Utilization of Waste Products in Refractory Materials

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Over 13 Mt of energy by-products is generated in the Czech Republic every year. Part of them is further applied in the manufacturing of building materials. The article describes experiences with application of the energy by-products for manufacturing of refractory materials in the company P-D Refractories CZ a.s. Alternative materials were used in lightweight insulation fireclay bricks. We can use class F fly ash as a grog and lightening agent for materials with bulk density over 900 kg · m^{-3} and classification temperature up to 1150 °C. Class C fly ash is being tested in a wide range of the refractory materials. For example, it can be used in fireclay bricks for stoves, acid-resistant fireclay bricks or refractory castables. Utilization of waste products means reducing of a raw material costs and it is also limited their adverse impact on the environment.

1 Introduction

Various kinds of waste materials have become significant raw materials source in the field of producing of building materials. The main reasons for their use are: decrease of final costs during manufacturing, limited natural resources, reduction in wastes disposal costs, etc. Chemical and mineralogical composition of waste materials is very often similar to the composition of raw materials, or they have characteristics that are favourable for final products. And also the price is obviously lower than natural or industrial raw materials.

In the Czech Republic is produced a big amount of energy by-products (EBP). These EBP are generated during burning of coal and desulphurisation in thermal power plants, or during burning of biomass, municipal waste, etc.

Thus EBP can be: fly ash, slag and cinder from high-temperature burning (also known as class F fly ashes – ASTM C618); fly ash from fluidized technology (class C fly ash); fly ash generated during burning of (biomass); products from the desulphurisation (FGD gypsum) and other fly ashes and cinder generated during burning in heat plants and boilers. Special product is called: cenospheres. These are hollow spheres obtained by floating of class F fly ash. They have very low bulk density and can be used as a lightening agent in ceramic industry.

Class F fly ash (FFA) was successfully tested and now is ordinarily used in cement, concrete, autoclaved concrete, mortars, bricks, ceramic tiles production [1–5]. The fly ash and cinder from high temperature combustion were tested in lightweight fireclay bricks. These materials come from Opatovice power plant, where is burned brown coal. The chemical composition is quite stable in every batch. There were designed four formulas based on clay, cenospheres and four lightening agents – fly ash, cinder, expanded clay and lightweight grog.

The usage of cinder is more advantageous than class F fly ash. The testing samples with cinder are more stable during firing as well as they have lower bulk density. But on the other hand, the samples with FFA have higher compressive strength [6].

But in the Czech Republic has occurred significant problem with class F production. Limits for nitrogen oxides are required so that in many power plants special equipment has been installed. This equipment for the Selective Non Catalytic Reduction (SNCR) method means that the ammonia solution is spread into combustion chamber. This causes significant problems with production of fly ash. Firstly, big customers, especially cement and concrete producers, will increase consumption of fly ash from power plants where SNCR method is not used. It is also supposed price increase. Secondly, fly ashes can no longer be used in ceramics due to ammonia leaking during firing.

Class C fly ash (CFA) is generated during burning a fine grain mixture of coal powder and limestone or dolomite in fluidized-bed boilers, which are burning the air-borne coal dust at lower temperatures (up to 900 °C) in comparison with the classic high temperature burning (up to 1450 °C). For this reason its chemical and mineralogical composition differs from composition of the class F fly ash. The main minerals are anhydrite, calcite, calcium oxide, quartz, etc. An advantage of the calcium dioxide addition to the ceramic body is a small irreversible contraction of the fired body during and after firing. That is caused by the presence of anorthite which arises in the fired body at temperatures above 950 °C through metastable gehlenite. Creation of gehlenite and anorthite is accompanied with an increase in the fired bodies volume. This volume change occurs at a temperature interval where intensive contraction takes place due to sintering and collapse of the metakaolinite lattice [7, 8].

