

REMOVAL OF COBALT AND NICKEL FROM ZINC SULPHATE SOLUTIONS USING ACTIVATED CEMENTATION

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(Received 21 August 2004, accepted 15 October 2004)

Abstract

The influence of different parameters (duration, temperature, zinc dust quantity, concentration of activators - copper and antimony) on the process of activated cementation of Co and Ni has been studied. We have worked with industrial zinc sulphate solutions. During the process of activated cementation of Co and Ni, copper (involved as $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$) and antimony (involved as Sb_2O_3) were used as activators. The lowest values of Co content have been obtained at a temperature of 80-85 °C, $C_{\text{Cu}} = 200\text{-}300 \text{ mg/dm}^3$ and 18 multiple surplus of zinc dust. After adding Cu to the solution, mainly the cementation of Ni is activated, and that of Co is activated to a lower degree. It was found that when $G_{\text{Sb}} : G_{\text{Co}}$ ratio is between 0.5 : 1 and 2 : 1, the solution is purified from Co and Ni to a great degree. After intensive stirring and increasing the duration of the process the cement sediments dissolve reversely. This holds true of Co to a greater extent, as compared to Ni. The results obtained will be used to establish optimal conditions for the carrying out of activated cementation in Zinc Production Plant in KCM SA, Plovdiv.

Keywords: zinc sulphate, cobalt, nickel, activated cementation, Sb_2O_3

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1. Introduction

The purity of the zinc sulphate solution, which is fed for electrolysis, is of great importance since the purity and structure of cathode zinc depend on it, as well as the coefficient of current utilization, the power consumption, the voltage of the tanks and other indices, which determine the zinc cost price [1].

The metal impurities, which are more precious than zinc, can influence the purity of the cathode sediment through co-sedimentation and some of the impurities (cobalt, nickel and copper) facilitate the reverse dissolution of zinc [2] by forming microgalvanic cells with it [1]. The harmful effect of these impurities is increased at higher temperatures and acidity of electrolyte, as well as at the simultaneous presence of Sb and Ge, Co and Cu and other elements in the solution.

When the chemical methods for cobalt sedimentation are used, the nickel practically remains in the solution. For this reason many of the zinc plants have recently orientated to the implementation of activated cementation of cobalt and nickel with zinc dust. Due to the activated cementation the zinc sulphate solution is purified more completely from other microimpurities, too, such as Ge, In, Se, Te etc. and at the same time the total purity of the solution is significantly improved. The cobalt and nickel sedimentation with zinc powder is possible in the presence of activating agents and high temperature (65-95 °C). The process is called activated cementation [1].

The additives supporting the process must have a more positive potential than zinc since they form with cobalt and nickel intermetallic compounds or mixed phases with a more positive potential [3].

The activators, which are used in the process, have been selected in an empirical way. It is common practice to use as activators compounds of arsenic and antimony in combination with copper ions. It has been found that cobalt sedimentation during the process is due to two reactions. One of them is formation of Co alloy or cobalt in hard solution. The second reaction is formation of basic cobalt salts and it is a function of the high local pH on the zinc surface and the concentration of Zn^{2+} ions. This high pH value is as a result of hydrogen liberation. The hydrogen formation stops when the core of metal zinc in the cemented fractions is exhausted and the basic cobalt salts can be dissolved back. These salts are dissolved much easier than Co alloys and

this is the main reason for the back dissolution of cobalt during the activated cementation process [4].

The examinations of the cemented product with Raman spectroscopy before the reverse dissolution of cobalt have ascertained equal spectra of the cemented product and Co(OH)_2 in ZnO matrix or a mixture of $\text{CoO} \times \text{ZnO}$ [5].

It is known from theory that in the presence of Zn^{2+} ions cobalt cannot settle in a pure form, but as a Co-Zn alloy which consists mainly of sub-potentially settled zinc [6]. As a rule the presence of Zn^{2+} ions slows down the cobalt cementation in the absence of activators.

With the absence of Zn^{2+} ions in the solution cobalt is cemented comparatively quickly until it reaches very low concentrations. It is assumed that the zinc sulphate solution influences negatively the cementation of cobalt and it happens most probably through adsorption of Zn^{2+} ions on the surface of zinc powder thus making its effect passive. The results obtained from the experiments conducted with the aim to study the influence of Zn^{2+} ions confirm their suspension effect on the cementation as a result of the adsorption of ZnOH^+ on the zinc powder [7].

