The object of this study is model solutions, spent sulfuric acid and chloride acid etching solutions, degreasing of metal products at enterprises.

The paper reports results of research on the possibility of obtaining sediments of predefined composition and reducing the consumption of chemical reagents in comparison with conventional cleaning schemes. The systematization of the elements of the technological scheme has been shown, which provides for the treatment of concentrated wastewater of the etching area in combined systems with obtaining sediments of predefined composition and is the basis for the implementation of resource-saving technology. Rational parameters were established for the state (pH=3–4, Eh=+0.3–(+0.33) V, and rH_2=16.3–19.38 V) and technological parameters (degree of iron extraction ψ=0.8, reagent consumption from the stoichiometric norm of B=0.8). Such parameters provide the proper conditions for the oxidation of organic compounds and their co-precipitation with insoluble iron hydroxy compounds (the maximum degree of extraction of organic impurities is 86 %). The formed precipitate corresponds to the $FeOOH \cdot nH_2O$ composition, contains 2–3 % of organic impurities, and is subject to burial. As a result of studies on the treatment of concentrated iron-containing wastewater, the obtained sediment is ready for further utilization by processing. The composition of this sediment corresponds to the natural mineral limonite FeOOH ($Fe_2O_3 \cdot nH_2O$) and is formed at pH values from 3.5 to 7.5 with rH_2 values from 26 V to 21 V and at technological regeneration parameters of pH=4.0–4.6; rH_2=23.34–32.25 V.

As a result of research into the deep purification of wastewater using a magnetic device, a suspension of sediment of ferromagnetic impurities (hydroxo compounds of iron) is obtained, which could be the basis for extraction or production of magnetically favorable dispersed material

Keywords: pickling and degreasing solutions, parameters, magnetic device, sediment of predefined composition

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DETERMINING RATIONAL PARAMETERS FOR THE TREATMENT OF CONCENTRATED WASTEWATER FROM ETCHING SITE BY USING COMBINED SYSTEMS PRODUCING SEDIMENTS OF PREDEFINED COMPOSITION

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1. Introduction

Concentrated wastewater from the etching area includes iron-containing chloride and sulfate spent technological solutions (STS) and STS from degreasing operations. As a result of the analysis of balance schemes of material flows of the etching area – environment system, it was determined that the bulk (up to 98 %) of waste comes from STS [1]. Such solutions are formed as a result of treatment of steel surfaces with acid solutions in order to clean them from corrosion products [2]. Hundreds of millions of tons of concentrated STS are produced annually at the enterprises of Eastern Europe, which require processing and disposal [3]. In addition, they belong to environmentally hazardous industrial waste of the 2–3 hazard class, their disposal requires significant costs [4, 5]. In practice, galvanic and other highly concentrated metal-containing wastes under the influence of external physical and chemical factors change into soluble forms and penetrate into soils and drainage waters, polluting the surrounding natural environment [6].

The current development of technologies in the most developed countries of the world involves the inclusion of elements of wastewater treatment and obtaining sediments of predefined composition as auxiliary elements for the basic production process [7]. In most countries, highly concentrated metal-containing waste in the form of sediments is subject to disposal on the territory of the enterprise or in special landfills after its preparatory treatment for transportation. The system of preliminary preparation for transportation requires a number of additional technological equipment for compaction, dehydration, drying of sediments, etc. The process is complex and requires additional costs for reagents – this significantly increases the cost of the disposal process.

Thus, solving the problem of obtaining sediments of predefined composition and reducing the consumption of chemical reagents in the treatment of concentrated wastewater in the etching area in combined systems is a relevant task.

2. Literature review and problem statement

Modern technological schemes for the treatment of concentrated wastewater in the etching area require rationalization. However, most attention is paid to the organization of local cycles of regeneration of etching solutions. Work [8] reports the results of research on the development of a technological scheme for the purification of washing water to the norms of "Technical water of category II" for use in production. It includes reagent cleaning with an alkaline reagent ($Ca(OH)_2$ solution) and a flocculant, filtering on a filter with polystyrene foam loading and processing part of the flow on a reverse osmosis unit. It is shown that this technology provides a closed cycle of resource consumption. This minimizes the discharge of waste into the environment and costs of the enterprise. However, when applying this technology, issues related to obtaining sediments suitable for further processing and disposal remain unresolved. Wastewater in its entirety, namely concentrated wastewater from degreasing operations, is also not considered.

The most common method of wastewater treatment is chemical or reagent [9]. In practice, wastewater from etching operations is subject to treatment with an alkaline reagent for the purpose of neutralization. The disadvantage of chemical (reagent) technologies for wastewater treatment from etching operations [9] is the high consumption of reagents and the formation of a significant amount of sediment, which cannot be disposed of and can be dissolved again due to complexation and the formation of colloidal micelles.

In addition, it is worth noting that the used iron-containing STS include harmful contaminants, such as petroleum products (including oils), fats, ionogenic surfactants (surfactants), and other impurities that are difficult to identify, control, and regulate. Thus, the sediments formed as a result of the chemical cleaning method, in terms of component composition, as a rule, do not meet the conditions of their subsequent processing for the purpose of disposal.

An option to overcome these difficulties may be electrochemical methods [10], which make it possible to obtain sediment to be disposed of and ensure a reduction in the consumption of chemical reagents. However, these methods have not found practical implementation due to the low stability of the membranes, especially under the conditions of an aggressive environment (etching solutions), the instability of the regimes, the complexity of the processes of oxidation of Fe^{2+} to Fe^{3+} in regeneration schemes. Their use for extracting iron requires high energy consumption and equipment complexity.

In work [11], systems for the automated control over the pH and Eh parameters of wastewater, which are used for dosing reagents, are given, which ensures the necessary quality of wastewater purification from heavy metals and other toxic impurities. However, sediments are sent only to dewatering.

The method of processing etching solutions to obtain such iron compounds as magnetite Fe_3O_4, hematite $\alpha-Fe_2O_3$, and maghemite $\gamma-Fe_2O_3$ is promising. These compounds of a crystalline structure quickly sediment during processing, their volume and humidity are much lower than those of iron hydroxides [9]. A fairly common method of such processing of spent etching solutions is the method of ferritization using variable magnetic fields [12]. At the same time, the energy efficiency of STS processing process increases, magnetite deposits are formed, which are easily disposed of. However, with this method, there is no increase in the degree of extraction of iron ions compared to the conventional thermal method.

An option for overcoming these difficulties is the use of a magnetic device in technological schemes of wastewater treatment as an element of auxiliary systems that provide deep purification of wastewater. This is the approach used in work [13]. The use of magnetic devices ensures a 3-fold reduction in iron concentration. However, their disadvantages are the limited possibilities of creating localized zones of high-gradient electric fields in the working zone of deposition, which leads to a low deposition force on impurity inclusions.

