Останнім часом значна увага приділяється розробці комплексної переробки промислових стічних вод, що забезпечує як належний ступінь очистки для організації оборотного водопостачання, так і подальшу утилізацію відходів очищення води. Представлено удосконалений процес феритизації, який дозволяє зменшити вихідні концентрації іонів нікелю у відпрацьованих електролітах нікелювання з 50–100 г/дм^3 до <0,2 мг/дм^3. Розроблено експериментальний ферит-реактор з використанням традиційного термічного та електромагнітного імпульсного способу активації процесу феритизації в діапазоні генеруючих частот до 0,9 кГц. Встановлені енергетичні переваги використання електромагнітної імпульсної активації в порівнянні з високотемпературною. Досліджено кінетику вилучення іонів нікелю та заліза з водних розчинів. Експериментально визначено вплив основних технологічних параметрів феритизації при різних способах активації. Найефективніші результати очистки висококонцентрованих стічних вод були досягнуті із застосуванням електромагнітного імпульсного (T=20 °C) та термічного (T=70 °C) способів активації процесу феритизації при вихідному співвідношенні концентрацій Fe^{2+}/Ni^{2+} в межах 3/1–4/1, сумарній концентрації іонів важких металів 20–25 г/дм^3, початковому pH реакційної суміші 9,5, тривалості процесу феритизації 15 хв. Виконано дослідження фазового складу і фізичних властивостей осадів феритизації. Здійснено порівняльний аналіз об'ємів осадів при різних способах ущільнення. Осади здебільшого характеризуються кристалічною структурою, феромагнітними властивостями і значною хімічною стійкістю. Це забезпечує реальні екологічні шляхи утилізації, що дозволяє уникнути втрат цінного та водночас токсичного металу – нікелю. Запропонований комплексний процес переробки рідких промислових відходів запобігає забрудненню навколишнього середовища, забезпечує ефективне і раціональне використання води, сировини та енергії в системі гальванічного виробництва

Ключові слова: очистка стічних вод, феритизація, промислові виробництва, електроліти нікелювання, важкі метали, відходи, утилізація

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RESEARCH OF THE TREATMENT OF DEPLETED NICKEL-PLATING ELECTROLYTES BY THE FERRITIZATION METHOD

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1. Introduction

Protection of water resources from depletion and pollution is one of the most important environmental problems. Toxic wastewater of galvanic production, as well as the waste of water treatment, is of particular danger to humans, which is related to the cancerogenic and mutagenic action of heavy metal compounds. The wastewater of electroplating production contains significant amounts of highly toxic nickel compounds, whose share reaches 20 % of the total content of heavy metals. Discharge of this wastewater into the environment, in addition to the environmental damage, leads to the loss of a valuable metal, whose natural sources are limited. It is known that the highly concentrated used solutions (electrolytes, eluates of ion-exchange filters) make up approximately 5 % of the total volume of all wastewater of galvanic production. At the same time, the content of pollutants in the concentrated wastewater exceeds 70 % of the total mass [1]. That is why it is important to employ the comprehensive treatment of wastewater from electroplating production with the closed resource circulation systems, which makes it possible to create the local systems of water treatment directly at a specific production area, specifically at the nickel plating line.

Analysis of the existing methods of treatment of electroplating production wastewater showed that, despite their diversity, the ion exchange, sorption, membrane, electrochemical methods are widely used in practice, while the reagent method is the most common [2]. The essence of this method is in binding the heavy metal ions by hydroxides of

Ca, Na, or Na carbonate, with the deposition of compounds that are difficult to dissolve. Its main disadvantages are not only the enhanced consumption of reagents, but also a low degree of wastewater cleaning from the ions of heavy metals. In addition, volumetric precipitates of reagent purification of wastewater are chemically unstable and poorly dehydrated, which considerably complicates and raises the cost of subsequent disposal.

The ferritization method is promising for the treatment of electroplating production wastewater [3]. Using this method makes it possible to receive almost insoluble compounds of iron and other heavy metals (M) as a result of treating their ions with the alkaline reagent (1) and oxygen from the air (2):

$$xM^{2+} + (3-x)Fe^{2+} + 6OH^- \rightarrow M_xFe_{3-x}(OH)_6, \quad (1)$$

$$M_xFe_{3-x}(OH)_6 + 0{,}5O_2 \rightarrow M_xFe_{3-x}O_4 + 3H_2O. \quad (2)$$

This method provides for a high degree of wastewater cleaning from the ions of heavy metals, as well as the possibility of environmentally-safe disposal of insignificant waste volumes, which are formed during treatment. The effectiveness of industrial application of these processes is determined by a substantial saving of materials, reagents, and the use of standard equipment. Given the significant number of electroplating industries in the world and particularly in Ukraine, effective and economical removal of heavy metal ions from wastewater is an extremely urgent problem. Solving it will improve the sanitary-hygienic state of the environment and will ensure the appropriate economic effect as a result of the rational use of water, raw materials, and energy.

