

# DISPERSED CARBON CATHODES FOR NONFERROUS METALS EXTRACTION FROM TECHNOLOGICAL WASTE WATERS

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## Abstract

The processes of copper and nickel electrodeposition on the dispersed particles of thermoexpanded graphite and the conductive soot have been investigated with the cyclic voltammetry method. It was shown possibility of copper and nickel electrolytic extraction from the aqueous solutions of their salts with concentration  $2 \text{ mg/dm}^3$ . Electrolysis in the reactor with dispersed three-dimensional flowing electrodes of the thermoexpanded graphite and the conductive soot showed possibility of nonferrous metals extraction to residual concentration lower than  $0.1 \text{ mg/dm}^3$ . The characteristics of the electrochemical reactor for purification of the printed circuit cards manufacturing washing water with productivity 100 L per hour are adduced.

The closed systems with the circulate water supply are most safe from ecological point of view. Application of these technologies in the galvananotechnic, hydrometallurgy and other branches of industry is possible with condition of the washing waters which are the low-concentrated (less then  $1 \text{ mg/dm}^3$ ) solution of the nonferrous metals salts purification without reagents methods.

One of the perspective methods of this problem solution is an electrolysis which allows to obtain nonferrous metals in the most concentrated kind and demands the minimum expenditure of energy for their further processing. But the electrolytic extraction of the nonferrous metals from the low-concentrated solutions is make difficult with the diffusion limits of electrical current. This problem may be solved with help of the bulk-porous flowing electrodes which have large surface area.

For the purification of waste water of electrolytic cadmium plating the electrochemical reactor with porous carbon cathode and titanium with plating of the rare metals oxides anode were used. For increase of conductivity the solution of sodium chloride with the concentration of  $80 \text{ g/dm}^3$  was added to the washing waters. The degree of  $\text{Cd}^{2+}$  extraction achieved was 98-99 % and for cyanides - 93 % [1]. For enhance of electrolysis efficiency and of cathode surface area it was offered the washing waters to let pass throw layer of the granulated conductive charge which played role of a cathode. During electrolysis the potential of the cathode was kept 50 mV lower than the reduction potential of a metal extracted [2].

For manufacturing of the copper plating from the cyanide electrolytes washing water the electrochemical reactor with charge of granules  $\text{Ni}_{0.9}\text{Fe}_{2.1}\text{O}_4$  which is placed between

stainless electrodes bipolar cathode was used with sufficient efficiency [3]. When the concentration of the inlet solution was  $60 \text{ mg/dm}^3 \text{ CN}^-$  and  $50 \text{ mg/dm}^3 \text{ Cu}^{2+}$  decreasing of  $\text{CN}^-$  concentration (down to  $< 1 \text{ mg/dm}^3$ ) and  $\text{Cu}^{2+}$  (down to  $10 \text{ mg/dm}^3$ ) was achieved. Electrolysis was carried out for 1 h with current density  $0.15 \text{ mA/cm}^2$  and voltage 25 V at the temperature  $20^\circ\text{C}$ . The space between electrodes can be filled with dispersed nonconductive material, for example ion-exchange resin [4]. In this case the electrolysis efficiency increases and rate of process may be enhanced in two times.

It has been shown that charged layer of the ionite which is in contact with the platinum electrode has influence on the stationary potential of the electrode [5]. From other hand, polarization of the platinum electrode leads to change of acidity of the surface layer of the titanium phosphate particles that leads to increase of sorption capacity in 2-3 times. When the multicomponent model solution which contained 0.001 M of the ions  $\text{Cu}^{2+}$ ,  $\text{Cr}^{3+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Ni}^{2+}$  were investigated it has been shown that in the case of activated with electrical field sorption the degree of these ions extraction was 80-99.9 % and when activation was absent it was less 46-90 %. The ions  $\text{Cu}^{2+}$ , which are characterised by most high sorption affinity to the titanium phosphate, are extracted in first turn while the highest degree of the solution purification from  $\text{Ni}^{2+}$  ions is achieved only after complete extraction from the solution of the  $\text{Cu}^{2+}$  cations.

