The Use of Black Fly Ash at the Production of Ceramics Materials - Part II

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Summary

This contribution is a presentation or results aimed at verification of possible utilization methods of ashes – solid wastes from combustion of black coal in fusion boilers as one of the components in ceramics production. Firing process of ceramics depends on properties of used ash and desired properties of ceramic material.
Firing process is positively affected by morphology of inorganic and organic matter: surface areas a pore volume, equal settling vellocity of individual components.
Dried bricks with constant addition of ash 25% wt. And 75% wt. of ceramic raw material were placed in laboratory owen.
Properties of ceramic bricks were tested at thermal holdups for 15, 60 and 90 minutes during firing in laboratory owen at 650 to 950°C.
Burnout of unburned coal residuals (UCR) starts in the ash at 650°C, which was completed using lower temperature gradient of 10 $K.min^{-1}$ at 950°C and using 25 $K.min^{-1}$ temperature gradient the burnout was not complete even at 1000°C, with only 20,7% of UCR from 25,5% LOI burned out.
Limiting condition is heating capacity of ash and ceramic raw material, which does not exceed 840 $KJ.kg^{-1}$. Burnout of UCR in ash is during temperature changes affected by content of inorganic matter. Burnout of UCR in ash is slower as burnout of coal, because UCR particles does not contain volatile matter.

Keywords: fly ash, ceramics, black coal, firing, unburned coal residuals

Introduction

Part I of the contribution presents the results of testing the possibility of using ash from combustion of black coal in EVO Vojany thermal power plant as a partial replacement of clays along with its characteristics. Products made using presented compound composition as a mixture of ash and brick-making clay fulfills the criteria for final ceramic products (Michalíková et al. 2014).

This – Part II – of the contribution reviews the effect of thermal holdup on ceramic compounds with admixture of ash and the conditions of UCR burnout during firing. Ash used in test was dry fly ash from electrostatic separators of K1 boiler.

Effect of thermal holdup on properties of fired ceramics with ash admixture

In ceramics production the firing process must be adjusted to properties of used ash and required properties of ceramic compound.

The effect of thermal holdup on properties of ceramic potsherds with added black coal fly ash was investigated using 70 mm × 35 mm × 12 mm (STN 72 1565) bricks with constant addition of 25% wt. of ash and 75% wt. of brick-making clay.

The period of thermal holdup was 15 min., 60 min. and 90 min. The effect of thermal endurance on properties of ceramic potsherds was tested at temperatures of 650, 700, 750, 800, 850, 900, 950°C.

Dried bricks were put into laboratory oven. In first series of tests first part of the bricks was fired at final temperature of 950°C with thermal holdup of 15 minutes at temperatures of 650, 700, 750, 800, 850, 900, 950°C. In second series of the test the bricks were fired with thermal holdup of 60 minutes at temperatures of 650, 700, 750, 800, 850, 900, 950°C. In third series of the tests the bricks were fired with thermal holdup of 90 minutes at temperatures of

650, 700, 750, 800, 850, 900, 950°C.

After slow cooling each of the bricks was weighted. Table 1 summarizes weights of the bricks fired for different periods of thermal holdup at temperatures of 650, 700, 750, 800, 850, 900, 950°C (Mihoková 2001, Michalíková et al. 2011).

After the bricks were cooled down to room temperature (20°C) each of the bricks were broken at about the middle of the brick. The rupture was used for visual evaluation of effect of thermal endurance of burnout of carbonate matter, in this case the unburned coal residuals.

In first series of the tests at thermal holdup of 15 minutes:

− At temperature of 650°C there is a visible ceramic look on the bricks – color of the brick is brown-red, brick core visible after the breakage is gray and thus not completely fired (width of unfired layer is 5.7 mm at 12 mm with of brick).

− At temperature of 700°C the unfired layer inside of the brick is 4 to 5 mm wide.

− At temperature of 750°C the unfired layer is 4 to 5 mm wide.

− At temperatures of 800 and 850°C the unfired layer is 4 mm wide.

− At temperature of 900°C the unfired layer is 3 mm wide.

− At temperature of 950°C the unfired layer is thicker than 1.5 to 2mm, but without complete burnout of carbon matter.

