1. Introduction

Production of dry construction mixes increases with each passing year [1, 2]. The growing popularity of these materials is explained by the series of advantages for construction operations: increased productivity, reduced number of operations to prepare the mixes to use, improved quality of work, and others. The dry construction mixes include multicomponent mixtures, which necessarily contain in their composition a binder, a filler, and the modifying additives [3]. Each of these materials has its function. A binding component enables the strength of the hardened solution, its integrity, as well as the adhesion to a work surface. Fillers make it possible to lower the content of a binder, which reduces the amount of water and leads to obtaining a denser material. Modifying supplements provide a solution with the required properties. Dry construction mixes are the multicomponent materials and include both inorganic and organic materials. Given the ambiguous effect of organic additives on the strength characteristics of a cement matrix and its resistance against various types of aggression, it is a relevant task to study the effects of cellulose esters on the properties of cement.

2. Literature review and problem statement

It is known [4] that the additives that retain water in mixtures are water-soluble cellulose esters. These are the cellulose derivatives whose general formula is \([C_6H_{11}O_2(OH)x]_n(OR)_y\), where \(n\) is the degree of polymerization; \(x\) is the number of OH groups, which are substituted in a single chain of a cellulose macromolecule (degree of substitution, DS); \(R\) is methyl, ethyl, propyl, and other radicals. Each link of a cellulose macromolecule includes in its structure three groups of \(\text{OH}\) (OR), which are capable of substitution and, consequently, the formation of the corresponding cellulose esters. The structural formula of methyl hydroxyethyl cellulose is shown in Fig. 1.
Paper [5] reports the results that suggest that cellulose esters slow down the hydration processes and do not allow water in the solution to be absorbed into the porous surface of the base and prevent evaporation. This leads to an increase in the time over which a solution retains its plasticity and the ability to form an adhesion contact. However, there were unresolved issues on the effect of viscosity and the concentration of additives on the strength parameters of the resulting material. After all, the parameter that determines the dosage of an additive (0.1–0.5 % by weight) is viscosity, which is defined in the solution with a concentration of 2.0 % by weight at 20 °C. The higher the viscosity of cellulose ester, the less its quantity that must be added to the dry mixture; however, but there is an issue related to that the large values of viscosity significantly increase the density of solutions, both based on cement and other binders [6].

The introduction of such additives is explained by the need to provide the resulting product with the required properties. However, it is known that organic additives can both improve the strength of products, mainly due to the plasticizing effect [7], and degrade it due to the hydrophobic action [8].

Researchers found that cellulose esters exert a very significant effect on the properties of solutions. They significantly slow down the processes of hydration in the early periods of hardening due to a significant reduction in physical water involved in the hydrolysis and hydration of clinker minerals [9]. The result is the formation of a mixture of large hydrocolloid particles, which also changes the character of the hardening progress [10].

This is confirmed by the results from studying the processes of hydration of such systems by calorimetry [11]. There is a decrease in the amount of hydration heat in the first 36 hours of hardening.

Such influence of cellulose esters on the hydration process of the cement matrix leads to a change in the sequence of processes that are characteristic of the cement matrix. There occurs the inhibition of the gel of ettringites, portlandite, and calcium hydro silicate [12].

The hydration processes are also affected by a molecular mass of cellulose esters. It was established in [13] that the effect of the impact is different. The higher the molecular mass of a cellulose ester, the greater the ability to slow the process.

Paper [14] noted the effects of cellulose esters not only on the ability to retain water but also on the rheological properties of the solution. The introduction of cellulose ester additives in the cement matrix leads to an increase in the viscosity of a porous solution and reduces the migration rate of the porous solution ions. This lowers the degree of cement hydration and inhibits the formation of a CSH gel.

The hydration processes inhibition when introducing cellulose esters is noted when using other types of cement as matrices in dry construction mixes. The data from [15] indicate the slowing down of the hydration process of aluminated cement while the duration of setting increases with an increasing concentration of the ester.

The above data indicate that the processes of hydration have been studied in detail while the issues of the influence of cellulose ether viscosity on the physical and mechanical characteristics of the cement matrix have not been considered. This is especially relevant because the production of dry construction mixes involves the cellulose esters of different grades, which have a wide range of viscosity indices.

