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ELECTROWINNING OF COPPER AND LEAD FROM AMMONIUM ACETATE SOLUTIONS

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This paper presents the results of laboratory studies on electrowinning of copper and lead from spent leachate obtained by leaching of copper concentrates with ammonium acetate solutions. The effect of electrolyte composition and the electrolysis current density on the process efficiency was investigated. The electrolyte was also pre-treated with ammonia before it was electrolysed under the same above-mentioned conditions.

Key words: copper concentrate, removing of lead, leaching, electrolysis

1. INTRODUCTION

In pyrometallurgical processing of copper concentrates, the relatively high content of lead in the concentrate, reaching up to 2.5%, poses a problem. Lead is concentrated mainly in by-products of pyrometallurgical processes, such as dust and sludge formed during removal of dust from metallurgical gases. There are two approaches to the problem of lead accompanying copper production: efficient capture of lead-containing waste from the pyrometallurgical production of black copper and its further processing to recover metallic lead, and reduction of lead content in copper concentrate (most often by hydrometallurgical methods) used as furnace feed material. Lead content in the concentrate can be reduced below 1% by leaching with concentrated ammonium acetate (Sanak-Rydlewska S., Bieszczad T., 2000, Sanak-Rydlewska S., 2000).

Electrolysis is one method for regenerating leachate. An advantage of this method is that some components can be removed from the system without introducing new ones (Bieszczad T., 1998). Whether a metal can be removed by electrowinning depends primarily on the standard potential of its electrode reaction. The metals easiest to recover are those with positive standard potentials (noble metals). More difficult to recover are metals whose standard potentials are negative, because gaseous

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hydrogen may develop together with metal deposition. In most cases, however, hydrogen evolution can be avoided owing to the high overpotential of hydrogen evolution on solid electrodes. In practice, the least noble metal that can be deposited by electrolysis in aqueous solutions is manganese, whose standard potential is –1.18 V. Less noble metals can be deposited in the form of amalgams at the mercury electrode or by electrolysis conducted in molten salts.

The best known and most widely applied electrolytic processes are electrorefining of copper and silver, and zinc production. About 53% of the zinc produced worldwide (and in Poland) is obtained by electrolysis (Gupta C.K., 1990). Electrowinning of copper is a final unit operation in the hydrometallurgical method for copper production (Łętowski F., 1976; Kozłowska-Kołodziej B., 1978; Kołodziej B., 1996). The method involving copper leaching-electrowinning is commercially used by many companies (Kuhn A.T., 1971). Electrolysis is conducted in solutions containing 20-70 g/dm^3 Cu^{2+} and similar amounts of sulphuric acid. In these processes the cathodes are made of copper whereas the anodes are made of lead-antimony (6-16%)-silver (0-1%) alloy. A method for obtaining copper from lean deposits that is gaining importance involves direct extraction from the deposit, followed by electrowinning (SX-EW-solvent extraction-electrowinnig) (Suttil K.R., 1993). Electrolysis done in a double membrane electrolysis cell (DMEC process) makes it possible to obtain cobalt and nickel from scrap metals. (Redden L.D., 1992). Electrolysis is also used in both electrorefining and electrowinning of lead from leachate produced by leaching spent lead batteries and other lead-containing materials (Kołodziej B, 1999). A breakthrough in regenerating solutions with very low metal contents can be the use of electrodes made of carbon fibre fabric. (Przyłuski J., 1994).

Electrowinning of metals (mainly copper) from the ammoniated solutions is much less frequent. This problem has been addressed in several papers (Marczenko N.A., 1957; Komkin W.D., 1960; Goerlich Z., 1972) examining the effect of cathodic current density, ammonia and copper ion concentrations, temperature and hydrodynamic conditions on the efficiency of electrowinning and the quality of deposits.

The use of state-of-the-art electrochemical processes in cells of unconventional design seems to be the future for precious metals recovery and waste utilization (combined with hydrometallurgy).

