UDC 628.34
DOI: 10.15587/1729-4061.2017.97256

DEVELOPMENT OF TECHNOLOGY FOR RECYCLING THE LIQUID IRON-CONTAINING WASTES OF STEEL SURFACE ETCHING

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Представлені результати проведених теоретичних та практичних досліджень процесів переробки ферумовмісних відходів травлення сталевих поверхонь, а саме: регенерації та утилізації відпрацьованих травильних розчинів, очищення промивних вод. На основі результатів досліджень обґрунтовані та практично апробовані нові технологічні підходи щодо перероблення відходів з метою мінімізації їх скидів у навколишнє середовище та зниження витрат підприємства

Ключові слова: рідкі відходи, регенерація, гідратація, відпрацьовані травильні розчини, окисно-відновні властивості, промивні води

Представлены результаты проведенных теоретических и практических исследований процессов переработки железосодержащих отходов травления стальных поверхностей, а именно: регенерации и утилизации отработанных травильных растворов, очистки промывных вод. На основе результатов исследований обоснованы и практически апробированы новые технологические подходы к переработке отходов с целью минимизации их сбросов в окружающую среду и снижения расходов предприятия

Ключевые слова: жидкие отходы, регенерация, гидратация, отработанные технологические растворы, окислительно-восстановительные свойства, промывные води

1. Introduction

Etching the steel surfaces implies their treatment with the solutions of acids (HCl, H_2SO_4) at elevated temperature. As a result, liquid iron-containing wastes are formed: used-up etching solutions (UES) and wash water (WW). UES belong to the highly-concentrated solutions, WW belong to the category of concentrated solutions [1].

During the search for a rational solution to process the liquid iron-containing wastes of steel surfaces etching, the research into processes of regeneration and utilization of EUS and WW was carried out. The purpose of regeneration is the possibility of reusing EUS as a reagent in the etching process. Purification (elimination of components) of WW will make it possible to get them back into production.

High concentrations of acids and ions of metals (exceeding 3 mol/dm^3), chemical aggressiveness of UES (pH lower than 1) necessitate their recycling in local cycles (separately from the main volume of wastewater). Thus, the development of technology of processing UES in order to restore their properties should be considered a relevant issue.

2. Literature review and problem statement

The main tasks of recycling processes are the extraction and returning to the production of valuable components, especially metals and salts, as well as preventing toxic substances from getting in the environment.

In metallurgical and chemical industries, a few basic methods of UES recycling are used. Thus, a well-known technique of recycling includes homogenization, neutralization and evaporation. In this case, to prevent deposition of slightly soluble calcium phosphate salts, neutralization is performed with the solution of ammoniac to the value of pH equal to 6–6.5 [2]. However, it is impossible to provide comprehensive recycling of UES in this way because the resulting sediment after filtration is landfilled, which leads to further contamination of the ecosystem.

In practice, UES are to be treated with lime. Such disposal requires high consumption of the reagent (3–4 m^3 of 10 % $Ca(OH)_2$ per 1 m^3 of UES). In addition, a large amount of lime slime is formed (up to 80 % of the volume that is treated), which is not subject to subsequent disposal. It is necessary to pay a fine for storing the slime [3–5].

Sometimes they use a regeneration method based on cooling UES [5, 6] in a crystallizer of isohydric type, which contains 300 g/dm^3 of $FeSO_4$ and 1 g/dm^3 of H_2SO_4, to t=–5 °C. Crystals of $FeSO_4 \cdot 7H_2O$ are separated on a centrifuge and packed and the regenerated solution is returned to the technological process, but this method is energy-intensive and suitable for the regeneration of insignificant amount of UES.

For the UES recycling, electrochemical methods are used: electrolysis or electro dialysis [7, 8], but these methods of treatment need sophisticated technological equipment and high electricity consumption.

A modern method, which is used at some enterprises in Turkey, involves deposition of iron ions in the form of slime and its further immobilization by burning in rotary kilns at 850–900 °C, with the use of tetraborate and sodium silicate as additives. The resulting product is resistant to leaching and can be used for further recycling in the form of building materials [9]. Although this method makes it possible to dispose of iron-containing waste of galvanic industries, it is unprofitable for operating galvanic enterprises due to the high economic cost and the need for additional technological equipment.

