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PRELIMINARY STUDY OF PURE ZINC RECOVERY FROM SPENT PICKLING LIQUORS BY COMBINING ANION EXCHANGE AND ELECTRODEPOSITION

HANNA ZAKIYYA[1] – TAMÁS KÉKESI[2]

Abstract: Zn recovery from spent pickling liquors (SPL) from hot dip galvanization was examined with modelled solutions by combining anion exchange separation and electrodeposition processes. The solution was purified to be suitable for the electrodeposition of Zn with the main goal of eliminating the iron content. The anion-exchange resin bed in a chromatographic column primarily retained Zn, while divalent Fe was removed in the loading and rinsing steps. At the end of the process, the elution of Zn was carried out by a significantly reduced Cl^- ion background. In parallel with the purification process, the potentiodynamic study (1 min runs at 40 mV/s polarization speed) of Zn electrodeposition in the series of Fe concentrations was examined. During the separation process, the preliminary reduction of the iron to its divalent state was found to be of utmost importance. The separation of iron could be improved by controlling the preliminary reduction. It was found that the effect of iron concentration on the polarization curves is complex. Initially, hydrogen bubble formation causes inhibition, but at higher iron concentrations a Zn-Fe deposit is soon formed, promoting hydrogen evolution, thereby depressing polarization but also the current efficiency. The loss of the dendritic structure obtained from pure zinc solutions also characterizes the effect of mixed Fe-Zn deposition. In order to recover pure zinc at the cathode, the pre-purification of the Zn electrolyte is essential.

Keywords: Spent pickling liquor, anion-exchange separation, Zn electrodeposition, Fe impurity

INTRODUCTION

The pollution caused by the by-product of the pickling process is harmful to the environment, but it can be considered also as a valuable secondary resource, especially for zinc. The main accompanying element, considered as impurity in this case, is iron. In the hot dip galvanizing (HDG) industry, either hydrochloric acid (HCl) or sulfuric acid (H_2SO_4) is used as the pickling reagent. The first mentioned is considered superior for providing a smoother pickled surface, less hydrogen blistering and lower operational temperature [1]. However, at the same time, this procedure produces a highly dangerous and corrosive spent pickling liquor (SPL) of decreased HCl, but increased Fe and Zn concentrations because of the dissolution of the bare or previously zinc-coated steel surfaces. It results in a dropping efficiency of pickling. Thus, the pickling reagent needs to be refreshed. On the other hand, the waste solution discharge specifications in Europe are rather strict, requiring lower concentrations than 0.5 mg/dm^3 of Zn and 10 mg/dm^3 of Fe, [2]. Though, SPL as a liquid waste contains 25 to 125 g/dm^3 zinc, 90 to 200 g/dm^3 iron, and approximately 7 to 10 M Cl^- ion, partly in the form of free HCl [3], [4], [5], [6], [7], [8]. The high metal concentration of this pickling waste makes

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[1] Institute of Metallurgy, University of Miskolc
H-3515 Miskolc-Egyetemváros, Hungary
zakiyya.hanna@student.uni-miskolc.hu

[2] Institute of Metallurgy, University of Miskolc
H-3515 Miskolc-Egyetemváros, Hungary
kekesi@uni-miskolc.hu

it a potential secondary source of either zinc or iron. Processes for recovering zinc from pickling industrial wastes have recently become more appealing. However, determining the best conditions for economically recovering Zn from this liquid waste still needs further investigation.

Instead of producing Zn of the ordinary grade, a pure Zn product is a more economical alternative. This can be achieved by a special solution purification method combined with electrodeposition, however the co-existence especially with iron at usually high concentration may be challenging. Metallic impurities have a complex effect on the electrodeposition process. According to previous reports [9] [10], the presence of metallic impurities does not only endanger the purity of the cathode, but it causes a decrease in current efficiency. One of the most devastating impurities in the electrodeposition of Zn is Fe. In the sulphate electrolyte system, iron concentration must be kept lower than 10 g/dm^3, otherwise, it may cause a significant loss in the current efficiency of Zn deposition [11]. There are several potential purification techniques available to produce a pure Zn electrolyte: e.g. partial neutralization, chemical precipitation, solvent extraction, and ion exchange [3] [12].

