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DEVELOPMENT OF FERRITIZATION PROCESSING OF GALVANIC WASTE INVOLVING THE ENERGY-SAVING ELECTROMAGNETIC PULSE ACTIVATION OF THE PROCESS

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Розглядається перспектива підвищення рівня екологічної безпеки промислових підприємств в результаті реалізації ресурсозберігаючої технології переробки відходів гальванічних виробництв методом феритизації з електромагнітною імпульсною активацією процесу. Експериментально визначено вплив різних способів активації процесу феритизації: термічного та електромагнітного імпульсного при сталіх технологічних параметрах ($C_S=10,41 \text{ г/дм}^3$; $Z=4/1$; $pH=10,5$; $\tau=25 \text{ хв}$; $v=0,15 \text{ м}^3/\text{год}$) на ступінь вилучення іонів важких металів з гальванічних відходів. Показано, що найкращі показники переробки були досягнуті при наступних режимних характеристиках генерації електромагнітних імпульсних розрядів: амплітуді магнітної індукції $0,298 \text{ Тл}$, частоті імпульсів від $0,5$ до 10 Гц . Такий спосіб активації забезпечує належний ступінь вилучення іонів важких металів – $99,97 \%$ для використання очищених розчинів в оборотній системі водопостачання підприємства. Виконано структурні дослідження фазового складу і фізичних властивостей осадів феритизації. Екологічно безпечні феритизаційні осадки, які отримані при термічному і електромагнітному імпульсному способі активації характеризуються високим ступенем ущільнення більш ніж 90% , кристалічною структурою з максимальним вмістом феритних фаз з магнітними властивостями. Крім того, як показали експерименти з вилучування важких металів, ці осадки характеризуються високим ступенем їх іммобілізації, який сягає $99,96 \%$, на відміну від гальванічних шлаків нейтралізації стічних вод $<97,83 \%$. Метод електромагнітної імпульсної активації має і незаперечні енергетичні переваги в порівнянні з високотемпературним: енергозатрати знижуються більш ніж на 42% . Запропонований процес переробки гальванічних відходів удосконаленим методом феритизації запобігає забрудненню навколишнього середовища, забезпечує ефективне і раціональне використання води, сировини та енергії в системі гальванічного виробництва

Ключові слова: феритизація, гальванічні відходи, важкі метали, електромагнітні імпульсні розряди, вилучування

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1. Introduction

Water pollution is one of the main risk factors for human health. Toxic wastewater from galvanic production, as well as waste water purification products, are of particular danger, given the high content of toxic compounds of heavy metals. Known methods of galvanic production wastewater treatment come down to its processing into low-soluble hydroxides with their separation in the form of galvanic sludge [1]. The ions of heavy metals easily leach from these

unstable substances into the soil and water objects, thereby causing irreparable damage to the entire ecosystem [2]. Ukraine annually accumulates in specially designated places about 2.26 million tons of toxic wastes from acids, alkalis, and salts, and 0.98 million tons of galvanic sludge, which is considerably greater than in other European countries [3]. That is why most enterprises have fully exhausted their capacities to host such wastes at own territory. At present, the volume of their processing and disposal is insufficient while there are not enough dedicated polygons.

That renders the issue of processing galvanic waste more important every year.

The most rational techniques for treating galvanic sludge are its processing and obtaining products for commercial application or extraction valuable components from these toxic sediments [4]. However, all known technologies involve multistage processes and require the use of a large number of different, including costly and hazardous, reagents, or considerable energy consumption [5]. In addition, the implementation of such technological processes demands serious investments. Therefore, of special importance is the possibility of further development and implementation of environmentally reliable, low-waste and energy-saving technologies. Employing such technologies makes it possible to effectively remove the ions of heavy metals from galvanic sediments and waste water and to construct closed water supply systems.

One of the promising methods for processing galvanic waste is the ferritization method [6]. Using this method makes it possible to receive chemically resistant compounds of heavy metal ferrites, harmless to the environment, from high-temperature treatment of solutions with an alkaline reagent and oxygen of air. In addition, this method ensures a high degree of heavy metal ions extraction from the reactive mixture [7].

Thus, it is a relevant task to improve ferrite processing of galvanic wastes by reducing energy consumption for implementing the technology.

