ISSN 1070-3632, Russian Journal of General Chemistry, 2014, Vol. 84, No. 11, pp. 2315–2319. © Pleiades Publishing, Ltd., 2014.
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Effect of Magnetic Field on the Electroflotation Extraction of Sparingly Water-Soluble Heavy and Non-Ferrous Metal Compounds from Wastewater

V. I. Il'in, A. V. Perfil'eva, and V. A. Kolesnikov

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

Received January 1, 2013

Abstract—Factors that determine the efficiency of extraction of dispersed particles of sparingly water-soluble heavy and non-ferrous metal (Fe, Ni, Co) compounds from wastewater by magnetic treatment followed by electroflotation are discussed. Optimum conditions of the process are found. The results show that exposure of water-dispersed systems to magnetic field can significantly improve the efficiency of the electroflotation extraction of sparingly water-soluble heavy and non-ferrous metal compounds, which can be useful for wastewater treatment industry.

DOI: 10.1134/S1070363214110516

INTRODUCTION

Over the past years essential progress has been made in the technologies of physicochemical treatment of wastewater, but the development of this field of science raises new and new problems. One of such problems consists in intensifying existing water treatment processes.

First of all we would like to note that the term "intensification" in this context suggests not only acceleration of the treatment process, but also improvement of the treatment quality.

The most widespread ways to intensify the wastewater treatment process are based on the introduction to water being treated of various chemical reagents, first of all coagulants and flocculants. Among the disadvantages of this approach to intensifying the wastewater treatment process we can mention the necessity to occupy additional working floors for accommodating the chemical feed plant, as well as increased salt contents in the purified water and more precipitate formation.

In this connection of considerable interest are methods for intensifying wastewater treatment processes without using chemical reagents. One of such methods is based on the exposure of the aqueous dispersion system to magnetic field.

Since 1950s, extensive research has been performed on the application of magnetic treatment of aqueous systems for prevention of scale formation in pipelines, heaters, and heat exchangers [1]. However, research on extraction of different-size dispersed particles of sparingly soluble compounds of heavy or nonferrous metals from wastewaters which are mostly lyophilic disperse systems is complicated because of the complexity of applied problems to be solved. In particular, one should find optimal conditions for successful extraction of particles with different granulometric compositions and surface characteristics.

Systematic research into the electrochemical purification of wastewater at the Mendeleev Russian University of Chemical Technology resulted in the development of scientific foundations of an electroflotation process for extraction of dispersed particles of sparingly soluble heavy or nonferrous metal compounds from aqueous dispersion systems [2]. Correlation of the engineering parameters and regimes of the electroflotation process with kinetic regularities Analysis of experimental data allowed assessment of the effect of various physicochemical parameters of aqueous dispersion systems on the formation of electrolytic bubbles and formation and extraction of dispersed particles on the basis of a correlation of the engineering parameters and regimes of the electroflotation process with kinetic regularities.

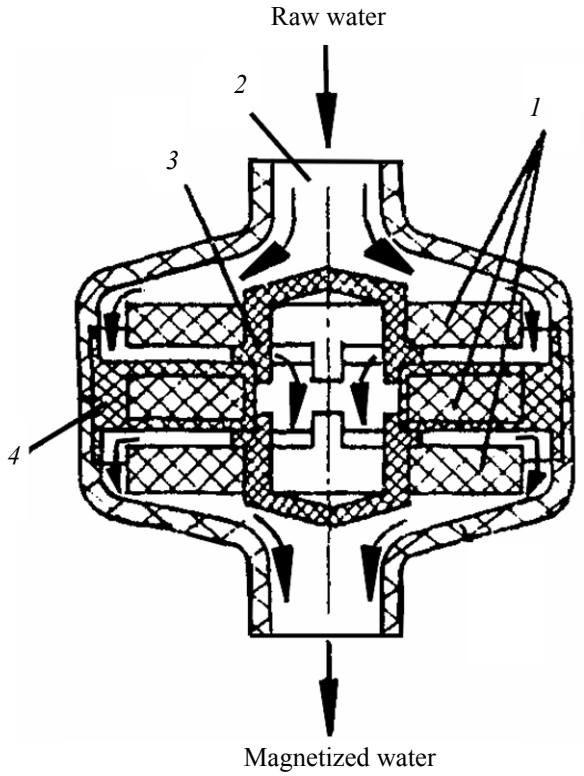

Fig. 1. Schematics of the device for magnetic treatment of aqueous solutions: (*1*) permanent magnets; (*2*) central channel; (*3*) cylindric chamber; and (*4*) partition.

