ISSN 1070-3632, Russian Journal of General Chemistry, 2014, Vol. 84, No. 5, pp. 1058–1060. © Pleiades Publishing, Ltd., 2014.
Original Russian Text © V.I. Il'in, 2012, published in Rossiiskii Khimicheskii Zhurnal, 2012, Vol. 56, Nos. 5–6, pp. 96–99.

Use of Precipitate Electroflotation for Increasing the Degree of Wastewater Treatment to Remove Nonferrous Metals

V. I. Il'in

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

Received November 1, 2012

Abstract—A method is suggested and studied of removing nonferrous metals of from waste waters. The method is, that waste water containing nonferrous metals is treated to adjust pH to 9–10, after which sodium orthophosphate solution is added at metal/phosphate ion weight ratio 1 : (0.5–0.7) resulting in formation of slightly water-soluble metal hydroxyphosphate whose solubility is inferior to that of corresponding metal hydroxide. To isolate resulting compounds, electroflotation method with insoluble anodes is employed. Efficiency of removing nonferrous and heavy metals meets norms established for water discharge into fish-industry reservoirs.

DOI: 10.1134/S1070363214050430

INTRODUCTION

A method commonly used in wastewater treatment to remove nonferrous metal cations is that based on chemical precipitation of metal compounds via reacting metal cations with suitable alkaline agents, followed by gravity separation of the resulting dispersed phase. However, in some cases, particularly in the presence of an aggregation-resistant dispersed phase, this method does not ensure degrees of treatment compliant with appropriate quality standards [1, 2], and a need arises in extra post-treatment step.

With a view to improving the efficiency of the method of wastewater treatment to remove nonferrous metals we suggested that precipitate electroflotation be carried out after the reaction between the metal cation and the alkaline agent. For details on physicochemical principles and dependences of the process efficiency on various factors, see [3].

Methodology

In our experiments we used model aqueous solutions and samples of real industrial wastewaters containing a dispersed phase of poorly soluble compounds and ions of nonferrous metals Ni, Co, Cd, Cu, Cr, Zn, etc. (to 100 mg L^{-1}). The electroflotation recovery of the dispersed phase comprising nonferrous metals was carried out on laboratory and industrial flow-type electroflotators using ruthenium-titanium oxide anodes and stainless-steel cathodes.

The concentrations of the nonferrous metals in aqueous solutions were determined by atomic absorption spectrometry (a KVANT-AFA spectrometer), and the phase composition of the dispersed phase, by IR spectroscopy (a UR-20 spectrophotometer, KBr pellets). The X-ray diffraction analysis was performed on a DRON-2 setup.

RESULTS AND DISCUSSION

Depending on the salt composition of aqueous solutions and the charge and concentration of the salt anions and nonferrous metal cations, at the optimal pH of formation of the dispersed phase of metal hydroxides their solubility (the equilibrium concentration of the metal cations) lies within the 0.5–1.0 mg L^{-1} range. Upon removal of the dispersed phase of nonferrrous metals from aqueous solutions by electroflotation procedure the concentration of the metal cations in the treated water decreases by 10–25% on the average due to their physical adsorption on the surface of hydroxide compounds.

A method was proposed and examined in which reduction of the residual concentrations of nonferrous metal ions in water being treated is achieved by adding compounds, comprising ionized groups of hydrophilic organic substances, to the dispersed system. The solubility of the resultant poorly soluble compounds is lower than that of the corresponding hydroxide compounds.

Residual total concentration (dissolved plus nondissolved forms) of the metal compounds and average size and ζ-potential of the dispersed phase particles in relation to the $[M^{n+}] : [PO_4^{3-}]$ concentration ratio in the initial mixture

$[M^{2+}] : [PO_4^{3-}]$	Residual concentration, mg L^{-1}	Phase composition of compound recovered (IR-spectroscopic data)	Average particle size, μm	ζ-potential of particles, mV
1 : 0	4.0–9.3	$M(OH)_2$	48–55	+(3…8)
1 : 0.5	0.01–0.02	$M_3(PO_4)_2 \cdot MHPO_4 \cdot nH_2O \cdot M(OH)_2$	75–90	+1…–3
1 : 1.0	0.01–0.08	$M_3OH(PO_4)_2 \cdot MHPO_4 \cdot nH_2O$	70–85	–(4…18)
1 : 1.5	0.4–5.0	$M_3OH(PO_4)_2 \cdot MHPO_4 \cdot nH_2O$	30–40	–(12…22)
1 : 2.0	7.2–17.5	$M_3(PO_4)_2 \cdot nH_2O$	28–36	–(35…38)

