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Research paper

High-Strength Concretes with Use of Ashes and Slag Waste of Circulating Fluidized Bed Boilers for Road Products

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Abstract

The results of studies on the influence of ash slag from circulating fluidized bed boilers on the heavy concretes properties are presented. Portland cement PPC 500 N, sand with the fineness modulus M = 1.05, 5-10 mm fractions granite macadam, "Fluid Premia–196" plasticizer were used in the studies. The studies were carried out using mathematical planning of the experiment.
Mechanical properties of concretes have been studied using ordinary hydraulic presses, and in the study of freeze-thaw resistance, the dilatometric method was applied, and the water absorption in a vacuum chamber is taken for the concrete porosity criterion. It is established that with increasing a degree of sand replacement with ash-slag, the strength properties of concrete decrease by 3-10% in comparison with concretes not-containing slag. However, the use of a plasticizer permits to compensate the reduction and to obtain high strength concretes.
As a result of the research, the optimal heavy concretes compositions with the use of ash slag to manufacture small products for road pavements have been determined.

Keywords: *ash slag of the circulating fluidized bed, durability, frost–thaw resistance, water absorption*

1. Introduction

It is known that in the world, the degree of electric energy consumption, including thermal power plants, is growing every year. Billions tons of ash and slag have been accumulated in the territories of thermal power plants. Utilization of these wastes is an urgent task of humanity, because they pollute the environment not only in places where they are accumulated, but also pose a threat to the people's health all over the world.
According to the studies data [1], the level of thermal power plants waste utilization in Ukraine does not exceed 10 — 13%, while in the countries of Europe: Germany and Denmark, it has reached almost 100%, in the UK and Poland — 50 —70%. This is due to the fact that fly ash- in developed countries is the same commodity as heat and electricity.
Development of complex technological techniques allows the use of waste from the thermal power stations in the technology of obtaining construction materials [2]. As a rule, waste from the coal burning in the thermal power plant boilers is gray colored, and their chemical composition is represented by oxides of silicon, aluminum, iron and calcium, as well as impurities in the form of magnesium, sulfur, sodium and potassium oxides. The phase composition of the ash slag is represented mainly by aluminosilicate glass, and also includes quartz, iron oxides.
There is no single common classification of ash slag wastes. The first classification was carried out in 1953 with the development of the ASTM standard (C 350-54T). In 1960, it was suggested to treat ash as a pozzolanic additive, and in 1968, natural pozzolanas and ashes were combined into the single ASTM C 618 standard under the general title of "mineral additives" [3].
The purpose of the study is to study the influence of ash salts from circulating fluidized bed boilers on the stability to freezing and thawing and, consequently, on the strength of heavy concretes designed for operation in the climatic conditions of Ukraine/

2. Materials and methods of the study

The following materials were used in the work: Portland cement PC 500 N (42,5) produced by "Haldeberg zement Ukraine"; sand with the fineness modulus M_f = 1.05 taken from the local deposits; ashes from boilers with circulating fluidized bed [4]; "Fluid Premia-196" hyperplasticizer based on modified polycarboxylates; crushed granite fraction of 5-10 mm taken from Kremenchuk deposit. For more complete detection of the ash slag and studying the hyperplasticizer's influence on the concrete freeze-thaw resistance and strength, a three-level experiment planning matrix was implemented in the study.
Freeze-thaw resistance was determined by the rapid method according to DSTU BV 2.7-47-96. Freeze-thaw resistance was determined by the rapid method. According to DSTU BV 2.7-47-96 several methods for determining the freeze-thaw resistance of concrete, including two rapid methods are established. The dilatometric method for determining the freeze-thaw resistance by freezing in the kerosene medium was used in the work. According to this method, the freeze-thaw resistance is determined by the maximum difference between volumetric deformations of concrete and standard samples. The standard sample is an aluminum cube

with a side length of 100 mm. Measurement of volumetric deformations was carried out using the "Beton-Frost" dilatometer (Fig. 1).