In addition, there is an unresolved issue about the impact of cellulose ester additives on the stability of the cement matrix under conditions of various aggressive environments. It is known that the cement stone collapses with time, especially under conditions of sulfate aggression [16, 17]. Given the influence of cellulose esters on the nature of the progress of processes of hardening the cement matrix, one can conclude that the additives would affect the corrosion resistance of materials. The effect of sulfate ions on cement resistance is considered in [18]; the mechanisms of sulfate aggression are given. It was established in [19] that a change in the component composition of the latter leads to a change in the destruction mechanisms of the cement matrix. This process is influenced by the concentration of the corrosive environment [20].

It is also necessary to consider the data from [21] on that the introduction of cellulose esters leads to an increase in the porosity of the resulting product. This effect can increase the risk of corrosion of the material.

Based on the above, it can be concluded that the use of cellulose ester additives as admixtures that retain water will necessarily lead to changes in the processes of the hardening of dry mixtures based on cement. However, the question remains of how the viscosity of cellulose esters affects the processes of cement matrix formation in dry construction mixes and the corrosion resistance of resulting products.

All this allows us to assert that it is expedient to study the effect of cellulose ester density on the strength and corrosion resistance of the cement matrix.
3. The aim and objectives of the study

The aim of this study is to establish the influence of methyl hydroxyethyl cellulose characteristics on the properties of the cement matrix, which is included in the composition of dry construction mixes. This would make it possible to obtain articles with better indicators of strength and to extend the term of their operation.

To accomplish the aim, the following tasks have been set:
- to examine the nature of the influence of the viscosity of cellulose ester additives on the normal density and setting duration of the cement matrix;
- to investigate the influence of the additives’ viscosity on the cement matrix strength;
- to determine the corrosion resistance of types of cement with the cellulose ester additives.

4. Materials and methods to study the properties of cement with the additives of methyl hydroxyethyl cellulose of different viscosity

In our study, we determined the following indicators of the cement with additives: normal density, setting duration, strength at the age of 2, 7, and 28 days.

The normal density and setting duration were determined in line with a standard procedure at Vic’s device in a slurry of normal consistency.

Determining the compressive strength employed a procedure given in DSTU EN 196-1:2007 (EN 196-1:2005, IDT). Methods of cement testing. Part 1. Determination of strength. Given that the values initially grow rapidly, and then gradually slow down, the test results were processed by a logarithmic approximation method.

Our study involved the Portland cement PC 400P–N. The chosen additives were methyl hydroxyethyl cellulose of varying viscosity: low (11,000–16,000 mPa·s), medium (17,000–23,000 mPa·s), and high (20,000–30,000 mPa·s). These components were introduced to dry construction mixes in the amount of 0.25–0.75 % by weight. The corrosion resistance was studied in aggressive solutions of sodium sulfate (3.0 % by weight), magnesium (0.3 % by weight), and calcium (0.2 % by weight). The values of the corrosion resistance coefficients of the samples were calculated as the ratio of the strength of the samples made from the slurry of normal consistency the size of 20×20×20 mm, which were exposed to aggressive solutions, to the strength of the samples that were exposed to tap water. The stability coefficient was determined at the age of 6 months [22]. Cement is considered corrosion-resistant if the coefficient of corrosion resistance at the age of 6 months is higher than 0.80.

5. The results of studying the effect of methyl hydroxyethyl cellulose of varying viscosity on the properties and corrosion resistance of cement

5.1. The effect of viscosity of methyl hydroxyethyl cellulose on the normal density and setting duration of the cement matrix

It was established that the selected methyl hydroxyethyl cellulose additives exerted different influences on the normal density and the setting duration of cement. The obtained results are given in Table 1 and unequivocally testify that increasing the content of each type of additive increases normal density.

| Mixture | Additive content, % by weight | Normal density, % | Setting duration, g-min |
|---------|------------------------------|-------------------|-----------------------|
| Portland cement | 0.00 | 33.3 | 0–54 | 1–30 |
| Cellulose ester of low viscosity | | | |
| LV I | 0.25 | 35.1 | 1–59 | 3–09 |
| LV II | 0.50 | 37.2 | 2–20 | 3–25 |
| LV III | 0.75 | 38.9 | 2–40 | 4–50 |
| Cellulose ester of medium viscosity | | | |
| MV I | 0.25 | 35.1 | 1–57 | 3–14 |
| MV II | 0.50 | 37.2 | 2–18 | 3–48 |
| MV III | 0.75 | 38.9 | 2–35 | 4–58 |
| Cellulose ester of high viscosity | | | |
| HV I | 0.25 | 40.4 | 1–52 | 3–12 |
| HV II | 0.50 | 42.8 | 2–35 | 4–20 |
| HV III | 0.75 | 47.1 | 3–05 | 5–30 |

There is a monotonous increase in the setting duration, both the beginning and end of this process. It should be noted that a significant increase in this indicator by 2–4 times occurs even at the minor concentrations of cellulose esters (Table 1).

