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Electrodialysis Technology. Theory and Applications.

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1. Introduction

First commercial equipment based on Electrodialysis (ED) technology was developed in the 1950s to demineralize brackish water (Juda & McRae, 1950; Winger et al. 1953). Since then ED has advanced rapidly because of improved ion exchange membrane properties, better materials of construction and advances in technology. In the 1960s, Electrodialysis Reversal (EDR) was introduced, to avoid organic fouling problems (Mihara & Kato, 1969). Over the past twenty years EDR has earned a reputation as a membrane desalination process that works economically and reliably on surface water supplies, reuse water and some specific industrial applications when designed and operated properly.

Some applications of ED/EDR were its use to reduce inorganics like radium (Hays, 2000), perchlorate (Roquebert et al., 2000), bromide (Valero & Arbós, 2010), fluoride (GE W&P, 2010), iron and manganese (Heshka, 1992) and nitrate (Menkouchi Sahlia et al., 2008) in drinking water. In addition the technology can be used to recycle municipal and industrial wastewater (Broens et al., 2004; Chao & Liang, 2008), recovering reverse osmosis reject (Reahl, 1990; Korngold, 2009), desalting wells (Harries et al., 1991), surface waters (Lozier et al. 1992), final effluent treatment for reuse in cooling towers (De Barros, 2008), whey and soy purification (MEGA a.s., 2010), table salt production (Kawahara, 1994) and many other industrial uses (Schoeman & Stein, 2000; Dalla Costa et al., 2002; Pilat, 2003). For this kind of applications, this technology had shown best hydraulic recovery and cost effective in front of other membrane technologies, specially compared with Reversal Osmosis (RO). In these sense, the lower residues produced during ED/EDR process, is another important advantage of this technique (AWWA, 2004). Moreover, electrodialysis is not always a cost effective option for seawater desalination and does not have a barrier effect against microbiological contamination.

This chapter reviews some aspects related with the theory of the technology, design, operation and maintenance (O&M), manufacturers, applications, operational costs and finally shows two cases studies involving the two world's biggest EDR systems, both located near to Barcelona (Spain). The first of them is located in Abrera (Valero et al., 2007) with a capacity of treatment of 220,000 m³/d (576 stacks in two stages, provided by GE Water & Process) and it is related with desalting brackish water to improve the quality of the produced drinking water. The second one is located in Sant Boi del Llobregat (Segarra et al., 2009) with a capacity of treatment of 57,000 m³/d (96 stacks in two stages, provided by MEGA a.s.) and represents a tertiary treatment of a wastewater treatment plant (WWTP) for agricultural reuse.

2. Theory

ED is an electrochemical separation process in which ions are transferred through ion exchange membranes by means of a direct current (DC) voltage. The process uses a driving force to transfer ionic species from the source water through cathode (positively charged ions) and anode (negatively charged ions) to a concentrate wastewater stream, creating a more dilute stream (Figure 1).

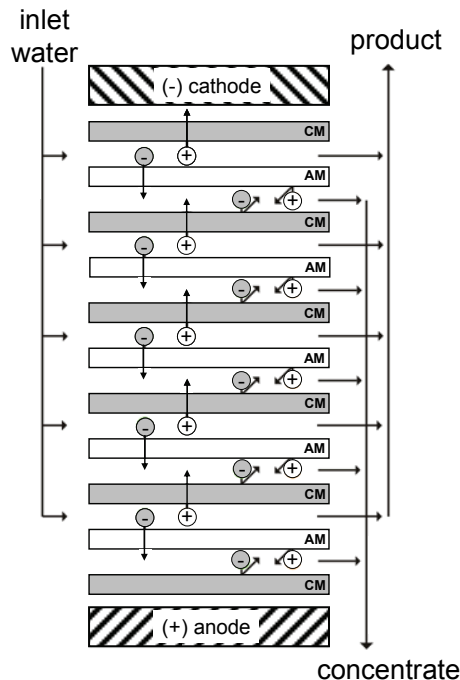


Fig. 1. Principles of ED

ED selectively removes dissolved solids, based on their electrical charge, by transferring the brackish water ions through a semi permeable ion exchange membrane charged with an electrical potential. It points out that the feed water becomes separated into the following three types of water (AWWA, 1995):

- product water, which has an acceptably low conductivity and TDS level;
- brine, or concentrate, which is the water that receives the brackish water ions; and
- electrode feed water, which is the water that passes directly over the electrodes that create the electrical potential.

EDR is a variation on the ED process, which uses electrode polarity reversal to automatically clean membrane surfaces. EDR works the same way as ED, except that the polarity of the DC power is reversed two to four times per hour. When the polarity is reversed, the source water dilute and concentrate compartments are also reversed and so are the chemical reactions at the electrodes. This polarity reversal helps prevent the formation of scale on the membranes. The setup is very similar to an ED system except for the presence of reversal valves (Ionics Inc., 1984).

2.1 Membrane stacks

All ED and EDR systems are designed specifically for a particular application. The amount of ions to be removed is determined by the configuration of the membrane stack. A membrane stack may be oriented in either a horizontal or vertical position.

