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Potentiodynamic Study of The Effects of Nickel on the Electrodeposition of Zinc from Chloride Media

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Abstract. The potentiodynamic experiments of the nickel effects on the zinc electrodeposition have been done to understand the impact of Ni impurities on the electrowinning of Zn from spent pickling liquor. The nickel chloride solutions of Ni concentrations 90 and 1 g/dm^3 *were used as the electrolytes. The latter was also mixed with 90 g/dm*^{3} *Zn in the experiments. All the runs were carried out at room temperature with 40 mV/s continuous polarization speed and with 1/s sampling rate. It was observed that nickel electrodeposition from chloride media containing 90 g/dm*^{3} *Ni started with the generation of hydrogen bubbles, entirely blocking the cathode surface. Only a slight current development was observed until the polarization potential ~ -0,8 V. The visual observation showed bubbles also formed at the anode, which may represent chlorine and/or oxygen evolution. While, in the electrodeposition of nickel with only 1 g/dm*^{3} *Ni concentration in the electrolyte, metal deposition was hardly observed, but visible hydrogen bubbles constantly blocked the cathode surface. A similar tendency was observed in the mixed-solution electrolysis cell; the initial tiny bubbles accumulated at the cathode surface more than in the pure Zn solution. The enhancement of* H_2 *evolution indicates how nickel deposition may contribute to the loss of useful current in the process of Zn electrodeposition. The mass of nickel deposited from the mixed solutions significantly decreases as the Ni concentration decreases in the electrolyte, while the mass of deposited zinc is relatively constant. It means that the purity of the produced Zn is appreciably higher – with respect to Ni – if nickel is efficiently eliminated from the solution before electrowinning.*

Keywords: Potentidynamic, Zn electrodeposition, Ni impurities, Electrodeposition from chloride media, Spent pickling liquor

