The Prospects of Application of Ashes from Combined Heat and Power Plants (Chpp) in the Primorsky Region for Creation of Protective Fibre-Reinforced Concrete with Improved Impermeability Characteristics

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Abstract. The article discusses the feasibility of usage of fly ashes from the Primorsky region heat power plants in production of fibre-reinforced concrete with improved impermeability characteristics. Based on the fact that ashes created by the Primorsky region heat power stations are chemically applicable as the filler in concrete composition, those of four Primorsky region heat power plants were analyzed. It is found that ashes of Vladivostokskaya HPP-2 and Artyemovskaya HPP comply with the required indicators of specific effective activity and can be classified as the first class materials applied in all kinds of construction operations. The development of the composition binder involving acidulous ash is the most promising.

1. Introduction

Composition materials synthesis has come into widespread use over the past decades. It allows obtaining composition materials for construction with wide range of properties. Binding materials are nominally divided into two types: binders obtained by means of mixing several components, and binders as the product of mechanochemical activation of Portland cement or other binder with chemical modifiers containing water-reducing component, mineral admixtures and, if necessary, special admixtures for obtaining binder with special properties.

To obtain composition binder raw materials available in the Primorsky region, such as fly ashes from HPP, were used. Composition binder being developed is designed for application as part of protective fibre-reinforced concrete with improved impermeability characteristics.

For this purpose we studied in the paper physical-mechanical and chemical properties of fly ash from the largest HPP in the Primorsky region: Vladivostokskaya HPP-2 and Artyemovskaya HPP, Primorskaya GRES, and Partizanskaya GRES. Possibility of dry separate screening was an important factor in ash selection. Now such method is implemented at the mentioned heat and power plants.

Wastes of the heat power plants are mainly divided into two groups: bottom ash and fly ash, which are different in the method of removal. Fly ash is a more efficient admixture for the concrete composition than bottom ash. One of essential characteristics of fly ash is its high hydraulicity conditioned by chemical interaction of silicone oxides and aluminum oxides with calcium hydroxide.
that is released during hydrolysis of clinker minerals with development of hydrated silicates and hydrated calcium aluminates that reflects upon hydrated cement strength.

Composition and structure of ash depends on a complex of cofactors: type and morphologic features of the fuel burned, fineness of grinding in the process of preparation, ash content, chemical composition of the mineral matter of fuel, temperatures in the burning area, particle residence time, etc.

2. Equipment and devices used in studies
Thermal analysis of ashes was carried out on thermal gravimetric analyzer Shimadzu DTG-60H at the rate of temperature elevation 20 deg./min., in the interval of 20 – 1,100 °C. Quality and quantity formula as well as properties of the source materials and composition binder were studied with the help of standard methods. Mineral composition and structure were analyzed by X-ray diffraction analysis on X-ray powder diffractometer D8 Advance by Bruker AXS. Figure 2.3 - Scanning electron microscope CarlZeissCrossBeam 1540XB

Specific volume activity of beta- and gamma-emitting nuclides in loads was determined by spectrometric method with the help of multifunctional spectrometric complex MSC “Gamma Plus”. The study was conducted according to the requirements of the following reference documents: GOST 27451-87 “Ionizing radiation measuring means. General specifications”, GOST 26864-86 “Ionizing radiation power spectrometers. Methods of basic parameters measurement”, Specifications 4362-002-46549900-06 (PLUS.412131.002TU) “Multifunctional spectrometric complex MSC “Gamma Plus”. Specifications”.

3. Results and discussion
According to the microstructure analysis, fly ash is represented in the form of hetero-granular finely-dispersed spherical particles with different size of granules beginning with nano-sized ones (fig. 1).
High dispersion ability of ash is the forecasting factor of its high activity in respect of the components of the binder in case of hydration. Polydisperse spheres present in ash have smooth glassy surface. According to the literature data, glassy phase, proportion of which depends on the burning conditions and the fuel used, is represented by X-ray amorphous aluminosilicate compounds.

Experimental tests have allowed defining the values of the main characteristics of fly ash that determine the possibility of its usage for construction materials production. Chemistry data of ashes indicate the differences by content of certain oxides, as a result of pulverized combustion of different types of coal (table 2.12). So, quantity of SiO$_2$ varies from 47.4 % to 63 %, Al$_2$O$_3$ – from 12.6 % to 29.3 %, CaO – from 3.4 to 12.5 %. This fact reflects upon ash properties and determines the field of its application as part of construction materials.

