# Increase of efficiency of electroflotation extraction of low-soluble manganese compounds from water solutions in presence of flocculants of anion, cation and non-ion types

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The process of electroflotation extraction of dispersed phase of manganese (II-IV) low-soluble compounds from water solutions with different ion composition is examined. The process of forming of dispersed phase in presence of $OH^-$, $CO_3^{2-}$, $PO_4^{3-}$ ions, as well as flocculants of anion, cation and non-ion types is studied. It was shown that efficiency of electroflotation process depends directly on dispersity and electrokinetic potential of particles, which are determined by acidity and ion composition of the medium. Maximal average hydrodynamic diameter of dispersed phase of low-soluble manganese compounds were observed in the pH area 10-11, what corresponded to minimal solubility of dispersed phase. In this case the process of electroflotation extraction passed with maximal efficiency, extraction degree achieved 96 %. Introduction of cation flocculant in solutions allowed to rise extraction degree up to 98 %. Addition of $CO_3^{2-}$ and $PO_4^{3-}$ ions in solutions caused shift of ζ-potential of dispersed phase in the area of negative values (-18 mV and -33 mV respectively), what finalized in complication of forming of flotation complexes "particle - $H_2$, $O_2$ bubbles" and to complication of coagulation processes. Extraction degree did not exceed 10 % in both cases. Addition of cation and non-ion flocculants in the examined solutions allowed to compensate negative charge of dispersed phase, to enlarge this phase and to rise extraction degree of manganese (II) low-soluble compounds to 98 %.

***Key words:*** manganese, electroflotation, size of particles, electrokinetic potential, flocculants, hydroxides, phosphates, carbonates.
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## Introduction

Manganese and its compounds are widely used in the industry and thereby often plays a role of contaminant in waste waters. Manganese is contained in liquid wastes of metallurgical and galvanizing enterprises of the mining and paint-and-varnish industries, works for production of fertilizers etc. In particular, ferromanganese is used for deoxidation of steels in order to remove excessive hydrogen from them [1, 2]. Manganese additions are used for smelting of high-strength, stainless and heat-resistant steels [3, 4]. Manganese dioxide is used in production of manganese-zinc batteries [5]. Presence of inorganic impurities, including phosphates, carbonates etc., which are the components of initial technological solutions, are the features of this kind of drains [6, 7].

Additionally, manganese is an insufficient raw material [8]. That's why manganese extraction from water systems is actual not only from the point of view of environmental measures, but also taking into account its significant economical base. Maximal allowable concentration (MAC) for manganese extraction from drinking water objects makes 0.1 mg/l [9], what meets the requirements of WHO, EU, USEPA [10].

Electroflotation is one of the prospective and up-to-date methods for purification of waste waters from low-soluble metal compounds [11. 12]. This method is efficient and expedient for initial concentrations of extracting metals within the range 10-100 mg/l; use of flocculants expands this range to 300 mg/l [13]. It is applicable for extraction of dispersed phase of manganese compounds from waste waters and processed man-caused solutions [14].

The aim of this research is to examine influence of $OH^-$, $CO_3^{2-}$, $PO_4^{3-}$ ions on solubility, average hydrodynamic diameter and electrokinetic potential of dispersed phase of manganese low-soluble compounds and efficiency of their electroflotation extraction from water solutions in presence of flocculants of different types.

## Technique of experimental researches

Laboratorial investigations were carried out in water solutions $MnSO_4 \cdot 7H_2O$. Concentration of $Mn^{2+}$ ions in solutions made 50 and 100 mg/l. Transition of $Mn^{2+}$ ions in dispersed state was conducted via adjusting of medium pH by alkali (NaOH) and addition of $Na_2CO_3$ and $Na_3PO_4$. Mass relationship $[Mn^{2+}]/[CO_3^{2-}, PO_4^{3-}] = 1/1.5$. Control of medium pH was realized by I-160 MI ion meter.

