# Properties of Fluid Ashes and Their Utilizability

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*Summary*

*This paper presents properties of ashes from combustion of black/hard coal in fluidized bed type boilers of EVO Vojany thermal power plant. Properties of ashes depend on inorganic components in coal and combustion temperature. Method for recovery of Fe component using low intensity magnetic separation from fluid bed ash is presented.*

*Keywords: coal, combustion, ash, fluidized boiler*

## Introduction

Burning of coal with similar properties in different types of boiler leads to formation of ashes with different physical, chemical, mineralogical, petrographic and petrologic properties. It is caused by different conditions in chamber. Temperature is the most important factor affecting polycomponency of ashes. Light fly ash and bed ash is formed in fluidized boilers.

Advantage of fluid combustion is lower energetic demand per unit of produced energy and positive effect on lowering $SO_X$ and $NO_X$ emissions.

This contribution is a presentation of properties of fluidized bed ash produced in thermal power plant EVO Vojany, Slovakia and method for recovery of Fe component using low intensity magnetic separation.

### *Physical, chemical and mineralogical composition of fluid ash particles*

Properties of ashes are affected by their history – conditions of their formation, properties of coal and technology used for its combustion. Combustion temperature in fluidized bed boilers is 800 to 850°C (Michalíková et al., 2003, 2007).

There is no difference in shape/morphology of particles formed by combustion of different types of coal in the same type of boiler (fusion, granulation or fluidized bed). The only difference is particle size distribution. Different morphology of particles is found when comparing ashes produced by combusting the same type of coal in different types of boilers (Kušnierová et al., 2011a, 2011b).

Physical properties include morphology, size distribution, surface area, mass and bulk density, hardness, optical properties, magnetism, electrical properties, thermal conductivity, compressibility and compactibility, fusibility and frost resistance (Fečko et al., 2003; Kušnierová et al., 2011a).

Morphology / particle shape of unburned coal residuals (UCR) is different than morphology of inorganic particles of ash. During combustion in fluidized bed type chambers the inorganic particles form mineral skeleton with shape similar to shape of original coal particle. UCR particles are highly porous.

Size distribution of ash affects surface activity more than any other physical factor. Size of light fly ash particles is 0–1 mm and bed ash 1–10 mm and more.

Surface area of ash is affected by morphological composition and content of UCR, quantitated as loss on ignition (LOI). Surface area of black coal light fly ash from two fluid boilers (EVO Vojany) is 30,69 $m^2 \cdot g^{-1}$ (K5) and 20,03 $m^2 \cdot g^{-1}$ (K6). Cause is high content of UCR in light fly ash (K5 = 33,47% and K6 = 18,9% LOI).

Density of black coal fluid light fly ash is 2,2–2,6 $g \cdot cm^{-3}$, and density of bed ash is 2,6–2,88 $g \cdot cm^{-3}$.

### *Chemical properties of fluid ashes*

Ashes from combustion of coal contain regardless of coal and boiler type these chemical elements: Si, Al, Fe, Mn, Ca, Mg, K, Ba, Mn and Na. Content of other elements is lower than 1% (Fečko et al., 2003; Michalíková et al., 2003).

### *Mineralogical and petrographic composition of fluid ashes*

Ashes contain silicates and alumosilicates of iron and iron oxides. These particles act as paramagnetic up to ferromagnetic mineral substances – substances with mineral susceptibility. Mineral novelties in ashes (see Table 1) are wollastonite $CaSiO_3$, kirschsteinite $CaFeSiO_4$, andradite $Ca_3Fe_2(SiO_4)_3$ and particles with chemical composition and properties similar to zeolites such as klinoptilolite a phillipsite (Kušnierová et al., 2011a; Michalíková et al., 2003).

Mullite phase and mullite $2SiO_2.3Al_2O_3$ is not present in fluid ashes as it is formed at higher temperatures

1 050–1 200°C, or 1 400°C, resp. Ash forming phase – inorganic minerals in coal – is partially up to fully molten during combustion and eutectic compounds are formed. Organic component – UCR – is transformed to macerals (Fečko et al., 2003).

