Electroflotation extraction of a heavy metal hydroxide mixture from a multi-component solution

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Considerable attention is paid to the issues of wastewater treatment in the metallurgical industry. Electrochemical wastes are certainly considered as the most dangerous in terms of negative impact on the environment and humans. The high content of heavy metals and extreme pH values make it impossible to discharge such wastewater without deep purification treatment. The electroflotation method for extraction of metals from multi-component systems is considered as the most efficient. As part of the work done, the influence of addition of flocculants and surfactants, as well as the background electrolyte, on the efficiency of extracting a mixture of metals Fe^{2+}, Ni^{2+}, Zn^{2+}, Co^{2+}, Cu^{2+}, was assessed. It has been established that systems with electrolyte based on sodium sulfate have higher stability due to changes in the surface layer and the "dispersed particle – gas bubble" interface, while addition of OS-20B surfactant leads to inhibition of the electroflotation process and decrease of the efficiency of heavy metals extraction. A similar effect was observed for a system with a background electrolyte based on sodium chloride and the addition of ALM-10 surfactant. Addition of flocculants did not have a significant effect on the efficiency of electroflotation purification and was considered as not advisable. Based on the obtained results, a conceptual scheme for the process of wastewater purification treatment from heavy metal ions using the electroflotation method is proposed.

Key words: electroflotation, wastewater, heavy metals, flocculant, surfactant, iron, nickel, zinc, cobalt, copper
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Introduction

Almost all heavy metals, which are used in the industry, are extremely toxic for humans and the environment [1–6]. Despite the fact that any of heavy metals are biogenic (copper, zinc, nickel, boron, iron, molybdenum et al.), even small exceed of their concentration in river or drinking water can lead to growth of oncologic diseases as well as to sharp and chronic poisoning of both humans and other biological objects.

Soil contamination by heavy metals occurs as a result of the effect of industrial wastewaters, fertilizers or use of insufficiently purified wastewaters in agriculture [7–9].

Production processes of ferrous and non-ferrous metals (mining, pyrometallurgical and hydrometallurgical processing) [10–11], as well as their electrochemical treatment processes [12–15] are considered as the main sources of introduction of heavy metals in the environment. Volumes of incoming heavy metals are proportional to production scale. At present time, due to the objective reasons, the most part of purification facilities, which are operated at such works, are in the conditions of physical and moral ageing, they can't solve preset problems and meet the modern strict requirements to purification. Intake of such sewages in natural object without corresponding level of preliminary purification of these sewages will lead to death of such objects, while their drainage in urban canalization can provide substantial damages to municipal equipment for deep biological purification.

At present time, the most researches are devoted to decrease of emission of heavy metals in the environment, such researchers can be classified in three basic directions: (a) development of new and more friendly ecological functional coatings [16, 17]; (b) putting into practice of the systems with closed water circulation at the industrial works [18]; (c) improvement of the technologies [19–21] and reactants allowing to extract efficiently heavy metals from water [22–26].

Electroflotation (EF) method is considered as the most prospective among numerous techniques for efficient extraction of heavy metals from wastewaters and technological solutions. EF method allows to extract non-soluble compounds of ferrous and non-ferrous metals, emulsions of inorganic substances, oil products and greases as well as surfactants [19–20, 27–29].

At the same time, efficiency rise of extraction of the mixture of hydroxides of ferrous and non-ferrous metals in composition of multi-component solutions, which are forming during surface treatment of various steels, is an actual

EF problem [27–29]. Alkali reactants, surfactants, flocculants and coagulants are used for intensification of the extraction processes [12, 13, 25].

Study of purification process of wastewaters at the shop area for application of galvanizing coatings via electroflotation is the aim of this research.

Materials and methods for research

The mixture of bivalent metals (Fe^{2+}, Ni^{2+}, Zn^{2+}, Co^{2+}, Cu^{2+}) with concentrations 20 mg/l (100 mg/l in total metals sum) was chosen as a test system. It simulates rinsing water, which is forming during technological cycle of processing of steel products at the stages "degreasing", "pickling", "coating application".

Na_2SO_4 and NaCl with concentrations 1 mg/l were used as electrolyte for creation of a permanent ionic force, while flocculants Praestol 2500 and Ferrocuyl 8737 were used as an additives for intensification of flotation processes.

