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MECHANISM OF THE ANODIC DISSOLUTION OF Fe70-Cu16-Co10 ALLOY ORIGINATED FROM REDUCED COPPER CONVERTER SLAG IN AMMONIACAL SOLUTIONS. RECOVERY OF COPPER AND COBALT

MECHANIZM ANODOWEGO ROZTWARZANIA W ROZTWORACH AMONIAKALNYCH STOPU Fe70-Cu16-Co10 OTRZYMANEGO W WYNIKU REDUKCJI ŻUŻLA PO PROCESIE KONWERTOROWANIA KAMIENIA MIEDZIOWEGO. ODZYSK MIEDZI I KOBALTU

Industrial copper converter slag was subjected to reduction roasting, in which Fe70-Cu16-Co10 alloy was obtained. This alloy was dissolved anodically in an ammonia-ammonium chloride solution. This resulted in the separation of the metals, wherein iron remained in the slime, while copper and cobalt were components of slime, electrolyte and cathodic deposit. A mechanism of the anodic dissolution process was developed. The alloy was a three-phase system and did not dissolve uniformly. A series of secondary processes took place in the system: precipitation of iron compounds and adsorption of copper and cobalt ions on the iron precipitates. A hydrometallurgical method of copper and cobalt recovery was developed.

Keywords: cobalt, copper, recovery, electrowinning

W wyniku redukcji przemysłowego żużla konwertorowego otrzymano stop Fe70-Cu16-Co10. Stop ten roztwarzano anodowo w roztworze amoniakalno-chlorkowym. W wyniku tego procesu następuje rozdział metali: żelazo pozostaje w szlamie, natomiast miedź i kobalt wchodzą w skład szlamu, elektrolitu oraz osadu katodowego. Opracowano mechanizm procesu anodowego roztwarzania stopu. Badany stop stanowił układ trójfazowy i roztwarzał się selektywnie. W układzie zachodziły procesy wtórne: wytrącanie się związków żelaza oraz adsorpcja jonów miedzi i kobaltu na powierzchni wytrąconych związków żelaza. Opracowano hydrometalurgiczną metodę odzysku miedzi i kobaltu.

1. Introduction

Metallic cobalt is a component of numerous materials having various practical applications. Due to its special properties (hardness, strength, etc.) it is used in ferromagnetic alloys (e.g. alnico) and, particularly, sintered hard alloys. The latter includes widia (tungsten carbide with an addition of approx. 10% Co) and stellites, which are used to cut glass and porcelain as well as in the production of mining drills. Cobalt is a component of "superalloys" (i.e. high-temperature creep resistant and heat resistant alloys), which are used in the aviation and space industries. Cobalt alloys are used also in biomedical engineering for the production of non-toxic implants, which are more resistant to attacks of organic acids in comparison to other alloys used in medicine. Some chemical compounds of cobalt reveal special significance, in particular, in the ceramic industry (glass and porcelain colouring) and in the production of catalysts.

The primary source of cobalt is oxide and sulphide ores, which accompany nickel or copper ores. Considerable amounts of cobalt can also be found in some intermediate and by-products from the pyrometallurgical treatment of ores and concentrates. These are: slags from the processing of copper matte in converter furnaces, cobalt alloys produced by reduction of copper converter slag, Cu-Fe-Pb alloys resulting from the flash furnace smelting technology, wastes from the hydrometallurgical processing of zinc ores and non-ferrous metal scraps. At the present time economical requirements impose the development of effective and inexpensive methods for the recovery of cobalt from secondary sources. Moreover, the increased demand for cobalt to approx. 50,000 t/year is forecasted in 2010, notwithstanding the varying

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global production trends for this metal over the past two decades [1].

A method for cobalt extraction from waste materials depends on their composition. Hydrometallurgy offers numerous opportunities in this regard. The hydrometallurgical route includes two main stages: leaching and then selective separation of metals from the leaching liquor. Hardly leached materials are often roasted in an additional stage under sulphurising, oxidising or reducing conditions. The aim of the pyrometallurgical processing is to transform the metallic compounds into sulphates, oxides or alloys, i.e. materials soluble in typical leaching solutions, even in water. Acidic, ammoniacal or iron (III) salts solutions are used usually in the leaching stage. The selection of the leaching solution (composition, concentration of components, pH) and process parameters (temperature, pressure, size of the grains, rate and type of agitation) is dependent on the qualitative and quantitative composition of the waste cobalt-containing material.

Acma [2] conducted recovery of cobalt from slag originated from the processing of copper matte in converter furnace. The slag was melted under reducing conditions at various temperatures to produce a metallic matte of varying chemical compositions. This product was subsequently leached with sulphuric acid. It was found that the rate and efficiency of the cobalt leaching depended mainly on sulphur content in the metallic matte, whereas carbon presence did not affect cobalt dissolution. However, Whyte et al. [3] observed decrease in the cobalt leaching from Fe-Co-Cu alloys (obtained from copper slags reduced in an electric furnace) at carbon contents higher than 0.5%. Thus, the Fe-Co-Cu alloys with low content of sulphur and high content of carbon can dissolve effectively in sulphuric acid solely under increased oxygen pressure (in autoclaves). Anand et al. [4] showed that leaching of the copper converter slag with sulphuric acid under higher oxygen pressure and at increased temperatures allows to recover up to 98% of cobalt.

The leaching of oxide or sulphide industrial slags is often preceded by roasting with the addition of ferric sulphate [5], pyrite [6], ammonium sulphate or sulphuric acid [7]. It was found that the roasting conditions affect efficiency of further cobalt dissolution. Cobalt was recovered completely from the slags roasted with concentrated sulphuric acid at a temperature of 350°C, and subsequently leached in water [7]. A similar method was applied for the recovery of cobalt from slags obtained through melting in an reverberatory furnace as well as from converter slags [8]. In this case, the maximum recovery of cobalt reached 87%.