Wastes of zinc plating are formed mainly from the process of galvanic coating and include the solutions containing high concentrations of metal or its compounds, the main of which is iron ion. These compounds exist in the solutions in the form of sulphates, chlorides, cyanates. The predominant way of recycling such wastes is treatment with the use of calcium oxide CaO and separation of sediment in the form of slime [10]. Although these methods are effective in terms of purification and subsequent recycling, cyanides and other organic components that require prior oxidation may exist in wastewater.

The most modern is a technique for recycling acidic iron-containing UES, which includes oxidation with hydrogen peroxide, followed by the neutralization and deposition with an alkali component and separation of sediment [11, 12]. After draining, hydroxides decompose to iron oxides, which are used to make dyes and enamels (iron oxide pigments). Filtrate – solution of potassium chloride with pH value of 9–10 – after the treatment with solution of orthophosphate acid to pH value of 8–8.5 is utilized in the form of liquid fertilizers. Wastewaters after cleaning are treated with sodium carbonate, clarified, and evaporated. The sediment is used to produce cement. Although this method allows obtaining useful components (liquid fertilizers, cement), it is unprofitable because of the large amount of power resources and consumption of expensive reagents [13].

One of the methods of UES recycling involves the use of ion exchange sorption [4], but for the complete regeneration of ion exchange resins, a double weight of reactants is necessary compared with the weight of components that are extracted. In addition, organic impurities, existing in UES, prevent the purification on ion exchange resins.

Thus, the methods considered may be divided by the totality of technological operations and methods of treatment into:

1) chemical oxidation of Fe^{2+} to Fe^{3+} and provision of optimal hydrolysis of resulting salts with the aim of extracting metal in the form of insoluble hydro-oxo compounds;

2) thermal methods of regeneration;

3) electrochemical oxidation of Fe^{2+} to Fe^{3+} with subsequent separation of components, for example, by extraction;

4) salting with subsequent additional purification of the solution, for example, adsorption;

5) treatment with alkaline reagent;

6) extraction of Fe^{2+} compounds on ion exchange resin.

Among the numerous existing methods of WW purification: reagent, ion exchange, sorption, membrane, biochemical, electrochemical – the reagent method is the most common. At the chemical WW purification from the ions of heavy metals, sodium hydroxide and sodium carbonate, and cheaper calcium hydroxide (lime, lime milk) are used as alkaline reagents. Every year at the enterprises of Ukraine, 10.0–12.5 thousand tons of electroplating sludge are formed as a result of neutralizing alkaline reagents [14].

Known membrane methods of the WW purification, reverse osmosis and ultrafiltration [3, 14], provide a sufficiently high degree of purification, allow returning purified water into production and regenerating the dissolved substances. In this case, consumption of electricity is insignificant. Plants of reverse osmosis and ultrafiltration are characterized by compactness and simplicity of operation. However, caught substances are accumulated on the surface of membranes over time, which reduces their permeability and selectivity [15]. Poor chemical resistance of aggressive media and high primary cost of membranes limit applying membrane methods: they are used only where media are non-aggressive and the concentration of metal ions does not exceed the TLV [14].

Sorption methods of galvanic wastewater treatment are quite common: adsorption and ionic exchange [3, 4, 14]. However, restrictions in the industrial use of these techniques are associated with the complications in sorbent regeneration.

As we see from the literature review, the existing methods of recycling of both UES and WW, which include oxidation of the solution, extraction of etched metal, are not always comprehensive. Disposal of the solution or its components and return of water to technological needs are not economically appropriate for businesses due to high cost of reagents and electricity. Such disposal requires additional technological equipment and implies extensive labor consumption.

Therefore, one should consider it a promising research direction to search for optimal solutions of comprehensive recycling of UES and treatment of WW of steel surfaces etching.

3. Aim and tasks of research

The aim of present work is to develop a technology for the regeneration of iron-containing etching solutions of steel surfaces.

Its application will make it possible:

– to purify wash water according to the requirements “Technical water” of category II, which is used for the preparation of electrolytes;

– to regenerate UES for their reuse in the process of steel surfaces etching, which minimizes their discharge into the environment and expenditures of an enterprise;

– to use UES of galvanic production as chemical reagents.

To achieve the set goal, the following tasks were to be solved:

– to analyze the reagent treatment of WW and to develop purification scheme of WW according to the requirements of "Technical water" of category II;

– to develop a scheme of regeneration of etching solutions (UES) for their subsequent reuse;

– to explore the efficiency of UES as a chemical reagent to extract zinc from the complex compounds of galvanic wastewater, oxidation of organic compounds in alkaline wastewater after degreasing operation;

– to explore acidic-base and redox properties of UES and WW, to substantiate the adopted technological solutions from the standpoint of the theory of concentrated aqueous electrolytes.

