

THE pH AND MEDIUM COMPOSITION IMPACT ON THE EFFICIENCY OF ELECTROFLOTATION-BASED EXTRACTION OF SLIGHTLY SOLUBLE IRON, CHROMIUM AND MANGANESE COMPOUNDS FROM WATER SOLUTIONS AND PHYSICAL-CHEMICAL PROPERTIES OF THESE COMPOUNDS

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ABSTRACT

The study demonstrates the pH and solution ion composition impact on the average hydrodynamic diameter d_m and electrokinetic potential (ζ -potential) of the dispersed phase of slightly soluble ferrous metals compounds. We examined formation dispersed phases of slightly soluble Fe (III), Cr (III), and Mn (II) compounds in the presence of OH^- , CO_3^{2-} , PO_4^{3-} ions as precipitating agents and anionic, cationic, and non-ionic flocculating agents. The electroflotation-based extraction of slightly soluble ferrous metals compounds was found to be directly linked to dispersity and electrokinetic potential of particles, that depend on acidity and ionic medium composition. The maximal hydrodynamic diameter of dispersed phases of the slightly soluble Fe (III), Cr (III), and Mn (II) compounds were observed at isoelectric point and corresponded with pH value of the minimal dispersed phase solubility. In this case, electroflotation-based extraction was more efficient, the iron (III), manganese (II), and chromium (III) removal α reached 98, 96, and 83 %, respectively. Cationic flocculating agent additives increased the iron, manganese, and chromium extraction up to 99, 98, and 94 %, respectively. If carbonate and phosphate ions were added, the electrokinetic potential of compounds of all examined slightly soluble metals changed to negative values: $-(12-19)$ mV in the presence of CO_3^{2-} ions and $-(35-43)$ mV in the presence of PO_4^{3-} ions. This shift hindered coagulation and decreased electroflotation-based extraction of the dispersed phases, especially in case of manganese compounds ($\alpha \leq 10\%$). Cationic and non-ionic flocculating agents additives balanced the high negative charge of the dispersed phases of slightly soluble ferrous metals compounds, enlarged the removal up to 98 % depending on the dispersed phase and flocculating agent.

Introduction

Metal ions are among the most widely distributed contaminants appearing in the water as a result of activity of different industrial enterprises. Ferrous metals occupy the especial place among the metals presented in waste waters. Usually ferrous metals include iron and manganese, sometimes also chromium [1]. Cleaning degree of waste waters with removing compounds of ferrous metals is determined by preset standard regulations and depends on kind of a water object as well as of a region where cleaned waste waters appear. Maximal admissible concentration (MAC) of water object of drinking destination makes (in correspondence with RF legislation) 0.1 mg/l for Fe (totally); 0.05 mg/l for chromium (VI); 0.5 mg/l for chromium (III); 0.1 mg/l for manganese (totally) [2]. In general it meets the requirements of WHO, EC and USEPA [3].

Ferrous metals are widely used in many industries, i.e. in metallurgy during steel melting. Ferromanganese is used for steel deoxidation in order to remove excessive oxygen from steels [4, 5]. Chromium and manganese additives are used in melting of high-strength steels for manufacture of tunneling and drilling machines as well as steels with increased corrosion and heat resistance [6, 7].

Chromium and manganese are also widely used in galvanic-chemical production, while manganese dioxide – in production of manganese-zinc batteries [8]. High-toxic chromium (VI) salts can be applied for manufacture of corrosion-resistant decorative coatings. The processes of acidic pickling of the components for scale and corrosion removal are typical both for galvanic and metallurgical technological processes. Thereby activity of metallurgical, galvanic-chemical and metal processing plants leads to forming of large amount of liquid metal-containing wastes and waste waters which contain ions and soluble compounds of Fe, Cr and Mn in different valence states.

Actuality of cleaning of waste waters with removal of ferrous metals ions is stipulated by not only ecological aspects, but also by economical ones. Manganese is a raw material in very short supply in Russian Federation [9] and its extraction from waste waters is considered as the important practical task. Chromium compounds also should be recycled with obtaining valuable components, i.e. chromium (III) based catalysts.

Electroflotation is one of the modern and prospective methods for cleaning of waste waters with metal ions removal [10, 11]. It is economically efficient and expedient for initial concentrations of extracted metal cations from 10

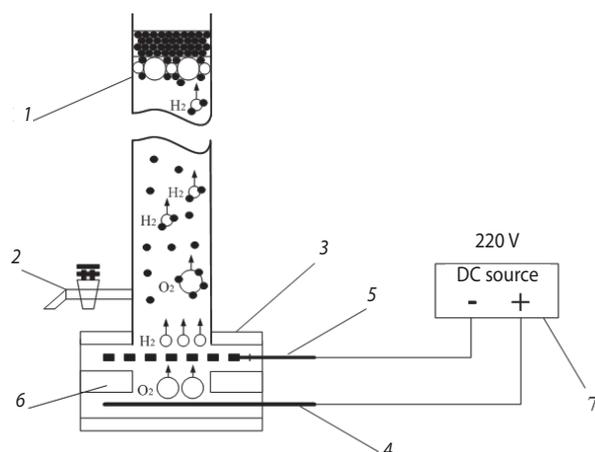


Fig. 1. The scheme of labour electroflotator:

1 – column; 2 – gate for taking samples;
3 – electrode block; 4 – anode; 5 – cathode;
6 – rubber packing; 7 – direct current source

to 100 mg/l; use of flocculating agents allows to expand this range to 300 mg/l [12].