The electrochemical reactors with the carbon fibrous materials cathodes were found the most effective for the purification of the washing waters [6-8]. When mercury was extracted in the cylindrical titanium electrochemical reactor with the cathode of carbon felt, which was prepared by thermal processing of the polyacrylonitrile filaments at  $900^\circ\text{C}$ , of 99.9 % yield was achieved. Through the electrochemical reactor the solution which contains  $20 \text{ g/dm}^3$  of sodium chloride and  $100 \text{ mg/dm}^3$  of mercury chloride is pumped with rate  $150 \text{ cm}^3/\text{cm}^2\cdot\text{hour}$ . When the current through the electrochemical reactor was 100 mA concentration of mercury at the outlet of the reactor was  $0.11 \text{ mg/dm}^3$ .

Behaviour of the electrodes of the fibrous carbon materials have been investigated during cathode and anode polarisation in the acidic and alkaline media [9-10]. The processes of reduction of the oxide surfaces and etching of the fiber surface were observed. When current density is higher than  $1000 \text{ A/m}^2$  some changes in the fibres structure are detected. Crack and partial destruction of the fibres take place. Moreover, when the electrochemical reactor with the cathode of carbon fibres is used for extraction of copper with high purification degree of the solution growing together of the fibres via copper crystals is observed that leads to change for the worse of the process parameters [11]. This forces to lead search of the dispersed carbon materials with developed surface which give possibility for realization of the "pseudoliquid" cathode which is deprived of this deficiency.

When choose the material for making of the cathode, it would be taken into consideration that in the processes of the metals electrical reduction ability of the electrode surface to adsorb metal ions plays an important role. It has been found that the ion exchange capacity of the carbon materials depends on oxidation degree of their surface which is determined by ability to formation of the surface complexes with the metals ions [12]. Oxidation of the carbon materials surface takes place by heating up  $200^\circ\text{C}$  in the air atmosphere, by action of strong oxidizers ( $\text{KMnO}_4$  in the concentrated  $\text{H}_2\text{SO}_4$ ), by the anode treatment in the electrolyte solutions.

Electrochemical oxidation of the carbon fibres in concentrated sulfuric acid leads to form of the oxygen-containing functional groups not only on the surface but in the bulk of the fibre. Such treatment is characterized by formation of the graphite oxide which can not be reduced to carbon by cathodic polarization [13]. Presence of the functional groups on the surface of the fibre essentially increases the cation exchange capacity. After exposure of the anodic treatment carbon felt in 0.1 M solution of silver nitrate on the voltammograms in condition of cathodic polarization of the electrode increase of silver reduction current peaks is occurred at the potential +0.3 V. Oxidation of the carbon fibre with the graphite structure surface can leads to form of the ionic intercalated compounds which form the bulk oxides by hydrolysis. The properties of these oxides strongly differ from the properties of the surface oxides. The bulk oxides are flaky CHO-compounds having oxygen covalently bonded between distorted layers of carbon hexagons. The layer spacing in bulk oxides ( $\approx 620$  pm) roughly corresponds to the layer spacing in graphite plus the oxygen van der Waals diameter ( $\approx 280$  pm). Bulk oxides are strong oxidants; their redox potentials are close to that of  $\text{MnO}_2$  [14]. Surface oxides are oxygen-containing functional groups such as -OH, -COOH and others, situated at edge positions of carbon layers. Their redox properties are more related to those of aromatic compounds with the same functional groups, *i.e.*, their reduction is only partly possible in aqueous solutions and requires potentials close to that of the hydrogen evolution.

The method of nonferrous metals extraction from low-concentrated solutions in the electrochemical reactors of flow type with the cathode of thermally expanded graphite (TEG) was offered by us [15]. Choice of the material is conditioned by that TEG has large specific area and surface oxides which as have been shown up are the adsorption sites of the nonferrous metals ions. The graphite particles with the metal coating precipitate on the bottom of the electrochemical reactor and can be extracted easily without interruption of the process. Powder of the metallized graphite is the valuable material for the antifriction wares production.

The results of copper and nickel extraction from the sulfate solutions with concentration less then  $1 \text{ g/dm}^3$  in the electrochemical reactors with dispersed cathode of TEG and conductive carbon black soot (CS) are presented in this paper.

## Experimental

TEG with the filling density of  $8\text{--}10 \text{ g/dm}^3$  was prepared by means of rapid heating (in the preliminary warmed up to  $900^\circ\text{C}$  electrical furnace) of the intercalated with sulphuric acid natural graphite GAK-2 utilizing  $(\text{NH}_4)_2\text{S}_2\text{O}_8$  as oxidizer [16]. CS was obtained by means of thermal treatment in argon atmosphere of technical carbon at the temperature  $1500^\circ\text{C}$  for 60 hrs.