To increase the adhesion level of extracted dispersive metal compounds and gas bubbles, which are generated during electroflotation, the following additives of surfactants with non-ionogenic nature were tested during "degreasing" stage:

– synthanol ALM-10 oxylatate of fatty high alcohols ($C_nH_{2n+1}O(C_2H_4O)_m$), with length of the carbon chain n = 10–13 and ethoxylation degree *m* = 7–10;

– OS-20B specimen, mixture of polyoxyethylene glycol of esters of fatty high alcohols $RO(CH_2CH_2O)_nH$, where R = 14–18 and *n* = 20.

To prepare model solutions, the following reactants were used: $FeCl_2 \times 4H_2O$, $NiSO_4 \times 7H_2O$, $ZnSO_4 \times 7H_2O$, $CuSO_4 \times 5H_2O$, $CoSO_4 \times 5H_2O$, Na_2SO_4, NaCl with *xch* qualification. Model solutions were prepared with distilled water.

The noted salty components correspond to typical contaminations of wastewaters from galvanizing production, from manufacture of printed circuit boards for electronic devices, from metallurgical and mining works (which are actively developing in Myanmar at present time).

Purification of model systems was conducted via electroflotation method according to the previously developed technique [27–29] with use of the labor unit; this unit contains permanent electric current source HY 1803D, lentic electroflotator with volume 500 ml, cross section square 10 cm² and height 80 cm. The unit has insoluble anode OPTA and cathode of stainless steel 12Kh18N10T. The scheme of the labor electroflotation unit with batch operation is presented in the **Fig. 1**.

In several cases, filtration of solution was carried out after electroflotation purification, using disenfranchised filters "Blue ribbon" (TU 2642-001-13927158-2003) with diameter of pores ~ 1 μm. pH control was realized via pH meter pH-410 with standard glass (ESK-1060|7) and silver chloride electrodes. pH of the solution was processed to the required value using NaOH and H_2SO_4 solutions; operating area pH = 8–11 ± 0.2 un.

Concentration of metal ions was determined via atomic absorption method in the Common use center named after D. I. Mendeleev, as well as using atomic emission spectrometer "Spektroskay" with magnetic plasma (Korolev city, Russia) [30, 31].

