Research Of The Influence Of Reftinskii SDPP`S Ash On The Processes Of Cement Stone`S Structure Forming

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Abstract. The article describes the experimental research of cement stone. Cement stone forming involves highly dispersive mineral additive – ground ash. It is stated that the substitution of some part of cement with activated ash leaves cement strength high. This is possible due to the activity of ash in structure forming processes. Activation of ash provides the increase in its puzzolanic activity, complete hydration processes. it is stated that ash grinding leads to a selective crystallization hydrated neoformations. Their morphology is different on outer and inner surfaces of ash spheres. The usage of ash can provide cement economy on condition that rheological characteristics of concrete stay constant. Besides, the usage of ash will improve physical and mechanic characteristics of cement stone and concrete.

1. Introduction
The usage of coal as solid fuel by thermal power plants makes it inevitable to cumulate a great amount of products of combustion. According to the data of Russian Heat Engineering Scientific Research Institute, annual burning of solid fuel leads to creating 40-50 million tons of bottom ash, the largest part of which goes to ash dumps [3]. Namely, about 5 million tons of technogenic wastes are created at Reftinskii SDPP every year. More than 4.5 million tons of waste gets to ash dumps polluting air and water, and altering chemical and mineral structure of soil.

One of the most effective ways of ash waste recovery is the usage of wastes in producing building materials as the basic minerals substituting some part of cement binder.

The primary factor holding back the usage of some ashes is their non-homogeneity in a chemical composition as well as in the dispersiveness. Reftinskii SDPP regularly burns Ekibastuz coal. This allows to receive fly ash with constant characteristics. The chemical composition of Reftinskii ash includes oxides: SiO₂ – 60.0÷62.0%, Al₂O₃ – 29.0÷31.0%, Fe₂O₃ – 4.0÷5.0%, CaO+MgO – 1.5÷2.5%. Its structure contains glass particles of nearly ideal spherical shape [3]. The size of a granule is 30-80 mcm, 80-100 mcm until 25 %.

By now, researchers from all over the world have developed a lot of works connected with effective filling of cement matrix with technogenic waste flour [2÷10].

The conclusions made by the scientists cannot be doubted. They show that the characteristics of cement composites greatly depend on a disperse systems` structures which are the basis of their creation [2, 4, 5, 7]. The structural endurance of a disperse system, its rheological characteristics, a
habit of action while flowing, the speed of destruction and reconstruction are closely connected [8, 10].

It is known that formation of a cement composite`s structure is a result of simultaneous actions of different factors and proceedings. The matter of interaction between products of cement stone hydration and mineral additives of ultra dispersive and nanometer range is the most complicated one while studying the process of structure forming.

Nano-additives are received through purposeful synthesis. They are referred to monomineral substances. Consequently, the view and depth of hydration processes will be rather similar. The usage of technogenic raw materials of polymineral nature will make it possible to provide the structure forming processes due to a range of chemical and physical processes. It is widely recognized that while using siliceous wastes, the interaction with hydration products takes place in a chemical way as a result of chemosorption of Portland cement by a silica additives.

2. Equipment and Instruments used in this research
Reftinskii ash grinding was executed in laboratory ball mill (LBM-7). Indices of dispersiveness were defined with the help of the meter SP-10. Cement composition samples have been kept in a water seal camera (WSC-1) at 20±2°C and relative humidity 100% from the moment of their creation until testing. Compression strength of cube samples of dispersive cement stone 20x20x20 mm in size was defined under a hand hydraulic press (HHP-1).

Microphotographs of dispersive cement stone have been taken with an optical microscope of the inverted type GX-51.

3. Results and discussions
During the research work the tested ash has been ground for 1, 2 and 3 hours. The index of surface area of the particles in received probes is represented in Figure 1.

![Figure 1](image_url)  
**Figure 1** – Index of surface area of ground ash probes with different time intervals of grinding

The activity of the ground ash was defined according to the results of testing cement stone strength by compressing it. The amount of ash in the cement stone varied (the percent of ash added is indicated in Table 1). The samples were prepared from the paste of normal thickness, ground ash was added
while substituting some part of cement binder. Strength test by compressing cube samples 20x20x20 mm in size was executed at the age of hardening at 2, 7 and 28 days. Obtained results were compared with those of control composition of Portland cement CEM II/A-S 32.5 (Table 1, Figures 2-3).

Table 1 – Results of compression test of samples

| Grinding time | Ash contents, % | Compression strength, kgs/sm² |
|---------------|-----------------|------------------------------|
| -             | 0               | 110 286 420 620              |
| 1 hour        | 10              | 149 339 382 480             |
|               | 15              | 176 348 401 502             |
|               | 20              | 107 328 390 440             |
| 2 hours       | 10              | 120 317 422 501             |
|               | 15              | 152 402 495 658             |
|               | 20              | 132 230 382 490             |
| 3 hours       | 10              | 127 310 360 420             |
|               | 15              | 148 305 365 410             |
|               | 20              | 135 340 350 402             |

As the experiment shows, the strength of cement stone varies significantly under the influence of ash dispersiveness and the quantity of added ash.

