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STUDY OF AGGLOPORITE PRODUCIBILITY FROM THE EKIBASTUZ COAL ASHES

Introduction

Currently, in Kazakhstan more than 500 million tons of ash and slag waste have been accumulated as a result of operation of coal-fired thermal power plants. It is supposed that wastes reserves will increase to 1 billion tons by 2030. It is known that storage of ash waste is a very costly 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 wastes leads not only to the withdrawal of significant land areas, but also causes very significant pollution of almost all environmental components in the area of their location [1].

In the republic, annual output of ash and ash and slag mixtures from coal combustion is about 19 million tons. There is practically no processing of ash and slag waste on industrial scale. As of January 1, 2022, share of recycled, reused, incinerated ash and slag waste was 0.75%.

The research subject of this work was the ash of Ekibastuz coal. Both hard coal of the Ekibastuz deposit and its ash are to some extent unique among the hard coals of other CIS deposits. In particular, this coal, which belongs to hard gas fat low-caking coal [2], has very high ash content, averaging 42%.

Another distinctive feature of this coal is fact that its ash is very refractory. According to the source [2], temperature of deformation beginning of this ash is 1175 °C, beginning of softening—1300 °C, beginning of liquid-melting state—1460 °C. In other words, even simple sintering of ash, not to mention formation of glass during melting, occurs at significant temperatures—above 1300 °C.

This behavior of Ekibastuz ash, which is unusual for coal ashes, is explained by initial mineralogical composition of internal overburden—that is, impurities in coal, amount of which is 42% on average. According to the source [3], these mineral impurities are quantitatively presented, in %: kaolinite—54, quartz—28, siderite—10, calcite—5, gypsum—2 and magnesite—1.

This implies that refractory minerals such as kaolin (which has a melting point of 1770 °C) and quartz (which has melting point of 1713–1728 °C). They are responsible for low-caking and high melting point of Ekibastuz coal ash, and very low content of low-melting minerals, such as siderite, calcite, gypsum and magnesite, only partially reduce overall sintering and melting temperature of this ash. It is this mineralogical composition of coal impurities that makes ash of Ekibastuz coals unique in their refractoriness.

In addition, as noted by some researchers, in particular [4], this ash is acidic, and not highly basic, which greatly limits its use unchanged as active mineral additive to Portland cements, since it initially does not have any noticeable hydraulic activity. In addition, it contains a certain amount of unburned carbon (coal, semi-coke), content of which for concrete is severely limited by requirements of state standards [5].

The article presents the experimental studies to assess possibility of using ash and slag waste generated during combustion of Ekibastuz coal for production of agglomerite—porous aggregate for production of lightweight concrete. The results of studying phase composition and structure of ash and slag waste using methods of X-ray phase and differential thermal and chemical analyzes are given. The results of heat treatment in a gradient furnace of experimental compositions of agglomerite gravel are described. The conclusions are drawn about possibility of using ash and slag waste in construction industry as agglomerite gravel grade 600.

Keywords: Ekibastuz coal, thermal power plant, ash and slag waste, ecology, agglomerite gravel, granules, secondary resources, building products, GOST

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Therefore, search for other ways to use Ekibastuz ash, apart from its use as active mineral additive to cements, is a rather urgent task in national economy [6–8]. We see one of these ways as an attempt to obtain from Ekibastuz ash a light artificial aggregate for lightweight concrete—agglomerite.

Materials and methods

The main goal of this work was baking of Ekibastuz ash from CRPP-3 with various additives to obtain agglomerite gravel with average density below 1.0 g/cm³. That is, such a density that agglomerite granules float in water, and also that they fully meet requirements of the state standards: GOST 11991-83 Agglomerite crushed stone and sand. Specifications and GOST 9757-90 Porous artificial gravel, crushed stone and sand. Specifications.

For firing, muffle furnace SNOL 6,7-1300 with a maximum temperature of 1310 °C was used.

In this work, to reduce caking and melting temperatures of Ekibastuz ash, we were guided by formulas of charge of ordinary window glass, which is known to be made on the basis of quartz sand [9].

For this, two formulations of glass mixtures were chosen as analogues:

1) two-component, in which soda with a small amount of Na₂SO₄ is added to quartz sand;

2) three-component, in which, in addition to soda and Na₂SO₄, calcium component was also added — calcite CaCO₃ (Na-Ca silicate glass).

