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DESIGN OF THE COMPOSITION OF ALKALI ACTIVATED PORTLAND CEMENT USING MINERAL ADDITIVES OF TECHNOGENIC ORIGIN (p. 6–15)

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This paper reports results of the development of cement compositions and production technology for common cement systems «portland cement clinker – mineral additives – alkaline activator – water-reducing admixture», which contain more than 60 % by weight of mineral additives. The additives have been selected from the group: granulated blast furnace slag, ash from thermal power plants (fly ash and disposed ash) and red mud (waste of alumina production). The relevance of the work relates to the need to improve a number of indicators that limit the widespread application of traditional cements, highly filled with waste (slag portland cement), in particular, early strength and setting terms.

We have devised basic principles of the structural arrangement of cement compositions, as well as show the technology of their production. It was established that in terms of the requirements based on acting Ukrainian and European standards, in particular EN 197-1, the designed cements are not inferior to the EN cements, CEM I, CEM II, CEM III, in their characteristics, but even outperform them for strength. The developed cement compositions, which contain the portland clinker in the amount not exceeding 40 % by weight, meet the requirements of the EN standard for the classes of compressive strength (at the age of 28 days) 32,5N – 32,5R; 42,5R – 52,5R.

We have investigated the influence of alkaline components on the structure formation processes of artificial stone in the alkaline activated cement at different levels. It was established that an increase in the alkalinity of a cement environment predetermines a decrease in the basicity of the phase composition of neo formations of cement at the micro

level, as well as contributes to increasing the total porosity of an artificial stone, which, at the same time, tends to closing and decreases over time.

Keywords: alkali activated cement, composite cement, related products, waste disposal, red mud, alkaline activation.

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ANALYSIS OF THE INTERACTION BETWEEN PROPERTIES AND MICROSTRUCTURE OF CONSTRUCTION CERAMICS (p. 16–25)

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We have defined the basic properties of ceramic bricks for various purposes. The microstructure and phase composition of ordinary, facing and clinker bricks were investigated. We have established the interrelation between the microstructure and phase composition of the examined materials and water absorption, mechanical strength at compression, and frost resistance. The research results allowed us to identify patterns in the formation of a ceramic sherd and explain the physical-chemical processes during sintering.

It was established that ordinary brick mostly contains the thermally altered clay substance with a low amount of the glass-phase. Given the above, due to the incomplete liquid-phase sintering, the ordinary brick has high water absorption values (10–14 %) at low strength (7.5–12.5 MPa).

Facing brick has the more developed glass-phase, which firmly binds the crystalline phase. The latter is represented

by such minerals as β -quartz, microcline, albite, mullite, etc. The main task in the facing brick production is to ensure the optimal dispersion of starting raw materials and to achieve even distribution of minerals throughout the entire volume of the product.

Clinker brick has a more complex mechanism of sintering because when using the starting particulate mass, it is required to obtain a dense homogeneous structure of products. The main features of the ceramic mass are the introduction to its composition of emaciated additives that would ensure the resistance of products against deformation during annealing, and marshes, which should ensure the intensive liquid-phase sintering at annealing. When annealing such articles, it is necessary to select the proper temperature-time mode, which would match the sintering interval of the basic clay material. This is required to ensure that, on the one hand, a strong dense structure of the product is obtained, with a water absorption of 4–5 %, and, on the other hand, that such kinds of defects as deformation, cracking, «over-annealing», swelling, etc. are avoided.

Research results could be applied under industrial conditions at enterprises in order to control product quality and eliminate possible causes of defects related to violation of the technological production mode.

Keywords: ceramic brick, ceramic material microstructure, sintering of clays, annealing of building ceramics.

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REMOVAL OF AMMONIUM IONS FROM AQUEOUS SOLUTIONS USING ELECTRODIALYSIS (p. 26–34)

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We report results of investigating the processes of electrochemical oxidation of ammonium in a two-chamber electrolyzer depending on the composition of the original solutions – anolyte and catholyte, current density, electrolysis duration. It is shown that the electrochemical oxidation of ammonia in aqueous solutions of ammonium sulfate proceeds at a rate of 14–55 mg/(dm³·hours) at a current density of 86.2–172.4 A/m² and the starting concentrations of a given ion of 10–120 mg/dm³. The rate of ammonium oxidation under these conditions increases with increasing starting concentrations of ammonium and with increasing current density.

The output of oxidized ammonium for current and specific consumption of electricity for water purification from ammonium are defined based on ammonium concentrations and current density and increase with an increase in the concentration of a given ion and a decrease in current density.

