

# **Development of fundamental principles of hydrometallurgical processes for the purpose of efficiency upgrading of metal extraction from low-grade stock**

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## **Abstract**

The data on leaching of complex alloys with the use of method of the combined electrochemical reactions; previously unknown physical and chemical characteristics of an alloy based on cadmium and titanium with leaching solutions in case of system parameters change; comparative data on change of structural characteristics of solutions during interaction of metals with alkaline solutions in case of presence of sulfurgraphite electrode and normal leaching are obtained.

When comparing of alloy electrochemical leaching results with leaching by solutions of sodium thiosulfate and sulfuric acid, it is shown that in case of electrochemical leaching, the extraction of metals is higher for: cadmium – 1.8 times, silver – 1.6 times, tin – 1.1 times, nickel – 1.5 times, and, in comparison with thiosulfate: cadmium – 2.2 times, silver – 1.9 times, nickel – 1.8 times.

Key words: ALLOY, ELECTROLEACHING, ELECTRODE, ANODE, CATHODE

## **Introduction**

In scientific and technical literature, there is large amount of data on development of scientific basis and new technologies of extraction of non-ferrous, rare and noble metals in inorganic aqueous solutions. The growth of the researches number directed on intensification and increase of metals extraction efficiency from poor, hard and multicomponent raw materials is noted. The researches on use of different chemicals, especially, which are not widely applied in the present-day technologies, techniques and equipment for metals extraction processes are being developed. The increase in scales and variety of researches areas are caused by decrease in quality of processed ores, involvement into production of multicomponent and

hard raw materials, necessity of recycling of technogenic waste and secondary raw materials.

Thiosulfate solutions are used for leaching of sulfide Ag-ores [1]. The influence of different components accelerating this process was investigated. Operation was carried out on the rotating disk made of  $\text{Ag}_2\text{S}$ ; the kinetics of its dilution in thiosulfate solution with adding of copper ammoniate (1 mmol/l) was studied. Catalytic effect of additive on dilution of  $\text{Ag}_2\text{S}$  is shown.

As the catalytic agent of thiosulfate leaching of  $\text{Ag}_2\text{S}$ , the complex compounds were considered:  $\text{Fe}^{3+}$ -EDTA,  $\text{Fe}^{3+}$ - oxalates and  $\text{Fe}^{3+}$ - citrates, which do not interact with thiosulfates, but are reduced by sulfides [2].

Electrolyzer for obtaining of noble metals by electrolyzing of the melted salts is suggested [3]. The electrolyzer includes hermetic cylindrical body, anode and central suspended cathode. At that, it contains the bath in the form of leakproof graphite container with the filter made of quartz fabric. The diaphragm in the form of the perforated graphite cylinder covered with quartz fabric is arranged between cathode and anode. The graphite separators are arranged between anode and diaphragm. Technical result is noble metals refining from insoluble nonmetallic impurity and proving of electrolyzer running time with a high speed of process.

The method [4] of zinc extraction from dusty wastes of metallurgical slag of brass production was suggested. The conditions of leaching and electrolyzing processes running are determined with possibility of leaching solution return to the process beginning. The analysis of scientific literature shows that traditional fundamental data on microstructure of condensed systems are used as scientific basis of new technical solutions and technologies in fundamental papers [5] and in the current publications devoting to the researches focused on development of new technologies of minerals processing [6]. The tendency of new technologies developers to increase the number of chemical operations in order to increase the efficiency of metals extraction into solution is noted in a number of papers. The analysis of fundamental studies development and designing of high technologies of non-ferrous metals extraction from complex minerals shows that the fundamental basis for development of innovative hydrometallurgical technologies is not optimized for complex, multicomponent and hard raw materials. Therefore, development of effective technologies in hydrometallurgy for extraction of metals from complex and low-grade mineral raw materials remains vital and relevant task.

