Chemical properties of fly ashes produced in the Arcelor Mittal power station and the Třinec ironworks power station

L Bulikova

Faculty of Civil Engineering, VŠB – Technical University of Ostrava, Ludvíka Poděště 1875/17 708 33 Ostrava-Poruba, Czech Republic

E-mail: lucia.bulikova@vsb.cz

Abstract. Fly ash is an inorganic secondary material coming from combustion of coal in power stations. Tested fly ashes were produced by different processes. Therefore they have different parameters. Their chemical properties were determined using chemical analyzes and compared. Results of laboratory tests show possibility to use of fly ashes in road construction as binder for soil treatment.

1. Introduction and background
Fly ash is an inorganic product of combustion of pulverized coal combustion in power and heating stations. Fly ash consists of small particles of siliceous glass and it is collected by electrostatic precipitation of flue gases. The chemical composition and reactions during combustion are influenced by the presence of water, oxygen, sulphur content, furnace type and burning process. Mineralogical composition of fly ash depends on the geological factors of coal and also on combustion conditions [1,2,5].

There are three types of coal-fired boiler furnaces used in power stations. They are referred to as dry-bottom boilers, wet-bottom boilers (high temperature combustion), and cyclone furnaces (fluid combustion). Traditional combustion of coal in furnaces is carried out at high temperatures in the range of 1200-1600°C, while fluid combustion at lower temperatures. Consequently, flue gas is desulfurized with limestone and the final product is gypsum. Produced calcium oxide CaO is low reactive due to high temperature in the furnace and typical product of high temperature combustion is siliceous fly ash. Fluid combustion is a technology, when coal is burned at 850°C along with sorbent (milled limestone), that is added due to the bonding of sulfur content in coal. During combustion, SO2 is absorbed by particles of CaO and anhydrite (CaSO4) is formed. This process affects considerable reduction of pollutants NOx in exhalations. Typical product of fluid combustion in Czech republic is calcareous fly ash [2,4,6].

2. Methods and result of tests
A set of methods for chemical and mineralogical analyses of two samples of fly ash from the Morava region was used. It includes Differential Scanning Calorimetry (DSC) and Thermal Gravimetric Analysis (TGA), Fluorescence Spectrometry, X-ray diffraction and Scanning Electron Microscopy, were carried out in the ICT VŠB TU Ostrava - Institute of Clean Technologies for Mining and Utilization of Raw Materials for Energy Use.

First one (SFA), produced by Arcelor Mittal Ostrava power station was collected from the tip near its source. Second one (CFA) was produced in the Třinec ironworks power station and it was collected
from dry storage silo. Both fly ash samples were produced by burning of coal from the Ostrava-Karvina coalfield.

Chemical analysis was performed to classify fly ash and determine its reactivity. The analysis showed that SiO₂, Al₂O₃ and Fe₂O₃ represented more than 70% content. The major differences between both samples of fly ashes are in higher content of sulfur trioxide SO₃ 7.5% and higher content of CaO 16.7% in case of CFA. The CaO content was only 4.9% in case of SFA (Table 1).

Table 1. Chemical composition of fly ash samples.

| Element   | SFA (%) | CFA (%) |
|-----------|---------|---------|
| SiO₂      | 42.7    | 40.9    |
| Al₂O₃     | 24.5    | 32.3    |
| Fe₂O₃     | 8.6     | 6.5     |
| CaO       | 4.9     | 16.7    |
| MgO       | 0.7     | 1.2     |
| SO₃       | 0.9     | 7.5     |
| K₂O       | 2.4     | 1.7     |
| LOI       | 11.4    | 7.8     |

Based on chemical composition of fly ashes, samples were classified as class F – siliceous and class C - calcareous (table 3) according to the ASTM C-618 classification. Siliceous fly ash (Arcelor Mittal Ostrava power station) is characterized by low volume changes and higher pozzolanic activity. Calcareous fly ash (Třinec ironworks power station) is characterized by higher volume changes and hydraulic properties for higher content of CaO. This fly ash is typical material that hardens in mixture with water without admixture of any binder. The contents of anhydrite (7.45%) and lime (5.66%) as highly reactive substances cause hydraulic behaviour of CFA (table 2). On the other hand SFA fly ash sample contains passive component- mullit (9.77%). X-ray diffraction quantified amorphous phase by method of internal standard ZnO. Amorphous phase is represented by siliceous glass principally.

