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Study of Physicochemical Properties of Polystyrene Concrete Based on Fly Ash and Water from Hydro-Ash Removal Facilities

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The article is devoted to improving the physical and chemical characteristics of polystyrene concrete by the means of adding industrial waste, thereby reducing the negative impact of ash and slag waste from thermal power plants (TPPs) of Kazakhstan on the environment. Fly ash, generated in large quantities as a result of fuel combustion at power plants, negatively affects the environment, polluting the air, soil, sewage, etc.
The article presents the results of the study of the chemical composition of ash and slag waste. Possible ways of ash utilization are considered. Also, the effects of adding the fly ash and water from hydro-ash removal facilities on the physical and mechanical characteristics of cement was investigated. For this purpose, samples with the addition of 5-10-15 % of fly ash by a weight of the prepared cement mixture. All samples of 3-7-28 curing days were tested. In the article standardized methods of cement dough testing were implemented: determination of standard consistency, setting time of cement dough, and determination of physical and mechanical parameters of concrete specimens in accordance with normative documents. The results of studies of the physical and mechanical properties of cement dough with the addition of fly ash from the ash dump and water from the hydro-ash removal facilities of TPP (thermal power plant) are given. The results of studies of standard consistency, setting time of cement dough, as well as tests of concrete compressive strength are given.

1. Introduction

Polystyrene concrete is a composite material, which includes Portland cement and its varieties, silica aggregate (silica sand or fly ash from thermal power plants), porous aggregate, which is polystyrene foam granules, as well as modifying additives (setting gas pedals, plasticizers, etc.). The use of polystyrene foam as a filler is characterized by weight reduction and improvement of thermal insulation properties of the composite material (Junkil Park Min Ook Kim, 2020). Polystyrene granules have a smooth surface to which cement does not adhere well. Therefore, the concrete turns out to be low-strength. In order to eliminate this disadvantage, active mineral additives are added to the mixture: ground slag, fly ash or silica. Their purpose is to improve the properties of the material (Laukaitis A. et al., 2005). In this article, fly ash is used instead of additives, and water from hydraulic ash collectors is used instead of ordinary water. Application of fly ash containing micro- and nanodispersions in cement compositions to replace part of cement leads to increase of plasticity of cement dough and improvement of compressive strength. In addition, as a result of redistribution of volumetric changes by addition of fly ash and water from the hydraulic ash trap channel, cracking is reduced. Fly ash in dry form has no binding properties. It is activated after it interacts with the cement binder component. Thus, cement consumption during concrete mix preparation is reduced to a large extent (Iyer R.S. and Scott J.A., 2001).
Every year a large amount of ash and slag waste (fly ash) emissions from thermal power plants increases. Currently, the world's annual production of ash and slag waste is about 750 million tons, and it is expected that in the near future this amount of waste will increase. This fact is one of the serious environmental problems associated with the threat to public health and environmental safety (damage to soil, plants, and atmosphere).

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Fly ash can even get into the soil and pollute groundwater with heavy metals. About 8 % of ash from coal ash and slag waste produced by Combined Heat and Power Plants (CHPPs) is recycled in Kazakhstan (less than 1.9 million tons).
The Republic of Kazakhstan ranks 8th in the world in terms of proven coal reserves, contains 3.4 % of the world's reserves in the subsoil, and is one of the ten largest coal producers in the world market. Utilization of massively produced ash from deposits is an urgent problem. One of the ways of its solution is its utilization in concrete production. An increase in environmental safety implies a reduction in the consumption of natural raw materials in concrete production and a reduction of industrial waste (Yao Z.T. et al., 2015).
The purpose of this study is to investigate the chemical composition of fly ash from ash dumps of thermal power plants, as well as the effect as an additive on the structure and properties of cement stone (Blissett R.S., Rowson N.A., 2012).
At present, the increase in requirements for the level of thermal insulation of building envelopes leads to the improvement and development of new materials and products (Reis J. et al., 2021). Such a material can be polystyrene concrete, which has good thermal insulation properties. However, polystyrene concrete based on cement binder is a complex system in which polar liquid (water) does not wet the hydrophobic surface of the aggregate - granular expanded polystyrene (Gu L., Ozbakkaloglu T., 2016). The use of "Fly Ash" containing micro- and nano-dispersions in cement compositions is known for replacing part of the cement, increasing the plasticity of cement dough and its' hardening. Introducing "fly ash" is expected to promote better adhesion of hydrate neoplasms on polystyrene. Therefore, it is necessary to conduct a research on the development of cement compositions with polystyrene and fly ash (Wang R., Meyer C., 2012).
Depending on the material, and fractional composition of fly ash and water from the hydro-ash removal facilities, the addition of ash to cement can affect the properties of the resulting material in different ways. Ash can affect the hydration and hardening of cement as well as the strength of the product. In some cases, fly ash increases the standard consistency and plasticity of the cement batter, making it easier to handle during construction (Zhang X.D., Han Y., 2016). The complex crystallization processes of cement play a crucial role in the strength of materials and the durability of the resulting material. The structure of the hydrated cement mass can influence the porosity, permeability, and mechanical properties of concrete.

