

ABSTRACT AND REFERENCES

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INVESTIGATION OF COMPOSITION AND STRUCTURE OF TRIPOLIPHOSPHATE COATING ON LOW CARBON STEEL (p. 4-10)**Olena Vlasova**

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The hypothesis on the matrix (composite) structure of the iron (III) tripolyphosphate precipitate and polyphosphate coatings on the steel substrate has been justified experimentally. According to the hypothesis, that iron (III) tripolyphosphate acts as a matrix forming agent while water-soluble sodium tripolyphosphate corrosion inhibitor is a filler.

Be means of the chemical synthesis method, it has been demonstrated that the chemical basis of the coating formed on the steel surface in the STPP solution is iron (III) tripolyphosphate.

It has been established that the composite structure of tripolyphosphate coatings and precipitates is determined by the nature of iron (III) tripolyphosphate.

The conducted investigation on the composition of the iron (III) tripolyphosphate precipitate and tripolyphosphate coating on steel, using the gravimetric method with washing have proved the presence of STPP. The results of X-ray spectral analysis have revealed that STPP in the structure of composite coating is situated not only as a filler inside the matrix but also as an additional layer on its surface.

The chemical protection mechanism of the tripolyphosphate coating on steel in atmospheric conditions has been justified.

The acquired knowledge would expand the theoretical and practical concept of the structure and properties of tripolyphosphate coatings on the steel substrate and their protection mechanism in conditions of atmospheric corrosion. The application of new knowledge in researches aimed at the development of ecologically safe methods of tripolyphosphate coating deposition with estimated complex of properties, would increase their efficiency.

Keywords: sodium tripolyphosphate, iron (III) tripolyphosphate, precipitate, coating, protective properties, matrix structure, chemical synthesis.

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OBTAINING OF Ni–Al LAYERED DOUBLE HYDROXIDE BY SLIT DIAPHRAGM ELECTROLYZER (p. 11-17)

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Ni–Al layered double hydroxides are promising cathode materials for Ni–Cd, Ni–Fe and Ni–MeH accumulators with improved characteristics. However, they are prepared using batch methods which cannot guarantee the stability of their characteristics. The main aim of the present work was the development of a continuous method of electrochemical synthesis of highly active Ni–Al layered double hydroxide in a slit diaphragm electrolyzer (SDE). A study on the influence of current density and anolyte composition (NaOH or NaOH+Na₂CO₃ at different ratios) on the electrochemical properties of Ni–Al hydroxide has been conducted. The LDH structure has been proven by means of X-ray diffraction analysis. It has been demonstrated that synthesis of Ni–Al LDH in SDE must be conducted at high current densities at which formation rate of hydroxyl anions would exceed the supply rate of cations. This would prevent the presence of aluminum cations in the solution that causes poisoning upon adsorption on the hydroxide surface. It has been demonstrated that introduction of sodium carbonate into the anolyte is not feasible, because of the possibility of complete hydrolysis of Al³⁺ in the presence of CO₃²⁻ with the formation of the Al(OH)₃ phase. This phase is capable of dissolving in alkaline electrolyte and poisoning the nickel hydroxide electrode. Optimal parameters for the synthesis of Ni–Al LDH in SDE have been established: current density – 18 A/dm², anolyte – NaOH solution. Ni–Al LDH, synthesized in SDE at these conditions, demonstrated the specific capacity of 237 mA·h/g. This exceeds capacities of chemically synthesized Ni–Al LDH (211 mA·h/g) and industrial sample (185 mA·h/g).

Keywords: Ni–Al layered double hydroxide, electrochemical synthesis, slit diaphragm electrolyzer.

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SYSTEM ANALYSIS OF THE SECONDARY CONDENSATION UNIT IN THE CONTEXT OF IMPROVING ENERGY EFFICIENCY OF AMMONIA PRODUCTION (p. 18-26)

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We established the mismatch between real and design coefficients of heat transfer, which is predetermined by the underestimation of condensation thermal resistance. The processes of heat exchange in a condensation column are identified and the equations for determining the coefficients of heat exchange, heat transfer and the concentration of ammonia in the circulation gas at the outlet of the column are derived. By applying the method of mathematical modeling, we defined necessary conditions for temperature distribution to exclude from the circuit of the unit for synthesis a turbo-compressor refrigeration unit with electric drive of capacity up to 4000 kW·h and reduction in the cooling temperature of circulation gas from 0 °C to – 5 °C at maximum thermal load with circulation gas on the complex of secondary condensation.

