ELECTROCHEMICAL RECOVERY OF ZINC FROM THE SPENT PICKLING BATHS COMING FROM THE HOT DIP GALVANIZING INDUSTRY. POTENTIOSTATIC OPERATION

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

Grupo IEC, Departamento de Ingeniería Química y Nuclear, *Universidad Politécnica de Valencia. P.O. Box 22012, E-46071 Valencia. Spain.*

*Corresponding author. Tel.: +34-6-3877632; fax: +34-6-3877639; E-mail address:

mongarga@iqn.upv.es (M. García-Gabaldón)

Keywords: electrochemical deposition, iron, hydrogen evolution reaction, pickling solutions, zinc electrodeposition

Abstract

An electrochemical reactor was developed to recover zinc from the spent pickling solutions coming from the hot dip galvanizing industry. These solutions mainly contain $ZnCl_2$ and $FeCl_2$ in aqueous HCl media. The effect of the applied potential on the figures of merit (fractional conversion, current efficiency, space-time yield and specific energy consumption) of the electrochemical reactor was analysed. Voltammetric experiments were performed previously in order to select the optimum conditions to be applied in the electrolysis experiments. From the i-V curves it was inferred that bulk zinc deposition started from potential values more cathodic than -0.99V. The hydrogen evolution reaction (HER) appeared from -0.45V and masked the zinc cathodic peak C1,

related to bulk zinc deposition, at high HCl concentrations. The presence of HCl inhibited iron deposition in synthetic samples. The additives present in the real baths, which diminish the massive hydrogen generation, allowed the observation of peak C1.

The potential values to be applied in the electrolysis experiments were chosen from the voltammetric experiments and ranged between -1V and -1.75V. In the absence of iron in solution, as the electrode potential was shifted towards more negative values, the space-time yield of zinc and its fractional conversion increased because of the increase in the electrode roughness and the hydrogen turbulence-promoting action. Simultaneously, the specific energy consumption decreased initially due to the increase in the zinc conversion rate but decreased for the most cathodic potential value due to HER. The presence of iron in synthetic solutions led to a decrease in current efficiency associated with the reverse redox Fe^{2+}/Fe^{3+} system and to the enhancement of the HER, which also induced increments in the local pH and the subsequent zinc redissolution for the most cathodic potential values. On the contrary, the additives present in the real spent pickling baths avoided the adverse effects of iron, and zinc electrodeposition was possible even at high cathodic potential values. In fact, a potential value of -1.75V was selected as the optimum since the conversion, the current efficiency and the space time yield obtained in the real baths were relatively high.

1. Introduction

Hot dip galvanizing processes offer a simple and effective way for corrosion protection of steel parts. This protection is based on covering the steel with a thin layer of metallic zinc that protects steel from corrosion by two ways: surface coating and sacrificial anode as zinc is lees noble than iron. This process consists of the following steps: alkaline or acidic degreasing, rinsing with water, pickling with dilute hydrochloric or sulphuric acid, rinsing with water, fluxing in aqueous $ZnCl_2/NH_4Cl$ baths, drying and dipping into molten Zn at temperatures of about 450ºC for a defined period [1].

As steel is introduced into the pickling bath, HCl reacts with iron and iron oxides to form ferrous chloride in solution. The same bath is used until the acid concentration falls to give unacceptable pickling times. The remaining acid is then usually used for stripping zinc from rejected galvanizing work until the acid is deemed spent. Zinc may also enter the pickling line via hooks, jigs, etc., that are used to suspend the work during dipping. Therefore, spent pickling baths contains hydrochloric acid, $ZnCl_2$ and $FeCl_2$ as principal compounds. The composition of the baths will change greatly depending on how long it has been used for pickling [2] but they mainly contain 80-150 g/l $FeCl_2$, 5-150 g/l $ZnCl_2$ and 10-80 g/l HCl [1].

Currently, many techniques exist to eliminate zinc and iron from wasted pickling solutions coming from hot dip galvanizing processes. The most widely used is the precipitation-filtration technique. Although the required equipment is relatively inexpensive, there are a number of disadvantages such as a large consumption of

3

chemicals and the expensive disposal of the generated hazardous waste [3] that makes this technique inappropriate.

Other techniques employed to treat the spent pickling baths are the diffusion dialysis, electrodyalisis and solvent extraction. These techniques do not allow any recovery of the products, but they permit the acid recovery. The electrodyalisis enables purification of water and concentration of the extracted component, but an additional treatment is needed to allow the acid and heavy metals separation and to permit the final separation and deposition of zinc and iron. Therefore this technique needs a complex purification system with a high investment cost [1]. The solvent extraction method makes the separation of zinc and iron possible but later treatment processes are needed and, thus, it becomes a complex system. The diffusion dialysis has proven successful in regenerating mixed acids until 80-85% of the original acid, but the high metal containing solution must be treated as hazardous waste. Its advantage is its low operating costs, but its investment costs are significant and it has low productivities [3].

