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Mineral binders and concretes based on technogenic waste

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Compositions of alkali-mineral binders based on wastes of alumina industry with application of research physicochemical methods have been developed. It has been established that impregnations with hot $CaCl_2$ solution accelerate the curing time. It has been established that the conditions of hardening significantly influence the physical-mechanical properties. The developed binding materials with a compressive strength of 40.0… 65.1 MPa belongs to hydration-condensation, alkaline-alkaline type. The results of studies on the ash slag influence from circulating fluidized bed boilers on the heavy concrete properties are presented. The studies were carried out using mathematical planning of the experiment. Mechanical concrete properties have been studied using in the study of freeze-thaw resistance, the dilatometry method was applied.

Keywords: alkali-mineral binders, compressive strength, DTA-analyses, fine-grained concretes, industry wastes, IR- spectrum, slags of TPP, X -ray analysis

Мінеральні в’яжучі та бетони на основі техногенних відходів

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Розроблено склади лужно-мінеральних в’яжучих на основі відходів глиноземного виробництва із застосуванням фізико-хімічних методів дослідження. Вивчено процеси твердіння лужно-мінеральних в’яжучих і бетонів на їх основі. Установлено, що просочення гарячим розчином CaCl2 прискорюють термін твердіння. Визначено, що умови твердіння істотно впливають на фізико-механічні властивості й формування структури лужно-мінеральних в’яжучих і бетонів. Доведено, що лужно-мінеральні в’яжучі на основі алюмосилікатних відходів тверднуть у різних умовах. Продуктом їхньої взаємодії є високоміцні, довговічні та водостійкі алюмосилікати, гідросилікати і гідроалюмосилікати. Приготовлено суміші з різним співвідношенням в’яжучого й заповнювача (від 5:1 до 1:5), виготовлено зразки й після термічної обробки виконано випробування за стандартною методикою. Результати випробувань підтвердили, що розроблені в’яжучі дозволяють одержати дрібнозернисті бетони із середньою густиною в сухому стані 1815 – 2311 кг/м^3, межею міцності при стисненні 15 – 28 МПа. Досліджено властивості золошлаків котлів із циркуляційним киплячим шаром. Установлено, що при твердненні цементно-золошлакових смішей протягом 60 діб не утворюються шкідливі новоутворення типу гідроалюмосульфатів кальцію. У дослідженнях використовували портландцемент ППС 500 Н, пісок з модулем тонкості М = 1,05, гранітний щебінь фракцій 5 – 10 мм, пластифікатор «Fluid Premia-196». Дослідження здійснювалися з використанням математичного планування експерименту. При вивченні стійкості до заморозання-відтавання застосовували дилатометричний метод, а для критерію пористості – водопоглинення у вакуумній камері. Зазначено, що зі збільшенням ступеня заміщення піску золошлаками міцність бетону знижується на 3 –10% порівняно з бетонами, що не містять шлаку. У результаті досліджень визначено оптимальні важкі бетонні композиції із застосуванням золошлаків ТЕС.

Ключові слова: DTA-аналізи, дрібнозернисті бетони, золошлаки теплоелектростанцій, ІЧ-спектральний аналіз, лужно-мінеральні в’яжучі, міцність на стиск, промислові відходи, рентгеноструктурний аналіз

Introduction

To date, mankind has accumulated a large number of technogenic wastes, which can be notionally named new deposits. The largest amount of industrial waste is generated by the following enterprises: chemical industry; non-ferrous metallurgy; ferrous metallurgy; power industry; building materials industry; agro-industrial complex; forestry and woodwork and timber industry; textile industry; metal-processing industry, as well as human domestic activities.

Metallurgy is one of the main industries where large amounts of technogenic waste are generated. Some metallurgical wastes have already undergone high-temperature treatment, crystalline structures in the waste have been formed, and they do not contain organic impurities. Other wastes such as those of iron ore enrichment have not yet found their application in construction. Thus, for example, wastes of iron ores, wet enrichment, are still being stored in refuse dumps occupying large areas and polluting the environment. Technogenic products of the metallurgical industry, it is advisable to divide into wastes of ferrous and non-ferrous metallurgy, as well as hydrometallurgy sludge.