Neutralization by sodium hydroxide after partial oxidation of ferrous to ferric ions can remove iron from the electrolytic liquors. However, this is not a perfect separation and it implies the consumption of neutralizing agents and a tight control of the pH, as well as the inclusion of alkali metal ions in the electrolyte solution. Researchers argue that these species may affect coulombic efficiency (QE) and deposit morphology [10] [13]. It is reported that by the addition of 50 g/dm^3 of Na$^+$ to pure Zn electrolyte, a decrease of 5–15% in the QE may be expected, because intermetallic compounds of zinc and sodium act as micro-anodes at the cathode surface [14]. Other chemical precipitations of iron, on the other hand, need a high consumption of chemicals that cannot be recovered or reused, as well as the costly disposal of potentially toxic sludge [6] [15]. Although solvent extraction is an effective procedure, it requires several processing steps and a costly and hazardous reagent, and in addition, some organic contaminants may be found in the purified aqueous phase [3] [16] [17]. The residual amount of organic compounds in the electrolyte may significantly affect the current efficiency because they exert a blocking effect that hinders the nucleation and crystal growth of the deposit [18]. In addition, the chemical similarity between the impurity metal and zinc would provide significant challenges in such separations too. Using an anion-exchange procedure might simplify the conditions. Ion exchange has been known for its high capacity, mechanical stability, selectivity besides its environmentally friendly and safe character. Removing dissolved Fe from the Zn electrolyte can be done by adjusting aqueous solution chemistry, which creates an exchangeable state between a particular ion or complex ion of the metal and the counter-ions in the resins [19]. Hydrochloric acid in the SPL might also be advantageous. The HCl medium is preferred for ultra-high purification because of its strong ability to produce anionic complexes [20] of varied sorbability in the resin:

$$[MeCl_n]^{z-} + z\overline{Cl}^{-} \leftrightarrow \left[\overline{MeCl_n}\right]^{z-} + zCl^{-} \quad (1)$$

The subscript *n* is the coordination number, and the superscript bar shows the species in the resin phase. By the distribution function *(Figure 1)* determined by the batch equilibration method, the separation of Zn ion and both Fe(III) and Fe(II) is possible at the concentration of HCl lower than 1 mol/dm^3 [6] [19] [20]. However, reducing the overall iron content to the divalent state may allow the application of higher HCl concentration for fixing Zn at its maximum distribution condition. Other researchers have also reported similarly strong retention of Zn in strongly basic anion-exchange resins of the same type (e.g. Lewatit MP-500 and Lewatit M-504) [21].

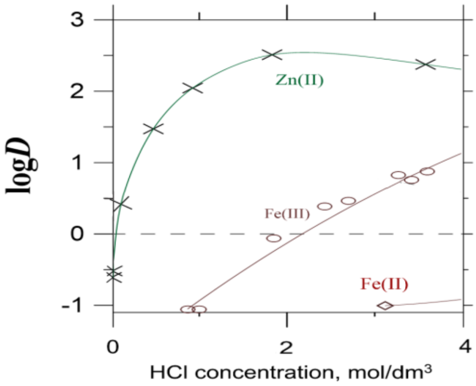

Figure 1

Anion-exchange distribution functions of Zn and Fe [19]

After eluting iron separately, the elution of Zn at a decreased HCl concentration may provide two electrolyte solutions for Zn or Fe recovery, respectively. The use of the Fe eluate has been demonstrated by earlier research [6]. The recovery of pure Zn from the purified $ZnCl_2$ solution needs further experimental investigation and optimization.

