

TREATMENT OF ACID MINE DRAINAGE BY ELECTRODIALYSIS

Daniella Cardoso Buzzi¹, Lucas Stéphan Viegas², Flávia Paulucci Cianga Silvas¹,

Marco Antônio Siqueira Rodrigues³, Denise Croce Romano Espinosa¹,

Ivo André Homrich Schneider², Andréa Moura Bernardes², Jorge Alberto Soares Tenório¹

¹USP; Av. Prof. Mello Moraes, 2463 – CEP 05508-030 São Paulo, SP

²UFRGS; Av. Bento Gonçalves, 9500 – CEP 91501-970 Porto Alegre, RS

³FEEVALE; BR-239, 2755 – CEP 93352-000 Novo Hamburgo, RS

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Abstract

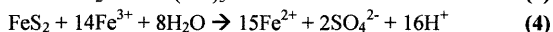
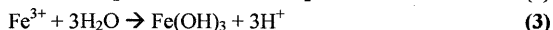
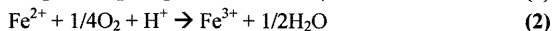
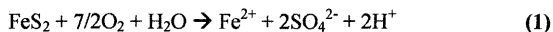
One of the major impacts caused by coal mining activity is water pollution from acid mine drainage (AMD). AMD is produced by the reaction of pyrite, water and oxygen, that is intensified in the acidophilic bacteria presence. This solution acts as a leaching agent of minerals present in the residue, producing a solution with dissolved metals and sulphuric acid. Conventional treatment of AMD consists of neutralization and precipitation of heavy metals, but is technically deficient. The electrodialysis (ED) has emerged as an attractive process for effluents treatment since it does not need reagents addition and generates no waste polluting in the environment. The ED used to treat the AMD is a membrane process that consists in the separation of cations and anions by the application of an electric field on a process cell. In this study the possibility of using ED to the AMD treatment was evaluated aiming water reuse.

Introduction

Acid Mine Drainage (AMD) is the result of the natural oxidation of sulphide minerals when exposed to the combined action of water and oxygen, that is intensified in the acidophilic bacteria presence. It is considered as the worst environmental problem associated with mining, particularly to coal mining [1].

The oxidation of pyrite in the presence of water promotes the formation of sulphuric acid which promotes the release of iron in the form Fe^{2+} and Fe^{+3} , sulphates and a host of other metals such as Al, Mn and Zn [2].

The reactions involved in the formation of AMD occur by chemical and biological processes, through the following equations [3].



Equation (1) shows the oxidation of pyrite (FeS_2), thus releasing Fe^{2+} and two H^+ . In equation (2), Fe^{2+} is oxidized to Fe^{3+} which hydrolyzes to form ferric hydroxide (an insoluble compound

at pH greater than 3.5) and in the process, as shown in equation (3), three more H^+ are released. Therefore, for every mole of FeS_2 five H^+ are released. However, since one H^+ is consumed for the oxidation of Fe^{2+} to Fe^{3+} , only four H^+ are actually produced [3].

After initiating the oxidation of pyrite, the Fe^{3+} itself can be reduced by pyrite, as shown in equation (4). Therefore, pyrite is still rusting while Fe^{3+} is produced. In this case, the conversion of Fe^{2+} to Fe^{3+} is the limiting step in pyrite oxidation reaction [3].

However, as the oxidation of Fe^{2+} to Fe^{3+} at pH 3 is very slow (approximately 100 days), the pyrite oxidation in this pH range also becomes slow, unless the iron oxidation is catalyzed by microorganisms that work in this pH range. It turns out that this pH range between 2.5 and 3.5, the bacterium *Thiobacillus ferrooxidans* quickly oxidize Fe^{2+} to Fe^{3+} [3].

The beginning of the exploration of coal in the region of Santa Catarina, in Brazil, was conducted by manual digging of many coal banks, in slopes. These excavations were carried out in mild and altered portions of the layer where it was possible to explore but, with the advancement of the banks, it became too hard to be operated manually. This way the mines were abandoned and then started opening a new coal bank [4].

The control of the generation of AMD is done by preventive methods, concentration and remediation [1]. The generation of AMD after starting, is very difficult to control and has a high cost of treatment [5].

Currently the mining industries have opted for the conventional effluent treatment followed by neutralization of the precipitation in the form of metal hydroxides [6].

