DOI: http://doi.org/10.21698/simi.2019.fp03

ENERGY-SAVING INTEGRATED FERRITISATION TREATMENT OF NICKEL-CONTAINING WASTEWATER

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Abstract

Modern requirements to electroplating waste treatment necessitate development of technologies that would allow on-site recycle and reuse of both treated water and residuals of water processing. The most prospective option for introduction of recourse-saving wastewater purification is associated with application the method of ferritisation. In this connection, the paper presents an advanced ferritisation process for reduction of initial concentrations of heavy metals (HM) in exhausted nickel electroplating electrolytes from 100 mg/L to 0.3 mg/L. Effects of main technological parameters of such wastewater treatment at thermal and electromagnetic pulse methods of activation of the ferritisation process were determined experimentally. Kinetics of removal of nickel and iron ions from aqueous solutions was investigated. Phase compositions and properties of sediments from wastewater treated were studied. The sediments are predominantly characterised by crystalline nanostructures, ferromagnetic properties and chemical stability, supporting opportunities for their environmentally sound utilisation. Proposed comprehensive process for treatment of liquid industrial waste flows would prevent contamination by toxic effluents; ensure rational use of water, raw materials and energy inputs.

Keywords*: ferritisation, nickel, sediment, utilisation, wastewater treatment*

Introduction

Toxic wastewater flows from electroplating plants pose particular hazards to human health. Release of these wastewater flows into the environment also results in losses of a valuable metal. Therefore, a comprehensive treatment of electroplating wastewater flows with closed systems of resource circulation directly on-site is relevant solution (Trokhymenko & Gomelya 2017).
Analysis of existing methods of electroplating wastewater treatment shows that, the reagent-based method still remains the most commonly used. This method involves precipitation of HM ions by alkaline reagent and is characterized by low degree of HM removal and formation chemically unstable bulky sediments.
The method of ferritisation is a rather prospective one for treatment of wastewater of electroplating plants (Pritosiwi 2012). The method allows to obtain almost insoluble compounds of iron and other HM by treatment of their ions with an alkaline reagent and air oxygen and provides a high degree of removal of HM ions from wastewater. In recent years, numerous studies have been conducted on wastewater treatment by ferritization (Chaiyaraksa & Klaikeow 2006; Pritosiwi 2012). The authors (Morgan et al. 2001; Petrick et al. 2008) demonstrated incorporation of HM ions into ferrite structure. In papers (Kochetov et al. 2010; Heuss-Aßbichler et al. 2016) the

ferritisation process was used for treatment of rinsing and concentrated copper-containing water, respectively.

These studies found that main factors affecting the process of wastewater treatment include pH, temperature (T) and duration (t) of the treatment process, initial concentrations of HM (C_Σ), and ratios (Z) of their concentrations. However, the traditional thermal activation method of ferritisation wastewater treatment is rather energy intensive, as it is carried out at temperatures above 60 °C. As an alternative to the thermal activation electromagnetic pulse discharges, can be applied (Yadollahpour et al. 2014). Therefore, in contemporary conditions, further improvement of the ferritisation method with minimisation of energy and reagents consumption is fairly relevant. Accounting the above, this study is dedicated to experimental research on influence of technological parameters and ways of activation for ferritisation process on quality of integrated treatment of exhausted nickel electrolytes.

Materials and Methods

Two laboratory installations were developed. The first one was used to study the ferritisation process at temperatures of 20 - 70ºC (Kochetov et al. 2014). Another installation was equipped with electronic block-unit for electromagnetic pulse activation of the process. Its mode characteristics: the electromagnetic signal included packs of pulses (16 pulses in a pack); pack spacing - 1300 ms; intervals between pulses - 20 ms; a pulse duration - 35 ms.

In laboratory experiments we used exhausted technological electrolyte of nickel electroplating units of one industrial plant of Kyiv. In the exhausted electrolyte, concentrations of heavy metal ions reached: Ni^{2+} = 67.9 g/dm^3 and Fe^{2+} = 0.12 g/dm^3, respectively. For the ferritisation process, solutions of iron (II) sulphate and 25% solution of sodium hydroxide were added to reach the required pH value. Technological parameters in the experiments varied within the following limits: $C_\Sigma = 11.7 \div 30.41$ g/dm^3; $Z = 2 \div 6$; pH values = $8.5 \div 10.5$; $t = 5 \div 15$ min.