2. Materials and Methods

Fly ash from the ash dump of Petropavlovsk TPP (Kazakhstan) was used in this study. Portland cement, M400 (JSC “Kokshetau Cement”, Kokshetau, Kazakhstan). Water from the hydro ash-removal facilities (CHPP JSC "Aluminum of Kazakhstan). Polystyrene granules, 5 mm in diameter, 5 % of cement weight. Polystyrene granules were pre-packed into cubic molds. M400 cement (15-20 % of the total weight) was mixed with ash (5 to 15 % of the cement weight). Superplasticizer was added to water in the amount of 0.05 to 0.2 % of the total weight of cement mixture, mixed and gradually added to the cement mixture.
After casting into 100 mm × 100 mm × 100 mm molds, the polystyrene granules and foam cement composite were cured for 28 days under ambient conditions.
To investigate the potential utilization of ashes sampled from ash dumps and ash collectors, the elemental composition was determined using an Epsilon 1 X-ray fluorescence spectrometer (Malvern Panalytical, Malvern, UK). An X-ray tube with a set of primary filters (U = 50 xB, I" = 0.5 mA; maximum power 5 VA; anode material - silver) was used as a source of X-ray radiation in the spectrometer.
Following cement dough tests were carried out in this research: determination of standard consistency, setting time of cement dough and determination of physical and mechanical parameters of concrete samples in accordance with normative documents. Samples were molded according to GOST 30744-2001 (Cements. Methods of testing with using polyfraction standard sand). Samples of cement composition were prepared, as a binding material using Portland cement, meeting the requirements of GOST 10178 (Portland cement and Pportland blastfurnace slag cement. Specifications), GOST 31108 (Common cement. Specifications), as fine and coarse aggregates used sand, meeting the requirements of GOST 8736-2014 (Sand for construction works. Specifications). All molded specimens hardened under normal conditions at temperature (20±3) ° and relative humidity (95±5) %. A laboratory mixer (SL-5) was used for mortar mixing, which provides all the necessary functions for mixing cement mortar in accordance with the standard. Determination of standard consistency and setting time of cement (or types/blocks if cement) was carried out on Vick's device according to GOST 310.3-76 (Cements. Methods for determination of standard consistency, times of setting and soundness).
Determination of flexural and compressive strengths were carried out on a hydraulic press PGM-100 MG4A. Specimens were prepared from cement and were tested according to GOST 310.4-76 (Cements. Methods of bending and compression strength determination).

3. Results and Discussion

For a purposeful use of fly ash and ash residue as a raw material, and for a safe storage and utilization of ash and slag waste (ASW), it is necessary to have information about their properties and characteristics (Szczerba J. et al., 2019).
Chemical properties of ash and slag ash vary greatly depending on the type of coal, combustion temperature, combustion technology, air/fuel ratio, and coal particle size. The main macroelements of ash include Si, Al, Fe, O, Ca, Ti, Mg, S, K, and Na, which make up to 98-99 % of ash and slag waste. Also, ashes contain various trace elements in concentrations of 0,1 % and less. Part of trace elements such as Sr, Ba, Sc, Y, La, Ti, Zr, etc. is concentrated in slag during coal combustion. At temperatures above 1000 ˚C, some elements volatilize from the high temperature zone and settle in electrostatic precipitators, cyclones (at 110-120 ˚C). To study the composition of fly ash (powder) and water from the hydro-ash removal facilities of the ash dump of TPP (liquid) (Petropavlovsk, Kazakhstan) 5 samples were taken for each investigated sample.