Examination of electroflotation process of extraction of low-soluble manganese compounds was carried out in laboratorial device with periodical action, having volume 0.5 l. Electrodes were manufactured from insoluble materials: anode from titanium plate with oxide ruthenium-titanium coating (ORTC), cathode from stainless steel net wit size of cells 0.5x0.4 mm and wire thickness 0.3 mm [15]. Square of both electrodes was 0.07 dm² and current volumetric density $i_v$ was 0.2-0.4 A/l. Filtration of solutions was conducted using ashless filters "blue ribbon" (diameter of pores 2-3 μm).

Examination of influence of flocculants types on physical and chemical properties ans electroflotation activity of low-soluble manganese compounds was carried out in presence of polyacrylamides and their co-polymers [16] of Superfloc (Kemira) series, for anion (A-137), cation (C-496) and non-ion (N-300) types. Molar charge of flocculants made 41.6; 55 % and 0 %, according to the data from a producer, while molecular weight was equal to 5; 3.8 and 3 mln. respectively. Concentration of flocculants was 2 mg/l.

Efficiency of electroflotation process was assessed by the value of extraction degree α (%), it was calculated in accordance with the following equation:

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

where $C_0$ and $C_\tau$ – initial and final manganese concentration in solution (in dispersed and ion forms).

Mass manganese concentration in solutions was determined via atomic-adsorption method using KVANT-AFA spectrometer. Average hydrodynamic diameter (dav, μm) of dispersed phase of low-soluble manganese compounds was determined using «Analysette NanoTec» analyzer via laser diffraction method. Electrokinetic potential (ζ, mV) of dispersed phase was measured via electrophoresis using «Malvern Zetasizer Nano» laser analyzer.

## Results and discussion

### *1. Influence of pH and medium composition on physical and chemical parameters of manganese compounds*

It is known that $Mn_{2+}$ can be deposited in the form of hydroxide $Mn(OH)_2$. At the same time, white deposit of manganese hydroxide is oxidized to brown compound $Mn^{3+}$ – MnO(OH) (hydrate of $Mn_2O_3$) in presence of air oxygen [17]. Existence of Mn non-soluble compounds with oxidation degrees from +2 to +4 ($Mn(OH)_2$, $Mn_3O_4$, $Mn_2O_3$, $MnO_2$) is possible in the alkali area of pH in correspondence with the state diagram "potential – pH" for manganese – water system [18]. Presence of these compounds is determined by oxidizing and reducing potential of medium.

The data regarding varying of Red/Ox potential (meaning potential of platinum electrode $E_h$, mV) of solution in presence of Red/Ox systems $S_2O_3^{2-}/SO_4^{2-}/S_2O_8^{2-}$ within pH range 9-11 were obtained for clarification of Mn compounds nature in water solutions (**Fig. 1**).

It was established in correspondence with the data of "potential – pH" diagram [17] that manganese (III) and (II, III) oxides, such as $Mn_2O_3$ and $Mn_3O_4$ ($MnO{\cdot}Mn_2O_3$, is possible in the systems containing $SO_4^{2-}$ and $S_2O_8^{2-}$ ions within pH range 9-11. Existence of manganese hydroxide $Mn(OH)_2$ is also possible in presence of $S_2O_3^{2-}$ ion.

X-ray phase analysis of flotation concentrates, which were prepared with preliminary drying, displayed that flotation concentrate contains only γ-$Mn_2O_3$ in presence of $S_2O_8^{2-}$ and $S_2O_3^{2-}$ ions. Analysis of the samples, which were prepared without preliminary drying, showed that existence of $Mn(OH)_2$ pr $MnO{\cdot}H_2O$ (pyrochroite) is possible in presence of $S_2O_3^{2-}$ and $SO_4^{2-}$ ions; the system containing $S_2O_3^{2-}$ ions is considered as dual-phase system with γ-$Mn_2O_3$ and $Mn_3O_4$. It confirms the experimental data obtained on the base of "potential – pH" diagram.

Experimental researches displayed that extraction degree α of manganese compounds in presence of the reducing agent ($S_2O_3^{2-}$) via electroflotation method does not exceed 93-94 %. In the case of electroflotation of solutions with the oxidizing agent ($S_2O_8^{2-}$) and sulphate ion $SO_4^{2-}$, α achieves 97 % after 10-12 min since the beginning of the process.