Recently, the use of magnetic adsorbents in water and wastewater treatment technologies in industry has been effective [14]. However, the high capital cost, the difficulty of separating the adsorbent from the solution, and the complex processes of its synthesis limit the use of magnetic adsorbents in industry.

Paper [15] considered the improvement of the technological scheme of wastewater treatment of the etching area by implementing technological combined schemes for the treatment of iron-containing wastewater using an auxiliary element of a magnetic device. At the same time, the possibilities of practical implementation of reverse osmosis are expanding. This makes it possible to obtain clean water that can be used for the preparation of technological solutions and mixed with technical water, for washing operations. However, the disadvantage is that the proposed technological scheme for the purification and further purification of iron-containing wastewater is multi-stage and requires the use of appropriate equipment.

In [16], a combined system is recommended, which is based on the distribution of wastewater into streams, taking into account the chemical nature of individual components, the intercomponent effect of ions on the structure of the water system. The hydrated ion model is considered as an element of this system. This ensures effective treatment of concentrated wastewater from galvanic production. Due to the combination of periodically operating local systems and continuously operating centralized systems, the specified scheme provides for the implementation of staged treatment of concentrated wastewater, which makes it possible to achieve high and stable quality of wastewater treatment of galvanic production. However, the proposed technological and technical solutions do not include the separation of the formed sediments according to the parameters of their chemical deposition and do not provide for obtaining sediments of predefined composition.

Work [17] describes the method of wastewater treatment of galvanic production, which is based on the co-precipitation of iron(III) ions with chromium ions with the formation of a mixed hydroxide. For the reduction of chromium(VI) ions to chromium(III), iron(II) compounds are used, which are dosed with an excess, while the unreacted iron(II) ions are converted into iron(III) ions by bubbling air with oxygen. Used solutions of etching baths are used as a source of iron(II) ions. The precipitation process is carried out by using classical precipitation reagents. The propensity of chromium(III) ions to isomorphic coprecipitation with iron(III) ions makes it possible to achieve a high degree of purification from chromium ions. The resulting sediment after filtering is sent for disposal by burial or incineration together with the main (organic) sediment, which contains organic impurities. The final filtrate, containing sulfate and sodium chloride, is returned to the production cycle.

The proposed technique in general makes it possible to strengthen the environmentally safe utilization and disposal of iron-containing STS, which are concentrated metal-containing waste. However, this technique can be implemented at enterprises of individual regions or regional centers, which provide for the treatment of wastewater of different composition and concentration at centralized treatment plants using unified technologies.

It is known that in the most common technologies for cleaning concentrated wastewater of the etching area from iron ions, there is no characterization of the obtained sediments and their composition. At the same time, all recommendations for obtaining sediments are only of a general nature and do not take into account the main technological parameters for obtaining sediments of predefined composition and required properties.

In the process of chemical precipitation of heavy metal ions from wastewater of galvanic production, precipitates are formed, the chemical composition of which depends on the ratio of reagents, that is, their excess or stoichiometric amount. To this day, it is recommended to calculate the consumption of reagents according to the stoichiometric rate, using their excess in practice.

But the precipitate often consists not only of insoluble metal hydroxide but of complex basic or acidic salts and an excess of reagent. At the same time, the true composition of the resulting sediment is difficult to predict or analyze. Therefore, the technological scheme proposed in [18] does not provide for obtaining sediments of a constant composition for subsequent processing in order to obtain certain marketable products.

It is known that the sediment formed at sewage treatment plants is diverse in composition and properties, therefore it is divided into two groups:

– group 1 is a liquid that contains water, that is, a suspended sediment that has flow properties. It includes sediment, for example, after a sedimentation reactor, sedimentation tank, flotation device, sandblast filter;

– group 2 – a solid body containing water, i.e., sediment belonging to capillary-porous materials and having the following properties: porosity, fragility, stickiness. This group includes dehydrated sediment or dried sediment under normal conditions or during thermal drying.

The composition, quantity, and main properties of sediment of groups 1 and 2 are determined by the conditions of wastewater generation, operating conditions of treatment facilities, treatment techniques, etc. Also, such sediments do not meet the requirements for chemical composition and specified properties for disposal by other methods.

Therefore, based on our review of the literature, it can be concluded that the technological parameters of the regeneration of concentrated etching solutions to obtain sediments of the recommended composition remain unexplored.

All this gives reason to assert that it is expedient to carry out research on the systematization of the main elements of the technological scheme for the treatment of concentrated wastewater of the etching area in combined systems with obtaining sediments of predefined composition. It is necessary to establish the state parameters: pH, rH_2, consumption of reagents to obtain sediment of a certain chemical model, which is suitable for further utilization by processing. To justify the use of a magnetic device for obtaining a sediment suspension for the production of magnetically favorable dispersed material. At the same time, it is necessary to reduce the costs of chemical reagents, taking into account the main theoretical provisions of chemical deposition, namely: consider such periods of sediment formation as induction, formation, and initial aging of the system.

3. The aim and objectives of the study

The purpose of our work is to substantiate the rational parameters for the consumption of chemical reagents, taking into account the technological parameters of the concentrated wastewater treatment processes of the etching area in combined systems. This will make it possible to obtain sediments of predefined composition and reduce the consumption of chemical reagents in comparison with conventional cleaning schemes.

To achieve this goal, the following tasks were set:

– to justify the main elements of the technological scheme of wastewater treatment with obtaining sediments of predefined composition;

– to determine the rational parameters and main elements of the technological scheme of wastewater treatment with obtaining sediments for disposal;

– to determine the rational parameters and main elements of the technology for obtaining sediments ready for further utilization;

– to determine the rational parameters for the regeneration of etching solutions with the production of sludge for disposal;

– to determine the parameters of deep magnetic purification of wastewater with the formation of ferromagnetic impurity sediment.

4. The study materials and methods

The object of our study was model solutions, spent sulfuric acid and chloride acid etching solutions, degreasing of steels from the "Hardware Factory" LLC (Ukraine). Model solutions contain ferric ions with a concentration from 0.02 mol/l to 0.7 mol/l and sulfuric and hydrochloric acids with a concentration from 5.5 mol/l to 2 mol/l, respectively. These model solutions are analogs of technological highly concentrated solutions and wastewater of the etching area.

The hypothesis of the study assumes that obtaining sediments of predefined composition for the purpose of further use (utilization, burial) depends on rationally selected technological parameters of wastewater treatment in the combined system.

The study of the thermodynamic stability of iron compounds under chemical deposition conditions, kinetic parameters of purification, and the main technological parameters of obtaining precipitates of predefined composition was carried out under laboratory conditions. Indicators of redox balance according to the rH_2 indicator and the study of the composition of etching solutions with an alkaline reagent were carried out under experimental and industrial conditions. The main elements of the technological scheme for cleaning concentrated wastewater of the etching area are shown in Fig. 1; Fig. 2 displays a photograph of the treatment facilities at the "Hardware Factory" LLC.

