



## Separation of copper and cobalt–nickel sulphide concentrates during processing of manganese deep ocean nodules

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### Abstract

Controlled sulphide precipitation was examined in this study for the recovery of copper and nickel–cobalt concentrates from liquors originating from leaching manganese deep ocean nodules in  $\text{FeSO}_4\text{--H}_2\text{SO}_4\text{--H}_2\text{O}$  solutions. The metal ions studied include  $\text{Co}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Fe}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Mn}^{2+}$  and  $\text{Zn}^{2+}$ . Promising results were obtained when copper and nickel–cobalt concentrates were precipitated with 5.5% solution of  $(\text{NH}_4)_2\text{S}$ . This was added at optimised flow rate of  $0.15 \text{ g S}^{2-}/\text{min}$  per 1 L of processed solution at the laboratory temperature,  $\text{pH}=1.0$  (copper precipitation) and  $\text{pH}=3.0$  (nickel–cobalt precipitation).

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**Keywords:** Manganese deep ocean nodules; Sulphide precipitation; Selective separation; Copper sulphide concentrate; Cobalt–nickel concentrate

### 1. Introduction

Ores or concentrates in which small amounts of valuable elements accompany the main metal have been often processed in metallurgical industry. If metals are produced from such materials by hydrometallurgical methods, minor valuable metals are precipitated from leach liquors before the extraction of the main metal. Sulphide precipitation makes high

degree of heavy metal removal possible over a broad pH range and has several advantages over hydroxide or carbonate precipitation, such as the low solubility and high stability of metal sulphides. Different reagents have been utilised as sulphide donors such as hydrogen, ammonium, sodium or calcium sulphides. A common problem associated with these precipitation agents is that they cause a rapid formation of metal sulphides, resulting in non-selective precipitation. In addition, such metal sulphides exhibit small particle size and difficult phase separation.

One possible approach to overcome these difficulties is using controlled addition of sulphide ions. Controlled addition of sulphide ions, i.e. controlled

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concentration of sulphide ions in processed solutions, makes possible selective separation of metals, which precipitate both from alkaline or acidic solutions. The optimum concentration of sulphide ions, which is adequate for selective separations of individual metals, depends significantly on the solubility products of the corresponding metal sulphides and on the pH value at which the precipitation is carried out. For example, controlled sulphide precipitation was successfully applied for selective removal of Co from manganese sulphate solutions (Bryson and Bijsterveld, 1991), Cu and Cd from nickel sulphate solutions (Jandová, 1996; Jandová and Leitner, 1998) or Co and Zn from ammonium solutions (Mishra and Das, 1992).

Controlled sulphide precipitation using  $(\text{NH}_4)_2\text{S}$  was examined in this study as a feasible approach for obtaining copper and nickel–cobalt sulphide concentrates from liquors originating from leaching nodules in  $\text{FeSO}_4\text{--H}_2\text{SO}_4\text{--H}_2\text{O}$  solutions after iron removal. Iron was precipitated as ammonium jarosite. In some cases, residual iron content after jarosite precipitation was removed by neutralizing precipitation using  $\text{NH}_4^+$  ions. Applying sulphide precipitation for separation of copper and nickel–cobalt concentrates from manganese sulphate solutions is advantageous because copper sulphide precipitation is operative in the acid pH range, cobalt and nickel precipitation in a weak acid pH range while Mn sulphide precipitation is successfully performed in the alkaline pH range (Monhemius, 1977). Due to the fact that the copper sulphide could be precipitated from very strongly acidic solutions, there is no problem to recover copper from sulphate solutions in the presence of Co, Ni and Mn. One of the problematic combinations is the cobalt–nickel–manganese separation from solutions containing high manganese concentrations. The pH of such solutions during the nickel–cobalt precipitation must be low enough to restrict the amount of manganese that could be co-precipitated.

Solubility products of metal sulphides of interest are listed in Table 1. Impurities such as  $\text{Mg}^{2+}$ ,

Table 1  
Solubility products of metal sulphides

Sulphide	CuS	ZnS	CoS	NiS	FeS	MnS
Log $K_s$	−47.7	−25.7	−22.0	−21.0	−18.8	−13.3

Table 2

Content of valuable metals in dry residue of nodules

Metal content [%]					
Co	Cu	Ni	Zn	Mn	Fe
0.128	1.21	1.23	0.12	27.07	4.12

$\text{Ca}^{2+}$  and  $\text{Al}^{3+}$ , which occur in leach liquors would generally be inert, because solubility products of their sulphides are more than 10000 times higher than those of cobalt or nickel and especially of copper.

