

KAUNAS UNIVERSITY OF TECHNOLOGY

VYTAUTAS ČESNAUSKAS

**BIOMASS FLY ASH ADDITIVE FOR PORTLAND CEMENT
AND SLAG CEMENT**

Summary of Doctoral Dissertation
Technological Sciences, Chemical Engineering (05T)

2018, Kaunas

This doctoral dissertation was prepared at Kaunas University of Technology, Faculty of Chemical Technology, Department of Silicate Technology during the period of 2012 – 2017.

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Editor: Brigita Brasienė (Publishing house “Technologija”).

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The official defence of the dissertation will be held at the public meeting of the Board of Chemical Engineering Science Field at 2 p. m. on 21st of June, 2018 in the Dissertation Defence Hall of Kaunas University of Technology.

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The summary of the Doctoral Dissertation was sent on 21 May 2018.

The doctoral dissertation is available on the internet <http://ktu.edu> and at the library of Kaunas University of Technology (K. Donelaičio Str. 20, 44239 Kaunas, Lithuania).

KAUNO TECHNOLOGIJOS UNIVERSITETAS

ČESNAUSKAS VYTAUTAS

**BIOKURO LAKIŲJŲ PELENŲ PRIEDAS
PORTLANDCEMENČIUI IR ŠLAKINIAM CEMENTUI**

Daktaro disertacijos santrauka
Technologijos mokslai, chemijos inžinerija (05T)

2018, Kaunas

Disertacija rengta 2012 – 2017 metais Kauno technologijos universiteto Cheminės technologijos fakultete, Silikatų technologijos katedroje.

Mokslinis vadovas:

prof. dr. Rimvydas KAMINSKAS (Kauno technologijos universitetas, technologijos mokslai, chemijos inžinerija – 05T).

Redagavo: Brigita Brasienė (Leidykla “Technologija”)

Chemijos inžinerijos mokslo krypties daktaro disertacijos gynimo taryba:

Prof. dr. Raimundas ŠIAUČIŪNAS (Kauno technologijos universitetas, technologijos mokslai, chemijos inžinerija 05T) – **pirmininkas**;

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Disertacija bus ginama viešame Chemijos inžinerijos mokslo krypties disertacijos gynimo tarybos posėdyje, kuris įvyks 2018 m. birželio 21 d. 14 val. Kauno technologijos universiteto, disertacijų gynimo salėje.

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Disertacijos santrauka išsiųsta 2018 m. gegužės 21 d.

Su disertacija galima susipažinti internetinėje svetainėje <http://ktu.edu> ir Kauno technologijos universiteto bibliotekoje (K. Donelaičio g. 20, 44239 Kaunas).

INTRODUCTION

Relevance of the work

Recently, the construction industry has been intensively developing, and the demand for various binding materials is growing steadily. Concrete is one of the most used materials in the world, and cement is necessary for its production. However, the cement industry is characterized by extremely high energy consumption and high pollution by carbon dioxide emission and other combustion products [1, 2]. Therefore, in order to reduce the environmental pollution and meet the needs of consumers, new alternatives to the ordinary Portland cement are searched [3–5].

However, as the requirements of the EU environmental and air pollution reduction rules (2008/50/EB) are tightened, the increasing use of renewable energy sources is in progress and the research for new applying possibilities of industrial waste are being sought [6–10]. One of these sources is biomass, during burning process, the heat energy is recovered [11]. With the increase in biomass utilization volumes, another problem – the utilization of biomass fly ash – is encountered. Despite the fact that ash contains a lot of micro-and macro elements useful for plant growth, the soil fertilization of biomass ash is limited due to the presence of heavy metals in the waste, and waste is stored in the landfills [12]. Biomass fly ash could be used as a mineral additive or an activator/binder in the cement-based binding materials [13–18]. Nevertheless, as many researchers point out, due to the richness of the biomass raw material and different technological processes used in the combustion process, the composition of fly ash varies, and an extensive investigation is required in each case [19–21].

One of the alternatives to ordinary Portland cement is slag cement. This type of cement is widely used in the production of concrete, which has high chemical resistance requirements or acts as a binder in the manufacture of massive constructions. In addition, the use of granular blast-furnace slag in slag cement production results in lower energy consumption and CO₂ emissions [22, 23]. However, this technogenic waste has latent hydraulic properties due to its glassy state phase [24, 25]. In order to increase the hydraulic activity of the blast-furnace slag, the waste is ground and/or activators, such as alkaline materials (sodium silicate, sodium hydroxide), sulfates, etc., are used [26, 27]. Whereas biomass fly ash contains alkaline oxides [19, 28–30]; therefore, it is expected that the additive of the latter material in the slag cement could destabilize the glassy state phase in the slag during the hydration of the slag cement without additional activation of the slag with other chemical reagents. Such complex use of biomass fly ash and granular blast-furnace slag in composite cements and their interactions and synergistic effects on the course of cement hydration or cement stone compressive strength are almost not investigated. Thus, the use of biomass fly ash as a mineral admixture for Portland cement or its application as a slag cement hydration

activator would allow discovering new possibilities of using biomass fly ash and reduce the pollution of the environment.

The aim of this work is to determine the influence of fly ash generated during the biomass combustion on the hydration, physical and mechanical properties of Portland cement and slag cement and to create new species of composite cements.

