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# RECOVERY OF COPPER AND COBALT FROM SLIME ORIGINATED FROM AMONIACAL LEACHING OF HIGH COPPER Cu-Co-Fe ALLOY

# ODZYSK MIEDZI I KOBALTU ZE SZLAMU OTRZYMANEGO W PROCESIE AMONIAKALNEGO ŁUGOWANIA WYSOKO MIEDZIOWEGO STOPU Cu-Co-Fe

The slime produced during ammoniacal leaching of Cu90-Co5-Fe5 alloy was treated in order to recover cobalt and copper. The chemical composition of the slime was determined. The slime was a mixture of Co-Fe-(Cu) alloy and $CoO{\cdot}Fe_2O_3{\cdot}\,xH_2O$. Slime was dissolved in HCl acid, and then iron was removed from solution by iron compound precipitation with concentrated ammonia. Copper was electrodeposited from purified, acidic solution. After copper recovery, solution was alkalized and series of electrolysis was carried out in order to recover cobalt. Since iron precipitates still contained some amounts of copper and cobalt, they were dissolved in $H_2SO_4$ and iron removal was repeated. From ammoniacal solution both copper and cobalt as Co-Cu alloy were electrowon. Total recovery of copper and cobalt was 40% and 55%, respectively.

*Keywords*: cobalt, copper, electrowinning, slime

Przeprowadzono odzysk miedzi i kobaltu ze szlamu otrzymanego w procesie amoniakalnego ługowania stopu Cu90-Co-5-Fe5. Określono skład chemiczny szlamu — stanowił on mieszaninę stopu Co-Fe-(Cu) i $CoO{\cdot}Fe_2O_3{\cdot}\,xH_2O$. Szlam roztworzono w kwasie solnym, a z uzyskanego roztworu wytrącono związki żelaza za pomocą stężonego roztworu amoniaku. Z oczyszczonego roztworu wydzielono katodowo miedź. Odmiedziowany roztwór zalkalizowano, po czym prowadzono odzysk kobaltu na drodze elektrolizy. Ze względu na współstrącenie się z żelazem znacznych ilości jonów miedzi i kobaltu, osad związków żelaza rozpuszczono w kwasie siarkowym, po czym strącanie przeprowadzono ponownie. Z uzyskanego roztworu amoniakalnego przeprowadzono katodowe współosadzanie stopu Co-Cu. Całkowity odzysk miedzi i kobaltu wynosił, odpowiednio: 40% i 55%.

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## 1. Introduction

In today's nonferrous metal processing large amounts of wastes and by-products with elevated strategic metals content are generated. Both economical and environmental reasons resulted in the development of effective and inexpensive methods for metals extraction from these sources. Recently, the recovery of cobalt from secondary sources has attracted some attention. Hydrometallurgical or pirometallurgical treatment of scraps of superalloys and cobalt alloys, spent magnets and catalysts was a research subject of many investigations (Ingier-Stocka et al., 1985; Clark et al., 1996; Tan and Shen, 2000). Process wastes such as metallurgical slags, which contain residual amounts of cobalt, represent also an important source of supply (Sukla et al., 1986; Tümen and Bailey, 1994; Banza et al., 2002). The main component of pirometalurgically reduced copper converter slags are Cu-Co-Fe alloys. This work is part of a series of investigations carried out on metal recovery from synthetic Cu-Co- Fe alloys (Burzyńska et al., 2003, 2004). In the earlier paper (Burzyńska et al., 2004b) dissolution of alloys in ammoniacal solutions was described. It was expected that process would enable metals separation in a relatively simple way, since copper and cobalt form soluble ammonia complexes, while iron should produce insoluble compounds (oxide, oxyhydroxide). However, it was found that dissolution of the Cu-Co-Fe alloys was strictly determined by their phase composition. The high-copper alloy (Cu90Co5Fe5) dissolved spontaneously in $Cu^{2+}$-ammonia-ammonium sulphate solution resulting solely in copper accumulation in the leaching solution, while cobalt and iron remained in the solid phase (as slime). The aim of this study was to conduct hydrometallurgical treatment of the slime generated during ammoniacal leaching of Cu90Co5Fe5 alloy in order to recover copper and cobalt.