Cell pairs form the basic building blocks of an EDR membrane stack (Figure 1). Each stack assembled has the two electrodes and groups of cell pairs. The number of cell pairs necessary to achieve a given product water quality is primarily determined by source water quality, and can design stacks with more than 600 cell pairs for industrial applications (Strathmann, 2004).

A cell pair consists of the following:

- Anion permeable membrane
- Concentrate spacer
- Cation permeable membrane
- Dilute stream spacer

In each stack, we can observe different flows (Figure 2):

1. Source water (feed) flows parallel only through demineralizing compartments, whereas the concentrate stream flows parallel only through concentrating compartments.
2. As feed water flows along the membranes, ions are electrically transferred through membranes from the demineralized stream to the concentrate stream.
3. Flows from the two electrode compartments do not mix with other streams. A degasifier vents reaction gases from the electrode waste stream.
4. Top and bottom plates are steel blocks that compress the membranes and spacers to prevent leakage inside the stack.

Effluent from these compartments may contain oxygen, hydrogen, and chlorine gas. Concentrate from the electrode stream is sent to a degasifier to remove and safely dispose of any reaction gases.

The first type of commercial ED system was the batch system. In this type of ED system, source water is recirculated from a holding tank through the demineralizing spacers of a single membrane stack and back to the holding tank until the final purity is obtained. The production rate is dependent on the dissolved minerals concentration in the source water

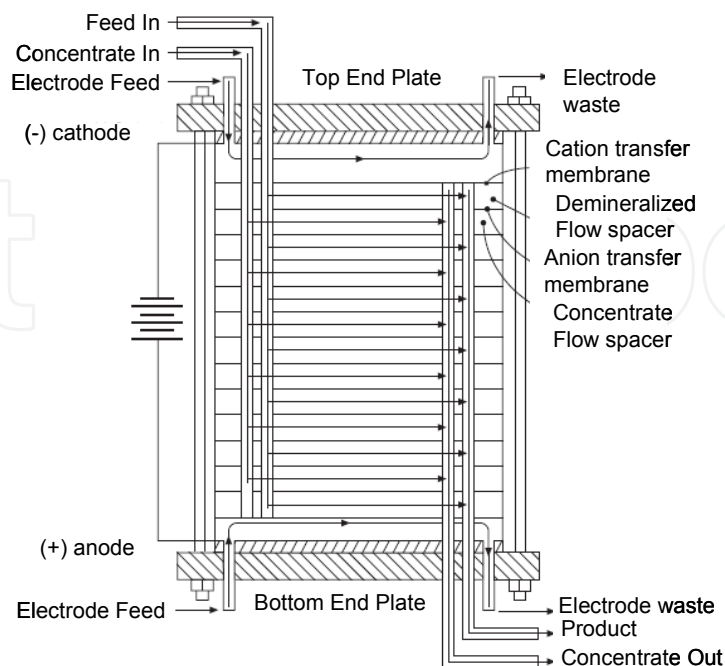


Fig. 2. Stack description (Ionics Inc., 1984)

and on the degree of demineralization required. The concentrate stream is also recirculated to reduce wastewater volume, and continuous addition of acid is required to prevent membrane stack scaling.

The second type of commercially available system was the unidirectional continuous-type ED. In this type of system, the membrane stack contains two stages in series; each stage helps demineralize the water. The demineralized stream makes a single pass through the stack and exits as product water. The concentrate stream is partially recycled to reduce wastewater volume and is injected with acid to prevent scaling. EDR was patented in 1969 (Mihara & Kato, 1969) and is a variation of this system which uses electrode polarity reversal to automatically clean membrane surfaces.

2.2 Membranes

The membranes are produced in the form of foils composed of fine polymer particles with ion exchange groups anchored by polymer matrix. Impermeable to water under pressure, membranes are reinforced with synthetic fiber which improves the mechanical properties of the membrane (AWWA, 1995).

The two types of ion exchange membranes used in electro dialysis are:

- Cation transfer membranes which are electrically conductive membranes that allow only positively charged ions to pass through. Commercial cation membranes generally consists of crosslinked polystyrene that has been sulfonated to produce $-\text{SO}_3\text{H}$ groups attached to the polymer, in water this group ionizes producing a mobile counter ion (H^+) and a fixed charge ($-\text{SO}_3^-$).
- Anion transfer membranes, which are electrically conductive membranes that allow only negatively, charged ions to pass through. Usually, the membrane matrix has fixed positive charges from quaternary ammonium groups ($-\text{NR}_3^+\text{OH}^-$) which repel positive ions.

Both types of membranes shows common properties: low electrical resistance, insoluble in aqueous solutions, semi-rigid for ease of handling during stack assembly, resistant to change in pH from 1 to 10, operate temperatures in excess of 46°C , resistant to osmotic swelling, long life expectancies, resistant to fouling and hand washable.

