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INTEGRATED TREATMENT OF RINSING COPPER-CONTAINING WASTEWATER

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Abstracts: A comprehensive ion-exchange based technology is proposed for treatment of copper-containing rinsing water with closed-circuit water supply and utilisation of the valuable metal. We applied the principle of ferritisation for wastewater treatment. The research results were used for development of the new environmentally sound method for utilisation of eluates of ion-exchange filters with production of a marketable product - copper ferrit and other ferromagnetic substances.

Key words: wastewater treatment, copper, utilization, ferritization.

1. Introduction

Modern development is accompanied by massive growth of releases of toxic waste that exceed the natural neutralisation capacity of ecosystems. Industrial wastewater discharges contain a substantial amount of pollutants, including the most hazardous ones – ions of heavy metals. Industrial facilities commonly apply reagent-based methods for treatment of wastewater and concentrated technologic solutions - i.e. neutralisation and precipitation of ions of heavy metals by alkaline reagents. As a result, industrial facilities accumulate stockpiles of poorly soluble sludges, which contain compounds of heavy metals and copper particularly.

Copper is an important element for the industry, but its natural resources are getting limited. Various sections of the industry, in particular, electronic, chemical and engineering facilities generate copper-containing wastewater and sludge. The actual performed wastewater treatment allows to use efficiently only 25% of primary copper. Environmental compliance demands the development of new technologies with on-site recycle reuse of both treated water and heavy metals extracted.

Depending on levels of heavy metals in copper-containing wastewater flows of industrial facilities, there are two types of wastewater: diluted (rinsing) and concentrated ones (exhausted electrolyte, pickling solutions, eluates of ion-exchange filters). The current research study is dedicated to development of the new resource-efficient technology for treatment of rinsing wastewater flows of copper electroplating facilities with re-use of purified water and valuable compounds of heavy metals.

2. Fundamentals of copper-containing wastewater processing

Detailed studies of published sources, as well as many years of our expedience of addressing the problem of efficient treatment of polluted wastewater, including inter alia copper pollution, suggest that now it is rather important to modernise reagent-based technologies of industrial wastewater treatment in order to ensure a reliable utilisation of toxic copper-containing sludges. Generally, sludges do not undergo any further processing and are disposed to landfills. However, these sludges are not stable and heavy metals may be leached from them by water. Besides that, the reagent-based treatment allows to reduce heavy metals contents in wastewater only to 0.1−0.2 mg/dm^3, or one order of magnitude higher than established by the Standard requirements (Hammer, 2006).

Notwithstanding numerous research studies, existing sludge utilisation technologies (e.g. their use in metallurgy) have not been applied yet, due to cost considerations. Utilisation of these sludges as components of construction materials is not acceptable due to environmental and health problems, as heavy metals compounds may be gradually leached by water from these construction items. Copper-containing wastewater may be also treated electrochemically, but electrochemical

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technologies are energy-intensive. Thus development of a rational technology for wastewater treatment with reliable utilisation of toxic waste is rather relevant.

Analysis of the contemporary situation in the sphere of treatment of wastewater contaminated by heavy metals in general and by copper in particular, suggests appropriateness of development of a comprehensive wastewater treatment technology with further waste recuperation. If the waste cannot be utilised in an economically viable manner, we believe that it is important to obtain leaching-resistant compounds of heavy metals allowing their environmentally safe landfilling. As our previous research works suggest (Kochetov et al., 1998), the most prospective option for introduction of low-waste processes is associated with application of local wastewater treatment installations for individual electroplating operations, including copper electroplating. That ensures purposeful extraction of valuable metals and design of closed circuit water supply systems.

Rinsing wastewater of copper electroplating facilities contain the following pollutants: suspended solids - up to 50 g/m^3, heavy metals (Fe^{2+} and Cu^{2+}) - up to 4 g-eq/m^3, COD - up to 50 g/m^3 at pH of 3 to 4. Due to the fact that wastewater flows of industrial facilities tend to contain relatively low concentration of heavy metals ions, it is appropriate to apply ion-exchange technologies instead of traditional reagent-based ones, as ion-exchange methods allow to concentrate pollutants and to process the water jointly with technological solutions.

3. Development of new Integrated Technology for copper-containing Wastewater Treatment

3.1 Wastewater purification

Practical experience of operating ion-exchange installations and numerous published data suggest that application of ion exchange technologies is appropriate when levels of organic substances and suspended solids do not exceed 6 and 3 g/m^3, respectively. Accounting for these considerations, we propose to use a two-section installation for treatment of wastewater flows of copper electroplating operations - after pre-treatment in the first section, water comes to the second section for ion exchange treatment (Fig. 1). The first section of installation includes two consecutive filters. The upper filter - filled with foamed polystyrene - allows to separate suspended solids, while in the lower filter organic substances are separated by sorbtion on activated charcoal. At the base of analysis of our research data we proposed the operating parameters for these filters, that ensure the necessary reduction of levels for suspended solids and organic substances in the purified water (Kochetov et al., 2003).

