

The Influence of the Vitreous Phase of Fly Ashes on Sintering Process

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Abstract

Fly ashes developing from hard bituminous coal burnt in conventional boilers are a precious material used in ceramic production by means of sintering. Depending on their physical and chemical properties, they can be used as a raw material in production of building ceramics with both porous and solid sintered structure. If fly ashes are picked up with the use of a few sections of electrostatic precipitator, the ashes from each of these sections display a large diversity of their physical and chemical properties. These differences affect the kinetics of sintering and forming of the liquid phase. Although the influence of granularity and the amount of alkalis on the sintering process of the fly ashes is rather obvious, the influence of vitreous phase is not so clear. In this paper, the extensive research was carried out on a dozen different fly ashes focusing on the properties of their vitreous phase. The differences in the chemical composition of the vitreous phase in ashes were also pointed out and to what extent it is organized: the number of broken Si–O–Si bridges, the degree of Si⁴⁺ \leftrightarrow Al³⁺ isomorphous replacements in tetrahedral positions. The achieved results together with the tests of fly ashes sintering gave grounds for putting forward a hypothesis concerning the role of the vitreous phase in sintering of fly ashes. To examine the vitreous phase the following methods were used: FTIR, NMR, XRD/Rietveld and classic chemical analysis.

Keywords: Fly ashes, Vitreous phase, Bowen's reaction series

WPŁYW FAZY SZKLISTEJ POPIOŁÓW LOTNYCH NA PROCES SPIEKANIA

Popioły lotne powstające z twardego węgla kamiennego spalanego w konwencjonalnych kotłach stanowią wartościowy materiał wykorzystywany w produkcji ceramiki metodą spiekania. Zależnie od swoich właściwości fizycznych i chemicznych mogą być użyte do produkcji ceramiki budowlanej o spieczonej strukturze porowatej lub gęstej. Gdy popioły lotne wychwytywane są przy użyciu kilku sekcji elektrofiltru pokazują znaczne zróżnicowanie właściwości fizycznych i chemicznych dla każdej sekcji. Różnice te oddziałują na kinetykę spiekania i powstawanie fazy ciekłej. Chociaż wpływ uziarnienia i ilości alkaliów na proces spiekania popiołów lotnych jest raczej oczywisty, to już wpływ fazy szklistej nie jest jasny. W tym artykule zrelacjonowano szerokie badania przeprowadzone na tuzinie różnych popiołów lotnych, skupiając się na właściwościach ich faz szklistej. Różnice w składzie chemicznym fazy szklistej popiołów zostały również wskazane oraz to w jakim zakresie jest ona uporządkowana: liczba zerwanych mostków Si–O–Si, stopień izomorficznych podstawe dla wysunięcia hipotezy dotyczącej roli fazy szklistej w spiekaniu popiołów lotnych. Aby zbadać fazę szklistą wykorzystano następujące metody: FTIR, NMR, XRD/Rietveld i klasyczną analizę chemiczną.

Słowa kluczowe: popioły lotne, faza szklista, seria reakcji Bowena

1. Introduction

During the process of coal combustion in a power plant, and heat and power station furnaces, waste materials such as slag and fly ashes are formed. This waste, besides small amount of residual coal, consists of a dehydroxylated and partially vitrified residue of barren rock. The coarse fraction is formed by slag, gathered under the fire grate. The fine fractions are formed by fly ashes which are carried away by a stream of gases from the furnace and collected by the electrostatic or sack filters [1].

In standard systems of dust extraction by electrostatic precipitator, fly ashes are separated from gases in a few zones placed in a row behind the combustion chamber. Fly ashes from all zones are stored in the retention silo, where they are collected as a mixture of ashes (Fig. 1). As one of very few industrial waste materials, coal fly ashes found wide range of application in various branches of the industry, for example as raw materials in production



Fig. 1. Scheme of dust extraction by use of electrostatic precipitator.

of ceramic materials by sintering [2, 3]. Ashes have their chemical composition similar to the clay raw material applied in sintering ceramic products. In contrast to clay, fly ashes are non plastic after water addition; furthermore they have different morphology of grains and different phase composition (amount about 60 % of vitreous phase). Despite these differences, fly ashes are applicable, because ashes can give interesting properties of sintered ceramic products.

