

# Establishment of regularities of electroflotation extraction of non-ferrous metal (Cu, Ni, Zn, Co, Fe) hydroxides from wastewater of various compositions in the presence of industrial surfactants

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The electroflotation process of extracting a mixture of Cu, Zn, Ni, Co, Fe hydroxides from wastewater containing NaNO<sub>3</sub>, NaCl, Na<sub>2</sub>SO<sub>4</sub>, Na<sub>2</sub>CO<sub>3</sub>, Na<sub>3</sub>PO<sub>4</sub>, NH<sub>4</sub>OH has been investigated. It was found that the maximum recovery rates of 97–99% are observed in the pH range from 8 to 11 for NaCl solutions. The electroflotation process is the least effective in Na<sub>3</sub>PO<sub>4</sub> solutions with recovery rates of 10–20%. The cationic surfactant SeptaPAV-SKhV-70 (СептаПАВ-СХВ-70) added to the solution increases the extraction ratio in the presence of phosphates by 40–50%. Low efficiency of the electroflotation process in Na<sub>3</sub>PO<sub>4</sub> is associated with a small particle size (about 20–30 μm) and a ζ-potential high negative value, what has an injurious effect on the formation of the flotation complex, negatively charged bubbles (H<sub>2</sub>, O<sub>2</sub>) and negatively charged particles. The addition of a cationic surface-active substance (SAS) reduces negative potential of the dispersed phase and increases particle sizes. All this contributes to the efficient passing of electroflotation process. Presence of a ligand (ammonia solutions) in the sewage reduces the recovery efficiency by 20–30%, especially for copper ions, which are strong complexing agents. Adding to the solution of small amounts (5 mg/l) of industrial surfactants STMs(a) (CTMx(a)) and Flon-1(c) (Флон-1(κ)) at total concentration of hydroxides of 100 mg/l leads to a more efficient passing of the electroflotation process. A process flowsheet for removing suspended matters (a mixture of metal hydroxides) using an electroflotation cell and a microfiltration module is proposed. A model series of electroflotation devices with a capacity of 1–10 m<sup>3</sup>/h was proposed for application of the described technical solutions. The separation time in the devices does not exceed 10 minutes, power inputs is up to 0.6 kW·h per 1 m<sup>3</sup> of the treated wastewater with a recovery rate of 97–99%. The cost of an installation for 10 m<sup>3</sup>/h does not exceed 1.5 million rubles.

**Key words:** electroflotation, Cu, Zn, Ni, Co, Fe hydroxides, wastewater, inorganic salts, industrial surfactants STMs(a), STMh(a), Flon-1(c).

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## Introduction

At the enterprises where galvano-chemical processes are used for surface treatment of various metals, the sewage contains a large quantity of non-ferrous metal ions (Cu, Ni, Zn, Cd, Co, Sn, Pb, Cr, Al, Fe) as well as various acids (HCl, HNO<sub>3</sub>, H<sub>2</sub>SO<sub>4</sub>, H<sub>3</sub>PO<sub>4</sub>), neutralizing of which produces inorganic salts (NaCl, NaNO<sub>3</sub>, Na<sub>2</sub>SO<sub>4</sub>, Na<sub>2</sub>CO<sub>3</sub>, Na<sub>3</sub>PO<sub>4</sub>) that affect coagulation, sedimentation and flotation [1–3]. There are published a wide range of works on wastewater treatment from non-ferrous metal ions using various methods: chemical, physico-chemical, membrane, sorption, and electrochemical [4–9]. Among the electrochemical methods for the purification of sewage from non-ferrous metal ions, electrocoagulation [5, 10–12] and electroflotation [13–16] are widely used. Processes of wastewater purification from non-ferrous metal ions get frequently complicated by the presence of emulsions, SAS, ligands, organic solvents, and other inorganic contaminants [14, 17–18]. In practice,

when treating the sewage of complex composition, several technologies are used together, being combined into working modules. Thus, coagulation, filtration, segmentation, pressure flotation, electroflotation and centrifugation are used for wastewater treatment from suspended substances (metal hydroxides) [1, 4, 8, 15, 19–20]. For the extraction of hydrophilic sediments (metal hydroxides) at low concentrations, electroflotation has a number of advantages [4, 15–16]. The treatment of alkaline water-ammonia effluents containing complexing agents as well as copper, zinc, nickel, cobalt, and iron ions is a complex task. Information on the treatment of such wastewater of complex composition and multicomponent systems is limited.

The laboratory tests permit to work through the technology of complete extraction of a mixture of non-ferrous metal hydroxides in the electroflotation module and reduce the load on the microfiltration module. This article is devoted to the experimental results obtained on investigating the model wastewater.

