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Sulfuric acid recovery from acid mine drainage by means of electrodialysis

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HIGHLIGHTS

- We study the recovery of sulfuric acid from acid mine drainage by electrodialysis.
- The effect of the applied current on the performance of an ED cell was investigated.
- An effective recovery of sulfuric acid was obtained in the experimental conditions.
- The main limitation of the process is due to the behavior of the cationic membrane.

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ABSTRACT

In the present work the recovery of sulfuric acid from acid mine drainage by means of 3-compartment electrodialysis (ED) is evaluated. An effective recovery of sulfuric acid free from Fe(III) species was obtained in the anodic compartment as a result of the co-ion exclusion mechanism in the membranes. The difference in the pH and pSO_4^{2-} values between the membrane phase and the external electrolyte promotes the dissociation of complex species inside the membranes. This phenomenon impedes the transport of Fe(III) and sulfates in the form of complex ions toward the anodic and cathodic compartment, respectively. The current efficiency values of the anion-exchange membrane at different current densities were approximately constant with time. However, the increase in the recovery of acid decreases as the current increases. This result is explained by the shift in the equilibrium at the membrane/solution interface as more SO_4^{2-} ions cross the anionic membrane and, by the enhancement of the dissociation of water when the limiting current density is exceeded. The main limitation of the process is related to an abrupt increase in the cell voltage due to the formation of precipitates at the surface of the cation-exchange membrane.

1. Introduction

Mining industries represent an important source of metals, as well as an essential economic activity for the regions where they are located. However, the generation of acid mine drainage (AMD) entails environmental problems due to the contamination of the surrounding watercourses. AMD is the result of the oxidation of sulfide minerals, mainly pyrite (FeS_2), when exposed to the combined action of water and oxygen. It contains considerable concentrations of Fe(III) and Fe(II) species, sulfates and other metals [1]. The hazards associated with these effluents stem from their acidic pH values and the toxicological effects of heavy metals on aquatic ecosystems [2,3]. Among the different technologies that could be used to minimize the impact of AMD and make the water reuse in other activities possible, ED is selected because it is a clean technology entailing several advantages. ED does not imply the addition of chemicals, can be operated in continuous mode and allows obtaining profitable by-products [4,5].

In particular, ED can be used to obtain a valuable product, such as sulfuric acid, from AMD. The sulfuric acid can be used as resource to offset the costs of treatment and make ED technologies more feasible than the typical treatment with limes [6]. However, in order to achieve this purpose, the treatment of AMD needs to be investigated previously. In ED systems, ion-exchange membranes are used to separate positively and negatively charged ions based on the fixed charges of the membranes. In consequence, the process of mass transfer through the membranes is accompanied by concentration polarization phenomena. The development of concentration gradients can limit the mass transfer through the membranes [7]. Moreover, concentration polarization affects not only the ionic transfer rates, but also the electrical resistance of membrane systems. This implies an important dependence of the current efficiency and the energy consumption of ED cells on the applied current. Additionally, other processes, such as the pH changes,

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the electrode reactions or the presence of membrane fouling, can also converge during ED operations, thus affecting the process performance. Finally, the appropriate choice of the membranes is another important requirement for the treatment of industrial wastewaters. In order to improve the reliability of the process, the membranes should not degrade in contact with oxidizing or very acidic solutions and should be mechanically stable.

Different electro-membrane processes (e.g. bipolar ED, electro-electrodialysis or distinct ED configurations) have been effectively used to recover sulfuric acid from various industrial wastewaters, such as nuclear decontamination effluents or rinsing waters used in metal electrorefining operations [8–10]. However, in the particular case of iron-containing AMD solutions, the speciation of iron entails the presence of various ionic species of different charge and mobility [1], thus adding a further complexity in the interpretation of the mechanisms of ionic transport through ion-exchange membranes. In addition, the peculiar transport of protons and the phenomena related to the proton leakage through anion-exchange membranes (AEMs) are other characteristics which have to be considered when recovering acids by means of electro-membrane processes. All these factors affect the performance of the ED operations and determine to a great extent the purity of the final products.

Therefore, the main objective of this study is to investigate the transport processes determining the mass transfer rates and energetic efficiency of ED processes used to treat AMD solutions. For this purpose, ion-exchange membranes featured as chemically and mechanically resistant are employed at different current densities. In order to evaluate the viability of the recovery of sulfuric acid from iron-containing solutions, we put special emphasis on the formation of different ionic species. This approach will allow us to interpret the different phenomena involved in the mass transport through the membranes. Finally, the main benefits and limitations of this technology are identified by evaluating the effect of the applied current density on the mass transfer rates and energy-related indicators.

