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Ratio of the ash concentration to the cement binder in the composition of concrete with the use of a modified additive

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Abstract. The paper presents studies of cement-ash binder in the composition of concrete with the use of a complex modified additive (CMA). The research is aimed at improving the conditions for the production of concrete works, in particular, improving the workability of a concrete mixture based on ash-cement binders. The main evaluation criterion of the study was the change in the viscosity of the composition with a change in the water-binding ratio. The measurements were carried out in two stages: at the first stage, the influence of the ash component on the water-binding ratio was estimated, at the second stage, the issue of changing the viscosity over time was considered. Laboratory tests were carried out using adapted methods for measuring the spread of the mixture and determining the setting time. According to the results of the first stage, the regularities of changes in the viscosity of the mixture by changing the water content were obtained, and the optimal ratios of water to the binder were obtained, depending on the percentage of the ash component. According to the results of the second stage, the regularities of changes in the viscosity (from the liquid to the solid state) of the mixture over the holding time, depending on the same percentage of ash were obtained. In conclusion, the data on the optimal water-binding ratio from the conditions for the manifestation of the ash-cement mixture of texotropic properties corresponding to the classical cement mixture, without the inclusion of ash, are presented.

1. Introduction

The history of concrete development dates back to ancient times, but still has an active development [1]. Modern technologies favor the future development of technologies for the use and production of concrete in construction [2-3]. New types of concrete are used in modern practice, such as fiberreinforced concrete, self-compacting concrete, carbon concrete, nano concrete, and others [4-7].

However, most of the transformation process of concrete as a construction material is not the development of new materials, but the use of additives that improve its physical and mechanical properties. The additive can be selected, for example, depending on the technological application of concrete or to improve certain of its indicators: speed of setting or hardening, increase in strength, water absorption, frost resistance, etc. [8].

The direction of industrial waste disposal is also actively developing. In the composition of concrete mixes or binders, waste or excess industry is added, mainly in order to reduce the cost of the product. The most common replacement additives are: rock crushing dropout, slag, ash, etc., [9]. In this paper, ash is used as a substitute for the binder. The addition of an ash component to the binder contributes to the deterioration of the physical and mechanical properties of concrete, therefore, the use of ash in the binder to save cement should not be used without the use of compensating additives

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(for example, the addition of a plasticizer for compaction of the mixture, in particular the porous structure of the ash component). In our case, a complex modified additive (CMA) developed by the authors of the paper is used, due to which the lost properties of concrete are restored [10]. The composition of CMA includes waste from the production of alcohol (post-alcohol bard), waste from the production of oils (soapstock), as well as alkali (caustic soda, NaOH). This additive can be used not only for heavy concrete, but also for light, for example, foam concrete [11].

In this paper, we will consider the task of evaluating the optimal water-binding ratio depending on the ash concentration, from the point of view of the conditions for the production of concrete works [12-17].

2. Methods

The tests were performed for a water-binding mixture with different ash percentages: 0, 4, 8, 10, 20, 30, 40%. In this case, the reference mixture (with which all subsequent comparisons of the results will be carried out) is a water-cement mixture without the addition of ash. The optimal water-binding ratio was determined for each of the compositions.

The composition of hydraulic ash includes: silicon dioxide (SiO_2) – up to 52%, aluminum oxide (Al_2O_3) – up to 18%; quicklime (CaO) – up to 13%, magnesium oxide (MgO) – up to 2%, iron scale (Fe_2O_3) – up to 7%, sulfur anhydride (SO_3) – up to 3%, alkali metals – up to 2%, ash residue – up to 7%.

The evaluation of the optimal water-binding ratio to the ash-cement composition was carried out in two stages:

The first stage included an assessment of the influence of the ash component on the water-cement ratio, performed by analyzing the results of measurements of the spread of the cement-ash mixture, Figure 1A.

The second stage included an assessment of the effect of the ash component on the time of change in the aggregate state of the mixture (from liquid to solid) after its mixing, performed by analyzing the results of measurements of the setting time of the mixture, Figure 1B.



A

Figure 1. Stages of laboratory tests.

Conditions for the first stage:

- The mixture spread was measured at two critical points: the minimum (the lower indicator of the water-cement ratio) and the approximate maximum spread of the mixture (the upper indicator). For the standard of the lower indicator, such a water-cement ratio is taken, at which the spread of the mixture will be as close as possible to the minimum radius of the scale of the measuring instrument. Accordingly, the standard of the upper indicator is taken to correspond to the maximum radius of the scale of the measuring instrument. For the conventional unit of increment of water to increase the ash component, the ratio is 0.5, that is, with an increase in ash by 10 g, the increase in water is 5 g. This

proportion is taken on the basis of preliminary measurements of the blurring of small samples of mixtures of different ash concentrations.

