Influence Of Plasticizing Additives on The Physical and Mechanical Properties of Gypsum Materials

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Abstract. The article presents the results of studies conducted to study the effect of superplasticizers of the FREM S3 brand based on naphthalene-formaldehyde resin and the SZhZ-3 brand based on polycarboxylate ether on water demand, setting kinetics and strength of gypsum materials used in ceramic industry enterprises producing porcelain and earthenware and sanitary ware. It is noted that the positive effect of the SDZ-3 additive on the formation of the optimal structure and strength of the gypsum material is significantly higher than that of the FREM S3 additive.

Keywords: gypsum material, water demand, setting kinetics, strength, naphthalene-formaldehyde resin, superplasticizer, polycarboxylate.

1 Introduction

In the ceramic industry, porous molds made of gypsum are used to form objects. The advantage of these molds, for example, is their low cost of production and ease of use compared to polymer molds [1-4].

The traditional material used for the production of porous molds is a gypsum binder based on α- or β-hemihydrates of calcium sulfate.

A positive factor in using this material is that the properties of gypsum molds and their pore structure parameters can be varied within wide limits by changing the water-gypsum ratio [5,6].

However, it also has a number of disadvantages, the main of which is the rapid deterioration of the active surface and the short service life of the molds due to the decrease in filtration capacity during operation, which leads to a gradual decrease in the quality of the resulting ceramic blanks [1].

Therefore, after 0-50 uses, they emerge as unusable and are thrown away as waste. For example, in a single LLC "EKOKERAMA" (Fergana city), as much as 5-6 lots of gypsum mildew waste are generated according to day. A lot of cash is spent on their series and transportation to landfills. However, in phrases of section and chemical composition, in contrast to maximum gypsum waste, they correspond to exceptional herbal gypsum stone.

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However, till now, this secondary product has now no longer been used withinside the manufacturing of constructing materials.
By increasing the lifespan of gypsum binders and molds made from these wastes, which are necessary for the ceramic industry, the ceramic industry will be able to generate additional income and prevent environmental pollution by reducing its need for gypsum purchased from outside for mold making and the costs of waste collection and transportation to landfills.
However, although our Republic has sufficient opportunities to process waste molds from ceramic industry enterprises, obtain gypsum binders from them, and increase the service life of molds made on their basis, research has not been conducted consistently, which makes it urgent to solve the problem of increasing the service life of gypsum binders and molds made on their basis from waste containing gypsum compounds.
The Department of "Building Materials and Products" of Fergana State Technical University is conducting extensive research on increasing the service life of gypsum binders and molds made on their basis, which are necessary for the ceramic industry. This article presents the results of a study conducted to study the effect of multifunctional plasticizers on the physical and mechanical properties of gypsum materials.

2 Research methods and materials

The studies investigated the effect of superplasticizer additives based on melamine formaldehyde FREMS3 and polycarboxylate ether SDJ-3 [7] on the properties of G-7 β-GRP and G-12 α-GRP obtained from waste molds by the “thermo-shock” method at 180-2400C [8,9].
The water requirement of gypsum paste was determined using a Suttard viscometer, the thickening kinetics using a Vika apparatus, and the strength of hardened gypsum was determined using samples measuring 4 × 4 × 16 cm according to GOST 23789–79 [10-13].
To comprehensively assess the effect of selected plasticizer additives on the properties of gypsum binders, the following indicators were determined: normal fluidity, set duration, flexural and compressive strength, porosity, and water absorption.
The effect of complex chemical additives on the reduction of water demand (St) of gypsum paste was calculated using the following formula:

$$S_t=[(Nq–Nq_g)/Nq]\cdot 100\%$$

Here, Nq and Nq_g are the normal density of gypsum paste without additives and with the addition of a plasticizer.

