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Ash Deposits CHP – as an Additional Source of Raw Material for Construction Production

Rimma K. Niyazbekova[a], Muratbek T. Userbaev[a], Gulnara A. Kokayeva[a], Lazzat S. Shansharova[a], Marat D. Konkanov[a], Saule A. Abdulina[b,*]

[a]S. Seifullin Kazakh Agro Technical University, 62, Zhenis avenue, 010011, Astana, Kazakhstan
[b]D. Serikbayev East Kazakhstan State Technical University, 19, Serikbayev str., 070000, Ust-Kamenogorsk, Kazakhstan
abdulina.saule@mail.ru

Issues related to the rational processing of industrial waste and the protection of the environment are of particular importance. The prerequisite for writing this article was the ecological situation in Kazakhstan.
Currently, many industrial enterprises have accumulated and continue to accumulate man-caused waste of production processes that not only pollute the atmosphere and, washed away by rain and snow, pollute the water basin of nearby areas. The work of CHP is one of the main polluters of the environment, mainly the air basin. CHP plants operating on traditional types of fuel contribute up to 30 % of the volume of harmful emissions of the atmosphere, pollute the land and water with combustion products and sewage.
Technogenic wastes occupy hundreds of thousands of hectares of fertile land. In them, the content of non-ferrous metals reaches up to 5 %, iron up to 45 %, in addition, some of them contain noble metals. The bulk of this waste is siliceous materials, which are the main source of building materials.
In Kazakhstan, as yet, they have not been engaged in the utilization of ash, these are technogenic waste from the thermal power station. Known methods of processing such raw materials do not fully comply with modern requirements of scientific and technological progress. Dumps of ash and slag materials occupy large areas, and their content requires significant operating costs, which affect the increase in the cost of production of energy. They are a source of environmental pollution, present a danger to public health and a threat to the plant and animal life of the surrounding areas. Especially dangerous are ash dumps located near water basins (rivers and lakes), because of the possible breakthrough of dams. Effective utilization of coal energy coal plants can help significantly reduce the negative impact on the environment and improve the economic performance of the enterprise. In general, ash is widely used in various industries and has good market prospects.
There are available technologies for ash utilization, some of which are widely used commercially. At present, the main quantity of ash is used in the construction industry - this is the production of cement, bricks, cellular concrete products, slag blocks, lightweight aggregates, roofing material, expanded clay, construction of dams for ash dumps, construction and repair of roads.
The use of ashes and slags of CHP as building materials is the most ambitious direction and can solve the problem of building materials shortage in the regions of Kazakhstan in the future. Due to the use of ash waste, we can save up to 30 % of cement and more than 50 % of natural aggregates, thereby reducing the thermal conductivity of concrete will reduce the mass of buildings and structures.
To attract investments in order to increase the level of processing and use of ash waste, it is possible to use interest in the purchase of ash and slag from the thermal power stations of Kazakhstan in those Western European countries and the Middle East, where there are not enough sources of mineral raw materials in sufficient quantities.
The solution of the above problems is necessary to increase the level of utilization of ash waste with a view to reducing their accumulation, improving the environmental situation in the vicinity of the CHP plant, as well as receiving income from the sale of products produced on the basis of ash waste.

