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The Influence of Addition of Fly Ash from Astana Heat and Power Plants on the Properties of the Polystyrene Concrete

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Abstract: Due to the constant increase in prices for energy resources, as well as the reduction in non-renewable resources in most developed countries of the world, the energy consumption standards of buildings are constantly decreasing, and the requirements for the level of thermal insulation of building envelopes are increasing. The increasing requirements in the level of thermal insulation of enclosing structures make the issues of improving and developing new materials and products become more urgent. Polystyrene concrete has good high-thermal and sound-absorbing properties. This serves as a means of reducing costs, improving thermal insulation, reducing the dead load (weight) on the building and outside, among many other advantages. However, concrete made with polystyrene foam as a substitute for large aggregates has insufficient strength, due to the fact that the cement has low adhesion to the polystyrene foam. Based on the research of scientists and authors on the possibility of using industrial waste, it was assumed that the addition of fly ash to the composition would strengthen the matrix and the degree of compression of the polymers by the cement matrix as a result of the presence of nanoparticles in the fly ash and their positive effect on the structure and properties of the composition. The aim of the study was to develop a heat-insulating polystyrene concrete based on a binder using fly ash and to investigate its physical and technical properties. The properties of fly ash have been studied for the purpose of safe use in mixtures to increase strength properties and improve adhesion to polymers. The involvement of industrial waste from the ashes of coal from Kazakhstani deposits will contribute to the ecological improvement of the environment of the megacities of Kazakhstan. The effect obtained from the optimal combination of the characteristics for a building material is the improved physical and mechanical properties of heat-insulating materials.

Keywords: cement compositions; polystyrene concrete; fly ash; waste; structure and strength

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1. Introduction

Concrete is the most widely used building material, and its properties have a significant influence on the durability and strength of structures. Cement is the most important component of concrete, and its quality directly affects the performance of the final product. However, traditional cement production processes are energy intensive and lead to significant greenhouse gas emissions, making it important to explore alternative materials that can partially replace cement in concrete without compromising its properties. One such material is fly ash, a by-product of coal combustion, which is produced in large quantities in thermal power plants. Polymer concrete has been gaining popularity in recent years due to its excellent chemical resistance, durability and low permeability as well as low thermal conductivity. However, the application of polymer concrete faces a number of problems such as low strength and low adhesion of cement to polymer. The low strength and adhesion of cement to polymer limit its use in load-bearing structures and hence the need for a stronger and more durable material is vital. Fly ash has been recognized as an alternative material for the partial replacement of cement in concrete due to its pozzolanic properties. It reacts with the calcium hydroxide in cement to form additional compounds that increase the strength and durability of concrete. The use of fly ash in concrete also reduces the environmental impact of conventional cement production by reducing the amount of cement required in the mixture. Currently, fly ash with an average particle diameter of approximately 3 microns is produced on an industrial scale. The fly ash can provide concrete strength comparable to that obtained with highly reactive pozzolana. To achieve early concrete performance, the concentration of fly ash should be slightly higher than the amorphous silica content and the total amount of water in the concrete can be reduced by about 10%; concrete using fly ash also shows less tendency to size crack [1–3].

Depending on the material, the fractional composition of the fly ash, the addition of fly ash to cement can have several effects on the properties of the resulting material. Different methods for the production of mixed fly ash cements and their effects on the mechanical properties of composites based on such cements have also been described [4–6].

The grinding regimes of fly ash also affect the physical and chemical properties of the fly ash as well as the quality of the fly ash cements [7–9]. Mechanical treatment of the fly ash has a positive effect on the physical-chemical properties of the ground fly ash [10,11]. Studies on the properties of cement and concrete showed that the pulverization of fly ash tends to increase its pozzolanic activity which is related to the higher specific surface of the fly ash. This, in turn, increases the pozzolanic reaction rate [12–14]. There is an optimal grinding time in terms of pozzolanic activity in terms of water demand. Grinding for 4 h increased the strength of the ASTM F-grade fly ash by 15–27% in 7 days. It was noted that the reactivity of fly ash can be improved by reducing its particle size. From this point of view, ultrafine fly ash particles were synthesized by processing class F fly ash (20–30 μm) into smaller particles with average particle size (<7 μm), closer to the silica fume particle size.

Fly ash can affect the hydration and hardening of cement, and the strength of the product. In some cases, fly ash increases the normal thickness and plasticity of cement dough, making it easier to work with during construction [15–17]. Fly ash positively affects the crystallization and microstructure of cement and improves the strength of Portland cement systems [18–20]. The complex processes of cement crystallization play a decisive 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 [21,22].

The use of fly ash in cement can lead to the formation of additional crystalline compounds, which can increase the strength and durability of the material [23–25]. Depending on the type of coal combusted, its material and fractional composition can significantly change the properties of cement pastes, hardening the cement and composites. Despite the large number of work carried out on the use of fly ash in cement composition and concretes, the increase in the strength of composites is mainly achieved by mechanical treatment or by chemical additives, which requires additional resources [26–28]. In addition, the use of fly ash is necessarily related to the composition of the coals and ashes. The Republic of Kazakhstan ranks 8th in the world in proven reserves of coal, contains 3.4% of the world's reserves in the subsoil and is one of the top ten coal producers in the world market. The main coals used in the combined heat and power plants are those from the Ekibastuz coal basin. The use of multi-tonnage ash from these deposits is an urgent problem. One of the ways to solve it is its application in the production of polystyrene concrete.

The aim of this study is to investigate the properties of cement compositions containing fly ash from thermal power plants in Astana. The work will focus on studying the effect of the elemental and fractional composition of the fly ash; the amount of additives on the hydration, hardening, normal thickness, beginning and end of setting of the cement dough; and the physical and mechanical properties of the polymer concrete which is currently in demand in the Kazakhstan market.

2. Materials and Methods

Standardized methods of testing cement dough were used in the work: determination of normal thickness, the setting time of cement dough, determination of physical and mechanical parameters of polystyrene concrete according to international standards. The particle size of fly ash was determined by means of a laser analyzer. The phase composition of hydrated concrete samples was studied by X-ray method, the structure of solidified samples was investigated by electron microscopy methods.

The following materials were used:

(1) Portland cement M400 (JSC "Kokshetau Cement", Kokshetau, Kazakhstan) was used as a binding material. The initial setting time of Portland cement is 107 min, the final setting time 260 min. The chemical and mineral compositions are described in Table 1.
(2) Superplasticizer MasterGlenium 116 (Master Builders Solution, Astana, Kazakhstan). The recommended dosage according to Master Builders Solution is 0.4–2.0% of the weight of the cement. The exact amount of the additive should be determined in the laboratory by making trial mixes. The current research found that 0.5% was the best consistency to add to the cement mix.
(3) Polystyrene granules of the same type weighing 14–20 kg per 1 m^3, granule size of 1.0–1.6 mm, manufactured by JSC "Sibur-Chimprom" (Russian Federation).
(4) Fly ash from the Astana main power plant was poured into a ball mill for 2.4 h by grinding balls according to [28] with a diameter of 40 mm.

Polystyrene granules were stacked in advance in the form of cubes from 60 to 80% of the total volume. Cement grade M400 was mixed with ash (5% to 15%). Superplasticizer was added to water 30% of the total weight of the cement mixture, stirred and gradually added to the cement mixture.

After pouring into molds of 100 mm × 100 mm × 100 mm, polystyrene granules and foam-cement composite were kept for 28 days in environmental conditions. After 28 days, the thermal conductivity was defined according to [29] with the help of heat conductivity meters ITP-MG4 (RNPO RusPribor Ltd., St. Petersberg, Russia).

