Conference paper

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Electroflotation extraction of sparingly soluble compounds of non-ferrous and rare-earth metals from liquid technological waste

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Abstract: The experimental results describing electroflotation extraction process are presented and analyzed for sparingly soluble compounds of non-ferrous and rare-earth metals, the influence of the disperse phase particle size and particle surface charge on the efficiency and electroflotation rate having been determined.

Keywords: anthropogenic wastes; electroflotation; Mendeleev XX; non-ferrous metals; rare-earth metals; technological solutions.

Introduction

The electroflotation (EF) extraction of inorganic compound disperse phase has been studied actively for the last 15–20 years for non-ferrous metal disperse phase particularly, a number of interesting reviews, articles and monographs having been published [1–6].

Previously the interaction of the ζ-potential and hydrodynamic radius of insoluble particles of non-ferrous metals and rare earth elements with the efficiency of the electroflotation process depending on the nature of the electrolyte and its concentration was not analyzed in the open literature.

Previous studies on the electroflotation process for extracting difficulty soluble compounds of non-ferrous metals have shown that high efficiency in comparison with classical flotation is related to the size of gas bubbles in the electroflotation process that come into contact with a dispersed phase whose size is in the range from 10 to 100 μm.

It is necessary to get the contact of 10–40 μm sized hydrogen bubbles, 20–100 μm sized oxygen bubbles with disperse phase, i.e. sparingly soluble non-ferrous and rare-earth metal compounds for carrying out the electroflotation process successfully.

The high efficiency of the EF process results from the fact that the particle size is 10–100 μm in dilute solutions at disperse phase concentration 10–100 mg/L, it ensuring the effective contact of the particle and

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Table 1: The electroflotation efficiency for some sparingly soluble metal compounds.

Me^{n+}	$Me(OH)_n$	$Me_x(CO_3)_x$	Me_xS_x	$Me_x(PO_4)_x$
Cu^{2+}	High	Average	Average	High
Ni^{2+}	High	Average	Low	Average
Zn^{2+}	Very high	Average	Average	High
Cd^{2+}	Very high	Average	Low	High
Mn^{2+}	High	Average	–	Average
Fe^{3+}	Very high	Average	–	Average
Al^{3+}	High	Average	Average	Average
Cr^{3+}	Low	–	–	–

gas bubbles. Conducting the electroflotation process without special reagents with particles of such size is difficult [6].

Experimental

Investigations of the EF process were carried out on the laboratory-scale non-flowing unit to determine the effect of the solution composition, the nature of the dispersed phase of difficulty soluble compounds of non-ferrous metals. The efficiency of the process was evaluated by the extraction ratio α, which was determined from the analysis of the metal concentration before the start (C_i), and after the completion of the process (C_f) and was calculated by the formula 1.

$$\alpha = \frac{C_i - C_f}{C_i} * 100\ \% \tag{1}$$

The REM concentration was determined on a Thermo Scientific XSeriesII inductively coupled plasma mass spectrometer, a non-ferrous metal concentration was determined on a QUANT-AFA atomic absorption spectrometer.

The particle sizes were evaluated using an Analysette NanoTec laser particle analyzer. Determination of the ζ-potential was carried out with the Malvern Zetasizer Nano laser analyzer of the characteristics of particles of the submicron and nano-range.

Results and discussion

This report presents experimental data on the effect of the solution composition, the pH of the medium, the nature of the dispersed phase, the particle size and the magnitude of the ζ potential on the efficiency of the EF process.

The nature of the metal and of the precipitant ion has been established to influence the EF process essentially. The research's results of the electroflotation efficiency for some sparingly soluble metal compounds, such as hydroxides, phosphates, carbonates and sulfides of some metals are represented in Table 1.

The experiment conditions: solution 1 g/L Na_2SO_4, J_v – 0.4 A/L, Me^{+n} concentration – 0.1 g/L, pH – 6–7 (Al, Fe, Cr), pH – 9–10 (Cu, Ni, Zn, Cd, Mn), τ – 20 min.