**Objective:** To improve the technology of electroflotation recovery of non-ferrous metal hydroxides (Cu, Zn, Ni, Co, Fe) from wastewater of various compositions in the presence of industrial SAS on a laboratory installation of non-flowing type.

**Main tasks:**

1. To determine the influence of the electrolyte nature and pH of the solution upon the recovery ratio of Cu, Ni, Zn, Co, Fe hydroxides (NaNO<sub>3</sub>, NaCl, Na<sub>2</sub>SO<sub>4</sub>, Na<sub>2</sub>CO<sub>3</sub>, Na<sub>3</sub>PO<sub>4</sub>, NH<sub>4</sub>OH electrolytes).
2. To investigate the effect of SAS of various nature on the recovery efficiency for a mixture of non-ferrous metal hydroxides from sulfuric acid and ammonia solutions of electrolytes.
3. To define passing conditions of the electroflotation process with a high recovery ratio for toxic contaminants, non-ferrous metal hydroxides.

### Research methodology

The electroflotation process study has been carried out on laboratory and experimental-industrial installations.

The influence of the wastewater composition, SAS, the nature of the ions forming the dispersed phase (hydroxide, carbonate, phosphate) and the role of a complexing agent have been studied on a non-flowing laboratory installation. The modes of gasing and mixing of solutions, current loads, the foam product stability and the time of water treatment in the apparatus have been studied at flow-through laboratory and experimental-industrial installations.

Table 1

**Characteristics of the surfactants in use**

Composition	MTMh	MTMs
Crude tall oils (%) by weight:		
Fatty acids	37.7	36.0
Tarred acids	31.8	15.9
Stearins	7.0	13.8
Esters	2.2	4.8
Aliphatic alcohols	11.2	15.7
Resins	9.1	11.8
Water	1.0	2.0
Molecular mass, g/mol		
	333	345

Table 2

**Influence of the background electrolyte nature upon the recovery rate of a mixture of non-ferrous metal hydroxides at different times of EF**

$\tau$ , min	Recovery rate $\alpha$ , %														
	NaCl					Na <sub>2</sub> SO <sub>4</sub>					Na <sub>3</sub> PO <sub>4</sub>				
	Me					Me					Me				
	Fe	Ni	Zn	Co	Cu	Fe	Ni	Zn	Co	Cu	Fe	Ni	Zn	Co	Cu
5	92	89	92	95	94	63	84	80	87	82	7	10	1	1	1
10	94	91	95	98	96	69	95	92	97	93	11	28	3	2	3
20	96	95	96	99	98	75	96	94	98	95	17	34	4	4	6
20*	99	99	99	99	99	81	99	95	99	99	83	94	94	94	95

\* Additional filtering.

Experimental conditions:  $c(\sum Me^{n+}) = 100$  mg/l,  $c(Me^{2+}) = 25$  mg/l;  $c$  (of electrolyte) — 1 g/l; pH—10;  $J_v = 0.4$  A/l.

The electroflotation process efficiency was evaluated by the recovery rate  $\alpha$  (%) calculated by formula (1):

$$\alpha = (C_{init.} - C_{con.})/C_{init.} \cdot 100\%. \quad (1)$$

The concentration of iron, chromium and aluminum ions was determined by atomic adsorption method on a KVANT-AFA (“KBAHT-AΦA”) device (Russia).

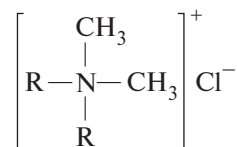
To determine the physical and chemical characteristics of the dispersed phase particles, an Analysette NanoTec/MikroTec/XT laser particle analyzer and a Malvern Zeta-sizer Nano laser analyzer of particle characteristics in the submicron range and nanorange were used.

The investigations has been carried out using the equipment of the CCU of Mendelev University of Chemical Technology.

The details of the principles are described in the works of the authors presented in the reference list [21–22].

The main characteristics of SAS produced from hardwood (MTMh) and softwood (MTMs) species (anionic surfactants) are presented in **Table 1**.

Amine-type nitrogen-containing cationic SAS (collectors) ( $R_1 - R_2 - NH_2$ ), as well as cationic surfactant SeptaPAV (СептаПАВ) based on didecylmethylammonium chloride were used in the work.



In this article, we will consider the electroflotation process of extracting a mixture of hydroxides (Cu, Zn, Ni, Co, Fe) for two different systems:

**System A.**  $H_2O + \sum Me(OH)_2 + \text{electrolyte}$  (pH = 8–11), where electrolyte: NaCl, NaNO<sub>3</sub>, Na<sub>2</sub>SO<sub>4</sub>, Na<sub>2</sub>CO<sub>3</sub>, Na<sub>3</sub>PO<sub>4</sub>, NH<sub>4</sub>OH.