Fig.. 1: Illustration of the dilatometer with the measuring electronic unit

The concrete strength was determined by testing the 100-mm side sample-cubes. On hydraulic presses, the concrete porosity was assessed by the degree of water adsorption in the vacuum chamber at the vacuum level of 0.7 Pa.

When planning the experiment the following input parameters were established: X_1 – cement consumption; X_2 – hyperplasticizer consumption; X_3 - degree of sand replacement with ash slag. Terms of the experiment planning are presented in the Table 1.

Table 1: Terms of the experiment planning

Variable factors		Variation levels			Variation interval
Natural appearance	Coded appearance	-1	0	+1	
Cement consumption	X1	400	500	600	100
Additive content	X2	0.8	1.4	2.0	0.6
Degree of sand replacement with ash slag ZSh-P	X3	-1	0	1	0.5

3. Basic material and results

For the more detailed study of ash slag properties, the technology of X-ray diffraction analysis (XRD) fig.2, spectroscopy fig. 3 and differential thermal analysis (DTA) were used.

Decoding of the X-ray diffraction pattern indicates that the maxima with vertices are 3.5149; 3.1959; 2.578; 1.8711; 1.1424 belong to anhydride $CaSO_4$ mineral, and with vertices – 3.3476; 2.4575; 2.2851; 2.1306; 1.9201; 1.6724 - belong to silicon oxide and correspond to the SiO_2 formula. Thus, the crystallized part of the ash slag consists of calcium minerals and silicon oxide. With the X-ray diffraction pattern, it is also evident that most of the ashes are represented by amorphous structures, which can be combined under the name of vitreous phase, which promotes the ash slag hydration.

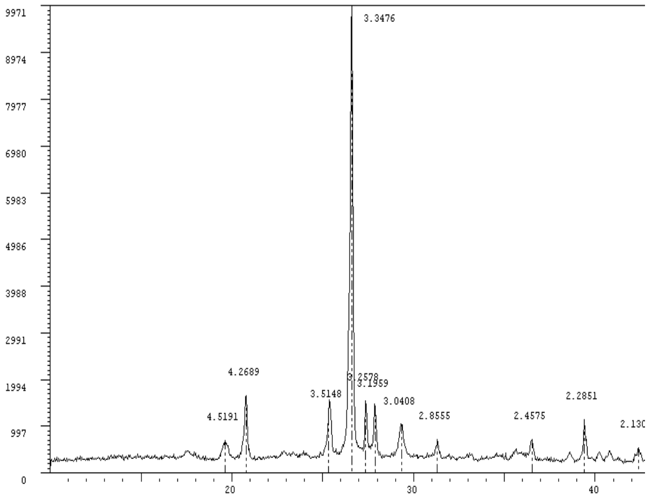

Fig. 2: X-ray diffraction pattern of ash-slag

The hydraulic activity of ash slags is associated with the presence of such compounds as lime in a free state or anhydride, which are able to react with water to form a water-resistant stone without introducing additional activators [2]. It is known that the different content of CaO affects both the change in the composition of the vitreous phase and the composition of the newgrowths crystallized, and the manifestation of hydraulic and pozzolanic properties of ash slags [2].

