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STUDY OF ASH AND SLAG WASTE TO BE USED AS SECONDARY RESOURCES

Introduction

Kazakhstan has a significant number of thermal power plants. Every year, the amount of ash and slag waste (ASW) generated at combined heat and power plants (CHPP), state district power plants (SDPP), as well as in boiler houses increases. The fuel and electricity sector is one of the main “pollutants” of the natural environment [1]. By burning coal, the plant obtains thermal energy and generate electrical energy. Negative side of this process is formation of by-products of coal combustion — fly ash and slag.

It is known that storing ash and slag waste is a very expensive undertaking. According to expert estimates, investments in the reconstruction of one ash and slag dump can reach 5 billion tenge, and construction of a new one costs 10–12 billion tenge. Storage of ash and slag waste not only leads to the withdrawal of vast land areas, but also causes very significant environmental pollution.

Comparative analysis

Deterioration of ecological situation is reasonably linked to atmospheric pollution. Long-term storage of thermal energy waste in ash dumps contributes to harmful substances and heavy metal ions entering the water and soil. The anthropogenic component of formation of water surface quality is already commensurate with the natural component, which poses a threat to sustainable water use. The annual yield of ash, fly ash and slag mixtures from coal combustion in ash dumps in Kazakhstan is more than 17 million tons. Over 300 million tons of ash waste have been accumulated in ash dumps [2].

Electricity production development and recycling of TPP waste, in particular, ash from coal combustion, is one of the main state priorities of Kazakhstan. **Figure 1** shows the volumes of ash and slag waste generation in Kazakhstan regions in 2022 [3–5].

The other regions of Kazakhstan use gas fuel. There is a need to reduce anthropogenic burden through introduction of regional regulations, changes in fees for pollution of water bodies and use of energy waste in manufacture of building materials. There is practically no processing of ash and slag waste on an industrial scale.

In Kazakhstan, about 8% of ash (less than 1.9 million tons) from coal ash and slag waste produced by thermal power plants and state district power plants is processed at the research and production level. If the ASW use remains at this level, then by 2030 the volume of accumulated waste will reach 1 billion tons [6].

According to expert estimates, investments in reconstruction of one ash and slag dump can reach 5 billion tenge, and construction of a new one costs 12–13 billion tenge [7].

One of the largest thermal power plants in Kazakhstan is Almaty Electric Station CHPP-3 JSC, which provides energy to about 70% of consumers in

The article presents the results of assessing impact of ash dumps on the natural environment under conditions of burning coal from the Ekibastuz deposit in Kazakhstan. It is shown that in the area of ash storage facility at Ekibastuz SDPP-2 and in the Almaty region, as a result of activities of three thermal power plants, huge amounts of ash dumps have been accumulated and significantly pollute the environment. Possibilities of obtaining popular building materials from them have been determined. The relevance and significance of this problem is enhanced by fact that manmade waste from thermal power plants is insufficiently processed while current ash waste accumulates and occupies huge areas, which withdraws them from land use. Utilization of ash dumps makes it possible to reduce the anthropogenic load on the environment and ensures the rational use of secondary raw materials. Possibility of obtaining agloporite from the ash of Ekibastuz coal used by the thermal power plant of Almaty is studied. The chemical and granulometric composition of ash and slag is determined. X-ray diffraction and differential thermal analyses are performed. The analysis of chemical composition of Ekibastuz ash describes the composition of the mineral substances of coal. The main components are silicon and aluminum oxides, and a large amount of iron oxide is also present. Knowledge of the chemical composition of ash is necessary to decide on the possibility of using it to obtain building materials. Thus, all studies conducted have shown the possibility of using ash and slag waste as secondary raw materials in order to reduce the anthropogenic load on the environment.

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the Almaty region. Waste from CHPP-3 is not processed, and current accumulated ash waste occupies huge areas which are withdrawn from land use. Storage of ash and slag waste not only leads to withdrawal of significant land areas, but also causes very significant pollution of almost all environmental components in the area where they are located.