**System B.**  $H_2O + \sum Me(OH)_2 + \text{electrolyte} + \text{SAS}$  (pH = 8–11), where SAS: Flon-1(cat.), STMs (an.); (Na<sub>2</sub>SO<sub>4</sub>, NH<sub>4</sub>OH).

### Experimental results

The experimental data presented in **Table 2** allow us to evaluate the kinetics of the process and its efficiency for each

metal. In the NaCl solution, the rate of electroflotation recovery is high; 90–95% of all metals are extracted in 5 minutes of the process. The hydroxide precipitate easily forms a flotation complex; it is stable under long-term electrolysis (up to 30 minutes) and has a flaky structure. In Na<sub>2</sub>SO<sub>4</sub> solutions, the structure of the precipitate becomes different compared to that in NaCl: small flakes on which the gas bubbles H<sub>2</sub>, O<sub>2</sub> are poorly fixed. The main reason is the negative surface of the dispersed phase ( $\zeta$ -potential  $\approx 20$ –25 mV). Fe<sup>2+</sup> ions are the least efficiently recovered: by 75% in 20 minutes (filtration provides a recovery rate of 81%), some of the ions are present in the solution as Fe<sup>2+</sup> cations (at pH = 8–10) or FeO<sub>2</sub><sup>2-</sup> anions (pH = 10–11). The interfacial characteristics of various metal hydroxides in aqueous solutions of electrolytes are presented in the review [4].

The influence of industrial SAS of various nature used in enrichment of aluminum oxide concentrates is studied. Previous investigations have shown that the positive SAS effect on electroflotation processes becomes apparent at low concentrations of 100–200 mg/l of metal hydroxides; 5–10 mg/l is sufficient.

It was found that the cationic surfactant Flon-1 has a negative effect: the extraction ratio is reduced. The effect is due to the fact that the charge of the dispersed phase metals hydroxide is positive at pH = 10, since Cu(OH)<sub>2</sub> and Zn(OH)<sub>2</sub> precipitates are present in the solution as well as partially Ni<sup>2+</sup>, Fe<sup>2+</sup>, Co<sup>2+</sup> ions, that form hydroxides at pH = 10–10.5 (Table 3). On the other hand, the anionic SAS have a positive effect on the kinetics of electroflotation process. The maximum degrees of extraction are achieved within the first 5–10 minutes. The main effect is associated with a change in the charge of the dispersed phase, small positive values of the electrokinetic potential at pH = 10, and the formation of negative  $\xi$ -potentials at pH > 10. Owing to the displacement of water molecules from the surface with the addition of anionic SAS, the surface is hydrophobized, which intensifies the process of electroflotation.

The weak effect of anionic SAS becomes evident as a result of the fact that in a solution of Na<sub>2</sub>SO<sub>4</sub> there is present the surface-active anion SO<sub>4</sub><sup>2-</sup>, which competes with anionic SAS on adsorption points on hydroxide precipitates.

In the wastewater of many industrial plants, there are ligands, an ammonia solution, tartrate ions, various amines along with non-ferrous metal ions, which can form complexes. In this case, the extraction of non-ferrous metal ions passes less efficiently than in solutions of NaCl, Na<sub>2</sub>SO<sub>4</sub>, NaNO<sub>3</sub>, where strong complexes do not arise.

The low recovery rates of ions, primarily Cu, Zn, correlate with the formation of ammonia complexes. Values of the stability constant of ammonia complexes Cu, Zn, Ni, Co, and Fe are presented below [23].

- 1) pK(Cu – NH<sub>3</sub>) = 12
- 2) pK(Zn – NH<sub>3</sub>) = 9.3
- 3) pK(Ni – NH<sub>3</sub>) = 7.5
- 4) pK(Co – NH<sub>3</sub>) = 5.13
- 5) pK(Fe – NH<sub>3</sub>) = 3.7

The strongest complexes are formed by copper ions (the maximum value of pK); the Cu(OH)<sub>2</sub> sediment formation is hampered. Adding cationic surfactant into the H<sub>2</sub>O –  $\Sigma Me(OH)_2$  – NH<sub>3</sub> – system provides high recovery rates, since the charge of the dispersed phase in excess of ammonia is negative. The  $\zeta$ -potential  $\approx -10$ –12 mV cat. SAS is adsorbed in the dispersed phase. In the presence of cat. SAS the degree of electroflotation extraction reaches the greatest possible values.

Anionic surfactant STMx has a positive effect on the electroflotation process, primarily affecting the ions, which are less prone to form complexes. The main effect is connected with the displacement of NH<sub>3</sub> molecules by anionic SAS and hydrophobization of the surface [4, 23]. The Cu-NH<sub>3</sub> complex is quite strong and 14% remains in the soluble form [Cu(NH<sub>3</sub>)<sub>6</sub>]<sup>2+</sup>.

