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Galvanic Sludge Recycling with the Extraction of Valuable Components

[1]*Yulia Egorovna Tokach,* [1]*Yury Konstantinovich Rubanov,*
[1]*Nadezhda Aleksandrovna Pivovarova and* [2]*Ludmila Nikolaevna Balyatinskaya*

[1]Belgorod State Techological University named after V.G. Shukhov,
Russia, 308012, Belgorod, Kostyukova st. 46
[2]Belgorod State National Research University,
Russia, 308015, Belgorod, Pobedy st. 85

Abstract: A recycling method of galvanic production was proposed, which includes galvanic sludge mixing with additives containing chlorine ions in the ratio $Cl^-: \Sigma Me^{n+} = 1{,}1:1$, mechanochemical activation of mixture obtained by dry grinding in the ball mill to a size of 0,5 - 5 microns, subsequent heat treatment in a muffle furnace at the temperature of 450 - 500°C, the resulting cake leaching by waste water own galvanic production at pH = 3, separating the precipitate from the solution by filtration and removal of metals from the resulting solution by electroflotation at elevated pH 8 - 10. Collector and foam former for elektroflotation process for extracting metal hydroxides was selected; sodium alkylbenzenesulfonates (sulphonol) were used as a collector in an amount of 250 mg/l and potassium xanthate in an amount of 3 mg per 100 g of metal ions in solution was used as a foam former. Fractional precipitation of metals is proposed in accordance with the pH value of metal hydroxides formation. The resulting precipitates were dried and subjected to calcination at 650 °C for metal oxides.

Key words: Galvanic sludge · Waste water · Mechanochemical activation · Heavy metals · Leaching, elektroflotation.

INTRODUCTION

Full-scale extraction of heavy metals from waste water, sludge and waste processing solutions of industrial plants is explained due to the need to protect not only the environment, but also the value of metals themselves. Furthermore, due to the gradual depletion of future natural source materials, such as ferrous and non-ferrous metals for many industries acquires particular significance full use of all kinds of industrial wastes.

Currently, more attention is paid to themselves technologies, which allows efficiently to extract metal ions from galvanic sludge and waste water and create the closed circulating water systems. Thus, it is possible to prevent the harmful effects of waste water and solid waste on the environment and transform them into secondary raw materials, thereby reducing their class of hazard (up to 4th and 5th) and bring considerable profit [1,2].

Galvanic wastes can be divided according to sources of their formation and technology for their subsequent processing into two types: sewage and galvanic sludge [3].

Despite wide opportunities of immediate utilization galvanic sludges in various sectors of the economy, the most appropriate methods of the utilization are the ones that allow to extract valuable metals [4]. Mainly two methods of extracting metals from galvanic sludge are applied: hydrometallurgical, pyrometallurgical.

The essence of a hydrometallurgical method - extraction (leaching) of metals from ores and concentrates in processing waste aqueous solutions of chemical reagents and followed separation from a solution a metal or its chemical agents.

Hydrometallurgical methods are suitable for the extraction of metals from raw materials with low concentrations of the metal, which can not be treated by

Corresponding Author: Yulia Egorovna Tokach, Belgorod State Techological University named after V.G. Shukhov, Russia, 308012, Belgorod, Kostyukova st. 46.

traditional methods, so the role of these methods in terms of happening depletion and degradation of crude ore is constantly increasing.

The advantages of hydrometallurgy include the ability of separation of metals with similar properties and simplification of processing in comparing with the pyrometallurgy. Use of hydrometallurgical techniques in a variety of cases, significantly reduces the environmental pollution with hazardous waste. Hydrometallurgy is used for non-ferrous metals (Al, Cu, Ni, Co, Zn).

The essence of the pyrometallurgical method of obtaining metals from sludge is follow: sludge dewatering and drying, low temperature reductive treatment with producing powder metallurgical concentrates, their melting and obtaining pure metals and alloys.

The activation process can contribute to the intensification of these methods. Activation by grinding as a new way to speed up the physical and chemical processes is becoming more widely used. The most promising use of activation refinement in dealing with complex use of mineral resources and reduce the harmful effects of products processing industry on the environment [5]. In particular, it may be the processes of leaching, extraction, selective and gross dissolution of substances, exchanging of burning of various concentrates to burning free process, based on mechanoactivation and used in the utilization and waste water treatment with separation of valuable (or harmful) components.

Energy costs for the activation is repaid by time savings and more complete extraction of soluble components.

The heavy metal salts, that contained in galvanic sludge, is a mixture of soluble compounds as hydroxides, carbonates, sulfides, removal of which presents a number of technical difficulties. First of all, it is the presence of various impurities and the instability of the waste composition, caused by changes in the parameters of the process [6]. One of the main methods for extracting metals from waste is leaching preliminary transfer into soluble compounds.

This paper presents the results of studies on transition of not readily soluble salts of heavy metals in the water-soluble compounds by chlorinating roasting and with the use of mechanical activation with subsequent leaching of solutions.

For the research electroplating galvanic sludge was used, that contains heavy metals at the following concentrations in mg/kg: Zn^{2+} - 46625; Ni^{2+} - 1433; Cu^{2+} - 12750; Fe^{3+} - 20100; Pb^{2+} - 45; Cd^{2+} - 9.

