UDC 661.856+004.92
DOI: 10.15587/2312-8372.2017.109145

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DETERMINATION OF OPTIMAL PARAMETERS FOR THE PRODUCTION OF COPPER-CONTAINING PARTICLES DURING PLASMA-CHEMICAL TREATMENT OF AQUEOUS SOLUTIONS

Вивчено процеси отримання мідьвмісних частинок при обробці розчинів контактною нерівноважною плазмою пониженого тиску. Встановлено оптимальні характеристики процесу. Визначено залежність процесу від pH та концентрації розчину. Доведено, що при певних параметрах можна отримувати частки у заданому діапазоні значень.

Ключеві слова: *нерівноважна плазма, водні розчини, мідьвмістні частинки малої розмірності.*

1. Introduction

Interest in micro- and nanoscale copper-containing particles is due to the specific properties of both the particles themselves and the materials modified by them [1, 2]. For example, the use of particles Cu_2O, CuO is common when creating new catalysts for various industrial processes, as a filler for varnishes and paints, Cu_2O is used in the production of galvanic cells, and other fields of engineering [1]. In this case, the characteristics and options for their practical application largely depend on the method of production, which usually determines their structure, size, physical and chemical properties, etc. [3]. In this regard, relevant studies are devoted to finding ways to improve the technological processes that allow to obtain particles with specified properties.

2. The object of research and its technological audit

The object of research is the process of obtaining copper-containing particles from aqueous solutions using contact non-equilibrium plasma of reduced pressure. One of the most problematic places in this process is the correct selection of parameters, both the medium and the plasma discharge, which is the main processing tool. This is due to the fact that the physicochemical mechanisms of the reactions are rather complicated and when they occur, synergistic effects are observed, the dependencies of which are not entirely clear.

Technological audit was conducted to identify the characteristics of this process from the point of view of obtaining copper-containing powders. The aim of technological audit is determination of the following process parameters: pH of the formation of copper-containing sediments in the treatment of solutions, the value of redox potentials sufficient for the reactions and conditions for the formation of particles with specified parameters. The study is carried out using laboratory equipment and software modules of the package HSC Chemistry 5.11 (Outotec, Finland).

The technological scheme of the process is shown in Fig. 1.

The scheme operates as follows: copper sulfate is mixed with water in the tank 10. Then the resulting solution is transferred to the plasma-chemical reactor 12, from which it enters the sedimentation tank 11. After separation, the wet sediment enters the dryer 15 and then onto the package 16.

Plasma-chemical reactor, in which the main transformations take place, in liquid media, is a device in which a whole complex of processes is combined. The main of them can be considered electrochemical, plasma-chemical, chemical, processes of cavitation of gas bubbles formed as a result of water decomposition, diffusion, heat exchange, etc.

The general scheme of the processes taking place in the plasma-chemical reactor using the example of pure water is shown in Fig. 2.

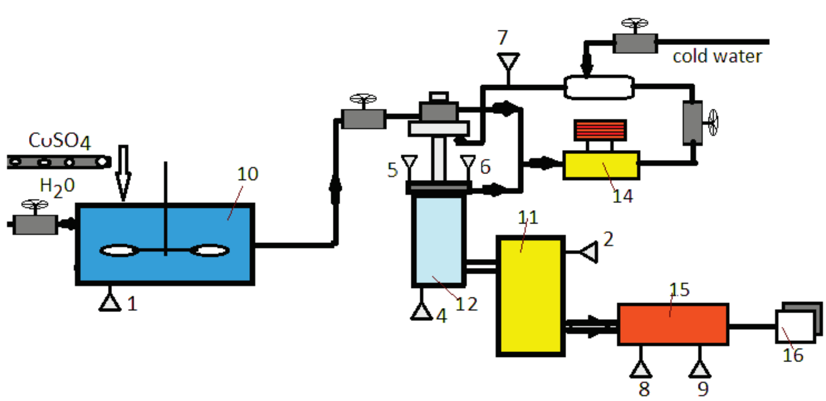

Fig. 1. Technological scheme for obtaining copper-containing particles from aqueous solutions using a contact non-equilibrium plasma of reduced pressure: 1–9 – sensors; 10 – tank with a stirrer; 11 – sedimentation tank; 12 – plasma-chemical reactor; 14 – heat exchanger; 15 – dryer; 16 – packaging

