

*The object of this study is wastewater from chloride and sulfate etching operations.*

*This paper reports results of research on ways to reduce the consumption of chemical reagents in wastewater treatment systems from etching operations. Spent etching solutions are subject to regeneration with return to the production process and partial dosing to the main stream of wastewater. It was found that at a ferrum concentration of 30 g/l in etching solutions, the solution must be treated with an alkaline reagent (10–20 % NaOH) to pH=3.5–4.0 in order to return to the technological process. In this case, the final concentration of ferrum is 11 g/l. The use of hydrogen peroxide (20–40 % H<sub>2</sub>O<sub>2</sub>) together with the alkaline reagent makes it possible to increase the degree of extraction by 30 %, that is, the final concentration of ferrum is 8 g/l. When discharging 1 m<sup>3</sup> of etching solutions, 0.5 m<sup>3</sup> is subject to regeneration and, after mixing with 0.5 m<sup>3</sup> of the commercial reagent (HCl) it returns to the technological process. Commercial acid consumption is reduced by 50 %. It was shown that the use of individual flows of waste solutions as a chemical reagent reduces the cost of reagents for their neutralization (saving alkaline reagent is 80 %). Thus, 1.2 kg/m<sup>3</sup> of a commercially available reagent (NaOH) is consumed per 1 m<sup>3</sup> of solutions (etching and degreasing) after mixing them, and, without mutual neutralization, this consumption is 6 kg/m<sup>3</sup>. To neutralize etching solutions, it is recommended to carry out the process in the range of pH=6.5–7.5. For a solution in which Fe<sup>3+</sup> ions predominate with an initial concentration of 0.53 mol/L, a degree of extraction of 0.9 is achieved, and the total consumption of the reagent (7.1 mol/l) exceeds the stoichiometric one by only 10 %.*

*Deep purification from ferrum-containing impurities using a magnetic device expands the possibilities of practical implementation of further desalting with inverse osmosis*

*Keywords: resource-saving technology, etching solutions, ferrum-containing impurities, magnetic device, reagent consumption*

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# DEVELOPMENT OF A RESOURCE-SAVING TECHNOLOGY FOR THE TREATMENT OF FERRUM-CONTAINING WASTEWATER FROM ETCHING OPERATIONS

**Mykola Yatskov**

PhD, Senior Researcher, Professor\*

Director

Rivne Technical Professional College of National University of Water and Environmental Engineering  
Orlova str., 35, Rivne, Ukraine, 33017

**Natalia Korchyk**

PhD, Associate Professor\*

**Nadia Budenkova**

PhD, Associate Professor\*

**Oksana Mysina**

Corresponding author

Senior Lecturer\*

E-mail: o.i.mysina@nuwm.edu.ua

\*Department of Chemistry and Physics

National University of Water

and Environmental Engineering

Soborna str., 11, Rivne, Ukraine, 33028

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## 1. Introduction

Etching steel surfaces involves treating them with solutions of strong acids (HCl, H<sub>2</sub>SO<sub>4</sub>) at elevated temperatures. As a result of this treatment, liquid ferrum-containing waste is formed – wastewater (WW): spent etching solutions (SES), which are characterized as highly concentrated solutions, and flushing water (FW), which belong to the category of concentrated solutions [1]. Such liquid waste contains up to 70 % of heavy metals, and, by volume, make up 10–15 % of the total amount of WW [2]. It should be noted that the volumes of spent etching solutions of steel surfaces make up 85 % of the total volume of highly concentrated wastewater in electroplating industries [3].

The main problem of the etching site is the processing of SES; for this purpose, they create local cycles of their neutralization, disposal, regeneration [4]. The most progressive is the creation of combined systems in which the main volume of wastewater is treated in centralized systems with

a partial return of water to the production process. SES are subject to disposal or regeneration with partial return of chemical reagents to the production process and partially dosed into the main WW stream from washing operations.

With such wastewater treatment, the task arises of reducing the total concentration of ferrum less than 1 mg/l. Widespread in practice is WW treatment with an alkaline reagent, which makes it possible to ensure the final total concentration of ferrum in WW up to 3 mg/l. To enable the concentration of ferrum in purified water less than 1 mg/l, additional (deep) purification of water is required.

For the purification of ferrum-containing WW, it is possible to use a magnetic method, since a significant part of ferrum-containing impurities is characterized by magnetic-susceptible properties [5]. Promising for deep wastewater treatment from ferrum-containing impurities is the introduction of environmentally friendly magnetic devices. The main element of such devices is a granular filter load, magnetized by an external device that generates a magnetic field [5].

The use of a magnetic device as an auxiliary element of the combined system for the purpose of deep purification of wastewater from ferrum-containing impurities is considered. The magnetic device contains a cylindrical body with a filter nozzle placed in it, a solenoid, an electrode system. In this case, the filter nozzle is made of porous ferroelectric, and the inner surface of the device housing contains an insulating coating of electrically conductive material. The filter nozzle can also be made of metallized barium titanate, and the insulating coating of the inner surface of the housing is made of fluoroplastic [6].

In practice, wastewater must be treated with lime, which requires high reagent costs (3–4 m<sup>3</sup> 20 % Ca(OH)<sub>2</sub> per 1 m<sup>3</sup> SES). At the same time, a large amount of sediment is formed (up to 80 % of the processed volume), which is not subject to further disposal [7]. Thus, the study of methods of processing SES, including the use of fewer reagents, as a stage of regeneration and neutralization, is an urgent problem.

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## 2. Literature review and problem statement

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Technical solutions offered in [4] include the main stages of wastewater treatment technology: effluent accumulation, treatment, and phase separation. Wastewater belongs to the category of acidic ferrum-containing waters from surface preparation operations, namely etching. A feature of this category of the WW water system is that metal ions are present in the form of an ionic associate. It is known that associates differ significantly from free ions, which must be taken into account to determine the cost factors for neutralization and precipitation of metals.

The most common processing method is the reagent method [7, 8]. In the reagent cleaning of WW from heavy metal ions, sodium hydroxide and sodium carbonate are used as alkali reagents, as well as cheaper calcium hydroxide (lime, milk of lime). However, the use of calcium hydroxide contributes to the formation of a significant amount of lime sludge, which cannot be disposed of.

