

INVESTIGATION ON NICKEL, ZINC AND SULPHUR CO-DEPOSITION DURING COBALT ELECTROWINNING

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ABSTRACT

It is well known that nickel and zinc are co-deposited during cobalt electrodeposition. Nickel has almost the same chemical, physical and electrochemical properties like cobalt. Furthermore, electrochemical potential of nickel is relatively higher than that of cobalt. For this reason nickel is preferentially reduced at the cathode in the presence of cobalt. In spite of its lower electrochemical potential in comparison to cobalt, zinc is reduced on the cathode because of its higher hydrogen-overvoltage. The co-deposition mechanism of sulphur at the cathode is not yet well understood. Investigations on the mechanism of sulphur co-deposition during cobalt electrolysis remain until without tangible results.

This work aimed to investigate the influence of some parameters on the co-deposition of nickel, zinc and sulphur during cobalt electrowinning. The following parameters have been investigated: Co^{2+} concentration in the electrolyte, current density and ammonium sulphate $[(\text{NH}_4)_2\text{SO}_4]$ additions. It has been established that important nickel, zinc and sulphur co-deposition takes place at relatively low Co^{2+} concentration in solution. The behaviour of these elements with regard to the cathodic phenomena has been established.

INTRODUCTION

Cobalt containing ores are usually treated by a sulphuric acid – electrowinning process. Many impurities are present in the leach liquor. Nickel and zinc are the most harmful impurities. They can hardly be completely removed from solution by precipitation, cementation or ion-exchange. These elements are therefore co-deposited with cobalt at the cathode during cobalt electrolysis. Furthermore, it has been observed that cobalt cathodes, obtained by electrolysis in sulphate media, contain up to 1,500 ppm of sulphur^[1, 2]. The

influence of the following parameters on the co-deposition of these impurities during cobalt electrowinning has been investigated in the present work: Co^{2+} concentration in the electrolyte solution, current density and $(\text{NH}_4)_2\text{SO}_4$ addition.

EXPERIMENTAL

Solution

A sample of an industrial cobalt sulphate solution from the Gécamines Shituru Plant (Katanga / D. R. Congo) was used in the experiments. Its chemical composition is given in **table 1**. The content of the different elements has been adjusted by evaporation, dilution with distilled water or addition of pure chemical reagents.

Table 1: Chemical composition of the cobalt solution

Co^{2+}	28 g/l	$S_{(\text{sulphate})}$	31.85 g/l
Ni^{2+}	0.07 g/l	$S_{(\text{total})}$	31.94 g/l
Zn^{2+}	2.65 mg/l	$\text{Fe}_{(\text{total})}$	0.17 g/l
Cu^{2+}	0.20 mg/l	H_2SO_4	7.37 g/l

Experimental procedure

Electrolysis experiments were carried out in a glass vessel containing the electrolyte in which three electrodes, two anodes and one cathode, were immersed. With reference to industrial practice, the cathode was a stainless steel and the anode material was a Co-Si alloy. The cathode had an exposed surface of 46.8 cm². The electrolyte was continuously agitated in order to ensure uniformity in solution composition. The cell was placed in a bain-marie. The bath temperature was measured using a quartz sheathed thermometer immersed in the electrolyte and automatically regulated by a thermostat. Regulation of current density was performed by varying the current intensity of the electrolysis cell. The intensity and voltage were measured by means of a potentiometer. Their values

were continuously recorded. The experiments were carried out with an electrolyte which had an initial pH-value of 6.3. The bath temperature has been kept constant at 80 °C in all test series. The ratio cobalt/Me (Me = nickel, zinc or sulphur) in the electrolyte remained unchanged in all experiments.

RESULTS AND DISCUSSION

Effect of cobalt concentration

Figure 1 shows the effect of cobalt concentration in the electrolyte on the cathodic co-deposition of nickel, zinc and sulphur. Nickel co-deposition decreases linearly with increasing cobalt concentration. The same behaviour is observed for zinc. Sulphur evolution exhibits a parabolic tendency with a minimum at about 50 g/l Co²⁺.