2. Literature review and problem statement

The expediency of ferritization for processing galvanic wastes is predetermined by that they simultaneously contain compounds of iron and other heavy metals, in particular nickel, copper, zinc. Recent years have seen numerous studies into processing galvanic sediments and used technological solutions by ferritization. Thus, paper [8] considers the process of treating galvanic sludge when the ions of iron, nickel, copper, and zinc are transferred to insoluble compounds. The disadvantage of such a ferritization is that the process was performed at a temperature of the reactive mixture above 60 °C, requiring significant energy costs. Study [9] noted the inclusion of Cu^{+2} ions into the structure of ferrites and the chemical stability of sediments, in relation to leaching of heavy metals' ions; work [10] examined the ferritization of highly concentrated chromium-containing wastewater. Authors of works [9, 10] investigated model solutions, rather than actual liquid wastes from galvanic production. In their research, the authors of [9, 10] indicate the optimal parameters for a ferritization process, namely: the ratio of concentrations $\text{Fe}^{2+}/\text{Cu}^{2+}$ is 3.5; $\text{Fe}^{2+}/\text{Cr}^{3+}$ is 7. The conditions for ferrite processing of waste from water treatment have a series of disadvantages as well – significant temperature, 80 °C and 65 °C, and a prolonged time of the process, 10 hours and 1 hour, for the ions of copper and chromium, respectively. Paper [11] applied the process of ferritization to clean the concentrated wastewater from copper lines at the starting concentration $>10 \text{ g/dm}^3$. It was established in studies by authors [8, 10, 11] that the main factors that influence the course of a wastewater cleaning process are the pH value, the temperature and duration of the ferritization process, as well as the ratio of heavy metals concentrations.

Thus, our analysis of the scientific literature [8–11] reveals that the processing of liquid and condensed galvanic

wastes by a ferritization method is typically performed at temperatures above 60 °C with a duration longer than an hour. Given this, the conventional thermal technique for activating the process is rather energy- and resource-intensive. An alternative to thermal activation could be the activation by electromagnetic pulse discharges. Authors of paper [12] used high-power discharges, which are significant in terms of energy costs. Study [13] investigated the process of cleaning the highly-concentrated wastewater from the nickel-plating line using the electromagnetic pulse activation of the ferritization process. However, study [13] failed to consider in detail the effect of rational changes in the mode characteristics of electromagnetic pulse discharge generation on the process of wastewater treatment from the ions of heavy metals and the structural properties of the sediment received. Thus, it is advisable to further improve the ferritization method involving the electromagnetic pulse activation of the process, with the aim to minimize energy resources while obtaining chemically resistant waste. In addition, further disposal of such stable waste would contribute to solving the issue of environmental safety and resource saving in galvanic production. Therefore, it is a relevant task to develop and comprehensively study a cost-effective processing of galvanic wastes.

3. The aim and objectives of the study

The aim of this study is to devise the regime characteristics for the electromagnetic pulse activation of ferrite processing of galvanic wastes. This would improve the degree of energy and resource saving in the process of neutralization of toxic liquid wastes from industrial production.

To accomplish the aim, the following tasks have been set:

- to conduct an experimental study into the influence of characteristics of electromagnetic pulse discharges in the activation of the ferritization process on the degree of extraction of heavy metals from the solutions of galvanic sediments;
- to experimentally examine the physical-chemical properties of ferrite sediments from the processing of liquid galvanic wastes;
- to investigate leaching of heavy metals from the sediments obtained.

4. Materials and methods to study the processing of galvanic waste by the ferritization method involving the electromagnetic pulse activation of a reactive mixture

For the experiments, two laboratory installations were used with a reactor's working volume of 1 dm^3 : with the thermal activation of the ferritization process at temperatures up to 75 °C [14] and the electromagnetic pulse activation at room temperature (Fig. 1).

Earlier study [13] has made it possible to conclude about the feasibility of the ferritization process at the following mode characteristics of pulse generation: the amplitude of magnetic induction is 0.08 and 0.3 Tl, the pulse rate is 0.1...1,000 kHz, the power is 35...120 W. Electromagnetic pulse activation was carried out by packets of pulses in the quantity from 1 to 5; the interval between packets is 10 s. The number of pulses in a packet is from 1 to 10, the period between pulses is 5...1,000 ms, the pulse duration is 5...1,000 ms.