## Objective

The alloy chemical composition %: Cd - 18.83, Ti - 16.93, Ag - 15.49, Sn - 13.28, V - 6.07, Co -

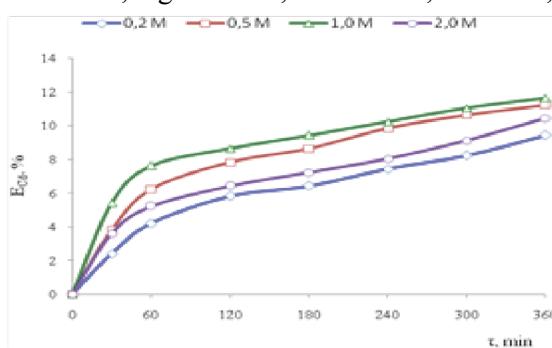
0.11, Ni - 2.18, Cu - 3.54, Mn - 3.71, Fe - 5.79, Pb - 1.19, light elements sum is 12.88. Researches of alloys electrochemical leaching process with the use of sulfurgraphite electrode were conducted.

## Methodology

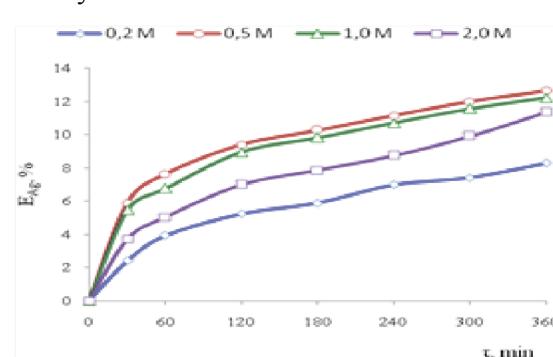
While studying, the experiments on transfer of metals into solution from multicomponent alloy and alloy based on lead and bismuth were carried out. The researches of influence of parameters of electoleaching process on metals extraction were carried out with carbon-sulfur electrode in case of current density of  $i = 150 \text{ A/m}^2$ , with stirring 480 r/min during 6 hours. Sodium hydroxide solution volume with concentration of 0.2 – 2.0 M is 200 ml,  $t = 25^\circ\text{C}$ , alloy weight is 1.0 g. The sulfurgraphite electrode was used as the anode, and the graphite electrode served as the cathode.

## Results

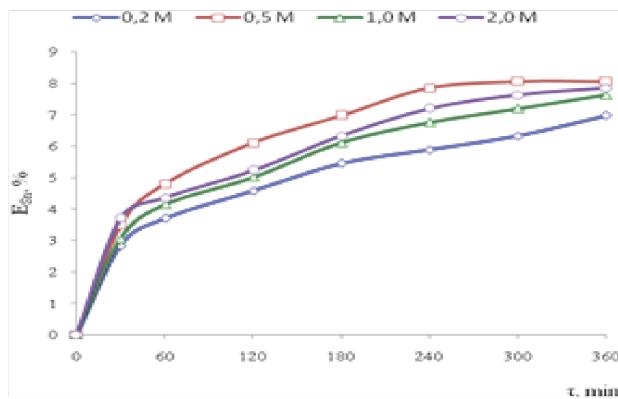
Dependence of extraction of cadmium, silver, tin and nickel when alloy electoleaching in case of sodium hydroxide concentration change in solution is presented in Fig. 1 (a, b, c, d). From presented data, it is seen that influence of sodium hydroxide concentration on extraction of cadmium and silver do not depend directly on the growth of leaching agent concentration. The degree of tin extraction is slightly lower than indicators for cadmium and silver, but nature of change of extraction degree is similar. The smallest indicators are characteristic for nickel; at that, direct dependence of nickel extraction into solution on growth of leaching agent concentration is observed. The degree of silver extraction when electoleaching during 6 hours increases in case of sodium hydroxide concentration 0.2 M to 8.2 %, 0.5 M to 8.2 %, 1.0 M to 12.2 %, 2.0 M to 12.6 %. In case of tin, these indicators at concentration of sodium hydroxide are 0.2 M – 6.9 %, 0.5 M – 7.6 %, 1.0 M – 7.8 %, 2.0 M – 8.0 respectively. For nickel, these indicators in case of concentration of sodium hydroxide are 0.2 M – 0.40 %, 0.5 M – 0.50 %, 1.0 M – 0.54 %, 2.0 M – 0.58% respectively.