Table 1: Composition of ashes from the Astana CHPP.

Element	Sample №1, % by weight (**Powder**)	Standard deviation values	Sample №2, % by weight (**Liquid**)	Standard deviation values
Al	10,763	1.0982179	10,377	1.1340931
Si	17,240	1.2933324	18,798	2.2719781
P	0,720	0.2246206	1,778	0.4569651
Cl	0,014	0.0324343	1,228	0.5103225
K	0,188	0.0246502	2,451	0.5164449
Ca	4,560	0.5427615	2,055	0.5512495
Ti	0,255	0.3763456	4,213	0.3500752
Mn	1,250	0.5964109	0,060	0.2389435
Fe	11,633	0.8165218	6,240	0.6279092

As can be seen from the analysis results, fly ash samples contain macroelements Al, Si, Ca, Fe, Mn, K, Ti and trace elements P, Cl, V, Cr, Cu, Zn, Ga, As, Rb, Sr.
The results show a solid confidence in evaluated average concentrations of macroelements, as most of calculated standard deviations fall into 68% interval of normal distribution. While only low-concentrated Mn macroelement shows higher degree of variance.
Fly ash particles are spheres and aggregates of compact shape with particle sizes ranging from 10 to 100 microns. From the above data it can be concluded that this sample is very finely dispersed.
Fly ash contains silicon dioxide (SiO), calcium oxide (CaO), aluminum oxide (AlO) and iron oxide (FeO). The components vary depending on the type of coal burned.

(a) (b)

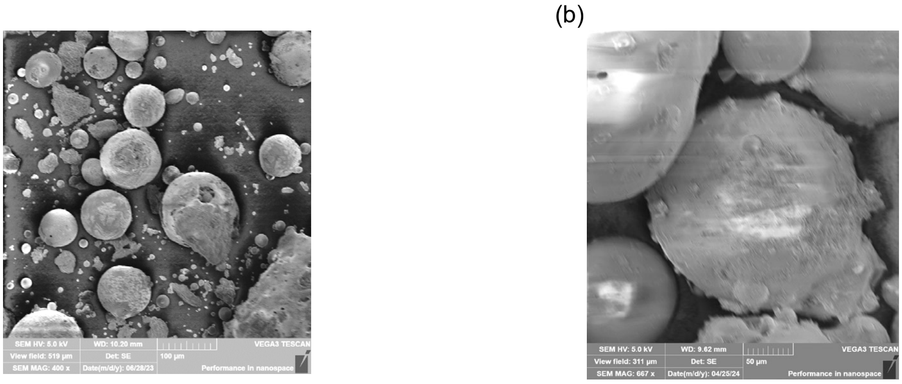

Figure 1: Microphotograph of fly ash (a) at x400 magnification; (b) at x1000 magnification

As shown in Figure 1, fly ash is formed as a result of rapid cooling of molten ash. Hence, most of the fly ash particles are in amorphous state. Fly ash particles are generally spherical in shape with diameters ranging from less than 1 μm to 150 μm, while cement particles are less than 45 μm in size. This spherical shape and particle size increases the flowability of the concrete mix and reduces the water requirement.

Studies (Wu H.-C., Sun P., 2007 and Xuhang, L. et.al., 2023) on the determination of the standard consistency of cement dough containing fly ash additives are of considerable interest. The standard consistency of the dough characterizes the water demand of cement and is a prerequisite for determining its setting time.The results of the study are summarized in Table 2.

Table 2: Results of the study to determine the standard consistency of cement dough

Sample	Standard consistency, %	Initial setting time (hour, minutes)
Control sample, Portland cement M400	27,75%	3 h. 28 min.
cement+3% fly ash	27,7%	3 h. 24 min.
cement+5% fly ash	26,25%	3 h. 18 min.
cement+8% fly ash	25,5%	3 h. 20 min.
cement+10% fly ash	25,25%	3 h. 16 min.
cement+15% fly ash	24,05%	3 h. 02 min.