4. Materials and methods for examining the UES regeneration and purification

The study was carried out on the used-up technological solutions and wash waters of steel etching at the enterprise TzOV "Plant of Metalware Products", (Makeyevka, Ukraine) under laboratory and experimental-industrial conditions.

The acidic-base and redox properties of UES, WW were studied by the methods of potentiometric titration and chemical sedimentation. Experiments were conducted in the reactor of periodic action at intensive stirring of reacting substances.

Quantitative analyses of the content of iron ions were carried out under laboratory conditions using the method of photometric determining with sulphosalicylic acid according to a well-known procedure [16]. The concentration of Fe^{3+} was determined in the process of reaction with alkaline solution of H_2O_2.

Potentiometric titration was carried out on the potentiometer EB 74 (made in Belarus) (under laboratory conditions) and under industrial research conditions using the portable pH meter "pH 602" (Ukraine). Potentiometric measurement was carried out using a standard procedure [16] by titrating the UES solutions with a standard solution of alkali.

5. Results of research into creation of the proposed technologies

5. 1. Results of research into technology of wash water purification

Wash waters belong to the category of acidic iron-containing concentrated solutions.

A specific feature of this category is that ions of metal exist in a solution in the form of ion associates. Associates are known to differ substantially from free ions, which needs to be considered to determine consumption coefficients for the neutralization of solutions and sedimentation of metals:

$$[Fe(H_2O)_6]^{3+} \rightarrow [Fe(H_2O)_5OH]^{2+} + \\ +H^+ \rightarrow [(H_2O)_4Fe(OH)_2Fe(H_2O)_4]^{4+}. \quad (1)$$

It should be noted that for high concentrations (larger than 1 g/dm^3), ion strength of solution increases, which leads to increasing solubility of iron hydroxides. Therefore, the wastewater purification was carried out with the use of combined reagents: calcium hydroxide and flocculant (Zetag 8180) (Germany); calcium hydroxide and silica gel. The treatment with alkaline reagent is typically performed at a certain ratio of Fe^{2+}: Fe^{3+}. For this purpose, wastewater is subject to previous oxidation (for example, by aeration).

Hydroxides, present in a sediment, absorb ions, which helps to reduce the amount of salts in wastewater. The resulting sediment contains crystalline compounds, which provides sufficient completeness of dehydration of slime (sediments).

At the first stage of the studies, we determined the possibilities of using the following treatment methods:

1) treatment with calcium hydroxide and flocculant (Zetag 8180);

2) treatment with calcium hydroxide and silica gel;

3) treatment with calcium hydroxide.

Results of the conducted studies are presented in Table 1.

Based on the presented data, we found that:

1) treatment with lime only is not effective due to the fact that dispersed substances are not separated;

2) treatment with lime and silica gel provides a high purification effect, but the sediment, which is complex by structure and difficult to pack, is formed;

3) treatment with lime with flocculant (Zetag 8180) is more effective.

Table 1

Results of treating the WW with different reagents

No. of entry	Methods of treatment	Concentration Fe_{final}, mg/dm^3	Sediment volume
1	Treatment with $Ca(OH)_2$ to (pH_{final}=8,5)	–	Dispersed substances are not separated
2	Treatment with $Ca(OH)_2$ + silica gel to (pH_{final}=8,5)	0.06	$V_{sediment}$=98 %, sediment is poorly separated
3	Treatment with $Ca(OH)_2$ + flocculant (Zetag 8180) to (pH_{final}=8,5)	0.13	$V_{sediment}$=20–30 %

After the reagent purification, the treated solution was subjected to filtration through the filter with a polystyrene foam loading in order to separate the dispersed substances, as well as for additional iron removal.

Subsequently, the portion of treated water was passed through a reverse osmosis system, which at further mixing with the main part of the flow makes it possible to obtain water of the "Technical water" quality of category II (Table 2).

Results of the conducted studies on the WW purification are shown in a technological schematic (Fig. 1).

Presented technological scheme was tested and implemented at TzOV "Plant of Metalware Products" (Makeyevka, Ukraine).