Relationships of residual manganese concentration in filtrate and degree of electro-flotation extraction of manganese low-soluble compounds from pH were obtained (**Fig. 2**).

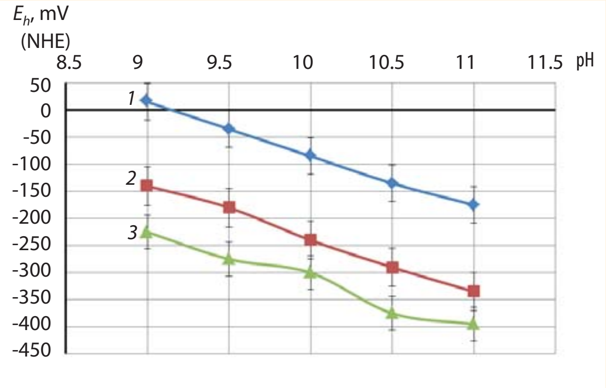

**Fig. 1. Dependence between platinum electrode potential Eh and medium pH in solutions of $MnSO_4$ ($C_{Mn2+}$ = 100 mg/l) in presence of 1 g/l of ions:**
*1* - $SO_4^{2-}$; *2* - $S_2O_8^{2-}$; *3* - $S_2O_3^{2-}$

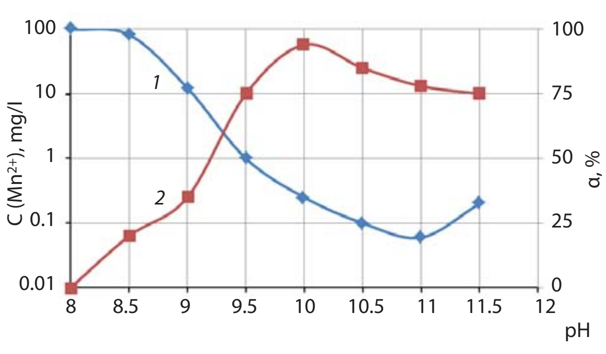

**Fig. 2. Influence of medium pH on residual concentration in filtrate and degree of electroflotation extraction of low-soluble manganese compounds ($C_{Mn2+}$ = 100 mg/l):**
*1* - filtration using decontaminated paper filter;
*2* - electroflotation, $\tau_{process}$ = 15 min.

It is shown that manganese is presented in solution mainly in the form of non-linked ions at pH < 8.5. Maximal content of low-soluble compounds is observed within pH range 10.5-11.5. When pH = 11.0, Mn concentration in solution does not exceed 0.06 mg/l. At the same time, maximal efficiency of electroflotation purification process is observed at pH = 10.0, extraction degree is 94 %. Increase of pH of solutions up to 11.5 and higher leads to decrease of extraction degree (α does not exceed 75 %). It can be concluded that choice of pH for conducting of electroflotation process based on the data about dispersed phase solubility is not optimal variant. Previously conducted researches had shown that efficiency of electroflotation process depends on physical and chemical parameters of dispersed phase of extracting compounds [19].

To solve the correlation problem for the data about solubility and efficiency of electroflotation process for extraction of particles of manganese low-soluble compounds (from one side) and their surface parameters (from other side), influence of medium acidity on average hydrodynamic diameter and ζ-potential of low-soluble compounds was examined.

The researches were conducted in solutions with low and increased content of sodium sulphate (0.001 and 0.01 M $SO_4^{2-}$). The solution 0.01 M $SO_4^{2-}$ characterizes a system with minimal salt content, what allows to reveal isoelectric area available for maximal possible removal of dispersed phase [20]. This solution can describe the system which is approximate to real waste waters containing essential amount of sulphate, included in composition of electrolytes (in addition to salt components of extracting metal). Obtained data are presented on the **Fig. 3.**

Analysis of dispersion parameters of manganese low-soluble compounds showed that size of particles in these compounds is practically identical in solutions with different background content (0.001 and 0.01 M $SO_4{}^{2-}$) (see Fig. 3, histograms *1* and *2*). Rise of pH in the examined solutions leads to increase of hydrodynamic diameter of particles dav from 25-27 μm (pH 8) to 50-55 μm (pH 10—11). Rise of pH to 11.5 and higher leads to decrease of size of particles.