In the initial experiments, precipitation curves of Co, Cu, Ni, Zn, Mn and Fe were established to determine optimum conditions for selective precipitation of their sulphides. In these experiments, the conditions of which were chosen using literature data (Bryson and Bijsterveld, 1991; Jandová, 1996; Jandová and Leitner, 1998; Mishra and Das, 1992), the influence of the following parameters was examined:

- pH value ranging over 1.0, 2.0 and 3.0
- flow rate of  $(\text{NH}_4)_2\text{S}$  addition, which was 0.03 g  $\text{S}^{2-}$ /min, 0.05 g  $\text{S}^{2-}$ /min, 0.10 g  $\text{S}^{2-}$ /min and 0.15 g  $\text{S}^{2-}$ /min per 1 L of processed solution.

The results obtained were used to establish conditions of two-stage sulphide precipitation leading to formation of copper and cobalt–nickel concentrates.

## 2. Experimental

### 2.1. Materials

In this study, copper and cobalt–nickel concentrates were obtained from manganese deep ocean nodules originating from the IOM area, located in the Clarion-Clipperton ore field. These nodules were mined in July 2001 during an expedition organized and sponsored by IOM, joint organization, Szczecin.

Table 3

Average composition of processed solutions

Solution no.	Metal concentration metals [g/L]					
	Co	Cu	Ni	Zn	Mn	Fe
1	0.078	0.586	0.823	0.096	18.11	0.035*
2	0.142	1.425	1.356	0.248	35.87	0.517

\* Solutions after the additional iron removal by hydrolytic precipitation.

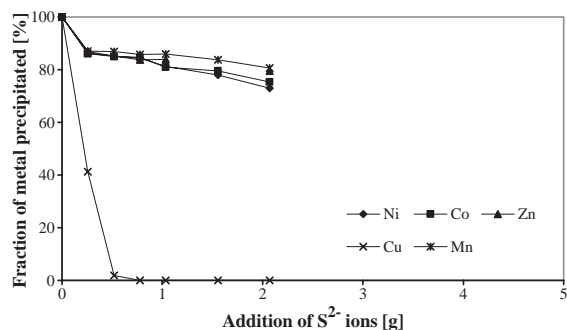


Fig. 1. Course of sulphide precipitation from solution no. 1: pH=1, flow rate of (NH<sub>4</sub>)<sub>2</sub>S addition of 0.03 g S<sup>2-</sup>/min per 1 L of processed solution.

Content of valuable metals in the nodules, as seen in Table 2, was determined after their decomposition by alkaline fusion using AAS method.

The nodules were leached in FeSO<sub>4</sub>-H<sub>2</sub>SO<sub>4</sub>-H<sub>2</sub>O solutions. Iron was removed from leach liquors by ammonium jarosite precipitation or by jarosite precipitation followed by pH-controlled hydrolytic precipitation with NH<sub>3</sub> aqueous solution. The average composition of the processed solutions is given in Table 3.

## 2.2. Procedure and equipment

Experiments were conducted at the laboratory temperature in a stirred glass vessel having a provision for pH control. The pH value of processed solutions, which varied from 1.0 to 3.0, was adjusted by addition of H<sub>2</sub>SO<sub>4</sub> and/or by addition of NH<sub>3</sub> solutions to reach the pre-selected constant value. Approximately 5.5%

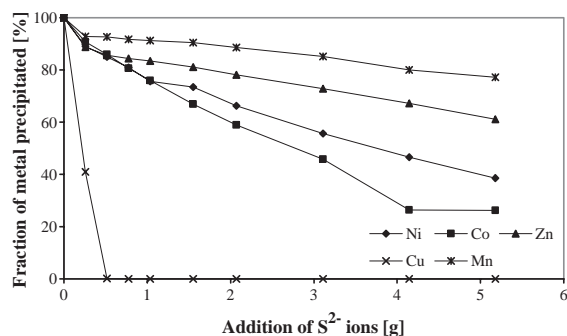


Fig. 2. Course of sulphide precipitation from solution no. 1: pH=2, flow rate of (NH<sub>4</sub>)<sub>2</sub>S addition of 0.03 g S<sup>2-</sup>/min per 1 L of processed solution.

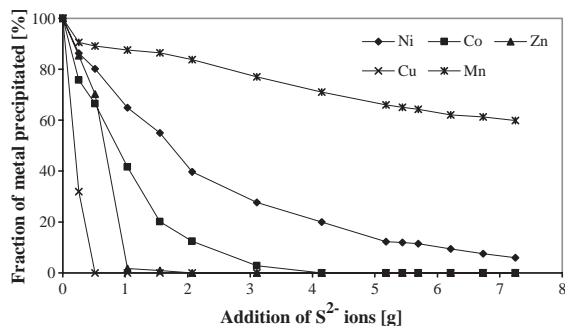


Fig. 3. Course of sulphide precipitation from solution no. 1: pH=3, flow rate of (NH<sub>4</sub>)<sub>2</sub>S addition of 0.03 g S<sup>2-</sup>/min per 1 L of processed solution.

