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Use of Ash and Slag Waste from Thermal Power Plants as an Active Component of Building Materials

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This paper presents the use of ash and slag waste generated from the combustion of coal at thermal power plants as a secondary raw material in various areas of industry. The process of separation of ash and slag is considered into the following components: coal, magnetic concentrate, and aluminum silicate concentrates. The possibility of using aluminum silicate concentrate in the building industry for the production of mineral binders and premixes is investigated. Mineral binding compositions based on gypsum were studied by thermogravimetric methods (differential scanning calorimeter DSC Q2000, thermogravimetric analyzer TG 209 F1). The influence of aluminosilicate microspheres on the quality of the building material was evaluated. The introduction of aluminosilicate concentrate into the building composition reduces the moisture content by 1 %, but the weight loss profile does not change. This indicates the redistribution of microspheres in the volume of the mineral binder composition and the formation of a new physical phase. When using a superplasticizer (Melflux 1641F1), the mechanism of water loss (additional peak) changes. There is a change in the formation of phase contact in the condensed system.

1. Introduction

Ash and slag waste (ASW) is formed as a result of burning solid fuel at the thermal power plants (TPPs). These wastes are a finely dispersed material, which consists of particles up to 0.14 mm in size. These wastes can be used as secondary resources and used in various areas of the national economy (Yu et al., 2015). To date, 172 coal-fired thermal power plants in Russia annually store more than 20 million tons of ash and slag waste , the total accumulation is about 1.5 billion tons (Aleksandrova and Korchevenkov, 2017).

Accumulated raw materials in unprocessed form are unsuitable for industrial use with the exception of road construction (road filling). The storage of waste on special sites increases the anthropogenic impact on the environment (Blisset and Rowson, 2012). Companies have to pay annual fines for environmental pollution.

The chemical composition of ash and slag waste includes a significant amount of iron, aluminum, silicon and other chemical elements (Franus, 2015). With the correct organization of processing, the following useful components can be obtained from them:

- iron concentrate with an iron content of 51-52 %;
- concentrate of precious metals (gold, platinum, palladium)
- aluminosilicate hollow microspheres;
- feedstock for the production of building materials, cement and foam silicate.

The involvement of ash and slag waste in the industrial turnover is one of the most effective ways to save resources. Throughout the world, ASW is actively used as a secondary raw material (tab. 1) (Malchik et al., 2016).

Table 1: Share of use of ash and slag waste in the world

Japan (% wt.)	China (% wt.)	European Union (% wt.)	USA (% wt.)	Russia (% wt.)
96	80	98	46	10

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The foam flotation method, which is based on the different ability of carbon to be retained on the interphase surface, due to the difference in specific surface energies, is suitable for the extraction of carbon from the ASW. The magnetic separation method is suitable for the extraction of magnetic concentrate from the ASW.
Ash and slag waste is used in various directions: backfilling of mines, soil compaction, creation of embankments over landfills, vertical sealing walls to prevent wastewater from seeping from the landfill, soundproofing of walls, agriculture, etc (Menshov et al., 2014).
In construction, ash has found the greatest application in cement and concrete technologies. The use of ASW reduces the cost of producing building materials (cement, dry mortar, concrete, foam blocks, bricks, paving slabs).
The production process of Portland clinker produces CO2 emissions (over 800 kg·CO_2 per t of clinker) (Giergiczny, 2019). To reduce the environmental impact associated with cement (concrete) production, the use of cement additives other than Portland cement clinker is increased. Ash can be used as such an additive (Scrivener and Gartner, 2018). The use of ash in the composition of cement and concrete is primarily determined by the chemical and phase composition close to the composition of cement.
Both in Russia and abroad, high-calcium ash is more actively used in them, but their use is still associated with certain difficulties (Jalal et al., 2015). Ash is characterized by fluctuations in composition and properties, high content of free CaO in them. To solve these problems, calcium chloride, hydrochloric acid, and other chlorides are added to the raw mixture (Yao et al., 2015). This often contributes to the development of cement stone corrosion (Niu et al., 2016).
The greatest value for various practical applications, including in construction technologies, is aluminum silicate concentrate. It consists of nano-and micro-sized hollow balls, the shell of which consists of almost pure aluminum oxide. The use of aluminosilicate microspheres in the production of dry building mixes improves their quality, operational properties, reduces the cost and increases the corrosion resistance of materials (Bazhenov and Murtazaev, 2008).
Ash and slag waste is used in various areas of construction for the production of dry mixes (Giergiczny, 2019; Abdollahnejad et al., 2020), backfilling of roads (Sirotyuk and Lunev, 2017), etc., mainly in its original state. This article examines the effect of aluminosilicate concentrate isolated from ash on the physicochemical properties of mineral binders. Also, the properties and composition of ash strongly depend on the type of coal and the combustion technology used, therefore, the study of the possibility of using fly ash generated at the Kashirskaya TPPs is an important and relevant area of research.

