

Electrodialysis in Hydrometallurgical Processes

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Abstract Electrodialysis (ED) is an ionic exchange membrane process for separation of different components and species. In desalination a large part of the energy is used to sustain a concentration difference between the solutions, but in the processes of exchanging in selective manners, the energy need is lower and more directed towards ohmic losses in the membranes. The latter has relevance to several hydrometallurgical industries, as they very often accumulate undesired species in their process streams and currently apply intensive (energy and chemical) routes to remove these species. Here, we describe the principle of ED and discuss opportunities for component and salt separation using ion exchange membranes by providing a brief review of ED in the hydrometallurgical sector.

Keywords: Electrodialysis, metal separation, hydrometallurgy, review.

1 Introduction

Electrodialysis (ED) is a membrane separation process based on the movement of ionized species in solution under the influence of an electric field. ED can be applied

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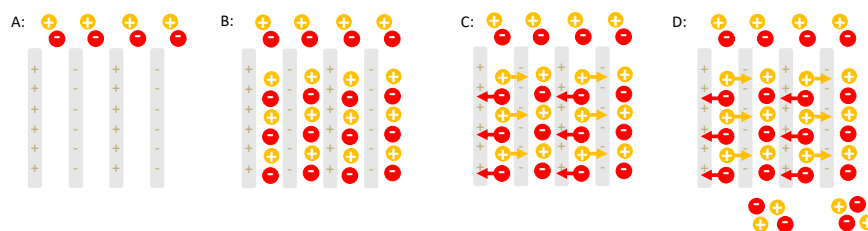


Fig. 1 Schematic description of ED with ion-selective membranes for the purpose of desalination. A solution containing salt (A) is fed into a membrane module (B), where a current is applied (C). In doing so, anions go through the AEM and the CEM, so that all ions gather and one ends up with a desalinated solution and a brine solution (D).

to concentrate ionic solutions, deionize salt solutions, or separate ionic and non-ionic species [1]. The industrial application of ED has its roots in the demineralization of brackish water, as first reported in the 1950s [2, 3]. Due to constant improvement of process design and membrane materials, ED nowadays represents an interesting alternative for different applications in water and wastewater treatment, the food industry, and the chemical and hydro-metallurgical sector [4].

In metal production and processing, large amounts of aqueous streams containing metallic as well as non-metallic species are generated upon removing the wanted bulk metals. Some of the remaining diluted compounds can be of great value, *e.g.* rare earth and noble metals, however their concentration in the solution is often too low to allow for profitable recovery using established processes. ED with ion-selective membranes can be a cost-effective alternative to recover resources and thereby increase circular economy in the metal processing industry.

Another challenge in hydrometallurgy is the undesirable impurities in the raw materials. When leaching ores to extract the mineral of interest, unwanted compounds like halogens and metals accumulate in the aqueous streams. Their presence can make the electrolysis more energy demanding or possibly be harmful and their removal requires a lot of chemicals. A pre-treatment with ED can provide selective removal of problematic compounds and save use of chemicals, energy and money.

This paper outlines the principles of ED operation and a review of selected efforts of implementing ED into the hydrometallurgical or otherwise relevant processes.

2 Principle of Electrodialysis

ED in its simplest form is based on alternating membranes with selectivity for anions or cations and then to apply a current. The resulting outcome is desalination like for instance desalination of a NaCl solution as shown in Fig. 1, where sodium (Na^+) is illustrated as yellow ions and chloride (Cl^-) as red ions. An anion exchange

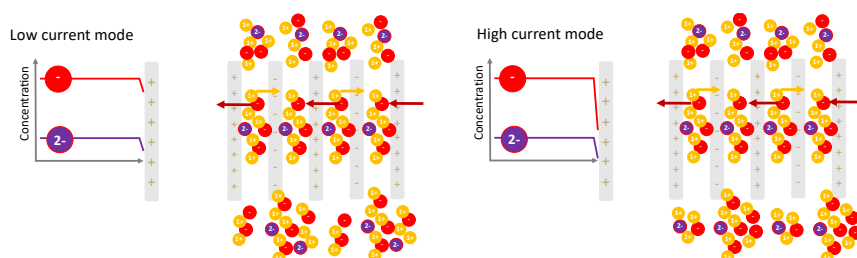


Fig. 2 Selective desalination by boundary layer concentration effects. Considering a simplified sea water solution consisting of NaCl and MgCl₂, one can have different removal rates of the different cationic species at different current rates.

membrane (AEM) is a polymeric material containing fixed positive charges that reject other cations, and *vice versa* for cationic exchange membranes (CEM).

Desalination of a binary mixture like sodium chloride and water is a simple form of ED. However in most realistic solutions one has a mixture of components and different concentration of the different components. Perhaps the most common example is sea water, which consists of not only water, Na⁺, and Cl⁻, but also ions like Mg²⁺, SO²⁻, K⁺, Ca²⁺, and more. In a simplified model for sea water solutions where one considers a lot of NaCl and much less MgCl₂, one can have different relative removal of the different components at different rates, a phenomenon referred to as boundary layer separation. This is illustrated in Fig. 2.