Voltammograms were taken off in the three electrodes cell with the potentiostat PI - 50 - 1.1 with rate of potential scan  $5 \text{ mV/s}$ . As the auxiliary electrode was used graphite plate with dimensions  $40 \times 10 \times 3 \text{ mm}$ . The potential values refer to the silver electrode, saturated with KCl. The working electrode was made up of compact TEG or CS by means of the dispersed material pressed in a glass tube with inside diameter of 3 mm when it was placed on a glass plate. The working surface was lower edge of the obtained carbon pivot and current conductor - pressed in it copper wire.

Dispersed working electrode was made up by means of fill up 10 mg of TEG in the glass tube with inside diameter of 3 mm which was installed in the cell filled with electrolyte

and copper current conductor with diameter 2.5 mm was lowered on deeper that the lower edge of TEG was at the glass tube cut. As a background electrolyte was used 0.01 M solution of sodium sulfate.

Extraction of copper and nickel from the solutions was carried out in the electrochemical reactor of flow type which was made up of glass tube with diameter 30 mm and length 150 mm with the dispersed cathode placed at the upper part in case of TEG or at the lower part in case of CS. As a current conductor was used nickel circle with diameter 29.5 mm and nichrom wire. A flow of the electrolyte was carried out through the split between the nickel circle edge and the glass reactor wall. As the anode graphite pivot with diameter 6 mm which was situated in the glass tube for preventing of contact with the cathode particles serves.

Pumping of electrolyte was carried out with the peristaltic pump PP1-05 which allowed to vary the flowing rate of a solution of 0.1 to 200 ml/min. The flowing rate was put such that electricity quantity which was passed through the set solution volume with the current value which was settled when voltage was 35V would be enough for extraction of all metal. Electrochemical reactor was supplied with electricity with the stabilised power source B5-49. The current value was controlled with the multimeter Sch-4300.

Determinations of copper and nickel in the solutions were carried out by the colorimetric methods [17]. The reagents of analytic purity were used for the solutions preparation.

The specific surface area was determined by the standard method of argon adsorption at the liquid nitrogen boiling temperature.

X-ray spectroscopy was carried out with the diffractometer DRON - 3M using  $\text{CuK}\alpha$  radiation.

## Results and discussion

TEG due to peculiarity of its preparation technology has residuals of the intercalant (sulfuric acid) in the crystal grating and the different oxygen-containing functional groups (lactone, quinone and other) [16]. In connection with this when electrode of TEG is cathodic polarized the processes of deintercalation and oxygen-containing groups reduction pass on it.

Accounting that concentration of the oxygen-containing groups which are able to reduction on the working surface of the electrode will decrease with increase of cathodic polarisation time, one can explain the current decrease with circling of the electrode. This was cause of necessity to investigate dependence of the polarisation current on time. For this in potentiostatic regime at the potential 1 V the electrode was polarized for 5 min. in the background electrolyte after that cyclic voltammetry was carried out. Then the procedure was repeated. The voltammograms are presented in Fig. 1. When time of polarization is more then 30 min. the current values do not change. That is why all further investigations carry out on the electrodes after preliminary polarization during 30 min. in the background electrolyte.

Absence of intercalated sulfuric acid in CS structure would lead to decrease of current value. But due to larger surface area of the particles ( $25 \text{ m}^2/\text{g}$  for TEG and  $270 \text{ m}^2/\text{g}$  for CS) the current value is one order higher than that for the electrode of pressed TEG. At the potential -0.35 V wide peak of the surface oxides reduction is occurred on the voltammogram. The potential value of hydrogen evolution on CS electrode is less 0.15 V positive than that on TEG electrode.

Thermal treatment of carbon materials leads to conductivity increase due to graphitization of the structure [12]. But X-ray powder patterns of CS and natural graphite did not confirm of graphite considerable quantity formation (Fig.2) although it had conductivity as compared with that for graphite.

As was mentioned above the reactions of the metal ions electroreduction are diffusion-controlled in low-concentrated solutions. It was interesting to study behaviour of TEG and CS electrodes in the solution containing of copper or nickel ions. In Fig. 3 the voltammograms of TEG pressed electrodes are presented.

