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Electroflotation Removal of the Dispersed Phase of Sparingly Water-Soluble Non-Ferrous and Heavy Metals from Aqueous Media. Effect of the Composition of the Aqueous Medium on the Removal Efficiency

V. I. Il'in, V. A. Brodskii, V. A. Kolesnikov, and A. F. Gubin

Mendeleev Russian University of Chemical Technology, Miusskaya pl. 9, Moscow, 125046 Russia
e-mail: lera@muctr.ru

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Abstract—The article describes the effect of the composition of the aqueous medium on the surface characteristics (ζ-potential, solubility, particle size, and dispersity) of the disperse phase of sparingly water-soluble non-ferrous and heavy metal compounds, as well as on their removal by the electroflotation method. The electroflotation efficiency can be improved by varying the surface characteristics of the dispersed phase by varying the pH and redox potential of the medium, as well as using different reagents and certain types of water-soluble polyelectrolytes of different functionalities under conditions optimal for their work.

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INTRODUCTION

Economic development inevitably entails impact on the environment, including aqueous systems. Annual state reports show that the anthropogenic load on natural ecosystems tends to increase. In some regions of the country pollution of water systems still remains very high [1, 2].

The problem of protection of water resources is largely solved owing to water treatment technologies and devices. Traditional chemical mechanical water treatment technologies fail to efficiently remove dispersed particles, first of all, sparingly soluble non-ferrous or heavy metal particles, from wastewaters. To intensify the process of removal of dispersed metal particles from aqueous media, one should find out how the composition of the aqueous medium affects the surface characteristics of metal particles (ζ-potential, size and dispersity, as well as solubility).

Electroflotation is a promising method for removal of dispersed particles from water. Electroflotation involves electrolytic generation of gas bubbles that float from the bulk of the liquid, and, in doing so, they aggregate with dispersed particles due to decreased surface energy of the floated particle and gas bubble at the liquid–gas interface. The aggregates are lighter than water and, therefore, they float to the surface [3].

Scientific research, practice, and service experience revealed some undeniable advantages of the electroflotation technology, the most important of which are the possibility of simultaneous removal of pollutants with different phase and disperse compositions, fairly low energy consumption (compared to electrocoagulation, from 0.1 to 0.3 kW h/m^3); generation of fine gas bubbles (diameter 20–100 μm) with a high adhesivity to pollutants to be removed; possibility of smooth adjustment of the generation rate and size of gas bubbles by varying current load; and a positive effect of electric on the physicochemical properties of the treated disperse system due to intensification of flake formation.

The above advantages explain the worldwide interest in the development and improvement of the electroflotation process [4].

In the present work we studied the effect of the composition of the aqueous medium on the electroflotation removal of dispersed non-ferrous and heavy metal compounds.

Study of the Effect of the Composition of the Aqueous Medium on the Efficiency of Removal of the Dispersed Metal Phase

Methodology of the Study

Experiments were performed using model solutions and real industrial wastewaters containing sparingly soluble compounds of metals (Ni, Co, Cd, Cu, Pb, Cr, Zn, Fe, Pb, Ca, Mg, etc.) and electrolytes (NaCl, $NaNO_3$, Na_2SO_4, etc.). The treatment process was performed on batch or flow laboratory and industrial electroflotation installations with a ruthenium–titanium oxide anodes and stainless steel cathodes.

The concentrations of metals in water were measured on a KVANT-AFA atomic absorption instrument.

The electrokinetic potentials (ζ-potentials) were measured on a Malvern Zetasizer Nano laser analyzer.

The particle size distributions were determined on an Analysette NanoTec/MicroTec/XT laser particle sizer.

The relative change in the concentration of dispersed particles over the course of their electroflotation removal from aqueous systems was estimated by the recovery (in %):

$$\alpha = 100 \times (c_0 - c_\tau)/c_0, \qquad (1)$$

where c_0 and c_τ are the initial and current concentration of dispersed particles, respectively.