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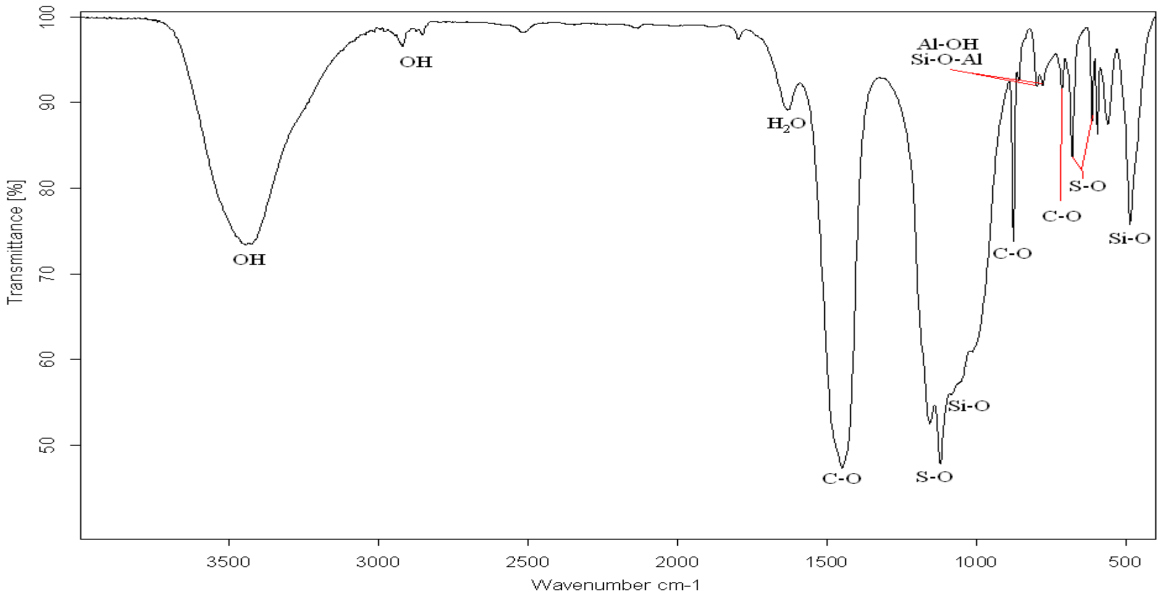

Fig.3: Spectral pattern of ash slags

The IR spectra of ash and slag contain bands characteristic of silicates and aluminosilicates with absorption bands in the region of 1050-1200 cm-1. The spectrum also contains a doublet characteristic of aluminosilicates within the range of wave numbers 770-810 cm^{-1}, which refers to vibrations of the Al-OH and Si-O-Al stretch oscillation. The deformation oscillations of the Si – O stretch are expressed in the absorption band within the range of wave numbers 500–400 cm^{-1}.

The presence of carbonates in the composition of ash and slag is proved by the presence of absorption bands, which are caused by C – O oscillations: valency - an intense band on the wave number 1440 cm^{-1}, a narrow intense band on 875 cm^{-1}; deformation - a weak band at 713 cm^{-1}, as well as bands at 2516 and 1795 cm^{-1}.

Sulfate groups are determined by the intense absorption band within the range of wave numbers 1090-1180 cm^{-1} and 680-650 cm^{-1}. According to the position of the maximum, it is possible to reliably determine the mineral in the sulfate group. In the composition of ash and slag, judging by the spectrum, only anhydrous sulfates are present.

The high-frequency region of the absorption bands with the values: 2918; 2850 and 3443 cm^{-1} refers to the stretch vibrations of connected OH-groups. The absorption band with a frequency of 1630 cm^{-1} refers to the stretch vibrations of water molecules. The presence of bands corresponding to valent deformation vibrations of OH-groups and the valent vibrations of water molecules is associated with the phenomenon of moisture adsorption from the environment due to the high activity of minerals that are part of ash and slag composition.

Thus, the studies have established that anhydrous calcium sulfate is present in the composition of ash and slag, and this may be anhydrite.

Studies have shown that ash slags belong to high-calcium ashes (CaO> 20 % wt), i.e. to basic ashes; as to the content of SO_3 - to sulfate ($S0_3$> 5 % wt) ashes. The main sulfate mineral is anhydride $CaSO_4$. [4].

The processes of cement-ash compositions hydration should be subordinate to the established general fundamental laws, which, in particular, consist in the fact that, at ordinary temperatures, the ash silica glass is slowly hydrated, which leads to the formation of C4AN13-19 or calcium carboaluminate with excess CH in the liquid phase. Then it can go into the hydrogranate, aluminum hydroxide or gibbsite. If these phases do not go into more stable hydrosulfoalluminates, the durability of the product will decrease [5-6].