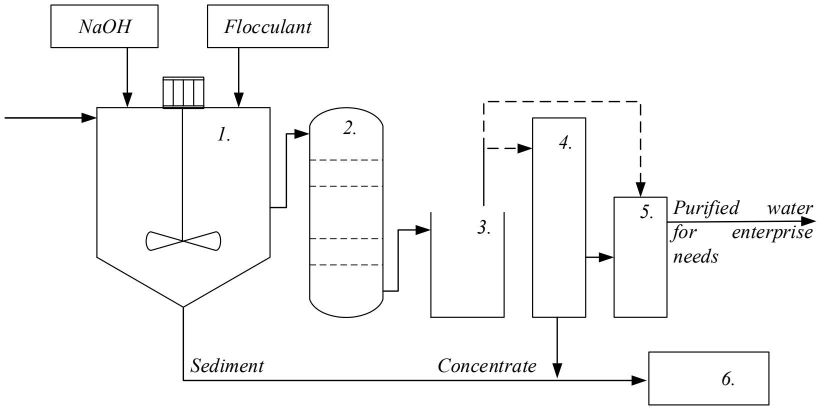


Fig. 1. Basic elements inv the technological scheme for treating concentrated wastewater of the etching area. Designation: 1 — chemical reactor; 2 — polystyrene foam filter; 3 — intermediate capacity; 4 — reverse osmosis installation; 5 — purified water capacity; 6 — sediment accumulator

The acid-basic and redox properties of the concentrated wastewater from the etching area and the conditions of its treatment for the purpose of purification, regeneration, and utilization were studied by the methods of potentiometric titration and chemical precipitation in a batch reactor with intensive agitation of reactants.

Quantitative studies on the content of ferric ions were carried out under laboratory conditions by the method of photometric determination with sulfosalicylic acid. Potentiometric titration was carried out under laboratory conditions using an EB 74 potentiometer and under industrial experimental conditions using a portable pH meter pH 602 (Ukraine). Magnetic cleaning was studied at an experimental setup for magnetic deposition.

Fig. 2. Wastewater treatment facilities at the "Hardware Products Factory" LLC

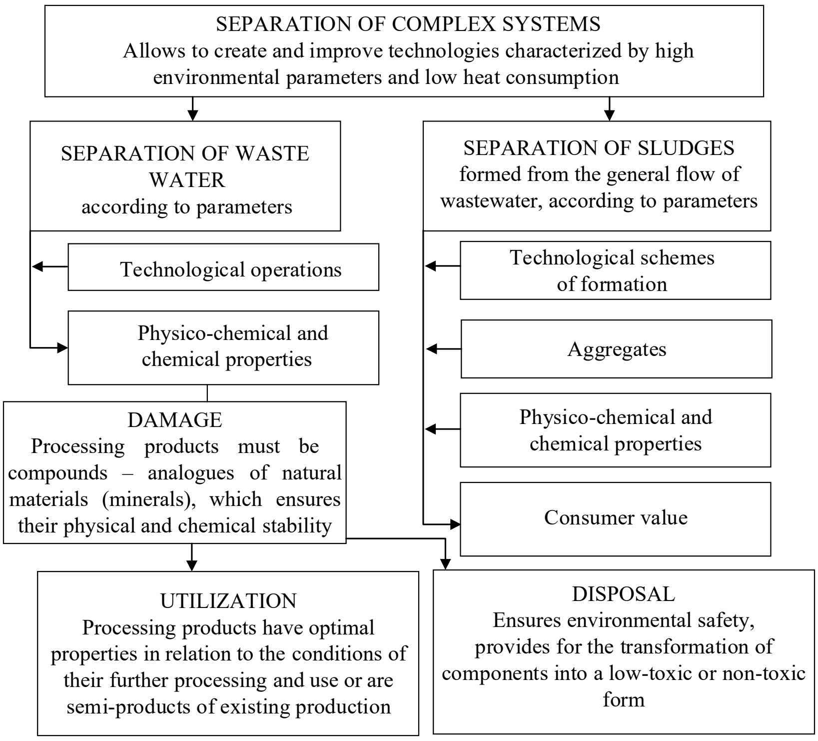
5. Results of research into the rational parameters of concentrated wastewater treatment processes at the etching site

5. 1. Basic elements in the technological scheme for wastewater treatment with the production of sediments of predefined composition

Based on the review of the literature [4] and earlier conducted studies, which were verified in papers [15, 18–20] and under industrial conditions (Fig. 2), we systematized elements of the technological scheme, which provides for the treatment of concentrated wastewater from the etching area in combined systems with obtaining sediments of predefined composition (Fig. 3).

In accordance with the principles of waste-free production, we believe that the very technology of wastewater treatment (chemical precipitation, electrocoagulation, galvanic coagulation, etc.) should provide for obtaining sediment of predefined chemical composition, physicochemical properties, and consumer values.

To this end, in order to improve the classical technology [19], wastewater should be divided into separate categories according to the parameters of its treatment. It depends on the technological operation (degreasing, etching, washing, etc.) and physical and chemical properties (pH, Eh, rH_2, qualitative and quantitative composition, etc.). At the same time, it is important to take into account the aggregate state of the sediment (liquid or solid), which is formed as a result of cleaning, to ensure the conditions for their further processing or disposal (Fig. 3).



SEPARATION OF COMPLEX SYSTEMS
Allows to create and improve technologies characterized by high environmental parameters and low heat consumption

SEPARATION OF WASTE WATER
according to parameters

Technological operations

Physico-chemical and chemical properties

SEPARATION OF SLUDGES
formed from the general flow of wastewater, according to parameters

Technological schemes of formation

Aggregates

Physico-chemical and chemical properties

Consumer value

DAMAGE
Processing products must be compounds – analogues of natural materials (minerals), which ensures their physical and chemical stability

UTILIZATION
Processing products have optimal properties in relation to the conditions of their further processing and use or are semi-products of existing production

DISPOSAL
Ensures environmental safety, provides for the transformation of components into a low-toxic or non-toxic form

Fig. 3. Basic elements in the technological scheme for the treatment of wastewater with the production of sediments of predefined composition

According to the results from our review of the literature, in this work it was determined that the main concept for improving the technological scheme of cleaning concentrated wastewater from the etching area coincides with the basic concept of chemical production, namely:

– minimization of chemical reagents of the technological process;

– return of purified water to production (after deep purification);

– waste disposal.

In order to substantiate the technical solutions regarding the construction of a combined system of concentrated iron-containing wastewater from the etching area with obtaining sediment of predefined composition, it is necessary to conduct experimental studies with the determination of state parameters. Such indicators include the concentration of components, pH, Eh, rH_2, temperature; technological parameters: speed and degree of extraction, speed of agitation, and dosing of reagents.