For the beneficial use of fly ash and bottom ash as raw materials, for safe storage and use of ash and slag waste (ASW), it is necessary to have information about their properties and characteristics [30]. To study the potential use of ash, selected from ash dumps and ash collectors, the elemental composition was determined with an X-ray fluorescent XRF spectrometer Epsilon 1 (Malvern Panalytical, Malvern, Great Britain). As an X-ray source in the spectrometer, an X-ray tube with a set of primary filters (U = 50 xB, I" = 0.5 mA; maximum power 5 VA; the anode material—silver) was used.

The characteristics of Portland cement 400 are shown in Table 1.

Table 1. Characteristics of Portland cement (Kokshe-Cement LLP) [31].

	Chemical Composition, wt %							
	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	Loss on Ignition	Sum
Portland cement	20.49	4.80	4.40	63.42	1.47	2.25	1.55	99.14

Following [31], the physical and mechanical parameters are determined in Table 2.

Table 2. Properties of cement slurries and pastes.

Cement	Setting Time, h-min		Bending Strength, MPa, in Days			Ultimate Compressive Strength, MPa, in Days		
	Start	End	3	7	28	3	7	28
Portland cement 400	1–47	4–20	2.67	3.5	4.22	20.7	30.12	41.0

The sand was used as a filler—crushed and sifted limestone.

Following [32], the following characteristics were determined: bulk density—1380 kg/m^3; sand fractions μ = 2.02 mm and belonging to the class of sands with medium size.

Portland cement was used as a binder with the following characteristics, determined according to [33]:

- Paste of normal thickness—24.5%,
- Beginning of setting—1 h 47 min,
- End of setting—4 h 20 min,
- Average value of compressive strength of samples of normal hardening at the age of 28 days—41.0 MPa,
- Residue on sieve 0.08 mm—8.4%.

The stability of disperse systems was studied by changing the ζ-potential of the particles. When the stability of the colloidal system was disrupted, one could visually observe an increase in the formation of large particles in the solution volume, precipitation or a change in the height distribution of particles.

During the formation of suspensions by the particles under study, lyophobic disperse systems are formed, which are characterized by a weak interaction between the dispersed phase and the dispersion medium, which leads to high instability of such systems and their tendency to decrease in dispersion with time. The study of the coagulation of such systems in solutions makes it possible to elucidate the conditions that ensure the aggregative stability of suspensions [34,35].

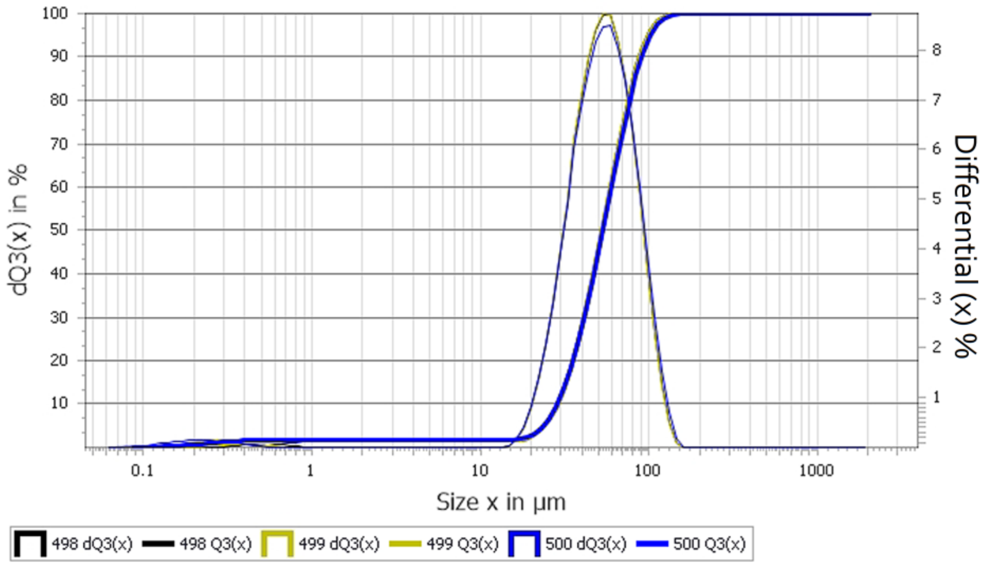
Experimental results have shown that, in general, particles in aqueous suspensions are characterized by the formation of aggregates. The average size of aggregates in aqueous suspension exceeds 20–30 nm. This indicates a low aggregation stability (the formation of aggregates occurs during the first hours), which is consistent with the low values of the ζ-potential. Particle size distributions in all samples were determined using the FRITSCH Analysette 22 laser method. The analyzer uses the principle of diffraction of laser radiation on dispersed samples: when it hits a powder particle, the laser beam is deflected at a certain angle depending on the particle size. The scattered beam hits the detector. The intensity of the radiation hitting each element of the detector and the subsequent mathematical processing of the signal make it possible to determine the size of the sample particles and evaluate their shape.

For a cement paste with fly ash, the normal thickness of the binder is slightly higher. The water demands of the cement change because when micro and nanodispersions are added in optimal amounts, the structure and properties of the suspensions and pastes change. The normal thickness of the cement paste is determined according to [36] with the help of Vick's device (DDC-1).

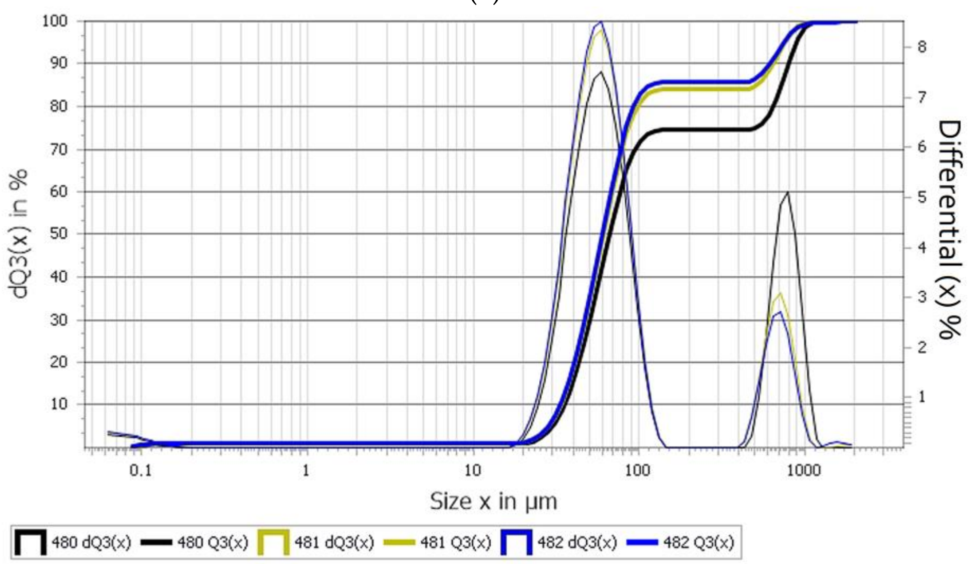
The physical and mechanical properties of Portland cement with the above additives also indicate an increase in strength indicators during all hardening periods. Numerous experiments with the use of fly ash and water from hydraulic ash collectors have made it possible to identify the optimal composition of cement compositions based on Portland cement. The experiments carried out made it possible to determine the optimal compositions of composites based on blocks of cement with the addition of fly ash microdispersions, which correspond to the maximum strength of cement samples after 28 days of hardening.