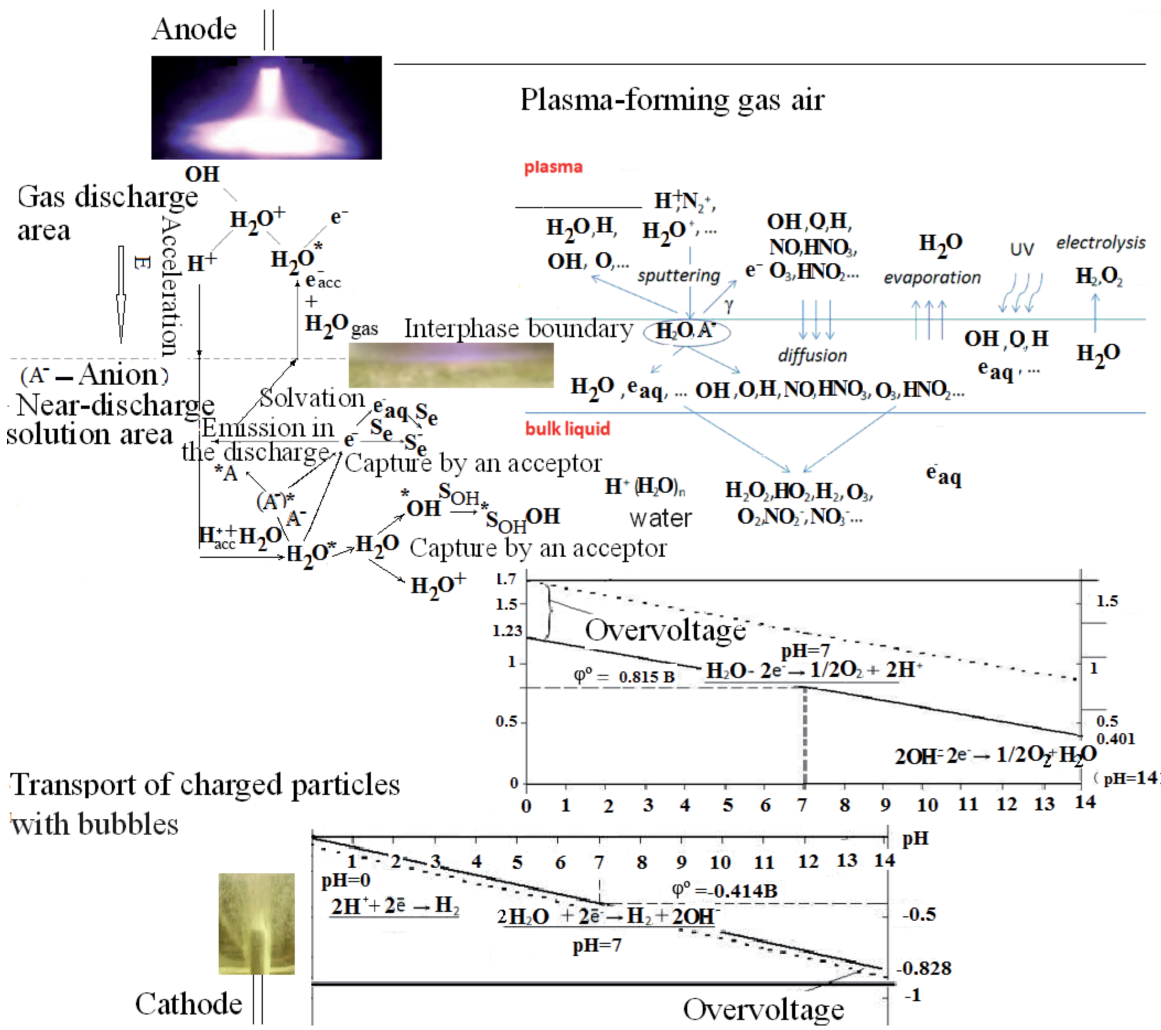

Fig. 2. Representation of the processes taking place in the plasma-chemical reactor during the treatment of pure water [4–6]

Let's note that the main processes leading to the appearance of new components of the solution, in accordance with Fig. 2 occur at the boundaries of the phase sections – interphase boundary and cathode. However, when using solutions, it is possible for chemical processes to proceed throughout the volume of the liquid.

