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Electrochemical Recovery of Zinc from the Spent Pickling Solutions Coming from Hot Dip Galvanizing Industries. Galvanostatic Operation

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The performance of an electrochemical reactor for zinc recovery from the spent pickling solutions coming from the hot dip galvanizing industry in galvanostatic operation is studied in this paper. These solutions mainly contain $ZnCl_2$ and $FeCl_2$ in aqueous HCl media. The effect of the applied current on the figures of merit (fractional conversion, current efficiency, space–time yield and specific energy consumption) of the electrochemical reactor is analyzed and compared with the values obtained in the potentiostatic operation. The applied current was selected in order to obtain similar electrode potential values to those applied in the potentiostatic operation and ranged between −150 and −700 mA. In the absence of iron in solution, as the current value was shifted towards more negative values, the space–time yield of zinc and its fractional conversion increased because of the increase in the zinc reduction rate, the electrode roughness and the hydrogen turbulence-promoting action. However, the increase in current values makes current efficiency to decrease due to the hydrogen evolution reaction (HER), which causes an increment in the specific energy consumption. 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. These adverse effects related to the presence of iron are greater in galvanostatic mode than in potentiostatic one. On the contrary, the additives present in the real spent pickling baths improve the zinc electrodeposition rate compared with the behavior of synthetic mixtures of zinc and iron solutions but the zinc redissolution is enhanced.

Keywords: zinc electrodeposition; galvanostatic operation; iron; hydrogen evolution reaction; pickling solutions

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 zinc at temperatures of about 450 °C for a defined period [1].

The pickling step, previous to the galvanizing process, generates a succession of effluents containing, among other substances, high concentrations of $ZnCl_2$, $FeCl_2$ and HCl. This gives rise to an environmental problem that has to be solved due to the hazardous nature of the effluents [2, 3]. In addition, the decrease of natural reserves of non-ferrous metals and the requirement of environmental protection, makes zinc electrowinning from spent pickling solutions an interesting alternative [4, 5]. Moreover, the electrolytic recovery of zinc present in the spent pickling baths can be a suitable technique because zinc electrowinning has been practiced for many years [6]. In fact, 80% of world zinc production is obtained by electrowinning [1].

In our previous paper [7], the potentiostatic recovery of zinc present in the spent pickling bath using an electrochemical reactor was studied. The major interfering reaction during zinc electrodeposition on the cathode surface was the hydrogen evolution reaction (HER), although iron presence also diminished the current efficiency. It was also observed that during the last instants of electrolysis, zinc concentration at the electrochemical reactor increased again due to local pH increases near the cathode surface.

In the potentiostatic operation, a constant potential on the working electrode with respect to the reference electrode is established, and the electrode potential determines which electron transfer reactions can occur and their absolute rates. Only species with a less negative redox potential than the applied one will be deposited on the electrode, therefore little current is wasted. On the other hand, in the galvanostatic operation a constant current is passed through the electrochemical reactor, and the electrode potential varies with time. When the concentration of the reactant finally drops to zero a sharp rise in potential takes place until a new electrode reaction begins [8, 9].

The potentiostatic way of operation is easy to put into practice on a laboratory scale by using a standard potentiostat. However, its industrial application is more difficult because of the high cost of high-power potentiostats. Another drawback of the potentiostatic mode in industrial applications is the requirement of reliable reference electrodes. Then, for most industrial electrochemical processes, constant current control is the most useful operating approach from both a practical and theoretical viewpoint [9]. The purpose of this work is to analyse the behaviour of an electrochemical reactor working in galvanostatic mode for the zinc recovery present in the spent pickling baths coming from the hot-dip galvanizing industries. The effect of the applied current on the “figures of merit” of the electrochemical reactor has been evaluated and compared with the values obtained in the potentiostatic operation.

2. EXPERIMENTAL

The expemiental setup used in this work was adequately described in our previous paper [7]. The electrochemical reactor used in this work consisted of a Pyrex glass of 100 ml 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 14.15 cm^2. Experiments were performed at different applied currents, which ranged from -150 to -700 mA. The applied current values were selected in order to obtain similar electrode potential values to those applied in the potentiostatic operation [7]. The electrolysis experiments were controlled using an AutolabPGSTAT20 potenitostat/galvanostat.

Samples were taken from the electrochemical reactor every 30 min, 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 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. To measure iron concentration it was used the same equipment changing the zinc hollow lamp for a Fe hollow lamp, the wavelength used was 248.3 nm, the applied operating current was 5 mA and the spectral bandwidth was 0.2 nm.

