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CORROSION STABILITY OF CEMENT MATERIAL MODIFIED BY CELLULOSE ETHER

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ABSTRACT

The influence of cellulose ether (methyl hydroxyethyl cellulose) on the corrosion resistance and physical and mechanical properties of the cement matrix was studied. Cellulose ethers were added into the cement in an amount of 0.25, 0.5 and 0.75 wt. %. It is established, that the adding of cellulose ether into the cement leads to an increase in the normal density of the cement paste and the extension of the curing time of the mortars. A monotonous increase in normal density is noticeable: on 5.4% at an additive concentration of 0.25 wt. % and on 16.8% at a concentration of 0.75 wt. %. This indicates the high water-retaining capacity of methyl hydroxyethyl cellulose. A significant decrease in the strength of the samples in the early curing period (2 - 4 times) also occurs, but the strength of the control cement samples is higher in all curing periods apart to the samples of cement with the additive. The cement mark with additives is reduced not so much. Those difference between control (clear cement) and project (cement with cellulose ether) samples for mark are: 0.25 wt. % - 14.3 %, 0.50 wt. % - 23.9 %, 0.75 wt. % - 40.5 %. At the age of 180 days, the presence of the additive of methyl hydroxyethyl cellulose also leads to the decrease in the strength of the samples when stored in tap water. With the amount of additive up to 0.25 wt. % toughness index decrease in compare to additiveless samples on a 12.5 % and at 0.75 wt. % those decrease rises up to 24.4 %.

With small amounts of cellulose ether additive (up to 0.25 wt. %). The corrosion resistance of the samples is similar to that for cement, or slightly exceeds it. Further increase of amount of additive leads to significant decrease of corrosion resistance of materials.

The manufacturing and using of dry building mixes with low concentration of water retention additives are better for conditions of contact with aggressive environment.

KEY WORDS: *cement, methyl hydroxyethyl cellulose, dry mixes, physical and mechanical properties, corrosion resistance*

INTRODUCTION

At this stage of human development, Portland cement is the main constructional material that used in building manufacturing. Its corrosion resistance in aggressive environments has been studied and various methods of improving this indicator have been developed [1]. However, in recent years, usage of dry building mixtures with components that gives different properties for the building mixture found wide usage. Dry building mix commonly composed with the necessarily basic binder, which is provide the required strength, fillers and modifying additives. One such additive is water-soluble cellulose ethers. These are derivatives of cellulose with the general formula $[C_6H_7O_2(OH)_{3x}(OR)_x]_n$, where n – is the degree of polymerization; x – is the number of OH groups substituted in the same cellulose macromolecule chain (the degree of substitution – C_3); R – is methyl, ethyl, propyl and other radicals. Each unit of the cellulose macromolecule has three groups of OH, which are capable of substitution and, as a consequence, the formation of corresponding ethers [2]. The main task of such additives is to retain moisture and provide the necessary plasticity for the paste [3]. Often methyl hydroxyethyl cellulose used as a water retention additive. The adding of such an additive leads to a dramatic change in the rheological properties of the solution and certain changes in the course of the processes of hydration of the binder. It is known, that the use of organic additives, at certain concentrations, leads to a decrease in the strength of cements [4-5], so it is advisable to study the effect of water retention additives on this indicator. Due to the usage of mortars in abodes with different environment, including industrial enterprises shops and in environments where there is a possibility of contact with aggressive agents, the effect of the addition of cellulose ether on the strength and corrosion resistance of the cement matrix were studied.

MATERIALS AND METHODS

The main purpose of the research is to study the effect of the concentration of water retention additive on the corrosion resistance of the cement matrix.

Portland cement CEM I 42.5 N and low viscosity methyl hydroxyethyl cellulose (11000-16000 mPa·s) were used as starting materials. Normal density and setting was calculated using VICAT's apparatus. Compressive strength of cements was determined according to the test procedure with small cement samples (size 20x20x20 mm). The additive of methyl hydroxyethyl cellulose was added into the dry mixture in such concentrations of 0.25, 0.50 and 0.75 wt. %.

Corrosion resistance in aggressive solutions of 3 % sodium sulfate (Na_2SO_4), 3 % magnesium sulfate ($MgSO_4$) and 0,2 % calcium sulfate ($CaSO_4$) was studied. The values of the corrosion resistance coefficients of the samples was calculated as the ratio of the strength of the samples contained in the aggressive solutions to the strength of the samples that were kept in tap water. The coefficient of resistance at the age of 6 months was calculated.

RESULTS AND DISCUSIONS

The results show that the introduction of even a small amount of cellulose ether leads to significant changes in the properties of the cement dough. There is a monotonous increase in normal density: 5.4 % at a concentration of the additive 0.25 wt. % and 16.8 % at a concentration of 0.75 wt. %. This indicates a high water-retention capacity of methyl hydroxyethyl cellulose (table 1).