The formation of hydrosulphoaluminate in the late period of the cement-ash system hardening may lead to the destruction of cement stone [7-8]. Taking into account this fact, a cement stone of 1:1 composition with slag was studied by means of the X-ray analysis. A fragment of the graphs is shown in Fig. 4

As can be seen from the X-ray diffraction pattern's fragment, the maxima inherent in ettringitis in the cement stone at the age of two months are absent. Studies of cement-ash-slag stone at the micro level with a scanning microscope confirmed the absence of needle crystals inherent in hydrosulphoaluminate (figure 5,6)

Studying microscopic photographs of a pure cement stone compared to a cement ash-slag stone, we can conclude the following: in a cement stone without ash-slag there are typical components of a cement stone like Portlandite and calcium hydrosilicates. In micrographs of cement-ash-slag stone the picture is almost the same, but with a large amount of portlandite. In our opinion, it is evidenced by an increase in the number of light crystals.

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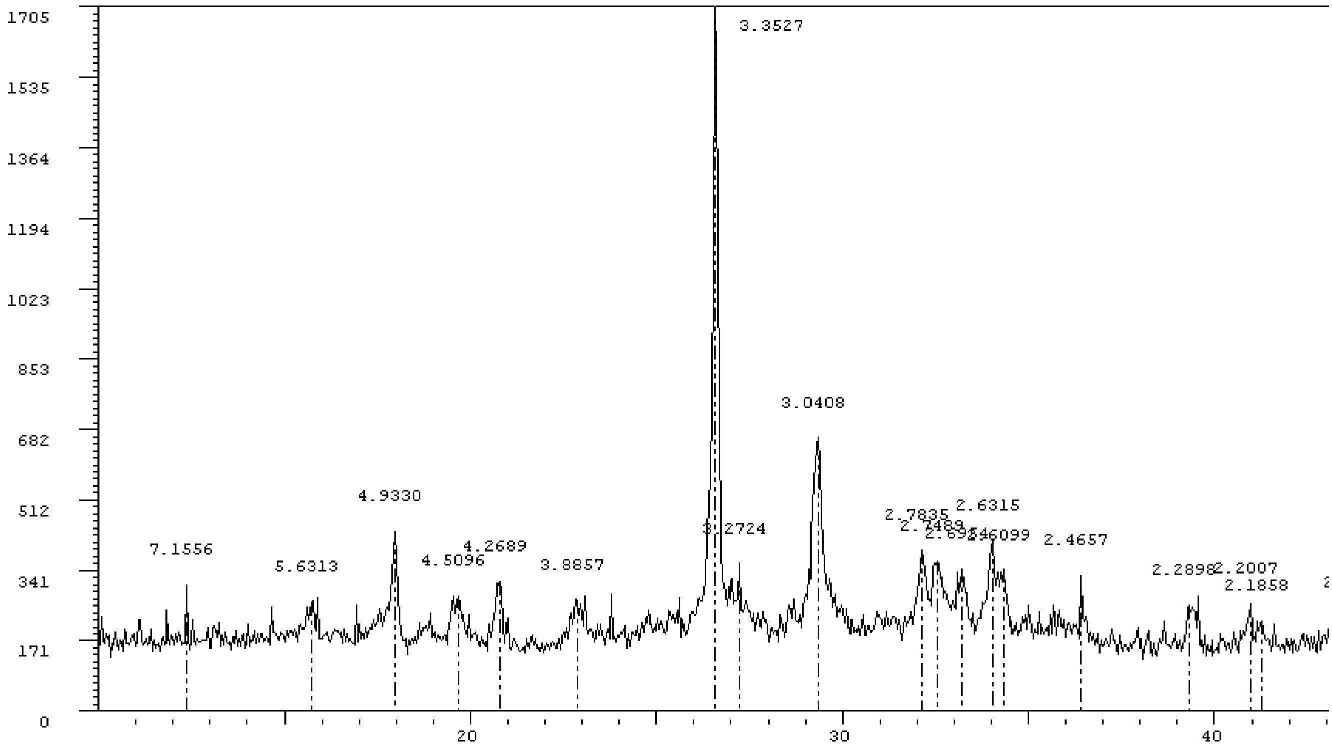