Metal recovery is essential to eliminate residual wastes, and its purity may increase the value of the recovered product. The efficiency of the Zn cathodic reduction is a critical aspect in the applicability of the intended process. Acceptable Zn deposition on the cathode is determined mainly by the composition of the bath, in which various components and settings may impact the deposition process and the final deposit structure. Although chloride solutions are advantageous for their high conductivity, the complexity of transition metal ions raises specific concerns. In the case of Zn, cathodic deposition from chloride media, the dissociation of the formed zinc-chloro-complex ions to release the electro-active cation must precede the reduction of Zn metal. Another problem comes from hydrogen evolution because of the lower standard and formal potentials of zinc. It is often challenging to deposit zinc on the cathode without severe hydrogen evolution interfering with the main cathodic reaction. Moreover, incomplete separation of Fe may also be a problem for purity – impaired by co-deposition – and current efficiencies. However, zinc electrodeposition over chloride media offers significant benefits in terms of solubility and electrical conductivity. Considering the challenges, the current work observes the possibility of elaborating an efficient anion-exchange separation to be included before the Zn electrodeposition to recover pure Zn from the SPL solution.

1. EXPERIMENTAL METHOD

1.1. Anion-exchange separation

A strongly basic anion-exchange resin with a polystyrene-divinylbenzene matrix and quaternary ammonium functional group under the commercial name Varion AP (Nitrokémia Co. – Hungary) was used for the current experiments. The model solution containing Fe and Zn was prepared – according to the usual concentrations in the industry – from analytical grade reagents with the concentrations specified in *Table 1*. All the solutions were prepared in a 1.8 mol/dm^3 HCl background. Before the separation process, the strongly basic anion-exchange capacity was examined, giving 1.4 mmol/cm^3 for the wet and filtered volume. The required quantity of resin was physically purified before being conditioned into the chloride form with 2 mol/dm^3 HCl, to ensure better condition for the sorption of zinc chloro-complexes.

Table 1

Composition of the loaded solution

Component	**Zn (mg/dm^3)**	**Fe (mg/dm^3)**	**HCl (mol/dm^3)**
Set value	10,000	10,000	1.8

In the chromatographic procedure, several stages were done with adjusting HCl concentration *(Figure 2)*. The HCl concentrations used were chosen based on the previously reported anion-exchange distribution functions *(Figure 1)*. The processes were started with feeding the prepared resin into the glass column with an inner diameter of 2.5 cm and approx. 25 cm in height. The ~120 cm^3 resin bed was free from air bubbles. To obtain a better separation while keeping technically good productivity, the flow was kept at a relatively low rate, adjusted to 1.5 bed volumes per hour (BV), which is lower than the commonly used 3 BV value. However, following the loading stages, the rinse flow rate was increased to 3 BV. Effluent samples – of 10 cm^3 volume – were collected regularly at planned intervals. At the end of the process, all the collected samples were analyzed by atomic absorption spectroscopy (AAS). These results were then transformed into elution curves to evaluate the efficiencies of the purification process.