Today, many foreign countries have experience in developing effective environmental and economic systems of non-waste technology. For Kazakhstan, this experience is useful in terms of using innovative solutions in the field of processing and recycling of ash and slag waste in domestic practice. Problem of recycling slag in construction remains an urgent task, since almost all research is limited to experimental developments. All this raises an urgent need to conduct targeted comprehensive studies of both the slag itself and materials based on it. Therefore, today waste management has become particularly relevant as one of the key areas for the development of a “green”

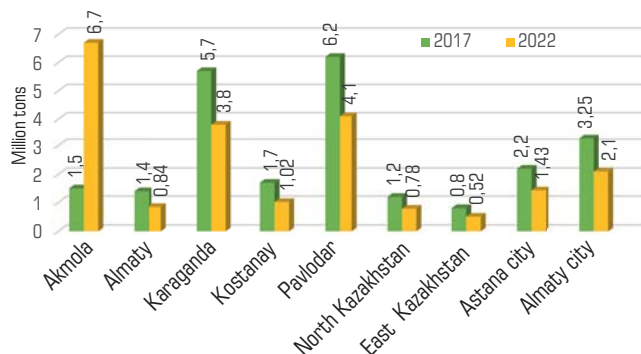


Fig. 1. Ash and slag waste generation in the regions of the Republic of Kazakhstan [4]

economy in Kazakhstan, i.e. conservation and effective management of ecosystems [8, 9].

By and large, ash is not a waste, but a valuable raw material — a man-made mineral source. Therefore, in England and Germany, ash and slag are completely used in the national economy (100%), up to 82% in Japan, 65% in the USA and China, and to 15% in Russia.

However, for various reasons, ash dumps find no utilization in Kazakhstan, since their physical and chemical properties are very poorly studied, and, in addition, processing of such waste produces other waste, the ash dumps are totally unsuitable for use because they contain a lot of unburnt coal. There are factors of disinterest. Therefore, ash dumps at storage facilities across Kazakhstan are increasing from year to year, causing, as mentioned above, environmental, economic and socio-economic damage amounting to a billion tenge.

World experience shows that fly ash can be used in various areas of the national economy, however, the most ash-intensive and environmentally and economically efficient areas, as already mentioned, are the construction and road industries.

When using fly ash as a mineral additive for cements and concrete mixtures, their physical, mechanical and operational properties are significantly improved. In connection with the above, the relevance of using fly ash as a component for cement and concrete mixtures is beyond doubt.

Of greatest interest to Kazakhstan is the experience of Germany, where the Federal Ministry of the Environment developed a Waste Prevention Program in 1972 [10]. In Germany, every manufacturing enterprise is interested in processing and there are large processing facilities in the country. There are about 20 such systems in Berlin alone. Germany is one of the leaders in waste recycling in Europe — 70% of waste is recycled here. Finland is in first place — 97% of waste is recycled in this country.

A review of previous scientific works showed that there is significant world practice of conducting research on ash dumps of thermal power plants [11, 12]. In neighboring countries, the level of use of ashes and slags from thermal power plants does not exceed 7–10%, while in developed countries it is about 50%, in France and Germany — 70%, in Finland — about 90% of their current output [13, 14]. Domestic enterprises practically neglect ash and slag waste.

Thus, in areas affected by ash dumps, unfavorable environmental situations result from dust formation, as well as leaching of ash components (radionuclides and heavy metals), their entry into the soil and groundwater, which, in turn, poses a danger to public health and a threat to flora and fauna in nearby areas. In addition, ash dumps are the cause for the alienation of large areas of land for the purpose of constructing ash dumps for the placement of ash waste, which are almost irrevocably withdrawn from useful use, even after their reclamation, and their maintenance requires significant operating costs, which increases the cost of energy production. One of the problems of storing ash waste at an ash dump is its location near large cities, in our example, within the Almaty metropolis. The problem of terrain deformation and alteration aggravates [15, 16].