It is noted that fly ash improves the mechanical properties of sintered products. It is the result of the presence of mullite in grains of fly ashes. Another interesting property is the presence of grains in a form of vitreous spheres, socalled microspheres. Microspheres are a source of closed porosity in the final product. Closed porosity decreases heat conduction, but does not increase water absorbability. Finally, fly ash has a high amount of vitreous phase, which actively participates during fly ashes sintering.

Fly ashes are used both for porous products [2-4] and solid products [5, 6]. In the first group of materials, porous ceramic products are wall products: hollow bricks and ceramic bricks. Silica fly ashes (from coal) characterised by a low amount of sulphur, formed in the conventional boiler dust, are used in this technology. Fly ashes were introduced to the ceramic mass as a leaning component in quantity more than 60 % [2]. Porous ceramic products are fired at the temperature range 900-1050°C, and the sintering process proceeds without the presence of the liquid phase. As every leaning component, fly-ashes allow to decrease the time of drying process. The fly ashes also increase sintering processes during the firing procedure, and finally improve parameters of the final material: mechanical strength, heat resistance, water absorption. The other group of materials are solid ceramic products, such as clinker brick and stoneware products. These products are formed in punch presses in a semi-dry or dry method from the granulated powders. The sintering process of these products precedes with the presence of liquid phase at the temperature range 1100-1250°C. Brown coal fly ashes found their application as an additive promoting the sintering process in these technologies [5, 6]. In both of these technologies, the mixture of fly ashes from all zones of the electrostatic precipitator are applied. However, fly ashes from different zones are distinguished by considerably different physical and chemical properties, and

Table 1	1.	Chemical	composition	of	fly ashes	[wt%].

Component	Power Plant A			Power Plant B			
Component	zone1	zone2	zone3	zone1	zone2	zone3	
SiO ₂	50.30	46.85	46.40	51.81	49.45	48.43	
Al ₂ O ₃	25.36	25.70	26.00	26.92	26.83	28.72	
FeO+ Fe ₂ O ₂	9.50	9.40	9.35	6.07	6.68	6.35	
CaO	3.80	5.70	4.90	4.71	4.86	4.63	
MgO	3.00	2.54	3.40	2.56	3.01	2.60	
SO3	1.03	1.10	1.08	1.02	1.04	1.17	
TiO ₂	1.08	1.85	1.93	0.25	0.77	0.94	
Na ₂ O	2.36	2.90	3.05	1.12	1.74	1.77	
K ₂ O	2.00	2.08	2.21	2.63	2.81	2.81	
LOI	0.50	0.90	1.06	2.80	1.94	1.47	

LOI: Loss of ignition

therefore must be treated as completely different potential raw materials for the sintered ceramic materials. However, the influence of grain size distribution and amount of alkalis on sintering process is obvious, the role of vitreous phase is not completely known [7, 8].

The better understanding of the role of the vitreous phase in technology of sintered ceramic materials is the aim of this work. During the research, fly ashes from two Polish power plants (A and B) were collected, for each of the three zones of electrostatic precipitator. These ashes were different from each other in their physical and chemical properties. In the paper, fly ashes from the conventional boiler dust were used without combustion of coal and biomass or calcium sorbent simultaneously.

2. Experimental results

2.1. Physical and chemical properties of fly ashes

The cone quartering method was applied for collecting a representative sample of fly ashes. The chemical analysis was performed according to the PN-EN 196-2:2005 standard; content of TiO_2 was measured by the extinction method. The XRD method with the Rietveld method was applied for the phase analysis and quantitative analysis of crystalline components of the material. To estimate an amorphous phase content also the XRD/Rietveld method with determined quantity of the internal standard sample in a form of corundum was applied. An assumption that the amorphous phase consists of a vitreous phase and amorphous carbon (loss of ignition) was made. The density of fly ashes was determined by a helium pycnometer. The results of research are presented in Tables 1, 2 and 3.

Chemical compositions of fly ashes are identical in terms of quality and close together in terms of quantity. Fly ashes from the I zones are characterized by lower quantities of

Table 2. Phase composition of fly ashes [wt%].

Dhase	Po	wer Plan	it A	Power Plant B			
Phase	zone1	zone2	zone3	zone1	zone2	zone3	
vitreous phase	73.3	82.3	82.9	71.8	80.8	82.8	
mullite	15.6	10.1	9.7	17.3	10.8	11.6	
β-quartz	10.5	6.6	6.5	8.3	5.4	3.5	
hematite	-	-	-	-	1.0	0.6	
amorphous phase	0.5	0.9	1.1	2.8	1.9	1.5	

Table 3. Density of fly ashes.