Electroflotation process can be realized only in the case when contaminating components in the solution are presented in the form of slightly soluble compounds or are sorbed during flotation on other slightly soluble compounds which are presented in the solution [13]. Extraction of metal ions as hydroxides via pH variation by alkali in the solutions is an efficient and simple method of their transition in the form of slightly soluble compounds. It is known that medium pH has an impact on solubility and size of oxides and hydroxides (d_{av} , μm), charge of their surface (ζ -potential, mV), efficiency of conduction of coagulation processes in general and forming of stable flotation complexes [14, 15].

The aim of this research is a study of the impact of dispersion parameters and electrokinetic potential of slightly soluble Fe (III), Cr (III) and Mn (II) with different nature on efficiency of their joint extraction from water and electrolytic solutions via electroflotation method.

The technique of experiment

Solutions containing ferrous metals ions – Fe (III), Cr (III) and Mn (II) – were the objects of this research. The metal ions were transferred in dispersed state due to variation of medium pH or use of different flocculating agents, such as NaOH, Na_2CO_3 and Na_3PO_4 . Mass relation between metal and ion – flocculating agent $[\text{Me}^{n+}]/[\text{An}^{x-}]$ made 1/1,5. Correction of pH values in the solutions was realized by alkali (NaOH) adding. pH control was conducted using I-160 MI ion meter.

The process of electroflotation extraction of slightly soluble metal compounds was conducted in non-flowing device with 0.5 l volume, having insoluble electrodes. Anode was presented by titanium plate with oxide ruthenium-titanium coating (ORTA), while cathode was a net of stainless steel with cell size 0.5×0.4 mm and wire thickness 0.3 mm. The square of anode and cathode was identical (0.07 dm^2). The scheme of this device is displayed on the **fig. 1**. Volumetric current density for realization of electroflotation process

made 0.2–0.4 A/l. This process was conducted in 0.01 M solution of SO_4^{2-} in order to increase electric conductivity. Filtration of solution was executed with use of ashless filters with pores diameter 2–3 μm .

Metal extraction degree from water solutions α (%) was calculated as relationship between difference of initial and final metal content in solution (from one side) and its initial content (from other side), summarized in dispersed and ion forms:

$$\alpha = [(C_0 - C_\tau) / C_0] \cdot 100\%.$$

Study of the impact of the nature of flocculating agents on dispersion parameters, electrokinetic potential and electroflotation activity of the particles of slightly soluble metal compounds was conducted in the presence of flocculating agents of Superfloc (Kemira) series, of anionic (A-137), cationic (C-496) and non-ionic (N-300) types. Molar charge of flocculating agents made (%) 41.6; 55 and 0, while molecular weight – 5; 3.8 and 3 mln respectively (according to the producer's data).

Measurement of mass concentration of metals in the solutions was conducted according to the standard technique on atomic absorbing spectrometer KVANT-AFA. The average hydrodynamic diameter of dispersed phase particles (d_{av} , μm) was determined by measuring correlating deviation function of diffused light intensity, using laser analyzer «Photocor Compact Z». Measuring of electrokinetic potential (ζ , mV) of the particles was based on measurement of electrophoretic mobility of liquid particles and was also conducted in «Photocor Compact Z» analyzer.

The results of theoretical calculations

1. Impact of medium pH on physical-chemical parameters and electroflotation activity of slightly-soluble compounds of ferrous metals

The impact of medium pH on solubility of Fe (III), Cr (III) and Mn (II) compounds was examined via filtration using ashless paper filters with 2-3 μm hole diameter. Relationship between residual concentration of examined metals and pH is presented on the **fig. 2**.

It was revealed that Fe^{3+} ions transferred by 99 % in the form of slightly soluble compounds just within the pH 4–5 interval. Minimal residual Fe concentration in filtrate does not exceed 0.4 mg/l for pH 7. Forming of slightly soluble Cr (III) compounds in water solutions is possible after pH reaches 5.0. Minimal residual Cr (III) concentration in filtrate is observed at pH 8.0 and makes 0.05 mg/l (more than 99.9 % of chromium transfers in the form of slightly soluble compounds). pH increase up to 9 and higher leads to severe rise of dispersed phase solubility, what can be explained (according to the “potential – pH” equilibrium diagram data) by dissolution of chromium hydroxide $\text{Cr}(\text{OH})_3$ in alkali medium with forming of chromate ions CrO_4^{2-} [16]. Forming of slightly soluble Mn compounds is possible in a strong alkali me-