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. The 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 people's health all over the world.

The complex technological techniques development allows the waste use from the thermal power stations in the obtaining construction materials technology [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.

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.

Review of the research sources and publications

According to the research publications [1], the utilization rate of thermal power plants waste in CIS countries does not exceed 10 - 13%, whereas in Europe: Germany and Denmark it reached almost 100%, in the UK and Poland – 50 - 70%. This is due to the fact that ashes and slag waste in developed countries are the same commodities as heat and electricity.

The development of sophisticated technological techniques permits the use of thermal power plants waste in the technology of obtaining building materials [2]. The phase composition of the ash slag is mainly aluminosilicate glass and also includes quartz, iron oxides [2]. Blast-furnace slag is mainly used in the cement industry. A great deal of work has been devoted to studying the process of their interaction with the minerals of Portland cement clinker, both domestic and foreign researchers. The expediency of blast furnace slag widespread use in the cement industry has been proven by numerous studies and practical recycling experience [3]. The processes of ashes and ash-slag interaction with the minerals of Portland cement clinker are the subjects of the modern researchers' studies [2, 4 – 7].

Efficient and prudent use of the components that make up mineral composites is an urgent scientific problem.

One of the fields of mineral origin waste management is their use in building materials technology. Some wastes can be used in cement production, while others can be a basis for other types of binders. The idea of producing alkaline-alkaline earth aluminosilicate hydraulic cement, as well as building concretes, belongs to the Ukrainian scholar V.D. Glukhovsky [8].

Today, cement, including slag-alkali binders, is widely used in construction. It is known that slag-alkali binders and concrete based on them are considered to be high-strength, frost-resistant, and durable materials. Slag alkali cement differs from the known compositions by the fact that it can be manufactured based on various industrial wastes and an alkaline composition [9].

In Azerbaijan, the goal of many researchers in the field of building materials technology is to develop composite binders using industrial wastes.

One of the research projects we are carrying out in this field is developed based on alkali-mineral binders and concrete.

Definition of unsolved aspects of the problem

Despite the large number of studies conducted, the utilization of industrial waste in Ukraine remains at a low level compared to European countries. Also, new technologies and, accordingly, new types of waste appear in the industry, which should be studied and areas of their use identified.

The problem statement is to develop an alkaline-mineral binder and high-strength concrete based on industrial waste

Basic material and results

Industrial aluminosilicate wastes from the Ganja Alumina Refinery Plant are used as mineral raw materials for the production of alkaline-mineral binder and concrete. Liquid glass with a density of 1.215 g / cm3 and a silicate module of 2.9 was used as the alkaline component, the chemical composition of which is characterized in percent for weight: Na_2O + $nSiO_2$ – 22.5; SiO_2, 16.87; Na_2O – 5.63; H_2O – 77.5.

It was established that the chemical composition of aluminosilicate waste is characterized by the following oxides in percent for weight: SiO_2 - 65.18; Al_2O_3 18.71; Na_2O –1.70; K_2O – 1.06; MgO 0.60; CaO – 0.72; TiO_2 – 0.21; MnO – 0.07; Fe_2O_3 – 7.56; p.p.p. – 4.76.

Sodium hydroxide NaOH, bentonite clay of the Dash-Salakhly deposit and Portland cement PC 500 of the Garadag plant was used as an additive, and quartz sand of the Imishli deposit of the Azerbaijan Republic with fineness modulus Mkr = 1.56 was used.

The method to accelerate hardening, temperature and the processing mode is important for alkaline-mineral binders. The choice of processing temperature is based on the DTA data (fig. 1).