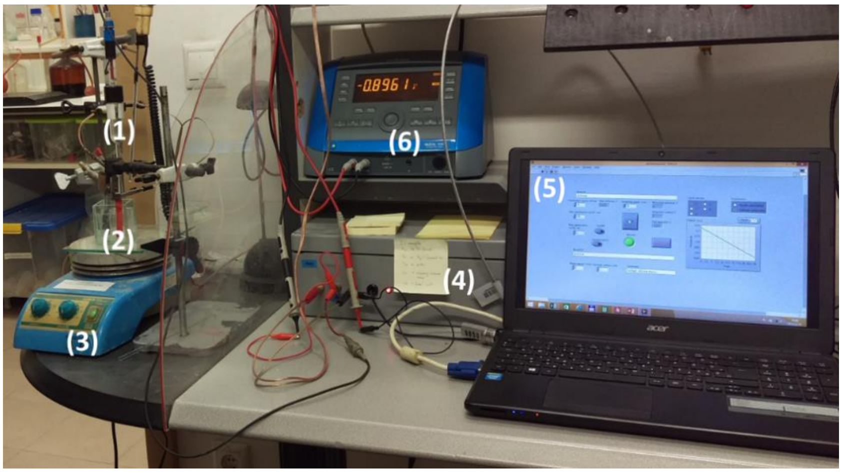
Introduction

The recycling process of spent pickling liquor (SPL) has currently become attractive, as it does not only solve the environmental problem but also provide a secondary resource of metals, particularly iron (Fe) and zinc (Zn). As hydrochloride acid (HCl) is used in the pickling stage of the hot-dip galvanizing (HDG) process to clean metal surfaces before the main coating stage, a direct recovery of the metal content should be based on processes in chloride solutions. The fresh acid content of 15-30 % HCl [1] gradually decreases because of the metals salt formation in the solution during service. After losing 75-85 % of its concentration [1], [2], [3], this liquid is still used as the stripping solution to remove unwanted zinc coatings from defected products before re-galvanizing [4]. Thus, SPL contains significant amounts of zinc in addition to iron and other metals, at various levels, making this material hazardous. Moreover, from the economic viewpoint, storing it in the landfill after the precipitation process and neutralising the acid are considered as loss of chemical, let alone the land and transportation cost. The ideal solution is circular technology with close to zero waste. The composition of SPL greatly depends on how the fresh liquid was used in the previous process. Therefore, the cathodic deposition of zinc should be considered in a wide range of concentrations of Zinc and the main impurities. This liquid may contain 25 to 125 g/dm^3 zinc, 90 to 200 g/ dm^3 iron, and 70 to 100 g/dm^3 free HCl and approximately 7 to 10 M total Cl$^-$ ion [5] [6] [7] [8] [9] [10]. Additionally, trace amount of Cu, Co, Ni, Pb, Cd, Cr and Mn can also be present in the solution [1], [2], [11]. Nickel with higher reduction potential interferes with the deposition of zinc in two conditions. Firstly, its more noble nature tends to be deposited in favour of zinc, which later impacts the purity of the deposit. Like iron, its lower overpotential to hydrogen also promotes more hydrogen evolution.

The nature and concentration of impurities along with temperature and acidity influence practical characteristics of the Zn deposition, such as current efficiency and cathode potential. The more noble impurities - more likely to be deposited - might be a serious problem for the purity of the product. Furthermore, they may reduce the overpotential of hydrogen, thus may promote hydrogen evolution. Beside the detrimental effects on purity, impurities may lower current efficiency and increase energy consumption [12]. In the electrodeposition process of zinc in the presence of nickel, the re-dissolution of deposited metals always takes place as the deposited nickel forms numerous galvanic micro pairs with zinc. At the same time, hydrogen evolves on the nickel zones enhancing the re-dissolution of the surrounding zinc [13], [14]. Manganese in the electrolyte solution behaves similarly to nickel to promote depolarization and speed up the zinc re-dissolution reaction [13]. Fortunately, neither nickel nor manganese can form anionic chloro-complexes, thus their elimination by the preliminary anion-exchange purification step designed for the removal of iron in the divalent state may be just as efficient. However, it should be fundamentally clarified how much of the more noble nickel impurity may remain in the purified solution if high-purity zinc is the desired cathodic product. Nickel may have no practical corrosive attack since its electrode potential (- 0.25 V) is significantly higher than that of zinc. However – as discussed above – the lowered hydrogen overpotential may result in more current loss and the preferential nickel deposition may cause unwanted impurity in the zinc cathode. This harmful mechanism has been demonstrated by earlier potentiodynamic experiments as the presence of iron significantly promoted the reduction of hydrogen. The electrode potential of nickel is however less negative than that of iron, therefore this effect can be even more disturbing if nickel is also contained in the electrolyte solution. At extreme cases, when the hydrogen evolution is intensive and the solution is close to neutral, the locally increasing pH may trigger the formation of hydroxide particles. Thus, an inhibiting layer can even be formed hindering the deposition of the less noble zinc. All these aspects of impurity co-deposition emphasize the importance of examining the effects of nickel contained in the purified zinc electrolyte. Therefore, the current experiments have been focused on the characteristic effects of nickel on the zinc electrodeposition.