It was established that isoelectric point pI on the relationship graph ζ—pH in the solution 0.01 M $Na_2SO_4$ is observed within pH range 9.0-9.5 (see Fig. 3, curve *3*) and is characterized by change of charge from positive to negative. If we take the solution 0.01 M $Na_2SO_4$, ζ-potential is negative not depending on medium pH (see Fig. 3, curve *4*). It can be explained by high sorption activity of $SO_4^{2-}$ ions in dispersed phase of metal low-soluble compounds [21]. In pH values are up to 10 and higher, ζ-potentials of particles in both solutions are practically identical.

Comparison and assessment of obtained data (see Fig. 2 and 3) allow to conclude that electroflotation process is mostly efficient within pH range 10.0-10.5. The extremal value of relationship between size of particles and pH is observed in this range. Rise of pH leads to shift of ζ-potential in the area of highly negative values, what complicates conducting of coagulation and flocculation processes [22. 23]. As a result, coagulation and elevation of flotation complexes on the surface of processing solution are very complicated, i.e. caused by difficulties in interaction of the particles with highly negative charge with low-dispersed bubbles of cathode hydrogen, which also have negative charge and make the main input in efficiency of electroflotation process [13].

### *2. Influence of flocculants nature on physical and chemical parameters of manganese compounds in presence of excessive $OH^-$, $CO_3^{2-}$ and $PO_4^{3-}$ ions*

Essential amount of phosphate ions and carbonate ions, which are able to form low-soluble compounds with metal ions, can be contained in liquid man-caused wastes of mining, metallurgical and galvanizing production. Such solutions contain hydroxides and hydrated oxides, hardly soluble

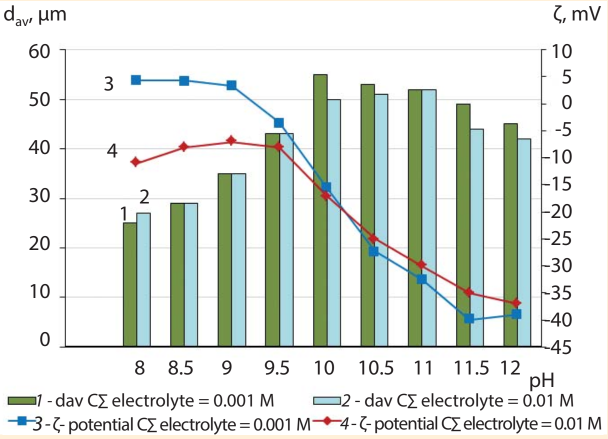

**Fig. 3. Relationship between ζ-potential and average hydrodynamic diameter $d_{av}$ of Mn low-soluble compounds ($C_{Mn2}$+ = 100 mg/l), and medium pH and background concentration**

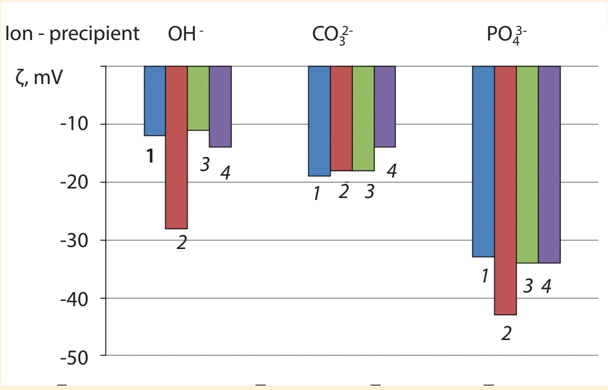

**Fig. 4. Relationship between electrokinetic potential (ζ) of low-soluble Mn compounds ($C_{Mn}$ = 100 mg/l) and nature of ion-precipient ($OH^-$, $CO_3^{2-}$, $PO_4^{3-}$) and flocculant:**
*1* — without flocculant; *2* — anion type; *3* — cation type; *4* — non-ion type; pH = 10-11, background electrolyte 0.01 M $SO_4^{2-}$, $C_{flocculant}$ = 2 mg/l

metal phosphates and carbonates as well as other compounds with complicated composition, whose electroflotation extraction is difficult ($\alpha \leq 10\%$) due to variation of physical and chemical properties of dispersed phase [6]. Use of flocculants that can vary physical and chemical properties of dispersed phase is considered as the up-to-date method for efficiency rise of electroflotation process.