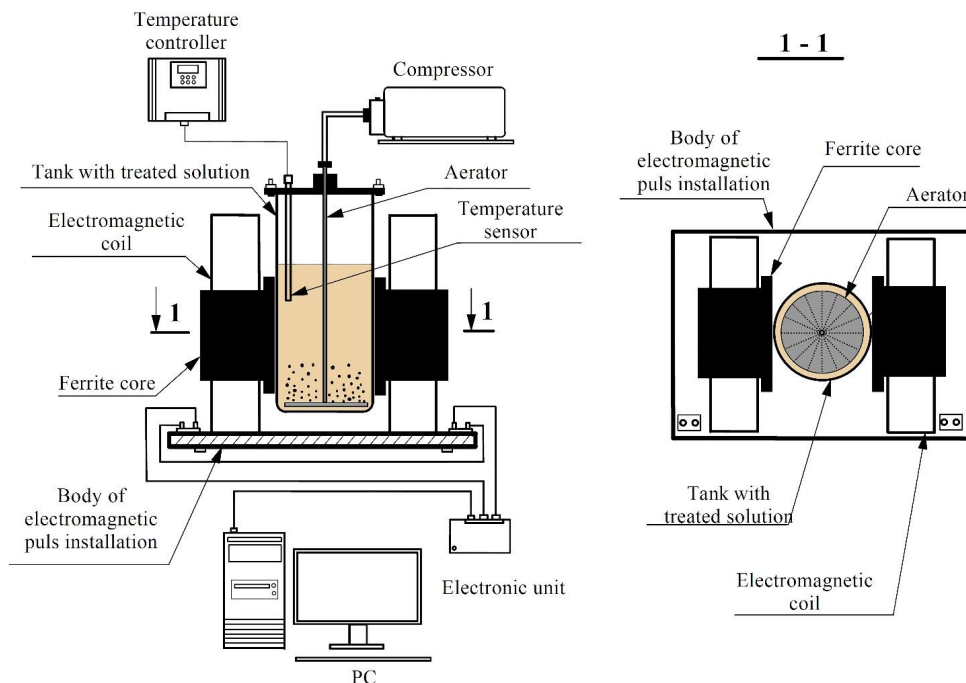


Fig. 1. Structural diagram of laboratory installation for processing galvanic wastes by the ferritization method involving electromagnetic pulse activation

We have examined a condensed sediment, which is the waste from the reagent purification of used electrolytes of nickel plating, copper plating, and galvanizing, as well as a used sulfuric acid solution from steel etching at one of the industrial enterprises in the city of Kyiv (Ukraine). Basic characteristics of the galvanic sludge and the used etching solution are given in Tables 1, 2. The sludge processing was carried out in two stages. At the first stage, dissolving of sediment in the used etching solution was conducted. The second stage of processing implied the ferritization of the obtained solution. To implement it, we adjusted the necessary ratio of concentration of iron ions and the total concentration of other heavy metals ions: $[Fe^{total}]/\Sigma ([Ni^{2+}]+[Cu^{2+}]+[Zn^{2+}])$ and added tap water. To adjust a pH magnitude, we used a 25 % sodium hydroxide solution followed by the aeration of the reactive mixture with oxygen from air.

The ferritization process of the obtained reactive mixture was conducted according to the optimal technological parameters, which were set by us in [11]:

- the total concentration of heavy metals ions $C_{\Sigma} = 10.41 \text{ g/dm}^3$;
- the ratios of ions concentrations

$$[Fe^{total}]/\Sigma([Ni^{2+}]+[Cu^{2+}]+[Zn^{2+}])Z=4/1;$$

- pH value 10.5;
- process duration $\tau=25 \text{ min.}$;
- the rate of aeration of the reactive mixture by oxygen from air $v=0.15 \text{ m}^3/\text{h}$.

Table 1

Basic characteristics of the galvanic sludge neutralization

| Content of heavy metals ions, g/dm ³ | | | | pH | Density (ρ), g/cm ³ | Moisture content (W), % | Dry residue, mg/dm ³ |
|---|------------------|------------------|------------------|------|--------------------------------|-------------------------|---------------------------------|
| Fe ^{total} | Ni ²⁺ | Cu ²⁺ | Zn ²⁺ | | | | |
| 0.203 | 4.732 | 2.631 | 1.425 | 9.81 | 1.016 | 93.06 | 3,040 |

Table 2

Characteristics of used sulfuric acid etching solution

| Etching material | H ₂ SO ₄ , g/dm ³ | Fe ^{total} , g/dm ³ | SO ₄ , g/dm ³ | pH | Suspended substances, g/dm ³ |
|------------------|--|---|-------------------------------------|------|---|
| Steel pipes | 41.0 | 46.6 | 79.89 | 1.45 | 0.35 |

We have examined the process of ferritization involving both thermal and electromagnetic pulse activation technique.

The plan of nine series of experiments is given in Table 3. To initiate the process of ferritization, we added magnetite (Fe₃O₄) to the reactive mixture [15].

Residual concentrations of heavy metals ions (ferrite, nickel, copper, and zinc) after processing of galvanic wastes by the method of ferritization were determined at the atom-absorbent spectrophotometer AA-6800 (Shimadzu, Japan).

Volume of the compacted sludge after centrifugation was determined at the centrifuge OPn-8 (Dastam M, Russia) at the division factor (Sf) 3,600 over 2 min. The rotor rotation frequency was 6,000 rpm.

Structural analysis of the sediment obtained was performed by a powder X-ray diffraction method in a stepwise mode with Cu-Kα radiation at the Ultima IV diffractometer (Rigaku, Japan). Video recording was carried out in the interval of angles 2θ 6–70° at a scanning step of 0.05° and an exposure time at a point of 2 s.

The scanning electron microscope-analyzer REMMA-101A (SELM I, Ukraine) was used to study the microstructure of sediment samples.

Stability of the resulting sediments in a neutral environment was determined by leaching the ions of heavy metal ions, according to EN 12457-1:2002 Part 1. Leaching was conducted under a dynamic mode. To this end, we used an installation with a rotation speed of 9 rpm.