3 Results and discussion

The effect of complex chemical additives on reducing the water demand of gypsum paste is illustrated in Figure 1.
For both the gypsum paste made from α-YaG and the paste made from a mixture of 60% α-YaG and 40% β-YaG, the addition of the SDJ-3 polycarboxylate plasticizer showed the greatest reduction in water demand (Figure 1). When using this supersuperplasticizer at a concentration of 0.4%, the normal viscosity of the gypsum paste based on α-YaG decreased by 44%, and for the mixture of 60% α-YaG and 40% β-YaG by 39%, and with a further increase in concentration, the normal viscosity value remained unchanged.

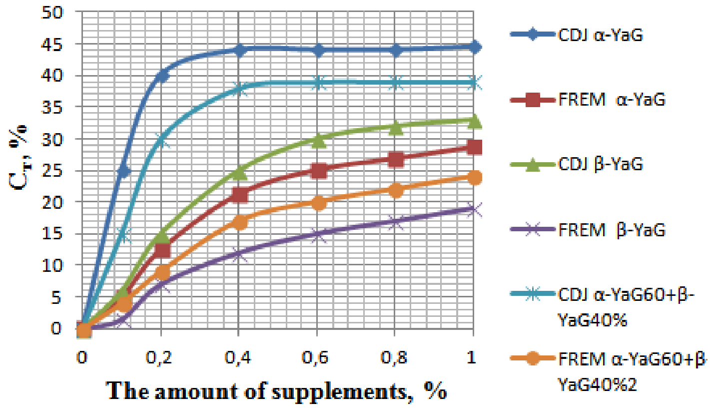


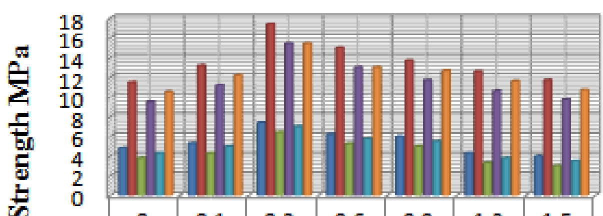
Fig. 1. The effect of complex chemical additives on the water demand of gypsum paste.

The melamine-formaldehyde based FREMS3 additive showed a lower water-reducing ability (23-27%) compared to the SDJ-3 plasticizer for gypsum compositions of all compositions. In this case, a higher concentration of FREMS3 additive is required to reduce water requirements.

Thus, the polycarboxylate ether-based SDJ-3 additive is effective in reducing water requirements during the preparation of gypsum paste.

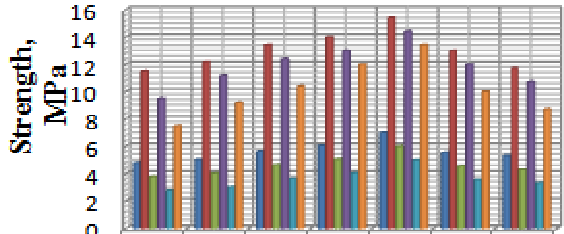
In order to evaluate the effectiveness of additives on strength, studies were conducted to determine the strength of gypsum stone of various compositions depending on the type and concentration of modifying additives. The tests were carried out on gypsum samples that had hardened for 2 hours. The test results are shown in Figures 2 and 3.

According to the obtained data, the use of the melamine-formaldehyde-based FREM 3S plasticizer additive at a concentration of 0.9% increased the flexural strength of the gypsum material obtained from α-YaG by 7 MPa and the compressive strength by 15.42 MPa. In the case of 60% α-YaG + 40% β-YaG, this value was 13.42. The maximum increase in the flexural and compressive strength of the applied gypsum binder compositions was observed when the polycarboxylate-based SDJ-3 additive was used in an amount of 0.30%.



	0	0,1	0,3	0,6	0,9	1,2	1,5
CDJ eg y.α-YaG.	4,8	5,28	7,42	6,25	6	4,3	4
CDJ сиқ.α-YaG	11,5	13,2	17,42	15	13,7	12,6	11,72
CDJ eg.β-YaG.	3,8	4,28	6,42	5,25	5	3,3	3
CDJ Tight.β-TaG	9,5	11,2	15,42	13	11,7	10,6	9,72
CDJ eg.α-YaG60+β-YaG40.	4,3	4,98	6,98	5,75	5,5	3,8	3,5
CDJ Tight.α-YaG60+β-YaG40	10,5	12,2	15,42	13	12,7	11,6	10,72

Fig. 2. Effect of the amount of SDJ-3 plasticizer additive on the strength of gypsum stone obtained from gypsum and mixed binder.