1. Experimental Methods

The characteristics of Zn deposition from chloride media affected by nickel were investigated by the protentiodynamic method. The model solutions used as electrolyte were prepared from analytical grade $ZnCl_2$ and $NiCl_2 \cdot 6H_2O$ dissolved in the distilled water. Basically, two pure nickel chloride solutions of Ni concentrations set first to 90, then regularly to 1 g/dm^3 , respectively, were used as the electrolytes. The results obtained with the pure nickel solutions were compared to those reported also previously for the pure zinc-chloride solution of 90 g/dm^3 Zn concentration - relevant to the SPL. In further experiments, the 1 g/dm^3 pure nickel solution was mixed with the pure Zn solution at different ratios (1:100, 1:200, 1:300, 1:400, 1:500, 1:1000 and 1:10000) to examine the effect of Ni concentration on the Zn electrodeposition. An electrolysis cell with the dimensions of 50x50x50 mm made of glass was used as shown in Fig. 1. The saturated calomel reference electrode (SCE) was connected to the surface of the cathode (working electrode) through a bridge tube ending in a Lugging-capillary tip (of ~ 1 mm diameter) and filled with the given electrolyte solution. The anode (counter electrode) was made of a pure zinc rod of 5 mm diameter, to compensate for the loss of Zn^{2+} concentration caused by the repeated cycles of cathodic deposition from the pure zinc, or the mixed Zn-Ni solutions. The initial cathode was made of a copper plate with the active surface of 2 cm^2 by masking at the edges and the back by acid resistant lacquer. The cathode surface was preliminarily polished with a 400-grit SiC paper giving a uniform surface, washed with distilled water, and finally dried before setting into the cell. All the runs were carried out at room temperature with 40 mV/s continuous polarization speed – giving the widest range of clear results - and with 1/s sampling rate.



where:

(1) reference electrode
(2) electrolysis cell
(3) magnetic stirrer
(4) potentiostat
(5) PC controller and LabView interface
(6) multimeter

Figure 1. Potentiodynamic electrodeposition equipment.

The system was connected to a special computer-controlled potentiostat designed at the University of Miskolc that was capable to produce rapid polarization runs, suitable for the investigation of the cathodic processes under fast changing conditions. It was controlled and the results were recorded by a special software – developed and run on the NI LabView platform. A magnetic stirrer and a rotating rod of 2 cm length at the bottom of the cell were used with rotation speeds from 0 to 800 r.p.m. To determine the composition of the deposits, weighing the cathode before and after the potentiodynamic process has been done. Then, these electrodes were immersed into 1 mol/dm^3 of HCl + cc. HNO_3 to dissolve the deposit on its surface prior to analysis by atomic adsorption spectroscopy (AAS). Hydrogen activity during the polarization set up was also studied at various pH values between 2.3 and 4.3 with blank hydrochloride acid solutions and results referring to the same pH as the model solutions were used for comparison.

2. Results and Discussion

The form of deposition of Zn on the cathode depends on the composition of the bath, in which various agents may influence the electrocrystallization process and the structure of the final deposit. Although, chloride solutions offer high rates of zinc deposition on the cathode surface, it is hard to obtain smooth and compact deposits. Moreover, the existence of the impurities promotes hydrogen evolution, which always means competition with and modification of the Zn electrodeposition. The polarization curves are presented with the current values, as the actual surface of the working electrode may change during the experimental run. Apparent current densities can be expressed from the plotted values referring to the starting (geometric) area of the active surface.

Nickel electrodeposition from chloride media containing 90 g/dm^3 Ni started with the generation of hydrogen bubbles, entirely blocking the cathode surface. As shown in Fig 2, there is just a slight current development observed until the polarization potential ~ -0,8 V. Magnification of the curve scale also showed that the polarization curve fluctuated initially, indicating the periodically evolving hydrogen bubbles. In acidic electrolytes the deposition of fresh nickel crystals is always followed by subsequent reduction of H^+ to H_{ads}, which firmly adheres to the electrode surface and 13 blocks further reduction process until it forms recombined hydrogen molecules which are then released as bubbles [15]. After the bubbles get detached, further metal deposition can take place at the same site. At higher overpotentials the hydrogen reduction is accelerated so much that this process can become virtually simultaneous referring to the overall cathode surface. The visual observation showed bubbles formed not just at the cathode surface, but also at the anode, which may represent chlorine and/or oxygen evolution.