It was found that, depending on pH of the medium and concentration ratio of the reacting components, the reaction of nonferrous metal cations Ni(II), Zn(II), Cu(II), Cd(II), Co(II), and Mn(II) with orthophosphate ions and the subsequent electroflotation removal of the resulting dispersed phase can give flotation concentrates with different phase compositions. For example, in acidic media (pH 3–5) with excess metal cations the most stable solid phase is metal phosphate hydrate $MHPO_4 \cdot nH_2O$. Increase in pH leads to formation of metal hydroxide whose surface sorbs the phosphate ions, $M(OH)_nPO_4^{3-n}$. At excess phosphate ions, precipitation of metal orthophosphate hydrate $M_3(PO_4)_2 \cdot nH_2O$ is observed; in an alkaline medium it is converted to metal hydroxyphosphate $M_n(PO_4)_{3-n}OH$ [4].

When determining the mechanism of the orthophosphate ion action as precipitant, account must be taken of the fact that, along with orthophosphate ion PO_4^{3-}, the aqueous solution also contains hydrogen orthophosphate ion HPO_4^{2-} produced by the hydrolysis reaction:

$$PO_4^{3-} + H_2O \rightarrow HPO_4^{2-} + OH^-. \tag{1}$$

Presumably, the reaction of the metal cations with hydroxyl and hydrogen orthophosphate ions proceeds by the following scheme:

$$\begin{aligned} aM^{2+} + (b - 2c)HPO_4^{2-} + 2cOH^- &= cM(OH)_2 \cdot dM_3(PO_4)_2 \\ &+ 2aM^{2+} + 2bHPO_4^{2-} + [d - (2b + c)]PO_4^{3-}, \end{aligned} \tag{2}$$

where a is the number of moles of M^{2+} ions; b, number of moles of HPO_4^{2-} ions; c, parameter characterizing the basicity of the reaction medium; and d, number of moles of PO_4^{3-} ions.

From the expression for reaction (1) constant we obtain

$$pH = K - \log ([HPO_4^{2-}]/[PO_4^{3-}]). \tag{3}$$

Considering reaction (2), this leads us to

$$pH = K - \log (2b / [d - (2b + c)]. \tag{4}$$

It is seen from expression (4) that, at constant pH and temperature of solution, the basicity c of the freshly precipitated primary solid phase will be determined by the number of the orthophosphate ions introduced into the reaction medium, $d - (2b + c)$.

In the solid phase–solution heterogeneous system, which is formed in the primary stage of the process, the following secondary reaction proceeds spontaneously:

$$\begin{aligned} &cM(OH)_2 \cdot dM_3(PO_4)_2 + 2bHPO_4^{2-} \\ &= (c - n)M(OH)_2 \cdot (d + n)M_3(PO_4)_2 \\ &\quad + [d - (2b + c)]PO_4^{3-} + 2H_2O. \end{aligned} \tag{5}$$

The neutralization reaction may result in substitution of nOH^- ions in the crystal structure of the solid phase by nPO_4^{3-} ions, as confirmed by IR-spectroscopic data for the flotation concentrate particles.

Along with reaction (5), a hydrolysis reaction may proceed in which the PO_4^{3-} ions in the crystal structure of the solid phase are replaced by OH^- ions. It was found that the secondary reaction, both neutralization and hydrolysis, causes changes in the composition of the solid phase.

The highest electrofloatability is exhibited by hydroxylphosphates of metals (Cu, Cd, Zn, Ni, Co). At the concentration ratio in the initial mixture $[M^{n+}] : [PO_4^{3-}]$ = 1 : 0.5–0.7 the residual total concentration (dissolved plus nondissolved forms) of individual nonferrous metal compounds after electroflotation removal of the dispersed phase is 0.01–0.02 mg L^{-1} (see table). The tabulated data show that the involvement of orthophosphate ions in wastewater treatment to remove individual metal cations causes changes in the phase composition, average size, and ζ-potential of the dispersed phase particles.