The absence of copper in the zinc sulphate solution influences most strongly the cementation of nickel. Its settling is less influenced by the absence of As activator than by the absence of copper. Even in the presence of As activator, copper influences to a greater extent the cementation of nickel [3].

Cd^{2+} ions with quantity up to 100 mg/dm^3 have a combined effect with Cu/Sb additive and they bring the concentration of cobalt in the solution to much lower values as compared to the influence of Cu/Sb only. It is known from practice that some plants feed lead (PbO , PbSO_4 or zinc powder alloyed with lead) in the process of removing cobalt and nickel. It is supposed that lead stabilizes the sediment and prevents the cemented cobalt from reverse dissolution [7].

The activated cementation process can be carried out with the help of the double alloys, too, Zn-Al and Zn-Cd [8]. With the purpose to increase the extent of cobalt settling it was suggested that the cementation be carried out with dust from a Zn-Sb alloy, mixed with 0.1 – 5 % graphite dust. The maximum settling of Co was achieved at 5 % graphite consumption [9]. A

process flow diagram is put forward to purify the solution from Cu, Cd, Co, Ni, As, Sb, Ge and Fe through cementation with the help of zinc pellets with $d=3-30\text{mm}$. The process is activated by Sb_2O_3 and carried out under $85-95\text{ }^\circ\text{C}$ of temperature. The final removal of impurities, however, is accomplished with the presence of zinc dust in the solution.

Potassium antimonyl tartrate $\text{KSbC}_4\text{O}_7\text{H}_4.1/2\text{H}_2\text{O}$ is most often used in practice as an activator containing antimony [10]. The deepest purification of Co^{2+} ions with an additive of $\text{KSbC}_4\text{O}_7\text{H}_4.1/2\text{H}_2\text{O}$ is achieved under a concentration of $5-10\text{ mg/dm}^3$ of Sb^{3+} ions in the solution. If the concentration values are higher, then the extent of cobalt purification decreases [11].

Except for this additive, Schlippe's salt - $\text{Na}_3\text{SbS}_4.9\text{H}_2\text{O}$ is also used. When this antimony-containing additive is added nickel and cobalt are co-settled with cadmium and they are taken out of the process with the spent electrolyte [12].

When a metal antimony activator is added we have ascertained a higher degree of cobalt settling as compared to the presence of Schlippe's salt activator. The optimal parameters of the process are: temperature of $70\text{ }^\circ\text{C}$ and copper concentration of 40 mg/dm^3 [13].

The arsenic-containing activator, which is used most often for the cementation of cobalt and nickel, is As_2O_3 [3].

Some authors put forward the following permanent factors for the activated cementation process with satisfactory results: temperature $50-90\text{ }^\circ\text{C}$, zinc dust concentration – 5 g/dm^3 , duration of process $15-60\text{ min}$ and ratio $\text{Co:Sb}=1:1$ [14].

Recently, researchers have been working on the possibilities to replace the activators used at present with new and more effective ones. The influence of the following elements has been studied: Sn II, Te IV, In III, Bi III, Pb II, Hg II, Se IV, Ge IV and Ag I on the extent of cobalt settling.

Among these elements it was found that tin is just as much efficient as antimony [7]. The best results were obtained with the following three combinations: Sb-Cu-Cd, Sb-Pb-Cu-Cd and Sn-Cu-Cd.

The main part of the data in the literature on cementation of cobalt and nickel refers to artificial solutions. There is scanty information on the cementation from industrial solutions. In this connection, the purpose of the

present work is to study the activated cementation of Co and Ni from industrial solutions at the presence of Sb_2O_3 activator and recommend conditions for obtaining the maximum degree of cementation of Co and Ni impurities.

2. Experimental

The initial solutions used during the experiments have been taken from the Zinc Production Plant in KCM SA, Plovdiv after purification from copper through cementation. The composition of the initial neutral solutions is shown in Table 1.