2. Experimental

The initial samples of the mineral binders composition for the study consisted of: the first sample - gypsum, lime, basalt (designation CTP 3.1); the second - gypsum, lime, basalt, aluminosilicate concentrate (designation CTP 4.1), the third - gypsum, lime, basalt, aluminosilicate concentrate, polymer additive Melflux (superplasticizer). The samples were obtained by the method of non-firing pressing. The method for obtaining building compositions is presented in the work of Petropavlovskaya et al. (2016).
Gypsum was used natural LLC "KNAUF Novomoskovsk" (Tula region) with a grain size of 5 mm or less. The main properties of gypsum are presented in table 2.

Table 2: Physico-chemical characteristics of gypsum

True density, kg / m^3	Total porosity, %	moisture content, %	Maximum moisture content, %
2300	0,24	0,3	0,1

As additives, lime from the Uglovsky lime plant in the Novgorod Region and basalt from the Bulatosky deposit in the Arkhangelsk Region were used.
The aluminosilicate concentrate was obtained from the fly ash of the Kashirskaya SDPP, due to complex separation by magnetic separation and flotation methods.
Superplasticizer Melflux 1641F 1 (manufacturer BASF Construction Additives) is a powder product obtained by spray drying on the basis of modified polyether carboxylate. The technical characteristics of the superplasticizer are presented in Table 3.

Table 3: Technical characteristic Melflux 1614F1

Bulk density, kg / m3	heat loss, % wt	pH of 20 % solution at 20 °C
400-600	2,0	6,5-8,5

To obtain an aluminum silicate concentrate from ash and slag waste, a complex method was used, including two stages (Ryabov et al., 2018).
Stage 1-Foam flotation. In contrast to traditional technologies of carbon extraction using kerosene, this study used a mixture of reagents consisting of kerosene and vacuum thermal gas oil with the addition of surfactants. As a foaming agent, it is proposed to use pine oil, reagents T-60, T-66, etc. Laboratory studies have shown the advantages of this approach.
Stage 2-Wet magnetic separation method. The method is based on the technology of separation of materials that differ in magnetic properties (magnetic susceptibility) and different behavior of materials in the zone of action of a magnetic field that changes the gravitational trajectory of materials.
The study of mass loss (TGA) by samples of mineral cutting compositions was carried out on TG 209 F1 (NETZSCH) timbers with a heating rate of 10 °C/min. The analysis was performed under the following conditions: the first stage is heating the sample from 30 to 600 °C at a speed of 10 °C / min, the second stage is holding it for 30 minutes at a temperature of 600 °C. The studies were carried out in aluminum crucibles with an inert gas (argon) supply of 40 ml/min. The sample weight was 10–20 mg.
The test samples were analyzed by differential scanning calorimetry (DSC) on a DSC 204 F1 device (NETZSCH, Germany) at a heating rate of 10 °C/min. The conditions of the analysis fully corresponded to the conditions of the thermogravimetric analysis. This makes it possible to accurately compare the thermal effects in the samples with their mass loss.
Mathematical processing of the experimental data of TGA and DSC was carried out using the software "NETZSCH Thermokinetics 3.1"