5. 2. Research results regarding the construction of a technological scheme of wastewater treatment with obtaining sediments for disposal

The surface preparation section includes the following operations: degreasing, two-stage washing (hot and cold), post-degreasing, etching, cold washing after the etching operation.

In order to obtain sediments in a form and composition that enable their burial or disposal during the disposal of toxic waste, we recommend including additional technological equipment.

It is known that the composition of sediments produced by the reagent cleaning method does not meet the conditions for their subsequent processing (disposal), as they contain harmful contaminants, such as fats, oil products, ionogenic surfactants, etc.

Table 1 gives elements of the technological scheme for the mutual neutralization and extraction of impurities of organic and inorganic origin from the concentrated wastewater of the etching area, which are the basis for the implementation of resource-saving technology.

Based on the results of the research reported in [20], the following parameters are presented for effective treatment of concentrated wastewater in the etching area:

– state parameters (elements of the technological scheme), namely the values corresponding to a strongly acidic oxidizing environment, are as follows: pH=3–4, Eh=+0.3–(+0.33) V and rH_2=16.3–19.38 V. Under these conditions, rational conditions for oxidation (coagulation) of organic compounds and their co-precipitation with insoluble hydroxocompounds of iron are provided;

– technological parameters: the value of the degree of extraction of iron is $\psi=0.8$ and the consumption of the reagent (from the stoichiometric norm) is $B=0.8$. At the same time, the maximum degree of extraction of organic impurities according to the HSC value is 86 %.

5. 3. Results of determining the main parameters and elements of the technology for obtaining sediments ready for further disposal

In the current paper, studies were conducted to determine the main kinetic and thermodynamic parameters of chemical precipitation, namely: pH, Eh, degree of conversion (extraction), speed (in the pH range from –1 to 10.2).

Table 2 gives data that allow determining thermodynamically stable forms of iron compounds under chemical precipitation conditions in the pH range from –1 to 10.2 and the Eh range from 0.7 V to –0.6 V.

Fig. 4 shows data on changes in the degree of iron extraction as a function of pH and the degree of iron extraction as a function of time.

Under the conditions of the equilibrium process in composite systems (Pourbet diagram), it can be stated that for the interval of Eh values from –0.414 to –0.1 V, the following equilibrium transformations $Fe^{2+}\leftrightarrow Fe(OH)_2\leftrightarrow H_2O$ correspond, and at the points of Eh values from – 0.1 V and more are as follows:

$$Fe^{2+}\leftrightarrow Fe(OH)_2\leftrightarrow Fe(OH)_3\leftrightarrow H_2O.$$

Table 1

Elements of the technological scheme for mutual neutralization and extraction of impurities of organic and inorganic origin from concentrated wastewater of the etching area

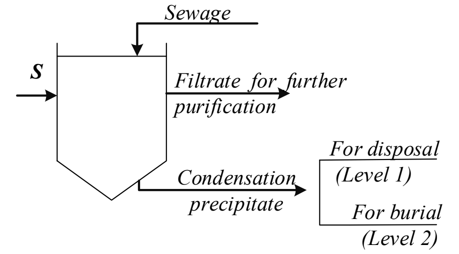
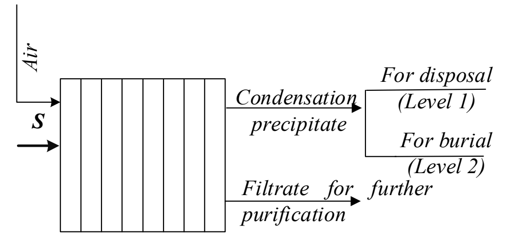
No.	Code	Installation type	Typical process	Element function (structure type)	Graphic representation
Level 1. Elements of the technological scheme for the treatment of concentrated wastewater of the etching area from components of organic and inorganic origin, including impurities (oils, fats, surfactants, cuprum ions, nickel, etc.)					
1	E1	Liquid-sludge conversion reactor	Chemical	Formation of condensation sludge during wastewater treatment	
2	E2	Separation reactor	Hydromechanical (filtration)	Sludge dewatering	

Table 2

Data for determining the thermodynamic stability of the form of iron compounds under chemical deposition conditions (theoretical calculations based on the Nernst equation)

Parameter	Value							
pH	–1	1.3	2.2	3.5	5.8	6.8	8.2	10.2
Iron concentration in solution, mol/l	0.6	0.198	0.16	0.12	0.075	0.064	0.038	0.0012
Eh, B (calculated value)	0.35	0.33	–0.043	–0.17	–0.36	–0.43	–0.61	–0.61
Form of ratio Fe^{3+}:Fe^{2+} (calculated value)	$4.3 \cdot 10^{-8}$	$3.2 \cdot 10^{-8}$	$2.6 \cdot 10^{-15}$	$1.3 \cdot 10^{-17}$	$5.7 \cdot 10^{-21}$	$2.9 \cdot 10^{-22}$	$1.2 \cdot 10^{-25}$	$3.9 \cdot 10^{-27}$

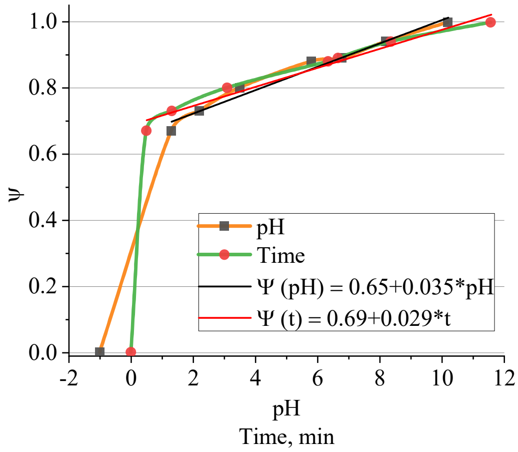


Fig. 4. Change in the degree of extraction of iron depending on pH and time: ψ is the degree of extraction

Topochemical reactions that take place during the purification of iron-containing wastewater from etching operations include the stages of formation of colloidally dispersed particles of hydroxocomplexes of iron and their crystals and have certain kinetic features. It is known that the nature and concentration of components affect the course of individual stages.

In this work, technological solutions of chloride and sulfate types with a total iron concentration of 0.6 mol/l were studied. At the same time, the concentration of Fe^{3+} for the sulfate type is no more than 8 %, and for the chloride type – from 50 % or more. Table 3 gives data on the experimental studies of kinetic parameters for individual stages of the process:

1) induction;
2) sediment formation;
3) separation of the sediment from the solution.

