Using thermal power plants waste for building materials

R S Fediuk, A K Smoliakov, R A Timokhin, V O Batarshin, Yu G Yevdokimova

Far Eastern Federal University, 8, Sukhanova St., Vladivostok, 690950, Russia

E-mail: roman44@yandex.ru

Abstract. The recycled use of thermal power plants (TPPs) wastes in the building materials production is formulated. The possibility of using of TPPs fly ash as part of the cement composite binder for concrete is assessed. The results of X-ray diffraction and differential thermal analysis as well as and materials photomicrographs are presented. It was revealed that the fly ash of TPPs of Russian Primorsky Krai is suitable for use as a filler in cement binding based on its chemical composition.

1. Introduction
The modern concept of construction is directed at the use of the recycled materials, in particular, various waste products. This solves a number of problems:
- saving the expensive materials;
- decreasing CO₂ emissions by reducing the production of construction materials;
- utilization of environmentally hazardous waste [1-2].

One of the biggest sources of waste is thermal power plants (TPPs), which convert energy from the coal burning. This paper presents the possibility of using the TPPs waste as part of the composite cement binder for concretes. Wastes of thermal power plants are mainly divided on two categories: a slag and a fly ash, differentiated by the way of their removal. According to Ovchinnikov, Zagorodnjuk, Lesovik etc., a fly ash is a more effective additive in cement compositions than a slag [3-4]. In this case, the volume of alite phase increases, while the aluminate phase decreases compared to the control sample, and so the strength of the cement stone increases as well [5-7]. The study of composition and origin of fly ash from Primorye TPPs is interest when selecting additives for composite binder.

2. Materials
The materials used in the study are fly ash from the large TPPs of Russian Primorsky Krai: Vladivostok TPP, Artem TPP, Primorye TPP and Partizansk TPP. The important factor is the ability of the selection of dry ash that is currently implemented in these TPPs.

Vladivostok TPP produces coal combustion using IIR technology (Implementation, Innovation, Reconstruction), which is built on the basis of modern aerodynamics receptions and after modernization in the combustion chamber creates two zones of burning - low-temperature vortex at the bottom of the firebox and high temperature one at the top, providing an intensive post-combustion. The dispersed flow of fuel and air, and recirculation movement inside the furnace are powerful tools of low-emission combustion with a high thermal efficiency of the furnace. Vladivostok TPP uses lignite as the basic fuel from Pavlovsky open-cast mine in Chikhez field. Pavlovsky lignite is the "B"-
grade coal. It is grossly dense and is dark brown in color is dominating matt gloss (sometimes semi-mat). The coal structure is streak-striped and lenticular-striped. The original plant material is dominated by the remains of coal woods stem, leaf and parenchyma bark. The composition is dominated by coal vitrinite (80...99%). The brown coals are mined by open-cut method. Main characteristics of this coal are as follows: in the first stage the calorific value is 2920 kcal / kg, moisture content is 41%, ash content is 8.8%.

Artem TPP runs on coal, and therefore there is a scientific interest is comparing fly ashes from Vladivostok TPP and Artem TPP. In addition, fly ashes from other power plants of Primorsky Krai were also studied: Primorye TPP (Luchegorsk settlement) and Partizansk TPP.

3. Methods
The study of samples microstructure was performed using a scanning electron microscope (Carl Zeiss CrossBeam 1540 XB). For analysis, the specially developed software package for automated processing was used, enabling the researchers to get almost all the morphological parameters of the microstructure (the size and shape of the structural elements, their orientation in space), and to assess the values of the porosity and the specific surface area [8-10]. The study of qualitative and quantitative the composition and the properties of the starting materials and the composite binder was done using the standard methods. The study of the mineral composition and structure is performed using X-ray diffraction (XRD) analysis on the powder XRD meter D8 Advance by Bruker AXS. The X-ray diffraction is the nondestructive method for analyzing substances in powder form. It provides the ability to conduct qualitative and quantitative analysis of crystalline phases of identifying the crystal structure of inorganic, organic and metal complex compounds in polycrystalline form, identifying the composition of polycrystalline materials, and the degree of crystallinity of polymers [11-13].

Based on the indicators during heating, the following methods of thermal analysis are distinguished:
- Differential thermal analysis (DTA) - shows the change in energy of the system (sample);
- Thermogravimetry (TG) - shows the change in mass.