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1. Introduction

In the Republic of Kazakhstan, the annual output of ash and ash and slag mixtures when burning coal is about 19 Mt, and in the ash dumps to date, more than 300 million tonnes of waste have been accumulated. Although ashes in the main mass are captured by various filters, nevertheless about 250 Mt of fine aerosols are annually supplied to the atmosphere in the form of TPP emissions. The latter are able to significantly change the balance of solar radiation near the earth's surface. They are the nuclei of condensation for water vapor and the formation of precipitation; and getting into the respiratory system of man and other organisms, cause various respiratory diseases. Unlike other industries, such as ferrous and non-ferrous metallurgy, smoke emissions of modern TPPs are carried out through a small number of very high pipes, a height of more than 180 m. Therefore, pollutants dissipate in the vast space of the lower troposphere. In the spheres of influence of various TPPs, it is established that in the nearest zone with a radius of 12-15 km, depending on the height of the pipe, 35 to 60 % of the emitted ash falls out (Plotnikov et al., 1990). As a solid fuel at TPPs, Ekibastuz coal is used most, characterized by high ash content (30 - 40 %). At present a huge amount of ash and slag has accumulated on the territory of Kazakhstan in the region of operating TPPs (>4,600 Mt). They occupy huge areas and negatively affect the environment. Ash of Ekibastuz coals contains up to 30 % of aluminum oxide (Glukhovsky et al., 1991). Only with the ash of Ekibastuz HEPS is annually dumped in the dump about 6 Mt alumina. Fuel ash and slags are products of thermochemical and phase transformations of inorganic components of fuel and largely consist of the minerals of the enclosing rocks. The predominant minerals in ash and slag materials of TPP are silicates. First of all, these are meta- and orthosilicates, as well as aluminates, ferrites, aluminaferrites, dehydrated clay minerals; Oxides, for example, quartz, corundum, alumina, calcium oxides, magnesium, etc., are present in significant amounts. In the ash dumps, secondary minerals can arise as a result of hydrochemical processes, for example, calcite, portlandtite, iron hydroxides, etc. Ashes and slags are a complex system, the properties of which depend on the type of fuel and the mode of its combustion, the design of the boiler and many other factors. This determines the need for comprehensive studies of the composition and properties of the mineral part of various coal burned at Kazakhstan power plants, since the main reason for the insufficient use of ash and slag in the national economy is the unsatisfactory state of the study of ash and slag as raw materials.
According to (Runova, 1990), the main type of fuel and energy resources in Kazakhstan is coal, the supplies of which are carried out mainly from Ekibastuz, Karaganda and Kuznetsk deposits. The Ekibastuz coal basin is one of the most significant in terms of reserves and ranks first in the world in terms of coal density: on an area of 62 km^2, coal reserves are estimated at 13×10^9 t or 200 t/m^2. And for open-pit mining, coal is one of the most promising areas in the world. Ash content of coals reaches 40 - 50 %. The main consumers of coal from this basin are in the Urals and in the Republic of Kazakhstan. At present, the production of alumina cement has been reduced in Kazakhstan. The use of low-grade bauxites leads to the formation in the cement of hydraulically inert compounds, for example, gehlenite, as a result of which the strength characteristics of the cement stone are reduced. At the same time, there is a huge amount of waste in the ash dumps, the use of which will promote the development of the production of special cements (Tao and Dong, 2017). However, without thorough investigation of such waste and their effect on hydration, hardening, and also operational properties associated with the use of cements and concretes in the high temperature and pressure zone, it is impossible to produce them.

2. Methodology of carrying out experimental researches

Portland cement of grade 400, alumina, expanding cements, water slurry from traps, fly ash, microspheres from ash disposal facilities of CHPP-2 in Astana were used to make the samples. Depending on the granulometric composition and type of waste, the methods of their introduction into the cement mixture of the composition of used water, the following were investigated:

- Chemical, phase, granulometric composition of ashes from "wet" ash collectors and microspheres;
- Properties of cement pastes - normal density, setting time;

The chemical and phase composition, structure and properties of ash and slag materials depend on the composition of the mineral part of the fuel, its calorific value, the combustion regime, the way they are captured and removed, the place of selection from the dumps (Zhang, 2017).
The chemical composition of the waste from the combustion of Ekibastuz coals, determined on the 797 VA “Computrace analyzer" (Metrohm), is mainly represented by SiO_2, Al_2O_3. Fe_2O_3, CaO, MgO, Na_2O, K_2O, TiO_2, SO_3, etc. Table 1 shows the composition of ashes from "wet" ash collectors and microspheres.
To study the phase composition of waste, electron-microscopic and X-ray phase analysis was used by the ionization method of recording the radiation intensity on a D8ADVANCE X-ray diffractometer (Bruker) using Cu-radiation. The surveys were carried out in the discrete scan mode in 0.020 2Ɵ increments. As a result of analyzes in fly ash, the main minerals were found: vitreous phase, mullite $2Al2O_3{\cdot}SiO2$, calcium orthosilicate

$2CaOSiO_2$, SiO2, oxides Al_2O_3, CaO, MgO, hematite $2Fe2O_3$, hedenbergite FeO·CaO·2SiO2. In the ashes from the "wet" ash collectors, as a result of hydrochemical processes, secondary minerals such as calcite, portlandtite, iron hydroxides appeared. In samples, whitens are represented by irregularly shaped crystals, there are also small crystals, which are an isomorphous mixture of iron compounds. The phase composition of the microspheres includes a vitreous phase, mullite, calcium aluminosilicates, quartz, hematite.