It was found that action of the second industrial surfactant STMh(an) is less effective, the difference in the recovery rate for the second surfactant (STMh) in a number of systems is 8–12% lower than that for STMs. Thus, despite the course of complexing processes, non-ferrous metals – NH<sub>4</sub>OH in the presence of SAS, as shown by Table 4, it is possible to extract efficiently the precipitation of non-ferrous metal hydroxides [4, 13].

It was established that the introduction of SAS into the solution affects not only the dispersed phase (charge change, particle sizes, surface hydrophobization), but

Table 3

**Influence of SAS upon the recovery rate of a mixture of non-ferrous metal hydroxides sulfate solutions at different electroflotation times**

$\tau$ , min	Recovery rate $\alpha$ , %														
	Na <sub>2</sub> SO <sub>4</sub>					Na <sub>2</sub> SO <sub>4</sub> + STMs (a)					Na <sub>2</sub> SO <sub>4</sub> + Flon-1 (c)				
	Me					Me					Me				
	Fe	Ni	Zn	Co	Cu	Fe	Ni	Zn	Co	Cu	Fe	Ni	Zn	Co	Cu
5	82	84	820	87	63	93	93	94	90	75	50	49	49	42	41
10	93	95	92	97	69	96	97	97	97	81	79	79	78	77	70
20	95	96	94	98	75	97	98	98	94	94	84	83	81	81	74
20*	98	99	95	99	81	98	99	99	99	91	99	99	93	98	95

\* Additional filtering.

Experimental conditions:  $c(\Sigma Me^{n+})$  — 100 mg/l,  $c(Me^{2+})$  — 25 mg/l;  $c(Na_2SO_4)$  — 1 g/l;  $c(SAS)$  — 5 mg/l; pH—10;  $j_v$  — 0.4 A/l.

Table 4

**Influence of SAS upon the recovery rate of a mixture of non-ferrous metal hydroxides in ammonia solutions at different electroflotation times**

$\tau$ , min	Recovery rate $\alpha$ , %														
	NH <sub>4</sub> OH					NH <sub>4</sub> OH + STMs (a)					NH <sub>4</sub> OH + Flon-1 (c)				
	Me					Me					Me				
	Fe	Ni	Zn	Co	Cu	Fe	Ni	Zn	Co	Cu	Fe	Ni	Zn	Co	Cu
5	66	61	12	70	40	97	94	95	93	54	94	94	93	89	89
10	82	78	54	80	47	97	95	96	93	80	97	98	97	97	93
20	83	80	55	81	50	98	95	97	94	86	98	98	98	99	95
20*	92	94	71	96	57	99	98	99	98	86	99	99	99	99	96

\*Additional filtering.

Experimental conditions:  $c(\Sigma Me^{n+})$  — 100 mg/l,  $c(Me^{2+})$  — 25 mg/l;  $c(NH_4OH)$  — 500 mg/l;  $c(SAS)$  — 5 mg/l; pH=8.0;  $J_v$  — 0.4 A/l.

also the release of H<sub>2</sub>, O<sub>2</sub> bubbles on the electrodes. The main effects manifest themselves during stabilization of the bubble size ( $\approx 25 \mu m$  H<sub>2</sub>,  $\approx 40 \mu m$  O<sub>2</sub>) the adsorption of SAS on the surface of the gas phase, which contributes to the effective operation of electroflotation not only in the laminar mode ( $Re < 1.0$ ), but also in the transition region  $1 < Re < 40$ , which is important from a practical point of view for increasing the saturation gas made [4, 13, 22].

To analyze the efficiency of wastewater treatment from a mixture of non-ferrous metal hydroxides, we can use  $\alpha_{av} = (z \cdot \alpha_{Me})/n$ , where  $n$  is an amount of metal instead of assessment of the recovery rate for each of the presented metals ( $\alpha$ ). It is important to note that the use of  $\alpha_{av}$  in this system is justified, since the toxicity of Cu, Zn, Ni, Co, and Fe ions is comparable, and one of the maximum permissible concentration (MPK) criteria is  $\approx 0.01$  mg/l for all ions, the maximum permissible discharge is at the level of 1–0.5 mg/l. In fact, the  $\alpha_{av}$  value characterizes the percentage of recovery of suspended matters (SM), namely a mixture of metal hydroxides.

The precipitates formed with Cu, Zn, Ni, Co, Fe cations and flocculating reagents NaOH, Na<sub>2</sub>CO<sub>3</sub>, Na<sub>3</sub>PO<sub>4</sub> have different solubility and largely determine the residual concentration of ions in the solution. The solubility of hydroxides decreases in the following row: Co(OH)<sub>2</sub> > Fe(OH)<sub>2</sub> > Ni(OH)<sub>2</sub> > Zn(OH)<sub>2</sub> > Cu(OH)<sub>2</sub>.