The membranes are permselective (or ion selective) that refers to their ability to discriminate between different ions to allow passage or permeation through the membrane. In these sense membranes can be tailored to inhibit the passage of divalent anions or cations, such as sulfates, calcium, and magnesium. For example, some membranes show good permeation or high transport numbers for monovalent anions, such as Cl^- or NO_3^- , but have low transport numbers and show very low permeation rates for divalent or trivalent ions, such as SO_4^{2-} , PO_4^{3-} , or similar anions. This is achieved by specially treating the anion membrane, and the effect can be exploited to separate various ions. The relative specificities vary, with the monovalent anion membrane showing the greatest specificity, for example, the ratio of chloride to sulfate ion transport numbers. (Xu, 2005).

It depends on the manufacturer by usually each membrane is 0.1 to 0.6 mm thick and is either homogeneous or heterogeneous, according to the connection way of charge groups to the matrix or their chemical structure (Xu, 2005). In the case of homogeneous membranes, charged groups are chemically bonded and for heterogeneous they are physically mixed with the membrane matrix. Different manufacturers of ion exchange membranes are available in the market (Table 1). Each one offers membranes for specific applications, and they have different properties involving, size, thickness, area resistance and composition.

Manufacturer/Reference	Country	Commercial brand
Asahi Chemical Industry Co.	Japan	Aciplex
Asahi Glass Col. Ltd	Japan	Selemion
DuPont Co.	USA	Nafion
FuMA-Tech GmbH	Germany	Fumasep
GE Water & Process	USA	AR, CR,..
LanXess Sybron Chemicals	Germany	Ionac
MEGA a.s.	Czech Republic	Ralex
PCA GmbH	Germany	PC
Tianwei Membrane Co.Ltd.	China	TWAED
Tokuyama Co-Astom	Japan	Neosepta

Table 1. Main manufacturers of ion exchange membranes.

2.3 Spacers

The spaces between the membranes represent the flow paths of the demineralized and concentrated streams formed by plastic separators which are called demineralized and concentrate water flow spacers respectively. These spacers are made of polypropylene or low density polyethylene and are alternately positioned between membranes in the stack to create independent flow paths, so that all the demineralized streams are manifolded together and all the concentrate streams are manifolded together too.

Demineralizing and concentrating spacers are created by rotating an identical spacer 180°. Demineralizing spacers allow water to flow across membrane surfaces where ions are removed, whereas concentrating spacers prevent the concentrate stream from contaminating the demineralized stream.

There is a spacer design with a “tortuous path” in which the spacer is folded back upon it self and the liquid flow path is much longer than the linear dimensions of the unit. Another kind of spacers is a “sheet flow” that consists of an open frame with a plastic screen separating the membranes. These spacers are operated at lower flow velocities, to achieve a degree of desalting in each pass through the stack, comparable to the tortuous path or sheet flow spacers. In general the increase of turbulence promotes mixing of the water, use of the membrane area, and the transfer of ions. Turbulence resulting from spacers also breaks up particles or slime on the membrane surface and attracts ions to the membrane surface. Flow velocity ranges from (18 to 35 cm/s, creating a pressure drop between the inlet and outlet. A velocity less than 18 cm/s promotes polarization, or the point of limiting density of water (AWWA, 1995).

Maximum pressure for ED and EDR systems is generally limited to 50 psi (345 kPa), and pressure is lost at each stage of the system. Since pressure must be maintained throughout the system, the impact of spacers on pressure is an important design consideration.

Different models and sizes of spacers satisfy specific design applications. The main difference in spacer models is the number of flow paths, which determines water velocity across the membrane stack and contact time of the source water with the membrane. Since water velocity is responsible for the degree of mixing and the amount of desalting that occurs across membranes, velocity is an important design parameter for spacer choice. Because the same spacers are used for both demineralized and concentrated water in EDR

systems, the flow rates of both these streams should be equalized to prevent high differential pressures across the membranes.

2.4 Electrodes

A metal electrode at each end of the membrane stack conducts DC into the stack. Electrode compartments consist of an electrode, an electrode water-flow spacer, and a heavy cation membrane. The electrode spacer is thicker than a normal spacer, which increases water velocity to prevent scaling. This spacer also prevents the electrode waste from entering the main flow paths of the stack (Ionics, 1984).

Because of the corrosive nature of the anode compartments, electrodes are usually made of titanium and plated with platinum. Its life span is dependent on the ionic composition of the source water and the amperage applied to the electrode. Large amounts of chlorides in the source water and high amperages reduce electrode life. Polarity reversal (as in EDR) also results in significantly shorter electrode lifetimes than for nonreversing systems (AWWA, 1995).

2.5 Operation

When DC potential is applied across the electrodes, the following take place (AWWA, 1995):

At the cathode, or negative electrode (-):

- Cations (Na^+) attraction
- Pairs of water molecules break down (dissociate) at the cathode to produce two hydroxyl (OH^-) ions plus hydrogen gas (H_2). Hydroxide raises the pH of the water, causing calcium carbonate (CaCO_3) precipitation.

And at the anode, or positive electrode (+):

- Anions (Cl^-) attraction
- Pairs of water molecules dissociate at the anode to produce four hydrogen ions (H^+), one molecule of oxygen (O_2), and four electrons (e^-). The acid tends to dissolve any calcium carbonate present to inhibit scaling.
- Chlorine gas (Cl_2) may be formed.