In order to achieve the aim of the work, the following goals had to be completed:

1. To investigate the chemical, mineral, and granulometric compositions, ash morphology, and pozzolanic activity of biomass fly ash;
2. To determine the influence of biomass fly ash additive on Portland cement hydration, physical and mechanical properties;
3. To find a method for the biomass fly ash activation and to study the influence of activated biomass fly ash on Portland cement hydration, physical and mechanical properties;
4. To explore the impact of activated biomass fly ash on Portland cement stone resistance to alkali – silica reaction and sulfate attack;
5. To determine the influence of activated biomass fly ash additive on slag cement hydration, physical and mechanical properties;
6. To propose technological recommendations for the application of biomass fly ash.

Scientific novelty of the dissertation

1. It has been found that the tribochemically activated biomass fly ash prepared as microfiller accelerates the hydration of Portland cement minerals, increases the compressive strength of cement stone, the resistance to alkali – silica reaction, and reduces the sulfate attack impact on the cement stone.
2. It was established that the activated biomass fly ash accelerates the slag cement hydration process and activates the latent hydraulic properties of granulated blast-furnace slag.

Practical significance of the dissertation

A new species of composite cements are created, and the technological recommendations for the application of biomass fly ash additive are proposed, according to which, the usage of biomass fly ash in Portland cement and slag cement production CO₂ emissions would be reduced to 12.5 mln. m³ per year, and in this way, the biomass fly ash, which is still disposed in landfills, would be utilized.

Approval and publication of the research results

The results of the research are presented in 5 publications: 3 of them were published in journals included in the Clarivate Analytics WoS database; 2 were reported at the conferences.

Structure and contents of the dissertation

The dissertation consists of an introduction, literature review, experimental part, results and discussion, conclusions, a list of references, and a list of publications on the topic of the dissertation. The list of references includes 176 bibliographic sources. The main results are discussed in 104 pages; they are illustrated with 15 tables and 39 figures.

Statements presented to the defense

1. Non-pozzolanic tribochemically activated biomass fly ash can be converted into an effective microfill, which accelerates the hydration process of Portland cement and slag cement minerals and increases the compressive strength of the cement stone.
2. Activated biomass fly ash activates the latent hydraulic properties of granulated blast-furnace slag and promotes the formation of gismondine and calcium silicate hydrates in the hardening system.

EXPERIMENTAL

The *biomass fly ashes* used in the experiment were collected in the electrostatic filters during the biomass (waste wood) combustion in fired power plant in Lithuania. Raw material was dried for 24 h at 100 °C, and when milled up to specific surface area, it reached 430 m²/kg.

Ordinary Portland cement CEM I 42.5 R was used in this work (JSC “Akmenės cementas”). The mineralogical composition of the clinker was as follows: 3CaO·SiO₂ 57.80 wt.%, 2CaO·SiO₂ 22.15 wt.%, 3CaO·Al₂O₃ 6.65 wt.%, and 4CaO·Al₂O₃·Fe₂O₃ 13.40 wt.%.

The *granulated blast-furnace slag* was milled in a ball mill for 8 h until the material specific surface area was close to that of Portland cement (350 m²/kg).

The main chemical composition and characteristics of the biomass fly ash, cement, and slag cement are shown in Table 1.

Ground reactive siliceous gravel contained opal SiO₂ and met the ASTM C1260-070 standard requirements for reactivity [31].

Other chemical reagents (CaO, HCl, NaOH, Na₂SO₄, trilon B, acetone, etc.).

Table 1. Chemical composition and characteristics of raw materials

Material Parameter, wt. %	Biomass fly ash*	OPC	Granulated blast-furnace slag
SiO ₂	45.08	19.52	36.3
Al ₂ O ₃	2.98	5.03	5.67
Fe ₂ O ₃	1.37	3.05	1.22
CaO	16.58	61.39	43.4
MgO	1.90	3.93	4.66
K ₂ O	4.47	1.06	0.52
Na ₂ O	0.37	0.12	0.65
MnO	0.56	-	-
SO ₃	2.26	2.5	1.56
P ₂ O ₅	2.07	-	0.34
TiO ₂	0.2	-	0.24
ZnO	0.12	-	-
BaO	0.10	-	-
Lost of ignition. %	8.89	3.4	5.44

*recount is not performed to 100%

Test of the Portland cement–biomass fly ash stone mineralogical composition. Samples (30×30×30 mm) were formed from the OPC paste with 0, 5, 15, and 25 wt.% biomass fly ash additive (activated and not ground) mixed with water (w/c ratio was determined according to the requirements of LST EN 196-

3:2005 [32]). During the first day, the samples were kept in forms at 20 ± 1 °C at 100% humidity. After 24 hours of hydration, the samples were transferred into the water and kept at 20 ± 1 °C for 2, 27, 89, and 179 days.

Part of the OPC samples with 5, 15, and 25 wt.% ground biomass fly ash additive after 28 days of hydration in the water were transferred into 5% Na₂SO₄ solution and were cured for 3, 6, and 9 months.