Table 1: Composition of ashes from "wet" ash collectors and microspheres

Components, %	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Na_2O	SO_3	CaO
Ash from "Wet" ash collectors	47.02	26.2	8.05	3.36	1.56	0.1	0.2	0.1
Fly ash	50.5	24.7	7.4	2.6	1.8	0.3	1.2	0.18
Microspheres	39.2	30.4	4.5	3.3	1.1	0.15	1.1	0.11

Inorganic phase, in turn, consists of the components:
- Amorphous, represented by glass and amorphized clay substance;
- Crystalline, including slightly modified grains of minerals of the initial fuel (quartz, feldspar and other, thermally stable minerals) and crystalline neoplasms that have arisen during fuel combustion (mullite, hematite, calcium aluminosilicate, etc.).

The density of the shell material is 2.4 - 2.5 g/cm; the average density of microspheres – 0.6 to 0.7 g/cm. The prevailing (more than 80 %) size of microspheres is 70 to 200 μm. The calculated specific surface area of the microspheres is 1,100 to 1,200 cm^2/g (Mi and Liu, 2016). As a result of hydrochemical processes, secondary minerals can appear in ash dumps, for example, calcite, portlandtite, iron hydroxides, etc. The phase composition from the data of X-ray phase analysis (Figure 1).

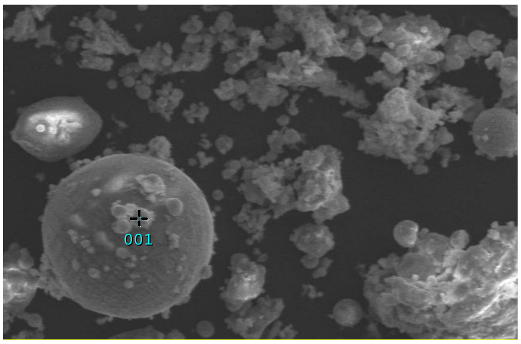

Figure 1: Micrograph of ash microspheres of CHPP-2 in Astana: the prevailing phase (up to 40 %) is mullite

When using fly ash, it was controlled:
- Hygroscopicity, % by weight – up to 0.15;
- Thermal conductivity in the bulk state – 0.08 ... 0.13 W/m×K;
- Temperature range of melting – 1,673 ... 1,823 K;
- Softening start temperature - tp = 1,673 K.

The study of the granulometric composition and determination of the main indicators of waste after drying are presented in Table 2 and Table 3.

Table 2: Granulometric composition of fly ash

Particle content, %, grain size, mm							
"Wet" ash collectors	20-10	10-5	2-1	0.5-0.25	0.25-0.1	0.1-0.05	<0.05
	-	-	1	4	3	5	35.2
Microspheres	-	-	-	1	1	2	44.3

Table 3: The main characteristics of fly ash

Characteristics	Indicators
Humidity, %	0.086
Specific surface, m^2/kg	180

3. Results

In the work, ash from wet ash collectors and aluminosilicate microspheres of the Astana thermal power station, operating mainly on Ekibastuz coal (Figure 2) were researched.
In the Figure 2 shows the particles that have different composition and size. The smallest of the particles are carried away by the flue gases. Particles of most of the ashes are spherical and have a smooth vitrified surface texture. The homogeneity of the particles is different. The particle size ranges from a few microns to 50-60 microns.
The aluminosilicate hollow microspheres are a dispersed material folded by hollow microspheres of 10 to 200 μm in size (Figure 3). The chemical analysis of ash microspheres presents in Table 4.