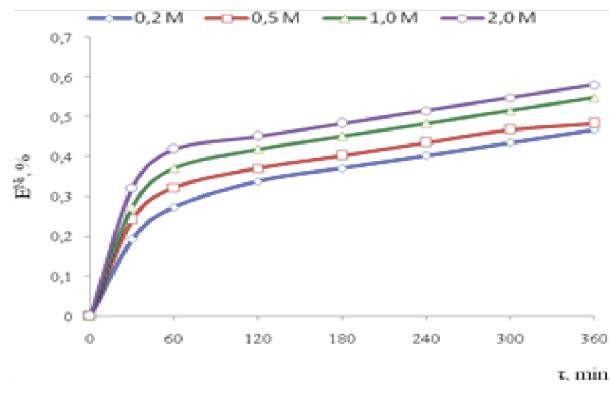
a



b



c



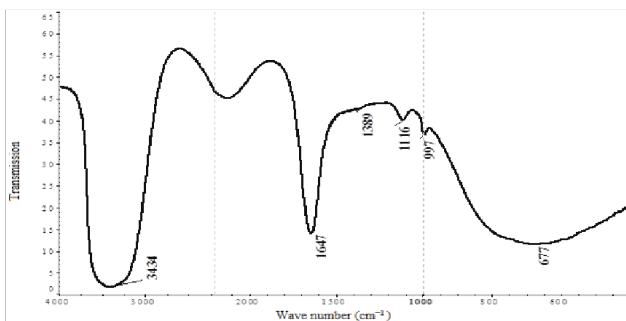
d

Current density is  $i = 150 \text{ A/m}^2$ ,  $t = 25^\circ\text{C}$ , graphite - cathode, sulfurgraphite electrode – anode

**Figure 1.** Extraction degree of cadmium (a), silver (b), tin (c) and nickel (d) when electrolyzing of an alloy depending on sodium hydroxide concentration

Data on research of microstructure of the solutions obtained as a result of alloy leaching are given below. Solutions were investigated by Fourier infrared spectrometer "Avatar 370" in the spectral range of 4000–400  $\text{cm}^{-1}$  from capillary layers in the KRS-5 windows. Spectra are recorded from layers with a transmission of 13–14% at a frequency of 1651  $\text{cm}^{-1}$ . Add-on to experiment: Transmission E.S.P.

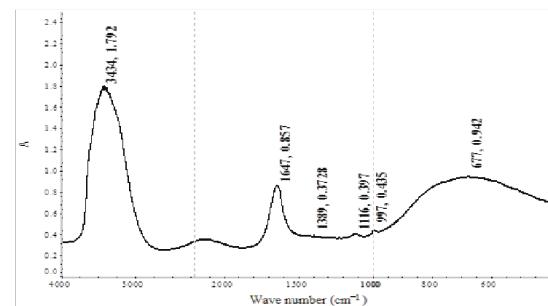
Let us dissolve  $C_{\text{NaOH}} = 0.2 \text{ M}$  in spectrum (Figure 2) of solution of the alloy obtained after electrolyzing (current density is 150  $\text{A/m}^2$ , at 25  $^\circ\text{C}$ , stirring speed is 480 r/min). The absorption bands of stretching  $v(\text{OH}) = 3434 \text{ cm}^{-1}$ , deformation  $\delta\text{HOH} = 1647 \text{ cm}^{-1}$ , and librational  $v_L \text{H}_2\text{O} = 677 \text{ cm}^{-1}$  vibrations of molecular water were recorded. The group  $[\text{S}_2\text{O}_3]^{2-}$  is 1116, 997  $\text{cm}^{-1}$ . The group  $[\text{CO}_3]^{2-}$  is 1389  $\text{cm}^{-1}$  [7].