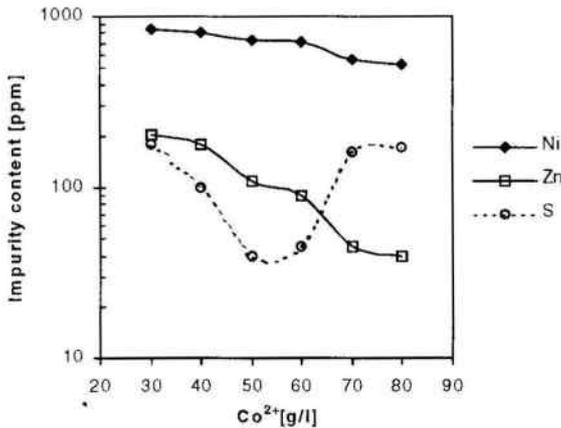


Figure 1: Influence of cobalt concentration on the co-deposition of Ni, Zn and S (T = 80 °C, J = 250 A/m²)

These results clearly indicate that the competition between cobalt, nickel and zinc ions on the cathode decreases with increasing cobalt concentration in the solution. Theoretically, the reduction on the cathode occurs with preference for the ion which has the greatest redox potential in the electrolyte. Standard redox potentials at 25 °C are given in table 2. Beside other parameters which have an influence on the cathode reaction, the sequence of cathodic deposition should be the following: hydrogen, nickel, cobalt and zinc. The reduction potential of an element is expressed by the following equation:

$$E_{M^{n+}/M} = E_{M^{n+}/M}^0 + \frac{RT}{nF} \ln[M^{n+}] \quad (1)$$

According to equation (1), if different ions would have the same value of potential, they could be reduced simultaneously at the cathode. In this context, for nickel and cobalt co-deposition, the following equation applies:

$$E_{Co^{2+}/Co} = E_{Ni^{2+}/Ni} \quad (2)$$

From equation (2), in the experimental conditions prevailing here, the Ni²⁺/Co²⁺ ratio in the electrolyte must be 0.169 for a simultaneous deposit of cobalt and nickel. This means that for an electrolyte, which contains for example 28 g/l Co²⁺, the concentration of nickel must be higher than 6.56 g/l before any co-deposition can be observed. However, the used solution contained only 0.07 g/l Ni²⁺ (Ni²⁺/Co²⁺ = 0.0025), as mentioned in table 1. Despite this fact, nickel co-deposition occurred. In the case of zinc, its concentration in solution must even be very high. In the present situation, the reduction of zinc in presence of cobalt could not occur, since the zinc content of the used solution was very low (2.85 mg/l Zn²⁺). This reasoning clearly demonstrates that the observed co-deposition of nickel and zinc during cobalt electrolysis is driven by other factors or mechanisms than their relative concentrations alone. K. Y. Sasaki and J. B. Talbot^[5] established, using the electrodeposition model of W. C. Grande and J. B. Talbot^[7, 8], that co-deposition of nickel from cobalt solutions takes place through monohydrolysis of nickel ions which are then present as Ni(OH)⁺.

Table 2: Standard reduction potentials at 25 °C

Elements	E ⁰ [volt]
H ⁺ /H ₂	0,00
Ni ²⁺ /Ni	-0,25
Co ²⁺ /Co	-0,28
Zn ²⁺ /Zn	-0,77

Effect of current density

The influence of current density on impurities co-deposition during cobalt electrolysis has been subject of numerous investigations.

The results of this work are presented in figure 2 which indicates impurities contents in cobalt cathode at different current densities. Zinc co-deposition increases with increasing current density. But the sulphur content goes down when the current density

increases, while nickel co-deposition remains almost unchanged.