Thermograms of the samples are obtained on TG analyzer Shimadzu DTG-60H. The heat interval is from 20 to 1,500°C and the temperature rise speed was 20°C/min. The temperature (T) is measured with a platinum thermocouple with accuracy of 5°C, and the signal is recorded on paper by a four-channel recorder with a scan speed of 2.5 mm/min. The temperature difference (∆T) between the studied substance and a standard proportional to the thermal effect is recorded in the form of DTA curve (sensitivity of 500 mV). Simultaneously, the curve of weight loss (TG) and its derivative (DTG) (sensitivity of 500 mV) are recorded. The samples weight is 113 mg. Weighing accuracy is 0.05 mg.

In the course of analysis of the literature, it was found that materials such as TPPs fly ash have some radioactivity. Due to the fact that the concept of the research is aimed at creating conditions for the environmental safety of a home, it is necessary to quantitatively check the background radiation of these materials. The specific (volumetric) activity of beta- and gamma-emitting nuclides in the samples was determined by spectrometric method using the USC Gamma Plus universal spectrometer complex.

The study is conducted according to the requirements of the following standard documents:
- GOST 27451-87 "Ionizing radiation measuring means. General specifications";
- GOST 26874-86 "Ionizing radiation power spectrometers. Methods of basic parameters measurement"
- TU 4362-002-46554900-06 (PLUS 412131.002TU) "Complex universal spectrometry USK Gamma Plus. Specifications".

The principle of operation is based on the complex transformation in the working volume of gamma rays and beta particles in the flashes of light (scintillation), the intensity of which is proportional to the energy lost by the gamma-quantum or beta-particle detector. As lights flash, they reach the photoelectron amplifier tube (PAT), and are converted into a stream of electrons, which
multiply under the influence of the applied potential difference, resulting in at the output of the PAT-generated pulses of electric current, the amplitude of which is proportional to the particle energy lost in the detector. This fact provides the fundamental ability to measure the energy spectrum of the detected gamma or beta radiation [14-16]. The signal detection unit is amplified, formed, and converted to a voltage pulse. This pulse is applied to the input of an analog-to-digital converter, where it is sorted in the amplitude and converted into a digital code that allows to record and store received the information in memory.

4. Results and Discussions
The selected ash should not contain any foreign inclusions. The composition and the structure of ash depend on the set of concurrent factors: the type and morphological features of combusted fuel in the course of ash production, the ash content of the fuel, the chemical composition of the mineral part of the fuel, the temperature in the combustion zone, and residence time of the particles in this zone, and others. (Figure 1).

![Image](image1.png)

**Figure 1.** The microstructure of Vladivostok TPP fly ash. Amplification 200 and 2000 times: a – amplification X200; b – amplification X2000.

The laboratory researchers have identified the basic characteristics of the fly ash and determine the possibility of its use for the production of polymer-mineral construction materials [17-19]. The main criteria for the selection of fly ash to study the possibility of its use as a component of nanomodifier follows:

- shape of the particles;
- particle size distribution;
- specific surface area;
- packing density;
- chemical content.

The fly ash samples of were taken from a large capacity silo, from where they could be shipped for delivery to consumers or, depending on the filling of the silo through the mixing device by the pressure system, may be moved to the ash dump. After sampling, singular samples were combined, mixed thoroughly, and reduced to laboratory sample by quartering. The laboratory samples of fly ash were sieved through a 0.08 sieve; as a result the significant part of unburned coal particles, magnetite beads and microspheres remained on the sieve, while ash passing through a sieve was selected for the study and for concrete production. Chemical analysis of the ashes is carried out in accordance with GOST 10538-87. This standard applies to brown and black coals, anthracite, oil shale, peat and coke and establishes the methods for determining silicon dioxide (SiO$_2$), iron oxide (Fe$_2$O$_3$), aluminum oxide (Al$_2$O$_3$), magnesium oxide (MgO), calcium oxide (CaO), potassium oxide (K$_2$O), sodium oxide (Na$_2$O), phosphorous oxide (P$_2$O$_5$), titanium dioxide (TiO$_2$), sulfur trioxide (SO$_3$), and mixed manganese oxide (Mn$_3$O$_4$) and fuel in the ash. The data on the chemical content of ashes (Table 1) indicate that the contents of the individual oxides in the fly ash derived from the combustion of
various kinds of pulverized coal have significant deviation. It determines the difference in the properties of ash and possible areas of use in the manufacture of building materials.

