ABSTRACT AND REFERENCES

TECHNOLOGY ORGANIC AND INORGANIC SUBSTANCES

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DEVELOPMENT OF THE TECHNOLOGY FOR OBTAINING ENGOBED CONSTRUCTION ARTICLES WITH THE "ANTIQUITY" EFFECT (p. 6-13)

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The physical and chemical processes that occur when obtaining engobe coatings for construction ceramics with the decorative "antiquity" effect were considered, the composition of the charge, the technology of manufacturing and applying of the coatings on a ceramic product were proposed. The coatings have dark brownish-lilac color with a volumetric effect of light "variability". Engobes can be used when decorating the front ceramic bricks of single annealing with keeping at the maximum temperature of 1,070 °C.

It was found that to provide a gradient volumetric decorative effect, it is recommended to introduce in the composition of engobe charge the microspheres of TPP fly ash in the amount of 3–5 %, and for the thick brown-lilac color – up to 60 % by weight of manganese ore. To ensure the necessary rheological indicators of the engobe slip and its high adhesion capacity, the fineness of grinding of charge components should be not more than 1 % by the residue on sieve No. 0063. The moisture content of the slip is 45 % and fluidity is 18 s.

The mechanisms of shrinkage processes of engobe coatings and the ceramic base at different methods for application of the engobe slip on the product were established. To decrease the difference of shrinkage of the coating and ceramics, it is recommended to apply the engobe slip of the developed composition on the dried ceramic semi-finished product.

After annealing at 1,070 °C, the products are of high quality with the indicator of water absorption of the coating of 5.2–5.4 % and hardness of ~5 by the Mohs scale.

The obtained data can be applied in modeling of processes of engobing the products and in the development of compositions of engobe coatings. The practical value of the results consists in creating a new kind of the decorated building products, which enables increasing the market of its sales and enhancing the competitive capacity.

Keywords: ceramic facing bricks, engobe, decorative coating, water absorption, manganese ore, annealing of building ceramics.

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IMPROVEMENT OF FUNCTIONAL PERFORMANCE OF CONCRETE IN LIVESTOCK BUILDINGS THROUGH THE USE OF COMPLEX ADMIXTURES (p. 14-23)

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When examining concrete in livestock buildings, signs of corrosion and destruction of concrete floors and walls were found. Experimental studies have identified main critical points that directly affected concrete continuity. Excessive moisture, use of corrosive acidic or alkaline disinfectants and presence of natural excretions of animals (urine and feces) were found in livestock buildings.

To solve this problem, admixtures were proposed: yellow iron oxide pigment and liquid glass which improve strength characteristics of concrete, its heat resistance and reduce penetrability.

It was proved by the conducted studies that introduction into concrete of admixtures in quantities from 0.5 % to 2 % has resulted in a 2.8 times smaller depth of chloride penetration as compared to the control specimens. This was due to a decrease in water absorption by concrete when introducing iron oxide, cuprous sulphate, peracetic acid and sodium silicate which reduced pore size in samples.

It was proposed as an innovation to assess thermal stability of concrete using the method of temperature-programmed desorption mass spectrometry (TPMS) based on the dependence of evolution of carbon monoxide and carbon dioxide from samples of carbonate-containing substances on the sample temperature.

Microbiological studies have identified microbes of Penicillium and Fusarium species, bacteria Escherichia coli and Pseudomonas aeruginosa, which cause corrosion of concrete in livestock buildings. Numerous experiments have shown that the proposed admixtures added to the concrete (based on yellow iron oxide pigment (1.5–2.0 wt. %), peracetic acid (0.2–0.3 wt. %), liquid glass (2–3 wt. %) and cuprous sulfate (0.5–1.0 wt. %) had antimicrobial properties and thus prospects for their use in animal husbandry.

Keywords: livestock buildings, corrosive medium, biological corrosion of concrete, bactericidal admixtures, concrete strength.