**Figure 2.** Infrared spectrum of solution after electrolyzing of an alloy with  $C_{\text{NaOH}} = 0.2 \text{ M}$

In Figure 4, the solution of infrared spectrum after leaching of an alloy is presented at concentration of solution  $C_{\text{NaOH}} = 0.5 \text{ M}$  (current density is 150  $\text{A/m}^2$ , at 25  $^\circ\text{C}$ , stirring speed is 480 r/min). The absorption bands of stretching  $v(\text{OH}) = 3416 \text{ cm}^{-1}$ , deformation  $\delta\text{HOH}=1647 \text{ cm}^{-1}$ , and librational  $v_L \text{H}_2\text{O} = 677 \text{ cm}^{-1}$  vibrations of molecular water were record-

The optical density is measured in a maximum of absorption bands. They characterize vibrations of  $v(\text{OH})$ ,  $\delta\text{HOH}$ ,  $v_L \text{H}_2\text{O}$ ,  $v_4(\text{E})$  thiosulfate ions,  $v_1(\text{A}_1)$  thiosulfate ions,  $v_3$  group  $[\text{CO}_3]^{2-}$  (Fig. 3). Optical density in maxima of absorption bands according to stretching vibrations of water  $v(\text{OH})$  was 1.792; to deformation vibrations of water  $\delta\text{HOH}$  - 0.857; to librational vibrations of water  $v_L \text{H}_2\text{O}$  – 0.942. In a maximum of the absorption band characterizing vibration  $v_4(\text{E})$  of thiosulfate ions at wave number 1116  $\text{cm}^{-1}$ , optical density was 0.397. Optical density in an absorption band maximum at wave number 997  $\text{cm}^{-1}$ , characterizing vibration  $v_1(\text{A}_1)$  of thiosulfate ions was 0.435. Optical density in a maximum of absorption band of stretching vibration of  $[\text{CO}_3]^{2-}$  group at wave number 1389  $\text{cm}^{-1}$  was 0.3728.

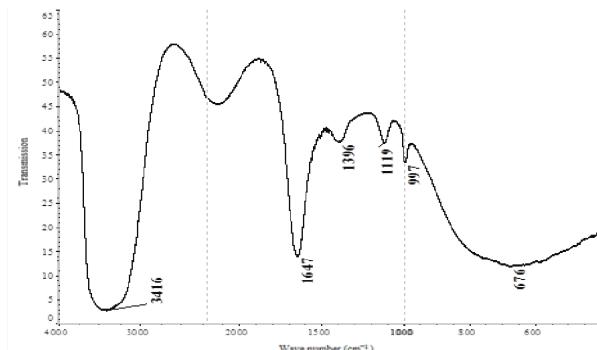


**Figure 3.** Infrared spectrum of solution after electrolyzing of an alloy with  $C_{\text{NaOH}} = 0.2 \text{ M}$

ed. The group  $[\text{S}_2\text{O}_3]^{2-}$  is 1119, 997  $\text{cm}^{-1}$ . The group  $[\text{CO}_3]^{2-}$  is 1396  $\text{cm}^{-1}$  [7].

The optical density is measured in a maximum of absorption bands. They characterize vibrations of  $v(\text{OH})$ ,  $\delta\text{HOH}$ ,  $v_L \text{H}_2\text{O}$ ,  $v_4(\text{E})$  thiosulfate ions,  $v_1(\text{A}_1)$  thiosulfate ions,  $v_3$  group  $[\text{CO}_3]^{2-}$  (Fig. 5). Optical density in maxima of absorption bands according to stretching vibrations of water  $v(\text{OH})$  was 1.581; to