Introduction of  $\text{Cu}^{2+}$  ions in the solution leads to change of the voltammograms and when the solution contains  $20 \text{ mg/dm}^3$  of copper the process of the metal deposition on TEG cathode becomes predominating. The sections of limited current which value depends on depolarizer concentration are observed on the curves. Other shape cyclic voltammograms on pressed TEG were in nickel-containing solutions (Fig 4). Standard electrode potential of nickel reduction reaction ( $-0.26 \text{ V}$  vs. hydrogen electrode) is lower than that of copper reduction ( $+0.34 \text{ V}$ ). Therefore the processes of sulfuric acid deintercalation, surface oxides reduction, hydrogen and nickel reduction proceed simultaneously. Current values of each these processes are comparable in the low concentrated solutions and no one is predominate. The break on the curves at potential  $-0.07 \text{ V}$  is caused with nickel deposition on TEG. The results of voltammetric tests of pressed TEG electrodes show that hydrogen evolution over voltage is  $-1.3 \text{ V}$  which will allow to use this material for extraction of nonferrous metals from aqueous solutions.

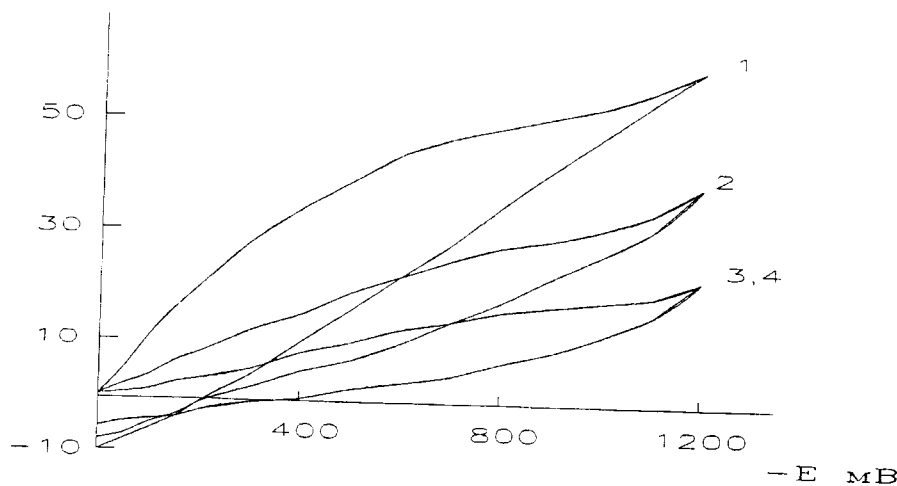


Fig.1. Cyclic voltammograms of pressed TEG electrode in the background electrolyte: 1 - without preliminary polarization; 2 - after polarization for 10 min.; 3,4 - after polarization for 30 and 40 min.

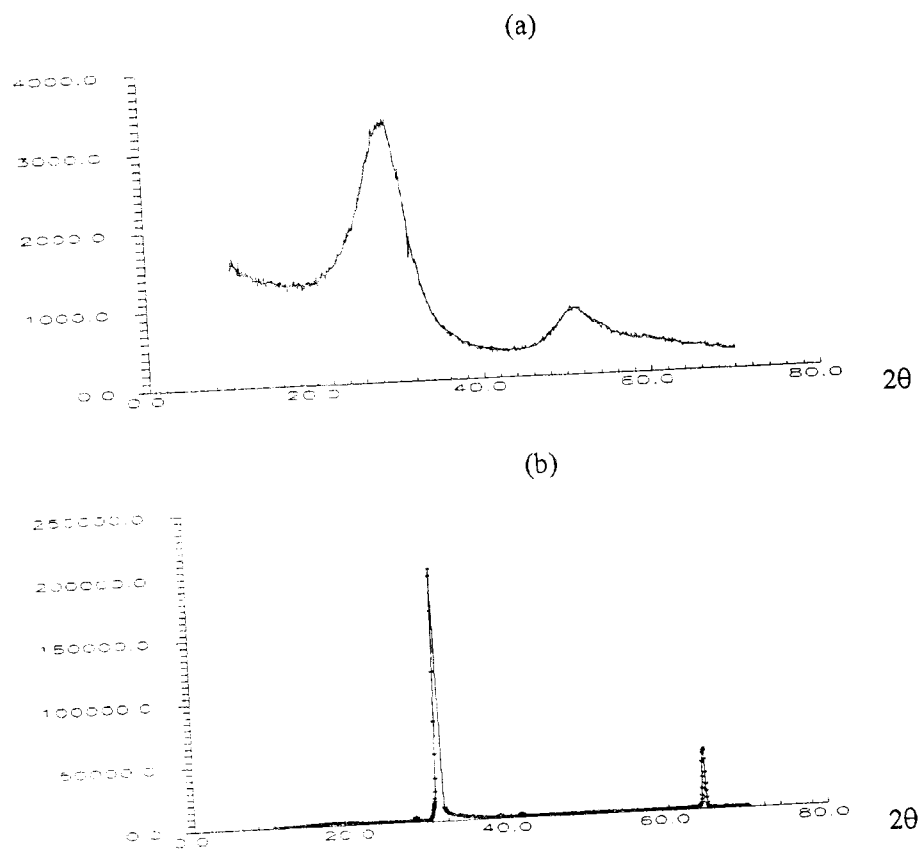


Fig. 2. X-ray powder patterns of CS (a) and graphite (b).