Test of the OPC–slag–biomass fly ash stone mineralogical composition. The control sample CEM III/A was prepared by using OPC and blast-furnace slag (EN 197-1:2011) [33]. The ground biomass fly ash was used to replace 5, 10, 15, 20, and 25 wt.% of the OPC or 10, 20, and 30 wt.% of slag. The samples for compressive strength and instrumental analysis (30×30×30 mm) were formed from the blast-furnace cement paste (water-to-solid ratio was estimated according to EN 196-3:2005 [32]) without sand and kept in moulds at 20 ± 1 °C and 100% humidity during the first day of hydration. After 24 h of formation, the samples were transferred to the deionised water and stored there for 6, 27, and 89 days at 20 ± 1 °C.

Interrupting the hydration process. After compressive strength measurements, the samples (30×30×30 mm) were crushed. The hydration of samples was stopped by using acetone. The dried cement stone grains (65 ± 5 °C; 24 h) were ground and put through a sieve with 80-µm mesh.

For the alkali-silica reaction test [34], 40×40×160 mm mortar prisms from the binder and reactive siliceous fine gravel (up to 0.125 mm) mortar were formed (binder-to-aggregate ratio 1:3; water-to-binder ratio 0.5). The binder in the samples was formed of OPC with 0, 5, 15, and 25 wt.% replacements with AFA. During the first day, the samples were kept in moulds at 20 ± 1 °C and 100% humidity. After 24 h of formation, the bars were transferred to the storage containers filled with 1 N NaOH solution maintained at 80 ± 1 °C. The mass and length changes of the mortar bars were periodically measured over 13-day period.

Prisms for the compressive strength analysis (40×40×160 mm) were formed following the standard EN 196-1:2005 (the ratio of cement to sand was 1:3 by weight; water-to-cement ratio was 0.5) [35]. AFA was added as a partial replacement of the OPC at levels of 5, 15, and 25% by weight of the total cementitious material. During the first day, the samples were kept in molds at 20 ± 1 °C and 100% humidity. After 24 hours of formation, the samples were transferred into distilled water and stored there for 7, 27 days, and 3 months at 20 ± 1 °C. The compressive strength of the samples was performed with Form+Test Mega 10-400-50 press.

Sieve analysis of biomass fly ash was carried out by using Sonic Sifter L3P shaker with 700, 600, 425, 212, 106, 80 µm size sieves. The mass of the sample was 3 g; the duration of sieving was 5 min; the vibration frequency was 1.0.

Particle size and distribution of raw materials was determined by a laser particle-size-analyzer CILAS 1090 LD 0.1–500 µm interval. The distribution of

solid particles in the air stream was 12–15 wt.%. The compressed air (2500 mbar) was used as a dispersing phase. Measuring time was 15 s.

Specific surface area measurements of the used materials were measured by the automatic Elektronischer Luftdurchlässigkeitsprüfer Blain equipment.

The pozzolanic activity was assessed using the modified Chapelle method [36]. This test consists of placing 1.000 g of mineral admixture into 500 ml of lime solution (1.200 g/l CaO). The solutions were kept for the first 48 h in a thermostat at 45 °C. At the end of this period, 50 ml of the solution was taken, and the CaO content was determined by titration with 0.05 N hydrochloric acid (HCl) solution using methyl orange as the indicator. The results were expressed as milligrams of fixed CaO per gram of pozzolanic additive. The rest of the solution (450 ml) was kept for 24 h at 45 °C. The process was repeated until the estimated value of the pozzolanic activity was insignificantly low (7 days).

The hydraulic activity of ground biomass fly ash was estimated by a Frattini test (EN 196-5:2005) [37]. 20 ± 0.01 g of investigated OPC sample with 0, 5, 15, and 25 wt.% AFA additive was mixed with 100 ml deionized water (40 ± 0.5 °C) and kept for 8 days in a thermostat at 40 ± 0.5 °C. At the end of this period, suspension was filtered, and 50 ml of the filtrate was taken for hydroxide ions (0.1 mol/l HCl) and CaO concentration (0.03 mol/l trilon B) determination.

The content of free calcium oxide in biomass fly ash was determined by the ethylene glycol method. 0.3 g of investigated material powders were mixed with 70 ml of neutral ethylene glycol and isopropyl alcohol solution. The sealed flask with a cork was thermostated at 70 ± 0.5 °C in a water bath and titrated with 0.2 N benzoic acid for free CaO determination.

The X-ray powder diffraction (XRD) data was performed using the D8 Advance diffractometer (Bruker AXS, Karlsruhe, Germany) with Bragg–Brentano geometry. The X-ray beam was filtered with a Ni 0.02 mm filter to select the CuK_α wavelength (operating voltage of 40 kV, emission current of 40 mA). The step-scan covered an angular range of 3–65° (2θ) at a scanning speed of 6 °C·min⁻¹ using a coupled two theta/theta scan type.

X-ray fluorescence (XRF) analysis was performed by using S4 Explorer with CuK_α radiation (operating voltage, 20 kV; emission current, 5 mA).

Simultaneous thermal analysis (STA) (differential scanning calorimetry and thermogravimetry) was carried out on a Netzsch STA 409 PC Luxx instrument with ceramic sample handlers and crucibles of Pt-Rh. At a heating rate of 15 °C·min⁻¹, the temperature ranged from 30 °C to 830 °C under the ambient atmosphere.

