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ELECTROWINNING OF COBALT FROM SULFATE-CHLORIDE AND SULFATE SOLUTIONS OF COBALT AND MANGANESE UNDER DYNAMIC CONDITIONS

The design of an electrolyzer for electrowinning in dynamic conditions is developed. The dependence of the results of electrowinning of cobalt and manganese from sulfate and sulfate-chloride solutions under dynamic conditions using a titanium cathode and a lead anode with 1 % of silver was studied. It was found that the best extraction results for the current yield and the specific energy consumption were obtained by electrolysis from sulfate solutions at a low concentration of manganese in an electrolyser without a perforated baffle plate separating the cathode and anode spaces.
Key words: cobalt, manganese, water solution, cathode, anode, electrowinning, anode slurry

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Introduction. Cathode processes take place in electrolytes that differ in nature – sulfate, chlorides and others with different concentrations of metal and impurities, pH value of the electrolyte, current density at the cathode and anode, temperatures, presence of additives of «inert» salts. In this regard, the mechanisms of the cathode process undergo significant changes, influencing the main technological parameters [1, 2, 12-14].

The aim of this work is to create conditions for implementation of continuous electrolytic process, to study the effect of the presence of a perforated baffle plate and Cl-ion in the solution on the main parameters of the electrowinning in dynamic mode: current yield, specific energy consumption, and cathodic cobalt quality.

Research method. Electrodeposition of cobalt was carried out from sulfate-chloride and sulfate solutions, cobalt sulfate $CoSO_4$ and manganese sulfate $MnSO_4$ chemically pure grades were used for the experiment, as well as their crystal hydrates $CoSO_4 \cdot 7H_2O$ and $MnSO_4 \cdot 7H_2O$. For the preparation of chloride solutions, cobalt chloride $CoCl_2$ and / or sodium chloride NaCl were used. The amount of chloride ion in the solution did not exceed its solubility in water and chlorine was not released from the electrolyte into the gas phase [3-12].

The research has been conducted in a dynamic mode. The concentrations of metal ions in the initial electrolyte were the following, g/dm^3: 18-55 Co and 0,7-10 Mn. The electrolysis was conducted with current value of I = 1 A, pH = 1,1-1,4 and temperature 50-60 °C in three stages, h: I – 5-6, II – 5-6, III – 5-6.

The electrical diagram of the installation is shown on Fig.1. The cathode is titanium, anode is made of lead with a content of silver up to 1 %. Electrowinning of cobalt in a dynamic mode was carried out from sulfate and chloride-sulfate solutions in a cell box with a perforated baffle plate made of plexiglas separating the cathode and anode space of electrolyte, or without it. The anode was placed in a bag of filter cloth, which served to collect the anode slurry. Inside the bag, a fresh electrolyte was supplied, which ensured the stability of the electrolyte composition in the anode space. The output of the spent electrolyte was carried out from the near-cathode space. The electrolyte level was kept constant. The rates of fresh electrolyte supply and removal of waste were regulated. With this method of electrowinning, the manganese anions MnO_4^- built up at the anode cannot appear in the cathode space, since the Mn^{2+} cations contained in the initial solution interact with anions according to the reaction

$$3Mn^{2+} + MnO_4^- + 2H_2O = 5MnO_2 + 4H^+. \quad (1)$$

Manganese is discharged to the anode slurry in the form of MnO_2 by the reaction (1), while it is impossible for MnO_4^- to enter the cathode space, which excludes the reduction of the anion MnO_4^- at the cathode by reaction

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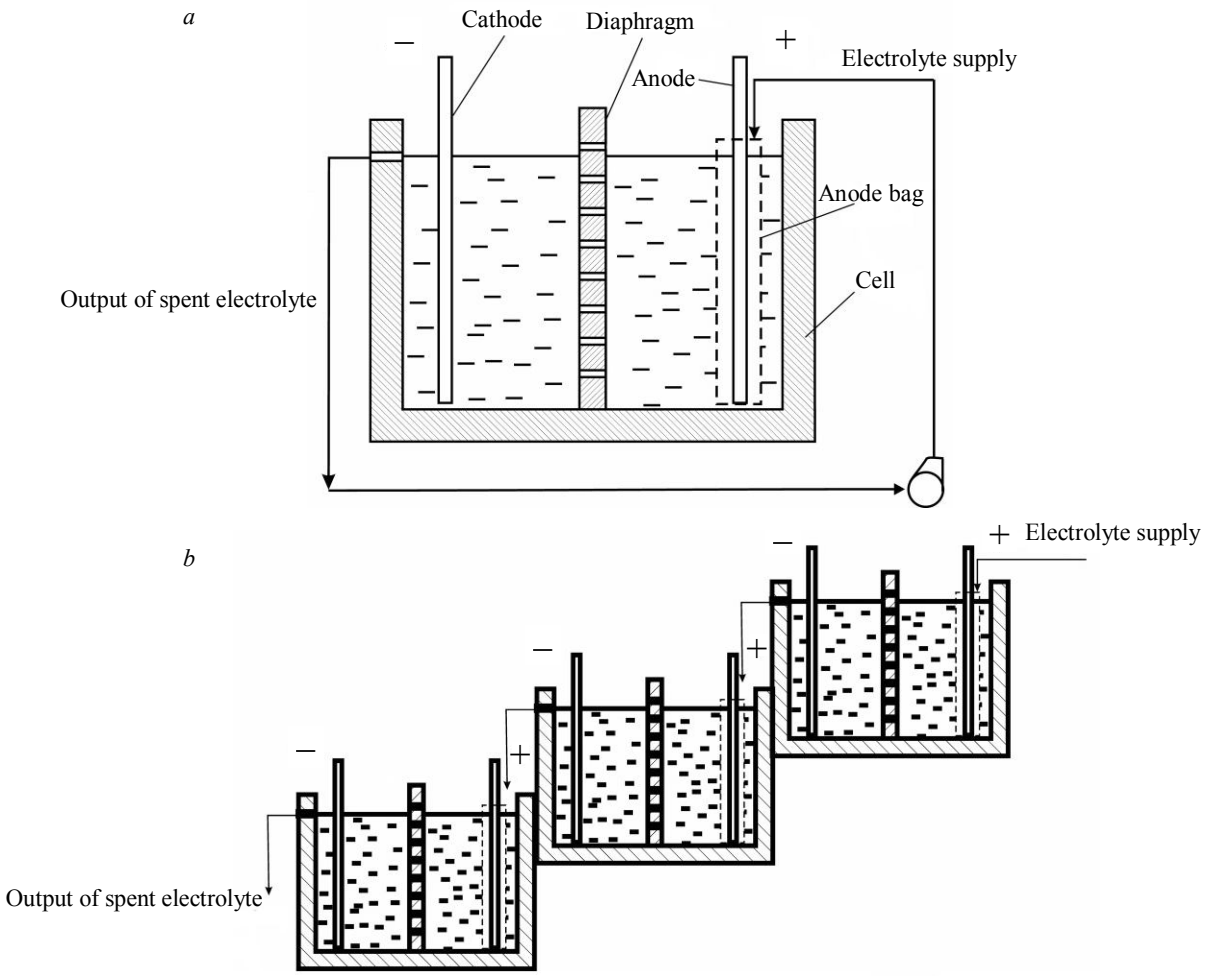


