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THE INFLUENCE OF WATER-REDUCING ADMIXTURE ON RHEOLOGICAL PROPERTIES OF CERAMIC SLIPS

In the article present the studies of water-reducing admixture sodium tripolyphosphate, sodium phosphonate and sodium polyacrylate effects upon rheological properties of the ceramic slip used for fabrication of flooring tiles. Availability use of complex dilutant contains sodium phosphonate and sodium silicates were shown. The optimal ratio of the water-reducing admixture components provided specified rheological properties of the ceramic slip was determined.

Introduction. The dynamics of present-day production of building materials is determined by complex technical and economic working conditions of enterprises. For example, JSC "Keramin" supplies more than 70 percent of production to all regions of the CIS and other countries, and imports most part of raw materials and energy resources from the CIS. The necessity of production growth, market maintenance and extension in the conditions of economic crisis, trends of increase of cost of all kinds of resources (including raw materials, energy, labour forces) require constant searching for new ways of cost reduction.

Ceramic slips that are used in the process of floor tile production are made by means of preparation of concentrated suspensions using separate or mixed wet-raw grinding. In addition, water suspensions should be rather fluent at minimum humidity and stable for definite time, which will allow to increase productivity and to reduce energy consumption while producing slip and moulding powder [1].

For instance, if humidity of slips used in the process of ceramic tiles production reduces by 1%, gas consumption for producing 1 t of moulding powder decreases by 2 m^3. With the annual volume of slip production on JSC "Keramin" (about 240 thousand tons) economic efficiency as a result of reducing of fuel and energy cost will make up near 1 billion 440 million rubles. Since slip production is applied at the majority of ceramic enterprises, researches aimed at reducing the humidity of ceramic suspensions are relevant from a practical point of view. Slip flowability, possibility of transportation on pipelines, their moisture-yielding ability during moulding powder production depends on rheological properties of suspension.

The aim of this work was to study the influence of different viscosity reducers (deflocculants) on the rheological properties of slips used in the manufacture of ceramic floor tiles , as well as decreasing ceramic suspensions humidity while maintaining their mobility.

Main part. A system similar to the ceramic slip, which is used on the JSC "Beryoza-storymaterialy" in the process of ceramic floor tile production, was chosen as a subject of investigation.

To prepare the slip we used refractory clay deposits of Veselovsk and Novoraysk and kaolin of Prosyanovsk and Glukhovetsk, silica sand and feldspar in Homel and Vishnevogorsk. The slip was prepared by wet grinding of all components in the laboratory ball mill "Speedy". Humidity of slip measurement was conducted using electronic humidity analyzer MA-90 according to [2]. Fineness of slip grinding was defined by sieve № 0063 residue value according to the method [3] and made within 1.5–2.0%. Engler slip viscosity (°E) and densification coefficient (K) were estimated by velocity of outflow from Engler viscosimeter orifice after 30 sec and 30 min of hold according to the method [4].

According to the literature data [1], various inorganic and organic compounds, including polymeric ones, as well as mixtures based on them, are used as ceramic slips viscosity reducing agents. In this investigation for slip deflocculation, there were admixed sodium tripolyphosphate (STPP) additives, sodium phosphonate and sodium polyacrylate, since they have a number of advantages over other deflocculants [5, 6].

Sodium tripolyphosphate is the most common class of deflocculant polyphosphates and possesses fluxing capacity. Polyphosphate anions are absorbed by clay particles, significantly increasing their negative charge. As a result, the viscosity of the ceramic slip is reduced. STPP disadvantages are relatively high cost and when hydrolysis at elevated temperature in alkaline medium is carried out, sodium orthophosphate is formed. This leads to the increase in the viscosity of the suspension over time.

We have investigated the use of sodium salts of phosphonic acids as a possible analogue of polyphosphates. Phosphonic acid is a compound of formula $RP(O)(OH)_2$, where R - an organic radical bonded with the atom P by the bond C-P [5]. With bases phosphonic acids form acidic and neutral salts - phosphonates . Organophosphonates interact with multivalent metal cautions forming complexes

that retain stability at elevated temperature aqueous solutions and are adsorbed on the surface of mineral particles, increasing their charge.