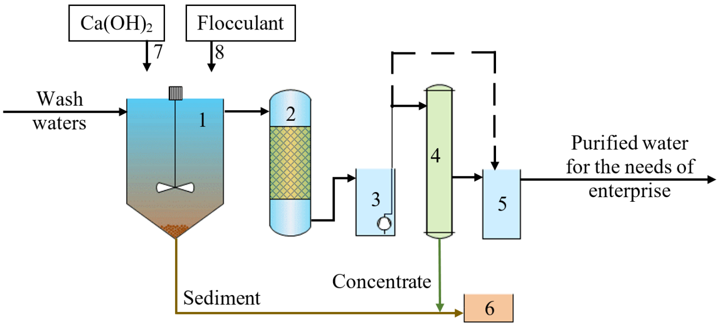

Fig. 1. Schematic of wash waters purification: 1 – chemical reactor; 2 – polystyrene foam filter; 3 – intermediate vessel; 4 – reverse osmosis system; 5 – vessel for purified water; 6 – sediment accumulator; 7, 8 – reagents

Table 2

Indicators of water purification

Indicator	Measurement units	Before purification	After purification	TLV Technical water of category II
pH	units	5÷6	7÷8	6÷9
Iron, Fe^{2+}	mg/dm^3	600	0/1	0.3
Chlorides, Cl^-	mg/dm^3	627	98	100.0
Sulphates, SO_4^{2-}	mg/dm^3	220	69.1	150.0
Nitrates, NO_3^-	mg/dm^3	400	13	15.0
Calcium, Ca^{2+}	mg/dm^3	100	222	250.0
Magnesium, Mg^{2+}	mg/dm^3	26.75	2.8	3.0
Hardness	mg-equ./dm^3	10	1.8	2.0

5. 2. Results of research into technologies for the regeneration of used-up etching solutions

An analysis of the scientific literature allowed us to choose hydrogen peroxide as an oxidant in the regeneration of UES. We conducted studies on the redox properties of UES both with H_2O_2 and without it at different pH values.

Ions of alkali earth metals and alkaline metals are known to be initiators of processes that are developed in the presence of hydrogen peroxide. Therefore, to regulate pH, we used both sodium hydroxide and calcium hydroxide [5]. In the experimental studies, along with pH determining by adding the alkaline reagents, the Eh values of the solutions were defined.

Based on the obtained practical and theoretical results, we believe that it is necessary to characterize properties of concentrated water systems in terms of hydration of ions and resulting ion associates. In this case, the difference between ion associates and usual complexes is not considered. In the present paper, authors believe that ionic associates differ considerably from free ions, which needs to be taken into account for determining the consumption coefficients in the neutralization of solutions and sedimentation of components of concentrated aqueous systems.

At increasing concentration of electrolyte, even a larger amount of water is included in the composition of hydrate membranes. In the end, a system, in which all the water is distributed between ions, is formed. This corresponds to the structure, made up of single-layer hydrated ions (boundary of complete hydration – BCH).

Thus, in the process of operation and treatment of etching solution there is a constant transition from an aquatic structure to the crystal hydrates. At any concentration, this system should be considered as a single unit (Table 3).

Table 3

Relationship between iron concentration in UES and BCH

Used-up etching solutions of steel surfaces	Mean concentration of ions, mol/l	Range of concentrations of area
Output	4.8	before the boundary of complete hydration
In the process of operation	5,3	boundary of complete hydration
Used-up	6–7	after the boundary of complete hydration
After neutralization	5	

For the purpose of choosing the optimal technique for the regeneration of etching solutions of steel surfaces, we conducted a series of studies, based on the following methods:

1) chemical oxidation;
2) thermal, with the use of catalyst;
3) electrochemical;
4) treatment with alkaline reagent.

Results of the research are shown in Table 4.

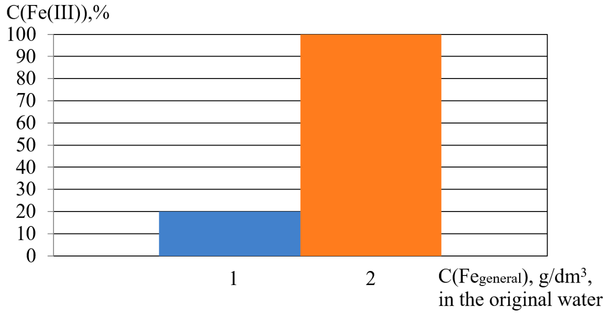

Fig. 2. Properties of solutions after iron sedimentation: 1 – iron concentration – 13 g/dm^3, pH=2, Eh=680 mV; 2 – iron concentration – 61 g/dm^3, pH=1, Eh=460 mV

According to the results of conducted research, for the regeneration of etching solutions of steel surfaces, the technological scheme, which includes the following operations, was accepted:

– used-up etching solutions are treated with a 40 % solution of lime milk until reaching pH=4.2, and with a solution of hydrogen peroxide;

– separation of decantate from sediment;

– additional strengthening of decantate with acid.