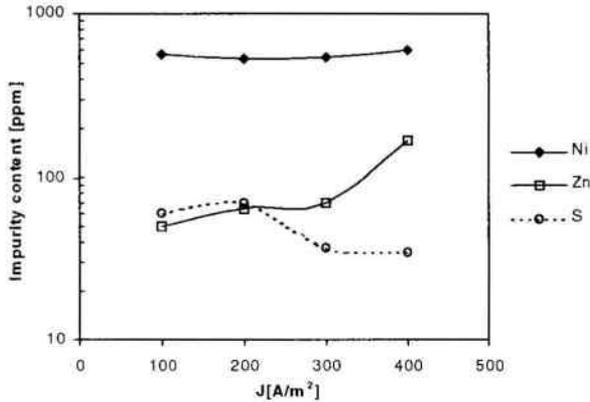


Figure 2: influence of current density on the co-deposition of nickel, zinc and sulphur ($T = 80\text{ }^{\circ}\text{C}$, $[\text{Co}^{2+}] = 35\text{ g/l}$)

N. Zech et al.^[6] established that the co-deposition of nickel during cobalt electrolysis was driven by mass transfer, which is strongly influenced by the current density. This hypothesis seems not to be confirmed in the present work, since the effect of current density on nickel co-deposition is visibly negligible. Nevertheless, the increase in zinc co-deposition with increasing current density could be influenced by mass transfer phenomena as shown in **figure 2**. It appears that zinc co-deposition strongly depends on mass-transfer effects than does nickel deposition in the investigated interval of current density.

Effect of $(\text{NH}_4)_2\text{SO}_4$ addition

$(\text{NH}_4)_2\text{SO}_4$ is usually added to the cobalt electrolyte solution in order to increase its conductivity and to decrease the cathodic over-voltage^[2]. The influence of this addition on impurities co-deposition has been investigated in the present work. The results shown in **figure 3** indicate that, under the experimental conditions prevailing in this work, $(\text{NH}_4)_2\text{SO}_4$ concentration in the electrolyte seems to have no influence on the co-deposition of nickel and zinc. In contrast, the sulphur content decreases from 500 to 100 ppm while the $(\text{NH}_4)_2\text{SO}_4$ addition was varied from 15 to 20 g/l. This sharp decrease in sulphur co-deposition indicates that the effect of $(\text{NH}_4)_2\text{SO}_4$ addition is very effective at dosages higher than 15 g/l. However, it was found that the sulphur content is lower for solution in which precipitation of impurities like nickel and zinc has been performed by precipitation with S^{2-} -ions than for solution in which no S^{2-} -ions have been added^[1, 3]. Sulphur deposition on the cathode could therefore be

due to the presence of S^{2-} ions in the electrolyte. It can also be presumed that the observed decrease in sulphur co-deposition with increasing current density could be due to the oxidation of S^{2-} by the increasing oxygen quantity which is released at the anode side. It is evident that increasing current density induces an important oxygen production at the anode.

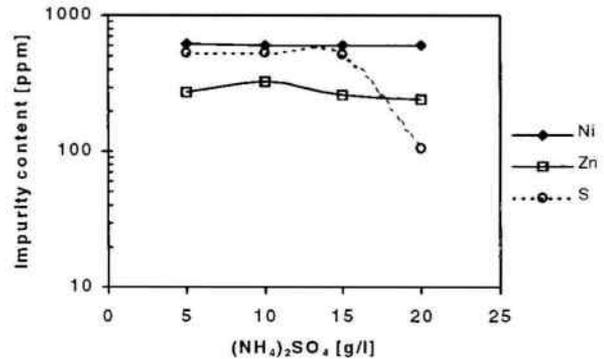


Figure 3: effect of $(\text{NH}_4)_2\text{SO}_4$ addition on nickel, zinc and sulphur co-deposition

The decrease in sulphur co-deposition with increasing $(\text{NH}_4)_2\text{SO}_4$ addition could be explained by the interaction between $(\text{NH}_4)^+$ and S^{2-} which considerably reduces the mobility of S^{2-} . It can not be excluded that sulphur ions could be absorbed by $(\text{NH}_4)^+$ ions, thereby decreasing their mobility in the electrolyte. Further works are necessary for a best understanding of the complex mechanism of sulphur behaviour during cobalt electrolysis.