Table 1. Chemical composition of the solutions for activated cementation

Solution 1	Component, mg/dm ³					
	Cu	Cd	Co	Ni	Ge	Sb
1	26	134	13.8	1.1	0.67	0.005
2	0.1	147.6	12.6	3.8	0.055	0.010

Zinc powder produced in KCM SA, $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, pure for analysis and Sb_2O_3 (Fluka), pure for analysis have been used to carry out the activated cementation process.

Each experiment is conducted with 1 dm³ volume of solution. The reagents are fed one by one and after reaching a certain temperature and respective duration of time a sample is taken for analysis.

The influence of the following five main factors on the process of activated cementation has been studied: temperature, duration, zinc powder quantity, Cu^{2+} quantity and Sb_2O_3 quantity which are determined by the Co:Sb ratio. We can conclude from the information from scientific sources that higher temperatures increase the speed of the process.

At higher temperatures, however, there is the risk of starting the reverse process – dissolution of the cement sediment. That's why it is necessary to determine exactly at what temperature the activated cementation process is carried out under a satisfactory speed in the right direction.

Most scientific sources indicate temperature of 65-90 °C. In our

experiments the temperature varied between 75-85 °C.

There is no unanimous opinion regarding the duration of the activated cementation. Some authors recommend 15-60 min [14], others – 3 h. The experiments were conducted with duration of 120-150 min.

Zinc powder plays the role of cementing agent for Co^{2+} and Ni^{2+} ions at the activated cementation. In most plants the fed quantity of zinc powder is a 10-18 multiple surplus.

In our experiments the fed quantity of zinc powder varied between 15, 18 and 20 multiple surplus. Copper plays the role of an activating additive supporting the cementation process. In the experiments Cu^{2+} ions were added in the form of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ in different quantities to supply Cu^{2+} to the following concentrations: 100, 150, 200 and 300 mg/dm^3 .

The antimony quantity is of vital importance for the process and that's why a significant number of experiments were made with the purpose to determine the necessary quantity. In our experiments antimony was supplied in the form of Sb_2O_3 . In order to determine the necessary quantity the $G_{\text{Sb}}:G_{\text{Co}}$ ratio was within the limits of 0.25:1 to 2:1.

3. Results and discussion

Part of the results from the activated cementation of Co and Ni at the ratio of $G_{\text{Co}}:G_{\text{Sb}} = 1:1$, as related to the concentration of the two impurities in the industrial sulphate solution, are represented in Table 2 and Fig. 1-4.

3.1. Influence of the temperature

It was found that at all three temperatures under which the experiments were conducted – 75 °C, 80 °C, and 85 °C the process goes on with satisfactory results with respect to the final minimal values of the cobalt and nickel concentrations.

The lowest values of cobalt content in the solution after cementation were obtained at 80 °C and 85 °C, and they are respectively 0.075 mg/dm^3 and 0.078 mg/dm^3 .

Table 2. Co and Ni content at activated cementation with 18 multiple surplus of zinc dust, different temperatures and Cu content ($G_{Co} : G_{Sb} = 1:1$)

t, °C	τ , min	$C_{Cu} = 100,$ mg/dm ³		$C_{Cu} = 200,$ mg/dm ³		$C_{Cu} = 300,$ mg/dm ³	
		$C_{Co},$ mg/dm ³	$C_{Ni},$ mg/dm ³	$C_{Co},$ mg/dm ³	$C_{Ni},$ mg/dm ³	$C_{Co},$ mg/dm ³	$C_{Ni},$ mg/dm ³
75	0	12.6	1.1	12.6	1.1	12.6	1.1
	60	0.45	0.15	0.20	0.20	0.50	0.10
	75	0.10	0.09	0.25	0.20	0.24	0.20
	90	0.45	0.30	0.12	0.25	0.80	0.03
	120	0.58	0.10	0.60	0.40	0.40	0.03
80	45	1.40	0.40	0.35	0.20	0.40	0.10
	60	0.60	0.50	0.09	0.30	0.08	0.10
	75	0.30	0.10	0.08	0.20	0.12	0.30
	90	0.17	0.30	0.20	0.25	0.10	0.20
	120	0.40	0.20	0.30	0.30	0.21	0.21
85	45	1.3	0.09	0.20	0.20	0.13	0.07
	60	0.85	0.02	0.31	0.10	0.09	0.15
	75	0.60	0.07	0.11	0.15	0.08	0.20
	90	0.70	0.20	0.05	0.20	0.31	0.20
	120	0.35	0.30	0.15	0.15	0.91	0.30