Transformation process during heating up of inorganic component of coal runs as a continuous change of original ash forming minerals up to liquefied mixture of chemical elements, molten minerals, eutectic compounds.

## Black coal light fly ash from EVO Vojany*Solid residuals after coal combustion in fluidized bed type boiler and their reactivity*

Relatively coarse bed fraction of solid residuals – ash – gets separated from finer light fraction in fluidized bed combustion process (Michalíková et al., 2003). Finest light fraction of solid residuals is removed using filters. Because of using different types of coal, composition of solid residuals after combustion (thermochemical properties (Horovčák et al., 2012)) is also different. Limestone is added to combustion process as a desulphurization agent. Bed ash differs from light fly ash by higher content of free lime (Michalíková et al., 2007). Quantity of anhydrite and amorphous alumosilicate is almost the same in both ashes. Mineral novelty ettringite – $3CaO{\cdot}Al_2O_3{\cdot}3CaSO_4{\cdot}32H_2O$ is formed when water is added to solid residual. Another new formation responsible for definite hardness of composite is amorphous CS(A)H gel. Relatively high content of anhydrite can be used as a partial or full replacement of gypsum in portland cements.

Pozzolanic and cementation properties of compound are affected by mineralogical and not chemical composition (Michalíková and Škvarla, 2010). Classification and restriction specifications emphasizing chemical composition are rather misleading (Michalíková et al., 2003, 2012).

New hydrated phase created by mixing of fluid ash with water does not only lower solubility as a component of original material but also has ion-exchange capabilities. Leachates reach the quality of drinking water after some time. Presence of free CaO can significantly increase pH of fresh ash leachates, but alkalinity decreases after some time as a result of interactions.

Mineral components in accessory rocks of coal (silicates and clay minerals) are transformed by melting and fast cooling to amorphous alumosilicate phases that along with amorphous $SiO_2$ and $Al_2O_3$ allows development of pozzolanic reaction and formation of hydrated calcium-silicate products with cement binder (Fečko et al., 2003; Michalíková et al. 2003).

One of the limiting factors for utilization of ashes in building industry is LOI. Fluid bed ash confirms EN STN 206-1 standard that allows 3–5% LOI.

Table 1. Mineral novelties of fluid ashes (McCarty et al., 1993)

Tabela 1. Mineralne składniki popiołów fluidalnych (McCarty i inni, 1993)

| Mineral novelty | Assumed chemical composition |
|---|---|
| Anhydrite | $CaSO_4$ |
| Hannebachite | $CaSO_4.1/2\ H_2O$ |
| Portlandite | $Ca(OH)_2$ |
| Gypsum | $CaSO_4.2H_2O$ |
| Calcite | $CaCO_3$ |
| Quartz | $SiO_2$ |
| Hematite | $Fe_2O_3$ |
| Magnetite | $Fe_3O_4$ |
| Ettringite | $Ca_6Al_2(SO_4)_3(OH)_{12}.6H_2O$ |
| Thaumazite | $Ca_6Si_2(SO_4)_2(CO_3)_2(OH)_{12}.24H_2O$ |

***Content of Fe and unburned coal residuals***

Assays of iron and loss on ignition in light fly ash and bed ash in fluidized bed type boilers K5 and K6 were done in chemical laboratory of Institute of Montanneous Sciences and EP and are presented in Table 2. Particle size distribution of fluid bed ash is shown in Table 3.

Loss on ignition in sample ranges from 0 to 0,4%. This loss on ignition can be accounted to random occurrence of thermally undecomposed $CaCO_3$ added to combustion process for desulphurization (Michalíková and Škvarla, 2010).

Properties of black coal fluid ashes regarding their possible utilization in building industry are characterized using the results of electron microscopy.

Fittingly selected samples were studied by distribution of chemical elements (using energy-dispersion microanalysis – EDX) showing concentrations of investigated elements. Electron microscopy observations and EDX analyses were performed on following samples: fluid light fly ash from K5 boiler and fluid bed ash from K5 boiler. Results are shown in Table 4 and Table 5.