Table 1: The rational part of the feed for chlorinating roasting

Metall	Concentration in sludge, g/kg	Required amount of chlorine ions, g
Ni^{2+}	1,433	1,733
Cu^{2+}	12,750	14,256
Zn^{2+}	46,625	50,617
Fe^{3+}	20,100	38,328
Total	80,908	104,931

X-ray diffraction of studied galvanic sludge is shown in Fig. 1.

To carry out the chlorinating roasting the necessary amount of chlorine ions was determined from the equation of reactions such as:

$$Me^{n+}(OH)_n + nNaCl \rightarrow MeCl_n + nNa(OH)$$

The required amount of chlorine ions, depending on the metal content in the sludge is shown in Table. 1.

Analyzed galvanic sludge was pre-dried in an oven at 105 °C to a residual humidity of 5%. The dry sludge in an amount of 100 g containing the extracted components in an amount of 8,090 g was mixed with 17,291 g of dry NaCl, containing 10,49 g of Cl^- and was milled in a ball mill to a particle size of 50 microns. The milled mixture was calcined in a muffle furnace at the different temperatures. In chlorinating roasting process a series of reactions takes, that result in the formation of soluble compounds of metals in the form of chlorides. [7]

Estimated chemistry processes occurring transition sulfides, hydroxides and carbonates of metals in the water-soluble chlorides is represented by the following scheme:

For Sulfides:

$$MeS + 2NaCl + 2O_2 \rightarrow MeCl_2 + Na_2SO_4$$

For Hydroxides:

$$Me(OH)_2 + 2NaCl \rightarrow MeO+Na_2O+ 2HCl$$
$$MeO + 2HCl \rightarrow MeCl_2 + H_2O$$

For Carbonates:

$$MeCO_3+ 2NaCl+0,5O_2 \rightarrow MeO+ Na_2O+ CO_2+Cl_2$$
$$2MeO+ 2Cl_2 \rightarrow 2MeCl_2+O_2$$

Fig. 2 shows X-ray diffraction after the process of co-grinding the sludge with NaCl in a ball mill for 2 hours.

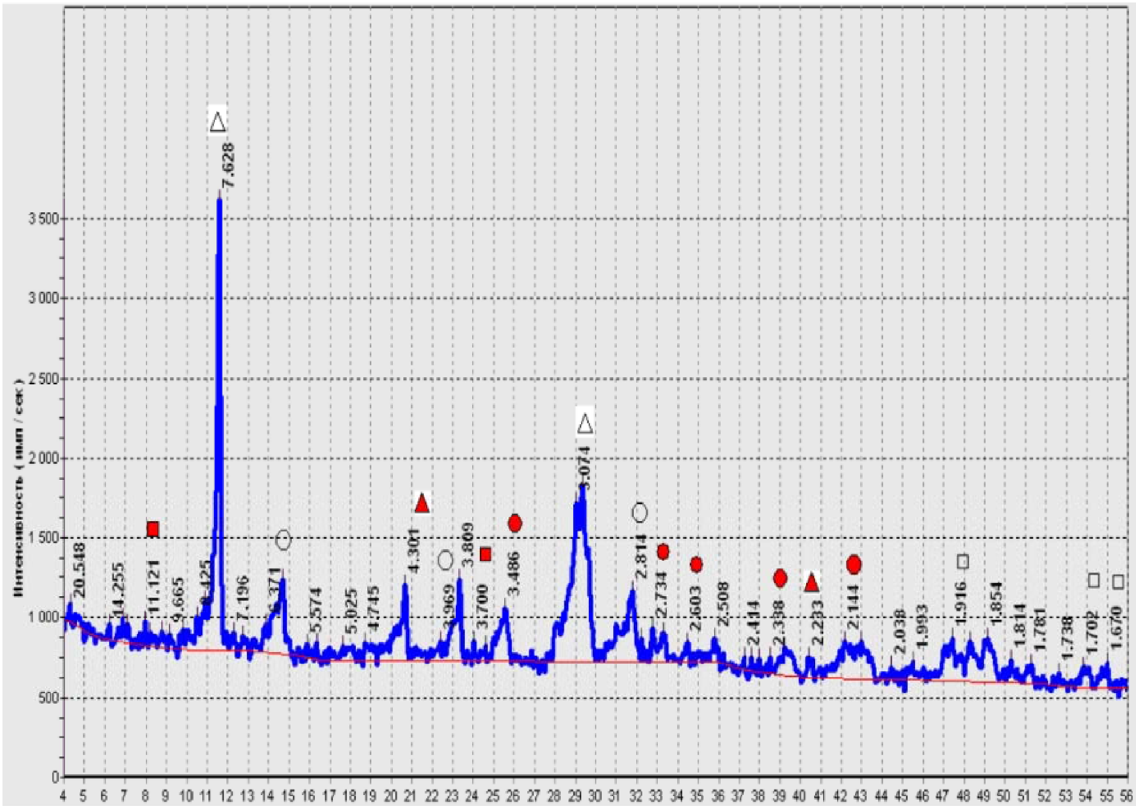

Fig. 1: X-ray diffraction of studied galvanic sludge ○- $Ni(OH)_2$; • - $Zn(OH)_2$; □ - $Cu(OH)_2$; ■- $Fe(OH)_3$; Δ- $CaSO_4 \cdot 2H_2O$; - SiO_2

Analysis of the resulting X-ray diffraction showed that the co-grinding process promotes early formation of metal chlorides as a result of mechanical activation.