2. INVESTIGATION METHODS

The measurements were performed in a rectangular Plexiglass vessel containing two identical acid-resistant-steel electrodes with an active surface of 50 cm^2 each, placed of 0.5 cm apart. The electrodes were connected to a 5351-type (UNITRA UNIMA) stabilised power supply that ensured pre-set current throughout the measurement. In each of the measurements, 100 cm^3 of electrolyte were used, flowing through the electrolytic cell at a constant rate of 75 cm^3/min, forced by a peristaltic pump. During the measurements the potentials were controlled between the cathode and anode, and between the cathode and the silver-silver chloride electrode connected via a 40% ammonium acetate salt bridge. In the study, 10% and 40% ammonium acetate solutions were used, which contained about 2 g/dm^3 Cu^{2+} and 0.2 g/dm^3 Pb^{2+}; 5 g/dm^3 Cu^{2+} and 0.5 g/dm^3 Pb^{2+}; and 10 g/dm^3 Cu^{2+} and 1 g/dm^3 Pb^{2+}. The selected electrolyte concentrations correspond roughly to those obtained after leaching of copper concentrate with ammonium acetate. The electrolysis was conducted at room temperature at three different currents: 50 mA, 100 mA and 500 mA. Leachate samples were analysed for Cu and Pb content by the ICP method.

3. ANALYSIS OF ELECTRODE REACTIONS

In the constant-current electrolysis, forced reactions occur on the cathode and anode. A general principle is that the first ions discharged at the cathode are those with the highest cathodic reduction potential. On the anode, anions with the lowest anodic oxidation potential are discharged first, followed by ions of successively higher potential. The problem of determining the product of electrode reactions is solved by calculating reduction and oxidation potentials for all ions present in the solution, according to the following equations:

$$\mathrm{P_k = E_{el} - \eta_k = E^0 + (2.303RT/nF)\log a_k - \eta_k} \tag{1}$$

$$\mathrm{P_a = E_{el}' + \eta_a = E'^0 + (2.303RT/nF)\log a_a + \eta_a} \tag{2}$$

where: P_k, P_a – anodic oxidation and cathodic reduction potentials, E_{el}, E_{el}' – half-cell potentials, E^0, E'^0 – standard half-cell potentials, η_k, η_a – cathodic and anodic process overpotentials, a_k, a_a – cation and anion activities, and F - faraday.

The electrolysed solutions contained the following cations and anions: NH_4^+, Cu^{2+}, Pb^{2+}, H$^+$, CH_3COO^- and OH$^-$ Their approximate decomposition potentials can be calculated from the equations specified above.

Among the cations, ammonia ions have the highest concentration in the solution. No data exist in the literature on cathodic reduction of NH_4^+ ion, but the simplest electrode reaction has been assumed, according to the equation:

$$\mathrm{2NH_4^+ + 2e \rightarrow 2NH_{3(g)} + H_{2(g)}} \,. \tag{3}$$

On the basis of the thermodynamic data of this reaction, ΔG^0 and then the standard potential E^0 can be calculated. The calculated standard potential is – 0.651 V. The potential of ammonium ion decomposition can be evaluated by this equation:

$$P_{NH_4^+} = -0.651 + 0.059 \log[NH_4^+] - \eta_{NH_3} - \eta_{H_2} . \tag{4}$$

The calculated electrode potential (the first two terms of equation (4)) is – 0.644 V for the 10% ammonium acetate solution and – 0.609 V for the 40% solution. The hydrogen evolution overpotential in acid (pH of the studied solutions is about 5) is about 0.5 V on the iron electrode (about 0.6 V on copper electrode); no data are available on the overpotential for ammonium evolution. With the overpotential for ammonia evolution equal to zero, the potential of NH_4^+ decomposition will be below – 1 V.

Cu^{2+} ions are reduced at the cathode according to the reaction:

$$Cu^{2+} + 2e \rightarrow Cu . \tag{5}$$

The standard potential of this reaction is + 0.337 V. The electrode potential calculated for the Cu^{2+} concentration of 2 g/dm^3 is + 0.293 V, and + 0.313 V for the concentration of 10 g/dm^3. These potentials will decrease as copper ions are removed in the course of electrolysis. It is difficult to estimate the overpotential of copper ion deposition on iron and metallic copper. It depends on many factors, of which the most important is cathodic current density. At low current densities the overpotential of deposition of metal ions on the parent metals is low. Because of this, one can expect that the potential of copper ion deposition will be close to the cathode equilibrium potential in a given solution. In ammoniated solutions the electrode reaction occurs according to the equation

$$[Cu(NH_3)_4]^{2+} + 2e \rightarrow Cu_{(s)} + NH_{3(g)} \tag{6}$$

the standard potential of which is $E^o = -0.5$ V [Milazzo G., 1963].