Conditions for experiments

| No. of entry | Activation technique | T, °C | Fe ₃ O ₄ | Magnetic induction amplitude in working zone, Tl | Number of pulse packets | Number of pulses per packet | Pulse frequency, Hz | Interval between packets of pulses, s | Period between pulses, ms | Pulse duration, ms |
|--------------|----------------------|-------|--------------------------------|--|-------------------------|-----------------------------|---------------------|---------------------------------------|---------------------------|--------------------|
| G1 | Low-temperature | 18 | – | – | – | – | – | – | – | – |
| G2 | Thermal | 75 | – | – | – | – | – | – | – | – |
| G3 | EMI | 18 | – | 0.298 | 1 | 1 | 100 | – | 5 | 5 |
| G4 | EMI | 18 | – | 0.298 | 1 | 1 | 1 | – | 100 | 900 |
| G5 | EMI | 18 | + | 0.298 | 1 | 1 | 1 | – | 100 | 900 |
| G6 | EMI | 18 | – | 0.086 | 1 | 1 | 1 | – | 100 | 900 |
| G7 | EMI | 18 | – | 0.298 | 4 | 10 | 10 | 10 | 50 | 50 |
| | | | | | | | 5 | | 100 | 100 |
| | | | | | | | 1 | | 500 | 500 |
| | | | | | | | 0,5 | | 1,000 | 1,000 |
| G8 | EMI | 18 | + | 0.086 | 5 | 10 | 1,000 | 10 | 10 | 10 |
| | | | | | | | 100 | | 50 | 50 |
| | | | | | | | 10 | | 100 | 100 |
| | | | | | | | 1 | | 500 | 500 |
| | | | | | | | 0,1 | | 1,000 | 1,000 |
| G9 | EMI | 18 | + | 0.298 | 5 | 10 | 1,000 | 10 | 10 | 10 |
| | | | | | | | 100 | | 50 | 50 |
| | | | | | | | 10 | | 100 | 100 |
| | | | | | | | 1 | | 500 | 500 |
| | | | | | | | 0.1 | | 1,000 | 1,000 |

Calculation of electrical energy consumption when using the thermal technique of activating the process was carried out by formula:

$$W = C \cdot V \cdot (T_2 - T_1), \quad (1)$$

where C is the specific heat capacity of water; V is the volume of a reactive mixture, dm³; T_1 and T_2 are, accordingly, the temperature of the starting and heated water, °C.

The calculation was carried out taking into consideration the coefficient of efficiency of electric heating, 95 %. For the electromagnetic pulse technique of activating the process, the amount of electricity consumed was determined based on the power of the device, which generates electromagnetic pulse discharges.

5. Studying the processing of galvanic wastes by the ferritization method involving electromagnetic pulse activation

5. 1. Results of extraction of heavy metals ions from the reactive mixture in the process of ferritization

Results from experiments on the extraction of heavy metals ions from the reactive mixture in the process of ferritization at various activation techniques are shown in Fig. 2. In all experiments, the residual concentrations of heavy metal ions in the solution are in the range from 0.05 mg/dm³ to 3.0 mg/dm³ regardless of the activation technique. In addition, the results of our study (Fig. 2) have confirmed that using the ferritization process at 18 °C is impractical without the application of electromagnetic pulse discharges (G1 experiment). The residual

concentrations of heavy metals in a solution at such an activation technique are >3.0 mg/dm³.

Fig. 2 shows that water after ferritization treatment with the thermal and electromagnetic pulse activation of the process in a series of experiments G3÷G9 meets the requirements of category 1 for galvanic production, in terms of the maximum permissible concentrations (MPC) of ions: ferrum (Fe^{total}), nickel (Ni²⁺), copper (Cu²⁺), and zinc (Zn²⁺). At the same time, the residual concentrations of ions: ferrum, nickel, and copper, do not meet the requirements of the above standard after the process of ferritization at 18 °C (G1).

As shown by the results from a series of experiments (G3÷G9), a change in the mode characteristics of electromagnetic pulse discharge generation affects the efficiency of extraction of heavy metal ions from the reactive mixture. It should be noted that reducing generating frequencies from 100 Hz to 1 Hz while increasing the period and duration of a pulse from 5 to 100 and 900 ms in experiments (G3; G4) leads to a slight decrease in the concentration of nickel and copper ions in the solution. Adding to the reactive mixture of magnetite (G5) at constant frequency, period, and pulse duration (G4) predetermines a decrease in the concentration of nickel ions from 0.82 mg/dm³ to 0.17 mg/dm³. The content of other ions of heavy metals (ferrum and zinc) in an aqueous solution remains almost unchanged. When reducing the amplitude of magnetic induction in the working area from 0.298 to 0.086 Ts in the series of experiments G4 and G6, the concentration of copper ions in the solution increases and that of nickel decreases. Significant reduction in the residual concentrations of copper ions in the solution is achieved in the series of experiments G7, during which the pulse frequency changed from 0.5 Hz to 10 Hz at a different number of their

packets. The content of the ferrum, nickel, and zinc ions in the solution is identical to experiments (G3÷G6).

In addition, additional experiments were conducted (G8, G9), in which we increased the number of pulse packets, frequency, and amplitude to achieve the best indicators of galvanic waste processing. However, at such an activation of the reactive mixture, we did not observe any improvement in the efficiency of heavy metal ions extraction. Their residual concentrations remained within the values of experiments G5 and G6.

