

## Ultra-Dispersed Ash Filler for Dispersed Binding Systems

Victoria Petropavlovskaya<sup>a</sup>, Mikhail Sulman<sup>a</sup>, Tatiana Novichenkova<sup>a,\*</sup>, Alexander Sidorov<sup>a</sup>, Kirill Petropavlovskii<sup>a,b</sup>

<sup>a</sup>Tver State Technical University, Tver, Russian Federation

<sup>b</sup>Moscow State University of Civil Engineering (MGSU), Moscow, Russian Federation  
tanovi.69@mail.ru

The paper shows studies of dispersed systems based on cement binder and dispersed aluminosilicate filler. Such dispersed filler in research is modified waste - ash from a thermal power plant from the Moscow region. This waste was generated by hydraulic ash removal. In the work ash was used, which has undergone additional training. It was divided into separate components. In these studies, an aluminosilicate component was used. It has fairly stable chemical and physical-mechanical properties. The treatment of ash powder proposed in this work makes it possible to obtain a system with a large number of contacts in a dispersed system. In this work, the effect of mechanical activation of ash-cement compositions on the physical and mechanical properties of cement stone is investigated. It is shown that in the process of additional grinding, the destruction of large-pore particles occurs. They may be present in small amounts in the ash after processing. The use of activated ash in cement compositions affects the properties and structure of the cement stone. This is facilitated by the active interaction of Portland cement minerals with aluminosilicate ash components. Highly dispersed particles of activated ash in the dispersed binder system allow you to regulate the internal structure of the stone. The highly dispersed composition of the ash powder requires additional plasticization of the dispersed system. The additional introduction of a plasticizer into the activated ash-cement composition helps to improve rheological characteristics, and, consequently, to increase the strength and density of the modified cement stone with the addition of highly dispersed ash filler.

### 1. Introduction

The area of the most urgent tasks of building materials science currently includes the issues of obtaining effective compositions that fully meet the priority goals of sustainable development - Sustainable Development Goals (SDGs) (Gusev et al., 2019).

Within the framework of ensuring the use of "rational consumption and production patterns", it is necessary to investigate all kinds of industrial waste to replace natural raw materials in the production of building materials (Abzaev et al., 2014). This will help preserve the natural environment, improve the ecological situation, reduce carbon dioxide emissions, and also reduce the area occupied by waste (Ciarán et al., 2015). So, as a result of the activities of enterprises of the fuel and energy complex and the mining industry, a lot of tonnage ash waste is generated (Domanskaya et al., 2019). They occupy huge areas, contribute to environmental pollution (Kazanskaya et al., 2018), and can cause many serious natural disasters, air pollution and water sources (Kharitonov et al., 2019).

At the same time, they can be successfully used in the construction industry (Duc Vinh Quang et al., 2020), which constantly needs large amounts of raw materials (Juenger et al., 2015).

Some technologies imply the use of waste ash in the production of cement (Kozhuhova et al., 2017). In view of the fact that one of the main problems in the production of Portland cement is the control of carbon dioxide emissions, the involvement of ash waste, as a component of the binder, can reduce this negative impact. So, according to statistics, about 60 % of carbon dioxide emissions are from limestone burning. And it is the main raw material in the production of Portland cement clinker. It is known that the production of 1 ton of cement contributes to the formation of 918 kg of CO<sub>2</sub> (Krivoborodov et al., 2020) and the release of CO<sub>2</sub> leads to the greenhouse effect and global warming.

Involving the maximum possible volume of ash and slag in the production of such a popular binder as cement will improve the environmental situation and reduce CO<sub>2</sub> emissions. In the modern world, such a task is urgent and in demand. According to many authors, the structuring role of fuel ash in building compositions is due to the type and technology of fuel combustion, as well as the method of ash waste disposal.

