A New Plasticizer Of Comprehensive Action On The Basis Of Sugar Industry Waste

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Abstract. The effect of a new plasticizing additive to construction cement concrete is studied. Its main component is molasses, which is a waste of beet sugar production. To regulate the mobility and strength of the concrete mixture, the rate of its setting and hardening, surfactants and compounds of alkali and transition metals were additionally introduced into the molasses. It is shown that the optimal variant of the additive in terms of mobility and strength of the concrete mixture exceeds the known commercial plasticizer PFM-NLK. The new additive, unlike PFM-NLK, allows to use sand of various fractional and mineralogical composition in the production of concrete. The possible influence of physical and chemical parameters and chemical composition of molasses on the characteristics of cement concrete is discussed.

1. Introduction

The use of additives of various types in the production of concrete mixtures and products is one of the most progressive directions in the field of construction materials technologies [1-4]. In recent years, hyper- and superplasticizers occupy a special place in their number [2, 5, 6]. Their basis, as a rule, are products of fine organic synthesis, having a sufficiently high cost, which inhibits their widespread use. In this regard, it is important to search for promising plasticizing additives to concrete mixtures in a number of different industrial waste. Of obvious interest in this regard are large-scale waste from sugar production with the prospect of their use both in natural and in modified form.

The main waste of sucrose production is molasses, which is a syrupy liquid of dark brown color with a specific smell of caramel and volatile amines formed during the decay of betaine [7].

It is reported about the use of molasses as a moderator of the processes of setting and hardening of concrete [8]. It is also known about its plasticizing effect on the concrete mixture. Thus, the introduction of molasses in an amount of 0.05-3% of the volume of concrete solution leads to a slow set of its strength at the age of 7 days [1]. The results of the molasses test allow us to refer it to the IV group of weakly plasticizing additives that increase the mobility of the concrete mixture from P1 to P2 (from 2-4 to 5-9 cm) without reducing its strength.

More pronounced plasticizing effect has molasses evaporated post-yeast bard, which is obtained by processing molasses. It belongs to the III group of medium plasticizing additives that increase the mobility of the concrete mixture from P1 to P3 (from 2-4 to 10-15 cm).
Molasses and products of its processing as plasticizers of concrete have a number of disadvantages, among which it is necessary to highlight their excessive slowing down effect and the volatility of the chemical composition.

In order to eliminate these shortcomings, we have conducted a study of new promising plasticizers containing molasses as the main component. The concrete mixture was obtained by mixing 3.5 kg of cement PC-500 D0, 11 kg of crushed stone, 6.5 kg of sand with the module of the size MK=1.1 and 2.2 kg of water. To regulate the mobility and strength of the concrete mixture, the rate of its setting and hardening, alkali and transition metal compounds, as well as additional surfactants were introduced into it. As the latter, alkylbenzenesulfonic acid, sodium lauryl sulfate, citric acid and salts of organic or inorganic acids were used. These components were used in dosages, which reduced the slowing effect of molasses, but did not lead to a noticeable decrease in the strength of concrete. Tests were carried out in comparison with the known commercial additive PFM-NLK. PFM-NLK and molasses-based additives were introduced into the concrete mixture in an amount of 1-2 % by weight of cement.

PFM-NLC is obtained by multistage organic synthesis. He is a copolymer based on polyethylenepolyamines sodium with the addition of air-entraining and waterproofing components [9]. PFM-NLK is an improved analogue of the well-known industrial plasticizer S-3. According to the manufacturer, it is able to increase the mobility of the concrete mixture from P1 to P5 (from 2-4 to 21-25 cm) without loss of strength at the age of three days [10].

However, these indicators PFM-NLK are achievable using only certain types of sand. So, in the South of Russia the most common type of construction sand is fine river sand with the module of size MK=1,1-1,3 and the content of quartz grains is about 70 %. As it turned out, in concrete mixtures using such sand, many well-known plasticizers, including PFM-NLK, significantly worsen their performance [11, 12]. For this reason, in our studies, PFM-NLK has proved to be only an average plasticizing additive (Fig. 1 and 2).

![Figure 1](image1.png)

CD – cone draft; 1 – without additives; 2 – with PFM-NLK; 3 – with additive No 1; 4 – with additive No 2.