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DEVELOPMENT OF SOLUTIONS CONCERNING REGULATION OF PROPER DEFORMATIONS IN ALKALI-ACTIVATED CEMENTS (p. 24-32)

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The essence of the problem related to proper deformations in alkali-activated cements (AAC) complicated with high content of gel-like hydrate formations was analyzed. Cement types diametrically opposite in their compositions and, accordingly, in the content of gel phases during hydration, that is, the alkali-actie vated portland cement (AAPC) and alkali-activated slag cement (AASC) were taken for consideration. Approaches to formation of an effective structure of artificial stone counteracting shrinkage deformation by means of interference in structure formation when using complexes of mineral and organic compounds were proposed. Such compounds in composition of complex organo-mineral admixtures jointly influence intensification of crystallization processes and formation of an effective pore structure and morphology of hydrate phases while reducing water content in artificial stone. Salt electrolytes of various anionic types and anion-active surface-active substances were considered as ingredients of the proposed complex modifying admixtures.

It has been found that the “salt electrolyte–surfactant” system is the most effective for AAPC modification. It was shown that modification of AAPC with this complex admixture based on $NaNO_3$ reduced shrinkage from 0.406 to 0.017 mm/m. Instead, the use of Na_2SO_4 provided AAC of this type with a capacity of expansion up to 0.062 mm/m. It was shown that the effect of compensated shrinkage of modified AAPC is associated with a higher crystallization of low-basicity hydrosilicates (CSH(B)) and calcium hydroaluminates ($CaO{\cdot}Al_2O_3{\cdot}10H_2O$). An additional effect is associated with formation of sulfate-containing sodium-calcium hydroaluminate (for the Na_2SO_4-based system) and crystalline calcium hydronitroaluminate (for the $NaNO_3$-based system) with a corresponding microstructure stress.

For further development, a complex admixture of “Portland cement clinker–salt electrolyte–surfactant” system was proposed for AASC modification. It provided shrinkage reduction from 0.984 mm/m to 0.683 mm/m. Minimization of the modified AASC shrinkage was explained by formation of sodium hydroalumosilicate of gmelinite type ($(Na_2Ca){\cdot}Al_2{\cdot}Si_4{\cdot}O_{12}{\cdot}6H_2O$) with a high degree of crystallization along with low-basicity calcium hydrosilicates. It was noted that the cement stone structure is characterized by high density, uniformity, and consolidation of hydrate formations.

Keywords: alkali-activated cement, salt electrolyte, complex organo-mineral admixture, structure formation, proper deformations, shrinkage.

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STUDYING THE INFLUENCE OF METAKAOLIN ON SELF-HEALING PROCESSES IN THE CONTACT-ZONE STRUCTURE OF CONCRETES BASED ON THE ALKALI-ACTIVATED PORTLAND CEMENT (p. 33-40)

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This paper reports results from comparative testing the reaction “alkali – active silica” in traditional Portland cement and alkaline Portland cement with the addition of metakaolin. The research is based on studying the process of structure formation in cements in the contact zone “cement stone – basalt”.

The research results allow us to conclude that the dynamics of the process of interaction of the reaction “alkali–silica” in cements may be constructive and destructive in character. That depends on the content of components that are able to actively interact with alkalis in the presence of reactive silica. The so-called “constructive” processes are accompanied by the binding of corrosion products during the formation of alkaline hydroalumosilicates. The research results were used as the basis for developing the mechanism of preventing the reaction “alkali – active aggregate” in concretes based on alkaline cement by introducing to the cement composition additional amounts of materials containing active aluminum, in particular, metakaolin.

Our study has shown that the introduction of a metakaolin additive could effectively control the processes of structure formation in the contact area “cement stone – active silica”, thereby changing the character of new structures. The mechanism of an alkaline corrosion process of an active aggregate in the presence of metakaolin has been established, according to which metakaolin enters the reaction at a rate of microsilica, providing for a very fast binding of the Na^+ and K^+ ions. Silicate gel of alkaline metals binds into insoluble zeolite-like new structures and hybrid hydroalumosilicates. As resilient structures, the latter condense and strengthen the contact area by enhancing its microhardness and strength.