Choice of analogues of glass batches was substantiated by the following considerations.

Firstly, as described above, melting point of quartz (in the case of building glass—quartz sand) is quite high — about 1700–1730 °C. Addition of alkaline and alkaline earth components (Na₂CO₃, Na₂SO₄, CaCO₃) can significantly reduce this temperature to the level of 1450 °C.

Secondly, process of obtaining industrial building glass is divided into four stages [10]:

1) silicate formation (at temperatures of the order of 800–900 °C);

2) glass formation, characterized by a significant transfer (melting) of previously formed silicates into glass with a large number of bubbles (at a temperature of about 1100–1200 °C);

3) clarification, in which initially added clarifiers and increase in temperature to 1450 °C lead to disappearance of bubbles in the glass;

4) homogenization (or averaging), proceeding at temperatures of the order of 1400–1500 °C, during which remains of previously unmelted silicates are melted and glass is mixed to average its composition.

For purposes of this work, the last two steps were not needed. On the contrary, in our case it was necessary to stop process at the stage of glass formation when number of gas bubbles in the glass would be maximum.

Choice of not one (two-component Na-containing) composition but two compositions, taking into account and Na-Ca-containing composition, was made at the very beginning of the research, taking into account known information that pure Na-glasses, as a rule, are more soluble and less chemically resistant. compared to Na-Ca-glasses. This, in turn, was important for us since one of the technical requirements for agglomerate according to regulatory documents was resistance of agglomerate substance to silicate decomposition. (As it turned out later, both compositions showed a very high resistance to silicate decay, and not just Na-Ca-glass).

Thirdly, for our case, presence of reducing agent (coal) in the Ekibastuz ash turned out to be a positive factor, which contributed to a significant acceleration of decomposition of Na_2SO_4 and its interaction with SiO_2 , due to which overall melting temperature also decreases.

In our case, baking soda Na_2CO_3 was used instead of calcine soda ash was added at the rate of no more than 5% by weight of soda in accordance with recommendation.

Results and discussions

Two formulations of aluminosilicate glasses were manufactured and tested: Na-aluminosilicate and Na-Ca-aluminosilicate glass. These glasses are aluminosilicate, and not silicate, as is case for ordinary building glass, in our opinion, these glasses should be called based on quantitative composition of Ekibastuz ash, in which aluminosilicates quantitatively prevail: sillimanite and mullite, and quartz has a subordinate value.

Formulations of tested aluminosilicate glasses are presented below:

1) Na-glass: 2) Na-Ca-glass:

1. Ash—85.58%; 1. Ash—93.89%;
2. Soda—11.02%; 2. Soda—5.63%;
3. Na_2SO_4 —0.55%. 3. Na_2SO_4 —0.5%;
4. Ca_2CO_3 —2.77%.

The formulations were first tested in the form of bulk charge in crucibles at various temperatures from 1200 to 1310 °C and various exposures. As a result, exposure for half an hour at a temperature of 1280 °C was recognized as the most optimal, which was later used to prepare granules of both types of glass. Temperature rise in the muffle was 10 degrees per minute.

Then, after revealing sintering interval at which foam glass was formed and which for both types of glass was 1250–1310 °C, they began to produce spherical granules with a diameter of 5 to 10 mm. To do this, mixture was mixed with water to bring it to a plastic state, from which granules were molded and dried before firing.

At the first stage, granules were produced without any binder additive.

In this case, they were not molded very well and had a very low strength after drying, which is why they often collapsed. Then, methylcellulose in the form of a powder was introduced into formulations, which was used in the production of dry building mixtures. Methylcellulose Valocel was used in the amount of 1–3% by weight of the charge. Variant with 2% methylcellulose was chosen as the optimal one. With such an amount of it, the molded mass was easily rolled into a bundle with a diameter of 5 mm, and granules that hardened after drying were strong enough and did not crumble. The dried but not yet fired pellets are shown in **Fig. 1**.

Radiographic analysis

As a result, X-ray patterns of original ash and two types of aluminosilicate glasses were obtained in order to study their phase composition on the X-ray diffractometer DRON-3 (**Fig. 2**).