Fig.1. Installation pattern: *a* – a scheme of electrolysis plant; *b* – electrolytic cascade

$$MnO_4^- + 5e + 8H_3O^+ = Mn^{2+} + 12H_2O, \quad (2)$$

and Mn^{2+} at the cathode is not restored: $E^0_{Mn^{2+}/Mn^0} = -1{,}18$ V.

Difficultly soluble manganese compounds in the anode slurry are accumulated in a cell out of dense filter cloth – the anode bag – and do not enter the cathode space, and the presence of a perforated baffle plate also prevents the passage of anode slurry particles to the cathode.

This method of supplying the initial solution to the electrolyser and discharging the spent electrolyte improves the quality of the cathode cobalt surface, reduces the manganese content therein. It is desirable, according to the reaction (1), to observe the molar ratio between the ion Mn^{2+} in the initial solution and the ion MnO_4^- in the anolyte: $Mn^{2+} / MnO_4^- \geq 3/2$.

The manganese concentration was determined by the volumetric persulfate method, cobalt – by the colorimetric method with nitroso-P salt and by weight with α-nitroso-β-naphthol.

The analysis of elemental composition of the cathodic cobalt and anode slurry surface was carried out on a scanning electron microscope CamScan MV 2300 with energy-dispersive INCA Energy, and Aztec software for microanalysis.

Results and discussion. The table gives the results of electrolysis from sulfate and chloride-sulfate solutions of Co (II) and Mn (II). The volume of the electrolyte is 400 cm^3; areas: cathode – 33, anode – 36 cm^2; distance between the electrodes is 7.8 cm; pH = 1.1 – 1.4.

From the data in the table it follows that an increase in the manganese content by an order of magnitude reduces the cobalt winning, by a factor of 1.5-2.5. The presence of a small amount of chloride ions improves the quality of cathodic cobalt – by the content of impurities and the surface state, which has less roughness, and contributes to the formation of complex compounds in the anode slurry.

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The results of electrolysis from sulfate-chloride and sulfate solutions of Co (II) and Mn (II)

Stages	Time, h	Residual concentration of ions on a solution, g/dm^3			Voltage, V	Current, A	Weight, g		Current yield, % by weight	Specific energy consumption, kW·h/kg	Winning, % by weight
		Co	Mn	Co:Mn			Cathode Cobalt	Anode slurry			
Sulfate-Chloride solution											
With a baffle plate (cathode – Ti, anode – Pb)											
0	0	41.0	1.2	34.2	0	0	0	0	0	0	0
I	5	38.5	1.0	38.5	6.8	1	1.22	0.53	22.2	27.9	6.10
II	11	34.8	0.8	43.5	7.1	1	2.40	0.95	19.8	32.5	10.39
III	17	31.9	0.7	45.6	6.5	1	3.47	1.56	18.6	32.0	22.20
0	0	40.0	10.6	3.8	0	0	0	0	0	0	0
I	5.5	39.0	9.9	3.9	5.0	1	0.65	1.48	10.7	42.5	2.97
II	10.5	37.9	9.0	4.2	4.9	1	1.20	2.75	10.4	42.8	11.02
III	15.5	36.0	8.0	4.5	5.2	1	1.69	4.61	9.9	47.7	13.14
Without a baffle plate (cathode – Ti, anode – Pb)											
0	0	42.0	1.1	38.2	0	0	0	0	0	0	0
I	6	37.0	1.0	37.0	4.6	1	3.48	0.90	52.7	7.9	11.90
II	12	32.8	0.8	41.0	4.8	1	6.04	1.25	45.8	9.5	21.91
III	18	30.3	0.7	43.3	5.0	1	8.07	1.42	40.8	11.2	27.86
0	0	34.8	9.6	4.5	0	0	0	0	0	0	0
I	6.5	33.3	9.0	4.3	5.3	1	1.30	1.37	19.7	24.3	4.31
II	13	31.8	8.2	4.3	4.9	1	2.41	2.26	18.3	24.5	8.62
III	19	30.6	7.8	4.4	4.5	1	3.33	3.45	16.8	24.5	12.07
Sulfate solution											
With a baffle plate											
0	0	43.4	1.18	36.8	0	0	0	0	0	0	0
I	6	42.7	1.16	38.8	5.40	1	1.39	1.88	21.0	23.4	1.61
II	12	41.8	1.15	36.3	5.43	1	2.93	1.57	22.2	22.2	3.69
III	18	40.8	1.13	36.1	5.41	1	4.69	1.44	23.7	20.7	5.99
0	0	55.9	10.22	5.5			0	0	0	0	0
I	6	55.0	10.21	5.4	4.9	1	0.88	0.14	13.35	31.3	1.61
II	12	54.8	10.08	5.4	5.1	1	1.52	0.61	11.5	40.3	1.97
III	18	54.0	10.06	5.4	5.0	1	2.20	1.46	11.1	41.1	3.40
Without a baffle plate											
0	0	40.0	1.06	37.7	0	0	0	0	0	0	0
I	5.5	35.5	0.92	38.6	5.77	1	3.60	0.35	59.58	8.81	11.25
II	11	27.8	0.78	35.6	5.59	1	6.06	0.56	50.12	10.15	30.5
III	16.5	17.8	0.69	25.80	4.95	1	8.01	0.70	44.16	10.2	55.5
0	0	41	9.8	4.2	0	0	0	0	0	0	0
I	6.5	38.5	9.52	4.0	4.83	1	1.72	0.45	24.12	18.23	6.10
II	13	36.5	8.73	4.2	4.63	1	3.32	0.93	23.2	18.16	10.98
III	19	34.4	7.2	4.8	4.58	1	4.75	1.43	22.73	18.34	10.10

Figure 2 shows the dependence of current yield of cobalt from solutions by time and mass ratio of Co/Mn from electrolyzers with a baffle plate and without it.