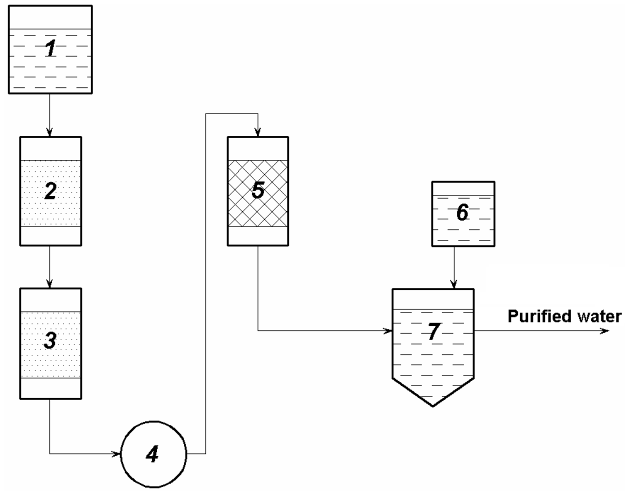

Fig. 1. Model technological scheme of rinsing wastewater treatment: 1 – rinsing water collector, 2 – filter with foamed polystyrene filler, 3 – adsorber with activated charcoal, 4 – pump, 5 – H-cationite filter, 6 – alkaline solution metering pump, 7 – mixer-neutralizer.

After the adsorption treatment, water is pumped to the ion-exchange filter for removal of heavy metals' ions. We propose to use an ion-exchange filter loaded with strongly acidic H-cationite and developed key operating parameters of the filter (Kochetov et al., 2003). When concentrations of sorbed ions in the discharge water of the ion-exchange filter reach 0.02 g-eq/m3, the cationite is exhausted and should be regenerated by sulphuric acid solution (1 mol/dm3). In terms of quality, the treated water of the proposed technological process meets all requirements to its secondary industrial use: suspended solids - up to 3 g/m3, concentration of heavy metals (Cu^{2+} and Fe^{2+}) ~ 0.02 g-eq/m^3, COD up to 3 g/m^3 and pH ~ 7.

3.2 Eluate processing

Acidic eluate after the regeneration of H-cationite filter by a sulphuric acid solution is actually the only waste product of the technology proposed. The eluate contains Cu^{2+} and Fe^{2+} ions in almost equal concentrations and their overall level reaches up to 20 g/l. The ion-exchange method could be scarcely efficient in both economic and environmental terms unless a solution would be found for rational utilization of the eluate (Hammer, 2006). Therefore, utilization of eluates is an important final stage of the comprehensive wastewater treatment.

Industrial facilities generally apply the traditional method of neutralization by alkaline reagents for treatment of acidic eluates. The method generates another wastewater flow with pH values over 9.5 that cannot be discharged to municipal sewers. The unstable sediment obtained is generally landfilled and pollutes the environment. Summing up - this method of eluate treatment is not environmentally acceptable and results in loss of valuable components.

So, identification and development of efficient and economically viable methods for utilization of concentrated copper-containing wastewater are rather important. In particular, the ferritization method

(Zapolsky, 2000) is quite promising in the case of treatment of liquid industrial waste, including eluates. In essence, the ferritization method is associated with formation of dispersed particles with magnetic properties in water contaminated by ions of heavy metals. The method allows easy separation of chemically inert sediments with ferrite structure and ensures a high degree of water purification, allowing to re-use secondary water for on-site industrial purposes.

4. Experimental study

Ferritization method allows to achieve co-sedimentation of Cu^{2+} and Fe^{2+} ions by alkaline reagents. Initially formed highly dispersed particles are in close contact, substantially accelerating formation of the crystalline structure of copper ferrite in the course of further oxidation of Fe (II) into Fe (III). The most environmentally acceptable option is associated with oxidation of bivalent iron by oxygen in the air. Application of chlorine or other oxidizing reagents is undesirable. The reaction results in formation of substances with ferrite structure according to the following scheme:

$$\mathrm{xCu^{2+} + (3-x)\,Fe^{2+} + 6\,OH^- + 0{,}5O_2 = Cu_x\,Fe_{3-x}\,O_4 + 3H_2O} \tag{1}$$

Cu^{2+} ions are known (Zapolsky, 2000) to catalyze oxidation/reduction processes, including oxidation of Fe (II) into Fe (III).

