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Dmytriieva N.,
Agafonova I.,
Bostan N.

RESEARCH FOR MODIFICATION OF CONCRETE WITH ASH-CONTAINING WASTE OF DNISTROVSKA PSPS (UKRAINE)

The object of reseaerch is concrete samples modified with ash-containing fillers and plasticizers. As practice shows, the use of secondary resources is an important issue in the field of construction and entails significant savings. The issue is also considered from the point of view of environmental protection. The study is aimed at determining the effect of modification of concrete with ash-containing waste on the strength characteristics using the example of the hydroelectric power station of the Dnistrovska PSPS (Sokyriany district, Chernivtsi region, Ukraine). The main hypothesis of the study is the assumption that varying components such as fly ash, water glass, and superplasticizers will make it possible to obtain concrete with specified strength characteristics. To achieve the aim, the authors decided to use in the study the superplasticizer SikaPlast-520N and BETO-plast, Portland cement M400 and sands of the quarries of the Parkan and Suklei regions (Moldova). According to the plan of the experiment, studies of the influence of hardening conditions on the structure and properties of modified concrete samples were carried out. Destructive testing of samples was carried out in the laboratory directly on a hydraulic press.

The results of experiments without the addition of liquid glass and the introduction of a minimum amount of fly ash and experiments with the introduction of a minimum amount of fly ash and the addition of 3 % water glass are presented. To determine the dynamics of strength gain, tests were carried out on 7, 14 and 28 days. The presented results of the study of the samples on day 7 show a gain of more than 50 % strength. This indicates the possibility of reducing the curing period of structural concrete in the formwork system. A more complete and objective idea of the quality of concrete is possible while taking into account the average strength of concrete and its homogeneity.

Today, there is no unified theory that can relate the different properties of cement and filler to the final properties of a composite material. The issue of modifying concrete compositions when using fine aggregate from other quarries requires additional research. At the same time, the results of the experiment show that the use of microfillers based on wastes from the Dnistrovska PSPS provide ample opportunities not only for saving binders, but also for improving the physical, mechanical and operational characteristics of concrete.

Keywords: *ash-containing waste, concrete modification, fly ash, concrete strength, Portland cement, superplasticizer.*

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1. Introduction

The use of secondary mineral resources is a topical area of the construction industry, providing an increase in the structural quality of materials, while saving the constituent components of materials, energy and labor costs. The issue of ecology is also important, since modern energy is a source of a large amount of waste, for example, ash and slag, which causes significant harm to the environment. The amount of fly ash produced worldwide is estimated at about 780 million tons per year [1, 2]. The problem of ash and slag waste dumps (ASW) is raised in many countries of the world, since they often occupy large areas. They are thus a source of environmental pollution, posing a threat to people, flora and fauna of the surrounding areas. At present, for example, the share of used ash and slag waste in Ukraine is about 1 %, in Russia – 10 %, and the USA – about 20 % of ash and slag waste. European countries, where industrial symbiosis is highly developed, use about 70% of the generated ash and slag waste: in the UK – 60 %, in Germany – 72 %, in Finland – 84 % [3]. In Moldova, based on the analysis of statistics [4], in 2017 about 396 thousand tons of waste was generated (in 2016 – 313 thousand tons), of which: 211 thousand tons of toxic waste and 185 thousand tons (740 106 m^3) municipal solid waste (MSW) [5].

The above figures confirm the relevance of the issue of recycling ash and slag waste on an industrial scale and require additional research on the modification of concrete compositions with local components or secondary industrial products. This is of practical importance both for the building materials industry and the ecological situation in the republic.

Thus, *the object of research* is concrete samples modified with ash-containing fillers and plasticizers. And *the aim of research* is to consider the effect of modifying concrete with ash-containing waste on the strength characteristics on the example of the hydroelectric power station of the Dnistrovska PSPS (Sokyriany district, Chernivtsi region, Ukraine).

2. Methods of research

To achieve this aim, studies of concretes based on liquid glass and fly ash were carried out using: superplasticizer SikaPlast-520N and BETO-plast, Portland cement M400 and sands of the open-cast mines of the Parkan and Suklei regions (Moldova).