During the short 15 minutes thermal holdup the presence of low temperature melting eutectics, especially FeO caused sintering of the outer parts of bricks along with isolation of the core – lowering up to diffusion towards the center of the brick.

Thermal endurance of 15 minutes is unsatisfactory for complete burnout of the unburned coal residuals in the brick.

Second series of the test at thermal holdup of 60 minutes:

− At temperature of 650°C there is a visible unburned layer with dark grey color 1 to 2 mm wide.

Tab. 1. Effect of thermal hold up on weight of the bricks

Tab. 1. Wpływ sesji wypalania na wagę cegły

t [°C]	**15 [min]**	**60 [min]**	**90 [min]**
650	44.60	43.96	44.27
700	44.36	43.50	43.13
750	43.59	43.80	43.55
800	43.90	43.28	43.00
850	43.51	43.19	42.90
900	43.48	43.40	43.61
950	43.45	43.35	42.90

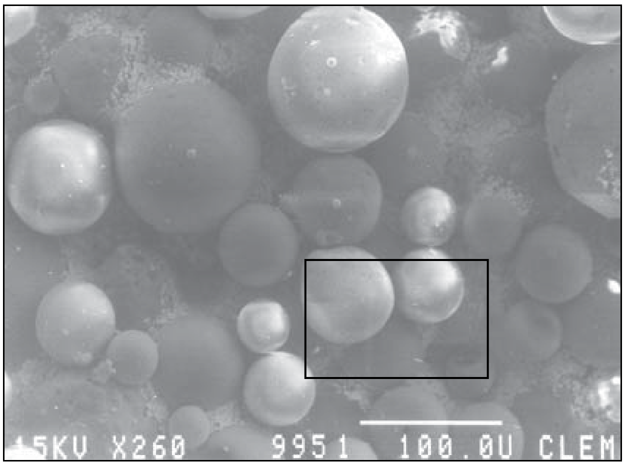

Fig. 1. Composition of inorganic black coal fly ash particles from fusion boiler. Particles have almost ideal spherical shape with adequate surface area

Rys. 1. Prezentacja nieorganicznych cząsteczek popiołu z węgla kamiennego pozyskanych z kotła fluidalnego. Cząsteczki mają niemalże idealny kulisty kształt z odpowiednim obszarem powierzchniowym

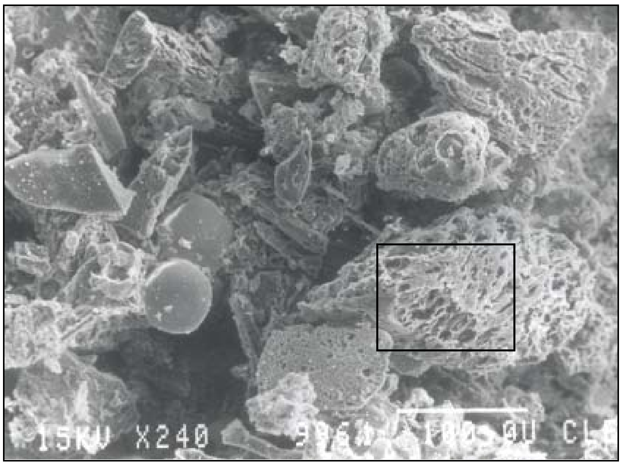

Fig. 2. Concentrate of particles of unburned coal residuals

Rys. 2. Stężenie cząsteczek w pozostałościach niespalonego węgla

− At temperatures of 700 and 750°C there is a lighter color layer inside of the brick 1 to 2 mm wide with fired UCR particles, no complete burnout of the whole volume.
− At temperature of 800°C the lighter color layer is only tenths of millimeter wide.
− At temperature of 850°C the layer inside of the brick is 0.1 to 0.2 mm wide with darker red color.
− At temperatures of 900 and 950°C the area of the rupture is homogeneous and the color of the bricks is red.

In all the bricks without dark unreacted core small pores with diameter of 0.02 to 0.1 mm are visible.