- To take into account the thixotropy of the mixture and its ability to change the viscosity over time, two measurements were performed for one batch. As the measurements were performed sequentially, comparisons of the spreading diameters of the mixture of one batch may indicate a potential effect of time (downtime) on the viscosity of the mixture. On the absolute time scale: the condition for preparing the solution to 2.5 minutes, conducting the first test within 2.5-4.0 minutes (including molding), conducting the second test within 4.0-5.5 minutes.

- The mixture corresponding to the standard of the lower indicator is conventionally called – batch 1, the upper – batch 2. Each of the batches consists of two dimensions: measurement 1 and measurement 2.

- To assess the effect of the ash component on the porosity of concrete, the mixture residues were measured after two consecutive measurements of one batch.

Conditions for the second stage:

- The measurements were carried out in three stages of testing: the first stage of testing included an assessment of changes in the setting time at fixed values of water-cement ratios of solutions of different ash concentrations; the second stage included an assessment of the obtained water-cement ratios by the spreading method, as well as an assessment of the applicability of the spreading method itself to ash-cement solutions, the rheology and thixotropy of which may differ from the classical cement; the third stage included an assessment of the applicability of the results of small samples to large-sized building structures being erected.

- The qualitative and quantitative composition of the components of the compared binders is presented in Table 1, where the classical method of concrete production belongs to type 1.

Туре,	Ash		Cement	Cement (PC400 DO), g		Water, g	
number	gram	%	gram	%	Lower	Upper	
Type 1	0	0	400	100	120.00	129.00	
Type 2	16	4	384	96	121.50	130.50	
Type 3	32	8	368	92	123.00	132.00	
Type 4	40	10	360	90	123.75	132.75	
Type 5	80	20	320	80	127.50	136.50	
Туре б	120	30	280	70	131.25	140.25	
Tyep 7	160	40	240	60	135.00	144.00	

Table 1. Qualitative and quantitative composition of binders and concrete.

3. Results and discussion

3.1. Stage one - flow tests

Figure 2A shows graphs of changes in the area by the percentage increase in the ash component: the nature of the curves indicates the non-linearity of the pattern. The obtained data allow talking only about the existing dependence, without being able to assess the regularity in the water demand with an increase in the percentage of the ash component, as the limits of the partial values of the flowes lie in different ranges.

Figure 2B shows graphical representations of the dependence of the spreading areas of the second dimension relative to the first $(S_1^2 - S_1^1; S_2^2 - S_2^1)$, as well as the spreading areas of the lower and upper indicators of the water-cement ratio $(S_2^1 - S_1^1; S_2^2 - S_1^2)$ on the ash concentration $(S_{number of measuring}^{number of measuring})$. The curves of Figure 2B have a more stochastic distribution, and therefore do not have a certain regular dependence.



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Figure 2. Dependence of the spreading areas on the ash concentration.

Figure 3 shows the results of the evaluation of the binder residues after the tests, within each batch. By comparing the binder residues after the tests, within each batch, indirect assumptions can be made about the change in the density of the material from an increase in the percentage of the ash component. If we compare all the partial values of changes in the residues, regardless of the batch, it is necessary to take into account the adjustment of the mass of the residue to increase the W/C ratio. The results of the partial values of the residues indicate an increase in the porosity of the mixture with an increase in ash, while a close proportional pattern is observed, as evidenced by the values of the coefficients of variation as close as possible to 1.0: R (C_a ; R_1)=-0.993; R(C_a ; R_2)=0,992 (C_a is an array of changes in the ash concentration, and R_i is an array of changes in the residues for mixtures 1 and 2). The error (the difference in residues) that is observed between the partial values of R_1 and R_2 can be explained by the high degree of viscosity and stickiness of mixtures of mixes 1 relative to mixes 2, which is why mass losses are possible in the process of rodding and forming samples.

Figure 4 shows the results of the analysis of water-cement ratios of mixtures of different ash concentrations corresponding to the flows of the reference mixture (without ash content). The red line corresponds to the reference dependence of the spread on the water-cement ratio. The black lines correspond to the same dependencies of mixtures of different ash concentrations. For each of the dependencies, linear equations are determined, which are used to extrapolate to the intersection with the vertical red lines corresponding to the areas of the upper and lower water-cement index of the reference mixture. So, for each composition of the mixture, the lower and upper indicators of the water-cement ratio were determined, at which a viscosity similar to the reference one is achieved.



Figure 3. Change in residues by change in ash concentration.

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Figure 4. Correction of the water-cement ratio.

