Chimica Techno Acta
published by Ural Federal University
journal homepage: chimicatechnoacta.ru

LETTER
2021, vol. 8(1), № 20218109
DOI: 10.15826/chimtech.2021.8.1.09

Continuous copper leaching technology

L.I. Mukhortova*, O.E. Nasakin, A.V. Eremkin, I.V. Glushkov

Federal State Budgetary Institution of Higher Education "Chuvash State University named after I.N. Ulyanov ", 19 Moskovsky Ave., Cheboksary, Russia, 428015
* Corresponding author: mlimait@rambler.ru

This short communication (letter) belongs to the MOSM2020 Special Issue.

Abstract

The parameters of the continuous technological process of leaching copper from fine copper waste using nitric acid as an oxidizer are studied. Optimal conditions for a continuous leaching process were established, in which solutions with a mass concentration of copper ions greater than 25 g/dm^3 were obtained.

Keywords

copper leaching
copper waste treatment

Received: 20.10.2020
Revised: 25.12.2020
Accepted: 25.12.2020
Available online: 13.04.2021

1. Introduction

Copper is one of the most popular metals for human economic activity and has been used since ancient times. In the global structure of copper consumption, 30% is used in construction, 30% for equipment production, 13% - in the transport industry, and the remaining 27% is distributed among other sectors of the economy. In 2019 there were produced 23.72 million tons of copper. In the copper market, Russia provides about 4.7% of world production. Currently, there is an excess of demand over supply in the amount of 94 thousand rubles·tons and according to analysts ' estimates, a further increase in demand for copper is forecast [1].

Unfortunately, the extraction of copper from natural sources is expensive and not very environmentally friendly, so it is more cost-effective to get copper from copper waste.

Hydroelectrometallurgical processes are widely used for processing copper waste to produce metallic copper. These processes can be divided into electrolytic refining and electroextraction [2,3]. Electrolytic refining is used as the final stage in pyrometallurgical processes for producing copper, including the processing of copper waste by melting. The technology of this process is well studied and covered in detail in many monographs and textbooks. As a result of electrofining, cathode copper with a purity of 99.7–99.9% and a spent electrolyte are obtained, in which copper sulfate and impurities of other metals accumulate. The spent electrolyte is periodically sent for regeneration, which is a process of electrical extraction of copper. Electroextraction is carried out in electrolyzers with an insoluble anode.

The electroextraction method can also be used for processing copper waste from previously obtained solutions of copper salts.

It is known that copper dissolves only in the presence of substances with oxidizing properties: concentrated sulfuric acid, oxygen, hydrogen peroxide and nitric acid. High values of redox potentials of nitric acid solutions allow dissolving copper. With concentrated nitric acid (mass fraction of acid more than 45%), the reaction proceeds according to equation (1), and with dilute acid (mass fraction of acid less than 40 %) – according to equation (2) [4]:

$$Cu + 4HNO_3 \rightarrow Cu(NO_3)_2 + 2NO_2 + 2H_2O, \quad (1)$$

$$3Cu + 8HNO_3 \rightarrow 3Cu(NO_3)_2 + 2NO + 4H_2O. \quad (2)$$

In this paper, the possibility of conducting a continuous process of copper dissolution with nitric acid while excluding the formation of toxic nitrogen dioxide is studied.

2. Experimental

The diagram of the experimental laboratory installation is shown in Fig. 1

A cylindrical reactor 1 with a diameter of 50 mm and a height of 250 mm with a false bottom located at a height of 20 mm has a jacket heated by water vapor obtained in a laboratory steam generator 5. Copper chips with a particle size of about 2×2×2 mm were loaded into the reactor until a 200 mm high copper column was obtained. Seven compositions of working solutions with different fixed concentrations of nitric acid were prepared for the experiments 10, 15, 20, 25, 30, 40 and 45% (mass). Before each experiment, working solutions with a volume of 500 cm^3 were prepared, heated to a set temperature and thermostated.