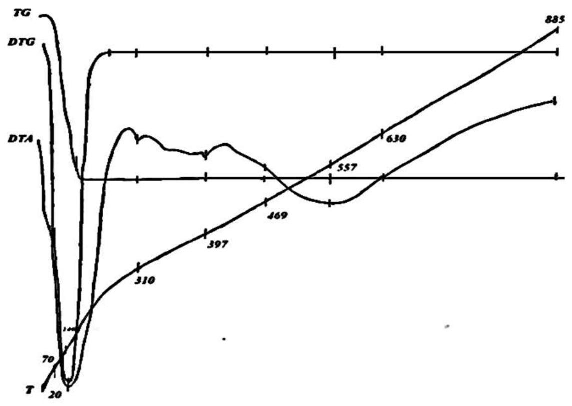

Figure 1 – Thermogram of an alkaline-mineral composition based on aluminosilicate waste

On the DTA curve, two endo-effects are observed having maxima of 70°C (weak) and 140°C (deep). This is because there are weakly coordinating water molecules in the system. In the range from 240°C to 885°C temperature, two particularly weak endo-effects were recorded, having maxima of 310°C and 367°C and one weak endo-effect at 557°C temperature. There is dehydration of the original minerals here. The DTG curve is similar to the DTA curve range from 240°C to 885°C temperature, two particularly weak endo-effects were recorded, having maxima of 310°C and 367°C and one weak endo-effect at 557°C temperature. There is dehydration of the original minerals here. The DTG curve is similar to the DTA curve.

As it can be seen from the TG curves, when a sample is heated from 20 to 885°C, an intensive mass loss of only 56.6% occurs, including 1.2% in the range of 20–70 C, 55.4% in the range of 70–170°C. After a temperature of 170°C, the process stabilizes, and no mass loss is observed.

Based on the DTA results of the initial alkaline-mineral raw material, a treatment temperature of 140 –150°C was adopted for 11 (2 + 7 + 2) hours.

It is known that, along with various hardening accelerators, impregnation with calcium chloride also accelerates the hardening of alkaline-mineral binders, especially since $CaCl_2$ is economically more profitable. Based on a series of experiments on the processing of samples with calcium chloride solutions, the treatment model was established: processing after manufacturing the samples with a hot (60°C) $CaCl_2$ solution with a density of 1.35 g/cm^3 for 1 h, then drying at the temperature of 140 –150°C for 2.5 (0.5 + 1.5 + 0.5) h.

Compositions of alkaline-mineral binders and the conditions of their heat treatment are given in table 1.

Table 1– Optimized composition of alkaline-mineral binder based on alumina silicate waste

№	Hardening conditions	Composition, in percent per weight					Ultimate strength, MPa
		Liquid glass	NaOH	Portlandcement	Clay	Alumino-silicate waste	
1	Chamber drier 140-150°C	35.2	9.7	10.4	8.6	36.1	40.00
2	Air dry flow 140-150°C	32.0	9.4	9.4	8.0	41.2	44.75
3	Impregnation with $CaCl_2$ hot solution 60°C	29.0	8.4	8.4	7.3	46.9	53.23
4	Autoclave 9 atm., temperature 174.5°C	29.1	8.5	9.5	6.1	46.8	65.1

The table shows that binders, hardened in an autoclave have the maximum strength. Processing with a hot solution of calcium chloride provides strength lower than that in an autoclave, but also higher than in other conditions, within the experiment.

Thus, we can conclude that the alkaline-mineral binder based on aluminosilicate waste hardens under various conditions. The product of their interaction is high-strength, durable and water-resistant aluminosilicates, hydro silicates and hydro aluminosilicates. The resulting binder material refers to hydration-condensation binders, such as alkaline-alkaline earth, with ratios of oxides: R_2O - RO - R_2O_3 - SiO_2 = (0.72 ∣1.5): (0.4 ∣0.73): 1: (2 03: 3.2).

At the next stage, the possibility of obtaining concrete based on the developed binder was studied.

A mixture prepared with a different binder/aggregate ratio from 5:1 to 1:5, samples were made and tests were carried out after heat treatment (tab. 2).

Table 2 – Optimized composition of fine-grained concrete based on alkaline mineral binder

№	Hardening conditions	Composition, by weight %						Ultimate compressive strength, MPa	Density, kg/cm^3
		Binder					Sand		
		Liquid glass	NaOH	Portlandcement	Clay	Alumino-silicate waste			
1	Chamber drier 140-150°C	19.6	5.4	5.4	4.6	19.5	45.5	15.73	1815
2	Air dry flow 140-150°C	19.5	5.5	5.3	4.7	24.1	40.9	18.77	2044
3	Impregnation with $CaCl_2$ hot solution 60°C	19.5	5.5	5.45	4.55	30.1	34.9	26.42	2254
4	Autoclave 9 atm., temperature 174.5°C	19.5	5.5	5.46	4.54	30.1	34.9	28.41	2311

The table shows that there is practically no difference between the strength indices of concrete hardened in an autoclave and treated with a hot solution of calcium chloride.