## 2. Experimental

### 2.1. Leaching of Cu90Co5Fe5 alloy

A block sample of synthetic alloy (67,68 g) was placed in a glass vessel containing 0.4 $dm^3$ of solution with the following composition: 0.08 M $Cu^{2+}$, 2.5 M $(NH_3+NH_4^+)$ and 0.5 M $SO_4^{2-}$. The electrolyte was agitated with magnetic stirrer and temperature was maintained constant at 50°C. Every 15 h, the leaching solution was replaced with the fresh electrolyte. After every 5 h of dissolution, the slime was mechanically removed from the specimen surface, washed with distilled water, dried in 55°C to the stable mass and collected. Operations were repeated until complete dissolution of the alloy sample. Leaching parameters resulted from earlier findings (Burzyńska et al., 2004b).

### 2.2. Processing of the slime

A sample of dry slime (9,06 g) was dissolved in hot 1 M HCl solution with $H_2O_2$ addition. To remove iron from the solution concentrated ammonia was added (to pH 10) and then iron precipitates were filtered. Filtrate was acidified again with HCl (to pH 0) and a series of 1h electrolysis's was carried out for copper recovery. After complete copper electrowinning, the solution was alkalized with concentrated ammonia (to pH 8) and a series of electrolysis's was conducted in order to recover cobalt. The iron precipitates were dissolved in 2 M $H_2SO_4$ solution. Since it still contained significant amounts of copper and cobalt, the precipitation with concentrated ammonia was repeated. After filtration, a series of electrolysis from ammoniacal solution (pH 10) was carried out for both copper and cobalt recovery. The electrolysis's were conducted in a cuboid PVC vessel at room temperature. Rectangular platinum cathode was suspended between two platinum anodes. The electrolyte was agitated with the magnetic stirrer. The copper coulometer was connected in the electric circuit. The process was conducted at constant current density, although its value was decreased (in a range of 0.49-0.38 A/dm$^2$) gradually to prevent metal powder deposition since the metal concentration in the bath decreased gradually. At the end of each electrolysis stage the cathodic deposit was stripped with hot 2 M $H_2SO_4$ + $H_2O_2$ solution and its composition was determined. At every stage of the slime processing, the volume and composition of resulted solutions were controlled. Copper, cobalt and iron ions concentrations were determined by AAS method, while chloride ion concentration by conductometric titration with 0.1 M $AgNO_3$ solution. The ions concentrations were converted into ions masses in the solution. The flow-sheet of the slime treatment is presented in Fig. 1.