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

3. RESULTS AND DISCUSSION

3.1. Synthetic solutions

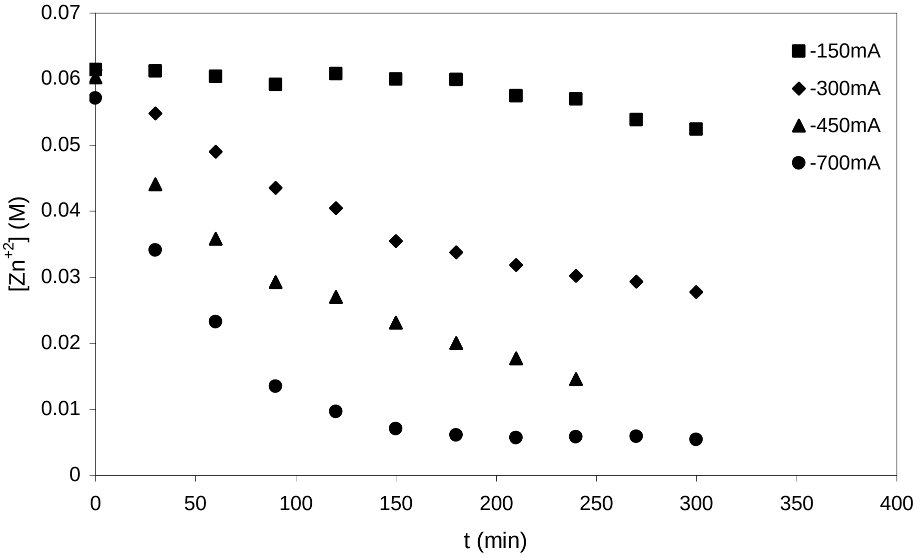

Figure 1. Evolution of zinc concentration vs. time as a function of the applied current. $[ZnCl_2]_0$ = 0.055 M, $[HCl]_0$ = 0.1 M.

Fig. 1 shows the variation of zinc ion concentration as a function of time at different applied current values for an electrolyte composed of 0.055M $ZnCl_2$ and 0.1M HCl. For the lowest cathodic current (-150 mA), the current density is too low and the zinc concentration value remains practically constant. For intermediate current values (-300 and -450 mA), zinc concentration initially diminishes with time following a linear tendency because the applied current is lower than the limiting value. When the limiting current value is surpassed an exponentially decrease is obtained as observed for the most cathodic current value (-700 mA), where zinc concentration diminishes exponentially from the beginning of the experiment. For a given time value, as current is made more negative zinc becomes depleted from de solution faster and, consequently, the amount of zinc in solution is lower.

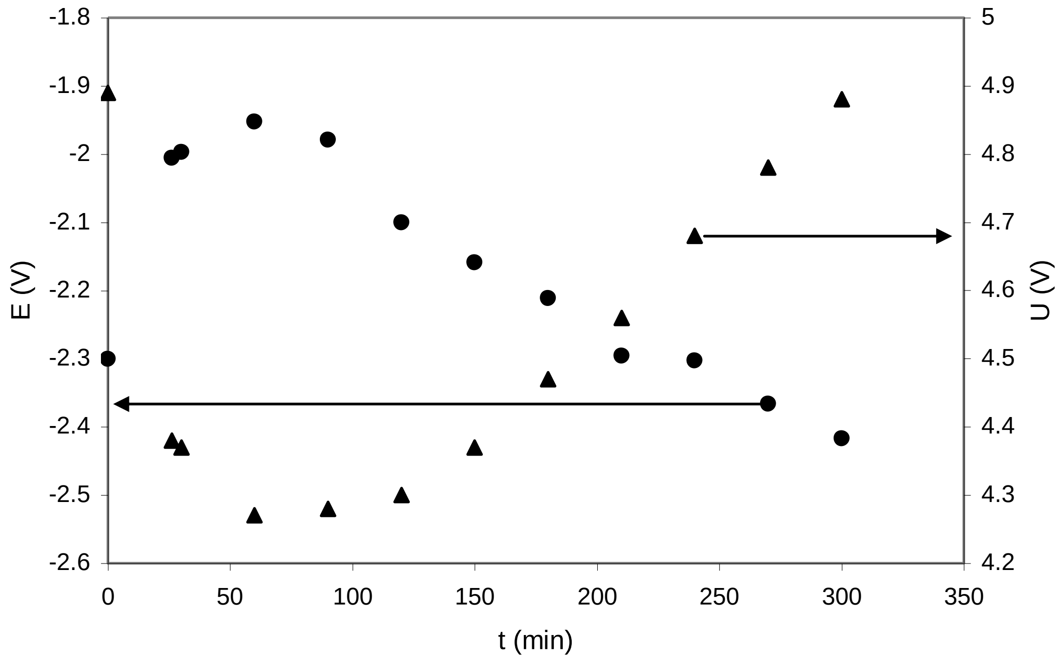

Figure 2. Electrode potential and cell voltage vs. time for an applied current of -700 mA. $[ZnCl_2]_0$ = 0.055 M, $[HCl]_0$ = 0.1 M.

Because the galvanostatic operation corresponds to an imposed global reaction rate, the electrode potential (E) and the cell voltage (U) change with time as can be observed in Fig. 2 for an applied current of -700 mA. Initially, the electrode potential is very cathodic (-2.3 V) because the resistance of the electrode to zinc electrodeposition is very high. As the graphite electrode is covered with zinc deposits, its resistance decreases, and consequently, the electrode potential becomes less negative, reaching a value of -1.95 V. Finally, as zinc is removed from solution, the hydrogen evolution reaction (HER) starts in order to maintain the applied current constant. HER process becomes more important for longer times and makes the electrode potential shifts to more negative values until reaching a value of -2.42 V. On the other hand, the cell voltage initially has a value of 4.9 V. As a consequence of the electrode activation and the decrease of the electrode overvoltage due to zinc deposition, the cell voltage decreases until a minimum value of 4.27 V. Afterwards, the cell voltage increases sharply because of zinc depletion from solution and the beginning of the hydrogen evolution reaction.

The effect of the applied current on the fractional conversion of zinc, X_{Zinc}, for an electrolyte composed of 0.055M $ZnCl_2$ and 0.1M HCl is shown in Fig. 3. When the applied current is -150mA zinc deposition is negligible during the first 3 hours, afterwards, X_{Zinc} increases linearly with time. For more negative current values, X_{Zinc} increases as current is made more negative.