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Tab. 1 Chemical composition of raw materials

[mass-%]	SiO_2	Al_2O_3	Fe_2O_3	MgO	CaO	Na_2O	K_2O	TiO_2	L.o.I. [%]
FFA	53,97	31,65	6,02	1,03	2,79	0,39	1,61	1,97	–0,58
CD	43,07	29,91	10,8	3,04	9,61	0,41	0,83	2,03	–37,16
CFA	42,6	24,1	7,13	0,59	19,6	0,21	0,56	4,63	–4,09
Expanded clay	49,08	26,73	11,02	2,08	3,81	0,52	2,49	3,68	–0,59
Cenospheres	58,09	27,85	5	1,61	0,72	0,99	4,77	0,78	–0,2
Clay A	48,6	34,84	2,57	0,36	0,28	0,1	1,98	0,83	–11,25
Clay B	44,93	34,43	2,19	0,32	0,29	0,24	1,6	1,27	–14,43
Clay C	55,14	20,33	9,45	2,15	0,98	0,14	2,61	1,1	–7,91

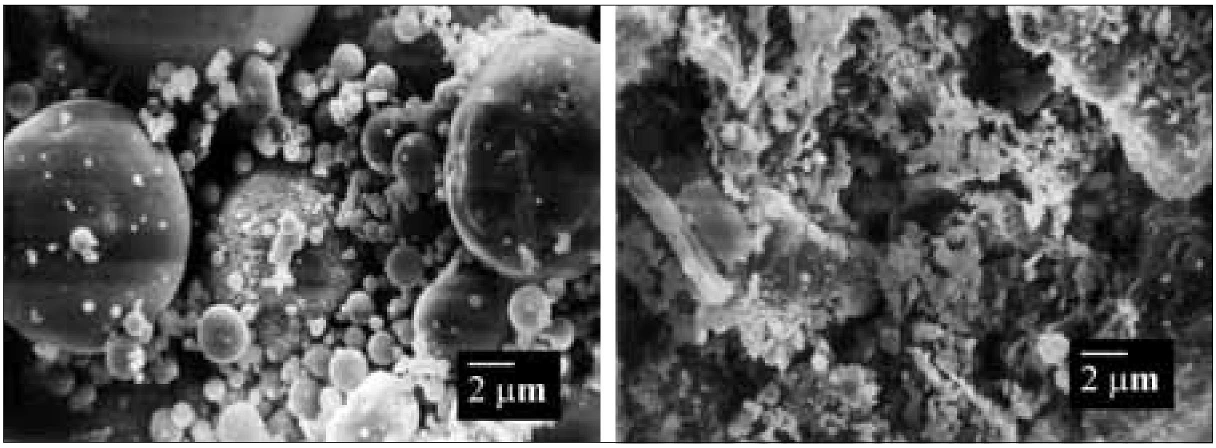

Fig. 1 Morphology of grains in class F fly ash (l.), and class C fly ash (r.)

The company P-D Refractories CZ a.s. is major producer of refractory and raw materials in Europe. Refractory clay mining, clay firing and manufacturing of the refractory materials have been proceeding for over 160 years. The assortment includes fireclay bricks, high-alumina bricks, silica bricks, insulating bricks, refractory clays and grog, magnetite bricks, ceramic chimney pipes, refractory mortars, mastics and castables. The properties of refractory materials depend on their chemical and mineralogical composition. The major part of produced materials is based on alumina and silica oxide.

This paper deals mostly with lightweight thermal insulation fireclay bricks. These materials are very important part of the thermal aggregates. The most important parameter is bulk density and classification temperature. Other parameters are compressive strength, thermal conductivity, additional linear changes, refractoriness, mineralogical composition, etc. The successful application depends on parameters mentioned above as well as on the parameters of combustion – type of aggregate, position of product, atmosphere in the furnace, etc.

2 Experimental procedure

2.1 Raw materials and their properties

In the research, conventional raw materials and energy by-products were used:

- Clay A – kaolinic refractory clay with good binding power and sinterability. Mineralogic composition of clay is 65 % kaolinite, 25 % illite-hydromuskovite, 3 % illite-montmorillonite and 5 % quartz.
- Clay B – kaolinic refractory clay, consisting mainly kaolinite and quartz.
- Clay C – montmorillonitic (foundry clay with very low sintering temperature. Dry clay has a light green colour, after firing the colour is dark red to brown. The mineralogical composition is montmorillonite (29 %), illite (27 %), kaolinite (11 %) and quartz (20 %).
- Expanded clay – special product based on fired mixture of clays with specific chemical composition. During burning, clay increase its volume (3–3,5 ×), so it is used as a lightweight aggregate.
- Expanded perlite – perlite is amorphous volcanic glass, which expandes when heated. Expansion of the material is 7–16 times to its origin+al volume. Thanks to very low bulk density (300–150 kg · m^{-3}) is used in wide range of lightweight building materials.
- Cenospheres – these are hollow spheres obtained by floating of class F fly ash. They have very low bulk density and can be used as a lightening agent in ceramic industry.
- Cinder – anorganic residue after the complete conversion of the carbon in coal to gaseous products. Cinder has high porosity (40–50 %) and elongated grains (Fig. 4).
- Class C fly ash – from Tisova power plant, where brown coal from north-western area of the Czech Republic is burned.

The chemical composition of the raw materials is shown in Tab. 1.

The basic difference between FFA and CFA consist in the mineralogical composition. FFA contain up to 80 % glassy phase as the main component, and up to 20 % mullite. CFA are characterized by their higher SO_3 content (anhydrite), free calcium oxide CaO and calcite. They do not contain either glass

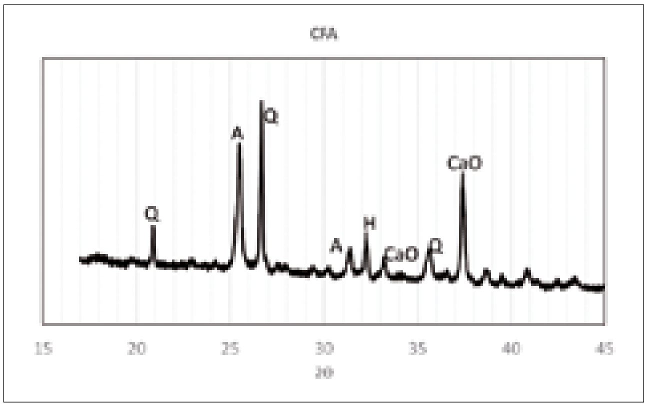

Fig. 2 X-ray analysis – class C fly ash (Q-quartz; A-anhydrite; H-hematite)

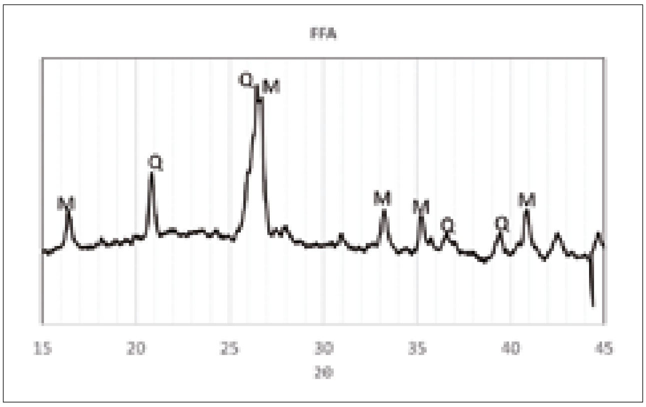

Fig. 3 X-ray analysis – class F fly ash (Q-quartz; M-mullite)

phase or mullite. Quartz is present in both types of fly ashes.

The difference between ashes can be also seen on pictures from electron microscope (Fig. 1). Due to combustion temperature over 1400 °C has FFA regular spherical particles while CFA has irregular shaped grains.

2.2 Preparation of test samples and test methods

Experimental works are built on results with class F fly ash and cinder from high temperature combustion [6]. In the first phase were formulated five batches based on clay, expanded clay, microspheres, cinder and expanded perlite. Formulas are shown in Tab. 2. This cinder is produced as residue during gasification of coal. The gas is fuel that is combusted in shaft kilns for fired refractory grog manufacturing. Thus this cinder varies from high temperature cinder. The main difference is in chemical composition due to lower temperatures and way of combustion.

The second phase of experimental works can be divided into two parts. In the first part, the attention was focused on lightweight fireclay bricks with bulk density about 1100 kg · m^{-3} and classification temperature up to 1150 °C after firing. The batches were formulated according to results of previous experiments with fly ash and cinder. The aim was to completely replace expensive cenospheres used as a lightening agent. The formulas are shown in Tab. 3.