It follows from the data in the table and in Fig.2 that the largest yield with respect to cobalt current was obtained with a small concentration of manganese from chloride-sulfate and sulfate solutions in an electrolyzer without a baffle plate, and the smallest yield with respect to cobalt current – at a high concentration of manganese from chloride-sulfate and sulfate solutions in an electrolytic cell with a baffle plate.

Figure 3 shows the dependence of the specific energy consumption by time and mass ratio of Co/Mn from electrolyzers with a baffle plate and without it.

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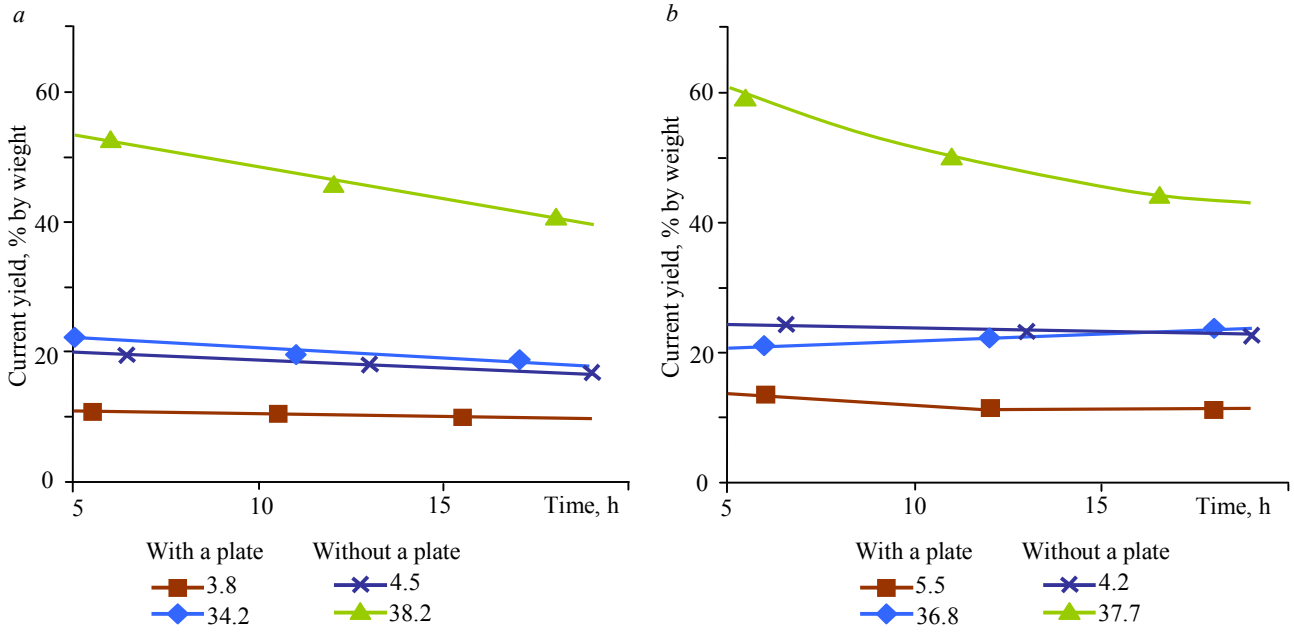


Fig.2. Dependency of current yield of cobalt from solutions by time and mass ration Co/Mn from chloride-sulfate (*a*) and sulfate (*b*) solutions

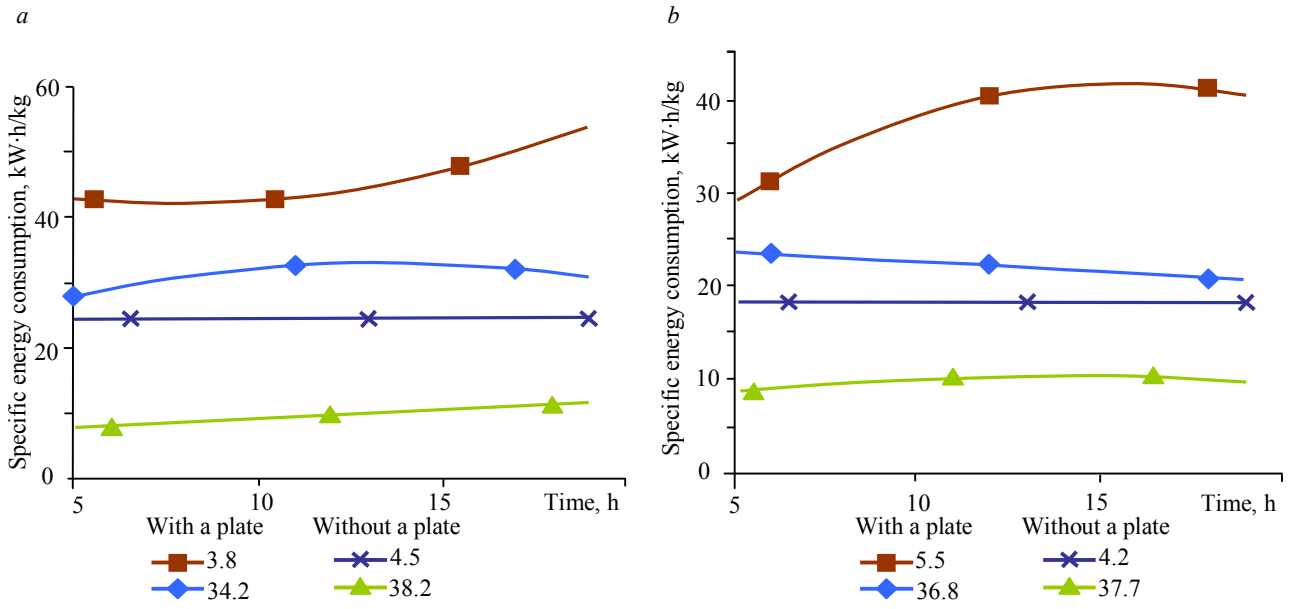


Fig.3. Dependency of specific energy consumption from time and mass ration Co/Mn from chloride-sulfate (*a*) and sulfate (*b*) solutions

It follows from the data in the table and in Fig.3 that the lowest specific energy consumption was obtained with a small concentration of manganese from the chloride-sulfate and sulfate solutions in the cell without a plate, and the largest specific energy consumption – at a high concentration of manganese from the chloride-sulfate and sulfate solutions in the cell with a plate.