At the next stage, the possibility of obtaining concrete based on slag of circulating fluidized bath of TPP was studied.

The following materials were used in the work: Portland cement PC 500 N (42,5), sand with the fineness modulus $M_f = 1.05$; slag from boilers with circulating fluidized bed; superplasticizer «Fluid Premia-196» based on modified polycarboxylates; as a coarse aggregate - crushed granite fraction of 5–10 mm taken from Kremenchuk deposit. For more complete detection of the slag and studying the hyperplastic bizer's influence on the concrete freeze-thaw resistance and strength, a three-level experiment planning matrix was implemented in the study.

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 slag.

Terms of the experiment planning are presented in the table 3.

Table 3 – 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 consumption	X2	0.8	1.4	2.0	0.6
Degree of sand replacement with ash slag	X3	-1	0	1	0.5

Freeze-thaw resistance was determined by the rapid method. The dilatometry 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.

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.

The chemical composition of the slag is shown in table 4. The properties of the slag were studied using X-ray diffraction (XRD) fig.2 and spectral analysis methods fig. 3.

The table shows that the content of calcium oxide CaO=5, 17%, and silicon oxide SiO_2=48.95%, according to these indicators, the slag can be attributed to acidic. The content of sulfur oxide SO_3 is more than 7% and according to this indicator, the slags are sulfate. The sulfur oxide may be in the composition of the slag in the form of gypsum $CaSO_42H_2O$ or anhydride $CaSO_4$. In both cases, they can react with the aluminate minerals of Portland cement and create hydrosulfite aluminates CA3S31H (ettringite) [14-16]. If they appear after cement hardens, the structure of the cement stone may be destroyed, which may lead to the destruction of concrete.

Table 4 – The chemical composition of the slag

Al	21.91	Al_2O_3	26.89
Si	44.37	SiO_2	48.95
S	6.80	SO_3	7.36
K	6.99	K_2O	3.90
Ca	7.94	CaO	5.17
Ti	1.02	TiO_2	0.81
Fe	9.57	FeO	6.12
Zn	0.04	ZnO	0.04
Mo	0.00	MoO_3	0.00
In	1.36	In_2O_3	0.76
W	0.00	WO_3	0.00

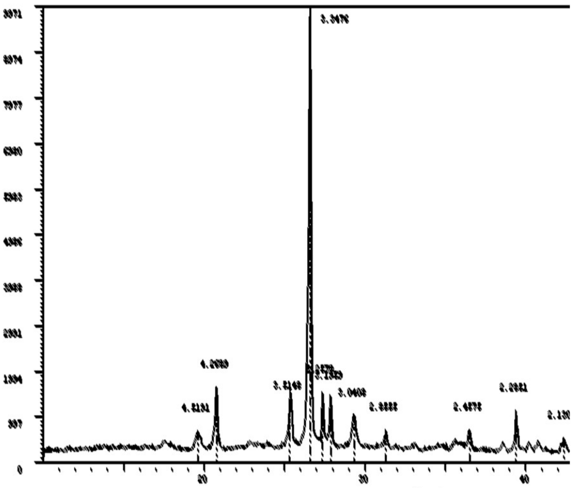

Figure 2 – X-ray diffraction pattern of ash-slag

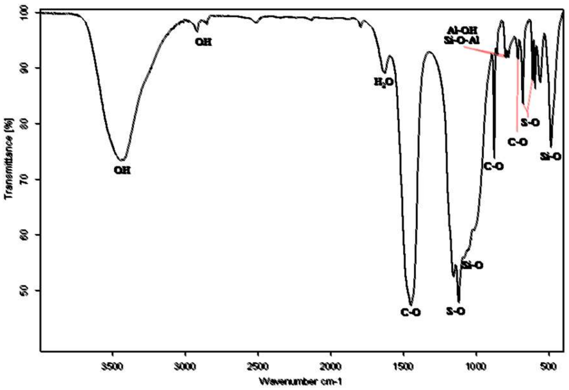

Figure 3 – Spectral pattern of ash slags

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 slag consists of calcium minerals and silicon oxide. With the X-ray diffraction pattern, it is also evident that most of the slags are represented by amorphous structures, which can be combined under the name of vitreous phase, which promotes slag hydration.

