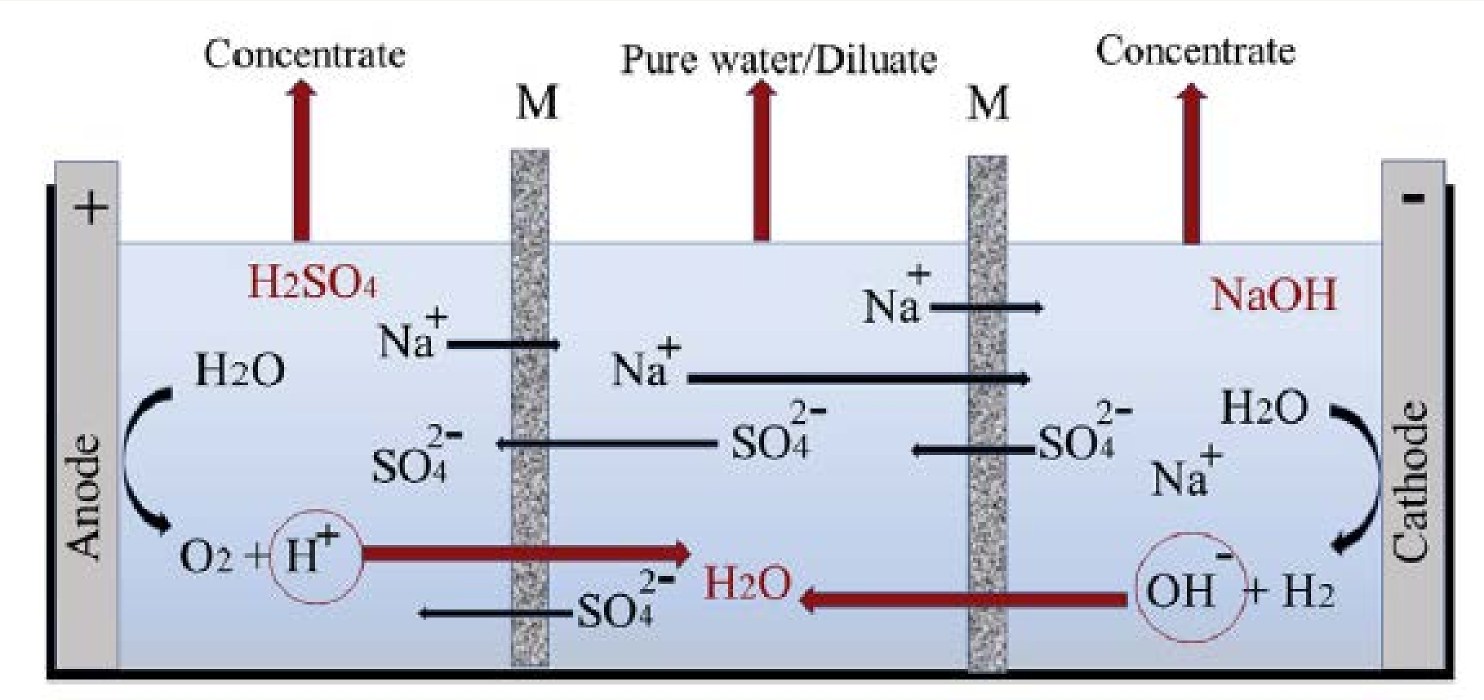
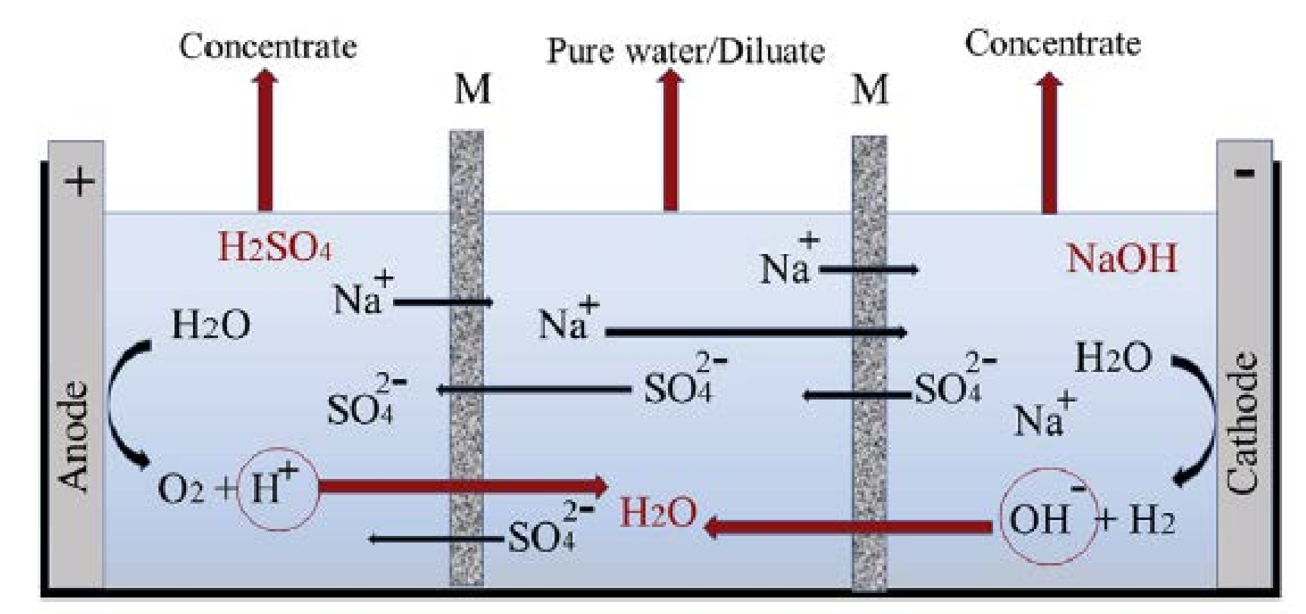
# ELECTRODIALYSIS