Effect of the Concentration of Hydrogen Ions

Study of the effect of the pH of the medium on the ζ-potential of dispersed particles showed that there is a certain pH range corresponding to the minimum solubility of hydrolysis products (0.3–1.5 mg/L), in which the surface of particles is recharged and the ζ-potential reaches a zero value. Thus, this pH range for nickel, manganese, and zinc hydroxides are 9.8–10, 9–9.2, and 8.8–9.0, respectively. However, the working pH range, in which the electroflotation process takes place, is shifted to the alkaline range by ~0.5–1 from the pH values corresponding to the isoelectric point, where ζ = 0 (Table 1). This is obviously explained by the fact that in the electroflotation process pH-dependent are not only the ζ-potential, but also size and dispersity of particles. Table 2 lists data relating to the effect of pH on ζ-potential, average particle size $\bar{d}$, fraction of fine particles ($d < 10$ μm), and recovery α for the dispersed phase of sparingly soluble copper, nickel, and manganese compounds.

Table 1. Characteristics of certain metal cations in water at various pH values

Metal cation[a]	pH value	
	isoelectric point (ζ = 0)	working range of electroflotation
Ni(II)	9.8–10	10.5–11
Cu(II)	8.2–8.5	9.0–9.5
Zn(II)	8.8–9.0	9.3–9.5
Cd(II)	9.0–9.2	9.8–10
Fe(II)	8.0–8.3	8.8–9.2
Fe(III)	6.0–6.2	5.5–7.5
Cr(III)	6.3–6.5	7.0–7.5
Mn(II)	9.0–9.2	10–10.5
Co(II)	9.0–9.2	9.8–10

[a] Initial concentration of metal cations 20–100 mg/L; water contains sodium sulfate, 50 mg/L.

Thus, the concentration of hydrogen ions is a key factor for the efficiency of electroflotation removal of the dispersed phase, on account, on the one hand, by the effect on the process of formation of dispersed particles, which controls the concentration ratio of metal ions and dispersed particles in the aqueous medium, and, on the other, by the effect on the surface properties of particles, such as solubility, ζ-potential, size, and dispersity. The recovery of the dispersed phase depends on the size and dispersity of particles: The highest recovery occurs at pH values, at which the average particle size is a maximum and the fraction of fine particles is a minimum.

Effect of the Redox Potential of the Medium

Mixed-valence metals (for example, Ni^{2+}/Ni^{3+}, Fe^{2+}/Fe^{3+}, Mn^{2+}/Mn^{3+}, Co^{2+}/Co^{3+}, Sn^{2+}/Sn^{4+}) form sparingly soluble compounds (oxides and hydroxides) with different phase compositions depending on the pH and redox potential of the medium. Thus, in the system nickel–water at pH from 8 to 12 and redox potential from –0.7 to +0.6 V, nickel exists as individual Ni(II) hydroxide and Ni(II) and Ni(III) oxides. Mixed-composition compounds can form at the phase interface.

It was found that the redox potential of the medium affects not only the phase composition of particles but also their surface properties, in particular, average size

Table 2. Characteristics of the finely dispersed phases of copper, nickel, and manganese compounds and their recoveries at various pH values of the medium

System	Parameter	pH						
		8.5	9	9.5	10	10.5	11	11.5
Cu–H_2O	ζ, mV	–10.5	–11.5	–13.5	–15	–16	–19	–28
	$\bar{d}$, µm	37	45	50	39	37	35	32
	$d < 10$ µm	2.4	2.6	2.0	3.8	4.2	4.3	5.1
	α, %	78	95	98	86	74	70	58
Ni–H_2O	ζ, mV	–9.5	–10	–13.5	–14.5	–17	–23	–28.2
	$\bar{d}$, µm	32	38	52	64	81	89	80
	$d < 10$ µm	6.5	5.6	4.2	2.8	2.2	1.5	2.1
	α, %	60	77	80	84	97	98	82
Mn–H_2O	ζ, mV	–3.6	–2.8	–3.4	–5.5	–21.8	–27.4	–35
	$\bar{d}$, µm	32	35	53	55	54	52	49
	$d < 10$ µm	6.5	6.0	4.8	3.4	3.7	4.1	5.3
	α, %	24	29	85	96	97	60	62

that increases from 15 to 30%, thus favoring a more efficient electroflotation process.

