



Contribution of nickel, zinc and sulphur co-deposition during cobalt electrowinning

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Synopsis

It is well known that the electrochemical precipitation of metals from aqueous solutions is conducted by the electrochemical standard potential scale. This scale indicates the order of nobility of different metals. Consequently, the standard potential scale shows the nocivity of metals when they are present as impurities in aqueous solutions containing metals. In the hydrometallurgy of cobalt, nickel and zinc are co-deposited during cobalt electrodeposition. Nickel has almost the same chemical, physical and electrochemical properties as cobalt. Furthermore, the 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. The presence of small amounts of zinc in solution leads to contamination of cobalt electrowon. In spite of its lower electrochemical potential in comparison to cobalt, zinc is reduced on the cathode because of its higher hydrogen-overvoltage. But, in the hydrometallurgy of zinc, small amounts of cobalt present solution will contaminate the zinc reduced at the cathode. This is easily explained by the fact that cobalt is more electropositive than zinc. The co-deposition mechanism of sulphur at the cathode is not yet well understood. Great attention has to be paid to the mechanism of co-deposition of sulphur during cobalt electrolysis.

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 cannot 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 Gecamines Shiturii Plant (Katanga/D. R. Congo) was used in the experiments. Its chemical composition is given in Table I. The content of the different elements has been adjusted by evaporation, dilution with distilled water, or addition of pure chemical reagents.

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 stainless steel and the anode material was 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.

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Table I
Chemical composition of the cobalt solution

Co ²⁺	28 g/l	S _(sulphate)	3 1.85 g/l
Ni ²⁺	0.07 g/l	S _(total)	3 1.94 g/l
Zn ²⁺	2.85 mg/l	Fe _(total)	0.1 7 g/l
Cu ²⁺	0.20 mg/l	H ₂ SO ₄	7.37 g/l

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 was 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⁺.

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 II. 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:

$$E_{M^{n+}/M} = E_{M^{n+}/M}^{\circ} + \left\{ \frac{RT}{nF} \right\} \times \ln [M^{n+}] \quad [1]$$

According to Equation [1], if different ions have the same value of potential, they could be reduced simultaneously at

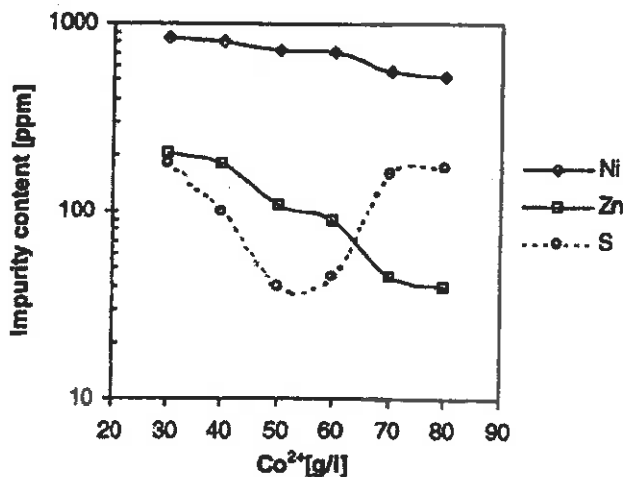


Figure 1—Influence of cobalt concentration on the co-deposition of Ni, Zn and S (T = 80°C, J = 250 A/m²)

the cathode. In this context, for nickel and cobalt co-deposition, the following equation applies

$$E_{Co^{2+}/Co} = E_{Ni^{2+}/Ni}^{\circ} \quad [2]$$

equation applies

From Equation [2], in the experimental conditions prevailing here, the Ni²⁺/Co²⁺ ratio in the electrolyte must be 0.17 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 I. Despite this fact, nickel co-deposition occurred. In the case of zinc, its concentration in solution must 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 by their relative concentrations alone. K. Y. Sasaki and J. B. Talbot⁵ established, using the electrodeposition model of W. C. Grande and J. B. Talbot⁷, that co-deposition of nickel from cobalt solutions takes place through monohydrolysis of nickel ions, which are then present as Ni(OH)₂.