Concentrations of heavy metal ions were determined by voltamperometry analyser AVA-3. Structural analysis of sediments was performed by X-ray diffractometer PHILIPS x'pert. Microstructure of precipitates were studied by scanning electron microscope-analyzer PEMMA-101A. Magnetic measurements were carried out using Petersen Instruments.

Results and Discussion

Wastewater treatment

Experimental research results for determination of influence of main technological parameters of the ferritisation process: pH, C_Σ, Z and t on efficiency of treatment exhausted nickel electrolytes for different methods of activation of the process are shown in Figure 1.

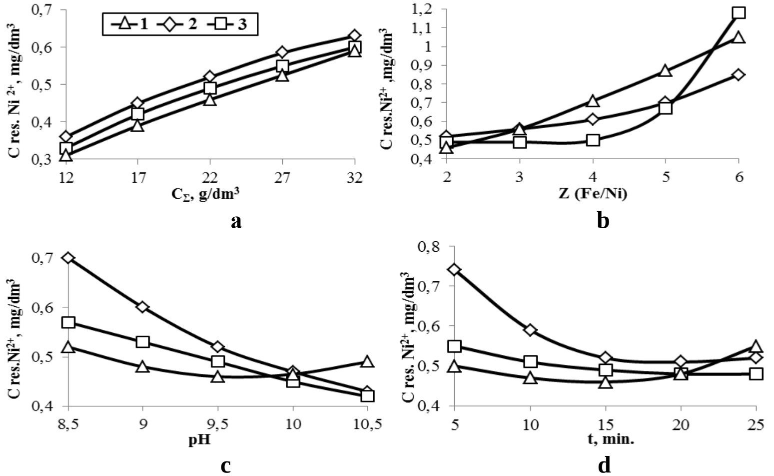


Figure 1. Dependence of residual concentrations of nickel ions C_{res} in the course of treatment of exhausted electrolyte solutions from concentration of the solution C_{Σ} (a), the ratio of concentrations of HM ions Z (b), pH (c) and duration of the process τ (d); 1 - the process of ferritisation at 20 ° C; 2 - thermal activation of the process; 3 - electromagnetic pulse activation of the process at 20 ºC.

Figure 1a indicates that at higher total contents of heavy metal ions in the initial reaction mixture, residual concentrations of nickel ions after the ferritisation increased, regardless of methods of activation of the process. Analysis of experimental research shows that the best result was obtained within the limits of Fe^{2+}/ Ni^{2+}ratios from 3/1 to 4/1 (Figure 1b).

Results of study of pH effects show that residual concentrations of nickel ions decrease with increasing pH (Figure 1c). Probably, this is due to the fact that at higher pH values, the predominant role in the process of nickel removal does not belong to sorbtion of Ni^{2+} ions, but to crystallization of insoluble nickel compounds on surface of ferromagnetic particles. In this case, structures and sizes of these particles have major impact on efficiency of wastewater treatment (Gawande et al. 2013).

As can be seen from graphic kinetics dependence for removal of nickel ions at Figure 1d, residual concentrations of metal ions in the solution decrease with the increase of duration of the ferritisation process from 5 to 15 min for both modes of activation. In a longer process residual concentrations of HM remain unchanged, due to the final formation of stable solid-phase products within initial 15 min.

As can be seen from the data obtained, for all studied values of technological parameters, residual concentrations of nickel ions in the treated solution were in the range from 0.3 mg/dm^3 to 1.2 mg/dm^3. Residual concentrations of iron ions in purified water were also investigated. Analysis indicates that in all ranges of the technological parameters studied and at different methods of activation of the process, concentrations of this metal were in the range from 0.1 to 0.35 mg/dm^3. This corresponds to high degree of removal for nickel and iron ions – 99.99%.

Besides that, results of experiments indicate that the electromagnetic pulse method of activation is highly efficient, and - with its clear advantages over the thermal one does not worsen the degree of removal of HM ions.

In order to estimate kinetic regularities of removal of nickel ions and metals from solutions (Figure 1d), we proposed mathematical models for different methods of the process activation. Types of regression equations that most adequately describe these dependencies have the following forms (Rossiter 2005):

- for nickel

$$\Delta C_{res.\ Ni} = \frac{t}{a+b\cdot t}, \quad (1)$$

- for iron

$$\Delta C_{res.\ Fe} = bt^2 + at, \quad (2)$$

here $\Delta C_{res.}$ – residual concentration of heavy metals ions, mg/dm^3; a, b – model factors; t – duration of the ferritisation process, min.