It should be noted that at high concentrations greater than 1 g/l, the ionic strength of the solution increases. This leads to an increase in the solubility of ferrum hydroxides, therefore, WW purification with a significant content of Fe<sup>2+</sup>, for example, after etching steels, is recommended to be treated with combined reagents. Usually, treatment with an alkaline reagent is carried out at a certain ratio of Fe<sup>2+</sup>:Fe<sup>3+</sup>. To do this, wastewater is subject to preliminary oxidation (conventional aeration) [4].

The practical implementation and operation of sewage treatment plants has difficulties that are associated with the instability of the composition of wastewater (a mixture of SES and FW). As a result of fluctuations in the concentration of acid and ferrum ions, there are incompleteness of the chemical precipitation reaction, excess reagent consumption, the formation of a highly dispersed precipitate, etc. To ensure a high cleaning effect, it is recommended to treat SES separately from the total flow of wastewater. The most advanced technology is regeneration (return of SES components to the production process), which includes the following operations [4]:

- extraction of disassembled metals;
- oxidation of Fe<sup>2+</sup> to Fe<sup>3+</sup>.

It is assumed that regeneration is carried out in centralized systems of sewage treatment plants or at special production sites – local cycles.

Two categories of SES are considered, namely: from the operations of chloride and sulfate etching.

Regeneration of the SES sulfate etching is carried out by neutralizing with lime milk or ammonia water in order to extract metals in the form of hydroxides.

The oxidation operation is carried out by oxygen in the air with continuous bubbling. To ensure the conditions for the formation of sediments of metals that are easily dehydrated, such pH values are recommended, which are equal to 4.8–5.2 and 9–10, respectively. In the case of use as a precipitating reagent of ammonium water, conditions are provided for the production of ammonium sulfate as a by-product. Thus, regeneration by neutralization with the use of chemical reagents (chemical processes) involves the transformation of the main components of SES, including acids, but does not allow them to be returned (in full) to the production process.

For the processing of spent etching solutions, the method of extracting metals by crystallization is sometimes also used [9]. According to this method, SES is cooled in an isohydric-type crystallizer, the resulting FeSO<sub>4</sub>·7H<sub>2</sub>O crystals are separated using a centrifuge. The regenerated solution is returned to the technological process. However, this method requires high energy costs, the use of multistage processes and is suitable for the regeneration of a small amount of SES.

The regeneration of sulfate acid, including the extraction of metals by crystallization [9], is carried out at the first stage by oxidation of Fe<sup>2+</sup> to Fe<sup>3+</sup> with oxygen in the air. After that, the acid mixture is evaporated for crystallization and precipitation of ferrum ions(III). Next, a cation is added to the resulting solution to extract the residual amount of ferrum ions(III). The resulting sulfate acid has a concentration of 50 %. Cationite is regenerated with chloride acid and a solution is obtained of ferrum(III) chloride. Thus, the regeneration of etching SES based on sulfate acid, which are used for decapitation of steels, can significantly increase their shelf life, improve the quality of steel surface treatment. In the process of regeneration, filtration and extraction of organic contaminants (fats, oils) from the SES is carried out.

One of the methods of processing spent etching solutions involves the use of ion exchange sorption [10]. However, the ion exchange sorption process for the complete regeneration of ion exchange resins requires double the amount of chemical reagents compared to the number of components to be extracted.

Thus, the use of mass transfer processes, involving the separation of SES components by crystallization, ionic exchange (cation) ensures its complex regeneration.

A well-known electrochemical method for the processing of SES, involving the reduction of acid from etching wastewater using diffusion dialysis [11]. However, this method has not found application in industry due to unsatisfactory technical and economic indicators. A method including the stage of electrolysis with selective membranes (electrodialysis) is also used [12]. Regeneration of sulfate acid by electrodialysis is carried out by preliminary neutralization using chemical reagents. After separating the sediment, the solution enters the middle chamber of the four-chamber electrolyzer. The electrolyzer includes one cation exchange and two anion-exchange diaphragms. The solution from the middle chambers is sent to the cathode chamber, where an alkaline solution is formed, which is then used to neutralize. The diluted acid from the first anode chamber is sent to the second chamber for concentration [12].

Thus, in the process of neutralization of SES, the components of the solution are subject to transformation: acid – neutralization, metal ions – into the form of hydroxides. In the

process of electrolysis, conditions are provided for the regeneration of the acid due to separation using selective membranes and the transformation of water (anode reactions) to form an acid. At the same time, in the cathode chamber (cathode reaction of water transformation), an additional product is formed – alkali. The method of electrochemical membrane regeneration of chloride etching solutions is also known [13]. However, electrochemical membrane regeneration methods have not found practical implementation due to the low stability of membranes, especially in aggressive environments (etching solutions) and due to its high energy consumption.

Regeneration of chloride etching SES implies the absence of any discharges [14]. The technological scheme includes the following operations (FW and SES together):

- neutralization and precipitation at a dosage of 15 % solution KOH to pH 7.5–8.5;
- oxidation of  $\text{Fe}^{2+}$  to  $\text{Fe}^{3+}$  by hydrogen peroxide;
- filtration with two washings of the precipitate of ferrum hydroxo compounds;
- drying of the precipitate of ferrum hydroxo compounds at a temperature of less than 120 °C.

The total processing time is 10–14 hours. The resulting precipitate is recommended for use in the form of ferrum-oxide pigments; liquid phase – in the form of liquid potash fertilizers [15]. The disadvantages of this method are the multistage process, the difficulty in using hydrogen peroxide to oxidize the total mass of ferrum ions, and expensive equipment for drying the precipitate.

Spent chloride galvanizing solutions contain high concentrations of metal or their mixtures with ferrum ions [16]. In solutions, these compounds are present in the form of chlorides, sulfates, cyanides. Calcium oxide is used for the processing of such solutions, followed by the separation of the precipitate in the form of sludge [17]. This method is effective, but the waste may contain cyanides and other organic contaminants.

Existing methods of processing SES from sulfate and chloride etching include oxidation at elevated pressure and temperature, crystallization, extraction, evaporation, thermal decomposition. This requires the use of special equipment, qualified maintenance, and can be practically implemented in the conditions of regional centers (waste processing) [13].

In practice, SES solutions are subject to treatment with an alkaline reagent for the purpose of regeneration and neutralization, which requires high reagent costs (3–4 m<sup>3</sup> 20 %  $\text{Ca}(\text{OH})_2$  per 1 m<sup>3</sup> SES). At the same time, a large amount of sediment is formed (up to 80 % of the processed volume), which cannot be disposed of [7].