	Pc	wer Plan	t A	Power Plant B			
	zone1	zone2	zone3	zone1	zone2	zone3	
Density [g/cm ³]	2.18	2.35	2.38	1.98	2.45	2.58	

Component	Po	wer Plan	it A	Power Plant B			
Component	zone1	zone2	zone3	zone1	zone2	zone3	
SiO ₂	48.26	45.41	44.92	53.95	50.71	50.29	
AI_2O_3	19.30	22.40	23.01	20.25	23.59	24.62	
FeO+ Fe ₂ O ₂	12.95	11.41	11.30	8.48	7.02	6.94	
CaO	5.11	6.88	5.91	6.58	6.01	5.59	
MgO	4.09	3.08	4.11	3.58	3.72	3.14	
TiO ₂	1.40	1.34	1.31	1.42	1.29	1.41	
SO3	1.47	2.25	2.33	0.35	0.95	1.13	
Na ₂ O	3.22	3.52	3.69	1.56	2.15	2.14	
K ₂ O	2.73	2.53	2.67	3.67	3.48	3.39	

Table 4. Chemical composition of vitreous phase of fly ashes [wt%].



Fig. 2. Grain size distribution of fly ashes from Power plant A.



Fig. 3. Grain size distribution of fly ashes from Power plant B.

alkalis (Na₂O, K₂O) when compared to those from the II and III zones. Alkalis are responsible for the formation of initial quantities of the vitreous phase during the sintering process

Besides, rather small yet systematic changes of SiO₂, SO₃ and losses of lignite quantities in subsequent electro-filters could be stated. Significantly greater differences between different fly ashes are the result of their different phase composition. For both power plants, the quantity of the vitreous phase increases significantly with the subsequent electrostatic zone at a cost of crystalline components: mullite and β -quartz. Density increases with the following zones. Fly ashes from the zones I have the lowest density, probably because they have a high amount of micro-spheres. Basing on the results of the chemical and phase composition of fly ashes, we can estimate the chemical composition of their vitreous phase. The results of this estimation are presented in Table 4.



Fig. 4. The ²⁷AI NMR spectra for mullite and fly ashes from Power plant A.



Fig. 5. The ²⁷AI NMR spectra for mullite and fly ashes from Power plant B.

To estimate the grain size distribution the Malvern particle analyzer was used. A logarithmic histogram of cumulative curve of grain size distribution of fly ashes from particular zones and both of power plants are presented in Figs. 2 and 3.

For both power plants, ashes from Zone II and Zone III of electro-filters have a similar grain size distribution and their grains are significantly finer than those from Zone I. The fly ashes from II and III zones of power plant A are more coarse-grained than the ashes from the same zones of power plant B. Fly ashes from Zone I of power plant A are more fine-grained than the ashes from the same zone of power plant B. Furthermore, two maxima of grain size could be observed. The maximum of coarse grains present in fly ashes from Zone I consists of microspheres [9]

According to the result from Table 4, the vitreous phase of fly ashes contains a high quantity of alumina. Theoretically, aluminium can occur as a cation in an octahedral position or in tetrahedral position as an aluminium oxygen anion $[AIO_4]^{5-}$. Substitution $[SiO_4]^{4-} \leftrightarrow [AIO_4]^{5-}$ in the vitreous phase causes the appearance of the negative charge which is compensated by cations like Na⁺, K⁺ or other. Fly ashes contain less than 20 percent of mullite. In mullite, aluminium is present in both listed coordinations. We use ²⁷Al NMR (nuclear magnetic resonance) measurements of fly ashes and mullite to estimate the proportion of aluminium in the tetrahedral and octahedral positions. ²⁷Al NMR spectrums are presented in Figs. 4 and 5. ²⁷Al NMR spectrum of the mullite contains 3 characteristic peaks: aluminium in octahedral position for 1 ppm, and two peaks for aluminium in the



Fig. 6. Infrared spectra FTIR of fly ashes from Power plant A.



Fig. 7. Infrared spectra FTIR of fly ashes from Power plant B.

tetrahedral position (47 and 62 ppm), which have different locations in the structure of mullite [10]. The peak marked with a star (*) indicates the crystalline impurity corundum, because mullite is formed from corundum and silicate [11]. When the areas under the tetrahedral and octahedral peak are comparable, it can be determined that mullite contains more or less 1.2:1. Another ratio is in the samples of fly ashes over 10:1. In the result: probably in the vitreous phase of fly ashes, aluminium is present only in the tetrahedral position. A very high ratio of aluminium tetrahedral to octahedral position may be a result of high quantity of aluminium cations substitution in the structure of mullite. Fly ashes will contain a small amount of corundum.