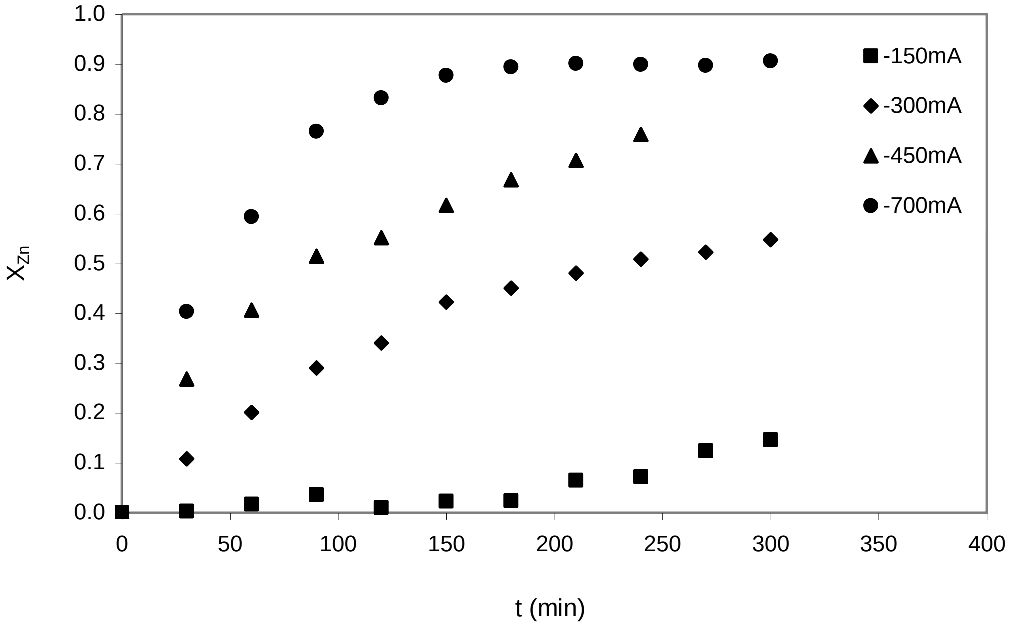

Figure 3. Fractional conversion of zinc vs. time as a function of the applied current. $[ZnCl_2]_0$ = 0.055 M, $[HCl]_0$ = 0.1 M.

As in potentiostatic operation, it is essential to consider several figures of merit, such as the current efficiency, ϕ, the mean value of the space-time yield, η, and the specific energy consumption, E_s for a better understanding of the behaviour of the electrochemical reactor and in order to compare the results with those obtained in potentiostatic mode or other chemical or physical process. These figures of merit are calculated by means of the following equations [10]:

$$\phi(t)(\%) = \frac{n \cdot F \cdot (C_0 - C(t)) \cdot V}{\int_0^t I(t) \cdot dt} \cdot 100 \qquad (1)$$

$$\eta(t) = \frac{M \cdot (C_0 - C(t))}{t} \qquad \left(g \cdot l^{-1} \cdot h^{-1}\right) \qquad (2)$$

$$E_s(t) = \frac{\int_0^t U(t) \cdot I(t) \cdot dt}{V \cdot C_0 \cdot X(t) \cdot M \cdot 3600} \qquad \left(kW \cdot h \cdot kg^{-1}\right) \qquad (3)$$

Figs. 4-6, represent, respectively the evolution of current efficiency, space-time yield and specific energy consumed at the different applied currents for an electrolyte composed of 0.055 M $ZnCl_2$ and 0.1 M HCl. As shown in Fig. 4, for the lowest cathodic current value, -150 mA, ϕ remains at low values due to the low zinc reduction rate and the presence of the HER process from the beginning of the experiment.

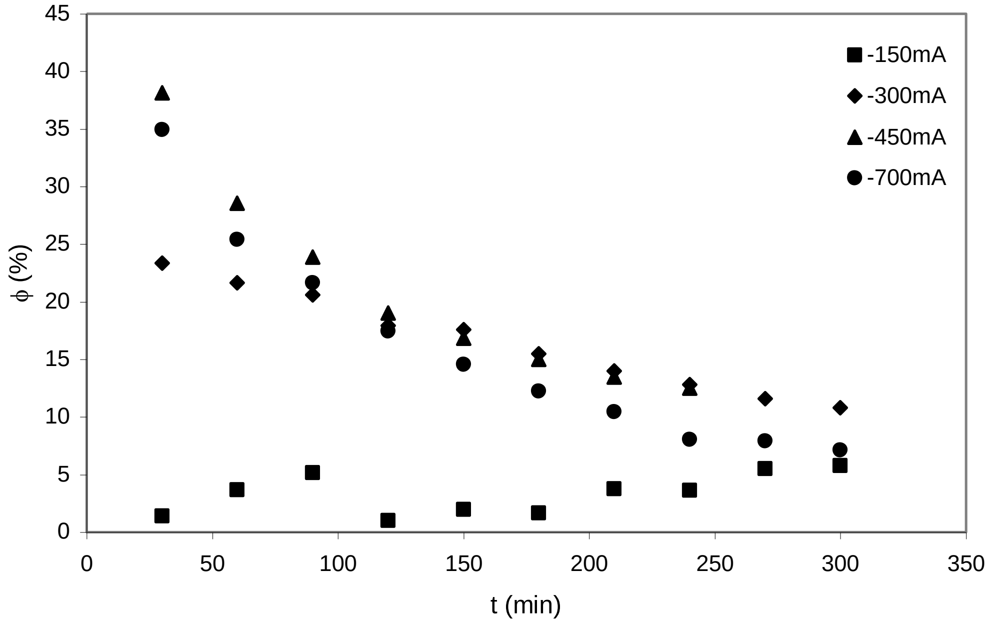

Figure 4. Current efficiency of zinc vs. time as a function of the applied current. $[ZnCl_2]_0$ = 0.055 M, $[HCl]_0$ = 0.1 M.