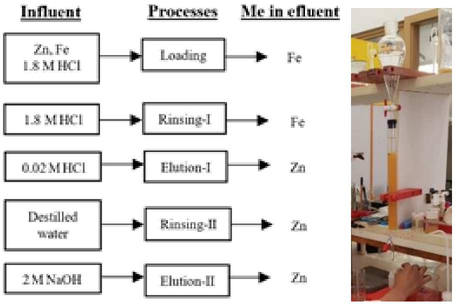

Figure 2

The anion-exchange separation of Zn and Fe in HCl solutions

1.2. Electrodeposition

To understand the potentiodynamic characteristics of an acceptable Zn cathodic deposition, several sets of electrodeposition experiments were performed and evaluated. The characteristics of zinc electrodeposition were examined at the designed settings of Zn and Fe concentrations, pH and stirring intensity. The effect of iron concentration was assessed to represent the SPL solutions of different degrees of purification. The electrolysis experiments were conducted in a rectangular cell made of glass with dimensions of 50 × 50 × 50 mm, as shown in *Figure 3*. A saturated calomel reference electrode was used with a 1 mm diameter Luggin-capillary tip facing the zinc cathode. Copper starting sheets served as working electrodes and were ground with sandpaper and cleaned with water before drying. The counter electrode (anode) was made of pure zinc to compensate for the loss of Zn concentration during the electrodeposition cycles. The electrolyte was refreshed after each parameter setting but not between the parallel potentiodynamic runs. However, the evaluation was based on the average values of the overpotential-current plots taken as the averages of the minimum three times repeated parallel results. A computer-controlled potentiostat had been developed and built at the University of Miskolc, which could generate rapid polarization response and was suited to observe cathodic processes under fast-changing circumstances. It was operated by a custom software developed on the NI LabView platform. All runs were conducted at room temperature with a constant polarization speed of 40 mV/s and a sampling rate of 1/s, providing the most extensive range of accurate findings. The effect of iron contamination was examined by dissolving the deposits and analyzing the solution samples by AAS after the electrodeposition runs.

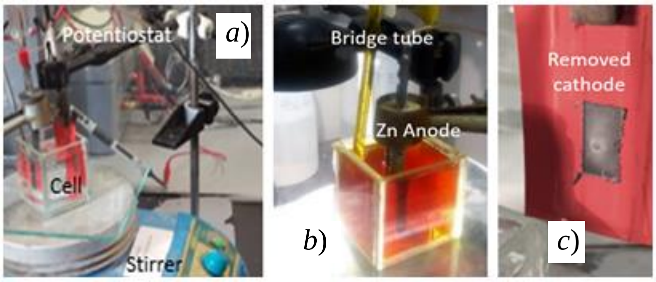

Figure 3

The experimental set-up with the cell (a), the electrodes in the Fe-contaminated solution (b), and the removed cathode (c)

2. RESULT AND DISCUSSION

2.1. Anion-exchange separation

The designed anion-exchange procedure could separate Zn and Fe directly at the loading stage. Related to the distribution functions in *Figure 1*, this purification process, as shown in *Figure 4*, implies that zinc was fixed entirely in the resin.

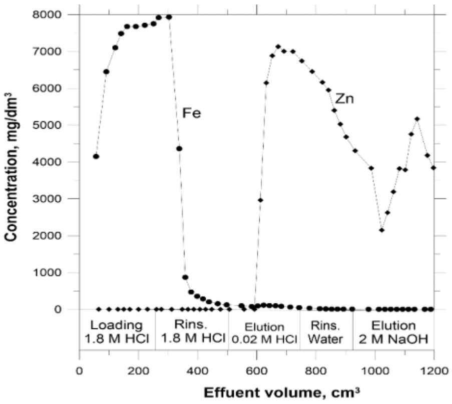

Figure 4

Elution curves obtained by the preliminary chromatographic separation

The stability of zinc chloro-complexes are significantly higher than those of Fe in the solution containing free Cl^- concentration lower than approximately 2 M. Thus, the complexation of Zn species according to the general reaction (1) was readily formed. No leakage of Zn can be observed during the loading and the rinsing steps. Meanwhile, the Fe content passed through the column. Though, a little portion of Fe was left behind, only removed from the column in the first elution step, causing slight contamination of the Zn effluent.

This portion of iron retained in the resin during the loading and the first rinsing stages should be considered as trivalent, which had not been fully reduced before loading. In a closed vessel, in contact with the sludge containing metallic iron, com-proportionation:

$$2\mathrm{Fe(III)} + \mathrm{Fe} = 3\mathrm{Fe(II)} \tag{2}$$

may assure the predominance of the divalent state, as the standard electrode potential of the Fe^{3+}/Fe^{2+} couple is +0.74 V, whereas that for the Fe^{2+}/Fe is –0.42 V. However, due to the high standard electrode potential of oxygen (>1 V) in direct contact with the slightly acidic aqueous solution, the ambient air may cause oxidation on the surface:

$$2\mathrm{Fe}^{2+} + 1/2\mathrm{O}_2 + 2\mathrm{H}^+ = 2\mathrm{Fe}^{3+} + \mathrm{H}_2\mathrm{O} \tag{3}$$

However, the formation of the chloro-complexes of iron, by the reaction expressed generally by *Equation (1)*, is practically possible in the trivalent state at relatively high free Cl^- ion concentrations. This may hinder reaction (2), and the reduction process is kinetically slow in stationary conditions, therefore, the presence of Fe(III) species cannot be excluded unless strict protective conditions are applied.