Ammonium oxidation rate increases by 1.66 times in solutions of ammonium sulfate ([NH₄⁺] = 90 mg/dm³, *j* = 172.4 A/m²) in tap water, compared with distilled water. This is due to the presence of chlorides in tap water, which act as a catalyst during ammonium oxidation at the expense of the intermediate formation of active chlorine. Under these conditions, we observed complete oxidation of ammonia compared with solutions on distilled water where the residual ammonium concentrations reach 1–3 mg/dm³.

It is shown that the presence of chlorides in catholyte at a concentration of 30 mg/dm³ almost does not accelerate the oxidation of ammonium. Our work demonstrated that in all cases, during oxidation of ammonium, pH of solutions decreases to 6.1–2.0, which is predetermined by the oxidation of ammonium to nitrates and the acidification of water by the formed nitric and sulphuric acids.

Based on the reported results, it can be concluded that the electrochemical method is the most promising method for the extraction of ammonium ions from water. Its application makes it possible to achieve a 100 % water purification.

Keywords: ammonium ions, electrodialysis, redox processes, anodic oxidation, specific electrical conductivity, output of substance for current.

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ESTABLISHING THE PATTERNS IN ANODE BEHAVIOR OF COPPER IN PHOSPHORIC ACID SOLUTIONS WHEN ADDING ALCOHOLS (p. 35–41)

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We have investigated the anodic polarization dependences of the copper electrode in phosphate-alcoholic solutions. The dependences derived can be divided into regions, each of which corresponds to the course of certain electrochemical reactions within the specified range of potentials. The first region corresponds to the anodic dissolution of copper, the second region – to the formation at the surface of copper of a passivating oxide-salt film and the diffusion regime of metal dissolution. Upon reaching the potential for the decomposition of water, the dissolution of a copper electrode is accompanied by the oxidation of H₂O molecules. We have established the relationship between patterns of copper dissolution and polarization dependences of the electrode. Electrochemical etching of copper is matched with the range of electrode potentials of 0–0.8 V. Formation of an oxide-salt film at potentials of 1–2 V predetermines the ionization of copper under diffusion mode and leads to the preferential dissolution of metal's micro-irregularities with the formation of the shiny surface of the electrode. Shifting the anode potential towards magnitudes exceeding 2 V leads to the emergence of point etching at the surface of copper because of a local disruption in the continuity of a passive film. Adding ethanol to the solutions of phosphoric acid reduces current density of the anodic copper dissolution in the stationary area to the values of 0.2–2 A·dm⁻². Ethanol helps obtain a shiny surface of copper. At (C₂H₅OH)>30 %, the polishing effect disappears. Butyl alcohol is an effective inhibitor of copper etching and in its presence j_a reduces to 0.1–1 A·dm⁻². Adding C₄H₉OH predetermines the formation of surface with a strong gloss and the minimum number of etching points. At (c(C₄H₉OH))>50 %, copper surface acquires a significant number of etching points. Inhibitory effect of glycerol is close to the action of butanol. The shape of the polarization dependence is predetermined by the C₃H₈O₃ content in solution. When increasing c(C₃H₈O₃)>20 %, polishing does not occur and the surface of the electrode has a matte appearance. The data obtained show that the anodic behavior of copper depends on the nature of an additive, which could be used to develop the polishing electrolytes or the dimensional copper treatment.

Keywords: electrochemical polishing, passive film, diffusion dissolution, pitting, anodic polarization, dimensional treatment.

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INVESTIGATION OF THE PROPERTIES OF Ni(OH)₂ ELECTROCHROME FILMS OBTAINED IN THE PRESENCE OF DIFFERENT TYPES OF POLYVINYL ALCOHOL (p. 42–47)

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Electrochromic films were prepared by cathodic template synthesis in the presence of two types of polyvinyl alcohol: with the hydrolysis degree of 99 % and 85 %. The prepared films show differences in structural, morphological, electrochromic and electrochemical characteristics. Both films were X-ray amorphous and had different shapes of the curve on the XRD patterns in the region of small 2θ angles, which corresponds to differences in the direction of 001. Comparison of the morphology of the films prepared from solutions containing PVA with different hydrolysis degrees revealed that the film prepared in the presence of 99 % hydrolyzed PVA has a relatively flat relief with small sizes of bumps. On the other hand, the film prepared in the presence of 85 % hydrolyzed PVA had worse uniformity. Its relief had wavy lines, the height of which reached 1.2 μm. Cyclic voltammograms of both films were also different. CVA of the film prepared in the presence of 85 % hydrolyzed PVA had sharp anodic and cathodic peaks that are similar in height. The potentials of the peaks were +600 and +700 mV. The film prepared in the presence of 99 % hydrolyzed PVA showed broader peaks, with the anodic peak shifted to more positive values (+900 mV). Electrochromic characteristics of both films also differed significantly. The film deposited in the presence 85 % hydrolyzed PVA had a high coloration rate (60 s), but lower coloration degree (18 %). On the other hand, the film deposited in the presence of 99 % hydrolyzed PVA had a coloration rate that is three times slower (200 s), but higher absolute coloration degree (24 %). Several mechanisms that explain such differences in the behavior of the films prepared in the presence of different PVA types have been proposed.

