The Use of Black Coal Fly Ash at the Production of Ceramic Materials - I. Part

Františka MICHALÍKOVÁ[1], Ivan BREZÁNI[2], Martin SISOL[3], Lucia MIHOKOVÁ[4], Beata STEHLÍKOVÁ[5]

[1] CSc.; Institute of Montanneous Sciences and Environmental Protection, Faculty BERG, Technical University of Košice, Slovakia; email: frantiska.michalikova@tuke.sk
[2] Eng.; Institute of Montanneous Sciences and Environmental Protection, Faculty BERG, Technical University of Košice, Slovakia; email: ivan.brezani@tuke.sk
[3] Eng., Ph. D.;Institute of Montanneous Sciences and Environmental Protection, Faculty BERG, Technical University of Košice, Slovakia; email: martin.sisol@tuke.sk
[4] Eng., Ph. D.; Technical University of Košice, Park Komenského 19, 043 84 Košice; email: lucia.mihokova@tuke.sk
[5] Eng., Ph. D.; Faculty BERG, Technical University of Košice, Park Komenského 19, 043 84 Košice; email: stehlikovab@gmail.com

Summary

In the contribution, methods of utilizing power plant fly ash for the bricks production are presented. The utilization of fly ash at maximum of 30 % (wt) meets the requirements to the bending strength (after drying and firing) of the probe bricks. The laboratory tests prove the justification of the application of fly ash in the brick manufacturEng.

Keywords: flyash, ceramics, unburned coal residuals, bricks

Introduction

One of the reasons for low utilization of ashes in industries is variation of their mineralogical and chemical composition, although their properties are similar to properties of natural resources.

World trend – utilization of industrial wastes – is motivated by economic advantages, especially preservation of resources, energy and a must for environmental protection. Ashes are widely available and cheap resource with valuable properties also in ceramics production.

Analysis

Brick-making technology is based on processing and forming of press-works from plastic paste, their consecutive drying and firing, where products gain their porous structure and in most applications red color of potsherds.

Utilization of fly ashes in bricks production is widely known.

Raw materials in bricks productions contain primarily these minerals: kaolinite, halloysite, montmorillonite, illite, sericite and chlorite, non-plastic minerals such as quartz, feldspars, mica, calcite, dolomite, siderite and gypsum.

Inorganic component formed after coal is burned is composed of ashes. Ashes from black coal combustion in fusion boilers contain up to 60% of glass phase because of high burning temperature. Mineral novelties are mainly alumosilicates of Al, Fe, Ca, Mg, zeolites – clinoptilolite, phillipsite with less frequent occurrence of magnetite mineral novelties.

Montmorilonitic raw materials are hard to process and fly ash addition of 30 to 50% volume can intensify production, in spite of extensive vulnerability during drying and firing [Vídeňská 1986, 1987].

By addition of ashes to 30% volume of illitic raw materials it is possible to lower occurrence of technological cracks and thus raise the strength of products.

Ashes act as lightweight aggregates, lesser as grogs and contain unburned coal reiduals (UCR) that lower heat consumption during firEng.

With further increase in ash content strength of products does not rise anymore and with content exceeding 50 % strength of the products declines along with specific weight and product – lightweight brick has better thermal insulation properties.

With ash content above 80%, raw material has new technological properties and 20% of brick clay acts as a binder between individual particles of ashes. Ash bricks are thus produced with lower strength and specific weight between 600 and 1200 kg. m^{-3}.

Our experimental research was aimed for preparation of mixture of ashes with brick production raw material and consecutive study of ceramics-technological properties. Intended part II of the article deals with visual determination of thermal hold-off during firing of bricks with ashes containing unburned coal residuals [Baulovičová, Mihoková, Michalíková et al. 2011].

Another part of the work was done using zeolitized ash. These problematics will be discussed in a stand-alone contribution.