FT-IR spectra were measured using a Perkin-Elmer Fourier transform infrared system Spectrum X spectrometer. The samples were prepared by mixing 1 mg of the sample in 200 mg of KBr. The spectral analysis was performed in the range of $4000 - 400$ cm⁻¹ with a spectral resolution of 1 cm⁻¹.

Scanning electron microscopy (SEM) was carried out on the FEI Quanta 200 FEG microscope. Accelerating voltage of 20 kV, a working distance of 10 mm, and a high vacuum were used for the SEM observation.

Isothermal calorimetry was used (“TAM Air III”) to investigate the heat evolution rate of OPC blended with 0, 5, 15, or 25 wt.% by weight of the BFA or AFA and slag cement blended with 0, 5, 10, 15, 20, and 25 wt.% AFA.

RESULTS AND DISCUSSION

Biomass fly ash influence on the hydration of ordinary Portland cement

In order to monitor the trend of variation of elements in the biomass fly ashes (BFA), a number of samples were collected. The results of the XRF analysis showed that SiO_2 (43-50 wt.%) and CaO (15-20 wt.%) are the main oxides in all the BFA samples (Fig. 1). The content of K_2O varies between 3-6 wt.%; whereas, Al_2O_3 , MgO , Fe_2O_3 , SO_3 , and P_2O_5 do not exceed 5 wt.%. For further research, sample 1, for which the chemical composition is given in Table 1, was chosen (close to the average composition).

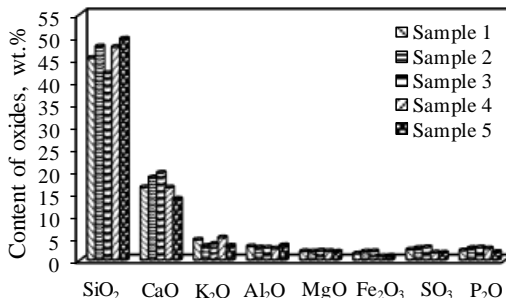


Fig. 1. Variation of chemical composition of the biomass fly ash samples

According to the XRD analysis data (Fig. 2), quartz (d -spacing: 0.425, 0.334, 0.181 nm), CaO (d -spacing: 0.277, 0.240, 0.169 nm), MnS (d -spacing: 0.324, 0.198 nm), Al_3PO_4 (d -spacing: 0.423, 0.334 nm), and calcite (d -spacing: 0.302, 0.228, 0.209, 0.189, 0.186 nm) were found in the BFA.

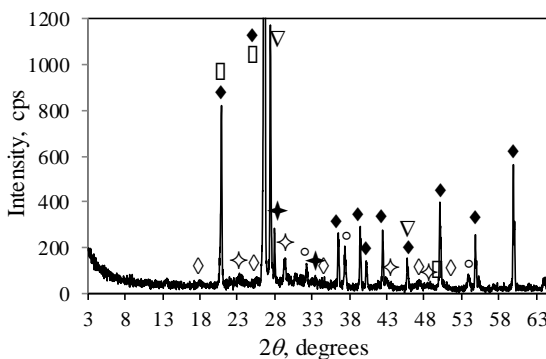


Fig. 2. X-ray diffraction pattern of biomass fly ash. Indexes: \blacklozenge – quartz (SiO_2); \square – calcium oxide (CaO); ∇ – manganese sulfide (MnS); \blacklozenge – calcite (CaCO_3); \star – potassium manganese sulfate ($\text{K}_2\text{Mn}_2(\text{SO}_4)_3$); \square – aluminum phosphate (Al_3PO_4)

It was established that the BFA is not pozzolana as pozzolanic activity reached only 22 mg CaO/g . Moreover, BFA particle diameter varies over very wide limits ($< 80\text{--}600\ \mu\text{m}$), and the particles larger than $80\ \mu\text{m}$ constitute 78.34 wt.% of the total amount.

It was determined that in the early stage of the cement hydration, BFA additive causes a shorter induction period and accelerates the recrystallization of ettringite into AFm. Although the biomass fly ash additive essentially unchanged the process of Portland cement hydration (no new hydrated phases were identified by the instrumental analytical methods), but it had a negative effect on the strength properties of cement (the dilution effect of binding material is seen). It was determined that after 28 days of hydration, the compressive strength of samples with 15 wt.% BFA additive was more than 10% lower than that of OPC (53 MPa); whereas, the compressive strength of the sample with 25 wt.% additive (35 MPa) was 30% lower than that of the OPC.

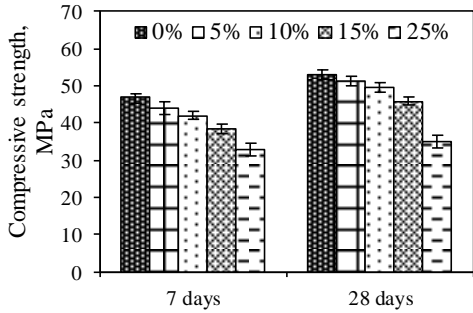


Fig. 3. Compressive strength of cement standard prisms with 0–25 wt.% of BFA additive after 7 and 28 days of hydration

Thus, the investigated biomass fly ash (as-received) is an unsuitable additive for the Portland cement.