The electrode processes could be much intensified by the use of highly active and chemically durable electrode materials.

Here we present the results of an experimental research on the process of extraction of dispersed particles from aqueous dispersion systems by magnetic treatment followed by electroflotation.

EXPERIMENTAL

In the experiments we used model aqueous solutions containing dispersed particles of magnetically sensitive iron group metal (Fe, Ni, Co) compounds at concentrations of 50–100 mg/L.

Magnetic treatment of the aqueous dispersion systems was performed in a device (Fig. 1) comprising ring-shaped permanent magnets inside a plastic housing, with a little spacing between the magnets and housing walls. The magnets are separated by a cylindroconical chamber and a ring-shaped partition for closing the central channel and dynamically impacting the water flow. Raw water enters the central channel and moves from top to bottom, flowing over the cylindroconical chamber, permanent magnets, and ring partition. In so doing, the water flow changes direction many times (axial along the conic chamber and central channel, radial from the periphery to centrum, and opposite along spacing between magnets). As the water flow moves along spacings between magnets it is exposed to magnetic field and gets magnetized. The magnets are fabricated from a ceramic material (strontium ferrite).

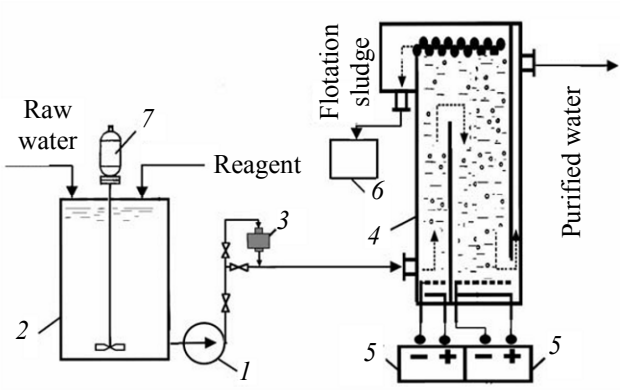

Fig. 2. Schematics of the laboratory stand for studying the effect of magnetic treatment on the process of electroflotation extraction of dispersed sparingly soluble heavy and nonferrous metal compounds from wastewater: (*1*) sewage regulator; (*2*) pump; (*3*) magnetic treatment device; (*4*) electroflotator; (*5*) dc power sources; (*6*) flotation sludge collector; and (*7*) stirrer.

The experimental study of the effect of magnetic treatment on the electroflotation extraction of dispersed particles from wastewater was performed on a laboratory stand mimicking operation of the water treatment equipment in the flow regime (Fig. 2).

Preliminary experiments allowed us to establish optimal parameters for treatment of aqueous dispersion systems: magnetic field strength 80–85 kA/m (1000–1070 erg), cross-sectional water flow rate 1–2 m/s, duration of exposure to magnetic field 0.03–0.05 s, volumetric flux density in flotation chambers 0.1–0.25 A/L.

The sewage regulator with a working solution (tap water with a hardness of 0.5 mg-equiv/L, containing individual metal cations or their mixture) was loaded with stirring with 1% NaOH until dispersed particles form in water being treated. The pH ranges for the most complete formation of hydroxide dispersions (the lowest contents of metal cations in the filtered sample) were 6.3–6.7 for iron, 10.5–10.8 for nickel, 9.2–9.5 for

Table 1. Results of magnetic treatment in the electroflotation removal of dispersed iron compounds

Stages of treatment of aqueous disperse systems	Recovery (%) at electroflotation time, min				Solubility of $[Fe^{3+}]$, mg/L
	2	3	4	5	
Disperse phase → electroflotation	66	77	88	98	0.50
Heavy metal cations → magnetic treatment → disperse phase → electroflotation	87	93	97	99	0.50
Disperse phase → magnetic treatment → electroflotation	88	94	98	>99	0.01

cobalt, and 9.5–10 for cation mixture. The pH values were adjusted with NaCl, $NaNO_3$, or Na_2SO_4 and measured with an I-160 MI laboratory ionometer.

The suspension was stirred for 5–7 min, and then the pump was switched on. After the suspension had filled the electroflotator, the dc power sources were attached, and water was passed in succession through the magnetic treatment device and electroflotator in a volume four times the working volume of the electroflotator plus communications at its inlet and outlet. The water feed rate was controlled with a valve installed after the pump. The flotation sludge was transferred to the collector at regular intervals.