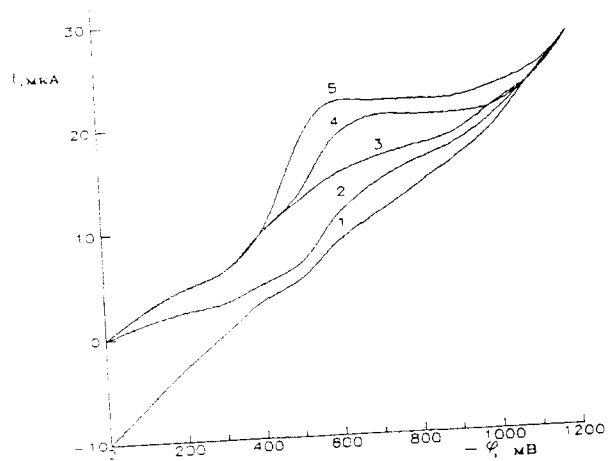


Fig 3. Cyclic voltammograms of TEG pressed electrode in the solution with different copper contents: 2 - 5; 3 - 10; 4 - 20; and 5 - 50 mg/dm<sup>3</sup>; 1 - the curve of reverse potential scan.

Cyclic voltammograms of CS pressed electrodes in solutions containing copper are shown in Fig. 5. Such as in the case of TEG electrodes polarization the process of surface oxides reduction is marked on voltammograms (curve 1). But presence of copper ions in the solution begins display only when their concentration is higher than  $100 \text{ mg/dm}^3$  (curves 3, 4).

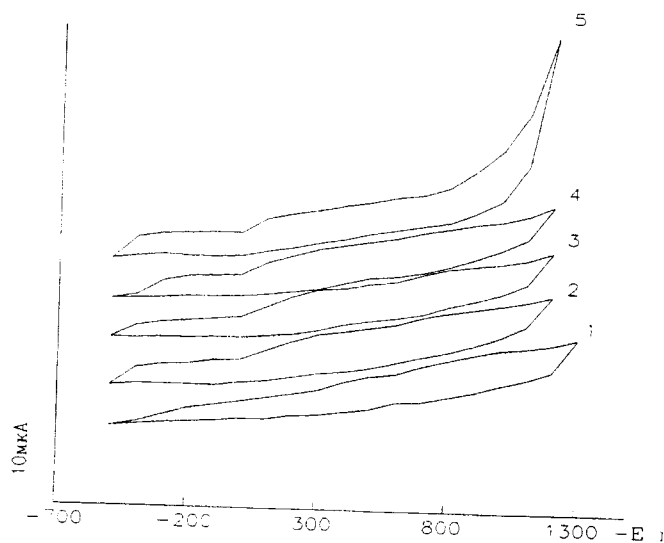


Fig. 4. Cyclic voltammograms of pressed TEG electrodes in the solutions with different nickel contents: 1 - 0; 2 - 10; 3 - 20; 4 - 50; 5 -  $100 \text{ mg/dm}^3$ .

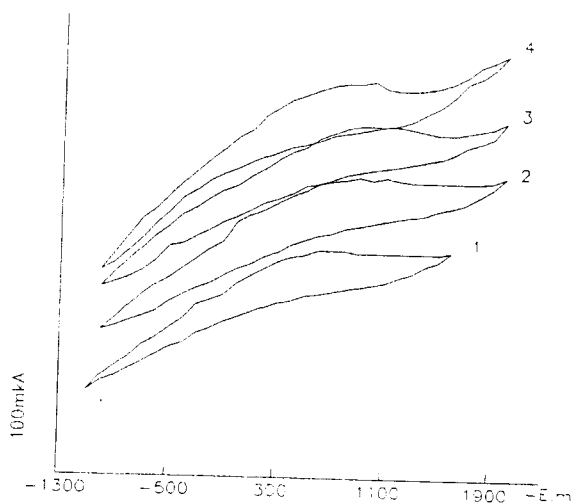


Fig. 5. Cyclic voltammograms of CS electrode in copper-containing solutions: 1 - 0; 2 - 50; 3 - 100; and 4 -  $200 \text{ mg of copper per } 1 \text{ dm}^3$ .

