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Study of the zinc recovery from spent pickling baths by means of an electrochemical membrane reactor using a cation-exchange membrane under galvanostatic control

J. Carrillo-Abad, M. García-Gabaldón *, V. Pérez-Herranz

IEC Group, Departamento de Ingeniería Química y Nuclear, Universitat Politècnica de València, Camí de Vera s/n, P.O. Box 22012, E-46071, 46900 València, Spain

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ABSTRACT

The performance of a cation-exchange membrane (CEM) used for recovering zinc from real spent pickling baths is studied in this work. These spent baths contain high amounts of $ZnCl_2$ and $FeCl_2$ in aqueous HCl media. The results obtained with this membrane are compared with those obtained with an anion-exchange membrane (AEM) treating the same effluent. The effect of the presence or absence of initial zinc in the cathodic compartment is also studied.

The absence of initial zinc in the cathodic compartment in the CEM experiments permits iron codeposition. Furthermore, the results obtained with the CEM are worse than those obtained with the AEM for all the figures of merit. This fact shows the need of filling the cathodic compartment with a synthetic zinc solution. The presence of zinc in the cathodic compartment from the beginning of the electrolysis not only inhibits iron codeposition but also favors zinc deposition as the hydrogen evolution reaction becomes a secondary reaction, improving by this way the results of all the figures of merit of the reactor with the CEM. A deep study about the effect of the applied current and the concentration of the synthetic zinc solution placed in the cathodic compartment permits to reach the equilibrium between the zinc transferred through the membrane and that deposited on the cathode. Therefore, the synthetic cathodic zinc is not consumed at any time. Moreover, under this circumstances iron codeposition is also avoided.

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1. Introduction

One of the most well known uses of metallic zinc is to protect iron or steel pieces from corrosion processes by coating them with it [1]. In order to coat the pieces, the oldest technique used is the hot dip galvanizing, which is based on dipping the pieces into molten zinc. Previously to the dipping process, these pieces must be cleaned by means of different pretreatments. The present paper focuses on the effluents coming from the pickling process, which consists of attacking the pieces surface with HCl for cleaning them from rust and impurities. The effluents coming from the pickling process contain high concentrations of Zn, Fe and HCl together with low concentrations of organic compounds, such as hydrogen evolution reaction inhibitors, and other heavy metals [2]. Therefore, spent pickling baths have to be treated before their disposal to accomplish with the environmental restrictions. However, the development of an adequate treatment for this effluent is very difficult because of the high complexity usually encountered in the hydrochloric acid effluents, where the target species are present in a heterogeneous mixture with different amounts of non-desirable compounds [3].

Owning to the inefficiency of the traditional methods for the treatment of spent pickling baths, as the precipitation-filtration process [4], many different techniques such as liquid–liquid extraction [5] or anionic resins [6] have been suggested [7]. In this way, the electrolysis in a membrane reactor is presented in this paper as an alternative for the treatment of the spent pickling baths in one single step. In a previous work [8], the authors performed an electrochemical study of the solution to obtain the kinetics of the electrochemical processes and, then, an undivided electrochemical batch reactor was used in potentiostatic and galvanostatic mode [9,10] to determine the viability of zinc recovery from spent pickling baths. During these experiments zinc redissolution was observed at high time values for all the experimental conditions. This process is related to the synergic effect of iron ions and dissolved chlorine gas that attacks zinc deposits causing their oxidation [11,12].

In order to prevent the zinc redissolution phenomena, an anion-exchange membrane (AEM) was initially used [13] to avoid

* Corresponding author. Tel.: +34 963877632; fax: +34 963867639.
E-mail address: mongarga@iqn.upv.es (M. García-Gabaldón).

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chlorine presence in the cathodic compartment. This membrane permitted zinc conversion values closer to 100% and higher current efficiencies. However, iron began to codeposit with zinc as the latter was being removed from the solution since the iron–zinc system deposits following the anomalous codeposition phenomenon [14–16], in which the less noble metal (zinc) deposits preferentially, and iron deposition depends on the zinc–iron ratio, the applied current and the pH value.

Therefore, in order to recover zinc in only one step and try to prevent iron codeposition simultaneously, a cation-exchange membrane (CEM), NAFION-117, is used in the present work. In this sense, the anodic compartment contains the spent pickling bath whereas the cathodic one is filled with HCl in the presence or absence of a synthetic zinc salt. By this way, chlorine presence in cathodic compartment is avoided as CEM acts as a barrier. Moreover, the zinc pass through the cation-exchange membrane is preferential over that of iron. This is related to the Fe(II) oxidation to Fe(III) in the anodic compartment together with the fact that NAFION-117 traps trivalent cations preferentially over the divalent ones [17–19]. Therefore, the influence of the concentration of the synthetic zinc solution initially present in the cathodic compartment together with the applied current will be evaluated. In addition, the results obtained with the CEM will be compared with those obtained with the AEM at the same working conditions. For a better understanding of the different experiments, a diagram of the electrochemical reactor with both membranes used is presented in Fig. 1.