Thus, the presence of a plate in the cell decreases the electrowinning performance parameters from the sulfate-chloride and sulfate solutions. Probably, the plate creates a barrier to the passage of cobalt ions to the cathode.

Figure 4 shows the results of X-ray spectral analysis of cathodic cobalt obtained by winning without a baffle plate on a titanium cathode and a lead anode with 1 % silver at a current of 1 A from a sulfate-chloride solution with the initial concentration, g/dm^3: Co 31.75; Mn 8.2 and a mass of cathode cobalt of 2.41 g.

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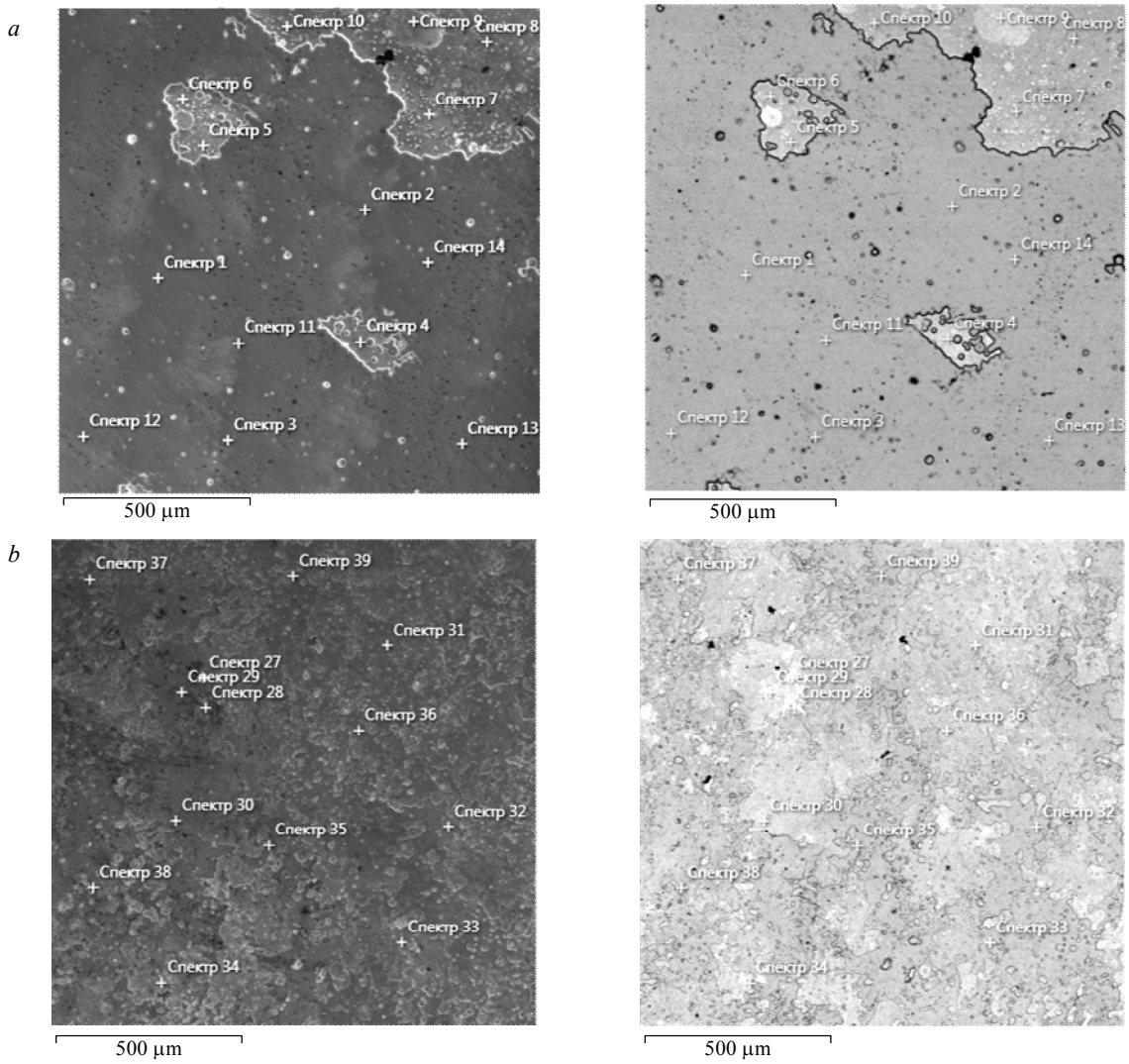


Fig.4. Results of X-ray spectral analysis of cathode cobalt obtained during winning without a plate on a titanium cathode with current of 1 A from sulfate-chloride solution with initial concentration, g/dm^3: Co 31.75, Mn 8.2 and cathode cobalt mass of 2.41 g:

a, *b* – microphotograph SE and BSE of cathode Co sample from internal and external sides of a cathode accordingly, zoom 150$^\times$; *c*, *d* – a single specter of cathode Co sample; place forming the caverns on internal and external sides of a cathode accordingly; *e* – summarized specter of cathode Co, external side of a cathode. Also see p.440