In order to remove the remaining Fe-contamination – if practically needed – the preliminary reduction should be more complete, whereas the first two stages of the separation should be carried out under protective atmosphere (N_2) to exclude the formation of any Fe(III) species. Also, the first rinsing step can be extended. As no leakage of Zn was observed during the first two steps, applying a slightly lower initial HCl concentration may also be beneficial in this respect.

2.2. Electrodeposition

Visual appearance of deposits from the first experimental series are shown in *Figure 5*. The surfaces of final deposits were captured after each process with different Fe(III) content in the electrolyte and various stirring speeds. The electrolysis started with a uniform deposition, followed by the formation of a spongy deposit, and ended with a dendrite structure. Although the observed dendrite formation seemed to decrease in the presence of Fe, excessive hydrogen evolution also took place in the cell. Thus, dendrite formation was suppressed by hydrogen evolution enhanced by iron co-deposition. It implies that the absence of dendrites does not indicate preferable conditions, as the presence of Fe results also in contamination. Initially, the deposition was hindered by growing hydrogen bubbles attached to the cathode surface. These conditions occurred in low iron concentrations, such as 5 g/dm^3. A more intensive cathodic process may occur after the initially growing bubbles are released, which dominantly happens at the edges, then all over the active surface. Compared with the iron-free deposition process, it is proved that the addition of iron promotes hydrogen evolution due to the lower overpotential of hydrogen on iron.

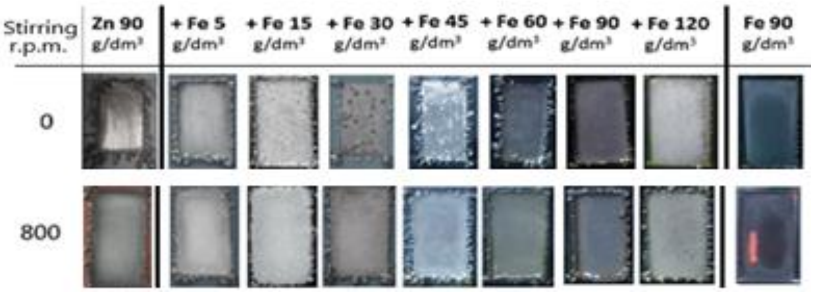

Figure 5

The final structure of the cathode obtained from the potentiodynamic experiments with different rates of Fe(III)additions to the stationary or vigorously stirred $ZnCl_2$ solutions

Metal deposition tends to be denser with increasing agitation speed. Stirring the Zn-Fe chloride solution can not only modify the convection regime toward the cathode surface, but it can also remove the bubbles. As a result, a porous metal deposit occurs at the highest examined stirring speed. It is also remarkable that the deposit morphology practically does not change by increasing the iron concentration in the electrolyte, but it seems to be the most compact when the iron concentration is between 45 and 60 g/dm^3 with the Zn concentration of 90 g/dm^3.

The observation of deposits from pure iron chloride solutions showed powder formation, which could be easily removed from the cathode surface. The solutions were getting darker because of the iron powder getting mixed in. The co-deposition of hydrogen gas is also involved in this phenomenon. It is showed from the resulted deposition that the iron deposition tends to be darker than that of zinc. So, it can be visually estimated that there was more zinc deposited from the solution with an iron concentration lower than 60 g/dm^3, as the deposition color is brighter. The bars in *Figure 6* shows that the amount of iron deposited from the mixed solution is increasing quickly as the Fe concentration is increased beyond 30 g/dm^3.