The increase in the normal density and the setting duration of the cement slurry indicates a significant capability of methyl hydroxyethyl cellulose to retain water in solutions. There is a dependence between the viscosity of the additives and the increase in these indicators: the higher the viscosity, the greater the normal density and the longer the setting duration of cement mortars.

5.2. Effect of the viscosity of methyl hydroxyethyl cellulose on the strength of the cement matrix

The introduction of cellulose ester additives of varying viscosity leads to a significant reduction in the strength of cement.

Introducing the additives of cellulose ester of low viscosity leads to a significant drop in the strength of the cement matrix compared with the starting cement in the early period of hardening (Fig. 2). The magnitudes of approximation \( R^2 \) credibility indicate a sufficiently high degree of conformity of the trend model with the source data on the additive-free cement and at the introduction of 0.25 and 0.50 % by weight of cellulose esters of low viscosity. The conformity is slightly less at the concentration of an additive of 0.75 % by weight.

Similar results were obtained when introducing to cement an additive of cellulose ester of medium viscosity. There is a decrease in the strength of cement stone over the entire range of concentrations; however, not as significant as in the previous case (Fig. 3).

The impact of the cellulose ester of high viscosity on cement strength is slightly different in character (Fig. 4).

Increasing the concentration of an additive is accompanied by its significant reduction. Under the general trend of a slow gain in strength in the early period of hardening, a low level at the age of 28 days is observed. Accordingly, increasing the concentration results in this indicator reaching 29.1, 24.9, and 16.3 MPa.
Technology organic and inorganic substances

Calcium sulfate

The high capacity of methyl hydroxyethyl cellulose to retain water is confirmed by a significant increase in the normal density of the cement slurry. It should be noted that the cellulose ester of high viscosity retains much more water than those of low and medium viscosity. Thus, the introduction of low and medium viscosity additives increases the normal density at, respectively, 0.25 % by weight and 0.75 % by weight, by 5.4–16.8 %, and for the ester of high viscosity – by, respectively, 21.3–41.4 % (Table 1). This explains a significant increase in the setting duration. Part of the water does not react with the clinker minerals, which slows down the progress of this process.

Such changes in the process of hydration processes cannot but affect the characteristics of strength.

As regards the influence of the concentration of a cellulose ester additive on the strength of the cement matrix, it should be noted that the strength of the starting cement is higher than its strength with the additives irrespective of the concentration of the latter. In addition to that the greatest decrease in a strength indicator occurs in the early periods of hardening (1–7 days) and is, depending on the concentration of an additive, 2.2–4.2 times, respectively. At further hardening, the difference in strength is less significant and, when reaching 28 days of hardening, they gradually become closer (Fig. 2–4).

Comparing the strength of cement with the same content of additives, it can be concluded that a higher grade of strength is demonstrated by cement with an additive of the ester of low viscosity. For example, at concentrations 0.25 % by weight, at the age of 28 days, it is 38.0, 32.0, and 29.5 MPa, respectively. The cement with a cellulose ether of medium viscosity has the strength parameters that are close to the previous ones, and the introduction of a high-viscosity additive reduces this indicator more significantly (Fig. 2–4).

The introduction of methyl hydroxyethyl cellulose to cement also influences the corrosion resistance of types of cement (Fig. 5).

The selected aggressive mortars contain sulfate-anions but, depending on the available cations, the destruction of the samples is likely to follow different mechanisms.

Given the presence of active ions in mortars, it is likely that the destruction in the systems sodium sulfate-cement and calcium sulfate-cement occurs due to the formation of calcium hydrosulfoaluminate, followed by the occurrence of mechanical stresses in the stone and, consequently, its gradual destruction.

5.3. The corrosion resistance of cement with the additives of methyl hydroxyethyl cellulose

Dry construction mixes are used under different conditions, including the conditions of aggressive environments. Therefore, indexes of corrosion resistance of the cement matrix are of importance.

Our results indicate, on the example of the methyl hydroxyethyl cellulose additive of low viscosity (Fig. 5), that the increase in the content of the additive in the cement leads to that the corrosion resistance monotonously reduces. The exception is a mixture with the additive in the amount of 0.25 % by weight; in this case, the resistance of the samples even slightly increases.

One should note a sharp drop in the corrosion resistance of the samples at the content of an additive of 0.75 % by weight. This mostly happens under conditions of a sodium sulfate solution.