Thus, one of the most problematic areas of this technology is the difficulty in choosing the parameters of the plasma-chemical treatment of the solution, leading to the production of the desired quality.

3. The aim and objectives of research

The aim of research is determination of the following parameters for the process of obtaining copper-containing particles: calculations of pH and redox potentials sufficient for the occurrence of reactions of copper-containing sediments formation during plasma-chemical treatment of solutions, as well as conditions for the formation of particles with specified parameters.

To achieve this aim it is necessary:

1. To study the characteristics of the process of obtaining sediments and evaluate them.

2. To determine the composition and size of the obtained particles and analyze the accumulated statistical characteristics.

4. Research of existing solutions of the problem

Among the methods for obtaining micro- and nanoparticles [1, 2], one can single out large groups of methods of chemical, electro-chemical, electropulse and plasma-chemical synthesis [3–11]. These methods are based on the reduction of metal ions in solutions under conditions favorable for the subsequent aggregation of atoms and ions with the formation of nanoparticles.

Let's note that the most easily controlled methods are based on the use of electrochemical processes of different directions [2].

The use of contact non-equilibrium plasma for production of new compounds [8] is the basis for the creation of new technologies that make use of the advantages of most of the above methods. In this case, there is a need for additional data to determine the optimal process parameters.

Thus, the results of the literature analysis allow to conclude that using the technologies of plasma-chemical treatment of liquid media to obtain compounds of ultra- and nanoscale character, it becomes necessary to select the parameters optimal for this process.

5. Methods or research

To find the preliminary conditions for formation of interphase boundaries, diagrams in the coordinates of the potential E-pH of the aqueous medium (the Purbe diagram) are used [12]. These diagrams clearly show the thermodynamically stable forms of the existence of elements (ions, molecules, atomic crystals and metals) in solutions at different pH values and oxidation-reduction potential E [13].

The choice of sulfuric solution is due to its cheapness, simplicity, stability of composition and high current efficiency close to the theoretical one. The Purbe diagrams for one element may differ depending on the temperature, the solvent and the presence of ligands in the solution. For the solution of $CuSO_4$ in water, the main reaction mechanism is considered to involve the interaction of ions and compounds Cu^+, Cu^{2+}, Cu, HSO_4^-, HSO_4, SO_4^-, SO_4^{2-}, $CuSO_4$, $S_2O_8^{2-}$, CuO, Cu_2O [14], hydroxides and sulfides of copper, ions of CuO_2^{-2} and $HCuO_2^-$ [9].

For calculations, the HSC Chemistry application package [13] is used, including built-in reference databases for thermodynamic, physical and chemical properties of inorganic and organic substances, and calculation modules, including the E-pH diagram calculation module. Thermographic and radiographic methods of research are also used.

6. Research results

The effect of pressure, concentrations, and temperatures is considered in the calculations. As a result, let's note that the most significant factors affecting the stability of compounds and elements in solutions are their concentration and pH. As an example, let's consider the E-pH diagram for the Cu-S-H_2O system shown in Fig. 3.