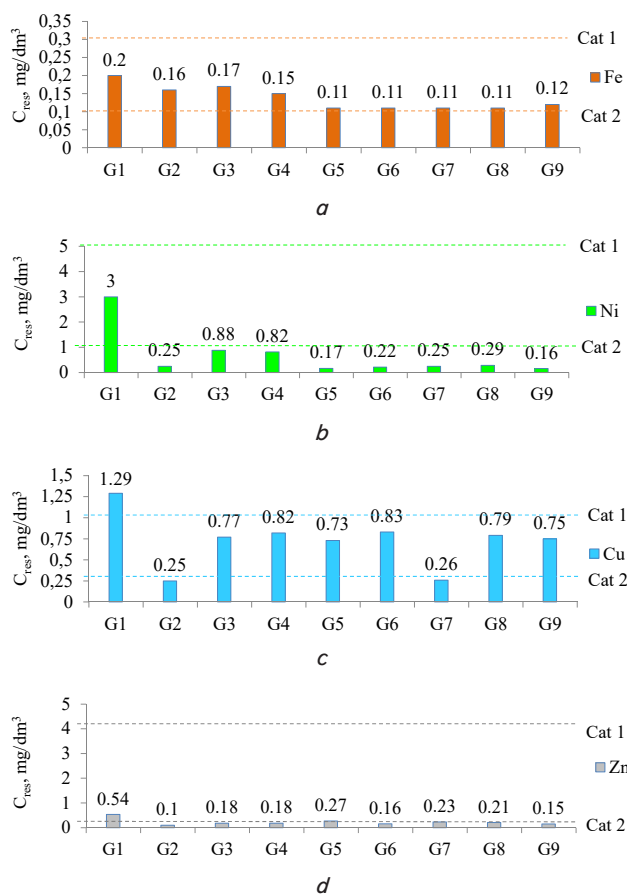


Fig. 2. Residual concentrations of heavy metals ions C_{res} during ferritization of galvanic waste: a – ferrum, b – nickel, c – copper, d – zinc

5. 2. Studying the properties of the obtained ferritization sediments

A black dispersed suspension forms in the solution in the process of ferritization at various techniques of its activation and different mode characteristics of generating electromagnetic pulse discharges, which is further crystallized with the creation of mostly dense ferrite structures (Fig. 3). The resulting sediment almost does not contain either crystallization or adsorbed water, as opposed to the hydroxide and hydroxo-carbonate sediments from the reagent wastewater treatment [16].

The structure of the obtained samples of ferritized sediments (G1÷G9) was investigated. Our study of the phase composition of sediments (Fig. 4) show the high crystallization of samples in all nine series of experiments the exception being a G1 series, with a low-temperature activation of the reactive mixture. The diffractogram of this sample contains the widened peaks of low intensity, whereas samples from the G2÷G9 series demonstrated, on diffractograms, the

intense narrow peaks in the range of angles 2θ $25\div 45^\circ$ and $55\div 65^\circ$. They mainly contain the phases of ferrites of heavy metals $Fe_2(Fe,Ni,Cu,Zn)O_4$ with the structure of an inverse spinel and a parameter of cubic lattice of $a=8.39 \text{ \AA}$ (Fig. 5). Fig. 5 shows that there are peaks that relate to the phases of iron-nickel oxyhydroxides, particularly nickel-plated limonite $(FeNi)O(OH)$, $a=2.96 \text{ \AA}$, and, in small quantities, sodium sulfate Na_2SO_4 , $a=5.84 \text{ \AA}$.

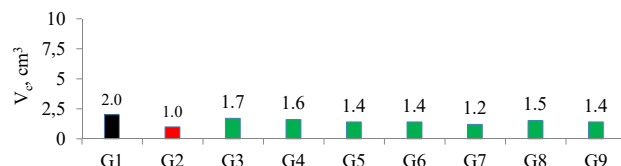


Fig. 3. Volume of compacted sediments V_c obtained in the processing of galvanic waste by the ferritization technique

It should be noted that x-rays of samples from G2 and G7 are almost identical, with a slight difference in reflex intensity. These samples have the highest degree of crystalline structure.

Data from electron microscopy of sediments (Fig. 6) testify to the formation of dispersed structures of sediments. Samples from the G2 and G7 series contain crystals of irregular shape in a porous space. Such structures have good sorption capacity both for heavy metal ions and to organic matter, and thus can be successfully used to clean flush waste water from industrial production [17].