The use of chemical reagents in wastewater treatment makes it possible to ensure the final total concentration of ferrum ions in WW up to 3 mg/l. To ensure the concentration of ferrum ions in purified water less than 1 mg/l, additional (deep) purification of water is required.

For the processing of waste etching solutions, it is progressive to create closed water supply systems using deep purification of ferrum-containing wastewater from etching operations. A number of post-treatment methods are known to improve water treatment processes. Much attention is paid to physical methods (non-reactive), which are based on the influence of external magnetic, electrical, ultrasonic, etc. fields on the components of the water system with various technological parameters of the cleaning process. The most commonly used effect is that of a magnetic field on the water system. In all cases, such an effect leads to a change in the physical properties of water – structure, its density, surface tension,

etc., which can cause phase-dispersed (PD) transformations. In magnetic water purification technologies, the most characteristic are PD transformations, which are accompanied by transformations between molecules and colloidal particles: phase formation↔dissolution; and between molecules and ions: ionization↔molarization. In practice, the most common are technologies that include the influence of a magnetic field as a factor in the intensification of reagent purification: coagulation, oxidation, reduction, settling, etc.

The intensification of the transition of phase formation↔dissolution is due to the physical impact on the formation of spatial structures of the water system. A device for magnetic-electric activation of reagent solutions is known, which involves the action of a magnetic field on the initial solution and subsequent electrocoagulation. Industrial tests showed a fairly high improvement in water transparency: the content of suspended particles decreased by 28.6–60.5 %, coloring – by 32.5–50.0 %, coagulant consumption decreased by 15.0–22.0 % [18].

It is believed that the effect of the magnetic field on the transformation between molecules and ions (molarization↔ionization) is associated with the phenomena of hydration of ions. At the same time, ionic associates that arise under the influence of a magnetic field are embryos of the solid phase and act as centers of crystallization. The effect of magnetic processing on the concentration of dissolved gases, primarily oxygen and carbon dioxide, is manifested in proton-electron changes in the water system.

This phenomenon is of effective importance in the treatment of wastewater by destructive methods; water softening systems and recycling of mineralized waters. Thus, it is shown that after magnetic processing, the boiling point of water decreases by several degrees and the heat of its evaporation decreases, which leads to significant energy savings [18].

Innovative technology and equipment for microarc processing in rotating magnetic fields is offered in [19] for various technological processes. This is used in the preparation of drinking water, the treatment of various types of wastewaters, the compaction of sludge, the oxidation of phenols, alcohols in WW, the neutralization and disposal of water after washing containers with petroleum products, etc. The versatility of the proposed technologies is determined by the complexity of the combined system, which provides intensive dispersion components and particles and their mixing. At the same time, intramolecular and interatomic bonds in objects of influence are weakened. Hydrodynamic effects are expressed in significant shear stresses of the liquid of developed turbulence, pulsations of pressure and flow rate. The hydroacoustic effect is achieved by small-scale pressure pulsations, intense cavitation of shock waves, and secondary nonlinear acoustic effects. Thermal effects contribute to hydrolysis reactions. At the same time, magnetic devices are included in the main system of treatment facilities, which also include an ozonation unit, a hydro cyclone, an electrolytic reactor, a type sump with thin-layer blocks, etc. When applying this technological system, environmental improvement is predicted, opportunities for pollution disposal, for the production of organic fertilizers, building materials, etc. are expanded [19]. Nevertheless, this technology is energy-consuming.

A fairly common method of processing spent etching solutions is the method of ferritization using alternating magnetic fields [20]. At the same time, the energy efficiency of the process of processing SES increases, magnetite precipitates are formed, which are easily disposed of. Nevertheless, with this method, there is no increase in the degree of extraction of ferrum ions compared to traditional thermal.

There is reason to believe that it is more promising to use magnetic and magnetic-electric wastewater treatment to extract ferrum-containing impurities as an element of auxiliary systems that provide deep wastewater treatment. As noted, the main element of the magnetic device is granular loading [5]. Magnetization of the load is carried out by an external generator of the electromagnetic field. Between the granules, the formation of effective capture zones occurs due to the high value of the intensity of the generated magnetic field  $H$ . In terms of intensity, the generated field is much higher than the magnetic field created by the external magnetizing system, and for the most part – a high degree of its heterogeneity  $gradH$ . The product of these two parameters  $H gradH$ , the so-called power factor, the value of which reaches  $1 \cdot 10^{12} - 1 \cdot 10^{14} \text{ A}^2/\text{m}^3$ , is essential precisely near the contact points of the granules and ensures the effective extraction of ferrum-containing impurities [5]. The effective use of the magnetic sorption method of purification of liquid products of chemical technology from ferromagnetic impurities is known [21]. The use of magnetic filter precipitators with a ferromagnetic filter matrix reduces the concentration of ferrum by 3 times. The disadvantages of known magnetic devices are the limited ability to create localized zones of high-gradient electric fields in the working area of deposition of electrically charged impurities, which leads to a low precipitating power effect on impurity inclusions.

Recently, the use of magnetic adsorbents in water and wastewater treatment technologies in industry has been effective [22]. However, the high capital cost, the complexity of separating the adsorbent from the solution and the complex processes of its synthesis limit the use of magnetic adsorbents in industry.

The results of studies of magnetic-electric wastewater treatment technology, carried out earlier, made it possible to design a device that creates a high-gradient electric field in the working deposition zone in combination with an extensive filtration surface. This increases the power effect on electrically charged impurities and especially with a low specific electric charge and, as a result, provides an increase in the overall efficiency and degree of wastewater treatment and, in general, fluid process media [6]. In this technological solution, the implementation of deep wastewater treatment of the etching area from ferrum-containing impurities using a magnetic device, followed by desalting with inverse osmosis, is relevant.

Based on a critical analysis of information sources, it was found that the existing methods of processing SES require special equipment, qualified maintenance, and can be practically implemented in regional centers. All methods include as a stage of treatment with chemical reagents for the purpose of regeneration and neutralization, which requires high costs of the latter. For the processing of spent etching solutions, it is progressive to create closed water supply systems using deep purification of ferrum-containing wastewater using a magnetic device. The above necessitates research that will become a reliable basis for the creation of a combined resource-saving technological system for the treatment of ferrum-containing wastewater from etching operations.

### 3. The aim and objectives of the study

The purpose of our research is to create a resource-saving technology for cleaning ferrum-containing WW from etching operations on steel surfaces. This will make it possible to reduce the consumption of chemical reagents and provide deep

wastewater treatment of the etching area from ferrum-containing impurities.