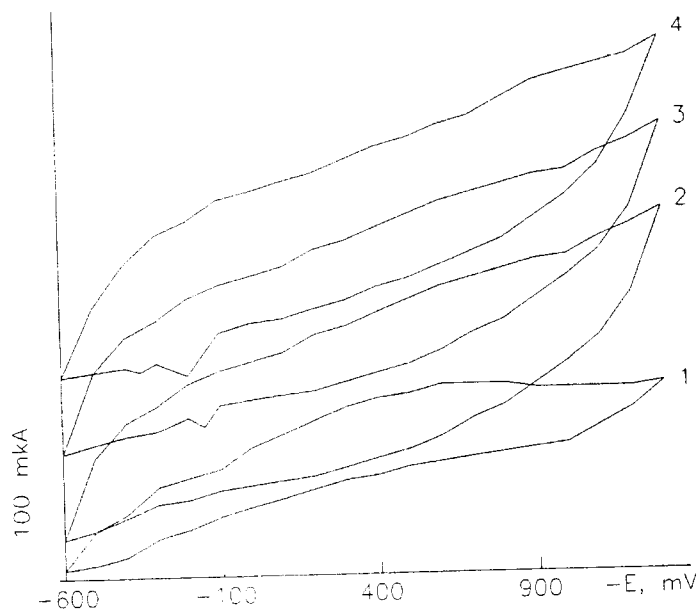


Fig.6. Cyclic voltammograms of CS electrode in nickel-containing solutions:  
1 - 0; 2 - 20; 3 - 50; and 4 - 100 mg of nickel per 1 dm<sup>3</sup>.

In the case of CS electrode polarization in nickel-containing solution any peaks of nickel reduction are not observed on the voltammograms (Fig.6). But one can see clear peaks of nickel oxidation on the curves of reverse potential scan and may affirm that nickel ions discharge on the particles surface with formation of the metal plating.

Absence of copper and nickel peaks reduction may be connected with large surface area of the electrode. Comparing voltammograms of CS electrodes in copper-containing and nickel-containing solutions we may say that due to large surface area of the electrode current density is so low and very many of copper and nickel clusters form on the particles surface. Unlike to nickel copper clusters are unstable in the solution and process of their disappearance is occurred. Because this the peaks of copper dissolution are not observed on the reverse scan curves.

With polarization of dispersed TEG electrode the same phenomenon is occurred (Fig. 7) but current values are higher on order of value as compared with that of the pressed electrodes and limited current of copper reduction begin to be occurred at concentration 2 mg/dm<sup>3</sup>.

As consequence of the voltammetry like for cathodes of pressed TEG on the voltammograms of dispersed electrodes in nickel-containing solutions discharge of nickel ions



is masked with parallel processes and only in the solutions which contain 200 and more  $\text{mg/dm}^3$  of nickel the peaks of nickel reduction display on the curves.

Comparing the voltammograms of dispersed TEG electrodes for the solution with low nickel concentration ( $1\text{--}20 \text{ mg/dm}^3$ ) one may say that at these concentrations deposition of nickel takes place because difference of current at same potentials in direct and reverse scan increases in cause of increase of nickel reduced results the accessory processes flow on the cathodes of tested carbon materials and this is a cause of that efficiency of electrolysis will not achieve 100 %. This conclusion is confirmed with the electrolysis results which are presented in Tables 1 and 2.

The electrolysis results confirmed the supposition which have been made on the basis of voltammetry data that copper will not deposit on CS particles. Electrolysis leads to formation of copper as well as nickel plating on surface of TEG particles and metallized particles which contain 10-12 % of graphite deposit on the bottom of the electrochemical reactor. But when electrolysis was carried out in the electrochemical reactor with dispersed CS cathode in the case of nickel-containing solutions the dispersed powder of nickel which practically did not contain of carbon was obtained and in the case of copper -containing solution the powder of copper oxide was obtained.