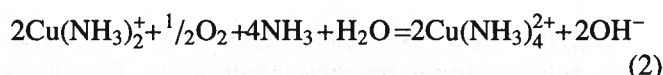Anand et al. [9] used ferric chloride solutions to leach copper converter slags and slags from the melting of copper matte. Both materials contained metal oxides and sulphides, with inclusions of pure metals. However, this method allowed to recover less than 50% of cobalt.

There is insufficient detailed data concerning the dissolution of cobalt alloys [10-12]. A number of studies on the dissolution of synthetic Cu-Co-Fe alloys of various compositions was carried out by a research group (L.Burzyńska, W.Gumowska and E.Rudnik) at Department of Physic Chemistry and Metallurgy of Non-Ferrous Metals, Faculty of Non-Ferrous Metals, AGH University of Science and Technology. The alloys were leached in acidic [13] and ammoniacal solutions [14]. It was found that the anodic dissolution of the Cu-Co-Fe alloys in sulphuric acid was an effective process and the anodic current efficiencies reached up to 100%. The passivation of the alloy anodes was not observed. During this process, iron and cobalt were transferred to the solution, while copper was deposited on the cathode or accumulated in the slime.

Ammoniacal leaching of Cu-Co-Fe alloys was dependent on the composition of the material. It was found that a high-copper alloy could dissolve spontaneously in an ammonia- ammonium sulphate electrolyte, while low-copper alloys could dissolve only in ammonia-ammonium chloride solution during electrolysis. Spontaneous dissolution of Cu90Co5Fe5 alloy was accelerated by the addition of some amounts of copper ions to the ammoniacal solution. It is known that $Cu(NH_3)_4^{2+}$ ions can oxidize metallic copper:

$$Cu + Cu(NH_3)_4^{2+} = 2Cu(NH_3)_2^+ \qquad (1)$$
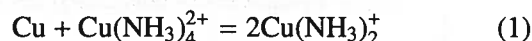
Oxygen dissolved in the solution can oxidize cuprous ions:

$$2Cu(NH_3)_2^+ + {}^1/_2O_2 + 4NH_3 + H_2O = 2Cu(NH_3)_4^{2+} + 2OH^- \qquad (2)$$

Homogeneous reaction (2) is faster than heterogeneous process (1) and the dissolution of the metal is autocatalyzed by cupric ions [19]. Hence, the presence of $Cu(NH_3)_4^{2+}$ in the ammoniacal solutions accelerate significantly the dissolution of metallic copper. Moreover, the dissolution rate increases intensively with increased Cu^{2+} concentration in the solution.

The ammoniacal leaching of the Cu-Co-Fe alloy was a selective process: copper was transferred on to the solution, whereas iron and cobalt remained in the solid phase.

Low-copper alloys dissolved only under the current. The anodic current efficiencies were approx. 97%. Under these conditions, iron and copper were remained mainly in the slime, whereas cobalt was deposited on the cathode.

Cobalt ions present in the leaching liquors are separated from the other metals in one of a number of ways. The most important of these include solvent extraction [20], ion exchange [21], cementation [22] and electrolysis [23]. The latter method is used successfully for aqueous solutions as well as for solutions impured by traces of organic compounds (e.g. SX-EW processes) [24]. Electrolysis is carried out at temperatures less than 100 °C. The process characterizes with low energy consumption, it do not require a considerable outlay, expensive apparatuses or expensive reagents. Moreover, the final product is the metal of high purity.

Legnica Copper Smelter produces several thousands tonnes of copper converter slag per annum. To date, cobalt has not been recovered from this source in Poland. The cobalt content in this slag reaches up to 1.5 %, hence, it would be able to obtain annually up to 300 tonnes of metal. Moreover, high metal price (44,000 $/t – November 2008) inclines to the development of a low-cost method for cobalt recovery from this industrial source.

At the Institute of Non-Ferrous Metals in Gliwice a method of the reduction of the copper converter slag in an electrical furnace was developed. Fe-Cu-Co-Pb alloys produced in such way contained 4-10% of cobalt. These alloys were used as the initial material for the hydrometallurgical recovery of cobalt and copper.

The present paper describes the anodic dissolution of Fe70-Cu16-Co10 alloy in an ammonia-ammonium chloride solution. A mechanism for this process was also proposed. The results of the copper and cobalt recovery from slime, cathodic deposit and electrolytes are also presented.

2. Experimental

2.1. Materials

The copper converter slags were supplied by the copper smelter at Legnica (Poland). The chemical composition of the slags was (in wt %): Cu (1.70-5.60); Co (0.90-1.45); Pb (3.42-7.61); Fe (30.40-38.00); As (0.05-0.12); Zn (3.10-6.40); Ag (0.005-0.014); S (0.17-0.78); Ni (0.045-0.095); SiO_2 (25.50-32.84); CaO (0.43-2.49); MgO (0.23-1.94). Batches of the slag (900 kg) were reduced in an industrial electric furnace (EMA Brzezie) at 80-90 V at a current of 900-950 A. The process was carried out in the presence of fluxing agents (limestone 8.6%, dolomite 8.6%) and reducing agents (coke breeze 2.7%, pig iron 2.0%). A temperature of 1,425-1,570°C was applied. The thermal treatment of the slag was performed at various dwell times in the furnace (112-142 min) and with a constant reduction time

(90 min). The sample described in the present paper was obtained at a dwell time in the furnace of 142 min. The product of the reduction was an Fe70-Cu16-Co10 alloy. The alloy was examined via scanning and optical microscopes. The chemical composition of the sample was determined by wet chemical analysis (AAS method) and SEM with an EDS analyser. The particular composition of the phases in the alloy was determined by SEM-EDS analysis. Volume fractions of the phases were determined by image analysis using the "Aphelion" software. Calculations were done on grey levels images of polished deposit surfaces (with an areas of 600 μm × 800 μm) observed with the use of the scanning microscope.