2. Literature review and problem statement

The feasibility of application of the ferritization method for wastewater at a nickel plating line is predetermined by the simultaneous content of nickel and iron compounds in them. In recent years, numerous studies on the treatment of wastewater and technological solutions by ferritization were carried out. The process of extraction of cobalt ions from concentrated solutions was explored in paper [4]. Inclusion of Co^{+2} ions into the ferrite structure and chemical stability of sediments was indicated. The optimal conditions of ferritization of diluted multi-component solutions of heavy metals were determined in article [5]. However, in these publications and works by other authors, model solutions rather than actual wastewater of electroplating production were studied. The process of ferritization for cleaning washing wastewater at a copper plating line was applied in paper [6], while ferritization of concentrated copper-containing wastewater was explored in article [7]. In these studies, it was revealed that the main factors, affecting the progress of the wastewater treatment process, are the values of pH, temperature (T) and duration (t) of the ferritization process, as well as the original concentrations of heavy metals (C_Σ) and the ratio (Z) of these concentrations. However, information about the studies of complex ferritization of recycling of depleted nickel-containing electrolytes and concentrated technological solutions with the disposal of formed waste of water treatment was not found in the literature.

It should be noted that wastewater treatment by ferritization is typically performed at the temperature above 60 C and additionally requires the use of a large quantity of iron compounds. Thus, the traditional thermal method of the process activation is power- and resource consuming [8]. Activation by electromagnetic pulsed discharges can be an alternative to thermal activation. But the authors of paper [9] used high power discharges, which are essentially power consuming. That is why further improvement of the ferritization method, which is aimed at minimizing power and reagent resources, can be considered a way to solve the problems of saving power and resources at the galvanic production. That is why a comprehensive research into cost-effective recycling of electroplating wastewater, which provides the necessary effect of water purification from the heavy metal ions and safe disposal of nickel-containing sediments, is relevant.

3. The aim and objectives of the study

The aim of this study is to conduct experimental research into determining the influence of technological parameters of the ferritization process, as well as the techniques of its activation on quality of the comprehensive treatment of highly concentrated wastewater from a nickel plating line.

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

– to conduct experimental studies of the basic technological parameters of cleaning depleted electrolytes of nickel plating from ions of heavy metals in various methods of activation of ferritization process;

– to explore the kinetics of extraction of iron and nickel ions from aqueous solutions by means of ferritization;

– to study experimentally physical and chemical properties of deposits of water treatment by ferritization;

– to perform economic substantiation of the developed processes of treatment of electroplating production wastewater.

4. Materials and methods to study the comprehensive treatment of nickel-containing wastewater

Two laboratory set-ups were developed. The first one was to study the process of cleaning wastewater by ferritization at temperatures of 20–70 °C [10]. The scheme of the second set-up for carrying out experiments with the use of electromagnetic pulse activation of the process at the temperature of 20 °C is shown in Fig. 1. Mode characteristics are: an electromagnetic signal was composed of a package of pulses (16 pulses in the package), the interval between the packages was 1,300 milliseconds, the period between pulses was 20 ms, pulse duration is 35 ms.

The depleted technological solution of nickel plating baths at one of the industrial enterprises in Kyiv (Ukraine) was applied in the laboratory experiments. The composition of the original electrolyte of nickel plating is presented in Table 1. The concentration of ions of heavy metals in the depleted electrolyte was: Ni^{2+} – 67.9 and Fe^{2+} – 0.12 g/dm^3, respectively. For implementation of the ferritization process, solution of sulphate of iron (II) of concentration within 7.8–36.7 g/dm^3, and 25 % sodium hydroxide was added to establish the desired pH value. The ferritization process was implemented in the periodic mode.

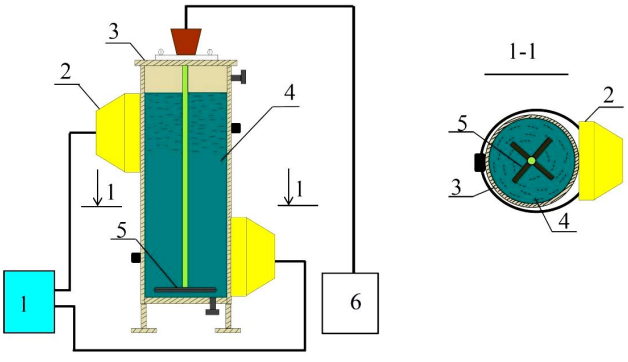

Fig. 1. Structural diagram of the laboratory set-up with electromagnetic pulse activation of the ferritization process: 1 — electronic unit-casing; 2 — pulsators; 3 — reactor; 4 — treatment solution; 5 — air distribution system; 6 — compressor

Technological parameters in the experiments varied in the following range:

– total concentration of ions of heavy metals C_{Σ}=11.7–30.41 g/dm^3;

– ratio of concentration of ions Fe^{2+} and Ni^{2+} Z=2–6;

– magnitudes of pH are 8.5–10.5; duration of treatment process τ=5–15 min.

Planning of four series of experiments are shown in Table 2.