Due to the inadequate existing techniques to treat the spent pickling solutions, the decrease of natural reserves of non-ferrous metals and the requirement of environmental protection, zinc electrowinning from spent pickling solutions appears an interesting alternative [4]. On the other hand, the electrolytic recovery of zinc is one of the oldest industrial processes, whose importance lies in the great worldwide demand for this metal that currently reaches an overall production of 9 million tonnes per year [5]. In fact, 80% of world zinc production is obtained by electrowinning [4].

In the present work, the cathodic electrodeposition of zinc present in the spent pickling baths coming from hot dip galvanizing industries is studied under potentiostatic operation and is compared with the behaviour of a synthetic sample in a concentration value similar to the real one. However, a previous study of the chemical and electrochemical behaviour of the metal ions must be done in order to examine the kinetic characteristics for the desired reactions and to take account of complexation of the cations and the irreversible nature of the electrodeposition processes [6].

2. Experimental

2.1- Voltammetric study

The cyclic voltammograms were obtained using a conventional three-electrode cell. The working electrode was a platinum disc of surface area 0.078 cm^2 enclosed in Teflon. Prior to each experiment, the Pt surface was mechanically polished with emery paper down to 4000 grid. An Ag/AgCl saturated KCl electrode was used as reference electrode and a platinum electrode was used as the counter electrode. Before each electrochemical experiment, the solution was deoxygenated for 10 minutes with ultrapure nitrogen. This inert atmosphere was maintained during the whole measurement. The electrochemical experiments were controlled using a Autolab PGSTAT20 potentiostat/galvanostat. Moreover, zinc was deposited under potentiostatic conditions (-0.45V, -1.4V and -1.5V) during 2 hours onto the Pt substrate. The structure, morphology and composition of the zinc coatings were examined by means of a JEOL JSM-3600 scanning electron microscope.

2.2- Electrolysis experiments

The potential values to be applied in the electrolysis experiments were chosen from the voltammetric experiments and ranged between -1V and -1.75V. The electrochemical reactor used in this work consisted of a Pyrex glass of 100ml with two graphite electrodes acting as working and counter electrodes and a standard Ag/AgCl satured KCl electrode acting as reference electrode. Both anode and cathode were made of two cylindrical graphite bars with an effective area of $14.15cm^2$. All the experiments were performed using the same potentiostat/galvanostat as that employed in the cyclic voltammetric experiments.

Samples were taken from the electrochemical reactor every 30min, and potential, current, cell voltage, pH and metal concentrations were recorded during the electrolysis. The determination of zinc was performed by atomic absorption spectrophotometry (AAS) on a Perkin-Elmer model AAnalyst 100 atomic absorption spectrophotometer using a Zn hollow cathode lamp at 213.9nm wavelength, 0.7nm spectral bandwidth and an operating current of 5mA. To measure iron concentration it was used the same equipment changing the Zn hollow lamp for a Fe hollow lamp, the wavelength used was 248.3nm, the applied operating current was 5mA and the spectral bandwidth was 0.2nm.

All solutions were prepared using analytical grade reagents and distilled water. Electrolytes containing $ZnCl_2$ and/or $FeCl_2$ in HCl were used in a concentration range similar to that present in the spent pickling baths. The zinc and iron concentrations were

respectively 0.055M and 0.035M, which are in accordance with the concentration values of these metal ions present in the diluted pickling-wasted baths. The HCl concentration was 0.1M. All the experiments were performed at room temperature.

3. Results and discussion

3.1- Voltammetric study

The zinc and iron concentration values present in the spent pickling baths are 2.75M and 1.75M, respectively. These values were determined by AAS following the operating conditions presented in Section 2.3 These measured values are similar to those reported in the literature [1, 2, 7]. This sample was diluted to 1:50, in order to perform the voltammetric and electrolysis experiments.

Fig. 1 represents the cyclic votammograms of different solutions performed on a platinum disk electrode at room temperature, scan rate of $60mVs^{-1}$, 0.1M HCl and under static conditions. For a zinc solution, curve a), the main features are the cathodic peak C1, which corresponds to the zinc bulk deposition, and the corresponding anodic stripping peak A1 centred at about -0.6V, which refers to the oxidation of the zinc previously deposited. This anodic peak appears even at higher HCl concentrations in solution (not shown), which indicates that zinc is also deposited in HCl concentrated media. Furthermore, due to the HCl presence, a cathodic peak related to HER (Hydrogen Evolution Reaction) process is observed at -0.45V (peak C2) [8].