New technologies for effluent treatment are being studied to replace conventional treatment systems, such as electrodialysis (ED), microfiltration, reverse osmosis, ion exchange, among others [7].

The ED has emerged as a new technology for effluent treatment and has proved efficient for the recovery of water and electrolyte concentration [7].

The ED is already considered a clean technology for effluent treatment, being attractive to different segments since it presents several advantages over traditional processes, such as: it is not necessary the reagents addition and generates no waste polluting in the environment [8].

The principle of ED is illustrated in Figure 1, which shows a schematic of a typical ED cell arrangement consisting of a series of anion and cation exchange membranes arranged in an alternating pattern between an anode and a cathode to form individual cells. An electrical potential is established between the anode and cathode, the positively charged cations migrate toward the cathode and the negatively charged anions towards the anode. The cations pass easily through the negatively charged cation-exchange membrane but are retained by the positively charged anion exchange membrane. Likewise the negatively charged anions pass through the anion-exchange membrane and are retained by the cation exchange membrane. Thus, a solution treated by ED generates two new solutions, a more focused and a more dilute [8].

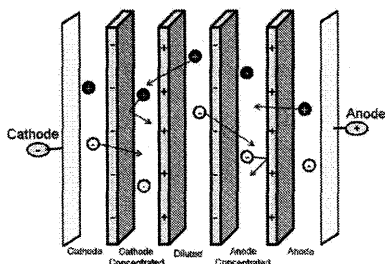


Figure 1. Schematic diagram the principle of ED.

The ED process essentially removes ions with positive and negative electric charges. Particulate substances and neutral or ionic molecular weight greater than the membrane pores, are not removed [8].

The evaluation of the efficiency of ED can be given by analyzing the following parameters: concentration polarization and limiting current and percent extraction [9].

Concentration Polarization and Limit Current

The polarization is the phenomenon that occurs when it is applied an electric current exceeding the current that can pass the membrane surface [10]. As in ED cells normally present turbulent flow, the solution polarization occurs in the boundary layer formed on the membrane surface and not within the solution. In this case, when the applied current is excessively high, the concentration of ions in the membrane boundary layer drops to zero. And similarly, on the other side of the membrane there was an accumulation of ions, as they arrive at a higher speed than they can diffuse to the solution [9].

If the current density limit, in ED, is exceeded, it will decrease the efficiency of the process, as it occurs an increase in electrical resistance of the solution and dissociation of water which would cause an increase in energy consumption [10].

It is possible to obtain initially, the value of this current density through the polarization curves, also called current-potential curves (CVC). Figure 2 shows a typical CVC, which is evidenced in three well defined regions.

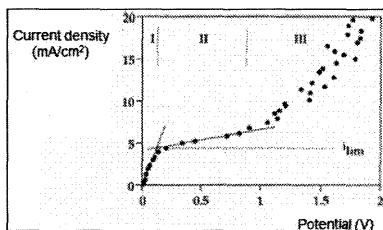


Figure 2. Graph of current density versus potential.

Figure 2 visualizes a first region (I), linear, which can be analyzed as almost equilibrium in the interface membrane/solution, where the system resistance can be attributed to ion transport in the membrane. The second region (II) in which the current varies slightly with the potential to form a plateau region, corresponding to the current limit, where with increasing current density the concentration polarization becomes more evident. And finally, the third region (III), which exceeded the limit of the current and there is an increase of current intensity with the applied potential, possibly due to current conduction by the species H^+ and OH^- , the dissociation of water [9,10].

Percent Extraction

An important parameter used to evaluate the efficiency of the ED is the percent extraction, defined as:

$$E_p(\%) = \frac{Ci - Cf}{Ci} \times 100 \quad (5)$$

Where, Ci is the ion concentration in the diluted in the beginning of the experiment and Cf is the ion concentration in the diluted at the end of the experiment [11].

Objective

The aim of this work was to investigate the possibility of using electrodialysis technique to the acid mine drainage treatment, from coal mining, aiming water reuse in the mining process.

Materials and methods

Sample Collection

The sample was collected in Criciúma, SC in an abandoned coal bank. The sample was allowed to rest for the settling of any solids and then it was filtered through a membrane of $0.45\mu m$ to then be chemically characterized. The analyses performed were pH, conductivity and concentration of the following parameters: Al, Ca, Na, K, Mg, Fe^{2+} , Fe^{3+} , Ni, Mn, Zn, SO_4^{2-} , Cl and NO_3^- .