Effect of current density

The influence of current density on impurities' co-deposition during cobalt electrolysis has been the subject of numerous investigations. The results of this work are presented in Figure 2, which indicates impurity contents in cobalt cathodes at different current densities. Zinc co-deposition increases with increasing current density. The sulphur content goes down when the current density increases, while nickel co-deposition remains almost unchanged.

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 depends more strongly on mass-transfer effects than does nickel deposition in the investigated interval of current density.

Effect of (NH₄)₂SO₄ addition

(NH₄)₂SO₄ is usually added to the cobalt electrolyte solution in order to increase its conductivity and to decrease the cathodic over-voltage^{1,2}. 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, (NH₄)₂SO₄ 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 (NH₄)₂SO₄ addition was varied from 15 to 20 g/l. This sharp decrease in sulphur co-deposition indicates that the effect of (NH₄)₂SO₄ addition is very effective at dosages higher than 15 g/l. However, it was found that the sulphur content is

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Table II
Standard reduction potentials at 25°C

Elements	E° [volt]
H ⁺ /H ₂	0.00
Ni ²⁺ /Ni	-0.25
Co ²⁺ /Co	-0.28
Zn ²⁺ /Zn	-0.77

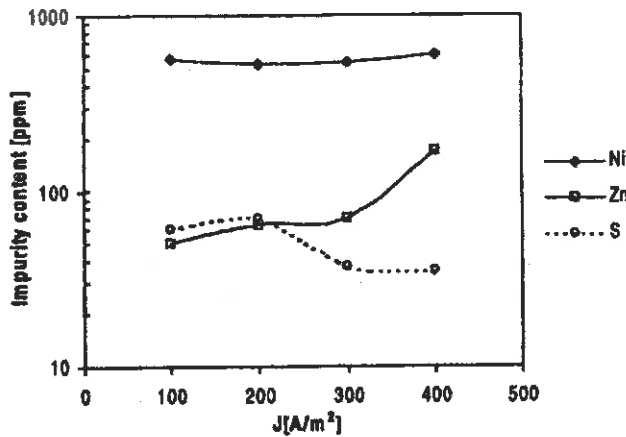


Figure 2—Influence of current density on the co-deposition of nickel, zinc and sulphur (T = 80°C, [Co²⁺] = 35 g/l)

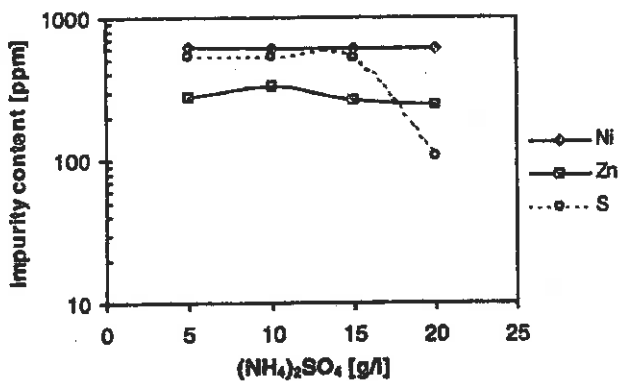


Figure 3—Effect of (NH₄)₂SO₄ addition on nickel, zinc and sulphur co-deposition

lower for solutions in which precipitation of impurities like nickel and zinc have been performed by precipitation with S²⁻ ions than for solution in which no S²⁻ ions have been added. Sulphur deposition on the cathode could therefore be due to the presence of S²⁻ 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 S²⁻ by the increasing oxygen quantity that is released at the anode. It is evident that increasing current density induces an important oxygen production at the decrease in sulphur co-deposition with increasing (NH₄)₂SO₄ addition could be explained by the interaction between (NH₄)⁺ and S²⁻ which considerably reduces the mobility of S²⁻. It cannot be excluded that sulphur ions could be absorbed by (NH₄)⁺ ions, thereby decreasing their mobility in

the electrolyte. Further works are necessary for a better 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 Me/Co ratio in the cathodic deposit. The influence of cobalt concentration in the electrolyte and the current density on the Me/Co ratio in the deposit are shown, respectively, in Figures 4 and 5. In all cases the Me/Co ratio in metal is higher than in the electrolyte. K. Twite *et al.*^{1,2} and A. Bouyaghroumni *et al.*⁴ observed that the Ni/Co ratio is higher in metal than in electrolyte.