**CEE 597T**

**Electrochemical Water and Wastewater Treatment**

- ED is a method for the removal of electrolytes from water by transporting electrolyte ions through ion-exchange membranes to other solution under the influence of constant DC (direct current) directed perpendicular to the membrane plane.
- The driving force of the process is the electrical potential gradient.
- ED is based on the phenomena of electrolytic dissociation of salts, directed movement of ions in an electric field, and selective transfer of ions through ion-exchange membranes.






$$2H_2O - 4e^- \rightarrow O_2 + 4H^+ \text{ or}$$
$$2SO_4^{2-} + 2H_2O - 4e^- \rightarrow O_2 + 2H_2SO_4$$

$$2H_2O + 2e^- \rightarrow H_2 + 2OH^- \text{ or}$$
$$2Na^+ + 2H_2O + 2e^- \rightarrow H_2 + 2NaOH$$

If electrolyte solution contains chloride ions, chlorine gas would be allocated in the anodic chamber along with the oxygen

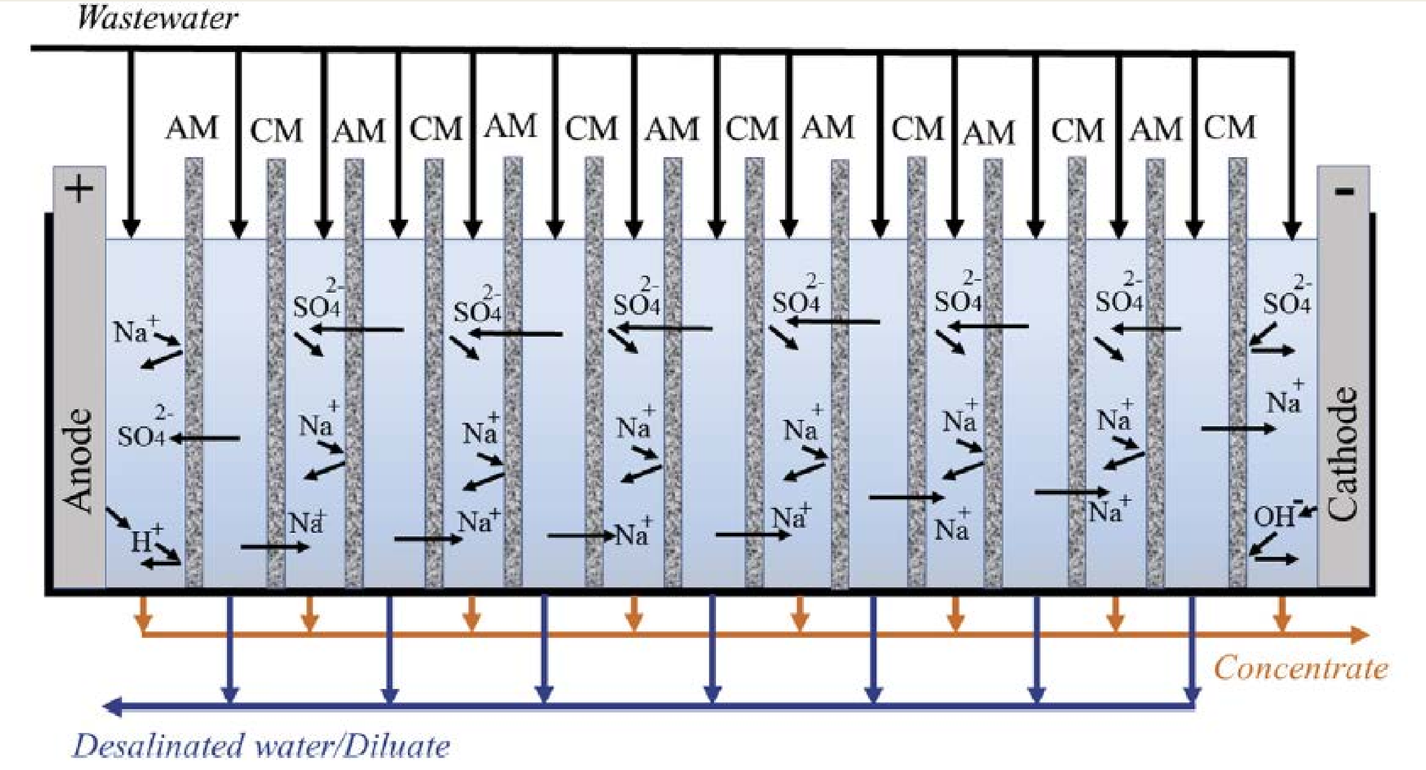
$$2Cl^- - 2e^- \rightarrow Cl_2$$

- Electrolyte solution (for example, $Na_2SO_4$) is fed to all compartments of a simple electrodialyzer
- When applying the potential difference to electrodes cations start to move toward the cathode (negative electrode) and anions move toward the anode (positively charged electrode).
- Electrolyte concentration of the middle compartment (dilute or retentate compartment) will gradually become desalinated and filled with clean water.
- At the same time electrode reactions will lead to the oxygen gas generation and formation of acid ($H_2SO_4$) at the anode and hydrogen gas evolution as well as alkali (NaOH) formation at the cathode. Thus, near-electrode compartments become enriched with alkaline or acid electrolyte (concentrate or permeate).