Table 2. Results of X-ray diffraction.

| Element    | SFA (%) | CFA (%) |
|------------|---------|---------|
| Quartz     | 12.08   | 11.65   |
| Hematite   | 1.43    | 3.39    |
| Calcite    | 1.97    | 1.93    |
| Zincite    | 9.14    | 9.08    |
| Periclase  | 0.73    | 1.31    |
| Mullite    | 9.77    | -       |
| Magnetite  | 1.26    | -       |
| Gypsum     | 1.47    | -       |
| Muscovite  | -       | 4.63    |
| Lime       | -       | 5.66    |
| Anhydrite  | -       | 7.45    |
| Amor.      | 62.2    | 54.83   |
Table 3. Classification according to ASTM C-618.

| Class | Fly ash | Ca, Fe, Sum of oxides (%) | CaO (%) |
|-------|---------|---------------------------|---------|
| F     | Siliceous | Considerable amount Fe (Al₂O₃+SiO₂+Fe₂O₃) > 70 | < 10    |
| C     | Calcareous | Considerable amount Ca (Al₂O₃+SiO₂+Fe₂O₃) > 50 | 10-20   |

Electron microscope micrographs of fly ash samples from the AM power station (SFA) and from the Třinec ironworks power station (CFA) are shown in figures 1 and 2. Spherical particles of SFA microspheres and mica particles were observed.

Microspheres are formed during combustion in the temperature range of 1200-1500 °C and they influence fly ash properties (density, porosity etc.). Particles of calcareous fly ash have shape of irregular grains, due to lower temperature combustion of coal in the Třinec ironworks power station [6,7].

![Figures 1 and 2](image1.png)

**Figure 1.** Siliceous fly ash (the SFA samples). **Figure 2.** Calcareous fly ash (the CFA samples).

The colour of fly ash is changed from light gray to black depends on the amount of unburned carbon or the presence of pyrite (dark) and shale (light) in coal. Colour is influenced by the amount of lime or iron too [5].

![Figure 3](image3.png)

**Figure 3.** Different colour of fly ash samples (left SFA, right CFA).
3. Application in road construction

Treatment and stabilization of soils change the properties of soils to improve their engineering utilisation. Bulk density, moisture content, plasticity, susceptibility to volume changes, shear strength and bearing capacity are the most improving properties of treated soil. Binders that are used in soil treatment are represented mainly by cement, lime or hydraulic road binder. Fly ash has been used as an alternative binder in last decades [1,3,5,7].

Fly ash is used to mechanical soil treatment. Mechanical treatment of soil improves mechanical properties of treated soil (e.g. shear strength or compressibility), workability. Siliceous and calcareous fly ash is used in geotechnical applications closely connected with road construction to increase strength properties of soils, to control contraction and swelling of soils, to reduce water content in soils and to modify a particle size distribution [1,7,8,10].

Soil treatment by fly ash in the Czech Republic is governed by the European standard EN 14227-15 Hydraulically bound mixtures - Part 15: Hydraulically stabilized soils, Technical Requirement TP 94 - Soil treatment and Technical requirements TP 93 - Design and construction of highway structures using fly ash and ash. Regulations contain technical requirements for materials, material testing, requirements for construction of road layers, effects of soil treatment and environmental aspects [7].

4. Conclusions

Fluid combustion is more effective than high temperature combustion therefore it becomes more useable. However, combustion products have chemical and mineralogical properties that may cause problems in their utilization.

Composition of fly ash depends on type of fuel and furnace. In the past, defects occurred at application of inappropriate materials to road embankments and therefore specific research helps to avoid similar mistakes.

Laboratory tests show the potential of utilisation of fly ashes from the Morava region in road construction. Based on initial results from chemical analyses fly ashes can be used in treatment of soils. In the further research it is recommended to verify mechanical parameters of mixtures with concrete type of soil. The next step in future work would be to check the mixture properties in large-scale tests on construction site using the appropriate machinery.

Acknowledgement

Financial support through the Student Grant Competition VŠB-TUO - Project No. SP2017/155 is gratefully acknowledged.

References

[1] American coal ash association 2003 Fly ash facts for highway engineers (Washington DC: FHWA) pp 47-52
[2] Fečko P 2003 Fly ashes (Ostrava: Editorial Centre VŠB-TU Ostrava) p 187
[3] Kresta F 2013 Secondary materials in highway construction (Ostrava: Editorial Centre VŠB-TU Ostrava) pp 54-66
[4] Brandštetr J, Havlica J 1996 Phase composition of solid residues of fluidized bed coal combustion quality tests and application possibilities Chemical Papers 50 pp. 188-194
[5] Mezencevová A 2003 Possibilities of utilizing power plant fly ashes Acta Montanistica Slovaca 8 pp 146-151
[6] Michalíková F, Sisol M, Krinická I 2010 Chemical and mineralogical properties of ash of coal combustion in thermal power plants Waste forum 11 pp 15-16
[7] Bulíková L, Kresta F 2017 Possibility of use of fly ash from the Morava region to soil treatment in road constructions Conference Fly ash in civil engineering 2017 pp 7-13
[8] Kresta F 2013 Fly ash utilisation in road construction in Czech Republic 5th symp. on ash, slag and waste landfills in power plants and mines pp 118-125
[9] Ministry of Transportation Department of Roads 2011 Design and construction of highway structures using fly and ash *Technical Requirement 93*

[10] Ministry of Transportation Department of Roads 2013 Soil treatment *Technical Requirement 94*