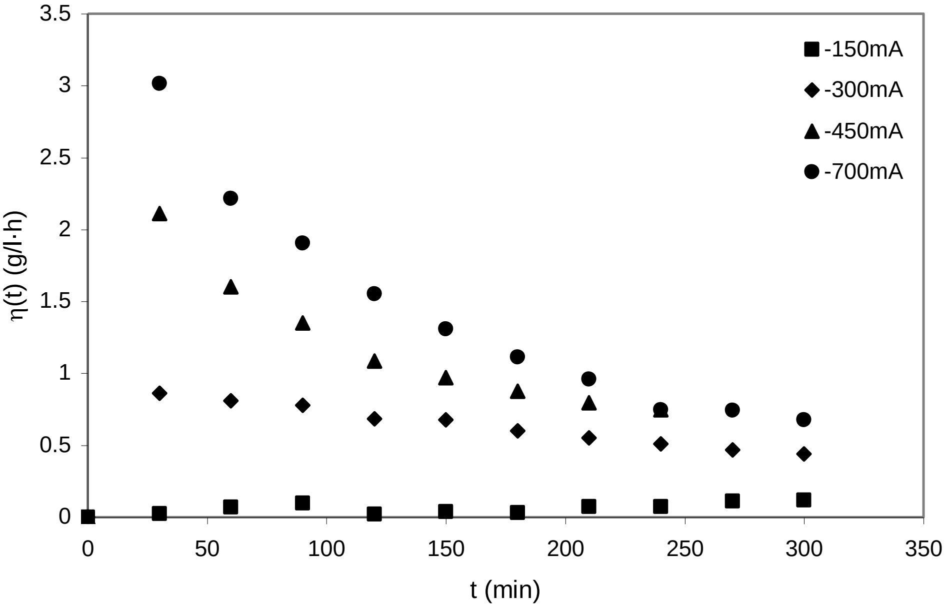

Figure 5. Space-time yield of zinc vs. time as a function of the applied current. $[ZnCl_2]_0$ = 0.055 M, $[HCl]_0$ = 0.1 M.

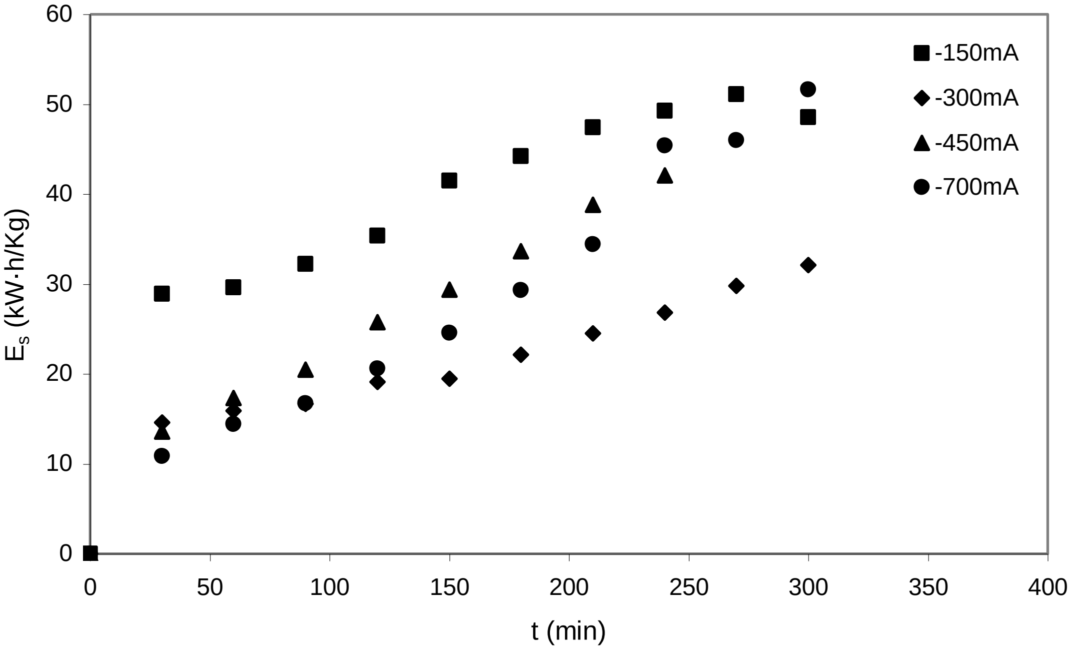

Figure 6. Energy consumption of zinc vs. time as a function of the applied current.$[ZnCl_2]_0$ = 0.055 M, $[HCl]_0$ = 0.1 M.

For the intermediate current values, -300 and -450 mA, ϕ grows with the applied current as the zinc reduction rate increases. However, for the most cathodic current, -700 mA, ϕ decreases again since HER is more important than zinc deposition. For current values greater than -150 mA, ϕ initially presents high values because zinc reduction is the main reaction but as HER process contribution is substantial, ϕ begins to decrease. As studied in potentiostatic mode [7], the contribution of hydrogen evolution is very important from the beginning of the experiments when the HCl concentration is as high as 0.1 M.