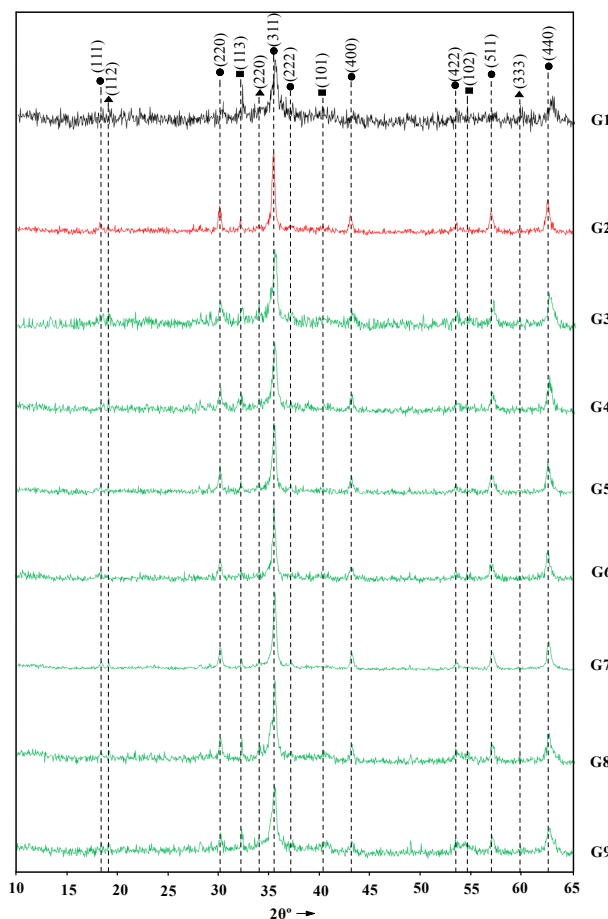


Fig. 4. Diffractograms of sediments obtained from processing galvanic waste by the ferritization method: ● – $(Fe,Ni,Cu,Zn)Fe_2O_4$; ▲ – $(FeNi)O(OH)$; ■ – Na_2SO_4

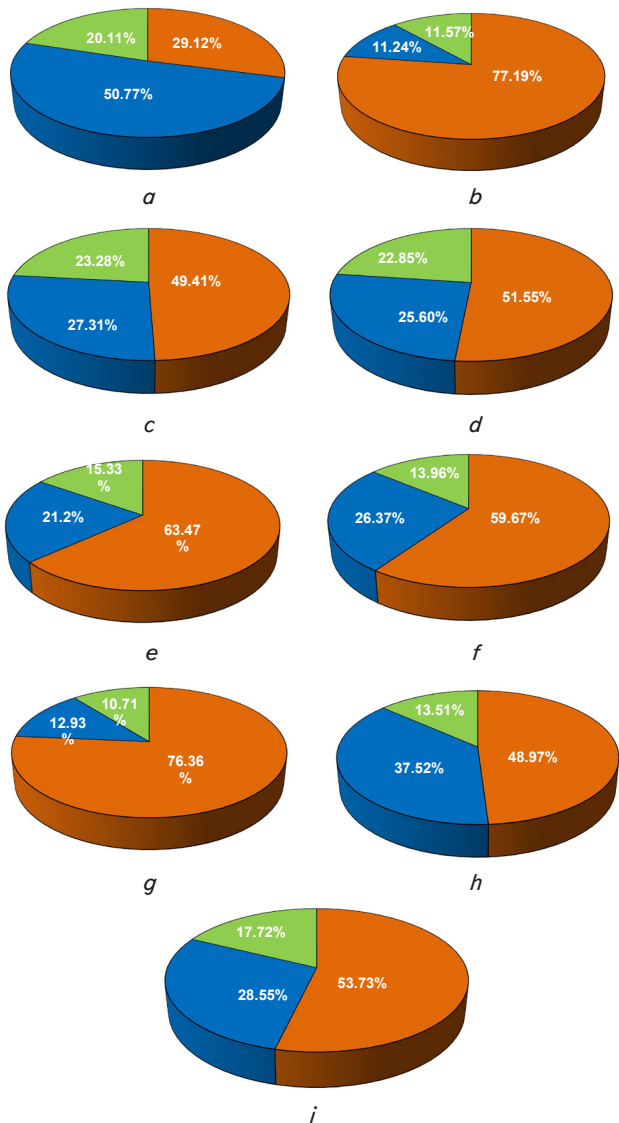


Fig. 5. Phase composition of sediments: a - G1; b - G2; c - G3; d - G4; e - G5; f - G6; g - G7; h - G8; i - G9; ■ - (Fe,Ni,Cu,Zn)Fe₂O₄; ■ - (FeNi)O(OH); ■ - Na₂SO₄

Chemical stability of the electroplating sludges from a reagent treatment of wastewater and the sediments obtained from ferrite processing of galvanic waste (samples from the G1, G2 and G7 series of experiments) were investigated by leaching the ions of heavy metals from them at pH=6.6.