To determine optimal temperature chlorinating roasting was carried out in the temperature range 500 - 650 °C. Dependence of the efficiency of metals extraction with the temperature of solution heat treatment is presented in Fig. 3, from which it can be concluded that the optimum calcination temperature is in the range 530 - 560 °C.

Temperatures below 530 °C is sufficient for the initial transition of initial metal compounds into water-soluble compounds and at temperatures above 560 °C the reverse decay of formed compounds is observed and the main products of the reaction output is reduced. Fig. 4 shows an X-ray diffraction of the sample after chlorinating roasting.

From the obtained X-ray diffraction it can be concluded that during the heat treating of the mixture sludge with the sodium chloride in the mixture the formation of chlorides of metal contained in the sludge is taken.

The study on the influence of roasting on the degree of metals extraction is shown in Fig. 5.

With increasing of firing time more than 90 minutes, the efficiency of metal extraction, as follows from Fig. 3.5, practically unchanged, thus it is advisable to carry out the calcination time in the range 80 ÷ 90 minutes.

Influence of Reduction Range of the Sludge on the Efficiency of Metal Extraction into the Solution: The purpose of this study was to determine the effect of the degree of reduction range of the material, which depends on the duration of grinding and, thus, the amount of mechanical energy input to the test material, on the efficiency of the leaching of metals.

As a result of the studies it was found that the preliminary mechanical activation of sludge with chlorine ions in the process of the chlorinating roasting intensifies the formation of water soluble compounds in the form of the metal chlorides. [8] Mechanical activation of the mixture was carried out in a ball mill at the different durations. Matching numbers and duration of mechanical activation of samples are presented in Table 2.

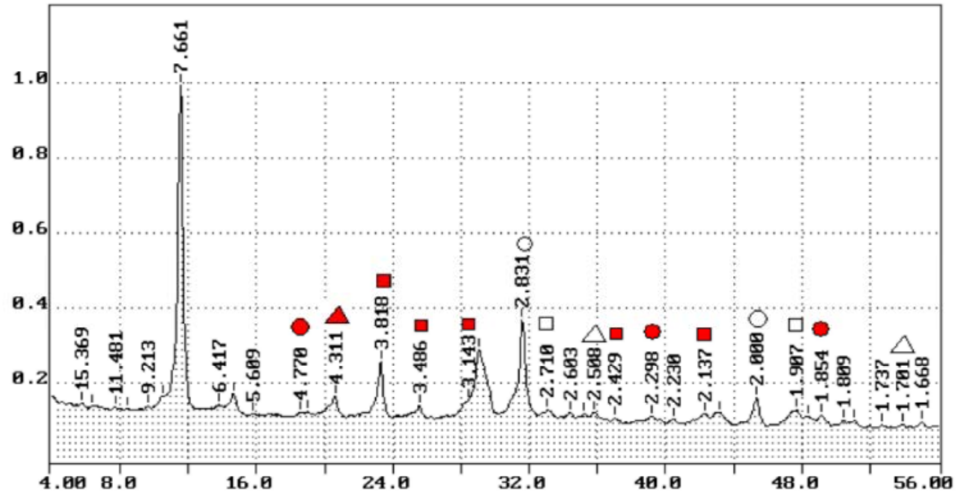

Fig. 2: X-ray diffraction of initial galvanic sludge mixed with the sodium chloride ○ - $NiCl_2{\cdot}4H_2O$; • - $ZnCl_2$; □ - $CuCl_2$; ■ - $FeCl_3$; Δ- NaCl; ▲- SiO_2

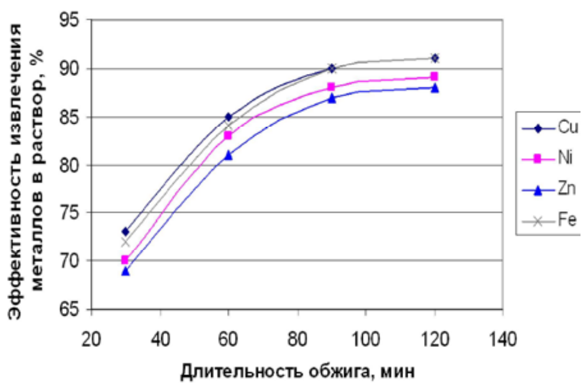

Fig. 3: Dependence of the efficiency of metals extraction with the temperature of solution heat treatment

Table 2: Matching numbers and duration of mechanical activation

Number of samples	1	2	3	4	5	6
Duration of mechanical activation, h	2	4	6	8	10	14

With processing of the sludge in a ball mill, with the degree of reduction range, structural changes occur in the substance. A plurality of defects forms and the substance becomes reactive. With processing of multiple reagents interact between them is chemical reaction. However, as the thermal activation of solid phase reactions, for the initiation of mechanochemical reaction it is necessary to bring to the powder a sufficient amount of mechanical energy. [9] Thus, the number of drum rotations of ball mill was selected most optimal.

In the process of mechanical activation in a ball mill the powder particle size was monitored using laser particle size analyzer MicroSizer 201. The measurement results are shown in Table 3.

Fig. 6 shows the dependence of residual concentration of metals in the sludge with the average particle size after mechanical activation of the galvanic sludges.