2.2. Anodic dissolution

A cuboid alloy anode (with a total area of 30 cm^2) was hung vertically between two rectangular platinum cathodes (each with an area of 90 cm^2) in a cuboid PVC vessel containing 1 dm^3 of the electrolyte. Measurements were carried out in the electrolyte: 2.5 M (NH_3 + NH_4^+) and 1.0 M Cl^-. The electrolyte was agitated with a peristaltic pump with a circulation rate of 15 dm^3/h. The bath temperature was maintained at 50 ±0.2°C. The anodic dissolution was carried out under galvanostatic conditions at an anodic current density of 350 A/m^2. The electrodes were weighed before and after the electrochemical measurement. After the electrolysis, the cathodic deposit, anodic slime and suspension were obtained (Fig.1). The suspension was filtered. The anodic slime and filtration sediment were thoroughly washed with water and dissolved in hot 2.5 M hydrochloric acid with a hydrogen peroxide addition. Dry, insoluble residues of the slime were studied via X-ray diffractometry and SEM. The cathodic deposits were dissolved in HNO_3 (1:1) solution. The concentrations of the metals in the solutions were determined by the AAS method.

2.3. Recovery of copper and cobalt

Anodic dissolution of the alloy resulted in the transfer of metals into solution and/or solid phases (slimes and cathodic deposits). Figs. 1-3 show the flow charts of the hydrometallurgical route for the cobalt and copper recovery proposed in this paper. In the subsequent stages, iron and lead free solutions of high concentrations of copper and cobalt ions were obtained. It should be noted that the anodic slime resulting from the electrolytic dissolution of the alloy contained some compounds insoluble in $HCl+H_2O_2$ solution (S_{insol} – Fig.1). This fraction was dried and analyzed with X-ray diffraction. It showed the presence of elemental sulphur, copper and iron sulphides.
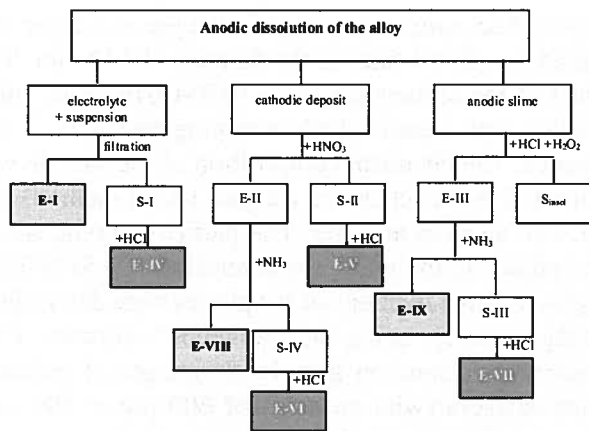
Fig. 1. I stage of the hydrometallurgical recovery of Co and Cu from the alloy: E – electrolyte; S – sediment

As a result of the dissolution of hydrated iron oxide precipitates (S-I, S-II, S-III, S-IV) in HCl, the solutions (E-IV, E-V, E-VI, E-VII) were obtained (Fig.1). They contained high concentrations of ferric ions as well as considerable amounts of Cu^{2+} and Co^{2+} (as result of the adsorption on iron precipitates). These solutions were connected (Electrolyte A – Fig.2). Iron was removed from the electrolyte A by precipitation of iron (III) oxides (S-V, S-VII) with ammonia.

Sediment S-VII (Fig.2) contained mainly Fe and Pb compounds and, hence, it was the waste product.
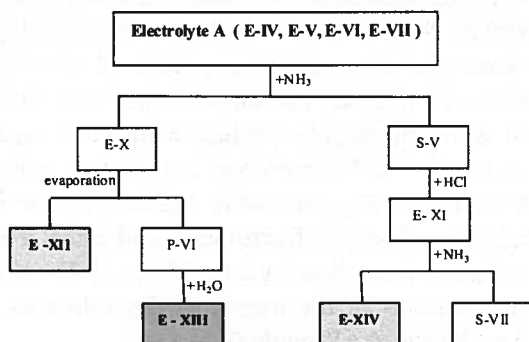

Fig. 2. II stage of the hydrometallurgical recovery of Co and Cu from the alloy: E – electrolyte; S – sediment; P – precipitate

Ammoniacal electrolytes (E-XII, E-XIV - Fig. 2) did not contain neither Fe nor Pb ions and were mixed with solutions (E-I, E-VIII, E-IX) from I stage. Obtained in such way Electrolyte B (Fig.3) was prepared for the copper and cobalt electrowinning follow the diagram shown in Figure 3.

High total volume of the ammoniacal electrolyte E-X was reduced by evaporation. The process was accompanied by precipitation of carmine and fine crystalline chemical compound. It is supposed that the precipitate (P-VI – Fig.2) was [Co(NH$_3$)$_5$Cl]Cl$_2$ [25]. Cobalt salt was dissolved in water (E-XIII) and then used in III stage of the cobalt recovery.