Table 1. The chemical content of the Primorsky Krai TPPs ashes

| TPPs            | The predominant type of coal | Content of elements on an oxide basis,% | LOI |
|-----------------|------------------------------|----------------------------------------|-----|
|                 | Luchegorsk and Bikin brown coals |                                        |     |
| Primorye TPP    | SiO₂                        | 55.3                                   | 2.3 |
| Vladivostok TPP | TiO₂                        | 0.5                                    |     |
| Artem TPP       | Al₂O₃                       | 12.6                                   |     |
| Partizansk TPP  | Fe₂O₃                       | 10.7                                   |     |
|                 | CaO                         | 12.5                                   |     |
|                 | MgO                         | 3.5                                    |     |
|                 | K₂O                         | 1.0                                    |     |
|                 | Na₂O                        | 0.4                                    |     |
|                 | SO₃                         | 3.4                                    |     |
|                 | CaO_free                    | 1.0                                    |     |
|                 | LOI                          | 2.3                                    |     |

| TPPs            | Primorye brown coal (Pavlovsky section) | Black coal | Neryungri black coal |
|-----------------|----------------------------------------|-------------|----------------------|
| Vladivostok TPP | 63.0                                   | 48.1        | 47.4                 |
| Artem TPP       | 0.5                                    | 0.0         | 0.9                  |
| Partizansk TPP  | 21.4                                   | 29.3        | 22.3                 |
|                 | 7.5                                    | 6.5         | 19.6                 |
|                 | 3.4                                    | 9.7         | 4.8                  |
|                 | 2.1                                    | 1.8         | 2.8                  |
|                 | 1.3                                    | 1.2         | 0.1                  |
|                 | 0.3                                    | 0.2         | 0.4                  |
|                 | 0.6                                    | 2.3         | 1.62                 |
|                 | <0.1                                   | no          |                      |
|                 | <5                                     |             |                      |

Given the focus of the research on the development and use of environmental-friendly materials, the radioactivity of ash has been evaluated. Ashes depending on the total effective specific activity of natural radionuclides A<sub>eff</sub> up to 370 Bq / kg are used to produce materials, products, and structures, of residential and public buildings. The results of determination of specific effective activity of fly ash by the spectrometric complex "USC Gamma Plus" are shown in Table 2.

Table 2. Determination of specific effective activity of the Primorsky Krai TPPs fly ash

| Indicator | The measurement result (A), Bq/kg |
|-----------|-----------------------------------|
|           | Primorye TPP | Vladivostok TPP | Artem TPP | Partizansk TPP |
| Activity ⁴⁰K | 496.9±101   | 392±89         | 342±68   | 516.9±101    |
| Activity ²³²Th | 153.6±20.3 | 31.5±19.7     | 29.5±15.7 | 193.2±22.3  |
| Activity ²²⁶Ra | 163.1±9.36 | 37.6±6.32     | 27.23±5.93 | 113.1±6.37  |
| A<sub>eff</sub> = A<sub>Ra</sub> + 1.31A<sub>Th</sub> + 0.085A<sub>K</sub> | >398 | 80±30 | 93±20 | >410 |

Ashes of Vladivostok TPP and Artem TPP belong to the first class of materials (less than 370 Bq / kg) in accordance to GOST 30108-94 "Building materials and elements. Determination of specific activity of natural radioactive nuclei". This material can be used for all kinds of construction work. Ashes of Primorye TPP and Partizansk TPP exceed the permissible parameters of radioactivity, so they are not suitable for use in construction. Thus, ashes of Vladivostok TPP and Artem TPP comply the most to GOST 25592-91 "Mixes of fly-ash and slag of thermal plants for concretes. Specifications", and they are used for further research.

The high content of Al₂O₃ (to 29.3%) and SiO₂ (to 63%) in the ash can cause crystallization compounds like mullite. The loss on ignition of less than 1.5% indicates a small amount of residual
fuel that minimizes products shrinkage processes during firing. Thermal studies of raw were performed on TG analyzer Shimadzu DTG-60H at a temperature rise rate of 20°C / min, in the range of 20-1,100°C. The results of thermal analysis are presented graphically in Figure 2.