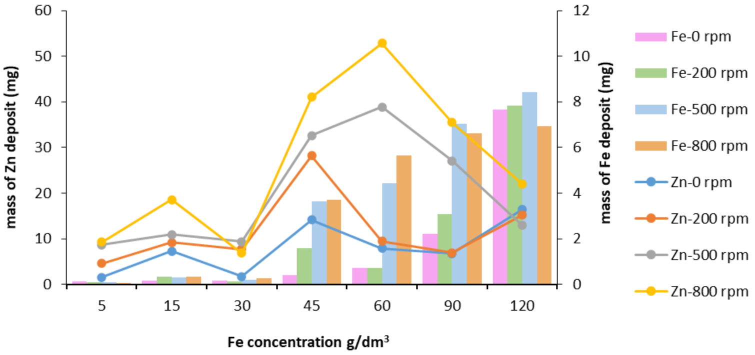

Figure 6

Deposit compositions obtained from solutions of 90 g/dm^3 Zn with various concentrations of Fe (1 min runs at 40 mV/s polarization speed)

However, zinc deposition – denoted with the solid lines – is also increased concomitantly. It is also seen that the intensity of stirring has a strong effect on the rate of zinc deposition. It can be also seen for iron in the 45–90 g/dm^3 Fe concentration range of the mixed solutions. At the highest iron concentration, however, stirring seems to lose its relative importance. Comparing the positions of the curves (indicating the Zn deposit) and the bars (standing for the Fe deposits), it is seen that from stirred solutions of 90 g/dm^3 Zn and various Fe concentrations, the obtained Zn deposit can be of different composition. Pure Zn can be obtained from agitated solutions of less Fe concentrations than 5 g/dm^3. In stationary solutions, however, the rate of deposition is so low that accurate measurements were impossible. The addition of Fe also increases the mass of Zn deposited.

With increasing contamination of Fe in the electrolyte solution, hydrogen evolution will increase because of its lower overpotential to Fe. The generated gas bubbles give an extra stirring at the surface of the cathode, enhancing the transport of the zinc ions too. It increases the rate of Zn deposition considerably, as seen in the 30–60 g/dm^3 range of iron concentration. With even more iron in the electrolyte, the mechanical effect of hydrogen evolution is outweighed by the more prominent Fe deposition causing smoother surfaces. Additionally, a strong H^+ reduction may strongly increase the local pH, triggering a local formation of hydroxide particles. It may inhibit the deposition of the less noble zinc. In the Fe range beyond ~60 g/dm^3, the increased rate of iron deposition results in more contaminated zinc deposits. This is especially true if the solution is not stirred intensively. Therefore, in order to obtain pure zinc from the SPL, it is necessary to apply the planned preliminary purification of the solution, removing iron efficiently and electrowinning zinc from a pure solution stirred vigorously.

Depositions from the pure Zn or Fe solutions are equally accompanied by hydrogen reduction, visually confirmed by the H_2 bubbles released. Nevertheless, the hydrogen evolution was more intensive from the Fe solution compared to that of the Zn solution. As shown in *Figure 7*, no limiting current appears in the polarization curves obtained by the potentiodynamic experiments of the pure 90 g/dm^3 Zn or Fe solutions. Stirring did not result in a reasonable tendency in the slopes of the polarization curves, indicating that there may be another cause of agitation or a rapid roughening of the cathode surface. Actually both can be present. The former is related to a strong evolution of H_2 gas noticed at higher polarizations, while the latter is caused by a strong dendrite formation, also observed. The initial slope of the polarization curves of Zn is significantly steeper than those of Fe, which indicates that more Zn^{2+} would be reduced to the metal with the same settings than with the Fe electrodeposition. The back-turns at the far ends of the polarization curves of Zn indicate looser deposits, producing dendrites at the surface of the cathode. However, stirring may detach the larger dendrites and the actual surface decreases, resulting in decreased currents as well. The unusual backdrop of the potential with further increasing current is caused by the rapidly growing actual surface of the spreading dendrites, which only appears in the zinc solution.