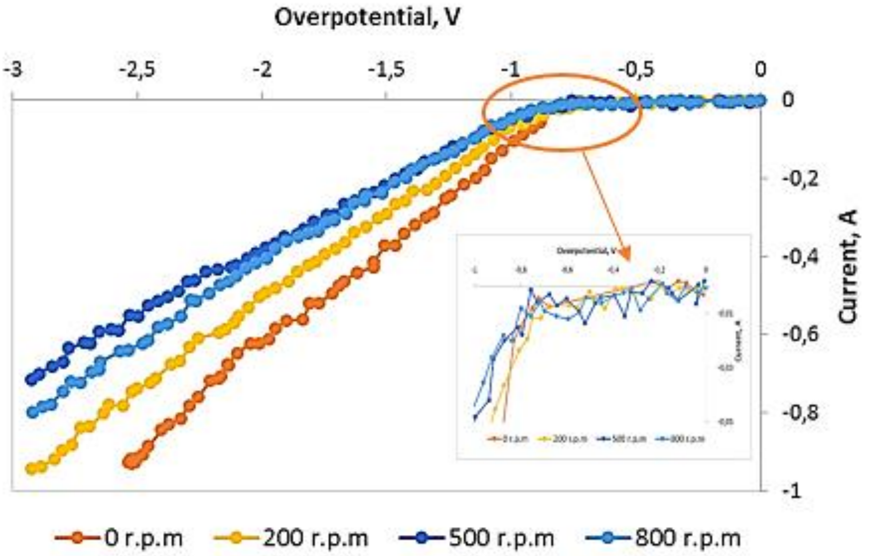


Figure 2. Polarization curves obtained with electrolytes of 90 g/dm^3 Ni (anode: graphite)

Under the examined conditions, stirring speed did not show visually any positive impact on the deposition of nickel; however, as can be observed from the polarization curves in Fig. 2, it could depress the slopes. It is possibly caused by the refinement of the Ni crystals deposited, thereby the microstructure of the cathode surface could get smoother, resulting in higher actual current densities with the same currents. The required overpotential is proportional to the actual current density. Unfortunately, the excessive production of hydrogen bubbles takes place simultaneously with the nucleation of Ni deposit, resulting in looser structures at higher currents. The flaky deposit produced at the cathode surface is easily detached and falls to the bottom of the cell. Figure 3 shows the condition of the cathode surface after the Ni electrodeposition procedure. It is also observed that during the electrodeposition, the solution pH is increased from 4 to 13.5 corresponding to an excessive reduction of hydrogen ions.

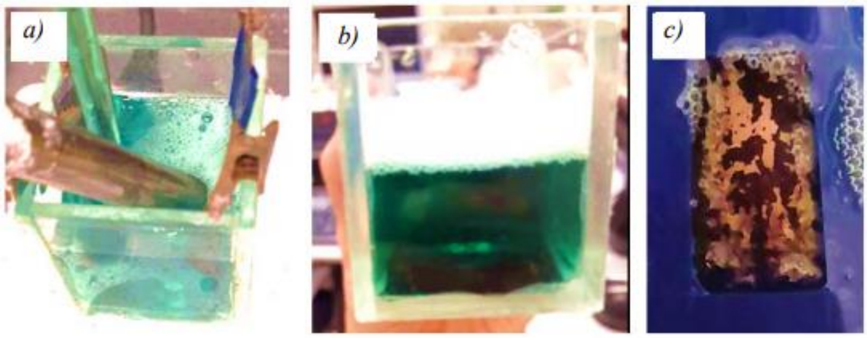


Figure 3. The conditions in the cell at the start (a), after the procedure of ~ 1 min duration (b) and the final surface of the cathode (c).

In the electrodeposition of nickel with only 1 g/dm^3 Ni concentration in the electrolyte, metal deposition was hardly observed, but visible hydrogen bubbles constantly blocked the cathode surface. There was virtually no current generated all over the examined potential range, as can be seen in Fig. 4. The results were the same with both copper and zinc starting plates for the cathode.