Colloidal particles or slimes that are slightly electronegative may accumulate on the anion membrane and cause membrane fouling. This problem is common to all classes of ED systems. These fouling agents are removed by flushing with cleaning systems. In EDR systems, the polarity of the electrodes is reversed two to four times each hour. When polarity is reversed, chemical reactions at the electrodes are reversed. Valves in the electrode streams automatically switch flows in the two types of compartments. Streams that were in demineralizing compartments become concentrate streams, and concentrate streams become demineralizing streams. The alternating exposure of membrane surfaces to the product dilute and brine concentrate streams provides a self-cleaning capability that enables purification and recovery higher than 90% of source water, reducing the burden on water sources, and minimizing the volume of waste that requires disposal (AWWA, 2004).

2.6 Design

In commercial practice, the basic apparatus for ED/EDR is a stack of rectangular membranes terminated on each end by an electrode. Flow of the process streams is contained and directed by spacers that alternate with the membranes. The membranes are arranged alternately cation and anion. The assembly of membrane spacers and electrodes is

held in compression by a pair of end plates. The apparatus thus resembles a plate-and-frame filter press. Stack is completed with pumps, piping and an electrical subsystem that includes: adjustable DC power supply, rectifiers to convert alternating current (AC) power to DC power, internal control system with controls, reversal timing (only for EDR), and alarms.

The design of an ED/EDR plant is based on the product water requirements of the application and the characteristic of the inlet water to be treated (Tsiakis & Papageorgiou, 2005). The parameters, which characterize the working optimum of an EDR, are the values of the applied voltage used in the electrical stages and the feed water pressure corresponding to the maximum separation percentage and minimum energy consumption. These values were obtained from the surfaces corresponding to separation percentage and consumed power versus applied voltage and pressure. It could be important to carry out a pilot study before the industrial design of the system (Valerdi-Pérez et al., 2001). Along the pilot study, operators had to check the quality of the product in different conditions, focused in the behaviour of several limiting parameters characterizing an ED/EDR system (Ionics, 1984):

- Limiting Current Density (Polarization)
- Current Leakage
- Back Diffusion
- Langelier Saturation Index
- Calcium Sulfate Saturation
- Pressure Drop
- Differential Pressure
- Water Transfer
- Temperature Limits

With these data, ED and EDR plants can be designed to remove from 50 to 99 percent of source water contaminants or dissolved solids. Source water salinities of less than 100 mg/L up to 12,000 mg/L TDS can be successfully treated to produce finished water of less than 10 mg/L TDS.

To calculate the efficiency of the process during the design step, we have to take into account the Faraday's Law. In these sense, the passage of 96,500 amperes of electric current for one second will transfer one gram equivalent of salt. One Faraday is equal to 96,500 ampere-second and that is equal to 26,8 amperes, of current passing for one hour. Thus, when 26.8 ampere-hours, one gram equivalent of salt will be transferred in each cell pair, we have a process 100 percent efficient. To determine the voltage requirements for a given system, the current is determined from Faraday's Law and the resistance is determined by the components of the membrane stack and the solution under treatment, according to the Ohm's Law (Lee et al, 2006; Valerdi-Pérez & Ibañez-Mengual, 2001).

Typically, maximum salt removal for any hydraulic stage is 55-60 percent with normal design values at 40-50 percent. To increase the amount of salt removal in a EDR system, additional hydraulic stages must be incorporated. Then in systems where high capacities are required, additional hydraulic stages are made by simply adding more stacks in series to achieve the desired water purity (Larchet et al, 2008).

In addition, to increase water recovery some functions can be incorporated into the EDR system to take advantage of a substantial increase in recovery and production rates at minimal costs. In this sense, three main flows can be recycled: concentrate stream, off-

specification product and electrode stream. With those products, water can be recycled back to the system feed, eliminating the need to send it to waste. To achieve this water recovery, it could be necessary to dose some chemical into the system. In this sense, an antiscalant (1-5mg/L) can be added into the concentrate stream to control calcium scaling, and acid (HCl) is continuously feed into the electrode flow and into the concentrate stream to maintain the Langelier Saturation Index (LSI) at +1.8 for calcium carbonate control.

3. Maintenance

Scheduled maintenance depends on the use and application of the system and varies with each manufacturer. Nowadays, ED and EDR systems are designed with fully automated control systems. Thus O&M procedures are scheduled to check control settings and operating parameters, supported with detection systems that recognize operation levels or critical conditions.

Several setpoints are implemented to operate the system. In these sense, operators check the values and alarms related with temperature, conductivity, pH, current voltage, intensity, flows and pressures. Data are collected or logged for the different streams and, in the case of EDR, during positive or negative polarity.

It could be necessary to clean the membranes periodically. Cleaning is a means of removing mineral scale, organic matter, biological growth (slime), colloidal particles, or insoluble constituents which build up on the surface of the membrane. To prevent scaling and fouling, ED and EDR units are equipped with a clean-in-place (CIP) system to allow periodic flushing of the membrane stack and piping with an acid solution. A chemical feed pump and storage tank form the main components of the CIP system.