Experimental

Evaluation of production of ceramics using black coal ash from fusion boilers

While dealing with grant projects, dissertation and diploma theses, possibilities of utilization of ashes from coal combustion in fusion type boilers. Utilization of ashes as partial replacement of natural resources – clays – in ceramics production is one of the possibilities. Ashes with their physical and chemical properties satisfy the needs in ceramics production, what is confirmed by practical experiences of ceramics plants worldwide. Particle size distribution of ashes (0 - 0,2 mm), surface area (3-6-10 $m^2.g^{-1}$), higher content of combustible content – unburned coal residuals make it possible to lower specific weight of ceramic potsherds, lowers the consumption of fuel in firing process and enhances thermal – technological properties of products.

Black coal ash from fusion boilers of EVO Vojany thermal power plant (combustion temperature 1400 – 1600°C) used in our tests contains more than 10.9% of unburned coal residuals characterized by loss on ignition (LOI), that lowers the consumption of fuel used for firing, acts partially as a grog and enhances strength of final products. Morphology of the ash is characterized by presence of hollow spherical glass inorganic particles (microspheres – cenospheres and plerospheres) and unburned organic particles.

Fig. 1 shows unburned coked coal residual particle with 82.18% LOI. Image of the particle morphology is characteristic for the burnup of coal. In micron size pores, spheres (cenospheres and plerospheres) of inorganic component are wedged. Surface area of UCR is higher by one order than the surface area of inorganic particles. Particles of UCR show high degree of internal porosity (surface area of 10 – 15 - 17 $m^2.g^{-1}$) [Michalíková et all.2003, 2009]. Their presence contributes to diffusion in pores of fired body.

Use of ashes in production of building ceramics

Videňská tested the use of solid waste from energetics – ashes – in bricks production. Presented results are examination of the possibility of partial replacement of clays by ashes. In bricks production, firing is the fundamental operation. Consumption of technological fuel when firing products based on ashes is considerably lower when compared to consumption of fuel when firing product made of pure clay.

This is caused by content of combustible particles (0, 5, 20 and more % LOI). During firing of such materials it is necessary to adjust firing process to ashes content. Specific demands of such mixture are related to burn up of char matter. It is necessary to determine mechanism and kinetics of oxidation of admixtures, so that the rate and temperature of firing corresponds with the desired quality of bricks in which "black cores" are undesirable.

During firing of materials with ash addition, material is heated by internal burning of combustible component. Combustion temperature of char particles at

Tab. 1 Characteristic chemical composition of black coal fly ash.

Tab. 1 Charakterystyka składu chemicznego popiołu lotnego z węgla kamiennego

Chemical component	SiO_2	Al_2O_3	Fe	TiO_2	CaO	MgO	K_2O	Na_2O	SO_3
[%]	50 – 57	25 – 30	3 – 11	0 – 1	2 – 4	1,5 – 3	2,5 – 5	0 – 2	0,5 – 1

Tab. 2 Mineralogical composition of black coal ash from EVO Vojany thermal power plant.

Tab. 2 Skład mineralogiczny popiołu z węgla kamiennego z elektrowni cieplnej EVO Vojany

Chamical composition	Mineral	Content [%]
		EVO Vojany
SiO_2	Quartz	4,1
$3Al_2O_3.2SiO_2$	Mullite	2,1
Fe_2O_3	Hematite	8,7
TiO_2	Rutile	-
TiO_2	Anatase	0,6
SiO_2	Cristobalite	-
C	Carbon	18,32
Glass phase		62,90