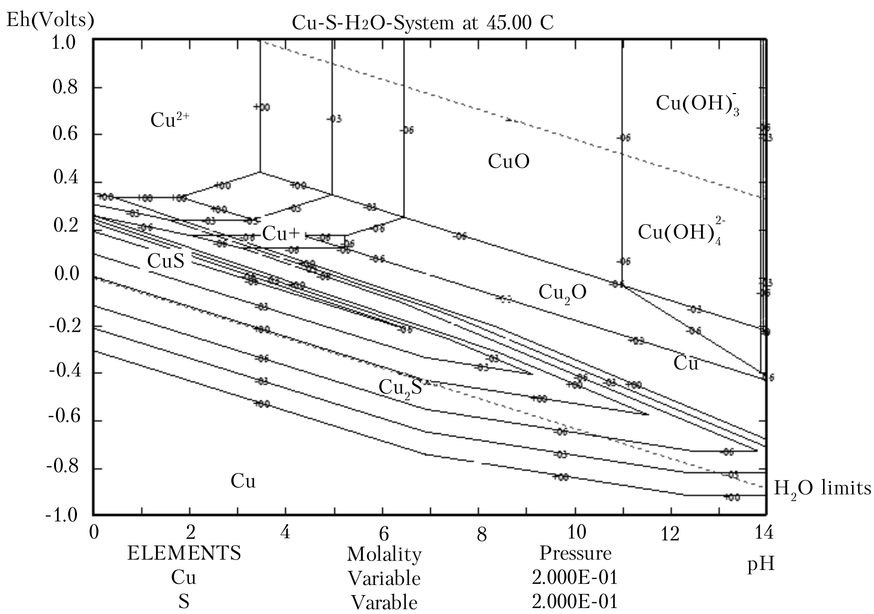

Fig. 3. E-pH diagram for the Cu-S-H_2O system at 45 °C, for Cu at a concentration of 1, 10^{-3}, 10^{-6} mol/l and a pressure of 0.2 bar

Let's note that with decreasing Cu concentration, the copper solubility fields increase in the form of Cu^+, Cu^2 ions in the acid medium, the sulfide stability fields decrease and the Cu stability field increases.

Obtaining loose (powder) sediments occurs with a sharp decrease in surface concentration. The current density is determined by the expression [8]:

$$i_k = zF(D/\delta)\, C^0, \qquad (1)$$

where i_k – the cathode current density, A/cm^2 (A/cm^2); D – the coefficient of Cu^{2+} ion diffusion in the aqueous solution, cm^2/s; δ – the thickness of the diffusion layer (0.05–0.1 cm); C^0 – Cu^{2+} ion concentration in the volume, g/l; F – number of Faraday (96500 coulombs); Z – the valence number of substance ions.

Let's note that the crystal structure of particles is formed not immediately, but after a certain time. It is established that the structure of primary particles is amorphous in mass [15]. Then a crystallization process takes place in the volume of particles and spherical coarse particles with a radius of about 10^{-6} m break up into many fine particles, but already of a crystalline structure. Thus, the size of the resulting crystalline particles is due not only to the conditions of germination of germs and growth of amorphous particles, but also to the conditions of their crystallization [15].

The quality of the powder is affected by the following factors: current density and copper concentration, process temperature. The rise in temperature increases the diffusion coefficient, but requires a higher current density to produce the powder. However, let's take into account that when the pressure in the reactor is 0.2 bar, the temperature of the solution does not exceed 55 °C.

pH of the solution is varied based on the calculated data, during the experiment for various concentrations of Cu.

Under the condition that the Cu solubility field falls into the field, the process of sedimentation of copper and its oxides at the electrode buried in the liquid is observed practically from the first seconds of treatment of the low-pressure contact non-equilibrium plasma (Fig. 4, *a*, *b*). In this case, an increase in the current intensity of the process, respectively, leads to an increase in the current density, which is accompanied by an increase in both the yield of the sediment and its density. However, at a lower concentration of Cu with the same parameters of the current strength, let's obtain more loose sediments (Fig. 4, *c*).

Taking into account that the sediment is amorphous for a certain time after preparation, the particle sizes can be corrected with stabilization. Based on the thermo- and radiographic studies, an approximate composition of the dry sediment is determined (Table 1).