Determination of Polarization Curves

To define the current to be applied during the ED it was, initially determined the current density limit. This test was conducted in an ED cell with 5 compartments in order to obtain the polarization curve, from which it was define the current density to be applied in trials of ED for AMD.

The assembly of this cell was carried out with the “placement in a filter press assembly” of Chinese origin membranes, cationic – HDX100 (pink) and anionic – HDX200 (green), with a surface area of $16cm^2$.

The cell was prepared as follows: in the central compartment, called Diluted, a solution of AMD was placed and other compartments, called Cathode, Anode, Concentrate Cathode and

Concentrate Anode, solutions of sodium sulphate (Na_2SO_4) were placed, to maintain conductivity in the system. Each container was connected to a pump that caused the recirculation of the solutions. Both ends of the cell, the cathode and anode were both Ti/Ru, in which successive currents were applied.

The currents applied varied gradually from 1 to 1mA, every 2 minutes with an interval of 3 minutes without current application. Every variation of current values were collected from the potential difference between electrodes and also anionic and cationic membranes, using Pt wires as electrodes, placed at the ends of each membrane. This test was performed in triplicate.

Electrodialysis

ED tests were also conducted in laboratory cell with 5 compartments, and for these tests the assembly was performed as follows: Diluted compartment, in the Concentrate Cathode and Concentrate Anode, AMD solutions were placed and in compartments, Cathode and Anode, solution of Na_2SO_4 to maintain conductivity in the system. Each container was connected to a pump that caused the recirculation of the solutions. Both ends of the cell, the cathode and anode were Ti/Ru, which were applied to the current predetermined polarization curves. Figure 3 presents the experimental cell used.

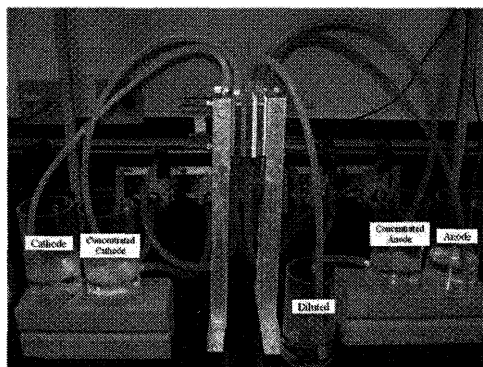


Figure 3. ED cell with 5 compartments.

The test was conducted for 24 hours and every 2 hours, in the first 6 hours and after the test, samples were taken for chemical analysis to verify the percent extraction, and also monitored the pH and conductivity of all compartments.

Results and discussion

Table 1 shows the chemical characterization of AMD, as the determination of pH, conductivity, cations and anions.

Table 1. Chemical characterization of AMD.

	Parameters	Sample AMD
	pH	2.84
	Conductivity ($\mu\text{S} \cdot \text{cm}^{-2}$)	1154
Cations	Aluminium ($\text{mg} \cdot \text{L}^{-1}$)	269.00
	Calcium ($\text{mg} \cdot \text{L}^{-1}$)	143.07
	Sodium ($\text{mg} \cdot \text{L}^{-1}$)	1,059.00
	Potassium ($\text{mg} \cdot \text{L}^{-1}$)	64.07
	Magnesium ($\text{mg} \cdot \text{L}^{-1}$)	19.24
	Ferrous ($\text{mg} \cdot \text{L}^{-1}$)	0.55
	Ferric ($\text{mg} \cdot \text{L}^{-1}$)	0.28
	Nickel ($\text{mg} \cdot \text{L}^{-1}$)	0.16
	Manganese ($\text{mg} \cdot \text{L}^{-1}$)	1.12
	Zinc ($\text{mg} \cdot \text{L}^{-1}$)	0.56
Anions	Sulphate ($\text{mg} \cdot \text{L}^{-1}$)	518.28
	Chloride ($\text{mg} \cdot \text{L}^{-1}$)	69.76
	Nitrate ($\text{mg} \cdot \text{L}^{-1}$)	143.07

The polarization curves were carried out and it was determined that the current limit for the cationic membrane was approximately 33mA and 25mA anion membrane.