For all the samples of fly ashes and mullite, the infrared spectroscopy IR measurements were carried out. Infrared spectra are presented in Figs. 6 and 7.

Infrared spectroscopy measurements confirm that fly ashes contain aluminium in the tetrahedral and octahedral position. Furthermore, fly ashes from the power plant "A" have more broken oxide bridges than fly ashes from the power plant "B", because the peak 900-1200 cm is shifted to the lower wave number.

2.2. Fly ashes sintering

The physical aspect of sintering is shrinkage of samples. "Bähr - Thermoanalyse" apparatus was used for dilatometric measurement, *i.e.*, a precise measurement of linear shrinkage during heating of fly ash samples. The samples of dimensions 3×3×15 mm were formed by the semi-dry method in a special punch press. Then, the samples were heated up



Fig. 8. The linear change of length of fly ash samples during sintering – Power plant A.



Fig. 9. The linear change of length of fly ash samples during sintering – Power plant B.

to 1000°C with heating rate 10°/min, and after 10 minutes of annealing in the maximum temperature, the samples were cooled down with 20°/min rate. The results of measurements are presented in Fig. 8 (power plant A) and 9 (power plant B).

Fly ash samples from different zones show very large differences in their linear shrinkage. Probably, the main factor for this is the grain size distribution of fly ashes. By comparing the results of linear changes in fly ash from Zone III of the first power plant, with more fine-grained ash from Zone II of the second power plant, we came to the conclusion that not only grain size distribution plays a meaningful role during the sintering process, but also amount of alkalis (mainly Na₂O). Comparing the results of linear changes in the fly ash from Zone II of the same power plant B with the ash from Zone III of the same power plant leads to the conclusion that other factors played a role during the sintering process, because these fly ashes are similar in terms of grain size distribution and chemical composition.



Fig. 10. The typical DTA/TG graph of fly ashes (fly ashes from Zone II power plant B).

For all fly ashes DTA (Differential Thermal Analysis) with TG (Thermo-gravimetry) research were made. DTA curves of all the examined ashes are very similar. The differences in TG curves follow the various losses on ignition in the temperature range 400-750°C. The typical fly ash DTA/ TG curves are presented in Fig. 10. In fly ashes at above 900°C, exothermic reactions can be noticed which are not accompanied by the weight loss. This effect is related to sintering processes. Probably this effect includes both the physical thickening of the material, as well as the chemical synthesis of new phases.

The results of DTA of fly ashes allowed us to set the hypothesis that during sintering new phases were formed. The hypothesis was verified by researching the phase composition of sinters from different temperatures. The samples of fly ashes were formed by a semi-dry method. The forming pressure of 15 MPa and humidity of mixture 11-12 % were used. After drying at 105°C, the samples were fired at 800, 900, 1000 and 1050°C, with holding them in the maximum temperature for an hour. For all sinters of fly ashes, the qualitative phase composition analyses were made. It is noted that, at about 900°C on X-ray photographs, very blurred and small peaks are observed which clearly identify new phases. But at about 1000 and 1050°C in the samples new phases are present, such as plagioclases and olivine. The next stage of research was the quantitative phase composition analysis of the sinters from 1000 and 1050°C, that were made from the fly ashes of Zone III only. The fly ashes from Zone III have the highest sintering tendency. The results are presented in Table 5. During sintering new phase products appear, and the vitreous phase content decreases. This is a devitrification process of the vitreous phase. New products of devitrification of the vitreous phase are: olivine and calcium rich plagioclases (anorthite). Both of fly ashes are characterized by a similar amount of olivine (~10 %) and very various amounts of plagioclases. An astonishing result is a significant increase of amount of mullite at such a low temperature of 1050°C. Sintered fly ashes contain more hematite and less β-quartz than fly ashes before heating.

3. Discussions

Fly ashes from individual zones are different particularly in grain size distribution, amount of alkalis and phase composition (also the amount of vitreous phase). All of these

Table 5. Phase composition of materials from the fly ashes as a function of sintering temperature [wt%].