dium; if $\text{pH} < 8$, manganese is presented in the solution mainly as non-linked ions. Maximal content of dispersed phase is observed in the interval $\text{pH} 10.5\text{--}11.5$, residual concentration does not exceed 0.06 mg/l . Technical literature data testify that Mn^{2+} can be precipitated as $\text{Mn}(\text{OH})_2$ hydroxide. At the same time, white sediment quickly oxidizes in oxygen presence to a brown compound $\text{Mn}(\text{III})$ – hydrate $\text{Mn}_2\text{O}_3 \cdot \text{MnO}(\text{OH})$ [16]. It was established that potential of platinum electrode in the solution containing MnSO_4 as well as 0.01 M SO_4^{2-} as phone electrolyte, lowers from -140 to -355 mV relating to the normal hydrogen equivalent when pH increases from 9 to 11. Existence of non-soluble Mn compounds with oxidation degree from $+2$ to $+4$: $\text{Mn}(\text{OH})_2$, Mn_3O_4 , Mn_2O_3 is possible in alkali area in correspondence with the equilibrium diagram “potential – pH ” for the system “manganese – water” [17].

X-ray phase analysis of flotation concentrates which were prepared without preliminary drying displayed that existence of manganese hydroxides and manganese hydrated (II) oxides - $\text{Mn}(\text{OH})_2$ or $\text{MnO} \cdot \text{H}_2\text{O}$ (pyrochroite) is possible in the system containing SO_4^{2-} ions. Flotation concentrate in the presence of oxidizer ($\text{S}_2\text{O}_3^{2-}$) is presented by two phases – $\gamma\text{-Mn}_2\text{O}_3$ and Mn_3O_4 , what confirms experimental data obtained on the base of the diagram “potential – pH ”. Flotation concentrates that were prepared on the base of $\text{Fe}(\text{III})$ are presented by hydroxides $\text{Fe}(\text{OH})_3$ and $\text{Cr}(\text{OH})_3$.

Data about solubility of dispersed phase allow to make a conclusion that the examined metals can be extracted out of solution if they are there together, and after extraction they will be presented as individual compounds. This is valid for consecutive extraction of Fe, Cr and Mn compounds within pH ranges 4–5; 7–8 and 10–11 respectively.

It is known that efficiency of electroflotation process depends not only on residual concentration of metals ions in the solution, but also on size of particles in dispersed phase, which according to [18] depends on surface charge of particles and is maximal in electric neutral area. In this connection, investigations of the impact of medium pH on the values of ζ -potential for dispersed slightly soluble $\text{Fe}(\text{III})$, $\text{Cr}(\text{III})$ and $\text{Mn}(\text{II})$ compounds were conducted. These investigations were executed in the solutions with low and increased content of sodium sulphate ($0,001$ and $0,01 \text{ M SO}_4^{2-}$). The solution with low salt content ($0,001 \text{ M SO}_4^{2-}$) allows to reveal isoelectric area, where the most complete removal of dispersed phase particles is possible [19]. The solution $0,01 \text{ M SO}_4^{2-}$ characterizes the system that is proximate to real waste waters and that contains not only salt components of extracted metal, but also essential amount of sulphate being presented in composition of a lot of electrolytes.

It was found out that re-charging of surface of particles of slightly soluble $\text{Fe}(\text{III})$, $\text{Cr}(\text{III})$ and $\text{Mn}(\text{II})$ compounds occurs in the solution $0,01 \text{ M SO}_4^{2-}$ (fig. 3).

pH value in the isoelectric point (IEP) makes 6.2 for slightly soluble compounds of $\text{Fe}(\text{III})$, $7,7$ for $\text{Cr}(\text{III})$ and 9.4 for $\text{Mn}(\text{II})$. At the moment of dispersed phase forming, slightly soluble compounds of chromium (III) are characterized by high positive charge ($+27 \text{ mV}$)m which is rather higher than a charge of $\text{Fe}(\text{III})$ and $\text{Mn}(\text{II})$ dispersed phases

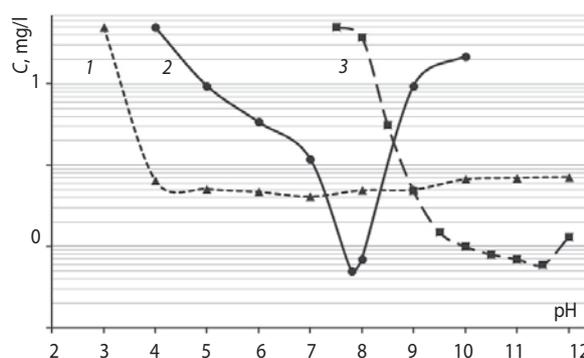


Fig. 2. Logarithmic relationship between residual concentration of metal ions in filtrate and medium pH : 1 – $\text{Fe}(\text{III})$, 2 – $\text{Cr}(\text{III})$, 3 – $\text{Mn}(\text{II})$, $C_{\text{init}} \text{Me}^{n+} = 50 \text{ mg/l}$