Numerical values of the residual concentration of metals in the sludge after leaching of the samples are shown in Table 4. Analysis of the results showed that with increasing the duration of the grinding fineness changed slightly. As can be seen from Table 3, 90 % of weight fraction of the particles decreased from 97.5 microns to 51.3 microns, i.e. 1.9 times. When you consider that reducing the particle size of 2 times the surface area is increased to 4 times, the residual concentration of metals in the sludge decreased more than 5 times (Zn^{2+} - in 6,8 times; Cu^{2+} - in 5,9 times; Fe^{3+} - in 8,7 times; Ni^{2+} - in 6,3 times). Therefore, to increase the solubility of substances affect not only increase the specific surface area, but also the duration of the mechanical activation process, i.e. increasing the amount of mechanical energy supplied.

In comparison with the initial concentrations of metals in the sludge extraction efficiency was: Zn^{2+} - 85,2%; Cu^{2+} - 83,1%; Fe^{3+} - 88,6%; Ni^{2+} - 84,3%.

It follows that the action of external forces increased energy reserve of grinding material by increasing the surface energy, which contributes to the acceleration of physical and chemical processes. Namely, the greater number of strokes imparted particulate substance and the larger the velocity of strokes and the less the interval between successive blows, than the greater the activity of the substance occurs and its reactivity.

Table 3: Dependence of particle size with the duration of grinding

No of samples	Correspondence of of the particle size (D, mm) with the specified weighting values part (?,%) Weight part, P, %	10	20	30	40	50	60	70	80	90	D_{cp}, mkm
1	Particle size D, mkm	1,22	2,10	3,53	5,87	9,42	15,3	26,4	47,1	97,5	23,16
2		1,25	2,15	3,41	5,39	8,54	12,2	19,9	33,1	81,0	18,55
3		1,27	2,31	3,73	5,82	8,78	12,7	21,5	33,6	59,7	16,60
4		1,13	1,88	3,08	4,93	7,97	12,0	19,6	32,8	62,0	16,15
5		1,25	1,97	2,88	4,08	5,99	9,26	15,9	25,2	55,8	13.59
6		1,19	1,86	2,73	3,42	3,64	7,4	13,6	22,4	51,3	11,95

Table 4: The residual concentrations of heavy metals after leaching of mechanically activated galvanic sludge

No of samples	Cocentration of heavy metals, mg/kg Zinc	Copper	Iron	Nickel
1	15302,4	3844,3	16383,5	1102,3
2	13986,8	3412,1	15153,5	993,6
3	11114,8	2789,7	10,979,0	903,2
4	10432,1	2270,7	6845,1	564,4
5	5834,4	1374,7	3625,2	375,2
6	2265,1	649,1	1865,5	176,9

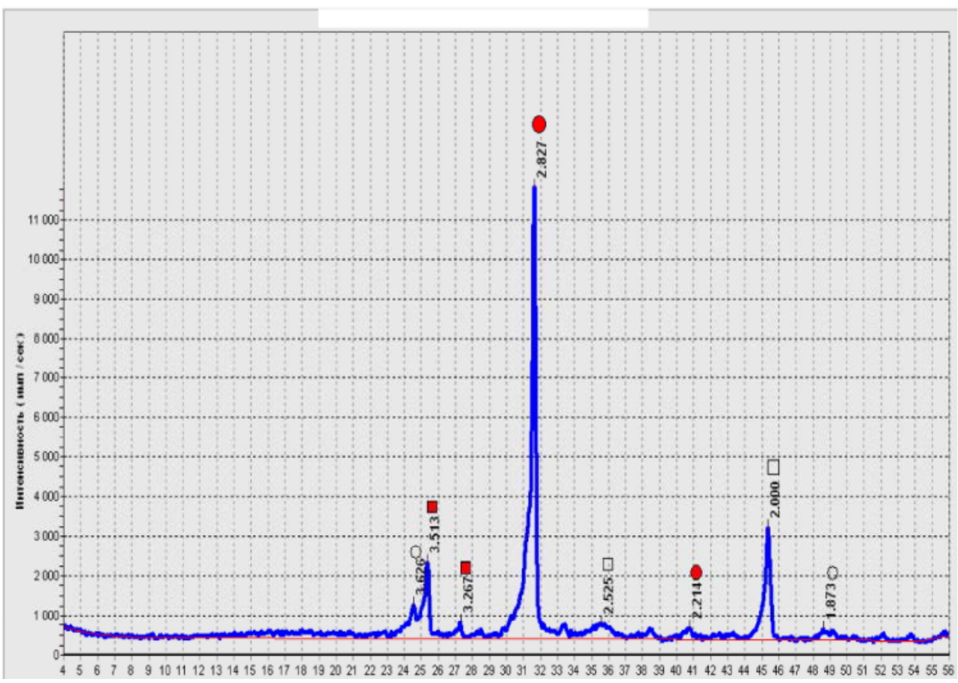

Fig. 4: X-ray diffraction of initial sludge mixed with the sodium chloride after heat treatment at the temperature 530 °C ○ - $NiCl_2$; • - $ZnCl_2$; □ - $CuCl_2$; ■ - FeCl3.