For the Cu(OH)<sub>2</sub> precipitate, the solubility product (SP) is  $5 \cdot 10^{-20}$ , whereas SP =  $1.6 \cdot 10^{-15}$  for Co(OH)<sub>2</sub>.

Precipitates of carbonates are more soluble than hydroxides. The SP values are  $1.4 \cdot 10^{-10}$  for CuCO<sub>3</sub> and  $1 \cdot 10^{-10}$  for CoCO<sub>3</sub>.

The solubility of phosphates is significantly lower than that of hydroxides and carbonates and is as follows: SP Cu<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub> —  $1.3 \cdot 10^{-37}$ ;  $9.1 \cdot 10^{-31}$  — Zn<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>;  $5.3 \cdot 10^{-31}$  — Ni<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>.

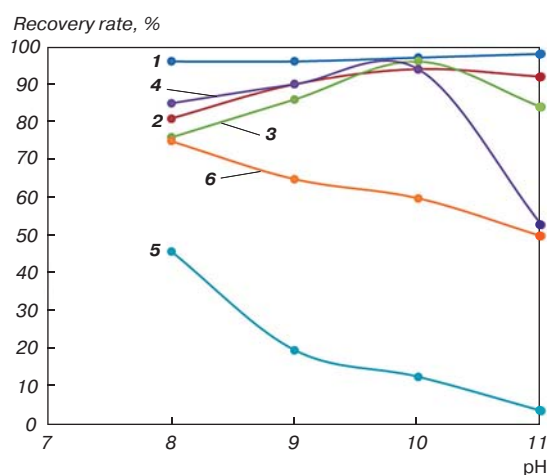
Complete information on the solubility of precipitates of hydroxides, carbonates, sulfides, and phosphates is provided in the reference books.

The recovery rate of the hydroxide mixture from pH of the medium and the nature of the background salts present in the wastewater (NaNO<sub>3</sub>, NaCl, Na<sub>2</sub>SO<sub>4</sub>, Na<sub>2</sub>CO<sub>3</sub>, Na<sub>3</sub>PO<sub>4</sub>) were studied.

The analysis of the experimental data presented in Fig. 1 has showed that the average rate of extraction of Cu, Zn, Ni, Co, and Fe ions in the pH range from 8 to 10 for NaCl is 96–98%. The process of electroflotation proceeds quite quickly, the stationary values of  $\alpha$  are set in 4–5 minutes. High efficiency of the electroflotation process for this system is determined by the structure of the dispersed phase, the particle size of 50–70  $\mu m$  and small values of the  $\zeta$ -potential at pH = 8–10 varies from  $\pm 2$  mV to  $-6$  mV.

The specified conditions create a high efficient formation of the flotation complex. In solutions of NaNO<sub>3</sub>, the recovery rate is by 6–10% lower than in solutions of NaCl, especially at pH = 8, where the solubility of the hydroxide precipitation environment a high degree of recovery of 81% (curve 2) is primarily due to the extraction of Ni ( $\alpha = 82\%$ ), Co ( $\alpha = 69\%$ ), Fe ( $\alpha = 69\%$ ) is not effective.

For Na<sub>2</sub>CO<sub>3</sub>, Na<sub>2</sub>SO<sub>4</sub> solutions, the  $\alpha_{av}$  values for pH = 8–10 practically coincide with that of NaNO<sub>3</sub>



**Fig. 1.** Influence of pH and the electrolyte nature upon the recovery rate of a mixture of hydroxides (Cu, Zn, Ni, Co, Fe):

1 — NaCl; 2 — NaNO<sub>3</sub>; 3 — Na<sub>2</sub>CO<sub>3</sub>; 4 — Na<sub>2</sub>SO<sub>4</sub>; 5 — Na<sub>3</sub>PO<sub>4</sub>, 6 — Na<sub>3</sub>PO<sub>4</sub> + SAS.

Experimental conditions:  $c(\Sigma Me^{n+})$  — 100 mg/l,  $c(Me^{2+})$  — 25 mg/l;  $c$  (of electrolyte) — 1 g/l;  $c(SAS)$  — 5 mg/l;  $\tau$  — 20 min;  $J_v$  — 0.4 A/l

solutions, at pH = 10, the value of  $\alpha_{av}$  is 94% ( $\text{Na}_2\text{SO}_4$ ); 96% ( $\text{Na}_2\text{CO}_3$ ); 94 % ( $\text{NaNO}_3$ ).