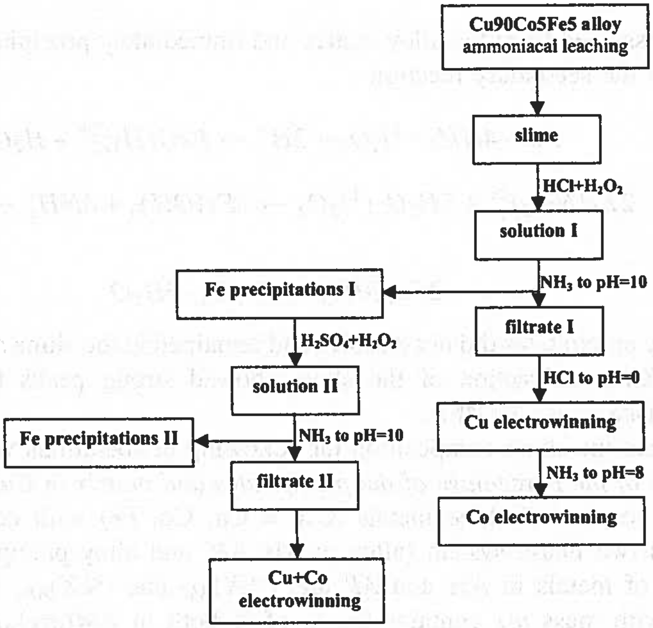

Fig. 1. The flow-sheet of the slime treatment

## 3. Results and discussion

### 3.1. Composition of the slime

The Cu90Co5Fe5 (detailed wt%: Cu 92.3% Co3.4% Fe4.3%) alloy was a two phase system (Burzyńska et al., 2004c). The alloy matrix was a copper based solid solution (Cu97.4% Co1.1% Fe1.5%), while the alloy precipitates were Fe-Co alloy with minor copper content (Cu16.7% Co34.9% Fe48.4%). Microscopy of the Cu90Co5Fe5 alloy after dissolution in ammoniacal solution revealed that the matrix was selectively leached, leaving the alloy precipitates behind as a porous structure (Burzyńska et al., 2004b). The chemical analysis of the solution and the slime showed that transfer of large amounts of copper and traces of cobalt to the leaching bath took place. The metals contents in the slime (Cu19.7±5.9% Co35.4±4.4% Fe44.9±8.6%) were similar to that of the alloy precipitates. Hence it was concluded that:

- copper dissolved autocatalytically from the alloy matrix:

$$Cu + Cu(NH_3)_4^{2+} \rightarrow 2Cu(NH_3)_2^{+} \tag{1}$$

$$2Cu(NH_3)_2^{+} + 4NH_4^{+} + 2OH^{-} + {}^{1}/_{2}O_2 \rightarrow 2Cu(NH_3)_4^{2+} + 3H_2O \tag{2}$$

- cobalt[1]dissolved from the alloy matrix

$$2Co + 12NH_4^{+} + 1^{1}/_{2}O_2 \rightarrow 2Co(NH_3)_6^{3+} + 3H_2O + 6H^{+} \tag{3}$$

- iron[1] dissolved from the alloy matrix and immediately precipitated as hydrated oxide in the secondary reaction

$$Fe + 4NH_3 + {}^{1}/_{2}O_2 + 2H^{+} \rightarrow Fe(NH_3)_4^{2+} + H_2O \tag{4}$$

$$2Fe(NH_3)_4^{2+} + 5H_2O + {}^{1}/_{2}O_2 \rightarrow 2Fe(OH)_3 + 4NH_4^{+} + 4NH_3 \tag{5}$$

$$2Fe(OH)_3 \rightarrow Fe_2O_3 \cdot 3H_2O \tag{6}$$

- the alloy precipitates did not dissolve and remained in the slime as the Fe-Co-(Cu) alloy (X-ray diffraction of the slime showed strong peaks for Fe-Co alloy (Burzyńska et al., 2004b)).

To determine the slime composition the following deliberations were carried out:

1. *Calculation of the percentage of the precipitates and matrix in Cu90Co5Fe5 alloy*

The alloy consists of three metals $X (X = \text{Cu, Co, Fe})$ with concentrations of $(\%X)_A$. This is two phase system (alloy matrix $AM$ and alloy precipitates $AP$). The concentrations of metals in $AM$ and $AP$ are: $(\%X)_{AM}$ and $(\%X)_{AP}$, respectively. An alloy sample with mass $m_A$ contains $(m_X)_A$ of X both in $AM (m_X)_{AM}$ as well as in

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[1] It seems that participation of cobalt and iron in cementation of copper could be neglected since their low contents in the alloy matrix

$AP$ $(m_X)_{AP}$. After dissolution metal $X$ was present both in the electrolyte $(m_X)_E$ and in the slime $(m_X)_S$. Hence:

$$(m_X)_A = (m_X)_{AP} + (m_X)_{AM} = (m_X)_E + (m_X)_S. \tag{7}$$

$X$ amounts in $AP$ and $AM$ are:

$$(m_X)_{AP} = \frac{\%X_{AP} \cdot m_{AP}}{100\%} \tag{8}$$

and

$$(m_X)_{AM} = \frac{\%X_{AM} \cdot m_{AM}}{100\%} = \frac{\%X_{AM}(m_A - m_{AP})}{100\%}, \tag{9}$$

where: $m_{AP}$ and $m_{AM}$ are masses of $AP$ and $AM$ in the alloy sample $m_A$.
From equations (1)-(3):

$$\frac{\%X_{AP} \cdot m_{AP}}{100\%} + \frac{\%X_{AM}(m_A - m_{AP})}{100\%} = (m_X)_E + (m_X)_S \tag{10}$$