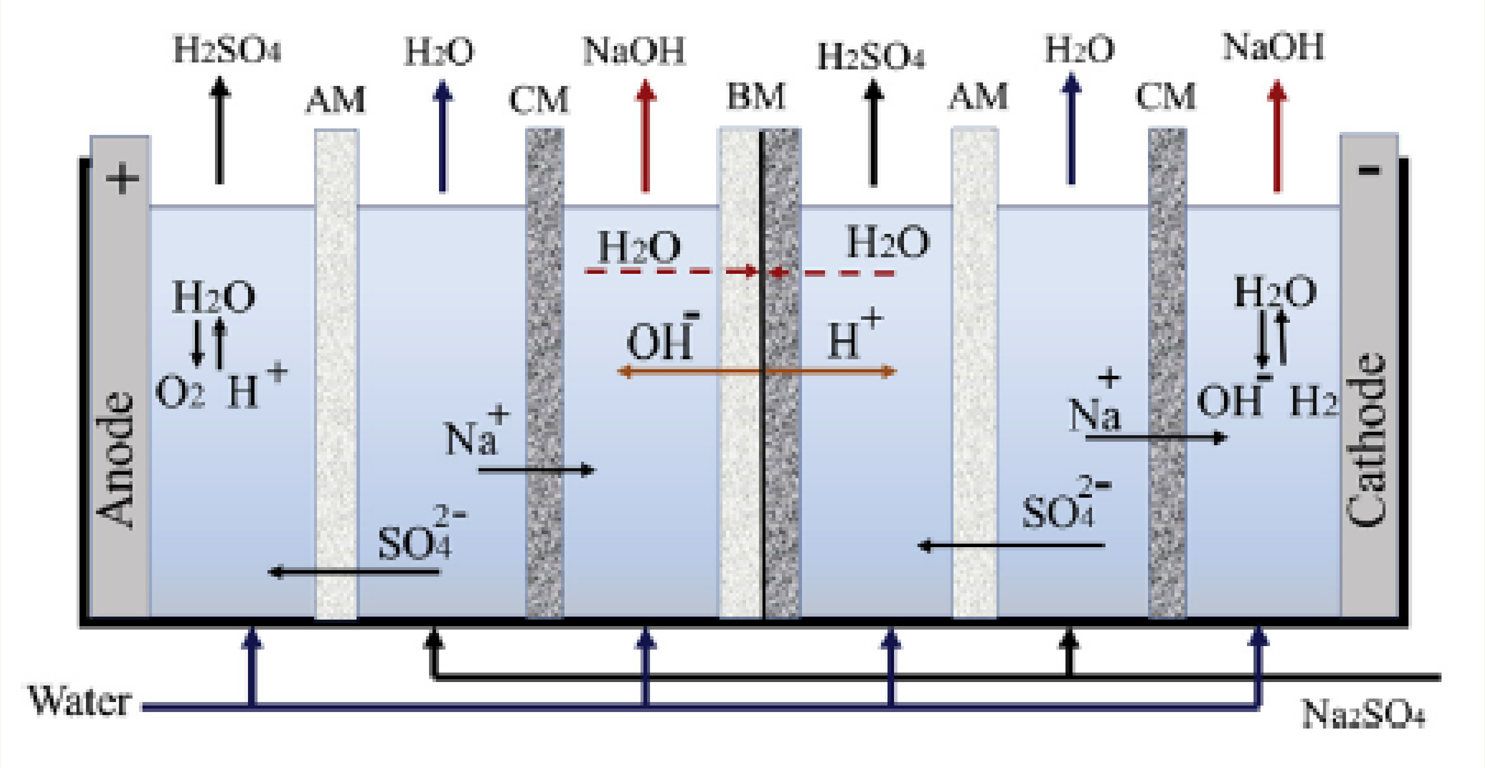
# Principles of Electrodialysis

- Use of three-compartment electrodialyzers is a cost-consuming process due to the loss of energy to the electrode side reactions.
- In this regard a significant improvement of cost efficiency can be achieved by using a large number of membranes. Usually electrodialyzers can contain up to 2000 of ion-Exchange membranes pairs. There are three ways of electrodialyzer operation depending on the type of used membranes.

- **1.** *The principle of work of conventional multichamber electrodialyzers* with membranes of different charge is similar to that of the simple electrodialyzer.
- Membranes are placed in between two electrodes. Electrolyte solution (wastewater) is usually fed to all compartments. While applying the direct current, cations move toward the cathode through the cation-Exchange membrane placed from the cathode side. Anion membrane is placed on the anode side. The cation-exchange and anion-exchange membranes are alternated. The anions move in the opposite direction toward the anode through the anion exchange membrane. While passing the anion-Exchange membrane, anions are retained in the concentrate stream by a cationic membrane located from the side of anode. On the contrary, cations are retained by the anionic membrane located on the cathode side. Thus, the overall process results into the increase of ions concentration in each odd chamber and decrease of ions concentration in each even compartment.



- **2. ED with bipolarmembranes** is an effective replacement to conventional water electrolysis and allows direct production of bases and acids through the water splitting to hydrogen and hydroxide ions without forming oxygen and hydrogen gas. The process gives significant cost savings especially when using multicompartment electrodialyzers. Generation of $O_2$ and $H_2$ gases during anodic and cathodic reactions, respectively, consumes up to half of useful energy in the process of conventional water electrolysis.
- Electrolyte solution is fed to the compartments between anion-exchange and cation-exchange membranes and water is fed to electrode and near bipolar membrane compartments. When electric field is applied, compartments on both sides of bipolar membrane start to be filled with electrolyte ions migrating from near compartments and with $H^+$ (from cathode side) and $OH^-$ (from anode side) ions migrating from intermediate part of bipolar membrane thus producing acid and base.



- **3. Substitutional ED with membranes** of the same type i.e., only cation-exchange or only anion-exchange membranes packed between two electrodes are used for special application such as for obtaining organic acids from their salts or reducing the acidity of citrus juices and rarely used in water treatment applications.