Pb^{2+} ions will be reduced at the cathode according to the equation:

$$Pb^{2+} + 2e \rightarrow Pb \tag{7}$$

The standard potential of this reaction is –0.126 V. By assuming, as previously, low overpotential of lead deposition, the potential of Pb^{2+} decomposition in a solution with a concentration of 0.2 g/dm^3 is close to –0.215 V, and –0.194 V for a solution with a concentration of 1 g/dm^3.

Cathodic reduction of hydrogen ions in acid solutions (the pH of the studied solution is about 5) occurs according to the reaction:

$$2H^+ + 2e \rightarrow H_2 . \tag{8}$$

The potential of the hydrogen electrode depends on the pH of the solution and is – 0.295 V for pH = 5. The overpotential of hydrogen evolution on the iron electrode (in acid solution) is high and amounts to about 0.5 V, hence the hydrogen evolution potential in this system is – 0.795 V.

Even a rough estimate of the discharge potentials of cations present in the studied system demonstrates that the copper deposition reaction has the highest potential and will take place first. Theoretically, deposition of lead should begin when the electrode potential, which decreases as the copper ion concentration drops, has reached the value – 0.214 V (for Pb^{2+} concentration of 1 g/dm^3), which corresponds to very low Cu^{2+} concentrations of about 10^{-10} g/dm^3. Actually, electrolysis of lead begins much earlier. When conducting a constant-current electrolysis one should remember that cation and anion discharge overpotentials are strongly affected by the current density, although in a different fashion, and concurrent deposition of several ions may occur.

Apart from cathodic reactions, anodic oxidation takes place. Water decomposition with oxygen evolution

$$2H_2O \rightarrow O_2 + 4H^+ + 4e \qquad E^0 = 0.401\,V \tag{9}$$

anodic oxidation of acetate ion [Isaacs N. S., 1974]

$$2CH_3COO^- \rightarrow C_2H_6 + 2CO_2 + 2e \qquad E^0 = -0.364\,V \tag{10}$$

and oxidation of Pb^{2+} ions

$$Pb^{2+} + 2H_2O \rightarrow PbO_2 + 4H^+ + 2e \qquad E^o = -0.5\ V \tag{11}$$

should also be considered in the studied system.

As the overpotential for oxygen evolution on iron is about 0.25 V, the oxygen evolution potential in this system will be about 1.18 V (assuming that the solution has pH of 5).

Assuming that the overpotentials for evolution of ethane and CO_2 are similar to that of oxygen (no data are available), the decomposition potential of the acetate ion would be about 0.1 V. This means that on the anode, the water decomposition reaction will proceed, accompanied by oxygen evolution.

The oxidation potential for reaction (11) in a solution with pH = 5 and lead content of 0.2 g/dm^3 is 0.954 V, and it rises with the decrease in Pb^{2+} ion concentration. The potential thus calculated should be increased to include the overpotential for PbO_2 deposition – there are, however, no literature data about this reaction. Under the conditions of the studied electrolysis, no deposition of solid PbO_2 on the anode was observed, but evolution of gaseous products could be seen. Consequently, the overpotential for PbO_2 deposition on the steel anode must be higher than 0.02 V.

4. DECOMPOSITION VOLTAGE

Knowledge of the decomposition potentials for various electrolytes as determined from I = f(V) dependencies allows prediction of the sequence in which these ions will undergo electrode reactions.

Current as a function of the voltage applied was measured for 10% and 40% ammonium acetate solutions containing 5 g/dm^3 Cu^{2+} or Pb^{2+}, as well as solutions containing both ions at the same time but in a concentration ratio of 10 to 1. Voltage was applied to the cell electrodes from a UNITRA UNIMA type 5352 M power supplier and the current was measured with an HC–81 ammeter. The dependence of the current response to the applied potential is shown in Fig. 1. The curves are almost independent of the ammonium acetate and the presence of the other ions at a 10 times lower concentration. Only two curves are shown – one characteristic of copper ions, the other of lead ions. The discharge potentials of copper and lead ions are –1.20 V and –1.63 V, respectively.