Influence of excessive of $OH^-$, $CO_3^{2-}$ and $PO_4^{3-}$ ions and flocculants of anion, cation and non-ion types on ζ-potential (**Fig. 4**) and size dav (**Fig. 5**) of particles of low-soluble manganese compounds was examined.

In presence of excessive $OH^-$, $CO_3^{2-}$ and $PO_4^{3-}$ ions, ζ-potential of low-soluble manganese compounds is ore negative, than in presence of $OH^-$ ions; it makes -18 mV and -34 mV respectively. Addition of flocculants of cation and non-ion types in the examined solutions does not lead to significant variation of ζ-potential. Addition of flocculants of anion type in the solutions containing $OH^-$ and $PO_4^{3-}$ ions, causes shift of ζ-potential towards more negative values (-28 mV and -43 mV respectively). The processes of coagulation and enlargement of dispersed phase occur in the solutions, containing excessive $OH^-$, $CO_3^{2-}$ and $PO_4^{3-}$ ions, in presence of cation and non-ion flocculants; dav diameter increases from 43-53 µm to 88-121 µm. It was shown that ζ-potential of dispersed phase of low-soluble manganese compounds decreases depending of nature of ion-precipient in the row of OH-, $CO_3^{2-}$ and $PO_4^{3-}$ ions.

### *3. Electroflotation extraction of manganese compounds containing excessive OH-, $CO_3^{2-}$ and $PO_4^{3-}$ ions*

Generalization of previously obtained data about efficiency of conduction of electroflotation process in presence of excessive $OH^-$, $CO_3^{2-}$ and $PO_4^{3-}$ ions and flocculants of different types was carried out at the final stage of this research [24, 25].

It was revealed that extraction degree 96 % is achieved 10 min later after beginning of the process with excessive $OH^-$ ions and does not vary afterwards (**Fig. 6**). Introduction of flocculants of all researched typed allows to increase process intensity more than by two times and to decrease time of solution processing to 4-6 min. Flocculants of cation type is mostly efficient, α rises up to 98 %, while flocculants of anion and non-ion types can't increase extraction degree of low-soluble manganese compounds, but decrease time of electroflotation processing.

In presence of excessive $CO_3^{2-}$ and $PO_4^{3-}$ ions, electroflotation process is oppressed, extraction degree does not exceed 5-10 % in both cases, forming of flotation complexes "Particle - $H_2$, $O_2$ bubbles" does not occur, foam layer practically does not form. Introduction of flocculants in these solutions allows to rise extraction degree and to intensify electroflotation process. So, α achieves 96-97 % in the system containing $CO_3^{2-}$ ions, not depending on flocculant type. In the system containing $PO_4^{3-}$ ions, cation flocculant is most efficient ($\alpha = 95$ %), while non-ion is less efficient (α does not exceed 91 %, process kinetics is retarding). The obtained results correspond to technical literature data about manganese extraction from hydro-mineral wastes at copper deposits in the Ural region [14].

### *4. Discussion about the results*

It was established that medium pH and $E_h$, ion medium composition and nature of flocculants have key influence on electroflotation process. This influence appears through three factors: variation of nature, charge and size of particles of low-soluble manganese compounds.