The Table 1 analysis shows that zinc hydroxides as well as copper and iron hydroxides are of most efficient floatability; chromium hydroxide, nickel sulfide and cadmium sulfide are of low floatability, it being related to particle size, 1–10 μm, and high negative ξ-potential, –10 … –30 mV.

So, based on the information represented above we can classify the electroflotation efficiency for some sparingly soluble heavy metal compounds into four groups:

I	Group (very high)	$-\alpha = 95-99\,\%$;	$\tau = 1-2$ min
II	Group (high)	$-\alpha = 90-95\,\%$;	$\tau = 4-6$ min
III	Group (average)	$-\alpha = 70-90\,\%$;	$\tau = 6-10$ min
IV	Group (low)	$-\alpha < 70\,\%$;	$\tau > 10$ min

Adding CO_3^{2-}, S^{2-}, PO_4^{3-} ions as a precipitating agent to the solution containing ions of non-ferrous metals Cu, Ni, Zn is proved to result in lowering the mean particle hydrodynamic radius of the disperse phase by the factor of 1.5–2 in comparison with the hydroxide.

The ζ potential shifts to negative values getting to –20; –40 mV. Fine-dispersed negative charged particles are extracted less efficiently. The application of flocculants influences positively because of increasing the ξ-potential, growing the particle size, the extraction level getting to 95–98 % [7].

Changes of the particle nature, ξ-potential value, mean particle hydrodynamic radius and other surface properties take place at the same time as a result of contacting the disperse phase with the electrolyte containing cations, anions, surfactants, flocculants, H_3O^+ ions and OH^- ions. All these things result in either increasing the electroflotation efficiency or depressing the process [8, 9].

A number of interesting results on the electroflotation extraction of sparingly soluble non-ferrous and rare-earth metal compounds as well as ones illustrating the influence of the charge and size of the particles in different electrolytes are represented below.

The shaft and water rubbish containing salt NaCl, Na_2SO_4, Na_2CO_3 components with 10–100 g/L, heavy metal ions, such as Fe, Ni, Zn, Cu – from 100 to 1000 mg/L is formed in treating wastewaters from the mineral source economic sector factories [10, 11]. The EF is carried out less efficiently in such kind of systems in comparison with dilute ones.

The extraction of Fe^{3+} from salt NaCl, Na_2SO_4, Na_2CO_3 solutions has been studied, the data being represented in Table 2.

The efficiency maximum for the extraction of Fe (III) disperse phase from NaCl, Na_2SO_4, $NaNO_3$ solutions, c_{salt} up to 100 g/L is found to get at $c_{in}Fe^{3+}$ up to 100 mg/L. When $c_{in}Fe^{3+}$ increases up to 500 mg/L the process efficiency is reduced because of increasing the disperse phase particle size and dominating coagulation processes. The α-value proves to decrease in increasing the salt concentration. The most abrupt α decrease takes place in $NaNO_3$ solution.

Adding the flocculant to $NaNO_3$ solution allows us to increase the extraction efficiency up to 95 %, the electrolyte concentration being 10–100 g/L.

The nature of the salt has been established to influence the disperse phase particle size and colloidal system stability, the particle size being within the range 50–60 μm.

The practice has shown that flotation and electroflotation processes are more difficult for carrying out in 10–100 g/L solutions in comparison with water solutions containing <1 g/L salt. It is due to following reasons:

- disperse phase nature transformation $Me(OH)_2 \rightarrow Me(OH)A_x \rightarrow MeA_2$;
- size decrease of disperse phase particles in increasing the salt concentration for NaCl, $NaNO_3$, Na_2SO_4;
- suppression of hydrogen release reaction when $NaNO_3$ is present as a result of reducing nitrate ions in $NaNO_3$ solutions of 5 g/L and higher concentration;

Table 2: Influence of the solution composition on the extraction efficiency of Fe^{3+} ions.[a]

$c_{in}Fe^{3+}$, mg/L	Na_2SO_4, g/L			NaCl, g/L			$NaNO_3$, g/L		
	1	10	100	1	10	100	1	10	100
100	99	98	98	98	98	98	99	98	90
300	99	99	97	99	87	85	90	7	0
500	58	18	0	99	85	84	23	2	0

[a]The experiment conditions: pH 6.5; J_v – 0.3 A/L; τ – 10 min.