The use of fly ash as an integral part of cement-based compositions can be explained from the point of view of the uniform distribution of the ash particles in the volume. The hydraulic activity of fly ash is determined by the chemical-mineralogical and granulometric composition. Fly ash from CHPP plants had 5 to 9.3% free lime. The hydraulic activity of ash is due to the presence of free CaO, which determines the high pH value of its aqueous extracts (the ratio of ash to water is 1:10).

The particle size distribution of the ash samples taken from ash dump and ash pond fly ash was studied using a laser particle size analyzer (FRITSCH Analysette 22 laser method) and is presented in the graphs (Figure 1). The powder sample was placed in an ultrasonic bath filled with liquid. Since the processes of solvation and hydration of solids in liquid media can distort the real particle sizes, the powder was stirred mechanically and with ultrasound, after which the resulting suspension was fed into the measuring cuvette. A laser beam scanned the suspension in the cuvette, deflecting at a certain angle depending on the diameter and optical properties of the particles. A collecting lens focused the scattered light onto a focal plane. The spectra recorded by the multichannel detector were processed in the software.

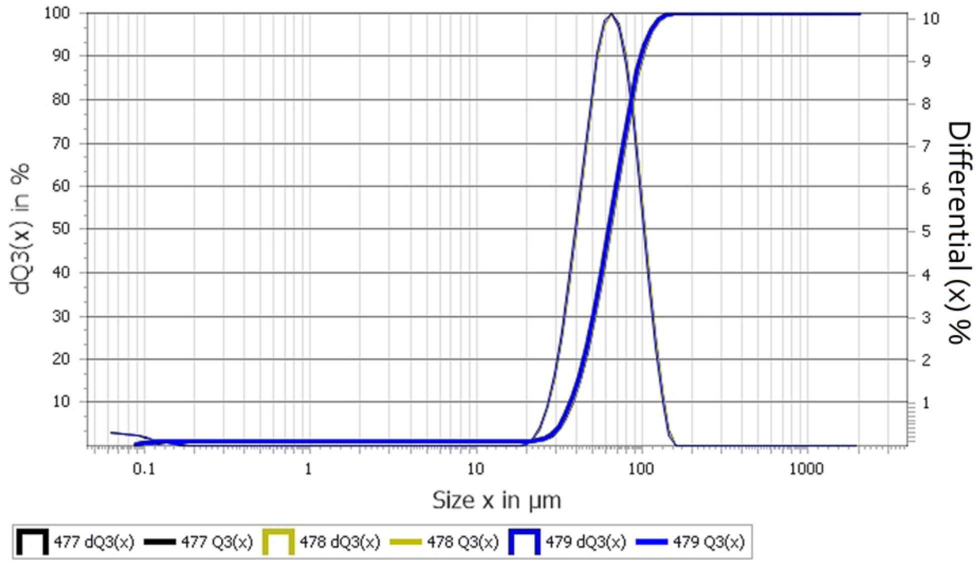


(**a**)

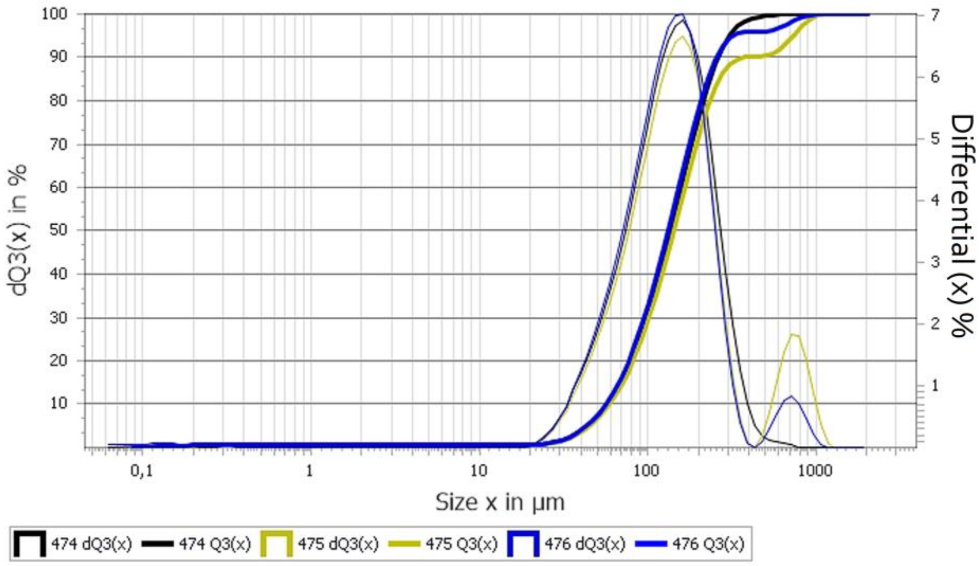


(**b**)

Figure 1. *Cont.*



(**c**)



(**d**)

Figure 1. Particle size distribution: (**a**) fly ash sample; (**b**) fly ash sample b; (**c**) ash samples from ash disposal area; (**d**) ash samples from hydraulic ash disposal area.

The method of determination of the compressive strength was performed in accordance with [37] on the testing press CONTROLS Pilot 500.

3. Results and Discussion

In the study, polystyrene concrete was made according to rational distribution by percent. Polystyrene concretes with a content of 5 to 15% fly ash from the total mass of the cement slurry were investigated. The content of polystyrene in all samples was 60% filling by volume of the sample.

The results of the sample composition analysis are shown in Table 3.

Table 3. Composition of ashes from the Astana CHPP.

No.	Item	Sample #1 (Powder)	Sample #2 (Powder)	Sample #3 (Powder)	Sample #4 (Liquid)	Sample #5 (Liquid)	Sample #6 (Liquid)	Sample #7 (Liquid)	Sample #8 (Liquid)
1	A1	17.346	19.755	19.608					
2	Si	40.919	50.989	52.327	13.720	9.509	10.431	7.887	5.853
3	P	0.610	0.695	0.717			6.514	22.341	20.289
4	S	0.199	0.091	0.079	2.436	1.219	1.253	1.207	
5	CI	0.126	0.171	0.172	0.003	0.007	0.204	0.000	1.138
6	K	1.629	2.094	2.207	3.260	1.089	1.814		3.418
7	Ca	9.926	4.155	3.350	74.143	78.754	72.453	57.317	56.565
8	Ti	2.847	2.998	3.170	0.608	1.033	1.0 d^3		
9	V	0.059	0.055	0.060		0.013			
10	Ml	0.405	0.321	0.303	0.168	0.255			
11	Fe	24.916	17.659	16.999	4.981	7.795	3.567	2.224	2.689
12	Ni	0.001	0.004						
13	Si	0.045	0.053	0.051					
14	Zn	0.018	0.069	0.032					
15	Ga	0.013	0.013	0.014					
16	As	0.004	0.004	0.004					
17	Rb	0.012	0.014	0.015					
18	Sr	0.236	0.230	0.237		0.023			
19	У	0.025	0.025	0.025					
20	Zr	0.140	0.155	0.166					
21	Nb	0.006	0.006	0.006					
22	Sтi	0.028	0.026	0.025	0.340	0.139	1.440	4.773	5.296
23	Te	0.018	0.021	0.017	0.288	0.113	1.261	4.243	4.573
24	Ba	0.287	0.251	0.254					
25	Eu	0.162	0.120	0.115	0.053	0.041			
26	Yb	0.017	0.015	0.016					
27	Re	0.000	0.000	0.000					
28	Os	0.000	0.000	0.000					
29	Ir	0.000	0.000	0.000					
30	Pb	0.004	0.008	0.009					
31	Nd		0.002	0.002					
32	Lu			0.014					
33	Rh				0.000			0.009	
34	Cr					0.10			

The issues of the utilization of ash from CHPPs in all regions of Kazakhstan are relevant, if we take into account the following factors: the proximity of ash dumps to urban developments; the limited areas for the expansion of ash dumps; the damage caused to the environment. As can be seen from Table 3, all the ash samples had calcium and silicate components and could be used in the building materials industry. The ashes belong to the inert materials and are characterized by the basic ash modulus M_b = 0.08. The calculated silicate modulus Ms = 1.82. M_b is the basic modulus (hydrosilicate modulus) M_b, which is the ratio of the sum of basic oxides to the sum of acidic oxides: M_b = (CaO + MgO + K_2O + Na_2O): (SiO_2 + Al_2O_3); M_s—silicate (silica) module M_s, showing the ratio of silicon oxide reacting with other oxides to the total content of aluminum and iron oxides: M_s = SiO_2: (Al_2O_3 + Fe_2O_3).