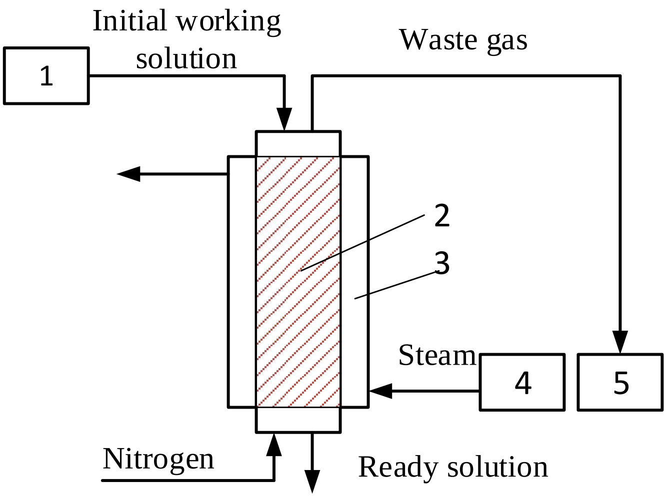

Fig. 1 Scheme of an experimental laboratory installation: 1 – a tank for preparing the working solution; 2 – a reactor with loaded copper chips; 3– a jacket for heating the reactor; 4 – a steam generator; 5 – an absorption tank

To stabilize the temperature in the reactor, the reactor was initially filled with water, the water was heated to a set temperature by applying steam to the jacket, then the water was drained and a hot working solution was immediately supplied. The working solution was fed to the upper part of the reactor through a sprinkler. The contact time was regulated by the flow rate of the working solution from 60 to 300 cm^3/s. The liquid level in the reactor was regulated by lowering the finished solution. The first 50 cm^3 of the finished solution was discarded. The content of copper ions in the solution was controlled by the iodometric method [5]. Waste gases from the reactor were displaced by a nitrogen current into an absorption flask filled with 50 cm^3 of a 10% solution of potassium iodide. At the end of the experiment, a qualitative test was made for the content of nitrogen dioxide in the absorption solution for the formation of pink staining with the Griess-Ilosvaya reagent [6].

To obtain reliable results, all experiments were repeated three times and the arithmetic mean values of the measurement results were calculated. In each experiment, the reactor was filled with a new sample of copper and a freshly prepared working solution was used. The relative error of the results does not exceed ±5%.

3. Results and Discussion

The main criteria for the effectiveness of the process of leaching copper with nitric acid are the concentration of copper ions in the solution at the reactor outlet and the formation of nitrogen dioxide.

During the experiment, it was found that the solubility of copper is mainly influenced by three factors: the contact time, the concentration of nitric acid and the temperature of the solution.

To determine the optimal contact time, experiments were performed with a working solution containing 30% nitric acid when the temperature and flow rate of the solution changed (Fig. 2).

The data presented in Fig. 2 show that the solubility of copper increases with decreasing consumption of the working solution and, accordingly, with increasing contact time. It follows that in production conditions, when the process is carried out in an industrial reactor, the efficiency of the leaching process will increase, since the contact time will increase at the same costs. It should be noted that at the same flow rates, the dissolution rate increases with increasing temperature and reaches a maximum value at 60 °C.

To determine the effect of nitric acid in the working solution on the amount of dissolved copper at a constant flow of the working solution of 60 cm^3/s, experiments were conducted which varied the temperature and composition of the working solution found that the mass fraction of nitric acid, 10 and 15% copper is not dissolved even when the temperature rises to 80 °C.

With a further increase in the concentration of nitric acid in the solution, the solubility of copper increases (Fig. 3).