Table 2 shows that increasing the amount of fly ash to 15 % reduces the amount of water for mixing cement dough by 3 %. Fly ash has an effect on the standard consistency of cement dough, which will affect the reduction of shrinkage due to the water-soluble effect of fly ash and reduce the risk of thermal cracking as a result of reduced heat release.Studies on the determination of standard consistency showed that the best results belong to the samples with 10 % and 15% fly ash addition respectively. Initial setting times were reduced by 30 minutes with the addition of 15% fly ash.

With an increasing dosage of ash as aggregate, the compressive strength increased as compared to the control specimen as shown in Table 3.

Ten samples were prepared for each set test period. The prism samples were placed in the testing machine and loaded to failure at a constant rate of load increase (0.05±0.01) MPa/s. The pre-made sample is placed between the press platforms in the prescribed manner: the cube is placed with its face on the lower base plate in such a way that the pressure exerted by the press on the cube is equal at each point of the surface. It is necessary to measure the sample with a ruler and record the data to the nearest 1 millimeter. It is also necessary to weigh the sample. The results are recorded on the screen of the press (GOST 10180-2012 Concretes. Methods for strength determination using reference specimens).

Table 3: Compressive strength test results

No.	Sample	Fly ash, %	Plain water, ml	Ash trap water, ml	Addition of plasticizer to the weight of cement,%	Curing time, days	Compressive strength, MPa	Standard deviation values
1	Control sample (M400)	0	225-250	-		3	10,8	0.6852489
2		0	225-250	-		7	15,9	1.169994
3		0	225-250	-		28	19,6	1.6686899
4	With fly ash	10	-	225-250	0,05-0,2%	3	8,5	1.240325
5		15	-	225-250	0,05-0,2%	3	10,0	1.5253216
6		10	-	225-250	0,05-0,2%	7	12,0	1.1042672
7		15	-	225-250	0,05-0,2%	7	15,2	1.2096471
8		10	-	225-250	0,05-0,2%	28	24,8	1.2252208
9		15	-	225-250	0,05-0,2%	28	27,3	1.1636864

Analysis of the results of physical and mechanical tests showed that in the first 3-7 days of curing, the introduction of fly ash in an amount of up to 10 % caused a decrease in the cement strength of a sample. After 28 days, the fly ash added specimens had a strength 7 % higher than the control specimens. The slow growth in strength of cement with fly ash is due to slower hydration processes. The final stable structure in such cement is reached later than in conventional cement mixtures. Relatively low standard deviation values show that the measurements have a reliable consistency.

Szostak B. and Golewski G.L. mentioned (2020) that during the early curing periods, water-thick interlayers filled with $Ca(OH)_2$ crystals were observed between cement particles and ash, which is also in agreement with other studies (Maria, H. et.al., 2022). Figure 2 shows microphotographs of hardening of ash-based cement specimens.

(a) (b)

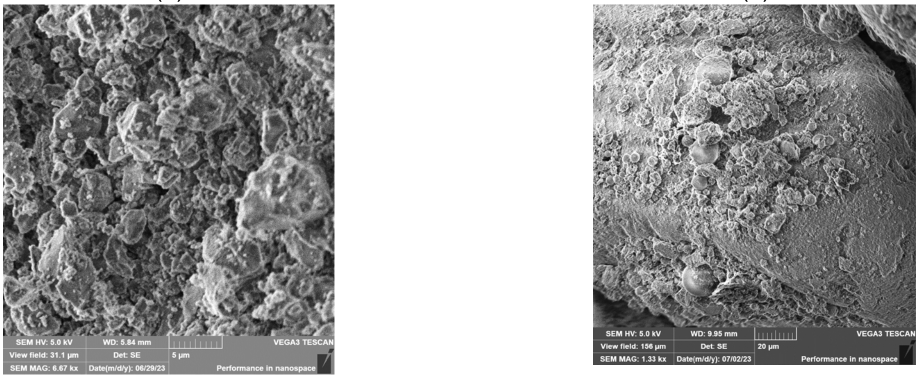

Figure 2: Microphotographs of fly ash and ash trap water based cement samples with 3 (a) and 28 (b) days curing time

As shown in Figure 2, as a result of the interaction of $Ca(OH)_2$ with the ash phase, the formation of calcium hydrosilicates and other new formations took place, thereby thickening and strengthening the cement stone. When ash is used in combination with Portland cement, calcium hydroxide, released during hydrolysis of Portland cement calcium silicates, reacts with aluminosilicate glass contained in the ash.
Figure 3 shows : IR spectroscopy of fly ash based cement sample after 28 days of curing.