The hardware-technological design is developed for the stage of secondary condensation based only on the absorption and steam-ejector refrigeration systems that utilize the heat of material flows of low (above 100 °C) and super-low (to 90 °C) potentials. We defined efficiency indicators for the reduction of specific energy consumption by electricity and natural gas, which are 60 kW·h/t NH₃ and 1.2 m³/t NH₃.

Keywords: production of ammonia, secondary condensation, identification, mathematical modeling of the processes of heat exchange, energy efficiency.

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MATHEMATICAL MODELING OF THE DYNAMICS OF HOMOGENEOUS REACTIONS IN THE CASCADE OF PERFECT MIXING REACTORS (p. 27-32)

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Present study tackles theoretical analysis and mathematical modeling of the process of homogeneous first-order reaction in the cascade of perfect mixing reactors of continuous action (PMR-C). The modeling of chemical reactors is based on the thermal and material balances in combination with chemical kinetics. The mathematical model of the dynamics of the process of homogeneous first-order reaction in the PMR-C cascade is represented in the form of equations of change in the molar fraction of substance over time and a change in the inner energy of the ideal flow of substance. In the present work, we calculated, by the mathematical model, the process of acetic anhydride hydrolysis in 5 sequentially connected PMR-C. Calculation by the model is performed by the Runge-Kutta method of third order. We obtained temperature profiles for the dynamics of the process of acetic anhydride hydrolysis for a cascade of PMR-C. The temperature gradient in reactor grows over time; consequently, it takes on a constant value. We analyzed the impact of the volume of reaction mixture on the depth of the course of the process both for the separate perfect mixing reactors and for the cascade of perfect mixing reactors. With an increase in the volume of mixture, the reaction rate increases, while the speed of reaching the necessary degree of conversion decreases. The speed of reaching the maximum degree of conversion for the cascade of reactors compared with one perfect mixing reactor of the same volume is considerably higher. Recommendations regarding the course of the process are formulated. We calculated the value of cost for conducting the process of acetic anhydride hydrolysis depending on the change in temperature. Minimum cost is attained at temperature 341 K and amounts to UAH 1.70 million per year.

Keywords: dynamics of the process, cascade of perfect mixing reactors, acetic anhydride, degree of conversion.

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THERMAL ANALYSIS AND IR-SPECTROSCOPIC RESEARCH INTO INTERACTION BETWEEN ORGANOSILICON COMPOUNDS AND NONMETALLIC MATERIALS (p. 33-38)

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It is established that the treatment of carbonate and silicate nonmetallic materials with organosilicon compounds is accompanied by the occurrence of endothermic and exothermic effects.

Exothermic effects are associated with the cleavage of radicals in the organosilicon compounds. It was found that the tuff impregnated with ethyl silicate hydrolyzate is characterized by a wider range of removal of radicals – C₂H₅. This may be due to their more intense interaction as compared to other non-metallic materials.

Occurrence of endothermic effects is caused by release of water, which formed as a result of interaction between nonmetallic materials and organosilicon compounds.

The strength of bond between organosilicon compounds and non-metallic materials decreases in a series of sodium phenyl silicate>potassium methyl silicate>sodium ethyl silicate.

An interaction between siliconates of alkali metals and silicate non-metallic materials is characterized by a stronger bond than that in the case of carbonate materials. The total loss of mass of impregnated silicates is 5.4–10 % versus 26.1–30.3 % in carbonates.

The data on IR spectroscopy of the impregnated nonmetallic materials also testify to the physical-chemical interaction between carbonates and silicates and organosilicon compounds. The fixation and interaction of siliconates in the composition of carbonates is evidenced by the occurrence on IR spectra of new bands at 2900–3000 cm⁻¹ and an increase in the intensity of bands responsible for oscillations in the bonds between silicon and oxygen. The evidence of this is also an increase in adsorbed water and a decrease in the intensity of absorption bands characteristic of anion. There is also an expansion in the range of bands responsible for the valence and deformational oscillations in the bonds between silicon and oxygen. There appear the bands that are caused by the deformational oscillations in the bond between C–H and adsorbed water.

The indicated peculiarities allow us to conclude that in the structure of silicates and carbonates there occurs both a physical fixation and a chemical interaction between siliconates of potassium and sodium.

Keywords: non-metallic materials, carbonates, silicates, organosilicon compounds, IR-spectroscopy, DTA, DTG, TG.

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FORMATION OF LEATHER BIOSTABILITY WITH THE USE OF CATIONIC POLYELECTROLYTES (p. 39-47)

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The creation of new preparations with a wide range of biocidal action on the pathogenic microorganisms, long-term protective action and, at the same time, with low toxicity for humans and safe for the environment, is a relevant direction in the development of modern technologies in the production of leather materials.

