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Effect of nickel in zinc electrowinning under periodical reverse current

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The effects of nickel impurities were investigated during the electrowinning of zinc in acidic media using periodical reverse current (PRC) along with anodic potential current response and cathodic current efficiency. The chemical and structural characteristics of the cathode deposit were also determined using nickel concentrations of 3, 5 and 10 $mg\,l^{-1}$ in sulphuric acid (200 $g\,l^{-1}$ H_2SO_4) containing 60 $g\,l^{-1}$ of zinc. The cathodic current efficiency drop caused by nickel was less detrimental in PRC than DC. It was found that the morphology of the deposit plays an important role in the redissolution process caused by impurities. The levelling effect caused by PRC decreases the rate of zinc redissolution, which results in an increase of current efficiency. However for concentrations equal to or greater than 10 $mg\,l^{-1}$, the levelling effect caused by PRC is no longer dominant. On the anode nickel did not affect the overpotential of the lead-silver electrode in PRC or DC modes.

1. Introduction

It has been shown that the use of periodical reverse current (PRC) during the electrowinning of zinc in acidic media can decrease energy consumption [1–5]. This was mainly attributed to the lower anodic overpotential observed at the lead electrode. Bérubé and Piron [2] explained that the beneficial effect was related to the desorption of shielding chemical species such as $OH_{(ad)}$ and to a different morphology of the anode obtained in PRC.

The use of PRC also increases the current efficiency of zinc electrodeposition in certain conditions [5]. It was found that the synergistic effect betwen PRC and lead impurities could influence the crystallographic growth of the zinc deposit, resulting in a higher hydrogen overpotential and consequently a higher current efficiency.

Hitherto very pure electrolytes were used in PRC studies. However, in industrial processes the electrolyte frequently contains impurities such as nickel [6–9] which originate with the zinc ore and remain in solution at trace levels, even after purification. During the electrowinning of zinc using direct current, a small concentration of nickel ([Ni] = 10 $mg\,l^{-1}$) in the acid electrolyte (60 $g\,l^{-1}$ Zn and 200 $g\,l^{-1}$ H_2SO_4) will cause redissolution of zinc after a certain time [7, 10–13]. This mechanism is not very well understood, and some investigators have attributed it to a galvanic effect between zinc and nickel [7, 8, 10–12].

No study has so far been undertaken on the effect of PRC on zinc electrowinning from electrolytes containing nickel impurities. The present investigation aims at a better comprehension of the mechanism involved with PRC and the effect of nickel at the anode and cathode during zinc electrowinning. For the purpose of this study, only nickel was added to the acid electrolyte, in order to avoid a synergistic effect with other species. Anodic potentials were recorded as well as the roughness and chemical analysis of the zinc deposit. Hydrogen current densities were measured in order to calculate the time before redissolution of the deposit.

2. Experimental details

2.1. *Cell*

The cell was composed of one lead–0.5% silver anode and one aluminium cathode (both supplied by Noranda). The anodic and cathodic total surfaces were equal (6 cm^2 each), and their active surfaces were delimited by epoxy coating. The electrodes held by Teflon holders, were separated by 3.7 cm, which is similar to industrial conditions. The whole cell was contained within a one litre beaker and put into a thermostated bath maintained at 40° C. An inverted burette was fixed over the zinc electrode to measure the volume of hydrogen cathodically evolved. The hydrogen current (I_{H_2}) was calculated using Faraday's law. The cathode was weighted before and after each experiment, and Equation 1 was checked each time.

$$I_{H_2} + I_{Zn} = I_{total} \quad (1)$$

2.2. *Electrode preparation*

The anode was preconditioned at the beginning of the project to obtain a surface layer of lead oxide. This procedure was developed by Cominco [14, 15] to

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produce an anode similar to industrial anodes after six months of service. It consisted of maintaining an anodic polarization of the lead-silver electrode at a potential greater than 2 V with respect to the standard hydrogen electrode (SHE) for a period of 8 h in a fluoride (2.1 M KF) and acid sulphate solution (0.4 M H_2SO_4). For electrowinning tests, the aluminium electrode was polished with 600 grit sandpaper before each experiment. Since a small amount of lead oxide was formed on the lead-silver electrode during a test, it was only brushed to remove excess oxide. This procedure made it possible to leave a lead oxide layer on the surface of the anode. Thus it was consequently not necessary to precondition the anode before each experiment.