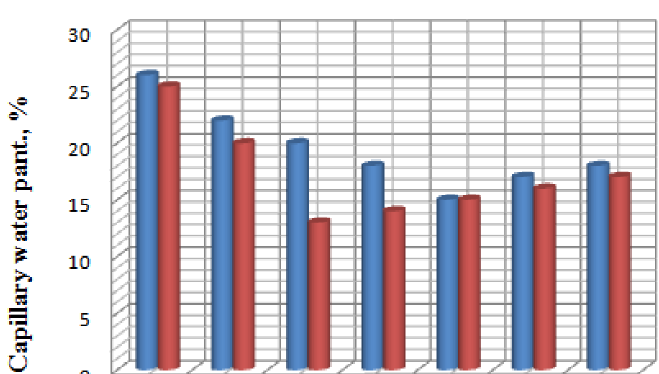


	0	0,1	0,3	0,6	0,9	1,2	1,5
FREM eg.α-YaG.	4,8	5,04	5,65	6,06	7	5,55	5,3
FREM Tight.α-YaG	11,5	12,2	13,42	14	15,42	13	11,72
FREM eg.β-YaG.	3,8	4,04	4,65	5,06	6	4,55	4,3
FREM Tight.β-YaG	9,5	11,2	12,42	13	14,42	12	10,72
FREM eg.α-YaG60+β-YaG40.	2,8	3,04	3,65	4,06	5	3,55	3,3
FREM Tight.α-YaG60+β-YaG40	7,5	9,2	10,42	12	13,42	10	8,72

Fig. 3. Effect of the amount of FREM 3S plasticizer additive on the strength of gypsum stone obtained from gypsum and mixed binder.

The increase in the strength of gypsum samples leads to a change in porosity and water absorption, which is directly related to the setting time of the ceramic mold. Therefore, the effect of the above plasticizers on the porosity and water absorption of gypsum samples was studied. Figure 4 shows the water absorption data of samples with the addition of SDJ-3 and FREM 3S additives. It can be seen that the plasticizer additives affected the water absorption indicators of gypsum samples with different amounts, consistent with the results of the study on the strength properties above.

α-YaG



	0	0,1	0,3	0,6	0,9	1,2	1,5
FREM.α-YaG.	26	22	20	18	15	17	18
CDJ .α-YaG	25	20	13	14	15	16	17

Fig. 4. 60 % α-YaG + 40 % β-YaG

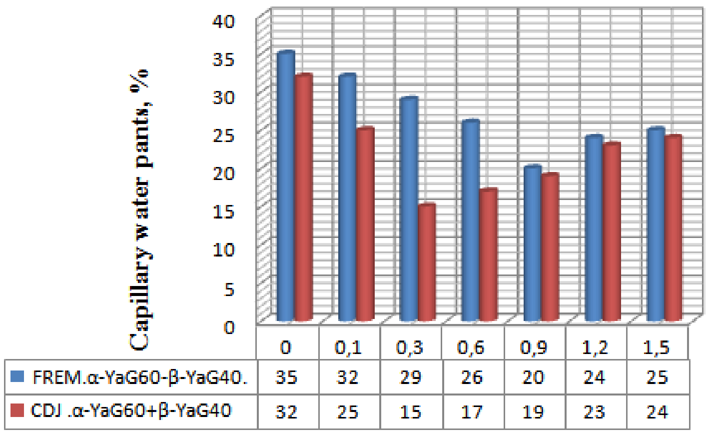


Fig. 5. Effect of type and amount of plasticizer additives on water absorption of samples made from binders of different compositions.