Zinc deposits obtained at -0.45V (peak C2) and -1.4V (peak C1) during 2 hours and under the experimental conditions presented in Fig. 1a) were analysed by SEM. The zinc percentage in the deposit obtained at -0.45V was negligible, since the HCl concentration in solution is quite high and this potential value belongs to the hydrogen evolution range. On the contrary, when the potentiostatic experiments were performed at -1.4V, the typical morphology of a zinc deposit [9] is obtained, and the deposit displays the hexagonal zinc plates aligned parallel to the substrate as usual for zinc electrodeposits [10].

On the other hand, for an iron solution, curve b), no cathodic peak related to Fe^{+2} reduction to metallic iron is observed since low pH values inhibits iron reduction process [8, 11]. However, it does show the cathodic peak associated with HER process, C2. Moreover, at the anodic scan, the anodic peak, A2, that appears centred at 0V agrees with the hydrogen oxidation to H^+ over a platinum surface [12]. The anodic peak A3 observed at 0.6V is related to Fe^{+2} to Fe^{+3} oxidation process.

Curve c) represents the cyclic voltammogram of a synthetic mixture of Fe/Zn in a concentration similar to that present in the diluted real sample (curve d)). The cathodic scan only presents the hydrogen reduction peak C2 as iron enhances HER process and consequently peak C1 is masked. The anodic scan shows a complex peak. This peak is a mixture of A1 and A2 peaks, which suggests the zinc deposition over the platinum electrode for the Fe/Zn mixture. The porosity observed by SEM in the majority of the deposit obtained in the conditions presented in curve c), obtained after 2h electrolysis at -1.5V, indicates that a large amount of hydrogen gas is formed as predicted by the cyclic voltammograms experiments [13]. On the other hand, the composition of this

sample reveals a zinc percentage of 99%. Moreover, studies with different amounts of zinc, iron and HCl in synthetic samples (not shown) revealed that the presence of iron displaces the cathodic peak C1 towards less cathodic potential values [8].

Finally, curve d) shows the voltammogram obtained for a 1:50 diluted real sample. The additives are added to the real bath to avoid the excessive hydrogen formation [14], and this fact permits the observation of peak C1, which is related with zinc reduction process, since otherwise it would be masked by the hydrogen evolution enhanced in the presence of iron. Moreover, in the reverse scan, the shape of the complex anodic peak, could suggest zinc and iron codeposition. This fact was confirmed by the measurement of the composition of the real sample, in which the zinc and iron percentages were approximately 70% and 30%, respectively"

Therefore, zinc bulk deposition process starts from potential values more cathodic than -0.99V. HER process appears from -0.45V and may mask the cathodic peak C1 at high HCl concentrations. The presence of HCl inhibits iron deposition in synthetic samples and masks the observance of peak C1, which is related to bulk zinc deposition. On the other hand, the additives present in the real pickling baths allow the observation of peak C1. According to these results, the potential values to be applied in the electrolysis experiments range from -1V, which represents the initial steps of the zinc electrodeposition, to -1.75V since at this potential value the zinc deposition is completed.

3.2- Electrolysis experiments

3.2.1. Synthetic solutions

Initially, the electrolysis of synthetic solutions in absence of iron has been studied, and, afterwards the iron effect over zinc electrodeposition has been evaluated. Fig. 2 shows a plot of the evolution of zinc concentration as a function of time at different electrode potentials for an electrolyte composed of 0.055M $ZnCl_2$ and 0.1M HCl. The applied potential values have been selected according to the zinc reduction peak C1 present in curve a) of Fig. 1. When the electrode potential is -1.125V the concentration of zinc in solution remains practically constant, because this potential value is far from the potential value corresponding to peak C1 observed in curve a) of Fig. 1, moreover, this fact confirms that peak C2 is associated with HER process. For more cathodic applied potentials, the concentration profile decays exponentially with time as zinc is depleted from solution, this behaviour being characteristic of a batch electrochemical reactor. On the other hand, the more negative the applied potential is, the higher the velocity of the zinc reduction reaction, and consequently, the amount of zinc in solution is lower. At the most cathodic potential value of -1.5V and for a high electrolysis time, an increment in the zinc concentration value is observed. This fact is related to zinc redissolution at high local pH values around working electrode interface [15, 16].