# *Classification of membranes used in ED*

- In general membranes used in ED processes can be divided into nonactive (porous), active (ion exchange), and ideally active (ion exchange).
- 1. **Nonactive membranes** contain pores of a certain size that allow mechanical passing of smaller compounds through the membranes. These membranes do not change the ion transport number ($t_i$) that means that cations and anions transport number in the solutions $t^0{}_c$ and $t^0{}_A$ is equal to the transport number of cations ($t_c$) and anions ($t_a$) in the membrane, respectively. It is worth to notice that the ion transport number is the fraction of the total electricity carried by a specific ion i. Nonactive membrane can be used for the separation of nonelectrolytes from electrolytes.

- **2. Active/selective membranes** change the ion transport number of either cations or anions depending on the membrane charge. For example, if a membrane increases the cation transport number ($t_c > t^0{}_c$), which is typical for negatively charged membranes (cation-exchange membrane carrying a negative charge of anions fixed in the membrane matrix), the anion transport number will be decreased ($t_a < t^0{}_a$) by the membrane.
- In contrast when positively charged membrane (anion-exchange membrane carrying a positive charge of cations fixed in the matrix) increases anion transport number ($t_a < t^0{}_a$), then ($t_c > t^0{}_c$) Pore size of these membranes is smaller than those of nonactive membranes. The smaller the pore size the more prominent the change in the ion transport number.

- **3. Ideally active (ideally selective) membranes** can let pass only cations or anions (if $t_c$ =1 then $t_a$ = 0 and in contrast if $t_a$=1 then $t_c$=0). All electricity is transferred through the membrane by counterions.
- The higher the cation and transport numbers in cathodic and anodic membrane, respectively, the higher the CE of ED.
- Transport of ions through ion-exchange membranes in ED is controlled by
- diffusion,
- electromigration, and
- convection

❑ The total flux Ji (mol/$m^2$s) of ions through the membrane can be found as follows:

$$J_i = \vartheta \cdot C_i - D_i \frac{dC_i}{dx} - \frac{z_i \cdot F \cdot C_i \cdot D_i}{R \cdot T} \frac{\partial \phi}{\partial x}$$

where v is the velocity of ion in solution due to convection (m/s); Ci is the concentration of ion i (mol/$m^3$); $D_i$ is the diffusion coefficient ($m^2$/s); x is the coordinate of direction (m); $z_i$ is the charge number of species; $\phi$ is the electric potential (V); R is the gas constant; and T is the temperature.

# *Ion Exchange groups*

- Depending on type, ion-exchange membranes can have acidic or basic ion exchange groups such as $SO_3^-$ ,$COO^-$, $SeO_2^{\ -}$ , -N$^+$≡, -N $(CH_3)_3$, -N$^+(R)_3$, etc., in their matrix. The nature of fixed charges and counterions significantly affects the selectivity of the membranes and electrical conductivity.
- Cation transfer membranes which are electrically conductive membranes that allow only positively charged ions to pass through. Most of commercial *cationexchange* membranes contain $SO_3^-$
- *Anion-Exchange* 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 for example, **[-$(CH_3)_3N^+$]** which repel positive ions.
- Membranes should have
- high mechanical and chemical strength,
- high conductivity, and
- high permeability for ions along with a
- high selectivity and low electrical resistance (2-10 $\Omega/cm^2$ area of the ion exchange membrane) and thickness.

# *ED systems: depending on the direction of dilute flow*

- one -pass flow systems (continuous process) when the desired degree of desalination is achieved in a single pass of dilute through the electrodialyzer;
- batch systems (discontinuous process) or circulating ones when dilute and feeding water of concentrated compartments circulate through the electrodialyzer several times until the desired value of desalination is achieved;
- partially circulating process, where a part of desalinated dilute is circulated through the electrodialyzer along with the feeding dilute.

# *Advantages*

- High water recovery in the range of 80%e90%.
- Ability to obtain highly concentrated brines, which facilitates their further processing and allows recovery of valuable components.
- Long service life of membranes, which can last up to 7-10 years.
- Lower requirements for water quality entering to treatment by ED compared to water treated by reverse osmosis. Water silt density index (SDI) for the process of ED should be usually below 12 while for reverse osmosis SDI should not exceed 3.
- Resistance of membrane to elevated temperatures, drying up, bacteria decontamination, and free chlorine content up to 1 mg/L. However, there is a possibility of membranes fouling with microorganisms.
- Mechanical strength of membranes and of manual cleaning of membranes.
- Membranes contribute to about 50% of ED equipment costs.
- Compact sizes of ED equipment.
- Simplicity of operation and ease of automation.
- Low operating pressures (0.3-0.4 atm) of electrodialyzers.
- No chemicals addition to the process except the occasional use of softeners.