Ammoniacal-chloride electrolyte B (Fig.3), containing mainly copper and cobalt complexes, was evaporat-

ed. As it was observed previously, cobalt salt was precipitated (P-VIII).It was then dissolved deposit in water (E-XVII) and mixed with electrolyte E-XIII (Fig. 2). This solution (E-XVIII) contained mainly cobalt ions (about 98%), which corresponded to 65% of the total cobalt content in the dissolved alloy.

The electrowinning of cobalt and copper was conducted from two electrolytes: E-XVI and E-XVIII. The electrolyte E-XVI was acidified with HCl to pH=0 and then copper was selectively deposited on the cathode. Copper free electrolyte was alkalized with NaOH to pH = 9 and cobalt was electrowon.

Electrolyte E-XVIII contained a certain quantity of copper, nickel and zinc ions. This electrolyte was acidified with HCl to pH=0 to selective copper recovery. In the next stage, the solution was alkalized to pH=9 with NaOH and the electrowinning of cobalt was carried out.
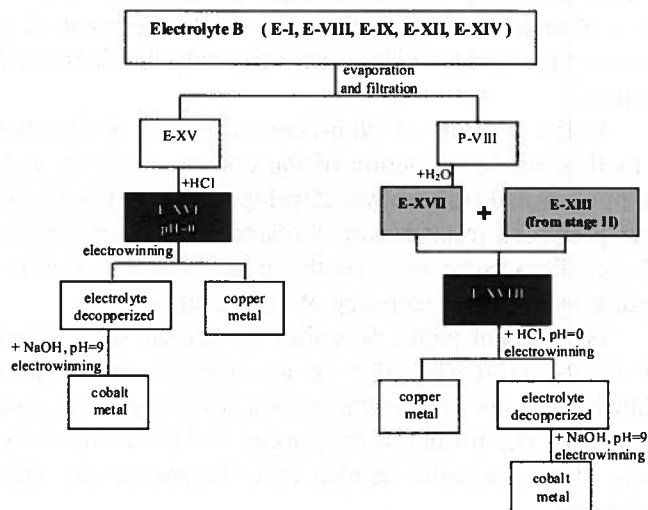

Fig. 3. III stage of the hydrometallurgical recovery of Co and Cu from the alloy: E – electrolyte; S – sediment; P – precipitate

3. Results and discussion

3.1. Characteristics of the material

The product of the reduction roasting was an iron base alloy with a general composition of Fe70-Cu16-Co10 (in wt%). The alloy contained also a few other elements (eg. As, Ni, Si, Sn), since the slag was an industrial material. Microstructure of the alloy is shown in Fig.4. Fe70-Cu16-Co10 alloy was a three-phase system. Phase I was the matrix, dark spherical precipitates represented phase II, while light streaks were phase III. The volume fractions of the individual phases in the alloy were estimated. It was found that phase I represented approx.70 vol%, phase II – approx. 26 vol% and phase III – 3-4vol. %
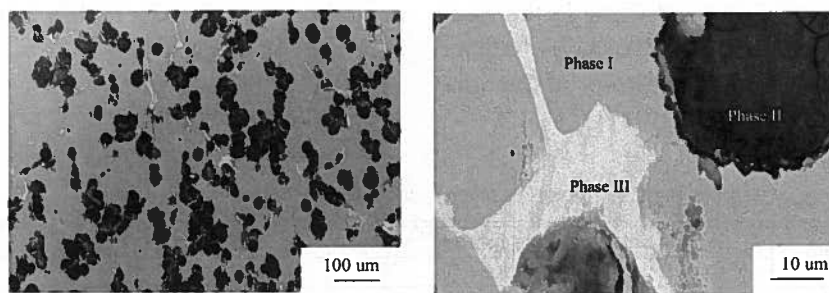
Fig. 4.   Microstructures of Fe70-Cu16-Co10 alloy

The alloy matrix (phase I) was a solid iron-based solution (79% Fe) containing comparable quantities of cobalt and copper (about 9.5 %). Phase II was also an iron-based alloy, but with a lower copper content (approx. 5%) than in the matrix. Phase III was a copper-based alloy with low additions of cobalt and iron, but with a relatively high content of tin (approx. 15%). The lead contents in each phase did not exceed 1%. Detailed compositions of the alloy and the individual phases are shown in Table 1.

TABLE 1

Chemical composition of alloy and the individual phases in alloy Fe70-Cu16-Co10

Material	Analysis	Chemical composition, wt %										
		Co	Cu	Fe	Pb	Zn	As	Ni	Ag	S	Si	Sn
Alloy	Chemical analysis	8.8± 0.3	21.1± 0.5	71.2± 1.9	0.006 ± 0.008	0.009 ± 0.003	–	1.2± 0.1	–	–	–	–
	SEM	9.7± 0.4	15.6± 0.9	70.1± 1.3	0 – 0.6	0 – 0.06	0.8±0.2	1.4± 0.0	0.0	0.8± 0.0	0.2± 0.0	1.1± 0.2
Phase I		10.0± 0.2	9.3± 0.5	78.7± 1.0	0 – 0.07	0.0	0.3± 0.2	0.9± 0.2	0 – 0.41	0.3± 0.1	0.1± 0.1	0.3± 0.1
Phase II	SEM	9.9± 1.8	5.5± 3.0	74.5± 6.4	0 – 1.0	0.0	0.3± 0.1	5.9± 1.1	0.3± 0.3	1.9± 0.5	0.4± 0.0	0.7± 0.3
Phase III		0.5± 0.1	78.8± 1.2	3.9± 0.1	0 – 0.33	0.0	0.7± 0.2	0.7± 0.5	0.2± 0.2	0 – 0.12	0.1± 0.0	14.7± 1.12