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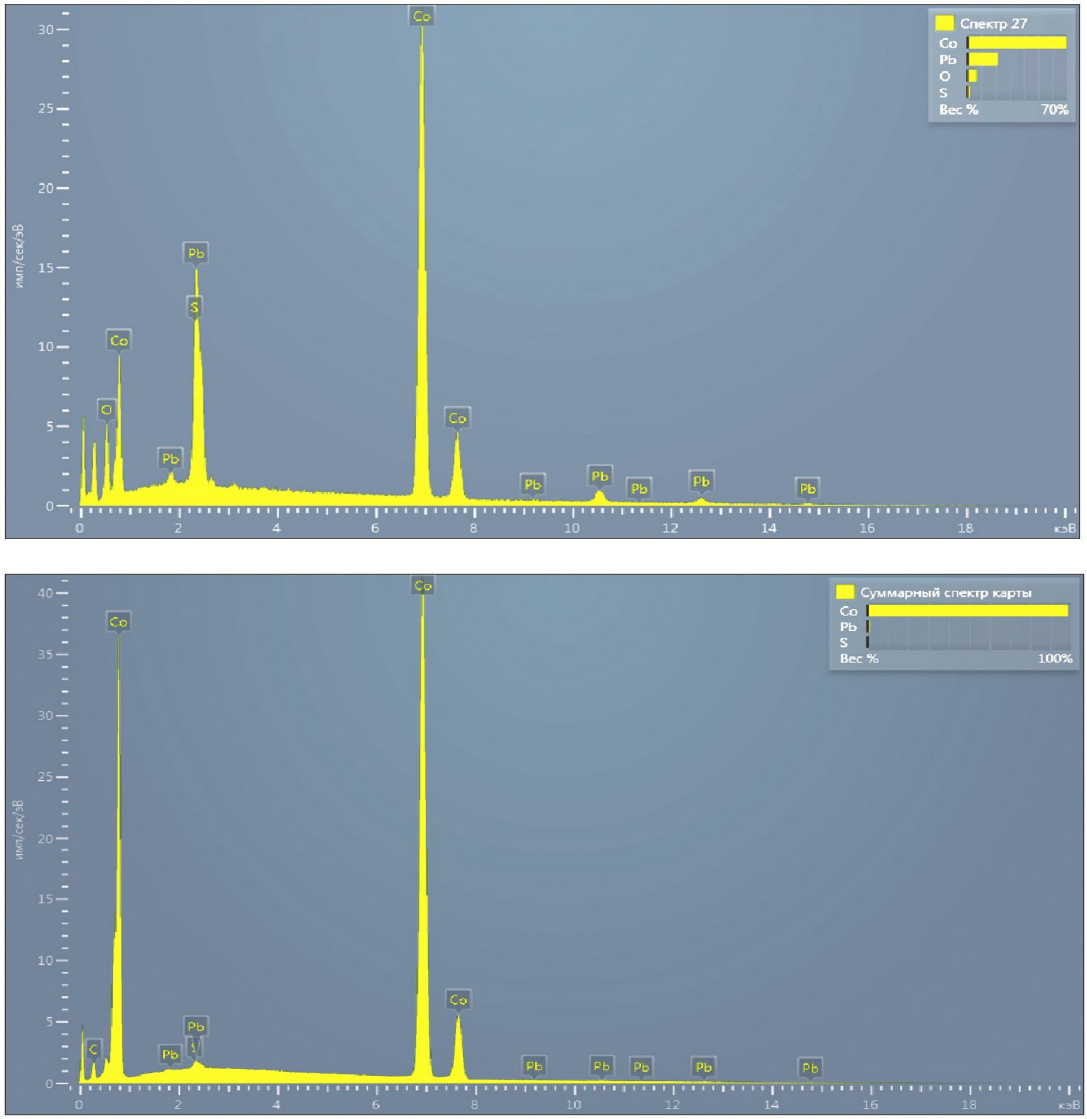


Fig.4. Ending

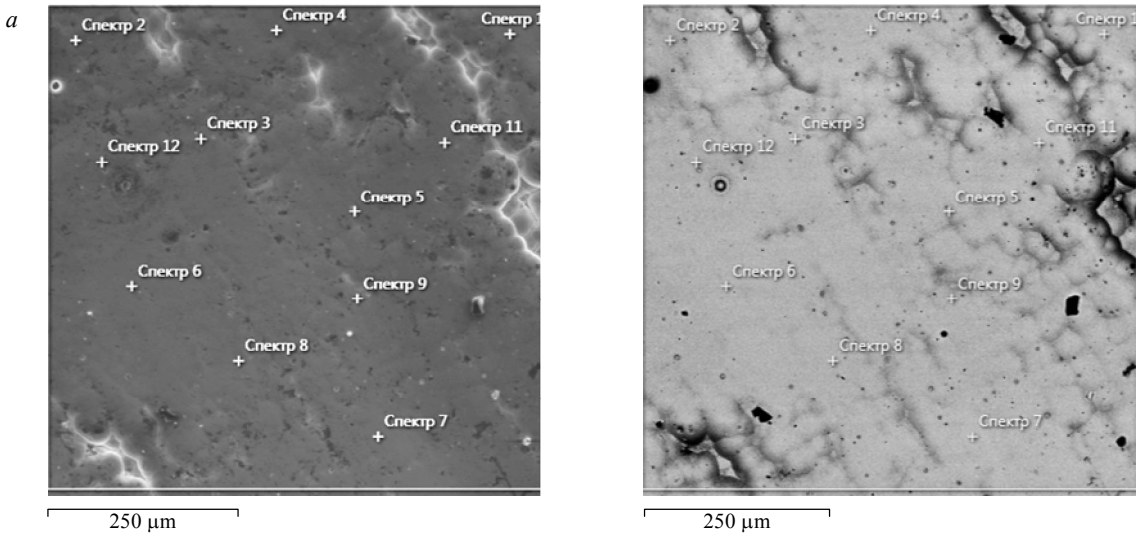
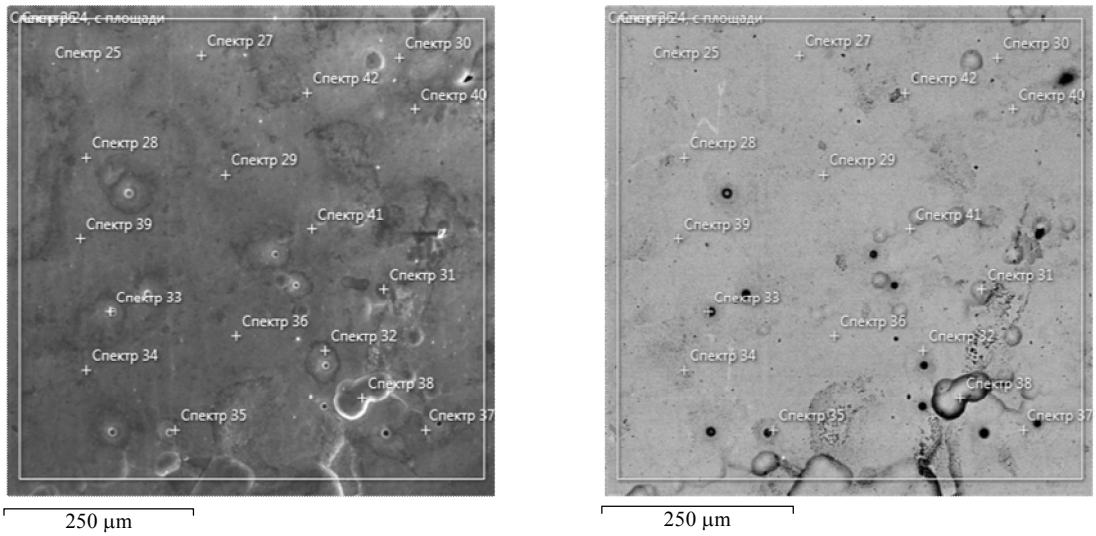