So, at the final stage of the wastewater treatment process, the eluate from the ion-exchange filter comes to the reactor for ferritization treatment. We seek to develop conditions for obtaining of copper ferrite $CuFe_2O_4$. This compound is used in radio-engineering, electronic and automatic devices as a magnetostriction material. As the industrial production of copper ferrite is rather energy-intensive - it is synthesized by high-temperature sintering at about 1000°C (Carter & Norton, 2007) studies of low-temperature synthesis may be of particular importance. At moral ratio Fe to Cu of 2:1 in the reaction mixture it is possible to obtain copper ferrite according to phase diagram of the system Fe-Cu-O, (Yund & Kullerd, 1964):

$$4Fe^{2+} + 2Cu^{2+} + O_2 + 12OH^- = 2CuFe_2O_4 \downarrow + 6H_2O \tag{2}$$

It is worth to note, that ions of copper and iron (II) are present in the eluate in almost equal molar concentrations, in order to produce copper ferrite, it is necessary to add excessive amounts of iron (II) ions to ensure Fe to Cu molar ratio of 2:1.

4.1 Experimental procedure

The experimental setup for research of ferritization process is shown in Fig. 2. In order to ensure the necessary stoichiometric ratio of iron to copper in the reaction mixture, the necessary volume of iron (II) sulphate solution is added to the reactor and then - at intensive stirring - 20% solution of sodium hydroxide is added to reach the required pH value. The resulting suspension of copper and iron (II) hydroxides after the alkaline treatment is then treated by air bubbling at rate of about 1 cm^3/s.

We studied the following factors of the ferritization process:

– temperature of the reaction mixture - from 25 to 80 °C;
– pH from 6 to 12;

The quantitative analyses were done by using photometric and potentiometric methods. (Lurye, 1984). Structure of the sediment was studied by X-ray diffractometry with application of DRON-3 diffractometer, using filtered Cu radiation.

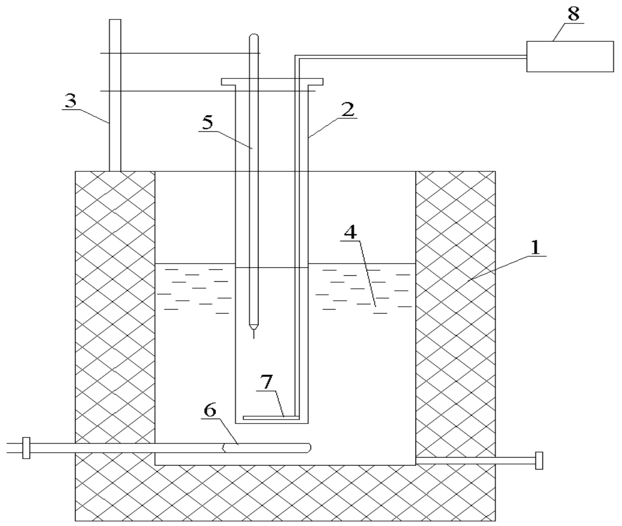

Fig. 2. The laboratory setup for ferritization process: 1 – thermostat case, 2 – cylinder with the treatment solution, 3 – stand, 4 – water, 5 – thermometer, 6 – tubular electric heater, 7 – air distribution system, 8 - compressor.

5. Results and discussions

Difractograms of all the samples studied show only peaks that are included into Table 1. Analysis of X-ray diffraction data suggests that structure of the obtained substances corresponds to spatial group F d3m (a cubic crystal lattice of spinel type) - i.e. the one of copper ferrite. The above assumption is supported by interfacial distances that meet relevant parameters of the standard sample of copper ferrite. In addition, the obtained crystalline substance displays ferromagnetic properties.

Lattice constant a of copper ferrite was estimated by equation:

$$a = d\sqrt{H^2 + K^2 + L^2} \tag{3}$$

where d is the interfacial distance measured in the precision area at the gravity centre of the diffraction peak with crystallographic indices 311.

Lattice constant of our samples, as estimated by equation (3), reaches 0.8534 nm or somehow higher than in the case of standard 0.8462 nm for copper ferrite obtained by the traditional methods (Clegg, 1998). Higher lattice constants of our samples in comparison to standard ones are most probably associated with inclusion of water molecules into crystalline ferrite lattice.

Table 1. Structural parameters of the compounds obtained.

Crystallographic indices, HKL	Interfacial distances d, nm	Relevant intensity of peaks I*, %
311	0,257	100
331	0,167	65
400	0,145	71
533	0,130	59
444	0,123	21

** the value of 100% corresponds to intensity of the highest peak*

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The latter assumption is confirmed by the fact that after high temperature thermal treatment of our samples (5 hours at 800°C), lattice constants of the samples became almost equal to the standard parameter. Besides that, X-ray diffractometry suggests that at higher temperatures contents of amorphous phase decrease with relevant increase of contents of crystalline copper ferrite.