2.3. *Reference electrode*

A mercury/mercurous-sulphate reference electrode was used to measure the anode potential. The potential of such an electrode was calculated by Bérubé and Piron [2]. They showed that at 40° C the value was 0.6413 V with respect to SHE. A thermostated Luggin capillary kept the electrode at the working temperature.

2.4. *Electrolyte*

Chemicals used were all reagent grade and the water was twice distilled. Each litre of electrolyte contained 200 g of sulphuric acid and 60 g of zinc from $ZnSO_4 \cdot 7H_2O$. Nickel was added afterward so that concentrations of 3, 5 and 10 $mg\,l^{-1}$ were obtained in the electrolyte.

2.5. *Electrical apparatus*

To produce the shape of the current signal to the galvanostat (when using PRC), a Wavetek wave generator (model 275) was used. The signal was transformed into current by the EG & G PAR potentiostat/galvanostat (model 173). The potential response read between the anode and the reference electrode was sent through a channel selector to a Tektronix oscilloscope (model 7623A) or to a Keithley multimeter (model 614).

2.6. *Chemical analysis*

The flame spectroabsorption technique was used to measure the nickel and lead content of each zinc deposit. The limit of detection of this method is of the order of 0.1 ppm with an accuracy of ~ 1–2%, and the results obtained give a global value of the nickel or lead content.

2.7. *Roughness analysis*

To measure the surface roughness, a 'Rank Taylor Hobson Leicester' surface analyzer was used. It gives the surface profile of the zinc deposit. From this profile the mean value of the peak height was calculated with an accuracy of 5%. This mean value is defined here as the deposit roughness.

2.8. *Experimental set-up*

It was shown that an inverse charge greater then 125 $C\,m^{-2}$ was detrimental to the lead electrode [2]. Since this type of electrode was used to perform all the experiments, the values of 50, 100 and 115 $C\,m^{-2}$ were chosen. The value of 0 $C\,m^{-2}$ corresponds to the DC mode. The inverse charge is obtained by multiplying the inverse current and the inverse time. The latter was fixed at 0.5 s The direct time was set at 100 s.

To study the effect of nickel during the electrowinning of zinc using PRC, two types of experiments were set up: one to determine the induction time, and another with a fixed time of deposition (1 h), for comparing parameters affecting the surface state of the deposit.

3. Results

The first part of this work shows the effect of nickel on the anode. This is important because previous research shows that PRC lowers the cell voltage on decreasing the anodic overpotential [2].

The second part of this research is on the cathode. It is based on the fact that with direct current and in acidic media, nickel has a detrimental effect by causing redissolution of the zinc after a period of time [7, 10–13]. Using PRC may affect the mechanism involved during this period; comparisons were made with results obtained using DC.

3.1. *Anode*

Nickel in the electrolyte did not influence the anodic potential during the electrowinning of zinc using PRC. Thus the beneficial effect resulting from the lower anodic overpotential is preserved when nickel is present. Table 1 summarizes the values of minimal anodic potential reached during a cathodic pulse. It shows that there is no major difference between electrolytes containing nickel and without nickel. The minimal anodic potentials reached after 0.5 s of

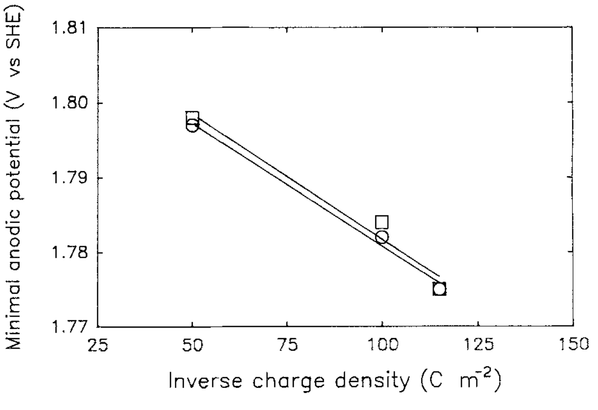

Fig. 1. Anodic response during a pulse of reverse current. Inverse charge of 100 $C\,m^{-2}$. (○) without nickel and (□) with 5 $mg\,l^{-1}$ of nickel.