In boundary layer separation, one can expect that at *low overall current*, one removes equally much of both components (here cations) so that after a short time the lower concentration specie (here Mg²⁺) is removed almost completely. In this case the degree of desalination is low, but the divalent magnesium ions are completely removed. In another mode where a *high overall current* is applied, the limiting current density of the lower concentration component (or specie) is reached immediately and one removes much more of the component (specie) of the higher concentration. In these cases one can obtain a brine with little magnesium and thus lower the relative content of the low concentration component (specie). There are many examples of systems where boundary layer separation is of interest, and each of them requires careful examination as several different fluid dynamic phenomena can occur and care should be taken when measuring and modeling systems as such [5].

2.1 Role of the Membrane

So far we have mainly discussed the ED process in terms of simple principles for binary salt solutions and possibly more complex solutions of ternary and higher order. In these cases the role of the membrane is to ensure that only cations go through the CEM and only anions go through AEM. However, ED systems offer many more solutions and also restrictions. A highly relevant example is selectivity of ions with

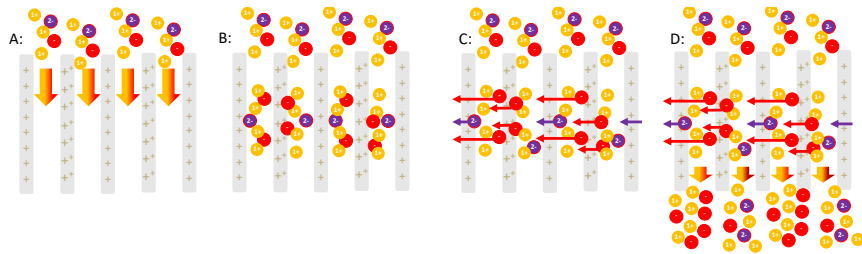


Fig. 3 Valence selectivity, particularly for monovalent ions, can be obtained by several types of membranes and used to separate higher valence species from monovalent species.

different valences, as shown in Fig. 3. Here, one applies only CEM or AEM, but has alternated membranes that reject higher valency ions. These membranes typically have special coatings to obtain such properties [6]. This means that one can use ED for either sulphate or magnesium/calcium removal in the case of seawater and for many different applications in the hydrometallurgical industry by surface modification of existing ionic membranes.

When considering selectivity of membranes, the common figure of merit is the permselectivity of the membrane, α . The permselectivity is interpreted in different ways, but is ultimately an empirical coefficient that compares a measure value to a theoretical value, as described in detail in Section 2.2. The permselectivity is sometimes treated as an ability to discriminate a positive ion over a negative ion by the application of the liquid junction potential theory model [7]. Several membranes do however offer close to unity discrimination of one salt over the other and the liquid junction theory does not account for the contribution of water in the permselectivity. Therefore, and at higher concentrations, the permselectivity also describes the ability to not transport water alongside the membranes, a phenomena often referred to as osmotic drag [8,9].

2.2 Energy use in Electrodialysis

The energy needed to drive an ED process in a unit cell with a binary salt mixture like water and NaCl, $E_{u.c.}^{ED}$, is the sum of the ohmic potential energy, IR , and the reversible potential of mixing the two different solutions, as summarised in Eq. 1. A unit cell is a pair of membranes and a pair of aqueous streams of high and low concentration ($C_{high/low}$). Typically the membranes have the higher resistances in an ED unit cell, but this depends much on the thickness of the flowing solutions (0.2-2mm) and the concentration of the solution (0.01-1M).

$$E_{u.c.}^{ED} = E_{u.c.}^{OCP} + IR_{u.c.} \quad (1)$$

where OCP is for open circuit potential, I is for current, R is for ohmic resistance of the unit cell and

$$E_{u.c.}^{OCP} = \bar{\alpha} E_{mix}^{rev} = \bar{\alpha} \frac{2\bar{R}T}{F} \ln \left[\frac{C_{high}}{C_{low}} \right] \quad (2)$$

where $\bar{\alpha}$ is the average apparent permselectivity for a pair of membranes, \bar{R} is the molar gas coefficient, T is temperature, and F is the Faraday constant.

Beyond these main energy costs (concentration difference and ohmic), other energy usage matters as well. Concentration polarisation leads to higher energy spending because of the very high ohmic resistance one can get on the dilute side of the membrane and the locally increased concentration difference across the membrane. Pumping water through the membrane module also requires energy. A third, secondary energy spending, relates to fouling mitigation and clean up, where filtering and membrane module cleaning are the main factors.

3 ED applications in hydrometallurgy

Generally, we find that ED efforts in the hydrometallurgical sector fall into a category of either recovering wanted species or removing unwanted species. Unwanted species are sometimes in the category of disturbing other parts of the process industry and other times in the category of being of environmental concern.