It is also important that the solubility of the dispersed phase increases from 10 to 100 times in going from hydroxide to oxide compounds.

Thus, by varying the redox potential of the system one can vary the phase composition and properties of the dispersed phase and, as a consequence, its flotation activity.

Effect of Anions

Study of the effect of anions (F^-, Cl^-, NO_3^-, SO_4^{2-}, CH_3COO^-, CO_3^{2-}, PO_4^{3-}, S^{2-}, HPO_4^{2-} , etc.) on the removal of dispersed metals from the aqueous medium established that NO_3^-, SO_4^{2-}, and CH_3COO^- anions at concentrations of up to 1 g/L have almost no effect on the efficiency of the electroflotation process. The presence of Cl^- anions favors more efficient removal of dispersed chromium and nickel compounds, whereas F^- ions favor better removal of dispersed copper, zinc, and cadmium compounds. The enhanced electroflotation efficiency is due to decreasing ζ-potential of particles.

In the presence of CO_3^{2-}, PO_4^{3-}, and S^{2-} anions, dispersed particles with different phase compositions and surface properties can form, depending on the pH of the medium and the component ratio in the initial mixture. Thus, in an alkaline medium, complicated compounds like $M(OH)_nPO_4^{3-n}$ or $M_2(OH)_2 \times M_2(OH)_2CO_3$ are formed, rather than simple compounds like tertiary phosphates or carbonates. In the presence of excess CO_3^{2-}, PO_4^{3-}, and S^{2-} anions (compared to stoichiometry), the average particle size and the fraction of the finely dispersed phase decreases compared to hydroxide compounds. For example, in the presence of S^{2-}, the average particle size of nickel compounds decreases from 52 to 43 µm, while in the presence of CO_3^{2-} and PO_4^{3-}, to 34 and 27 µm, respectively. In the presence of PO_4^{3-}, the fraction of the dispersed phase with the particle size below 10 µm increases from 2.2 to 10.5 wt %. The dispersed system Cu–Na_2S–H_2O having copper sulfide particles smaller than 5 µm deserves special mentioning.

Decreased average particles sizes and increased fractions of fine dispersions in the presence of CO_3^{2-}, PO_4^{3-}, and S^{2-} anions are characteristic of systems containing Co, Fe, Cd, Ca, Mg, Zn, etc.

Indifferent electrolytes at concentrations of 10–100 g/L decrease the recovery of dispersed particles to 5–10%.

Effect of Cations

Industrial wastewaters almost always contains together Fe^{2+}, Fe^{3+}, Ca^{2+}, Mg^{2+}, as well as, depending

Table 3. Effect of metal cations on the electroflotation recovery of the dispersed phase of sparingly soluble metal compounds

Dispersed phase	Cations		
	increase recovery	no effect on recovery	decrease recovery
Cu	–	Zn^{2+}, Ni^{2+}, Fe^{3+}, Co^{2+}	Mg^{2+}, Ca^{2+}
Ni	–	Zn^{2+}, Cu^{+2}. Co^{2+}	Cr^{3+}, Mg^{2+}, Ca^{2+}, Fe^{3+}
Zn	–	Ni^{2+}, Cu^{2+}, Cd^{2+}, Fe^{2+}, Fe^{3+}, Co^{2+}	Cr^{3+}, Ca^{2+}
Cd	–	Ni^{2+}, Cu^{2+}, Zn^{2+}, Fe^{2+}, Fe^{3+}, Co^{2+}	Cr^{3+}
Mn	Fe^{3+}	Cu^{2+}, Zn^{2+}	Ni^{2+}, Cr^{3+}, Co^{2+}
Pb	Fe^{2+}, Fe^{3+}, Cu^{2+}	–	–
Sn	Fe^{3+}, Cu^{2+}, Zn^{2+}	Cu^{2+}	Cr^{3+}, Ca^{2+}
Al	Fe^{3+}	Mg^{2+}, Ca^{2+}	Cr^{3+}, Ni^{2+}, Cu^{2+}, Zn^{2+}