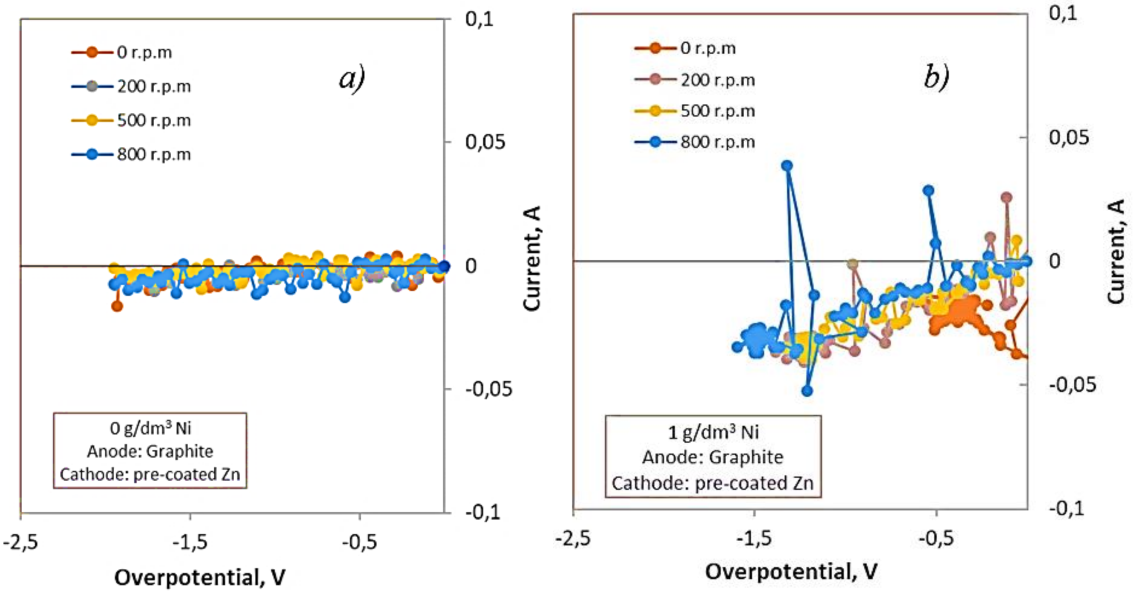


Figure 4. Polarization curves obtained on Zn-pre-coated copper plates with 0 (a) or 1 g/dm^3 Ni (b) in the chloride electrolyte of pH 4.3.

With the blank pH 4.3 solution, as seen in Fig. 3.*a*, there was almost no current observed even at higher cathodic polarizations. With 1 g/dm^3 Ni added to the solution, as presented in Fig. 4.*b*, slight cathodic currents occurred, indicating that at this pH Ni deposition can be the initial process and hydrogen evolution can develop when the nickel coverage is almost complete, as seen in Fig. 2 referring to high-Ni electrolyte solutions. The fluctuation of the curves gives information on the gaining and evolving action of the hydrogen bubble formation. The enhancement of H_2 evolution indicates how nickel deposition may contribute to the loss of useful current in the process of Zn electrodeposition. According to the measurements taken at regular intervals during the experiment with the 1 g/dm^3 Ni solution, the pH was virtually stable during the approximately 1 min long polarization run, as shown in Fig. 5. (The pH measurement had to be taken in different partial runs for assuring current free conditions.) The starting and the final pH values (4.2 ~ 4.4) were the same within the limits of experimental error for all the polarization runs.

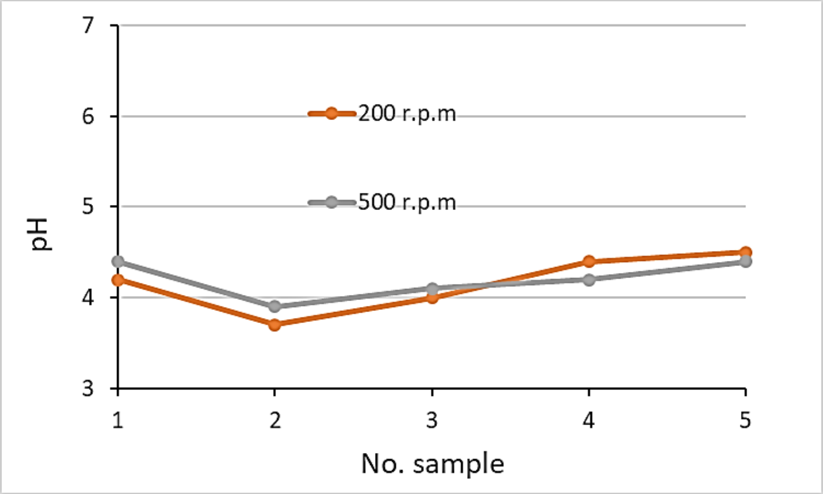


Figure 5. The change of the pH value during the polarization experiments with 1 g/dm^3 Ni in the chloride electrolyte.