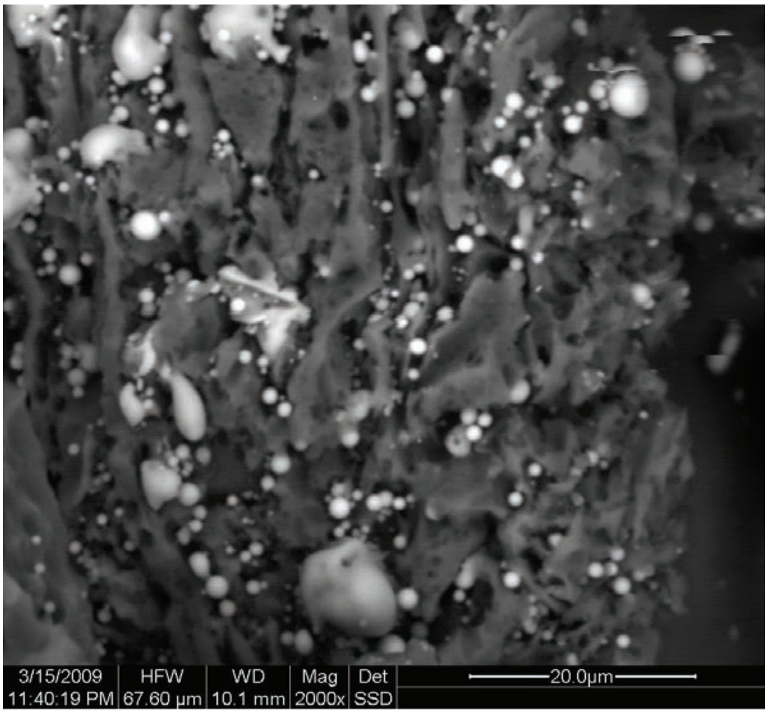

Fig. 1 Unburned coal residual particle – surface micromorphology of typical UCR particle with 0-5 μm microspheres wedged in pores of unburned coal (2000 x magnification).

Rys. 1 Niedopał - Mikromorfologia powierzchni za pomocą UCR mikrosfer o wielkości 0-5 mikrometrów, w porach spalonego węgla (powiększenie 2000 x)

some places considerably exceed the mean temperature of firing, accelerating physico-chemical processes at some places (welding effect – sintering).

Strengthening of potsherds without deformation at higher temperatures is delimited by physical processes and chemical reactions. Sintering takes effect in two phases: at first in solid phase and after appearance of liquid phase [Pytlík 1995]. Conditions for formation of primary melt, that allow formation of other phases and structures for the transformation of iron (III) oxide to iron (II) oxide are reached during burn up of combustible component. Higher temperature leads to faster oxidation. Exceeding of a certain temperature slows up to stops the oxidation, because the pores in potsherds are being closed. If the char particles do not burn in time, reducing properties of carbon will invoke chemical reactions accompanied by formation of liquid phase. Fe_2O_3 is transformed using carbon to a bivalent form and remains in this form till the maximum temperature of firing is reached and forms along with other oxides low melting eutectics. Eutectics strongly enrich potsherds with melt, especially at maximum temperature of firEng. Melt wit finely scattered carbon forms black glass cores in potsherds, that consecutively using different physico – mechanical reactions increase the sensitivity of products during cooling, black cores negatively affect technological properties of product after firEng.

Burning inside of product has zonal (diffusive) character. Line of burning relocates intensively towards the center of the product and takes place at temperature range of 700 to 1500°C. Combustion temperature is at relatively equal conditions expressed as a ratio of outer area (Sp) and real volume of product (Vs). Burn up of residual fuel is intensified by increasing Sp/Vs ratio.

In order to achieve high technological quality of potsherds it is necessary to fire dried product at optimum temperature – achieve and for some time retain certain maximum temperature during firing process [Pytlík 1995]. Burning of organic char particles contained in ashes and clays is achieved in temperature range 500-800°C by oxidation hold-off, which enables elimination of temperature gradients in potsherds, penetration of oxidation atmosphere to the center of product and burn up of organic matter [1]. From DTA curves it is possible to determine the temperature at which the leakage of water vapors from inside of the fired product stops. During the leakage of steam capillaries are formed and up to this temperature air needed for burning of carbon can penetrate the potsherds through these capillaries.