on the industry, Cu^{2+}, Zn^{2+}, Cr^{3+}, Al^{3+}, Ni^{2+}, and other cations. Therewith, the following variants are possible: (1) cation form a dispersed phase at close pH values, for example, Cu^{2+}–Zn^{2+} at pH ~9.8, Cr^{3+}–Fe^{3+}–Al^{3+} at pH 6.5–7.5, and Ni^{2+}–Fe^{2+}–Cd^{2+} at pH 10–11; and (2) cations form a dispersed phase at pH values differing from each other by 2–5. Examples of the second variant are provided by the following systems: Cr^{3+}–Cu^{2+}, Ni^{2+} (**I**), Cr^{3+}–Fe^{2+}, Ni^{2+}–Cd^{2+} (**II**), Fe^{3+}–Cu^{2+}, Zn^{2+} (**III**), Fe^{3+}–Ni^{2+}, Cd^{2+} (**IV**), Al^{3+}–Cu^{2+}, Zn^{2+} (**V**), and Al^{3+}–Fe^{2+}, Cd^{2+} (**VI**). Thus, the pH values in systems **I**, **III,** and **V** differ by 2–3 and those in systems **II**, **IV**, and **VI** differ by 3–5. Metals in these systems are present in the ionic and dispersed forms. Thus, in the Cr^{3+}–Ni^{2+} system at pH 6–7 nickel is present in the ionic form, and chromium is present as a hydroxide (dispersed particles).

Metal cations when present together in water mutually affect the electroflotation process. The character and strength of this effect depend on the metal cation and on the pH of the medium, corresponding to the formation of the dispersed phase (hydroxide formation).

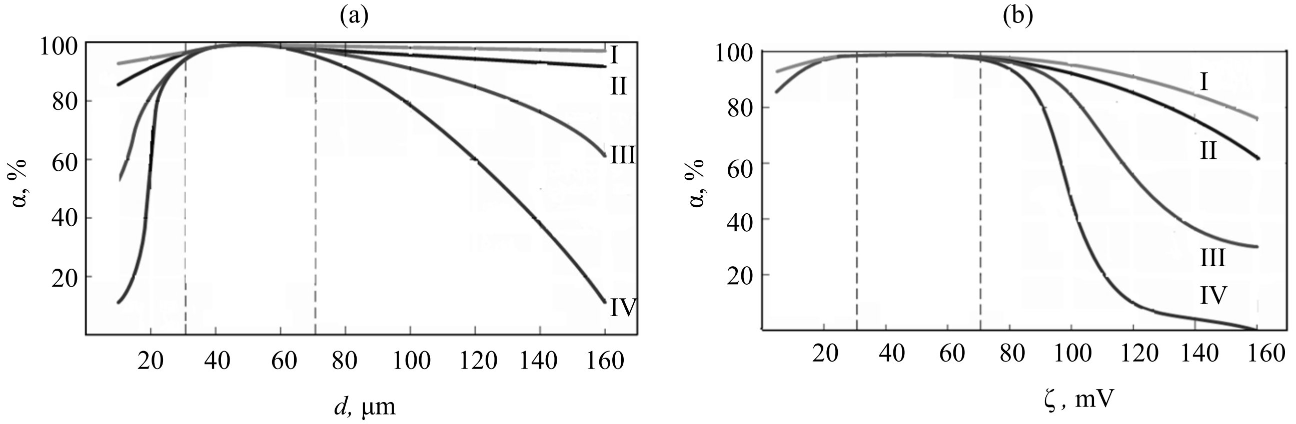
Binary systems and close pH values for hydroxide formation. The recovery of dispersed particles of individual copper and zinc compounds at pH 9.5 is about 97%, whereas on the electroflotation of the Cu–Zn system, the recovery of the dispersed phase of both metals is even higher (α ~ 99%). With the Zn–Ni system, the recovery of the dispersed phase is no higher than 30–40%. In the Cu–Ni system, the component metals have only minor mutual effect on the recovery of the dispersed phase (α = 97–98%), but at a 1 : ≥10 [Cu] : [Ni] ratio the recovery decreases by 5–15%.