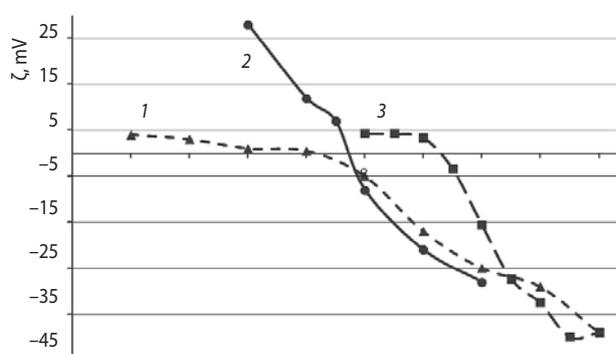


Fig. 3. Relationship between ζ -potential of the particles of slightly soluble compounds of ferrous metals and pH media in $0,001 \text{ M SO}_4^{2-}$: 1 – $\text{Fe}(\text{III})$, 2 – $\text{Cr}(\text{III})$, 3 – $\text{Mn}(\text{II})$, $C_{\text{init}} \text{Me}^{n+} = 50 \text{ mg/l}$

($+3\text{--}5$) mV respectively). Rise of medium pH is accompanied by re-charging of dispersed phase particles, lowering of ζ -potential to $-(25\text{--}40) \text{ mV}$ for all investigated systems.

The value of pH in the isoelectric point (IEP) is equal to 6.2 for slightly soluble $\text{Fe}(\text{III})$ compounds, 7.7 for $\text{Cr}(\text{III})$ and 9.4 for $\text{Mn}(\text{II})$. At the moment of dispersed phase forming, slightly soluble compounds of chromium (III) are characterized by high positive charge ($+27 \text{ mV}$) what is rather higher than dispersed phases charges for $\text{Fe}(\text{III})$ and $\text{Mn}(\text{II})$ – ($+3\text{--}5$) mV respectively). Rise of medium pH finalizes in recharging of the particles of dispersed phase, decrease of ζ -potential to $-(25\text{--}40) \text{ mV}$ for all examined systems.

If solutions contain excessive background ($0,01 \text{ M SO}_4^{2-}$), charge of the particles of dispersed phase for slightly soluble compounds of $\text{Fe}(\text{III})$ and $\text{Mn}(\text{II})$ is negative along whole pH interval; at the same time, during forming of dispersed phase it is within the interval (5–10) mV . Charge of slightly soluble chromium (III) compounds in pH interval 6–7 is low positive ($+3\text{--}5$) mV . This fact can be explained by high sorption activity of SO_4^{2-} ions on lately formed particles of dispersed phase [20]. Increase of pH value for solutions containing M SO_4^{2-} up to 8–10, leads to lowering of the electrokinetic potential values down to $-(25\text{--}40) \text{ mV}$. Decrease

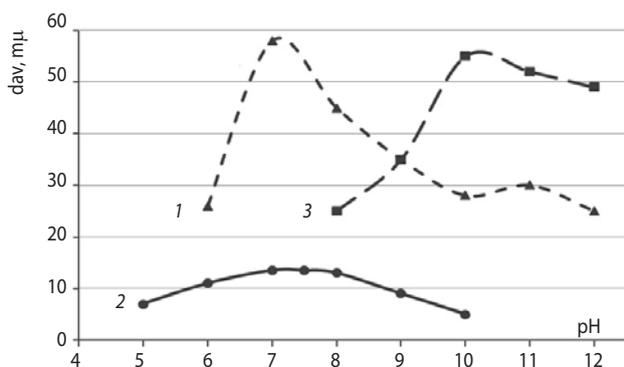


Fig. 4. Relationship between average hydrodynamic diameter d_{av} of particles of slightly soluble compounds of ferrous metals and medium pH in 0,01 M SO_4^{2-} :
 1 – Fe (III), 2 – Cr (III), 3 – Mn (II),
 $C_{init} Me^{n+} = 50 \text{ mg/l}$

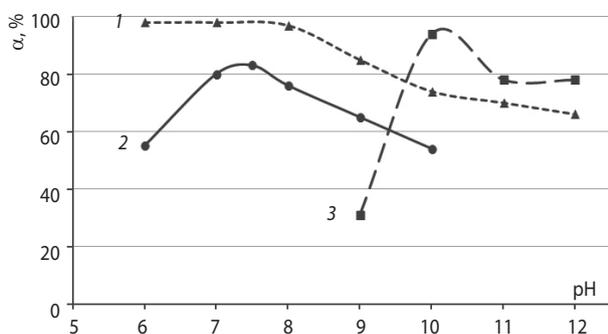


Fig. 5. Relationship between degree of electroflotation extraction of the particles of slightly soluble ferrous metals compounds and medium pH in 0,01 M SO_4^{2-} :
 1 – Fe (III), 2 – Cr (III), 3 – Mn (II). Process duration $\tau_{ef} = 10 \text{ min}$, $C_{init} Me^{n+} = 50 \text{ mg/l}$

of the values of ζ -potential in alkali area can be explained by sorption of excess of OH^- ions on dispersed phase of Fe and Mn compounds, as well as of CrO_4^{2-} chromate ions on dispersed phase of solving chromium (III) hydroxide.