Running the process under optimal conditions not only leads to decreased solubility of the solid phase but also is accompanied by the flocculation (an increase in the particle size) and electrostatic (a decrease in ζ-potential of the particles) phenomena.

We determined the optimal process conditions for higher degrees of wastewater treatment to remove dissolved and nondissolved forms of nonferrous metal compounds (Cu, Cd, Zn, Ni, Co, Al, Cr, Mn) occurring in wastewaters as a mixture.

It was found that, at the concentration ratio in the initial mixture $[\Sigma M^{n+}] : [PO_4^{3-}] = 1 : 0.5-1.5$ and pH 9–10, the residual concentration of the metal compounds after electroflotation recovery of the dispersed phase is 0.3–0.5 mg L^{-1}. In the extra filtration step the concentration of dissolved forms of nonferrous metal compounds in the treated water samples decreases to 0.01–0.05 mg L^{-1}.

With a view to increasing the degree of wastewater treatment via exhaustive recovery of the dispersed phase, a 0.05% solution of organic flocculant polyacrylamide was added to the water being treated after formation of the dispersed phase, before initiation of electroflotation. A maximum degree of treatment was reached in the case when the weight ratio of the metal recovered to the flocculant added (polyacrylamide) was 1 : (0.05–0.008). Examination of the particle size distribution showed that, in the presence of the organic flocculant, the average size of the particles increases due to their coalescence and formation of agglomerates. This leads to more efficient capture of the particles by gas bubbles and, thereby, to formation of stable complexes between particle agglomerates and gas bubbles, with the result being that higher degrees of treatment, specifically to residual concentrations of 0.005–0.01 mg L^{-1}, are achieved. Lower residual concentrations of the metal cations in the treated water compared to the filtered sample suggest that dissolved forms of metals are partially removed from the water via sorption on the resulting complexes having a highly developed surface.

The beneficial influence on the efficiency of nonferrous metal recovery from wastewaters, exerted by the techniques proposed, has stimulated their testing for water hardness reduction applications.

To this end, we examined the process of removal of calcium and magnesium cations from different water categories (process water, underground water, brines, etc.). It was found that, with sodium hydroxide as precipitant, the calcium and magnesium cations are fixed into poorly soluble compounds. The residual hardness of the treated water was estimated at 1–2 meq L^{-1} (20–40 mg L^{-1}). Extra treatment procedure with the use of orthophosphate ions provides for removal of calcium and magnesium ions as a mixed-composition dispersed phase comprised of carbonates, hydroxides, and phosphates to residual water hardness of 0.1 meq L^{-1}. With this procedure it is possible to avoid in certain cases the step of water hardness removal by ion-exchange process and to use low-hardness waters for makeup purposes in recycling water systems.

CONCLUSIONS

Addition of orthophosphate ions to the wastewater being treated causes changes in the phase composition and particle size distribution of the nonferrous metal compounds recovered as manifested in a decrease in ζ-potential of the particle surface, an increase in the average particle size, and a decrease in solubility of the solid phase. As a result, higher electroflotation efficiencies and increased degrees of wastewater treatment are achieved.

The method proposed is suitable for application in chemical industry, ferrous and nonferrous metallurgy, and heavy engineering sector for wastewater and water treatment purposes.

REFERENCES

1. *Water Quality Standards for Water of Water Bodies Used for Commercial Fishing, Including Standards of the Maximum Permissible Concentrations of Harmful Substances in Waters of Water Bodies Used for Commercial Fishing* (Approved by Order no. 20 of the Russian Federal Fisheries Agency of January 18, 2010).
2. *Hygienic Standards GN 2.1.5.1315-03: Maximum Permissible Concentrations (MPCs) of Chemical Substances in Water of Household and Cultural Use Water Bodies* (effective since June 15, 2003).
3. Kolesnikov, V.A., Il'in, V.I., Kapustin, Yu.I., et al., *Elektroflotatsionnaya tekhnologiya ochistki stochnykh vod promyshelennykh predpriyatii* (Electroflotation Technology of Industrial Wastewater Treatment), Moscow; Khimiya, 2007.
4. Shchegrov, L.N., *Fosfaty dvukhvalentnykh metallov* (Divalent Metal Phosphates), Kyiv: Naukova Dumka, 1987.