Table 1

Composition of the electrolyte of nickel plating

Components	Concentration, g/dm^3	pH
$NiSO_4 \cdot 7H_2O$	230...320	3.5...5.5
$NiCl_2 \cdot 6\ H_2O$	40...60	
H_3BO_3	25...40	
Saccharine	0.8...2.0	
1.4-butadinol	0.2...0.5	
Chloramine B	2.0...2.5	

Table 2

Conditions for conducting experiments for recycling the depleted electrolyte of nickel plating

No. of series of experiment	Total concentration of ions of heavy metals, (C_{Σ}), g/dm^3	Ratio of concentrations of ions of Fe^{2+} and Ni^{2+}, (Z)	pH	Duration of ferritization, (τ), min.	Bubbling (O_2), m^3/h
1	12÷32	2	9.5	15	0.12
2	22	2÷6	9.5	15	
3	22	2	8.5÷10.5	15	
4	22	2	9.5	5÷25	

Concentrations of iron and nickel ions in purified wastewater were determined on the volt-amperemeter analyzer AVA-3 (Burevestnik, Russia).

The quality of wastewater treatment was established according to the degree of its purification, which is calculated from formula:

$$a = \left(C_{\text{orig}} - C_{res}\right) \cdot 100\,\% / C_{\text{orig}}, \quad (3)$$

where C_{orig} and C_{res} are, respectively, the original and residual concentration of nickel irons in wastewater, mg/dm^3.

The sediment, obtained after ferritization was compacted under usual conditions (gravitation field) for 1 day and in the centrifuge OPn-8 (UCL 4.2) with the rotor RU-180 L (Dastam M, Russia) at separation factors (Sf) of 900 and 3,600 within 2 min. Separation factor was determined from formula:

$$\Phi_p = \frac{\omega^2 \cdot R}{g} \cong \frac{n^2 \cdot R}{900}, \quad (4)$$

where $\omega=\pi n/30$ is the angular velocity of the drum, m/s; R is the radius of the rotor, m; g is the free fall acceleration, m/s; n is the drum rotation frequency, rpm. The values of n were 3,000 and 6,000 rpm.

Structural analysis of sediment samples was conducted with the use of the method of powder X-ray diffractometry on the automated diffractometer XRD-6000 (Shimadzu, Japan). We used CuKα-radiation with the wave length of 1.54 Å and arc graphite monochromator, voltage in the tube was 40 kV, current 30 mA; the mode of continuous scanning was at the rate of 1,2°/min.; angular range of research (2θ) was from 5 to 90°; sample rotation rate was 30 rpm. Diffractograms were deciphered with the help of database ICCD PDF2+ – 2003 (The International Centre for Diffraction Data, the USA) and software Match V.1.9a (Crystal Impact, the USA).

To study the microstructure of samples of sediments, the scanning electronic microscope-analyzer REMMA-101A (SELMI, Ukraine) was used.

Calculation of the amount of consumed thermal power when using the thermal way of the process activation was performed using formula:

$$W = C \cdot V \cdot \left(T_2 - T_1\right), \quad (5)$$

where C is the specific thermal capacity of water; V is the volume of wastewater, m^3; T_1 and T_2 are respectively the temperatures of the original and heated water, °C.

The calculation was carried out taking into consideration efficiency for electric heating, which is 95 %. For the electromagnetic pulse method of the process activation, the amount of consumed electricity was determined by the passport power device of the device that generates electromagnetic pulse discharges.

5. Results of research into comprehensive treatment of depleted electrolytes of nickel plating

5. 1. Treatment of highly concentrated nickel-containing solutions

The results of experimental studies of determining the influence of the basic technological parameters of ferritization process are the following: pH, C_{Σ}, Z and t on effectiveness of treatment of depleted electrolytes of nickel plating for different ways of process activating was shown in Fig. 2. The obtained data indicate that at all the studied values of technological parameters, residual concentration of nickel ions in the treated solution was within the range from 0.1 to 1.2 mg/dm^3.

Dependences, shown in Fig. 2, indicate that an increase in total content of ions of heavy metals in the original reaction mixture leads to increased residual concentrations of nickel ions after ferritization regardless of the way of the

process activation. It should be noted that the total content of ions of heavy metals in depleted electrolytes of nickel plating does not significantly affect the degree of wastewater purification.

Analysis of the conducted studies of ferritization treatment of wastewater in a wide mole range of original ratios of concentration of nickel to concentration of iron (2–6) showed that it was possible to achieve the best result within the rations of correlation of Ni^{2+}/Fe^{2+} from 3/1 to 4/1 (Fig. 2, *b*).

When analyzing the impact of the pH magnitude of the original reaction mixture on the quality of ferritization wastewater treatment (Fig. 2, *b*), one can observe the tendency to a decrease in residual concentration of nickel ions at an increase in magnitudes of pH in the range of 8.5–10.0 for all techniques of activation.

Fig. 2, *d* shows kinetic dependences of removal of nickel ions from the depleted electrolyte. For all cases of activation of ferritization process, residual concentration of metal ions in the solution decreases within the first 15 minutes of the ferritization process and does not change during the further experiment both for thermal and electromagnetic pulse methods of activation.