Fig. 3 represents the evolution of current versus time for the same experimental conditions as those presented in Fig. 2. When the applied potential is more cathodic than -1.125V, the current curve shows a maximum value, which is the consequence of two opposite effects. Current sharply rises during the initial period as zinc nucleates on

the graphite electrode, causing an increase in roughness, and thus, in total current [9, 16]. For longer times, zinc deposition begins to be diffusion controlled, and as zinc ion is depleted, current slowly decreases, this factor being predominant at longer times of the experiment. In the case of a potential value of -1.125V, since Zn deposition is almost negligible the maximum in current is not observed. If the evolution of current is compared for every potential value, it is observed that the more negative the applied potential is the higher the cathodic current value is, due to the greater rate of zinc electrodeposition, as predicted in the voltammetric curves presented in Fig. 1.

The effect of the applied potential on the fractional conversion of zinc, X_{Zn}, for an electrolyte composed of 0.055M $ZnCl_2$ and 0.1M HCl is shown in Fig. 4. This Figure also presents the local pH profile for the most cathodic applied potential. When the applied potential is -1.125V zinc deposition is negligible, especially at the initial stages of the electrolysis, as observed in Fig. 2, whereas for more negative potential values, zinc fractional conversion increases as the applied potential is made more negative. Note that at -1.5V and when the electrolysis time is higher than 200 min, the zinc conversion decreases probably due to the zinc redissolution occurring nearby the electrode as a consequence of the great local pH increase observed in this Figure. This phenomenon of zinc redissolution was also observed by other authors [11,17].

For a batch electrochemical reactor in the potential range at which zinc deposition is mass-transfer controlled, assuming that the electrolyte is well-mixed at all times, the fractional conversion as a function of time is given by [18]:

$$X(t) = 1 - \exp(-k \cdot a_e \cdot t) \tag{1}$$

where k represents the mass transfer coefficient and a_e the active specific area of the electrode. The product of $k \cdot a_e$ is an important parameter in the design equations for all the electrochemical reactors supporting a mass transport controlled reaction, and may be calculated from the logarithmic representation of equation (1) versus time. Fig. 4 presents, as solid lines, the fitting of the experimental data to the theoretical expression presented in equation (1).

For the potential value of -1.125V, the $k \cdot a_e$ parameter is not calculated because under these conditions zinc reduction rate is negligible as mentioned above. Thus, this potential value does not show any theoretical line in Fig. 4. For the rest of applied potentials, the experimental values of conversion present a deviation from the theoretical model due to the fact that zinc deposition process is not only diffusion controlled but also charge transference controlled [8] and equation (1) is applied for processes controlled only by diffusion. Moreover, the theoretical model does not consider zinc redissolution.

The obtained values of $k \cdot a_e$ are 0.002 min^{-1}, 0.0028 min^{-1} and 0.0116 min^{-1} for the respective potential values of -1.25V, -1.375V, -1.5V. The increase of this parameter may be explained in terms of the turbulence of the H_2 bubbles generated on the cathode, the increased area of the zinc deposit and the greater rate of Zn electrodeposition that originates higher concentrations gradients in the proximities of the electrode. Regarding with hydrogen evolution, it becomes an evident feature when comparing zinc deposits at different potential values. For low electrode potentials the observed zinc deposit is thin, grey, smooth and hard, whereas at more cathodic electrode potentials, the area of the

zinc deposit is bigger and the deposit becomes darker, spongy, soft, and shiny. Therefore, the higher the cathodic potential value the greater the HER ratio, which increases the turbulence and, thus, the k parameter. On the other hand, the greater area of the spongy deposit increases the a_e parameter.

In order to rationalize the performance of a given electrochemical reactor or to compare between the performance of electrochemical reactors and other processes, it is essential to consider several figures of merit, such as current efficiency, ϕ, the mean value of the space-time yield, η, and the specific energy consumption, E_s, which are calculated with the following equations [19]:

$$\phi(t)(\%) = \frac{n \cdot F \cdot (C_0 - C(t)) \cdot V}{\int_0^t I(t) \cdot dt} \cdot 100 \qquad (2)$$

$$\eta(t) = \frac{M \cdot (C_0 - C(t))}{t} \qquad \left(g \cdot l^{-1} \cdot h^{-1} \right) \qquad (3)$$

$$E_s(t) = \frac{\int_0^t U(t) \cdot I(t) \cdot dt}{V \cdot C_0 \cdot X(t) \cdot M \cdot 3600} \qquad \left(kW \cdot h \cdot kg^{-1} \right) \qquad (4)$$

Figs. 5-7 show, respectively, the variation of the current efficiency, the space-time yield and the specific energy consumed at different electrode potential values and for an electrolyte composed of 0.055M $ZnCl_2$ and 0.1M HCl. At the lowest cathodic potential value, the current efficiency falls due to the zinc reduction reaction slowness and the greater importance of parallel reactions [20] (Fig. 5). The current efficiency increases as

the electrode potential is made more negative because of the approach to the potential value of peak C1 observed in curve a) of Fig. 1 as the contribution of the zinc reduction reaction is higher, but at -1.5V hydrogen evolution is more important than zinc deposition and, consequently, this fact causes a decrease of ϕ in relation to the values obtained at -1.25V and -1.375V. For all the applied potentials under study, ϕ presents high values during the initial steps but it drops at longer times due to the decrease in zinc concentration and the increase of hydrogen evolution reaction. Since the HCl concentration in solution is quite high (0.1M), hydrogen evolution appears from the early stages of all experiments [8] as observed previously in Fig. 1 by the presence of peak C2, and the maximum value of the current efficiency obtained is close to 45%.