**Table 1 – Chemistry of ashes at the Primorsky region HPP**

| Prevailing coal type | Primorskaya GRES | Vladivostokskaya HPP-2 | Artyemovskaya HPP | Partizanskaya GRES |
|----------------------|------------------|------------------------|-------------------|-------------------|
| SiO$_2$              | 55.3             | 63.0                   | 48.1              | 47.4              |
| TiO$_2$              | 0.5              | 0.5                    | 0.0               | 0.9               |
| Al$_2$O$_3$          | 12.6             | 21.4                   | 29.3              | 22.3              |
| Fe$_2$O$_3$          | 10.7             | 7.5                    | 6.5               | 19.6              |
| CaO                  | 12.5             | 3.4                    | 9.7               | 4.8               |
| MgO                  | 3.5              | 2.1                    | 1.8               | 2.8               |
| K$_2$O               | 1.0              | 1.3                    | 1.2               | 0.1               |
| Na$_2$O              | 0.4              | 0.3                    | 0.2               | 0.4               |
| SO$_3$               | 3.4              | 0.6                    | 2.3               | 1.62              |
| Free CaO             | 1.0              | 0.4                    | <0.1              | -                 |
| o.i.                 | 2.3              | 1.4                    | 0.6               | <5                |
According to the requirements of GOST 25818 – 91, by the type of coal combusted the ashes are divided into:
– acidulous – anthracitic, black coal and brown coal, containing up to 10 percent of calcium oxide (Vladivostokskaya HPP-2, Artyemovskaya HPP, Partizanskaya GRES);
– base – brown coal, containing more than 10 percent of calcium oxide by weight (Primorskaya GRES).

High content of Al\textsubscript{2}O\textsubscript{3} (up to 29.3 %) and SiO\textsubscript{2} (up to 63 %) in ash can be the reason of crystallization of mullite-based compounds. Based on determination of losses on ignition that comprise less than 5 percent, there are traces of fuel remains in the ashes. This fact suggests positive influence on increase of hydrated cement strength in case of substitution of Portland cement by up to 50 percent of fly ash.

The results of thermal analysis are graphically represented at Fig. 2.

During heat treatment of ash in the range of 40–200 °C water loss occurs due to adsorption by finely-dispersed surface of particles. Carbonates are degraded into CaO and CO\textsubscript{2} at 712 °C. Intense endoeffect with weight loss at 500–700 °C testifies to the burn-up of residual fuel that is probably represented by coal particles as well as coke and semi-coke residues. Relatively small exothermic effect with maximum at 932 °C reflects crystallization of mullite-based compounds in aluminosilicate phase.

\[ \text{Figure 2} \] – The results of DTA and TGA of fly ash from Vladivostokskaya HPP-2

According to the results of X-ray diffraction analysis, diffractive crystalline reflections of mullite phase are identified in addition to quartz crystals (fig. 3).
Figure 3 – The results of X-ray fluorescence analysis of fly ash from Vladivostokskaya HPP-2. K – quartz, Ka – calcite, M – mullite

So, the ash under discussion is very close to aluminum silicates due to high content of silicone oxides and aluminum oxides up to 80-90 percent, of which silicone oxide is about two-thirds. Fly ash almost has no unburnt particles where harmful components are as a rule concentrated. Ash consists of crystalline and noncrystalline phases. Crystalline phase is represented by quartz, field spars, mullite and others, while noncrystalline phase is in the form of glass. So, one may suppose that ashes from the Primorsky region heat power stations are chemically applicable for usage as the filler in concrete composition.

According to the classification of GOST 24640-91 the ashes under discussion are low-calcium (acidulous) and may be used as active mineral admixtures possessing pozzolanic properties. In accordance with pozzolanic properties (as per classification of RILEM association) fly ashes from Vladivostokskaya HPP-2 and Artyemovskaya HPP may be taken for further studies.

During the following studies a radioactivity background of ash was estimated (table 2).

| Item      | Primorskaya GRES | Vladivostokskaya HPP-2 | Artyemovskaya HPP | Partizanskaya GRES |
|-----------|------------------|------------------------|-------------------|--------------------|
| Activity $^{40}$K | 496.9±101        | 392±89                 | 342±68            | 516.9±101          |
| Activity $^{232}$Th | 153.6±20.3       | 31.5±19.7              | 29.5±15.7         | 193.2±22.3         |
| Activity $^{226}$Ra | 163.1±9.36       | 37.63±6.32             | 27.23±5.93        | 113.1±6.37         |
| $A_{\text{eff}} = A_{\text{Ra}} + 1.31A_{\text{Th}} + 0.085A_{K}$ | >398             | 80±30                  | 93±20             | >410              |

4. Conclusions

Analyzing the results, it should be noted that specific effective activity of ashes at Vladivostokskaya HPP-2 and Artyemovskaya HPP is less than 370 Bq/kg. So, according to GOST 30108-94 “Building materials and elements. Determination of specific activity of natural radioactive nuclei” they may be classified as the first class materials applied in all kinds of construction operations.

Radioactive background of ashes at Primorskaya GRES and Partizanskaya GRES exceed the limits, so their usage in the construction industry should be restricted.

So, according to GOST 25592-91 “Mixes of fly-ash and slag of thermal plants for concretes” ashes from Vladivostokskaya HPP-2 and Artyemovskaya HPP comply with the indicators of specific effective activity.

As further studies showed, the use of HPP waste as nanodispersed component of composition binder is more efficient as compared to commercial additives. It is conditioned by the additional useful
function – clearing of ash disposal areas. In addition to the above, if viewed from that angle, development of the composition binder involving acidulous ash is the most promising.

As a result, a composition binder consisting of cement (55%), acidulous ash (40%), and lime-stone (5%) was developed by means of intergrinding with superplasticizer up to specific surface of 550 kg/m² with activity of 77.3 MPa. It makes possible to develop a cement stone of a denser structure.

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