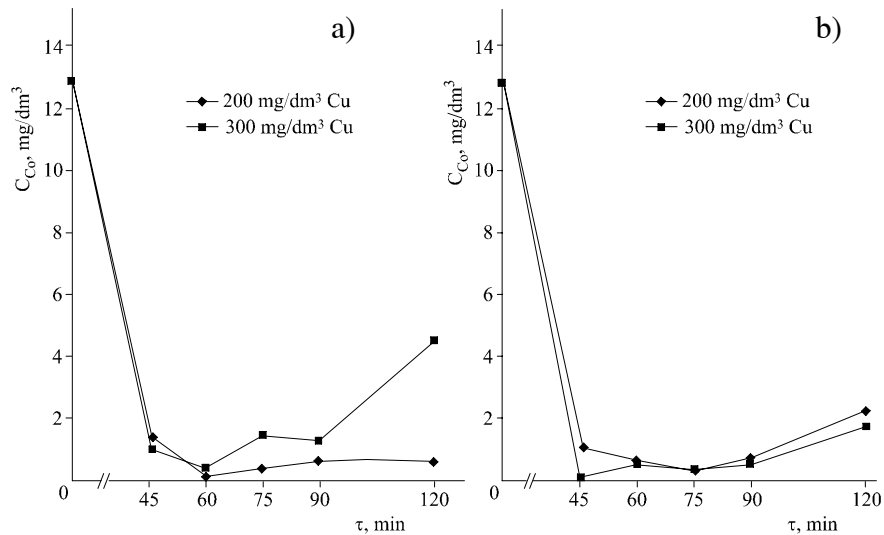


Fig.1. Influence of time on the Co content at differing Cu contents and zinc dust surplus (a – 15x, b – 20x, $t = 80$ °C, $G_{Co} : G_{Sb} = 1:1$)

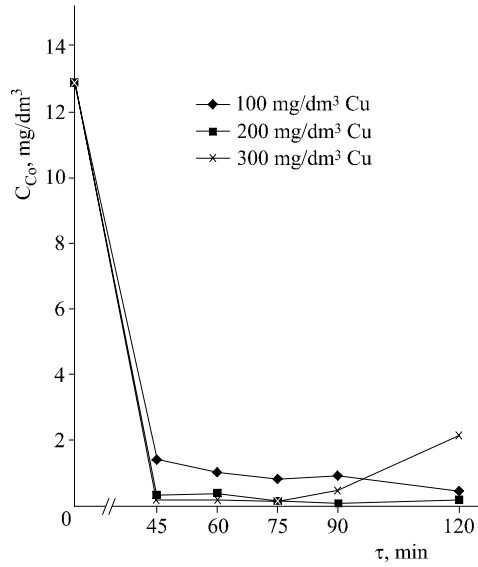


Fig.2. Co content at 18 multiple surplus of zinc dust and different Cu contents in the solution ($t = 85\text{ }^{\circ}\text{C}$; $G_{Co} : G_{Sb} = 1:1$)

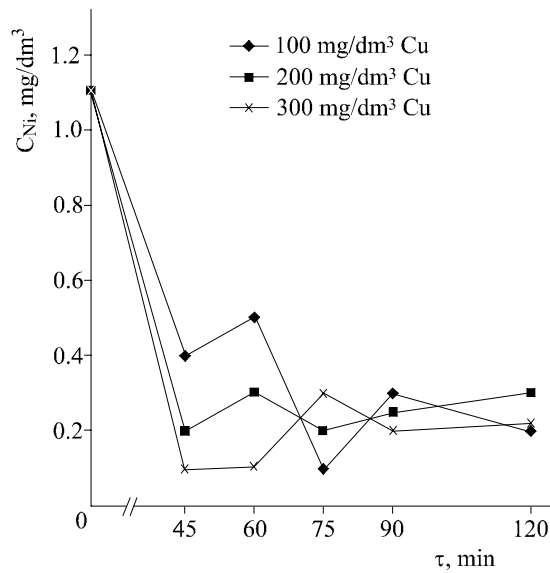


Fig.3. Influence of 18 multiple surplus of zinc dust on the cementation of Ni ($t = 80\text{ }^{\circ}\text{C}$; $G_{Co} : G_{Sb} = 1:1$)