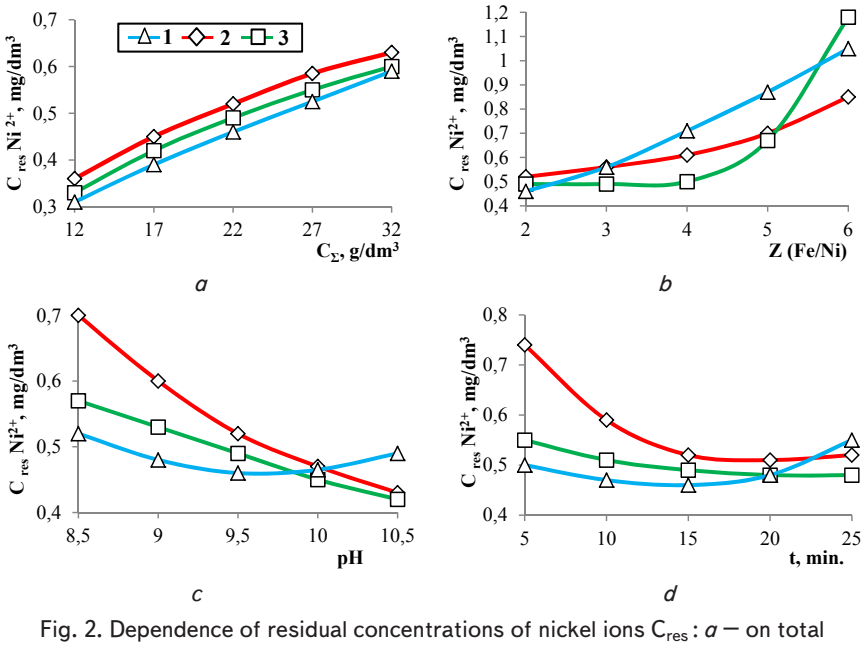

Fig. 2. Dependence of residual concentrations of nickel ions C_{res}: *a* – on total concentration of heavy metals in original solution of depleted electrolyte C_{Σ}; *b* – on the ratio of concentration of ions of heavy metals Z; *c* – on magnitude of pH; *d* – on duration of ferritization process τ. 1 – the process of ferritization at 20 °C, 2 and 3 – with thermal and electromagnetic pulse activation of the process, respectively

The mathematical models [12] were proposed to explore kinetic patterns of removal of ions of heavy metals from solutions. The assessment of adequacy of these models to the experimental data of wastewater treatment at various methods of activation was made. According to the tables of the Fisher criterion [13], by the level of significance of a=0.05 and numbers of freedom degrees 1 and 3, the value of $F_{1,3}(0.05)=10.3$ was found. Because the values of the Fisher criterion F_{comp} were obtained in the comparison of the experimental and calculated data (Table 3), $F_{comp}>F_{1,3}(0.05)$, the constructed mathematical models are considered to be adequate with a probability of 95 %.

Table 3

Values of the Fisher criterion (F) of comparison of experimental and calculated data of kinetics of heavy metal ions removal from wastewater

The way of activation of ferritization process			
High temperature		Electromagnetic pulse	
C_{res}, of Ni^{2+}, mg/dm^3	C_{res} of Fe^{tot}, mg/dm^3	C_{res}, of Ni^{2+}, mg/dm^3	C_{res}, of Fe^{tot}, mg/dm^3
229.48	100.68	217.31	22.23

Analysis of the values of residual concentrations of iron ions in purified water indicates that in all ranges of the studied technological parameters and at different ways of activation of the ferritization process, the concentration of this metal was in the range from 0.1 to 0.35 mg/ dm^3.

5. 2. Study of the properties of sediments

In the process of ferritization at different techniques of its activation, a black dispersed suspension is formed in the solution, which is later crystallized with formation, in particular, of dense ferrite structures. The resulting sediment does not actually contain either crystalline or adsorbed water unlike hydroxide and hydrocarbonic sediments of the reagent wastewater treatment [14].

Based on the ideas about the mechanism of the ferritization process [15], one should expect a rather complicated phase composition of sediments, in which there are usually various modifications of oxides, hydroxides and ferrites of iron and nickel. Indeed, the above-mentioned compounds were detected on all roentgenograms of all samples of sediments (Fig. 3). Thus, for the sediment sample of the low temperature ferritization (Fig. 3, *a*), which was obtained at: C_{Σ}=22 g/dm^3; *Z*=2; pH=9.5; τ=15 min, the phases of cubic structure were identified: of magnetite Fe_3O_4 with the crystalline lattice 8.39 Å and hematite γ-Fe_2O_3 – 8.33 Å. These compounds have ferromagnetic properties. In addition, there were detected diffracted maxima, related to the phase of iron oxyhydroxide – lepidocrocite γ-FeO(OH) with the lattice parameter of 10.48 Å, which is also the ferromagnetic component of the resulting sediment. Various modifications of NiOOH, $Ni(OH)_2$, and NiO were identified. We will note that the diffractograms of sediments samples of thermal and electromagnetic pulse activation of the ferritization process have almost identical view (Fig. 3, *b*). In these sediments, a higher degree of the crystalline structure in comparison with a sample of ferritization sediment at 20 °C, which is proved by more intensive and at the same time lower reflexes. During thermal and electromagnetic pulse activation, we clearly identified the phase of nickel ferrite $NiFe_2O_4$ with the structure of inverse spinel with lattice parameter *a*=8.34 Å, as well as the peaks that belong to compounds Fe_3O_4, γ-Fe_2O_3, γ-FeO(OH), NiOOH, NiO.