Fig.5. Results of X-ray spectral analysis of cathode cobalt obtained during winning without a baffle plate on a titanium cathode and lead anode with current of 1 A from sulfate solution with initial concentration, g/dm^3: Co 27.78, Mn 0.75 and cathode cobalt mass of 8.01 g:

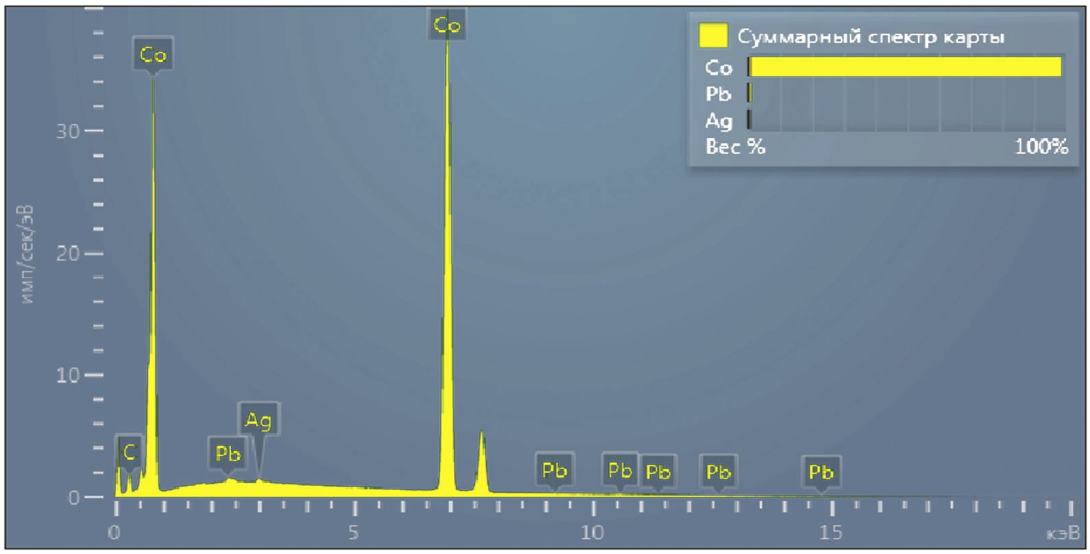
a, *b* – microphotographs SE and BSE of cathode Co sample from external (zoom 200 ×) and internal (zoom 300 ×) sides of cathode accordingly; *c*, *d* – summarized specter of a plate section from internal and external sides to the cathode accordingly. Also see p.441

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b



c



d

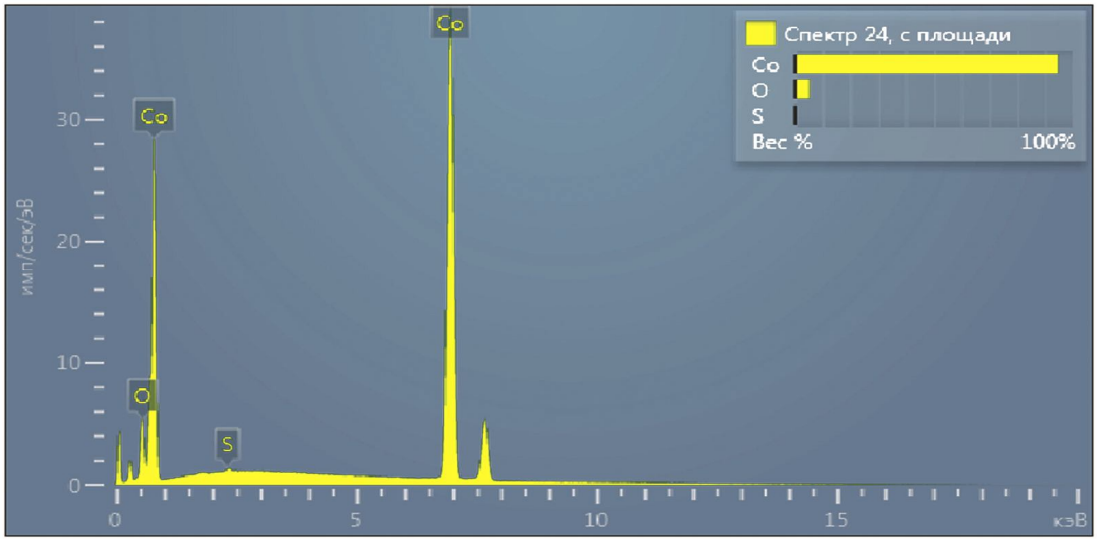


Fig.5. Ending

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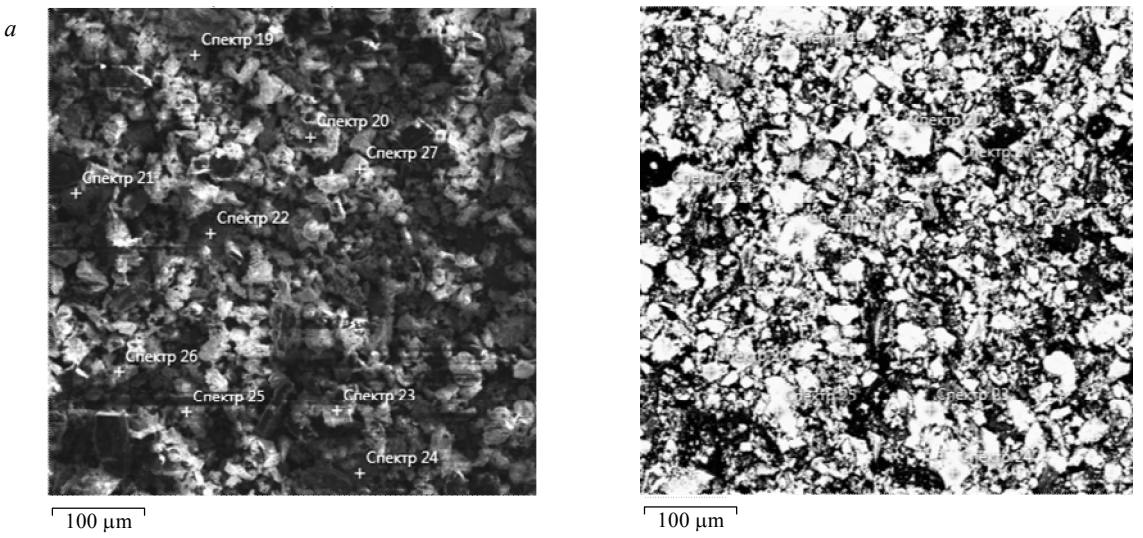