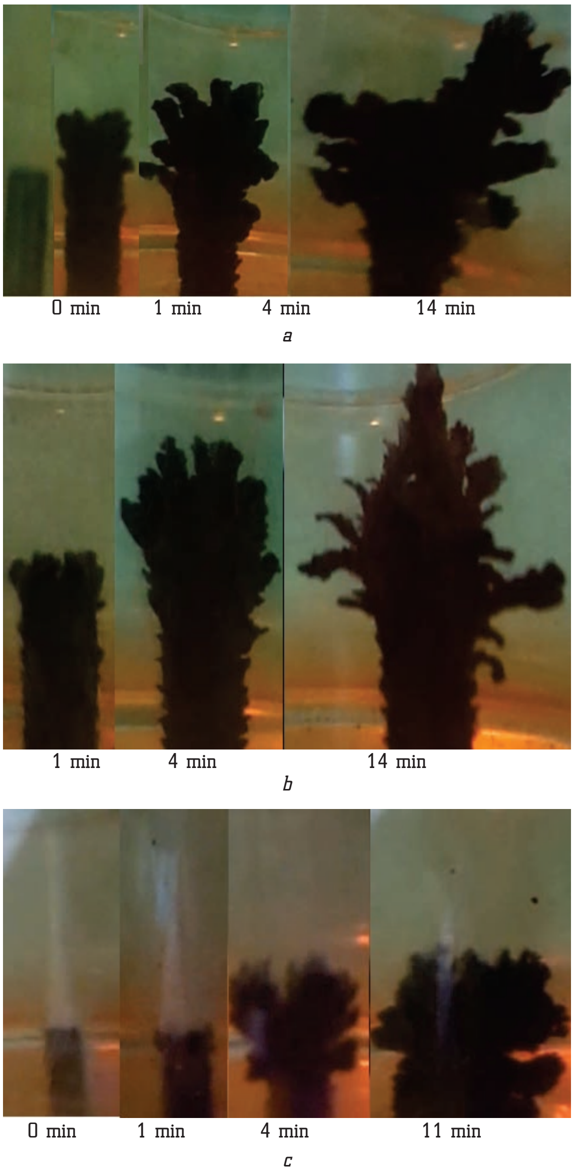

Fig. 4. Growth of sediment on the cathode (solution of $CuSO_4$ in water) at: *a* – pH=3.95; current intensity of the process I=140 mA, C(Cu)=0.156 mol/l; *b* – pH=3.65; current intensity of the process I=200 mA, C(Cu)=0.156 mol/l; *c* – pH=4.35; current intensity of the process I=200 mA, C(Cu)=0.08 mol/l

A distinction of this type of plasma-chemical treatment of liquid from ordinary electrolysis is the possibility of working with highly diluted solutions, which reduces the risk of sediment contamination by undesirable impurities.

Let's note that a decrease in the liquid layer contributes to an increase in the yield of oxide compounds. Also, when the thickness of the processed liquid layer is reduced, the size of the sediment particles decreases, obviously, this is due to an increase in the number of germs and a decrease in concentration. The dimensional characteristics of the particles are described in detail in [14, 15] and are in the range of 10–100 nm.

Table 1

An approximate composition of the copper-containing sediment obtained under different conditions for treating the solution with contact non-equilibrium plasma

Pressure, bar	Initial concentration, C(Cu), mol/l	Current strength, A	Thickness of the liquid layer, m	Approximate ratio of $Cu:CuO:Cu_2O$
0.1	0.0156	100	0.25	2:1:1
0.1	0.0257	100	0.2	2:1.1:1.2
0.1	0.0515	120	0.15	2:1.3:1.4
0.1	0.08	180	0.1	1.6:1.1:1.3
0.1	0.008	180	0.01	1:3:3.5
0.2	0.156	120	0.25	2.5:1:1.4
0.2	0.156	140	0.2	2.1:1.1:1.2
0.2	0.08	200	0.15	2.5:1.5:2
0.2	0.04	200	0.1	1.4:2.1:1.7
0.2	0.008	200	0.01	1.5:4:2.5

This allows to conclude that it is possible to improve the technological scheme by:

1) control of the inlet pH of the solution, ensuring the optimal yield of copper compounds;

2) use of the spent solution in the tank with the initial solution for its acidification;

3) refinement of the reactor block for the purpose of processing the solution in film mode or close to it, which should lead to an increase in the yield of copper oxides and a decrease in the particle size.