2. Experimental

2.1. Membranes and reagents

The ion-exchange membranes used in the present study are heterogeneous HDX membranes (provided by Hidrodex®). The AEM (HDX 200) contains quaternary amine groups attached to the membrane matrix. The cation-exchange membrane (CEM, HDX 100) is charged with sulfonic acid groups and has a similar morphology to that of HDX 200. Both membranes have remarkably high ion-exchange capacities, which are 1.8 and 2.0 mmol · gr^{-1} for the AEM and the CEM, respectively [11]. The structure of both membranes is reinforced with two nylon fabrics with the function of increasing their mechanical stability. Prior to conducting the experiments, the membranes were equilibrated in the solutions to be used subsequently during at least 24 h.

The composition of AMD varies substantially depending on the source from which samples are collected. In a previous study, the composition of different AMD solutions obtained from a carboniferous area in Criciúma/SC (Brazil) was elucidated [11]. The AMD solution with the highest concentration of sulfates was selected as a basis for the present investigation, since the principal aim of this work is the recovery of sulfuric acid from AMD. Synthetic solutions with a composition approximate to that of the original AMD solution were prepared by mixing 0.02 M $Fe_2(SO_4)_3$ and 0.01 M Na_2SO_4 (Panreac®). The solution to be concentrated in the anodic compartment was prepared from H_2SO_4 (J.T. Baker). Distilled water was used to prepare the synthetic solutions. The content of the most concentrated species in the original AMD source is summarized in Table 1, together with the concentrations and pH value of the synthetic solutions.

Table 1
Composition of the original source of AMD and the synthetic solutions used in the ED experiments.

Solution	Fe(III) (mol · L^{-1})	Na(I) (mol · L^{-1})	SO_4^{2-} (mol · L^{-1})	pH
AMD source	0.037	0.017	0.082	2.48
Synthetic solution: 0.02 M $Fe_2(SO_4)_3$ + 0.01 M Na_2SO_4	0.040	0.020	0.070	1.68

2.2. ED experiments

The principle of the process proposed in this work is shown in Fig. 1. The pilot plant used in the experiments consists of an ED cell divided in three compartments with recirculation. At the beginning of the experiments, the feed of the central and the cathodic compartment simulates the composition of AMD (0.02 M $Fe_2(SO_4)_3$ and 0.01 M Na_2SO_4), and the anodic reservoir contains 0.07 M H_2SO_4. The streams are pumped through the ED cell with a flow rate of 50 L · h^{-1}. Under the application of a constant current the AEM, placed between the anodic and the central compartment, facilitates the transport of SO_4^{2-} ions toward the anode. In addition, H^+ ions are generated at the anode surface as a product of the water oxidation reaction. As a result, the concentration of sulfuric acid increases in this compartment. Simultaneously, the central solution becomes depleted of positively charged ions that are transferred through the CEM. The ratio between the volume of the central and the side reservoirs was set to 4:1, so that the increase in the cell voltage could be limited and the passage of SO_4^{2-} ions to the anodic compartment could be ensured during the 10 h of operation. The effective area of the membranes and the electrodes was of 100 cm^2. A power supply was used to impose the current between anode and cathode. The anode consisted of a mixed metal oxide (RuO_2/IrO_2: 0.70/0.30) coated sheet of titanium (Magneto special anodes B.V., The Netherlands) and a sheet of AISI 304 stainless steel was used as cathode. The electrode reactions are given by Eqs. (1)–(5):

$$\text{Cathode}: 2H_2O + 2e^- \rightarrow H_2\uparrow + 2OH^- \quad (1)$$

$$Fe^{3+} + 1e^- \rightarrow Fe^{2+} \quad (2)$$

$$Fe^{2+} + 2e^- \rightarrow Fe^0 \quad (3)$$

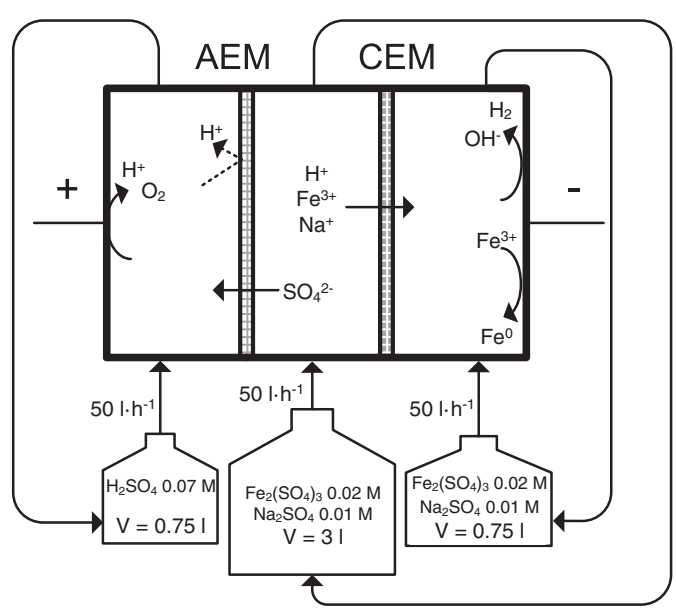

Fig. 1. Configuration of the ED cell used in the experiments for the recovery of sulfuric acid from AMD solutions.