Data from the electronic microscopy (Fig. 4) indicate the formation of dispersed structures of sediments. In comparison with traditional ferritization at 20 °C at electromagnetic pulse activation of the process, sediment has a high crystallinity degree with the spinel structure of the matrix. The porous space contains crystals of irregular shape. The sample of ferritization sediment at 20 °C has an amorphous jelly-like structure with some areas, on which nucleation of the crystalline phases is observed.

The results of research into specific amounts of ferritization sediments (Fig. 5) indicate a high effectiveness of compaction of the resulting sediment by centrifugation at separation factor *Sf*=900. Compared to sediments, deposited in the gravitational field, we will note that centrifugation increases sediment density approximately by 2 times. At an increase in Sf from 900 to 3,600, specific volume of sediment decreased on average by 10 %.

Graphic dependences in Fig. 5, a show that an increase in C_Σ leads to an increase in specific volume of sediment at different ways of suspension activation in the gravitation field on average by 30 %; at centrifugation with *Sf*=900 and 3,600 – by 20 %. The data in Fig. 5, *b* show that an increase in *Z* leads to an increase in specific volume of sediment irrespective of the way of activation in the gravitation field on average by 25 %; at centrifugation with *Sf*=900 and 3,600 – by 30 % and 25 %, respectively. The impact of pH of the medium on effectiveness of compaction of resulting sediments was studied. The data in Fig. 5, *c* indicate that specific volume of the formed sediment decreased at an increase in pH of the reaction suspension irrespective the way of activation of ferritization process, specifically, at sedimentation in the gravitation field on average by 15 %; at centrifugation with *Sf*=900 and 3,600 – by 5 %. As Fig. 5, *d* shows, at an increase in duration of the ferritization process, compactness of sediment in the gravitation field by 15 % is observed; at centrifugation *Sf*=900 and 3,600 – by 5 %.

It was shown that the most effective results of sediment compacting were achieved through centrifugation with *Sf*=3,600 with the use of the thermal and electromagnetic way of activation at *Z*=4/1. Under these conditions, specific volume of sediments decreased from 40 % to 34 % in comparison with sediment of ferritization process at 20 °C. Humidity of sediments decreased from 82 % to 79 %, respectively, density decreased from 1.129 g/cm^3 to 1.186 g/cm^3.

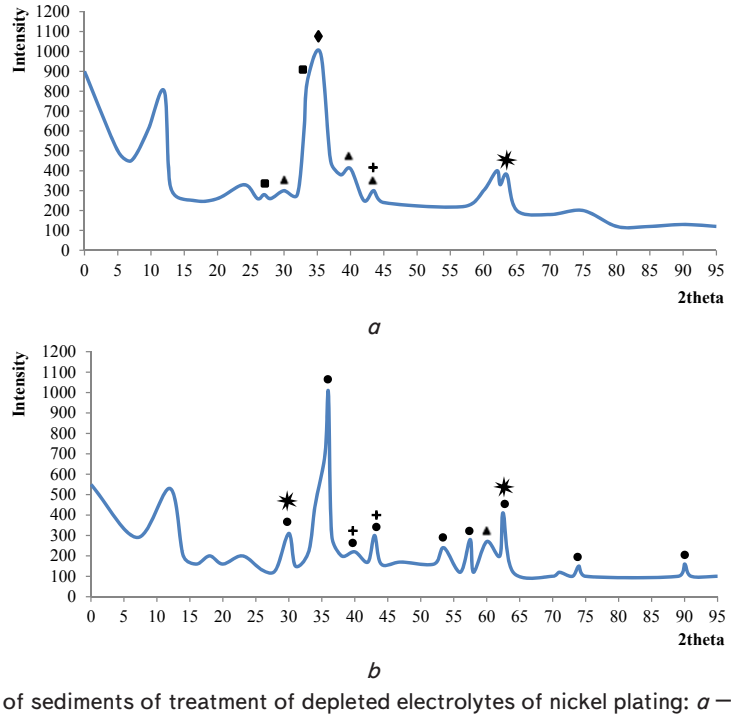

Fig. 3. Diffractograms of sediments of treatment of depleted electrolytes of nickel plating: *a* – ferritization process at 20 °C; *b* – with the use of thermal and electromagnetic pulse activation of the process. Identified phases: $NiFe_2O_4$ (•), γ-Fe_2O_3 (*), NiO (+), γ-FeO(OH) (■), γ-Fe_2O_3 (▲), NiOOH (♦)