The growing scale of construction in Kazakhstan requires a significant amount of mineral raw materials for the building materials industry. Intensification in this direction involves the use of industrial waste instead of primary natural resources to reduce the cost of building materials. The use of solid mining waste in the building materials industry is more economical compared to the production of building materials based on special-purpose extraction of mineral raw materials.

The aim of this work is to study properties of ash and slag waste from coal combustion at the Ekibastuz deposit in Kazakhstan, to evaluate the waste as a source of the

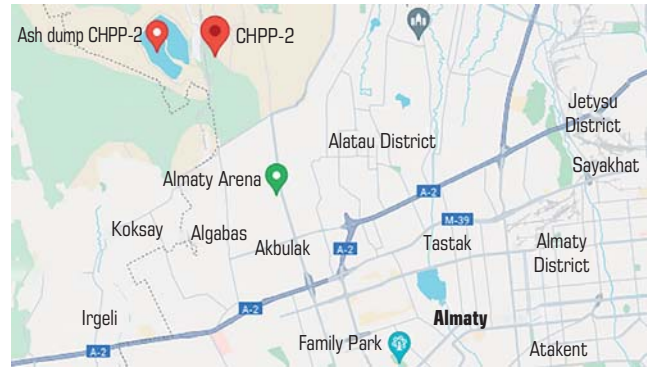


Fig. 2. Location of CHPP-2 ash dump in Almaty

environmental pollution and to determine feasibility of obtaining demanded building materials from the waste.

Materials and research methods

By burning coal, thermal power plants receive thermal energy and generate electrical energy. The negative side of this process is the formation of by-products of coal combustion — fly ash and slag. The composition of the ash and slag material was determined by the quantitative ratio of its constituent minerals, which depend on the mineralogical composition of the initial fuel feedstock.

In this work, ash and slag waste from CHPP-3 of the Almaty power plant was studied. The Almaty power plant unites 3 thermal power plants (CHP-1, CHPP-2, CHPP-3), which provide heat and electricity to consumers in Almaty and in the Almaty region of Kazakhstan. All thermal power plants use coal from the Ekibastuz deposit. At the ash dump of CHPP-3, ordinary samples from 3–5 to 15–16 kg in weight were taken to make group samples later on.

To determine phase composition of the material under study, a modernized DRON-3M diffractometer based on CuK α radiation with software was used. X-ray patterns of samples were obtained in the range of 2θ (angles) from 10 to 70 $^{\circ}$.

Chemical composition was determined using energy dispersive spectrometer EDX-8000. Knowledge of chemical composition of ash and slag