Fig.6. Results of X-ray spectral analysis of anode slurry resulted from winning without a plate on a titanium cathode and a lead anode with 1 % of silver and current of 1 A from sulfate-chloride solution with initial concentration, g/dm^3: Co 31.75, Mn 8.2 and anode slurry mass of 3.45 g:

a – microphotographs SE and BSE of anode slurry, zoom 500$^\times$; *b* – summarized specter of anode slurry

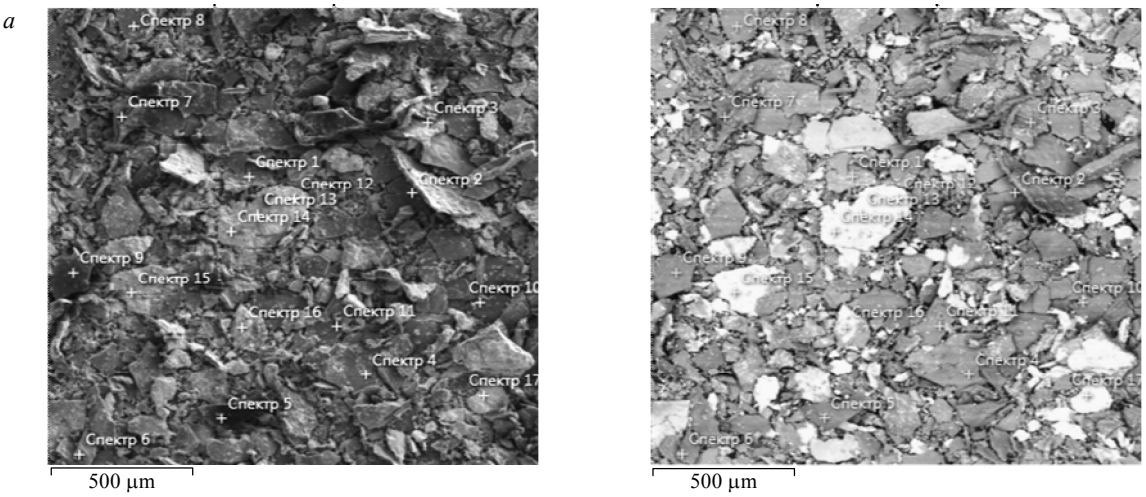
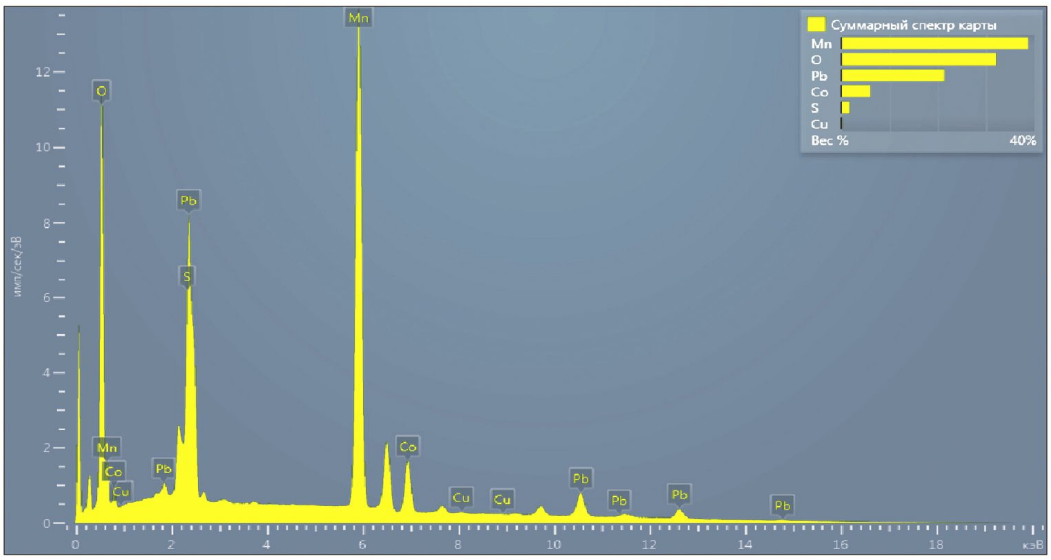


Fig.7. Results of X-ray spectral analysis of anode slurry resulted from winning without a plate on a titanium cathode and a lead anode with 1 % of silver and current of 1 A from sulfate solution with initial concentration, g/dm^3: Co 27.78, Mn 0.75 and anode slurry mass of 0.702 g:

a – microphotographs SE and BSE of anode slurry, zoom 120$^\times$; *b* – summarized specter of anode slurry; *c* – multi-layered picture; *d-g* – element distribution map of a sample section of anode slurry. Also see p.443 and 444

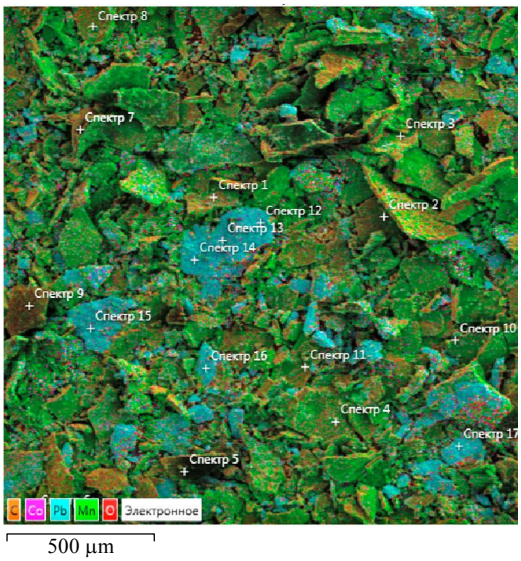
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b



