloride solutions, which are procedural steps for further analysis. After this treatment, the membrane resistance is measured with the membrane in equilibrium with .01 n sodium chloride. The resistance in the now path area is only slightly higher than the edge area indicating effective removal of the organic foulant. The ion exchange capacity for the edge and flow path area are nearly equal, also indicating foulant removal. Water content of membranes decreases with organic fouling due to displacement by the foulant. The water content data shows no evidence of foulant.

Property	Edge Area	Flowpath Area
As Rec'd Resistance (ohm/cm2)	21.9	435.0
Recovered Resistance (ohm/cm2)	12.5	14.1
Ion Exchange Capacity (Meq/dry gm)	2.29	2.25
Water Content	47.0%	47.3%

Figure 4: Analysis of Acrylic-Based Anion Membranes with Reversible Organic Fouling

This plant was commissioned in 1985. The analysis was performed in 1987 after 1,500 hours of operation without any cleaning. The plant is presently operating with its original membranes. Fouling is controlled by monthly flushes with sodium chloride brine.

Figures 5 and 6 present data from both types of membranes operated on a moderately fouling water. All data shown is after the treatment in hydrochloric acid and sodium chloride. Clearly the styrene divinyl-benzene based membrane increases in electrical resistance and decreases in

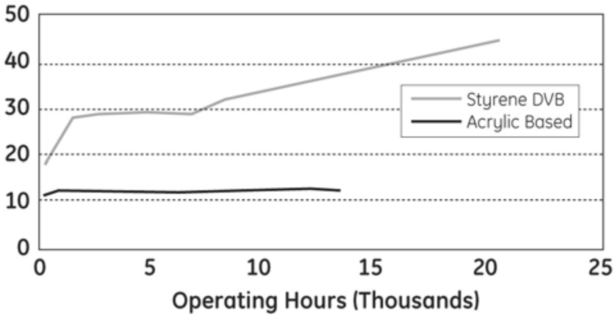

Figure 5: Electrical Resistance Effects of Organic Fouling on Anion Resin Membranes

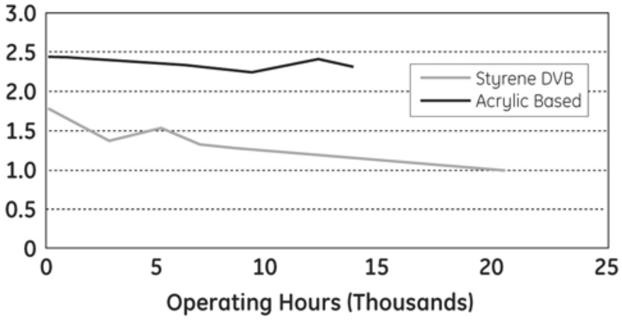

Figure 6: Ion Exchange Capacity Effects of Organic Fouling on Anion Resin Membranes

ion exchange capacity with increasing operating time. There was little effect on the acrylic based membrane.

This test was conducted between 1978 and 1981. In 1982, the plant was equipped with the new anion exchange membranes. A performance analysis conducted in November 1990 showed that after eight years of operation, performance had not measurably deteriorated.

In 1980 a 100,000 gpd plant was installed in Texas to treat municipal water derived from surface sources in a boiler feed application. After 14 months of operation, performance had seriously declined. Analysis of the styrene divinyl-benzene based anion exchange membranes showed acid and salt flushes could return the ion exchange capacity to 50% of its original value. The electrical resistance could not be restored, and remained three times greater than normal. The membranes were seriously and irreversibly fouled by organics. The new acrylic-based anion exchange membranes were installed as replacements. These membranes were operated for nine years with no irreversible fouling.

Additional Applications

The first major cooling tower blowdown recovery EDR installation is installed at Eskom's Tatuka power station in Southern Africa. The EDR feed is taken from the effluent of a side stream softening clarifier. The 1.15 mgd of product is returned to the cooling tower. The 290,000 gpd of brine is further concentrated in evaporators and then used for coarse ash quenching and fly ash conditioning.[2] The plant, which has been in operation for six years, is now being expanded to 3.4 mgd to meet the full needs of this 3,600 MW power station. Additional EDR systems are now in operation and under construction for similar applications.

Reclamation of biologically treated wastewaters is a more recent application of EDR. Several pilot studies showed EDR works on these waters. In Italy 2400 hours of pilot testing was performed on biologically treated refinery wastewater.[3] Based on the results, a 1.08 mgd plant was installed to recover this water for use as boiler feed. The plant has been in operation for two years without significant problems.

In the Middle East a 317,000 gpd plant recovers a blend of 60% secondary treated municipal wastewater and 40% cement manufacturing wastewater. On site pretreatment consists of chlorination, clarification and multimedia filtration. The plant is in its sixth year of operation with the original membranes.

Newer plants are now in operation on similar applications. A 1 mgd facility in the Far East and a 300,000 gpd system in Texas are now in operation recovering municipal wastewaters for industrial use.

Conclusion

To date, over 40 EDR systems are treating surface and wastewaters around the world. Five surface water and three wastewater facilities have production capacities in excess of 1 mgd. Pretreatments range from simple contact filtration with chlorination to clarification and filtration with lime softening. Not one of these plants has had to replace cation or acrylic anion membranes as a result of colloidal bacterial, organic, metals or polymer fouling. In addition, no plant has required membrane replacements due to attack by oxidizing disinfectants. While a few plants have required disassembly and washing to remove deposits when serious pretreatment problems have occurred, many plants have never been cleaned in this manner. These are the reasons EDR has a reputation as a membrane process that works on surface and wastewaters.

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