Table 1. Normal density and curing time of cement mixtures with additives

Mixture composition, wt. %		Normal density, %	Setting time, h-min	
Cement	Additive		Start	Finish
100,00	0,00	33,3	0-54	1-30
99,75	0,25	35,1	1-59	3-09
99,50	0,50	37,2	2-20	3-25
99,25	0,75	38,9	2-40	4-50

There is also a change in the setting time: with the increase in the mixture of amount of the additive, a significant increase of this indicator by 2 - 4 times were occurred. This leads to the conclusion that in the initial stages of hydration of the cement matrix there is not enough moisture for the processes of hydration of clinker minerals, which takes its toll on the speed of curing time. This is confirmed by the results shown in Fig. 1.

A significant decrease in the strength of the samples in the early curing period (by 2 - 4 times) was noticed, but the strength of the control cement samples was higher in all curing periods, regardless to the project samples with the additive. Those, the mark strength of cement with additives reduced not so much and at the concentration of the additive equals: 0.25 wt.% - 14.3%, 0.50 wt.% - 23.9%, 0.75 wt.% - 40.5%.

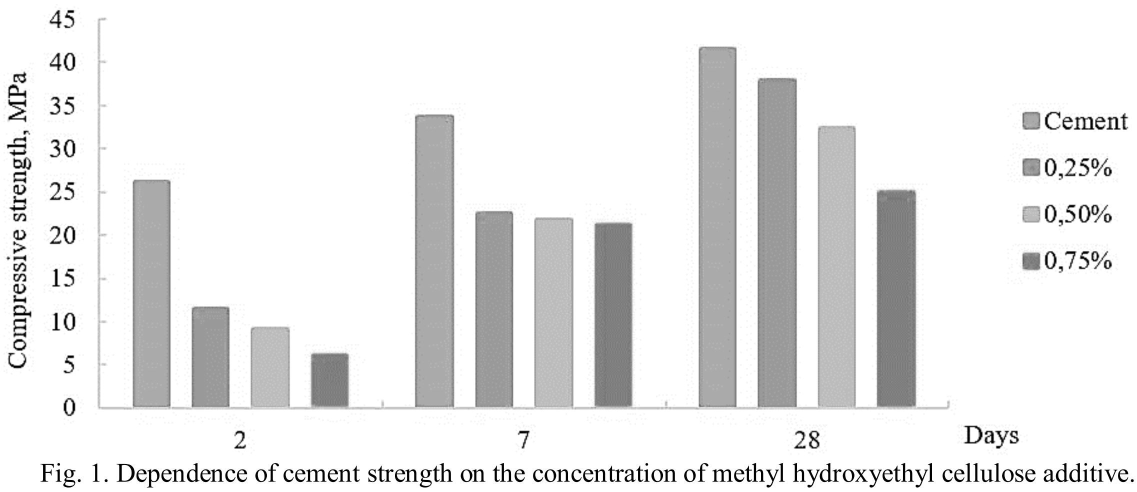

Fig. 1. Dependence of cement strength on the concentration of methyl hydroxyethyl cellulose additive.

At the age of 180 days (Fig. 2) the presence of the additive methyl hydroxyethyl cellulose in mixture also leads to a decrease in the strength of the samples when stored in tap water. Even at 0.25 wt. % of the additive is present in the additive, the strength index decreases by 12.5 % wt compared to the additiveless sample and by 24.4% at 0.75 wt. % of the additive.

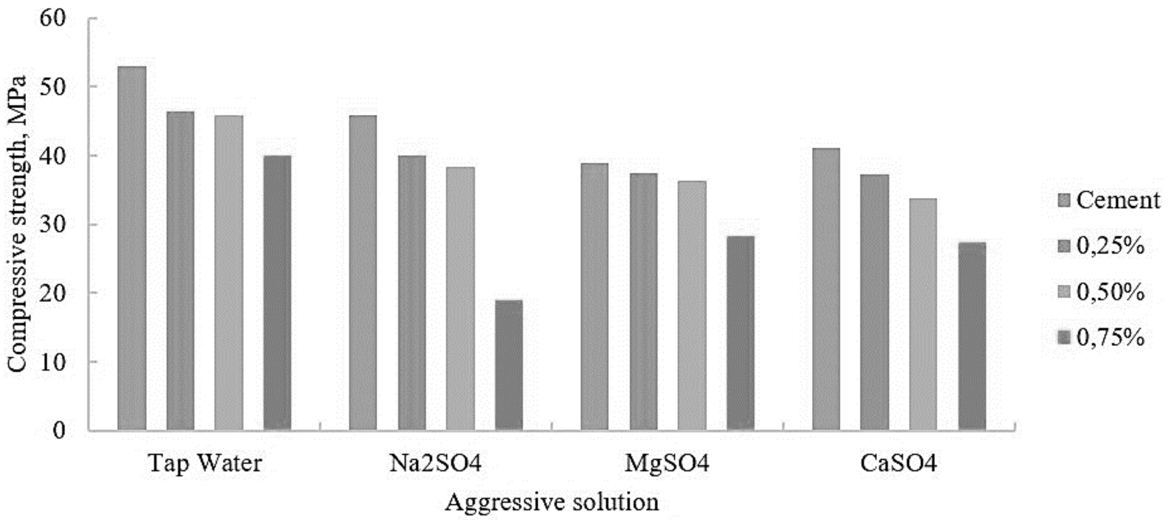

Fig. 2. The strength of the samples at the age of 180 days in aggressive solutions.