Tribochemical activation of the biomass fly ash

In order to improve the properties of biomass fly ash, in the next stage of research, a mechanical activation of BFA was carried out. The BFA was additionally ground to such an extent that it meets the requirements of micro-fillers (EN 12620: 2003 + A1: 2008). Specific surface area of activated BLP was 430 m²/kg.

After milling, 100 wt.% of the particles are lower than 450 μm, and the uniformly distributed particles are dominated by the diameters less than 63 μm, constituting 70 wt.% of the total amount (Fig. 4). Thus, these prepared biomass fly ashes (AFA) can be used as a microfiller. It was determined that the pozzolanic activity of additionally milled biomass fly ash was higher than BFA, but it remained very low and reached only 30 mg CaO/g.

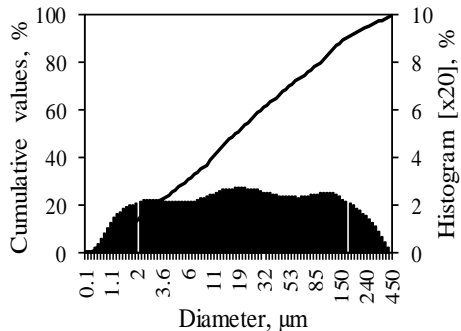


Fig. 4. Particle size distribution of the activated biomass fly ash (AFA)

According to the XRD data (Fig. 5), it can be noted that after the milling, the main difference between BFA and AFA mineral composition is the formation of Portlandite, as the characteristic peaks typical to this compound (d spacing: 0.489, 0.262, 0.192 nm) were identified in the XRD curve. Portlandite formation can be explained by the fact that during the grinding process, CaO becomes very active, joins the environmental humidity, and becomes portlandite. The formation of $\text{Ca}(\text{OH})_2$ was confirmed by the STA (Fig. 6), as significant endothermic effects at 440 °C are attributed to the decomposition of portlandite.

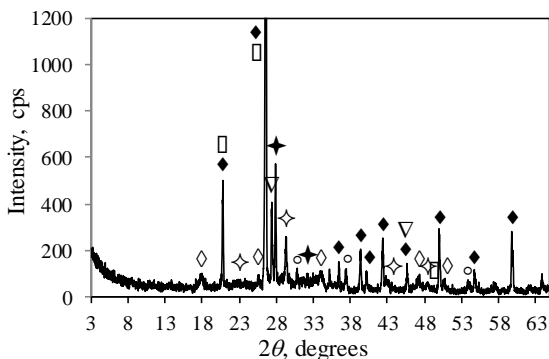


Fig. 5. X-ray diffraction pattern of activated biomass fly ash. Indexes: \diamond – portlandite ($\text{Ca}(\text{OH})_2$); \blacklozenge – quartz (SiO_2); \circ – calcium oxide (CaO); ∇ – manganese sulfide (MnS); \diamond – calcite (CaCO_3); \blacktriangle – potassium manganese sulfate ($\text{K}_2\text{Mn}_2(\text{SO}_4)_3$); \square – aluminum phosphate (Al_3PO_4)

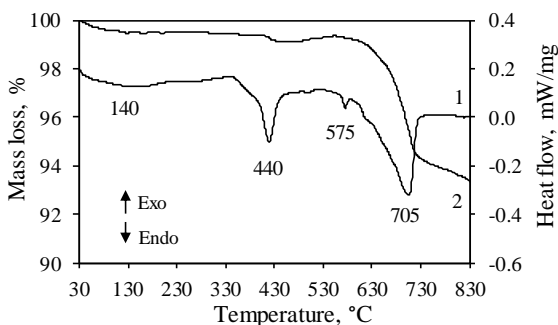


Fig. 6. STA curves of activated biomass fly ash (AFA) sample

The grinding of BFA results in the mechanical fly ash particle milling and changes the composition of the compounds; therefore, this process can be called a tribochemical activation of biomass fly ash.

The influence of activated biomass fly ash on the hydration and hardening of Portland cement paste

In the next stage of research, the influence of AFA additive (5, 15, and 25 wt.%) on the cement hydration process was investigated. The results of physical tests – setting time and normal consistency of different cement compositions – showed a negligible increase of setting time and a continuous increase of normal consistency according to the increasing percentage of the added AFA additive that were determined (Table 2). This is explained by the partial substitution of cement by adding a character with fly ash, causing excessive consumption of water and absorption of part of the water for hydration.

Table 2. Influence of the AFA additive on the physical properties of Portland cement paste

Amount of additive, %	Water-to-solid ratio	Initial setting time, min	Final setting time, min
0	0.255	89	139
5	0.265	95	153
15	0.275	105	155
25	0.285	104	160

In order to assess the influence of fly ash additive on the initial hydration of cement, the measurement of heat evolution during the hydration process (calorimetric analysis) was performed. As shown in Figure 9, two intense peaks of heat evolution were found in the calorimetric curves of the investigated Portland cement samples with 0-25wt.% AFA additive. The first, active heat evolution, is caused by wetting the cement powder and an initial kinetic reaction, during which Ca^{2+} , OH^- , SiO_4^{4-} , and SO_4^{2-} ions pass into the solution, and the second is related to the reaction between the deeper layers of calcium silicate particles and water. In the second peak, at the later hydration period, a shoulder that is associated with an aluminate hydration reaction and the formation of ettringite is observed. It can be assumed that the AFA additive slightly reduces the duration of the induction period but significantly accelerates the initial cement hydration. It is possible that during the induction period, Ca^{2+} ions adsorbed on the surface of the fly ash or finely ground fly ash can act as crystallization centers, around which portlandite and calcium silicate hydrate begin to crystallize. Moreover, AFA additive, as well as BFA,