Results of study of magnetic properties of sediments depending on reaction conditions are shown in Fig. 3. The results suggest that heating of the reaction mixture from 25 to 80°C results in more than 3-fold increase of magnetic susceptibility. As for pH value, maximal magnetic properties were observed at the level of 9.0−10.0. At lower pH values, the rate of iron oxidation decreases. At pH values over 10.0 magnetic properties of sediments somehow decrease as diamagnetic copper substances are formed, such as copper oxide. Therefore, maximal yields of crystalline copper ferrite are observed at 80°C and pH of 9.0−10.0 (as confirmed by X-ray phase analysis).

Duration of the ferritization process depends on temperature and may reach 20−30 min at temperatures over 60°C and approximately 5 hours at temperature of 20°C. The formation process of crystalline ferrite structure may be accelerated by addition of $CuFe_2O_4$ crystals, that serve as centers of crystallization of the new solid phase of copper ferrite. The necessary amount of the crystallization initiator reaches about 0.05 g/dm^3.

After cooling of the reaction mixture, the ferromagnetic sediment is separated by filtering at magnetic filter. The ferrite sediment from magnetic filters is dried and removed for utilization.

Depending on amounts and quality of the product, we may assess economic factors and select the most appropriate utilization option:

- direct industrial application of the ferromagnetic substance;
- production of glazing enamels for ceramic tile;
- landfilling.

But even in the case of landfilling, the ferrite compounds are thermodynamically stable. This means a substantially enhancement of environmental safety of the precipitated products in terms of compliance with MACs for migration of heavy metals to environmental media. Besides that, after the ferritization treatment, the water meets all requirements for its re-use for industrial purposes.

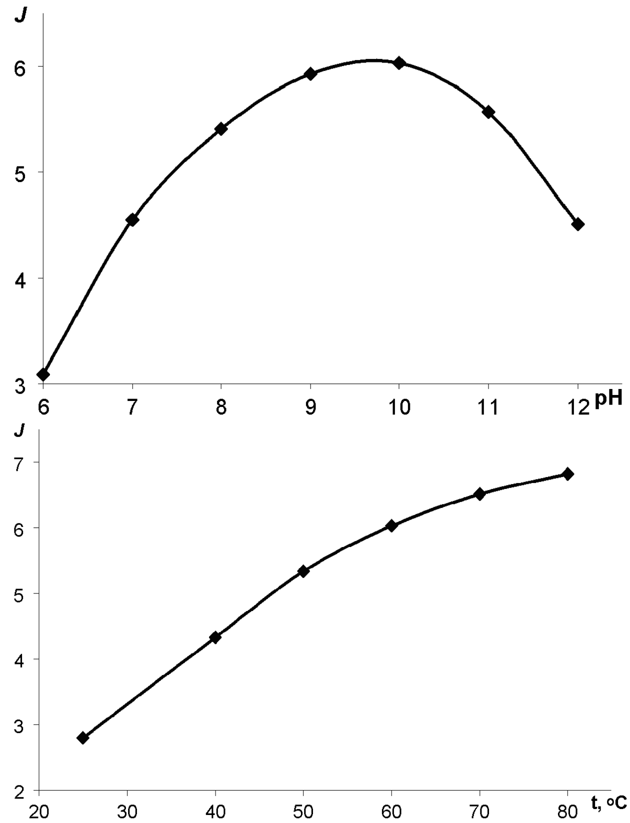

Fig. 3. Magnetic susceptibility of sediments depending on temperature (a) at pH = 10 and depending on pH (b) at temperature of 60°C.

6. Conclusions

Current lack of recycling technologies results in irreversible loss of the valuable components after industrial wastewater treatment. As result of our studies, we propose the comprehensive technology for treatment of wastewater contaminated by copper ions and other heavy metals. We have applied the principle of ferritization in order to produce dispersed particles with magnetic properties in wastewater. These insoluble and chemically inert particles can be easily concentrated and separated from wastewater and thus recycled effectively. Moreover, due to application of ferritization method quality of the treated wastewater meets all requirements needed to reuse it as process water on site.

Introduction of the technology at industrial facilities would allow to avoid discharge of toxic wastewater to surface water bodies and reduce water treatment costs due to re-use of treated water in closed-circuit water supply systems. In addition, the method allows to select optimal options for environmentally sound utilization of waste of the wastewater treatment process, accounting for particular needs of a specific facility. The benefit of our new processing technology is the by-product copper ferrite, which can be used as a marketable substance.

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