The hydraulic activity of slags is associated with the presence of such compounds as lime in a free state or anhydride, which can react with water to form a water-resistant stone without introducing additional activators [7]. 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 slags [7].

The IR spectra of 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 wavenumbers 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 wavenumbers 500–400 cm^{-1}.

The presence of carbonates in the composition of slag is proved by the presence of absorption bands, which are caused by C – O oscillations: valency – an intense band on the wavenumber 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 wavenumbers 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 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 $CaSO_4$ [12].

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 hydrosulfoallluminates, the durability of the product will decrease [6,13].

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 ettringite in the cement stone at the age of two months are absent. Studies of cement-slag stone at the micro-level with a scanning microscope confirmed the absence of needle crystals inherent in hydro sulphoaluminate (figure 5-6).

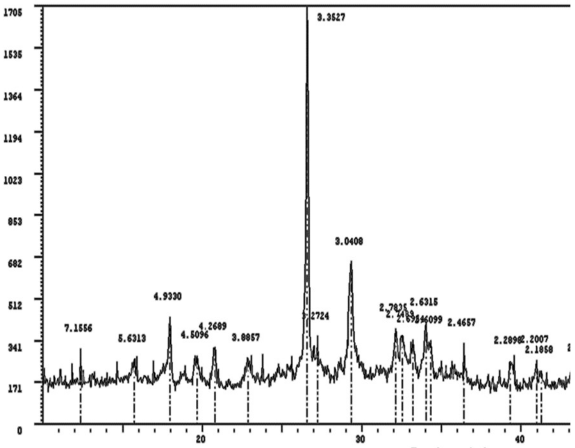

Figure 4 – X-ray diffraction pattern’s fragment of cement-slag stone after hardening for 60 days in wet conditions

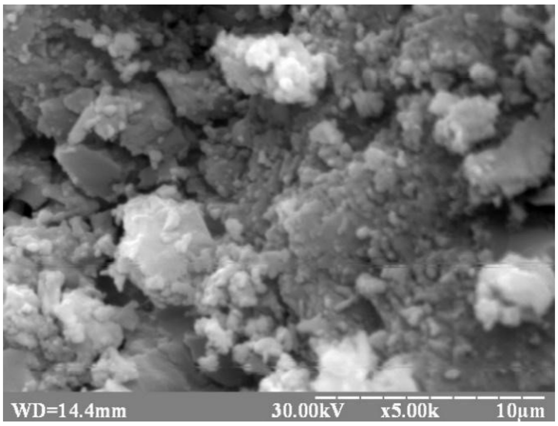

Figure 5 – Electron-microscopic photographs of the cement - slag stone fracture surface after its hardening for 60 days in wet conditions

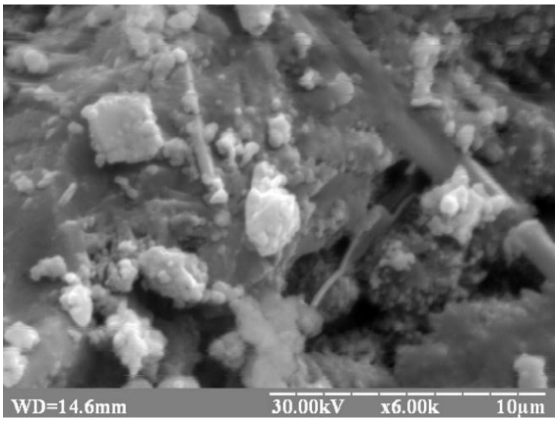

Figure 6 – Electron microscopic photographs of the cement stone fracture surface after its hardening for 60 days in wet conditions

Studying microscopic photographs of a pure cement stone compared to a cement slag stone, we can conclude the following: in a cement stone without slag, there are typical components of a cement stone-like Portlandite and calcium hydrosilicate. In micrographs of cement-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 fig 5.