Sodium polyacrylates (SPA) along with phosphonates belong to organic deflocculants. Polyacrylic acid is a polymer compound of general formula $[CH_2CR(COOH)–]_n$ [6]. Sodium polyacrylates with polymerization degree from 10 to 200 and molecular mass from 1,000 to 20,000 are good deflocculants: polymer anion is easily absorbed by clay particles, providing exclusive dispersing force and stability for a long time. Polyacrylates deflocculant effect depends on the length and nature of the radical R.

In the first step investigated the rheological properties of the slip of 35% moisture content based on the content of the above additives. Deflocculants injected into the slip in an amount of 0.1-0.8 (0.9)% by weight calculated with the reference to a dried substance.

In Fig. 1 it can be seen that slip viscosity decreases if the quantity of sodium tripolyphosphate additive is increased from 0.1 to 0.7%, sodium phosphonate is increased from 0.1 to 0.6% and sodium polyacrylate from 0.1 to 0.7%.

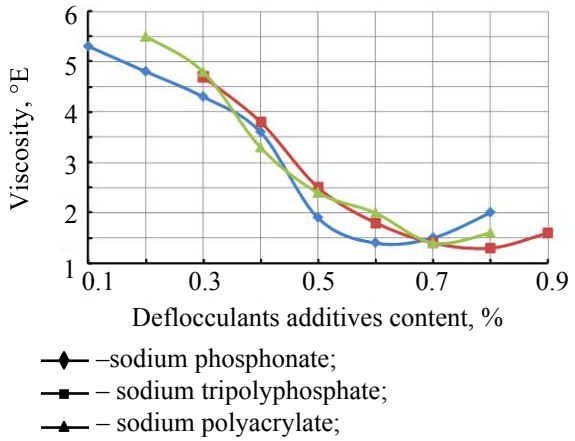

Fig. 1. Relation between viscosity of slip with humidity 35% and kind and quantity of admixed deflocculant

Minimum values of viscosity of the slip 1.4-1.6 ° E in the form of horizontal areas are observed when the content of additives in the range of 0.7-0.9% STPP, 0.6-0.7% sodium phosphonate and 0.7-0. 8% SPA. With further increase in the content of additives the viscosity is increased. Increased efficiency of sodium phosphonate additive in comparison with additives of sodium tripolyphosphate and SPA is explained by the fact that sodium phosphonate along with banding in complexes cations of polyvalent metals provides steric effect due to the adsorption of anion part containing organic radical on the mineral particles of slip[5].

There is a relation between densification coefficient variation and deflocculant additives content in Fig. 2. Fig. 2 shows that by increasing the amount of administered STPP 0.1 to 0.5%, sodium phosphonate from 0.25 to 0.1% SPA and from 0.45 to 0.1% densification coefficient is deacreased.

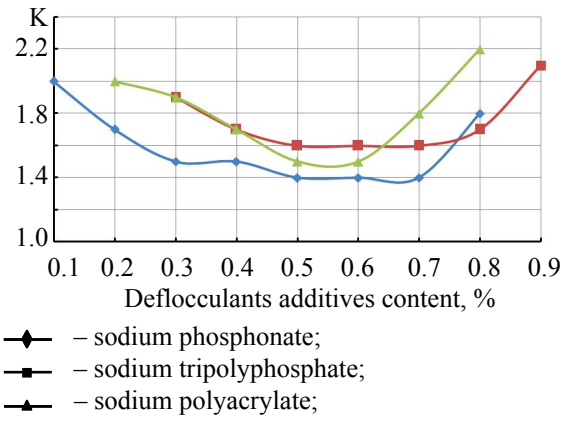

Fig. 2. Relation between densification coefficient (K) of slip with humidity 35% and kind and quantity of admixed deflocculant

Minimum values of slip K that equal to 1.4-1.6 and have a form of horizontal grounds are observed in case when additives content is in the limits of 0.5-0.7% of sodium tripolyphosphate, 0.25-0.75% of sodium phosphonate and 0.45-0.65 % of sodium polyacrylate. When we further increase the content of additives densification coefficient is increased again. It should be noted that sodium phosphonate in this case is the most effective additive, because it reduces K to 1.6 with content of 0.25%, whereas for the SPA and the STPP it is the value of 0.5 and 0.45% respectively. The widest range of additive (0.5%) in which minimum value of K is observed is also characteristic of sodium phosphonate. STPP and SPA for the specified interval (0.25%) is less than 2 times.