3. Results and discussion

The results of the thermogravimetric study of samples of mineral compositions are presented in Figures 1,2 and 3. In the temperature range of 80-200 °C there is a mass loss of the test samples. The weight loss is no more than 17 %. On the DTG curve, three distinct peaks of mass loss can be distinguished, with a maximum at points 121, 150, and 180 °C. In the range of 80-125 °C, there is a loss of adsorption water. The greatest mass loss is observed in the range of 125-200 °C. This is due to the loss of chemically bound water. Since gypsum is part of the composition in the form of crystallohydrate.
This is confirmed by the presence of three endoeffects on the DSC curve in the region of 100-190 °C.
The presence of an exoeffect in the temperature range of 420-510 °C is associated with the rearrangement of the crystal structure of the mineral binder component.

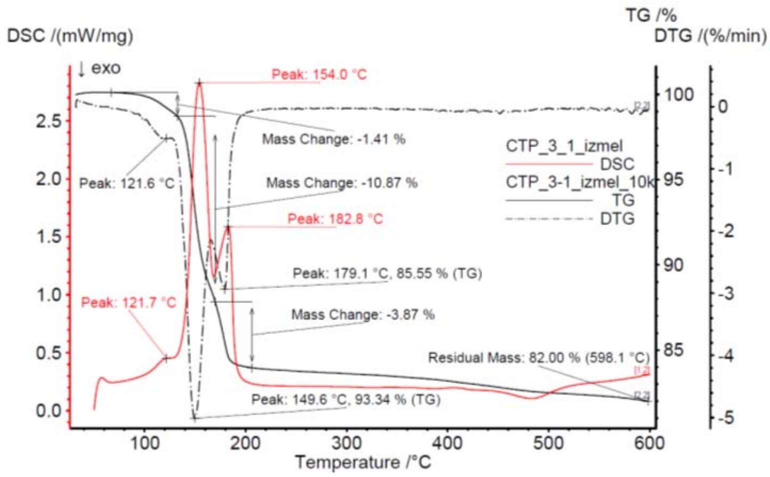

Figure 1: DSC, TG and DTG curves of sample CTP 3.1-izmel

All three samples were characterized by three peaks of mass loss in the region of 80-200 °C. But in samples using the aluminosilicate component, there is a lower mass loss of 1 %. This indicates a lower water content in the samples and, accordingly, a change in the structure during the formation of mineral building materials.
The studied crushed samples of building compositions allow us to estimate only the content of the equilibrium moisture. However, when forming the structure of mineral binding compositions using aluminosilicate microspheres, the physical imp act of the latter can be observed. This effect is called micro-filling, since the ash introduced into the material fills the voids between the particles of the main component, compacting it [Celik et al., 2015].