The conducted researches of relationships between sizes of particles of dispersed phase of slightly soluble compounds of Fe (III), Cr (III) and Mn (II) (from one side) and medium pH (from other side) displayed that average hydrodynamic

diameter of particles of slightly soluble compounds of Fe (III) and Cr (III) within pH interval 7–8 passes the maximal value which is equal to 58 and 14 μm respectively. The average hydrodynamic diameter of Mn (II) compounds passes the maximal value at pH 10 and reaches 55 μm (fig. 4).

Thereby, at the first stage of this work we displayed the impact of medium pH on physical-chemical parameters of dispersed phase of slightly soluble compounds of Fe (III), Cr (III) and Mn (II). It can be mentioned that size of dispersed phase depends directly on electrokinetic potential of dispersed phase and its solubility.

The process of electroflotation cleaning of solutions with removal of slightly soluble compounds of Fe (III), Cr (III) and Mn (II) within pH interval 6–12 is examined and displayed on the fig. 5.

It is shown that electroflotation process passes with maximal efficiency in the area of minimal solubility of dispersed phase, which coincides with the isoelectric point and maximal hydrodynamic diameter of dispersed phase. Thereby, extraction degree of slightly soluble Fe compounds makes 97–98 % for pH equals to 10. Slightly soluble Cr (III) compounds are extracted with minimal efficiency: α does not exceed 85 % within pH interval 7–8.

The obtained data manifest on existence of principal possibility to conduct selective extraction and separation of slightly soluble Fe and Cr compounds with Mn compounds, what is interesting from practical point of view.

The impact of solubility, dispersion parameters and ζ -potential of the particles of slightly soluble compounds of Fe (III), Cr (III) and Mn (II) on their electroflotation activity within pH interval 6–12 was analyzed (table 1).

It was shown that efficiency of electroflotation extraction of slightly soluble Fe (III) and Cr (III) compounds depends on the value of ζ -potential of the particles of dispersed phase. The most extracting efficiency was displayed for the particles with charge close to 0, and the same area is characterized by minimal values of residual concentrations. This effect was stipulated by more easy passing of coagulating processes between the particles in solution and more easy interaction in the system “dispersed phase – oxygen/hydrogen bubbles” [21, 22]. Efficiency of electroflotation extraction of slightly soluble compounds of Cr (II) is rather less that efficiency of extraction of Fe (III) compounds, with extraction degree

Table 1. The impact of solubility, dispersion parameters and ζ -potential of the particles of slightly soluble compounds of Fe (III), Cr (III) and Mn (II) on their electroflotation activity within pH interval 6–12

pH	Dispersed phase											
	Fe (III)				Cr (III)				Mn (II)			
	$C_{res}, \text{ mg/l}$	$d_{av}, \mu\text{m}$	$\zeta, \text{ mV}$	$\alpha, \%$	$C_{res}, \text{ mg/l}$	$d_{av}, \mu\text{m}$	$\zeta, \text{ mV}$	$\alpha, \%$	$C_{res}, \text{ mg/l}$	$d_{av}, \mu\text{m}$	$\zeta, \text{ mV}$	$\alpha, \%$
6	0,47	26	1	98	3,4	7	5	55	–	–	–	–
7	0,41	58	0	98	1,2	11	2,3	80	–	–	–	–
8	0,49	45	–5	97	0,05	14	1	76	37	25	–3,6	<10
9	0,5	35	–17	85	0,07	9	–11	65	0,49	35	–2,5	31
10	0,67	30	–25	74	9,4	5	–27	54	0,1	55	–6	94
11	0,7	28	–29	70	21,9	<1	–32	<10	0,07	52	–27	78
12	0,71	25	–39	66	–	–	–	–	0,13	49	–35	76

$C_{init} Me^{n+} = 50 \text{ mg/l}$, $i_v = 0,2-0,4 \text{ A/l}$; $\tau_{ef} = 10-15 \text{ min}$, background – 0,01 M SO_4^{2-}

Table 2. The impact of nature of a deposition ion and flocculating agent on dispersion parameters, ζ -potential and electroflotation activity of the particles of slightly soluble compounds of Fe (III), Cr (III) and Mn (II)