In ED systems, acid is continuously fed into the electrode stream of the cathode to prevent scaling. In EDR systems, on the other hand, electrode clean-in-place (ECIP) is a routine preventive-maintenance procedure to remove scale or fouling from the electrode system. In addition during the preventive maintenance a CIP process is a required procedure that flushes scale or reversible fouling from the membrane stack and hydraulic piping. The chemical solution circulated through the stack depends on the type of contamination. The following chemical solutions used in the CIP process are the only chemicals that should be used for stack cleaning (AWWA, 1995):

- Hydrochloric acid solution. Periodic cleaning with a 2 to 5 percent hydrochloric acid (HCl) solution is the most frequently used method to remove scale and biofouling.
- Sodium chloride solution. A 3 to 5 percent NaCl solution removes organic foulants, which are present in many surface waters, from the membranes. The solution should be at least 3 percent NaCl (0.55N chloride) and have a pH between 8.0 and 10.0, adjusted with NaOH. A pH greater than 11 can damage the anion membrane. This solution should then be circulated through the system. After the NaCl application, the operator should flush the membranes with HCl to remove excess salt.
- Chlorine solution. A 10- to 50-mg/L chlorine solution disinfects the membranes and hydraulic piping.

The use of chlorine is one of the advantages of ED/EDR membranes in front of other membranes technologies. They can operate on waters with up to 0.5 mg/L chlorine to control the biological nature of feed water, and can be shock-chlorinated up to 30 mg/L for maximum cleaning efficiency if required. Additionally, ED/EDR presents some other advantages, for example it is possible to repair and disassembly the stack and if it is

necessary, it is easy to manually clean the membranes or replace them. In these cases, stacks should not be allowed to remain dry for long periods of time because membranes may become damaged. Generally, disassembly requires that each piece be removed separately, with the exception of the top electrode, which can be replaced without the removal of any of the membranes. It is important to maintain correct component orientation and to store membranes in water. The stack should be rebuilt in the order it was disassembled; incorrect assembly can reduce performance or cause scaling.

Besides the cleaning procedure, the most frequent manual operation is to check the intermembrane voltage to prevent "hot spots" or current leakage. The intermembrane voltage has to be similar along the entire stack, and operators had to check it frequently. Excess current can melt or "burn" the membranes and spacers. Normal design practices limit this voltage to 80% of the current that would cause burning. The limit is determined by water temperature, conductivity of the source water, membrane stack size, and the internal manifold that splits flow into concentrate and dilute streams. When operators find increases of current in a located point, they had to check the voltage along some days to prevent a "hot spot".

4. EDR vs RO

Most of desalting processes are related with membrane pressure technologies in general and especially with RO. In this way, RO represents a worldwide solution for many desalination problems, but EDR could be a cost effective solution for many industrial applications of different size (Strathmann, 2010). The RO process requires extensive pretreatment, higher pumping power and more chemicals. RO also has a lower water recovery rate if the water has positive scaling tendencies.

Only EDR could be inappropriate in two cases: desalting sea water directly as drinking water (because is not cost effective) and if the problem to solve is a microbiological contamination (because EDR not provides a barrier effect). In the case of the emerging contaminants, it will depend of the chemical status of each compound, and it needs to check it.

Then it is possible to point out some advantages in favour of EDR in comparison with RO. Most of these advantages are included in O&M tasks, and are listed below (Strathmann, 2004, GE W&P, 2010):

1. The EDR system does not require high feedwater quality and is less sensitive to pre-treatment problem in comparison with an RO system. EDR system is able to operate with Silt Density Index (SDI) average of 12 compared to 3 for the RO system. High SiO₂ content water can be treated without forming precipitation on ion exchange membranes
2. The EDR system is capable of operating with a continuous free chlorine residual of up to 1 ppm. The RO system will require a dechlorination process to protect RO membrane from degradation by free chlorine oxidation. The EDR ability to operate with chlorine residual minimises biological fouling of the membrane in a more reliable system.
3. The EDR system has a nominal initial brackish water recovery in the range of 80%-90%. The RO system normally has a water recovery in a much lower range, 65%-75%. The high EDR water recovery reduces this project's feedwater usage and wastewater discharge cost.
4. The EDR membrane is not attacked by bacteria or affected by high temperatures. Therefore no special storage solutions are necessary for long term storage. The RO system requires special storage solutions and controlled storage temperatures. The EDR

membrane can be cleaned with acid and brine/caustic flush while the RO membrane requires special and expensive cleaning chemicals. It is important to determine if these chemicals can be discharged to the environment without further treatment.

5. The EDR rugged thick membrane technology has ensured membrane life of 7 to 10 years. The RO membrane is designed for 5-7 years due to the membrane sensitivity to various operating factors.
6. The reversal feature of the EDR system controls membrane scaling with no chemical addition. The RO system requires the addition of acid and a sequestering agent. The resulting waste from the RO system is highly acidic requiring caustic neutralisation and may not be discharged to the environment.
7. The EDR membrane can be manually cleaned without damaging the membrane properties. This is due to the "plate and frame" configuration. The RO membrane has a spiralwound configuration, it can not be cleaned manually, and therefore it must be replaced.