Binary systems, different pH values for hydroxide formation. Of the highest practical interest among such systems are Ni^{2+}–Cr^{3+}, Cu^{2+}–Cr^{3+}, Ni^{2+}–Fe^{3+}, and Cu^{2+}–Fe^{3+}, which are the most commonly present in industrial wastewaters.

It was found that the electroflotation of a mixture of nickel and iron at pH 10.5 (the most favorable pH for removal of nickel dispersed phases, α = 97%), the recovery of nickel particles decreases by 20–40%, whereas the recovery of iron particles is no higher than 90%. As the pH decreases to 8.5–9, the recovery of nickel particles increases to 85–90 %. Similar effects are observed with the Cu^{2+}–Fe^{3+} and Zn^{2+}–Fe^{3+} systems.

The Cr^{3+}–Ni^{2+} system behaves in a different way. The electroflotation of a 1 : 10 Cr^{3+}: Ni^{2+}system in all the pH ranges studied the recovery of the dispersed phase of nickel is 40–50%, and the chromium recovery is no higher than 20%. When the content of Cr^{3+} in the mixture is increased so that the Cr^{3+}: Ni^{2+} ratio becomes 1 : 3–5, an even stronger suppression of the electroflotation process is observed. Similar phenomena take place in the Zn^{2+}–Cr^{3+}, Cu^{2+}–Cr^{3+}, Cd^{2+}–Cr^{3+}, and some other systems. The summarized data on the effect of metal cations on the efficiency of the electroflotation removal of dispersed metal phases at pH 9.5–10 are presented in Table 3.

The different effects of cations on the recovery of dispersed metal phases can, first of all, be explained by the fact that cations can interact with the dispersed phase by different mechanisms: adsorption, ion



Dependence of the electroflotation recovery of dispersed metal phase on the (a) average size and (b) ζ-potential of particles. For I, II, III, and IV, see text.

exchange, coprecipitation, and cocrystallization; therewith, compounds with different phase compositions and surface properties are formed, which differently affect their electroflotation activity.

Analysis of the particle size distribution allows us to conclude that the enhanced eflectroflotation efficiency in binary systems is associated both with increased average particle size and with decreased fraction of the finely dispersed phase.

Ternary systems. Electroflotation of a mixture of Cu^{2+}, Ni^{2+}, and Cr^{3+} ions in the pH range 7–10 at varied weight concentrations of the ions at their initial total concentrations 10–100 mg/L was studied. Changing the pH of the medium and the component ratio in the mixture, especially increasing Cr^{3+} concentration, increased the residual concentration of Cu^{2+} and Ni^{2+} cations, implying decreased recovery of the dispersed phase.

The electroflotation of a 1 : 1 : (>0.5) Cu–Ni–Fe system resulted in a decreased recovery of the dispersed phase. Thus, the recoveries of individual dispersed particles of copper, nickel, and iron are 80, 88, and 90%, and the recoveries from the mixture are 55, 58, and 59%, respectively. Therewith, the average particle size decreases from 50–52 to 30 μm.

In the case of a Cu–Ni–Co system that is the most commonly present in nonferrous metal industry wastewaters, the recoveries of the dispersed phase were high (98–99% for each metal) at different component ratios.

Quarternary and more component systems. Study of the recoveries of the dispersed phase from a Al–Zn–Cd–Pb system with the [Zn–Cd–Al] : [Pb] ratio of 1 : (1–3) at pH 7–9 showed that the lowest flotation activity is characteristic of lead compounds (α = 20–30%). If nickel or copper are present instead of aluminum, the recovery of the dispersed phase of lead reaches 96–98%.