Comparing the values of logarithms of solubility products (SP) of manganese carbonate and hydroxide ($\lg SP_{MnCO_3} = -9.41$; $\lg SP_{Mn(OH)_2} = -12.8$) [26], we can conclude that manganese carbonate solubility is higher that

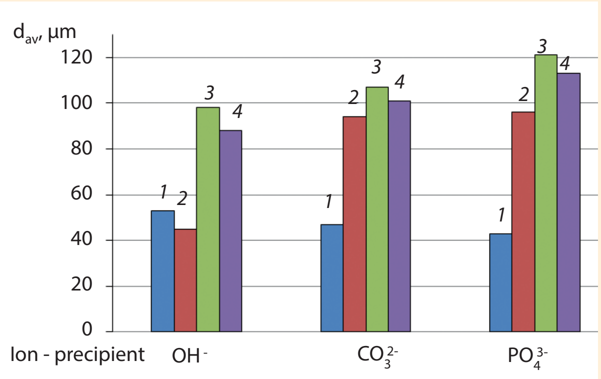

**Fig. 5. Relationship between average hydrodynamic diameter (dav) of low-soluble Mn compounds ($C_{Mn} = 100$ mg/l) and nature of ion-precipient ($OH^-$, $CO_3^{2-}$, $PO_4^{3-}$) and flocculant:**
*1* – without flocculant; *2* – anion type; *3* – cation type; *4* – non-ion type; pH = 10-11, background electrolyte 0.01 M $SO_4^{2-}$, $C_{flocculant} = 2$ mg/l

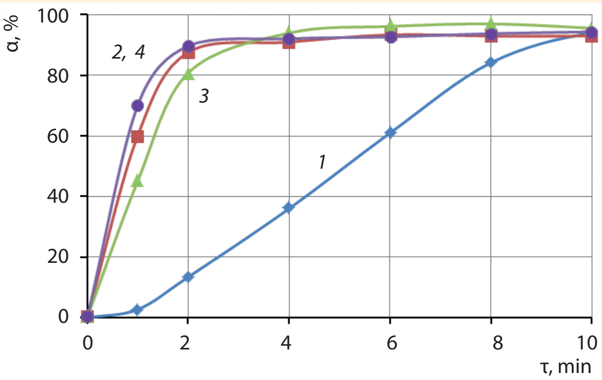

**Fig. 6. Relationship between extraction degree of low-soluble Mn compounds ($C_{Mn} = 100$ mg/l) and processing time in presence of $OH^-$ ions:**
*1* – without flocculant; *2* – anion type; *3* – cation type; *4* – non-ion type; pH = 10-11, background electrolyte 0.01 M $SO_4^{2-}$, $C_{flocculant} = 2$ mg/l

| Ion-precipient, Nature of flocculant | | Measuring parameter | | | | | |
|---|---|---|---|---|---|---|---|
| | | $d_{av}$, μm | < 10 μm, % | ζ, mV | α, % (τ 2 min.) | α, % (τ 10 min.) | $C_{res}$, mg/l (electroflotation+ filtration) |
| OH- | - | 53 | 4 | -12 | 13 | 96 | 0.10 |
| | Anion | 45 | 2,2 | -28 | 88 | 94 | 0.07 |
| | Cation | **98** | **0** | **-11** | **81** | **98** | **0.06** |
| | Non-ion | 88 | 1,5 | -14 | 87 | 96 | 0.07 |
| $CO_3^{2-}$ | - | 47 | 2,4 | -19 | 0 | <10 | 0.25 |
| | Anion | 94 | 0 | -18 | 77 | 96 | 0.10 |
| | Cation | **107** | **0** | **-18** | **94** | **97** | **0.10** |
| | Non-ion | 101 | 0 | -14 | 94 | 96 | 0.12 |
| $PO_4^{3-}$ | - | 43 | 5,2 | -33 | 0 | <10 | 0.08 |
| | Anion | 96 | 1,2 | -43 | 82 | 92 | 0.06 |
| | Cation | **121** | **0** | **-34** | **85** | **95** | **0.05** |
| | Non-ion | 113 | 0 | -34 | 10 | 91 | 0.05 |
| $CM_n^{n+}$ = 50-100 mg/l; pH = 10-11; background electrolyte 0.01 M $SO_4^{2-}$; $C_{flocculant}$ = 2 mg/l; $i_v$ = 0.2-0.4 A/l; $\tau_{process}$ =10-15 min; decontaminated paper filter | | | | | | | |