In the present article we report the results of examining the antibacterial properties of leather, modified with a composition of natural minerals (zeolite, montmorillonite) and polyhexamethyleneguanidine hydrochloride (PHMG-HC) – cationic polyelectrolyte. PHMG-HC is related to the biocides with a wide range of antimicrobial action, it provides surfaces that are treated with a long-lasting bactericidal effect (up to 8 months), which is why it is called a unique biocide with prolonged action. However, up to now, the use of PHMG-HC to provide leather materials with antibacterial properties has not been explored.

The research was conducted using the lining leather, impregnated with the dispersed solutions of zeolite and montmorillonite. The modification of leather with PHMG-HC, the substance included in the register of preparations permitted by the EU, was carried out at the stage of after-tanning processes in the production of leather. We propose to use the preparation as a polyfunctional material that fixes the filling and greasing materials in the

dermis structure and simultaneously provides it with antibacterial properties.

As a result of research, we established special features of the anti-bacterial properties of leather depending on the treatment of a semi-finished product with the solutions of PHMG-HC at different concentration and the type of mineral filler. It is shown that the examined samples acquire a certain level of biostability when treated with the solution of PHMG-HC at concentration not lower than 2.5 %.

It is determined that the structure of natural minerals and their location in the leather dermis affect the degree of absorption of the biocide by a semi-finished product. It was found that the leather materials, modified with PHMG-HC, exert a pronounced bactericidal effect on the bacteria of the genus *Escherichia coli*, *Pseudomonas aeruginosa*, *Bacillus subtilis*.

Research results demonstrated the possibility of obtaining leather materials with special antibacterial properties when using environmentally safe biocidal preparation (polyhexamethyleneguanidine hydrochloride) and accessible and cheap natural minerals (zeolite, montmorillonite).

Keywords: leather, cationic polyelectrolyte, polyhexamethyleneguanidine hydrochloride, zeolite, montmorillonite, biocide, antibacterial properties.

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ELECTROCHEMICAL WATER SOFTENING IN A DIAPHRAGM ELECTROLYZER (p. 48-55)

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The results of studies in electrochemical softening of water in a diaphragm electrolyzer with inert anodes and a porous diaphragm were presented. It was shown that the most significant degree of softening of water at the lowest current and electric power consumptions was observed when water was fed to the anode chambers and moved in parallel flows in the electrode chambers. The total hardness of natural water was reduced to 1.4–1.6 mmole/dm³, alkalinity to 3.8–4.3 mmole/dm³, pH by 0.3–0.6 and acidity practically did not change. The recommended process scheme for water softening involves parallel movement of

catholyte and anolyte streams in the electrolyzer at a ratio of their consumptions (7–8):(3–2) and their separate extraction from the electrode chambers. Catholyte is filtered to remove insoluble hardness salts and mixed with anolyte. The degree of water softening is regulated only by changing the strength of direct current applied to the electrodes. The technology makes it possible to completely abandon the use of chemical reagents, simultaneously stabilize and disinfect softened water and avoid secondary contamination of water with chemicals. The design of an industrial monopolar electrolyzer with an inactive diaphragm for electrochemical change of pH and Eh was developed. The electrolyzer features a solid anode and a perforated cathode or perforated electrodes closely pressed against the diaphragm. The softening technology is advisable to use for local water preparation for production operations and before softening hard water with ion-exchange filters or electrolysers. The developed technology of water softening and purification has been introduced at a number of enterprises in Slovakia and Ukraine, in particular, for industrial water treatment in galvanic plants and flour mills.

Keywords: water softening, diaphragm electrolyzer, active reaction, oxidation-reduction potential.

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DEVELOPMENT OF THE MATHEMATICAL MODEL OF THE BIOTREATMENT PROCESS OF WATER-SOLUBLE GASEOUS EMISSIONS (p. 56-62)

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In the experimental research, the kinetic characteristics of hydrogen sulfide, sulfur dioxide and ammonia biooxidation were determined. It was found that the hydrogen sulfide and sulfur dioxide oxidation rates varied from 12 mg/g of biomass per hour in the region of the minimum pollution concentrations to the maximum value of 40 mg/g·h. As for ammonia, the variation range was 1.5–5 mg/g·h, respectively. The analytical description of the dependence of the specific degradation rate of pollutants on their concentration was proposed. The obtained quantitative values and variation nature

of the specific oxidation rate prove the technological possibility of using the trickle-bed bioreactor for treatment of water-soluble gaseous emissions.