Complex Metal Ions Extraction from Concentrated Solutions by Electroflotation Method: Application of electroflotation extraction method of metal ions from solutions is due to its efficiency. Varying the electrical parameters of the process we can provide optimum dispersion of air bubbles, without destroying the foam layer. Along with the electrode unit processes at the electroflotation device volumetric flow chemical reactions is taken, which lead to phenomena such as a change in the nature and the flotation concentrate solubility, dissolution or the formation of sludge, the destruction of complexation substances that improves the quality of the process.

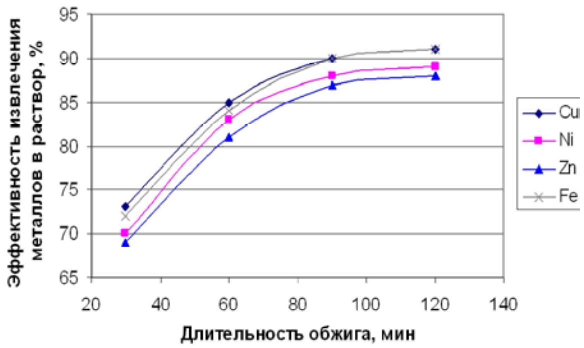

Fig. 5: Dependence of the efficiency of metals extraction into the solution with the duration of roasting

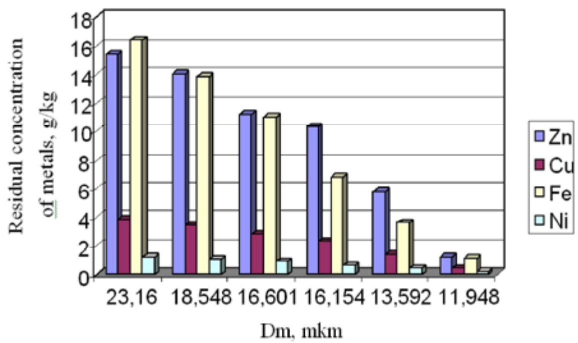

Fig. 6: Dependence of residual concentration of heavy metals in the sediment after leaching with medium particle size

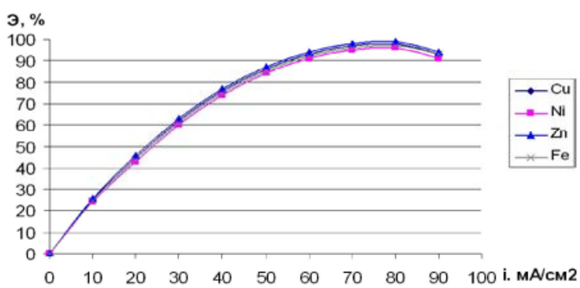

Fig. 7: Dependence of the efficiency of elektroflotation metal extraction with current density

Investigations were carried out with solutions obtained by leaching of studied electroplating galvanic sludges after chlorinating roasting with pre-mechano-chemical activation.

It is known that the magnitude of the load current at the electroflotation depends on the treating solution, the nature of float compound, concentration shape and material of the electrodes and it is an important parameter for controlling the amount of released gases and the size of the microbubbles, which is decisive for the formation flotation complexes «bubble - disperse phase» and then separating it from the formed foam concentrate. At low current value, i.e. in a laminar flow regime, the degree of gas saturation is low, whereby the process is not efficient enough. At high load current, there is considerable turbulence in the flow, which also reduces the efficiency of extraction. Deleterious effect in this case due to coalescence of bubbles accompanied by a significant reduction in useful surface of the gas phase in a heterogeneous system and decrease the probability of formation flotation complexes (it is reduced proportion of bubbles participating in the flotation elementary event). On the other hand, such large bubbles, which have a higher kinetic energy when collision with an already formed flotation complex not fixed on the surface thereof and divides it. The presence of convective flow induced by sparging and also due to less stable foam flotated pollutant [10].

From the literature sources it is also known that at low concentrations of the object to retrieve the effect the current density is expressed weakly as residual concentration decreases to a lesser extent, thus the efficiency of extraction is decreasing. By increasing the initial concentration of metal ions the formation of flotation complex is not complete, gassing enough is not enough, i.e. load growth needs. At the same time, as already mentioned, this leads to a large turbulence of the solution. This contradiction leads to a decrease in the extraction efficiency [11].

Below the experimental data of matching the optimum current for the efficient extraction of metals are shown.

Efficiency of the electroflotation process carried out at current densities of 0 - 90 mA/cm^2 for 20 min. Collector and foam former for elektroflotation process for extracting metal hydroxides was selected; sodium alkylbenzenesulfonates (sulphonol) was used as a collector in an amount of 250 mg/l and potassium xanthate in an amount of 3 mg per 100 g of metal ions in solution was used as a foam former.

Fig. 7 shows curves showing the dependence of the efficiency of metal recovery with current density. Curves pass through a maximum current density in the range 70 - 80 mA/cm^2.

It should be noted that the correct choice of the current density maximizes the extraction efficiency in minimal time. Intensification of electroflotation process by increasing the current density above the optimum reduces the efficiency of the process.

Flotation of hydrophobized sediment has the peculiarity that at first recoverable metals pass into the sediment and then subject to flotation by collectors.