$m_{AP}$ values were calculated. Then the percentage of the precipitates (% $AP$) and matrix (% $AM$) in the alloy were estimated:

$$(\%AP) = \frac{m_{AP}}{m_A} \cdot 100\% \tag{11}$$

and

$$(\%AM) = 100\% - (\%AP). \tag{12}$$

Calculations were carried out individually for each element (Cu, Co, Fe) for three independent leached alloy samples. Average values of (%$AP$) and (%$AM$) in the alloy were: 8.6 wt% and 91.4 wt% (± 0.1%), respectively.

2. *Behavior of the metals during leaching*

By using %$AP$ and %$AM$ values, $(m_X)_{AP}$ and $(m_X)_{AM}$ were calculated and compared with that in the slime $(m_X)_S$ (tab.1). Hence, it was possible to assess that in the slime:

- copper $(m_{Cu})_S$ originated from the alloy precipitates $(m_{Cu})_{AP}$ and partially from the alloy matrix $(m_{Cu})_{AM}$ : $(m_{Cu})_S \approx (m_{Cu})_{AP} + 1\%(m_{Cu})_{AM}$;
- cobalt $(m_{Co})_S$ originated from the alloy precipitates $(m_{Co})_{AP}$ and partially from the alloy matrix $(m_{Co})_{AM}$ : $(m_{Co})_S \approx (m_{Co})_{AP} + 78\%(m_{Co})_{AM}$;
- iron $(m_{Fe})_S$ originated both from the alloy precipitates $(m_{Fe})_{AP}$ and the alloy matrix $(m_{Fe})_{AM}$ : $(m_{Fe})_S \approx (m_{Fe})_{AP} + (m_{Fe})_{AM}$.

Since all alloy precipitations remained in the slime, it was assessed that:

$$\frac{(m_{Cu})_{AP} + (m_{Co})_{AP} + (m_{Fe})_{AP}}{(m_{Cu})_S + (m_{Co})_S + (m_{Fe})_S} \cdot 100\% = 73.8\%. \tag{13}$$

It means that 73.8% of the total amount of metals in the slime occurred as the Fe-Co-(Cu) alloy. Remainder amounts of metals formed chemical compounds.

TABLE

Comparison of experimental results (Gumowska, 2002) with calculations

| Value | Metal | SERIES 1 | SERIES 2 | SERIES 3 |
|---|---|---|---|---|
| experimental | | | | |
| $m_A$, g | total | 5.9395 | 9.7548 | 9.7934 |
| $(m_X)_S$, g | Cu | 0.1544 | 0.2248 | 0.2391 |
| | Co | 0.2220 | 0.3208 | 0.4273 |
| | Fe | 0.3414 | 0.4984 | 0.5507 |
| $(m_X)_E$, g | Cu | 5.1947 | 8.6732 | 8.5856 |
| | Co | 0.0171 | 0.0254 | 0.0251 |
| | Fe | 0 | 0 | 0 |
| calculated | | | | |
| $m_{AP}$, g | total | 0.5126 | 0.8418 | 0.8452 |
| $(m_X)_{AP}$, g | Cu | 0.0856 | 0.1406 | 0.1411 |
| | Co | 0.1789 | 0.2938 | 0.2950 |
| | Fe | 0.2481 | 0.4074 | 0.4091 |
| $m_{AM}$, g | total | 5.4269 | 8.9130 | 8.9482 |
| $(m_X)_{AM}$, g | Cu | 5.2858 | 8.6813 | · |
| | Co | 0.0597 | 0.0980 | 0.0984 |
| | Fe | 0.0814 | 0.1337 | 0.1342 |

### 3. *Determination of composition of the chemical compounds in the slime*

The slime consists of the Fe-Co-(Cu) alloy (from *AP*) and chemical compounds of Cu, Co and Fe (from *AM* dissolution), hence:

$$(m_X)_{CC} = (m_X)_S - (m_X)_{AP}, \tag{14}$$

where: $(m_X)_{CC}$ — mass of $X$ in chemical compound in the slime.