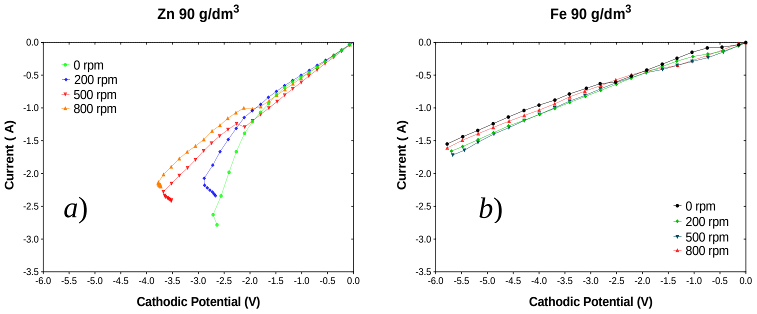

Figure 7

The effect of stirring speed on the polarization curves of zinc (a) and iron (b) deposition, respectively

On the other hand, the active surface did not seem to change significantly with the pure iron-electrolyte. Generally, the deposit tended to be smooth and finally powdery with increasing polarization. The applied stirring hardly affected the deposition of iron from the pure solution, indicating that hydrogen evolution was the dominant process.

The comparison of the graphs obtained with pure Zn solutions to the others resulting from the addition of iron can be seen in *Figure 8*. The stirring of the pure Zn electrolyte depressed the irregular growth. It can be inferred from the decreasing slope as the stirring speed is increased. As seen in the images of the finally obtained cathode surfaces *(Figure 5)*, there were fewer dendrites at higher stirring speeds. In case of solutions with added iron, the stirring may promote metal deposition by detaching the H_2 bubbles from the cathode surface. The potentiodynamic results in *Figures 7.a* and *8.a, b, c, d* do not show a definite tendency in the effect of Fe concentration over the whole range of the stirring speeds. The highest cathodic currents can be obtained with 60 g/dm^3 Fe in the 90 g/dm^3 Zn solution. It confirms the results shown in *Figure 6* obtained by the analysis of the deposits. In general, the curves are steeper, as the stirring speed is increased in the Zn electrolytes contaminated with Fe. The current was increased not only by the faster deposition of the metal alone but also by hydrogen reduction. In the mixed Zn-Fe solutions, the effects of increased metal ion transport, actual surface area and hydrogen deposition are superimposed, thus, the tendencies and the correlations with any of these factors cannot be clear.