Third series of the test at thermal holdup of 90 minutes:
− At temperature of 650°C there is a 1-2 mm wide layer of grey color visible in the middle of the brick.
− At temperatures of 700 and 750°C there is a lighter color ceramic layer 0.1 mm wide without visible presence of unburned coal residuals.
− At temperature of 800 and 850°C appearance of the rupture is homogenous.
− At temperatures of 900 and 950°C appearance of the rupture of the brick is homogenous with darker red color comparable to outer parts of the brick.

At lower temperatures (650-750°C) not even 90 minutes of thermal holdup was satisfactory for complete burnout/firing of the brick and therefore we applied the test with 2 hours of thermal holdup and fired bricks were used for bending strength measurements. The bricks were after breakage completely homogenous.

From available source – optimum firing curve of brick-making material from Hanušovce brickworks (maximum firing temperature of 1050°C) it is clear that all the bricks will have enough time for complete burnout of unburned coal residuals and proper firing of ceramics in industrial conditions.

The limiting condition is heating value of ash and brick-making compound mixture. Theoretical value of heating value should not exceed 840 $KJ.kg^{-1}$ (Pytlík 1995). This limit will not be exceeded with lower than 30% ash addition with 10.9% LOI as there are admixtures added to the compound (Václavík et al. 2012).

The process of ceramic product firing is positively affected by morphology of inorganic component – unburned coal residuals, surface area and porosity (Michalíková et al. 2011).

Surface area of organic and inorganic fly ash components with different content of UCR is as follows:

Surface area [$m^2.g^{-1}$], denoted as:
SM: surface area measured at one place,
SA: surface area from several measurements,
OP: pore volume in cm^2 per 1 gram of sample.

Note:
Because of settling velocities the UCR particles cumulates in coarsest size classes (Bakalár et al. 2005). Pore volume of UCR particles is 0,014 – 0,009 $cm^3.g^{-1}$, higher porosity boosts burnout.

Ash – inorganic component after flotation of UCR and magnetic separation "cleaned" of UCR and magnetite Fe has of one order higher pore volume – 0,0021 $cm^3.g^{-1}$ when compared to UCR.

Surface areas of UCR are also of 1,5 – 1,6 orders higher than inorganic component.

Results of measurement of surface areas of organic and inorganic component are an important information, because they significantly affect physical properties of ceramic compounds.

E.g.: inorganic component – coarse ash in size class 0,12 – 0,18 mm contains up to 86,10% LOI, has large surface area SM: 15,91 $m^2.g^{-1}$, SA: 15,81 $m^2.g^{-1}$, pore volume: 0,014 $cm^3.g^{-1}$.

Inorganic component of ash with particles of UCR/LOI and novelties of magnetite mineral separated using low intensity magnetic separation process only has 0,61% LOI, surface area is 1,46 – 2 $m^2.g^{-1}$, pore volume is 0,0021 $cm^3.g^{-1}$ (Michalíková et al. 2009).

Note:
Parameters of coal combusted in fusion boiler of EVO Vojany thermal power plant:
• Combustion heat: 32 $MJ.kg^{-1}$, heating capacity: 25 – 30 $MJ.kg^{-1}$
• Combustion heat of ash with 82,48% LOI: 27,59 $MJ.kg^{-1}$
• Combustion heat of combustible matter: 33,87 $MJ.kg^{-1}$ (82,48% LOI)

For instructive purposes see Figure 1 – snapshot of inorganic component of black coal fly ash from fusion boilers.

Figure 2 shows a picture of UCR particles with visible porous and rugged surface adequate to measured surface areas.

Burnout of unburned coal residuals in ash

Presence of unburned coal residuals in ash – loss on ignition depends mainly on type of burned coal, content of volatile matter in coal, fineness and firing process. Utilization of ashes in ceramic industry requires the knowledge of temperatures of unburned coal residuals burnout and its kinetics (Michalíková et al. 2009).