Han et al. (1982) showed that the solid product of coprecipitation of cobalt with Fe(III) in ammoniacal solution was spinel structure $CoO{\cdot}Fe_2O$. Similar suggestions aroused from XRD of slimes produced during anodic dissolution of Cu-Co-Fe alloys in ammoniacal solutions (Burzyńska et al., 2004b). In the present study the molar ratio of iron to cobalt in the remainder slime was exactly 2:1:

$$\frac{(m_{Fe})_{CC}}{M_{Fe}} : \frac{(m_{Co})_{CC}}{M_{Co}} = 2 : 1, \tag{15}$$

where: $M_{Fe}$ and $M_{Co}$ are molar masses of iron and cobalt. For that reason the final composition of the dry slime was accepted as a mixture of Co-Fe-(Cu) alloy and $CoO{\cdot}Fe_2O_3{\cdot}xH_2O$ phase contaminated with copper ($x \leqslant 2$ was estimated).

### 3.2. Copper electrowinning

At first, the sample of slime was dissolved in 0.25 dm$^3$ HCl solution. Chloride media has not found practical application generally, since chloride ions generate corrosion problems, however they seemed beneficial in the dissolution of Fe-Co alloy in the slime. Moreover, hydrogen peroxide was added for faster Fe-Co alloy dissolution. Pregnant solution (solution I) contained: 1.07 g $Cu^{2+}$, 2.54 g $Co^{2+}$ and 3.77 g $Fe^{3+}$. It is known (Das and Gopala Krishna, 1996) that copper can be directly electrowon from the acidic electrolytes only when iron contamination is fairly low (less than 1g/dm$^3$). The standard reduction potential for $Fe^{3+}/Fe^{2+}$ is 0.77V, whereas that of $Cu^{2+}/Cu$ is 0.34V. Thus, the reduction of $Fe^{3+}$ ions takes place first and consumes most of the current. Moreover, during electrolysis the cathode copper may be attacked by $Fe^{3+}$ resulting in the formation of a redox system. Consequently, the dissolution of deposited copper and reduction of $Fe^{3+}$ ions may happen. Hence, to avoid losses in the current efficiency and the production of poor quality cathode copper, iron elimination from the electrolyte is

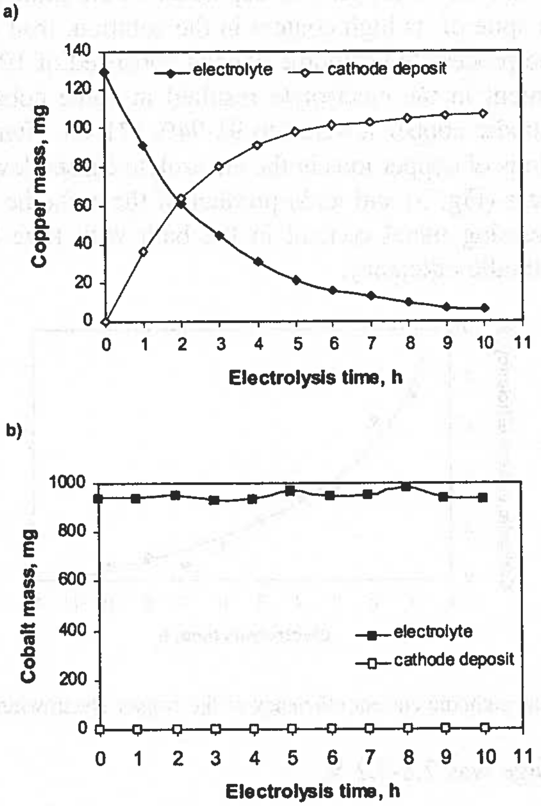

Fig. 2. The influence of time on the $Cu^{2+}$ and $Co^{2+}$ contents in the bath and amount of deposited metals at the current density of 0.38 A/dm$^2$