Fig. 3. Participation of young scientists in laboratory research

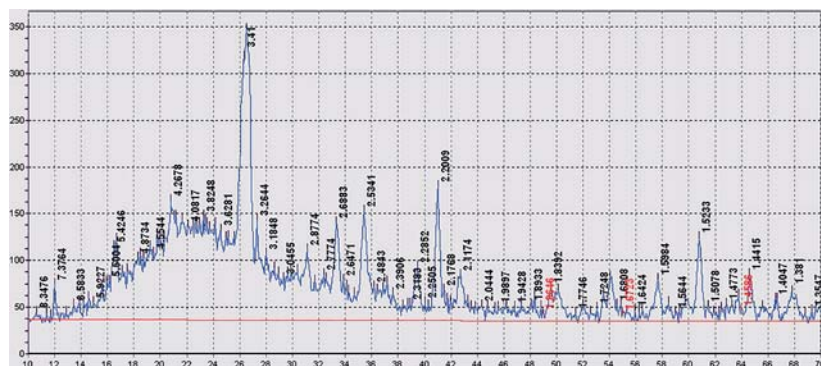


Fig. 4. Radiograph of fly ash

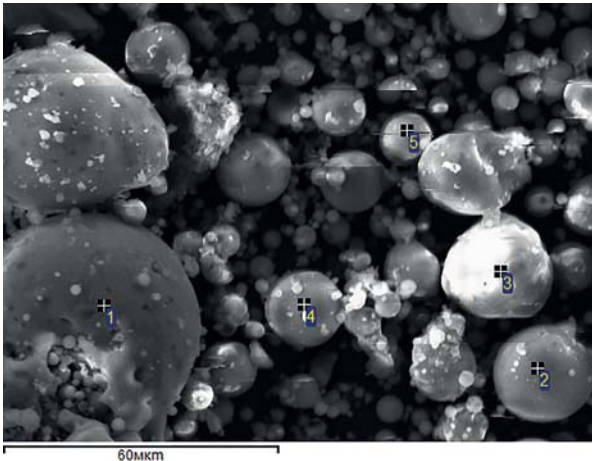


Fig. 5. Micrograph of ash fractions on scanning electron microscope [4]

waste is a necessary condition for judging about its properties and deciding on possibility of using it in various sectors of the national economy. To determine chemical composition of ash and slag waste, ash samples were taken from electric precipitators and ash and slag dumps in accordance with the methodology RD 34.09.603-88 "Guidelines for organizing control of the composition and properties of ash and slag sold to consumers by thermal power plants." This technique makes it possible to analyze the content of various elements in ash and slag, which is important for assessing their possible use in the production of building materials or other industries. This instrument allows analyzing chemical composition of materials by measuring the X-ray emissions caused in irradiation of a sample by electron beam. Thus, an accurate and reliable technology was used to obtain data on chemical composition of fly ash.

The particle size distribution analysis was carried out using Analyzette 22 MicroTec Fritsch GmbH (Germany) device. Microphotograph of fly ash was taken with Superprobe-733 scanning electron microscope with software.

Physical and mechanical properties of fly ash were determined in accordance with the state standards GOST 30744-2001 and GOST 8736-2088. The samples were fired in a SNOL 6.7-1300 muffle furnace; BL-10 laboratory mixer was used to mix the samples. The samples were subjected to strength testing 1 day after steaming and after water storage of the steamed samples for 7, 14 and 28 days. The content of fly ash in the binders was 5, 10, 15 and 20% by weight. The compression strength tests of the samples were carried out in accordance with GOST 10180-90 using laboratory press PM-20MG4 with software, thanks to which data obtained shows their brand strength.

The object of study is the elemental composition of ash and slag waste from CHPP-2. The subject of study is the optimized use of ash and slag.

Table 1. Phase composition of fly ash depending on fraction

| Mesh sieve number | Particle size, μm | Content of the fraction on sieve, % | Distribution of phase composition depending on fraction, % | | | | |
|-------------------|-------------------|-------------------------------------|--|-----------|-------------|--------|---|
| | | | mullite | α- quartz | sillimanite | carbon | glass phase (occupied by halo square, sm ²) |
| 0.5 | 500 | 0.14 | 28 | 54 | – | 18 | 6 |
| 0.45 | 450 | 2.26 | 44 | 21 | 24 | 11 | 14 |
| 0.25 | 250 | 3.36 | | | | | |
| 0.1 | 100 | 25.8 | 46 | 18 | 28 | 8 | 14.5 |
| 0.09 | 90 | 0.84 | | | | | |
| 0.08 | 80 | 12.12 | 42 | 20 | 31 | 7 | 18 |
| 0.063 | 63 | 4.5 | 47 | 17 | 29 | 7 | 20 |
| 0.05 | 50 | 21.46 | 50 | 21 | 29 | – | 22 |
| 0.045 | 45 | 21.38 | 47 | 25 | 28 | – | 23 |
| 0.04 | 40 | 7.9 | 51 | 14 | 35 | – | 23 |

The ecological situation in Almaty is complex. The Development Strategy Almaty-2050 reports that more than 122 thousand tons of harmful substances are emitted into air every year in the city. Transport emission is 65%. This is more than 500 thousand city cars and about 200 thousand non-resident cars. According to the data of local administration, Almaty CHPP-2 which burns high-ash Ekibastuz coal produces 27% of emission. The ash dump of Almaty CHPP-2 is located within the Alatau district of the city (Fig. 2)

At the ash dump of CHPP-2, ordinary samples from 3–5 to 15–16 kg in weight were taken to manufacture group samples later on [17].