Deposition ion		Fe (III), pH 7–8			Cr (III), pH 7–8			Mn (II), pH 10–11		
Nature of flocculating agent		d_{av} , μm	ζ , mV	α , %	d_{av} , μm	ζ , mV	α , %	d_{av} , μm	ζ , mV	α , %
OH ⁻	–	58	0	98	14	1	83	53	–12	96
	Anionic	112	–15	95	49	–25	90	45	–28	94
	Cationic	105	+3	99	53	+8	94	98	–11	98
	Non-ionic	92	–2	99	12	–2	68	88	–14	96
CO ₃ ²⁻	–	55	–15	92	11	–12	65	47	–19	<10
	Anionic	92	–30	95	42	–32	72	94	–18	96
	Cationic	122	–6	98	55	–5	95	107	–18	97
	Non-ionic	115	–10	98	35	–8	92	101	–14	96
PO ₄ ³⁻	–	43	–35	88	8	–28	32	43	–33	<10
	Anionic	105	–41	90	26	–35	64	96	–43	92
	Cationic	93	–24	92	34	–17	89	121	–34	95
	Non-ionic	112	–22	80	38	–20	85	113	–34	91

$C_{\text{init}}\text{Me}^{n+} = 50 \text{ mg/l}$, $C_{\text{floc}} = 2 \text{ mg/l}$, $i_v = 0.2\text{--}0.4 \text{ A/l}$; $\tau_{\text{ef}} = 10\text{--}15 \text{ min}$, background – 0.01 M SO_4^{2-}

80 and 98 % respectively and with pH 7, what is caused by dispersion parameters of extracting slightly soluble compounds. Electroflotation behaviour of dispersed phase of slightly soluble compounds of Mn (II) is firstly determined by dispersion parameters and solubility of manganese compounds. In this connection electroflotation process passes with maximal efficiency with pH 10 and α reaches 94 %.

It should be noted that colour and structure of flotation complexes of Mn (II) dispersed phase vary during electroflotation from light brown in the beginning of flotation to dark reddish 10–15 min later. We can suggest that oxygen which is extracting on the electrode, acts as oxidizer and, as a result, Mn(OH)₂ transits to the form of oxides $\gamma\text{-Mn}_2\text{O}_3$ and Mn₃O₄.

2. Impact of nature of flocculating agents on physical-chemical parameters and electroflotation activity of slightly-soluble compounds of ferrous metals

Waste waters and processed technological solutions of galvanic-chemical, metallurgical and metal processing production facilities can contain substantial amount of CO₃²⁻, PO₄³⁻ and other ions, able to form hardly soluble compounds with ferrous metal ions. In this case waste waters will contain not only hydroxides and hydrated oxides, but also less soluble metal phosphates and carbonates as well as other compounds with complicated composition, which are subjected to electroflotation extraction from water solutions with significant difficulties [23, 24]. In this connection, the impact of nature of different deposition ions (OH⁻, CO₃²⁻, PO₄³⁻) as well as flocculating agents (of anionic, cationic and non-ionic types) on surface properties and electroflotation activity of the particles of slightly soluble compounds of Fe (III), Cr (III) and Mn (II) is examined. The obtained data are presented in the **table 2**.

It was shown that adding of carbonate and phosphate ions in the solutions containing Fe³⁺ ions leads to decrease of extraction degree by 6–10 % due to shifting of electrokinetic potential in the area of negative values (–15–35) mV. At the same time the values of Fe (III) phosphate and hydroxide solubility

($\lg K_{\text{Sp}}\text{FePO}_3 = -21.89$, $\lg K_{\text{Sp}}\text{Fe(OH)}_3 = -37.5$) show that competition of these ions will finalize in forming of slightly soluble phosphates in solution. Fe (III) and Cr (III) carbonates in solutions are completely hydrolyzed. Adding of carbonate ions in the system containing Cr³⁺ ions suppresses electroflotation process. So, if concentration of carbonate ions exceeds 50 g/l, extraction degree is not more than 47 %. This impact can be firstly explained by increase of chromium hydroxide solubility in products of soda hydrolysis with forming of soluble chromium hydrocomplexes, e.g. [Cr(OH)₄]⁻ [25].

Comparing the values of logarithms of productions of manganese carbonate and hydroxide solubility ($\lg K_{\text{Sp}}\text{MnCO}_3 = -9.41$, $\lg K_{\text{Sp}}\text{Mn(OH)}_2 = -12.8$) [26], it can be concluded that manganese carbonate solubility is a little higher than manganese hydroxide solubility. Thereby variation of flakes colour from white to dark brown can be explained by variation of the chemical dispersed phase. X-ray analysis displayed that the product obtained as a result of manganese electroflotation extraction from solution containing MnSO₄ and Na₂CO₃, is dual-phase one and contains both MnCO₃, as well as Mn₃O₄ (Mn·Mn₂O₃); it should be mentioned that carbonate ions are presented excessively in this solution relating to Mn ions within pH interval 10–10.5. The value of logarithm of production of manganese phosphate solubility is rather smaller than the value of logarithm of production of manganese hydroxide solubility ($\lg K_{\text{Sp}}\text{Mn}_3(\text{PO}_4)_2 = -36.21$) [26], i.e. dispersed phase is presented only by slightly soluble manganese (II) phosphate.