Table 1. Experimental results for DC and PRC electrowinning*

*Inverse charge** (Cm^{-2})	*Nickel in solution* ($mg\,l^{-1}$)	*Minimal anodic potential* (V_{SHE})	*Induction time* (*min*)	*Roughness* (μm)	*Nickel in deposit* (*ppm*)	*Lead in deposit* (*ppm*)
0	0	–	–	10.24	0	9
0	3	–	86	13.26	31	10
0	5	–	57	8.89	55	9
0	10	–	45	–	110	11
50	0	1.80	–	9.11	0	12
50	5	1.80	62	9.19	54	15
100	0	1.78	–	7.75	0	13
100	3	1.78	113	9.35	32	12
100	5	1.78	70	6.85	51	16
100	10	1.78	44	–	107	15
115	0	1.77	–	7.79	0	15
115	5	1.77	70	7.45	53	16

* The value of $0\,C\,m^{-2}$ for the inverse charge corresponds to the DC mode.

cathodic pulse are practically the same. As shown in Fig. 1, an increase of the inverse charge lowers the value of the minimal anodic potential even in the presence of nickel. Similar results were obtained by Bérubé and Piron [2], but without nickel.

The value of the anodic potential during direct current, which is not given in Table 1, was equal to 1.89 V (SHE) for all the experimental conditions using PRC. In DC mode, the anodic potential was equal to 1.91 V (SHE). Thus PRC reduces the anodic overpotential, as previously demonstrated [2].

3.2. *Cathode*

Using PRC for the electrowinning of zinc with nickel impurities in the solution causes redissolution of the deposit after a longer period of time compared to the use of direct current. Thus PRC lowers the detrimental effect of nickel.

3.2.1. Calculation of the induction time. Fig. 2 shows typical values for the hydrogen current during an experiment. In both cases the hydrogen current density was low at the beginning of deposition, and its value started to rise after a period of time called the 'induction time'. Induction time was longer in PRC than in DC. This was measured graphically by taking the time at which the intersection of the two tangents occurs (Fig. 2). Table 1 summarizes the induction time values for PRC and DC obtained with different amounts of nickel in solution.

With values lower than $1\,mg\,l^{-1}$ of nickel in solution, there was no variation in the hydrogen current after 4 h of electrowinning either in PRC or DC. Nickel concentrations over $3\,mg\,l^{-1}$ were necessary to observe the higher value for the hydrogen current.

Fig. 3 shows the effect of using PRC results in a higher induction time. However, at a value of $10\,mg\,l^{-1}$ of nickel in solution, PRC does not have any effect, since the induction time is approximately the same as that obtained with DC (45 min in DC and 44 min in PRC).

3.2.2. Impurities in the deposit. Fig. 4 shows that the amount of nickel in the deposited zinc did not vary from the PRC mode to the DC mode. In this figure, typical results are given (PRC with an inverse charge of $100\,C\,m^{-2}$). The same amount of nickel in the deposit was, however, obtained using 50 or $115\,C\,m^2$ (Table 1). Fig. 4 also shows that there was a linear relationship between the concentration in the

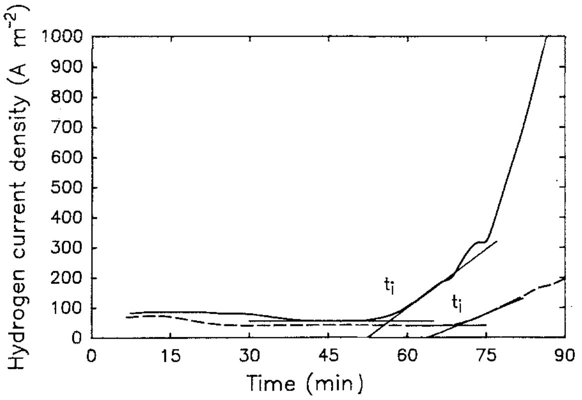

Fig. 2. Hydrogen current density at the zinc cathode against deposition time. Solution contains: $5\,mg\,l^{-1}$ nickel; total current density: $500\,A\,m^{-2}$. (——): DC (– –) PRC at $100\,C\,m^{-2}$.