(NH<sub>4</sub>)<sub>2</sub>S solution was added continuously into the vessel with the flow rate ranging from 0.03 g to 0.15 g S<sup>2-</sup>/min per 1 L of processed solution. During the precipitation tests, the liquid samples were withdrawn at selected time intervals, filtered and diluted for metal analysis by AAS. In every run, approximately 500 mL of leach solution was processed.

A two-stage precipitation, during which copper and cobalt–nickel concentrates were obtained, was conducted as follows: the pH value of processed leach liquor solution was adjusted to 1.0 and maintained at this value during addition of 5.5% (NH<sub>4</sub>)<sub>2</sub>S solution at the controlled flow rate of 0.05 or 0.15 g S<sup>2-</sup>/min per 1 L of treated solution. After the completion of copper precipitation, which was determined by the examination of copper concentration in the processed solution, the reaction mixture was stirred for 15 min to achieve steady-state conditions. The precipitate was then filtered,

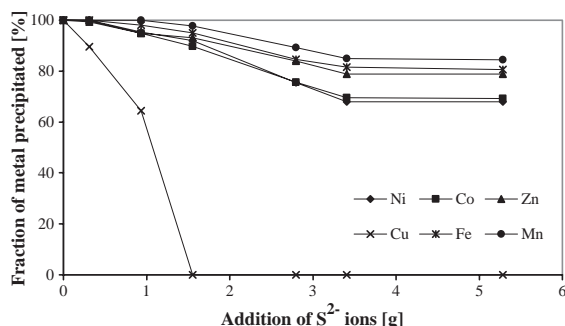


Fig. 4. Course of sulphide precipitation from solution no. 1: pH=1, flow rate of (NH<sub>4</sub>)<sub>2</sub>S addition of 0.15 g S<sup>2-</sup>/min per 1 L of processed solution.

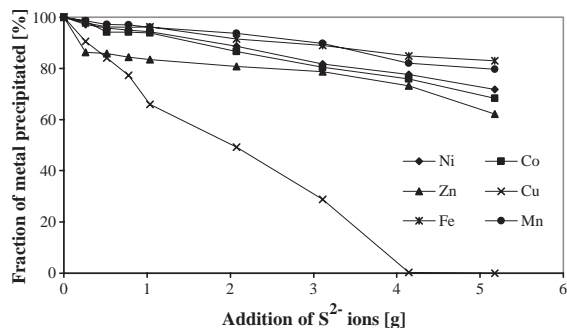


Fig. 5. Course of sulphide precipitation from solution no. 2: pH=1, flow rate of (NH<sub>4</sub>)<sub>2</sub>S addition of 0.03 g S<sup>2-</sup>/min per 1 L of processed solution.

washed, dried and analysed for its chemical and mineralogical composition using XRF and XRD methods. The pH value of the filtrate was adjusted to 3.0 using NH<sub>3</sub> solution and maintained at this value during the subsequent nickel–cobalt precipitation. The regime of nickel–cobalt precipitation was identical to that used for copper precipitation.

### 3. Results and discussion

Selected precipitation curves measured under various conditions are illustrated in Figs. 1–8. From the course of precipitation curves of valuable metals and of Fe, it was obvious that the optimum pH value for copper precipitation is approximately 1.0 while cobalt and nickel was possible to precipitate without significant manganese and iron co-precip-

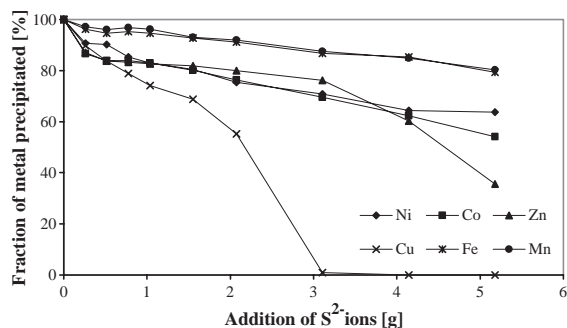


Fig. 6. Course of sulphide precipitation from solution no. 2: pH=2, flow rate of (NH<sub>4</sub>)<sub>2</sub>S addition of 0.03 g S<sup>2-</sup>/min per 1 L of processed solution.