Fig.4: X-ray diffraction pattern's fragment of cement-ash-slag stone after hardening for 60 days in wet conditions.

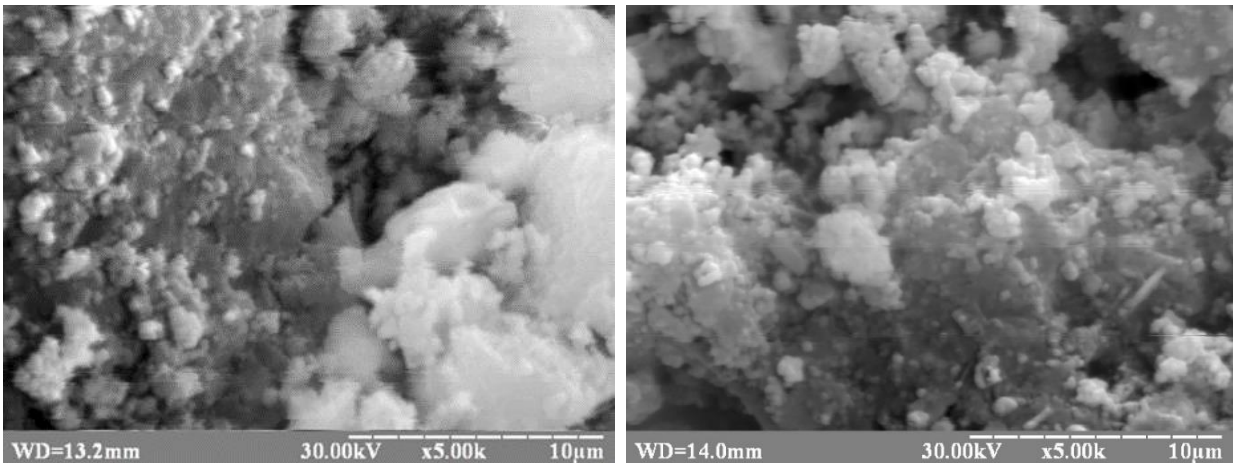

Fig. 5: Electron-microscopic photographs of the cement ash-slag stone fracture surface after its hardening for 60 days in wet conditions