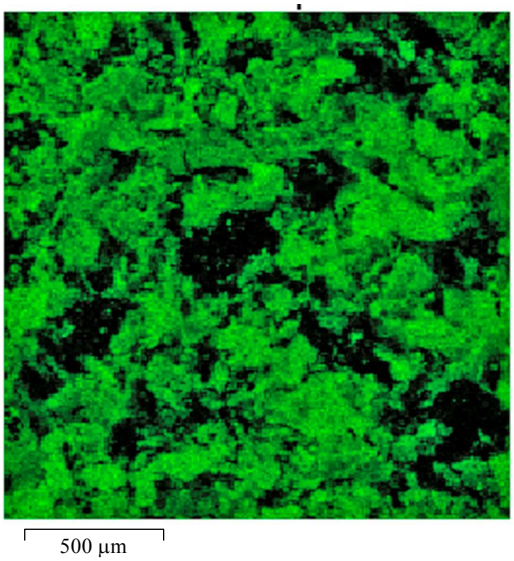
c

Multi-layered picture EDS 1



d

Mn K-series



e

Pb M-series

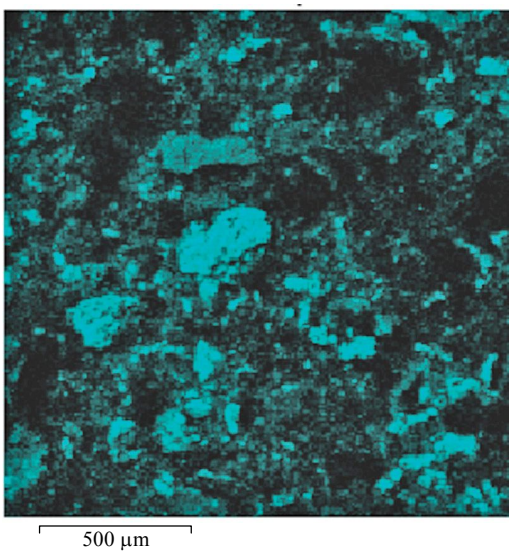


Fig.7. Continuation

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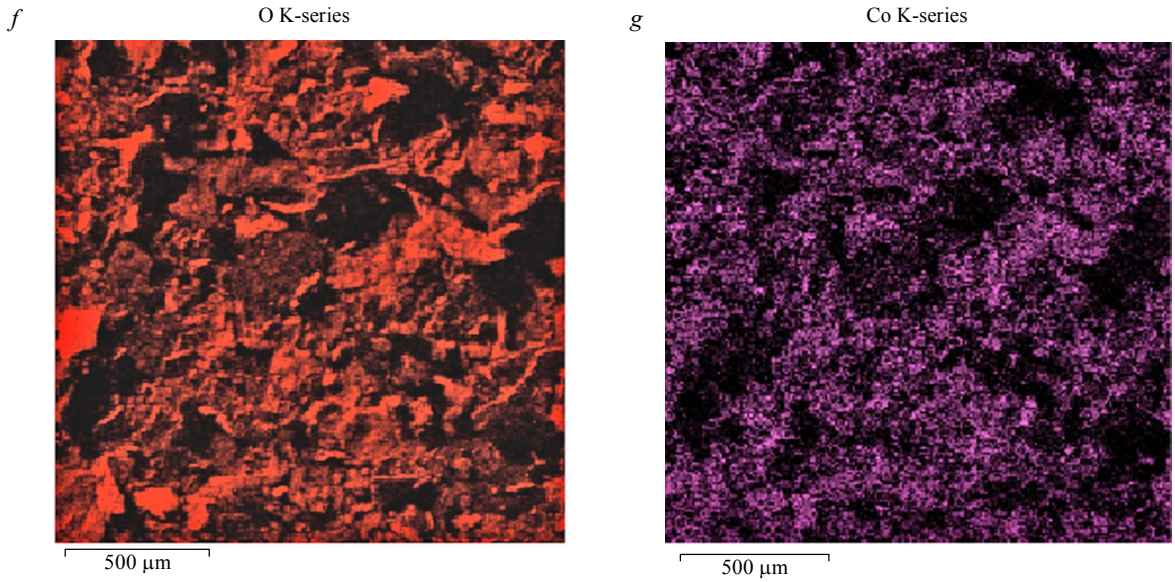


Fig.7. Ending

The X-ray spectral microanalysis (Fig.4) showed that the outer surface of the sample is fairly uniform in composition – the main phase of cobalt is metallic, but it has several small caverns that contain impurities and lead, presumably in the form of sulfate. In the main area of the plate, places without caverns have a composition of metallic cobalt.

The surface of the plate, which is internal to the cathode, has an uneven chemical composition, the main phase is cobalt, impurities are presumably in the form of lead sulphide.

Figure 5 shows the results of X-ray spectral analysis of cathode cobalt obtained by winning without a plate on titanium cathode and lead anode with 1 % of silver at a current strength of 1 A from a sulfate solution with the initial concentration, g/dm^3: Co 27.78, Mn 0.75 and a mass of cathodic cobalt of 8.01 g.

The X-ray spectral microanalysis (Fig.5) showed that the sample surfaces are homogeneous in composition, including structural one, the main phase is cobalt metal, the plate has minor damages. From the total specter of elements distribution, it can be seen, that impurities that are insignificant in content are distinguished on the external and internal sides of the plate, which are unevenly distributed over the entire surface of the plate.

Figure 6 shows the results of X-ray spectral analysis of anode slurry obtained by winning without a plate on a titanium cathode and a lead anode with 1 % of silver at a current strength of 1 A from a sulfate chloride solution with the initial concentration, g/dm^3: Co 31.75, Mn 8.2 and anode slurry mass of 3.45 g.

The X-ray spectral microanalysis showed that the main phase of the sample is lead and manganese oxide. Lead is in the sample in a free state (it got into the slurry presumably when the anode is stripped off) and in the form of lead sulfate, cobalt is found in small amounts, possibly in the form of sulfate.

Figure 7 shows the results of X-ray spectral analysis of the anode slurry obtained by winning without a plate on a titanium cathode and a lead anode with 1 % of silver at a current of 1 A from a sulfate solution with the initial concentration, g/dm^3: Co 27.78, Mn 0, 75 and anodic slurry mass of 0.702 g.

The X-ray spectral microanalysis showed that the main phase of the sample is manganese oxide. Lead is in the sample in a free state (it got into the slurry presumably when the anode is stripped off), less often in the form of an oxide, cobalt is found in small amounts in the form of sulphate, sometimes found in the form of cobalt oxide

Conclusion. Electrowinning of cobalt from water solutions of cobalt and manganese under dynamic conditions using a titanium cathode and a lead anode with 1 % of silver should be carried out from sulfate solutions at a low concentration of manganese in an electrolyser without a perforated baffle plate separating the cathode and anode spaces.

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