Hydrogen evolution and metal deposition was studied also with model chloride solutions containing high (90 g/dm^3) Zn or Ni, and also with 90 g/dm^3 Zn + 1 g/dm^3 Ni metal concentrations, compared with the 1 g/dm^3 Ni solutions. These results are shown for comparison in Fig. 6. In the mixed solution, the initial small bubbles accumulated at the cathode surface more than in the pure Zn solution. The bubbles formed contribute to the total current on the one hand, but on the other, they may partly block the active sites as they accumulate. Corresponding to the findings presented in Fig. 3, no appreciable deposition of any species was observed on the prepared copper cathode surface from the 1 g/dm^3 Ni – pH 4.3 electrolyte. With the high (90 g/dm^3) nickel concentration, some nickel initially deposited on the copper cathode, followed by excessive hydrogen reduction beyond approx. – 1 V cathodic polarization. This condition gives a lower gradient to the relevant polarization curve because of the competition of nickel ion with the hydrogen reduction and the mechanism implies the accumulation and subsequent release of the hydrogen bubbles covering the freshly deposited Ni crystals. It could be observed at the initial stage that the cathode surface was entirely covered with hydrogen bubbles.

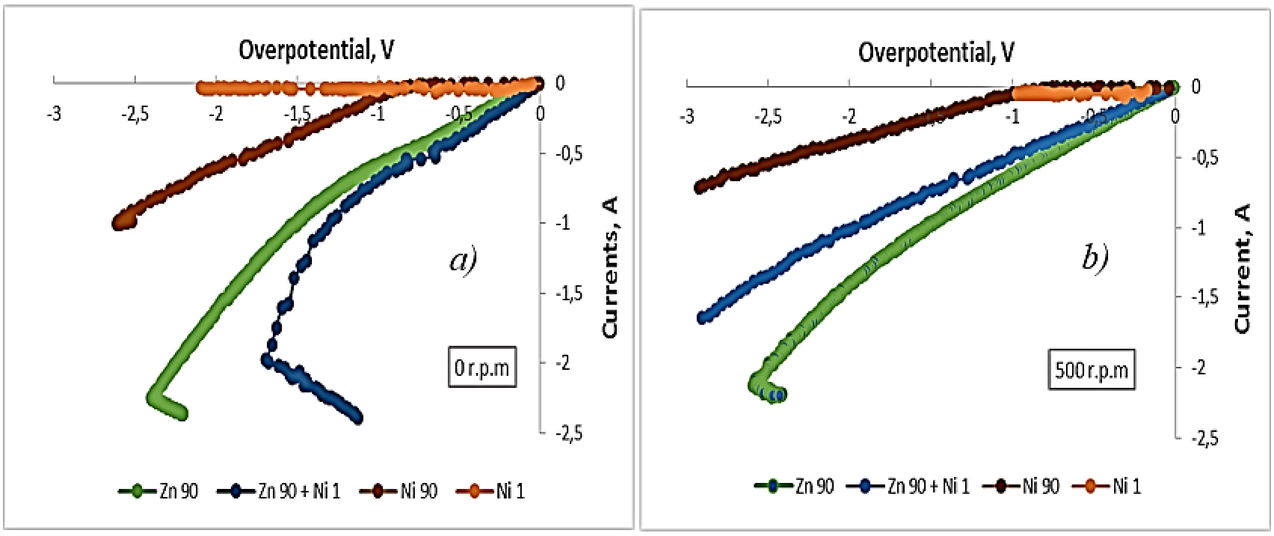


Figure 6. Cathodic polarization curves of Ni, Zn and mixed-solutions of pH 4.3 without (a) and with (b) agitation. (1 min runs at 40 mV/s polarization speed, applying Zn anodes).