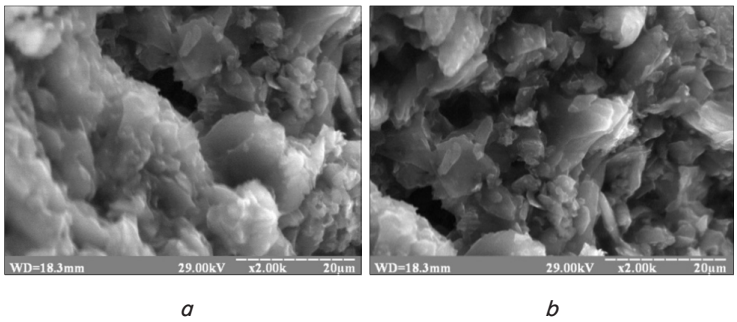

Fig. 4. Microphotographs of sediments samples of treatment of depleted nickel plating electrolytes: *a* – ferritization process at 20 °C; *b* – with the use of thermal and electromagnetic pulse activation of process

5. 3. Determining power efficiency

The assessment of power consumption of the treatment process at various methods of activation and technological ferritization parameters was performed. The amount of electricity, consumed by the treatment process is determined by the duration of the technological stages of the process, such as dosing, mixing, aeration, heating, and centrifugation. Diagrams in Fig. 6 compare power efficiency of the ferritization process using electromagnetic pulse method of activation with the high temperature method at different technological parameters of the process.

These data demonstrate that ferritization recycling of solutions of depleted electrolytes of nickel plating using the electromagnetic pulse method of activation compared with the thermal method makes it possible to decrease power consumption by 10–15 times.

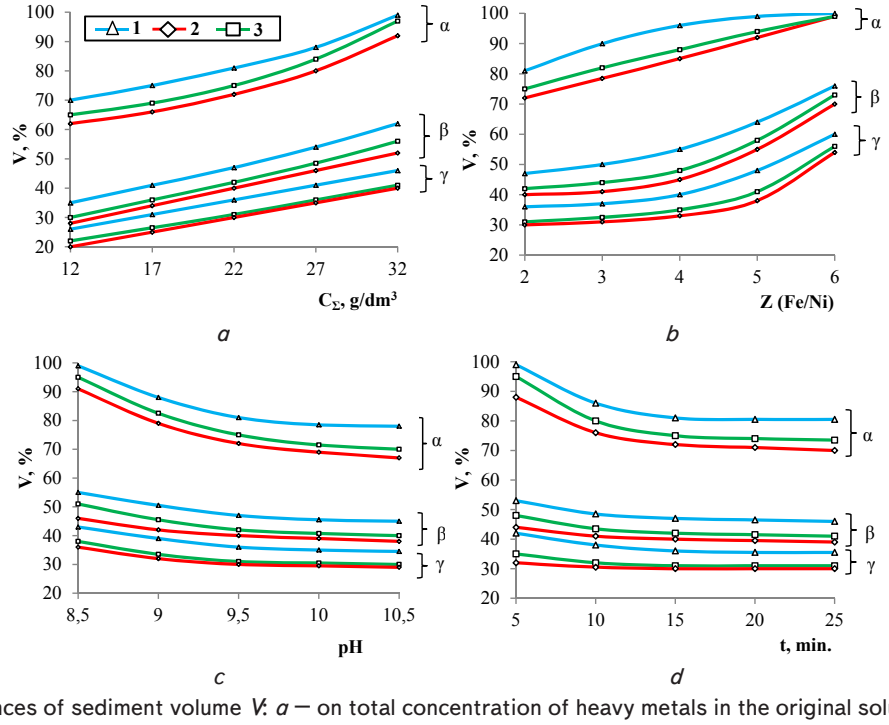

Fig. 5. Dependences of sediment volume *V*: *a* – on total concentration of heavy metals in the original solution of depleted electrolyte C_Σ; *b* – on the ratio of concentration of ions of heavy metals Z; *c* – on magnitude of pH; *d* – on duration of ferritization process τ. Sediment was obtained at: α – gravitational sedimentation, β and γ – centrifugation with *Sf*=900 and 3,600, respectively; activation of process: 1 – high temperature; 2 – electromagnetic pulse; 3 – low temperature