Test aimed to evaluation of using ashes as grog in brick production following components were used:

- ***Ash:*** Sample of black coal ash was taken off a dumping hopper of electrostatic dust separator of K1 boiler in EVO Vojany power plant. Chemical analysis of the sample revealed 10.9 % LOI and 5.95% Fe content. Before the mixing with clay, ash was dried.

- ***Brick making raw material:*** Brick works TEMAKO, s.r.o. in Hanušovce n/Topľou provided sample of basic brick making raw material.
- ***Preparation of ash and brick making raw material mixture:*** Sample was dried and comminuted to 100% passing 0.2 mm. Mixing of the individual samples was carried out at following volumetric quantities:

Compound no.1:
0 % ash + 100 % brick making raw material
Compound no.2:
10 % ash + 90 % brick making raw material
Compound no.3:
15 % ash + 85 % brick making raw material
Compound no.4:
20 % ash + 80 % brick making raw material
Compound no.5:
25 % ash + 75 % brick making raw material
Compound no.6:
30 % ash + 70 % brick making raw material

These compounds were kneaded by hand and after cellaring, testing bodies in compliance with technical normative STN 72 1565, part 4 were prepared. Part of the testing bodies was used after drying for flexural strength tests. Parallel part of the bodies was fired in electric box furnace Riedhammer (SK 170) at 970ºC and firing curve ensuring the possibility of complete burn up of combustible matter from compound.

Testing bodies "small bricks" with 70 x 35 x 2mm dimensions were fired at 900 °C in laboratory furnace, consecutively their technological parameters were estimated and calculated such as portion of mixing water, amount of shrinkage by drying, flexural strength after drying, color after firing, temperature of firing, total shrinkage, suction capacity, flexural strength after firing and weight loss after firing (see Tab. 3). Based on these parameters we concluded, that rising addition of ashes to brick making raw material does not significantly affects properties of ceramics potsherds when compared to potsherds made using zero ash addition. Positive difference was increasing suction capacity (apparent porosity that affects thermal conductivity of potsherds and thus improves thermal insulating properties caused by burn up of unburned coal residuals). Negative difference was decrease in flexural strengths after drying and firing with increasing portion of ash in mixture.

Six different pilling periods of mixtures were evaluated before formation of testing bodies: immediate, 20 minutes, 1 day, 2 days, 3days and 7 days after mixEng. Increase in pilling period increased plasticity of the mixture already after 1 day of pillEng. More than 7 days of pilling increases plasticity of the mixture and thus enhances its properties including strengths.

Interpretation of strength measurements

Purpose of the tests was to consider the possibility of utilization of black coal ash from fusion boilers from EVO Vojany in ceramics production.

Flexural strength after drying and firing is determined according to normative STN 72 1565, part 7

Tab. 3 Resulting technological parameters of ash and basic compound mixture

Tab. 3 Uzyskane parametry technologiczne popiołu i mieszaniny substancji podstawowej

Parameter	**0 % Ash**	**10 % Ash**	**15 % Ash**	**20 % Ash**	**25 % Ash**	**30 % Ash**
Content of water in mixture [%]	22.25	23.78	23.38	23.88	24.65	24.18
Shrinkage by drying [%]	7.85	7.71	7.57	6.71	7.0	6.14
Flexural strength after drying [MPa]	5.78	5.61	4.88	4.84	4.28	4.56
Color after drying	ocherous brown	brown	brown - grey	grey	darker grey	dark grey
Temperature of firing [°C]	900	900	900	900	900	900
Total shrinkage [%]	14.28	14.28	14.28	14.28	14.28	14.28
Suction capacity [%]	16.06	18.26	18.97	19.09	20.78	21.78
Flexural strength after firing [MPa]	6.56	6.99	6.48	6.31	5.63	5.93
Weight loss after firing [%]	7.54	5.43	5.00	5.50	5.88	6.28
Color after firing	brick red	brick red	brick red	brick red	brick red	brick red

using 20 x 20 x 120mm testing bodies.