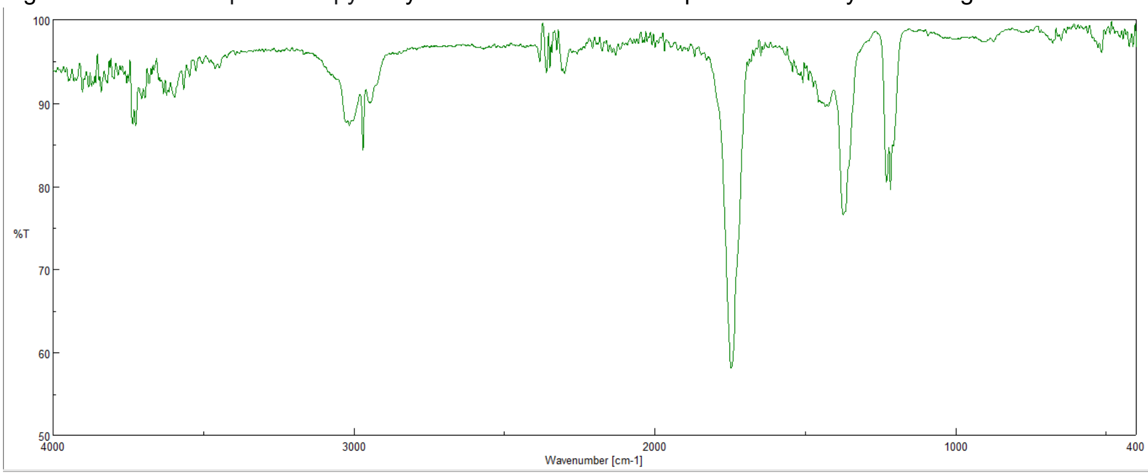

Figure 3: IR spectra: Fly ash based cement sample after 28 days of curing

Studies of the influence of fly ash microspheres on the processes of hydration and hardening of polystyrene concrete have shown that the absorption band at 3600 cm^{-1} belonging to $Ca(OH)_2$, and the increase in the intensity of bands in the region of 1400-1600 cm^{-1}, caused by vibrations localized on O-H bonds in hydroxyl groups and in water molecules, The deformation vibrations of OH-groups and H - O - O - H, testify to high adsorption ability and presence of C-S-H coating on fine particles of cement and microspheres.

4. Conclusions

Studies have shown that the mineral part of TPP ashes consists of a glassy phase by 90-92 %. The main component of this phase is silica, which to a large extent forms the physical and chemical properties of the ash. It participates in the processes of hydration, hardening of binder, as well as in synthesis processes forming various hydrosilicates.
The physical and mechanical properties of Portland cement with the additives also indicate an increase in strength values during all curing periods. Numerous experiments using fly ash and water from the hydro-ash

removal facilities allowed us to determine the optimal composition of cement mixtures based on Portland cement.

For the first 3-7 days of curing, the introduction of fly ash in amounts up to 10 % caused a decrease in the cement strength of the concrete. After 28 days, the fly ash added samples had strengths 7 % higher than the control samples. The slow increase in the strength of cement with ash is due to slower hydration processes.

CaO, SiO_2, Al_2O_3, and Fe_2O_3 constitute a major part of the cement samples. As CaO increases, the content of SiO_2, Al_2O_3, and Fe_2O_3 decreases. However, when CaO increases the content of alkalis including Na_2O and K_2O as well as SO_3 increases. Besides, replacement of ordinary water with the water obtained from hydro-ash removal facilities from TPPs for manufacturing of cement samples is a feasible solution of environmental and economic problems related to ash and slag waste utilization.

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