As it was found out in the experiment, increasing of the ash dispersiveness has a great influence upon cement growth kinetics. This phenomenon can be explained from the viewpoint of cluster formation as it is indicated by Solomatin [2, 8]. In case of 10% doze of ash the filling rate in the system is quite low. We can observe the decrease of strength because of lack of finely dispersed phase at packing the structure (Figure 2).

Figure 2 – Compression strength of samples with ash: a) 10%; b) 20%
According to the obtained indices of strength, the best grinding time is 2 hours. The further increase in the dispersiveness of ash (with surface area 4020 sm²/gr) leads to some positive and negative effects. The positive one is pozzolanic intensity and microfilling effect. The negative one is the decrease in strength because of increase in water consuming quality of the system. At the age of 28 days the strength growth of cement composite is 6% on condition that the cement contains ground ash 15% of cement weight in amount, with surface area 3200 sm²/gr (Figure 3).

In our opinion the process forming a monolithic structure of microfilled cement stone becomes possible while developing strong epitaxis contact interlocks with fragments of ash spheres and on the surface of unbroken spheres.

We developed a microscopic research of the samples of 90 days old. Their resistance was tested when they were 28 days old. This research was necessary for the analysis of the cement stone structure made from activate ash of 15% and cement (Figures 5-8).

It was stated that the dominating mechanisms of the interaction between cement, ash and water are physical and chemical processes: crystallization and epitaxis contacts.

Figure 5 shows the process of oriented growing and increasing of crystals on the surface of ash microsphere.

The process of crystal growing corresponds to chemoepitaxis and is divided into several stages: delivery of cations, anions, tetrahedral units, and products transforming into liquid in case of hydration of cement minerals; forming of layers on the parts where possible defects can be located; forming of near-surface centres of crystallization; nucleation of the layer of their fusion until blanket layer formation.

The defects of ash microspheres (Figure 6) appearing in the process of mechanoactivation, are an energetically beneficial location for the nucleation and growth of the firm epitaxis layer.

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**Figure 3 – Compression strength with ash contents 15%**
Figures 7, 8 demonstrate the process of forming the hydrates of filamentary morphology of C-S-H phase, platelike shape and six-sided calcium hydroalumimates and some quantity of hydrogarnets on the inner surface of ash microspheres. Regular joints of hydrosilicates and hydroaluminates in the form of dendrites of needle-shaped formations, platelike shape and six-sided crystals appear on the inner surface of the sphere.

As the results of the research state, agglomeration of ash microspheres (50 mcm in diameter) provides the formation of hydration phases in the zone of “free” space of the sphere. Neoformations are hydroalumuates of C₄AH₁₉ type (a variation C₄AH₁₃), and some quantity of hydrohelenite. This is possible due to the penetrating qualities of the screen in relation to cations.

We applied the slow-nucleation theory for the description of hydration process in the observed system containing ultradispersed ash. The theory states that the interaction of cement and water on the initial stage produce ions Ca²⁺, OH⁻, SiO₄⁻. Micro defects and destructions lead to the situation when the surface of the sphere begins to act as a screen through which Ca²⁺ penetrates first of all and
participates in the synthesis of neoformations together with ash minerals and alumosilicate glass. The growth of crystals of dendrite-like shape is possible only in case of “free” space and ash activity. Some early scientific works [11, 12] do not contain any information about hydrate phases. They have not been defined.

By the age of 90 days crystals are developed enough and provide more strength in cement stone, form micropor stone of high waterproofing qualities. Formation of such crystals can be possible only in case of mechanoactivation of ash.

The samples under test began to crack, chips appeared. This regularly happens with samples during compression testing. In microcracks (Figure 7) 60 days after testing one can notice neoformations and growth of crystal phases. Their morphological peculiarities are needle and tetrahedral shape, which are inherent for hydrosilicates. This can be explained by the “free” space in a microcrack and a long lasting reactive capacity of mechanoactivated ash. This capacity provides a self-healing process in cement stone for some period of time.

Conclusion
While studying the mechanisms of strength improvement of cement compositions containing mechanoactivated ash of some definite dispersiveness and granule forms one should pay a great attention to learning the processes of crystal forming which provide the strength of hardening systems. In the long run, it will be an undisputable factor in using ash in different types of cement composites. The structural typology of cement composite homogeneously mixed with microfilling (if its dispersiveness prevails that of cement binder) provides strength increase of contact zone due to the growth of junctions between particles, influence of capillary force and densification of a structure.

The active role of particles of ash microspheres in forming cement binding structure is proved by the results of electronic microscopic investigation.

Reftinski SDPP experimental mechanoactivated ash with surface area 3200 sm²/gr provides up to 15% of cement saving.

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