The most valuable component of fly ash is microspheres, a light fraction of fly ash, which is a fine powder consisting of hollow thin-walled particles of a spherical shape and aluminosilicate composition. The size of fly ash particles varies.

Aluminosilicate hollow microspheres are a dispersed material composed of hollow microspheres ranging in size from 10 to 200 microns. The density of the shell substance is 2.4–2.5 g/cm^3; the average density of the microspheres is 0.6–0.7 g/cm^3 bulk density. The predominant (more than 80%) size of the microspheres is 70–200 microns. The calculated specific surface of the microspheres is 1100–1200 cm^2/g. The average chemical composition of ash is shown in Table 3.

The phase composition according to X-ray phase analysis was as follows:

- The predominant phase (up to 40%)—mullite;
- Hygroscopicity, % by weight—up to 0.15;
- Thermal conductivity in the bulk state—0.08–0.13 W/m·K;
- Melting temperature range—1400–1550 °C;
- Softening start temperature—tp = 1400 °C.

When mixing cement with water at the earliest stages of the formation of a cement-water suspension, its structure can be considered from the standpoint of the main laws of colloid chemistry, which make it possible to explain the processes of a gradual transition of the system from a plastic state to a solid one. Cement particles in a cement-water suspension form a solid phase in a dispersion medium, in our case, water, immediately after mixing.

In this work, the kinetics of cement hydration was studied by evaluating the change in time of the distribution of its particles by size (PSD) in an aqueous suspension of low concentration at 20 °C with the addition of various amounts of ash. Experiments showed that all additives of fly ash affect the hydration of cement particles, as evidenced by the increase in the geometric dimensions of the particles compared to cement without additives.

In aqueous cement slurries with fly ash additives, the structure formation is determined by the level of hydration of the cement particles, the surface properties of the particles, and the composition of water. As a result of the experiments, it was revealed that the introduction of fly ash up to 60% influenced the processes of hydration of the cement particles and contributed to aggregation in cement suspensions. The hydration processes were affected by the surface properties of the particles. The addition of fly ash changed the surface properties of the cement particles, which affected the hydration of the cement. The positive effect of the water from hydraulic ash collectors at the thermal power plant on structure formation in cement suspensions and the setting time of the cement paste was noted. Aggregation in cement suspensions determines the course of gyration processes, contributes to a decrease in the water-cement ratio, and, consequently, to an increase in the frost resistance of hardened composites (Table 4). The normal thickness decreased to 23–24% when using water from gyro-ash collectors with the introduction of 60% and 80% ash, respectively.

Table 4. ζ-potential and the average size of the studied particles in optimal amounts in aqueous solutions.

Composition	d_{cp}, nm	Holding Time, h	ζ-Potential, mV	Water
Portland cement	11	3	−17.07	Tap water
Portland cement + 5% fly ash	10	3	−16.04	Tap water
Portland cement + 10% fly ash	12	3	−15.7	Tap water
Portland cement + 15% fly ash	12	3	−14.2	Tap water
Portland cement + 5% fly ash	13	3	−12.4	From CHPP hydraulic ash traps
Portland cement + 10% fly ash	14	3	−9.06	From CHPP hydraulic ash traps
Portland cement + 15% fly ash	12	3	−8.7	From CHPP hydraulic ash traps

For the studied compositions and binders, an elongation of the setting time was observed. This is because fly ash affects the processes of early structure formation in cement suspensions and pastes, and contributes to the aggregation of particles.

The study of the electrokinetic properties of additives at the boundary with distilled water and water from wet ash collectors showed that as a result of the action of various ions in water, a charged layer is formed at the boundary with the surface of the additives, which differs in sign and size. Therefore, a different structure formation in cement systems with additives was also expected.

The best results were shown by samples with the addition of water from the ash collectors, the water–cement ratio decreased to 23% compared to the control 26%. Experiments on the study of the properties of cement pastes and hardened composites have shown that cement with fly ash additives in optimal amounts, unlike types of cement without these additives, has a higher strength. It is important to establish the influence of additives on the setting time of cement. The results of the study of the effect of additives on the setting time of cement are shown in Table 5.

Table 5. Results of the study of the effect of additives on the setting time of cement.

Type of Binder	Type, Amount of Additive,% of Dry Cement	Beginning of Setting, Hours Minutes	End Setting, Hours Minutes
Portland cement M400		1 h 47 min.	4 h 20 min.
Portland cement with additive	fly ash		
	10	1 h 45 min.	4 h 30 min.
	15	1 h 50 min.	4 h 35 min.
	30	1 h 56 min.	4 h 40 min.
	60	2 h 50 min.	5 h 05 min.

Table 5 shows that the addition of fly ash from the Astana Heat Power Plant affected the setting time of the cement dough. The onset of setting of the cement dough with the addition of 10% fly ash in comparison with cement without additions is reduced by 5 min.

As the data of elemental composition analyses showed, the ashes used were rich in silica and aluminum. Aluminosilicate particles act as pozzolans in the cement stone and the initial setting times of cement pastes were slightly different from those without additives. Hardening processes are associated with corrosion of the surface of ash particles by calcium hydroxide $Ca(OH)_2$ released during cement hydration. Before the corrosion process develops, the ash grains are very weakly bound to the cement stone. This may be the reason for the extension of the setting time of the cement dough.

Studies to determine the normal thickness of a cement paste containing an additive of fly ash in its composition are of considerable interest. The research results are shown in Table 6.

Table 6. Results of determining the normal thickness of cement paste.

Type of Composite	Type, Amount of Additive, % of Dry Cement	Normal, Density, %
Portland cement M400	-	26.0
Portland cement + 5% fly ash	10	27.0
Portland cement + 10% fly ash	15	27.8
Portland cement + 15% fly ash	20	28.0
Portland cement + 10% fly ash + water from hydraulic ash collectors	60	24.0
Portland cement + 10% fly ash + water from hydraulic ash collectors	80	23.0

Table 6 shows that increasing the amount of fly ash to 60% reduces the amount of water for mixing the cement dough by 2%. Fly ash has an effect on the normal thickness of the cement dough, which will influence the reduction in shrinkage as a result of the water-reducing effect of fly ash and a reduction in the risk of thermal cracking as a result of a reduction in heat release.

The study of the fractional composition of ash sampled from the ash ponds company showed the following. More accurately the particle size distribution can be represented as a histogram—the dependence of the number of particles on the size of the particles (Figure 1). The samples of the studied mineral wastes had a wide enough range of particle size distribution, which corresponds to the important condition of applicability of the materials as fillers in polymer compositions, i.e., they have a suitable granulometric composition.