As a result of research, it was established that at iron concentration of 17 g/dm^3, which corresponds to the area of concentration to the boundary of complete hydration of ions (BCH), the maximum degree of conversion α=1 is achieved (Table 5). And at the concentration of 90 g/dm^3 (area after BCH), the degree of conversion α=1 is achieved, in this case, the values of Eh are equal to +600 mV and +460 mV, respectively, and oxidant consumption per unit of iron (II) mass is the same.

Table 4

Results of research into regeneration of etching solutions

No. of entry	Method of treatment	Results of research
1	Oxidation with hydrogen peroxide	Iron is not removed, it only transforms from one form to another
2	Oxidation by the method of bubbling and with ozonation catalyst Cu at temperature range from 40 °C to 70 °C	Iron is not removed
3	Electrochemical treatment using the iron electrodes	Iron is not removed
4	Treatment with sodium hydroxide with or without a catalyst	Iron is partially removed when treated with alkaline reagent without a catalyst, but with the formation of a large amount of sediment that is complex by structure and poorly dehydrated
5	Treatment with sodium hydroxide and calcium hydroxide in the presence of silica gel with a catalyst	Iron is partially removed, but with the formation of dispersed substances that are difficult to sediment
6	Treatment with sodium hydroxide and calcium hydroxide at pH 1÷2 and 4÷4.2 in the presence of a catalyst was compared	The best result is obtained with the use of calcium hydroxide in treatment up to pH 4÷4.2

Table 5

Examining the acidic-basic and redox properties of UES under the action of reagent $Ca(OH)_2$

No. of entry	Consumption of 20 % solution $Ca(OH)_2$, ml/l	pH values, units	Eh value, without dosage of solution H_2O_2, mV	Eh value, with dosage of solution H_2O_2, mV
1	250	0.15	–	–
2	500	0.35	500	–
3	600	0.7	–	500
4	650	2.4	–	720
5	700	4.4	–110	680
6	800	4.6	–	410
7	900	4.9	–	–
8	1100	5.3	–120	–
9	1300	9	–460	110

As was considered previously in paper [4], formation of complex compounds is characteristic for UES of steel surfaces, which is why conversion processes, providing the regeneration of UES, can be characterized by the following types of reactions:

– reactions, accompanied by a change in the state of a complexing agent at the solution oxidation;

– reactions, accompanied by a change in the inner sphere of a complexing agent when etched metal is removed.

Thus, the interspherical mechanism of electron transfer (at oxidation) occurs through ligands (area after BCH) or water (area before BCH), which are common for the coordination spheres of both regenerating particles.

In this case, the reaction by the second mechanism is the most energy-efficient.

As the research demonstrated (Table 5), without adding to the reagent of oxidant H_2O_2 at pH>4, the redox potential of Eh decreases to –110 mW. In the case of preliminary introduction of oxidant H_2O_2, the redox potential of UES increases up to values +720÷+400 mV and such a solution may be returned into production. Thus, in order to regenerate the solutions of UES, it is necessary to carry out the following operations:

– adding an alkaline reagent up to pH=4;

– adding an oxidant;

– adding an alkaline reagent up to pH=5.

According to the data of potentiometric titration of UES (C_{HCl}=200 g/dm³, $C_{Fe}^{3+} = 30$ g/dm³), 7.5 mol of alkali are needed for the neutralization by stoichiometry. Consumption of the reagent equals to 0.4–0.65 (in the pH range of 0.4–10.2) from stoichiometry. In practice, 4.9 mol (in this case, 98 % prior to pH 7) are consumed.

Thus, it is important to note that the reagent consumption is determined by the initial concentration of acid.