However, the condition of the ash or slag does not always meet the technical requirements for fillers (Domanskaya et al., 2016) and may require additional enrichment or the introduction of auxiliary operations (Potapova et al., 2017). They increase the efficiency of ash waste utilization. Researchers often use milling to increase the activity of waste ash. The joint grinding of a cement binder, ash, limestone and a chemical additive affects the intensification of hydration processes during hardening and increases the activity of the composite binder to 62 %, as studies show. The strength of cement with the addition of ash at the age of 3 days of natural hardening is 2 times higher than the strength of the control composition. But researchers also noted a change in the rheological properties of the cement mixture. These studies, like many others, focus on the most demanded and studied waste - fly ash (fly ash) with the high calcium content. Acidic ashes with low calcium content are less studied. Such waste is not yet widely used in modern building technologies, especially in the building materials industry. It takes up huge storage areas. Since, according to the technology, such ash waste is removed with the help of water, this is reflected in its properties. Such ash is characterized by a heterogeneous composition, as well as the presence of a sufficiently large volume of impurities.

Difficulties in the processing of acidic ash waste in the production of modern types of cement and concretes are the inconsistent particle size composition. First of all, this concerns the content of particles in the range of the largest fractions in the composition of the ash and slag mixture (Samchenko, 2018).

The waste hydro ash removal must be separated into separate fractions for effective use. It will be possible to apply each individual component exactly where it will make the greatest contribution to the creation of building composites. Separation, flotation, dispersion, activation in various grinding devices and other methods of ash treatment contribute to the efficiency increase. In order to replace part of the cement with highly dispersed waste, the possibility of using for this ash-enriched product of processing ash-and-slag mixtures was investigated. In this work, we studied the effect of mechanical activation of the cement and aluminosilicate parts of ash on the properties of the organomineral composition. The role of the combined use of mechanical activation and plasticization has been investigated.

## 2. Materials and methods

The ash of the Kashirskaya thermal power plant was selected for the study (Figure 1). It was formed as a result of burning brown coal. The nature of the combusted fuel was reflected in the material composition of the ash. Like other ashes from burning brown coal, the ash-and-slag mixture has parts of mineral and organic components. In work, ash was used, which was pre-treated by the flotation method. Flotation divides ash and slag waste into several separate parts - carbon, aluminosilicate, iron-containing. This is reflected in the chemical composition (Table 1) of each of the enrichment products. In these studies, the aluminosilicate component of the thermal power plant ash and slag waste was used. It mainly contains aluminum and silicon compounds – 21.5 % Al<sub>2</sub>O<sub>3</sub> and 57.8 % SiO<sub>2</sub>. To achieve a homogeneous composition of the ash component, it was subjected to additional mechanical treatment in an activator. After impact grinding, the enriched ash product has a fairly constant particle size distribution with a mode of 13.56 μm. This processing of the ash product provides an optimized dispersed mineral binder system with a large number of contacts.

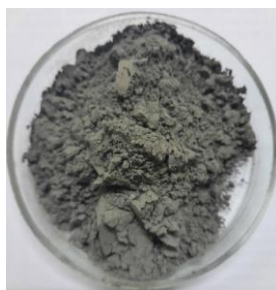


Figure 1: Appearance of activated fuel ash

Portland cement from Lafarge Holcim, production of the Russian Federation, was used in work as the initial binder. The mineralogical composition of the original Portland cement, which was used in the composition, in Table 2 is given.

Table 3 shows the oxide composition of the cement. As regards the content of Na, Mg, Mn and Fe oxides, ash and cement have a similar percentage. The aluminat phase, under certain conditions, can cause the formation of calcium hydrosulfoaluminoferrites, calcium hydroferrite and hexagonal calcium hydroaluminate.

Table 1: Chemical composition of the ash

Oxide /element	Content, %											
	Na <sub>2</sub> O	MgO	Al <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>	K <sub>2</sub> O	CaO	TiO <sub>2</sub>	MnO	Fe <sub>2</sub> O <sub>3</sub>	P <sub>2</sub> O <sub>5</sub>	SO <sub>3</sub>	C
Iron-containing	0.2	1.5	8.4	21.7	0.6	3.4	0.4	1.0	58.0	0.2	0.05	0.8
Aluminosilicate	0.6	1.6	21.5	57.8	2.1	2.3	0.9	0.1	4.6	0.4	0.1	3.2
Carbon	-	-	-	-	-	-	-	-	-	-	-	52.8

Table 2: Chemical composition of the cement

Content, %											
Alite	Belite	Alum	Ferrite	Lime	Portlandite	CaO	Quartz	Arcanite	Gypsum	Hemi-hydrate	
65.8	11.3	4.4	10.8	1.7	0.8	2.3	0.2	0.9	3.8	0.1	