Based on the experimental research, the mathematical description of the non-stationary biooxidation process of water-soluble gaseous hydrogen sulfide, sulfur dioxide and ammonia was developed. The developed mathematical model is based on the mass balance in the trickling layer of the bioreactor in the course of absorption and biodegradation processes. The analytical dependencies consider the emergence of dynamic balance between the harmful matter arrival intensity and oxidation. The state of dynamic balance determines the boundary of the bioreactor efficiency. The results allow evidence-based calculations of the hydrogen sulfide, sulfur dioxide and ammonia biotreatment process in the trickle-bed bioreactor.

Keywords: emission treatment, biotreatment process, hydrogen sulfide, sulfur dioxide, bioreactor.

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**MATHEMATICAL MODELING AND
COMPUTER SIMULATION OF
THE FILTRATION PROCESSES IN EARTH DAMS
(p. 63-69)**

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We built a mathematical model of the filtration consolidation of the body of an earth dam with engineering inclusions and erosion zone in a two-dimensional setting. It considers the presence of a damaged conduit in the body of a dam. We also took into account the impact of anthropogenic factors: temperature and the concentration of salts, subsidence of the upper boundary and the displacement of internal points in the region of dam over time. The existence of erosion zone (as a result of damage to the conduit) is considered. Taking into account the erosion zone exerts a significant effect on the overall picture of filtration processes occurring in the body of a dam. Erosion zone has the largest impact on the distribution of excess heads and their gradients. We developed a software application to automate the calculation of numerical solution of a boundary problem using the method of radial basis functions that make it possible to conduct numerical experiments by changing the input parameters and the form, as well as represent results of these experiments in the form of charts and numerical data according to each temporal layer. The software application was developed in the integrated programming environment Microsoft Visual Studio 2008 in the language C#. The impact of the existence of a conduit, erosion zone, temperature and the concentration of salts in the body of a dam was explored at different temporal layers. The distribution of all the desired functions and their impact can be displayed graphically. A series of numerical experiments were performed and their analysis conducted. It is shown as a result that the existence of damage in a conduit in the body of a dam leads to the formation of erosion zone.

This, in turn, leads to the gradual filtration destruction of soil material of the dam and its possible complete destruction. The results obtained might help to prevent and to evaluate the consequences of possible accidents without conducting field experiments, and, consequently, to save resources and time.

Keywords: hydropower engineering, problem of filtration consolidation, osmotic phenomena, free surface, object-oriented programming.

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DEVELOPMENT OF TECHNOLOGY FOR RECYCLING THE LIQUID IRON-CONTAINING WASTES OF STEEL SURFACE ETCHING (p. 70-77)

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Results of the conducted theoretical and practical research into processes of recycling the iron-containing wastes of steel surfaces etching are presented, namely, regeneration and utilization of used-up etching solutions and purification of wash water. Based on the results of research, new technological approaches to waste recycling with the view of minimizing their discharge into the environment and reducing costs of an enterprise were substantiated and practically tested.

The existing technologies for recycling the iron-containing wastes of steel surfaces etching require updating in order to minimize their discharge into environment and to reduce the expenditures of an enterprise. It is known that in the theoretical approach to the concentrated solutions of electrolytes, so many correction coefficients were introduced to the theory of calculations that the results of calculations lose their physical essence. Therefore, for the concentrated solutions, it is necessary to determine the basic parameters experimentally.

After exploring the technology of wash water purification, it was established that the most effective way is treatment with lime with flocculant (brand Zetag 8180) and filtering through a filter with polystyrene foam. A part of the treated water was passed through a reverse osmosis system, which, at subsequent mixing with the main part of the flow, makes it possible to obtain water of the “Technical water” category II quality.

In order to develop a technology for the regeneration of used-up etching solutions, we conducted research into redox properties of UES both with H₂O₂ and without it at different pH values. The optimal scheme of treatment is the one that includes alkalization with a 40 % solution of Ca(OH)₂ until achieving pH=4.2, and treatment with a hydrogen peroxide solution.

The technology of recycling of used-up etching solutions with the application of UES as a chemical reagent makes it possible:

- 1) with the alkalization, to provide optimal extraction of zinc from complex compounds, which also increases at a co-sedimentation of zinc and iron;
- 2) to provide optimal conditions for the oxidation of organic compounds in alkaline wastewater after degreasing operations.

Keywords: liquid wastes, regeneration, hydration, used-up etching solutions, redox properties, wash water.

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