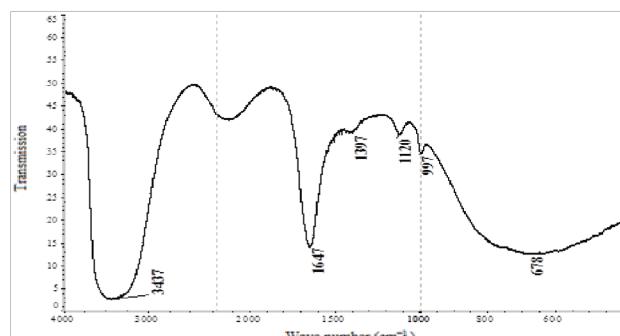
deformation vibrations of water  $\delta$  HOH – 0.861; to librational vibrations of water  $v_L$  H<sub>2</sub>O – 0.928. In a maximum of the absorption band characterizing vibration  $v_4(E)$  of thiosulfate ions at wave number 1119 cm<sup>-1</sup>, optical density was 0.427. Optical density in



**Figure 4.** Infrared spectrum of solution after electrolysis of an alloy with solution C<sub>NaOH</sub> – 0.5 M

In a spectrum (Fig. 6) of solution of the alloy obtained after leaching at concentration of solution C<sub>NaOH</sub> – 1.0 M (current density is 150 A/m<sup>2</sup>, at 25 °C, stirring speed is 480 r/min). The absorption bands of stretching v(OH) - 3437 cm<sup>-1</sup>, deformation δHOH - 1647 cm<sup>-1</sup>, and librational v<sub>L</sub> H<sub>2</sub>O - 678 cm<sup>-1</sup> vibrations of molecular water were recorded. The group [S<sub>2</sub>O<sub>3</sub>]<sup>2-</sup> is 1120, 997 cm<sup>-1</sup>. The group [CO<sub>3</sub>]<sup>2-</sup> is 1397 cm<sup>-1</sup> [7].

The optical density is measured in a maximum of absorption bands. They characterize vibrations of v OH, δ HOH, v<sub>L</sub> H<sub>2</sub>O, v<sub>4</sub>(E) thiosulfate ions, v<sub>1</sub>(A<sub>1</sub>) thiosulfate ions, v<sub>3</sub> group [CO<sub>3</sub>]<sup>2-</sup> (Fig. 7). Optical

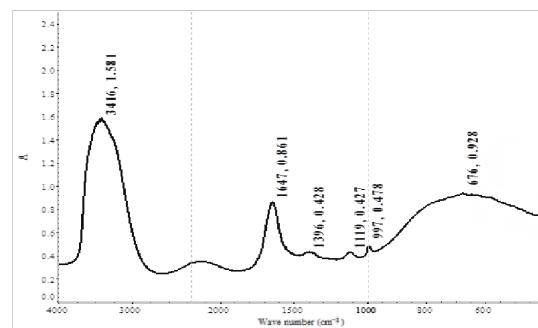


**Figure 6.** Infrared spectrum of solution after electrolysis of an alloy with solution C<sub>NaOH</sub> – 1.0 M

Experiments on chemical leaching of an alloy in order to compare the data of electrochemical leaching were conducted. Sulphuric-acid and thiosulfate leaching was used. Leaching was carried out at the room temperature and solvent concentrations: 5.0 g/dm<sup>3</sup>, 10.0 g/dm<sup>3</sup>, 15.0 g/dm<sup>3</sup>, 20.0 g/dm<sup>3</sup>.

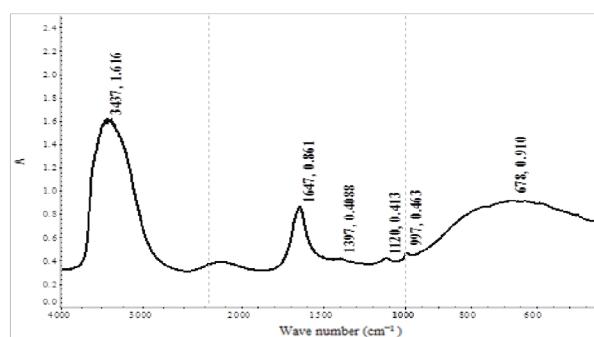
Figures 8 show that extraction of cadmium and silver from an alloy at usual chemical leaching is

an absorption band maximum at wave number 997 cm<sup>-1</sup>, characterizing vibration v<sub>1</sub>(A<sub>1</sub>) of thiosulfate ions was 0.478. Optical density in a maximum of absorption band of stretching vibration of [CO<sub>3</sub>]<sup>2-</sup> group at wave number 1396 cm<sup>-1</sup> was 0.428.