As can be seen from Figure 1, sample 1 was characterized by a large number of particles ranging from 10 to 50 microns in size, sample 2—less than 100 microns. Sample 3 was a mixture of fly ash and larger ash fractions, which can be seen in Figure 1.

It was revealed that the investigated powders of finely dispersed mineral industrial waste had a wide particle-size distribution, with the content of both small and large fractions, hence, such granulometric composition would have a positive effect on the rheological properties, namely, to reduce the viscosity of the composition. Considering that the viscosity of the composition is one of the decisive factors in the choice of the filler, especially for extrusion and injection molding methods, the selected fillers met the criterion of particle size distribution.

Numerous experiments carried out to select the optimal composition allowed us to identify the optimal composition of polystyrene concrete containing up to 15% fly ash; concrete compositions are shown in Table 7.

Table 7. Compositions of polystyrene concrete.

Samples	Cement (%)	Polystyrene (% by Sample Volume)	Ash (%)	Superplasticizer MasterGlenium 116 (%)	Water (mL)
Polystyrene concrete without additives	100	60	-	-	660
Polystyrene concrete with the addition of fly ash	95	60	5	-	660
Polystyrene concrete with the addition of fly ash	90	60	10	-	660
Polystyrene concrete with the addition of fly ash	85	60	15	-	660
Polystyrene concrete with fly ash and superplasticizer	95	60	5	0.30	660
Polystyrene concrete with fly ash and superplasticizer	90	60	10	0.30	660
Polystyrene concrete with fly ash and superplasticizer	85	60	15	0.30	660
Polystyrene concrete with fly ash and superplasticizer	85	60	15	0.1	660
Polystyrene concrete with fly ash and superplasticizer	85	60	15	0.2	660
Polystyrene concrete with fly ash and superplasticizer	85	60	15	0.15	660

The analysis showed that the thermal conductivity decreased as the proportion of expanded polystyrene and superplasticizer increased. This is because 98% of closed-cell EPS is air and the rest is polystyrene. Furthermore, it lies in the fact that the superplasticizer absorbs water and swells within 48 h of concrete hardening process. During the 28 days of drying, the samples lose water in their structure. For this reason, artificial micropores are formed outside the pores of the expanded polystyrene in the cement zone of the material [38–40].

The prepared control samples, a sample with the addition of a superplasticizer, a sample with the addition of fly ash, a sample with the addition of fly ash and a superplasticizer, are shown in Figure 2.

Figure 2. Prepared samples, where 1—control sample; 2—sample with the addition of superplasticizer; 3—sample with the addition of fly ash; 4—sample with the addition of fly ash and superplasticizer.

With an increase in the dosage of fly ash as a substitute for aggregate, the compressive strength increased compared to the control sample, as shown in Table 8. The highest compressive strength values for all types of concrete with fly ash and polystyrene were obtained for sample No. 21, and the lowest values of thermal conductivity were also obtained for sample No. 21.

Table 8. Physical and mechanical properties of the tested polystyrene concrete.

No.	Sample	Fly Ash %	Days	Thermal Conductivity	Compressive Strength (MPa)
1		0	3	0.35	2.25
2	Control sample	0	7	0.34	5.85
3		0	28	0.34	10.22
4		5	3	0.30	1.46
5		10	3	0.29	1.74
6		15	3	0.29	1.82
7		5	7	0.30	3.79
8	With the addition of fly ash	10	7	0.29	4.40
9		15	7	0.29	5.70
10		5	28	0.3	8.28
11		10	28	0.29	9.74
12		15	28	0.29	10.8
13		5	3	0.170	1.84
14		10	3	0.166	2.14
15		15	3	0.166	2.42
16		5	7	0.169	4.01
17	With the addition of fly ash and superplasticizer	10	7	0.166	5.34
18		15	7	0.165	6.29
19		5	28	0.169	9.82
20		10	28	0.166	10.99
21		15	28	0.165	12.48

With the repeated measurement of the parameter characterizing a certain property of a material, a number of different results were obtained. This was due to the limited accuracy of the measuring instruments, subjective features of the experimenter who took the readings and the variability in the studied properties due to the influence of random, uncontrollable factors on them, along with those factors taken into account. For each specimen with 3–7–28 days curing (5–10–15% fly ash) five tests were carried out ($n = 5$).

Since the best strength and thermal conductivity values were obtained for specimens containing 60% polystyrene and 15% fly ash, the statistical data were investigated for these specimens.

The arithmetical mean (mathematical expectation) of the 28-day curing strength of the 15% fly ash specimen was: 10.8 MPa. Mean square deviation: S = 0.10. Mean square deviation (standard) S showed the limits of variability of the studied property, i.e., the degree of dispersion of its individual values relative to the average. Average thermal conductivity for the sample with 15% fly ash and 28 days of hardening was 0.29. Mean square deviation: S = 0.01. Statistical processing of the test results, in addition to determining the variability of the measured quality index and the accuracy of the study, involved the estimation of confidence probability ($1 - p$) or the level of significance p of the obtained result.

The accuracy index e was equal to 1.058%. All five tests were homogeneous; there was no gross error in their performance.

Analysis of the results of the physical and mechanical tests showed that in the early 3–7 days of hardening the introduction of ash in an amount up to 15% caused a decrease in the cement strength of the polystyrene concrete. On the 28th day, the difference from polymer concrete containing no ash became minimal. After 28 days, the samples with the fly ash addition had a strength higher than the control by 6.7%. The slow strength growth of the cements with fly ash is explained by the slower processes of their hydration. The final stable structure in such cements is achieved later than in conventional cement concretes. In the early periods of hardening, water-thick interlayers filled with $Ca(OH)_2$ crystals were observed between the cement particles and the ash which was also consistent with other reports in the literature [41,42]. Subsequently, due to the interaction between $Ca(OH)_2$ and the ash phases, the formation of calcium hydrosilicates and other new formations began, compacting and hardening the cement stone.

Because of this, the structure of the hardened ash polystyrene concrete was more dense. Secondary hydrate phases formed as a result of the pozzolanic interaction of ash with cement stone are carbonized more easily and to a greater extent than the new hydrate formations of additive-free cement. Carbonization is accompanied by a significant increase in the strength of the hardened cement mortar. An increase in ash content above 15% led to a more significant decrease in the strength properties of cements.

Dependences of strength and thermal conductivity on the amount of fly ash are shown in Figure 3.

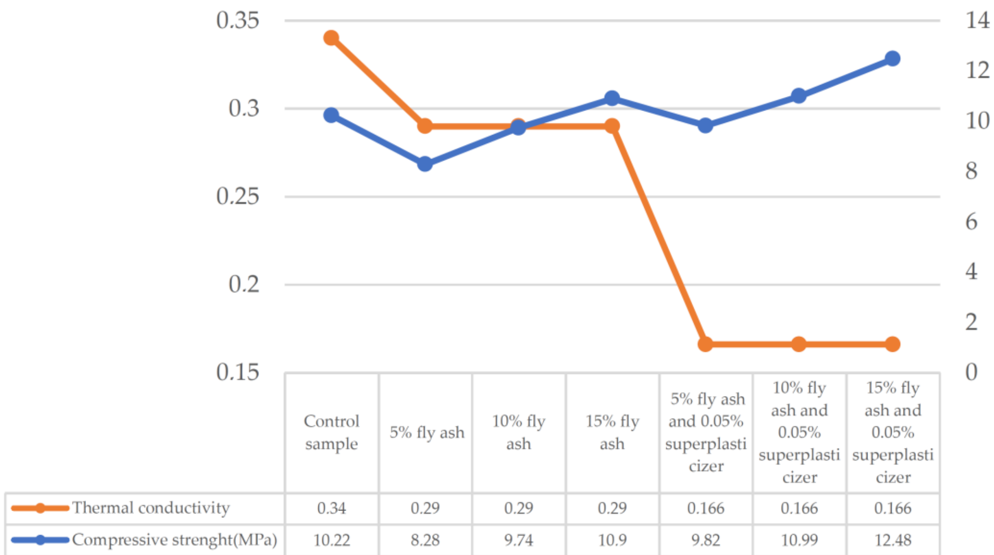


Figure 3. Dependence of polystyrene concrete compressive strength on thermal conductivity.