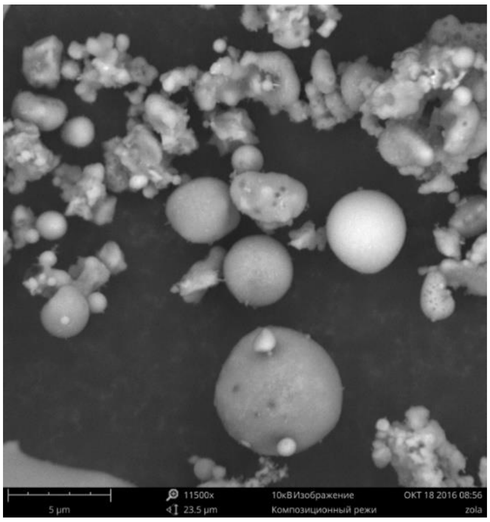

Figure 2: Hollow ash aluminosilicate microspheres

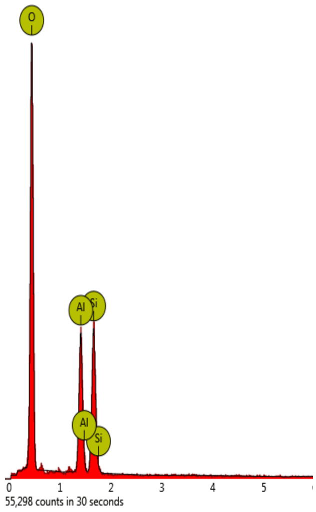

Figure 3: Elemental analysis of ash

Table 4: Chemical analysis of ash microspheres

Element Number	Element Symbol	Element Name	Weight Concentration	Error
8	O	Oxygen	63.7	0.0
14	Si	Silicon	19.4	0.1
13	Al	Aluminium	16.9	0.0

As can be seen from Figure 3 and Table 4, the chemical analysis of ash shows the predominance of particles of an aluminosilicate composition in it. Cements based on aluminosilicate microspheres play an important role in the development of heat-resistant materials that undergo phase transformations at temperatures above 773 K.
In this work we were researched the properties of cement pastes of normal density and setting time
When studying the influence of the compositions of cement compositions and the use of the cement base, the amount of cement was reduced by 5 - 7 %, which compensated for the energy costs of the mixture at home. The choice of the number of components of the mixture and their ratio is related to the given density of composites, its strength and economic feasibility.
It should be emphasized that careful mixing of components is one of the most important conditions for the successful implementation of any cement technology. Good mixing of cement particles with water promotes a more complete and rapid physical and chemical interaction, as well as a uniform coating of the aggregate grains with a thin layer of cement paste.
Experiments on the properties of cement pastes and solidified composites have shown that cement with recommended additives, in contrast to cements without these additives, has higher strength and heat resistance. The recommended time for cement is 2-5 min. An increase in the specific surface area of cements above the optimum can lead to aggregation of the part, and in cement pastes and suspensions to an increase in water retention. This phenomenon, in turn, has an undesirable effect on the strength properties of solidified cement, and also adversely affects the frost resistance of materials. The data obtained after 5 min of grinding and the study of the properties of cement pastes, by determining the time of setting, indicates a sufficient fineness

of grinding of cement particles. The results of the experiments showed the positive effect of microspheres on the strength properties of portland cement and aluminate cements. The recommended number of microspheres is 5 % of the weight of the cement. In cases with aluminous and expanding cements, due to the presence of rapidly hydrating aluminate phases, it is necessary to use the optimum amount of superplasticator. In order to increase the ductility and workability of cement paste, it is recommended to use a superplasticizer PMF-NLK in an amount of up to 0.2 % of the weight of the cement. The use of nanoadditives in the composition, as a result of their complex physico-chemical effect at the stage of formation and hardening of the cement binder, led to an increase in the strength characteristics of the final product.

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

Type of binder	Time of initial setting, hour. min.	time of final setting, hour. min.
Portland cement M500	2 h, and 20 min	4 h
Portland cement with the addition of wet ash 2 %	2 h and 10 min	3 h and 55 min
Portland cement with the addition of wet ash 3 %	2 h	3 h and 50 min
Portland cement with the addition of wet ash 4 %	1 h and 55 min	3 h and 50 min
Portland cement with the addition of wet ash 5 %	1 h and 40 min	3 h and 40 min
Portland cement with the addition of wet ash 7 %	1 h and 35 min	3 h and 35 min
Alumina cement	2 h and 10 min	3 h and 40 min
Alumina cement with the addition of wet ash 2 %	2 h	3 h and 40 min
Alumina cement with the addition of wet ash 3 %	2 h	3 h and 35 min
Alumina cement with the addition of wet ash 4 %	1 h and 50 min	3 h and 30 min
Alumina cement with the addition of wet ash 5 %	1 h and 40 min	3 h and 20 min
Alumina cement with the addition of wet ash 7 %	1 h and 35 min	3 h and 20 min