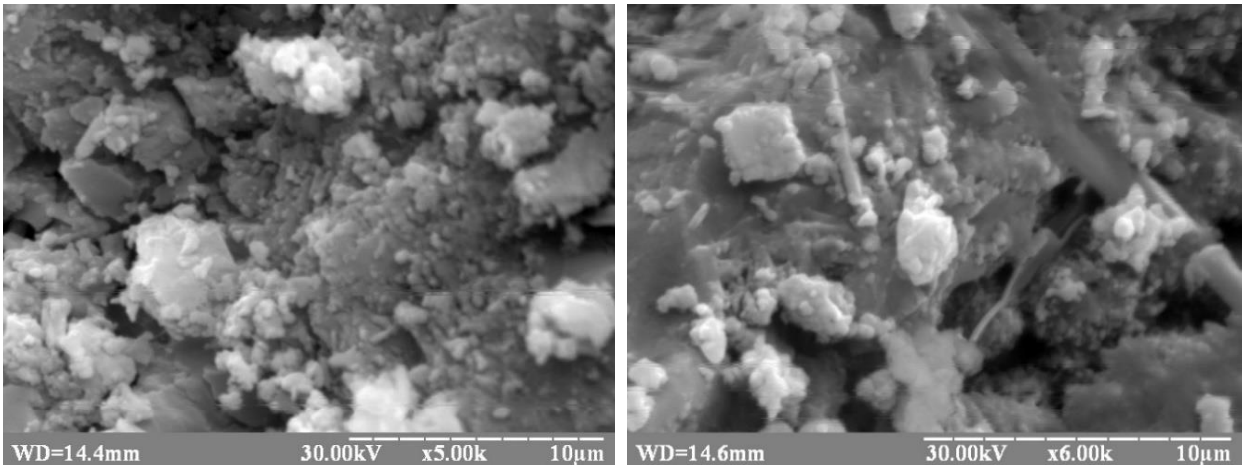

Fig. 6: Electron microscopic photographs of the of the cement stone fracture surface after its

After the absence of hydro-sulfoaluminate traces had been established in the cement-ash-slag stone, samples of concrete were prepared according to the experimental design matrix (table 2).

Table 2: Experiment planning matrix

No	x_1	x_2	x_3
1	2	3	4
1	600	2	ash slag
2	400	2	ash slag
3	600	0.8	ash slag
4	400	0.8	ash slag
5	600	2	sand
6	400	2	sand
7	600	0.8	sand
8	400	0.8	sand
9	600	1.4	0.5+0.5
10	400	1.4	0.5+0.5
11	500	2	0.5+0.5
12	500	0.8	0.5+0.5
13	500	1.4	ash slag
14	500	1.4	sand
15	500	1.47	0.5+0.5
16	500	1.4	0.5+0.5
17	500	1.4	0.5+0.5

Mixing of the concrete mixture components was carried out in a compulsory-type concrete mixer with a skip capacity of 150 liters. Dosing of the mixture components was carried out using electronic scales with an accuracy of 0.1 kg. Dosed components of the mixture were charged into the mixer in the following sequence: crushed stone + sand (ash) + cement. The components were mixed without adding water for three minutes. The plasticizer in the dosage amount was added to water and mixed with water using a mixer for 30 seconds. The ready mixture of water and plasticizer was added into the mixer. The components mixing lasted during 5 minutes.

After 5 minutes, the mixture was discharged from the mixer and tested for fluidity. From the finished mixture, samples were made in the form of cubes with a side of 10 cm and prisms sized 10 x 10 x 40 cm. The samples consolidation was performed using a vibration table with the oscillations amplitude of 0.5 mm and the frequency of 50 Hz. After a day, the samples were taken out of the forms. The samples were hardened under the laboratory conditions for 28 days. Additional conditions for the concrete samples hardening were not created. After 28 days of hardening, the samples were tested according to the experiment plan.

The results of the samples testing for compressive strength are presented in Table 3 and in Fig. 7.

Analysis of the samples testing results shows that when the sand is completely replaced with ash slag and at the minimum cement consumption within the limits of the experiment, the strength of the concrete is reduced by 6.5% (compositions 4 and 8). With a maximum amount of cement strength is reduced by only 3.6% (compositions 1 and 5). The concrete strength within the experimental design matrix varies from 38.6 to 75 N/mm^2. With the mean values of the concrete components consumption, the strength of the samples varies from 44.4 to 73.6 N/mm^2.

Table 3: Properties of concretes

Batch	Compression strength N/mm^2	Water absorption W_m , %	Frost resistance, cycle
1	2	3	4
1	72,3	5,22	480
2	43,4	8,76	238

3	70,1	7,3	332
4	38,6	9,86	105
5	75,0	3,82	633
6	45,1	5,05	380
7	72,7	4,1	580
8	41,3	6,26	365
9	73,6	4,71	538
10	44,4	6,64	360
11	61,1	5,25	487
12	59,5	5,26	408
13	63,6	6,65	390
14	65,4	5,58	435
15	66,7	5,31	424
16	67,0	5,36	416
17	68,0	5,1	464