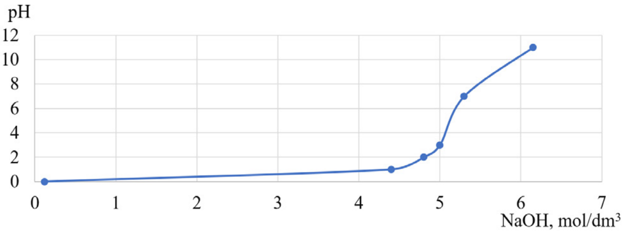

Fig. 3. Curve of potentiometric titration of the solution iron(III)-chloride solution (Fe — 30 g/dm³, HCl — 200 g/dm³)

The mismatch between theoretical and experimental data testifies in favor of the argument that properties of the above-described category of UES, which are demonstrated during their treatment, must be described based on the qualitative understanding of the structure of solutions.

The initial conditions of iron sedimentation from UES correspond to the areas of concentrations before the BCH. Water molecules that are quite close to ions of metal, may have chemical reaction with it. In this case, aqua-complexes transform to hydro-complexes.

As a result, consumption of alkaline reagent for the formation of insoluble hydro-oxo-compounds decreases.

As one can see, the curve of potentiometric titration (Fig. 3) has two jumps in the potential, which allows us to divide the sedimentation process into two stages. At the first stage, there occurs the neutralization of free acid (2) and the formation of crystalline centers of basic salt (3).

$$\left(H^+ + OH^- = H_2O\right), \qquad (2)$$

$$Fe^{3+} + OH^- \leftrightarrow (FeOH)^{2+}. \qquad (3)$$

At the second stage of sedimentation, there occur the processes of formation and sedimentation of metal hydroxides with regard to the dominating type of hydration:

– when ions in the form of $Fe(H_2O)^{3+}$ prevail, that is, a physical type of hydration, the reaction proceeds through the formation of basic salt (4);

$$(FeOH)^{2+}+2OH^{-}\leftrightarrow Fe(OH)_3\downarrow; \tag{4}$$

– when hydrated ions prevail (5), for example, in the form of $Fe(OH)^{2+}$, that is, a chemical type of hydration (specific hydration).

$$(FeOH)^{2+}+2OH^{-}\leftrightarrow Fe\ (OH)_3\downarrow. \tag{5}$$

Results of the presented research are reflected in the proposed concept for the regeneration of etching solutions of steel surfaces, which is represented by the following technological scheme (Fig. 4). This technology for the regeneration of UES of etched steel surfaces was tested and implemented at the enterprise TzOV "Plant of Metalware Products", Makeyevka, Ukraine. Due to the introduction of the proposed technology, the facility returns almost 9 UAH/m^3 of liquid waste, considering all the expenditures for reagents and electric power.

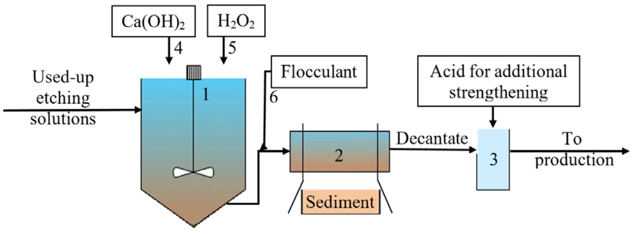

Fig. 4. Schematic of regeneration of etching solutions: 1 — chemical reactor; 2 — filter-press; 3 — vessel for additional strengthening; 4, 5, 6 — reagents

Purification of liquid waste of technological cycle of etching steel surfaces results into the formation of sediments.

Iron-containing sediment after the process of UES regeneration was obtained by the scheme: alkalization of iron (III) of chloride electrolyte of NaOH solution with its subsequent settling for 1.5–2.0 hrs. The resulting sediment is a viscous highly concentrated suspension of dark brown color. Humidity of the sediment is 92–94 %, its density is 1170 kg/m^3.

The sediment is characterized by low specific resistance of $15–18\cdot10^{11}$ m/kg, indicating the possibility of using standard equipment for the treatment of this sediment.

Efficiency of a vacuum filter at the dehydration of iron-containing sediment is 12–13 kg/m^2·h, thickness of cake equals 5–6 mm, its humidity is 82–84 %. The cake is well separated from the filter cloth. The filtrate of dark gray color contains a small amount of dispersed substances. The output sediment is characterized by considerable corrosion activity relative to aluminum.

Ferrum-containing sediment after WW purification was obtained by the alkalization of iron (III) chloride electrolyte using lime followed by settling for 1–2 hours. The sediment is a viscous highly concentrated suspension of light brown color.