Keywords: electrochromism, electrodeposition, thin films, Ni(OH)₂, nickel, polyvinyl alcohol, hydrolysis degree, nickel hydroxide.

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CALCULATION OF POLYCONDENSATION EQUILIBRIA IN AQUEOUS SOLUTIONS OF SILICA AND SILICATES (p. 48–55)

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We proposed some complication of the previously used calculation model to expand capabilities of the theoretical description of acid-base and polycondensation equilibria in water-silicate systems. A fuller account of the balance of H^+ ions enables the mathematical modeling of a structure and physicochemical properties of aqueous solutions not only of soluble silicates, but also of silicic acid, and with the same set of introductory thermodynamic parameters. The basis of the modified calculation model is a numerical solution of the system of eight linear and nonlinear equations by the Newton method.

We used the new model to calculate parameters of the molecular mass distribution of silicon-oxygen species and pH value in aqueous solutions of silicic acid, as well as alkaline silicates and silicates of amines (amino silicates). We determined ranges of values of input thermodynamic parameters, which make possible self-consistent description of three non-trivial experimentally observed effects. These are a rheological anomaly in solutions of amino silicates, absence of this anomaly in solutions of alkaline silicates, and predominantly monomeric nature of silicic acid in a low-concentrated aqueous solution of silica. We showed that a self-consistent description of three effects is possible only if the sum of indexes of dissociation constants (pK_a) and polycondensation constants (pK_p) of a silanol group, is less than 11.6. We also calculated concentrations of hydrolytic and polycondensation structures in compositions of anions and cations for these solutions and analyzed dependences of these concentrations on parameters of the calculated model. In particular, we showed that the modification of the calculated model leads to a significant increase in calculated values of pH and a degree of dissociation of silanol groups for a silica solution, while the average degree of polymerization stays almost unchanged. In addition, we found that the degree of depolymerization of a siloxane bond may be nonmonotonically dependent on pK_a value in solutions of amino silicates.

Keywords: soluble silicates, amino silicates, silicic acids, anomalous rheology, polycondensation.

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STUDYING THE INFLUENCE OF THE INTENSITY OF MECHANOCHEMICAL ACTIVATION ON THE PROCESS OF STEAM CONVERSION OF COAL (p. 56–62)

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We continue to study the process of converting coal into synthesis-gas under conditions of aerosol nanocatalysis and reasonably expect would-be benefits of industrial technology. The advantages include a possibility to change the rate of reaction by influencing the intensity of mechanochemical activation of the catalyst. We investigated the process in a reactor where the mechanochemical activation is performed by the rotation of the catalytic system. The effect of activation intensity on chemical reactions under conditions of aerosol nanocatalysis has been proven earlier for the fluidized and vibro-liquefied layer of the catalytic system. Previous studies have shown that the mechanochemical activation affects the composition of conversion products, namely the ratio of CO:H₂. That would make it possible in the future to quickly reorient the production of synthesis-gas in line with the needs of market for organic products. The research results showed that at a temperature of 750 °C, 1 bar, MCA intensity of 2–4 Hz and with an excess of coal (C:H₂O=5.5:1), the obtained ratio CO:H₂=1:1.99–1:2.10 can be used for obtaining alcohols. At a temperature of 750 °C, 1 bar, MCA intensity of 0–1 Hz and with an excess of coal (C:H₂O=5.5:1), the obtained ratio CO:H₂=1:1.19–1:1.35 can be applied for obtaining esters. We also noted the possibility of obtaining synthesis-gas with a ratio of 1:2.3 (2.5), which can be applied for obtaining hydrocarbons. This ratio was derived in the following mode: temperature 750 °C, pressure 1 bar, the ratio coal:water = 1:0.87, MCA intensity 3–4 Hz. The specified process to obtain hydrocarbons was investigated at 230 °C, 1 bar, in a vibro-liquefied layer of the catalyst aerosol at ratio CO:H₂ = 1:3 at 3 Hz and CO:H₂ = 1:2 at 3 and 5 Hz. The results of this paper are continuation of a global study

into coal processing with obtaining the required industrial product. This special feature is the advantage of conducting a given process based on the aerosol nanocatalysis technology.

Keywords: aerosol nanocatalysis, mechanochemical activation, catalytic system, composition of synthesis-gas, steam conversion.

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