3.1 Metallic value recovery

The literature has shown that it is possible to recover between 70-99% of valuable metals such as gold, noble metals, rare-earth metals, copper and silver by use of ED. Intensive research has been directed to the opportunities of recovering Cu from electroplating wastewater. In the range of initial Cu-ion concentrations from 1-4g/L, removal rates between 70-85% were achieved using ED [10–12]. When coupling ED to an in-situ complexation reaction step [13, 14] and an electrolysis step [15], recoveries >99% were obtained. Reig *et al.* [16] applied Selective ED to remove As and recover Cu and Zn from acidic metallurgical process waters. Non-selective and selective membranes were used in this approach. The recoveries were 80% for Cu(II), 87% for Zn(II), and 95% for As(V). In another report, full recovery of Ag ions from rinse water of an industrial plant with an initial concentration of 100mg/L was achieved by applying ED [17]. Scarazzato *et al.* used HEDP-acid to form a stable complex with 4.5g/L copper (Cu(II)-HEDP). They reported the highest Cu²⁺ recovery of 99.7% with HEDP (94.4%) and water using ED [14]. Iizuka *et al.* proposed a process for separating a mixed solution of Li (0.02M) and Co (0.02M), based on bipolar membrane ED coupled with metal-ion chelation. The selectivity for Li and Co in the metal recovery cells was 99% [18]. Hershey *et al.* investigated on the separation of radioactive strontium ($1.3 \cdot 10^{-7}$ M) from cesium ($7 \cdot 10^{-6}$ M)

based on the formation of strontium chelate complexes with EDTA and DTPA by ED. 94% of the cesium were reserved in the feed cell while 2.2% of it transferred to the anode cell with 85% of the strontium [19]. Roman *et al.* proposed a method based on the combination of membrane processes consisting of membrane-based solvent extraction and ED stages for the recovery of a solution of Zn and Fe with high concentration of hydrochloric acid. 99% of the initial HCl and 75% of the initial Zn was recovered in the concentrated phase [20]. Recently, efforts have been made to produce Li from brines, ores and spent Li-ion batteries. ED can be used to produce Li salts with purity >95% while keeping a high extraction efficiency rate (around 80%) and low energy consumption [21].

3.2 Metal removal

ED can further be used to extract species that can be harmful to the environment, like Pb, Cu, and Cd. The selective separation of metal ions from *e.g.* electroplating baths in the galvanic industry allows the reuse of both the concentrate solution in the electroplating bath and the diluate as rinse water. Santarosa *et al.* [22] studied the performance of different IEMs on the removal of Ni and Zn from synthetic solution and real industrial effluents and achieved removal of up to 90%. ED has also proven to be efficient for the separation of Ni and Co ions in sulfate solution [23]. The use of cadmium cyanide baths in the electroplating industry generates a strong concern due to high toxicity associated with Cd and CN. Applying ED, Cd and CN were recovered from synthetic wastewater in concentration ranges from 1-3g/L Cd yielding removals of 5-22% for Cd and 17-46% for CN. However, when other metal ions such as Co, Cr or Fe were present in the solution, the concentrate was not feasible for reuse in the electroplating bath since transport of these former metal ions occurs with Cd and CN ions [1]. Lead removal from wastewater is an important challenge in the battery industry. For ED applications, removal between 80-90% has been reported for Pb concentrations in synthetic wastewater ranging from 100-1000ppm [24, 25].

Electrodialytic Remediation is a process to remove contaminants disposed in solid material like harbor sediment or wastewater sludge. In different setups, 44-82% Cu, 65-81% Pb, 78-91% Zn and 98% Pb were removed from harbor sediments [26, 27]. Extensive studies have been performed to evaluate the feasibility of ED processes in the treatment of wastewater sludge and bio-ashes from sludge incineration. These waste products from wastewater treatment are rich in phosphor. In order to use the sludge, *e.g.* as fertilizer, heavy metals must be removed. With ED remediation, 70% of Cd removal from sludge suspended in citric acid or in distilled water was obtained [28], while when treating the ashes 75% of Cd removal was achieved [29]. Removal of Cu, Cr, Pb, Zn and Ni from sewage sludge [29–31] and ashes [31, 32] has also been investigated.

4 Outlook and perspectives

To preserve resources and increase environmental and economical sustainability, it is of interest to design industrial processes as closed loop systems. As a process-integrated method, ED is a promising technology for the purification of metal-containing effluents. This can be fit into several existing hydrometallurgical processes. Clearly, several efforts of ED into the hydrometallurgical sector have been made. We see several examples with room for higher recovery and for tailoring membranes with respect to selectivity and conductivity. For mixed species solutions, the selectivity of the membranes is a challenge that should be further addressed in future work. While most research focuses on pristine membrane properties like selectivity and conductivity, little is documented on the sustainability of these properties and the durability of the bulk membrane material. However, when transferring membranes to industrial applications, this research field needs exploration.

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