Abstract

Nowadays, 43% of the worldwide zinc production is used in the hot dip galvanizing process. Previously to the introduction of the pieces into the zinc molten bath, these pieces need a series of superficial treatments. Amongst these treatments, it is worth to mention the pickling one, which is based on the immersion of the pieces in a hydrochloric acid bath in order to eliminate rust rests, as the most polluting step from the galvanizing process, since the spent pickling baths contain high $ZnCl_2$ and $FeCl_2$ concentrations in HCl media. In the present Doctoral Thesis a study in depth of the electrochemical zinc recovery is carried out, showing it as a clean and efficient alternative. The purpose of this technique is the recovery of the most valuable component, in its metallic state that could be reintroduced directly in the hot dipping galvanizing process.

Previously to the use of the electrolysis to treat the spent pickling baths, an electrochemical study of the dissolution was done by means of the cyclic voltammetry technique. This study determined that bulk zinc deposition appears from -1V, and its reduction peak is close to -1.5V. From the different cyclic voltammetries performed was concluded that the zinc deposition is an irreversible process, controlled not only by diffusion but also by the charge transfer kinetics. The zinc deposition process is based on a previous step that consists of the formation of a zinc hydroxide film. In addition, it was also concluded that zinc and iron are deposited following an anomalous co-deposition process that permits zinc deposition preferentially over iron, since the zinc hydroxide film inhibits iron deposition. However, the stability of this zinc hydroxide film depends, mainly, on the zinc and iron concentration ratio, the pH and the applied current.

The potential and the current values applied in the electrochemical reactor in the potentiostatic and galvanostatic operation modes were determined from the previous electrochemical study. The analysis of the different figures of merit (X, ϕ, η y E_s) resolved that the potentiostatic mode looses its characteristic selectivity as a consequence of the HER (hydrogen evolution reactor) process. Moreover, it was also determined that the chlorine gas generated at the anode attacks the zinc deposits causing its redissolution, which is enhanced in iron presence. Iron presence also diminishes the process current efficiency. On the other hand, zinc-iron co-deposition was detected

once zinc conversion surpasses the 50% and the pH value was greater or equal to 2.

As a consequence of the negative effect of the chlorine presence near the cathode, an electrochemical membrane reactor was used. In this reactor the membrane would act as a barrier between both compartments. The use of an AEM (anionic exchange membrane) prevented the zinc redissolution phenomenon, improving the results obtained over those achieved in the barrier absence. However, since this membrane did not solve the iron co-deposition problem, it was changed by a CEM (cationic exchange membrane). Thanks to this configuration, the iron co-deposition was prevented although the results got worse due to the zinc absence in the cathodic compartment during the initial moments of the electrolysis. Adding zinc in the cathodic compartment of the CEM experiments permitted to obtain of similar results to those achieved with the AEM. From the CEM studies, it was determined that high current values improved the results obtained for the zinc recovery but also allowed the iron co-deposition phenomenon. In addition, the polarization curves of the membrane showed that operating at higher currents values than the limiting current causes the membrane fouling. Nevertheless, combinations amongst the applied current and the initial zinc concentration in the cathodic compartment allowed achieving an equilibrium between the zinc that passes through the CEM and the zinc that deposits on the electrode, preventing, by this way, iron co-deposition phenomenon.