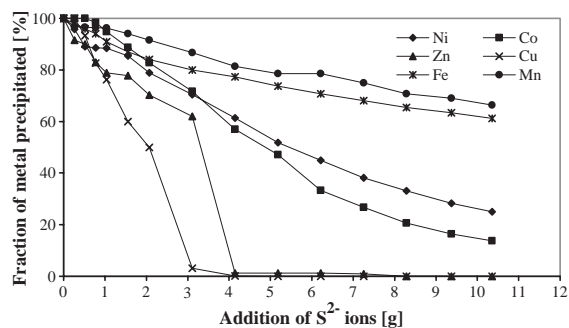


Fig. 7. Course of sulphide precipitation from solution no. 2: pH=3, flow rate of (NH<sub>4</sub>)<sub>2</sub>S addition of 0.03 g S<sup>2-</sup>/min per 1 L of processed solution.

itation at pH approximately 3.0. Solutions with increased iron content are not suitable for sulphide precipitation due to very probable contamination of nickel–cobalt concentrates with Fe and, therefore, due to higher consumption of expensive (NH<sub>4</sub>)<sub>2</sub>S. Increasing the flow rate of sulphide addition did not significantly influence the co-precipitation of Co, Ni, Zn, Mn and Fe during copper precipitation. However, it is probable that the increased rate will play more important role during nickel–cobalt precipitation.

The results of two-stage sulphide processing of solution nos. 1 and 2 (see Table 3) are given in Tables 4 and 5. Experiment no. 1 corresponded to processing of solution no. 1 at flow rate of (NH<sub>4</sub>)<sub>2</sub>S addition of 0.05 g S<sup>2-</sup>/min. Experiment no. 2 corresponded to processing of solution no. 2 at flow rate of (NH<sub>4</sub>)<sub>2</sub>S addition of 0.15 g S<sup>2-</sup>/min. In

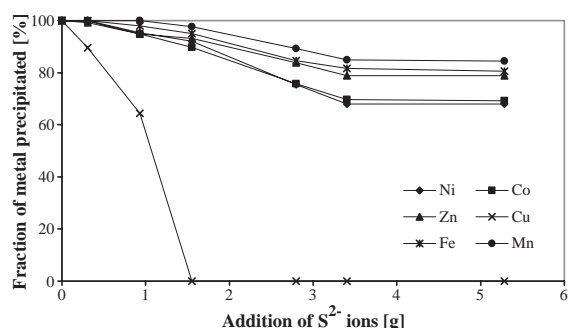


Fig. 8. Course of sulphide precipitation from solution no. 2: pH=1, flow rate of (NH<sub>4</sub>)<sub>2</sub>S addition of 0.15 g S<sup>2-</sup>/min per 1 L of processed solution.

Table 4  
Composition of copper sulphide concentrates

Experiment no.	Elemental content [%]									
	S	Cu	Co	Ni	Zn	Fe	Mn	Si	Al	Mg
1	54.54	43.57	0.16	1.12	0.03	0.15	0.06	<0.01	<0.01	<0.01
2	47.54	44.25	0.15	1.41	0.05	0.26	0.33	0.59	0.06	0.02

Table 5  
Composition of nickel–cobalt sulphide concentrates

Experiment no.	Elemental content [%]										
	S	Cu	Co	Ni	Zn	Fe	Mn	Si	Al	Mg	Ti
1	49.83	0.37	4.58	35.65	4.40	1.90	0.77	0.11	0.12	0.03	<0.1
2	52.85	<0.01	4.12	33.08	6.41	0.71	0.62	0.94	0.34	0.02	0.21

both of these experiments, more than 98% Co, Cu, Ni and Zn was separated, while manganese and iron co-precipitation was negligible. According to XRD analysis, copper concentrates were formed by the dominant CuS (covellite) and by elementary sulphur. The nickel–cobalt sulphides were mostly amorphous with the indications of Ni<sub>2</sub>S<sub>3</sub>, CoS and elementary sulphur.

#### 4. Conclusions

Controlled sulphide precipitation with (NH<sub>4</sub>)<sub>2</sub>S as a precipitation agent enabled efficient selective separation of copper and cobalt–nickel concentrates during hydrometallurgical processing of manganese deep ocean nodules. This procedure was based on reductive leaching in FeSO<sub>4</sub>–H<sub>2</sub>SO<sub>4</sub>–H<sub>2</sub>O solutions. If two-stage precipitation method was used with the flow rate of (NH<sub>4</sub>)<sub>2</sub>S addition of 0.15 g S<sup>2-</sup>/min per 1 L of processed solutions, approximately 98% of Cu, Co and Ni could be separated from manganese as low contaminated copper and cobalt–nickel concentrates. Both these concentrates represent valuable raw materials for production of copper, nickel and cobalt by commonly used technology. The mother liquor—a solution containing MnSO<sub>4</sub>—should be utilised for the separation of MnCO<sub>3</sub>, which is a suitable starting material for manganese electrowinning (Premchand and Jana, 1990).

This study will be continued and experiments proposed will be focused on establishing conditions of

selective zinc separation preceding nickel–cobalt precipitation.

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