Fig. 5 shows the space-time yield profile for the different applied currents under study.

η increases sharply over the initial period due to the nucleation of zinc onto the graphite electrode, which causes a decrease in the electrode resistance because of zinc deposition. Then, the space-time yield decreases with time owing to the zinc removal from the solution and similar values are reached for the different applied currents at the end of the electrolysis experiments. For the lowest cathodic current, η is low and remains practically constant due to the low zinc reduction reaction rate. On the other hand, the more negative the applied current is the higher the space-time yield because of the turbulence promoting action of hydrogen evolution, the roughness increase of the electrode surface and the higher velocity of the electrochemical reactions [11].

The effect of the applied current on the specific energy consumption is observed in Fig. 6. For all the applied currents, E_s increases with time due to the higher contribution of hydrogen evolution reaction as zinc is depleted from solution. The lowest cathodic current of -150 mA, presents the highest E_s value since represents the slowest zinc reduction rate. It is noteworthy that as current shifts to more cathodic values E_s diminishes owing to the higher contribution of the zinc reduction reaction to the total reaction rate.

As studied in potentiostatic mode, in order to compare the performance of the electrochemical reactor for the different applied currents, the time (t_{100}) at which a 100% zinc fractional conversion is reached, assuming a current efficiency of 100%, has been determined. In galvanostatic operation, t_{100} can be calculated from the following equation [10]:

$$t_{100} = \frac{nFVC_0}{I} \tag{4}$$

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

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

I (mA)	t_{100} (min)	X_{Zinc}	Φ (%)	η (g·l^{-1}·h-^{1})	E_s (kW·h·kg^{-1})
-150	131.66	0.018	1.73	0.033	34.39
-300	65.77	0.255	24.87	0.934	13.83
-450	43.05	0.346	34.08	1.900	14.81
-700	26.24	0.353	35	3.014	10.86

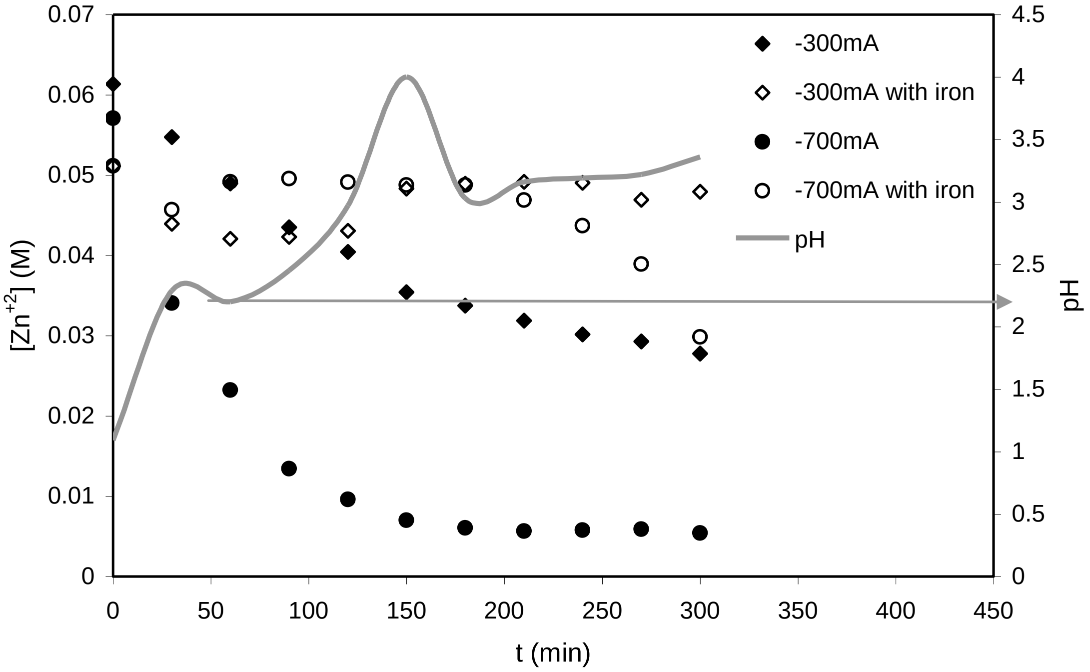

Figure 7. Evolution of zinc concentration vs. time as a function of the applied current. $[ZnCl_2]_0$ = 0.055 M, $[FeCl_2]_0$ = 0.035 M, $[HCl]_0$ = 0.1 M.

As a consequence of the increase in the zinc electrodeposition rate with the applied current, t_{100} decreases. For the most cathodic applied current values, -450 and -700 mA, the values of X_{Zinc} and ϕ, are close to 35%, which are very similar to those obtained in potentiostatic mode [7]. However, for the lowest cathodic current values, -150 and -300 mA, 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 applied current is shifted towards more cathodic values because of a greater zinc reduction rate, the turbulence-promoting action of hydrogen evolution and the increased roughness of the electrode surface. On the other hand, energy consumption decreases with the applied current due to the increase in the zinc reduction rate in relation to the secondary reactions, such as the HER process.