Flexural strength after drying σpo,s is a tension at which the dried body fractures under flexural stress. It is declared in MPa.

Flexural strength after firing σpo,p is a tension at which the fired body fractures under flexural stress. It is declared in MPa.

Main purpose of the test is determination of force F that needs to be equally applied on the body so that the body fractures under flexural stress. Flexural

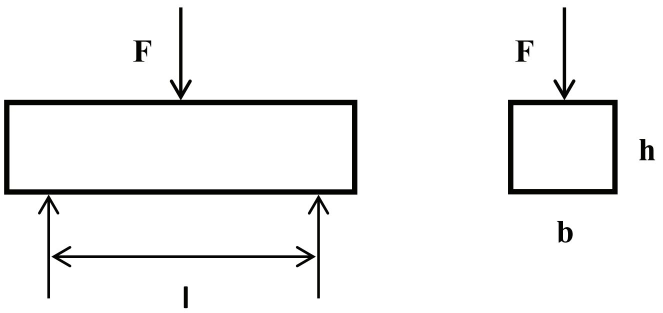

Fig. 2 Three-point bending setup for flexural strength measurement (left) and setup for compressive strength measurement (right)

Rys. 2 Trójpunktowe zginanie (po lewej) i pomiar wytrzymałości na ściskanie (po prawej)

Tab. 4 Flexural strengths of testing bodies made from mixture of ash and brick making raw material immediately after mixing

Tab. 4 Badanie wytrzymałości na zginanie próbki z mieszaniny popiołu i cegły – badanie niezwłocznie po zmieszaniu

	Flexural strength after drying		**Flexural strength after firing**	
Ash content [%]	**I.series**	**II.series**	**I.series**	**II.series**
	σ_{po} [MPa]	**σ_{po} [MPa]**	**σ_{po} [MPa]**	**σ_{po} [MPa]**
0 %	4,94	5,78	5,28	6,56
10 %	4,66	5,61	4,88	6,99
15 %	4,93	4,88	5,46	6,48
20 %	4,24	4,84	5,82	6,31
25 %	3,95	4,28	5,79	5,63
30 %	3,33	4,56	4,80	5,93

Tab. 5 Flexural strengths of testing bodies made from mixture of ash and brick making raw material 20 minutes after

Tab. 5 Badanie wytrzymałości na zginanie mieszaniny popiołu oraz cegły po 20 minutach

	Flexural strength after drying		**Flexural strength after firing**	
Ash content [%]	**I.series**	**II.series**	**I.series**	**II.series**
	σ_{po} [MPa]	**σ_{po} [MPa]**	**σ_{po} [MPa]**	**σ_{po} [MPa]**
0 %	5,28	6,39	6,68	7,66
10 %	5,55	6,49	6,83	6,63
15 %	4,54	5,76	6,04	6,87
20 %	5,59	5,64	7,32	6,65
25 %	5,19	4,65	7,58	6,98
30 %	4,25	4,15	7,15	6,90

Tab. 6 Flexural strengths of testing bodies made from mixture of ash and brick making raw material 1 day after mixing

Tab. 6 Badanie wytrzymałości na zginanie mieszaniny popiołu oraz cegły po 1 dniu

Ash content [%]	Flexural strength after drying		Flexural strength after firing	
	I.series	II.series	I.series	II.series
	σ_{po} [MPa]	σ_{po} [MPa]	σ_{po} [MPa]	σ_{po} [MPa]
0 %	6,54	5,63	6,37	7,00
10 %	6,10	5,19	6,95	5,82
15 %	5,94	5,27	6,57	5,68
20 %	4,77	5,01	5,94	6,35
25 %	4,88	3,94	7,48	5,48
30 %	4,20	3,65	6,17	6,16

Tab. 7 Flexural strengths of testing bodies made from mixture of ash and brick making raw material 2 days after mixing