It is shown that introduction of flocculating agents of cationic and non-ionic types in the examined solutions allows to compensate high negative charge of dispersed phase of ferrous metals slightly soluble compounds in the presence of phosphate and carbonate ions, to increase dispersed phase and to rise extraction degree for such compounds, what corresponds well with previously obtained data [27].

In this case, surface charge of forming electrolysis gases, which is negative for hydrogen and positive for oxygen [12], also has the impact on efficiency of electroflotation process. The data presented previously by

the authors displayed that if charges of a particle and gas bubble are contrary, it can be explained by zero charge for one of them. Then forming of flotation complex will pass effectively and maximal degree of their electroflotation extraction is reached [12, 20]. Negatively charged hydrogen provides the most efficient extraction of positively charged particles of dispersed phase of contaminants, while positively charged oxygen provides the same operation with negatively charged particles. If a particle has high negative ζ -potential, forming of flotation complex is hindered and flotation efficiency is decreased severely. Low flotation activity of phosphates and carbonates of the examined metals in comparison with hydroxides can be considered as the experimental proof. At the same time it was revealed that the most efficient extraction of dispersed phase is observed in the presence of flocculating agents of cationic and non-ionic types. In this case surface charge of particles is more positive than in solutions without flocculating agents, or in the presence of flocculating agent of anionic type. It provides more easy interaction of the particles with fine-dispersed hydrogen bubbles (20–40 μm) with negative charge [12, 28] and supports to form stable flotation complexes, intensifying thereby electroflotation process in general.

Conclusions

It is shown that increase of medium pH leads to passing through extremal point for the values of average hydrodynamic diameter of dispersed phase particles of slightly soluble compounds of Fe (III), Cr (III) and Mn (II). This extremal point is equal to more than 50 μm for Fe (III) and Mn (II) compounds and 14 μm for Cr (III) compounds. At the same time electrokinetic potential is located in the area of the isoelectric point or low negative values of potentials within the range (0–(–6)) mV. Maximal efficiency of electroflotation process is observed in these conditions: extraction degree of dispersed phase reaches 96–98 % for Fe (III) and Mn (II) compounds and 88 % for Cr (III) compounds.

It was established that nature of dispersed phase is the main factor having the impact on efficiency of electroflotation process. The particles formed during introduction of OH^- ions in the solution are extracted with maximal efficiency; it is connected with maximal absolute value of ζ -potential. Extraction of dispersed phase in the presence of carbonate ions is hindered. This effect is probably stipulated by the nature of dispersed phase, which presents itself hydroxides of the researched metals being a base for sorption of CO_3^{2-} ions. Owing to it, electrokinetic potential moves in the area with more negative values – (12–19) mV and size of dispersed phase decreases by 10–15 % in comparison with solutions containing OH^- ions. Lowering of efficiency of electroflotation process in the presence of PO_4^{3-} ions is caused by severe decrease of ζ -potential of dispersed phase for slightly soluble phosphates (–(35–43) mV). Extraction degree reduces along the following row: Fe (III) phosphates, Cr (III) phosphates, Mn (II) phosphates, while extraction degree of manganese phosphate does not exceed 10 %.

Introduction of flocculating agents in the solutions containing phosphate ions and carbonate ions allows to rise extraction degree first of all due to enlargement of dispersed phase of extracting compounds. Flocculating agent of cationic type is recognized as the most efficient one. Introduction of cationic flocculating agent in the examined solutions compensates negative charge of extracting metals compounds, what causes intensification of coagulation processes and electroflotation process in general.