To achieve the set aim, the following tasks have been solved:

- to find ways to reduce the consumption of chemical reagents for the regeneration of etching solutions;
- to reduce the consumption of chemical reagents by applying mutual neutralization of solutions and pre-oxidation of  $\text{Fe}^{2+}$  to  $\text{Fe}^{3+}$ ;
- to investigate the use of reagent-free methods for deep post-treatment of wastewater after reagent treatment.

## 4. The study materials and methods

The object of the study was model solutions, spent sulfate acid and chloride acid solutions of steel etching of the enterprise TzOV “Plant of hardware products”. The research was carried out under laboratory and pilot industrial conditions.

Acid-base and redox properties of FW and the conditions for their processing for the purpose of purification, disposal, regeneration were studied by methods of potentiometric titration and chemical precipitation in a reactor of periodic action with intensive mixing of reactants.

Quantitative analyzes for the content of ferrum ions were carried out in the laboratory by the method of photometric determination with sulfosalicylic acid. Potentiometric titration was carried out under laboratory conditions on the potentiometer EV 74 and under industrial research conditions using the portable pH meter pH 602 (Ukraine). Magnetic purification of FW was studied at an experimental installation for magnetic deposition. The installation consists of a tubular working housing made of stainless nonferromagnetic steel with an internal diameter of 25 mm, filled with a ferromagnetic filter nozzle in the form of steel chip granules with an equivalent diameter of 2–4 mm. The magnetic field was created using a sectional solenoid, to which a constant current was supplied. The magnetization system was placed around the working case. The electric power of the solenoid was supplied by a constant current, and with a range of variability of the magnitude of the intensity of the magnetizing field  $H$  in the range from 30 to 120 kA/m. At the inlet and outlet of the installation, samplers were installed to determine the degree of purification of  $\psi$  wastewater from ferrum-containing impurities in a magnetized filter nozzle.

The degree of purification  $\psi$  was calculated by the relative change in the content (concentration) of ferrum-containing impurities in terms of the total ferrum content before precipitation in the nozzle and after precipitation according to the formula:

$$\psi = \frac{C_0 - C}{C_0}, \quad (1)$$

where  $C_0$  is the ferrum concentration at the inlet of the magnetic filter,  $C$  – the value of the ferrum concentration after precipitation.

## 5. Results of studies of resource-saving processing of spent etching solutions

### 5.1. Research on reducing the consumption of chemical reagents for the regeneration of etching solutions

In the current work, studies have been carried out on the regeneration of SES from etching operations in an

acid-oxidizing medium using hydrogen peroxide (Fig. 1). Hydrogen peroxide contributes to the formation of ferum(III) hydroxo complexes, which are capable of forming insoluble compounds in an acidic medium. As an alkaline reagent, it is recommended to use a 10–20 % solution of NaOH. It should be noted that the use of milk of lime adversely affects the surface of the metal subjected to etching.

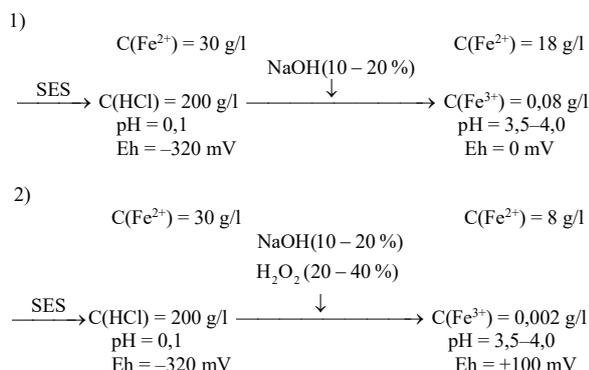


Fig. 1. Scheme of regeneration of the spent technological solution from etching operations

Based on the presented data, it was established that the use of hydrogen peroxide makes it possible to increase the effect of ferrum extraction from etching solutions by 30 % while the total cleaning effect is 70 %. The conducted studies provide a reduction in the consumption of commercial chloride acid by 50 %.

Fig. 2 shows the sequence of adding reagents for the regeneration of spent etching solutions.

We established the consumption of reagents, their concentration and dosing time (Fig. 2), which makes it possible to obtain a precipitate of hydroxo compounds of ferrum of stable composition.

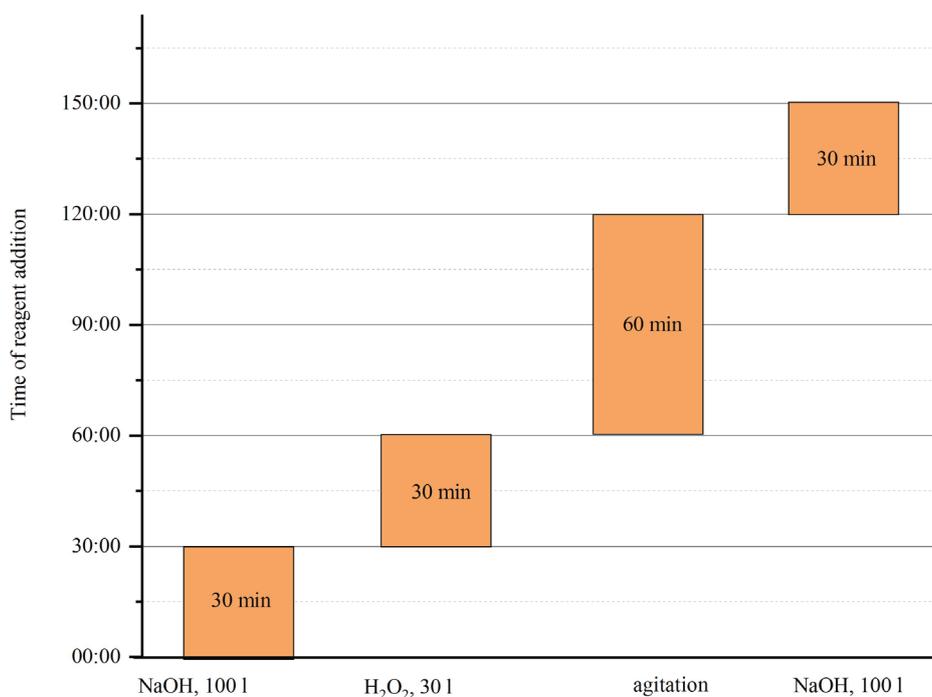


Fig. 2. The sequence of adding reagents for the regeneration of spent etching solution: NaOH – 20 % per 1 m<sup>3</sup>; H<sub>2</sub>O<sub>2</sub> – 20 % per 1 m<sup>3</sup>

### 5.2. Investigation of reducing the consumption of chemicals by mutual neutralization of solutions and pre-oxidation of Fe<sup>2+</sup> to Fe<sup>3+</sup>

After reagent treatment with 1 m<sup>3</sup> of SES, 0.7 m<sup>3</sup> of clarified filtrate is formed, of which 0.5 m<sup>3</sup> returns to the technological process. This saves a clean reagent of 0.5 m<sup>3</sup>. At the same time, 0.2 m<sup>3</sup> is sent to the local cycle of mutual neutralization with the technological solution from degreasing operations.