Water samples were taken every 10 min at the outlet of the electroflotator. Analysis for heavy and nonferrous metals in water was performed by atomic absorption spectrometry on a KVANT-AFA instrument by a standard procedure.

The size and dispersity of particles suspended in the aqueous medium was determined on an Analysette NanoTec/MicroTec/XT laser particle sizer. The electrokinetic potential (ζ-potential) was measured on a Malvern Zetasizer Nano laser analyzer.

The phase composition of the dispersed phase was determined by IR spectroscopy (UR-20 spectrophotometer) in KBr tablets. X-ray phase analysis was performed on a Dron-2 instrument.

Data processing was performed using Microsoft Excel. For the result we took an arithmetic mean of all measurements provided they differed from the mean value no more than 10% at the confidence probability p = 0.95.

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

$$\alpha = 100 \times (c_0 - c_t)/c_0,$$

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

RESULTS AND DISCUSSION

Generally, magnetic treatment of aqueous dispersion systems before electroflotation can be accomplished in two ways.

In the first approach, magnetic field is applied on an aqueous system containing heavy and nonferrous metal cations, after which an alkaline reagent is added to form dispersed particles. In the second approach, magnetic field is applied on an aqueous system already containing disperse systems formed under the action of an alkaline reagent.

Preliminary experiments showed that magnetic treatment of aqueous systems containing iron compounds at concentrations of 100 mg/L by both approaches enhances efficiency of electroflotation extraction of the dispersed iron phase (Table 1). Thus, when magnetic treatment was applied, the 2-min recovery was 87–88%, whereas in the absence of magnetic treatment the same recovery could be reached within 4 min. Magnetic treatment for 5 min, both by the first and second approach, results in the same recovery (99%), but the lowest solubility of dispersed particles of 0.01 mg/L is attained in the second case, i.e. at the following sequence of stages: dispersed phase → magnetic stirring → electroflotation.

Magnetic treatment of an aqueous system containing sparingly soluble nickel and cobalt compounds allows the electroflotation time to be shortened, on average, 1.2–1.5 times (from 10 to 8–6 min) compared to magnetic treatment of an aqueous system containing no heavy metal cations.

Table 2 lists the results of research on the effect of magnetic treatment on the surface properties and recoveries of dispersed particles of iron group com-

Table 2. Effect of magnetic treatment on the surface properties and recoveries of particles of sparingly soluble heavy and nonferrous metal compounds

Disperse phase M^{n+}–H_2O–NaOH	Without/with magnetic treatment				
	average particle size, μm	fraction of particles smaller than 10 μm, %	ζ-potential, mV	recovery, %	solubility of $[M^{n+}]$, mg/L
Fe^{3+}	60/140	2.6/0.7	4.2/1.2	96–98/99.9	0.2/0.01
Ni^{2+}	50/80	2.8/1.1	–14.5/–8.5	92–95/98–99	0.4/0.20
Co^{2+}	55/85	3.2/1.0	–9.2/–3.3	90–92/98–99	0.3/0.10
Ni^{2+} Fe^{3+}	37/78	4.1/0.8	–3.2/–1.2	10–12/95–98 30–45/98–99	0.7/0.30 0.2/0.01
Co^{2+} Fe^{3+}	38/75	4.9/0.8	–2.8/–1.1	50–62/96–98 70–75/98–99	0.5/0.20 0.1/0.01
Co^{2+} Ni^{2+} Fe^{3+}	34/70	5.1/1.2	–2.5/–1.2	80–90/97–99 85–92/97–99 90–95/97–99	0.3/0.10 0.3/0.10 0.2/0.03

pounds from aqueous dispersion systems. The resulting data show that magnetic treatment increases the mean particle size and decreases the fraction of a finely dispersed phase, as well as decreases the solubility of the compounds. In our opinion, the fact that magnetic treatment decreases the dispersity and solubility of the dispersed phase is explained by a change in the surface properties of particles, namely, a decrease of the ζ-potential and quantity of bound water in the precipitate.