We have investigated the natural shrinkage deformations (expansion) of the developed compositions of concretes based on the traditional and alkaline Portland cements. It has been shown that the introduction of a metakaolin additive to the system formulation makes it possible to reduce the system expansion indicators from 0.44 to 0.01 mm/m, thereby maintaining the defect-free structure of cement stone and concrete and improving the durability of concrete.

Keywords: alkaline cement, “alkali–aggregate” reaction (AAR), “alkali–silica” reaction (ASR), contact area.

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MODELING A RHEOLOGICAL ANOMALY IN THE SYSTEM Na_2O – SiO_2 – NH_3 – ZnO – H_2O (p. 41-48)

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A universal calculation model for theoretical description of structural and physicochemical properties of aqueous solutions of modified silicates with the involvement of complexing agents is offered. The model takes into consideration three types of equilib-

rium: acidic-basic, metal-complex and, for silicate oxygen anions (SOA), as well as polycondensation. The developed mathematical apparatus makes it possible to apply the model to virtually any type of water glass and its mixtures. For a particular case of the sodium-zinc-ammonium liquid glass, the model provides a numerical solution of the system with seventeen linear and nonlinear equations by using the Newton method.

The new model was used to explain the experimentally observable effect of the rheological anomaly in aqueous solutions of liquid glass modified by zinc and ammonia. The effect is typical, most of all, for the solutions of amino silicates, where the rheological anomaly is associated with the shift of the molecular-mass distribution (MMD) of the SOA towards the process of polycondensation at heating. The calculation results show that such shift also takes place in this system and is explained by the transformation of amino complexes of zinc in hydroxo complexes. The total process can be expressed by equation $[Zn(NH_3)_4]^{2+}+3OH^-\rightarrow[Zn(OH)_3]^-+4NH_3$, which is explained by the essential difference of magnitudes of enthalpy of formation of these complexes. This leads to a decrease in pH and to the shift of the MMD of SOA toward an increase in the degree of polymerization (a decrease in average basicity of SOA). The presence of other complex particles, such as $[Zn(NH_3)_3]^{2+}$, $[Zn(OH)_4]^{2-}$, $[Zn(OH)_2]$, etc., does not play a significant role.

The use of the proposed model allowed the calculation of dependences of parameters of the MMD of SOA, pH magnitudes and concentrations of complex and polycondensation structures on the composition of the solution and temperature. The evolution of relative content of different zinc and silicon containing structures in the course of a change in temperature and total concentration of zinc was traced in detail. It was concluded that the rheological anomaly in the studied system exists due to a special combination of thermodynamic parameters and is unlikely to be widespread among metal-complex silicates.

Keywords: soluble silicates, modified water glass, zinc complexes, abnormal rheology, polycondensation.

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A STUDY OF AN ELECTROCHROMIC DEVICE BASED ON $Ni(OH)_2$/PVA FILM WITH THE MESH-LIKE SILVER COUNTER ELECTRODE (p. 49-55)

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The study is devoted to the development and testing of the electrochromic device based on $Ni(OH)_2$/PVA (polyvinyl alcohol) composite and mesh counter-electrode. A copper wire with a layer of

electroplated silver layer is proposed as a mesh material. Glass coated with fluorine-doped tin oxide after special treatment was used as a substrate for electrochrome deposition. The treatment lies in the shallow dissolution of the surface by means of soft electrochemical etching. The distance between the mesh and electrochromic electrodes was small and equal to 1.5 mm.

The proposed design of the electrochromic device can lead to lower cost. However, it limits the range of possible applications for light windows or upper parts of view windows, building partitions.

Over the course of the studies, it was demonstrated that the electrochromic device is operational and can be used for further scaling. Parameters of electrochemical cycling – working voltage window and current density, were found. It was found that the use of galvanostatic regime for color switching results in linear characteristics of the device.

The use of the chosen voltodynamic regime results in a decrease of specific characteristics of the device – coloration degree and reversibility during bleaching.

It was found that due to the small potential difference of nickel oxide and silver electrodes, the polarity of voltage during coloration and switching changes. Additionally, it is noted that no gas evolution was observed over the course of the experiments.

Keywords: nickel hydroxide, polyvinyl alcohol, electrochromic device, mesh electrode, etching, counter-electrode, silver.

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