The research found that:

1. The amount of unburned carbon in the ash of CHPP-3 according to the results of determining of ignition loss according to GOST 21216-2014 was 16.16%.

2. As a result of interpretation of this X-ray pattern (see **fig. 2a**), the following minerals were identified in the following amounts, in % of the crystalline phase: hematite Fe_2O_3 — 12.1%, quartz SiO_2 — 32.4%, sillimanite Al_2SiO_5 — 25.9%, mullite — $\text{Al}_{4.96}\text{Si}_{1.06}\text{O}_{9.52}$ — 29.6%.

In addition, there is also a small amount of amorphous substance (amorphous substances) in the ash, which is noted by a low-intensity “halo” with a maximum intensity of up to 100 pulses / sec in the region of angles 14–32°. This is probably amorphous carbon, represented by coal or semi-coke and a very small amount low-melting glass phase, obtained from the melt of low-melting primary minerals: siderite, calcite, gypsum and magnesite. As can be seen from the above numerical values, the secondary minerals formed in the Ekibastuz ash during the combustion of coal at a thermal power plant are in good agreement quantitatively with the source data [2] on the amount of primary minerals-impurities in the Ekibastuz coal.

When comparing the X-ray patterns of the original Ekibastuz ash from CRPP-3 with the X-ray patterns of glasses (see **figs. 2b** and **2c**), the following can be seen:

—The intensity of the 3.36A · peak, which is responsible for mineral quartz in the initial ash (see **fig. 2**), on the X-ray pattern of Na-glass (see **fig. 2b**) fell from 650 pulses/sec to 220 pulses/sec (that is, almost 3 times). On the X-ray pattern of Na-Ca-glass (see **fig. 2c**), this characteristic peak of quartz disappeared completely;

—The intensity of amorphous “halo” responsible for glass phase, on the contrary, on the X-ray patterns of both glasses increased significantly to a value of 140 pulses/sec compared to the intensity of 100 pulses/sec of primary ash. Such increase in the intensity of “halo” indicates that as a result of firing of Ekibastuz ash, significant additional amount of glassy phase of aluminosilicate glass was obtained in it by melting (which is also noted visually).

Comparing the X-ray diffraction patterns of the Na-glass and Na-Ca-glass with each other (see **figs. 2b** and **2c**) shows that in Na-Ca-glass primary quartz has disappeared completely (only incompletely melted mullite remains), while in Na-glass, although its amount has decreased significantly, all quartz has not completely passed into glass.

It is this factor that can explain high temperature viscosity of Na-glass compared to Na-Ca-glass.

The same factor, that is, high saturation of Na-glass with silica SiO_2 and presence of certain amount of free silica, undermelted into glass, all other characteristics of Na-glass are explained: the ability of granules to keep their shape without “spreading” and “sagging” at high temperatures, higher strength, higher chemical resistance (resistance to silicate decomposition), less diffusion of gases from bubbles through viscous surface of molten granules, and as a result—a slightly higher porosity and slightly lower average density of Na-glass compared to Na-Ca-glass.

Thus, lion's share (25.9 + 29.6 = 55.5%) is formed by the minerals sillimanite and mullite, which can be formed from kaolinite (which was originally 54% according to [2] at temperatures of 1100–1150 °C and 1150–1390 °C, respectively. In second place (32.4%), quartz appears in quantitative terms (which has not undergone morphological changes—28% according to [2]), in third place (12.1%)—hematite Fe_2O_3 formed due to siderite FeCO_3 (10% according to [2]).

Ash of CRPP-3 showed very weak sintering, slight thermal shrinkage and complete absence of at least a slight local melting during holding in a