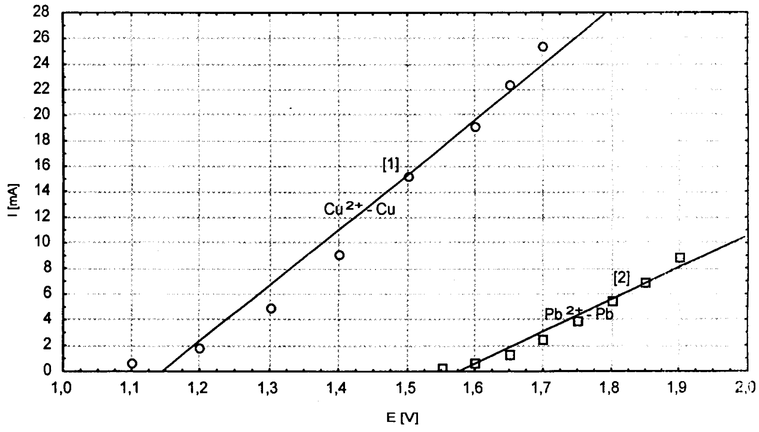

Fig. 1. Current – voltage dependence 1 – 40% solution CH_3COONH_4 + 5g/dm^3 $Cu(CH_3COO)_2$
2 – 40% solution $CH_3COOONH_4$ + 5g/dm^3 $Pb(CH_3COO)_2$

5. MEASUREMENT RESULTS AND INTERPRETATION

After one hour's leaching of copper concentrate with ammonia acetate, the solutions contained about 2 g/dm^3 Cu^{2+} and about 0.2 g/dm^3 Pb^{2+}. As concentrated ammonia acetate solutions have a high buffer capacity for lead (II), the same solution can be used several times for leaching [Bieszczad T., unpublished data]. Solutions of such high concentrations must not go into the wastewater. A method of solving this problem is electrowinning of metals from the leachate. This paper presents the results for solutions whose composition is similar to spent leaching solutions.

5.1. ELECTROWINNING OF COPPER AND LEAD FROM PURE ACETATE SOLUTIONS

The solutions to be used in electrolysis were made by dissolving appropriate amounts of copper (II) and lead (II) acetates in 10% or 40% ammonium acetate solution. In each case the Cu^{2+} concentration was 10 times higher than the Pb^{2+} concentration (roughly corresponding to the composition of spent solution after leaching of copper concentrate).

5.1.1. ELECTROLYSIS OF 10% CH_3COONH_4 SOLUTIONS

The results of electrolysis conducted in a 10% ammonium acetate solution containing about 2.5 g/dm^3 Cu^{2+} and about 0.25 g/dm^3 Pb^{2+} are shown in Table 1.

Table 1. Results of electrolysis conducted in a 10% ammonium acetate solution containing about 2.5 g/dm^3 Cu^{2+} and about 0.25 g/dm^3 Pb^{2+}

No.	I [A]	t [min]	$c_{Cu^{2+}}$ [g/dm^3]	$c_{Pb^{2+}}$ [g/dm^3]	$E_{K–A}$ [V]	E_K vs. ref. el. [V]	Current efficiency [%]
1	0.025	0 200	2.501 0.686	0.248 0.053	1.7–2.0	– 0.38 to – 0.65	~ 92
2	0.1	0 100	2.501 0.939	0.248 0.076	1.9–2.1	– 0.52 to – 0.67	~ 89
3	0.5	0 30	2.683 1.493	0.270 0.119	2.6–2.8	– 1.18 to – 1.29	~ 40

The symbols used in the table are defined as follows: I - current of electrolysis (A), t – time elapsed prior to sampling (min), $c_{Cu^{2+}}$, $c_{Pb^{2+}}$ - analytically determined concentrations of Cu^{2+} and Pb^{2+} (g/dm^3), $E_{K–A}$ - potentials of the cathode and anode (V), E_K vs. ref. el. – potential of cathode vs. the saturated silver-silver chloride electrode (V), current efficiencies calculated for electrowinning of copper (%).

The approximate current efficiencies, computed from the obtained results, depend on the electrolysis current. The highest efficiencies were obtained for the lowest currents. In all electrolyses, lead deposited along with copper and its concentration in the solution was markedly lower. The amount of deposited lead increased with the decrease in the electrolysis current. In the studied system, one should consider the possibility of unfavourable secondary chemical dissolution of deposited metallic lead and copper by ammonium acetate. This process will be affected mostly by the quality of the formed deposits, temperature and hydrodynamic conditions in the system. In the first electrolysis, a fairly compact deposit, resembling slightly soiled copper, formed on the cathode. In the next electrolysis, the deposit was brown, whereas in the last one the deposit was dark and spongy with a highly developed surface. In the electrolysis conducted at the highest current density, hydrogen evolved on the cathode, which explains the low current efficiency and the structure of the deposit. In all cases oxygen evolved at the anode.