The most efficient electroflotation process is observed at pH 10 at a 1 : (1–2) [Cu–Ni–Zn–Cd] : [Pb] ratio. At other ratios and pH values, the residual concentrations of metal cations are appreciably higher compared to the electroflotation of individual compounds. Thus, as the concentration of lead cations is increased 3 times, the electroflotation efficiency decreases 1.5–2 times.

The resulting data allow the aqueous systems studied to be divided into 4 groups in terms of the efficiency of electroflotation removal of dispersed phases (Cu, Zn, Ni, Co, Cd, Mn, Fe, Cr, Pb) at pH 9.5–10, depending on the average size and ζ-potential of particles (see figure):

Group I: the electroflotation efficiency is very high (average particle size 30–70 μm, ζ-potential from +5 to –15 mV, α = 95–99%, electroflotation time 3–5 min, residual concentration of metal cations 0.3–0.5 mg/L);

Group II: the electroflotation efficiency is high (α = 85–95%, electroflotation time 5–10 min, residual concentration of metal cations 0.3–0.5 mg/L);

Group III: the electroflotation efficiency is medium (α = 50–85%, electroflotation time 10–20 min, residual concentration of metal cations 0.01–0.05 mg/L);

Group IV: the electroflotation efficiency is low (α < 50%, electroflotation time > 20 min, residual concentration of metal cations 0.3–1.5 mg/L).

Thus, to purify certain aqueous systems from dispersed particles, special measures should be taken to intensify the electroflotation process and enhance its efficiency, specifically, to reduce the residual concentrations of metal cations for Group I and IV systems and increase the recovery of the dispersed phase and decrease the electroflotation time for Group III and IV systems.

The residual concentrations of metal cations present in aqueous systems along with the dispersed phase of sparingly soluble compounds of the same metals can be decreased by varying their surface characteristics and phase composition. Thus, the concentrations of metal cations present in aqueous systems along with the dispersed phase containing phosphates, oxides, sulfides, and carbonates of the same metals are decreased by introducing into the system a solution of an iron(II) or an iron(III) salt (or their mixture) in a certain concentration and performing electroflotation at pH 9–10. As a result, the concentration of metal cations in the aqueous system decreases to 0.01–0.1 mg/L.

The positive effect of iron(II) or iron(III) salts is likely to be explained with the formation of different metal species, in particular, ferrites and magnetites (by X-ray diffraction data). Obviously, such compounds possess good adsorption, coagulation, and flotation activities.

Another approach involves addition, before electroflotation at pH 8–10, to a metal hydroxide-containing system of orthophosphate ions in a certain weight ratio with respect to the metal to be removed. As a result, the metal hydroxyphosphate is formed, which is less soluble that the corresponding metal hydroxide and has good adsorption and flocculation characteristics. This allow the residual concentration of the metal cations in water after electroflotation to be decreased to 0.01–0.05 mg/L.

The possibility to decrease the concentration of mixed-valence metal cations (Ni, Fe, Mn, Co) by varying the redox potential of the system during the electroflotation process was explored. The efficiency of the process depends on the anodic current density, electrolysis time, and temperature and ionic composition of waters to be treated. If electroflotation is performed under optimal conditions, the concentration of dissolved metal species in the treated water can be decreased from 0.5–1.0 to 0.01–0.05 mg/L.

Ways to Intensifying the Electroflotation Process

The following equation was proposed to describe the electroflotation process [3]:

$$\alpha = 1 - e^{-K\tau}, \tag{2}$$

where α is recovery, %; τ, electroflotation time, min; *K*, a constant relating to the electroflotation rate, defined as follows:

$$K = \frac{0.15iE}{r_\mathrm{b}} \frac{0.15ir_\mathrm{p}^{1.5}}{r_\mathrm{p}^2}, \tag{3}$$

where *i* is the volume current density, A/L; r_b, bubble radius, μm; *E*, a coefficient relating to the efficiency of particle trapping by gas bubbles; and r_p, particle radius, μm.