As in potentiostatic mode [7], for a better understanding of the real sample is necessary to evaluate the iron effect on zinc electrodeposition. For this purpose, 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 (0.055 M $ZnCl_2$ and 0.035 M $FeCl_2$ in 0.1 M HCl). Fig. 7 shows the zinc concentration evolution in the presence and absence of iron for the current values of -300 and -700 mA. The solid line presents the pH profile for the lowest cathodic current value of -300 mA in the presence of iron. For the current value of -300 mA, initially the rate of zinc depletion is slightly higher in the presence of iron but zinc redissolution appears at time values higher than 150 min owing to the local pH increase shown in Fig. 7. On the other hand, for the current value of -700 mA, in presence of iron, the zinc reduction rate becomes negligible during the first steps of electrolysis, due to the local pH increase, that causes zinc redissolution [12]. For time values higher than 210 min, zinc concentration begins to decrease since zinc reduction rate becomes more important than zinc redissolution rate, although the zinc reduction rate is still low compared to that in the absence of iron. It is noteworthy to mention that potential values obtained in the presence of iron are more cathodic than those obtained without iron as can be seen in table 2, which indicates the enhancement of the HER process in the presence of iron [13].

Table 2. Comparison of the average electrode potential value for synthetic solutions with and without iron and for the diluted real solution.

	$E_{withoutFe}$ (V)	E_{withFe} (V)	E_{RS} (V)
-300mA	-1.24	-1.94	-1.78
-700mA	-2.17	-2.96	-2.63

Iron concentration was also measured and resulted invariable for all the current values under study. This fact may be related to the high acidity of the solution and the zinc presence that inhibits iron deposition [14, 15]. The presence of iron in solution greatly affects the zinc current efficiency as can be observed in Fig 8, where current efficiency of zinc deposition at -300 and -700 mA with and without iron is compared. This effect is also observed by other authors [16, 17]. The decrease in current efficiency observed in the presence of iron for both current values, is associated with the reverse redox system of Fe^{+2}/Fe^{+3} taking place at the two electrodes consuming high amounts of energy [18], and to the enhancement of the HER process, which also competes with zinc electrodeposition.

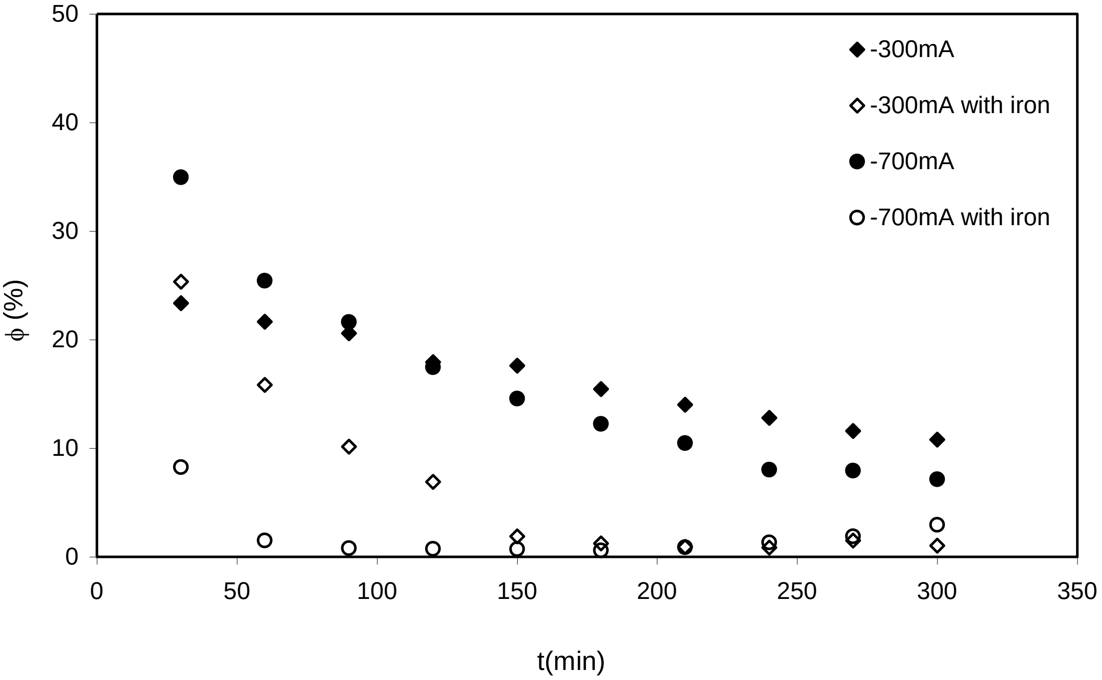

Figure 8. Evolution of current efficiency vs. time as a function of the applied current. $[ZnCl_2]_0$ = 0.055 M, $[FeCl_2]_0$ = 0.035 M, $[HCl]_0$ = 0.1 M.

In general words, the iron presence in the synthetic samples produces worse effects in galvanostatic mode in terms of zinc fractional conversion and current efficiency than in the potentiostatic one [7] since in galvanostatic mode only is possible to control the global reaction rate which makes impossible to select the reaction of interest as occurs in potentiostatic mode.

3.2. Electrolysis of real spent pickling solutions

In this section, the performance of the electrochemical reactor when processing real and synthetic solutions will be evaluated by means of the comparison of their figures of merit. The selection of the applied currents was made from the current values obtained in potentiostatic mode. Because of the similitude of these values with those applied when processing the synthetic sample, the selected current values were the same for better comparison of all data. Iron concentration was also measured at real samples and resulted invariable for all the applied currents under study.

Fig. 9 presents the zinc concentration evolution with time for all the applied current values and for a 1:50 diluted real sample. In this case, an anomalous behaviour is observed due to zinc redissolution, which is observed for all the applied current values. For the lowest cathodic current values, -150 and -300 mA, the zinc concentration initially diminishes and after a following increase, it remains practically constant. For the most cathodic current values, -450 and -700 mA, a great decrease in zinc concentration is previously observed after which zinc concentration in solution starts to increase due to the zinc redissolution phenomenon also observed in potentiostatic mode for all the potential values under study [7]. Comparing both operating modes, it is inferred that zinc redissolution phenomenon is enhanced when treating the real spent pickling baths in comparison with synthetic zinc solutions. These effects are associated with the local pH increase [15, 19] that causes zinc redissolution.