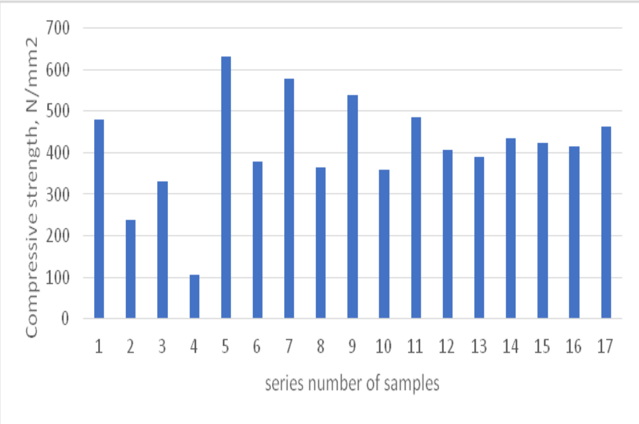

Fig. 7: Diagram of strength changes when compressing concrete samples

The fact of the strength reducing at the samples compression with increasing the sand replacement degree with ash slag, can be explained by the fact that the ash slag is not so strong mineral like quartz. Grains of ash-slag have internal pores reducing their durability. The reduction of concrete strength is associated with the increased porosity. Increasing porosity leads to an increase of water absorption. The results of research on water absorption of concrete in the experiment are presented in Table. 4 and in fig. 8

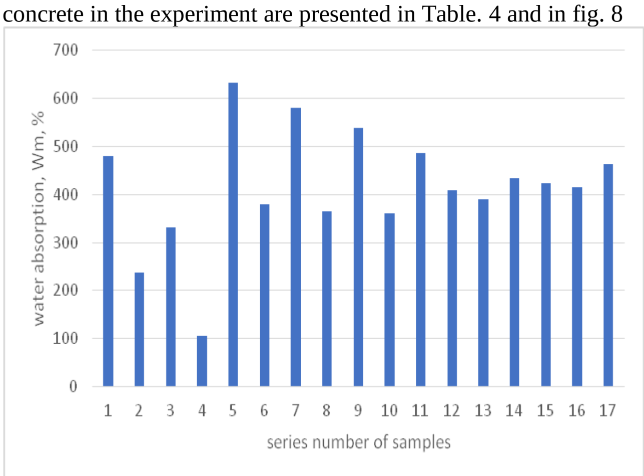

Fig. 8: Diagram of water absorption change in concrete

The diagram analysis shows that the maximum water absorption of 9.86% is observed in concrete batch 4, in which sand is completely replaced with ash slag. Specimens of batch 8, in which sand is not replaced by ash-slag, but other components of concrete are the same, showed the water absorption of 7.26%, which is by 26% lower. This fact confirms that ash slag contributes to increasing the porosity of the concrete and, naturally, reduces the strength, which is shown in Fig. 9.
Obviously, an increase in the porosity of the concrete will reduce not only the strength, but also frost resistance. The results of the concrete samples study for frost resistance are presented in Fig. 9.