![Figure 2. The results of DTA and TG of the Vladivostok TPP fly ash.](image)

During heat treatment of the ash in the range of 40-200°C, loss of the water occurred which is adsorbed by the highly dispersed surface area of the ash particles. Carbonate decomposition is observed at a temperature of 712°C. The residual fuel burning occurs at 500-700°C. The nature and intensity of loss of mass during this indicates the amount of unburnt residues that are particles of coal, coke and semi-coke residue. Relatively small exotherm with a maximum of 932°C reflects the crystallization of compounds in aluminosilicate phase like-mullite. XRD analysis showed that a clearly expressed mullite phase determined the ash besides quartz (Figure 3).

![Figure 3. XRD results of Vladivostok TPP fly ash. K - quartz, Ca - calcite, M - mullite](image)

5. Conclusion

The tested material is a relatively homogeneous multicomponent. By composition it is closest to aluminosilicates due to the high content of silicon and aluminum oxides (up to 80-90%), of which about two-thirds of silicon oxide. At the same time, the fly ash has almost no unburned particles, in which harmful components tend to concentrate. The fly ash consists of crystalline and amorphous phases. The crystalline phase contains quartz, feldspar, mullite, and so on. The amorphous phase is represented primarily in the form of a glass. Thus, the fly ash consists of minerals that are widely used separately as a filler dispersed in composite binders. Therefore, it is possible to assume that the ashes of Primorsky Territory TPPs are suitable for use as a filler for cement by their chemical composition. Based on the GOST 24640-91 classification, the selected fly ashes are of low-calcium (acidic) and serve as additives, the components of the material composition (active mineral additives having pozzolanic properties). According to the RILEM committee (International Committee of Material Testing Laboratories) classification, both Vladivostok TPP fly ash and Artem TPP fly ash have normal pozzolanic activity.
Hydration product binders have a high adhesion beans silica component, which has a significant amount of structural defects and also contributes to the growth of a preliminary mechanical activation in the preparation of the composite binder allowing to strengthen and improve the processes of hydration of clinker minerals, and leading to the formation of more neoplasms by increasing the active nucleation sites on the particle surface.

References
[1] Ibragimov R 2016 ZKG International. 69 (6) 34-39
[2] Serrano-Guzman M and Perez-Ruiz D 2011 Transportation Research Record 1(2205)138-146
[3] Ovchinnikov R V 2014 Dissertation of the candidate of technical sciences
[4] Zagorodnjuk L H, Lesovik V S, Volodchenko A A and Yerofeyev V T 2016 International Journal of Pharmacy and Technology 8(3) 15146-15155
[5] Polat R, Demirbofa R and Khushefati W H 2015 Construction and Building Materials 81 268-275
[6] Baeza F J, Galao O, Zornoza E and Garcés P 2013 Materials 6 (3) 841-855
[7] Fediuk R S 2016 IOP Conf. Series: Materials Science and Engineering 116 012020
[8] Al-Rahman L A and Raja R I 2013 Research Journal of Applied Sciences, Engineering and Technology 6 (22) 4297-4304,
[9] Arifin A M T, Abdullah S, Zulkifli R and Wahab D A 2014 Applied Mechanics and Materials 471 335-340
[10] Fediuk R S and Yushin A M 2016 IOP Conf. Series: Materials Science and Engineering 116 012021
[11] Sun F, Pan Y, Wang J, Wang Z, Hu C and Dong Q 2010 Polymer Composites 31 (1) 163-172
[12] Ramesh R, Madheswaran M and Kannan K 2010 Progress In Electromagnetics Research B 21 235-255
[13] Ibragimov R A and Pimenov S I  2016 Magazine of Civil Engineering 62 (2) 3-12
[14] Oosterhuis D M and Bondada B R 2010 Journal of Plant Nutrition 24 (3) 413-422
[15] Nambiar E K K and Ramamurthy K 2008 Materials and Structures/Materiaux et Constructions, 41 (2) 247-254
[16] Glagolev E, Suleimanova L, and Lesovik V. 2016 International Journal of Environmental and Science Education 11(18) 12383-12389.
[17] Cai J, Hu X, Xia B, Zhou Y, Wei W 2017 International Journal of Heat and Mass Transfer 105 623-637
[18] Sazonov T V, Fershalov Y Y, Fershalov M Y, Fershalov A Y, Ibragimov D I 2014 Applied Mechanics and Materials 635-637 155-158
[19] Pelin G, Pelin C-E, Stefan A, Dinca I, Fica A, Andronescu E, Trusca R 2016 Bulletin of Materials Science 39(3) 769-775