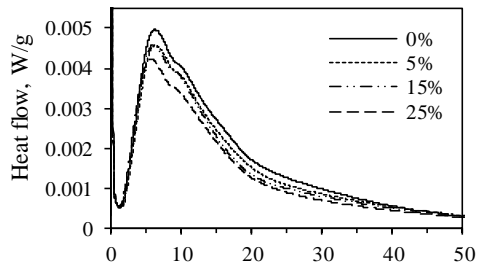


Fig. 7. Calorimetric curves of thermal flow in cement samples with 0–25 wt.% of the AFA additive

accelerates the reaction between C_3A and ettringite (Fig. 7). However, all of the samples with the AFA additive up to 50 h of hydration emit less heat energy. This can be explained by the fact that the AFA additive does not have binding or pozzolanic properties; therefore, the hydration with less cement emits less heat energy.

The investigation of the compressive strength of samples, in which the content of AFA additive varied from 5 to 25 wt.%, showed that this additive had a positive effect on the strength properties of cement. It was estimated (Fig. 8) that after 28 days of hydration, the compressive strength of the samples with 5–15 wt.% AFA additive was higher than that of the OPC samples. It should be noted that even for samples with 25 wt.% AFA additive, the compressive strength was less than 10% lower (48.3 MPa) than that of the OPC samples (53 MPa).

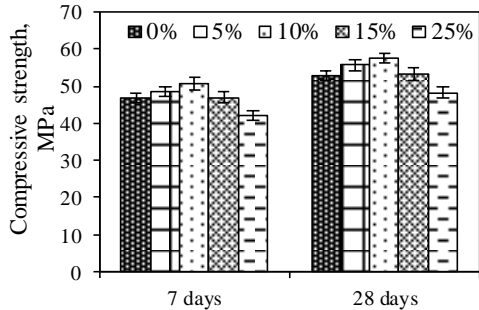


Fig. 8. Compressive strength of cement standard prisms with 0–25 wt.% of AFA additive after 7 and 28 days of hydration

The results of XRD analysis showed that after 28 days of hydration, the intensity of CSH and portlandite peaks grows with an increasing amount of AFA additive from 5 to 25 wt.% in the samples. The higher intensity of CH diffraction peaks may be associated with the more intense hydration process of calcium silicate, or it may be associated with the additionally mixed CH amount, because it is one of the AFA components. However, the higher intensity of the CSH peaks can be associated only with the more intense hydration process of calcium silicates.

Moreover, according to the FT-IR analysis data, it can be noted that the addition of AFA, as well as BFA, promotes the recrystallization of ettringite to monosulfohydroaluminate.

The results of thermogravimetric analysis (Table 3) showed that the mass loss of portlandite decomposition (420–480 °C) grew when the amount of AFA additive was increased in the samples. The higher mass loss was observed in the area of calcium silicate hydrate dehydration (80–140 °C). Even when 25 wt.% of AFA additive was used, larger amounts of portlandite and CSH were formed than in the OPC sample, and there was a significant acceleration of the calcium silicate hydration process. In the samples with AFA additive, greater amounts of both hydration products (CSH and portlandite) were formed. This indicates that in those samples, the pozzolanic reaction does not occur; otherwise, part of the CH would react with the active components, and the amount of CH should decrease.

Table 3. Thermogravimetric analysis results of cement samples with AFA additive cured for 28 days under normal conditions

Amount of additive, wt. %	Mass loss, wt. %									
	After 7 days of hydration					After 28 days of hydration				
	80–140 °C	420–480 °C	680–760 °C	80–140 °C	420–480 °C	680–760 °C	80–140 °C	420–480 °C	680–760 °C	
0	1.58	1.83	1.83*	3.66	3.66*	1.68	2.0	2.0*	4.69	4.69*
5	1.61	1.88	1.84*	4.09	3.80*	1.72	2.16	2.12*	5.05	4.76*
15	1.70	1.99	1.86*	4.61	3.73*	1.81	2.32	2.19*	5.12	4.24*
25	1.74	2.15	1.92*	4.65	3.19*	2.08	2.67	2.44*	5.25	3.79*

* data based on the estimated portlandite and calcite content in the AFA

Thus, the tribochemically activated biomass fly ash is an available additive for Portland cement, because up to 15 wt.% of the cement can be replaced with this additive without impairing the strength properties of Portland cement.

Chemical resistance of the ordinary Portland cement with the activated biomass fly ash additive

The influence of AFA additive on the chemical resistance of cement hydrates was evaluated after the hydration tests of Portland cement and cement with 5, 15, and 25 wt.% AFA additives in 1M NaOH and 5% Na₂SO₄ solutions.