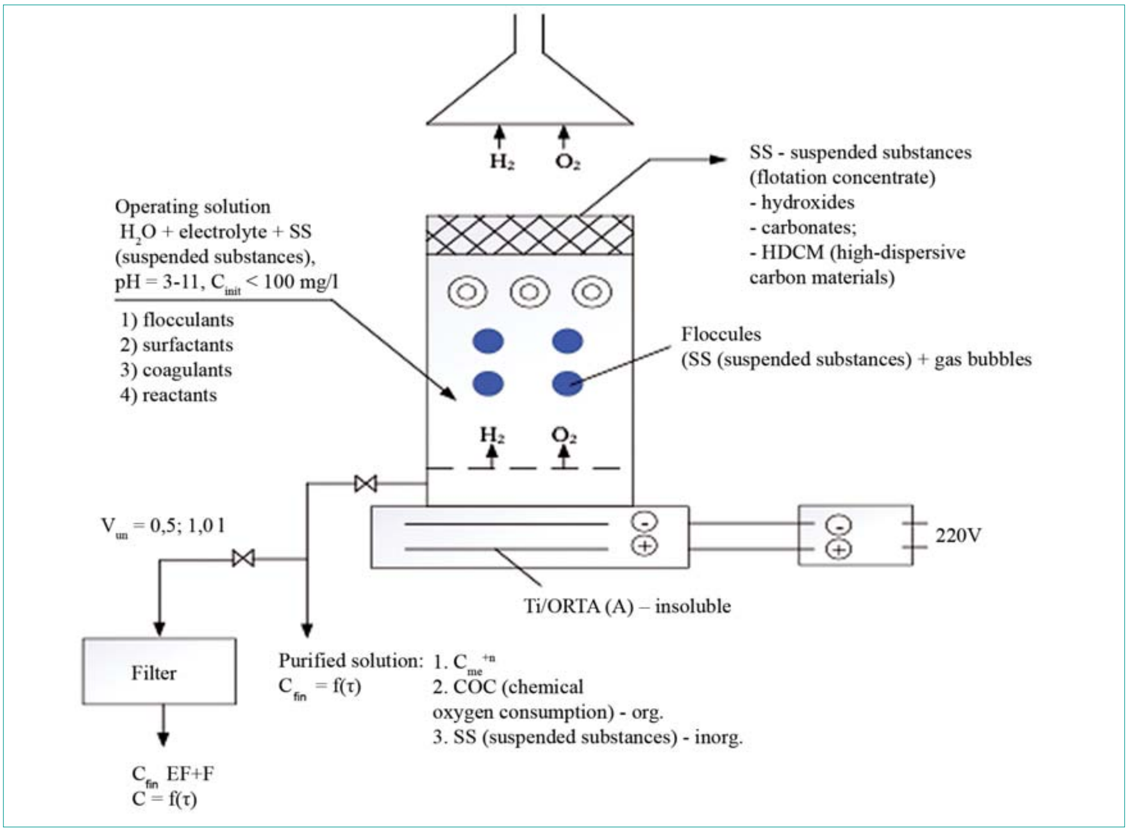

Fig. 1. Scheme of the labor electroflotation unit with batch operation

Efficiency of electroflotation process was assessed via extraction degree α (%), which was calculated via the formula

$$\alpha = (C_{init} - C_{fin})/C_{fin} * 100\,\%,$$

where C_{init} and C_{fin} – initial and final concentration of metals ions in water, mg/dm^3.

Experimental results and their discussion

It was established within the framework of several preliminary investigations that optimal pH value for electroflotation extraction of individual metals and mixtures is 10.0; minimal residual concentration of metals ions 0.1-0.5 mg/l is observed in this case. Optimal time for electroflotation process is 20 min [19].

Mutual effect of extracting metal cations on the processes of joint deposition and electro-flotation extraction was not examined in this research, owing to parallel investigations on this theme [28], where this material was already described.

However, this question is rather actual and will be examined in the future, during pilot-industrial testing. Electrokinetic parameters (such as surface charge of particles in dispersed phase) were determined in this work using laser analyzer of particles «Analysette NanoTec/MikroTec/XT», which is devoted for determination of particles distribution by their sizes via laser diffraction; its operation is based on the physical principle of electromagnetic scattering according to the standard technique [32]. These researches were carried out in the Common use center named after D. I. Mendeleev.

The experimental data on efficiency of electroflotation extraction for individual metals out of a mixture with background electrolyte NaCl are presented in the **Table 1** and **Fig. 2**.

The examined flocculants Praestol 2500 and Ferrocuyl 8737 provided no effect in the conditions of background electrolyte NaCl, what s good from the technical point of view and testifies on unification of this system.

Table 1. Influence of efficiency of electroflotation extraction of heavy metals mixture in presence of flocculants and with background electrolyte NaCl during 20 min

Organic additives	Fe	Ni	Zn	Co	Cu
Without additives	96	95	96	99	98
Flocculant FERROCUYL 8737	97	96	96	98	97
Flocculant PRAESTOL 2500	91	99	96	98	99

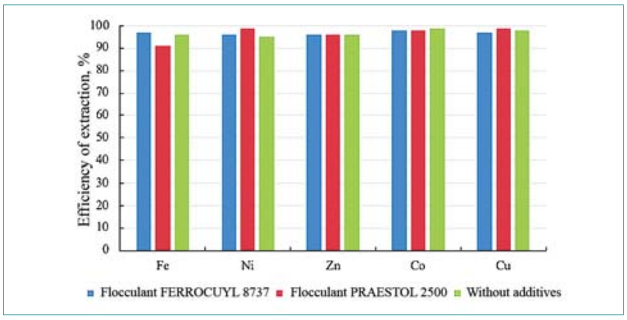

Fig. 2. Efficiency of extraction of heavy metals mixture in presence of flocculants and with background electrolyte NaCl

The data of Fig. 2 testify evidently, that addition of flocculants leads either to small (1–2 %) extraction efficiency rise or to its decrease for all metals except nickel.

Lowering of extraction efficiency for iron compounds (when using Praestol flocculant) can be explained by negative surface charge of iron hydroxide, while for all other hydroxides we observe positive surface charge for preset pH value.

The data on efficiency of electroflotation extraction of individual metals out of the mixture with background electrolyte NaCl are presented in the **Fig. 3**.

It can be seen from the Fig. 3 that influence of addition of surfactants on efficiency of electroflotation extraction of metals was expressed distinctly in comparison with a flocculant. So, addition of surfactant OS-20B didn't provide essential influence on extraction efficiency, while addition of surfactant ALM-10 significantly (more than by 15–20 %) decreased extraction efficiency of metals. This appearance is caused mainly by the mechanism of reactant effect, i.e. by decrease of tension on the separation boundary of the phases "Surfactant : Dispersed particle : Air bubble".