Conclusion made from results of thermal analysis of ash with 25.5% LOI (Michalíková et al. 2009) presented in Figure 3, which was realized using the principle of sample heat up in oxidizing atmosphere with constant temperature gradient of 10 $K.min^{-1}$ a 25 $K.min^{-1}$ is:

- Burnout of unburned coal residuals – in in ceramic compound with 25.5% LOI starts at temperature of about 650°C.
- Maximum exothermic effect caused by burnout is at temperature of 780°C.
- At lower temperature gradient of 10 $K.min^{-1}$ the burnout is completed at 950°C with decrease in weight to 74.51°C corresponding with loss on ignition (100% - 74, 51= 25,5%) and thus complete UCR burnout.
- At higher temperature gradient of 25 $K.min^{-1}$ the burnout is not complete even at 1000°C (20.27% of UCR is burned out)

The UCR burnout in ash takes place at lower temperatures with respect to inorganic component content. The higher the ash content, the higher temperature is needed to start the burnout and to achieve complete burnout of UCR (Michalíková et al. 2009).

For example the starting burning temperature of flotation concentrate with 84% LOI was determined as 500°C with burning completed at 640°C.

Coal passed during its combustion in boiler region of high temperatures (1400 – 1600°C), where the volatile matter burned out. Unburned coal residuals – UCR is composited of pure carbon corresponding with the ignition temperature of 500°C.

Green TG curve is thermo gravimetric with corresponding green axis on the left side. Red DTG curve is a derivation of a TG curve with corresponding red axis on the right side. Blue DTA curve is a differential thermal curve with corresponding blue axis on the right side.

Unburned coal in ash needs some time for complete burn out after achieving ignition temperature, which depends on content of unburned residuals and this time cannot be compensated by elevated temperature. Time factor is more important for complete burn out of unburned residuals than temperature gradient. Burn out time of unburned residuals in ash is longer when compared to bur out time of coal with the same particle size distribution, because ash particles does not contain volatile matter.

Conclusion

Testing of black coal ash from combustion of coal in fusion boilers proved the possibility of