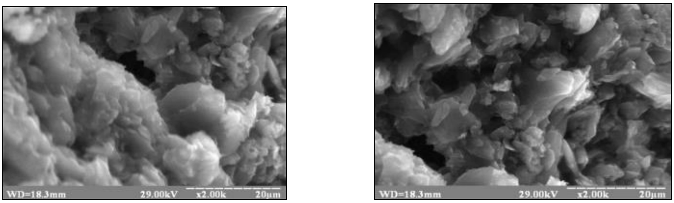
After linearizing transformations of functions 1 and 2 by the method of least squares, the factors of models were calculated. The detailed algorithm for solving the equations which is presented in (Kochetov et al. 2016). Calculated values of residual concentrations are well consistent with the experimental data; proposed models are considered adequate with 95% probability.

Study of sediments properties

In the process of ferritisation, with different methods of its activation, a black dispersion suspension is formed in the solution, that subsequently crystallises with formation of dense ferrite structures in particular. The samples were studied by X-ray diffraction and magnetic measurements. Those researches verified that content of the ferrite phase reaches 89 % and the crystals of obtained sediments are in the nanoscale range. In the case of both thermal and electromagnetic pulse activation, a phase of nickel ferrite $NiFe_2O_4$ was clearly identified with the structure of the inverse spinel and a lattice parameter a = 8.34 Å, as well as peaks attributed to Fe_3O_4, γ-Fe_2O_3, γ-FeO(OH), NiOOH, NiO.

The data we obtained explain why the best results of ferritisation treatment of are achieved at ratios of Fe^{2+}/ Ni^{2+} in the range of 3/1 ÷ 4/1. In our opinion, this is due to the fact that at other ratios, in addition to the formation of the ferrite phase, intermediate solid-phase reactions might take place in the solution. As a result, the phases formed are of limited stability in alkaline media and residual concentrations of nickel ions are increased.

Electron microscopy results (Figure 2) confirm formation of sediments with disperse structures. In comparison to traditional ferritisation at 20°C, in the case of the electromagnetic pulse activation, the precipitate has a high degree of crystallinity with the spinel matrix structure.



a **b**

Fig. 2. Microphotography of samples of sediments after ferritisation wastewater treatment: a - at T = 20 ºC; b - with application of electromagnetic pulse activation.

Structural analysis results were confirmed by experimental data on specific volumes, magnetic susceptibility of ferritic sediments and also HM leaching from sediments (Kochetov et al. 2016).

Our leaching experiments are shown that obtained compounds are chemically and thermodynamically stable. The amount of leachable HM from ferritisation sediments at pH from 5.5 to 8.5 is extremely low. They are characterized by a high degree of HM immobilization in sediments (up to 99.95 %). This means a substantially enhancement of environmental safety of the precipitated products. Depending on amounts and quality of the product the most appropriate utilization option can be selected: production of ferromagnetic sorbents; introduction of sediments into special purpose construction materials.

Energy efficiency of the developed processes

Energy intensity of the treatment process with different activation methods of ferritisation was also evaluated. The provided data suggest that the electromagnetic pulse mode of activation of the ferritisation process allows to reduce electric power consumption in 10 to 15 times in comparison with thermal activation.

Conclusions

Therefore, results of analysis of modern technologies for treatment of concentrated wastewater flows, as well as our research studies, clearly indicate prospects of application of the ferritisation method, due to its technical, economic and environmental advantages. Our research results have demonstrated efficiency of application of electromagnetic pulse discharges to activate the ferritisation process with a range of generating frequencies up to 0.9 kHz, and pulse duration of 35 ms. Influence of the main technological parameters on quality of the wastewater with application of different activation for the ferritisation process has been experimentally studied. It was found that this activation allowing to make the technology cheaper and attractive for investments. The most efficient results at initial HM concentrations of 20 – 25 g/dm^3; pH of the reaction mixture of 9.5, and duration of the process of 15 minutes. In this case, the experimental results indicate a high degree of wastewater treatment with removal of heavy metal ions (99.99%) that allows to use effluents in recycled water supply systems.

Kinetic regularities of nickel and iron ions from aqueous solutions by the ferritisation method were determined, and mathematical dependencies of HM removal were proposed.

Sediments obtained with high-temperature and electromagnetic pulse activation of the ferritisation process have high chemical stability and ferromagnetic properties, allowing to identify environmentally sound options for their utilisation.

Acknowledgements

The authors acknowledge financial support for this research provided by the Ministry of Education and Science of Ukraine under the project 5 DB-2018 and the Science and Technology Center in Ukraine under the project # 6363.

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