For the lowest cathodic potential value of -1.125V, the space-time yield is negligible and remains practically constant due to the slower rate of the zinc reduction reaction (Fig. 6). For electrode potentials more negative than -1.125V, η presents high values during the initial period and it may be attributed to the nucleation of zinc onto the graphite electrode. The space-time yield slow decrease at longer times is related to the removal of zinc from solution. For a given time value, the space-time yield increases when the cathodic potential becomes more negative, because of the turbulence promoting action of hydrogen evolution, the roughness increase of the electrode surface and the higher velocity of the electrochemical reactions [21].

As shown in Fig. 7, when the electrode potential is -1.125V, the specific energy consumption is quite high because the zinc reduction reaction rate is still low, but when the applied potential is made more cathodic (-1.25 and -1.375V), E_s decreases due to the higher contribution of the zinc reduction reaction. If the applied potential in made more

cathodic, -1.5V, the contribution of the hydrogen evolution reaction is very important from the early stages of the experiment and, consequently, E_s increases. If Figs. 5 and 7 are compared it is observed that its behaviour is reversal, as can be predicted by the comparison of equations (2) and (4).

In order to compare the performance of the electrochemical reactor for the different electrode potentials, the time at which a 100% zinc fractional conversion is reached, assuming a current efficiency of 100% (t_{100}) has been determined from the following equation [18]:

$$\int_0^{t_{100}} I \cdot dt = n \cdot F \cdot V \cdot C_0 \tag{5}$$

where t_{100} represents the time when the charge passed in the reactor corresponds to the stoichiometric value. For this time value, the four figures of merit, X_{Zn}, ϕ, η and E_s have been evaluated and are reported in Table 1.

As a consequence of the increase in current with the applied potential, t_{100} decreases. For the most cathodic electrode potentials, -1.375 and -1.5V, and for t_{100}, a recovery of zinc of about 34% is possible with a current efficiency close to 35%. However, for the less cathodic potential values, -1.125 and -1.25V, the fractional conversion and the current efficiency obtained for t_{100} considerably decrease, due to the slow zinc deposition rate. For t_{100} the space-time yield increases when the electrode potentials is shifted towards more cathodic values because of the turbulence-promoting action of hydrogen evolution and the increased roughness of the electrode surface. On the other

15

hand, energy consumption initially decreases due to the increase in the conversion rate of zinc. However, for the most cathodic potential value E_s increases due to HER.

In order to evaluate the iron effect on zinc electrodeposition, a synthetic solution with the same zinc and HCl concentrations as the previous one and the same iron/zinc ratio as that present in the real sample is prepared (0.055M $ZnCl_2$ and 0.035M $FeCl_2$ in 0.1M HCl). Fig. 8 shows the zinc concentration evolution in the presence and absence of iron for the potential values of -1.25V and -1.5V. The solid line presents the pH profile for the most cathodic potential value of -1.5V in the presence of iron. For the potential value of -1.25V, the rate of Zn depletion is practically the same in the presence and absence of iron. However, for the potential value of -1.5V, the zinc reduction rate becomes negligible in the presence of iron due to the great local pH increase shown in Fig. 8, that causes zinc redissolution [15]. This fact is related to the enhancement of the HER process in the presence of iron, which produces a greater H^+ consumption at -1.5V [11]. This fact is also observed by the comparison of curves a) and c) shown in Fig. 1.

Iron concentration was also measured and resulted invariable for all the potential values under study. This fact may be related to the high acidity of the bulk solution and to the presence of zinc that could inhibit iron deposition [8, 11]. It is noteworthy that although iron deposition does not take place, its presence in solution greatly affects the zinc current efficiency as it can be observed in Fig 9, where current efficiency of zinc deposition at -1.25V and -1.5V with and without iron is compared. The decrease in current efficiency observed in the presence of iron for both potential values, is associated with the reverse Fe^{+2}/Fe^{+3} redox system taking place at the two electrodes

consuming high amounts of energy [22], and to the enhancement of the HER process, which also competes for zinc electrodeposition.