As follows from Eq. (3), the intensity of the electroflotation process can be enhanced indefinitely by increasing current density. However, in reality this is not the case. Experiments show that the dependence of recovery on current peaks at an optimum current value. The following explanation can be given for this result. At low currents, the process occurs slowly, because the system is poorly saturated by gas bubbles. Increasing current increases recovery, because water is better saturated by gas bubbles. As a result, the electroflotation rate also increases. However, the rate of the electroflotation process increases only until an optimal current value is reached. Further increase of current may entail such consequences as foam destruction and hydrodynamic suppression of electroflotation. This phenomenon is well known in the flotation practice.

The electroflotation process can be intensified in a different way, specifically, by increasing the size of dispersed particles in the aqueous system being treated.

One of the common approaches to intensifying the removal of aggregatively and sedimentatively stable dispersed metal particles in wastewater treatment processes is the use of chemical reagents (inorganic coagulants, electrolytes) that affect the surface properties of particles to induce their aggregation and coagulation [5]. In this case, for optimal coagulation conditions one should increase the specific consumption of the reagent at decreased particle size and increased concentration of contaminants, maintain the optimal pH of the system, and use organic flocculant additives.

Over the past decade novel water-soluble polymer flocculants, specifically polyelectrolytes of different

Table 4. Effect of flocculant additives on the electroflotation removal of the dispersed phase of sparingly soluble metal compounds from wastewaters

Dispersed phase	Process parameters							
	without flocculant			with flocculant			τ_1/τ_2	$\alpha_1 - \alpha_2$,%
	$\bar{d}_1$, μm	α_1, %	τ_1, min	$\bar{d}_2$, μm	α_2, %	τ_2, min		
$Pb(OH)_2$	5	3–5	30	50	93–95	8	3.5	90–92
$Cr(OH)_3$	16	65–68	15	78	95–98	7	2	27–30
$Mn(OH)_2$	53	90–95	10	150	98–99	5	2	4–9
$CuCO_3$	51	60–65	10	140	92–96	4	2.5	28–32
$MnCO_3$	45	8–10	10	150	96–98	4	2.5	85–88
$NiCO_3$	37	75–80	10	100	93–98	5	2	13–18
NiS	47	53–56	14	100	92–95	7	2	40–42
$Ni_3(PO_4)_2$	32	22–25	14	100	92–95	7	2	70–73
$Cu_3(PO_4)_2$	37	65–72	10	120	98–99	5	2	26–34
$Ca_3(PO_4)_2$	8	14–16	10	80	97–99	5	2	83–85
$\sum M(OH)(PO_4)$	30	50–60	10	95	98–99	5	2	38–49

natures with widely varied molecular weights, charge densities, working pHs and temperatures of the medium, as well as weight fractions of the main substance. It is suggested that the use of novel flocculants as individual additives will intensify the process of electroflotation removal of dispersed metal phases.

The practical use of flocculants in electroflotation was preceded by a search for the most effective and universal polyelectrolytes. More than a hundred of domestic and foreign commercial polyelectrolytes, such as poly(epichlorohydrin-co-dimethylamines), poly(diallyldimethylammonium chlorides), polyacrylamides and mixtures (copolymers), including 10% of nonionogenic, 40% of cationic, and 50% of anionic polyelectrolytes.

Of the polyelectrolyte tested as flocculants, the best results were obtained with Superfloc polyelectrolytes which, what is more, showed a low toxicity.

It was found that the flocculating power of polyelectrolytes of the same ionic type increases with increasing molecular weight and charge density of the polyelectrolyte and scarcely depends on the value and sign of the ζ-potential of particles to be floated. A high flocculating power is characteristic not only of polyelectrolytes whose macroions have the sign opposite to the sign of the particle ζ-potential, but also polyelectrolytes whose charge has the same sign as the sign of the particle ζ-potential. This mostly relates to anionic polyelectrolytes.