Table 3: Oxide and elements composition of the cement

Content, %												
Na <sub>2</sub> O	MgO	Al <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>	K <sub>2</sub> O	CaO	TiO <sub>2</sub>	Mn <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	P <sub>2</sub> O <sub>5</sub>	SO <sub>3</sub>	Cl	
0.13	1.20	4.86	20.21	0.70	64.60	0.20	0.10	3.29	0.08	3.19	0.03	

Physical-mechanical test of cement showed: Blaine specific surface – 3.931 cm<sup>2</sup>/g, prism weight – 560 g, standard consistency – 29.4 %, W/C = 0.38, cone spread – 108 mm, the beginning of the setting of the cement paste – 235 min, end of the setting of the cement paste – 308 min, 28 d compressive strength – 53.1 MPa. The content of the ash component varied from 0 to 30 %. At the first stage, the precursor cement was used in the research, and at the second stage, activated cement was used. Impact grinding of ash and cement was carried out separately. The activation was performed in vortex-layer devices. A polycarboxylate-based "Lakhta" additive was used as a hyperplasticizer. The makers of additives – are Rastro Company, Russia. The assessment of the physical and mechanical properties of the ash-cement composition was carried out in accordance with the requirements of the relevant standards: GOST 31108-2020 Common types of cement. Specifications; GOST 30744-2001 "Cements. Methods of testing with using polyfraction standard sand". The features of the mineralogical composition of the gypsum stone were evaluated by the method of powder diffractometry on diffractometer "ARL X'tra". The amorphous phase was quantified using the crystallinity utility of the winxrd.

### 3. Results and Discussion

In this work, the possibility of using mechanical activation of ash-cement compositions to improve their physical, mechanical and operational properties was investigated. For this, formulations with activated ash based on the original cement (Figure 2), as well as based on activated ash and activated cement (Figure 3) were investigated. An increase in the strength of samples with activated cement and aluminosilicate ash component (Figure 3) by 67 % confirms the effectiveness of using ash in this composition to control its properties.

The inclusion of ash grains in the dispersed binder system in accordance with a given granulometric composition (Figure 4) changes the internal structure of the stone. Ash and cement grains of different diameters in the established optimal volumetric ratio form a dense packing and have a decisive influence on the structure formation process. The investigated mineralogical composition of the activated cement and ash is shown in Table 4. It is shown that the main components in the composition of the hardened ash-cement activated composition after hardening are quartz, microcline, portlandite, calcite, alite, belite and tetracalcium alumoferrite. The rest of the mineral components are contained in small amounts, less than 1 %. The amorphous phase in the composition of the hardened stone is about 10 %.

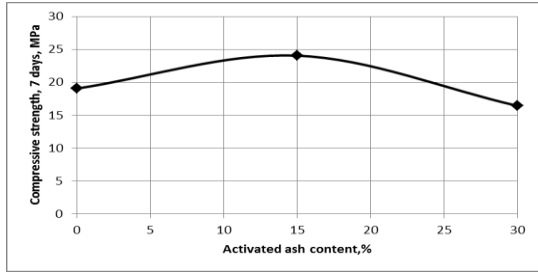


Figure 2: Change in the strength of the cement and activated ash composition

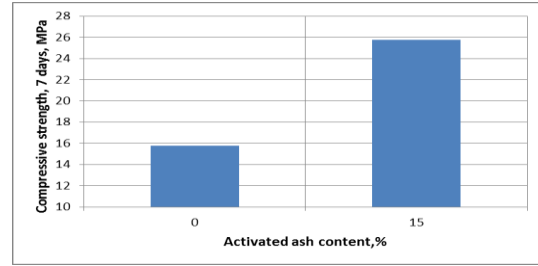


Figure 3: Change in the strength of the activated cement and ash composition

Table 4: Mineralogical composition of the activated cement and ash

Minerals/ phase	Content, %												
	Quartz	Calcite	Dolomite	Portlandite	Albite	Microcline	Anhydrite	Ettringite	Alite	Belite	Tricalcium aluminate	Tetracalcium aluminoferrite	Amorphous phase
Composition	63.8	2.0	0.5	2.9	7.0	6.3	0.7	0.5	3.2	1.7	-	1.4	10.0

