

Technical note

# Mechanism of cobalt removal from zinc sulfate solutions in the presence of cadmium

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## Abstract

The effect of cadmium and copper, temperature and reaction time on the removal of cobalt from zinc sulfate solutions using zinc dust was experimentally studied. The results show that the rate and extent of cobalt removal are enhanced when cementation takes place in the presence of less than 400 mg/L of cadmium. Cementation residues were analyzed using electron probe micro-analysis (EPMA) to investigate the distribution of phases in the cementation products and the mechanism of cobalt removal. It was found that formation of Zn–Co and Zn–Cd alloys on the zinc dust particles can enhance cobalt removal whereas the presence of Zn–Cu and Cu–Cd alloys can inhibit cobalt removal.

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## 1. Introduction

Most of the world's zinc is produced by electrowinning from a sulfate electrolyte. Trace impurities (e.g., Co) present in the zinc electrolyte solution can catalyse hydrogen evolution effectively, lowering the current efficiency (Boyan et al., 2004). Therefore, adequate purification of the zinc electrolyte before electrowinning is essential. Cobalt is commonly removed by cementation by the use of zinc dust and activators (e.g., Cu and Sb ions or Cu and As ions) required to enhance the kinetics of cobalt removal (Nelson et al., 2000; Jari, 2004; Van der Pas and Dreisinger, 1996). Several mechanisms have been proposed to explain the role of Cu and Sb in the enhancement of the removal of Co. Most of these studies try to correlate Co removal with

the type of alloy formed on the zinc dust (Yamashita et al., 1997; Takeshi et al., 1998). Fischer et al. (1969) found that the reaction path of cobalt cementation cannot be estimated thermodynamically from potential differences between Co and Zn but from the presence of mixed Co and Zn phases observed in cementation products. Many articles and patents on cobalt removal from zinc sulfate electrolytes have focused on identifying different alloys that may form during cobalt cementation. Several cobalt alloys are suggested and said to act as preferential cathodic substrates for cobalt deposition (Fountoulakis, 1983; Karavasteva, 2001). However, the mechanism of removal of Co from zinc sulfate solutions using zinc dust in the presence of Cd<sup>2+</sup> is still not very well understood.

The objective of this research was to elucidate the mechanism of Co removal from zinc sulfate electrolytes using cementation with zinc dust in the presence of Cd<sup>2+</sup>. In this work, residues obtained from the

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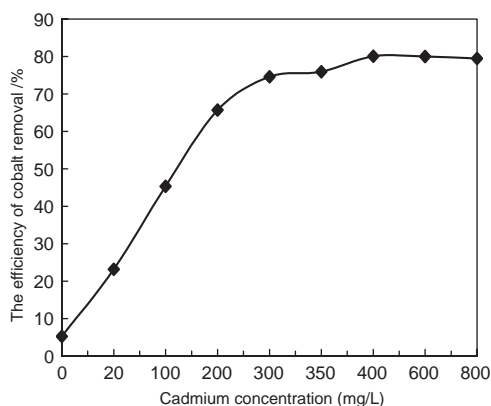


Fig. 1. Effect of cadmium concentration on cobalt removal.

cementation process were analyzed using EPMA to investigate the mechanism of cobalt removal.

## 2. Experimental

Batch cementation tests were carried out in a 1-L beaker. An axial type impeller was used to agitate the solution at 1000 rpm. The synthetic solution contained 140 g/L Zn added as analytical reagent  $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ , 3 g/L (the high concentration is to observe the phase more easily by EPMA) Co added as analytical reagent  $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$ , Cd (when used) was added as analytical reagent  $3\text{CdSO}_4 \cdot 8\text{H}_2\text{O}$ , and Cu (when used) was added as analytical reagent  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ . The pH was measured with a pH 2401 electrode from Radiometer. It was maintained at 4 by adding sulfuric acid to the solutions to prevent precipitation of Zn salts. A thermostat controlled the temperature. Zinc dust was added based on the stoichiometric amount required and zinc dust with a size distribution  $D_{\text{Zn}}$  53–63  $\mu\text{m}$  was used. Care was taken to prepare the cementation products for EPMA analysis: residues after the cementation process were

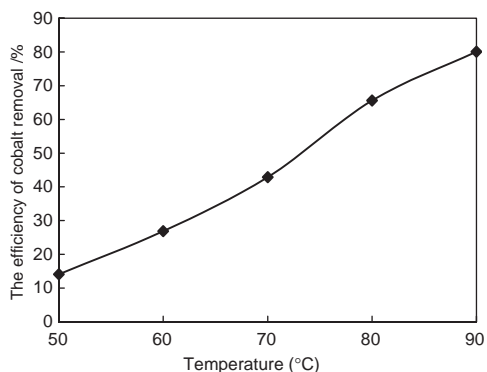


Fig. 2. Effect of temperature on cobalt removal.

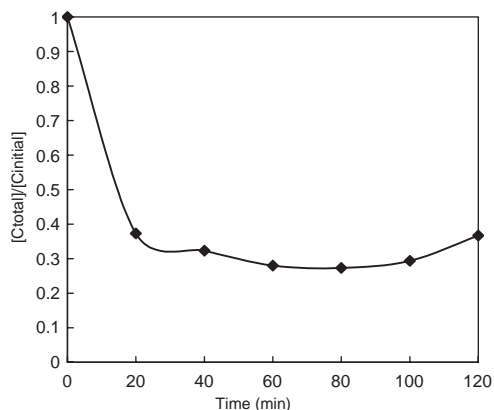


Fig. 3. Effect of the process time on cobalt removal.

filtered, washed with distilled water, and dried at room temperature.

The residues obtained after the cementation process were analyzed by EPMA.

## 3. Results and discussion

### 3.1. Effect of cadmium ion

The removal of Co as a function of the amount of  $\text{Cd}^{2+}$  initially added to the electrolyte is shown in Fig. 1. The data shown in this figure was obtained at 90 °C after 1 h of reaction. It is seen that in the absence of  $\text{Cd}^{2+}$  less than 10% of the cobalt initially present was removed.

As the  $\text{Cd}^{2+}$  concentration is increased, the amount of Co removed increases linearly up to close to 300 mg/L  $\text{Cd}^{2+}$ , then it plateaus at close to 400 mg/L at which point up to 80% of the Co originally present was removed. It is clear that  $\text{Cd}^{2+}$  is an important activator that should be present in small quantities during Co removal: purification circuits that totally eliminate Cd

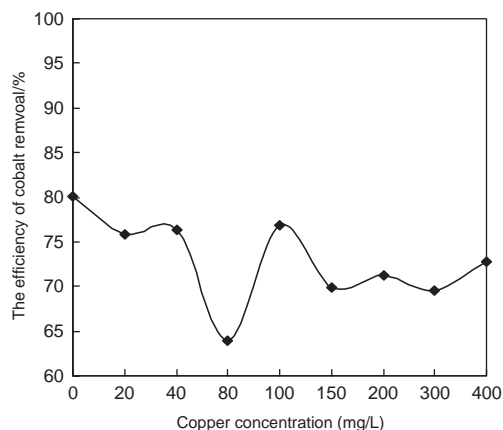


Fig. 4. Effect of copper concentration on cobalt removal.

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