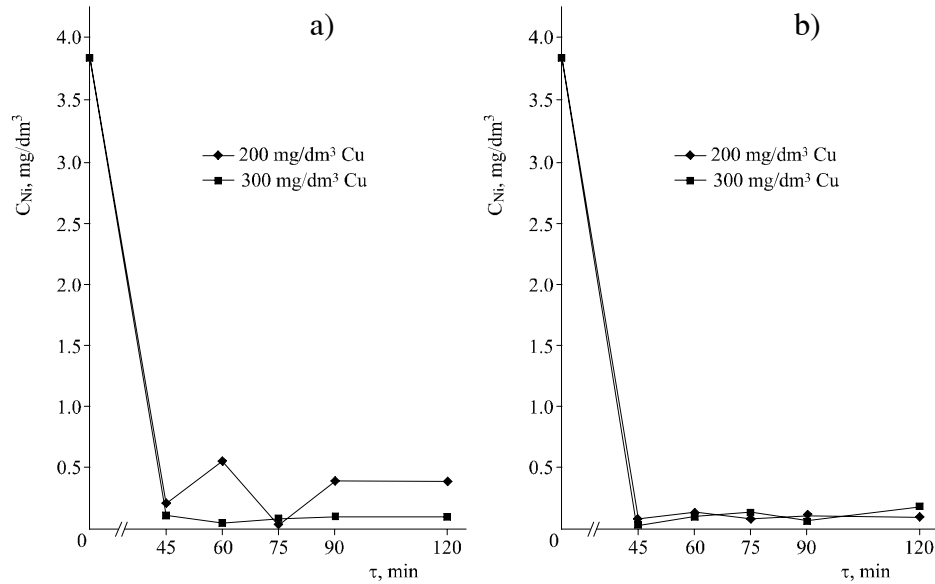


Fig.4. Influence of the zinc dust quantity on the cementation of Ni
(a – 15x; b – 20x; $t = 85\text{ }^{\circ}\text{C}$; $G_{Co} : G_{Sb} = 1:1$)

It was also observed that there is a process going on of reverse dissolution of the cemented quantity of cobalt. Nickel possess low values of concentration at all three temperatures and they remain permanent and stable all the time. The lowest concentrations of nickel are $0.02\text{ mg/dm}^3\text{ Ni}$ under temperature of $85\text{ }^{\circ}\text{C}$ and 0.03 mg/dm^3 under temperatures of $80\text{ }^{\circ}\text{C}$ and $75\text{ }^{\circ}\text{C}$.

3.2. Influence of the process duration

We can conclude from the results obtained that the concentration of cobalt reaches its minimal values after a certain period of time. But after that they begin increasing again, which is due to the process of reverse dissolution of the cemented cobalt.

The activated cementation process for cobalt passes through a minimum, which in this case is within the interval of 45-75 min. With the increase of the temperature the time necessary to reach the minimum reduces. After 45 min. and under a temperature of $85\text{ }^{\circ}\text{C}$ the concentration starts increasing.

Regarding the concentration of nickel the achieved low values most often remain unchanged throughout the process.

3.3. Influence of the zinc dust quantity

From the presented data we can see that when the zinc dust is in quantities 15-20 multiple surplus over the stoichiometric necessary quantity for the sedimentation of copper, cadmium, cobalt and nickel, then values of cobalt and nickel concentration are achieved that meet the requirements for a solution which is to undergo electrolysis.

Very low values of the cobalt concentration are reached at 18 multiple surplus and temperature of 80-85 °C – 0.075 mg/dm³ and 0.078 mg/dm³. At 15 and 20 multiple surplus values above 1 mg/dm³ have been recorded. The most possible reasons for these results are partial pelletization of the zinc dust particles or influence of the other factors: temperature and quantity of Cu²⁺ ions.

All the results obtained for the concentration of nickel meet the requirements for pure solution by varying within the interval of 0.02-0.4 mg/dm³.

3.4. Influence of the copper ions content

The Cu²⁺ ions content plays an important role for the cementation of nickel, and a minor one for the cementation of cobalt. The fed quantities of Cu²⁺ ions are: 100, 150, 200 and 300 mg/dm³.