At the same time, we have created variants of additives based on molasses (additives No 1 and No 2) provide better mobility of the concrete mixture compared to PFM-NLK (Fig. 1). Additive No 2 is significantly higher than PFM-NLC in this indicator during the entire test period. Additive No 1 retains the mobility of the mixture at the level of PFM-NLK. Obviously, the main contribution to the result is made by sugars, which are the main components of molasses [13, 14].
In addition, the additive No 2 provides a greater set of concrete strength at different stages of its hardening in comparison with PFM-NLK (Fig. 2).

Additive No 2 provides an increase in the strength of concrete at three-day age, it is 19.6 % compared to concrete without additives and 13.0% compared to PFM-NLK. At the age of 7 days, these figures are 13.9 and 3.0 %, respectively, and at the age of 28 days – 12.3 and 8.3 %. Additive No 1 in the initial stages of hardening is inferior to PFM-NLC, but at the age of 28 days provides almost the same increase in the strength of concrete.

We have analyzed the effectiveness of additives based on molasses depending on its physical and chemical parameters and chemical composition [15, 16]. Five molasses samples obtained from different beet sugar producers were studied (Table 1).

The results of tests of molasses samples showed that their plasticizing properties and strength properties of concrete vary within a wide range. From Table 1 it can be seen that the content of individual components of molasses is also different depending on the manufacturer. First of all, it is the content of fermented sugars, reducing substances and calcium salts.

The content of calcium salts in the molasses can not be a significant factor, because they are one of the main components of cement. In addition, molasses samples have different pH values. However, this difference is leveled by a highly alkaline reaction of the concrete solution.

The test results showed no clear dependence of the concrete strength on the sugar content. This suggests an additional impact on the characteristics of concrete such components of molasses as reducing agents and betaine.

**Table 1.** Physico-chemical parameters and chemical composition of molasses.

| Samples of molasses | No 1  | No 2  | No 3  | No 4  | No 5  |
|---------------------|------|------|------|------|------|
| Density, g/l        | 1180 | 1258 | 1260 | 1355 | 1200 |
| pH                  | 7.8  | 7.7  | 7.6  | 7.2  | 7.2  |
| Dry substances, %   | 74.2 | 73.1 | 74.0 | 82.0 | 78.6 |
| Sugar, %            | 46.4 | 46.5 | 46.5 | 46.0 | 45.0 |
| Amount of fermentable sugars, % | 46.6 | 45.8 | 46.4 | 46.4 | 45.7 |
| Reducing substances, % | 0.83 | 0.78 | 0.81 | 0.80 | 0.72 |
| Ca-salts, %         | 1.20 | 1.22 | 1.23 | 1.56 | 1.10 |

**Figure 2.** The rate of strength development of concrete with different additives.
The reducing substance is a sugar, reducing alkaline solutions of copper and other polyvalent metals. As part of molasses these include glucose, fructose, maltose and lactose. Their open forms contain an aldehyde or ketone group, which in the presence of transition metal cations are oxidized to the corresponding carboxylic acids. Such reactions can take place between iron (III) cations contained in the alkaline concrete mixture and reducing molasses sugars. The resulting salts of carboxylic acids, based on their intended structure, may show a certain surface activity. This can affect the mobility and strength of the concrete mixture.

It is also necessary to take into account the possible effect of betaine contained in the molasses on the test results of the considered plasticizing additives. As it is known, betaines are amphoteric surfactants used as emulsifiers, dispersants, antistatic agents and wetting agents [17]. Betaine molecules are bipolar ions of the following structure:

$$\text{R}(\text{H}_3\text{C})_3\text{N}^-\text{CH}^-\text{COO}^-$$

It is known that cement particles in the process of hydration acquire a positive charge, which contributes to their interaction with dipolar betaine molecules. The resulting complexes are able to exhibit surface-active properties, depending on their concentration, pH of the medium and the sequence of the concrete mixture components introduction.

The studied additives on the basis of molasses not only provide the necessary dynamics of mobility and strength of the concrete mixture. They allow to use sand of different fractional and mineralogical composition in the production of concrete. Therefore, these additives can be considered as new high-performance plasticizers of complex action.

2. References

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