Table 3

Kinetic parameters of purification of concentrated iron-containing wastewater from etching operations

Type of solutions	pH	Concentration, mol/L	Speed, 10^{-3} mol/s
Sulfate	1) pH –0.5÷1.15	0.6–0.28	1.69
	2) pH 1.15÷6.7	0.28–0.239	0.038
	3) pH 6.7÷11	0.239–0.009	0.53
Chloride	1) pH –1÷1.3	0.6–0.19	6
	2) pH 1.3÷5.8	0.19–0.01	0.002
	3) pH 5.8÷10.2	0.01–0.001	0.005

It was established that autocatalysis is more pronounced for solutions of the chloride type (the speed of the process is 3.6 times higher than for the sulfate type). The phenomenon of "impedance" corresponds to a decrease in the rate of sediment formation, and it is more pronounced for the chloride type compared to the sulfate type (compared to stage 1, by 3000 times).

Based on our experimental data, it was established:

– the initial etching solution has the following composition: C(HCl)=140 g/l, iron content $C(Fe_{total})$=80 g/l;

– after 12 hours, the total iron concentration increased to 120 g/l, and the acid concentration decreased to 100 g/l;

– the maximum rate of etching is 8 g/l.h, the minimum is 6 g/l.h, the average value is 6.3 g/l.h.

Taking into account the obtained data for individual components, the calculated ratio $C(Fe_{total})$:C(HCl) for the original solution is 0.57, for the spent solution – 1.2.

Table 4 gives the results of experimental studies on the composition of etching solutions after treatment with an alkaline reagent to a pH of 4.

On the basis of experimental studies, it was established that at the same pH value, the Fe^{3+}:Fe^{2+} ratio takes a value in the range of 0.039–4.6. At the same time, the maximum value of the ratio (Fe^{3+}:Fe^{2+}) corresponds to the minimum value of Fe (total):HCl 0.52, and the minimum value of the ratio (Fe^{3+}:Fe^{2+}) corresponds to the maximum value of Fe (total):HCl 1.5.

Features of the composition of solutions are associated with known equilibrium processes of intercomponent interactions, which include the formation of coordination complexes:

$$\left[Fe(H_2O)_6\right]^{3+} \rightarrow \left[Fe(H_2O)_5OH\right]^{2+} + \\ +H^{+} \rightarrow \left[(H_2O)_4Fe(OH)_2Fe(H_2O)_4\right]^{3+}. \qquad (4)$$

Ligands are known to prevent the formation of hydroxides in an alkaline environment:

$$\left[Fe(H_2O)_6\right]^{3+} + 4Cl^{-} \rightleftarrows \left[FeCl_4\right]^{-} + 6H_2O, \qquad (5)$$

and at pH>4, $\left[FeCl_3(OH)\right]^{-}$ is formed.

The main technological parameters for obtaining sediment of predefined composition, taking into account the theory of chemical deposition, are given in Table 5.

On the basis of experimental research on the treatment of concentrated iron-containing wastewater, the following technological parameters have been established: pH=3.5–4.0; Eh=0.1 V; the ratio of Fe^{3+}:Fe^{2+} forms can be 0.4 % and significantly increases when hydrogen peroxide is added to 52 %, which corresponds to a change in Eh values from 0.1 to 0.7 V. As a result, the conditions for the chemical precipitation of iron ions in the form of hydroxo compounds in an acid-oxidative environment are provided. The degree of conversion (extraction) increases by 30 % when they are neutralized (the degree of conversion (extraction) is from 89 % to 99.8 %, respectively, at pH 6.8 and pH 10.2). At the same time, it was established that autocatalysis (induction stage) is more pronounced for chloride-type solutions (the speed of the process is 3.6 times higher than for sulfate-type). The phenomenon of "impedance" corresponds to a decrease in speed at the stage of sediment formation, and it is more pronounced for the chloride type compared to the sulfate type (compared to the induction stage, by 3000 times).

Table 6 gives elements of the technological scheme for the treatment of concentrated iron-containing wastewater of the etching area with the production of sediments ready for further utilization by processing.

As a result of studies on the treatment of concentrated iron-containing wastewater, the sediment obtained is ready for further utilization by processing. The composition of the precipitate corresponds to the natural mineral limonite FeOOH ($Fe_2O_3 \cdot nH_2O$) and is formed at pH values from 3.5 to 7.5 with rH_2 values from 26 V to 21 V (Table 6).

Table 4

The composition of etching solutions after treatment with an alkaline reagent

Solution type	Acid concentration	Concentration Fe(total), g/l	Concentration Fe^{3+}, g/l	Concentration Fe^{2+}, g/l	Ratio Fe^{3+}:Fe^{2+}	Ratio Fe (total):HCl
Sulfate acid after treatment with 10 % NaOH	128	66.3	2.5	63.8	0.039	0.52
Sulfate acid after treatment with 10 % NaOH	6.4	9.4	2.5	6.6	1.42	1.5
Sulfate acid after treatment with 10 % NaOH	116.8	61.3	5.5	55.6	0.1	0.52
Sulfate acid after treatment with 10 % NaOH	116.8	63.8	3.0	60.8	0.05	0.55
Sulfate acid after treatment with 10 % NaOH	125.9	70.0	25.0	45.0	0.6	0.56
Sulfate acid after treatment with 10 % NaOH	120.5	63.7	18.8	44.9	0.42	0.53
Sulfate acid after treatment with 10 % NaOH	102.2	97.5	20.6	76.9	0.26	0.95
Sulfate acid after treatment with 10 % NaOH	100.4	83.8	24.4	59.4	0.41	0.83
Chloride	120	38.5	0.055	38.4	0.0014	–

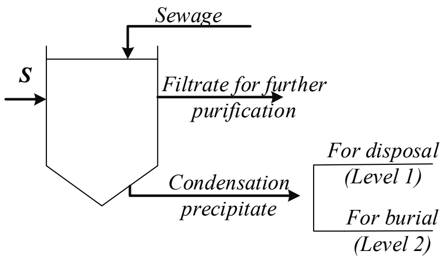
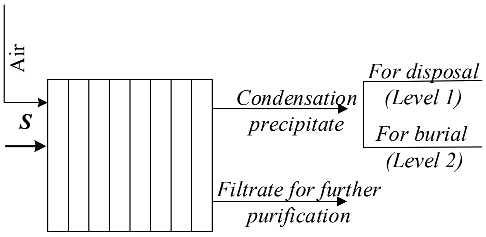
Table 5

Basic technological parameters for obtaining a precipitate of predefined composition