Studies of the effect of hardening conditions on the structure and properties of modified concrete samples were carried out according to the experimental plan. A series of samples were made, in the form of cubes with dimensions of 10×10×10 cm for the three variable factors presented in (Table 1).

Table 1

Levels of variable factors

Variation factor levels	Name of factors		
	The amount of fly ash, % by weight of cement	The amount of C-3, % of the mass of the solution	Liquid glass, % of the solution mass
	X1	X2	X3
–1	10	0.3	0
0	20	0.65	3
+1	30	1	6

For the stages of the experiment, plans were developed for each stage of research. Conventionally, they can be called the letters A1 (sand of the Parkan quarry) without adding liquid glass and introducing a minimum amount of fly ash and A2 (sand of the Suklei quarry) using: superplasticizer SikaPlast-520N, as well as B1 (sand of the Parkan quarry) and B2 (sand of the Suklei quarry) – superplasticizer BETO-plast.

The method of processing the research results consisted in the analysis and generalization of the constructed diagrams of the dependence of the influence of variable factors on the compressive strength of the material.

Before making the samples, the inner surfaces of the molds were thoroughly cleaned and coated with a thin layer of grease that does not stain the surface of the samples and does not affect the properties of the concrete surfaces. After filling the mold with an excess of concrete, it is installed and rigidly fixed on the vibrating platform and vibrated until it is completely compacted, and with the help of the cement paste that appears, the surface is smoothed with a trowel (Fig. 1).

Fig. 1. Production of concrete samples

After manufacturing, the samples were stored for 24 hours in molds covered with a damp cloth in a room with an air temperature of +20±2 °C. After that, the samples were taken out of the mold, marked and held until the test in a normal hardening chamber at a temperature of +20±2 °C and a relative humidity of 95–100 %.

3. Research results and discussion

Multicomponent concretes are now getting more and more practical application, which include: binder, coarse and fine aggregates and fillers (chemical and mineral additives).

In recent years, a great deal of experience has been accumulated in the use of waste heat power engineering, such as ash and slag, as mineral additives in the manufacture of mortars and concretes.

The doctrine of V. Jung is considered to be the scientific justification for the possibility of using microdispersions (MD) in the composition of cement. He developed the concept of cement stone, called it «micro-concrete» and substantiated, in fact, that the hardened cement stone contains a large amount of unreacted cement grains, which can be changed without loss of strength by the corresponding fractions of MD [6].

The main provisions for the use of finely dispersed MD in cement systems were laid by the authors of [6, 7]. The development of this scientific direction was continued by the authors of studies [8, 9].

So, the secondary use of ash and slag waste of JSC «Moldavska PS» in 2017 by other enterprises amounted to 25.931 tons (in 2016 – 22.846 tons) [4].

The main direction of using ashes and slags in the construction complex is their replacement of part of Portland cement [10]. At the same time, a number of ashes have unsatisfactory characteristics when used instead of part of the binder. Therefore, it is necessary to look for other directions for the effective use of ash, as well as to study the mechanism of their effect on the structure and properties of concrete.

The mechanism of the effect of the ash-containing mixture on the structure and properties of concrete when replacing a part of the mass fraction of fine aggregate, the effect of the water-cement ratio and hardening conditions is not fully understood.

The main indicator of the quality of structural concrete is its strength. Compressive strength is the most important classification indicator characterizing the technical properties of concrete. It is known that the variability of the strength characteristics of concrete is of a random nature and obeys the probabilistic and statistical laws [11].

The main hypothesis of the study is the assumption that varying components such as fly ash, water glass, and superplasticizers will make it possible to obtain concrete with specified strength characteristics.

The testing of samples by destructive methods was carried out in the laboratory directly on a hydraulic press of the PSU-125 type (Russia), undergoing pressure testing with a gradual, uniform increase in the load (Fig. 2–5).

In laboratory studies, the following characteristics of the components of multicomponent concrete were determined:

- sand moisture – 5 %;
- sand size modulus – 2.3;
- bulk density of sand – 1400 kg/m^3;
- bulk density of crushed stone – 1280 kg/m^3;
- modulus of the size of the ash-containing mixture of the state district power station – 1.4.

To determine the dynamics of strength gain, tests were carried out on days 7, 14 and 28.