The obtained results showed that all strong indicators for concrete with polystyrene containing fly ash were greater than for the control sample of concrete. The highest value was obtained for concrete containing 60% polystyrene and 15% fly ash since the increase in strength was 22.11%. The lowest value was associated with a control sample that did not contain ash and superplasticizer. The best performance in thermal conductivity was also shown by a sample containing 60% polystyrene and 15% fly ash in comparison with the control sample, where the difference in thermal conductivity was 51.47%. Figures 4–7 show micrographs of the hardened samples, which showed that fly ash particles containing aluminates promoted the formation of calcium hydrosulfoaluminates and were actively adsorbed on the surfaces of the particles.

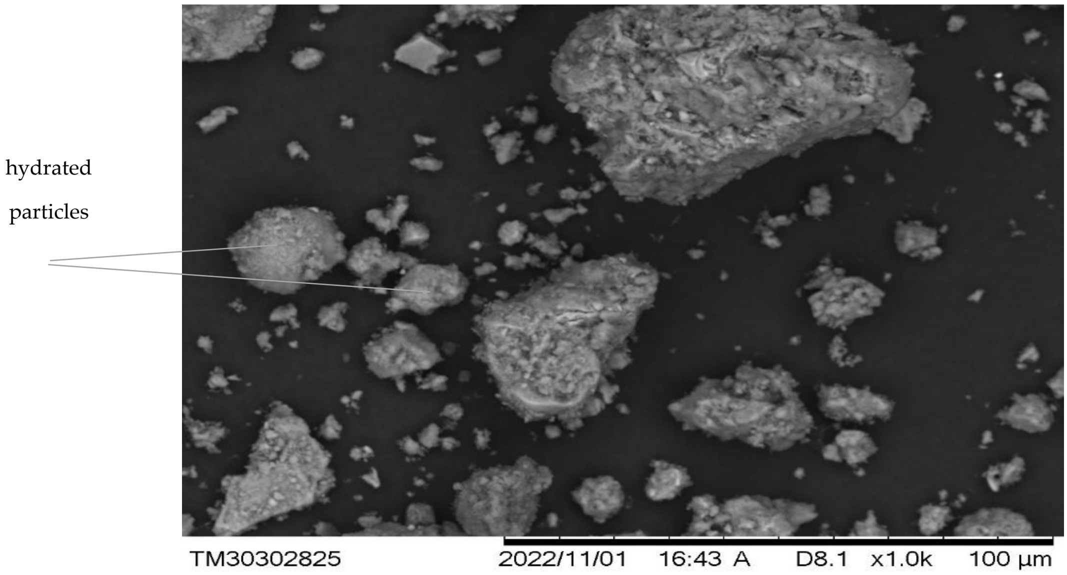


Figure 4. Micrographs of hardened samples without additives after 28 days of hardening, ×1000.

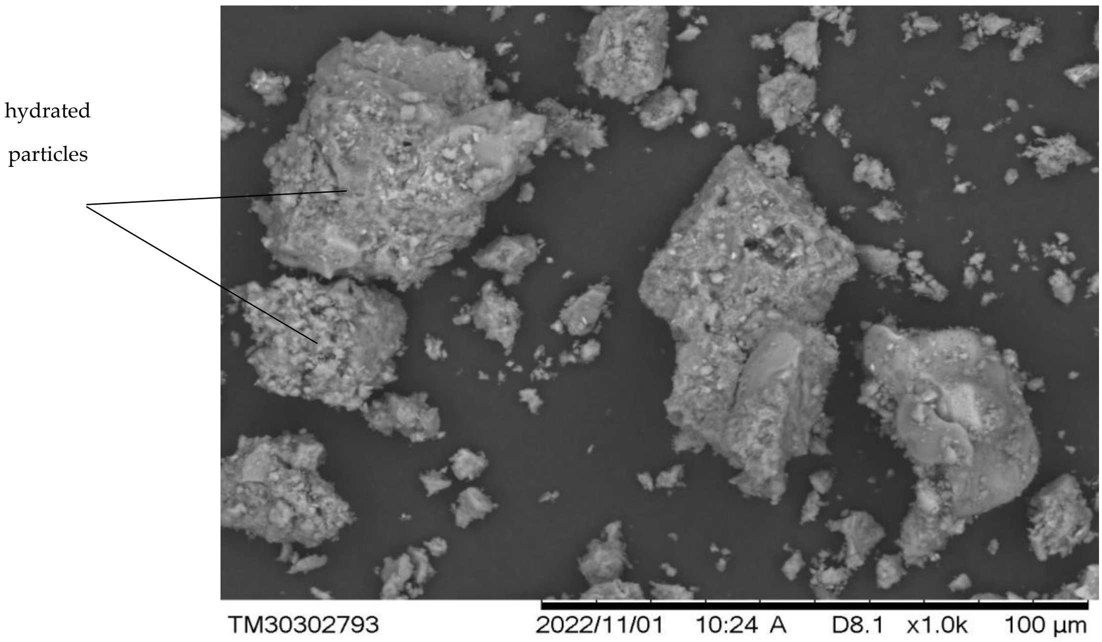


Figure 5. Micrographs of hardened samples of PC + 15% fly ash after 28 days of hardening, ×10,000.

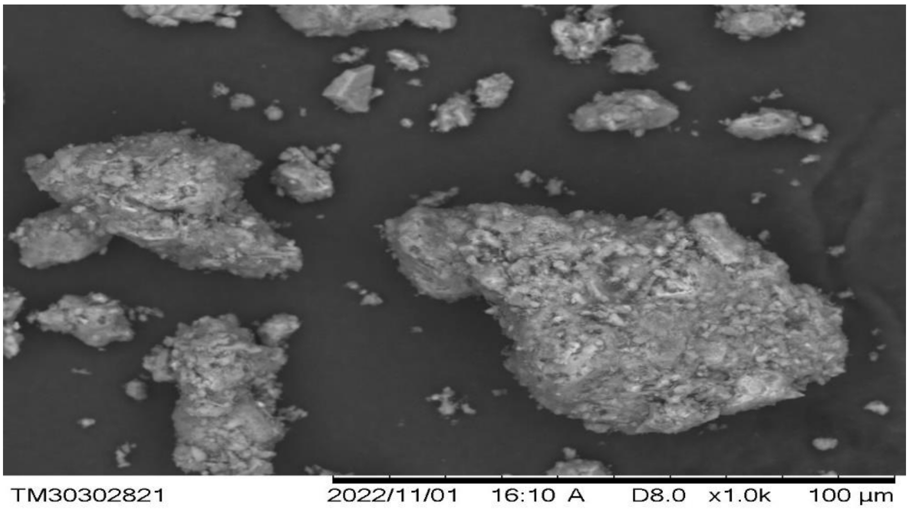


Figure 6. Micrographs of hardened samples without additives, ×7000.