Whereas membranes have surface area of 16cm^2 and that 80% threshold is usually used, the current density to be applied to the ED for this AMD, should be $20\text{mA}/16\text{cm}^2$ or $1.25\text{mA}/\text{cm}^2$. For this case, the current density limit is set based on the curve obtained for the anionic membrane, thus to avoid polarization in the membrane cationic.

From the obtained polarization curves, it was determined that a current of 20mA to the system, would be applied for 24 hours of ED testing. In this trial, the pH and conductivity were monitored in each compartment, every 2 hours of testing during the first 6 hours and after 24 hours. Table 2 presents the results of this monitoring.

Table 2. Experiment monitoring of ED.

Time	Parameters	Anode	Concentrated Anode	Diluted	Concentrated Cathode	Cathode
Initial	pH	5.85	2.84	2.84	2.84	5.85
	σ ($\mu\text{S} \cdot \text{cm}^{-2}$)	1400	1154	1154	1154	1400
2h	pH	2.71	2.80	2.99	2.91	10.58
	σ ($\mu\text{S} \cdot \text{cm}^{-2}$)	1822	1414	1005	1324	1627
4h	pH	2.49	2.64	3.04	3.04	10.88
	σ ($\mu\text{S} \cdot \text{cm}^{-2}$)	1930	1694	881	1372	1846
6h	pH	2.36	2.49	3.10	3.22	11.07
	σ ($\mu\text{S} \cdot \text{cm}^{-2}$)	2080	1930	737	1425	1950
24h	pH	2.09	2.06	4.83	3.87	11.09
	σ ($\mu\text{S} \cdot \text{cm}^{-2}$)	2760	3570	6.38	1751	1970

The results in Table 2 suggest that over the 24 hour test, there was a decrease in the conductivity of the diluted compartment and an increase in the conductivity of the other compartments, as it was expected. Because the aim of this work is the dilution of AMD in the central compartment

and the concentration of that sample in the Concentrated Anode and Concentrated Cathode compartments.

The increase in conductivity in the Anode and Cathode compartments is due to the release of H^+ and OH^- , respectively, by the electrodes to the solution of each compartment. The analysis of pH in these compartments corroborates this explanation. Because there is a decrease in pH in the Anode compartment and an increase in the Cathode compartment.

The chemical characterization, the AMD in diluted compartment along the ED test are shown in Figure 4 and Figure 5 for the analysis of extraction of cations and anions, respectively.

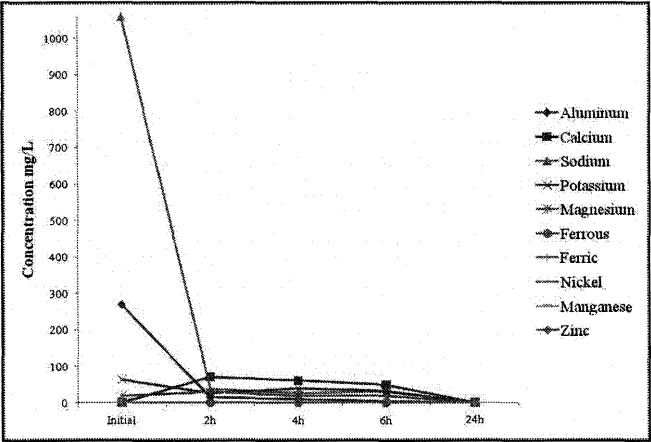


Figure 4. Extraction of cations.

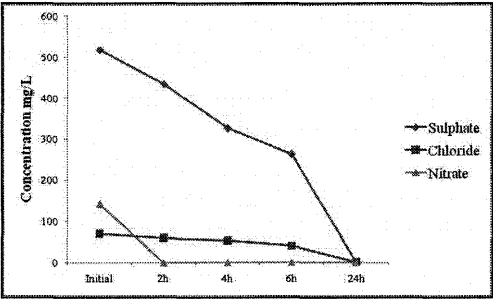


Figure 5. Extraction of anions.

From results presented in Figure 4 and Figure 5, it appears that the ED process was efficient for the extraction of cations and anions, removing over 99% of them after 24 hours of testing.

Conclusion

The ED can be used for the treatment of AMD from the abandoned coal bank. ED performed is efficient for the removal of cations and anions present in this effluent, removing more than 99% of this contamination in 24h.

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