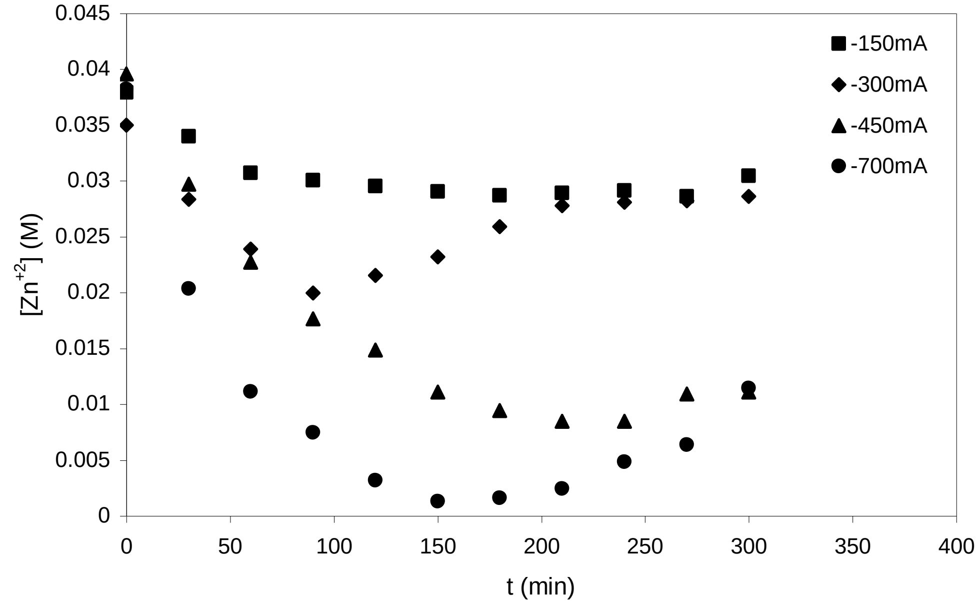

Figure 9. Evolution of zinc concentration vs. time as a function of the applied current. 1:50 diluted real sample.

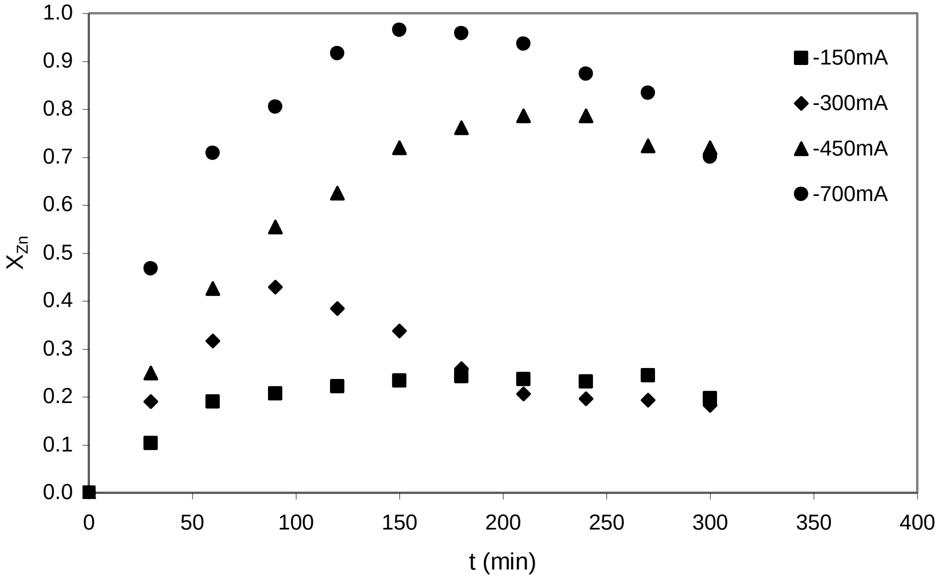

Figure 10. Fractional conversion of zinc vs. time as a function of the applied current. 1:50 diluted real sample.

The zinc conversion profile as a function of the applied current is shown in Fig. 10. The conversion behavior is the same as that observed in previously Fig.3, i.e the more cathodic current is the higher conversion rate. However, zinc redissolution appears for current values more cathodic than -150 mA. At -150 mA zinc conversion remains practically constant with a value close to 20%. For the rest of applied currents under study, a maximum value of fractional conversion is observed due to the zinc redissolution, phenomenon mentioned previously. Although the conversion values achieved are very similar, X_{Zinc} is lower in the case of real samples, as it is extracted from the comparison of Fig. 3 and Fig. 10, which is explained by the higher local pH values reached in the case of real samples which enhances the zinc redissolution and the subsequent decrease of the zinc conversion rate. However, X_{Zinc} of real samples are higher than those obtained for iron-zinc mixtures, this can be explained by the performance of HER inhibitors present at real samples that allow to obtain lower potential values in comparison to those obtained in the case of the synthetic iron-zinc mixture as can be seen at Table 2.