In planning circulation and the use of leaching electrolytes in a closed cycle, one should be prepared for its enrichment in copper and lead ions. The data for solutions with higher Cu and Pb content are given in Table 2.

Table 2. Results of electrolysis conducted in a 10% ammonium acetate solution with increased content of copper and lead

No.	I [A]	t [min]	$c_{Cu^{2+}}$ [g/dm^3]	$c_{Pb^{2+}}$ [g/dm^3]	E_{K-A} [V]	E_K vs. ref. el. [V]	Current efficiency [%]
4	0.5	0 50	5.275 1.075	0.591 0.084	2.6	– 1.10 to – 1.02	~ 85
5	0.5	0 100	10.626 1.242	1.263 0.102	2.6	– 1.04 to – 1,02	~ 95

The electrolyses were performed at current of 0.5 A because of much higher concentrations of electrodeposited ions. The current densities produced under such conditions are much higher and increase with the concentration of copper and lead in the solution. The electrolysis voltage and the potential of the cathode vs. the saturated silver-silver chloride electrode are similar and almost independent of the ion concentration in the solution. On the cathode a black powdery deposit is formed, easily peeling off the electrode, and probably a very small amount of hydrogen evolves.

Electrolyses of solutions with the lowest concentrations of copper and lead were also performed with the distance between the electrodes increased to 2 cm. This change slightly improved the current efficiency of the process at the highest current density, whereas the other parameters of the process and the cathodic deposit remained the same as in the system with the electrodes spaced 0.5 cm apart.

5.1.2. ELECTROLYSIS OF 40% CH_3COONH_4 SOLUTIONS

The measurements were conducted in a 40% ammonium acetate solution, with the other conditions remaining unchanged. The results for the lowest concentrations of copper and lead ions at various electrolysis currents are given in Table 3.

The electrolysis voltage and the potential of the cathode vs. the saturated silver-silver chloride electrode are similar to those in the electrolysis done in a 10% CH_3COONH_4 solution. The current efficiencies are also similar – the highest value was observed for the lowest current density and amounted to 95%. The greatest changes in the lead concentration in the solution were obtained for the lowest electrolysis currents.

The results of measurements for higher concentrations of copper and lead at electrolysis current of 0.5 A are given in Table 4.

Table 3. Results of electrolysis conducted in a 40% ammonium acetate solution containing about 2.5 g/dm^3 Cu^{2+} and about 0.25 g/dm^3 Pb^{2+}

No.	I [A]	t [min]	$c_{Cu^{2+}}$ [g/dm^3]	$c_{Pb^{2+}}$ [g/dm^3]	E_{K-A} [V]	E_K vs. ref. el. [V]	Current efficiency [%]
6	0.05	0 200	2.962 1.020	0.287 0.059	1.9–2.1	– 0.52 to – 0.85	~ 98
7	0.1	0 100	2.962 1.281	0.287 0.080	2.1	– 0.91 to – 0.87	~ 85
8	0.5	0 30	3.040 1.980	0.280 0.155	2.8–2.6	– 1.28 to – 1.09	~ 36

Table 4. Results of electrolysis conducted in a 40% ammonium acetate solution with increased content of copper and lead

No.	I [A]	t [min]	$c_{Cu^{2+}}$ [g/dm^3]	$c_{Pb^{2+}}$ [g/dm^3]	E_{K-A} [V]	E_K vs. ref. el. [V]	Current efficiency [%]
9	0.5	0 50	5.301 1.891	0.614 0.198	2.6	– 1.12 to – 1.09	~ 69
10	0.5	0 100	12.758 4.022	1.531 0.354	2.6	– 1.00 to – 1.07	~ 88

The cathode deposits formed in both electrolyses are spongy, brittle and black, and easily peel off the electrode. After electrolysis with higher metal content, small grains of metallic copper were easily discernible in the deposit.

