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SYNTHESIS OF NICKEL HYDROXIDE IN THE PRESENCE OF ACETATE ION AS A «SOFT» LIGAND FOR APPLICATION IN CHEMICAL POWER SOURCES (p. 6–12)

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Nickel hydroxide is widely used as the active material in chemical power sources. The formation mechanism of nickel hydroxide includes two fast phases of the formation of an initial amorphous particle and slow aging (crystallization) stage. Characteristics of nickel hydroxide can be improved by slowing down the first stage through the reaction of nickel cation with «soft» ligand and formation of a weak complex. It is proposed to use acetate ion as a «soft» ligand, which forms a complex with Ni²⁺ without the outer sphere. The influence of acetate ion on the crystal structure, particle morphology and electrochemical properties of nickel hydroxide chemically precipitated at high supersaturation using nickel sulfate in the presence and absence of sodium acetate is studied. The crystal structure of the samples is studied by means of X-ray diffraction analysis and sample morphology – by means of scanning electron microscopy, electrochemical properties – cyclic voltammetry. A comparative analysis of the characteristics of the samples prepared in the presence and absence of sodium acetate is carried out. The results of XRD analysis revealed that synthesis in the presence of acetate ion leads to the formation of a bi-phase system that contains low crystallinity β-Ni(OH)₂ and α-Ni(OH)₂. This also leads to a higher content of smaller particles with a larger surface area. The comparative analysis of electrochemical characteristics revealed the formation of a more active samples in the presence of acetate ions, which predominantly behaves like the α-form. The sample activity increased during cycling. Synthesis in the presence of acetate ion results in the increase of specific discharge peak current (equivalent to electrochemical activity) by 1.93 times, in comparison to the sample synthesized under the same condition but in the absence of acetate ions.

Keywords: nickel hydroxide, α-Ni(OH)₂, electrochemical activity, alkaline battery, acetate.

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IMPROVING THE RESISTANCE OF CONCRETE FOR SLEEPERS TO THE FORMATION OF DELAYED AND SECONDARY ETTRINGITE, THE ALKALI-SILICA REACTION, AND ELECTRIC CORROSION (p. 13–19)

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The paper reports results of examining the influence of modifier admixtures on the corrosion resistance of concrete for reinforced concrete sleepers based on the criteria of electric resistance, resistance to alkaline corrosion and corrosion due to the crystallization of delayed and secondary ettringite. This study was conducted within the framework of resolving the issue on premature destruction of reinforced-concrete sleepers caused by the progressing crack formation at the stage of heat treatment and subsequent operation. It has been established that the introduction of pozzolanic admixtures containing active Al₂O₃ in their formulation to the composition of concrete for sleepers makes it possible to minimize the risk of corrosion predetermined by the reaction between aggregates' silica and alkali and corrosion as a result of crystallization of delayed and secondary ettringite. The high efficiency of pozzolanic admixtures containing active Al₂O₃ regarding the specified types of corrosion is due to binding alkali into the insoluble alkaline hydroalumosilicates, contributing to the compaction of the system with a decrease in the content of Na⁺/K⁺ ions in the solution. A decrease in the content of alkali in the porous solution predetermines blocking the «alkali-silica reaction» and increasing the temperature of ettringite stability to higher values. This reduces the potential number of secondary ettringite forming cycles and the probability of delayed ettringite formation. The alternative mechanism of action of active Al₂O₃ on pozzolan implies binding the SO₄²⁻ and Ca²⁺ ions from a porous solution into low-sulfate forms of calcium hydro-sulfoaluminates, which excludes the crystallization of delayed and secondary ettringite.

Reducing the consumption of cement and water through the use of admixtures-plasticizers makes it possible to increase the electrical resistivity of the modified concrete for sleepers above the level of a control composition without admixtures. The obtained results provide an opportunity to ensure the design durability of concrete in reinforced-concrete sleepers through their comprehensive modification by plasticizers and active mineral admixtures that contain active Al₂O₃.

Keywords: alkali-silica reaction, delayed ettringite, secondary ettringite, electrical resistance, metakaolin, fly ash, silica fume, plasticizer.

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DEVELOPMENT OF THEORETICAL FOUNDATIONS FOR THE HOT METAL DESULFURIZATION WITH MAGNESIUM REDUCED BY THE HEAT FROM EXOTHERMAL TRANSFORMATIONS (p. 20–29)

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The process of hot metal desulfurization by magnesium, reduced by the heat from exothermic reactions, has been investigated. Our research into the thermodynamics of magnesium oxide reduction in line with various protocols has established that it is in principle possible to reduce magnesium oxide by carbon, silicon, manganese, iron, and aluminum. We have calculated starting temperatures for MgO reduction by iron, manganese, silicon, aluminum, and carbon, which are 2,956, 2,546, 2,313, 1,585 and 1,875 °C, respectively. It has been determined that the most rational method to reduce magnesium oxide is the process based on binding the products of reduction into a CaAl₂O₄ compound.