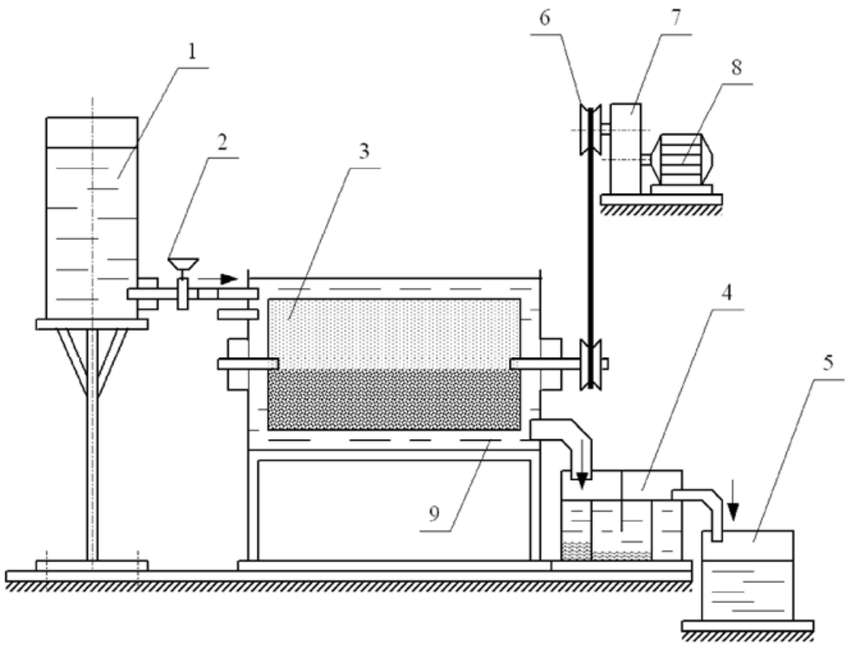

Fig. 8: Scheme of laboratory installation for copper depositing on a rotating drum 1 - pressure tank, 2 - adjusting valve, 3 - cylinder, 4 - sump, 5 - collector of the solution, 6 - pulley, 7 - gear, 8 - motor, 9 - bath.

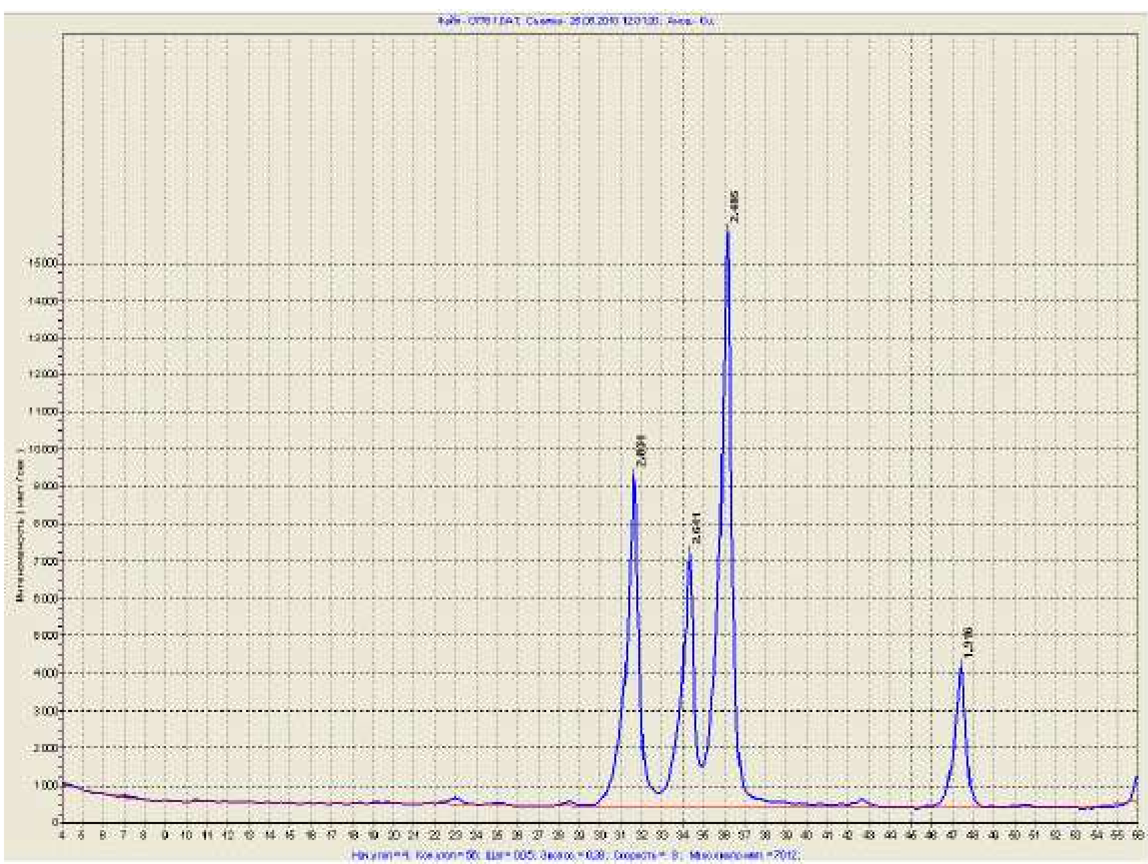

Fig. 9: X-ray diffraction of sediment, got with pH =8 after calcinations ● ZnO

Selectivity can be increased by adjusting the conditions of the medium. Thus, the ions can be separated by changing the shape of extracted substance by changing pH. By changing the pH of the medium can be phasically besiege certain groups of ions, then spending their selective flotation. For example, at low pH can extract iron hydroxide, gradually increasing the pH to allocate sequentially hydroxides of copper, zinc and nickel.