Studies of the average density of the solidified (Figure 5) found that the dispersed ash component responds positively to the plasticization of the dispersed system with a chemical additive-plasticizer. The introduction of a plasticizer also helps to improve the rheological characteristics of the compositions, and, consequently, to increase the strength and density of the modified cement stone with the addition of an activated ash component. When comparing the diffraction patterns (Figures 6, 7) on the recorded diffractogram of the cement composition with the addition of 30% activated ash, an increase in the intensity of quartz reflections is observed (Figure 7). The diffraction pattern of the sample with activated ash also contains mullite reflections. The presence of an amorphous phase is noted (Figure 7). This is evidenced by an amorphous halo in the range from 15 to 40  $\Theta$ . The shape of the reflections in the diffractogram of the second sample is closer to the normal distribution, which is the result of activation.

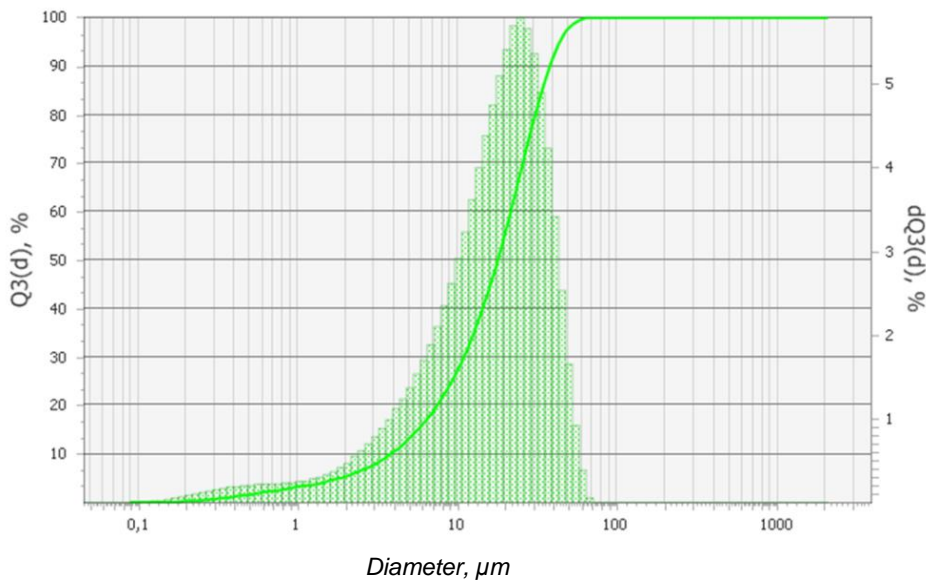


Figure 4: Particle-size distribution of the activated cement and ash composition

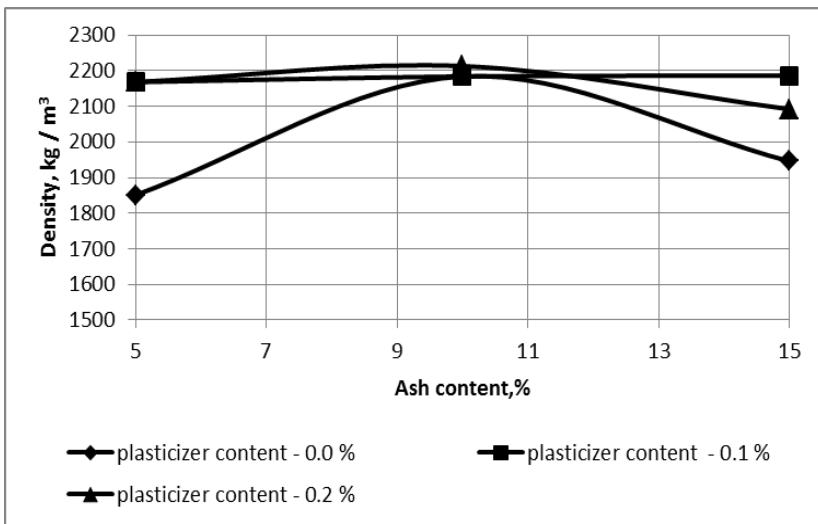


Figure 5: Change in the density of the activated cement and ash composition with the addition of a plasticizer