In the 2nd part were formulated batches based on clay, expanded perlite and fly ash (Tab. 4). The aim was to get samples with bulk density up to 600 kg · m^{-3} and CT up to 900 °C. These materials are used as insulation in thermal power plants.

The raw material mixtures for the production of testing samples were prepared by dry mixing according to the given formulas. The mixture was then moistened at the pressure moisture about 12 mass-%. Testing samples with a green body size of 100 mm × 100 mm × 60 mm were pressed at 20 MPa. The green bodies were fired

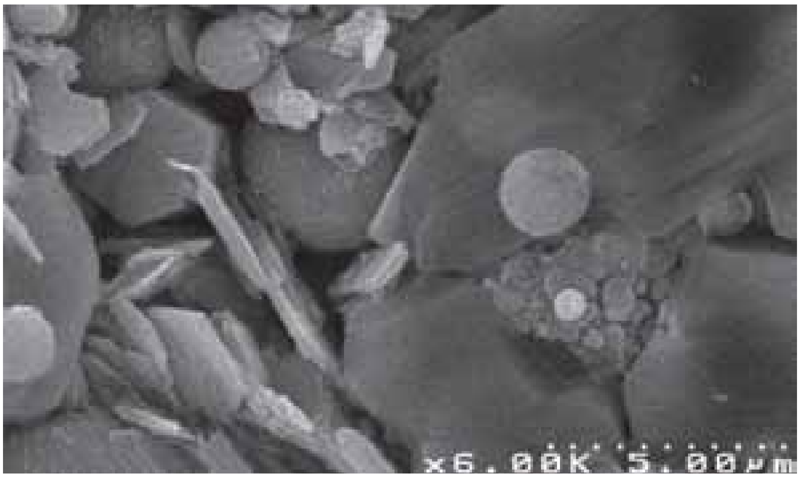

Fig. 4 Morphology of grains – cinder

Tab. 2 Formulas for the 1st phase of experimental works

		Lightening Agent 1	Lightening Agent 2	Lightening Agent 3
A	25 % clay A	60 % expanded clay	5 % cenospheres	10 % expanded perlite
B	30 % clay B	70 % cinder		
C	40 % clay B	60 % cinder		
D	25 % clay A	60 % expanded clay	5 % cenospheres	10 % cinder
E	40 % clay B	25 % expanded clay	5 % cenospheres	10 % cinder

Tab. 3 Formulas for the 2nd phase of experimental works – 1st part

[mass-%]	Ref	Var A	Var B
Expanded clay 0–4 mm	33	33	33
Expanded clay 0–1 mm	27	27	27
Cenospheres	5	0	0
Cinder	10	0	0
Class C fly ash	0	15	20
Clay	25	25	20

Tab. 4 Formulas for the 2nd phase of experimental works – 2nd part

Component	1	2	3	4	5
Clay B/C [mass-%]	70	40	40	30	20
Expanded perlite [mass-%]	30	30	40	30	40
Fly ash [mass-%]	0	30	20	40	40

Tab. 5 Bulk density, compressive strength and firing shrinkage after firing at 1070 °C

	BD [kg · m^{-3}]	CS [MPa]	FS [%]
A	1100	10,1	–2,47
B	1130	2,9	–3,13
C	1150	3,2	–2,59
D	1090	8,7	–2,96
E	1100	8,8	–2,86

Fig. 5 Black core in sample B

Tab. 6 Chemical composition after firing – 1st phase

[mass-%]	SiO_2	Al_2O_3	Fe_2O_3	MgO	CaO	Na_2O	K_2O	TiO_2
A	51	29,8	8,2	1,8	3,5	0,6	2,2	2,8
B	46,3	37,7	6,9	1,9	4	0,3	1	1,9
C	47,8	36,8	6,6	1,8	3,8	0,3	1	1,7
D	50,7	29,2	7,8	1,9	3,8	0,9	2,6	2,9
E	50,7	31,5	7,1	1,6	3,3	0,7	2,2	2,9

Tab. 7 Bulk density, compressive strength and firing shrinkage after firing at 980 °C and 1050 °C

	Temp. [°C]	BD [kg · m^{-3}]	CS [MPa]	FS [%]
Var-A	980	1045	7.98	–0,46
	1050	1057	8.02	–1,26
Var-B	980	1027	6.99	–0,71
	1050	1016	7.65	–0,96

in tunnel kiln at several temperatures – 1070 °C in the 1st phase, 980 °C, 1050 °C and 880 °C, 1000 °C in the 2nd phase.