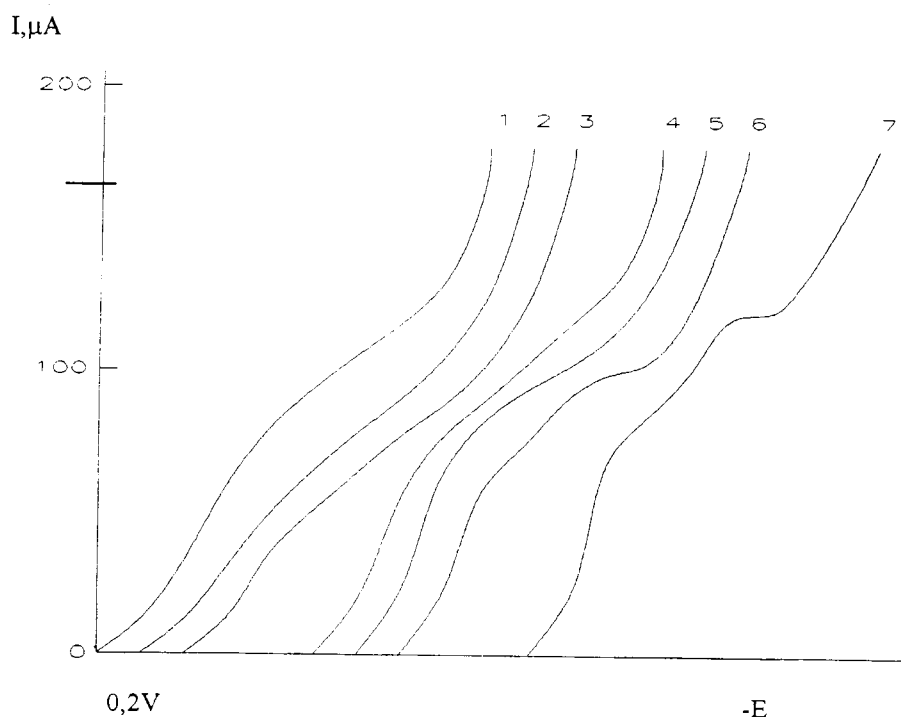
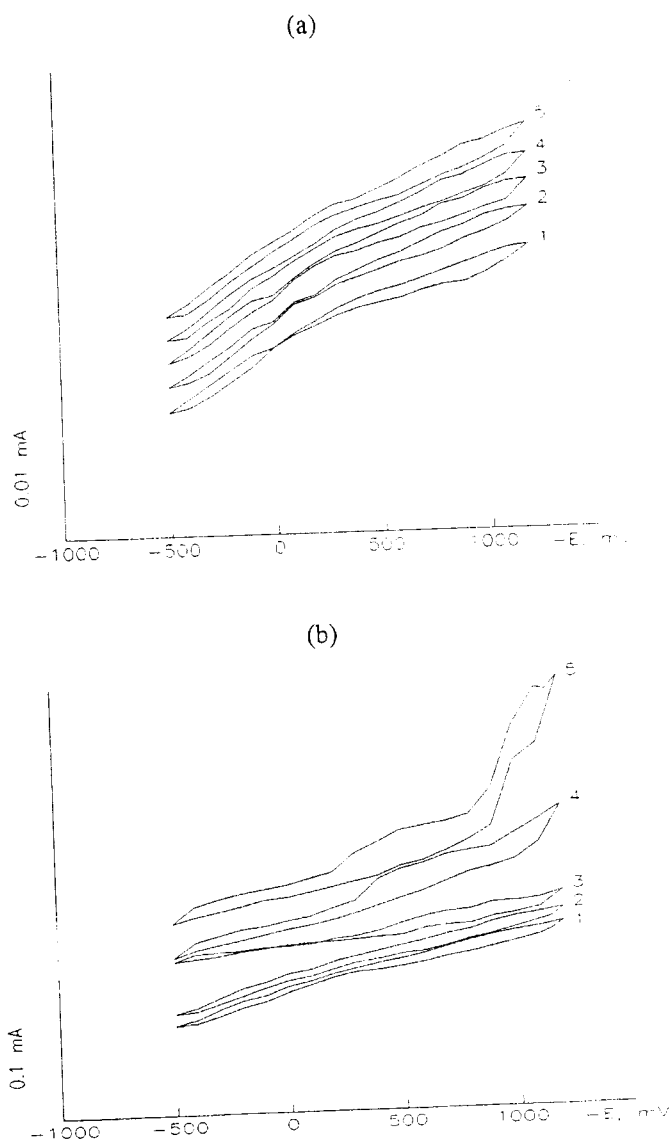


Fig.7. Voltammograms of dispersed electrode in the solutions with different copper contents: 1 - 0; 2 - 0.1; 3 - 0.2; 4 - 0.5; 5 - 1.0; 6 - 2.0; and 7 - 5.0 mg of copper per  $1 \text{ dm}^3$ .