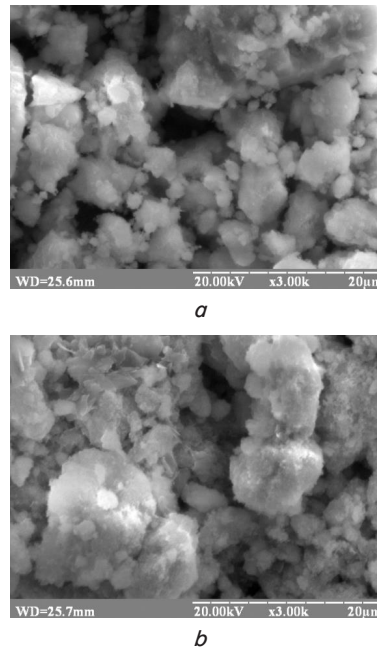


Fig. 6. Microphotographs of sediment samples at magnification x3,000: a - thermal (G2); b - electromagnetic pulse (G7) ferritization activation

The results from experiments, given in Table 4, showed that for galvanic sludge the content of heavy metal ions in the leaching eluate does not meet the requirements by DSanPiN 2.2.7.029-99 and the EU Directive 86/278/EU in terms of MPC in soil. The normative values for the concentration of nickel and copper ions are particularly exceeded.

As shown by the research results (Table 4), leaching of ions of heavy metals from ferritization sediments, first of all, depends on the techniques of activation of the process of processing galvanic waste. It should be noted that all the investigated concentrations of heavy metals in the eluate at all activation techniques, except for a low-temperature one, meet the requirements by DSanPiN 2.2.7.029-99 and the EU Directive 86/278/EU. When using the electromagnetic pulse activation, the concentrations of iron, copper, and zinc ions in the eluate have the higher values compared with the conventional thermal activation technique, but the difference is insignificant and is within 0.1 mg/kg. The nickel ions are leached approximately by 2 times more intensively under the thermal activation technique compared to the electromagnetic pulse activation.

Table 4

Results of leaching metal ions, mg/kg

| Metals | Galvanic sludge | Sediment from the ferritization processing of sludges | | | MPC in soil | |
|---------------------|-----------------|---|---------|-----------------------|----------------------|---------------------|
| | | Process activation technique | | | DSanPiN 2.2.7.029-99 | Directive 86/278/EU |
| | | Low-temperature | Thermal | Electromagnetic pulse | | |
| Fe ^{total} | 0.86 | 0.41 | 0.20 | 0.21 | - | - |
| Ni ²⁺ | 660 | 10.91 | 0.78 | 0.47 | 4.0 | 50 |
| Cu ²⁺ | 47.6 | 3.24 | 0.72 | 0.83 | 3.0 | 50 |
| Zn ²⁺ | 16.52 | 1.17 | 0.33 | 0.41 | 23.0 | 150 |

6. Discussion of results from studying the processing of galvanic wastes by the advanced ferritization method

Based on the results shown by a diagram in Fig. 2, we can argue about the prospects of using a ferrite method with the electromagnetic pulse activation for processing liquid and condensed galvanic wastes. The process of ferritization ensures a sufficiently high degree of heavy metal ions extraction from the reactive mixture with the formation of environmentally safe insoluble compounds – 99.97 %. This relates to that in the process of the extraction of ions of heavy metals, a special role belongs, rather than to the sorption of the specified ions on the surface of the sediment formed, to the crystallization of insoluble compounds of metals, in particular hydroxides and oxo-hydroxides, on the surface of ferromagnetic particles. At the same time, the extraction efficiency of heavy metals ions in the processing of galvanic waste is significantly influenced by the structure and size of these particles. The use of electromagnetic pulse discharges to activate the ferritization process, in comparison with the conventional thermal activation, makes it possible to save up to 42 % of energy costs. In this case, neither the degree of removal of heavy metals ions from the reactive mixture nor the crystalline structure of the sediment is compromised. It was established that the best results among those mentioned above were demonstrated by samples from the *G7* series of experiments – the amplitude of magnetic induction is 0.298 Tl and the pulse frequency is from 0.5 to 10 Hz, as evidenced by the data from Table 3. The water purified after the ferritization processing of galvanic waste can be used in a circulating water supply system [18].

Analysis of results from studying the compaction of ferritization sediments through centrifugation, shown in Fig. 3, makes it possible to establish that the volume of compacted sediment (V_c) depends on the process activation technique. The volume of sediments is reduced by half when using ferritization with the electromagnetic pulse and thermal activation (the *G2* and *G7* series of experiments) in comparison with the sediment from a low-temperature ferritization at 18 °C (*G1*). This is probably due to an increase in the number of dense phases in the formed sediment. This sediment contains ferrites, as well as various modifications of iron and nickel oxyhydrates, which increase the sediment density. Based on the results of our study (Fig. 3), it can be argued that the mass fraction of ferrite phases in the composition of the formed sediment (*G2*, *G7* series) is much larger in comparison with the sediment from a low-temperature activation (*G1*). Results from studying the specific volumes of ferritization sediments make it possible to indirectly assess the ferromagnetic properties, given that sediment with a minimum specific volume is characterized by the maximum magnetic susceptibility [19].