**Figure 5.** Infrared spectrum of solution after electrolysis of an alloy with solution C<sub>NaOH</sub> – 0.5 M

density in maxima of absorption bands according to stretching vibrations of water v OH was 1.616; to deformation vibrations of water δ HOH – 0.861; to librational vibrations of water v<sub>L</sub> H<sub>2</sub>O – 0.910. In a maximum of the absorption band characterizing vibration v<sub>4</sub>(E) of thiosulfate ions at wave number 1120 cm<sup>-1</sup>, optical density was 0.413. Optical density in an absorption band maximum at wave number 997 cm<sup>-1</sup>, characterizing vibration v<sub>1</sub>(A<sub>1</sub>) of thiosulfate ions was 0.463. Optical density in a maximum of absorption band of stretching vibration of [CO<sub>3</sub>]<sup>2-</sup> group at wave number 1397 cm<sup>-1</sup> was 0.4088.



**Figure 7.** Infrared spectrum of solution after electrolysis of an alloy with solution C<sub>NaOH</sub> – 1.0 M significantly lower, than at electrochemical leaching. Leaching of cadmium depending on various concentration of sulfuric acid (5.0 g/dm<sup>3</sup>; 10.0 g/dm<sup>3</sup>; 15.0 g/dm<sup>3</sup>; 20.0 g/dm<sup>3</sup>) showed that extraction ratio increases from 1.8% to 5.8%, from 4.2% to 6.6%, from 2.6 to 6.2%, from 2.8% to 6.4% respectively. 10.0 g/dm<sup>3</sup> concentration of sulfuric acid is the optimum.

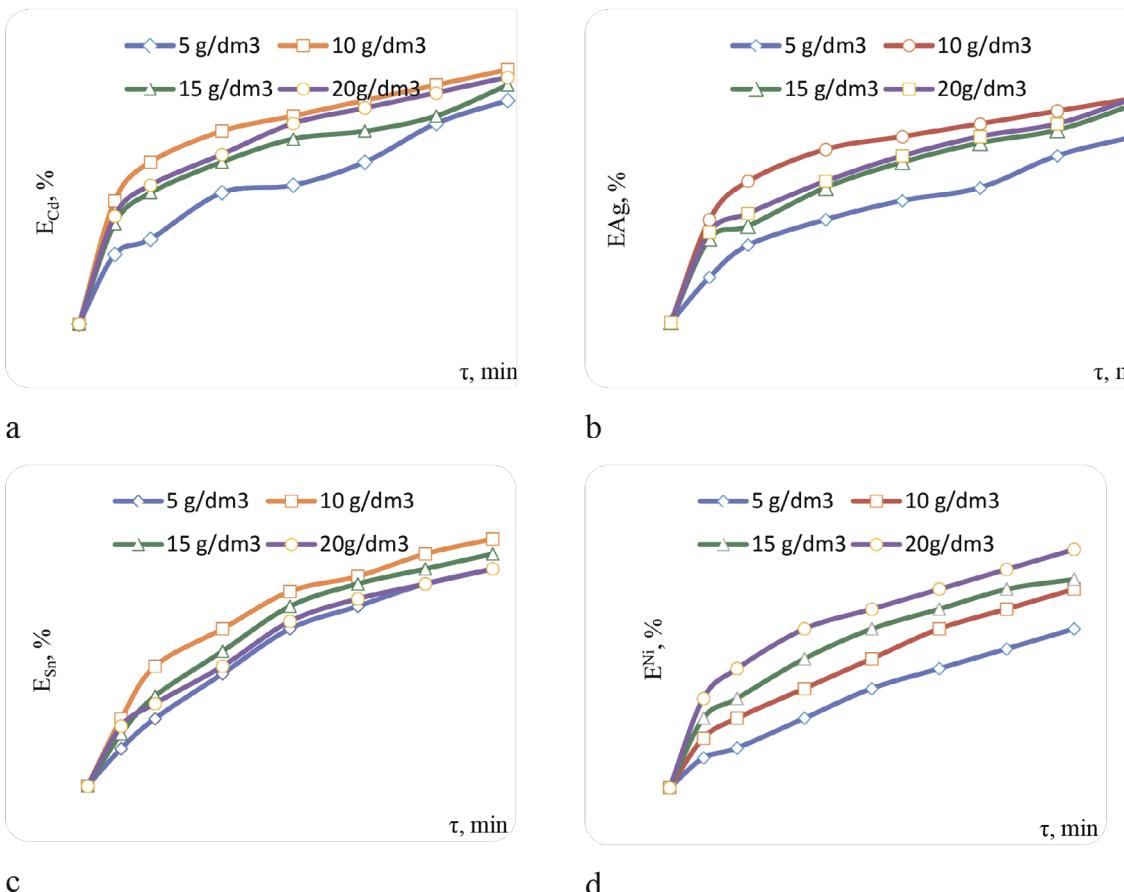
Results of extraction of silver (figure 8) show that