Taking into consideration the results of laboratory tests the experimental electrochemical reactor have been projected and made experimental sample of electrochemical reactor with dispersed TEG cathode for copper extraction from washing waters of the printed circuit production section. The results of production tests are presented in the Table 3.



**Fig. 8.** Voltammograms of dispersed TEG electrode in nickel-containing solutions:  
 (a) 1 - 0; 2 - 1; 3 - 2; 4 - 5; and 5 - 10 mg of nickel per 1 dm<sup>3</sup>;  
 (b) 1 - 20; 2 - 50; 3 - 100; 4 - 200; and 5 - 500 mg of nickel per 1 dm<sup>3</sup>.

**Table 1**  
Dependence of current efficiency of copper and nickel extraction on electrolyte concentration in the electrochemical reactor with dispersed TEG cathode

N	$C_{inlet}$ mg/dm <sup>3</sup>	I, mA	$C_{outlet}$ , mg/dm <sup>3</sup>		Extraction of metal, %		Current efficiency, %	
					Cu	Ni	Cu	Ni
1	1	4.0	0.1		92.0		2.5	
2	1	2.0	0.4	0.3	60.1	6.2	5.3	6.2
3	5	2.2	0.6	0.2	88.4	12.0	9.5	12.0
4	10	2.5	0.1	0.1	99.0	15.6	15.6	15.6
5	20	2.8	0.3	0.15	98.5	18.3	17.2	18.3
6	50	3.5	0.2	0.1	99.5	30.9	29.8	30.9
7	100	3.7	0.5	0.2	99.6	39.0	37.2	39.0
8	200	4.0	0.7	0.4	99.5	46.1	44.5	46.1
9	500	6.0	0.6	0.2	99.8	52.8	50.0	52.8

**Table 2**  
Dependence of current efficiency of copper and nickel extraction on electrolyte concentration in the electrochemical reactor with dispersed CS cathode

N	$C_{inlet}$ mg/dm <sup>3</sup>	I, mA	$C_{outlet}$ , mg/dm <sup>3</sup>		Extraction of metal, %		Current efficiency, %	
					Cu	Ni	Cu	Ni
1	1	2.0	0.1	0.1	95.0	95.0	5.5	5.5
2	5	2.2	0.1	0.1	98.0	98.0	9.2	9.2
3	10	2.5	0.1	0.1	99.0	99.0	18.0	18.0
4	20	2.8	0.1	0.1	99.5	99.5	18.8	18.8
5	50	3.5	0.1	0.1	99.8	99.8	32.1	32.1
6	100	3.7	0.1	0.1	99.9	99.9	38.2	38.2
7	200	4.0	0.12	0.1	99.8	99.9	45.6	46.2
8	500	6.0	0.2	0.1	99.9	99.9	52.3	52.7

**Table 3**

The results of production testing of the experimental sample of electrochemical reactor made at SPU "Electronprylad"

N	Copper containing in inlet water, mg/dm <sup>3</sup>	Copper containing in outlet water, mg/dm <sup>3</sup>	I, A	Voltage, V	Productivity, dm <sup>3</sup> /h
1	200	10	5.0	60	25
2	150	5	4.0	35	25
3	120	7	4.0	35	50
4	100	5	5.5	35	50
5	100	2	3.2	35	50
6	70	5	3.5	50	50
7	20	2	3.2	35	70

On the basis of these experimental results some modernisation of the reactor construction was made. As a result the reactor has next parameters:

sizes, m	1.5x0.35x1
copper contents in inlet water, mg/dm <sup>3</sup>	100
copper contents in outlet water, mg/dm <sup>3</sup>	2
current value, A	8
voltage, V	35
expenditure of dispersed TEG, g/m <sup>3</sup> of water	10
productivity, dm <sup>3</sup> of water/hour	60.

Purified water was given back to washing bath. Expenditure of electrical energy for purification of 1 m<sup>3</sup> water was 4.5 kW·hour. The electrochemical reactors with dispersed carbon cathodes allow to achieve the same parameters of nonferrous metals extraction degree from low-concentrated water solutions and of a specific outlay of the cathode material in comparison with reactors with carbon fibrous cathodes.

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