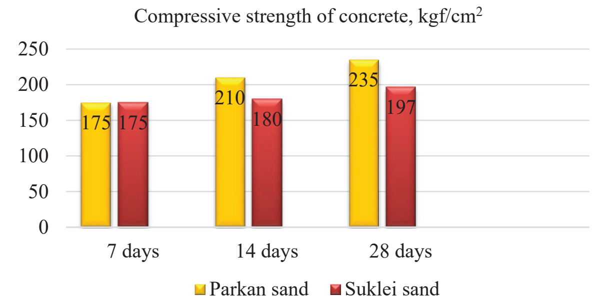

Fig. 2. Diagram of concrete compressive strength gain of the compositions of experiment A1 with the introduction of the minimum amount of fly ash

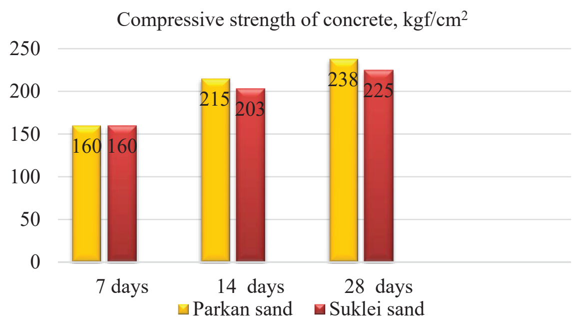

Fig. 3. Diagram of concrete compressive strength gain of the compositions of experiment A2 with the introduction of the minimum amount of fly ash

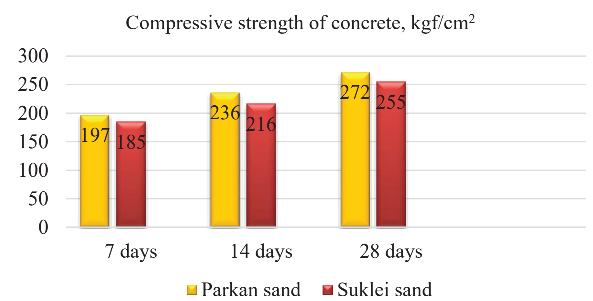

Fig. 4. Diagram of the compressive strength of concrete samples of experiment B1 with the introduction of a minimum amount of fly ash and the addition of 3 % water glass

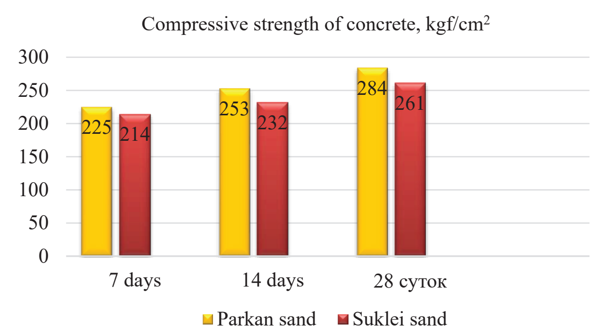

Fig. 5. Diagram of the compressive strength of concrete samples of experiment B2 with the introduction of a minimum amount of fly ash and the addition of 3 % water glass

The research results show that the strength characteristics of the samples prepared using the sand of the Parkan open-pit mine are higher than those using the sand of the Suklei open-pit mine.

It should be noted that on the 7th day all the samples show 50 % of the strength gain of the indicators on the 28th day, which indicates the possibility of reducing the curing period of structural concrete in the formwork system. According to the regulatory framework: SNiP PMR 52-01-02*«Concrete and reinforced concrete structures»; DBNV.2.6-98:2009 and DSTU BV.2.7-176:2008 [12, 13] indicators of concrete axial compression strength of specimens of experiments B1 and B2 correspond to class according to B20 (C16/20), specimens of experiments A1 and A2 – B15 (C12/15).

Today, there is no unified theory that can relate the different properties of cement and filler to the final properties of a composite material. Different researchers give different amounts of the optimal filler content. Determination of the composition, ratio and degree of preparation of the components is experimental. At the same time, the results of the experiment show that the use of microfillers based on wastes from the Dnistrovska PSPS provide ample opportunities not only for saving binders, but also for improving the physical, mechanical and operational characteristics of concrete.