Based on the established rational conditions for magnesium oxide reduction, the exothermic mixture for hot metal desulfurization was calculated, %: MgO – 15.0; FeO – 56.0; CaO – 7.0; Al – 22.0. Experimental study has confirmed the most successful technical solution for the introduction of the calculated exothermic mixture to the melt aimed at desulfurization, which implies the application of a device for the introduction of active reagents into the melt, which

is equipped with a chamber that collapses under the influence of the heat of liquid hot metal. Its use makes it possible to achieve the mean level of desulfurization of 65–70 %. We have performed, under industrial conditions, an experimental desulfurization of chromium hot metal using the designed exothermic mixture. According to the research conducted, the achieved degree of hot metal desulfurization in a ladle was at the level of 38 %; for the material of castings – at the level of 45.7 %. Thus, there is a reason to argue about resource and energy savings when applying the proposed technology for the out-of-furnace hot metal desulfurization by reduced magnesium.

Keywords: out-of-furnace hot metal treatment, desulfurization, magnesium oxide, aluminothermia, complex oxides, exothermic mixture.

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DETERMINING THE EFFECT OF THE COMPOSITION OF AN ALUMINOSILICATE BINDER ON THE RHEOTECHNOLOGICAL PROPERTIES OF ADHESIVES FOR WOOD (p. 30–38)

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Main rheotechnological properties of aluminosilicate adhesives for gluing wood arrays have been investigated. It was established that for adhesives based on the alkaline aluminosilicate binding agent with a composition of Na₂O·Al₂O₃·4.5SiO₂·17.5H₂O dynamic viscosity in the range of speeds from 0 to 200 RPM varies from 6.933 sP to 368.4 Sp, and the mean plastic viscosity takes the magnitude of 86.27 sP. At the same value of surface tension and cohesive work, the smallest angle of wetting (cosΘ=0.7973) and the largest coefficients of wetting (s=0.8986) and spreadability (f=-6.5 mN/m), as well as the work of adhesion forces (W_a=58.23 mN/m), wetting (W_w=58.23 mN/m), are demonstrated by beech backing, followed by alder, ash, pine, birch, and oak.

For adhesives based on the alkaline aluminosilicate binding agent with a composition of Na₂O·Al₂O₃·6SiO₂·20H₂O dynamic viscosity in the speed range from 0 to 200 RPM varies from 5.340 sP to 374.4 sP, and the mean plastic viscosity takes the magnitude of 85.72 sP. At the same value of surface tension and cohesive work, the smallest angle of wetting (cosΘ=0.5876) and the largest coefficients of wetting (s=0.7938) and spreadability (f=-19.34 mN/m), as well as the work of adhesion forces (W_a=74.46 mN/m), wetting (W_w=27.56 mN/m), are demonstrated by alder backing, followed by pine, oak, birch, beech, and ash.

For the adhesive with a composition of Na₂O·Al₂O₃·4.5SiO₂×17.5H₂O, at low values of shear rate, from 0.0378 to 1.05 1/sec, the shear force increases from 26.21 dyne/cm² to 48.64 dyne/cm².

The data obtained significantly exceed the same indicators for a liquid glass at high shear rates, from 14 to 39 1/sec. For the adhesive with a composition of $\text{Na}_2\text{O}\cdot\text{Al}_2\text{O}_3\cdot 6\text{SiO}_2\cdot 20\text{H}_2\text{O}$, at low shear speeds there is a sharp increase in the shear effort, from 40 to 110 dyne cm^2 . This is due to the dispersion processes in the silica component. At an increase in the shear speed values from 5 to 42 1/sec, the shear effort increases from 110 to 158 dyne/ cm^2 . This relates to the stabilization of viscosity values with the formation of a homogeneous adhesive structure.

Keywords: aluminosilicate adhesive, dynamic and plastic viscosity, surface tension, wetting angle, shear force, wood backing.

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DEVELOPMENT OF NANOMODIFIED RAPID HARDENING CLINKER-EFFICIENT CONCRETES BASED ON COMPOSITE PORTLAND CEMENTS (p. 38–48)

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It has been shown that significant reduction of «carbon trace» in construction technology is achieved by production of clinker-effective concretes based on composite Portland cements. Studies have shown that uneven distribution of grain fractions of the filler mix and their increased specific surface area lead to growth of water demand, stratification, bleeding in the concrete mix and a decrease in concrete strength. To achieve higher grain packing density, an approach based on optimizing particle size distribution in the concrete mix components was implemented. It was found that increased early strength of concretes based on low-emission composite cements is achieved by introduction of polycarboxylate (PCE) superplasticizers and alkaline-sulfate activation. To establish connection between environmental and technical properties of concretes, clinker efficiency in concrete was determined. An increase in strength of modified concrete based on composite Portland cement CEM II/B-M 32.5 R (clinker factor 0.65) create the possibility for a significant reduction of specific consumption of clinker per unit strength, up to 4.5...3.0 kg/(m³·MPa); accordingly, CO₂ intensity 3.9...2.6 kg CO₂/(m³·MPa). Significant intensification of the processes of early structure formation in nanomodified clinker-efficient concretes is ensured by a comprehensive approach: optimization of the component mix, introduction of the PCE superplasticizer and nanomodifiers. Using the laser diffraction method, it was proved that main contribution to development of specific surface of the nanomodified