After no traces of hydro sulfoaluminate were found in the cement-slag stone, concrete samples were prepared according to the matrix of the experimental design (table 5).

Table 5 – Experiment planning matrix

№	x_1	x_2	x_3
1	600	2.0	ash
2	400	2.	ash
3	600	0.8	ash
4	400	0.8	ash
5	600	2.0	sand
6	400	2.0	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	0.5+0.5
12	500	0.8	0.5+0.5
13	500	1.4	ash
14	500	1.4	sand
15	500	1.4	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 (slag) + cement. The components were mixed without adding water for three minutes. In our work, we used a complex additive consisting of the plasticizer “Fluid premia 196” and the hardening accelerator TEMP-3. Dosing of the plasticizer was carried out according to the experimental matrix, and the amount of the hardening accelerator was constant 1% of the mass of cement. A mixture of water, accelerator and plasticizer was prepared in advance. A plasticizer and a hardening accelerator in measured amounts were added to water and mixed with a mixer for 30 seconds. The finished mixture was added to the concrete mixer. Mixing the components lasted 5 minutes. After 5 minutes, the mixture was discharged from the mixer. From the finished mixture, the samples were made in the form of cubes with a side of 10 cm. The samples were compacted using vibration with an oscillation amplitude of 0.5 mm and a frequency of 50 Hz. A day later, samples were taken from the molds. Samples were laboratory cured for 28 days. After 28 days of curing, the samples were tested according to the experimental matrix.

The results of the samples testing for compressive strength are presented in Table 6 and fig. 7.

Table 6 – Properties of concretes

Batch	Compression strength N/mm^2	Water absorption W$_m$, %	Frost resistance, cycle
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

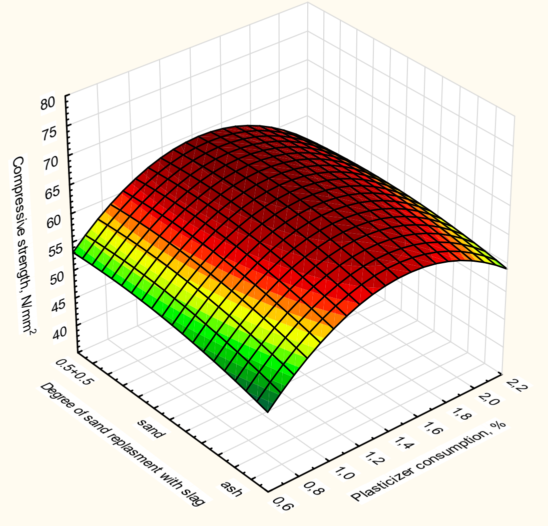

Figure 7 – 3D Surface Plot of strength against the degree of sand replacement with slag and Plasticizer consumption

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.

The fact of the strength reducing at the compression of the sample with increasing the sand replacement degree with slag can be explained by the fact that the slag is not so strong a mineral like quartz. Grains of slag have internal pores reducing their durability. The reduction of concrete strength is associated with the increased porosity.

Analysis of 3D Surface confirms that with increasing substitution of sand by slag, concrete strength decreases slightly. With an increase in the consumption of plasticizer to 1,4 – 1,6%, the strength of concrete increases. With a further increase in the consumption of plasticizers, the strength decreases. This fact can be explained by the fact that a large amount of plasticizer increases the plasticity of the concrete mixture and at the same time sedimentation of the mixture occurs.

Increasing porosity leads to an increase in water absorption. The results of research on water absorption of concrete in the experiment are presented in Table 6 and fig. 8.