The type of ash	Fly as plan	sh from F t A (III zo	Power one)	Fly ash from Power plant B (III zone)			
Component	20 [°C]	1000 [°C]	1050 [°C]	20 [°C]	1000 [°C]	1050 [°C]	
vitreous phase	82.7	43.4	42.9	82.7	71.3	55.7	
mullite	9.7	8.9	14.0	11.6	17.6	20.7	
β-quartz	6.5	6.5	3.7	3.5	-	1.3	
hematite	-	4.1	4.8	0.6	2.1	3.1	
plagioclases	-	28.8	26.6	-	1.6	8.1	
olivine	-	8.3	8.1	-	7.4	11.1	
C amorph.	1.1	-	-	1.5	-	-	



Fig. 11. Schedule of Bowen's reaction series.

differences translate to their tendency to sintering. However, the influence of grain parameters and amount of alkali on sintering process is obvious, the role of vitreous phase is not completely known [7, 8]. During sintering at over 900°C, the vitreous phase of fly ashes is observed as gradually devitrified. Olivine (Mg,Fe)₂[SiO₄] and plagioclases calcium rich in Ca[AlSi₂O₈] are new products of the devitrification process of the vitreous phase. Furthermore, the vitreous phase is a source of substrates to continue a further synthesis of mullite. Both processes are discussed below in more details.

The chemical composition of the vitreous phase is very similar to the igneous rock of basalt type, the so-called basic igneous rock. Basic igneous rock contains 40-54 % of SiO₂. All fly ashes have a similar amount of SiO₂ to the basic igneous rock (Table 4). It turns out that during heating in the vitreous phase of fly ashes the initial reaction series takes place similar to the typical igneous rock. These are the so-called Bowen's reaction series [12]. According to Bowen's reaction series (Fig. 11.), olivine and anorthite are always formed in the first stage of igneous rocks crystallization. Both of these phases are poor in SiO₂. The second, anorthite takes silica and sodium oxide and then transforms to albite:

$$Ca[Al_2Si_2O_8] + 4SiO_2 + Na_2O = 2Na[AlSi_3O_8] + CaO$$
 (1)

During taking silica, olivine is transformed to the pyroxenes:

$$(Mg,Fe)_2[SiO_4] + SiO_2 = (Mg,Fe)_2[Si_2O_6]$$
 (2)

In sintered fly ashes, pyroxenes were not found as new product of devitrification. Probably this is only the effect of too short time of fly ashes sintering. The sintered fly ashes from power plant A contain a higher amount of plagioclases, because these contain higher amount of sodium oxide, which is taken to the reaction (1). As a result, plagioclases in sintered fly ashes from the power plant A are sodium oxide richer than plagioclases in sintered fly ashes from the power plant B.

Mullite which is formed by the reaction in the solid phase crystallizes in the needle form grains. The needles of mullite bond the ceramic material and give high mechanical strength of them. Furthermore, mullite is a chemically durable phase. The synthesis of mullite from alumina and silica is very difficult because of low mobility of silicon and aluminium ions. Therefore high temperature must be used for synthesis of mullite. Admixtures, such as iron oxide, cause the fall of



Fig. 12. Diagram of phase composition change of fly ashes while heated.

the temperature of synthesis. The mixture of mullite and cristobalite can be obtained by firing some of clay mineral (kaolinite) at the temperature of about 1200°C. During heating the samples of fly ashes at the temperature of about 1050°C, the amount of mullite is increased, but probably in such a low temperature there is no nucleation process. Bowen's reaction series precludes the formation of mullite (nucleation process). In this case, the grain growth of mullite takes place probably. The vitreous phase of fly ashes is the source of substrates for the mullite formation. From the vitreous phase also hematite extracts, which gives characteristic red-brown colour of the sinters. We also observed a strange tendency to a gradual decrease of the β-quartz amount, but another polymorph of crystalline silica does not increase in amount. Probably, β-guartz has been dissolved in the liquid phase which is proof of silica. The liquid phase is involved in the mass exchange process, and during reaction (1) and (2) the liquid phase gives silica. The diagram that shows the phase composition change while sintering of fly ashes is presented in Fig. 12.

4. Conclusions

In summary, fly ashes from individual zones must be treated as completely different potential raw materials for the sintered ceramic materials. Utilization of the fly ashes from Zone II and III, as raw materials for clinker bricks or stoneware production is potentially possible. In these ceramic materials fly ashes can be applied as a fluxing agent. It is potentially possible to use the fly ashes from Zone I, as raw materials for hollow bricks and ceramic bricks production.

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