Table 3: Electrolyte nature influence on the residual metal ion concentration after the electroflotation (EF) and filtration (F).[a]

Salt nature	The residual metal ion concentration, mg/L							
	Cu^{2+} (pH 8.5)		Zn^{2+} (pH 9)		Ni^{2+} (pH 10.5)		Fe^{3+} (pH 6.5)	
	EF	F	EF	F	EF	F	EF	F
Na_2SO_4	10	0.1	2.6	2.0	64	0.15	2	0.2
NaCl	11	1.0	1.9	1.4	5	0.1	2	0.5
$NaNO_3$	30	0.5	5.9	2.0	60	0.05	11	0.4

[a]The experiment conditions: c_{Me}^{n+} – 100 mg/L, c_{salt} – 100 g/L, τ – 10 min, J_v – 0.4 A/L.

Table 4: The influence of the electrolyte nature on the size, ζ-potential and electroflotation efficiency of sparingly soluble nickel compounds.[a]

Ni^{2+}	Electrolyte			
	No electrolyte	NaCl	$NaNO_3$	Na_2SO_4
d_{mean}, μm	50	41	31	38
ζ, mV	–	−18	−38	−24
<10 μm, %	3.1	3.6	6.3	4.0
<1 μm, %	0.1	0.2	0.3	0.3
κ, mC/c	0.4	134	89	80
α, % (τ12 min)	98	94	30	81

[a]The experiment conditions: C_{in} (Ni^{2+}) = 50 mg/L, C (electrolyte) = 100 g/L, J_v = 0.2–4 A/L.

– oxidation of variable valence metals such as Fe, Ni, Co, Mn, Ce as a result of evolving chlorine in pH – 7–10 solutions;

The possibility of extracting Zn^{2+}, Cu^{2+} from NaCl, Na_2SO_4, $NaNO_3$, solutions has been proved experimentally, c_{salt} being up to 100 g/L. Initial concentrations of zinc or copper ions are up to 200 mg/L. The optimal pH values are established to be 8.5–9.0. The extraction efficiency is high within a wide range of salt concentrations, it being 95–99 %; but the process rate decreases in increasing the salt concentration. The more abrupt process slowing-down as well as the metal extraction efficiency decrease prove to take place for $NaNO_3$ solutions and for Ni^{2+}, Fe^{2+} ions.

The data related to the residual ion concentration for such metals as Zn^{2+}, Cu^{2+}, Ni^{2+}, Fe^{3+} and its dependence on the salt nature after the electroflotation (EF) process and additional filtration (F) in different electrolytes are represented in Table 3.

The Zn^{2+} ion disperse phase flotation is the most efficient, the Ni^{2+} disperse phase flotation being the least efficient one. The process for all metal ions such as Zn^{2+}, Cu^{2+}, Ni^{2+}, Fe^{3+} metals is the most efficient in NaCl solutions. The low electroflotation efficiency in NaCl solutions is established to be connected with changing the disperse phase surface properties and forming negative charge particles as well as with decreasing current efficiency for the hydrogen evolution reaction to 5–10 %.

The influence of the electrolyte nature and solution temperature on the surface properties and electroflotation efficiency of sparingly soluble nickel compounds has been studied; the results obtained being represented in Table 4.

The significant decrease of the mean hydrodynamic diameter of sparingly soluble nickel compound particles to 20–40 % (Δd_{mean}) is shown to take place in sodium chlorides, sodium nitrate and salt cake, the fine-dispersed phase particle content increasing correspondently.