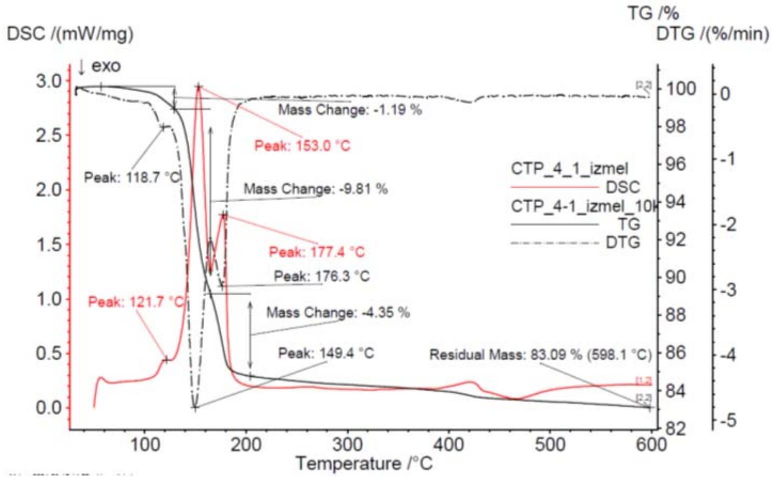

Figure 2: DSC, TG and DTG curves of sample CTP 4.1-izmel

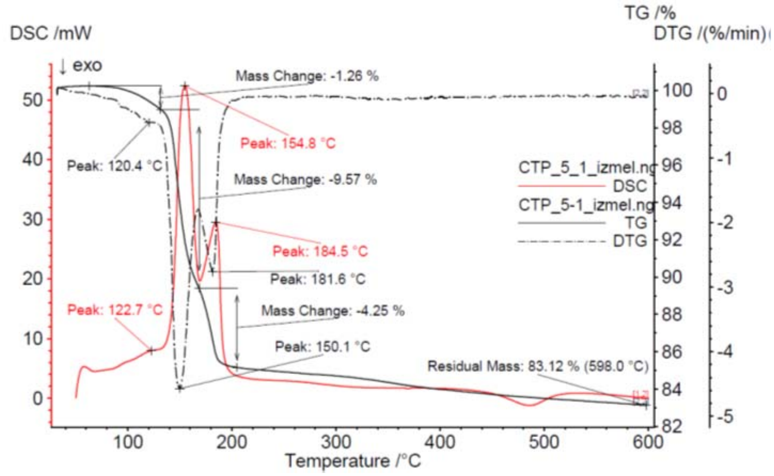

Figure 3: DSC, TG and DTG curves of sample CTP 5.1-izmel

When comparing the studied samples, the three peaks of water loss are in the same temperature ranges. Accordingly, it can be assumed that there is no chemical interaction of the aluminosilicate concentrate with the components of the building mixture. This fact indicates that when this additive is introduced, a new physical phase is formed.

In order to assess the structure during the formation of gypsum building material, a thermogravimetric study of two groups of samples was carried out. The first group consists of crushed samples that reproduce the average composition of the mineral astringent composition (designation-izmel). The second group is a lumpy material that reproduces the structure of the building material (designation-kycok). The need for this approach in the study is caused by the low mass of the image (less than 20 mg) required for the study.

Figures 4,5 and 6 show the results of the study of samples of building materials in the crushed state and in the form of lump material.

According to the results of thermogravimetric analysis, samples of lump material PAGE 3.1 and PAGE 4.1 in the temperature range of 80-200 °C has a greater mass loss compared to the crushed material. This may be due to the formation of internal closed cavities in which water is held.

According to the previously conducted physical and mechanical studies, when adding aluminum silicate concentrate to a building material, its performance characteristics increase (Petropavlovsk et al., 2020). This is reflected in the reduction of the content of physically and chemically bound water in the sample CPT 4.1 compared to the sample PP 3.1. It should be noted that when using the Melflux superplasticizer, a decrease in the water content in the test sample is observed (PAGE 5.1) by 3 % of the mass. in comparison with the sample PAGE 3.1 (Fig. 6). Also, the process of water loss in the range of 80-200 °C consists of 4 peaks. It can be assumed that the addition of a superplasticizer changes the formation of phase contact in the condensed system.