The most complete flotation occurs in environments finding appropriate metal hydroxide form (Table 5).

In the process of electroflotation with solutions, that has the pH value less than 4, decrease the efficiency of metals extraction is observed, which is due to the decomposition of collectors in acidic media with the release of free fatty acids RCOOH and transition metals in solution. When separation of metals at high pH values ??and a reduction in the efficiency of their removal from the transition metals to other chemical forms which do not interact with the collector in an aqueous solution.

Table 5 shows that increasing the pH to hydrate metals flotation properties are as follows: Fe (III), Cu (II), Zn (II), Ni (II). The dependence of the degree of metals extraction from aqueous solution pH was used for selective isolation.

Selective Metals Extraction from Complex Solutions: Studies in the selective extraction of metal ions from the solution after leaching of electroplating galvanic sludge performed by controlling of medium conditions. Changes in pH of the solutions was performed by the pH = 2 to pH = 12. This stepwise precipitated certain group of ions and then selective flotation was conducted [12].

According to the Table 5, the pH of hydrate of copper and zinc formation are in the same range, so the first step necessary to select the copper from acidic medium without admixture with pH = 2 - 3. For this purpose, a way of extracting copper with an iron scrap was used. Fig. 8 is a schematic diagram of the laboratory setup depositing copper on an iron scrap in a rotating drum.