The lowest values for the concentration of cobalt are at 200÷300 mg/dm³ copper ions. At a concentration of 100÷150 mg/dm³ Cu²⁺ ions cobalt concentration values are observed even above 1 mg/dm³.

The results obtained give the reason to make the following conclusions:

- The lowest values of cobalt concentration - 0.075 mg/dm³ and 0.078 mg/dm³ have been obtained respectively at: t=80 °C, C_{Cu} = 200 mg/dm³ and 18 multiple surplus of zinc dust and t = 85 °C, C_{Cu} = 300 mg/dm³ and 18 multiple surplus of zinc dust.

- The results, which were obtained for nickel in the course of the process, are under 1 mg/dm³. The lowest concentration is 0.02 mg/dm³ and it has been

obtained at $t = 85\text{ }^{\circ}\text{C}$, $C_{\text{Cu}} = 100\text{ mg/dm}^3$ and 18 multiple surplus of zinc dust.

- In order to reach the minimum of the process for the shortest possible time the following parameters are suitable – temperature $85\text{ }^{\circ}\text{C}$ and 45 min. duration, but in this case the reverse dissolution process comes to the front.

- From the point of view of stability of results in the course of time, the best conditions are at $t=75\text{-}80^{\circ}\text{C}$, 300 mg/dm^3 concentration of copper ions and 18 multiple surplus of zinc dust.

Based on the conclusions made at $G_{\text{Co}} : G_{\text{Sb}} = 1:1$ experiments have been conducted under different $G_{\text{Co}} : G_{\text{Sb}}$ ratios and $C_{\text{Cu}} = 100\div 300\text{ mg/dm}^3$, temperature $75\text{-}85\text{ }^{\circ}\text{C}$ and 18 multiple surplus of zinc dust over the stoichiometric necessary quantity for the sedimentation of copper, cadmium, cobalt and nickel (Table 3 and Fig. 5-7).

*Table 3. Co and Ni content at activated cementation with 18 multiple surplus of zinc dust and differing temperatures
($G_{\text{Co}} : G_{\text{Sb}} = 1:1$; $C_{\text{Cu}} = 200\text{ mg/dm}^3$)*

τ , min	Co, mg/dm^3			Ni, mg/dm^3		
	$75\text{ }^{\circ}\text{C}$	$80\text{ }^{\circ}\text{C}$	$85\text{ }^{\circ}\text{C}$	$75\text{ }^{\circ}\text{C}$	$80\text{ }^{\circ}\text{C}$	$85\text{ }^{\circ}\text{C}$
0	13.8	13.8	13.8	3.8	3.8	3.8
45	0.60	0.26	0.22	0.5	0.10	0.10
60	0.57	0.13	0.25	0.18	0.24	0.10
75	0.45	0.21	0.26	0.13	0.07	0.04
90	1.2	0.55	0.38	0.10	0.09	0.02

The results proved that the decrease in the quantity of added antimony ions worsens the activated cementation process with regard to the concentration of cobalt. The lowest value obtained for Co at the tested temperatures is under 0.9 mg/dm^3 while values of $4\div 6\text{ mg/dm}^3$ have been recorded at the same time.

At $t = 80\text{ }^{\circ}\text{C}$ the lowest values for C_{Co} (under 0.6 mg/dm^3) are within the interval of 60-90 min. These results are unstable in time and are higher than the results obtained under the same conditions and at $G_{\text{Co}} : G_{\text{Sb}} = 1 : 1$.

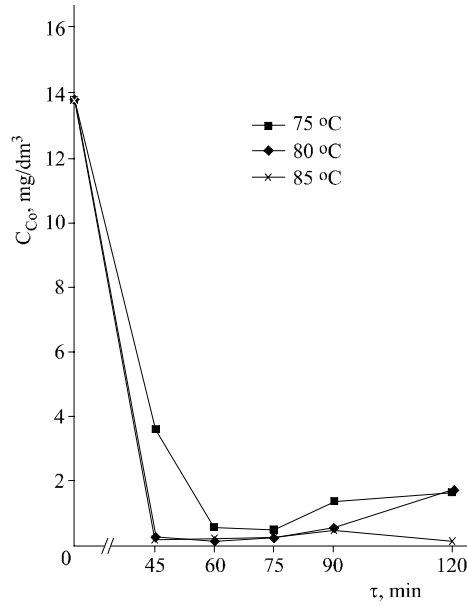


Fig.5. Influence of the temperature on the activated cementation of Co (18 multiple surplus of zinc dust ($G_{Co} : G_{Sb} = 1:0.5$; $C_{Cu} = 200 \text{ mg/dm}^3$))