3.2.2. Electrolysis of real spent pickling solutions

The applied potential values have been selected according to the zinc reduction peak C1 present in curve d) of Fig. 1. The zinc concentration profile for all the applied potential values is shown in Fig. 10. The fact that zinc electrodeposition takes place even at high cathodic potential values suggest that the additives present in the real sample avoid HER process [14], otherwise, this reaction would be enhanced in the presence of iron. In synthetic solutions containing mixtures of Zn/Fe, the HER reaction made impossible zinc electrodeposition for a potential value of -1.5V as can be observed in Fig. 8. Iron concentration was also measured at real samples and resulted invariable for all the potential values under study.

Fig. 11 shows the evolution of zinc conversion for the different applied potentials and the local pH profile for the most cathodic value of -1.75V. The conversion behavior is the same as that observed previously in Fig. 4, i.e. the more cathodic potential is the higher conversion value. However, zinc redissolution appears for potential values more cathodic than -1V since the local pH values obtained are quite high for all the applied potentials.

Regarding with the fitting of the experimental data to the theoretical expression represented in equation (1), it can be observed that the experimental values of conversion present a deviation from the theoretical model due to the fact that zinc

deposition process is, as mentioned above, not only diffusion controlled but also charge transference controlled and the theoretical model does not consider the zinc redissolution process. The obtained values of $k \cdot a_e$ are 0.0014 min^{-1},0.0032 min^{-1} and 0.015 min^{-1} for the respective potential values of -1.25V, -1.5V and -1.75V. If the values of $k \cdot a_e$ for real and synthetic samples are compared for the same potential values, it can be concluded that they are greater for the synthetic samples since in the real samples zinc redissolution phenomenon is present for every potential value under study, which diminishes the amount of zinc deposited on the electrode surface.

If the current efficiency obtained for synthetic mixtures of Zn/Fe and for real samples are compared (Figs. 9 and 12, respectively), it can be concluded that real samples present slightly greater values. This fact is related to the presence of additives, like hydrogen evolution inhibitors, in real samples which improve the current efficiency against the worse effects of the Fe^{+2}/Fe^{+3} redox system and HER process [11].

The space-time yield and the specific energy consumption (not shown) present the same behaviour with the applied potential as that explained previously for synthetic samples in the absence of iron (Figs. 6 and 7, respectively), i.e. as the applied potential is shifted towards more cathodic values the space-time yield increases and E_s decreases. It is noteworthy that the space-time yield presents greater values in synthetic samples due to the fast local pH increase occurring in the real samples, which leads to diminish the zinc reduction rate. On the other hand, real samples present better values in terms of energy consumption than those obtained for the synthetic ones because of the inhibitors, which diminishes the HER rate.

Table 2 presents the values of the figures of merit for the t_{100} parameter in order to compare the results of the real solutions with those presented in Table 1. Whenever the figures of merit for t_{100} are compared (Table 1 vs. Table 2), it can be observed that the synthetic solution in the absence of iron has better values (except in terms of energy consumption) than those obtained for the real bath under the same applied potential values. The higher values of zinc conversion and space-time yield presented in Table 1 are related to the lesser local pH increase that favours zinc electrodeposition. Regarding with the data presented in Table 2, the potential value of -1.75V may be selected as the optimum since the conversion and the current efficiency are relatively high, and although the specific energy consumption is the highest, the space-time yield is also considerably higher.

4. Conclusions

An electrochemical reactor was developed to recover zinc from the spent pickling solutions coming from the hot dip galvanizing industry. These solutions mainly contain $ZnCl_2$ and $FeCl_2$ in aqueous HCl media. The different figures of merit and the product of the mass transfer coefficient and the specific surface area were calculated in order to select the best electrochemical reactor operating conditions.

Voltammetric experiments were performed previously in order to select the optimum conditions to be applied in the electrolysis experiments. From the i-V curves it was inferred that bulk zinc deposition started from potential values more cathodic than -0.99V. The hydrogen evolution reaction (HER) appeared from -0.45V and masked the zinc cathodic peak C1, related to bulk zinc deposition, at high HCl concentrations. The presence of HCl inhibited iron deposition in synthetic samples and masked the observance of peak C1. The additives present in the real baths, which diminish the massive hydrogen generation, allowed the observation of peak C1.

The potential values to be applied in the electrolysis experiments were chosen from the voltammetric experiments and ranged between -1V and -1.75V. In the absence of iron in solution, as the electrode potential was shifted towards more negative values, the space-time yield of zinc and its fractional conversion increased because of the increase in the electrode roughness and the hydrogen turbulence-promoting action. Simultaneously, the specific energy consumption decreased initially due to the increase in the zinc conversion rate but increased for the most cathodic potential value due to HER. Even though iron deposition does not take place for any experimental condition

under study, its presence in synthetic Zn/Fe solutions led to a decrease in current efficiency associated with the reverse redox Fe^{2+}/Fe^{3+} system and to the enhancement of the HER, which also induced increments in the local pH and the subsequent zinc redissolution for the most cathodic potential values.