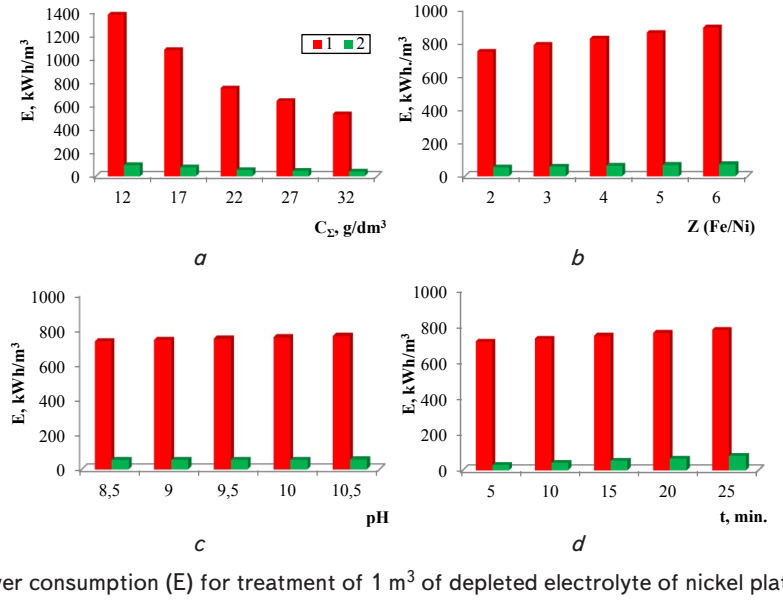

Fig. 6. Diagrams of power consumption (E) for treatment of 1 m³ of depleted electrolyte of nickel plating by the ferritization technology for: *a* – total concentration of heavy metals in the original solution of depleted electrolyte C_Σ; *b* – ratio of concentration of ions of heavy metals Z; *c* – magnitude of pH; *d* – duration of ferritization process τ. Activation of the process: 1 – high temperature; 2 – electromagnetic pulse

6. Discussion of results of research into treatment of depleted electrolytes of nickel plating

First of all, based on the results of research, it is possible to conclude about the prospects of application of the ferrite method for cleaning concentrated wastewater from the compounds of heavy metals. Compared with the traditional reagent treatment, this method has undoubted power and environmental benefits. The ferritization process provides for rather high level of cleaning wastewater from ions of nickel and iron – 99.99 %, which makes it possible to use purified water in the circulation system of water supply. In addition, the results of experiments with the extraction of heavy metals from wastewater indicate high efficiency of using electromagnetic pulse method of activation of the ferritization process. At significant power efficiency, such activation compared to the thermal activation does not worsen the degree of cleaning solutions of depleted electrolytes from ions of nickel and iron. For the electromagnetic pulse activation, discharges of medium power in the range of generating frequencies of up to 0.9 kHz with pulse duration of 35 ms were used. Subsequently, we consider it appropriate to examine the increase an increase in power efficiency of the process by decreasing the power of discharges of electromagnetic pulse activation.

Results of the study indicate that it is possible to enhance the quality of wastewater treatment by increasing the value of pH of the original reaction mixture in the range of 8.5–10.5 at the electromagnetic pulse and thermal activation of the process. This is obviously due to the fact that the predominant role in extracting nickel ions from wastewater in the alkaline medium is not played by sorption of Ni^{2+}, but by crystallization of insoluble compounds of nickel, including hydroxides, on the surface of ferromagnetic particles. In this case, effectiveness of extraction of compounds of heavy metals is especially influenced by have structure and dimensions of particles [16, 17].

Analyzing kinetic curves of wastewater treatment (Fig. 2, *d*) we can conclude that it is advisable to carry out the ferritization process within 15 minutes. During this time, chemically resistant solid-phase products of the reaction are finally formed. The resulting substances have a dispersed structure, and therefore good sorption capacity towards both ions of heavy metals and to organic substances. That is why sediments of ferritization treatment of electrolytes can be successfully used to clean washing wastewater of galvanic production [18]. In addition, due to high chemical stability of sediments, the ecological ways of their disposal are real, for example, introduction of alkali concretes to the matrix, which provides highly reliable encapsulation of toxic substances [19–21].

The study of the properties of sediments explain why the best results of ferritization treatment of solutions of depleted electrolyte of nickel plating are achieved at the ratios of Fe^{2+}/Ni^{2+} within 3/1–4/1. Obviously, this is due to the fact that at other ratios, in addition to the formation of ferrite phase, intermediate solid-phase products of ferritization reaction remain in the sediment, which are limitedly resistant in an alkaline medium [22]. This leads to a certain increase in residual concentration of nickel ions in the solution.

The data of the structural analysis of ferritization sediments (Fig. 3, 4) correlate well with the results of research into specific volumes of ferritization sediments (Fig. 5) in view of the fact that sediments with a smaller specific volume correspond to a better-ordered structure. The results of studies of specific volumes of ferritization sediments make it also possible to assess indirectly the ferromagnetic properties, because the sediment with the minimum specific volume is characterized by maximum magnetic susceptibility [23].

Analysis of physical and chemical properties of the sediments indicates that application of ferritization process at 20 °C at sewage disposal plants of enterprises is environmentally unacceptable, because existence of chemically unstable phases was identified in the resulting sediments. This prevents further disposal of resulting waste of sewage treatment. That is why we consider the use of such process for wastewater treatment inappropriate.

Results of the study make it possible to propose the technological scheme of treatment of highly concentrated wastewater from a nickel-plating line, taking into consideration specific features of a particular production In subsequent research, based on the kinetic model, it is possible to develop the technique of engineering calculation of the degree of purification of industrial wastewater of electroplating production from ions of heavy metals.