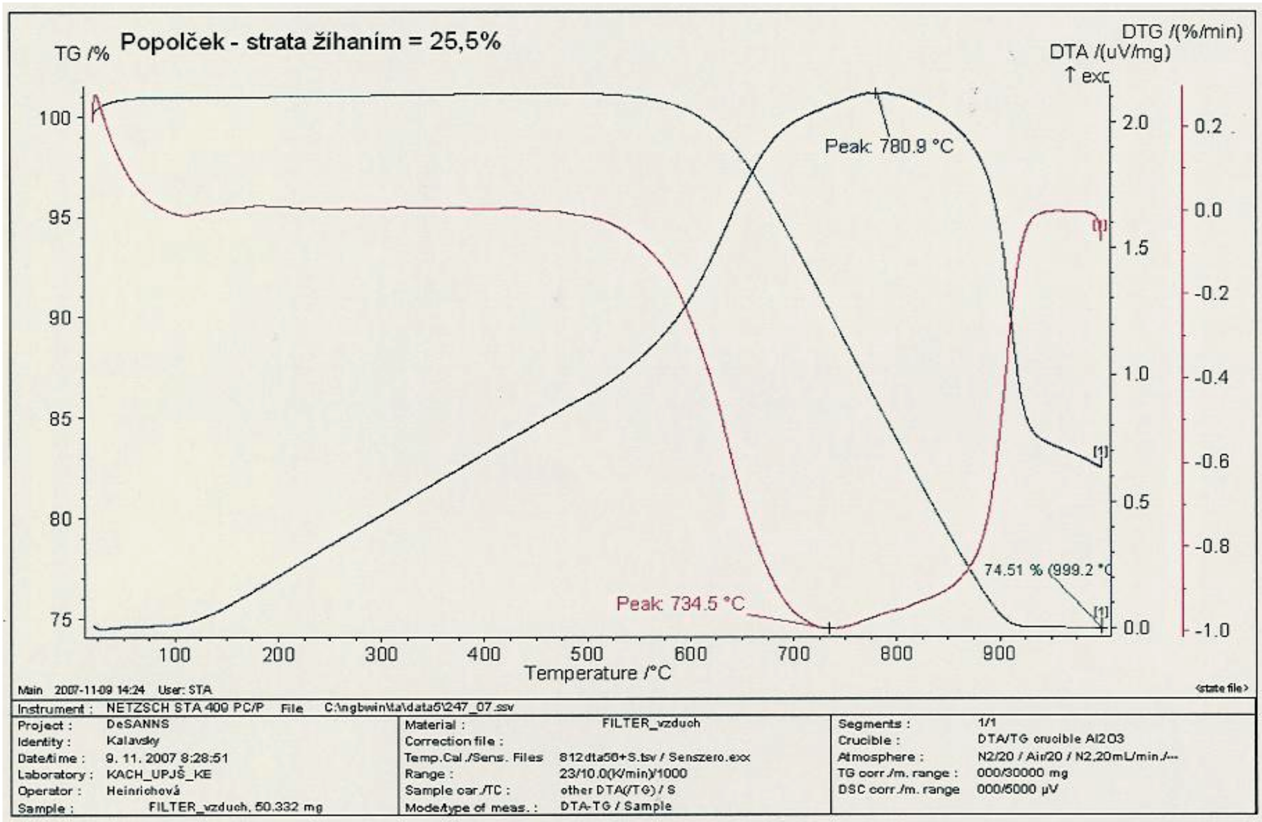

Fig. 3. TG, DTA and DTG curve of ash burnout with LOI = 25.64%, temperature gradient 10 $K.min^{-1}$

Rys. 3. Krzywe TG, DTA i DTG wypalania popiołu ze stratą prażenia równą 25,64%, gradient temperatury wynosi 10 $K.min^{-1}$

its usage as a partial replacement of material in ceramics production. Results of tests in laboratory conditions revealed, that best properties – flexural strength after firing had a compound of 10 – 15% of ash and 85 – 90% brick making material, where the mixed compound was left for two days.

During the test 0 – 30% of ash was mixed into the brick making material resulting in workable mixture from which the testing bricks were molded. Some conditions of the realized test could not be influenced because of the nature of used devices. For example the control of diffusion in muffle furnace could not be completely guaranteed, which could lead to change of needed oxidizing atmosphere to partially reducing atmosphere during testing.

Results of our laboratory research can be used as an objective base for development of prognoses regarding the utilizability of black coal ash from thermal power plants in industrial ceramics production.

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Wykorzystanie popiołu lotnego z węgla kamiennego do produkcji materiałów ceramicznych – część II

W artykule dokonano prezentacji wyników, które mają na celu zweryfikowanie możliwych metod wykorzystania popiołu – odpadów stałych ze spalania węgla kamiennego w kotle fluidalnym, jako jednego ze składników produkcji materiałów ceramicznych. Proces wypalania ceramiki zależy od właściwości użytego popiołu i docelowych właściwości materiału ceramicznego.

Na proces wypalania dobrze wpływa morfologia materii organicznej i nieorganicznej: powierzchnia właściwa a ilość porów, równa prędkość opadania poszczególnych komponentów.

Osuszone cegły, ze stałym dodatkiem popiołu 25% wag oraz 75% wag. nieprzetworzonego materiału ceramicznego, zostały umieszczone w piecu laboratoryjnym.

Właściwości cegieł ceramicznych zostały sprawdzone podczas 15, 60 i 90 minutowych sesji wypalania w piecu laboratoryjnym w temperaturze od 650 do 950°C.

Wypalanie pozostałości niespalonego węgla (PNW) rozpoczyna się w temperaturze 650°C i kompletne wypalenie uzyskuje się przy użyciu niższego gradientu temperatury o wartości 10 $K.min^{-1}$ w temperaturze 950°C. Przy użyciu gradientu temperatury o wartości 25 $K.min^{-1}$ wypalanie nie było skończone nawet w temperaturze 1000°C, a PNW wyniósł zaledwie 20,7% z 25,5% stratą prażenia (StP).

Warunkiem ograniczającym jest zdolność grzewcza popiołu i materiału ceramicznego, która nie przekracza 840 $KJ.kg^{-1}$. Wypalanie PNW w popiele następuje przy zmianie temperatury wywołanej zawartością materii nieorganicznej. Wypalanie PNW w popiele jest wolniejsze od wypalania węgla, ponieważ cząsteczki PNW nie zawierają substancji lotnych.

Słowa kluczowe: popiół lotny, ceramika, węgiel kamienny, wypalanie, pozostałości niespalonego węgla