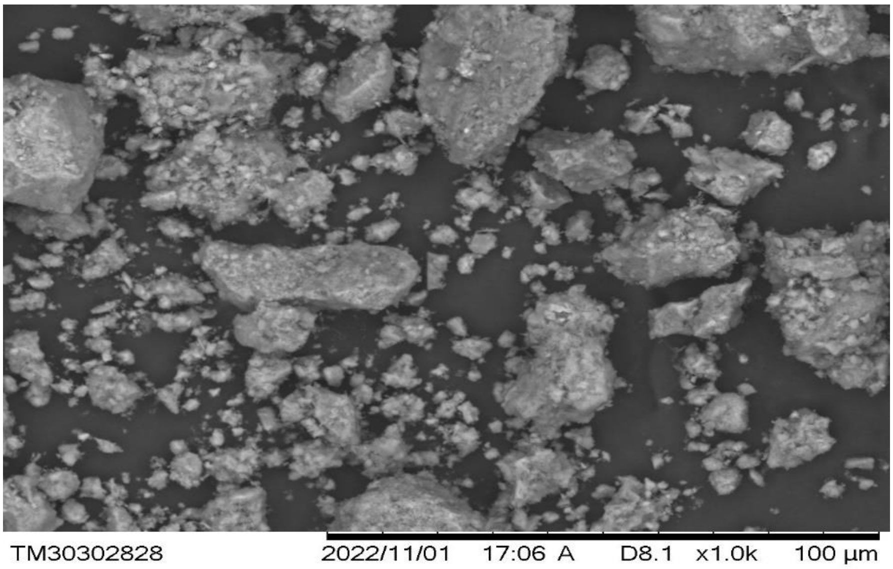


Figure 7. Micrographs of hardened samples of PC + 15% fly ash, ×7000.

Figure 6 shows that the hydrated particles had a large volume compared to the cement without additives. The presence of fly ash probably accelerates the hydration of the cement particles. This was also confirmed by the data in Figures 6 and 7, which showed that the samples with 15% fly ash addition, cured for 28 days at 7000× magnification had a significant decrease in porosity and an increase in the volume of the hydrated phase.

As can be seen from the figures, the structure of the samples cured with and without additives indicated the formation of internal pores, which reduced the thermal conductivity of the samples. The degree of hydration corresponded to the data for determining the strength of the samples.

When adding fly ash containing calcium aluminates, as a result of hydration, calcium hydrosulfoaluminates are formed, which contribute to an increase in strength. The formation of calcium hydrosulfoaluminates was evidenced by the data of the X-ray phase analysis (Figures 8–10).

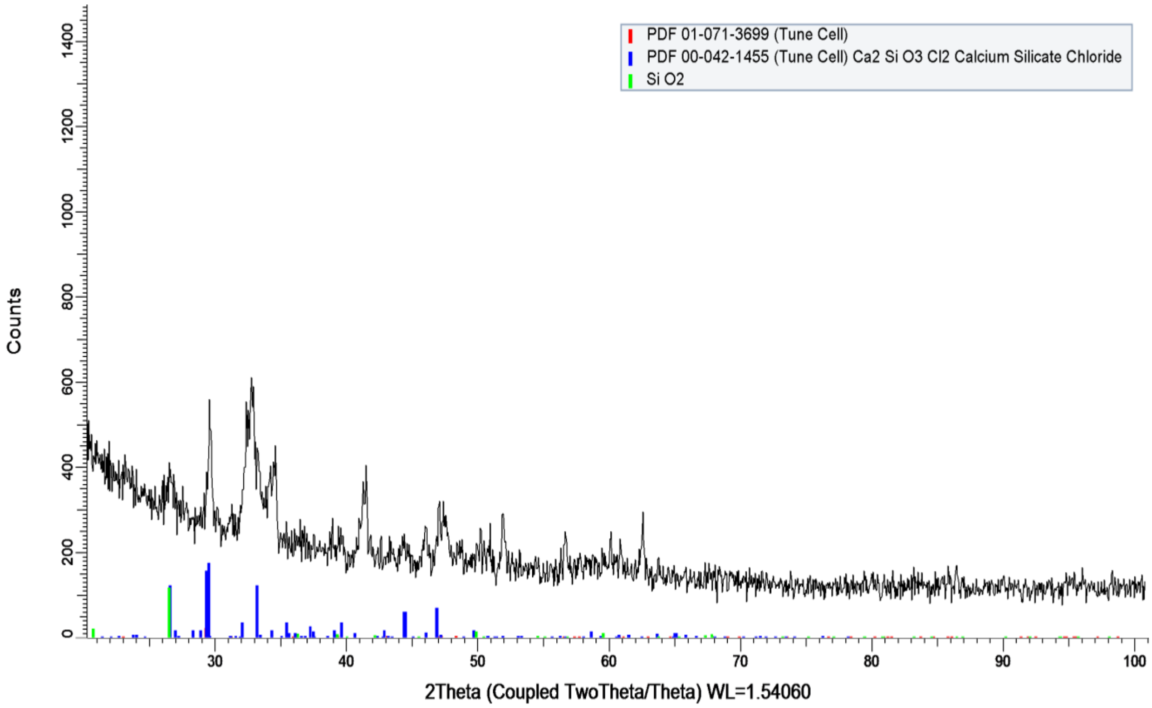


Figure 8. X-ray patterns of samples of PC + with fly ash 15% and superplasticizer, hardened within 3 days.

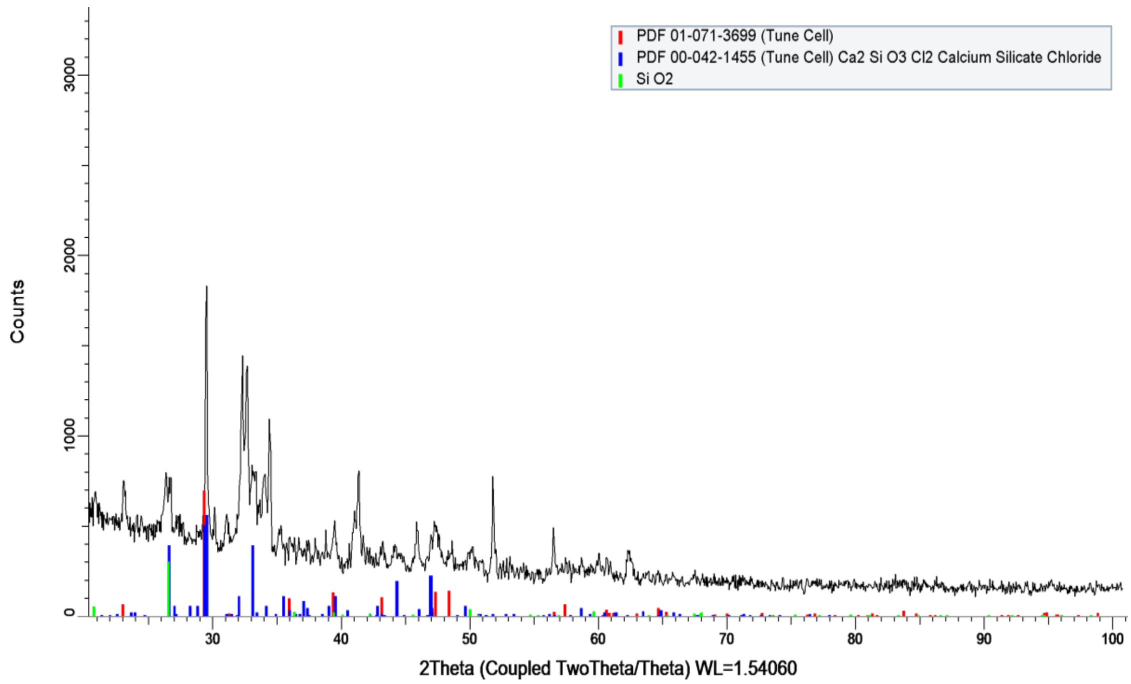


Figure 9. X-ray patterns of samples of PC + with fly ash 15% and superplasticizer, hardened within 7 days.