These data indicate that the SDJ-3 complex additive, obtained from local raw materials, has a slightly higher performance than the FREM 3S additive. However, the high cost of FREM 3S (190,000 soums/kg) and its use in a high concentration (0.9%) are considered economically inefficient and may lead to an increase in the cost of the structure.

It should also be noted that one of the important indicators in the production of large-sized porous molds is the setting speed of the gypsum paste. If the gypsum paste starts to set too quickly, it becomes difficult to pour it onto the metal base of the mold, which leads to the appearance of defects on the surface of the mold. Therefore, in the next stage of our work, the effect of plasticizer additives on the setting time of gypsum binders was studied.

Figure 5 shows the effect of plasticizers on the setting time of gypsum paste.

The introduction of the sulfat melamine formaldehyde-based FREM 3S additive in an amount of 0.1% to 0.5% practically did not change the setting time of the binders, and the polycarboxylate-based SDJ-3 plasticizer significantly slowed down the setting time, which was confirmed by previous studies of the strength properties of the material and literature data on the properties of this type of additives.

The differences in the bite duration of the studied additives are explained by differences in the mechanisms of their influence on gypsum systems.

When water interacts with the binder, the binder particles partially stick together, forming flocs, and do not have time to react with water. Floccules of binder particles accelerate sedimentation, that is, the dispersed system becomes ageratively and sedimentationally unstable. Plasticizing additives are deflocculants of the binder, that is, they break up the aggregated binder particles into much smaller components, thereby increasing the efficiency of its use and the stability of the dispersed system.

The mechanism of action of superplasticizers is based on the combined manifestation of electrostatic and steric effects, as illustrated in Figure 6. This steric effect is caused by the hydrophobic polyether chains on the side of the polycarboxylate ether molecules.

α-YaG

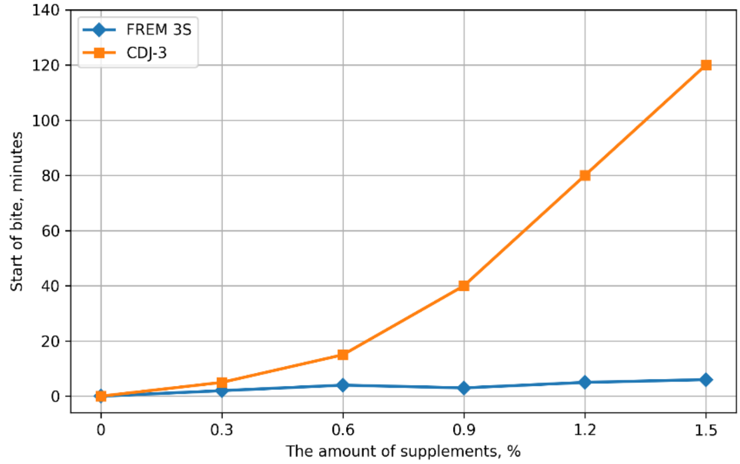


Fig. 6. 60 % α-YaG + 40 % β-YaG

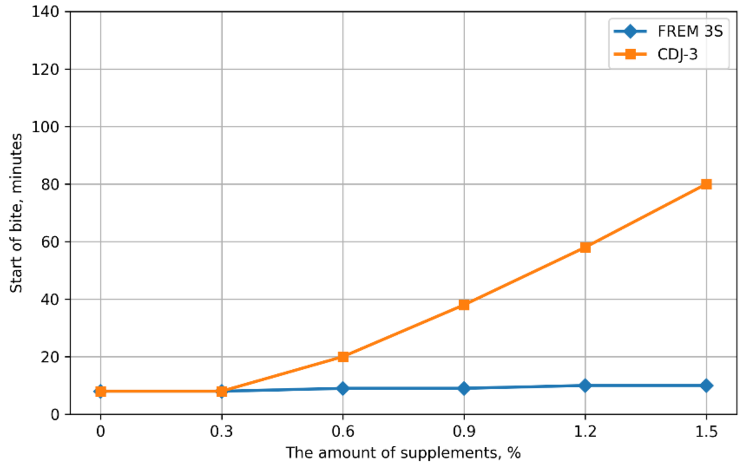


Fig. 7. Effect of plasticizers on setting time of gypsum paste.