During alkalization of the solution up to pH = 11, the recovery rate in  $\text{Na}_2\text{CO}_3$  drops to 84%, in  $\text{Na}_2\text{SO}_4$  — up to 53%, in  $\text{Na}_3\text{PO}_4$  — up to 4%. The indicated effect of a decrease in the  $\alpha$  value correlates with a growth in the negative values of  $\zeta$ -potential to 20–25 mV ( $\text{Na}_2\text{CO}_3$ ) — 25–30 mV ( $\text{Na}_2\text{SO}_4$ ) and — 30–40 mV  $\text{Na}_3\text{PO}_4$ . With a change in  $\zeta$ -potential, the particle size of the dispersed phase of oxides decreases up to  $30 \pm 5$   $\mu\text{m}$ . The most significant effect is shown for the  $\text{Na}_3\text{PO}_4$  solution (curve 5).

The prime reasons for low efficiency are the negative charge of the surface of the dispersed phase, the complexity of the flotation complex formation (negative particles, the negative charge of  $\text{H}_2$ ,  $\text{O}_2$  bubbles), and the low recovery rate [4, 9, 11].

On the other hand, the addition of a cationic SAS to the solution (curve 6) increases the efficiency of the electroflotation process by 25% (pH = 8) by 40% (pH = 11). The cationic SAS action is efficient for the dispersed phase of metal phosphates in an alkaline area, where the  $\zeta$ -potential magnitude change from –20 mV (pH = 5) and to –40 mV (pH = 11).

The Mendelev University of Chemical Technology and its industrial partner Evroekoplast JSC have held testing of the EF equipment production pieces with the capacity of 5 and 10  $\text{m}^3/\text{h}$  with insoluble anodes Ti/TiO<sub>2</sub>, RuO<sub>2</sub>.

Electroflotation cell for 5  $\text{m}^3/\text{h}$ . A single-sectional apparatus with overall dimensions 1820×800×1600 mm, current load 25 A, voltage 20 V (salinity 1 g/l).

Electroflotation cell for 10  $\text{m}^3/\text{h}$ . A two-sectional apparatus with overall dimensions 2500×300×1600 mm, voltage 32 V, current load 50 A.

The efficiency of the EF device is 94–96% in the flow mode, the presence of organic emulsions and SAS in the sewage stabilizes the foaming process, reduces the time of wastewater treatment and increases the purification efficiency. The production pieces of equipment are presented in Fig. 2.

Thus, using electroflotation with the greatest possible rate of extraction, one can reduce the load on the microfiltration module and to ensure its effective operation (Fig. 3).

For wastewater containing non-ferrous metal hydroxides, it is recommended to add industrial anionic surfactant STMs at the rate of 5–10  $\text{g}/\text{m}^3$  at a suspended matter concentration of 100–200  $\text{g}/\text{m}^3$ . The price for 1 kg of the STMs surfactant is 20–30 rubles/kg. With the content of ligands ( $\text{NH}_3$ ) and complexing agents Cu, Zn, Ni, Co in water, high recovery rates are achieved when the cationic surfactant Flon-1 is introduced into the system.

Table 5 contains the microfilter flushing calculations at different values of the electro-



Fig. 2. The production pieces of equipment, output: a — 1  $\text{m}^3/\text{h}$ ; b — 5  $\text{m}^3/\text{h}$ ; c — 10  $\text{m}^3/\text{h}$

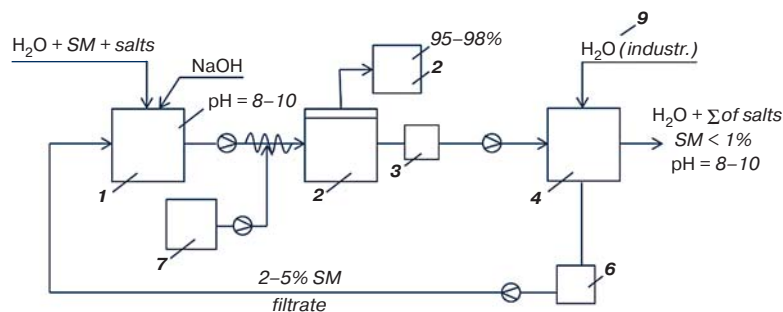


Fig. 3. The module for removal of suspended matters (a mixture of metal hydroxides): 1 — tank for neutralization of waste water; 2 — EF; 3 — industrial tank; 4 — microfilter; 5 — flotation mud (SM); 6 — tank for filtrate; 7 — tank with SAS; 8 — flocculator; 9 — water for washing the filter

Table 5

**Reducing the load on the microfiltration module at different efficiency of the electroflotation cell**

Parameter	Microfiltration			
	SM, $c_{con}$ , mg/l			
	100	50	25	5
Efficiency of electroflotation, $\alpha$ , %	0	50	75	95
Number of washes per hour	8–10	4–6	2–3	1
Quantity of pollutions				
[kg/hour]	1.0	0.5	0.25	0.05
[kg per 24 hours]	24	12	6	1.2

flotation cell efficiency in the presented module of the suspended matter removal (Fig. 3).