Research results and discussion

Primary laboratory research. Intensification in this direction involves utilization of industrial waste instead of primary natural resources to reduce cost of building materials. In this direction, scientists at the Satbayev University are conducting large amount of research on production of secondary raw materials from on industrial waste [16, 17]. Young scientists and PhD students of the University take active part in these studies (Fig. 3).

By burning coal, thermal power plants obtain thermal energy and generate electricity. The negative side of this process is formation of by-products of coal combustion — fly ash and slag. The composition of ash and slag material was determined by quantitative ratio of its constituent minerals dependent on mineralogical composition of initial feedstock of fuel. Using DRON-3 X-ray diffractometer, X-ray diffraction pattern of ash from TPP-2 was obtained (Fig. 4).

The chemical composition, %: SiO₂ — 57.7; Al₂O₃ — 29.6; (Fe₂O₃+ FeO) — 6.4; CaO — 1.1; MgO — 0.35; SO₃ — 1.3; K₂O — 0.03; Na₂O — 0.52; tensile strength — 3.0.

Analyzing phase composition of fly ash, it can be stated that only glass phase, which contains a microsphere, has its pozzolanic and hydraulic activity, and the rest is mullite (3Al₂O₃·2SiO₂), quartz (SiO₂), sillimanite (Al₂O₃), hematite (Fe₂O₃) and carbon (C) which possess no pozzolanic and hydraulic activity.

In addition, the following micro elements are present in the ash: P, Sc, Mn, Pb, Ti, As, Zr, Ge, Ga, W, Ni, Cr, which do not exist independently in ash, do not form independent compounds, but are the part of minerals and glass phase.

Specific surface — 290 m²/kg; true density — 2.1 g/cm³, bulk density — 780 kg/m³.

Figure 5 shows an electromicroscope image of fly ash. Fly ash particles are spherical, glassy and hollow, their sizes vary from 1 micron to 50 microns. Large particles contain smaller spherical particles in their cavities, as shown by the arrow in the figure. On the surface of large particles there are, as a rule, tightly "glued" tiny scattering balls. Electron microscopy allows for a deeper understanding of the microstructure of materials and their properties, which is of great scientific importance. As a result, it is possible to determine the surface area, hydrophobicity, thermal stability and the strength of fly ash. This is important for understanding how fly ash interacts with the environment [18, 19].

The mechanism of particle formation can be described as follows:

- under conditions of hydraulic removal from furnace, ash with elevated temperature comes into contact with water, resulting in the formation of small glass balls;
- after a moment, large melts due to action of water begin to turn into balls, during which small balls are captured by them into their cavity;
- "massive balls" cool down more slowly, so already cooling small balls stick to their surface;

It should be especially noted that on microscope screen, balls and fly ash balls have shiny and white (light) surface, which is typical for texture of glass. Color fades in the picture. Particles of unburned carbon here and there give a black background.

Granulometric composition. These properties of fly ash entering system of hydraulic ash removal channels depend on many factors, including [20]:

- design of boiler furnaces;
- operating conditions of boilers;
- system of dust preparation and supply of coal dust for combustion;
- type of mills and their operational condition;
- device with which fly ash is fed into hydroash removal system of TPP.

The granulometric composition of the Ekibastuz SRPP by fractions is distributed as follows: up to 0.5 mm — 0.14%; 0.45 mm — 2.26%; 0.25 mm — 3.6%; 0.1 mm — 25.8%; 0.09 mm — 0.84%; 0.08 mm — 12.12%; 0.06 mm — 4.5%; 0.05 mm — 21.46%; 0.045 mm — 21.38%; 0.04 mm — 7.9% (Table 1).