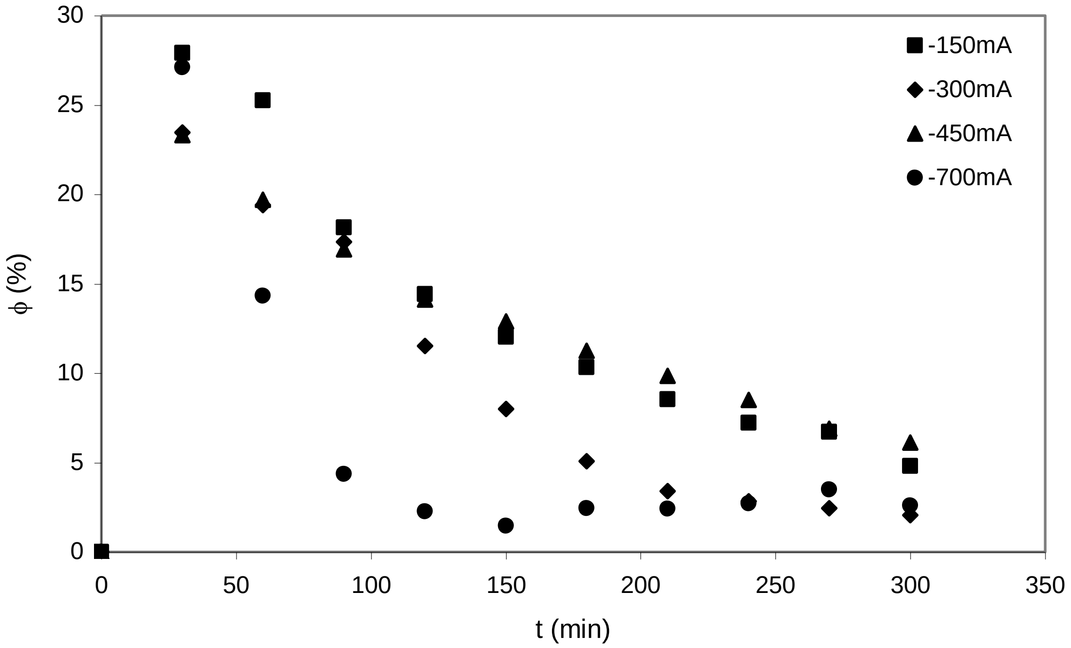

Figure 11. Current efficiency of zinc vs. time as a function of the applied current. 1:50 diluted real sample.

When the current efficiency of synthetic iron-zinc mixtures and real samples are compared (Figs. 4, 8 and 11 respectively), it can be concluded that the synthetic sample in the absence of iron presents the greatest current efficiencies. This fact is related to the worse effect of the Fe^{+2}/Fe^{+3} redox system and the enhancement of the HER process by the iron presence. If the comparison between iron-zinc mixtures and real samples is made, it can be observed that real sample has greater current efficiencies values due to the presence of additives in real samples, like hydrogen evolution inhibitors [12, 20], which improve the current efficiency against the worse effects of the Fe^{+2}/Fe^{+3} redox system and HER process [8].

The space-time yield and the energy consumption (not shown) present the same behaviour with the applied current as that explained previously for synthetic samples in the absence of iron (Figs. 5 and 6, respectively), i.e. as the applied current is shifted towards more cathodic values the space-time yield increases and the 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 real samples, which decreases the zinc reduction rate. Regarding with the energy consumption, real samples present better values than those obtained in the synthetic ones in presence of iron because of the presence of inhibitors which diminishes the HER rate.

Table 3. Figures of merit for the electrochemical recovery of zinc corresponding to t_{100} for a 1:50 diluted real sample.

I (mA)	t_{100} (min)	X_{Zinc}	Φ (%)	η ($g \cdot l^{-1} \cdot h$-^{1})	E_s ($kW \cdot h \cdot kg^{-1}$)
-150	81.33	0.195	19.04	0.3565	16.10
-300	37.5	0.221	21.86	0.8099	21.86
-450	28.29	0.235	23.33	1.293	23.114
-700	17.57	0.274	27.22	2.337	20.836

Table 3 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 3), it can be observed that the synthetic solution in the absence of iron has better values than those obtained for real one for the same current 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, and decrease the presence of parallel reactions which decrease the current efficiency of the zinc reduction process. The current value of -700 mA may be selected as the optimum since has the better values of the figures of merit.

4. CONCLUSIONS

An electrochemical reactor in galvanostatic mode was used 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 were calculated in order to select the best electrochemical reactor operating conditions.

The applied current was selected in order to obtain similar electrode potential values to those applied in the potentiostatic operation and ranged between −150 and −700 mA. In the absence of iron in solution, as the current value was shifted towards more negative values, the space–time yield of zinc and its fractional conversion increased because of the increase in the zinc reduction rate, the electrode roughness and the hydrogen turbulence-promoting action. However, the increase in current values makes current efficiency decrease due to the hydrogen-reduction side reaction, which causes an increment in the specific energy consumption. Even though iron deposition does not take place for any experimental conditions under study, its presence in synthetic zinc/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.

Regarding with the behavior of the real samples, the additives present in the real spent pickling baths avoided, partially, the adverse effects of iron as proved the higher current efficiencies and fractional conversions obtained with real samples in comparison to those obtained in the synthetic iron-zinc mixtures.

In the case of real baths, if the values of the four figures of merit for t_{100} are compared for both operating modes, it is inferred that although they are very similar, are slightly better in galvanostatic mode since under our experimental conditions it is impossible to select the reaction of interest and the HER contribution is always present from the beginning of the electrolysis. Finally, -700mA was selected as the optimum current value when processing the real spent pickling baths in galvanostatic mode.

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