manganese hydroxide solubility. X-ray phase analysis showed that product, which was obtained after electroflotation extraction of manganese from solution containing $MnSO_4$ and excessive $Na_2CO_3$ (pH = 10.5), contains both $MnCO_3$ and $Mn_3O_4$ ($MnO·Mn_2O_3$). Technical literature data display that the deposit also can contain the following compounds: $MnO(OH)_2$, MnO(OH), $Mn(OH)_2CO_3$, $Mn(OH)_2SO_4$, $Mn(OH)SO_4(H_2O)_2$ [27]. The logarithm of manganese phosphate SP is significantly smaller than logarithm of manganese hydroxide SP ($lgПР_{Mn_3(PO_4)_2}$ = -36,21) [26], i.e. it can be suggested that presence of phosphate ions in the solution with excessive alkali does not lead to formation of manganese phosphates. Influence of ion composition of the solution and nature of flocculant on average hydrodynamic diameter dav, ζ-potential and efficiency of electroflotation extraction of low-soluble compounds with alternative valence is generalized in the **Table**.

It is shown that ζ- potential of the particles of dispersed phase in presence of $OH^-$, $CO_3^{2-}$ и $PO_4^{3-}$ ions and cation flocculant is more positive by 10-20 mV, than in presence of anion flocculant. It allows to rise extraction degree by 1-4 %. This effect can be stipulated by simplification of particles interaction with more positive surface charge and with fine-dispersed hydrogen bubbles (20-40 μm), which have negative charge [13, 28, 29], what leads to efficiency rise of electroflotation process. Electroflotation process is suppressed in presence of $CO_3^{2-}$ and $PO_4^{3-}$ ions. It was caused by complications in passing of coagulation processes among particles with increased negative surface charge. Efficient extraction of the particles of low-soluble manganese compounds in presence of $CO_3^{2-}$ and $PO_4^{3-}$ ions and anion flocculant is certainly provided due to formation of large macro-floccules, which are larger more than by 2 times than dispersed phase in the corresponding systems without flocculating additives. Consequent filtration of solutions allows to decrease concentration of $Mn^{n+}$ ions down to 0.05-0.1 mg/l.

Influence of ion composition of solution and nature of flocculant on average hydrodynamic diameter $d_{av}$, ζ-potential and efficiency of electroflotation extraction of manganese low-soluble compounds (II-IV)

## Conclusions

It is shown that nature of dispersed phase is the main factor having influence on efficiency of electroflotation extraction of manganese low-soluble compounds. Average hydrodynamic diameter in presence of $OH^-$, $CO_3^{2-}$ and $PO_4^{3-}$ ions differs not more than by 20 % and is situated within the range 43-53 μm (pH = 10-11). In absence of flocculants, the most efficient extraction is observed for the particles forming in the conditions with excessive $OH^-$ ions (α = 96 %). It is explained by minimal absolute value of electrokinetic potential (-12 mV) and maximal average hydrodynamic diameter (53 μm) of dispersed phase. Electroflotation process in presence of $CO_3^{2-}$ and $PO_4^{3-}$ -ions is complicated (α < 10 %). Lowering of efficiency of purification process can be explained by variation of nature of the dispersed phase and shift of ζ-potential of the particles of manganese low-soluble compounds in the area of more negative values – (18-33) mV, what complicates formation of flotation complexes “particles – bubbles $H_2$, $O_2$». Addition of flocculants in solutions containing $CO_3^{2-}$ and $PO_4^{3-}$ ions allows to rise extraction degree due to enlargement of dispersed phase of extracted compounds. Addition of cation flocculant leads to the most efficient enlargement of the particles of dispersed phase provides maximal efficiency. Size of particles achieves 98-121 μm not depending on their nature, fine-dispersed phase with size up to 10 μm is absent. Extraction degree achieves 95-98 %. Practical use of obtained results is important from the point of view of selective separation and extraction of metals from multi-component systems Fe (III), Cr (III) and Mn (II), which are typical for metallurgical waste waters during steel making and galvanizing processes [15]. The results of this research allow to choose the scientifically substantiated approach for extraction of residual concentrations of manganese low-soluble compounds with alternative valence from waste waters after separation of Fe and Cr compounds.

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