It was noticed that results of the chemical analyses of the alloy dependent in some extent on the method used (AAS, SEM-EDS). It seems obvious, since AAS method allows to determine an average composition of the bulk of the sample, while SEM-EDS examination is a surface analysis.
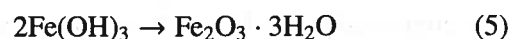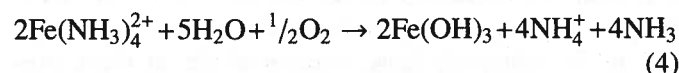
3.2. Anodic dissolution

In the process of the anodic dissolution of the Fe70-Cu16-Co10 alloy in the ammonia-ammonium chloride solution, the metals were transferred into the electrolyte, cathodic deposit, and slime. It was found that the electrolyte contained mainly ammine complexes of cobalt (48-80%) and copper (20-48%). Some amounts of nickel (0.2-8%) and traces of zinc (0.0-0.5%) ions were also detected. Ferrous (ferric) ions were absent in the bath.

The cathodic deposits consisted of 36-47% Co, 9-40% Cu, 16-50% Fe, and 3-4.5% Ni. A considerable amounts of iron in the cathodic deposits resulted from the embedding of the slime particles drifting in the bath (suspension). Large amounts of the slime were produced

during electrolysis, since the alloy was a high-iron material.

The slime consisted of two fractions: anodic slime compactly adhered to the alloy electrode and precipitates of the suspension in the electrolyte. Both types of the slime were enriched in iron compounds. It was found that iron ions dissolved from the anode immediately precipitated as hydrated oxide:

$$Fe + 4NH_3 - 2e \rightarrow Fe(NH_3)_4^{2+} \tag{3}$$

$$2Fe(NH_3)_4^{2+} + 5H_2O + {}^1/_2O_2 \rightarrow 2Fe(OH)_3 + 4NH_4^+ + 4NH_3 \tag{4}$$

$$2Fe(OH)_3 \rightarrow Fe_2O_3 \cdot 3H_2O \tag{5}$$

Reaction (4) occurs in presence of oxygen dissolved in the electrolyte. Moreover, the oxidation of Fe^{2+} to Fe^{3+} ions was favoured by the anode potential (0.4-0.9 V, vs. NHE), increasing gradually with the electrolysis time.

The main components of the anodic slimes were: iron (75-80%), copper (12-16%), and cobalt (6-8%). The

chemical analysis of the precipitates drifting in the electrolyte showed the presence of iron (96-97%), copper (0.5-2%), and cobalt (2-2.3%). The details of the elemental analysis for the metals are summarised in Table 2.

TABLE 2

Contents of the metals in slimes, cathodic deposit, and electrolyte

Metal	Run	Anode slime		"Drifting" slime		Cathodic deposit		Electrolyte	
		g	%	g	%	g	%	g	%
Co	1	0.2125	7.5	0.0078	2.3	0.0804	46.8	0.0312	52.6
	2	0.2710	7.8	0.0089	1.9	0.1088	40.6	0.0327	47.9
	3	0.2180	6.4	0.0173	2.3	0.1106	36.3	0.0458	79.7
	average		7.2±0.6		2.2±0.2		41.2±4.3		60.1±14.0
Cu	1	0.3535	12.4	0.0056	1.7	0.0406	23.7	0.0336	47.2
	2	0.5820	16.5	0.0035	0.8	0.1060	39.6	0.0280	43.6
	3	0.4715	13.9	0.0037	0.5	0.0275	9.0	0.0112	19.5
	average		14.3±1.7		1.0±0.5		24.1±12.5		36.7±12.3
Fe	1	2.2700	79.9	0.3216	95.9	0.0425	24.8	0.0000	0.0
	2	2.6400	75.2	0.4459	97.0	0.0419	15.6	0.0000	0.0
	3	2.6987	79.4	0.6692	96.9	0.1571	51.5	0.0000	0.0
	average		78.2±2.1		96.6±0.5		30.6±15.2		0.0±0.0
Ni	1	0.0067	0.2	0.0000	0.0	0.0077	4.5	0.0002	0.2
	2	0.0124	0.4	0.0000	0.0	0.0107	4.0	0.0054	8.0
	3	0.0081	0.2	0.0005	0.1	0.0093	3.0	0.0000	0.5
	average		0.3±0.1		0.0±0.0		3.8±0.6		
Zn	1	0.0000	0.0	0.0000	0.0	0.0004	0.2	0.0000	0.0
	2	0.0002	0.0	0.0003	0.1	0.0004	0.2	0.0003	0.5
	3	0.0001	0.0	0.0006	0.1	0.0005	0.2	0.0001	0.3
	average		0.0±0.0		0.1±0.0		0.2±0.0		0.4±0.2
Pb	1	0.0010	0.0	0.0002	0.1	0.0000	0.0	0.0000	0.0
	2	0.0012	0.1	0.0009	0.2	0.0000	0.0	0.0000	0.0
	3	0.0010	0.1	0.0007	0.1	$5.8 \cdot 10^{-5}$	0.0	0.0000	0.0
	average		0.1±0.0		0.1±0.0		0.0±0.0		0.0±0.0
Total mass of metals	Run	Σ		Σ		Σ		Σ	
	1	2.8437		0.3352		0.1716		0.0650	
	2	3.5068		0.4592		0.2678		0.0664	
	3	3.3974		0.6908		0.3051		0.0571	

Specific microstructure (Fig.4) and various compositions of the alloy phases (Table 1) determined their different behaviours in the dissolution process. It was expected that only iron based phases (I and II) could dissolve under the current flow. An autocatalytic dissolution of copper from the phase III could also arise with a gradual accumulation of the copper ions in the electrolyte. However, this process seems to be impossible due to the relatively large content of tin in these precipitates [19]. The microscopic observations confirmed that copper-coloured III phase was present on the alloy surface after anodic dissolution. It is noteworthy also that the ammoniacal dissolution of the iron-rich alloy generates considerable quantities of slime, which may cover the reaction surface. Moreover, a number of secondary reactions were also possible in the system. Therefore, an attempt was made to describe the mechanism of the anodic dissolution of the Fe70-Cu16-Co10 alloy.