7. Conclusions

1. The influence of the basic technological parameters on the quality of treatment of concentrated wastewater of a nickel plating line – depleted electrolytes at various methods of activation of the ferritization process was studied. It was found that the most effective results of wastewater treatment are achieved using electromagnetic pulse (T=20 °C) and thermal (T=70 °C) techniques of activation of the ferritization process with the following parameters: original ratio concentrations of Fe^{2+} to Ni^{2+} is within 3/1– 4/1; total concentration of ions of heavy metals is 20–25 g/dm^3; original value of pH of the reaction mixture is 9.5; duration of the ferritization process is 15 min. In this case, the degree of wastewater purification from ions of heavy metals, which makes it possible to use water in the circulation water supply system of enterprises, is achieved.

2. Kinetics of extracting iron and nickel ions from aqueous solutions by the ferritization method was explored. The mathematical dependences, which make it possible to predict with enough precision the degree of wastewater purification from ions of heavy metals at the lowest specific energy consumption, were proposed.

3. Sediments of high-temperature and electromagnetic pulse activation of the ferritization process are characterized by the crystalline structure and ferromagnetic properties. Such sediments compared to waste of traditional reagent wastewater purification are easily separated on magnetic filters, have high chemical resistance and capacity for further recycling. The analysis of specific volumes of sediments shows that the best results of compaction were achieved by centrifugation with separation factor of 3,600, using electromagnetic pulse or thermal activation

at the ratio of concentrations of ions of iron and nickel of 3/1–4/1.

4. It was found that electricity consumption of electromagnetic pulse activation of ferritization compared with high temperature activation decreases by order of magnitude, which makes it possible to significantly reduce the costs for ferritization technology of wastewater treatment, and therefore, makes it attractive for investments.

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Дослідження кінетики процесу Фішера-Тропша є досить важливим завданням, так як даний процес дуже чутливий до температурного режиму, та характеристик каталізатору. Також даний процес супроводжується багатьма побічними реакціями, які негативно впливають на швидкість та селективність реакції. Синтез Фішера-Тропша є альтернативним джерелом отримання якісного палива не з нафти, а з вугілля або біомаси. Тому дослідження кінетики реакції Фішера-Тропша спрямовані на підвищення селективності і активності каталізаторів, визначення констант швидкості хімічних реакцій є актуальними.

Вибір каталізатору є одним з основних факторів, що впливають на якість і вихід продукту по синтезу Фішера-Тропша. Для дослідів виготовлено два зразка кобальтових каталізаторів. Перший зразок каталізатору Co/γ-Al_2O_3 містить наночистинки кобальту одного розміру. Другий зразок каталізатору (Co)/γ-Al_2O_3 отриманий методом просочення носія розчином нітрату кобальту. Каталізатор отриманий методом просочення (Co)/γ-Al_2O_3 виявив на порядок вищу активність в порівнянні з монодисперсним. Однак монодисперсний каталізатор показав високу селективність за нижчими вуглеводнями.

Для розрахунку кінетики процесу Фішера-Тропша та для знаходження констант швидкості реакцій, було створено програмний модуль, який розроблявся в середовищі MS Visual Studio 2017 на мові C# з використанням технологій .NET Framework v4.6. За допомогою розробленого програмного модуля було розраховано константи швидкості реакції процесу Фішера-Тропша. Проаналізувавши отримані дані, видно, що відносна похибка лежить в межах 2...3 %, що свідчить про адекватність запропонованої моделі розв'язку зворотної задачі хімічної кінетики. Тому можна засвідчити, що дану модель розрахунку констант швидкості можна використовувати для дослідження процесу Фішера-Тропша

Ключові слова: реакція Фішера-Тропша, кобальтовий каталізатор, зворотна задача кінетики, константа швидкості

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MATHEMATICAL MODEL OF OBTAINING A HYDROCARBON FUEL BASED ON THE FISCHER-TROPSCH PATHWAY IN A STATIONARY LAYER OF THE COBALT-BASED CATALYST

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1. Introduction

At present, the processes for obtaining a synthetic liquid fuel from gases that contain a mixture of carbon monoxide and hydrogen include the Fischer-Tropsch process (FT-synthesis) [14]. The FT-synthesis is an alternative source for obtaining high-quality fuel from coal or biomass, rather than petroleum.

Given a decrease in the oil stocks in the world, mankind has begun to look for alternative sources in order to obtain fuel whose production volumes grow every year. Conversion of synthesis-gas to liquid hydrocarbons using the Fischer-Tropsch process (FT-synthesis) [1–4] is an alternative technique for obtaining the motor fuel.

The Fischer-Tropsch synthesis is an important technology, aimed at converting coal, natural gas, or biomass, into valuable products, such as motor fuels or raw materials for petrochemicals [1, 3]. The process is named after Franz Fischer and Hans Tropsch [3, 4], who showed the possibility of this reaction in 1923, by converting a mixture of carbon monoxide and hydrogen into hydrocarbons using an iron catalyst.