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Investigation of the possibilities to modify the building ceramics by utilising MWCNTs

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HIGHLIGHTS

- MWCNTs + CMC modifying additive changes the microstructure of the semimanufacture.
- 0.0045% MWCNTs + CMC improves the properties of ceramic products.
- Density of ceramic body (1000 °C) increases by 4.7%, compressive strength – 32%.
- MWCNTs additive has no influence on mineralogical composition of the ceramic bodies.

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ABSTRACT

Research deals with the possibility to improve the properties of ceramic products by utilising the modifying additive of multi-walled carbon nanotubes (MWCNTs), mixed with carboxymethylcellulose (CMC), which has the properties of dispersant, (MWCNTs + CMC).

It was found that after the insertion of modifying additive (MWCNTs + CMC, sufficient to reach 0.0045 mass percent of MWCNTs in the overall formation mass) into ceramic products' formation mass, plasticity as well as stability of the formation mass increase considerably and microstructure of semimanufacture changes. Density and strength of the semimanufactures become higher. Modified structure of the semimanufactures influences physical and mechanical properties of the burned ceramic bodies, as well as values of structure parameters. However, for the case when burning out sawdust additive is used in the composition of the formation mass, modifying additive has no noticeable influence on the properties of ceramic body. In this case, the absence of influence can be explained by considering that dry porous sawdust on the surfaces easier and more intensively absorb water dispersion with the particles of modifying additive, and therefore distribution of these particles in the formation mass is limited. Carbon nanotubes, adsorbed locally on sawdust particles, burn out together with sawdust. In such a way the positive influence of modifying additive is blocked. This interpretation was confirmed by the positive effect of modifying additive, when the other burning out additive–dispersed anthracite, which is distinguished by its hydrophobic properties, was introduced into the formation mass.

1. Introduction

Aqueous dispersion of clay is a colloidal system. The colloidal stability of aqueous dispersions of clay particles is critical in the development of clay processing operations such as filtration, sedimentation and ceramics processing [1].

The charge of clay's mineral particles existing in aqueous dispersion of clay is negative [2–5]. However, at certain pH values, the charge of clay's mineral particles can be equal to zero or can have positive value [6]. Authors Stumm and Morgan [7] note that the charge of the particles of minerals: feldspars, kaolinite, montmorillonite, albite, at pH values accordingly 2–2.4, 4.6, 2.5, 2.0 is equal to zero, i.e. at these pH values points of zero charge (PZC) are reached. Lewis [6] notes that when pH values of clay colloidal system are lower than those at which PZC is achieved, the clay

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colloidal particles have a net positive charge, but when pH values are higher than those at which PZC is achieved, the clay colloidal particles have a net negative charge. Clay slurry prepared during the ceramics processing is not acidic so the charge of clay mineral particles in the clay slurry is negative and this corresponds to [2–5].

It is generally known that the sign of electrical charge of all colloidal particles in the same colloidal dispersion is the same, and that the stability of colloidal dispersion is determined by electric repulsion between two approaching colloid particles having the same sign of electrical charge. With the increasing repulsion stability of colloidal dispersion is increased. And vice versa – with the decreasing repulsion stability decreases. When repulsion is decreased to zero the coagulation occurs.

The coagulation in clay slurry leads to the increase of viscosity. When high amounts of solid contents are utilised in clay dispersion, the liquidity is highly desired during the ceramics processing [4], as it leads to the improvement of the rheological properties of clay slurry and increase of density and mechanical strength of ceramic products as well.

In ceramic engineering, in order to have liquefying effect in clay and water mixtures the deflocculants are used. In the research of Welzen et al. [8] it was estimated that in order to avoid coagulation of clay colloid, surface-active agents (surfactants), such as thrimethylammonium bromide and sodium dodecylsulfate, can be used. In addition, it was stressed in this research that the effect of these surfactants is linked to pH of medium. The influence of surfactant sodium dodecylsulfate on flow behaviour of sodium montmorillonite and sodium calcium bentonite dispersions was investigated in the research of Permien and Lagaly [9], where it was estimated that the effect of this surfactant depends on dispersion's pH. In the research [10], montmorillonite clay was modified with octadecylamine (an aliphatic amine surfactant with 18 carbon atoms) and then modified montmorillonite clay was melt-mixed was mixed with natural rubber by using two roll mill. Then the impact of surfactant content and organoclay content on core characteristics, mechanical properties and morphologies of natural rubber nanocomposites was investigated. It was estimated that with the increase of surfactant content the morphologies of natural rubber nanocomposites revealed exfoliated structure and good dispersion of the organoclay in the natural rubber matrix. This resulted in the improvement of mechanical properties of the natural rubber nanocomposites.