As the charge density of the polyelectrolyte increases, the electroflotation recovery of the dispersed phase increases, and polyelectrolyte consumption much decreases.

In the long run, the role of polyelectrolytes is to ensure particle aggregation to form larger particles which are better entrapped by gas bubbles. One more essential advantage of polyelectrolytes for electroflotation consists in that they favor formation of finer bubbles and their faster floating up. Therefore, by increasing current one can increase the volume concentration of bubbles in the dispersion medium, thereby increasing the probability of their collision with particles to be floated, and, as a result, intensify the electroflotation removal of the dispersed phase, not destroying the formed aggregates.

The major improvements in the electroflotation purification of wasterwater from suspensed particles, obtained due to the use of specially selected polyelectrolytes and optimization of the working conditions of the electroflotation process involving polyelectrolytes include an up to 5 times reduction of the process time, increase of the recovery to up to 99%, extension of the concentration range of contaminants in the raw wastewater from 10–250 to 2–1500 mg/L, reduction of the working volume current densities by 15–25%, etc.

Table 4 presents the results of research in the electroflotation removal of the dispersed phase from wastewaters in the presence of flocculants (volume current density 0.05–0.15 A/L, initial concentration of the dispersed phase 10–150 mg/L).

It was shown that the flocculation of dispersed particles in the presence of polyelectrolytes may occur under the action of electrostatic forces decreasing the particle ζ-potential both in absolute value and by a bridging mechanism. In cases where the charge of polyelectrolyte macroions coincides in sign with the particle ζ-potential, the polyelectrolyte adsorption process occurs by an ion-exchange mechanism, i.e. ions in the diffuse part of the electric double layer near the particle surface are expelled by ionized polylectrolyte groups bearing the same charge, as evidenced by the results of in-solution isotope labeling experiments.

CONCLUSIONS

Our experiments showed that the ionic composition of the aqueous medium affects the surface characteristics of the dispersed phase of sparingly soluble non-ferrous and heavy metal compounds (ζ-potential, solubility, size, and dispersity) and thus affects the efficiency of their recovery by the electroflotation method.

Intensification and efficiency enhancement of the electroflotation process can be reached by varying the surface characteristics of the dispersed phase by varying the pH and redox potential of the medium and using reagents and water-soluble polyelectrolytes of certain types and functionalities under conditions optimal for their work.

The results of the present research have a practical interest for improving technologies of removal of the dispersed phase of sparingly soluble non-ferrous and heavy metal compounds from wastewaters.

REFERENCES

1. *Gosudarstvennyi doklad "O sostoyanii i ispol'zovanii vodnykh resursov Rossiiskoi Federatsii v 2010 godu"* (On the Use of Water Resources in the Russian Federation in 2010 State Report), Moscow: Priroda, 2011.
2. *Gosudarstvennyi doklad "O sostoyanii i ob okhrane okruzhayushchei sredy Rossiiskoi Federatsii v 2010 godu"* (On Environmental Protection in the Russian Federation in 2010 State Report), Moscow: Tsentr Mezhdunarodnykh Proektov, 2011.
3. Kolesnikov, V.A., Il'in, V.I., Kapustin, Yu.I., et al., in *Elektroflotatsionnaya tekhnologiya ochistki stochnykh vod promyshlennykh predpriyatii* (Electroflotation Technology of Industrial Wastewater Treatment), Moscow: Khimiya, 2007.
4. Il'in, V.I., *Elektroflotatsiya v protsessakh vodopodgotovki, ochistki, obezzarazhivaniya stochnykh vod i obrabotki osadkov* (Electroflotation in Wastewater Pretreatment, Purification, and Detoxification and Precipitate Treatment), Moscow: Mendeleev Ross. Khim. Tekhnol. Univ., 2008.
5. *Nalco Water Handbook*, New York: McGraw-Hill, 1987.