In order to neutralize the degreasing solutions, potentiometric titration of the SES degreasing solution with a solution of sulfate acid and SES degreasing with an etching solution was carried out (Fig. 3, 4).

The introduction of etching SES or sulfate acid solution (Fig. 3, 4) provides conditions for the formation of ferrum perhydroxo complexes at pH from 12 to 6.5, coagulation conditions for surfactants and oils (entering the process solutions during degreasing) until reaching a pH of 3–4 and Eh, equal to +0.30 to +0.33 V [23].

From the above figures, it follows that to ensure optimal conditions (the formation of ferrum perhydroxo complexes and surfactant coagulation), spent technological solutions of etching can be used instead of commercial acid.

Considering SES with a ferrum concentration of 37 g/l and sulfate acid of 200 g/l in terms of the concept of molar concentration of the components, namely a solution with a total mass of 237 g/l, we calculated the total number of moles of solute C<sub>S</sub>=2.49 mol/l. It can be argued that SES from etching operations refers to concentrated solutions of electrolytes (C<sub>S</sub>≥0.02 mol/l), for which there is a non-additive effect (unequal total consumption of the reagent when processing the same metal mass with different initial concentrations). Due to the absence of the theory of concentrated electrolyte solutions, the practical consumption of the chemical reagent was determined empirically on the basis of data from potentiometric titration and chemical analysis of ferrum content in the initial and treated solutions. In this case, the values of the degree of extraction were calculated by formula (1).

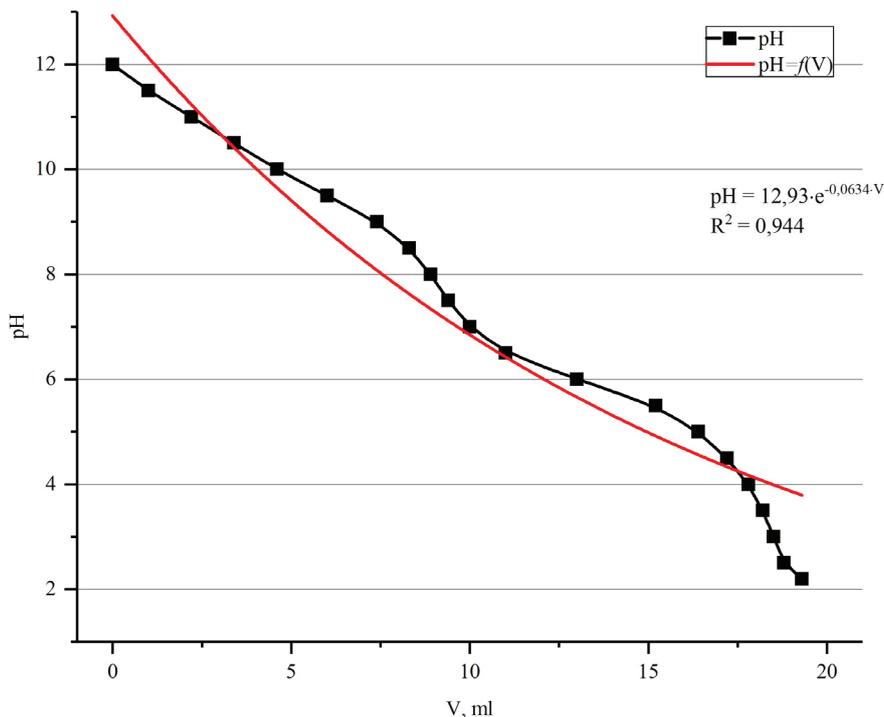


Fig. 3. Results of potentiometric titration of the spent etching solution of degreasing with sulfate acid solution ( $V_{IN}=50$  ml,  $\text{pH}_{IN}=12$ )

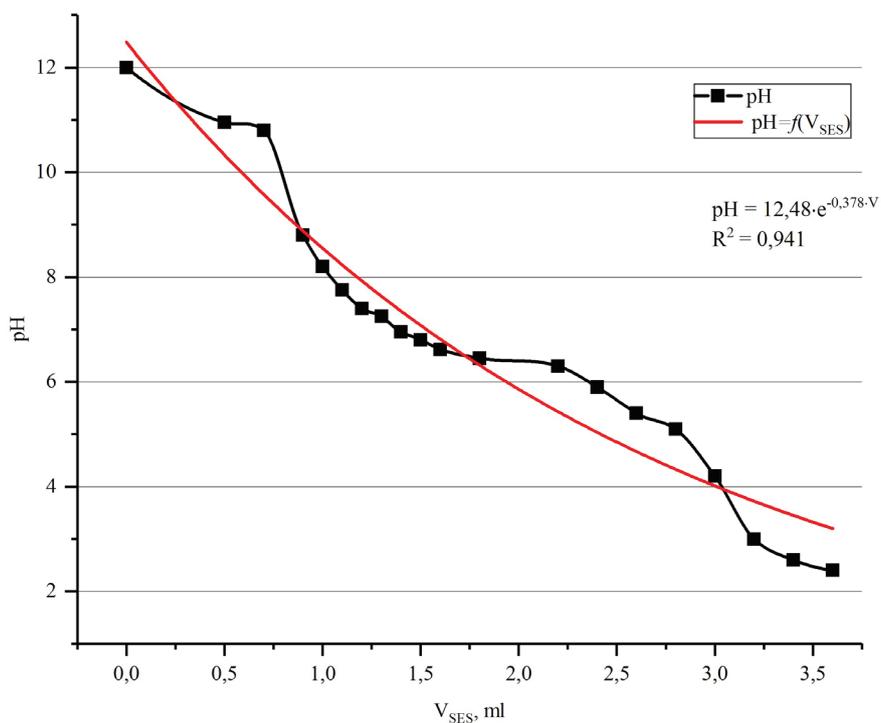


Fig. 4. Results of potentiometric titration of the spent etching solution with degreasing solution with etching solution ( $V_{IN}=50$  ml,  $\text{pH}_{IN}=12$ )

Fig. 5, 6 show the changes in the degree of ferrum extraction depending on pH and the degree of extraction of ferrum on the reagent flow rate for solutions of chloride and sulfate type (average values).