5.2. ELECTROWINNING OF COPPER AND LEAD FROM AMMONIATED SOLUTIONS

The solutions used in earlier experiments were treated with ammonia following the same procedure in each case: 5 cm^3 of concentrated ammonia water was added to 100 cm^3 of a 10% or 40% CH_3COONH_4 solution with an appropriate Cu^{2+} and Pb^{2+} content, the solution was filtered off, and 100 cm^3 of the filtered solution was taken for electrolysis. The treatment with ammonia had two goals: to complex copper ions and to partially precipitate lead by increasing the pH of the solution. The first objective was reached; the solution turned deep blue, a colour characteristic of tetra-ammino copper complexes. Analyses showed that the high stability of the acetate complexes of lead prevented precipitation of the sparingly soluble lead (II) hydroxide. The results of electrolyses conducted in ammoniated solutions, shown in the tables below, were obtained under conditions analogous to those specified earlier.

5.2.1. ELECTROLYSIS OF 10% $CH_3COONH_4 + NH_3$ SOLUTIONS

The results of measurements done in ammoniated 10% ammonium acetate solutions at various currents of electrolysis are given in Table 5.

Table 5. Results of electrolysis conducted in an ammoniated 10% ammonium acetate solution containing about 2.5 g/dm^3 Cu^{2+} and about 0.25 g/dm^3 Pb^{2+}

No.	I [A]	t [min]	$c_{\mathrm{Cu}^{2+}}$ [g/dm^3]	$c_{\mathrm{Pb}^{2+}}$ [g/dm^3]	E_{K-A} [V]	E_K vs. ref. el. [V]	Current efficiency [%]
11	0.05	0 200	2.466 1.040	0.222 0.035	1.5–1.6	– 0.51 to – 0.62	~ 72
12	0.1	0 100	2.466 1.054	0.222 0.041	1.9–2.1	– 0.62 to – 0.83	~ 71
13	0.5	0 30	2.407 1.334	0.214 0.062	2.4	– 1.27 to – 1.09	~ 36

The voltage of electrolysis and of the cathode vs. the saturated silver-silver chloride electrode are similar to those in electrolyses without ammonia (Table 1), whereas the current efficiencies are lower at low current densities. For currents of 0.05 A and 0.1 A the copper deposit produced on the cathode was glossy and relatively compact, whereas at 0.5 A the cathode was covered with a spongy deposit. One should note the high depletion of lead ions in ammoniated solution.

The results of electrolyses of solutions with higher copper and lead concentrations are shown in Table 6.

Table 6. Results of electrolysis conducted in ammoniated 10% ammonium acetate with increased content of copper and lead

No.	I [A]	t [min]	$c_{\mathrm{Cu}^{2+}}$ [g/dm^3]	$c_{\mathrm{Pb}^{2+}}$ [g/dm^3]	E_{K-A} [V]	E_K vs. ref. el. [V]	Current efficiency [%]
14	0.5	0 50	4.828 1.633	0.437 0.136	2.3	–1.19 to – 1.24	~ 65
15	0.5	0 100	10.313 1.532	1.219 0.075	2.6	– 1.03 to – 1.00	~ 89

The obtained current efficiencies are lower than those obtained in corresponding non-ammoniated solutions. In both cases, simultaneous evolution of gaseous hydrogen on the cathode was noted. The black deposit forming on the cathode easily peeled off the electrode, and at higher concentrations it became greasy.

5.2.2. ELECTROLYSIS OF 40% CH_3COONH_4 + NH_3 SOLUTIONS

The results of measurements conducted in ammoniated solutions at various currents of electrolysis are shown in Table 7.

Table 7. Results of electrolysis conducted in an ammoniated 40% ammonium acetate solution containing about 2.5 g/dm^3 Cu^{2+} and about 0.25 g/dm^3 Pb^{2+}

No.	I [A]	t [min]	$c_{\mathrm{Cu}^{2+}}$ [g/dm^3]	$c_{\mathrm{Pb}^{2+}}$ [g/dm^3]	$E_{K–A}$ [V]	E_K vs. ref. el. [V]	Current efficiency [%]
16	0.05	0 200	2.533 0.847	0.198 0.027	1.6–2.6	– 0.58 to – 0.90	~ 85
17	0.1	0 100	2.533 1.250	0.198 0.063	2.0–2.1	– 0.57 to – 0.98	~ 65
18	0.5	0 30	2.533 1.680	0.198 0.125	2.4	– 1.15 to – 1.24	~ 29

The highest current efficiencies and the highest depletion of lead ions were noted for the lowest current densities. Irrespective of the current value, a black, spongy, easily peeling deposit is formed at the cathode

Table 8 presents the results of electrolysis of ammoniated solutions with higher concentrations of copper and lead.