when concentration of sulfuric acid is 10.0 and 20.0 g/dm<sup>3</sup>, extraction ratio is the maximum - 7.6%, and when concentration is 15.0 g/dm<sup>3</sup>, extraction ratio is 7.4%, when concentration is 5.0 g/dm<sup>3</sup> – 6.3%.

Data on change of resolving extent of tin and nickel from time at various concentration of sulfuric acid are given in the figures 8. As is seen from the data provided, extraction ratio of tin during chemical leaching is little lower in comparison with electrochemical leaching (as compared with cadmium and silver) (figure 1). Thus the smallest extraction ratio is

observed (figure 8) at 5.0 g/dm<sup>3</sup> (6.3%) concentration of original solution and the greatest resolving extent of tin is observed at solutions with original concentration of 10.0 g/dm<sup>3</sup> (7.2%).

Extraction ratio of nickel during electrochemical leaching of an alloy (figure 1) is much higher, than during chemical one (figure 8). The maximum extraction ratio of nickel in the course of leaching by sulfuric acid, when the concentration is 20.0 g/dm<sup>3</sup>, reaches 0.37%.



**Figure 8.** Extraction ratio of cadmium (a), silver (b), tin (c) and nickel (d) during leaching of alloy depending on the concentration of sulfuric acid

Resolving of an alloy was carried out at various concentrations of sodium thiosulfate. Extraction ratio of cadmium, silver and nickel depending on resolving time at initial concentration of sodium thiosulfate 5.0 g/dm<sup>3</sup>, 10.0 g/dm<sup>3</sup>, 15.0 g/dm<sup>3</sup> and 20.0 g/dm<sup>3</sup> is given in figures 9 (a, b, c).

Analysis of research results presented in figures 9 (a, b, c) shows that chemical leaching by means of sodium thiosulfate has lower indicators as compared with electrochemical leaching.