As the deposition occurs, it continuously grows with a uniform pattern, implying the co-deposition of nickel and hydrogen. At the end of the polarization cycle, some dendrites were observed in the 90 g/dm^3 nickel electrolyte. The fine outgrowths were formed at the edges of the active cathode surface where a better nickel ion supply could be produced. Dendrite formation also occurs from the zinc solution of high (90 g/dm^3) concentration, but nickel dendrites tend to grow with more extended tips, reaching further into the solution and appearing in a relatively uniform pattern at the cathode edge. However, Zn dendrites develop more branches and side-arms, as demonstrated by the first two photos in Fig. 7.

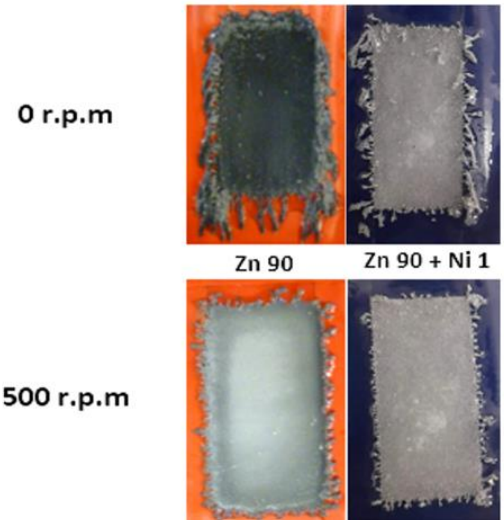


Figure 7 The final deposits from the 90 g/dm^3 Zn and from the mixed 90 g/dm^3 Zn + 1 g/dm^3 Ni solutions at different stirring rates.

This dendrite formation is the reason for the back-turns (hooks) at the relevant polarization curves especially seen in the concentrated stationary solutions. As the surface area rapidly grows with the dendrites formed, the actual current density drops, even if the current is further increased, thus less polarization is required under such conditions. The potentiostat cannot increase the current in such a pace as the surface gets rougher. However, stirring the electrolyte enhances the supply of ions over the entire cathode surface, thus fewer and smaller dendrites can develop. In this way some extra polarisation can be reached. Beside the ion transfer, it helps the hydrogen bubble removal.

In the mixed solution, 1 g/dm^3 nickel addition to the 90 g/dm^3 Zn exerts an inhibiting effect of metal deposition but enhances the evolution of hydrogen. This is supported by visual observations, and it results in the shifting of the characteristic polarization curve to the right after the intensive hydrogen evolution starts at about – 1 V overpotential. However, at the same time, hydrogen blocks partly the cathode surface, promoting dendrite formation and loose or even powdery metal deposition. As the metal of higher redox potential (Ni, if available at the surface) is preferably deposited, the possibility of a local Zn-Ni couple arises, which may promote the re-dissolution of previously deposited Zn too. These two anomalous processes result in the rapid increase of the current even with decreasing cathodic potentials, while visually less deposit formation can be observed. Since the hydrogen reduction on the cathode surface was unavoidable, some loose powdery deposition was also observed on the cathode surface. Stirring of the electrolytes generally helped reach higher cathodic polarizations with less hydrogen evolved. The slopes of the polarization curves are seen decreased in Fig. 6.b. The currents reached are lower (Fig. 6), dendrite formation is strongly depressed (Fig.7), the final deposits are denser, and the crystals are finer. However, such intensive stirring techniques are difficult to put into practice in the conventional electrolytic cell arrangements.