If the values of $k \cdot a_e$ for real samples and synthetic samples in the absence of iron are compared for the same potential values, it can be concluded that they are greater for the synthetic samples since in the real samples Zn redissolution phenomenon is present for every potential value under the study, which diminishes the amount of zinc deposited on the electrode surface. On the other hand, the additives present in the real spent pickling baths avoided the adverse effects of iron, and zinc electrodeposition was possible even at high cathodic potential values. Actually, a potential values of -1.75V was selected as the optimum since the conversion, the current efficiency and the space time yield obtained in the real baths were relatively high.

Nomenclatures

a_e specific area of the electrode ($m^2 \cdot m^{-3}$)

C_0 initial concentration of the ion to be deposited ($mol \cdot l^{-1}$)

$C(t)$ ion concentration in solution for a specific time ($mol \cdot l^{-1}$)

E_s specific energy consumption ($kW \cdot h \cdot kg^{-1}$)

F Faraday constant ($96500 \ C \cdot eq^{-1}$)

I current intensity applied (A)

k mass transfer coefficient ($m \cdot min^{-1}$)

M molecular weight of the metal to be deposited ($g \cdot mol^{-1}$)

n number of equivalents per mole

t_t time when the charge passed in the reactor corresponds to the stoichiometric value

$U(t)$ cell voltage at a given time (V)

V volume of the solution (l)

X fractional conversion of the metal to be deposited

Greek letter

ϕ current efficiency (%)

η space-time yield ($g \cdot l^{-1} \cdot h^{-1}$)

References

[1] U. Kerney, Treatment of spent pickling acids from hot dip galvanizing, Resour. Conserv. Recy. 10 (1994) 145-151.

[2] C. Stocks, J. Wood, S. Guy, Minimization and recycling of spent acid wastes from galvanizing plants, Resour. Conserv. Recy. 44 (2005) 153-166.

[3] G. Csicsovszki, T. Kékesi, T.I.Török, Selective recovery of Zn and Fe from spent pickling solutions by the combination of anion exchange and membrane electrowinning techniques, Hydrometallurgy 77 (2005) 19-28.

[4] L. Muresan, G. Maurin, L. Oniciu, S. Avram, Effects of additives on zinc electrowinning from industrial waste products, Hydrometallurgy 40 (1996) 335-342.

[5] A. Recéndiz, I. González, J.L. Nava, Current efficiency studies of the zinc electrowinning process on aluminum rotating cylinder electrode (RCE) in sulphuric acid medium: Influence of different additives, Electrochim. Acta 52 (2007) 6880-6887.

[6] M. García-Gabaldón, V. Pérez-Herranz, J. García-Antón, J.L. Guiñón, Electrochemical study of the activating solution for electroless plating of polymers, J. Appl. Electrochem. 37 (2007) 1145-1152.

[7] H. Samaniego-Peña, I. Ortiz-Uribe, M.F. San Román- San Emeterio, Valorización de efluentes de decapado ácido metálico. Recuperación de zinc. Doctoral Thesis Universidad de Cantabria (2006)

[8] M. Garcia-Gabaldón, J. Carrillo-Abad, V. Pérez-Herranz, E.M. Ortega-Navarro, Electrochemical study of a simulated spent pickling solution, Int. J. Electrochem. Sci. 6 (2011) 506-519.

[9] S.C. Das, P. Singh, G.T. Hefter, The effects of 4-ethylpyridine and 2-cyanopyridine on zinc electrowinning from acidic sulfate solutions, J. Appl. Electrochem. 27 (1997) 738-744.

[10] K. Saber, C.C. Koch, P.S. Fedkiw, Pulse current electrodeposition of nanocrystalline zinc, Mater. Sci. Eng A. 341 (2003) 174-181.

[11] P. Díaz-Arista, O.R. Mattos, O.E. Barcia, F.J. Fabri Miranda, ZnFe anomalous electrodeposition: stationaries and local pH measurements, Electrochim. Acta 47 (2002) 4091-4100.

[12] D.J. Walton, L.D. Burke, M.M. Murphy, Sonoelectrochemistry: Chlorine, hydrogen and oxygen evolution at platinised platinum, Electrochim. Acta 41 (1996) 2747-2751.