4. Conclusions

Under normal humidity conditions of hardening, when part of the fine aggregate is replaced by fly ash, the mechanism of influence on the structure, associated with the optimal distribution of particles by size, prevails. But fluctuations in strength are present in both test lots, therefore a more complete and objective idea of the quality of concrete is possible while taking into account the average strength of concrete and its homogeneity. Therefore, the issue of modifying concrete compositions requires additional research. In this case, samples with strength indicators closer to the average are characterized by a higher homogeneity of concrete in terms of strength.

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Dmytriieva Nina, *PhD, Associate Professor, Department of Construction Technology, Odessa State Academy of Civil Engineering and Architecture, Ukraine, ORCID: http://orcid.org/0000-0002-4828-1644, e-mail: dmitrieva.nv76@gmail.com*

Agafonova Irina, *Senior Lecturer, Department of Civil Engineering and Economics, Bender Polytechnic Branch of Transnistrian State University named after T. G. Shevchenko, Moldova, ORCID: http://orcid.org/0000-0003-4330-2642, e-mail: barkaririna@bk.ru*

Bostan Nina, *Senior Lecturer, Department of Civil Engineering and Economics, Bender Polytechnic Branch of Transnistrian State University named after T. G. Shevchenko, Moldova, ORCID: http://orcid.org/0000-0003-4336-6398, e-mail: boniqa@mail.ru*

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Kontsevoi A., Kontsevoi S.

MODELING OF A TWO-FLOW GAS PURIFICATION FROM CARBON OXIDES (IV) BY METHYLDIETHANOLAMINE SOLUTION

The object of research is the stage of purification of process gas of ammonia production with a capacity of 1360–1500 t/day in a two-section plate absorber. The paper substantiates the possibility to replace the monoethanolamine (MEA) absorbent solution with the activated solution of methyl diethanolamine (aMDEA) on the example of the Ukrainian multi-tonnage production, working under the two-flow purification scheme. One of the most problematic areas is the lack of a mathematical model for the absorption of carbon monoxide (IV) by a new absorbent for two-flow purification schemes. In the course of the study, the method of compiling the material balance was used, which takes into account the peculiarities of the interaction of the aMDEA components with CO_2, and numerical integration to calculate the number of plates.

An algorithm for calculating material and heat balances for finely and roughly regenerated solutions has been developed and implemented in Excel. The algorithm and the program provide for multivariate calculations with varying concentration parameters for gas and solution and their temperature. Thermal calculations take into account the adiabatic heating due to the exothermic absorption reaction and determine the temperature of the solutions at the outlet of each part of the absorber. Analysis of the material balance calculations in comparison with the data on the MEA solution shows a decrease in the solution consumption by 5.5 % when using aMDEA, which will help to reduce the energy costs for pumping and regeneration. By kinetic calculation, the number of plates for the absorber was determined to be 13. With the number of 15 in a standard absorber, the calculated number of plates allows the gas to be purified to a content of 0.01 % CO_2. An increase in the temperature of the solutions at the inlet to both sections by 10 degrees does not significantly affect the number of plates. Thus, mathematical modeling of a two-section plate absorber showed a real possibility of replacing an 18 % MEA solution with a 40 % aMDEA solution. It is proposed to implement this on existing equipment without changing the technological scheme.

Keywords: *process gas, carbon monoxide (IV), methyldiethanolamine, piperazine, two-section plate absorber, numerical integration.*

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1. Introduction

Purification of process gas from carbon monoxide (IV) in the production of ammonia is traditionally carried out by chemisorption methods, first of all, with a solution of monoethanolamine (MEA) or a hot solution of potash K_2CO_3, activated with diethanolamine. The chemistry of purification by these methods is provided in [1]. Technological schemes, apparatus designs are considered by the authors of works [2, 3]. A comparative analysis of purification methods is provided in [4, 5].

In the XXI century, a purification method was proposed using a solution of methyldiethanolamine (aMDEA) with a concentration of up to 50 %, activated with piperazine $C_4H_{10}N_2$ (diethylenediamine) with a concentration of up to 5 % [6]. The advantage of MDEA is easy regeneration