Figure 5 shows the results of the obtained water-binding ratios for the change in the percentage content of the ash component. Based on the analysis of the distribution of the dependence curve in Figure 5A, we can conclude that there is a relatively linear pattern between the increment of the ash concentration and the water demand (as evidenced by the high coefficient of determination $R_2=998$ – within the analysis of the first batches and $R_2=9932$ – within the analysis of the second batches). The proportionality of the dependence of the water-binding ratio on the ash concentration is represented by the following ratio for batch 1 - 0.031 (in the mass equivalent of the amount of water by weight of ash in the range from 0.27 to 0.32), for batch 2 – 0.033 (from 0.36 to 0.49). The revealed range indicates an unequal increment of water by the increment of the ash component, Figure 5B (where on the ordinate axis - the increment of ash in relation to cement, on the abscissa axis – the ratio of the increment of ash by weight).



Figure 5. Dependence of the water-binding ratio on the ash concentration.

3.2. Stage two - testing of the setting time

Figure 6A, B and C show the obtained indicators of the time of setting of stage 2 of stages 1, 2 and 3, respectively. The results for the lower water-binding ratio are shown on the left, and the results for the upper ratio are shown on the right. On all the charts of the time of setting, the first peak corresponds to the beginning of setting, the second – to the end. The arrangement of the types of solutions to be compared in ascending order from bottom to top, where red corresponds to type 1 - standard water-cement solution, relative to which comparisons are made.

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According to the test results shown in Figure 6A, the samples with a water-binding ratio for the lower indicator show a reduction in the setting time depending on the ash content, while the samples for the upper indicator show an inverse pattern, as evidenced by the average correlation coefficients: - 0.85 and 0.95, respectively, for the lower and upper indicators of the water-binding ratio. The different proportionality of the dependencies is explained by the influence of the amount of water on the timing and nature of setting.

According to the results of the tests presented in Figure 6B, there is a close relationship between the partial values of the parameters of the setting time of the samples for the lower parameters of the water-binding agents (the coefficient of variation does not exceed 8.9%), and for the upper ones there is a slight discrepancy with an increase in the ash concentration from 20 to 40% (the coefficient of variation does not exceed 19.9%). Therefore, it is necessary to adjust the previously determined water-binding ratio for the spread according to the upper indicators for 20, 30 and 40 % of the ash concentration in the direction of reduction.

According to the results of the tests presented in Figure 6C, for the lower indicators of waterbinding agents, there is an average to close relationship between the partial values of the parameters of the setting time of the samples (coefficient of variation in the range from 7.5 to 29.5%), for the upper indicators, the statistical data of the partial values are similar to the lower indicators (coefficient of variation in the range from 12.2 to 17.2%). In contrast to the beginnings, the values of the ends of the grasps of large samples exceed the values of small samples from 4 to 19% (for the lower indicator) and from -9 to 2% (for the upper one). This pattern of exceeding the beginning of the terms, and later on the contrary, the ends, indicates a small, but the influence of the sample dimension on the measurement results, which is also confirmed by a large run-up of these setting periods, ranging from 50 to 300% (for the lower indicator) and from 0 to 320 % (for the upper one).

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Figure 6. Setting time of standard samples of stage 2.

4. Summary

The results of the study of the mobility of the mixture by the method of spreading measurements confirmed the dependence of the water-binding ratio on the percentage of the ash component. The dependence has a strict regularity, has an inversely proportional linear character. The reason for the dependence (a decrease in the spreading area with an increase in the ash concentration) may be the absorbent properties of the ash. Comparisons of the measurements between each other (measurements 1 relative to measurements 2) in both mixes (corresponding to the upper and lower water-binding ratio) showed the manifestation of the rheological and texotropic properties of the binder, as the results of the second measurements (in all cases) showed large areas of flow relative to the first. However, comparing the data of the ratio (vagueness of measurements relative to each other) on the change in the ash content, we can conclude that the ash component affects the rheological and texotropic properties of the binder, and, consequently, changes in viscosity over time. The latter becomes relevant when there is an increased requirement for the workability of the concrete mixture in the production of concrete works.

The results of the tests of the setting time of the samples indicate the influence of ash on the setting time indicators. At a low water content, the absorbent properties of the ash become dominant, as a result of hardening (or more correctly, in this case, a change in the aggregate state) of the sample occurs due to physical drying of the material, rather than from hardening as a result of crystallization of the cement mortar. With high water content, the excess water compensates for the absorbing ash demand, the sample does not dry out, and the setting of the samples is already due to the crystallization of the cement during hydration. Consequently, in the case of a high water content, with an increase in the ash component and a concomitant decrease in cement, the setting time increases. The influence of sample sizes on the setting pattern was also revealed, which was clearly observed when testing classical samples (the largest size of the three stages). When measuring the classical samples of the largest sizes this effect was not expressed.

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