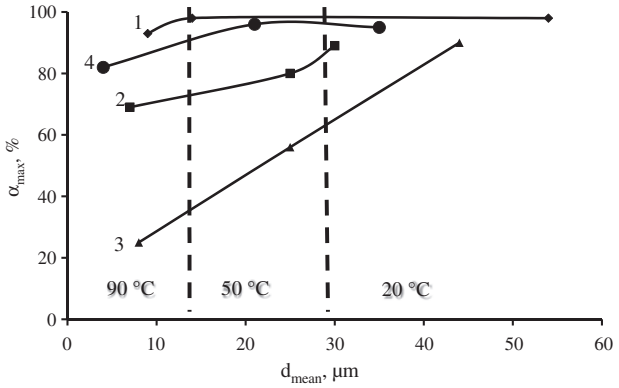

Fig. 1: Dependence of the maximum copper extraction efficiency on the mean hydrodynamic disperse phase particle diameter in electrolyte solutions at temperatures 20, 50, 90 °C: 1 – no electrolyte; 2 – NaCl; 3 – $NaNO_3$; 4 – Na_2SO_4. *c* (Cu^{2+}) – 50 mg/L, *c* (electrolyte) – 100 g/L, pH – 9–9.5; J_v – 0.2–0.4 A/L.

The extraction occurs most efficiently in the solution without electrolyte, which is explained by maximum particle size; it is the least efficient when nitrate-ions are present, the particle size being minimum, <31 μm and the hydrogen release reaction suppression takes place.

The disperse parameters of sparingly soluble copper compounds in different electrolyte solutions have been studied as well. Adding salts to disperse phase copper particle solutions is shown to result in decreasing the mean hydrodynamic diameter of the particles as well as increasing the fine-dispersed phase content significantly. Particles in NaCl solution are the smallest ones, their size being 29 μm.

Disperse phase copper particles have been shown to be extracted most efficiently from the solutions with no salt, α_{max} = 98 %, the extraction efficiency being minimum for NaCl and $NaNO_3$ solutions, α_{max} – <90 %.

The temperature influence on the disperse parameters of sparingly soluble copper compounds in electrolyte solutions has been appraised.

The Fig. 1 shows the dependence of the mean hydrodynamic diameter and maximum extraction efficiency α_{max} for disperse phase particles on the electrolyte nature and the solution temperature.

Increasing the ambient temperature up to 50 °C has been shown to result in decreasing the mean hydrodynamic particle diameter to 14–25 μm regardless of the electrolyte nature, increasing temperature up to 90 °C causes d_{mean} decrease to 4–9 μm and the extraction efficiency decrease.

The flotation process plays an important part in chemical engineering systems for producing rare-earth elements and their compounds from water solutions. Recently some interesting results have been obtained in studying the electroflotation extraction of some rare-earth elements like Ce^{3+}, Ce^{4+}, Y^{3+}, Sc^{3+}, La^{3+} and their mixtures from process liquors [10–14] (Fig. 2).

The analysis of dependences $\alpha = f(pH)$ demonstrates that there are two regions of electroflotation process in Na_2SO_4 solution. $La(OH)_3$ is extracted at pH = 10–11, similar to $NaNO_3$, NaCl. The extraction degree reaches 50–60 %.

Cerium is the most common element and it is used in many industries quite often. It should be noted however that ore materials mainly contain cerium in the form of compounds Ce (III), Ce (IV) compounds being used in industrial processes.

The comparison of the results obtained has been allowed us to single out the main factors having a maximum effect on completeness and efficiency of electroflotation extraction of sparingly soluble (III, IV) cerium compounds depending on the solution pH (Table 5).

The electroflotation extraction of sparingly soluble (III) cerium compounds occurs with maximum completeness and efficiency within of range pH 7–9, the range of pH for sparingly soluble (IV) cerium compounds being 4–7. The extraction efficiency achieves 97–96 % without using flocculants. The extraction of Ce (III) and Ce (IV) disperse phase particles is quite hard at pH = 10. It appears to be due to decreasing the particle chare to –60 mV, the effect not being significant for Ce (IV) compounds.

New data on EF extraction of sparingly soluble scandium compounds have been published [14].