The tests Portland cement and alumina cement with additives and without additives were carried out in accordance with the methods of GOST 310.1; GOST 310.2; GOST 310.3. The activity of the mixed binder was determined in accordance with GOST 310.4. The water absorption of the mixed binder was studied in accordance with GOST 12730.3. The porosity indices were determined in accordance with GOST 12730.4 on the kinetics of water absorption. The parameters characterizing the porosity were the average pore size λ and the pore homogeneity index α. Based on the test results, the relative water absorption by mass at the time t_1 = 0.254 h - Wt_1 and t_2 = 1 h - Wt_2 was calculated. Then, the parameters Δ1, α and Δ were determined using these nomograms. The finely divided disperse filler introduced into the binder can significantly change the rheological and structural and mechanical properties of the binder. With an increase in the degree of filling of cement with a finely ground mineral additive, as a rule, its water demand increases. It increases with increasing water requirement of the most used additive. It is important to determine the effect of modifying additives on the timing of setting the cement. The results of the study of the effect of additives on the setting time for cement are presents in Table 5. For the test compositions, astringents, a significant reduction in the setting time is observed. This is due to the fact that the additives bind calcium hydroxide, formed during the hardening of cement, in low-basic hydrosilicates of calcium, which leads to an acceleration of the processes of structure formation. Studies aimed at determining the normal density of cement paste, containing in its composition the additive of wet ash are of considerable interest. The results of the studies are presents in Table 6. As can be seen from Table 6, the normal density of the cement paste without additives is 29 %. For the cement dough containing nano-additives, the normal density of the binder is slightly lower and is 27.8, 27 and 26 % respectively for the PCs, 27.5, 26.8 and 25.5 % for the ACs. The reduction in the water demand for cement with these additives is due to the fact, that when micro and nanodispersions are added, its porosity is reduced, and the silica content is increased.

Table 6: Results of the determination of the normal density of the cement test

Indicator name	Cement without additive	Cement with the addition of wet ash 2%	Cement with the addition of wet ash 3 %	Cement with the addition of wet ash 5 %
Portland cement 400 Normal density, %	29	27.8	27	26
Alumina cement Normal density, %	28.8	27.5	26.8	25.5

In the technological process, an important operation is the method of introducing the additive into the cement. In practice, cement additives are introduced in several ways. The most traditional method is when additives in cement are introduced with mixing water, while thoroughly mixing the cement paste (separate way of preparation).
Another way of introducing the additive is to co-crush cement and additives. For disperse systems prone to aggregation of particles when water is added, the additive is introduced together with the plasticizer.
The criterion for evaluating the effectiveness of the method of introducing additives into cement is the strength of the cement stone for compression. Structural and mechanical properties of Portland cement with various additives are presents in Table 7.

Table 7: Structural and mechanical properties of Portland cement with various additives

Name of indicators	Cement with the addition of wet ash 2 -3 - 5 %	Cement without additive
Portland cement:		
Compressive strength, MPa	60	
	65.4	48
	68.2	
Transverse strength, MPa	2.48	
	2.54	2.4
	2.6	
Alumina cement:		
Compressive strength, MPa	62	
	66.4	48
	68	
Flexural strength, MPa	2.5	
	2.6	2.4
	2.72	

4. Conclusions

The most important indicators of the operational properties of concrete are the kinetic characteristics of their change in time. For concretes hardening for a long time under air-humidity conditions, one of such characteristics is the strength and kinetics of its variation with time. Comparative studies of the strength of Portland cement modified with active mineral additives were carried out.

- Found that active mineral additives slightly reduced the time of setting Portland cement;
- Found that mineral additives have a positive effect on the uniformity of the change in the volume of cement stone;
- Revealed that the cement stone on Portland cement with mineral additives is more intensively gaining strength compared to samples without additives.

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