Influence of AFA additive on the alkali – silica reaction

As biomass fly ash contains a number of alkalis, in the next stage of the research, the influence of AFA additive (5, 15, and 25 wt.%) on the course of the alkali-silica reaction in the cement mortars was determined. It has been found that the mass of all the investigated samples during the maintenance in 1 M NaOH solution at 80 °C for up to 14 days (Figure 13b) increased exponentially; however, in samples with the AFA additive, the mass gain was less than in the pure OPC sample. The reduced mass increase is probably due to the fact that the addition of AFA additive provides a better grain-size composition in the mixture and a denser cement stone structure. The biggest change in length (Figure 13a) is observed in the pure cement sample (0.095%) as well; whereas, in the samples with AFA additive, the length expansion is lesser and varies from 0.088% (sample with 25 wt.% additive) to 0.023% (sample with 15 wt.% additive). It has been observed that the expansion rate of all the mortars was high in the initial stages, and after that, it seemed to decrease. According to the applied methodology, the critical value of length expansion is 0.1%. Thus, the expansion of reference mortar prepared with the OPC was only slightly less than the critical value; meanwhile, the expansion results for the mortar mixtures containing activated biomass fly ash showed a reduction in the expansion compared to the plain cement mortars.

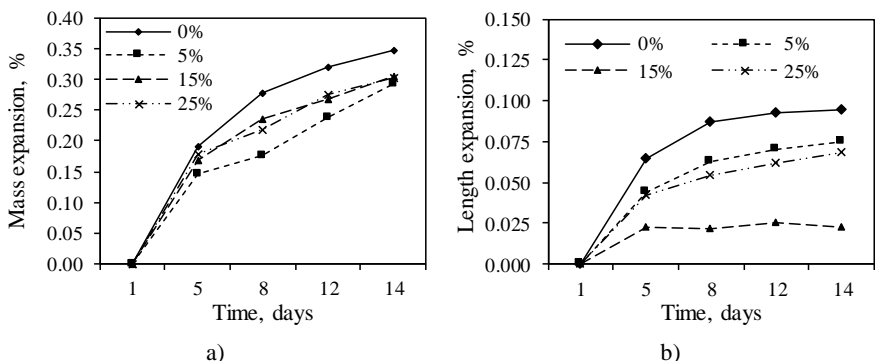


Fig. 9. Length expansion a) and mass expansion b) of cement samples with AFA additive after 14 days of storage in 1 molar NaOH solution at 80 °C

Influence of the AFA additive on the sulfate attack of cement stone

Based on visual observations, it is seen that after 9 months of maintenance in a 5% sulfate environment, the edges of cement sample without AFA additive (Fig. 10) was strongly influenced by the sulfate, and relatively bright cracks in the whole sample were observed. Meanwhile, in the cement samples with AFA additive up to 25 wt.%, only minor lesions were observed in the upper edge.



Fig. 10. Optical photos of cement samples (30×30×30 mm) with 0 and 25 wt.% of the AFA additive after 9 months of maintenance in 5% Na₂SO₄

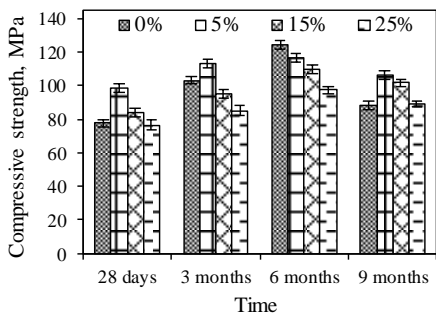


Fig. 11. The compressive strength of the cement samples (30×30×30 mm) with the AFA additive after 28 days of hydration in water and after 3, 6, and 9 months curing in 5% Na₂SO₄ solution

The results of samples of compressive strength showed that the AFA additive positively affects the resistance of the cement stone to the sulfate attack. It was determined that after 6 and 9 months of maintenance in a 5% Na₂SO₄ solution, the compressive strength of Portland cement sample decreased by 28.65%; whereas, up to 8.71% reduction of compressive strength was fixed in the samples with 5-25

wt.% AFA additive. Nevertheless, after 9 months curing in the sulfate environment, the samples with AFA additive exhibited higher compressive strength than the Portland cement sample without AFA (88.48 MPa). The decrease in the compressive strength of the samples is likely to result in the formation of secondary ettringite and gypsum during the hydration in the sulfate environment. In addition, with increasing hydration time from 6 to 9 months in the 5% Na₂SO₄, the decrease of intensity of the calcium silicate hydrates' main peaks in the XRD curves were observed, i.e., the decalcification of calcium silicate hydrates took place, which resulted in the cement stone structure porosity, softening, and lost compressive strength. However, these processes were more pronounced in a Portland cement sample without AFA additive.