In the research [4] investigation results of the influence of inorganic anions on the rheological properties of clay mineral dispersions are described. This research is concluded that the inorganic anions have the liquefying effect – they decrease the viscosity and increase the stability of clay colloidal dispersion against salts.

It is noticed [3] that relatively small amount of organic anions, such as natural polyanionic humate, aromatic multifunctional gallate, salicylate, less than one species per nm^2, adsorbed on the Al–OH sites of clay minerals (montmorillonite, kaolinite and aluminium oxide) stimulates significant increase of colloidal stability of the dilute suspension. In the research mentioned it was noted that the layer of organic anions was adsorbed on the surface of mineral particles. Such polyanionic surface modification process takes place spontaneously in any natural aquatic system containing clay and metal oxide as well as dissolved organic material. Static and electrostatic stabilization of mineral particles, influenced by organic anions, increase repulsion between uniformly negatively charged particles. Therefore, the edge-to-edge aggregation of clay particles is hindered and the resistance is increased significantly.

Authors of the research [11] have investigated the influence of polymers on the apparent and plastic viscosities as well as water loss of sodium bentonite suspensions and concluded that low-viscosity carboxymethylcellulose acts as a deflocculant, and this polymer, among the other polymers analysed, showed the highest resistance against the changes of rheological properties and the increase of the stability of bentonite suspension.

In the research [12] it is noticed that carboxymethylcellulose (CMC) is a polysaccharide which is widely used in industry, including mineral processing. In this research the adsorption of CMC on talc was investigated by using modern investigation methods, such as adsorption and electrolytic mobility measurements, FTIR, fluorescence spectroscopy, AFM and molecular modelling. CMC adsorption on talc was found to be influenced significantly by the changes of solution conditions, such as pH and ionic strength. The investigation results suggest that the main driving forces of CMC adsorption on talc are the combination of electrostatic interaction and hydrogen bonding.

The CMCs, despite of the average number of carboxymethyl groups per anhydroglucose unit, i.e. degree of substitution (DS), are anionic polymers [13,14]. The fact that CMC is an anionic polymer is also noted in references [15,16].

In the research [17] it is noted that in order to modify the rheology of the mixture of kaolin, deflocculated with sodium polyacrylate, sodium CMC is frequently added and that this addition increases mixture's viscosity and it becomes more elastic. It is concluded that these rheological changes do not involve the adsorption of the polymer. It is proved by the fact that aggregation of the clay particles occurs in the presence of the sodium CMC. In the research [18] it has been shown that CMC in the bentonite suspension helps to remove the yield stress and to increase mixture's viscosity.

It is indicated, that the amount of CMC added to kaolin clay slurry ranges from 0.01% to 10% [19], the amount of sodium carboxymethylcellulose (Na CMC) is 0.3% [17].

The analysis of above mentioned researches is related to the investigations of the possibility to improve the quality of ceramics and, other investigations of the influence of CMC on the improvement of ceramics quality, showing the existing contradictions on this matter. On one hand, it is stated that in order to improve ceramics quality, clay fluidity must be increased. On the other hand, the positive influence of CMC is explained by its behaviour as an agent increasing viscosity of clay slurry. We suppose that the contradictions could exist due to the fact that no considerations have been made regarding the synergistic effect of CMC. The synergistic effect of CMC could be explained by considering the following assumptions. On one hand, when CMC dissolves in water, it produces organic anions [13,15,16]. Therefore its positive action as a retarder of coagulation of negatively charged clay particles is quite understandable, having in mind the fact that the addition of negative charged inorganic anions [4] as well organic anions [3] increase the fluidity of clay slurry. On the other hand, the CMC water solution is a hydrophilic colloid, in which colloidal particles are charged negatively. Therefore, when CMC colloid is mixed with clay dispersion (clay slurry), where positively charged metal ions (cations) exist, coagulates with the formation of gel and, as a consequence, the viscosity and elasticity of clay slurry is increased.

Water soluble CMC is widely used in ceramics manufacturing processes. This fact confirms the sale of ceramic grade CMC in large quantities.

Our interest is focussed on the estimation of whether it would be possible to modify the clay slurry and improve the quality of ceramics by using other additives with negatively charged particles, instead of those used so far. As a promising positive effect in this matter could be the utilisation of water dispersion of carbon nanotubes (CNTs). The CNTs can be dispersed in water only when their surface is modified via adsorption of surfactants on its surface. In such dispersions the CNTs are being negatively charged [20,21]. In this sense it would be especially interesting to