5. Applications

Over the last ten to fifteen years, numerous advances in membrane and system technology have made EDR an especially attractive technology, both in terms of performance and cost-effectiveness.

Many applications of EDR technology can be founded worldwide. From small installations that have only one stack to the biggest one equipped with 576 stacks. Different suppliers and applications are involved. Desalting process is applied mainly to brackish water process, tertiary wastewater production and specific industrial applications, ranging from mining to pharmaceutical and food & beverages industries.

Table 2, shows a list of some of the worldwide industrial installations. Different suppliers and membrane manufacturers are available. The biggest supplier is General Electric Water

LOCATION	COUNTRY	APPLICATION		Production m ³ /d	YEAR
EURODIA					
Montefano	Italy	Groundwater	Nitrate removal	1.000	1991
Munchenbuschsee	Switzerland	Groundwater	Nitrate removal	1.200	1996
Kleylehof	Austria	Groundwater	Nitrate removal	3.500	1997
GENERAL ELECTRIC WATER & PROCESS (formerly ionics Inc)					
Abrera, BCN	SPAIN	Surface water	bromide reduction	200.000	2008
Magna, Utah	USA	Groundwater	As, Perchlorate reduction	22.728	2008
Sherman, Texas	USA	Surface water	salinity reduction	27.700	1993-96-98
Suffolk, Virginia	USA	Groundwater	Fluoride reduction	56.000	1990
Sarasota, Or	USA	Groundwater	Hardness & salts reduction	45.420	1995
Maspalomas	SPAIN	Groundwater	salinity reduction	37.000	1986
Barranco Seco, Canary Is.	SPAIN	Waste Water	Reuse	26.000	2002
Bermuda WaterWorks	Bermudas	Groundwater	Hardness & Nitrate reduction	2.300	1989
Falconera, Valencia	SPAIN	Groundwater	Nitrate reduction	16.000	2007
MEGA a.s.					
Sant Boi, BCN	SPAIN	Waste Water	salinity reduction	55.296	2010
Dolni Rozinka	Czech Rep.	Uranium mining	Desalination of sludge	1.752	2007
ZIAR nad HRONOM	Slovakia	Waste water	Desalination of sludge	350	2003
Arak	Iran	Waste water	cooling tower	4.800	2008 -10
Alberta	Canada	Well water	Gas well water desalination	40	2008

Table 2. Some worldwide EDR systems

& Process (USA), that acquired Ionics Inc. in 2004. Ionics Inc. developed the first ED commercial system in the 1950s (Juda and Mc Rae, 1950). Now is it possible to use different suppliers of this technology, involving the whole system, or associated with membrane manufacturers as internal suppliers. In this sense, could cite: MEGA (Czech Republic), Eurodia (France), Hydrodex (Brasil) and Tecnoimpanti (Italy).

6. Case studies

We show two technical cases involved the biggest EDR plants for drinking water and reuse water for agricultural applications, respectively. Both are located near Barcelona (Spain). The first one is the Abrera Drinking Water Treatment Plant (DWTP) and the second the Depurbaix Waste Water Treatment Plant (WWTP).

6.1 Case study 1: The Abrera DWTP.

The Llobregat and the Ter rivers, typical Mediterranean catchments in Northeast Spain, supply water to more than 4.5 millions inhabitants residing in the metropolitan area of Barcelona. Aigües Ter Llobregat (ATLL) a public company of the Autonomous Government of Catalonia has been appointed to manage the system that includes two DWTP and one sea water reverse osmosis (SWRO) plant, with a whole capacity of continuous treatment of 14 m³/s.

The Abrera DWTP takes raw water directly from the Llobregat River. It presents a low and irregular flow and some quality problems such as high salinity with a significant presence of sulphates, Ba²⁺, Sr²⁺, Na⁺, Ca²⁺, K⁺, Cl⁻ and specially Br⁻ (Fernández-Turiel et al., 2000). Furthermore, many problems are associated with the increase in micropollutant and microbiological levels due to both urban and industrial sewage. These problems produce many interruptions of the process, some of them lasting many hours. Consequently, the high levels of bromide (ranging between 0.5-1.2 mg/L), NOM and T, produce high concentrations of trihalomethanes (THMs) after chlorination (Chang et al., 2001; Rook, 1977), showing a high brominated profile.

The total THMs represent the sum of the concentrations of four THMs; chloroform (CHCl₃), bromoform (CHBr₃), bromodichloromethane (CHBrCl₂), and dibromochloromethane (CHBr₂Cl). They have been regulated since 1998 in the European Union (Council Directive 98/83/CE), and in Spain since 2003, with a parametric value of 100 µg/L established in 2009 (Real Decreto 140/2003).