Research of secondary raw materials

One of the most promising areas for use of waste from the fuel and energy sector is recycling as a source of secondary raw material [21–23].

Currently, the Satbayev University is accomplishing an ambitious project of building a plant for processing ash and slag waste. The plant will process ash coming from CHPP-1, CHPP-2 and CHPP-3. The ash will be used to produce feedstock for manufacturing materials for the construction industry [4, 24, 25]. There is no doubt that construction of a plant for processing ash and slag waste must begin in close proximity to coal-burning stations. This will increase production profitability. The largest number of publications on the use of ash and slag waste relates to the construction industry, including the development of technologies that allow the use of waste in several directions. The main fields of use are: cement production, concrete production, production of ceramic products, use in road construction, etc.

Ash cement. Production and use of ash cement is considered promising as it consists of ash and cement without mineral additives. One of these methods is the joint grinding of cement and ash at specified ratios in a ball mill in the presence of dry superplasticizer C-3 in an amount of 1.0...1.5% by weight of cement. The input materials for producing high-strength ash cement were: Portland cement grade TsEM 1 32.5, fly ash from TPP-2 and dry superplasticizer S-3 produced by JSC Poliplast. Pre-dried cement and fly ash at specified ratios are loaded into a ball mill. Grinding duration is 6 hours. After 3 hours from the moment of loading cement and fly ash, the required amount of C-3 is added into the mill. After unloading, the specific surface area is instrumentally determined.

Using the resultant mixtures, samples 4×4×16 cm are prepared and tested in accordance with GOST 30744-2001 with regard to the presence of a superplasticizer in the composition of the cementash binders. Therefore, the spread of the cone is kept within 110–112 cm.

Steaming of the samples is carried out according to the regime of 2+10+2 hours at an isothermal heating temperature of 95°C.

The results obtained are given in Table 2, from which it can be seen that:

- in comparison with the original cement without pre-grinding, the compressive strength of the pre-ground binder, consisting of cement and ash with the addition of superplasticizer NeoLit-400, is significantly higher and reaches 40.3...55.5 MPa (versus 26.2 MPa) after steaming and 65.5...75.8 MPa (versus 44.3 MPa) at the age of 28 days;
- the same is valid for the bending strength: 5.8...7.8 MPa (versus 4.8 MPa) after steaming and 7.9...8.9 MPa (versus 4.5 MPa).

The observed effects are explained as follows:

- during intensive grinding in the mill, the particles of cement and fly ash are partially amorphized, which enhances their reactivity;
- NeoLit-400 superplasticizer particles present in the mill are adsorbed onto active surfaces and centers, which contributes to finer grinding of particles of the above-mentioned components;
- when mixing the above-mentioned mixture with water, the effectiveness of the presence of N-400 increases even more, namely: [26]:

Table 2. Properties of obtained samples

| Binder composition, wt. % | | Specific surface area, cm ² /g | Water/cement ratio | Flow rate, mm | Tensile strength, MPa | | | |
|---------------------------|-----|---|--------------------|---------------|-----------------------|----------------|-----------------------|----------------|
| cement | ash | | | | After steaming | | At the age of 28 days | |
| | | | | | in bending | in compression | in bending | in compression |
| 100* | — | 289 | 0.45 | 110 | 4.8 | 26.2 | 5.3 | 44.3 |
| 70 | 30 | 550 | 0.33 | 112 | 7.8 | 55.5 | 8.9 | 75.8 |
| 50 | 50 | 570 | 0.35 | 112 | 6.7 | 50.3 | 8.3 | 70.3 |
| 30 | 70 | 580 | 0.37 | 112 | 5.8 | 40.3 | 7.9 | 65.5 |