required. After iron removal 0.129 g $Cu^{2+}$, 0.940 g $Co^{2+}$ and 0.026 g $Fe^{3+}$ remained in the solution (filtrate I), and $Cl^-$ ions content was 44.4 g. In spite of the fact that the coprecipitation with iron caused undesired losses in copper and cobalt from the solution, copper electrowinning was carried out. Fig.2 shows changes in the $Cu^{2+}$ and $Co^{2+}$ contents in the bath with time as well as the amount of deposited metals. The initial volume of the solution was 1 $dm^3$. After 10 h of electrolysis the final electrolyte volume was 0.95 $dm^3$, because of drawing of the solution samples.

From the acidic electrolyte copper was deposited on the cathode. Cobalt did not (in the initial stages), in spite of its high content in the solution. Iron remained also in the bath. After 6 h of the process the cathodic deposit consisted of 100% copper, however decreasing $Cu^{2+}$ content in the electrolyte resulted in some cobalt codeposition and the purity of the cathodic copper lowered to 91-94% (71.4% after 10 h).

Low concentrations of copper ions in the electrolyte caused low current efficiencies of the cathodic process (Fig. 3) and main product of the cathodic reaction was hydrogen. Moreover, decreasing metal content in the bath with time favored additionally decreasing in the cathodic efficiency.

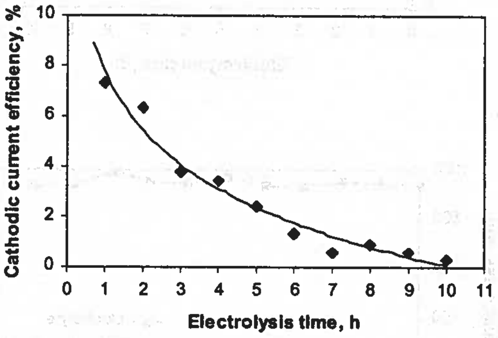

Fig. 3. Changes in the cathodic current efficiency of the copper electrowinning at 0.38 A/$dm^2$

Electrolysis voltage was 2.8-3.2 V.

### 3.3. Cobalt electrowinning

After copper electrowinning, the solution was alkalized with ammonia. Cobalt was removed from the solution with the following composition: 0.006 g $Cu^{2+}$, 0.938 g $Co^{2+}$ and 0.024 g $Fe^{2+}$. The electrolysis's were conducted with variable current densities: initial 2 hours — at 0.49 A/$dm^2$, 3-9 hours — at 0.43 A/$dm^2$ and the rest — at 0.38 A/$dm^2$ (at voltage 2.8-2.6 V). The initial volume of the solution was 0.975 $dm^3$. After 10 h of electrolysis the final electrolyte volume was 0.951 $dm^3$, because of drawing of the solution samples and pH maintenance with ammonia (16 $cm^3$ totally). The changes in the contents and the amounts of deposited metals with the time are showed in Fig. 4.