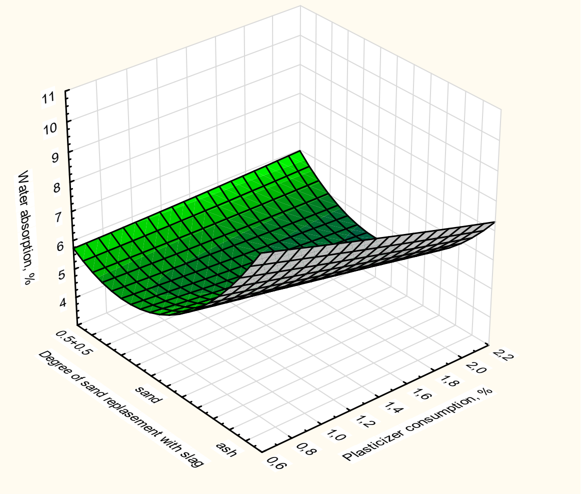

Figure 8 – 3D Surface Plot of water absorption against the degree of sand replacement with slag and Plasticizer consumption

The 3D Surface analysis shows that the maximum water absorption of 9.86% is observed in concrete batch 4, in which sand is completely replaced with slag. Specimens of batch 8, in which sand is not replaced by slag, but other components of concrete are the same, showing the water absorption of 7.26%, which is 26% lower. This fact confirms that slag contributes to increasing the porosity of the concrete.

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.

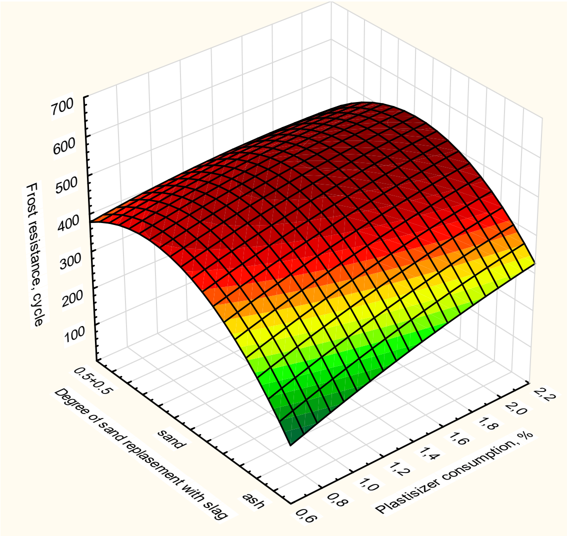

Figure 9 – 3D Surface Plot of frost resistance against the degree of sand replacement with slag and Plasticizer consumption

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 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 [17–19].

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 [20].

The influence degree of ash and ash slag on the concrete properties depend 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 [21].

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 the 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 7.

Table 7 – Optimal compositions of concrete with the use of ash and slag boilers with circulating fluidized bed

No	Class of conc.	Materials consumption per 1 m^3 of concrete mixture					
		Cement, kg	Crushed stone, kg	Sand, kg	Ash slag, kg	Plasticizer, kg	Water, liter
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	6.9	290
9	B55	600	900	270	270	7.2	300

Conclusion

The results of the studies permit the following conclusions.

1. Alkaline-mineral binders have been developed using local industry waste (liquid glass, NaOH, Portland cement, clay, aluminosilicate waste), hardening under various conditions; various factors influence the construction and technical properties of alkaline-mineral systems based on alumina production waste was studied and the composition of the alkaline-mineral binder was optimized.

2. It has been established that the hardening conditions have a significant effect on the physical-mechanical properties and structure-forming of alkaline-mineral binder and fine-grained concrete.

3. The compositions of fine-grained concrete based on alkaline-mineral binders and river sand have been developed, hardening under various conditions with the following physical-mechanical properties: mean dry density 1815.9 ... 2311.2 kg / m3, compressive strength 15.73 ... 28.41MPa.

4. It was established that in the chemical and mineralogical composition of the ash and slag of boilers with a circulating fluidized bed there are no salts and minerals that can adversely affect the hardening of cement-ash and slag compositions.

5. The results of X-ray diffraction analysis and microscopic studies prove that when hardening cement with slags, compounds such as hydrosulfite aluminates that can destroy concrete are not formed.

6. The use of slag as a fine aggregate in concrete leads to a decrease in strength by 3-5% and helps to reduce the water-cement ratio, which leads to an increase in the strength of concrete.

8. As a result of the studies, the optimal compositions of concrete were selected using slags as fine aggregate

9. It is advisable to use slag of boilers with a circulating fluidized bed as a fine aggregate in concrete in areas of their accumulation in terms of improving the environmental situation.

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