After firing, the body properties (bulk density (BD), water absorption (WA), apparent porosity (AP), apparent density (AD) compressive strength (CS), classification temperature (CT), chemical composition) were defined. Firing shrinkage (FS) was calculated according to the following formula:

$$FS = \frac{(l_f - l_d) \times 100}{l_d} \; [\%]$$

Where l_d is the length of dried test samples and l_f is the length of fired test samples.

3 Results and discussion

3.1 Use of cinder from coal gasification

The cinder contains approx 18 mass-% of water, thus water addition was different for every formula. There were not problems with workability, testing samples were compact after pressing as well as after firing. Edges and corners were not spalling. Bulk density, compressive strength and firing shrinkage after firing is shown in Tab. 5.

Samples B and C with 70 % and 60 % of cinder had five times lower compressive strength than sample A – reference sample. These samples have also the highest bulk density – 1130 and 1150 kg · m^{-3} respectively. Despite higher BD the samples are brittle. This is caused due to formation of "black core" (Fig. 5). Black core is a consequence of organic compounds combustion in a reducing environment. Carbon monoxide diffuses from surface deeper to the sample. CO decomposes together with formation of carbon. Newly formatted carbon is less active and is hard to burn it out.

Samples D and E had similar bulk density, about 1100 kg · m^{-3} and their compressive strength was higher than 8 MPa. In the Tab. 6 is shown chemical composition of samples after firing. Important is content of alumina dioxide and iron oxide. According to the company standard samples are required to have at least 28 mass-%. of Al_2O_3 and 8,3 mass-% of Fe_2O_3 on average.

3.2 Utilization of class C fly ash

Part 1: The aim was to complete replace cinder and cenospheres in formula D (previous phase) and find out if it is possible to obtain samples with same properties. After firing at 980 °C and 1050 °C was concluded that there is not a significant difference between samples. Bulk density and compressive strength is a little bit lower for the samples with 20 mass-% of CFA. And also compressive strength is lower.

After firing samples have almost 50 % of SiO_2. With increased amount of CFA increases calcium dioxide and decreases alumina dioxide value. However, amount of Al_2O_3 follows company standard.

It can be also seen on the Fig. 6 that there is no considerable difference in appearance

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Tab. 8 Chemical composition after firing

[mass-%]	SiO_2	Al_2O_3	Fe_2O_3	MgO	CaO	Na_2O	K_2O	TiO_2
Var-A	48,69	30,03	7,35	0,78	7,7	0,34	2,13	2,63
Var-B	49,11	27,73	7,5	0,77	9,49	0,34	2,03	2,7

Fig. 6 Samples A and B after firing

Tab. 9 Bulk density and firing shrinkage

	BD [kg · m^{-3}]	FS [%]	BD [kg · m^{-3}]	FS [%]
	880 °C		1000 °C	
1B	633	–1,00	647	–3,32
2B	505	–1,22	620	–6,67
3B	518	–1,17	628	–6,09
4B	494	–1,7	634	–6,39
5B	525	–2,75	588	–5,11
1C	624	–0,94	855	–11,10
2C	503	–1,81	677	–9,48
3C	518	–3,39	740	–7,27
4C	551	–3,75	673	–8,76
5C	520	–1,82	612	–6,56

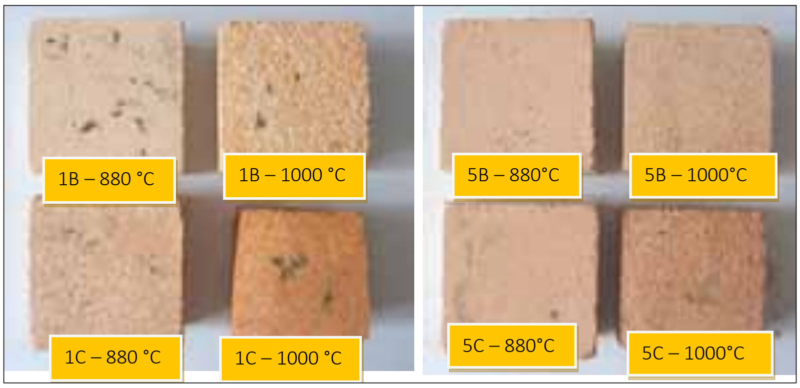

Fig. 7 Samples after firing – clay B and clay C

of samples – colour, shape. Fired samples were compact, without cracks and without spalling.