Based on the results of potentiometric titration, the consumption of a chemical reagent (NaOH) per 1 mol of a substance (acid, ferrum) in a wide pH range (from - 0.5 to 11) was determined. From the above data, it can be seen that the

main amount of alkaline reagent is spent on neutralizing the acid. Accordingly, the non-additives of the consumption of chemical reagent for the deposition of ferrum ions can be explained by the intensification of the phenomena of chemical hydration of ions and the formation of ionic associates [24].

The research results showed that the use of separate streams of spent etching solutions as a chemical reagent leads to a decrease in the consumption of reagents for their neutralization.

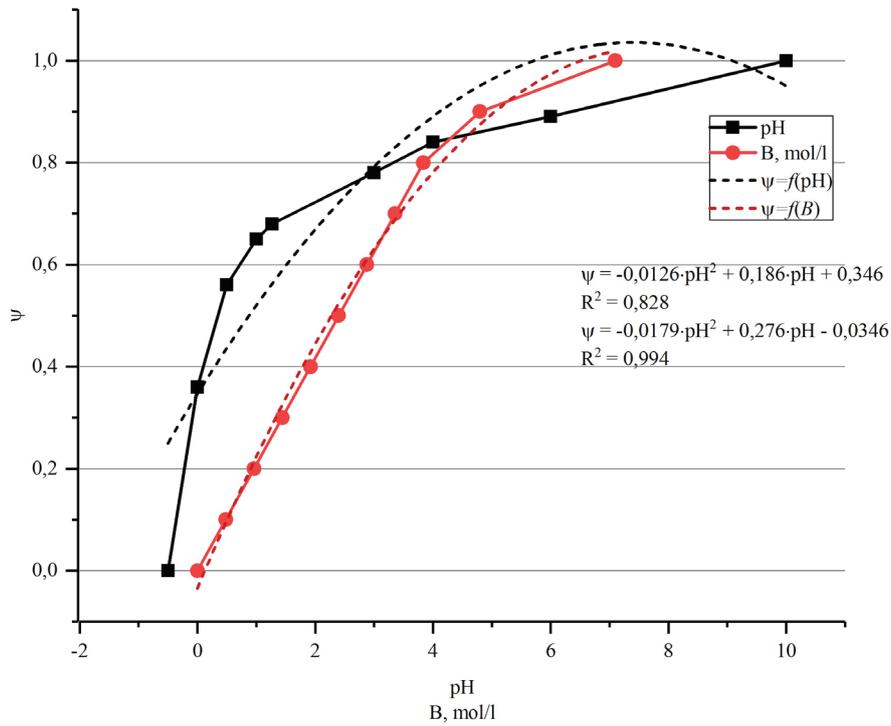


Fig. 5. Change in the degree of extraction of ferrum depending on pH and the consumption of reagent for chloride etching solution:  $\psi$  – degree of extraction; B – consumption of reagent, mol/l

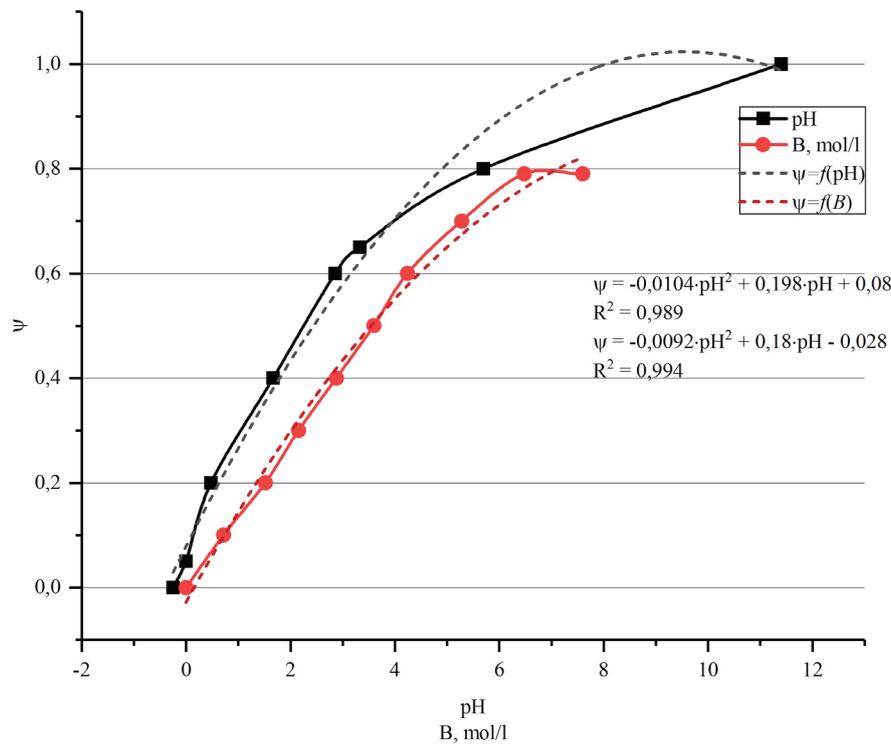


Fig. 6. Change in the degree of ferrum extraction depending on pH and the consumption of reagent for sulfate etching solution:  $\psi$  – degree of extraction; B – reagent consumption, mol/l

**5. 3. Research of methods of deep post-treatment of wastewater after reagent treatment**

For deep purification of water systems from ferrum-containing impurities, it is promising to introduce magnetic devices in which a granular filter load is used as the main element, magnetized by an external device that generates a magnetic field [5].

The projected degree of extraction of ferrum-containing wastewater,  $\psi$ , depending on the intensity of the external magnetic field at a filtration rate of 100 m/h and the length (height) of the nozzle layer of 0.8 m is 0.6–0.7. It was assumed that the particle size of impurities is in the range from 2 to 4 microns.

The results of studies of wastewater treatment from the etching site (sulfate-chloride solution) are given in Tables 1, 2.