Effect of cobalt concentration on Me/Co ratio in the metal deposit

For a good interpretation of the test results, it was necessary to observe the effect of some parameters on the ratio Me/Co in the cathodic deposit. The influence of cobalt concentration in the electrolyte and the current density on the ratio Me/Co in the deposit is shown respectively in **figures 4 and 5**. In all cases the ratio Me/Co in metal is higher than in the electrolyte. K. Twite et al.^[2] and A. Bouyaghroumni et al.^[4] observed that the Ni/Co ratio is higher in metal than in electrolyte.

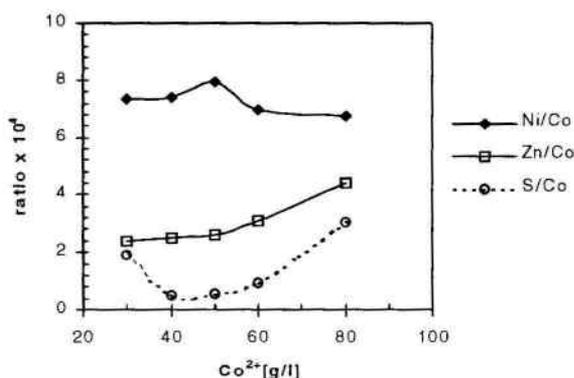


Figure 4: Effect of cobalt concentration in solution on the ratio cobalt/impurity in the metal ($J = 400 \text{ A/m}^2$)

On the other hand, it was been observed that the Ni/Co ratio on the cathode is linearly depending of Ni/Co ratio and the $(\text{NH}_4)_2\text{SO}_4$ concentration in the electrolyte^[2]. The Me/Co ratio is higher in the deposit than in the electrolyte, and this goes up with increasing cobalt concentration in the electrolyte and increasing current density. In contrast, the Ni/Co ratio decreases with increasing Co^{2+} concentration in solution. The behaviour of S/Co is difficult to understand.

Effect of current density on Me/Co ratio in metal

The influence of current density on Me/Co ratio in the deposit is shown in **figure 5**. The Ni/Co and Zn/Co ratios increase while the current density varies from 100 to 400 A/m^2 . It appears that the increase in current density increases nickel and zinc co-deposition on the cathode, in addition to increase in current efficiency^[4]. But the S/Co ratio decreases with increasing current density.

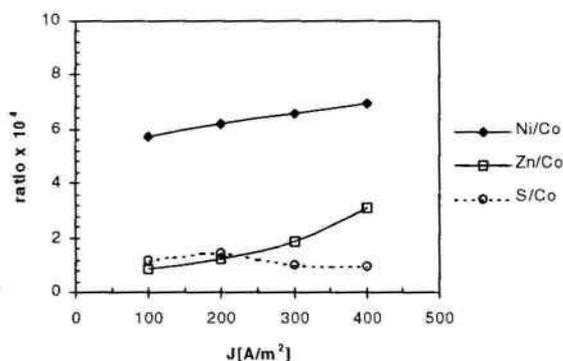


Figure 5: Effect of current density on the ratio cobalt/impurity in metal ($J = 400 \text{ A/m}^2$)

CONCLUSIONS

It has been found that both Co^{2+} concentration in solution and current density strongly influence nickel, zinc as well as sulphur co-deposition during cobalt electrowinning. Within the range of cobalt concentration in the electrolyte studied in this work, high cobalt concentrations decrease the nickel and zinc co-deposition. It has been demonstrated that co-deposition of nickel is not only depending on the hindering of the more noble metal by the less noble one. On the other hand, zinc and cobalt co-deposition was also found to be a function of the current density, increasing at higher current densities.

Sulphur co-deposition is difficult to understand, but it can be presumed that sulphur behaviour depends on the presence of S^{2-} in the electrolyte. Further research works are necessary.

From the test results, it was recommended to have an electrolyte with high Co^{2+} concentration of approximately 50 g/l, low $\text{Ni}^{2+}/\text{Co}^{2+}$ and $\text{Zn}^{2+}/\text{Co}^{2+}$ ratios and a current density of about 400 A/m^2 to obtain a good quality electrolytic cobalt.

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