# *Disadvantages*

- Membrane passivation and polarization due to mostly concentration polarization.
- Necessity in the solution pretreatment from suspended solid and hardness before the process (up to seven stages). The allowed concentration of suspended solids for ED is 3 mg/L, COD is below 5 mg $O_2$/L, boron and iron content below 0.1 mg/L.
- Frequent membrane replacement (often after 6-12 months).
- Impossibility to remove uncharged molecules and organic compounds. However, ED can be used for the desalination of noncharge compounds such as pharmaceuticals, sugar, and vine.
- Concentrate solution requires additional treatment or recycling. To improve the efficiency of the process and reduce the amount of formed wastewater to be recycled or utilized, recirculation of concentrate solution is often used.
- Ion transport number in membranes usually differs from the ion transport number in the electrolyte solution.
- Electroosmotic transfer of solvent molecules captured by migrating ions through the membrane can be observed during ED and change the composition and volume of electrolyte solution in electrodialyzer compartments.
- Electrophoretic movement of particles can cause additional precipitates on the surface of membranes.

*ED is suitable technology for the following cases:*

- Treatment of water with a higher tendency to fouling or variable quality of feed
- High recovery is required
- High concentration of concentrate is required (up to 200 g/l)
- High silica waters
- Suitable for existing plants without need of external pre-treatment

# Electrodialysis Applications

**Reduce Electrolyte Content**

- Potable from brackish water
- Food products – whey, milk, soy sauce, fruit juice
- Nitrate from drinking water
- Cooling tower water
- Boiler feed water
- Rinse water for electronics processing
- Effluent streams
- Electroless plating baths
- Blood plasma to recover proteins
- Pickle brines to recover flavor
- Sugar and molasses
- Amino acids
- Potassium tartrate from wine
- Chloride purge in Kraft paper process
- Photographic developer regeneration
- Fiber reactive dyes

**Recover Electrolytes**

- Pure NaCl from seawater
- Ag(I) salts from photographic waste
- Ni(II) from electroplating rinse waters
- Zn(II) from galvanizing rinse water
- Salts of organic acids from fermentation broth
- Amino acids from protein hydrolysates
- Acids from metal pickling baths and rinse
- HCl from cellulose hydrolysate

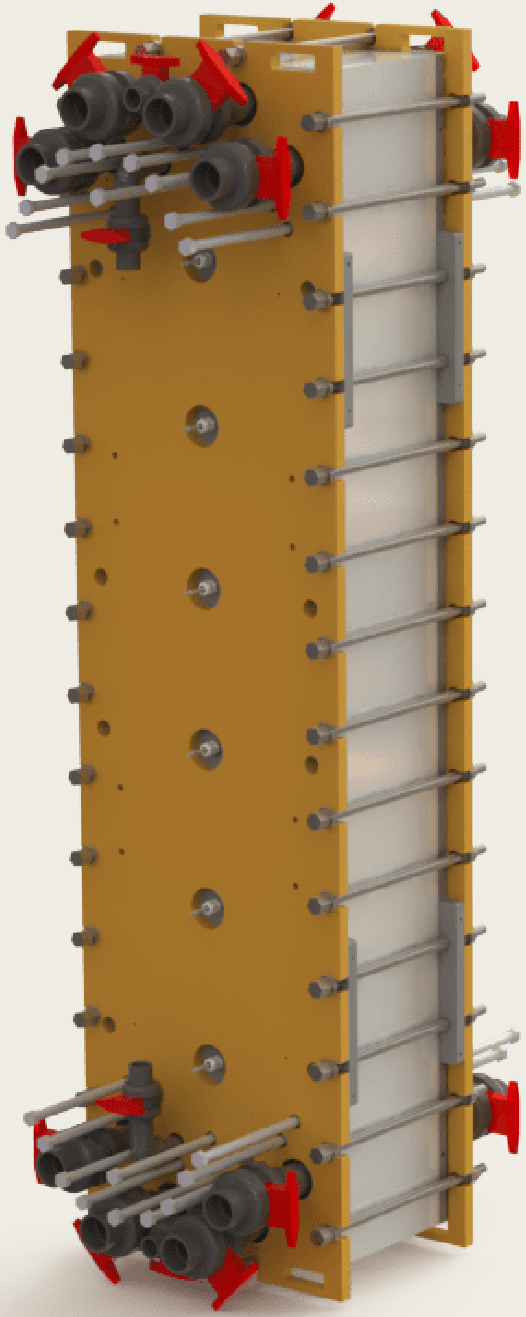
- **Miscellaneous**
- Salt splitting
- Metathesis
- Concentrate reverse osmosis brines
- Ion substitution