3.3. Preliminary calculations

In order to develop a model, some preliminary calculations were made. It was accepted that the decrement of the anode mass Δm_A, determined gravimetrically in each experiment, corresponded to the total mass of the phases removed from the electrode during the electrolysis. The mass of the individual phase m_i in the dissolved sample was equal:

$$m_i = \frac{\%W_i \cdot \Delta m_A}{100\%} \tag{6}$$

where $\%W_i$ is the volume fraction of the phase i in the alloy. Since particular densities of the alloy phases were unknown, it was believed that these were similar values. Therefore, the volume fractions of the separated phases were assumed to be mass fractions. The results of these calculations are shown in Table 3.

TABLE 3

Calculated masses of individual phases in the dissolved alloy samples

Run	Δm_A	m_I	m_{II}	m_{III}
			g	
1	3.4940	2.4458	0.9084	0.1398
2	4.5411	3.1788	1.1807	0.1816
3	4.3710	3.0597	1.1365	0.1748

The masses of the constituent metals in each phase $(m_M)_i$ were estimated using its chemical composition $\%M_i$:

$$(m_M)_i = \frac{\%M_i \cdot m_i}{100\%} \qquad (7)$$

Detailed calculations were made individually for all the elements and for each run of the electrolysis. A set of results were obtained for the main components (Cu, Co, and Fe) and are shown in Table 4. The last column of Table 4 shows the total mass of other elements present in each of the phases.

TABLE 4

Calculated contents of the cobalt, copper, and iron in the individual phases of the dissolved alloy samples

Run	Phase	m_{Co}	m_{Cu}	m_{Fe}	m_{Co} $+m_{Cu}$ $+m_{Fe}$	m_R^*
				g		
1	I	0.2438	0.2279	1.9241	2.3958	0.0500
2		0.3169	0.2963	2.5008	3.1140	0.9648
3		0.3050	0.2852	2.4071	2.9973	0.0624
1	II	0.0901	0.0501	0.6763	0.8165	0.0919
2		0.1171	0.0652	0.0790	1.0613	1.1194
3		0.1127	0.0627	0.8461	1.0215	0.1150
1	III	0.0007	0.1102	0.0055	0.1164	0.0234
2		0.0009	0.1432	0.0071	0.1512	0.0304
3		0.0008	0.1378	0.0068	0.1454	0.0294

* m_R – total mass of remaining elements (Ni, Pb, Zn, S etc.)

3.4. Model

The calculated data from Tables 3 and 4 were compared with the experimental findings from Table 2. It allowed to propose the model of the system behaviour. It was assumed that the following processes determined the composition of the slimes:

- anodic dissolution of phases I and II. Both phases are solid solutions, and thus iron, cobalt, and copper ions are transferred to the electrolyte. Over time, this process can lead to an increase in the content of iron

(III) compounds in the slime and the enrichment of the electrolyte with cobalt and copper ions,

- the autocatalytic dissolution of copper from phase III does not occur due to the considerable contents of tin in the precipitates,
- the adsorption of copper and cobalt ions on the iron (III) compounds produced in reactions (4) and (5).

1. According to this model, the total mass of metals in the slime is the sum of the mass of iron from phases I and II (Table 4) and of phase III in its entirety (Table 3). Apart from iron, phase III also contains copper and cobalt. On this basis, we calculated the composition of the slime resulted solely from the selective alloy dissolution (Table 5).

2. The mass of slime adhering to the anode and "drifting" in the electrolyte was determined as the sum of the masses of the following chemical elements: Co, Cu, Fe, Ni, Zn, and Pb (AAS method). In addition, a part of the "drifting" slime becomes embedded in the cathodic deposit, and in consequence the deposit also contains iron. This iron mass (Table 2) was taken into consideration in the calculations of the experimental total slime mass (total mass of the elemental metals). The composition of this slime is provided in Table 5. A comparison of the calculated (exclusively selective dissolution) and experimental composition of slime allows us to state that these differ considerably.

3. The data set forward in the literature [15] shows that iron hydroxides adsorb Co^{2+} and Cu^{2+} ions from the electrolyte. Data (Table 4) concerning the calculated composition of phases I and II (these phases undergo selective dissolution) make it possible to calculate the mass of copper and cobalt, which following the process should be located fully in the electrolyte and cathodic deposit. The experimental data indicates that the sum of the masses of copper and cobalt in these two phases (electrolyte and cathodic deposit) is considerably smaller. It was assumed that this effect is caused by the process of adsorption, which results in the enrichment of slime in copper and cobalt. The mass of adsorbed metals $(m_{Co})_{ads}$ and $(m_{Cu})_{ads}$ may be calculated:

$$(m_{Co})_{ads} = (m_{Co})_{phaseI} + (m_{Co})_{phaseII} - (m_{Co})_{electrolyte} - (m_{Co})_{cathodicdeposit} \qquad (8)$$

A similar dependence applies to copper. The mass of the adsorbed metals thus calculated, con-

verted into the unit mass of iron, and are shown in Table 5.

4. In point 1, we gave the method of calculating the mass of slime generated exclusively as the result of the selective dissolution of phases I and II.