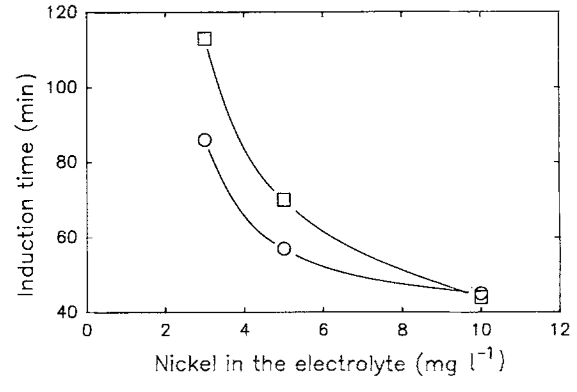

Fig. 3. Induction time observed at different nickel concentrations in (○) DC and (□) PRC with $100\,C\,m^{-2}$ of inverse charge.

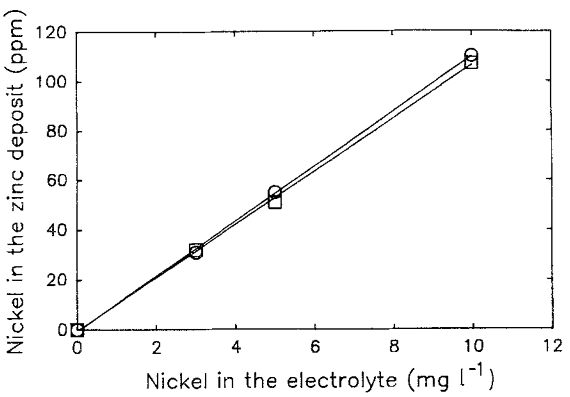

Fig. 4. Nickel in the deposit as a function of the nickel in the electrolyte in (○) DC and (□) PRC with $100\,\mathrm{C\,m^{-2}}$ of inverse charge.

electrolyte and the amount in the deposit. This linear relation was observed by others in direct current [10, 13].

Based on the observation made in Table 1, lead had no influence on the induction time. The only factor that affected the lead content was the inverse charge, as observed previously [2].

3.2.3. Roughness of the deposit. As already explained the cathode was polished at the beginning of each experiment. Therefore the roughness at the start of an experiment was equal to $1.5\,\mu$m, which constituted a reproducible starting value for the roughness. As the deposition occurred, zinc precipitated at the surface, causing the deposit to increase its roughness. The roughness values in Table 1 were obtained after 1 h of deposition. Therefore, it was not possible to obtain roughness values for experimental conditions resulting in induction times less than 60 min, as in the case of $10\,\mathrm{mg\,l^{-1}}$ of nickel solution.

For a given deposition time, Table 1 shows that PRC mode with high inverse charge gives a deposit with a smoother surface. This was caused by dissolution during the current reversal because the peaks of the deposit offer a path less resistive to the current [16]. Similar dissolution is observed in industrial plating [17] where a pulsing current is used to get smoother surfaces.

4. Discussion

4.1. *Effect of impurity on the anode*

In a previous study [2] it was shown that when using an inverse charge lower than $125\,\mathrm{C\,m^{-2}}$, the potential of the anode remains in the domain of stability of the lead oxide. In these conditions, contamination of the electrolyte, and thus the zinc deposit, by lead remains low [2]. Table 1 shows that for PRC or DC modes, the lead in the zinc deposits was equal to or lower than 16 ppm.

Nickel did not influence the potential of the anode. In PRC, its value during the direct time was equal to + 1.91 V (SHE), regardless of the nickel concentration in the electrolyte. At this potential, the Ni^{2+} ions can react with H_2O to form NiO_2. The nickel dioxide formed at the surface of the lead–silver electrode did not significantly affect the oxygen overpotential, since no difference was found in the anodic potential in the presence or absence of nickel in the solution. During the reversal time, the anodic potential remained in the domain of NiO_2, and only desorption of chemical species such as $OH_{(ad)}$ could have occurred. Thus nickel did not change the behaviour of the anode in direct or inverse time and the beneficial effect reported in [2] remains the same.

4.2. *Redissolution mechanism on the cathode*

Increasing the concentration of nickel in the solution will result in a greater amount of nickel in the zinc deposit. This is mainly shown in Fig. 4 where the amount of nickel is directly proportional to its concentration in the electrolyte. Also on this figure there was no meaningful difference between PRC and DC mode. This is because the deposition time in PRC is about 200 times longer than the dissolution time (100 s direct current and 0.5 s inverse current).