Presence of unburned coal residuals was not detected in coarser size classes of fluid bed ash. Using

Table 2. Iron and unburned coal residuals content (LOI)

Tabela 2. Zawartość żelaza i niespalonych pozostałości po antracycie (LOI)

| Boiler | Fluid ash | Loss on ignition [%] | Fe content [%] |
|---|---|---|---|
| K5 | bed | 33,47 | 2,78 |
| | light fly ash | 0,80 | 11,53 |
| K6 | bed | 18,91 | 3,07 |
| | light fly ash | 0,75 | 9,85 |

Table 3. Yields of size fractions and loss on ignition in sample of fluid bed ash from K5 boiler

Tabela 3. Wydajności wielkości frakcji oraz straty na zapłonie w próbce ze złoża fluidalnego K5

| Size fraction [mm] | Yield [%] | Loss on ignition [%] |
|---|---|---|
| + 6,3 | 10,00 | – |
| 5,6 – 6,3 | 3,16 | – |
| 4 – 5,6 | 7,37 | – |
| 2 – 4 | 19,43 | – |
| 1 – 2 | 20,27 | 1,20 |
| 0,355 – 1 | 22,60 | 0,86 |
| 0 – 0,355 | 17,17 | 0,51 |
| Feed | 100,00 | 0,70 |

Table 4. EDX area analyses of characteristic particles of fluid light fly ash from K5 boiler in EVO Vojany

Tabela 4. Analiza EDX cząsteczek charakterystycznych lekkiego popiołu lotnego z kotła K5 w EVO Vojany

| | Content of element [%] | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| EDX particle | Si K | Al K | K K | Ca K | Fe K | Mg K | S K | Ti K | Mn K |
| 221 | 45,1 | 17,0 | 3,4 | 24,6 | 8,1 | 0,0 | 0,0 | 1,3< | 0,5< |
| 222 | 1,0 | 0,5 | 0,4< | 91,5 | 0,6< | 1,0 | 5,0 | 0,0 | 0,0 |
| 223 | 42.6 | 17,6 | 3,4< | 19,2 | 11,3< | 0,0 | 0,0 | 5,9< | 0,0 |
| 224 | 78,7 | 11,3 | 5,7 | 1,7 | 1,8 | 0,4< | 0,0 | 0,2< | 0,1< |

Table 5. EDX area analyses of characteristic particles of fluid bed ash from K5 boiler in EVO Vojany

Tabela 5. Analiza EDX cząsteczek charakterystycznych popiołu fluidalnego z kotła K5 w EVO Vojany

| | Content of element [%] | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| EDX particle | Si K | Al K | K K | Ca K | Fe K | Mg K | S K | Ti K | Mn K |
| 211 | 57,3 | 19,4 | 7,8 | 8,1 | 5,6 | 0,6< | 0,0 | 1,2 | 0,0< |
| 212 | 17,2 | 7,1 | 1,2 | 3,8 | 63,8 | 2.7 | 0,0 | 0,1< | 4,1 |
| 213 | 10,7 | 6,5 | 0,7 | 5,6 | 75,2 | 0,5< | 0,0 | 0,2< | 0,5< |
| 214 | 41,6 | 21,2 | 1,2 | 22,9 | 11,2 | 0,2< | 0,0 | 1,4 | 0,2< |

magnetic separation in laboratory conditions we were able to prepare magnetic concentrates from fluid bed ash with over 50% Fe content in form of magnetite mineral novelty. EDX area analyses identified particles with 78 up to 90% Fe content (Michalíková et al., 2007, 2012; Rabatin et al., 1986),

Particle 211: By its chemical composition it is a modification of calcium-potassium alumosilicate that can originate in ash forming phase from sloam in coal. Particle is similar to Ca leucite novelty.

Si:57,3 : 28,09 = 1.33
Al: 17.4 : 27.00 = 0.64
K: 7.8 : 39.1 = 0.20
Ca: 8.1 : 40.08 = 0.20
Fe: 5.6 : 55.85 = 0.10
$K_{0,2}$ (Ca, Fe) $_{0,4}$ Al $_{0,64}$ Si $_{1,33}$ ... is similar to leucite with Ca: Ca,K($AlSi_2O_6$).

Particles 212 and 213 are typical for fluid bed ashes with high Fe content.