Fig. 1. Formed and dried granules

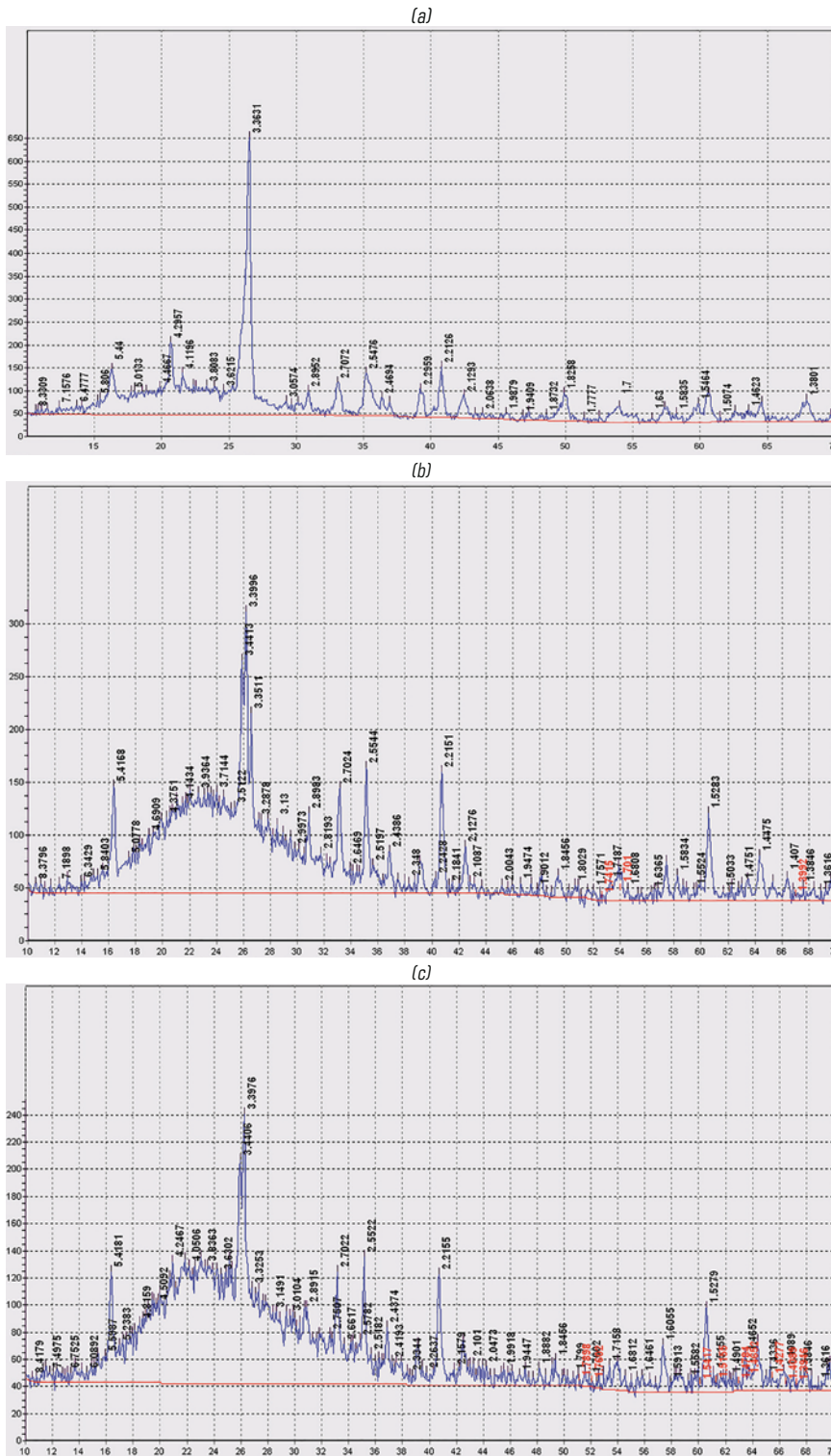


Fig. 2. X-ray of the ash from CHP-3 from the combustion of Ekibastuz coal (a), X-ray pattern of Na-glass (b) and X-ray pattern of Na-Ca-glass (c)

muffle furnace at a temperature of 1310 °C for 1 hour. In general, material turned out to be rather fragile and loose, relatively easily destroyed under pressure.

This result is in good agreement with the earlier source data [1], in which sintering start temperature for Ekibastuz ash was determined as 1300 °C. Therefore, we draw the conclusion that without addition of alkali

or alkaline earth elements to this ash, which reduce sintering and melting temperatures, agglomerite cannot be obtained at a maximum temperature of 1310 °C.

Study results of physical and mechanical properties of obtained two types of agglomerite.

Table presents the physical and mechanical properties of obtained varieties of agglomerite [11, 12].

Ratio of bulk density to compressive strength in the cylinder

Determination of bulk density of two types of agglomerite gravel was determined according to clause 6 of GOST 9758-2012, and compressive strength in cylinder was determined according to p.25 of this GOST.