The results show that with an increase in the content of nitric acid in the working solution, the rate of copper dissolution also increases, but with a mass fraction of nitric acid of 40% and 45%, the absorption solution turns

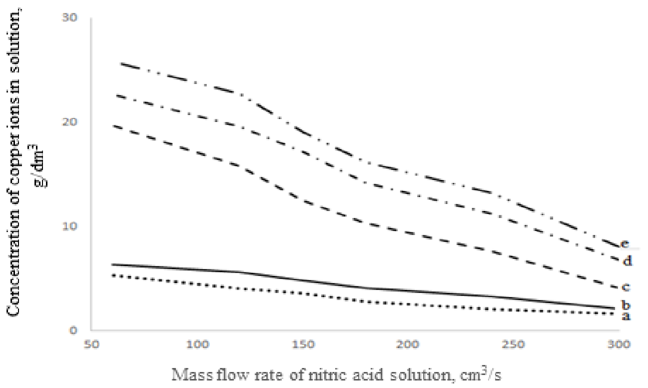

Fig. 2 Dependence of the concentration of copper ions in the solution on the flow rate of the working solution and temperature: a – 20 °C; b – 30 20 °C; c – 40 °C; d – 50 °C; e – 60 °C

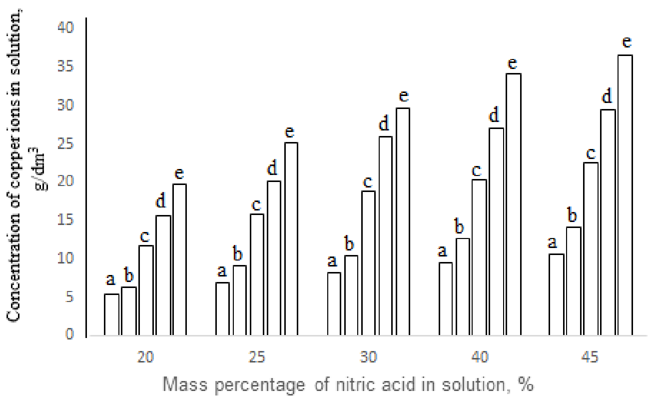

Fig. 3 Dependence of the concentration of copper ions in the solution on the content of nitric acid and the temperature of the solution: a – 20 °C; b – 30 20 °C; c – 40 °C; d – 50 °C; e – 60 °C

pink when the Griss–Ilosvay reagent is added, which indicates the formation of nitrogen dioxide. Therefore, it is optimal to use working solutions with a mass fraction of nitric acid of 30-35%. An increase in temperature also contributes to an increase in the rate of the copper oxidation reaction, but at temperatures above 60 °C, there is a significant entrainment of nitric acid with the nitrogen current and the cost of heat energy increases.

4. Conclusions

The experimental data obtained show that the process of copper leaching can be carried out in a continuous manner to produce solutions containing more than 25 g/dm^3 of copper ions. It was found that the maximum concentration of copper ions without the formation of nitrogen dioxide is achieved when using working solutions with a mass fraction of nitric acid of 25-30%, a temperature of 60 °C and a flow rate of 60 cm^3/s of the working solution.

5. References

1. WBMS: proizvodstvo medi v 2019 godu neznachitel'no vyroslo [WBMS: copper production in 2019 increased insignificantly] [Internet]. Moscow: JSC "Metallservis"; c2020 [cited 2020 Oct 10]. Russian. Available from: https://mc.ru/news/nw/news_id/11688
2. Naboichenko SS. Smirnov VI. Gidrometallurgiya medi [Hydrometallurgy of copper]. Moscow: Metallurgiya; 1974. 272 p. Russian.
3. Bredikhin VN, Manyak NK, Kaftanenko AYa. Med' vtorichnaya: monografiya [Secondary Copper: monograph]. Donetsk: DonNTU; 2006. 416 p. Russian.
4. Lidin RA, Molochko VA, Andreeva LL. Khimicheskie svoystva neorganicheskikh veshchestv [Chemical properties of inorganic substances]. Moscow: Khimiya; 2000. 408 p. Russian.
5. Lurie YY. Analiticheskaya khimiya promyshlennykh stochnykh vod [Analytical chemistry of industrial waste waters]. Moscow: Khimiya; 1984. 448 p. Russian.
6. Bykhovskaya MS, Ginzburg SL, Halizova OD. Metody opredeleniya vrednykh veshchestv v vozdukhe i drugikh sredakh [Methods for determining harmful substances in the air and other environments]. Moscow: Medgiz; 1960. 312 p. Russian.