On the other hand, it was been observed that the Ni/Co ratio on the cathode is linearly dependent on the Ni/Co ratio and the (NH₄)₂SO₄ concentration in the electrolyte². 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 Co²⁺ 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 the 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/m². It appears that the increase in current density increases nickel and zinc co-deposition on the cathode, in addition to increased current efficiency⁴. The S/Co ratio decreases with increasing current density.

Conclusions

It has been found that both Co²⁺ 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 dependent on the hindering of the more noble metal by the less noble one. On the other

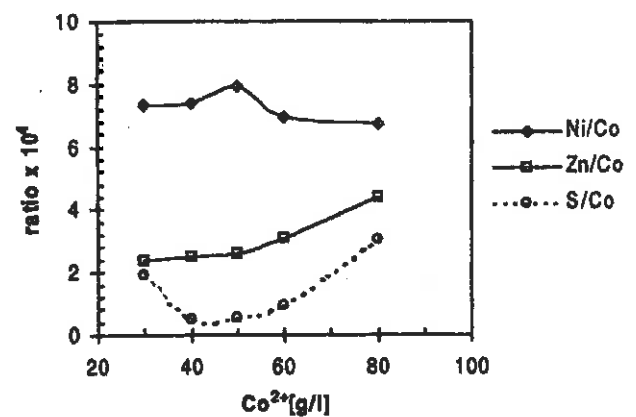


Figure 4—Effect of cobalt concentration in solution on the ratio cobalt/impurity in the metal (J = 400 A/m²)

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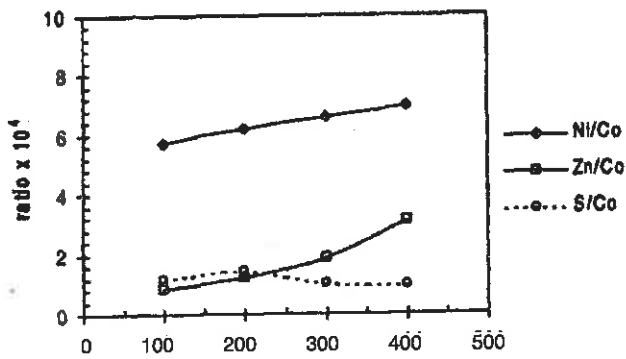


Figure 5—Effect of current density on the ratio cobalt/impurity in metal ($J = 400 \text{ A/m}^2$)

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.

Acknowledgements

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IDC donates R3.2 million to Wits University*

In line with the Industrial Development Corporation's (IDC) Leadership in Development strategy that aims to help produce top quality chemical and metallurgical engineers, the corporation is donating R3.2 million over a three-year period to upgrade undergraduate facilities at the University of the Witwatersrand's School of Chemical and Metallurgical Engineering.

An initial amount of R1 066 667 has already been used to transform an old facility into a state-of-the-art laboratory with 45 computers and an improved capacity to accommodate and meet students' needs. The hydrometallurgical research capacity of the school has also been boosted by this donation, which has been used to purchase a new high-temperature muffle furnace to upgrade the current facility.

The distillation laboratory is also currently being expanded to accommodate undergraduates' experiments, and additional gas chromatographs were bought for analysis purposes.

'We see ourselves as a catalyst for the development of South Africa's talent in business, engineering and entrepreneurship and view this donation as our contribution to the global competitiveness and innovation of the South African chemical and metallurgical industries,' said Qhena ◆

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