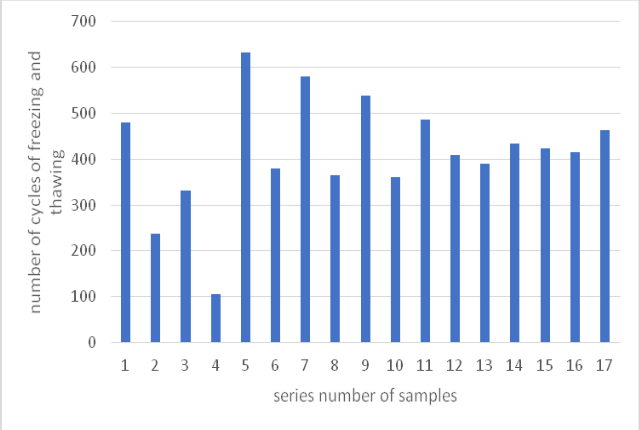

Fig. 9: Diagram of the concretes frost resistance changes

Analogues are compositions number 1 and number 5 with a maximum amount of cement and 4 and 8 with a minimum amount of cement. Frost resistance of samples number 1 is 480 cycles, that of number 8 is 633 cycles. The frost resistance reduction makes 24%. When comparing water absorption of the same compositions, the water absorption increase of composition 1 is 36%.
With the minimal amount of cement, the analogues are compositions 4 and 8. The frost resistance of composition 4 is three times lower than the frost resistance of composition 8. Analyzing the water absorption of these compositions, it can be stated that the water absorption increase of composition 4 makes 57%. It is obvious that the frost resistance of the concrete does not change in proportion to the water absorption change.
In concrete micropores sizing 10-5 cm, usually there is bound water that does not turn into ice even at extremely low temperatures (to -70 °C), therefore micropores do not significantly affect the concrete's resistance to freezing-thawing. The latter depends on the particular macropores and on their structure.
A number of laboratory studies have shown that concrete containing fly ash and ash slag may be less resistant to frost during freezing and thawing [9-12].
Concrete with fly ash can provide satisfactory resistance to freezing-thawing provided waterproof cement is used and W/C (water-cement ratio) does not exceed 0.45. In this case, of course, it is assumed that the concrete has an adequate porous structure [13].
The influence degree of ash and ash slag on the concrete properties depends not only on its amount in the mixture, but also on other parameters, including the composition and ratio of other ingredients in the concrete mixture, the type and size of the particular component, the hardening conditions in the process of molding and hardening, as well construction methods [14,15].
In the studies, all the technological parameters were the same for all batches of samples. The concrete water/cement ratio did not exceed 0.45 due to the use of a plasticizer. Obviously, samples of concrete batch 4 showed the lowest frost resistance because, due to the small amount of cement and the maximal replacement of sand with ash slag, a relatively large macropore structure was formed in which the water freezes when the temperature drops.
Based on the studies performed, optimal compositions of heavy concretes were suggested with the use of ash slag instead of silica sand for manufacture of small road products. All the concrete components provide frost resistance of products not less than 200 cycles, thus meeting the requirements of Ukrainian standards.
The optimal compositions of concretes are presented in table. 4.

Table 4: Optimal compositions of concrete with the use of ash and slag boilers with circulating fluidized bed

No	Class of concrete	Materials consumption per 1 m^3 of concrete mixture					
		Cement, kg	Ballast stone, kg	Sand, kg	Ash slag, kg	Plasticizer, kg	Water, l

3	B25	400	1116	335	335	4.8	200
4	B30	420	1100	320	320	5.0	210
5	B35	450	1068	312	312	5.4	220
6	B40	490	1035	300	300	6.0	248
7	B45	525	1000	290	290	6.3	260
8	B50	580	950	280	280	6.96	290
9	B55	600	900	270	270	7.2	300

4. Conclusions

The results of the studies perform permit to state the following conclusions.
1. In the chemical-mineralogical composition of ash-slags from circulating fluidized bed boilers there are no salts and minerals which can have a negative influence on the process of cement-ash-slag compositions solidification.
2. When the studied cement-ash-slag mixture with water is hardening, there can not be formed minerals of the hydro-sulfoaluminate group, which may have both a positive and a negative effect on the cement stone, depending on their formation period.
3. Replacement of sand as the concrete component with ash-slag causes reduction of the concrete strength and frost resistance due to increased porosity caused by the porous structure of ash slag.
4. The use of synthetic plasticizers of the “Fluid Premia-196” type permits to reduce the negative influence of ash-slag on the properties of concrete by reducing the water/cement ratio and improving the impact of the concrete mixture.
5. The results of the studies performed have permitted to suggest the optimal concrete compositions using ash slags for the production of road products, without reducing their frost resistance.

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