Tab. 7. Badanie wytrzymałości na ściskanie – popiołu i cegły po 2 dniach

Ash content [%]	Flexural strength after drying		Flexural strength after firing	
	I.series	II.series	I.series	II.series
	σ_{po} [MPa]	σ_{po} [MPa]	σ_{po} [MPa]	σ_{po} [MPa]
0 %	7,76	-	8,34	-
10 %	6,97	-	9,73	-
15 %	5,92	-	7,79	-
20 %	4,19	-	6,94	-
25 %	3,86	-	6,43	-
30 %	3,18	-	5,62	-

Tab. 8 Flexural strengths of testing bodies made from mixture of ash and brick making raw material 3 days after mixing

Tab. 8 Badanie wytrzymałości na ściskanie mieszaniny popiołu oraz cegły po 3 dniach po zmieszaniu

Ash content [%]	Flexural strength after drying		Flexural strength after firing	
	I.series	II.series	I.series	II.series
	σ_{po} [MPa]	σ_{po} [MPa]	σ_{po} [MPa]	σ_{po} [MPa]
0 %	4,99	-	6,57	-
10 %	5,35	-	6,55	-
15 %	5,21	-	6,69	-
20 %	4,75	-	6,41	-
25 %	4,23	-	6,36	-
30 %	3,52	-	6,21	-

Tab. 9 Flexural strengths of testing bodies made from mixture of ash and brick making raw material 7 days after mixing

Tab. 9 Badanie wytrzymałości na ściskanie popiołu i cegieł – po 7 dniach po zmieszaniu

	Flexural strength after drying		**Flexural strength after firing**	
Ash content [%]	**I.series**	**II.series**	**I.series**	**II.series**
	σ_{po} [MPa]	**σ_{po} [MPa]**	**σ_{po} [MPa]**	**σ_{po} [MPa]**
0 %	6,11	6,57	7,85	6,97
10 %	5,71	6,46	6,57	6,98
15 %	5,09	5,66	6,49	7,68
20 %	4,79	5,63	6,19	6,51
25 %	4,29	5,14	5,85	5,74
30 %	4,58	4,61	6,72	5,97

strength of testing bodies was measured using three-point bending setup with support span of 100mm. Width b and height h of the fractured body was measured after fracturEng. Flexural strength was calculated using Eq. 1-2.

$$\sigma_{po,S} = \frac{3}{2} \cdot \frac{F \cdot l}{b \cdot h^2} \quad (1)$$

$$\sigma_{po,P} = \frac{3}{2} \cdot \frac{F \cdot l}{b \cdot h^2} \quad (2)$$

Parameters of Eq. 1 are shown on Fig. 2.

Flexural strengths after drying and firing of testing bodies formed from mixtures immediately after mixing and up to 7 days of pilling are shown in Tab. 4-9. Flexural strength after drying decreases with increasing portion of ash in the mixture. Decrease in flexural strengths after firing is less significant, that is with increased portion of ash in the mixture is the decrease in absolute measured values of flexural strengths lower than the decrease in strengths after dryEng.

Conclusion

Purpose of this contribution was to evaluate the possibility of utilization of black coal ash – solid waste from combustion in thermal power plant fusion boilers – in ceramics industry

Results show that tested ash with its physical and chemical properties (particle size distribution, surface area, higher content of unburned coal residuals) improves properties of final products, acts partially as a grog, enhances strength and decreases specific weight of ceramic potsherds.

Best results – bending strengths after drying and firing – were measured for mixture containing 10 to 15% ash and 85 – 90% brick making raw material with pilling period of 2 days.

Ash with known loss on ignition can be used in ceramics production directly, without any processEng. Unburned coal residuals content is positive. Burn up of combustible matter in ash heats the product by internal burn up. Presented results can be used as an objective background for the evaluation of possibilities for utilization of ash in ceramics and brick making industry.