Particle 213 is formed predominantly by magnetite $FeFe_2O_4$ with hercynite molecule $FeAl_2O_4$ and Ca admixture.

Si: 10,7 : 28,09 = 0.38
Al: 6.5 : 27.0 = 0.24
Ca: 5.6 : 40.08 = 0.14
Fe: 75.2 : 55.85 = 1.35
$(Ca\ Fe)^{2+}\ (Al\ Fe^{3+})_2O^{4+}$ Si

Particle 214 corresponds with its chemistry to calcium alumosilicate with Fe content. Its chemistry points at possible relation to Ca alumosilicate with feldspathoids group – minerals which resemble feldspars in rocks.

### *Magnetic separation of fluid bed ash from EVO Vojany*

Dry low intensity magnetic separation was realized using dry electromagnetic separator Mechanobr with magnetic induction of 0,2–0,3 T. Magnetically separated were particles of fluid bed ash in 0–2,8 mm size fractions (Michalíková et al., 2012; Rabatin et al., 1986). Results of separation and achieved Fe contents in individual size fractions are shown in Table 6.

Highest Fe contents were repeatedly achieved for 0,5–1 mm a 1–2 mm size fractions.

## Conclusion

Knowledge of physical, chemical and mineralogical properties of solid wastes from combustion of coal in fluidized bed boilers of EVO Vojany thermal power plant provides information about the possibilities of their utilization in industry. Mineral novelties can be utilized as active components in building industry – in cements and mortars.

Pozzolanic properties affected not only by of chemical but mineralogical composition of ashes as well is the most important factor for utilization of fluid ashes in building industry.

Fluid bed ashes have higher reactivity caused by higher Ca content and are thus better suited for production of alkali activated binders than ashes from fusion and granulation type boilers.

Using low intensity magnetic separation it is possible to prepare magnetic concentrates with over 50% Fe content from fluid bed ashes. Magnetic product can be used in iron smelting as a component (5–8% wt.) as it is up to standard (Michalíková et al., 2007, 2012; Michalíková and Škvarla, 2010; Rabatin et al., 1986).

Possibilities of utilization of solid wastes from coal combustion are given by their physical properties (particle size distribution, surface area, morphological parameters) affected mainly by combustion process and presence – type of dominant ash forming minerals in coal responsible for formation of different novelties similar to natural minerals.

Fluid bed ash has lower loss on ignition than the limit set in EN STN 450 (STN 72 2064) standard and can thus be directly utilized in cement concrete production.

Composition of mineral novelties is not ideal as found in natural minerals.

For the evaluation of applicability of their utilization it is necessary not only to compare the costs of products produced using ashes with the cost of simi-

Table 6. Results of dry low intensity magnetic separation of fluid bed ash: 0–2,8 mm size fractions

Tabela 6. Wyniki suchej mało intensywnej separacji magnetycznej popiołu fluidalnego o wielkości 0–2,8 mm

| Size fraction [mm] | Yield of size fraction [%] | Yield of magnetic product [%] | Fe content in magnetic product [%] | Average Fe content [%] |
|---|---|---|---|---|
| 0 – 0,5 | 33,63 | 4,09 | 49,02 | 50,61 |
| 0,5 – 1 | 27,47 | 2,52 | 53,28 | |
| 1 – 2 | 24,89 | 0,43 | 51,38 | |
| 2 – 2,8 | 14,01 | 0,05 | 39,00 | |
| Σ | 100,00 | 7,08 | | |

lar products produced using natural raw materials but to consider establishing, operation, closing and recultivation charges of settling pits.

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## *Właściwości i wykorzystanie popiołów lotnych*

*Niniejszy referat prezentuje właściwości popiołów pochodzących ze spalania antracytu w złożach fluidalnych w elektrowni cieplnej EVO Vojany. Właściwości popiołów zależą od składników nieorganicznych w węgli oraz temperatury spalania. Zaprezentowano również metodę odzyskiwania składnika Fe przy użyciu mało intensywnej separacji magnetycznej od złoża.*

*Słowa kluczowe: węgiel, spalanie, popiół, kocioł fluidalny*