To minimize the THMs problem, ATLL searched for a new technology based on a membrane process. In this sense, the concern about THMs at the Llobregat DWTP has to do with changes in the treatment process, starting with enhanced coagulation in 1994, followed by the inclusion of a new step of GAC filtration in 1995, after sand filters. Subsequently, several changes have been carried out to improve the process. In 1999 ATLL carried out some trials using a pilot plant of Reverse Osmosis (RO) during a period of 6 months. The study showed that RO technology had a low recovery and certain instability due to the frequent shutdowns of the process because of the poor quality of raw water (floods, high turbidity, high fouling potential, chemical pollution...). Additional problems were the sensibility to high concentrations of sulphates, barium, calcium, alumina, and the disinfectant chlorine, that can be used at different points of the process. Later, to assess the reduction of the salts concentration (Kimbrough & Suffet, 2005) and consequently the THMs-Formation Potential (THMs-FP, 25°C, 48h), a pilot study was carried out during 28 months using a pilot plant of

EDR technology. Results showed that the EDR step improved the chemical and aesthetic quality of drinking water (Devesa et al., 2009, García et al., 2010) and allows a THMs-FP after 48h that is lower than the regulated level of 100 µg/L (Valero et al., 2007).

The final decision was the enlargement of the plant production from 3 m³/s to 4m³/s and the inclusion of a new EDR step after Granular Activated Carbon (GAC) filtration, with a production capacity of 2.3 m³/s. EDR takes feedwater from GAC step by means of a derivation of filtered water pipeline.

In addition, EDR permeates are aggressive showing a pH ranged between 6.5 and 7.3 and a LSI that varies between -1 and -2. Thus, a remineralization step is necessary, to supply EDR product water without blending with GAC filtered water. In this sense remineralization of EDR produced water was applied using lime contactors and CO₂ dosing. Only if the quality of raw water makes it possible, conventional treatment will be blended to produce up to 4 m³/s.

This plant is the world's largest desalination plant using this technology, and a new example of a large scale application of a desalting technology to improve the quality of drinking water. The work was carried out by the Spanish temporary consortium SACYR-SADYT using EDR technology provided by General Electric Water&Process.

The main characteristics of the DWTP are:

- Conventional process: pre-oxidation with potassium permanganate, coagulation, flocculation, oxidation with chlorine dioxide, sand filtration, GAC filtration and final chlorination using chlorine gas.
- Average current flow supplied by the DWTP: 2.3 m³/s. Maximum extended flow of the DWTP: 4 m³/s

Design of EDR's Stage:

- Maximum flow treatment : 2.3 m³/s (58 MGD)
- Range conductivity inlet water: 900-3000 µS/cm.
- Temperature range inlet water: 5-29 °C
- Pump station : 9+3 pumps of 1030m³/h to 60 mca
- Cartridge filters: 18 filters with 170 cartridges each of 50 inches and 5 µm.
- 9 modules with 576 stacks wit 600 cell pairs each one, in double stage.
- Homogeneous membranes: AR204 (anionic) and CR67 (cationic)
- Wet technology.
- Voltage range: 340-450 V 1st stage, 320-390 V 2nd stage.
- Bromides reduction: 60-80 %
- Conductivity reduction: 60-80 %
- Maximum volume of brines: 154 Tm/d, sent via a pipeline to the sea at the mouth of the Llobregat River.
- Water recovery >90% (including off-spec and concentrate recycle).
- Remineralization (when necessary) with Ca(OH)₂ up to 7 Tm/d and CO₂.

Every module is provided with reversing systems of flow for the changes of polarity, automatic valves and pumps equipped with electronic frequency variators that allow a full automated system. EDR process is operated according with the levels of THMs expected in the final drinking water. Then 1 to 9 modules were worked when necessary to blend with conventional treatment product to get the THMs levels at the lower cost.

The plant started operating on a trial basis in June 2008, and came into the normal operation from April 2009. Along the period April, 2009 to August, 2010, more than 20 hm³ had been



Fig. 3. Details of the EDR step at the Abrera DWTP.

produced through the EDR line. THMs's average values in the water product of the DWTP ranged between 40 and 60 $\mu\text{g/L}$. The energetic average consumption for the EDR process (stacks and pumps) has been lower than 0.6 kWh/ m^3 . During the indicated period the hydraulic performance has been higher than 90%, with a reduction of salts (measures like conductivity) higher than 80% in summer. Specific consumptions of HCl were of 0.08 Kg HCl/ m^3 and for antiscalant in the rejection of brine 0,002 Kg/ m^3 (Valero et al., 2010)

Due to the large size of the industrial plant, additional R&D studies will be focused on O&M procedures. Maintenance related to cleaning membranes and spacers, the measure of the inter-membranes voltages and "hot spots" detection, would be simplified using specific tools designed by the technical staff.

The cost of the new enlargement project was 61,218,478€. Given the considerable interest of these works, their repercussion on the quality of the supply and the technology used, a subsidy of 85% of the budget of the works was obtained from European Union funds.

6.2 Case study 2: The Depurbaix WWTP.

The project is located in Sant Boi de Llobregat, near Barcelona. It is a brackish water desalination facility for some of the effluent treated in the Depurbaix WWTP, which produces more than 57,000 m^3/d using EDR technology (Segarra et al., 2009).

The facility is one of the largest in the world that treats wastewater for agricultural use. The work was carried out by the Spanish temporary consortium BEFESA-ACSA using EDR technology provided by MEGA a.s.