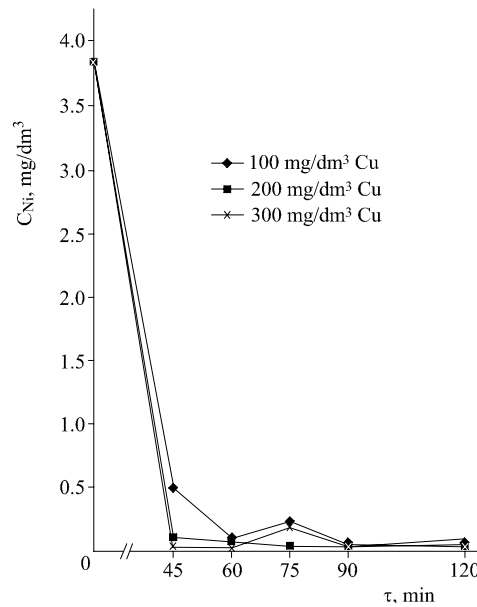


Fig.6. Influence of the Cu content in the solution on the activated cementation of Ni ($t = 85 \text{ °C}$; $G_{Co} : G_{Sb} = 1:0.5$)

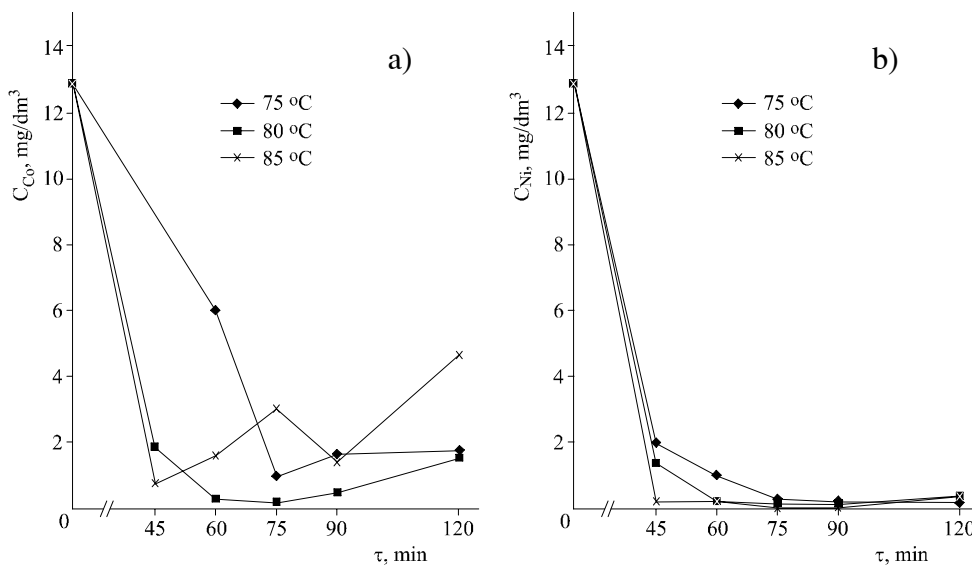


Fig. 7. Influence of the temperature on the process of activated cementation of Co (a) and Ni (b) at $C_{Cu} = 200 \text{ mg/dm}^3$ and 18 multiple surplus of zinc dust ($G_{Co} : G_{Sb} = 1:0.25$)

Nevertheless, the results obtained for C_{Ni} under the differing conditions are within the interval of $0.02 \div 0.2 \text{ mg/dm}^3$ and they completely meet the requirements for a solution which is to undergo electrolysis.

The activated cementation which is conducted with Sb_2O_3 activator at $G_{Co} : G_{Sb} = 1 : 0.25$ ratio does not meet the requirements for obtaining pure electrolyte with regard to cobalt and that's why these conditions are not recommended for industrial implementation of the process.