Humidity of the output sediment was 92.4 %, its density was 1200 kg/m^3. The sediment has low specific resistance of $10–12\cdot10^{11}$ m/kg, which indicates high efficiency of the sediment treatment using dehydration equipment. Performance efficiency of drum vacuum filter during the sediment dehydration was 15–17 kg/m^3·h and its thickness was 6–7 mm. The cake has humidity of 86.5 % and is easily separated from the filter cloth. The filtrate is transparent, it contains light stuck substances.

5. 3. Results of research into technology of recycling the used-up etching solutions

Local treatment of used-up etching solutions of steel surfaces allows us to apply them as reagents for the purification of other categories of liquid waste of galvanic production.

In present work, we conducted a whole range of studies to determine the optimal method of UES recycling through their use as reagents. As a result of the studies, it was established that the most effective is the use:

a) for the purification of acidic wastewater after an operation to prepare a surface (etching), which contain iron ions with concentration 20 g/dm^3, pH=0.2÷0.4 and Eh=+0.4 V;

b) for the purification of alkaline wastewater after preparing a surface (after operations of ammoniate zinc plating) with concentration of zinc ions 8 g/dm^3; pH=10 and Eh=+0.43 until achieving pH=8 and Eh=+0.43÷+0.5 V, as it is shown in Fig. 5.

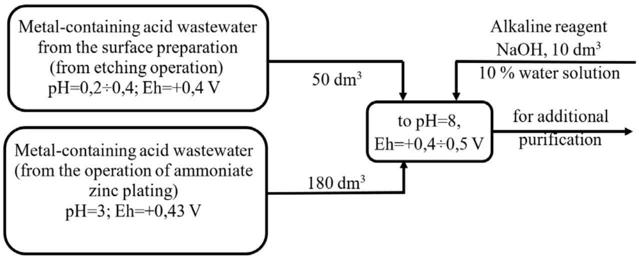

Fig. 5. Use of wastewater flows of galvanic production as chemical reagents

The use of UES as a chemical reagent with subsequent alkalizing provides optimal extraction of zinc from complex compounds. The efficiency of extraction of zinc from complex compounds increases at the co-sediment with iron. At pH=8 and Eh=0.43÷0.5, there occurs the transition of zinc to a non-soluble form of the double oxide $ZnFe_2O_4$ type.

The use of UES of steel surfaces allows us to not only improve the purification effect, but also significantly reduce the costs of an enterprise and reagents, which is shown in Table 6.

Table 6

Comparison of reagent consumption with and without using as chemical reagents for separate flows of wastewater from the galvanic production

Reagent	Amount of reagents per 100 dm^3 of metal-containing wastewater after metal coating	
	with use of wastewater flows as chemical reagent	without introduction of acid wastewater as chemical reagents
Alkaline reagent NaOH	1000 g/ per 100 dm^3	2000 g/per 100 dm^3
Effect of purification by zinc ions, %	up to 90 %	up to 30 %

We also investigated conditions for using UES for the purification of alkaline wastewater after operations of the surface preparation (degreasing). It may be implemented in the following fashion: acidic UES at pH=1.5 and Eh=+ 600÷+1110 mV are used for the purification of alkaline wastewater after degreasing at pH=10÷12 and Eh=200÷÷300 mV until achieving pH=3÷4 and Eh=+300÷+330 mV.

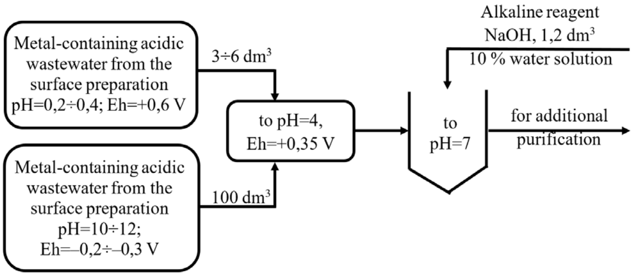

Fig. 6. Use of wastewater flows of galvanic production as chemical reagents

The use of acidic UES as a chemical reagent makes it possible to provide optimal conditions for the oxidation of organic compounds in alkaline wastewater after degreasing operations. At pH=2.9÷4 and Eh=+0.2÷+0.3, strong oxidizers and ion metals of variable valence (Fe, Cu, Cr), which are present in UES, as catalysts form the oxidation area of the majority of organic compounds. An oxidation of organic substances can be accompanied by the sorption of intermediate and resulting products on the hydro-oxo complexes of metals, which are formed at pH>3.5. It further reduces the content of organic substances by 15–30 %, contributing to the creation of optimal conditions for purification (Table 7) [5].

