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THE STUDY OF ELECTRODIALYSIS TREATMENT OF WASTEWATER THROUGH THE SYNTHESIS OF ULTRAMICRODISPERSED METAL OXIDE POWDERS

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Abstract: It is shown that in the process of electrochemical synthesis of metal oxide powders waste water is produced, the discharge of which is not desirable due to environmental considerations and because of the content of valuable substances. This paper presents the results of the research into the process of electrodialysis treatment of wastewater generated in the synthesis of ultramicrodispersed metal oxide powders on alternating current in a concentrated solution of sodium hydroxide, obtained by neutralization with acetic acid alkali seized by oxide powders of nickel and iron. This reduces the amount of wash water by 60 %. It was found that the concentration of sodium acetate after electrodialysis falls by 33 times. The cleaning time of 200 cm^3 water wash using 3-cell electrodialysis is 5.6 hours. Application of 30-cell electrodializators reduces the cleaning solution by 10 times.

Production of ultramicrodispersed metal oxide powders and creation of nanocomposites is an important direction of development of modern nanotechnology. Nanosized powder of nickel oxide is used as electrode material. It is used in catalysis including the synthesis of nanocarbon material and as an active element of gas sensors. High-performance ultrahigh frequency dielectrics are developed on the basis of complex mixtures of nickel and cobalt oxides. Iron oxide is used in production of suntraps and in medicine. There are various methods of obtaining nanodispersed metal oxide powders: precipitating pyrolysis, organometallic copolymerization, sol-gel method, hydrothermal synthesis, precipitation by urea, alkali metal carbonates and ammonia.

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Chemical technologies are known to have some disadvantages: large amount of contaminated wastewater, accumulation of waste mineral salts, which are difficult to utilize, complexity of setting up the unified manufacture with the fast change of range of low-tonnage products due to a variety of necessary oxidants or reductants [1, 2]. These disadvantages cause serious environmental consequences.

The development of production based on electrochemical processes using alternating current is a prospective direction in reducing the negative impact of chemical industry on the environment. It allows abandoning the use of chemical oxidants and reductants, reducing substantially or eliminating mineral salts wastes and using original raw materials more effectively.

The substitution of chemical stages by electrochemical ones in the process of ultramicrodispersed metal oxide powders synthesis makes for:

– developing a unified technological scheme of production;

– carrying out the process selectively, due to the possibility of setting the desired value of electrode potential;

– reducing the amount of wastewater and waste by creating a closed-loop cycle technology of water consumption and exclusion of chemical oxidants or reductants.

The wastewater produced in the process of electrochemical synthesis of metal oxide powders should not be discharged without control because of environmental considerations and because they contain valuable substances. In this connection the problem of creating a closed-loop cycle technology of water consumption and recycling reagents in the production of a desired product is of current importance. This study presents experimental data on the possibility of using electrodialysis treatment of wastewater [3 – 8] for a closed-loop cycle of water consumption in the process of metal oxide powders synthesis, in particular, the mixtures of oxides of nickel and iron synthesis with the use of alternating current.

Production of metal oxides by electrochemical method using AC comprises the following steps [9 – 12] (Fig. 1):

1) preparation of a sodium hydroxide solution;

2) electrolysis on asymmetric alternating current (20 Hz) in a solution of sodium hydroxide when exposed to ultrasonic radiation;

3) upholding of gel oxides of nickel and iron;

4) separation of the precipitate nickel and iron oxides by decantation;

5) neutralization of the alkali entrained by powder of metal oxides with acetic acid;

6) separation of the oxide powders of nickel and iron on a vacuum filter;

7) washing of powders of nickel and iron oxides with water;

8) electrodialysis treatment of wash water;

9) drying the resulting product;

10) packaging of the product.