Influence of background electrolyte on the base of Na_2SO_4 on extraction efficiency of metals from a mixture was examined at the next stage. The obtained experimental results are presented in the **Fig. 4** and **Fig. 5**.

Opposite influence of a flocculant on extraction efficiency of metals is observed for the system with Na_2SO_4 electrolyte. So, Praestol additive inhibited electroflotation processes in all experiments and essentially (more than by 10 %) decreased extraction efficiency of metals. In the meantime, Ferrocuyl flocculant additive allowed to increase slightly extraction efficiency of cobalt and iron, what can be very important for choosing purification process, taking

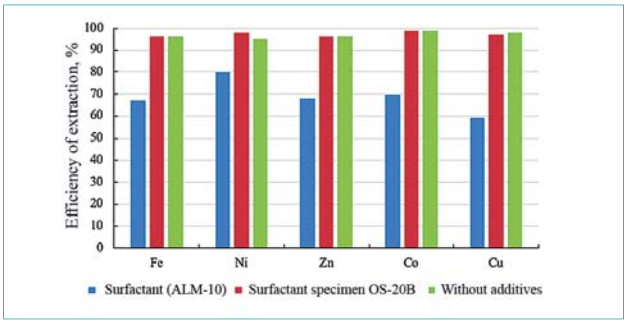

Fig. 3. Efficiency of extraction of heavy metals mixture in presence of surfactants and with background electrolyte NaCl

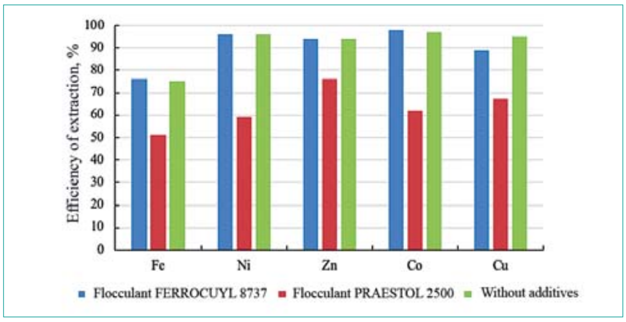

Fig. 4. Efficiency of extraction of heavy metals mixture in presence of flocculants and with background electrolyte Na_2SO_4

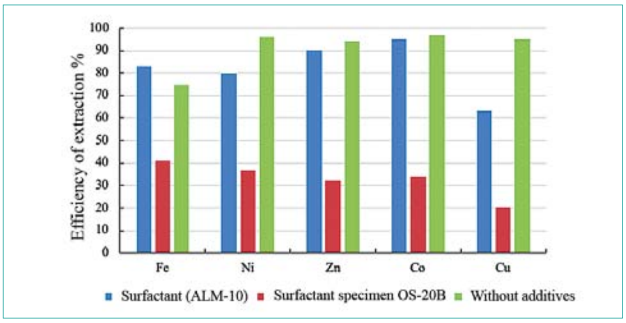

Fig. 5. Efficiency of extraction of heavy metals mixture in presence of surfactants and with background electrolyte Na_2SO_4

into account very strict requirements of maximal permissible concentration for cobalt ions.

The Fig. 5 testifies that additive of surfactant ALM-10 provides no significant influence on electroflotation efficiency. At the same time, additive of surfactant OS-20B leads to dramatic decrease of efficiency and practically completely inhibits the process of electroflotation extraction; it is caused by variation of the surface layer of a dispersion particle due to accumulation of a sulphate ion (counter-ion).

Based on the obtained data, the technological scheme for application of electroflotation method in the processes of wastewaters purification with removal of heavy metals ions was designed (**Fig. 6**).

Wastewaters with complicated composition contain the mixture of heavy metals hydroxides and organic contaminations, which are forming at machine-building works, first of all from galvanizing production facilities, manufacture of printed circuit boards for electronic devices, as well as from production of paints and lacquers, from battery-operated works and metal processing shops.

This purification scheme can be used for the above-mentioned processes, its operating principle is described below.

Purified wastewater with the above-mentioned composition is forwarded to the tank for reactant purification *1*, where surfactants and flocculants are added by pumps *14* and *15*. Then wastewater is directed to drainage and, using the pump *11*, to thin-layered settling tank *2*, where sediment is forming and is subjected to dewatering in the press filter *5*.