No.	C, mol/l	t, °C	v_{pr}, rev/min	$V_{(precipitate)}$, %				NaOH consumption, % of stoichiometric	Deposition type
				0 h	4 h	8 h	24 h		
1	0.02	20	90	12.5	11.0	8.2	8.0	100	amorphous-crystalline
2			180	12.5	11.0	8.2	8.0	100	amorphous-crystalline
3			270	11.7	10.9	9.9	9.7	100	amorphous-crystalline
4	0.1		180	25.7	16.8	13.9	13.6	100	amorphous-crystalline
5			270	25.3	21.0	19.4	19.0	100	amorphous-crystalline
6	0.5		180	50.1	44.9	34.3	33.6	100	amorphous-crystalline
7			270	52.1	47.5	34.5	33.8	100	amorphous-crystalline
8	0.02	35	90	10.6	9.0	8.8	8.6	100	amorphous-crystalline
9			180	10.6	9.0	8.8	8.6	100	amorphous-crystalline
10			270	10.7	9.0	8.8	8.6	100	amorphous-crystalline
11	0.1	35	180	20.2	18.6	18.3	18.0	100	amorphous-crystalline
12			270	20.6	20.2	18.6	18.2	100	amorphous-crystalline
13		75	180	16.4	16.2	14.9	14.8	100	crystalline
14	0.5	35	180	48.6	42.7	32.7	32.1	100	amorphous-crystalline
15			270	48.6	42.2	32.7	32.1	100	amorphous-crystalline
16		50	180	46.6	46.1	32.3	31.7	100	amorphous-crystalline
17		80	180	19.1	19.0	18.2	18.0	100	crystalline

Table 6

Elements of the technological scheme for the production of sediments ready for further utilization by processing

No.	Code	Installation type	Typical process	Element function (structure type)	Graphic representation
Level 2. Elements of the technological scheme for the treatment of concentrated iron-containing wastewater of the etching area with the production of sludge ready for further disposal by processing					
1	E1	Liquid-sludge conversion reactor	Chemical	Formation of condensation sludge during wastewater treatment	
2	E2	Separation reactor	Hydromechanical (filtration)	Sludge dewatering	

5. 4. Results of research on the regeneration of etching solutions with obtaining sediment for disposal

In order to determine the conditions for the maximum extraction of iron(III) ions and to predict the main composition of the sediment, in addition to pH, the redox balance was studied according to the rH_2 indicator (Table 7, Fig. 5).

According to our data, it can be concluded that the given conditions for the regeneration of etching solutions (pH=4.0–4.6; rH_2=23.34–32.25 V) allow obtaining sediment of the recommended composition for disposal, which corresponds to the natural mineral limonite FeOOH ($Fe_2O_3 \cdot nH_2O$).

Table 8 gives elements of the technological scheme for the regeneration of etching solutions with the production of sediment ready for further disposal by processing.

As a result of our research, the technological parameters for regeneration (pH=4.0–4.6; rH_2=23.34–32.25 V) were established, making it possible to obtain sediment of the recommended composition for disposal, which corresponds to the natural mineral limonite FeOOH ($Fe_2O_3 \cdot nH_2O$) (Table 8).

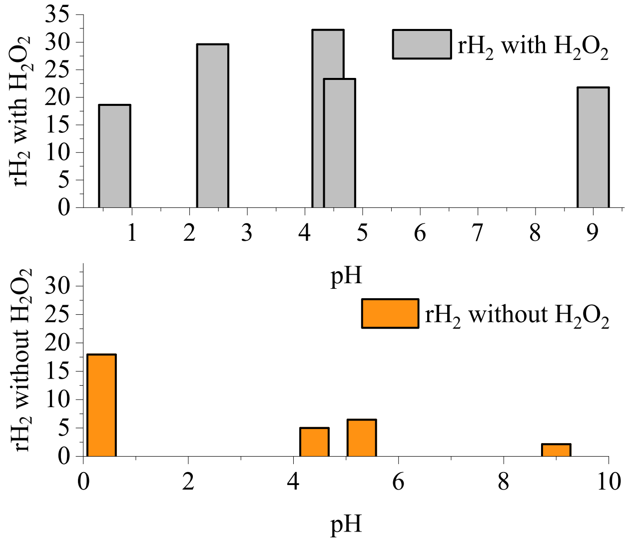


Fig. 5. Influence of hydrogen peroxide on redox equilibrium in the process of etching solution regeneration

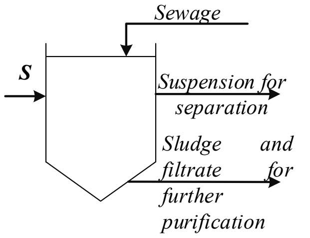
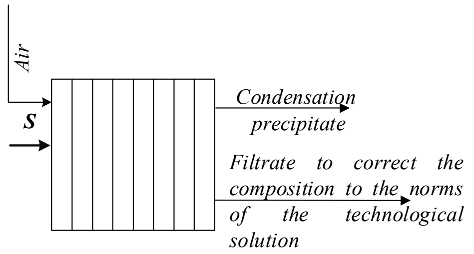
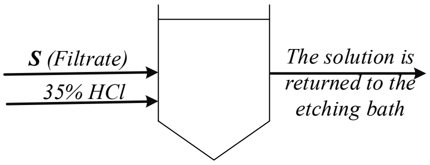
Table 7

Indicators of redox equilibrium of the process of regeneration of etching solutions

Consumption 20 % NaOH, ml	pH	Eh without H_2O_2 , V	Eh with H_2O_2, mV
125	0	–	–
250	0.35	0.500	–
300	0.7	–	0.500
325	2.4	–	0.720
350	4.4	–0.110	0.680
400	4.6	–	0.410
450	4.9	–	–
550	5.3	–0.120	–
650	9	–0.460	0.110

Table 8

Elements of the technological scheme for the regeneration of etching solutions with the production of a precipitate ready for further disposal by processing

No.	Code	Installation type	Typical process	Element function (structure type)	Graphic representation
Level 3. Elements of the technological scheme for the regeneration of etching solutions with the production of a precipitate ready for further disposal by processing					
3	E3	Liquid-sludge conversion reactor	Chemical	Formation of condensation sludge during wastewater treatment	
4	E4	Separation reactor	Hydromechanical (filtration)	Separation of slurry and sludge dewatering	
5	E5	Liquid-to-liquid oxidation reactor	Chemical	The chemical reagent HCl is dosed	

5. 5. Results of investigating deep magnetic post-treatment of wastewater with the formation of ferromagnetic impurity sediment

It is recommended to use a magnetic device in technological cleaning systems as an auxiliary element for deep purification of wastewater from iron-containing impurities [20]. The main element of such a device contains a granular filter load that is magnetized by an external device that generates a magnetic field.

The predicted extraction rate ψ of iron-containing wastewater depending on the strength of the external magnetic field at a filtration speed of 100 m/h and a length (height) of the nozzle layer of 0.8 m is 0.6–0.7.