A washing step is the most time consuming in the process of producing metal oxides. In the traditional method of washing of ultramicrodispersed powders of metal oxides of nickel and iron from the electrolyte solution 100 dm^3 per 1 dm^3 of water gel must be used. Water consumption can be dramatically reduced. For this purpose we used pre-neutralization of alkali entrained by metal oxides with acetic acid. The resulting slurry

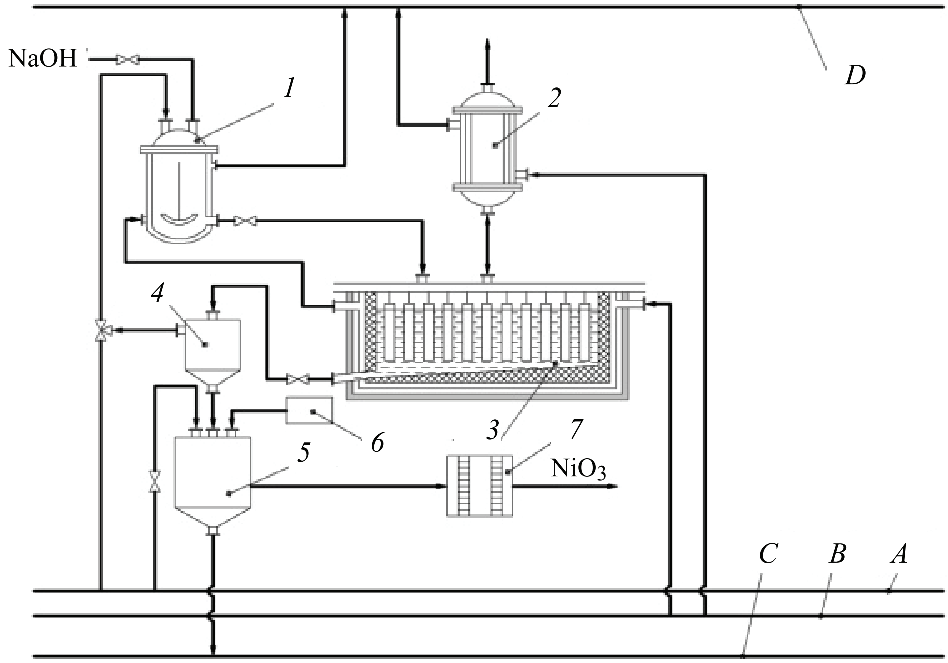

Fig. 1. Technological scheme of the process of synthesis of metal powders by electrolysis alternating sinusoidal current upon application of ultrasonic radiation:
1 – reactor for the preparation of the alkaline solution; *2* – condenser; *3* – electrolysis; *4* – sump; *5* – filter; *6* – dispenser acetic acid; *7* – dryer, *A* – distilled water; *B* – refrigerant; *C* – sodium acetate solution to electrodialysis purification; *D* – coolant drain line

settles, then it is separated by decantation. Alkali, after monitoring and adjusting its concentration is used repeatedly. The precipate with the powder of nickel oxide and iron, and alkali solution is neutralized with 80 % acetic acid. The sodium acetate, resulting from neutralization reaction, is filtered much easier than pure alkali solution. Furthermore, the washing of the gel takes from 1 dm^3 to 40 dm^3 of water, which generally reduces the amount of washing water for this process step to 24 dm^3. The washing time is reduced by 60 %.

The consumption of acetic acid required to neutralize the alkali is calculated as follows:

$$m_{CH_3COOH} = (V_s \rho_s W_{NaOH} M_{CH_3COOH} / M_{NaOH}) \cdot 10^4 / W_{CH_3COOH},$$

where m_{CH_3COOH} is mass of acid is required to neutralize, mg; V_s is the volume of sodium hydroxide solution, cm^3; ρ_s is the density of sodium hydroxide solution, g/cm^3; W_{CH_3COOH} is mass fraction of acetic acid, %.

The analysis of the metal oxide powders obtained by neutralization of alkali with acetic acid and without it showed that they do not differ in their physical and chemical characteristics. The sodium acetate resulting form neutralization is collected and sent for the electrodialysis treatment.