Taking into consideration the adsorption of copper and cobalt by iron compounds, we calculated the total composition of slime (Table 5), which follows from the course of two processes:

Comparison of the calculated and actual composition of slimes

Metal	Calculated composition of slime		Actual composition of slime	$\left(\frac{m_{Cu}}{m_{Fe}}\right)_{adsorption}$	$\left(\frac{m_{Co}}{m_{Fe}}\right)_{adsorption}$
	Selective dissolution	Selective dissolution and adsorption			
	%				
Fe	92.61 ± 4.84	80.93 ± 2.11	80.07 ± 4.34	0.075 ± 0.013	0.077 ± 0.005
Cu	4.02 ± 0.00	12.32 ± 1.62	10.11 ± 0.86		
Co	0.024 ± 0.003	6.44 ± 0.64	6.94 ± 0.29		

- the selective dissolution of phases I and II
- the adsorption of copper and cobalt by iron compounds.

By taking into consideration both processes leads to the high compatibility of the calculated composition of slime with the experimental data.

The results of the experiment include the following:
- general composition of the alloy – wet analysis
- compositions of the alloy and individual alloy phases – SEM-EDS analysis
- compositions of the anodic slime, "drifting" slime, electrolyte and cathodic deposit – wet analysis

Each of the analyses carries a certain error, but the compatibility of the experimental data with the accepted model (selective dissolution + adsorption) is nevertheless considerable.

3.5. Electrowinning of metals

3.5.1. Electrowinning of copper

The electrowinning of copper was conducted using electrolyte containing ammoniacal-chloride complexes of copper and cobalt and acidified with HCl to pH = 0 (E-XVI - Fig. 3). The initial composition of this electrolyte was as follows: 0.5480 g Co/dm^3; 2.3480 g Cu/dm^3; 0.1036 g Ni/dm^3; 0.0266 g Zn/dm^3. Under these conditions, copper was deposited selectively on the cathode. It led to the decrease in the concentration of Cu^{2+} ions in the electrolyte with time. Hence, the cathodic current density was reduced (from 100 – 40 A/m^2) in successive stages of the electrolysis to avoid formation of copper powder. The total time of electrolysis was 35 hours.

Cathodic deposits of a 99% purity were obtained, however, the presence of small quantities of cobalt and nickel was also detected. The content of cobalt in cathodic copper increased in the course of electrolysis from 0.26 % to 1.0%, while the nickel content increased initially from 0.04% to 0.25%, and then was maintained at a constant level. The cathodic current efficiencies decreased from 68% to 3% with the gradual decrease in Cu^{2+} concentration in the electrolyte. The recovery of copper from the electrolytes was very high (99.9%).

It is noteworthy that approx. 93% of copper was recovered from the initial alloy sample (some loses of copper were caused by numerous electrolyte samples taken to chemical analysis).

3.5.2. Electrowinning of cobalt

a. Electrolysis from the solution E-XVI (after copper removal)

The electrolyte after copper removal was alkalized with NaOH to pH=9 (cobalt can not deposit from an electrolyte with pH=0). A series of electrolyses was conducted in order to obtain cathodic cobalt deposits. The initial composition of the electrolyte was as follows: 0.5260 g Co/dm^3; 0.0122 g Cu/dm^3; 0.0950 g Ni/dm^3; 0.0260 g Zn/dm^3.

Electrolysis was conducted at a current density of 100 A/m^2 for 5.5 hours. Cathodic cobalt deposits with a purity 97.5 ± 0.3% were obtained. Copper was a sole impurity and it was completely (0.0122 g) co-deposited with cobalt during the initial stages of the process. The cathodic current efficiencies were low (15-0.2%).

b. Electrolysis from electrolyte E-XVIII

This electrolyte is the aqueous solution of cobalt salt $[Co(NH_3)_5Cl]Cl_2$, contaminated with a small quan-

tity of Cu, Ni, and Zn. The initial composition of the electrolyte was as follows: 0.9360 g Co/dm^3; 0.0864 g Cu/dm^3; 0.0027 g Ni/dm^3; 0.0012 g Zn/dm^3. This electrolyte was acidified with hydrochloric acid to pH=0 and copper electrowinning was performed. After total copper recovery (the concentration of Cu^{2+} ions in the electrolyte was 0 g/dm^3), the solution was alkalized to pH=9 with NaOH, and the cobalt electrowinning was carried out. The cathodic deposit were high purity (99.5% Co). The sole contamination was nickel, which was totally codeposited with cobalt during the initial stage of the electrolysis. Zinc remained in the electrolyte. The efficiency of the process was low (about 14%).

The total recovery of cobalt from the electrolytes was 99,8%. It was found that about 92% Co was recovered from the initial sample of the alloy.

4. Conclusions

1. Fe70-Cu16-Co10 alloy produced by reduction of the industrial copper converter slag was a three-phase system.
2. The mechanism of the anodic dissolution of the alloy depends on the composition and mass fraction of the individual phases in the material.
3. The composition of anodic slimes, which were the main source of copper and cobalt, depends mainly on the course of secondary processes occurring on the surface of the anode, such as: the precipitation of iron(III) compounds and the adsorption of copper and cobalt ions on their surface.
4. A hydrometallurgical method of copper and cobalt recovery from was developed. The total recoveries of copper and cobalt from the alloy were 93% and 92%, respectively.
5. Copper with a purity of 99% was obtained.
6. The purity of cathodic cobalt deposits depended on the composition of the electrolyte and reached 99.5% (electrowinning from solutions of cobalt salt [Co(NH$_3$)$_5$Cl]Cl$_2$) or approximately 97.5% (electrowinning from solutions remained after copper recovery).