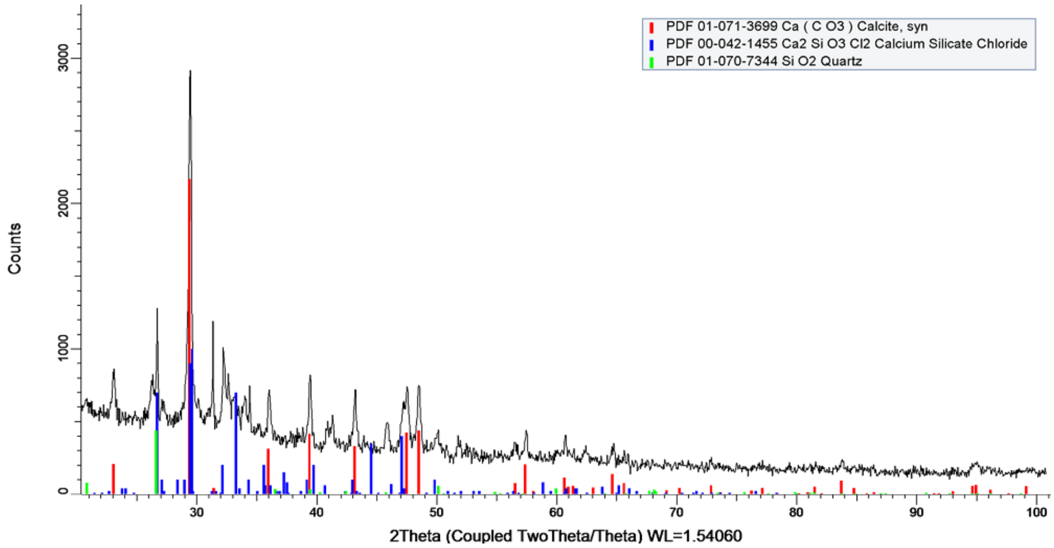


Figure 10. Radiographs of samples of PC + with fly ash 15% and superplasticizer, hardened within 28 days.

Silica and aluminosilicate-rich dry ash act as pozzolans in the cement stone. This increases the degree of hydration of the cement stone as well as its strength and density. The presence of pozzolans in the fly ash is primarily responsible for the increase in water-filled capillary pores required for the hydration of the cement component. Studies on the determination of the setting time show that, in the early age of concrete hardening, pozzolans do not actively participate in gelation. The binding of calcium oxide at this stage of hardening is due to adsorption only. The active participation of pozzolans occurs at a later date, due to the formation of very thin, surface-spreading reaction zones, as the particles are firmly embedded in the cement gel. The development of the inner surface of the gel and its strength and density by this time are considerably higher than those of pure Portland cement.

4. Conclusions

Thus, the conducted studies have shown that the introduction of fly ash additives of Astana CHPPs can have a favorable effect on the properties of concrete. The study of the elemental composition of the ash showed that the nature and degree of influence of fly ash on the properties of ash–cement compositions largely depend on the qualitative characteristics of the ash.

The results of the determination of particle size by means of a laser analyzer showed that the positive effect of fly ash on polystyrene concrete properties is due to a physical effect which is shown by the fact that fine particles are usually of a finer granulometric composition than those of Portland cement. It was revealed that the granulometric characteristics of the fine aggregates and cement particles affected the volume of voids and the water consumption of the polystyrene concrete mixture. The introduction of fine particles of fly ash, having sizes of up to 100 microns, increased the influence of the Portland cement grains on the reduction in porosity of the concrete mixture, which reduced the need for water to obtain concrete of a given consistency.

The addition of fly ash affected the composition of the cement mixture, the degree of hydration of the Portland cement, and the setting time and hardening of the hydrate phases. For a given consistency of cement, a reduction in the normal thickness from 26 to 23% could result in an overall improvement of its technological properties. It was found that replacing 15% of cement with fly ash reduced the normal densities by about 11.4%. Fly ash had an effect on the normal thickness of the cement dough, which contributed to a reduction in shrinkage due to the water-reducing effect of the fly ash.

The results of the physical and mechanical tests revealed that the samples of polystyrene concrete with ash from an Astana CHPP, introduced in an amount up to 15%, after 3 and 7 days due to a decrease in the rate of hydration of the cement and minerals, had a lower strength compared to the polystyrene concrete without additives. However, after 28 days of hardening, these samples had a strength 6.7% higher than that of the control samples as a result of carbonization and the formation of calcium hydrosilicates. Silica and aluminosilicate-rich dry ashes act as pozzolans in the cement stone. This increases the degree of hydration of the cement stone as well as its strength and density. The presence of pozzolans in the fly ash is primarily responsible for the increase in the water-filled capillary pores required for hydration of the cement component. Studies on the determination of the setting time show that, in the early stages of concrete hardening, pozzolans do not actively participate in gelation. The binding of calcium oxide at this stage of hardening is due to adsorption only. In later periods, pozzolans are actively involved, due to the formation of very thin, surface-spreading reaction zones, as the particles are firmly embedded in the cement gel. The development of the inner surface of the gel, its strength and density by this time are significantly higher than those of pure Portland cement. The structure of samples cured over a period of 28 days was distinguished by the formation of smaller pores compared with the concrete without additives, which had a positive effect on the strength of the samples. The study of the phase composition also showed the formation of hydrosulfoaluminates, which are the cause of lower porosity.

In the practice of modern construction, one of the most important tasks is to ensure quality thermal protection of buildings, contributing to energy and resource savings. In accordance with Euro-norms, the requirements for the levels of thermal insulation of external enclosing structures are increasing, which makes the development of effective materials using industrial waste relevant. The results of determining the thermal conductivity of polystyrene concrete samples showed that the use of fly ash as an additive in the mixture had a positive effect. The thermal conductivity coefficient after 3 days decreased on average by 14% with the introduction of fly ash from 5 to 15%. When adding superplasticizer, the decrease in thermal conductivity was recorded at more than 40%. It is possible that aluminosilicate microspheres contribute an additional effect in increasing the thermal protection of polystyrene concrete.

Ash binder can be widely used for the production of polystyrene concrete, commercial concrete, mortars and finished products. The fly ash from the thermal power plant in Astana can be used as an additive to cement without reducing the activity of the material. In order to use the fly ash effectively, a set of technological and physical-mechanical tests should be carried out.

Lightweight structural cement composites with polystyrene foam to improve thermal insulation prevent the segregation of the polystyrene granules through the adhesion given by the fly ash aggregate. At the same time, a properly selected dosage of superplasticizer and water provides sufficient flowability of the mixture for easy working and handling. This was confirmed by the MSCT results and flowability indicators, respectively. The porosity of the air voids of the composites remained practically unaffected by the change in the EPS volume, which is evident from the analysis of the pore data.

Moreover, the ultrahigh strength is an effective tool to combat the deteriorating effect of polystyrene on the strength of concrete.

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