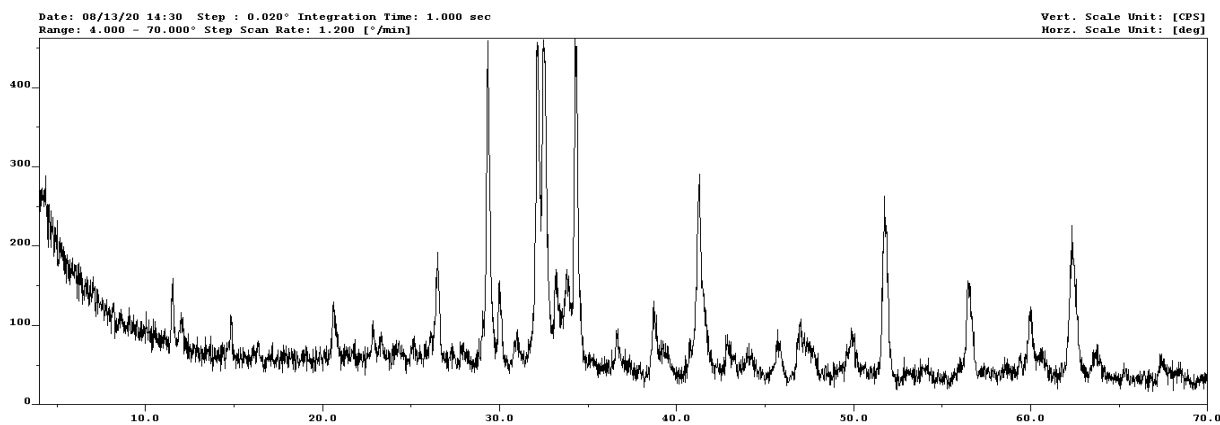


Figure 6: Registered diffraction pattern of the activated cement

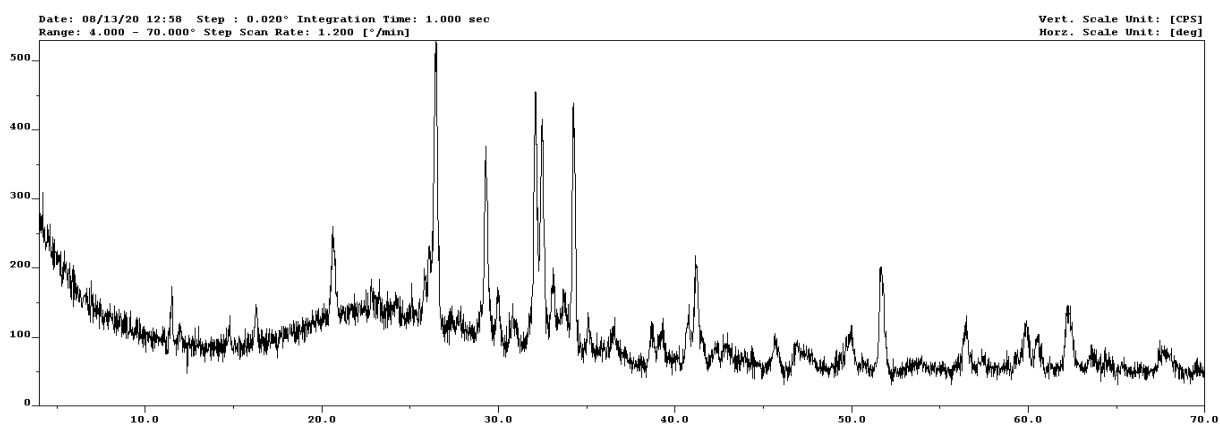


Figure 7: Registered diffraction pattern of the cement composition with the addition of 30 % activated ash

#### 4. Conclusions

This work confirms the efficiency of using ash and slag waste in building materials. The use of preliminary separation of ash and slag waste, a new method of activation and selection of grain composition with activated ash in the new binder makes it possible to regulate the properties of the cement stone due to the active interaction of Portland cement minerals with the aluminosilicate components of the ash. The inclusion of ash grains in the dispersed binder system regulates the internal structure of the cement stone. Controlling the grain composition ensures the formation of a compacted structure of the ash-cement stone and an increase in its physical and mechanical properties. The optimum content of activated ash in the activated cement is 15 %. The activation of the ash-cement composition affects its water demand. The introduction of the hyperplasticizer improves the rheology of the mixture and increases the efficiency of the introduction of the activated ash additive.

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