Data from a structural analysis of ferritization sediments, shown in Fig. 4, 5, correlate well with the results of research into the specific volumes of sediments (Fig. 3), given that the more orderly structure is matched with sediments with a smaller specific volume. Available data on the mechanism of the ferritization process suggests a rather complex phase composition of the sediments obtained. The sediment may contain various modifications of oxides and oxyhydrates of ferrum, nickel, copper, and zinc, which by nature are ferromagnetic, but, due to the small dimensions, they demonstrate paramagnetic properties [17]. Our analysis of structural studies has revealed that samples from

the *G2* and *G7* series of experiments, obtained under the thermal and electromagnetic pulse activation technique, are, respectively, characterized by the maximal content of ferrite phases with magnetic properties (≥ 89 %). In these series of experiments, the phase composition of sediments is practically identical. It should be noted that in addition to the formation of ferrite phases the sediment still has intermediate solid-phase products of the ferritization process, which are limitedly stable in alkaline medium [20]. This does lead to a certain increase in the residual concentration of heavy metal ions in the processed solution. The presence of sodium sulfate on the radiograms of sediments relates to that the obtained ferritization sediments were not washed with water.

By analyzing the results of leaching heavy metal ions from the electroplating sludge (Table 4), it was established that the vast majority of the remaining heavy metal concentrations do not meet the requirements by acting standards, concerning MPC in soil, especially nickel and copper. Storing such sediments at open sites and dumps is environmentally dangerous, given that the accumulation of heavy metals in soils above the specified permissible norms leads to hazardous pollution thereby disrupting the viability of the entire ecosystem.

The leaching of nickel ions depends on the composition and structure of the sediment obtained, principally on the presence of the nickel limonite phase $(\text{FeNi})\text{O}(\text{OH})$. It is known [21] this phase is unstable in an aqueous solution: it is the quantitative content of this phase that can define the magnitude of leaching nickel ions. The greater the content of this phase is, the higher the value of the nickel ions concentrations after their leaching.

The results of leaching heavy metals indicate that samples of the ferritization sediment obtained under the thermal and electromagnetic pulse activation technique are characterized by a high degree of immobilization of toxic metals – 99.96 %. It should be noted that hydroxide galvanic sludge, as opposed to ferrite sediments, have a lower degree of immobilization of toxic metals (< 97.83 %), thereby causing irreparable damage to the entire ecosystem. The results from studying the leaching of heavy metals from the sediments of ferritization processing obtained by the thermal and electromagnetic pulse ferritization activation techniques have shown a reliable fixation of these metals as part of new structures with chemically and thermally stable structure of inverse spinel.

Our analysis of physical and chemical properties of ferritization sediments indicates the apparent environmental impossibility to use the ferritization process with a low-temperature activation for galvanic waste treatment, as the formed sediments demonstrated the existence of chemically unstable phases. That prevents further safe disposal of the formed secondary products. Therefore, the use of such a method for processing galvanic wastes is inappropriate.

The sediments, which were obtained by the thermal and electromagnetic pulse activation of the waste recycling process, as opposed to the sediments from a low-temperature ferritization, are chemically stable and have real environmentally safe ways of disposal. For example, they can be used to produce construction, ferrite, pigment, and sorptive materials [22–25].

The devised ferritization technology with the electromagnetic pulse process activation is advisable to use at enterprises with an annual accumulation of up to 100 m³ of

liquid galvanic waste. It is efficient to use a reactor with a capacity of up to 0.5 m³ for waste recycling.

In the future, we consider it expedient to investigate a possibility of using the products from processing galvanic wastes as a component for alkaline cements and, by leaching heavy metal ions, to determine the immobilizing properties of these materials in different environments.

7. Conclusions

1. The influence of mode characteristics of electromagnetic pulse discharges generation on the efficiency of heavy metal ions extraction (Fe, Ni, Cu, Zn) during processing of galvanic wastes by the ferritization method has been experimentally studied. It is shown that the most effective results were achieved at the following parameters of electromagnetic pulse discharges generation: the amplitude of magnetic induction is 0.298 Tl, the range of generating frequencies is from 0.5 to 10 Hz. In this case, a high degree of heavy ions extraction is achieved, up to 99.97 %, and the resulting aqueous solution is usable in a circulating water supply system.

2. Our analysis of structural studies has shown that the ferritization sediments that were obtained by the thermal and electromagnetic technique of activation

and at the rational technological parameters of ferritization ($C_{\Sigma}=10.41$ g/dm³; $Z=4/1$; $pH=10.5$; $\tau=25$ min; $v=0.15$ m³/h), are characterized by the maximum content of ferrite phases with magnetic properties (≥ 89 %) and the degree of sediment compaction >90 %. Such sediments, in comparison with the waste from a conventional reagent treatment of wastewater, have high chemical resistance and capacity to further disposal.

3. The results from studying the leaching of heavy metals ions (Fe, Ni, Cu, Zn) from the sediments, which were obtained by the thermal and electromagnetic pulse techniques for the ferritization process activation, have showed a reliable fixation of these metals in the composition of the formed compounds with the structure of an inverse spinel. The obtained sediments are characterized by a high degree of heavy metal immobilization, 99.96 %, in contrast to the hydroxide sludge from galvanic production, <97.83 %.

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