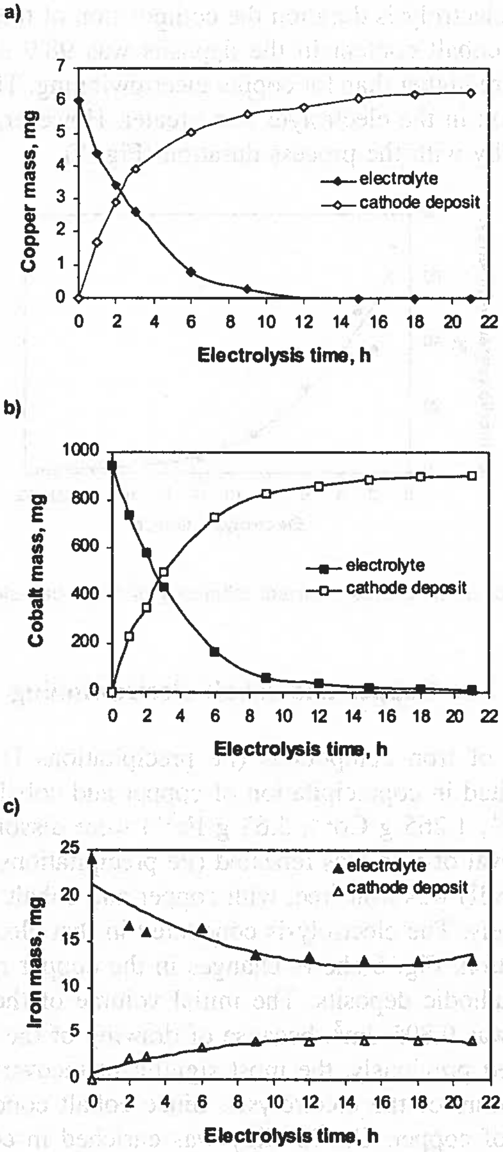

**Fig. 4.** The influence of time on the metal ions contents in the bath and amount of deposited metals

It was found that in ammoniacal electrolyte all metals codeposited. Because of low concentrations of copper and iron in the bath they did not played significant roles, however behavior of these two elements was different. Copper was totally recovered from the solution, while iron content in the bath remained almost stable after 9 hours of the electrolysis's. Cobalt was electrowon completely. It was observed that process was more effective during first six hours, and then recovery of metals slowed down.

Independently on the electrolysis duration the composition of the cathodic deposit was almost the same and cobalt content in the deposits was 98.9 ± 0.7%. The cathodic current efficiencies were higher than for copper electrowinning. This was obvious, since the cobalt concentration in the electrolyte was greater. However, the efficiency values also decreased gradually with the process duration (Fig. 5).

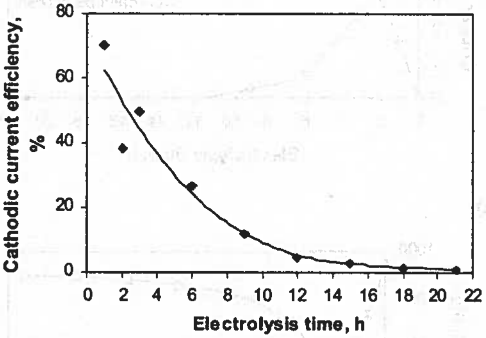

Fig. 5. Changes in the cathodic current efficiency of the cobalt electrowinning

### 3.4. Copper and cobalt electrowinning

The precipitation of iron compounds (Fe precipitations I) with ammonia from chloride solution resulted in coprecipitation of copper and cobalt ions. Therefore precipitates (0.905 g $Cu^{2+}$, 1.265 g $Co^{2+}$, 3.63 g $Fe^{2+}$) were dissolved in sulphuric acid (solution II) and removal of iron was repeated (Fe precipitations II). Obtained ammoniacal solution (filtrate II) was iron free, with copper and cobalt ions contents 0.335 g and 0.548 g, respectively. The electrolysis conducted in that electrolyte brought about Co-Cu alloy codeposition. Fig. 6 shows changes in the copper and cobalt contents in the bath and in the cathodic deposits. The initial volume of the solution was 1 $dm^3$ and the final volume was 0.895 $dm^3$, because of drawing of the solution samples.

As it was observed previously, the most significant recovery of both metals was observed for first 8 hours of the electrolysis. Since cobalt concentration in the bath was higher than that of copper, Co-Cu alloy was enriched in cobalt. Changes in the composition of the cathodic deposit are showed in Fig. 7.

In Fig. 7 the current efficiency of the Co-Cu alloy deposition is also showed. Its values decreased gradually with the time of the electrolysis from 60% in the first stage to 0% when the recovery of metals from the bath was completed. Electrolysis voltage was 2.8-3.2 V.