It was found that introducing Ni to the Zn electrolyte also change the nature of H^+ reduction. More hydrogen reduction was observed in the mixed solution. This is supported by visual observations, and it results in the shifting of the characteristic polarization curve to the right after the intensive hydrogen evolution starts at about – 1V overpotential. The importance of electrolyte agitation also has been proved by the potentiodynamic results. Increased stirring rates result in denser zinc deposits and depressed hydrogen evolution at the cathode. The mass of nickel deposited from the mixed solutions significantly decreases as the Ni concentration decreases in the electrolyte, while the mass of deposited zinc is relatively constant from the agitated solutions (Fig 8). It means that the purity of the produced Zn is appreciably higher – with respect to Ni – if nickel is efficiently eliminated from the solution before electrowinning.

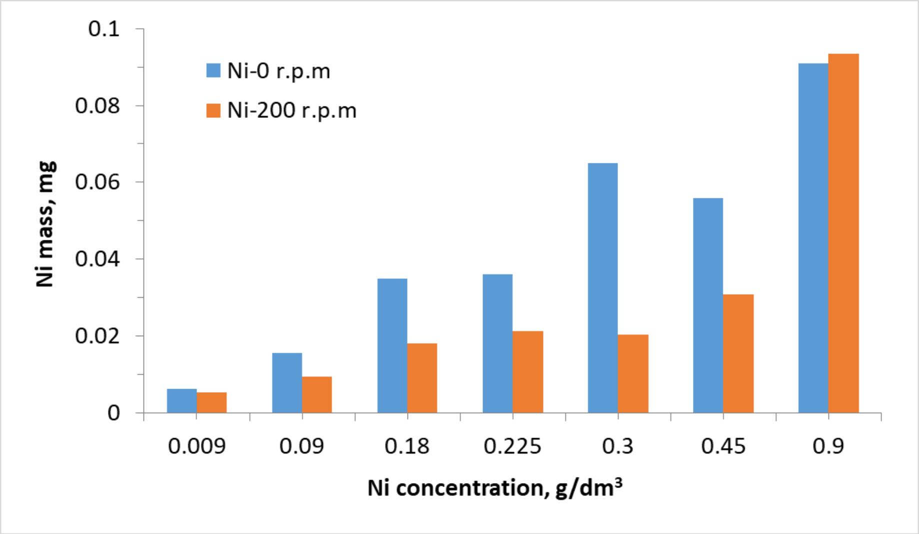


Figure 8. The mass of Ni impurities on the deposit of 90 g/dm^3 Zn – pH 4.3 mixed electrolyte.

Stirring at a rate of higher than 200 r.p.m increases the rate of zinc electrodeposition – almost equally compared to the rate from stationary solution. This may be attributed to the virtual elimination of hydrogen evolution. However, the electrodeposition of Ni from the solutions of low concentrations had little response to the effect of stirring. The main effect was the Ni concentration, which determined the contamination of the deposited zinc layer. Nickel concentration did not influence the electrodeposition of Zn in the examined ranges of concentrations. Anode gases evolved at the inert surface can cause added turbulence in the whole cell virtually enhancing the beneficial effects of forced electrolyte circulation. The strongest effect of stirring was seen in the change of the deposit morphology, efficiently eliminating the growth of long dendrites.

3. Conclusion

The presence of Ni in the zinc chloride solution changes the electrolyte nature and conditions for metal deposition. Visually, nickel co-deposition with zinc can be seen from the brighter colour of the deposit, proved by chemical analysis. Nickel affects the deposition of zinc by promoting hydrogen evolution by lowering the overpotential of gas evolution. Hydrogen evolution in relation to nickel deposition is a combined mechanism, where the primary step is always the reduction of the metal ion. The effect of nickel concentration in the electrolyte – even at lower levels than 1 g/dm^3 - was found to influence the purity of the obtained Zn deposit. The structure of the deposited zinc is also influenced by the nickel contamination, making it more inclined to form rougher crystals or even longer dendrites. Although Ni concentration did not influence the amount of Zn deposition in the examined ranges of concentrations, it still affected the purity of Zn deposition. Thus, purification before electrodeposition is necessary to be done.

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