Nickel concentration and the morphology of the deposit are factors affecting induction time. It has been shown by other workers [7, 10–12] that, in DC, the amount of nickel in the electrolyte is related to the induction time. The same result was confirmed in this study as shown by Fig. 3. However, PRC techniques made it possible to obtain zinc deposits having the same nickel content but with different roughness. Thus the roughness could explain the difference in induction time observed in Fig. 3. By using a concentration of $5\,\mathrm{mg\,l^{-1}}$ of nickel in the deposit for PRC and DC modes, a higher roughness was found to lower the induction time, as shown in Table 1. This was found even more strikingly at $3\,\mathrm{mg\,l^{-1}}$. An increase in the roughness of $4\,\mu$m corresponds to a decrease of 27 min.

The process by which nickel causes redissolution of the zinc deposit is explained in the literature for DC [7, 8, 10–12] and this explanation could reasonably apply also for PRC, because it refers to galvanic corrosion of zinc caused by nickel. However, more emphasis should be put on the morphological aspect of this process to increase the induction time.

The mechanism by which the morphology of the zinc deposit influences the induction time could be explained as follows. As the roughness increases during zinc deposition, the real surface of the deposit increases and thus the applied current density slightly decreases, maintaining a constant value of the applied current. Also peaks on the surface cause some small heterogeneity on the current distribution. Therefore the current density could decrease in some regions and increase in others. This causes some local changes in the cathodic overpotential.

In the case of electrowinning without nickel impurities, this would not affect the mechanism of zinc deposition and hydrogen evolution. However hydrogen overpotential on nickel is lower compared to that on the zinc surface, and a small amount of nickel at the surface combined with a more negative local cathodic potential could be enough to increase the hydrogen evolution locally after a certain time. The nickel current will increase if the solution is stirred by more hydrogen evolution, because with such a small concentration in solution, nickel current is ruled by mass transport. A greater amount of nickel will then precipitate at the surface, resulting in a larger area where hydrogen could evolve easily. The increase in the current of hydrogen could be so large that it could explain galvanic corrosion of zinc responsible for the observed zinc redissolution. Imposed current remains constant and part of the hydrogen current comes from the corrosion of zinc.

In the case of nickel concentrations of $10\,\mathrm{mg\,l^{-1}}$ or higher, there was no difference in induction time between PRC and DC conditions (Table 1 and Fig. 3). This could be attributed to the fact that, when a larger concentration of nickel is present at the surface, it is easier to start the higher hydrogen evolution at a given roughness and thus to start the autocatalytic redissolution of the deposit. The large nickel content would then become the dominant factor over the beneficial PRC levelling effect.

Since the beneficial effect of PRC came from its levelling action, it is expected that other ways of obtaining a smoother surface, by using additives or other types of pulse current, would also lower the detrimental effect of nickel impurities in the solution. Maintaining the surface at a roughness that delays the beginning of redissolution would increase the induction time even for nickel concentrations in the electrolyte of $10\,\mathrm{mg\,l^{-1}}$ or higher.

5. Conclusion

The beneficial effects of PRC on the anodic side were not influenced by the presence of nickel in the electrolyte. The anodic potential remains in the domain of stability of the nickel dioxide, which did not influence the oxygen overvoltage. Consequently, PRC made it possible to lower the anodic overpotential of the lead–silver electrode even in presence of nickel.

Using PRC affects the morphology of the zinc deposit and results in a smoother surface compared to that obtained with DC. It is the levelling action of PRC that lowers the detrimental effect of nickel in the electrolyte observed on the cathode for concentrations lower than $10\,\mathrm{mg\,l^{-1}}$ in solution. At concentrations of $10\,\mathrm{mg\,l^{-1}}$ and over, the levelling action of PRC still exists, but it was the large nickel content that became dominant and the induction times in these cases were equal in PRC and DC modes.

It was not possible in this study to obtain the roughness at which the zinc starts to redissolve for a given nickel concetration, but it was shown that morphology plays an important role in the redissolution process. A smoother surface tends to delay redissolution of the zinc deposit in the presence of nickel impurities.

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