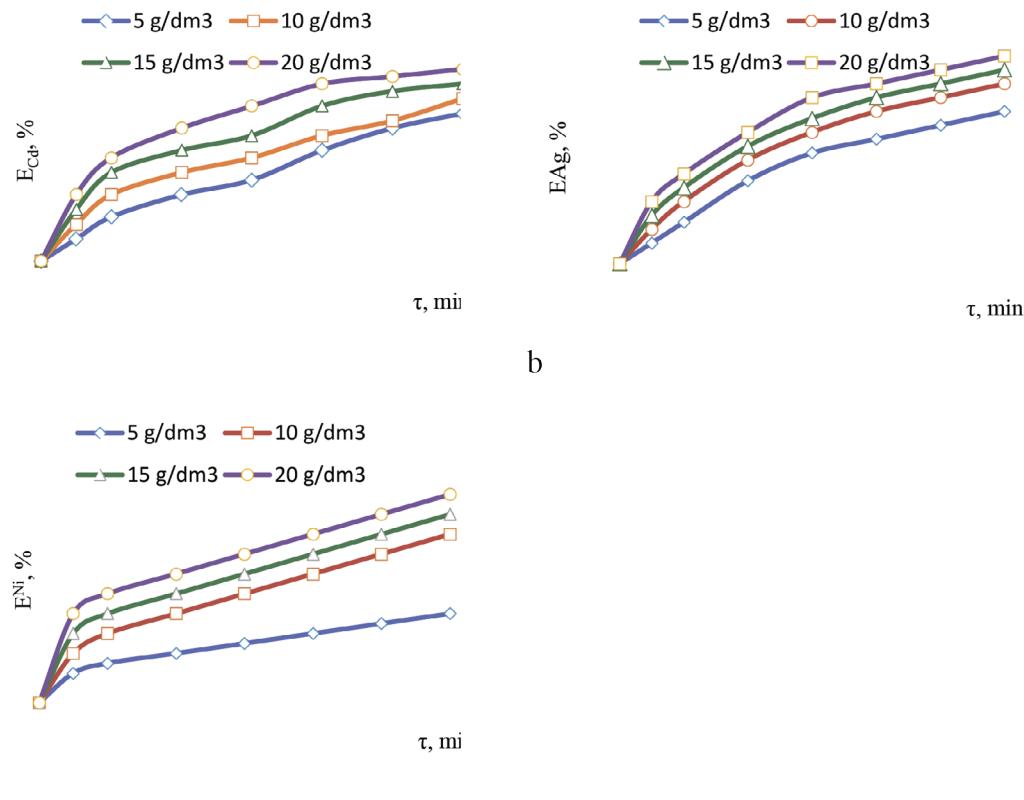
When concentration of sodium thiosulfate reaches 5.0 g/dm<sup>3</sup>, cadmium extraction by thiosulfate solution reaches 4.01% within 6 hours. When high concentration of sodium thiosulfate – 20.0 g/dm<sup>3</sup>, cadmium

extraction is 5.2%. When concentration of sodium thiosulfate is 5.0 g/dm<sup>3</sup>, extraction of silver reaches 4.81% within 6 hours. When high concentration of sodium thiosulfate – 20.0 g/dm<sup>3</sup>, extraction of silver is 6.5%.

As is seen from figure 9 (a, b, c), extraction of nickel at all concentrations of sodium thiosulfate of 5.0 – 20.0 g/dm<sup>3</sup> – is low, 0.14 – 0.34% respectively.

### Conclusion

Microstructure of leaching solutions is investigated by infrared spectroscopy method. The conclusion that microstructure of inorganic aqueous solution is influenced by almost all physical and chemical factors and that the microstructure of inorganic aqueous solutions is of molecular nature is confirmed.



**Figure 9.** Extraction ratio of cadmium (a), silver (b) and nickel (c) during leaching of alloy depending on the concentration of sodium thiosulfate

It is established that interaction of alloy and solution, which contains molecular entity including sulfur, occurs within all range of concentrations applied in experiment of solutions.

When comparing the results of electrochemical leaching of an alloy with leaching by solutions of sodium thiosulfate and sulfuric acid, it is shown that during electrochemical leaching the extraction of metals is higher for: cadmium – 1.8 times, silver – 1.6 times, tin – 1.1 times, nickel – 1.5 times, and, as compared with thiosulfate: cadmium – 2.2 times, silver – 1.9 times, nickel – 1.8 times.

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