Table 7

Comparison of reagent consumption with or without the use of separate wastewater flows of galvanic production as chemical reagents

Reagent	Amount of reagents per 100 dm^3 of metal-containing wastewater after the surface preparation	
	with use of wastewater flows as chemical reagent	without use of wastewater flows as chemical reagent
Alkaline reagent NaOH	100÷120 g	500÷520 g
Acidic reagent H_2SO_4	–	1800 g

The patent of Ukraine [16] protects the described method for recycling the used-up etching solutions.

6. Discussion of results of research into UES regeneration and its use as a reagent

The existing technologies of recycling iron-containing wastes of etching steel surfaces require updating in order to minimize discharge into the environment and reduce the cost of production. In addition, for the non-concentrated systems, determining the basic technological parameters is not difficult. The problem becomes more complicated when considering the concentrated water systems in connection with the strengthening of all forms of intermolecular interactions in the solution (ion-ion, ion-dipole, and dipole-dipole), and complexing. In the calculation, so many correction coefficients are introduced into such solutions that the results of calculations lose their physical essence. Therefore, for the highly concentrated solutions, it is necessary to experimentally determine the basic technological parameters.

The research was conducted within the framework of the scientific research work in the Department of Chemistry and Physics at the National University of Water Management “Physical-chemical methods for the purification of water systems” (state registration number 0112U005999 as of Feb 3, 2016).

After examining the technology of wash water purification, it was determined that the most effective way is the treatment with the flocculant Zetag 8180. Consequently, the solution was subjected to filtering through a filter with polystyrene foam. The filter was used to separate dispersion, as well as for additional iron removal. Then a part of the treated water was passed through the reverse osmosis system. This provides, at subsequent mixing with the main part of the flow, obtaining water of the “Technical water” quality of category II.

In order to develop the technology of UES regeneration, studies were conducted of the redox properties both with H_2O_2 and without it at different pH values. As a result, the optimum scheme of treatment was established, which includes the alkalization with a 40 % solution of $Ca(OH)_2$ until achieving pH=4.2 and treatment with the solution of H_2O_2.

As a result of examining the technology of UES utilization, it was found that UES can be used as a chemical reagent for the extraction of zinc from the complex compounds of wastewater of galvanic production. UES might be also used for the oxidation of organic compounds in alkaline wastewater after degreasing operations.

Research into processes, associated with the use of UES as a reagent, is not over yet. Many theoretical and experimental problems have not been solved when using acidic UES as a chemical reagent for the oxidation of organic compounds in alkaline wastewater after degreasing operations.

In the future, the authors will work on expanding the scope of application of UES as chemical reagents. Disadvantages of the developed technologies include the formation of hydroxide sediment. Finding the ways of disposing of or using such slime is the aim and the subject of further studies.

7. Conclusions

The paper presents results of research into recycling the liquid iron-containing wastes of steel surfaces etching. Technological solutions for the regeneration and utilization of UES and WW were developed. This technology provides a closed resource consumption cycle, minimizes waste discharge into environment and expenditures of an enterprise. In addition:

– the technological scheme of wash water purification to the standard of “Technical water of category II” was developed and practically implemented. The scheme includes a reagent purification with alkaline solution $Ca(OH)_2$ with flocculant, a filtering through the filter with a polystyrene foam loading, treating the part of the flow in the reverse osmosis system;

– the technological scheme of regeneration of acidic UES was developed and tested under industrial conditions. The scheme includes alkalization with a 40 % solution of $Ca(OH)_2$ until achieving pH=4.2 and treatment with a solution of hydrogen peroxide. The decantate is separated from sediment and additionally strengthened with acid;

– using wastewater flows of galvanic production as chemical reagents: UES and subsequent alkalization provides optimal extraction of zinc from complex compounds at a co-sedimentation with iron (and the formation of double oxide $ZnFe_2O_4$); UES also provide optimal conditions for the oxidation of organic compounds in alkaline wastewater after degreasing operations. This allows a significant decrease in the expenditures of an enterprise and reagent consumption;

– the mismatch between theoretical and experimental data indicates that the properties of the above-described category of UES must be characterized on the basis of qualitative understanding the structure of solutions. The initial conditions of sedimentation of iron from UES correspond to the area of concentration before BCH. The water molecules that are quite close to the ion of metal may react with it. In this case, aqua-complexes transform into hydro-oxo complexes. As a result, alkaline reagent consumption for the formation of insoluble hydro-oxo compounds decreases.

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