As a result of the research, a technological solution has been proposed, which implies that the magnetic device is used as an auxiliary element in the technological systems of wastewater treatment of the etching area. Wastewater after reagent treatment with the addition of coagulant, flocculant, alkaline reagent, and after a polystyrene foam filter, is fed to a magnetic filter with granular loading.

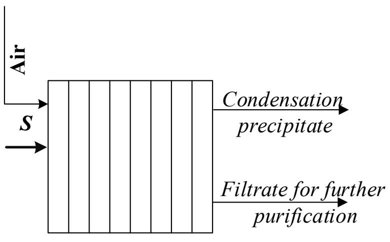
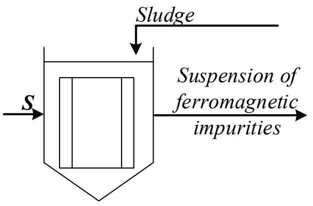
Thus, for a solution with an initial concentration of iron ions in wastewater of 0.6 g/l, it was established that after treatment with an alkaline reagent (10–20 % NaOH), the concentration of iron is $0.32.10^{-3}$ g/l, that is, it decreases by 1875 times. The use of a magnetic device makes it possible to reduce the total concentration of iron to $0.096.10^{-3}$ g/l (the degree of extraction of iron ions after the magnetic device is ψ=70 %). In general, the content of iron ions decreases by 6250 times.

Table 9 gives elements of the technological scheme of deep purification of iron-containing wastewater of the etching area using a magnetic device with the formation of a precipitate of ferromagnetic impurities.

On the basis of indicators of wastewater treatment from the etching area, it can be stated that the use of a magnetic device will enable deep purification of wastewater from iron ions. At the same time, a suspension of sediment of ferromagnetic impurities is obtained (Table 9).

Table 9

Elements of the technological scheme of deep post-treatment of iron-containing wastewater of the etching area with the use of a magnetic device with the formation of a precipitate of ferromagnetic impurities

No.	Code	Installation type	Typical process	Element function (structure type)	Graphic representation
Level 4. Elements of the technological scheme of deep post-treatment of iron-containing wastewater of the etching area with the use of a magnetic device with the formation of a precipitate of ferromagnetic impurities					
6	E6	Separation reactor	Hydromechanical (filtering)	Sludge dehydration	
7	E7	Reactor for separation in an electromagnetic field	Physical (Electromagnetic)	Deep purification and separation with obtaining a precipitate of ferromagnetic impurities	

6. Discussion of results of investigating rational parameters of concentrated wastewater treatment processes of the etching area

Taking into account the multicomponent composition of wastewater and further processing of sediments for the purpose of disposal (practical use), a combined system can be recommended. Such a system consists of a set of decentralized but coordinated structures, each of which is designed to transform a separate category of wastewater through an independent processing stage. In turn, decentralized structures can be connected into a single centralized system with automatic control (Fig. 3).

In accordance with the above, the main elements of the technological scheme, which provides for the treatment of concentrated sewage solutions of the etching area in combined systems with obtaining sediments of predefined composition, have been determined. These technological schemes can be arranged in the appropriate sequence depending on the purpose of cleaning:

– level 1: technological schemes for cleaning concentrated wastewater of the etching area from components of organic and inorganic origin, including impurities (oils, fats, surfactants, copper ions, nickel, etc.). At the same time, condensation sediments are obtained, ready for further transportation for burial (disposal);

– level 2: technologies for cleaning concentrated iron-containing wastewater from the etching site with obtaining sediments ready for further utilization by processing;

– level 3: technological schemes for the regeneration of etching STS with obtaining sediment ready for further utilization by processing;

– level 4: technological schemes of deep purification of iron-containing wastewater of the etching area using a magnetic device with the formation of a precipitate of ferromagnetic impurities.

Taking into account the increased ability to oxidize, STS of etching (chloride and sulfate solutions), which make up 85 % of the total volume of acidic metal-containing wastewater, should be classified as particularly aggressive liquid waste. Therefore, the problem of solving the processing of these types of waste in local cycles is significant.

Our research on the construction of a technological scheme for cleaning from components of organic and inorganic origin with obtaining sediments for subsequent burial or disposal allows saving the alkaline reagent by 80 %, excluding the use of acidic commodity reagent [20]. This is achieved by using the etching solution as an acidic reagent to neutralize the spent technological degreasing solution.

The combination of the proposed elements of the technological scheme makes it possible to obtain a precipitate that corresponds to the following chemical model $FeOOH \cdot nH_2O$. As a result of chemical transformations and secondary heterogeneous interactions, the sediment is chemically unstable and subsequently undergoes decomposition – dehydration [18]. This sediment contains 2–3 % of organic impurities and is subject to burial, and after special processing, roasting – disposal (Table 1). After the removal of organic impurities, wastewater with residual iron concentrations is recommended to be processed according to a technological scheme that enables the production of sediment of the specified composition for disposal (Table 2, Fig. 4).

On the basis of our research on devising a technology for obtaining sediments ready for further utilization by processing, rational state parameters and technological parameters have been established. The rational state parameters correspond to the following conditions: pH=3–4, Eh=(+0.3)–(+0.33) V, and rH_2=16.3–19.38 V. Rational technological parameters ensure the degree of iron extraction $\psi=0.8$ and the consumption of the reagent (from the stoichiometric norm) $B=0.8$ (Table 2, Fig. 4).

To devise a technology for obtaining sediments for disposal, theoretical calculations of redox and acid-basic conditions in the range of pH and Eh values obtained experimentally were carried out. Based on calculations from the Nernst equation, it was determined that in the defined pH and Eh intervals, the content of the $Fe(OH)_3$ form is <0.01 %. Under real conditions, it was experimentally determined that in the original solution the pH value is 1, and the Eh value is 0.35 V, while the ratio of Fe^{3+}: Fe^{2+} forms is 0.119 (10.6 %). In the range of pH=3.5–4.0, the value of Eh≈0.1 V, respectively, the ratio of Fe^{3+}: Fe^{2+} forms can equal 0.004 (0.4 %). This ratio increases significantly with the addition of hydrogen peroxide to 52 %, which corresponds to a change in Eh values from 0.1 to 0.7 V. As a result, the conditions for the chemical precipitation of iron ions in the form of hydroxo compounds are provided. These transformations correspond to the following equilibrium: $Fe(OH)_3 \leftrightarrow H_2O$ (Pourbet diagram). The use of hydrogen peroxide together with an alkaline reagent allows one to increase the degree of conversion by 30 % during their neutralization (Table 2, Fig. 4).

The obtained information on thermodynamics (Table 2, Fig. 4) and kinetics (Table 3) of the processes of cleaning concentrated iron-containing wastewater from etching operations in combined systems is necessary for their subsequent modeling under industrial conditions.