A similar process also occurs when the samples are stored in aggressive solutions. Thus, when the concentration of the additive in the amount of 0.25 wt.% the drop in strength took 12.9% in solution of Na_2SO_4, 3.4 % - $MgSO_4$, 9.2 % - $CaSO_4$, and at amount of 0.75 wt.% of additive respectively –8.6 %, 27.1 %, 33.6 %.

It should be noted that selected corrosive solutions could lead to different types of corrosion. In the presence of sodium sulfate there is an exchange reaction between calcium oxide and calcium sulfate, which leads to the formation of two-calcium gypsum. The latter, in turn, reacts with the formation of etringitis, which leads to the expansion of the system and, consequently, the reduction of strength.

In the case of a solution of magnesium sulfate, there are also exchange reactions between calcium hydroxide and magnesium sulfate to form magnesium hydroxide, which is formed in the cement stone in the form of flakes that do not have mechanical strength. In addition, calcium sulfate is formed, which is also formed with increasing volume, thereby reducing the strength of the samples.

Upon contact of the samples with a solution of calcium sulfate, a reaction occurs with the formation of a significant amount of etringitis, which significantly reduces the strength of the cements.

Thus, on the intensity of corrosion processes in cement matrix of dry building mixtures would be influenced concentration of water-retention additive, amount of calcium oxide that reacts during the hydration process of clinker minerals with water and amount of tricalcium aluminate in cement.

It is possible to make conclusion on corrosion resistance in various corrosive environments using the data of corrosion resistance coeficients (table 2).

Table 2. Corrosion resistance coefficients of the samples

Mixture composition, wt. %		Corrosion resistance coefficient after 180 days of curing in solutions		
Cement	Additive	Na_2SO_4	$MgSO_4$	$CaSO_4$
100,00	0,00	0,87	0,73	0,78
99,75	0,25	0,86	0,81	0,81
99,50	0,50	0,85	0,79	0,73
99,25	0,75	0,48	0,71	0,68

In general, cements are considered corrosion resistant if the corrosion resistance is above 0.80 at the age of 180 days. Depending on the type of aggressive agent, the corrosion resistance of the mixtures differs.

Under the conditions of sodium sulfate solution the best result in the original cement. In addition, the introduction of the additive methylhydroxyethyl cellulose in an amount of up to 0.5 wt.% Does not significantly reduce this figure and these cements are resistant to this aggression, but with the introduction of 0.75 wt.% There is a sharp decrease in corrosion resistance. This negative influence can be explained by of the significant amount of methyl hydroxoethyl cellulose on the processes of crystal structure formation of cement stone. Due to the high water-retention ability of additive and, as conclude from, shortage of amount of necessary what at the first stages of curing (reactions of hydration and hydrolysis of clinker materials).

When storing the samples in the solution of magnesium sulfate is noted low corrosion resistance of the original cement. At the same time, samples with the addition of methylhydroxyethyl cellulose at concentrations up to 0.5 wt.% Have significantly higher corrosion resistance, and at a concentration of 0.25 wt.% Even meet the requirements for corrosion resistance and significantly exceed this indicator in the original cement.

The calcium sulfate solution also shows a decrease in the strength of the cement samples with increasing concentration. But it should be noted that, as in the previous case, at a concentration of 0.25 wt.% Additives have a better corrosion resistance compared to the original cement. This can be explained by the fact that small concentrations of the additive during curing fill the micropores of the cement stone and, thus, close access to the middle of the samples. As the concentration of the additive increases, the strength of the material decreases and the strength decreases more strongly.

Comparing the effects of various corrosive solutions on the corrosion resistance of cements with the addition of methylhydroxyethyl cellulose, it can be concluded that the negative impact on the strength of the cements, they are arranged in the following order: calcium sulfate, magnesium sulfate, sodium sulfate.

CONCLUSIONS

1. The addition of methyl hydroxyethyl cellulose leads to increase of the normal density of the cement paste (on 5.4 – 16.8 %) and prolongs the curing time (by 2 – 4 times);

2. Adding of cellulose ether leads to monotone decrease of samples strength with increasing of additive amount: at the concentration 0.25 wt. % decrease on 14.3 %, 0.50 wt. % – on 23.9 %, 0.75 wt. % – on 40.5 %. The most significant decrease of strength appears at earlier curing terms;

3. At low amount of cellulose ether (up to 0.25 mass %) corrosion resistance of samples is the same to the cement or slightly exceeds it;

4. With increasing of concentration of cellulose ether in cement matrix there are significant decrease of corrosion resistance of samples occurs. At concentration of additive 0.75 wt. % these decrease of index are extreme.

Thus, the manufacturing and using of dry building mixes with low concentration of water retention additives are better for conditions of contact with aggressive environment

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