Thus, for the tested slip with humidity 35% viscosity values 1.4-1.6 ° E and densification coefficient K 1.4-1.6 were obtained with the content of certain STPP, sodium phosphonate and SPA deflocculants additives. According to the production conditions of JSC “Beryozastroymaterialy”, acceptable viscosity values for floor tile slip make up to 2°E and K up to 1.8.

For the purposes of decreasing the suspension humidity, slip with humidity 33% was made and its rheological properties were studied. The results are shown in Fig. 3 and 4.

By comparison Fig. 1 and 3 it can be noted that rate of curves of viscosity and intervals of deflocculant additives content in which minimal viscosity values in the form of horizontal grounds are observed practically haven’t changed, but the mini-

mum values of the viscosity increased from 1.4-1.6 ° E for slip with humidity 35% ° E to 1.6–1.8°E for slip with humidity 33% ° . In Fig. 4 it can be seen that if admixed sodium tripolyphosphate content is increased from 0.4 to 0.7%, sodium phosphonate from 0.55 to 0.4% and SPA from 0.5 to 0.7% slip densification coefficient decreases. Minimum value K that equals to 1.6 -1.7 and have a form of horizontal grounds are observed in case when additives content is in the limits of 0.7-0.8% of sodium tripolyphosphate. When we increase the content of sodium phosphonate from 0.4 to 0.55% we can observe a reduction in value of K to 1.6. When the content of sodium phosphonate additives is within 0.55-0.75% it is noted a minimum value of K 1.4-1.6 as a horizontal ground. If we increase the amount of sodium polyacrylate from 0.4 to 0.7% the value of K_3 reduces to 1.8. For all further deflocculants increasing in the content leads to an increase in densification coefficient.

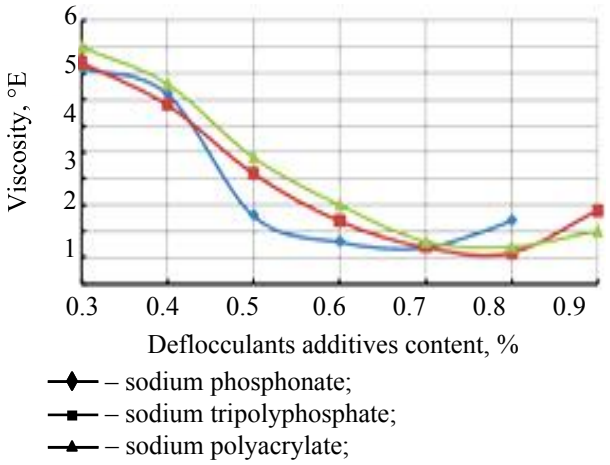

Fig. 3. Relation between viscosity of slip with humidity 33% and kind and quantity of admixed deflocculant

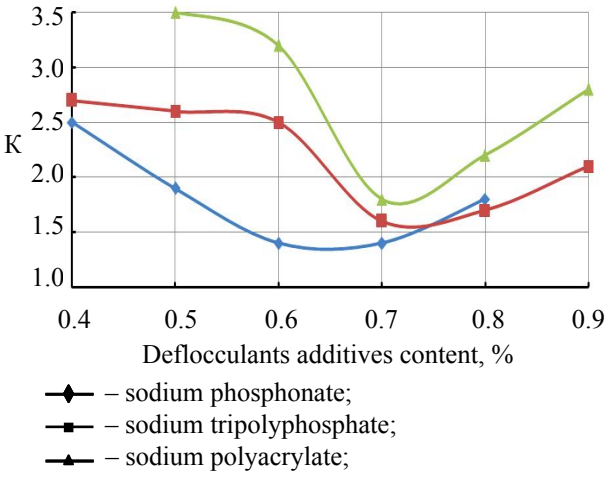

Fig. 4. Relation between densification coefficient (K_3) of slip with humidity 33% and kind and quantity of admixed deflocculant.

By comparison Fig. 2 and 4 it can be noted for slip with humidity 33% intervals of deflocculant additives in which minimal values in the form of horizontal grounds are observed have changed considerably. The minimum value of K for STPP increased from 1.4-1.6 to 1.6-1.7, for phosphonate sodium remained at the same level (1.4-1.6), for SPA minimum horizontal ground value of K is absent.