## *Electrodialysis in water treatment*

- Zero Liquid Discharge
- Wastewater from paper machine
- Desalination of high -silica water
- RO brine treatment
- Condensate treatment from fertilizer production (NPK, $NH_4NO_3$)
- Textile wastewater
- Cooling tower blowdown treatment

# *Electrodes*

- 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.



# Parameters Influencing the Efficiency of Electrodialysis

- ***Current Density and Cell Voltage***
- The higher the current density of ED units operation, the higher the demineralization efficiency and faster the process.
- However, too very high current densities increase the concentration gradient leading to significant decrease of ion concentration at the membrane surface.
- Higher cell voltage increases the CE of ED in the range of small electrolyte concentrations.
- When high voltage is applied to ED cell containing high electrolyte concentrations (>20 g/L), the effect of concentration polarization becomes more prominent and CE of ED significantly decreases.

## *Electrolyte Composition and Concentration*

- Efficiency of ED process depends on the dilute composition and concentration.
- The lower the concentration of electrolyte, the higher the electrochemical activity of membrane and consequently the higher the efficiency of desalination.
- Presence of gas bubbles, suspended solids, phosphates, microorganisms, and other compounds in the amount exceeding the maximum allowable concentrations for particular ED process significantly depresses the efficiency of desalination and membrane performance.

## *Flow Rate of Dilute and Concentrate Feed*

- Flow rate of water in dilute and concentrate compartments affects membrane polarization and hence the efficiency of desalination.
- If the feed rate of the solutions is below the critical level, polarization of membranes and decomposition of water into hydrogen ions and hydroxide ions start to be prominent.
- From another side generated hydrogen and hydroxide ions are involved in the transfer of current, which leads to the decrease of CE and transfer of desalinated ions.
- At some high value of water flow, CE can decrease to zero and suppress the efficiency of ED. In this regard, there is an optimal value of flow rate, which should be determined empirically for each particular process.

# *Worldwide Industrial Installation*

| 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 (fomerly 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 | salinty 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 | salinty 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 | salinty 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 |

| Industrial applications | Stack and process design | Status of application | Limitations | Key problems |
| --- | --- | --- | --- | --- |
| Brackish water desalination | Sheet flow, tortuous path stack, reverse polarity | Commercial | Concentration of feed and costs | Scaling, costs |
| Boiler feedwater production | Sheet flow, tortuous path stack, reverse polarity | Commercial | Product water quality and costs | Costs |
| Waste and process water treatment | Sheet flow stack, unidirectional | Commercial | Membrane properties | Membrane fouling |
| Demineralization of food products | Sheet flow or tortuous path stack, unidirectional | Commercial pilot phase | Membrane selectivity and costs | Membrane fouling, product loss |
| Table salt production | Sheet flow stack, unidirectional | Commercial | Costs | Membrane fouling |
| Concentration of reverse osmosis brine | Sheet flow stack, unidirectional | Pilot phase | Costs | Waste disposal |

# References


- Mika Sillanpää, Marina Shestakova, Electrochemical Water Treatment Methods, 1st Ed., Elsevier, 2017
- Comninellis, Christos, Chen, Guohua (Eds.), Electrochemistry for the Environment, Springer, 2010.
- Fernando Valero, Angel Barceló and Ramón Arbós, Electrodialysis Technology, Theory and Applications, cdn.intechweb.org/pdfs/13751.pdf
- https://www.youtube.com/watch?v=wYkkLUckmg4
- https://www.youtube.com/watch?v=NYJMf_gj6b0
- https://youtu.be/3xt3dSty8Us