2. Methodology and materials

The reactor used in this work was well defined in our previous work [13]. An equal volume (250 cm^3) of anolyte and catholyte is poured in their respective chamber after cell assembly. The same Ag/AgCl reference electrode and graphite cathode and anode have been used in this set-up. Both cathode and anode are totally immersed in the solution and they are symmetrically placed with respect to membrane surface. The membranes used are a NAFION-117 as CEM and an IONICS AR-204-SZRA-412 as AEM. The anode and cathode are made of two cylindrical graphite bars with an effective area of 14.15 cm^2.

The average composition of the spent pickling bath used in this work is presented in Table 1. The 1:10 diluted spent pickling bath is placed in the anodic compartment and a synthetic solution composed of 0.1 M HCl or 0.1 M HCl and $ZnCl_2$ in a concentration range from 0.02 M to 0.1 M, is placed in the cathodic one for the CEM experiments. On the other hand, in the AEM experiments, the 1:10 diluted spent pickling bath is poured in the cathodic compartment whereas the anodic one is filled with a 0.1 M HCl solution (Fig. 1). The synthetic solutions containing $ZnCl_2$ and/or HCl have been made from analytical grade reagents and distilled water. All experiments were made at room temperature.

Table 1
Average composition, in mol/l and g/l, of the spent pickling bath used in this work.

	Zn	Fe	HCl
M	1.9780	1.0578	2.1380
g/l	129.3242	58.8129	78.0356

Galvanostatic experiments are performed at different applied currents, which range from 700 to 1750 mA. The equipment used for the electrolysis experiments is an Autolab PGSTAT20 potentiostat/galvanostat. Potential, cell voltage, current, pH and temperature are recorded during the electrowinning. On the other hand, 1 ml samples are taken from the reactor every 30 min and zinc and iron determination is performed by atomic absorption spectrophotometry (AAS) as described in our previous works [9,10,13]. The determination of zinc is carried out on a Perkin–Elmer model Analyst 100 atomic absorption spectrophotometer using a zinc hollow cathode lamp at 213.9 nm wavelength, 0.7 nm spectral bandwidth and an operating current of 5 mA, whereas iron concentration is measured using the same equipment, changing the Zn hollow lamp for a Fe hollow lamp. The parameter values used for iron determination are: a wavelength of 248.3 nm, an applied operating current of 5 mA and a spectral bandwidth of 0.2 nm.

3. Results and discussion

As mentioned above, Nafion-117 is selected, in this work, as CEM in order to try to avoid the iron codeposition problem because this membrane favors zinc transport over that of iron. Divalent iron must be oxidized to its trivalent form in the anodic compartment and, therefore, it will be retained by Nafion-117 preferentially. With the purpose of comparing different aspects of the zinc electrodeposition, galvanostatic experiments are performed and the evolution of the concentration of zinc and iron in both the anodic and cathodic compartments is followed by means of atomic absorption spectrometry. Various figures of merit of the electrolytic cell are calculated. Firstly, zinc and iron removal rate is calculated using Eq. (1):

$$X(t) = \frac{n_0 - n(t)}{n_0} \quad (1)$$

where n_0 are the initial mols of zinc or iron present in solution and $n(t)$ corresponds to the mols of this species at a given time. Furthermore, the current efficiency, which is an indicative of the efficiency of the zinc deposition process and relates the current used to deposit it with the total current input, is calculated by using Eq. (2) [20]:

$$\phi(t) = \frac{n \cdot F \cdot (n_0 - n(t))}{\int_0^t I(t)dt} \cdot 100\ (\%) \quad (2)$$

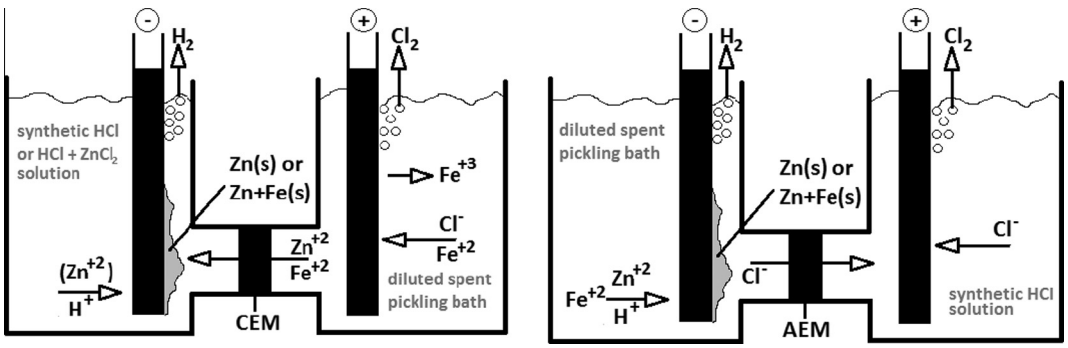

Fig. 1. Simplified diagram for both membrane reactors.

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