7. SWOT analysis of research results

Strengths. Among the strengths of this research, it is necessary to note the obtained results for the optimum ranges of process parameters – pH of the solution and its concentration, as well as the thickness of the layer of the treated solution. Using the same data with respect to the optimal ranges of input variables allows to solve the problem of choosing a rational control system.

The criteria for choosing this are:

1) possibility of obtaining high-quality products with a significant reduction in specific energy inputs and reagents;

2) minimization of costs for modernization process itself, using the means of automatic control of the technological process.

Weaknesses. The weaknesses of this research are related to the fact that the proposed solutions are based on the assumption of the possibility of an accurate measurement of input variables in real time. However, such assumption leads to errors due to uncontrolled disturbances. As a result, the errors in determining the input variables can lead to incorrect operation of the system and, in some cases, to parametric failures of the control system. Therefore, in order to prevent this drawback, special attention should be given to the quality of the input product, which imposes special obligations on the operating personnel – the operators of the system, i.e. the role of the subjective factor grows.

Opportunities. Additional opportunities to achieve the aim of research are in the following likely external factors. The growth of consumption of powders of nanosized copper oxide compounds leads to increased competition among producers. However, this circumstance can be considered stimulating in the sense that when using the appropriate instrumentation and control equipment allowing, taking into account the resulted research results, to provide an acceptable quality of process control. At the same time, the data obtained as a result of the implementation can become the basis for further development of the described study. In particular, the influence of operating conditions on the magnitude of the error in estimating input variables can be investigated to clarify the obtained dependences.

Threats. The difficulties in implementing the research results are related to the following factors: the first – the risk of obtaining products of lower quality than the predicted. This risk is justified, since the obtained scheme of the process is based on the assumption of the possibility of precise control of input parameters, which are considered as the most significant. The second factor is the market of raw materials. A long-term forecast for the invested funds may show that the use of secondary raw materials (waste), which is a source of environmental pollution in a number of industries, may be more appropriate.

Thus, SWOT analysis of research results allows to identify the main directions for the successful achievement of the research objectives. Among them: refinement of the obtained dependencies, in order to improve the quality of process management, increase the competitiveness of the obtained products and reduce specific costs for production.

8. Conclusions

1. The characteristics of the process of obtaining sediments are studied. At a concentration of $C(Cu)=10^{-1}–10^{-2}$ mol/l, the optimum pH range lies in the range 3.5–4.5. Let's note that an increase in the current intensity of the process is accompanied by an increase in both the yield of the sediment and its density. Reducing the Cu concentration at the same current parameters gives more loose sediments. At the same time, a decrease in the liquid layer promotes an increase in the yield of oxide compounds. Also, when the thickness of the processed liquid layer is reduced, the particle size of the sediment decreases.

2. The composition and sizes of the obtained particles are determined. With a thickness of the treated solution layer of 0.25 m, the oxide part is 50 % and 49 % at 0.1 and 0.2 bar, respectively, and at 0.01 m – 86 %, and 87 %. The dimensional characteristics of the particles are in the range 10–100 nm.

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ОПРЕДЕЛЕНИЕ ОПТИМАЛЬНЫХ ПАРАМЕТРОВ ПОЛУЧЕНИЯ МЕДЬСОДЕРЖАЩИХ ЧАСТИЦ ПРИ ПЛАЗМОХИМИЧЕСКОЙ ОБРАБОТКЕ ВОДНЫХ РАСТВОРОВ

Изучены процессы получения медьсодержащих частиц при обработке растворов контактной неравновесной плазмой пониженного давления. Установлены оптимальные характеристики процесса. Определена зависимость процесса от pH и концентрации раствора. Доказано, что при определенных параметрах можно получать частицы в заданном диапазоне значений.

Ключевые слова: неравновесная плазма, водные растворы, медьсодержащие частицы низкой размерности.

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