Part 2: In these part were tested five batches based on clay (B or C), expanded perlite and CFA. The aim was to modify currently produced lightweight refractory brick with bulk density about 500 kg · m^{-3} and classification temperature about 900 °C. Clay C was chosen because of its low sintering temperature (950 °C).

Samples 1, which are based on clay and expanded perlite, have the highest bulk density. It can be seen have very similar BD at 880 °C but after firing at 1050 °C have higher values samples with clay C due to higher degree of sintering. At the same time, values of FS are also much higher. Influence of CFA addition on firing shrinkage was not so significant as supposed.

At samples fired at 880 °C occurred problem with volume changes and cracks. Calcite and anhydrite decompose what leads to the formation of free calcium dioxide. The temperature is too low to create gehlenite and anortite. Exceeding CaO react with water (air humidity) forming calcium hydroxide. Crystals of arising hydration product damage structure and cracks start to appear. On the picture (Fig. 8) can be seen testing samples one month after firing at 880 °C.

3.3 Class C fly ash in other types of refractory materials

It was proven that some energy by-products are applicable for manufacturing of lightweight thermal insulation fireclay bricks. However, the range of refractory materials is very wide and class C fly ash is being tested also in other types of refractories. For instance:

- Refractory castables: CFA was tested in lightweight castable based on lightweight grog, alumina cement and other additives. The addition of fly ash was 15 %, there were no problems with workability. On the other hand, fly ash causes faster hardening of alumina cement. Bulk density of green samples was about 900 kg · m^{-3}.

  CFA (up to 20 mass-% was also added to dense refractory castable with CT up to 1150 °C. In addition to problems with hardening of cement, mixture was difficult to work. With increasing amount of CFA also increased amount of water needed to get the same consistency. After removing samples from moulds, they were brittle and had very low strength.
- Fireclay bricks for stoves and fireplaces: the aim is to reduce raw materials costs (replacement of clay and fine grog) and also to get lighter (in colour) body after firing. The maximal addition of CFA is 10 %.
- Refractory mortars: class fly ash has been tested in refractory mortar based on refractory grog, clay and sand. This mortar is modified for use in fireplaces and stoves where is maximal temperature up to 1000 °C. The addition 10 % means that mortar still has good properties and CFA contributed to higher strength of green body.

Despite relative good results with class C fly ash there are several problems in general. For further experimental works is important to find optimal addition of fly ash to every single supposed quality. Next is necessary to solve problem with cracking due to additional hydration. Potential use in manufacturing also means investments in storage silos and the technology is supposed to be changed.

It is assumed that EBP utilization will still be actual from economical as well as ecological point of view. Company P-D Refractories cooperates with universities on research projects granted by the Government of the Czech Republic and the European union. Class C fly ash utilization will be solved within the project FLUIDPOP – subsidized from Operational Programme Enterprise and Innovation for Competitiveness. The authors cannot predict market trends but it is necessary to be prepared for several future possibilities.

Fig. 8 Cracks and additional volume changes after firing

4 Conclusion

It was proved that energy by-products are applicable for the production of refractory materials. Class F fly ash, cinder and class C fly ash are applicable as a lightening agent and grog for lightweight fireclay bricks.

The research and development will consider class C fly ash utilization in a wide range of refractory materials. But on the other hand it is necessary to solve several technical and technological problems. As the most serious problem is the additional volume change due to hydration after firing.

It is inevitably to add sufficient amount of clay to bind all of the calcium dioxide (formation of anorthite and gehlenite). Nevertheless, the more clay is in the sample, the more sintered the sample is. Further experimental works will be concentrated on finding an optimal ratio of clay and fly ash as well as determining appropriate firing temperature.

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