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REFERENCES

- Ershova E. V., Zublyuk E. V., Krishtopa O. A., Lapteva A. M., Renizova L. I., Rudnev A. V. Mineral and raw material base of ferrous and alloying metals in Russia. *Razvedka i okhrana nedr.* 2016. No. 9., pp. 88–95.
- Sanitary Rules and Regulations 2.1.4.1074-01. Drinking water. Hygienic requirements to water quality from centralized systems of drinking water supply. Quality control. 90 p.
- Water Framework Directive (WFD) 2000/60/EC: Directive 2000/60/EC of the European Parliament and of the Council of 23 October 2000 establishing a framework for Community action in the field of water policy. 73 p.
- Vdovin K. N., Feoktistov N. A., Sinitkiy E. V., Gorlenko D. A., Durov N. A. Melting of high-manganese steel in the electric arc furnace. Technology. Message 1. *Izvestiya veshnikh uchebnykh zavedeniy. Chernaya metallurgiya.* 2015. Vol. 58. No. 10. pp. 735–739.
- Soifer V. M. Deoxidation of acidic carbon electric steel by ferromanganese in a ladle. *Metallurgiya mashinostroeniya.* 2020. No. 5. pp. 2–5.
- Kolpishon E. Yu., Ivanova M. V., Shitov E. V. Nitrogen-containing steels with equivalent composition. *Chernye metally.* 2007. No. 2. pp. 10–12.
- Gorynin I. V., Malyshevskiy V. A., Kalinin G. Yu., Mushnikov S. Yu., Bannykh O. A., Blinov V. M., Kostina M. V. Corrosion-resistant high-strength nitrogen steels. *Voprosy materialovedeniya.* 2009. No. 3 (59). pp. 7–16.
- Aleksandrov V. I., Koshel A. A., Yudin V. S. Manganese-zinc elements. *Innovatsii v nauke.* 2017. No. 4 (65). pp. 62–65.
- Beloglazov I. N., Zyryanova O. V., Saltykova S. N. Processing of manganese-bearing raw materials with manufacture of high-quality product. *Zapiski gornogo instituta.* 2013. Vol. 12. pp. 273–277.
- Mohtashami R., Shang J. Q. Electroflotation for Treatment of Industrial Wastewaters: A Focused Review *Environmental Process.* 2019. pp. 1–29.
- Kuokkanen V., Toivo K., Rämö J., Lassi U. Recent Applications of Electrocoagulation in Treatment of Water and Wastewater – A Review. *Green and Sustainable Chemistry.* 2013. No. 3. pp. 89–121.
- Kolesnikov V. A., Ilyin V. I., Kapustin Yu. I. et al. Electroflotation technology for cleaning of waste waters at industrial works. Moscow, Khimiya. 2007. 304 p.
- Romanov A. M. Electroflotation in Waste Water Treatment: Results and Perspectives. In: Gallios G. P., Matis K. A. (eds) Mineral Processing and the Environment. NATO ASI Series (Series 2: Environment). Springer, Dordrecht. 1998. Vol. 43. pp. 335–360.
- Brodskiy V. A., Gaidukova A. M., Kolesnikov V. A., Ilyin V. I. Impact of medium pH on physical-chemical parameters and efficiency of electroflotation extraction of slightly soluble compounds of ferrous metals from water solutions. *Khimicheskaya fizika.* 2017. Vol. 36. No. 8. pp. 56–63.
- Kokarev G. A., Kolesnikov V. A., Kapustin Yu. I. Intra-phase appearances on separation boundary oxide/solution in electrolyte. Moscow, Izd. Tsentr RKhTU. 2004. 72 p.

16. Poling L. General chemistry. Moscow, Mir. 1964. 583 p.
17. Atlas of Eh-pH diagrams. Intercomparison of thermodynamic databases. National Institute of Advanced Industrial Science and Technology Research Center for Deep Geological Environments. Naoto TAKENO. May 2005. 285 p.
18. Amanbaev T. R. Simulation of flotation process in dispersed systems. *Teoreticheskie osnovy khimicheskoy tekhnologii (TOKhT)*. 2014. Vol. 48. No. 2. p. 203.
19. Belkacem M., Khodir M., Abdelkrim S. B. Treatment characteristics of textile wastewater and removal of heavy metals using the electroflotation technique. *Desalination*. 2008. Vol. 228, Nos. 1–3. p. 245.
20. Brodskiy V. A., Kolesnikov V. A., Gibin A. F., Ilyin V. I. Mechanism of charge forming in dispersed particles of hardly soluble metal compounds in water solutions. *Khimicheskaya fizika*. 2012. Vol. 31. No. 10. p. 46.
21. Tzoupanos N. D., Zouboulis A. I. Coagulation–flocculation processes in water/wastewater treatment: the application of new generation of chemical reagents. *6th IASME/WSEAS international conference on heat transfer, thermal engineering and environment (HTE'08)*. pp. 309–317.
22. Bratby J. Coagulation and Flocculation in Water and wastewater Treatment. IWA Publishing, London, Seattle, 2006. 583 p.
23. Zaletova N. A. General phosphorus and phosphates in waste waters. *Collection of scientific works based on the materials of International scientific and practical conference in 16 parts: Modern society, education and science*. 2015. pp. 48–50.
24. Rubanov Yu. K., Tokach Yu. E., Nechaev A. F., Ognev M. N. The galvanic productions waste waters and sludges processing with the heavy metals ions extraction. *European Journal of Natural History*. 2009. No. 6. pp. 79–80.
25. Ripan R., Chetanu I. Inorganic chemistry. Vol. 2. Moscow, Mir. 1972. 871 p.
26. Kumok V. N., Kuleshova O. M., Karabin L. A. Solubility productions. Novosibirsk. Nauka. 1983. 267 p.
27. Brodskiy V. A. Role of surface parameters of dispersed phase and medium composition in intensification and rise of efficiency of electroflotation process in cleaning of waste waters. Dissertation ... of a Candidate of Chemical Sciences. Mendeleev University of Chemical Technology of Russia. Moscow. 2012. 195 p.
28. Alam R., Shang J. Q., Khan A. H. Bubble size distribution in a laboratory-scale electroflotation study. *Environ. Monit. Assess.* 2017. Vol. 189. p. 193.



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