Acknowledgement:
This work was supported by the research grant project VEGA, no. 1/1222/12, and APVV 0423-11

Literatura - References

1. *Bakalár, T., Búgel M., Schlosser S.,Onderková B.: Odstraňovanie ťažkých kovov z vodných roztokov = Heavy metal removal from water solutions. In: Acta Montanistica Slovaca. Roč. 10, mimoriadne č. 1 (2005), p. 275-279. - ISSN 1335-1788*
2. *Baulovičová L., Michalíková F. 2002. Popolček - odpad z energetiky ako surovina vo výrobe tehál. Medzinárodná konferencia "ODPADY 2002", Spišská Nová Ves, 7.-8.11.2002, p. 227- 232, ISBN 80-968214-2-3*
3. *Fečko, P., Kušnierová, M., Raclavská, H., Čablík V., Lyčková, B.: Fly ash. VŠB: Technical University of Ostrava, Ostrava 2005, 191 p., ISBN 80-248-0836-6*
4. *Lembák, M., Václavík, V.: K problematice využití odpadů z těžby černého uhlí pro stavební účely. RECYKLING 2004 "Možnosti a perspektivity recyklace stavebních odpadů jako zdroje plnohodnotných surovin". Sborník přednášek konference. 11. - 12. března 2004.VUT Brno, p. 94 - 102. ISBN 80-214-2583-0*
5. *Mihoková, L.: Použitie energetického odpadu – popolčeka vo výrobe tehál, Diplomová práca 2001, F BERG, TU Košice*
6. *Michalíková, F., Škvarla, J., Brezáni, I. Popolček ako prísada vo výrobe keramiky 2011.In: História a súčasný stav ťažby nerastných surovín na východnom Slovensku : 1. vedeckotechnická konferencia : Solivary, 30. - 31.marec 2011. - Košice : TU, 2011 p. 200-204. - ISBN 978-80-553-0641-4*
7. *Michalíková, F., Fečko, P., Ovčaří, P., Sisol, M., Kozáková, I. 2009: Properties of unburned coal residues measured by metallographic microscope. In: 13th Conference on Environment and Mineral ProcessEng. Part 4. - Ostrava : VŠB-TU, 2009 p. 213-220. - ISBN 9788024820187*
8. *Pytlík P.: Cihlářství. Brno 1995, FS VUT v Brne*
9. *Sičáková A. 2009: Úvod do stavebných materiálov. Vybrané kapitoly, Stavebná fakulta TU Košice, Stavebná fakulta, 10 p. ISBN 978-80-553-0492-2*
10. *Šimáčková, H., Nejedlík, M., Vyvážil, M., Jančová, J., Ledererová, J., Svoboda, M., Čablík, V. Economic view of possibilities of CCPs utilization in building products. Inżynieria Mineralna, 2011, roč. XII, č. 2(28), p. 11-21*
11. *Václavík V.,Dirner V., Dvorský T.: The use of blast furnance slag. Source: Metalurgija, Volume 51 Issue 4 p. 461-464. Published: Oct-Dec. 2012*
12. *Vídeňská M. 1986. Vyhořívání uhlíkatých látek. 1.Modelové představy a asymptotické případy řešení. Silikáty č.1, 1986, p. 33-37*
13. *Vídeňská M. 1987. Aplikace modelu vyhořívání při využití úletových popílků v keramice. Silikáty č.1, 1987, p. 55-62*

Streszczenie

W artykule przedstawiono metodę produkcji cegieł z wykorzystaniem popiołu lotnego z elektrowni. Udział popiołu lotnego w ilości 30% (wagowo) spełnia wymagania dotyczące wytrzymałości na zginanie (po wysuszeniu i wypaleniu) cegieł. Badania laboratoryjne wykazały skuteczność zastosowania popiołów lotnych w produkcji cegły.

Słowa kluczowe: popiół lotny, ceramika, niedopał, produkcja cegieł