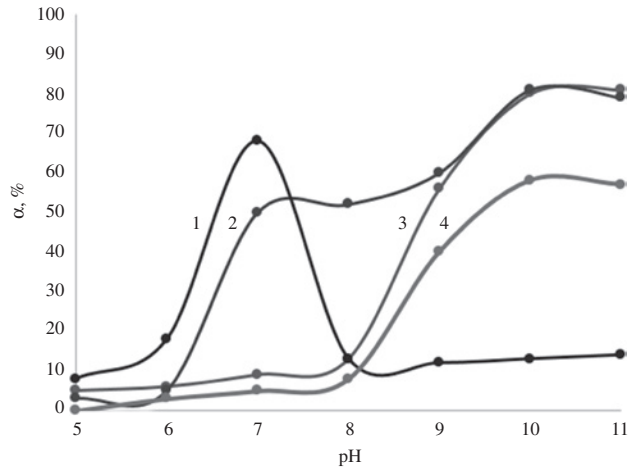

Fig. 2: Electroflotation extraction of sparingly soluble lanthanum compounds from process liquors: 1 – carbonate background; 2 – sulfate background; 3 – chloride background; 4 – nitrate background. C_0 (La^{3+}) = 50 mg/L, C (electrolyte) = 1 g/L, J_v = 0.4 A/L, pH = 5–11, τ = 20 min.

Table 5: Influence of the medium pH on the disperse parameters, ζ-potential and electroflotation efficiency of sparingly soluble (III, IV) cerium compounds.

pH	Disperse phase					
	Ce (III)			Ce (IV)		
	d_{mean}, μm	ζ, mV	α, %	d_{av}, μm	ζ, mV	α, %
6	12	39	27	19	−16	96
7	9	33	96	20	−16	97
8	12	−16	97	20	−16	96
9	14	−21	96	21	−18	95
10	12	−60	62	21	−21	93

[a]The experiment conditions: c_0 (Ce^{3+}) = 100 mg/L; c_0 (Ce^{4+}) = 100 mg/L; i = 0.4 A/L; τ = 10 min.

The main conclusions

The obtained experimental results on the EF process make it possible to formulate a number of basic conclusions:

- high extraction ratio are typical for amorphous precipitates having a size of 50–100 μm and a minimum value of the ζ-potential or close to an isoelectric point (for example, copper, nickel, cadmium, iron hydroxides);
- low extraction ratio for particles having a size of 10–30 μm and high negative values of the ζ-potential of 20–30 mV (oxides, sulfides, phosphates)
- strong suppression of the EF process is observed in solutions of $NaNO_3$ with a concentration of 100 g/L due to the suppression of the hydrogen evolution on the cathode and the reduction of the gas saturation due to the cathodic reduction of NO^{3-} ions;
- the efficiency of the EF process reduces with an increase of the dispersed phase concentration more than 500 mg/L due to the course of sedimentation processes. The process is more effective in the concentration range of 10–200 mg/L;
- the temperature increasing of the solution leads to a decrease of the particle size of the dispersed phase, primarily in solutions of electrolytes ($NaNO_3$), which leads to a reduction in the extraction ratio from 80 to 20 %.

Conclusions

The electroflotation method allows us to extend appreciably the manufacturing capability of traditional ways for the reagent treatment and separation of heterogeneous mixtures, giving chance to use natural raw material completely and reduce valuable substance losses in manufacturing.

Scientific research, practice and routine of applying have proved a number of real advantages of the electroflotation method. The most important of them are high rate being 5–10 min and high separation efficiency being around 99 %. The other pluses are possibility of simultaneous extracting different phase-disperse content additives of 10–100 μm size particles; low power inputs being within the range 0.1–0.3 kWh/m^3.

The advantages mentioned above explain the attention payed to developing and improving the electroflotation process in many countries of the world.

Table of symbols

α	the efficiency of the electroflotation process, %
C_i	the metal concentration before the electroflotation process, mg/L
C_f	the metal concentration after the completion of the electroflotation process, mg/L
ζ	zeta-potential, mV
J_v	the volumetric current density, A/L
τ	the time of conduction of the electroflotation process, min
d_{av}	the mean hydrodynamic particle diameter, μm

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