Table 1

Indicators of treatment of wastewater from the etching area (model studies)

Volume 40 % NaOH, l/m <sup>3</sup>	pH	Ferrum concentration after reagent purification, g/l	Ferrum concentration after magnetic device with $\psi=0.7$ g/l
0	0.7	2.5	–
50	1	–	–
100	1.8	$0.32 \cdot 10^{-3}$	$0.096 \cdot 10^{-3}$
200	2	$0.24 \cdot 10^{-3}$	$0.072 \cdot 10^{-3}$
250	2.6	$0.12 \cdot 10^{-3}$	$0.036 \cdot 10^{-3}$
450	12	$0.12 \cdot 10^{-3}$	$0.036 \cdot 10^{-3}$

Table 2

Indicators of purification of ferrum-containing wastewater from etching operations

Indicator name	Unit of measure	Before purification	After purification	Maximum permissible concentration of process water of category II [4]
pH	unit	5÷6	7÷8	6÷9
Ferrum, Fe <sup>2+</sup>	mg/l	600	0.096	0.3
Chlorides, Cl <sup>-</sup>	mg/l	627	98	100.0
Sulphates, SO <sub>4</sub> <sup>2-</sup>	mg/l	220	69.1	150.0
Magnesium, Mg <sup>2+</sup>	mg/l	26.75	1.8	3.0
Hardness	mg-equiv./l	10	0.8	2.0

Thus, deep wastewater treatment from ferrum-containing impurities is ensured using a magnetic device. At the same time, the possibilities of practical implementation of inverse osmosis for desalination are expanded.

## 6. Discussion of results of resource-saving treatment of ferrum-containing wastewater from etching operations

The concept of improving the technological scheme of wastewater treatment from surface preparation operations was formulated in accordance with the environmental requirements of chemical technologies. The basic principle is to reduce the consumption of chemical reagents at the inlet and outlet of the technological process, including water, which is ensured by its deep purification with return to production and disposal of waste.

The surface preparation area includes the following operations: degreasing, two-stage washing (hot and cold), post-degreasing, etching, cold washing after etching operation [23].

In order to reduce the consumption of chemical reagents and ensure effective subsequent neutralization of toxic waste, we recommend including additional technological equipment for local cycles of treatment of process solutions and wastewater from washing operations that provide:

- regeneration of solutions from etching operations (total volume of regeneration up to 50 %);
- mutual neutralization of solutions from etching and degreasing operations (total volume up to 50 %).

In local schemes, solutions are regenerated by treatment with alkaline reagent and hydrogen peroxide in an acid-oxide medium in order to deposit ferrum ions in the form of

hydroxo compounds, followed by separation into a vacuum filter with a chemical-resistant cloth (Fig. 1).

Fig. 1 shows that at a ferrum concentration of 30 g/l in etching solutions in order to return to the technological process, the solution must be treated with an alkaline reagent (10–20 % NaOH) to pH=3.5–4.0. In this case, the final concentration of ferrum is 11 g/l. The use of hydrogen peroxide (20–40 % H<sub>2</sub>O<sub>2</sub>) together with an alkaline reagent makes it possible to increase the degree of extraction of ferrum from etching solutions by 30 %, and the final ferrum concentration is 8 g/l. The total degree of extraction is 70 % under the same conditions with an alkaline reagent consumption of 1.5 mol of NaOH per 1 mol of Fe<sup>2+</sup>. The clarified solution to restore the ability to etch is enhanced by concentrated HCl in a ratio of 1:1. When 1 m<sup>3</sup> of etching solutions of 0.5 m<sup>3</sup> is discharged, it is subject to regeneration and, after mixing with 0.5 m<sup>3</sup>, the commercial reagent (HCl) is returned to the technological process. As a result of the proposed technological solutions, the consumption of commercial HCl is reduced by 50 % [25]. Under experimental and industrial conditions, the consumption of reagents, their concentrations, dosing time were established (Fig. 2), which ensures the extraction of sediment of hydroxo compounds of ferrum of stable composition for its further disposal (processing) [26].

It should be noted that with an acid consumption of 1000 kg per day, it becomes necessary to discharge the spent solution with a volume of 0.5 m<sup>3</sup>, followed by replenishment with a new commercial reagent. Thus, the consumption savings of the commercial reagent per year is up to 500,000 conditional units.

Based on the data shown in Fig. 3, 4, it is possible to determine the consumption of SES and chemical reagents, respectively, in order to mutually neutralize or neutralize them. When using individual streams of spent technological solutions from etching and degreasing operations as chemical reagents, the savings of alkaline reagent are 80 %, the use of an acidic commercial reagent is excluded. Thus, 1.2 kg/m<sup>3</sup> of commercial sodium hydroxide reagent is consumed per 1 m<sup>3</sup> of SES (etching and degreasing) after mixing them, and without mutual mixing (neutralization), this consumption is 6 kg/m<sup>3</sup>. Thus, the savings are about 17000 conditional units (at the lowest price). At the same time, the cleaning effect increases from 80 to 99 % [23].

For subsequent purification in order to neutralize, the wastewater generated in local cycles enters the facilities of centralized systems.

The main purpose of neutralization of SES and wastewater from washing operations (80 % of washing operations and 20 % of local treatment cycles) is to extract ferrum ions in the form of insoluble hydroxo compounds, which is achieved by dosing of alkaline reagent (NaOH solution with a concentration of 1 %). In matters of processing SES in order to neutralize, minimization of reagent costs remains relevant. If we consider the technology of neutralization of SES by neutralizing the acid and chemical deposition of ferrum in the form of hydroxo compounds, it is considered necessary to achieve pH=9, which corresponds to the completion of the reaction of the formation of ferrum(II) hydroxide. At the same time, the practical consumption of alkaline reagent is several times higher than stoichiometric ones. It is known that the consumption of reagents depends on the initial concentration of metal ions and increases with a decrease in their concentration.

For a solution with an acid concentration of 200 g/l (HCl or H<sub>2</sub>SO<sub>4</sub>) and ferrum ions of 37 g/l based on the

results of potentiometric titration, it was found that 64 % of the total mass of the reagent was spent to pH 3.2. This ensures a degree of extraction of 64 %. By pH 6.7, the total consumption of the reagent is 71 %, with the degree of extraction of 69 % (Fig. 5, 6). Practically, the consumption of reagents corresponds to stoichiometric calculations. In the pH range of 6.7–11, 31 % of the total amount of the reagent is consumed, while the degree of transformation (degree of extraction) is almost 1 and the consumption of the reagent exceeds the stoichiometric one by 10 times. The total consumption of the reagent is 20 % higher than stoichiometric. In order to reduce the consumption of the reagent, preliminary oxidation of  $\text{Fe}^{2+}$  to  $\text{Fe}^{3+}$  is recommended, for example, with oxygen in the air or hydrogen peroxide.