The following set parameters were used for the calculation: cell capacity of 10 m<sup>3</sup>/h, three-shift operation mode (24 hours), sorption filter with filtration charging. Washing was carried out at a pressure of 0.8–1.4 bar, with a suspended matter concentration of 5–10 mg/l and an NTU turbidity of 20–40 units one time per hour. The washing time is 45–60 seconds. As the concentration of pollutants increases, the frequency of flushing increases. The EF efficiency for the calculations was 50, 75, and 95%.

The use of electroflotation permits to dramatically reduce the load on the mechanical filter, which ensures high efficiency of its operation and reduces the amount of hydroxide sediment after flushing the filter.

### Conclusions

The investigations have shown that high extraction rates of contaminants, in particular, mixtures of non-ferrous metal hydroxides, in the electroflotation process ensure the efficiency of the entire process chain of equipment at sewage disposal plant.

The advantages of the electroflotation processes are as follows:

- short process time (5–10 min.) and high degree (up to 99%) of purification;
- the possibility of simultaneous extraction of impurities that have different phase-dispersed composition from 10 to 100  $\mu\text{m}$ ;
- relatively low power consumption (from 0.1 to 0.5 kW·h/m<sup>3</sup>);
- the possibility of smooth regulation of the gas bubble flow to control the process;
- the positive influence of the electric field upon the change in the physical and chemical properties of the purified dispersed system, which intensifies the process of coagulation and flocculation owing to the change in the current load;
- the useful capacity of flotation devices is 10–20 times less than that of precipitation tanks, the time of deposition and electroflotation differs by 3–5 times;
- production of foam products with a lower humidity (90–95%) than that of the sediment formed in the precipitation tanks (95–99.8%).

The advantages listed above explain the attention paid to the development and improvement of the electroflotation process in many countries of the world, including Russia.

To implement the described technical solutions, a model line of electroflotation devices with a capacity of 1–10 m<sup>3</sup>/h is suggested [14, 22]. The separation time in the devices does not exceed 10 minutes, power inputs are up to 0.5 kW·h per 1 m<sup>3</sup> of the treated wastewater with a recovery rate of 97–99%. The cost of an installation for 10 m<sup>3</sup>/h does not exceed 1.5 million rubles, the specific output of the equipment is 5 m<sup>3</sup> of the water being purified per 1 m<sup>3</sup> of a plant.

To organize a highly efficient water treatment system with water rotation, it is necessary to use two additional modules M2 — a sorption module for removing the soluble organic compounds and M3 — a membrane module (reverse osmosis) of demineralization. The cost of these modules depends on the manufacturer (domestic, foreign) and varies in the range of 1.7–2.2 million rubles per 1 m<sup>3</sup> of the water to be purified.

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### References

1. Information and Technical Guide to the Best Available Technologies (ITC 36-2017). Surface Treatment of Metals and Plastics using Electrolytic or Chemical Processes. Moscow: Buyro NDT. 2017. 228 p.
2. Filatova E. G. Wastewater Treatment from Heavy Metal Ions, Based on the Physico-Chemical Processes. Review. *Izvestiya Vuzov. Prikladnaya Khimiya i Biotekhnologiya*. 2015. No. 2. pp. 97–109.
3. Skugoreva S. G., Ashihmina T. Ya., Fokina A. I., Ilyalina E. I. Chemical Grouns of Toxic Effect of Heavy Metals (Review). *Theoretical and Applied Ecology*. 2016. No. 1. pp. 4–13.
4. Kolesnikov V. A., Ilin V. I., Brodsky V. A., Kolesnikov A. V. Electroflotation During Wastewater Treatment and Extraction of Valuable Compounds from Liquid Technogenic Waste: a Review. *Theoretical Foundations of Chemical Engineering*. 2017. Vol. 51, Iss. 4. pp. 361–375. DOI: 10.7868/S0040357117040054.
5. Sergi Garcia-Segura, Maria Maesia S. G. Eiband, Jailson Vieira de Melo, Carlos Alberto Martínez-Huitle. Electrocoagulation and Advanced Electrocoagulation Processes: A General Review about the Fundamentals, Emerging Applications and its Association with other Technologies. *Journal of Electroanalytical Chemistry*. 2017. Vol. 801. pp. 267–299.
6. Kyzas G., Matis K. Flotation in Water and Wastewater Treatment. *Processes*. 2018. Vol. 6. p. 116. DOI: 10.3390/pr6080116.
7. Peleka E. N., Gallios G. P., Matis K. A. A Perspective on Flotation: a Review. *Journal of Chemical Technology & Biotechnology*. 2018. Vol. 93, Iss. 3. pp. 615–623. DOI: 10.1002/jctb.5486.