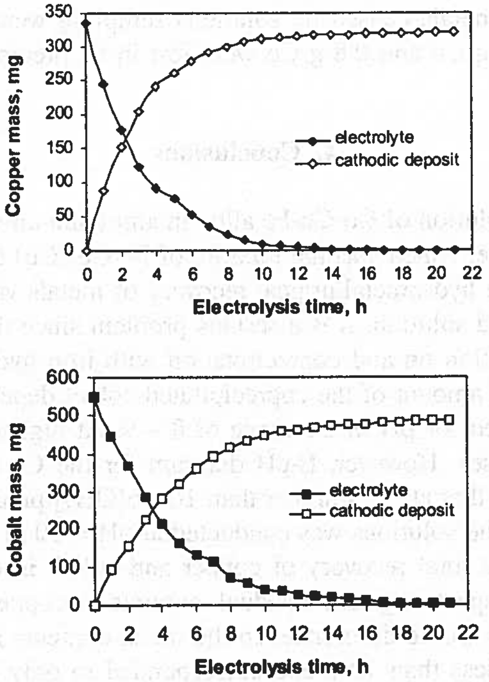

Fig. 6. The influence of time on the $Cu^{2+}$ and $Co^{2+}$ ions contents in the bath and amount of codeposited metals

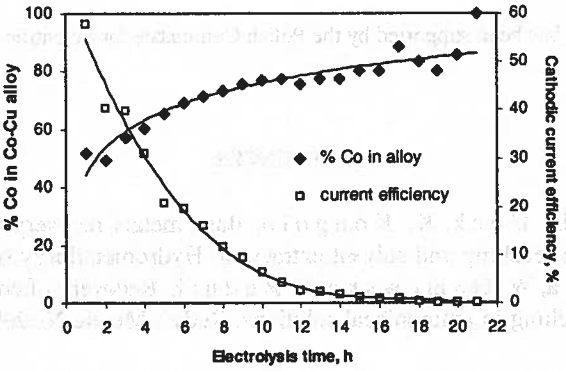

Fig. 7. Changes in the cathodic current efficiency and Co-Cu alloy deposit with the electrowinning time

## 3.5. Copper and cobalt mass balance

Total mass balances of electrodeposited copper and cobalt were made. The initial solution contained: 1.07 g $Cu^{2+}$, 2.54 g $Co^{2+}$ and 3.77 g $Fe^{3+}$ (solution I). During all electrolysis's (Cu, Co, Cu+Co electrowinnings) 0.43 g Cu and 1.39 g Co were recovered. Losses of metals caused by solutions sampling were: about 6 mg Cu and 33 mg Co. About 0.6 g Cu and 0.8 g Co were lost in Fe precipitations II.

## 4. Conclusions

Spontaneous dissolution of Cu-Co-Fe alloy in ammonia-ammonium sulphate solution produced the slime, which was the mixture of Fe-Co-(Cu) alloy and $CoO \cdot Fe_2O_3 \cdot xH_2O$ compound. The hydrometallurgical recovery of metals values required removal of iron from the treated solution. It is a serious problem since the loss of the valuable metals through adsorption on and coprecipitation with iron hydroxide occurs. Han et al. (1982) showed that amount of the coprecipitated cobalt depends on the pH and the maximum was observed for pH in the range of 8 – 9. At higher pH values the cobalt coprecipitation decreases. However, E-pH diagram for the $Co\text{-}NH_3\text{-}H_2O$ system (Vu and Han, 1977) shows that at pH's higher than 10 $Co(OH)_2$ precipitates. Therefore the removal of iron from the solutions was conducted at $pH = 10$ in spite of high losses of cobalt and copper. The total recovery of copper and cobalt in two electrolysis stages was 40% and 55%, respectively. The residual amounts of copper and cobalt remained in the iron precipitates. Some differences in the metal contents in the solution and the cathode deposit were less than 10% and corresponded to only a few milligrams of a metal. All metals deposited as monolithic deposits.

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