According to the obtained results, the acceptable viscosity value and K of floor tile slip with humidity 33% are provided by admixing 0.7-0.8% of sodium tripolyphosphate or 0.55-0.75% of sodium phosphonate. Using of SPA can lead to sharp rise of K due to the absence of a horizontal ground of densification coefficient minimum value. However, by forming a slip with a reduced humidity content of 33% by adding of STPP or sodium phosphonateis connected with their higher costs.

In [7, 8] has been shown the effectiveness of the application of thinning ceramic-ray slips of organic deflocculants in combination with conventional inorganic additives: sodium silicate, soda, etc. Along with deflocculating effects, characteristic for definite components, the effect of synergy is observed. [9] Trial experiments showed that by adding of soda in the range from 0.1 to 0.8 % dilution of the slip hardly occurs; and if we add sodium silicate in the same range the slip is diluted, but has a high densification coefficient. When selecting the inorganic component it was taken into account that the sodium silicate forms a homogeneous mixture with sodium phosphonate , which simplifies the preparation time.

Slip values based on deflocculants proportions

Name and value of electrolytes and Additives ratio		Viscosity, °E	densification coefficient K	discharge coefficient of deflocculants
sodium silicate	phosphonate sodium			
7.5	1	5.7	2.2	1
5.75	1	5.5	2.1	
2.5	1	5.1	2.0	
6.6	1	4.5	2.5	1.3
5.0	1	3.6	2.4	
4.5	1	2.2	2.4	
4.0	1	1.8	1.8	
3.5	1	1.8	2.0	
3.0	1	2.1	2.2	

As can be seen from the data shown in the Table , the minimum values of the viscosity and densification coefficient of the slip are obtained by the ratio of sodium silicate and sodium phosphonate 4 : 1. Consequently, by adding a relatively small addition of sodium phosphonate to sodium silicate

allows to get the slip with an acceptable viscosity and K . We can assume that a synergistic effect for the given deflocculants is exposed to the full extent when we add them simultaneously in ratios close to 4 : 1. The specified composition was successfully tested as a viscosity reducing agent for slip floor tiles with humidity33% at the central laboratory of " Beryozastroymaterialy " plant.

Conclusion. Rheological properties of floor tile ceramic slip, using sodium tripolyphosphate, sodium phosphonate and SPA as viscosity reducing agents, were investigated. It was determined that sodium phosphonate is the most effective viscosity reducing agent. Deflocculating effect of complex composition of sodium silicate and sodium phosphonate in the ratio 4 to 1 was defined. The cost of composition containing sodium silicate and sodium phosphonate is lower than that one of sodium phosphonate or sodium polyacrylate, which predetermines economic efficiency of its application in production process.

References

1. Rheology applied to ceramics (theory and practice) / L. Boscardin [et al.]. – Modena, 2006. – 473 p.

2. Дятлова, Е. М. Химическая технология керамики и огнеупоров. Лабораторные работы / Е. М. Дятлова, В. А. Бирюк. – Минск: БГТУ, 2003. – 41 с.

3. Лукин, Е. С. Технический анализ и контроль производства керамики / Е. С. Лукин, Н. Г. Андрианов. – М.: Стройиздат, 1986. – 269 с.

4. Практикум по технологии керамики / под ред. И. Я. Гузмана. – М.: ООО РИФ «Стройматериалы», 2005. – 336 с.

5. Энциклопедия полимеров. В 3 т. Т. 1 / гл. ред. В. А. Каргин. – М.: Советская энциклопедия, 1972. – С. 39.

6. Химическая энциклопедия. В 5 т. Т. 5 / гл. ред. Н. С. Зефиров. – М.: Большая Российская Энциклопедия, 1998. – С. 275.

7. Влияние состава комплексного разжижителя на основе оксиэтилидендифосфоновой кислоты, жидкого стекла и соды на структурно-механические свойства суспензии глины / Г. В. Мозговой [и др.] // Стекло и керамика. – 2011. – № 8. – С. 32–34.

8. Реология глин Троицкого месторождения / Ю. И. Гончаров [и др.] // Стекло и керамика. – 2004. – № 11. – С. 16–22.

9. Pishch, I. V. Flow properties of slip for producing ceramic sanitary ware / I. V. Pishch, Yu. A. Klimosh, E. I. Gapanovich // Glass and Ceramics. – 2006. – Vol. 63, N 7–8. – P. 259–261.

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