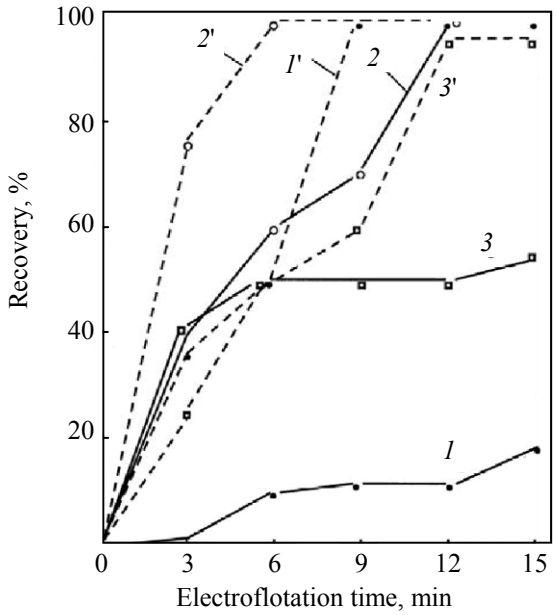

Fig. 3. Kinetic dependences of the recovery of iron compounds from (*1*) Na_2SO_4, (*2*) NaCl, and (*3*) $NaNO_3$ by (*1*–*3*) electroflotation and (*1*'–*3*') electroflotation with preliminary magnetic treatment.

Thus, the increased efficiency of electroflotation extraction of dispersed particles on magnetic treatment is explained by the fact that such treatment increases the mean size of particles, thereby enhancing their ability to be floated by gas bubbles. Increasing volume current density increases the volume concentration of bubbles in the dispersed medium, which increases the probability of collisions of floated particles and thus intensifies the electroflotation process.

Enhanced performance of the electroflotation process combined with magnetic treatment of the solutions was also observed in the research on the effect of permanent magnetic field on the electroflotation extraction of iron particles from concentrated solutions of sodium salts ($NaNO_3$, NaCl, Na_2SO_4, concentration 50–100 g/L). Thus, magnetic treatment of Na_2SO_4 solutions shortens the electroflotation time 5 times and increases the recovery of the dispersed iron phase from 20 to 99% (Fig. 3, curve *1′*). The use of magnetic treatment allows a 99% recovery of iron compounds from a NaCl solution to be obtained within 6 min (Fig. 3, curve *2′*), whereas without magnetic treatment the same recovery is reached only within 12 min (Fig. 3, curve *2*). Magnetic treatment of a $NaNO_3$ solution increases the recovery of iron compounds from 50 to 95% after a 12-min process (Fig. 3, curve *3′*).

Exposure of sodium salt solutions to magnetic field also results in increasing mean particles size and

decreasing content of a finely dispersed phase. Moreover, anions are directly incorporated into the precipitate, thus changing the phase composition of the dispersed phase: Along with hydroxide, it contains different forms of oxohydroxides and oxides.

Processing of the experimental kinetic results of the electroflotation extraction of dispersed particles by the integral method [3] showed that the electroflotation processes without preliminary magnetic treatment are described by a first-order equation and only have different rate constants varying from 0.9 to 1.5 min^{-1}, whereas the kinetics of electroflotation processes with preliminary magnetic treatment follows an equation different from the first-order one. Thus, the order of the kinetic equation for the electroflotation extraction of dispersed iron phase from sulfate solutions at the initial concentration 0.2 kg/m^3 is 2, and the rate constant is 0.85 $m^3\ kg^{-1}\ min^{-1}$. In the case of nitrate solutions, the order of the kinetic equation is 3, and the rate constant is 21.5 $m^6\ kg^{-2}\ min^{-1}$.

As to chloride solutions, the experimental kinetic curves for the extraction of iron particles from these solutions allow no definite conclusions as to the order of the kinetic equation for the electroflotation process, because the process occurs at a nonuniform rate.

Analysis of experimental results shows that the electroflotation extraction of dispersed particles, combined with magnetic treatment, compares in efficiency with treatment with flocculants. According to calculations, replacement of flocculation by magnetic treatment allows the capital and operational costs of wastewater treatment to be reduced by 65–75% and 95%, respectively, because this excludes the need in flocculants and in the equipment for their preparation and dosing in wastewater.

Note that the iron-containing flotation sludge can be used as a pigment in manufacturing paint materials and as a raw material for manufacturing ferrites [4].

CONCLUSIONS

Preliminary treatment of permanent magnetic field on an aqueous dispersion system under optimal conditions affects the phase and dispersed composition, which reveals itself in decreasing surface ζ-potential of particles and increasing mean size of the latter, as well as in decreasing fraction of a fine dispersion phase and decreasing solubility. As a result, the efficiency of the electroflotation extraction of the dispersed phase of sparingly soluble iron, nickel, and cobalt compounds enhances substantially.

Magnetic treatment seems to be one of the most promising ways to intensify and increase performance of the electroflotation extraction from aqueous solutions of dispersed heavy and nonferrous metal compounds for diverse industries.

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