The results of potentiometric titration of the SES solution, which is dominated by  $\text{Fe}^{3+}$  ions (with an initial concentration of 0.53 mol/L), showed that by neutralizing the acid pH=7, a degree of extraction of 0.9 is achieved. The total consumption of the reagent is 7.1 mol/l and exceeds the stoichiometric one only by 10 % (Fig. 5).

Thus, in order to reduce the consumption of the reagent, it is recommended to carry out the process in the range pH=6.5–7.5, followed by purification by the reagent-free method, namely magnetic separation. It is also recommended to provide for the preliminary oxidation of  $\text{Fe}^{2+}$  to  $\text{Fe}^{3+}$ .

It is proved that the mutual neutralization of solutions from etching and degreasing operations reduces the consumption of commercial acid by 50 %. To neutralize the SES degreasing, the use of individual streams of spent etching solutions saves the alkaline reagent by 80 % (Fig. 3, 4).

The use of a magnetic device as an auxiliary element of the combined system for the purpose of deep purification of wastewater from ferrum-containing impurities is considered. The magnetic device contains a cylindrical body with a filter nozzle placed in it, a solenoid, an electrode system. In this case, the filter nozzle is made of porous ferroelectric, and the inner surface of the device housing contains an insulating coating of electrically conductive material. The filter nozzle can also be made of metallized barium titanate, and the insulating coating of the inner surface of the housing is made of fluoroplastic. The design of a magnetic device has been patented, which allows for the separation of magnetic and non-magnetic impurities of wastewater due to the fact that a high-gradient electric field is generated in the working area of the device in combination with a branched magnetic surface of the filtering load. This increases the power effect on impurities of wastewater to be separated (especially with a low specific electric charge), and as a result, the degree of extraction of ferrum  $\psi$  from wastewater increases [6]. At the same time, the magnetic device provides for the separation of wastewater impurities into ferromagnetic and non-ferromagnetic fractions by acting on the medium of the magnetized force created by the solenoid.

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

Based on the indicators of WW purification from the etching area (Table 1, 2), it can be argued that the use of a magnetic device will provide deep wastewater treatment from ferrum ions, as well as partially remove ions that cause

water hardness. This is very important for the subsequent desalting of inverted osmosis and makes it possible to solve the problem of returning flushing water to production processes, which is the most difficult for sulfate etching.

The study of the resource-saving technological system for the treatment of ferrum-containing wastewater from etching operations was limited to the fact that:

- its practical implementation is associated with the creation of an automated control system (ACS) for non-stationary processes;

- the use of the chemical reagent hydrogen peroxide  $\text{H}_2\text{O}_2$  for the partial oxidation of  $\text{Fe}^{2+}$  to  $\text{Fe}^{3+}$  requires special storage conditions due to its instability.

It should be noted that no studies have been conducted to study the composition and methods of disposal (processing) of ferrum-containing sludge. This causes certain limitations in the use of the obtained results and can be interpreted as a disadvantage of this study. In the future, it is advisable to study the composition and subsequent disposal of ferrum-containing sludge. Currently, studies have been carried out and methods patented of disposal of ferrum-containing sludge in combination with chromium-containing [27]. The subject of future research is joint processing, including the disposal of ferrum- and zinc-containing sludge.

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## 7. Conclusions

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1. As a result of experimental studies, it was shown that the regeneration of solutions from etching operations is carried out by the method of treatment with alkaline reagent and hydrogen peroxide. It was found that at a ferrum concentration of 30 g/l in etching solutions in order to return to the technological process, the solution must be treated with an alkaline reagent (10–20 % NaOH) to pH=3.5–4.0. In this case, the final concentration of ferrum is 11 g/l. The use of hydrogen peroxide (20–40 %  $\text{H}_2\text{O}_2$ ) together with an alkaline reagent makes it possible to increase the degree of extraction by 30 %, that is, the final ferrum concentration is 8 g/l. At the same time, the total degree of extraction is 70 % under the same conditions with an alkaline reagent consumption of 1.5 mol of NaOH per 1 mol of  $\text{Fe}^{2+}$ . When dumping 1 m<sup>3</sup> of etching solutions of 0.5 m<sup>3</sup>, it is subject to regeneration and, after mixing with 0.5 m<sup>3</sup>, the commercial reagent (HCl) is returned to the technological process. The consumption of commercial acid is reduced by 50 %.

2. In order to reduce the consumption of chemical reagents for neutralization of SES, degreasing and etching is recommended to use individual SES flows as a chemical reagent. It was shown that the use of individual flows of waste solutions as a chemical reagent can reduce the cost of reagents for their neutralization. Thus, 1.2 kg/m<sup>3</sup> of commercial reagent (NaOH) is consumed per 1 m<sup>3</sup> of solutions (etching and degreasing) after mixing them, and without mutual neutralization, this consumption is 6 kg/m<sup>3</sup>. The savings of alkaline reagent is 80 % while excluding the use of an acidic commercial reagent. As a result of the proposed technical solutions, the consumption of commercial HCl for degreasing solutions is reduced by 50 %.

To neutralize etching solutions, it is recommended to carry out the process in the range of pH=6.5–7.5. For a solution dominated by  $\text{Fe}^{3+}$  ions with an initial concentration of 0.53 mol/L, a degree of extraction of 0.9 is achieved, and the total consumption of the reagent (7.1 mol/l) exceeds stoichiometric by

only 10 %. It is also recommended to provide for the preliminary oxidation of  $\text{Fe}^{2+}$  to  $\text{Fe}^{3+}$ . This makes it possible to ensure the consumption of reagents corresponding to stoichiometric.

3. The use of a magnetic device provides deep wastewater treatment from ferrum ions, and also makes it possible to partially remove ions that cause water hardness. This is very important for the subsequent desalting of the inverse osmosis and solves the problem of returning flushing water to production processes, which is the most difficult for sulfate acid etching of steel surfaces.

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#### Conflict of interest

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The authors declare that they have no conflict of interest in relation to this research, whether financial, personal, au-

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#### Data availability

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The data will be provided upon reasonable request.

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