Then purifying liquid is forwarded to electroflotation module *3*, where high-efficient extraction of heavy metals compounds (95–99 %) occurs. Contaminants are removed to the surface with assistance of moving force of oxygen and hydrogen bubbles, then flotation mud *9* (containing mixture of metals) is forming. This mud is directed to the press filter *5* for its consequent dewatering.

Purified water is forwarded by the pump *12* to the filter for mechanical purification *4*, where additional filtration with obtaining purified water occurs. Filter rinsing is carried out by industrial water, while rinsing water is directed to the corresponding tank *8* and afterwards, using the pump *13*, it is directed to the tank for reactant processing for secondary purification *1*.

Conclusion

Based on the obtained experimental results, the conditions for application of electroflotation method for purification of a multi-component mixture of metals Fe^{2+}, Ni^{2+}, Zn^{2+}, Co^{2+}, Cu^{2+} were suggested.

Taking into account very high cost of flocculants and their rather low efficiency, it was concluded that it is inexpedient to use them as reactants for intensification of purification process; however, use of flocculants can be efficient for further dewatering of forming mud.

Thus, it is possible to replace the surfactants, which are used at present time and which were examined within the experimental framework, by reactants with other properties,

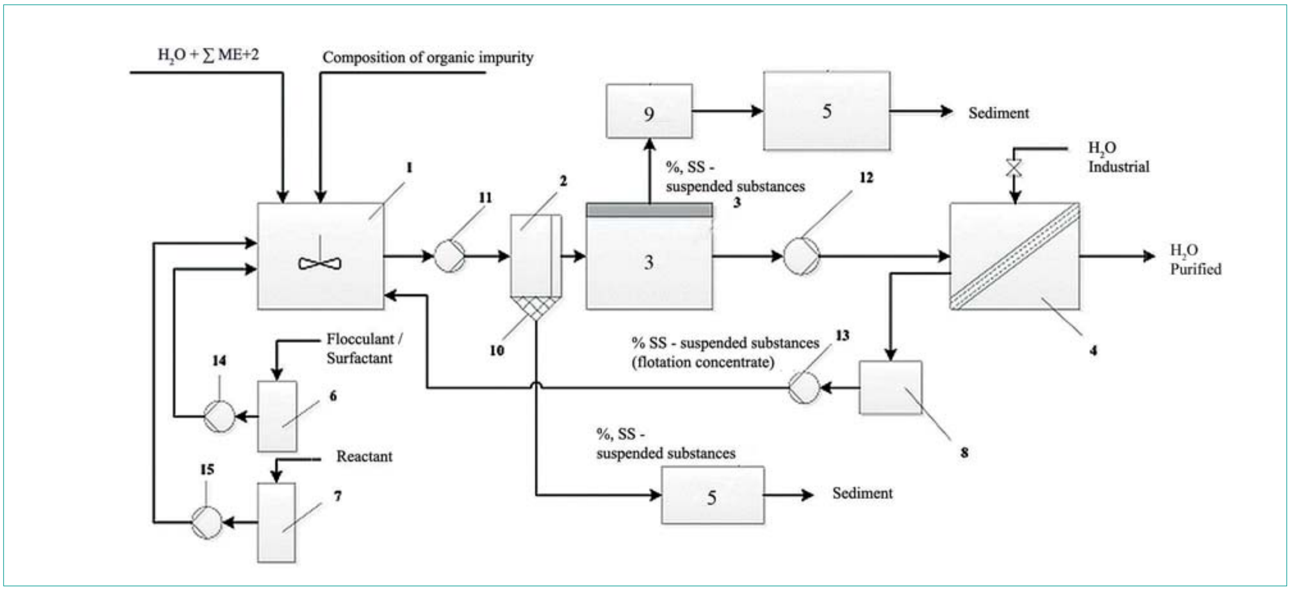

Fig. 6. Principal block scheme for processing of wastewaters and concentrates at galvanizing production (heavy metals ions)
1 – Tank for reactant processing; 2 – Thin-layered settling tank; 3 – Electroflotator; 4 – Filter for mechanical purification; 5 – Press filter; 6 – Tank for a flocculant or surfactant; 7 – Tank for reactants; 8 – Tank for rinsing water; 9 – Flotation mud; 10 – Sediment for a settling tank; 11,12,13 – Water supply pumps; 14,15 – Dosing pumps

which provide intensification of purification process or have no effect on it. Adsorption processes for removal of surfactants, with consequent additional water purification with removal of metal ions via electroflotation can be used as an alternative variant.

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