The discrepancy between theoretical and experimental studies is explained by the fact that actual processes of chemical deposition occur in non-equilibrium and decomposition systems (Table 4). This happens under the conditions of addition of chemical reagents in the cleaning process, the presence of other metal ions in etching solutions, including the ions of Ni^{2+}, Cr^{3+}, Cu^{2+}, and the influence of various kinetic factors.

The properties of solutions after treatment with an alkaline reagent can be explained by the fact that the process of precipitation of iron ions is significantly influenced by intercomponent interaction (emergence effect). In addition, cations bind to groups of anions to form coordination complexes (4):

The facts were established in favor of the “chemical” concept (sulfate etching solutions) of the influence of anions, namely the formation of sparingly soluble salts of the type $[Fe_2SO_4(OH)_4]$, i.e., ion association is the initial stage of solid phase formation.

It is known that ligands prevent the formation of hydroxides in an alkaline medium (5).

For chloride solutions, the degree of extraction of iron will be greater compared to sulfate etching solutions. This is explained, among other things, by the lowest stability of the corresponding chloride complexes.

Taking into account the technological parameters for obtaining sediment of the given composition (Table 5), the recommended cleaning technology allows obtaining sediment that corresponds to the natural mineral limonite FeOOH ($Fe_2O_3 \cdot nH_2O$). This precipitate is formed at pH values from 3.5 to 7.5 with rH_2 values from 26 V to 21 V. The resulting precipitate is easily dehydrated, and FeO(OH) (goethite) precipitate is formed, which is suitable for further use (Table 6).

To devise a technological scheme for obtaining sludge for disposal, it is recommended to direct 50 % of the total volume of the etching solution to local regeneration cycles. Regeneration of solutions from etching operations is carried out by treatment with an alkaline reagent and hydrogen peroxide in an acid-oxidizing environment in order to precipitate iron ions in the form of hydroxo compounds [19]. Schematically, this process can be represented as follows:

– oxidation of iron(II) ions to iron(III) ions, which is achieved when hydrogen peroxide is used;

– the formation of insoluble Fe^{3+} hydroxo compounds when adding an alkaline reagent to pH=4 [15, 19].

As mentioned, the chemical processes taking place are affected by all types of interactions between ions and water with the formation of complexes. Therefore, they belong to redox reactions, which are accompanied by a change in the state of complex formation.

On the basis of the theory of chemical processes, it can be stated that the reaction of extraction of hydrated ferric ion is more thermodynamically probable in comparison with extraction from chloride or sulfate complex compounds.

As a result of our research, it was established that with an initial concentration of iron of 20 g/l in the spent technological solution, the maximum degree of oxidation $\alpha=1$ ($\alpha=Fe^{3+}:Fe^{2+}$) is achieved, and at a concentration of 90 g/l, the degree of oxidation is $\alpha=0.8$. It should be noted that the consumption of the oxidizer reagent per 1 mass of iron (II) is the same. It can be assumed that the obtained data indicate that the mechanism of electron transfer through a water molecule occurs at a concentration of iron ≤20 g/l, and at 90 g/l – through the Cl^- ligand – formulas (4), (5).

According to the obtained data on indicators of redox balance (Table 7, Fig. 5), it can be concluded that the given conditions for the regeneration of etching solutions (pH 4.0–4.6; rH_2 23.34–32.25 V) allow obtaining sediment of the recommended composition for disposal, which corresponds to the natural mineral limonite FeOOH ($Fe_2O_3 \cdot nH_2O$).

Table 8 gives elements of the technological scheme of regeneration of solutions, which allows one to obtain sediment of the recommended composition for disposal. This sediment corresponds to the natural mineral limonite FeOOH ($Fe_2O_3 \cdot nH_2O$), as well as for technological purification schemes (Table 6).

It is recommended to use a magnetic device to design a technological scheme that includes deep wastewater treatment.

As a result of research on the deep purification of wastewater using a magnetic device (Table 9), a suspension of sediment of ferromagnetic impurities (hydroxocompounds of iron) is obtained, which may become the basis for extraction or production of magnetically susceptible dispersed material.

The resulting suspension of particles of hydroxocompounds of iron (ferromagnetic impurities), which is formed as a result of washing the nozzle of the magnetic device, can be the basis for extraction or production of magnetically favorable dispersed material.

The study of determining the parameters in the processes of cleaning concentrated wastewater of the etching area in combined systems with obtaining sediments of predefined composition is limited to the type of intercomponent interactions and is practically recommended for the use of etching solutions based on sulfuric and hydrochloric acids.

The disadvantage of technological schemes is the use of hydrogen peroxide to regulate the oxidation-reduction properties of wastewater to obtain sediments of predefined composition. Also, hydrogen peroxide is unstable during storage and is an expensive reagent.

In the future, it is expedient to investigate the possibilities of electrochemical methods for regulating redox properties for subsequent wastewater treatment with the aim of extracting sediments of predefined composition.

7. Conclusions

1. The basic elements of the technological scheme, which includes the separation of wastewater and sludge, which are formed according to technological operations and cleaning parameters, have been established. It involves the treatment of concentrated wastewater of the etching area in combined systems with the production of sediments of predefined composition.

2. On the basis of studies conducted on the treatment of concentrated wastewater of the etching area, the state parameters (pH=3–4, Eh=(+0.3)–(+0.33) V, and rH_2=16.3–19.38 V) and technological parameters (iron removal rate $\psi=0.8$, reagent consumption (from the stoichiometric norm) $B=0.8$) were determined. The sediment corresponds to the following chemical model: $FeOOH \cdot nH_2O$, it contains 2–3 % organic impurities and is subject to burial or disposal.

3. As a result of research on the purification of concentrated iron-containing wastewater from the etching site, the sediment obtained corresponds to the natural mineral limonite $FeOOH \cdot nH_2O$. This sludge is formed at pH values of 3.5 to 7.5 with an rH_2 value of 26 V to 21 V and is suitable for further disposal by recycling.

4. As a result of our research, the technological parameters of the regeneration of etching solutions (pH 4.0–4.6; rH_2 23.34–32.25 V) were established, allowing one to obtain sediment of the recommended composition for disposal, which corresponds to the natural mineral limonite FeOOH ($Fe_2O_3 \cdot nH_2O$).

5. The use of a magnetic device enables deep purification (reduction of the total concentration of iron to $0.096 \cdot 10^{-3}$ g/l) of wastewater from the etching area from iron ions. At the same time, a suspension of sediment of ferromagnetic impurities (hydroxocompounds of iron) is obtained, which can be the basis for extraction or production of magnetically susceptible dispersed material.

Conflicts of interest

The authors declare that they have no conflicts of interest in relation to the current study, including financial, personal, authorship, or any other, that could affect the study and the results reported in this paper.

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Data availability

The data will be provided upon reasonable request.

Use of artificial intelligence

The authors confirm that they did not use artificial intelligence technologies when creating the current work.

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