cementing matrix is made by ultrathin particles ($K_{isa}=761.2 \mu\text{m}^{-1}$ vol. %) of nano-SiO₂. It was established that synergistic combination of mineral additives in composite Portland cement and complex nano-SiO₂+C-S-H-PCE nanomodifier provide increased early strength (after 12 hours – $R_c=6.4$ MPa) and obtaining rapid hardening concrete class C50/60 ($f_{cm2}/f_{cm28}=0.51$). Thus, there are reasons to argue that it is advisable to develop nanomodified clinker-efficient concretes in order to ensure rapid construction and solve problems connected with necessity of implementation of a strategy of low-carbon development.

Keywords: clinker-effective concrete, composite Portland cement, polycarboxylate type superplasticizer, alkaline activator, nanosilica, early strength, CO₂ emission index.

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DEVELOPMENT OF ENGOBE COATINGS BASED ON
ALKALINE KAOLINS (p. 49–56)

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The properties of alkaline kaolins as promising raw materials during manufacturing engobe coatings for construction ceramics were studied. The chemical and mineralogical composition and peculiarities of thermal transformations of kaolins were determined; the compositions of engobe coatings were developed, their rheological properties were studied and physical and ceramic indicators after annealing were determined; the peculiarities of the formation of the coating structure were established.

The relevance of expansion of the raw material base is very high, since existing formulations of ceramic masses and coatings include mainly high-quality clays, kaolins, feldspars, quartz sands and others. Natural supplies of such raw materials are getting rapidly exhausted, which negatively affects the results of production. Thus, the search for alternative raw materials should take into account not only its availability, but also the ability to ensure high quality of ceramic products.

The research results revealed that alkaline kaolins are complex raw material containing kaolinite, quartz and feldspar minerals (microcline or albite), that is why they can replace the listed materials that are introduced into the composition of engobes by separate components. To correct the rheological properties of the developed engobe coatings, it is possible to use traditional electrolytes – rheotan and liquid glass – in the amount of up to 0.7 % by weight. During the thermal treatment, alkaline kaolins sinter actively at the temperatures of 1,100–1,150 °C and contribute to the intensive formation of the strong stone-like engobe layer with water absorption of 3–6 % on the product surface. This coating, in addition to creating a decorative effect, increases the durability of construction products on average by 30–35 %.

The obtained data have both scientific and practical significance, as they allowed substantiating the expediency of using alkaline kaolins as complex raw material in the production of engobe ceramics. This makes it possible to reduce the number of separate components in the composition of coating and to intensify sintering of engobe, which generally leads to the improvement of product quality.

Keywords: ceramic facing brick, engobe, decorative coating, water absorption, annealing of construction ceramics, alkaline kaolin.

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IMPROVING THE CONTROLLABILITY AND EFFECTIVENESS OF THE CHEMICAL-TECHNOLOGICAL PROCESS OF THE TECHNOLOGY FOR HYDROGEN THERMOBARIC CHEMICAL STIMULATION OF HYDROCARBON RECOVERY (p. 57–66)

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An innovative technology of complex hydrogen and thermobaric chemical effects (CHTBCE) on the productive formation of oil (gas) wells has been developed with the aim of stimulating hydrocarbon recovery. The basis of this technology is the integrated use of the anomalous properties of hydrogen under the conditions of a multi-stage thermal-gas-chemical technological process (CTP). Improving the effectiveness of the technology requires a significant improvement in the controllability of the underlying CTP.

An experimental complex has been created for studying the kinetics of thermobaric chemical processes and physical modeling of the complex effect, including hydrogen, on the change in the filtration-capacitive characteristics and rock permeability. The complex allows to reproduce the technological features of the implementation of the chemical-technological process, provides its course in conditions as close as possible to real reservoir.

It has been experimentally proved that by adding activators and inhibitors of chemical reactions to the base process fluids, it is possible to obtain different types of processes and their individual stages in the nature of the flow. It is shown how the use of hydroreactive agents based on aluminum makes it possible to obtain hydrogen and increase the permeability of rocks at the low-temperature stage of the process. The introduction of polymeric nitrile paracyanogen also activates and retains the high-temperature stage of the process at which hydrocracking of heavy hydrocarbons occurs.

A methodology for determining the most effective chemical-technological process of CHTBCE technology is proposed and developed. The method is based on a comparative analysis of the results of the effects of different types of CTP on the restoration of the permeability of formation damage rock core samples.

The research methodology created allows to experimentally determine the most effective CTP of the CHTBCE technology for use in wells with various reasons for the decrease in productivity.

Keywords: well, production stimulation, thermobaric chemical process, core sample, permeability, bottom-hole formation zone.

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