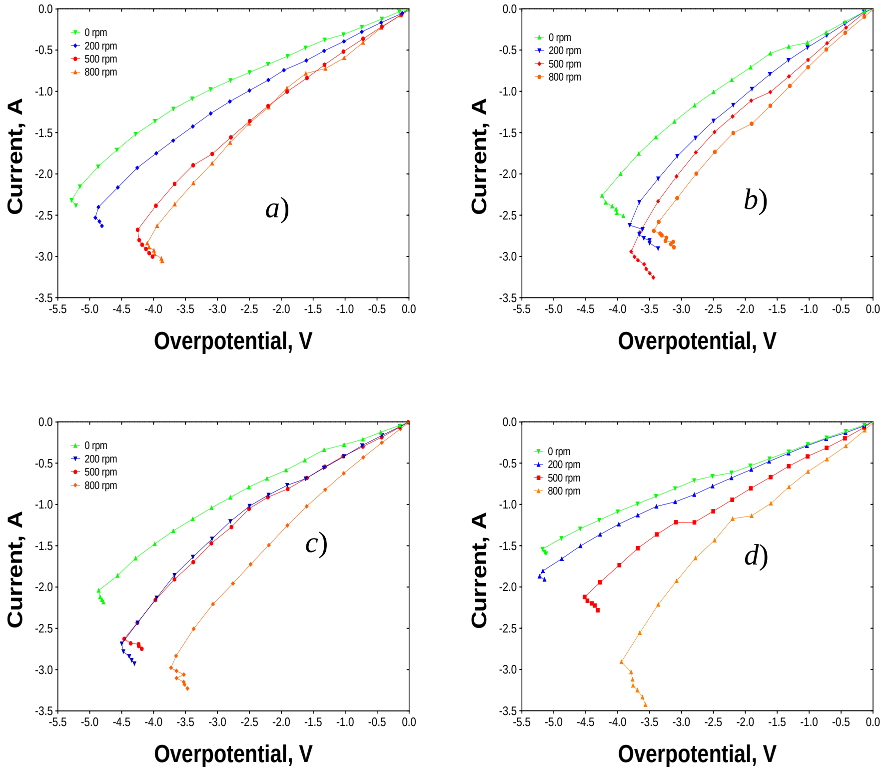

Figure 8

Effect of stirring speed on the deposition of zinc from solutions of 90 g/dm^3 Zn contaminated with iron at (a) 45 g/dm^3, (b) 60 g/dm^3, (c) 90 g/dm^3, and (d) 120 g/dm^3

The addition of iron to the stationary Zn solution caused a definite decrease in the obtained current. This is caused by the partial blocking of the active surface as hydrogen bubbles are formed initially, and at higher currents the streaming hydrogen gas can prevent the growth of the actual surface by blocking or removing the dendrites as seen in the photograph series of *Figure 5*. Comparing the relevant graphs of *Figures 7.a* and *8.a, b, c, d* suggests that at the same polarizations reached in the stationary Zn solutions, the currents attained in the cases of 45–90 g/dm^3 Fe contamination are getting significantly lower than those reached in the pure solution. However, the latter shows a break in the tendency caused by an onset of progressive dendrite formation, increasing the actual active surface. As the currents reached in pure Fe solutions *(Figure 7.b)* are also significantly lower than those obtained in the pure Zn solutions, and the addition of Fe makes the structure of the Zn-based deposit similar to that of Fe *(Figure 5)*, the effect of Fe in the Zn solutions can be attributed to the smoother surfaces obtained This effect may dominate, as the evolution of hydrogen accounts for a greater part of the current obtained in the pure Fe solutions. The highest total currents at relatively lower polarizations could be obtained in the 90 g/dm^3 Zn solutions with ~60 g/dm^3 Fe contamination, where the roughness of Zn deposition was still present, but an also significant Fe deposition could take place. It is corroborated by the analytical results shown in *Figure 6*. At this relatively high iron concentration the hydrogen evolution dropped in favor of metal deposition and the surface was less blocked by initiated gas bubbles, thus, also enhancing zinc deposition. Further increasing the iron concentration, as far as 120 g/dm^3, however resulted in the overwhelming dominance of iron deposition. It mostly produces powdery deposits and smoother surfaces, but the solution becomes turbid indicating that some dark Fe powder can be detached from the cathode. The backdrop potentials were also shifted to more negative values, confirming that less metal could be deposited at the lower ranges of polarization without agitation because of hydrogen blocking. It also proves that iron in the solution promotes hydrogen evolution at the cathode. The results expressed by the polarization curves are in parallel with those obtained by the analysis of the deposits.

CONCLUSIONS

The devised anion-exchange separation can perfectly remove iron in Fe(II) state. Relatively low concentration of chloride ions, naturally present in the treated solution form anionic chloro-complex species of zinc, which are strongly fixed in the resin bed of strongly basic anion-exchange resin in the chloride form. Elimination of iron during the anion-exchange procedure can be enhanced by a perfect preliminary reduction to Fe(II) state, applying vigorous stirring over iron chips under protective atmosphere. Less than 5 g/dm^3 Fe contamination in the chloride solution of 90 g/dm^3 Zn concentration may not harm significantly the purity of the zinc deposited on the cathode. The presence of more iron in the zinc chloride solution changes the nature of metal deposition. The final Zn deposit tends to be darker as more iron is added. As the evolution of hydrogen is appreciably stronger in the iron containing solutions, the adherence of the deposited crystals is decreased and the larger Zn dendrites are lost, but iron powder may also get mixed in the electrolyte during the process of electrodeposition. Increasing iron concentration indicated more hydrogen reduction on the cathode surface.

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