A series of experiments has been conducted under the following conditions: $t = 75 \div 85 \text{ }^\circ\text{C}$; $C_{Cu} = 100 \div 300 \text{ mg/dm}^3$; zinc dust quantity – 15, 18 and 20 multiple surplus and $G_{Co} : G_{Sb} = 1 : 2$ ratio. The results give us the reason to make the following conclusions:

After reaching the minimal values for C_{Co} at $t = 75 \text{ }^\circ\text{C}$ and $t = 85 \text{ }^\circ\text{C}$ and $C_{Cu} = 100 \div 300 \text{ mg/dm}^3$, their stability is observed in the 60-90 min. interval. These minimal values are in the $0.1 \div 0.8 \text{ mg/dm}^3$ interval. The values for C_{Co} at $C_{Cu} = 100 \text{ mg/dm}^3$ at all three temperatures are above 1 mg/dm^3 .

At $t = 85\text{ }^{\circ}\text{C}$ and $C_{\text{Cu}} = 200\div 300\text{ mg/dm}^3$ the minimal values for cobalt concentration are within the interval of $0.2\div 0.4\text{ mg/dm}^3$. These values are obtained quickly in the course of time (45-60 min) and after that the process of reverse dissolution of cobalt is observed.

Regarding the concentration of nickel at all three temperatures there are results under 1 mg/dm^3 , which remain stable in the course of time.

While the process is going on, with the increase of the quantity of Cu^{2+} ions the minimal values for cobalt concentration are reached more quickly. The same thing is observed with the increase of temperature, too, but the process of reverse dissolution of cobalt is recorded.

The results, obtained for C_{Co} at 15 multiple surplus of zinc dust are approximately by $0.1\div 0.3\text{ mg/dm}^3$ higher than those obtained at 18 and 20 multiple surplus. At all three multiple surpluses the results which are obtained for C_{Co} and C_{Ni} are under 0.2 mg/dm^3 and they meet the requirements for electrolysis. It is obvious from the results that at $C_{\text{Cu}} = 100\text{ mg/dm}^3$ no values are recorded for C_{Co} lower than 1 mg/dm^3 , while at $C_{\text{Cu}}^{2+} = 200\div 300\text{ mg/dm}^3$ there are results which meet the requirements for electrolysis.

The lowest values for $C_{\text{Co}} = 0.11\text{ mg/dm}^3$ and $C_{\text{Co}} = 0.13\text{ mg/dm}^3$ are obtained respectively at $t = 75\text{ }^{\circ}\text{C}$, $C_{\text{Cu}} = 300\text{ mg/dm}^3$ and 18 \div 20 multiple surplus of zinc dust. It was found from the results that any concentration of copper ions contributes to the cementation of nickel from the zinc sulphate solution.

4. Conclusions

1. The lowest values for C_{Co} in the zinc sulphate solution (0.075 mg/dm^3 and 0.078 mg/dm^3) are obtained respectively at:

$t = 80\text{ }^{\circ}\text{C}$, $C_{\text{Cu}} = 200\text{ mg/dm}^3$ and 18 multiple surplus of zinc dust

$t = 85\text{ }^{\circ}\text{C}$, $C_{\text{Cu}} = 300\text{ mg/dm}^3$ and 18 multiple surplus of zinc dust

These values for C_{Co} are obtained at $G_{\text{Co}} : G_{\text{Sb}} = 1:1$.

2. It was found that with the decrease of the quantity of Sb activator the final content of Co in the solution increases. Nevertheless, with the low content of antimony in the solution there are still satisfying values for C_{Co} ,

which meet the requirements for zinc electrolysis.

3. The experiments conducted indicate that the best results are obtained at 18 multiple surplus of zinc dust in relation to the stoichiometric necessary quantity for the sedimentation of Cu, Cd, Co and Ni.

4. The addition of copper in the solution activates to a greater extent the cementation of Ni and to a smaller extent the cementation of Co.

5. It was found that at $C_{Cu} = 150 \div 200 \text{ mg/dm}^3$ in the solution the cementation of Co and Ni is going on to the greatest extent.

6. By intensive stirring and increasing the duration of the process reverse dissolution of the cement sediment is observed. This is true for a greater extent of Co than Ni.

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