* Original cement, without resin and superplasticizer

Table 3. Compositions, average density and strength of aerated concrete under steaming conditions

| No. | Binder composition, wt. % of cement | Binder to ash ratio, % | Contents of foam blister B °D | Powder content, % | Average dry density, kt.AG | Compressive strength, MPa |
|-----|-------------------------------------|------------------------|-------------------------------|-------------------|----------------------------|---------------------------|
| 1 | 40/3.5 | 40/35 | 0.3 | 0.027 | 790 | 4.5 |
| 2 | 40/1.5 | 40/25 | 0.5 | 0.026 | 720 | 3.9 |
| 3 | 40/1.0 | 40/20 | 0.6 | 0.023 | 670 | 2.8 |

- due to its plasticizing properties, the required amount of water is reduced; despite this, the mobility of the mixture increases;
- N-400 destroys flocs — aggregates of cement grains and fly ash, as a result of which the water trapped in them is released, thereby participating in hydration processes;

in a hardening hydration system (cement-ash-SP-water), superplasticizer (SP) molecules split off the Na+ ion, and remaining anions consist of hydrocarbon radical and certain amount of hydrophilic SO₃-groups distributed along the length of the molecule, as a result of which the anions are adsorbed “flat” on positively charged particles of cement and fly ash and hydration products, transferring to them negative charge, thereby adhesion of particles of hydrate new formations [27, 28].

Ash-based gas concrete. One of the ways to produce cellular concrete is to introduce fly ash into its composition, which is due to significantly lower average density of solid waste materials; efficiency of fly ash increases when polystyrene foam is additionally introduced into the ash-based gas concrete mixture. In laboratory conditions, to obtain effective aerated concrete, we proceeded as follows [29].

Water in the required amount of 95% is poured into the working container of the mixer with a rotation speed of 410 rpm, then the mixer impeller is turned on, after which ash and CEM I 42.5 cement are fed in successively with bassanite (CaSO₄0.5H₂O) and polystyrene foam granules with a size ranging from 2–3 mm. This mixture is stirred for 3 minutes, and then, without stopping, the required amount of an aqueous suspension of aluminum powder is introduced, after which the mixture is further stirred for 1 minute.

After mixing is completed, the cellular mixture is poured into molds 10×10×10 cm within 30 seconds. The molds are filled with the solution in one pass. The height of the fill is 9.0...9.5 cm. The molds with cellular concrete mixture are kept at filling stations at a room temperature (20...22°C) during swelling process. After filling the molds with an aerated concrete mixture and swelling, the resulting “top” is trimmed after 2 hours. Then, 3 hours later, the samples with the mold are placed in a steaming chamber and steamed in the mode of 3 + 8 + 3 hours (temperature rise to 85°C + isothermal exposure to this temperature + descent).

The results obtained are given in Table 3. It is seen that at the cement to ash ratio of 40:20...35 in the presence of expanded polystyrene, the steamed samples have the following physical and mechanical properties: the average density is in the range of 670...790 kg/m³, and the compressive strength is 2.8...4.5 MPa. It should be mentioned that a patent has been received for the composition and method of producing aerated ash concrete [30].

Conclusions

In terms of chemical composition and properties, ash and slag waste from the Almaty CHPP-2 is both a source of soil pollution and a profitable and promising raw material. They can be classified as manmade mineral raw materials, which, unlike natural minerals, accumulate over time and are not depleted, which increases prospects for their study and use. Therefore, ASW processing is a very promising area for innovation and investment, which has a multi-purpose focus and a beneficial impact on the environmental and economic development of industrial centers.

The use of manmade mineral waste as additives or components for the production of various building materials contributes to the creation of low- and waste-free technologies for processing raw materials, rational use of mineral resources, and solving the environmental problem of the ecosystem.

Extraction of useful components and complete utilization of ash and slag waste owing to their beneficial properties for the production of building materials can free up space occupied by dumps, reduce the negative impact on the environment, offer useful products and reduce the rate of consumption of non-renewable natural resources. Fly ash from CHPP-2 can serve as an effective component in the production of aerated ash concrete and ash cement.

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