Table 8. Results of electrolysis conducted in an ammoniated 40% ammonium acetate with increased content of copper and lead

No.	I [A]	t [min]	$c_{\mathrm{Cu}^{2+}}$ [g/dm^3]	$c_{\mathrm{Pb}^{2+}}$ [g/dm^3]	$E_{K–A}$ [V]	E_K vs. Ref. el. [V]	Current efficiency [%]
19	0.5	0 50	5.327 2.171	0.628 0.196	2.5–2.6	– 1.19 to – 1.13	~ 64
20	0.5	0 100	10.130 2.841	1.265 0.332	2.6	– 1.33 to – 1.28	~ 74

The obtained current efficiencies are not high, a results of the noticeable evolution of gaseous hydrogen. Under conditions of electrolysis No. 19, the deposit formed on the cathode was similar to deposits obtained in earlier electrolyses, whereas during the electrolysis of the solution with the highest metal content, a black, greasy deposit formed on the cathode.

6. SUMMARY

The electrolysis of solutions with low content of metals has drawn interest due to its possible application to industrial fluid and wastewater treatment. In this study electrolysis was used to investigate regeneration of concentrated ammonium acetate solutions formed as a result of leaching of lead from copper concentrate.

Theoretical calculations and the experimental values of decomposition potentials show that in the system under study, copper and lead are co-deposited on the cathode, with gaseous hydrogen being also evolved at high current densities.

The current efficiency of the process, calculated relative to copper, is almost independent of the ammonium acetate concentration and of whether or not the solution is ammoniated. The current efficiency decreases (for the same composition) with the increase in current density, and increases with an increase in copper and lead.

The lower the cathodic current density, the higher the changes in lead ion concentration. Greater changes are noted in ammoniated solutions.

The voltages of electrolysis and the potentials of the cathode vs. the saturated silver-silver chloride electrode increase with the increase in current density, and are independent of the ammonium acetate concentration.

The cathodic current density and electrolyte composition affect the quality of the cathodic deposit. Deposits obtained at low current densities are more compact, whereas those obtained at higher current densities are spongy and easily peel off the electrode.

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W artykule przedstawiono wyniki badań laboratoryjnych nad procesem elektrowydzielania miedzi i ołowiu z roztworów modelowych, o składzie podobnym do tego, jakie uzyskuje się w procesie ługowania koncentratów miedziowych roztworami octanu amonowego. Dla roztworów modelowych przebadano wpływ składu roztworu elektrolitu i wielkości prądu elektrolizy na wydajność procesu. Zastosowano również wstępną obróbkę elektrolitu amoniakiem, po której poddano roztwór elektrolizie w takich samych warunkach, jakie stosowano dla roztworów bez dodatku amoniaku.

Z przeprowadzonych obliczeń teoretycznych i z wyznaczonych doświadczalnie napięć rozkładowych wynika, że w badanym układzie na katodzie zachodzi reakcja współwydzielania miedzi i ołowiu a przy wysokich prądach także gazowego wodoru. Wydajność prądowa procesu, liczona w stosunku do miedzi, prawie nie zależy od stężenia octanu amonowego i od tego czy roztwór poddawany procesowi elektrolizy zawierał amoniak, czy nie. Wydajność maleje (przy stałym składzie roztworu) ze wzrostem prądu elektrolizy, natomiast rośnie ze wzrostem stężenia miedzi i ołowiu w elektrolicie. Zmiany stężenia jonów ołowiu są tym większe im mniejszy jest prąd elektrolizy. Większe zmiany stężeń ołowiu występują w roztworach amoniakalnych. Napięcia elektrolizy, jak i potencjały katody względem nasyconej elektrody chlorosrebrowej, rosną ze wzrostem prądu elektrolizy, natomiast nie zależą od stężenia octanu amonowego.

Przy niskich wartościach prądu otrzymuje się osady bardziej zwarte a przy wyższych, gąbczaste, łatwo odpadające od elektrody. Ponieważ otrzymane osady w procesie elektrolizy stanowią mieszaninę miedzi i ołowiu, w przyszłości będą przedmiotem badań nad ich rozdziałem, w celu odzyskania czystych metali.