8. George K. Z., Matis K. A. Electroflotation Process: a Review. *Journal of Molecular Liquids*. 2016. Vol. 220. pp. 657–664. DOI: 10.1016/j.molliq.2016.04.128.
9. Ksenofontov B. S., Kozodaev A. S., Taranov R. A., Vinogradov M. S. Experimental Validation of Waste Water Treatment Processes Aimed at Metals Removal. *Tsvetnye Metally*. 2019. No. 10. pp. 96–100. DOI: 10.17580/tsm.2019.10.16
10. Sillanpää M., Shestakova M. Electrochemical Water Treatment Methods: Fundamentals, Methods and Full Scale Applications. Elsevier, 2017. 310 p.
11. Chen G. Electrochemical Technologies in Wastewater Treatment. *Separation and Purification Technology*. 2004. Vol. 38, Iss. 1. pp. 11–41.
12. Dina T. Moussa, Muftah H. El-Naas, Mustafa Nasser, Mohammed J. Al-Marri. A Comprehensive Review of Electrocoagulation for Water Treatment: Potentials and Challenges. *Journal of Environmental Management*. 2017. Vol. 186. pp. 24–41.
13. Chen X., Chen G. Electroflotation. In: *Electrochemistry for the Environment*. Springer Science+Business Media, LLC, 2010. p. 263.
14. Kolesnikov V. A., Kolesnikov A. V., Ilin V. I. Electroflotation in Wastewater Treatment from Oil Products, Dyes, Surfactants, Ligands, and Biological Pollutants: a Review. *Theoretical Foundations of Chemical Engineering*. 2019. Vol. 53, Iss. 2. pp. 205–228.
15. Brodskiy V. A., Malkova Yu. O., Zhukov D. Yu., Kolesnikov V. A. Effect of the Physico-Chemical Properties of the Disperse Phase of Poorly Soluble Compounds of Non-Ferrous and Rare Earth Metals on Their Combined Recovery from Aqueous Solutions by Electroflotation. *Tsvetnye Metally*. 2019. No. 10. pp. 78–84. DOI: 10.17580/tsm.2019.10.13
16. Kuzin E. N., Averina Yu. M., Kurbatov A. Yu., Sakharov P. A. Wastewater Treatment in the Electroplating Industry Using Composite Coagulants-Reducers. *Tsvetnye Metally*. 2019. No. 10. pp. 91–96. DOI: 10.17580/tsm.2019.10.15
17. Pyae Aung, Thu Aung Hein, Kolesnikov A. V. Investigation of Electroflotation Extraction Processes of a Mixture of Insoluble Copper and Nickel Compounds in The Presence of Organic Composition Used in the Treatment of Metal Surfaces. *Electroplating & Surface Treatment*. 2020. Vol. 28, Iss. 4. pp. 38–45. DOI: 10.47188/0869-5326\_2020\_28\_4\_38
18. Kolesnikov A. V., Htay T. Z., Kolesnikov V. A., Kovalenko V. S. Extraction by Electroflotation of Iron, Chromium and Aluminium Hydroxides from Aqueous Solutions of Sodium Chlorides and Sulphates in the Presence of  $Mg^{2+}$ ,  $Ca^{2+}$  and Surfactants of Different Types. *CIS Iron and Steel Review*. 2020. Vol. 20. p. 61–65. DOI: 10.17580/cisr.2020.02.13
19. Desyatov A. V., Baranov A. Ye., Baranov Ye. A., Kakurkin N. P., Kazantseva N. P., Kazantseva N. N., Aseev A. V. The Experience in Using Membrane Technologies for Purification and Desalination of Water. Moscow: Khimiya, 2008. 240 p.
20. Kuzin E. N., Kruchinina N. E. Purification of Circulating and Waste Water in Metallurgical Industry Using Complex Coagulants. *CIS Iron and Steel Review*. 2019. Vol. 18. pp. 72–75. DOI: 10.17580/cisr.2019.02.15
21. Kolesnikov V. A., Menshutina N. V., Desyatov A. V. Equipment, Technologies and Design of Sewage Treatment Systems. Moscow: DeLi plus, 2016. 288 p.
22. Kolesnikov A. V., Meshalkin V. P., Davydova T. V., Kolesnikov V. A. Scientific And Technological Basics of Increasing Resource Efficiency of Electroflotation Processes of Extraction of Difficult Insoluble Inorganic Compounds (OXIDES, Carbides, Hydroxides) from Aqueous Solutions. *Doklady Akademii Nauk. Khimiya, nauki o materialakh*. 2020. Vol. 494, Iss. 1. pp. 55–61. DOI: 10.31857/S2686953520050076
23. Pavlenko V. I., Volodchenko A. N., Klimenko V. G. A Handbook of General and Inorganic Chemistry. Izdatelstvo BGTU, 2010. 86 p.