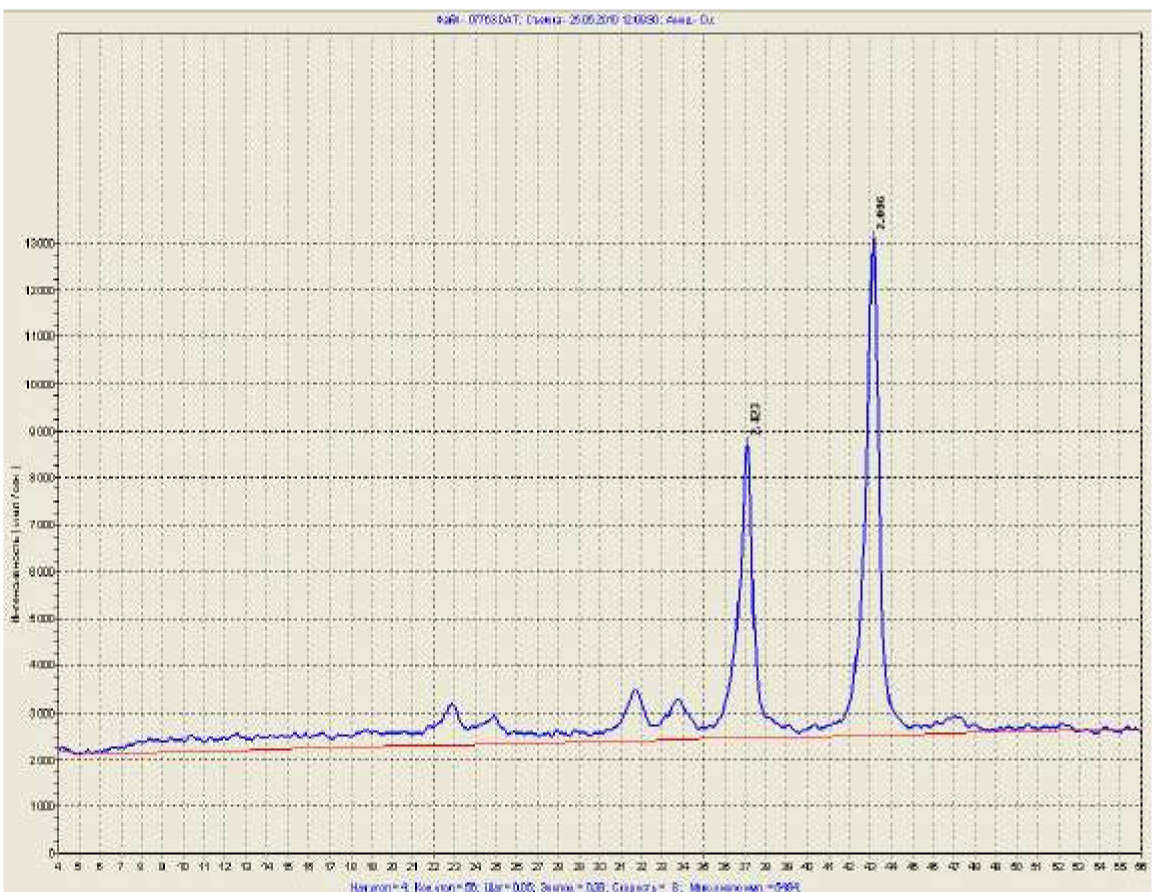

Fig. 10: X-ray diffraction of sediment, got with pH =11 after calcination ●·NiO

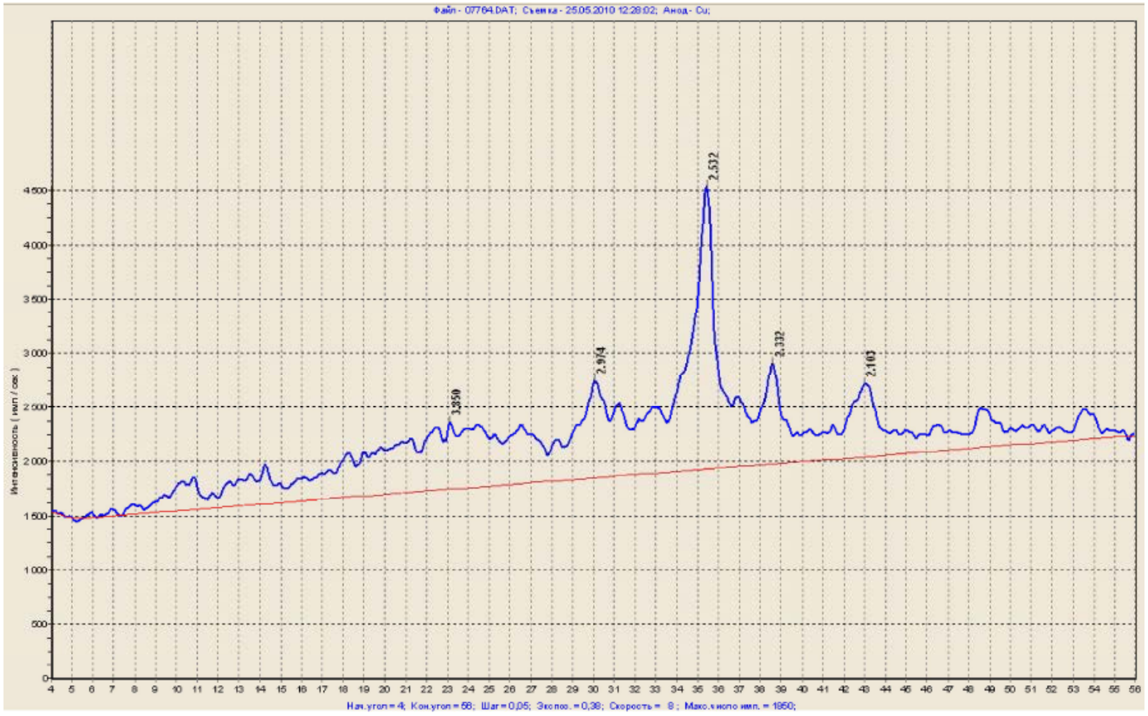

Fig. 11: X-ray diffraction of sediment, got with pH =5 after calcination ☐Fe_2O_3

Table 5: The range of the pH to precipitate the hydroxides of metals from solutions

Hydroxides	pH
$Fe(OH)_3$	4 - 6
$Cu(OH)_2$	7 - 9,5
$Zn(OH)_2$	7,5 - 9,0
$Ni(OH)_2$	9,5 - 11,5

Table 6: The residual concentrations of metals in the sludge

Metal	Initial concentration of metal, mg/kg	Final concentration of metal, mg/kg	Efficiency of extraction E, %
Cu^{2+}	12750	768	94
Fe^{3+}	20100	804	96
Zn^{2+}	46625	466	99
Ni^{2+}	1433	112	92

Extraction of ferric hydroxide was carried out at pH 4 - 5.5. This medium corresponds to finding in the form of ferric hydroxide. Alkalization of medium to pH 6.5 - 8.5 promoted to copper and zinc hydroxides precipitation.

The solution after leaching from the pressure tank *1* through the adjusting valve *2* gets into the bath *9*, inside of which is installed a rotating drum *3*. The drum formed with a perforated lateral surface. Iron scrap is placed inside the drum. Rotation of the drum is provided by an electric motor *8* via a gear *7* and a belt transmission *6*. The sediment with copper from the bath enters the collection sump *4* and collector of the solution 5.

At the second step extraction of the iron was produced at pH 4 - 5.5. At third step - zinc extraction at pH 6.5 - 8.5 and in the fourth stage flotation of nickel produced at pH = 10.5 - 11.

The efficiency of stepwise metal hydroxides extraction is shown in Table 6. The obtained residual sediments was dried and subjected to calcination at a temperature of 650 °C for getting of metal oxides. XRD patterns of the samples after calcination (Fig. 9 - 11) correspond to the extracted metal oxides.

The paper presents a technology of simultaneous neutralization of waste water and sludge of electroplating galvanic production, which allows to minimize the effects of toxic substances influence on the environment and provides to get valuable products in the form of a metal powder which can be used for industrial purposes.

CONCLUSION

Preliminary mechanical activation of mixture galvanic sludge with NaCl at a ratio Σme^{n+}: Cl^{-}=1:1,1 intensifies transition of not readily soluble heavy metal compounds in water-soluble form by more than 5 times in size reduction factor of 2 times.

The optimum temperature of chlorinating roasting for complex heavy metals extraction from galvanic sludges is 530 - 560°C for timing up to 90 minutes.

For the selective recovery of metals from solutions it is appropriate to pre produce cement copper precipitation in an acidic medium, with followed fractional getting of hydroxides and removing them into the foam concentrate.

The optimum concentration of reactants, flotation collectors for the extraction of heavy metals from leach solutions is for sodium alkylbenzenesulfonate 250 mg/l, for potassium xanthate 5 mg per 100 g of metal ions.

The optimum current density for the electroflotation recovery of metal ions from solutions is 80 mA/cm^2.

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