According to the technological regulations washing water contains up to 3 % of sodium acetate. This washing water is supplied to the electrodialysis treatment. Platinum anode, a cathode made of stainless steel, anion and cation

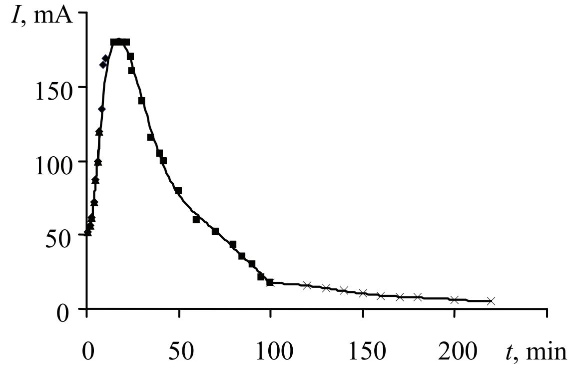

Fig. 2. Current dependence on time electrodialysis

exchange membranes, separating the anode and cathode chambers from the desalination chamber are installed into electrodialyzer. The washings from the process of metal oxide powder mixture are fed into electrodialyzer using a peristaltic pump at a predetermined flow rate by the experimenter. Washings can be cleaned in a cascade of electrodialyzers, which consists of several units, or in multi-chamber electrodialyzer.

The experiments were conducted in a three-chamber electrodialyzer of filter-press type, the volume of each chamber was 55 cm^3. Desalting chamber was separated from concentrate chambers type membranes MK-40 and MA-40. In demineralization chamber of the electrodialyzer 3 % sodium acetate solution was fed and 0.3 % acetic acid solution was fed into the concentration chamber (anode chamber), and 0.3 % sodium hydroxide was fed into cathode chamber. Kinetics of electrodialysis is shown in Fig. 2.

These data indicate that during the initial period of time (from 0 to 15 min) the amount of current increases. This phenomenon is probably related to the increased number of ions in the cathodic and anodic chambers. Then, the current begins to decrease – the process of desalination starts, and electrical resistance of the solution in the desalination chamber increases. In general, the concentration of sodium acetate after electrodialysis decreases by 33 times. The purification time of the wash water using a three-chamber electrodialysis is 5.6 hours. Application of 30-chamber electrodialyzer can significantly reduce the time of solution purification. This electrodialyzer is different from others as it has desalination and concentration chambers. The thickness of chambers is 2.5 mm. Therefore, during the desalting stage the same amount of wash water is reduced by 10 times.

Thus, application of electrodialysis enables to clean wash water from sodium acetate and send it to the washing cycle of metal oxide powders. Concentrated solutions of acetic acid and sodium hydroxide may be directed to the adjustment process of working solutions. The results obtained will be used for the next steps in the development of recommendations for the design of experimental industrial process of synthesis of metal oxides with closed cycle water consumption.

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Исследование электродиализной очистки сточных вод, образующихся в синтезе ультрамикродисперсных порошков оксидов металлов

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Ключевые слова и фразы: ацетат натрия; гидроксид натрия; порошки оксидов металлов; электродиализ.

Аннотация: Показано, что в процессах электрохимического синтеза порошков оксидов металлов образуются сточные воды, сброс которых не желателен как из-за экологических соображений, так и содержания в них ценных веществ. Представлены результаты исследования процесса электродиализной очистки сточных вод, образующихся в синтезе ультрамикродисперсных порошков оксидов металлов на переменном токе в концентрированном растворе гидроксида натрия, полученных путем нейтрализации уксусной кислотой щелочи, захваченной порошками оксидов никеля и железа. При этом снижается объем промывной воды на 60 %. Найдено, что концентрация ацетата натрия после электродиализа падает в 33 раза. Общее время очистки 200 см^3 промывной воды при использовании трехкамерного электродиализатора составляет 5,6 ч. Применение 30-камерного электродиализатора позволяет сократить время очистки раствора в 10 раз.

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