In accordance with GOST 9757-90 [9] bulk density with values 500 to 600 inclusive refers to bulk density grade 600. Therefore, both types of glasses obtained are assigned to this brand.

According to Table 5 of GOST 9757-90 [9], agglomerite gravel with a compressive strength in cylinder more than 1.2 to 1.5 MPa belongs to the P100 strength grade, and agglomerite gravel with a compressive strength in a cylinder in the range of 2.5–3.0 MPa refers to strength grade P250, which is reflected in the above table.

According to Clause 1.3.4 and Table 6 of GOST 9757-90 [9], grade of agglomerite gravel according to bulk density 600 must correspond to the strength grade P100.

The photographs of Na-Ca-glass and Na-glass cylinder compressive strength data obtained on the press, respectively, are shown Fig. 3.

Resistance to silicate degradation

Determination of resistance of agglomerite gravel against silicate decomposition was evaluated by alternating steaming and cooling of gravel granules in accordance with Clause 31 of GOST 9758-2012.

According to the requirement of Clause 1.3.7 of GOST 9757-90 [9], agglomerite gravel must be resistant to silicate decay. Weight loss in determining resistance against silicate decomposition for agglomerite gravel should be no more than 8%.

As can be seen from table, agglomerite gravel from two types of glass turned out to be very resistant to silicate decomposition and is not subject to dissolution. In this respect, Na-glass again showed an advantage over Na-Ca-glass.

In general, the very high resistance of two glasses and agglomerite gravel from them allows them to be used without problems in lightweight concretes as lightweight aggregates. Comparison of actually obtained characteristics of two types of agglomerite gravel with requirements of GOST 11991-83 was not considered here due to fact that requirements of this standard are lower than requirements of GOST 9757-90.

In addition to the above characteristics of obtained glasses, their indicators were also determined, such as their average and true density, as well as their porosity. These indicators are not standardized by GOST 9757-90.

Main physical and mechanical characteristics of glasses of two types of agglomerite

No.	Physical and mechanical characteristics, unit of measurement	Na-glass	Na-Ca-glass
1	Average Gravel Density, g/sm ³	0.95	0.98
2	Bulk density of gravel, kg/m ³	505.47	514.92
3	Brand according to bulk density of gravel	600	600
4	Cylinder crushing strength, MPa	2.99	1.39
5	Strength brand of gravel (by GOST 9757-90)	P250	P100
6	Weight loss in determination of resistance against silicate decay, %	0	0.07
7	Porosity, %	62.0	60.8
8	True density g/sm ³	2.5	2.5

Average density was calculated as follows: average diameters of several granules of one or another type of glass were measured, corresponding volumes of granules were calculated, granules were weighed, and then average density was calculated as arithmetic mean of 5 measurements.

As a result, it was found that average densities of the two glasses were quite close and, respectively, for the Na glass and Na-Ca glass were 0.95 and 0.98 g/cm³.

True density of two glasses was determined by accelerated method using the Le Chatelier device according to clause 4.15.2 of GOST 8269.0-97 [10]. It turned out to be the same for two types of glasses and equal to 2.5 g/cm³.

Porosity of two glasses was calculated from values of average and true density of corresponding glasses according to clause 12 of GOST 0758-2012.

Actual porosity values turned out to be close and respectively amounted to: 62.0% for Na-glass and 60.8% for Na-Ca-glass. In this parameter, an advantage again turned out to be for Na-glass.

Conclusion

As a result of research, it has been found that:

1. Utilization of ash and slag waste from combustion of Ekibastuz coal is possible by obtaining agglomerite gravel for use as a filler for lightweight concrete.

2. Two compositions of agglomerites are obtained and tested: Na-glass and Na-Ca-glass with an ash content of 85.6 and 93.9% respectively.

3. Evaluation of physical and mechanical properties of obtained types of agglomerite gravel shows that they correspond to grade 600 in terms of bulk density and grades P100 and P250 in terms of strength under compression in a cylinder according to GOST 9757-90.

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(a)



(b)



Fig. 3. Strength indications of agglomerite gravel when squeezing in a cylinder:

a – gravel based on Na-Ca-glass; b – based on Na-glass

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