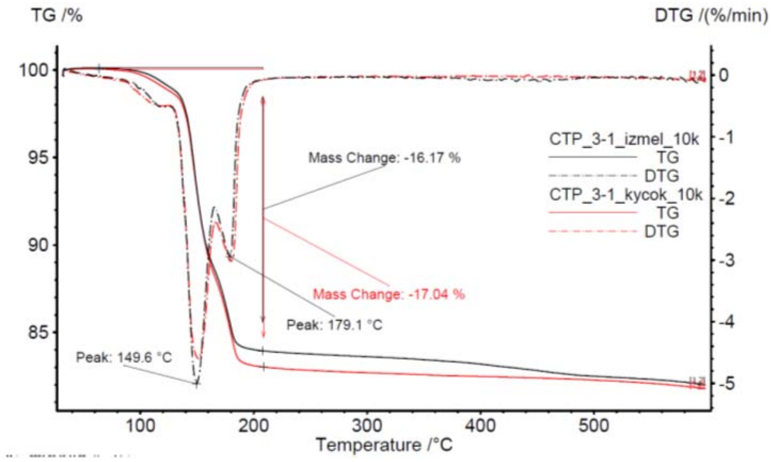

Figure 4: TG and DTG curves of sample CTP 3.1

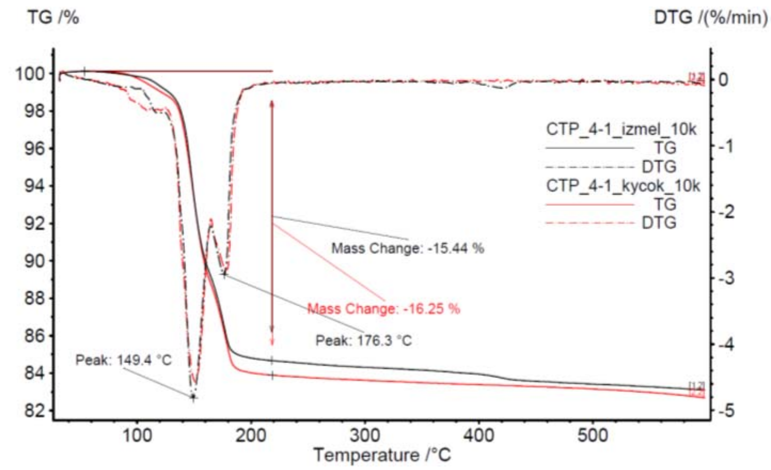

Figure 5: TG and DTG curves of sample CTP 4.1

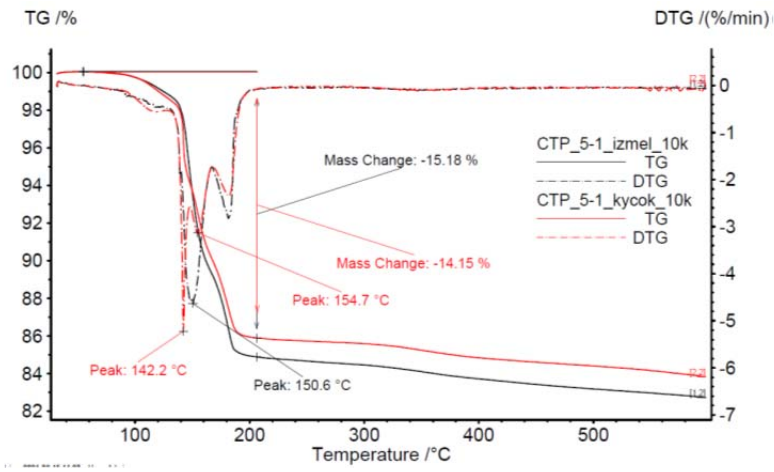

Figure 6: TG and DTG curves of sample CTP 5.1

The distance between the grains of the forming crystals changes in the field of short-range forces. When a non-fired structure is formed, an interaction occurs between the dissolved substance and the grain surface by the mechanism of chemical adsorption. To confirm this fact requires further investigation.

4. Conclusions

The use of aluminosilicate microspheres changes the structure of mineral binding compositions based on gypsum, which increases their quality characteristics: water absorption and the content of equilibrium moisture in the finished composition decreases, which is associated with a decrease in the porosity of the finished product. The introduction of aluminosilicate concentrate reduces the content of adsorbed and chemically bound water by 1%. In this case, the range of water loss and the morphology of the peaks do not change. This indicates a change in the physical structure of the mineral binder. The effect can be based on the high concentration of microdispersed particles in the composition of the raw mixture, which fill the voids in the bulk of the main phase. When adding a superplasticizer, the moisture content decreases by 3% and an additional peak of water loss appears, this indicates a change in the structure of the formation of the condensed phase.

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