REFERENCES

[1] T. Nishijama, H. Fujii, Instabilities in the consumption and production for cobalt. Nonrenewable Resources **7**, 4, 281-285 (1998).

[2] E. Acma, The effect of sulfur and reduction temperature on cobalt dissolution during sulfuric acid leaching of metallic matte. Can. Metall. Q., **36**, 1,: 25-29 (1997).

[3] R. M. Whyte, J. R. Orjans, G. B. Harris, J. A. Thomas, Development of a process for the recovery of electrolytic copper and cobalt from Rokana converter slag. Advances in extractive metallurgy, Ed. Sones M.S., 57-68 (1977).

[4] S. Anand, K. Sarveswara Rao, P. K. Jena, Pressure leaching of copper con-verter slag using dilute sulfuric acid for extraction of cobalt, nickel and copper values. Hydrometallurgy **10**, 305-312 (1983).

[5] H. S. Altundogan, F. Tümen, Recovery of copper, cobalt and zinc from copper smelter and converter slag by roasting with ferric sulphate. Hydrometallury **44**, 261-267 (2002).

[6] F. Tümen, N. T. Bailey, Recovery of metal values from copper smelter slags by roasting with pyrite. Hydrometallurgy **25**, 317-328 (1990).

[7] L. B. Sukla, S. C. Panda, P. K. Jena, Recovery of cobalt, nickel and copper from converter slag through roasting with ammonium sulphate and sulphuric acid. Hydrometallurgy **16**, 153-165 (1986).

[8] C. Arslan, F. Arslan, Recovery of copper, cobalt and zinc from copper smelter and converter slags. Hydrometallurgy **67**, 1-7 (2002).

[9] S. Anand, P. Kanta Rao, P. K. Jena, Recovery of metal values from copper converter and smelter slags by ferric chloride leaching. Hydrometallury **5**, 355-365 (1980).

[10] M. Kwarciński, W. Baranek, K. Anyszkiewicz, S. Bratek, Technologia przerobu stopu kobaltowego otrzymanego z kongijskich rud miedziowo – kobaltowych. Polskie Towarzystwo Mineralogiczne – prace specjalne **12**, 101-111 (1998).

[11] J. Włodyka, Electrochemical dissolution of Co-Ni-Fe-Cu alloy. Rudy i Metale Nieżelazne **46**, 8, 369-372 (2001).

[12] M. Niinae, N. Komatsu, Y. Nakahiro, T. Wakamatsu, J. Shibata, Preferential leaching of cobalt, nickel and copper from cobalt – rich ferromanganese crusts with ammoniacal solutions using ammonium thiosulphate and ammonium sulfite as reducing agents. Hydrometallurgy **40**, 111-121 (1996).

[13] L. Burzyńska, E. Rudnik, W. Gumowska, The influence of phase structure on the dissolution of Cu-Co-Fe alloys in sulphuric acid and the metals recovery. Hydrometallurgy **71**, 457-463 (2004).

[14] L. Burzyńska, W. Gumowska, E. Rudnik, Odzysk miedzi ze stopu Cu-Co-Fe. Cz. I. Ługowanie w roztworach amoniakalnych. Rudy i Metale Nieżelazne **48**, 4, 166-169 (2003).

[15] L. Burzyńska, W. Gumowska, E. Rudnik, The influence of chemical com-position of Cu-Co-Fe alloys on their dissolution in ammoniacal solutions. Hydrometallurgy **71**, 447-455 (2004).

[16] L. Burzyńska, W. Gumowska,, E. Rudnik, E. Ziomek, Odzysk miedzi ze stopu Cu-Co-Fe. Cz. II.

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Odzysk miedzi z roztworu po ługowaniu amoniakalnym. Rudy i Metale Nieżelazne **49**, 2, 69-73 (2004b).

[17] L. Burzyńska, E. Rudnik, J. Partyka, Recovery of copper and cobalt from slime originated from ammoniacal leaching of high copper Cu-Co-Fe alloy. Archives of Metallurgy and Materials **50**, 4, 1027-1039 (2005).

[18] L. Burzyńska, E. Rudnik, P. Barteczko, Recovery of copper and cobalt from low copper Cu-Co-Fe alloy. Archives of Metallurgy and Materials **51**, 2, 299-308 (2005).

[19] Z. Zembura, W. Ziółkowska, L. Burzyńska, B. Chołocińska, T. Woroniecki, Zastosowanie metody hydrometalurgicznej do odzysku miedzi z surowców odpadowych, Rudy i Metale Nieżelazne **31**, 6, 182-185 (1986).

[20] K. C. Nathsarma, P. V. R. B. Sarma, Processing of ammoniacal solutions containing copper, nickel and cobalt for metal separation. Hydrometallurgy **33**, 1-2, 197-210 (1993).

[21] Y. Wang, C. Zhou, Hydrometallurgical process for recovery of cobalt from zinc plant residue. Hydrometallurgy **63**, 3, 225-234 (2002).

[22] T. M. Dreher, A. Nelson, G. P. Demopoulos, D. Filippou, The kinetics of cobalt by cementation from an industrial zinc electrolyte in the presence of Cu, Cd, Pb, Sb and Sn additives. Hydrometallurgy **60**, 2, 105-116 (2001).

[23] S. C. Das, T. Subbaiah, Electrowinning of cobalt. I.Winning from pure cobalt sulphate bath. Hydrometallurgy **12**, 3, 317-333 (1984).

[24] K. G. Mishra, P. Singh, D. M. Muir, Electrowinning of cobalt from sulphate solutions contaminated with organic impurities. Hydrometallurgy **65**, 2-3, 97-102 (2002).

[25] L. Kolditz, Chemia nieorganiczna, PWN Warszawa.