6. Discussion of results of studying the effect of methyl hydroxyethyl cellulose on the properties of the cement matrix
A slightly more complex process can proceed in the presence of magnesium sulfate. First, the exchange reactions, most likely, lead to the formation of magnesium hydroxide, which has no mechanical strength, and, second, there is a possibility to form calcium hydrosulfaloaluminate.

If we compare the possible reactions, the most aggressive should be a solution of magnesium sulfate. This happens on the example of an additive-free cement: its coefficient of corrosion resistance is the lowest in this very solution (0.73 against 0.87 in a solution of sodium sulfate and 0.78 in a solution of calcium sulfate) (Fig. 5).

Completely different results are obtained when cellulose ester is introduced. Thus, the introduction of 0.25 % by weight improves the coefficient of corrosion resistance in the solutions of magnesium and calcium sulfates and leaves practically at the same level in a solution of sodium sulfate. And even when introducing an additive in the amount of 0.50 % by weight can improve the coefficient of corrosion resistance in a solution of magnesium sulfate in comparison with this indicator for the additive-free cement. A further increase in the content of additives in cement leads to a sharp drop in this indicator (Fig. 5).

This indicates the need for a cautious introduction of the additive of methyl hydroxyethyl cellulose to dry construction mixes based on the cement matrix.

Thus, at the small concentrations of methyl hydroxyethyl cellulose, there is some improvement in the corrosion resistance of materials, and, at significant, sharp deterioration. This is due to changes in the character of the clinker hydration process and the reduction of strength indicators with an increasing cellulose ester content in the material.

The obtained results prove that the increase in the viscosity of cellulose ester leads to a greater reduction in the strength of the cement matrix. When producing dry construction mixes, it is advisable to use methyl hydroxyethyl cellulose of low and medium viscosity. This would make it possible to achieve the required density of mortars and give them larger strength and resistance in aggressive environments.

Thus, the obtained results show that the viscosity of cellulose esters affects not only the ability to retain water in mortars but also affects the strength of the matrix and its resistance to corrosion.

There are studies into the influence of cellulose esters on the processes of hydration [5, 6, 9–14], but the viscosity factor of cellulose esters has not yet been explored and not taken into account in the design of mixtures.

Further investigations should be directed towards studying the effect exerted on the cement matrix by other components of dry construction mixes (these include, first of all, the dispersible powders) and the complex influence exerted by all main components of dry construction mixes on the physical and mechanical properties of the cement matrix.

Our results could be used in the production of these materials in order to optimize their compositions and forecast their stability in various aggressive environments.

6. Conclusions

1. Introducing cellulose ester in cement leads to an increase in the normal density of the slurry and prolongs the setting duration of mortars. The normal density of mortars increases with the introduction of the cellulose ester of low (LV) and medium viscosity (MV), by 5.4–16.8 %; for the ester of high viscosity (HV), by 21.3–41.4 %, while setting duration increases by 2–4 times.

2. The viscosity of the additives of ester differently affects the strength of the cement matrix. Regardless of the viscosity of the cellulose additives, there is a decrease in the strength indicator in the early periods of hardening (1–7 days); it is, depending on the concentration of the additives, 2.2–4.2 times, respectively. Low-viscosity cellulose ether reduces the strength of cement stone the least, that of high-viscosity cellulose – the largest. As the viscosity of the cellulose ether grows, so does its negative impact on the strength of cement. Its reduction, compared with an additive-free cement, at the age of 28 days, is, for the ether of low viscosity, at concentrations: 0.23 % by weight – 14.3 %, 0.50 % by weight – 23.9 %, 0.75 % by weight – 40.5 %; for the ether of medium viscosity, it is, respectively: 23.8; 26.2; and 33.3 %; for the ether of high viscosity, 28.6, 45.2, and 61.0 %.

3. The corrosion resistance of the cement matrix depends significantly on the concentration of methyl hydroxyethyl cellulose. At an insignificant amount of the additive (0.25 % by weight), this indicator is even somewhat improved. Compared to an additive-free cement, which is stored under similar aggressive conditions, there is the increased corrosion resistance of the samples containing the cellulose ether additives in a solution of magnesium sulfate, by 10.9 %, and in a solution of calcium sulfate – by 3.8 %. In a solution of sodium sulfate, the indicators are practically the same. Increasing the concentration of the additive up to 0.75 % by weight results in the significant reduction in the resistance of the samples in the solutions of sodium sulfate, magnesium and calcium sulfates, by 44.8 %, 2.9 %, and 12.8 %, respectively.

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