The main characteristics of the EDR system are:

- Inlet water: tertiary treatment of the WWTP + anthracite/sand filters. Average conductivity 3.040 $\mu\text{S/cm}$
- Expected EDR product water: 55,296 m^3/d .
- Expected plant product water after blending: 57,024 m^3/d .
- Pump station : 2+1 pumps

- Cartridge filters: 4 filters with 300 cartridges each one (20 μm).
- 4 modules with 96 stacks with 600 cell pairs each one, in double stage.
- Heterogeneous ion-exchange membranes: RALEX AM(H) (anionic) and CM(H) (cationic)
- Dry technologie
- Conductivity reduction: 60-80 %
- Water recovery >85%.

The plant started operating on a trial basis in January 2010 and came into the normal operation from September 2010. The full automatic modular system allows the operation according to the expected use of the product water.



Fig. 4. EDR stacks at the Depurbaix WWTP.

7. Discussion

In recent years membrane technology has become an important useful tool for the desalination of seawater, the use of brackish water and polluted water resources which were not suitable for producing drinking water, and for the physicochemical and microbiological improvement of the water obtained by conventional treatment.

Based in the important advantages of ion-exchange membranes (rugged, resistant to organic fouling, chlorine stable, broad range for pH and Temperature,..) compared with other membranes technologies, the improvement of EDR allows to use it for many applications that are cost effective than other technologies with a better commercial marketing like UF or RO. Maybe the use of EDR still has a label of a technology to solve local problems involving small communities or specific industrial applications. However, during last years big systems are in operation showing good performances and cost effective results. In this sense the T. Maybry Carlton WTP located at Sarasota (FL, USA) was pioneer in operate a big system since 1995. In that case, EDR was selected due to its ability to

maximize recovery of freshwater and minimize wastewater volume. The plant produces 45.420 m³/d and is equipped with 320 stacks. Later, improvement of EDR allows installing more systems worldwide, some of them in Spain related with drinking water and water reuse. EDR was introduced in the Canary Islands during the 80's, but during last years some big facilities were building in the Spanish Mediterranean area: two plants (16,000 m³/d each) in Valencia to reduce nitrate levels and two more in Barcelona: the first to reduce bromide levels and then the THMs formation (200.000 m³/d, 576 stacks) and the last to reduce salinity for reuse water for irrigation (55.296 m³/d, 96 stacks).

In addition, desalination of brackish water using membranes technologies like ED and specially EDR it is a cost effective method to supply good quality drinking water and could be a good solution for some industrial water utilities. Besides, EDR systems now are simpler and more reliable, which means that the demineralization of difficult-to-treat water is easier for municipalities to handle. In addition, the costs are becoming easier to swallow.

Some aspects could be improved in a near future: spacer configuration, membranes chemistry, materials and configuration of electrodes, specific antiscalants for EDR, elimination of degasifiers and the increase of the production of the stacks.

Finally, there are some interesting works related with the use of hybrid systems to get synergies between technologies (Turek, 2002; Kahraman, 2004), and some innovations are under study to improving the EDR technology (Balster et al., 2009; Charcosset, 2009; Ortiz et al., 2008; Turek et al., 2008; Veerman et al., 2009).

8. Conclusions

- EDR should be effectively applied for water and salt recovery from an industrial effluent for pollution prevention and for resource recovery.
- The growing popularity among municipalities of the EDR systems is related with its capacity to reduce TDS and some inorganics elements like nitrates, sulphates, radon, bromides and others, with high water recovery and easily operation and control by adjusting amount of electricity applied to membrane stack.
- The correct operation of big EDR systems, compared with classical membrane pressure systems like RO, allows extending EDR to new cost effective applications.
- Future steps of EDR systems could improve the design of membranes and spacers as well as a more compact design, lowering the capital and O&M costs.
- EDR could be in a near future the technology of choice for many applications because its efficiency to desalt water needed in different fields like drinking water, reuse water and many industrial applications, like food, beverages and mining among others.
- Hybrid systems between different membranes technologies including EDR, could be useful solutions for specific applications, and could improve recovery and reduce waste.

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The book comprises 14 chapters covering all the issues related to water desalination. These chapters emphasize the relationship between problems encountered with the use of feed water, the processes developed to address them, the operation of the required plants and solutions actually implemented. This compendium will assist designers, engineers and investigators to select the process and plant configuration that are most appropriate for the particular feed water to be used, for the geographic region considered, as well as for the characteristics required of the treated water produced. This survey offers a comprehensive, hierarchical and logical assessment of the entire desalination industry. It starts with the worldwide scarcity of water and energy, continues with the thermal - and membrane-based processes and, finally, presents the design and operation of large and small desalination plants. As such, it covers all the scientific, technological and economical aspects of this critical industry, not disregarding its environmental and social points of view. One of InTech's books has received widespread praise across a number of key publications. Desalination, Trends and Technologies (Ed. Schorr, M. 2011) has been reviewed in Corrosion Engineering, Science & Technology – the official magazine for the Institute of Materials, Minerals & Mining, and Taylor & Francis's Desalination Publications. Praised for its “multi-faceted content [which] contributes to enrich it,” and described as “an essential companion...[that] enables the reader to gain a deeper understanding of the desalination industry,” this book is testament to the quality improvements we have been striving towards over the last twelve months.

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