[13] A. Recéndiz, I. González, J.L. Nava, Current efficiency studies of the zinc electrowinning process on aluminum rotating cylinder electrode (RCE) in sulphuric acid medium: Influence of different additives, Electrochim. Acta 52 (2007) 6880-6887.

[14]   http://www.fosfamet.cl/PROCESO_DE_DECAPADO_PARA_METALES.doc (Accessed 17 January 2011)

[15] J. Dobryszycki, S. Biallozor, On some organic inhibitors of zinc corrosion in alkaline media, Corr. Sci. 43 (2001) 1309-1319.

[16] F. Simescu, H. Idrissi, Corrosion behaviour in alkaline medium of zinc phosphate coated steel obtained by cathodic electrochemical treatment, Corr. Sci. 51 (2009) 833-840.

[17] E. Gómez, X. Alcobe, E. Vallés, Characterisation of zinc+cobalt alloy phases obtained by electrodeposition, J. Electroanal. Chem. 505 (2001) 54-61.

[18] M. García-Gabaldón, V. Pérez-Herranz, J. García-Anton, J.L. Guinon, Electrochemical recovery of tin and palladium from the activating solutions of the electroless plating of polymers: Potentiostatic operation, Sep. Purif. Technol. 45 (2005) 183-191.

[19] M. García-Gabaldón, V. Pérez-Herranz, J. García-Anton, J.L. Guinon, Electrochemical recovery of tin from the activating solutions of the electroless plating of polymers: Galvanostatic operation, Sep. Purif. Technol. 51 (2006) 143-149.

[20] T. Boiadjieva, M. Monev, A. Tomandl, H. Kronberger, G. Fafilek, Electrochemical studies on Zn deposition and dissolution in sulphate electrolyte, *J. Solid State Electrochem.* 13 (2009) 671-677.

[21] M.F. Dahab, D.L.Montag, J.M. Parr, Pollution prevention and waste minimization at a galvanizing and electroplating facility, Water Sci. Technol. 30 (1994) 243-250.

[22] A.E. Saba, A.E. Elsherief, Continuous electrowinning of zinc, Hydrometallurgy 54 (2000) 91-106.

Figures and Tables

Fig. 1: Cyclic voltammograms obtained for different solutions: a) 0.055M $ZnCl_2$ in 0.1M HCl; b) 0.055M $FeCl_2$ in 0.1M HCl; c) 0.055M $ZnCl_2$ & 0.023M $FeCl_2$ in 0.1M HCl, d) 1:50 diluted real sample.

Fig. 2. Evolution of zinc concentration vs. time as a function of the applied potential. $[ZnCl_2]_0 = 0.055M$, $[HCl]_0 = 0.1M$.

Fig. 3. Current intensity vs. time as a function of the applied potential. $[ZnCl_2]_0 = 0.055M$, $[HCl]_0 = 0.1M$.

Fig. 4. Fractional conversion of zinc vs. time as a function of the applied potential. $[ZnCl_2]_0 = 0.055M$, $[HCl]_0 = 0.1M$. (Dots are the experimental values and lines represent the fitting to equation 1)

Fig. 5. Current efficiency of zinc vs. time as a function of the applied potential. $[ZnCl_2]_0 = 0.055M$, $[HCl]_0 = 0.1M$.

Fig. 6. Space-time yield of zinc vs. time as a function of the applied potential. $[ZnCl_2]_0 = 0.055M$, $[HCl]_0 = 0.1M$.

Fig. 7. Energy consumption of zinc vs. time as a function of the applied potential. $[ZnCl_2]_0 = 0.055M$, $[HCl]_0 = 0.1M$.

Fig. 8. Evolution of zinc concentration vs. time as a function of the applied potential. $[ZnCl_2]_0 = 0.055M$, $[FeCl_2]_0 = 0.035M$, $[HCl]_0 = 0.1M$.

Fig. 9. Current efficiency of zinc vs. time as a function of the applied potential. $[ZnCl_2]_0 = 0.055M$, $[FeCl_2]_0 = 0.035M$, $[HCl]_0 = 0.1M$.

Fig. 10. Evolution of zinc concentration vs. time as a function of applied potential. 1:50 diluted real sample.

Fig. 11. Fractional conversion of zinc vs. time as a function of applied potential. 1:50 diluted real sample. (Dots are the experimental values and lines represent the fitting to equation 1)

Fig. 12. Current efficiency of zinc vs. time as a function of the applied potential. 1:50 diluted real sample.

Table 1. Figures of merit for the electrochemical recovery of zinc corresponding to t_{100} for a synthetic solution of 0.055M $ZnCl_2$ in 0.1M HCl

Table 2. Figures of merit for the electrochemical recovery of zinc corresponding to t_{100} for a 1:50 diluted real sample