As a result, their water-saving effect reaches more than 50%. The mechanism of action of superplasticizers on gypsum systems is provided by the peculiarity of the dominance of steric effect on them.

The mechanism of action of the polycarboxylate-type superplasticizer SDJ-3 during the modification of gypsum particles is based on the simultaneous manifestation of 2 factors: the first is electrostatic repulsion of gypsum particles, and the second is steric repulsion, which is achieved by the hydrophobic polyether chains on the side of the polycarboxylate ester molecule (Figure 7).

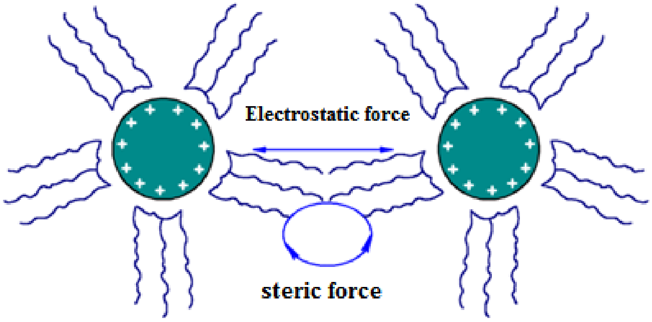


Fig. 8. Mechanism of action of hyper plasticizers on gypsum systems

The steric component of the mechanism of action of the polycarboxylate additive depends on the length of its side chains. The longer the side chains of the plasticizer, the more pronounced the effect of steric repulsion of gypsum particles [10,14-15].

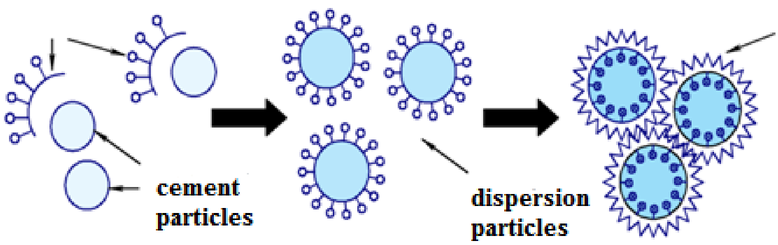


Fig. 9. Mechanism of influence of SDJ-3 complex polymer-mineral additive on the binder hardening process.

Unlike the polycarboxylate additive, the melamine formaldehyde-based superplasticizer FREM 3S works solely due to electrostatic repulsion forces. The weak retarding ability of FREM 3S is explained by the arrangement of macromolecules in the adsorption layer. The spatial-network structure of FREM 3S molecules has a less pronounced effect on the hardening process of the binder than the linear structure characteristic of polycarboxylate additives.

The obtained data suggest that the use of polycarboxylate-based plasticizers in an amount of more than 0.3% significantly slows down the setting period of the gypsum material, so it is not possible to use them in larger quantities. In addition, a higher concentration of the additive leads to an increase in the water-gypsum ratio and a decrease in the productivity of the process of manufacturing large-sized porous molds.

4 Conclusion

Gypsum mixtures based on α- and β-calcium sulfate hemihydrates were obtained and their technical properties were determined.

With an increase in the proportion of α-modification of calcium sulfate hemihydrate in the mixture, the normal viscosity of the gypsum paste decreases and the setting time increases.

Compressive strength changes in proportion to the increase in the proportion of α-YaG in the gypsum mixture. With an increase in the content of α-YaG, the strength of gypsum stone dried to constant weight increases from 10.1 to 21.3 MPa.

The introduction of plasticizer additives reduces the water requirement of gypsum mixtures, which leads to a decrease in porosity and water absorption, and increases their strength. For the composition of 60% α-YaG + 40% β-YaG, the porosity of gypsum stone decreased from 35.7% to 22.1 and 18.4% with the addition of 0.5% of SDJ-3 and FREM 3S plasticizers, respectively.

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