Table 4. Thermogravimetric analysis results of the cement samples with AFA additive cured for 3, 6, and 9 months in the 5% Na₂SO₄ solution

Amount of additive, wt.%	Mass loss, wt.%					
	After 3 months		After 6 months		After 9 months	
	80-140 °C	450-485 °C	80-140 °C	450-485 °C	80-140 °C	450-485 °C
0	2.12	2.70	2.75	3.12	2.01	2.39
5	2.19	2.82	2.42	2.95	2.20	2.52
15	2.10	2.63	2.29	2.73	2.19	2.52
25	2.10	2.68	2.21	2.70	2.05	2.43

The results of the previous studies were confirmed by the data of thermogravimetric analysis (Table 4). Due to the involvement of portlandite in the reaction with Na₂SO₄, its amount in cement stone decreased (450-485 °C). After 9 month maintenance of samples in a Na₂SO₄ solution, the greatest reduction in the mass loss of portlandite decomposition (comparing samples after 6 and 9 months of maintenance in a sulfate environment) was found in the Portland cement sample (24%); whereas, in the cement samples with 15 and 25 wt.% of AFA additive, the mentioned decrease of mass loss was about 10%. It was observed that the largest changes in the mass loss was as well fixed in the cement samples without AFA additive, which was affected by the decreased CSH (80-140 °C) content. Meanwhile, the smallest changes in the mass loss occurred in the cement sample with 15 and 25 wt.% AFA additives throughout all the hydration period. Probably, an additional alkaline source mixed with fly ash (the additive is strongly alkaline, pH = 12.89) slows down the decalcification process of calcium silicate hydrates.

To sum up, it can be stated that the AFA additive had a positive effect on the resistance of cement stone to the sulfate attack.

Biomass fly ash–granulated blast furnace slag type cement. Hydration and hardening

At this stage of research, an activated biomass fly ash was used as a slag activator in the cement system due to a high alkali and sulfate content in it (4.84 wt.% $K_2O + Na_2O$ and 2.26 wt.% SO_3 (Table 1), pH = 12.89).

The ground granulated blast-furnace slag (specific surface area is equal to $350 \text{ m}^2/\text{kg}$) was used in the experiment. Particles with a diameter of $\leq 42.27 \mu\text{m}$ constituted 50% of the total amount, and an average particle size was equal to $15.17 \mu\text{m}$ (Fig. 12).

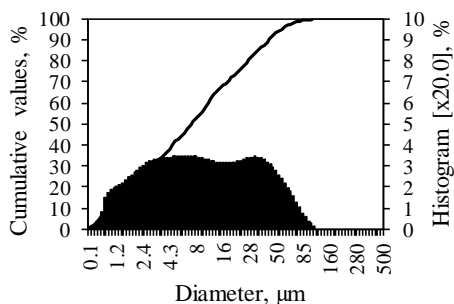


Fig. 12. Particle size distribution of ground granulated blast furnace slag

According to the XRD analysis data (Fig. 13), dicalcium silicate (d-spacing: 0.279, 0.274, 0.278, 0.260 nm), melilite (d-spacing: 0.307, 0.286, 0.245 nm), akermanite (d-spacing: 0.308, 0.287, 0.176 nm), calcite (d-spacing: 0.302 nm), quartz (d-spacing: 0.334 nm), merwinite (d-spacing: 0.268, 0.267, 0.203, 0.191 nm), and diopside (d-spacing: 0.322, 0.298, 0.294 nm) were found in the blast-furnace slag. Furthermore, an amorphous component in the slag composition is characterized by a broad peak in the angle of diffraction from 23° to 37° .

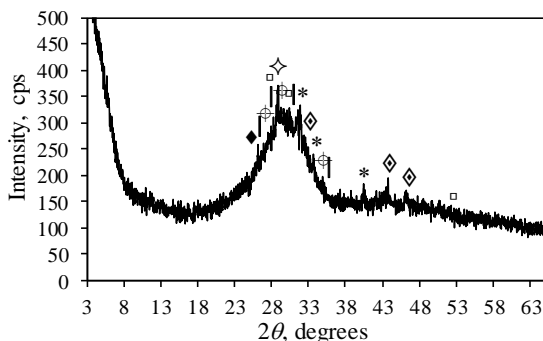


Fig. 13. X-ray diffraction pattern of ground granulated blast-furnace slag. Indexes: \blacklozenge – quartz (SiO_2); \diamond – calcite ($CaCO_3$); $*$ – dicalcium silicate (Ca_2SiO_4); $|$ – melilite ($Ca_4Al_2MgSi_3O_{14}$); \square – akermanite ($Ca_2MgSi_2O_7$); \blacklozenge – merwinite ($Ca_3Mg(SiO_4)_2$); \oplus – diopside ($Ca(MgAl)(Si,Al)_2O_6$)

In the next stage of the study, the mixtures of two different series of slag cement with AFA additive were prepared, in which the fixed content of Portland cement or slag was maintained.

The system (60-x) wt.% slag – 40 wt.% OPC – x wt.% activated biomass fly ash

The influence of AFA additive on physical–mechanical properties of the slag cement was investigated in this part of the research. The AFA replaced 10, 20, and 30 wt.% of slag; whereas, a part of Portland cement was constant and consisted of 40 wt.%.

The results of the research showed that in the slag cement, a part of the slag component could be replaced by the AFA additive without impairing the strength properties of slag cement. The most suitable replacement value was 10 wt.%; since, the compressive strength of such slag cement sample during the determination of the strength class (after 28 days of hydration) was the same as that of slag cement without additive (Fig. 14). However, the mentioned change in slag cement was not very effective as the additive (slag) was replaced with another additive (AFA). In this case, only part of the ecological and economic problem is solved: biomass fly ash for landfilling is consumed, but the CO₂ emissions in the environment are not reduced during the cement production.

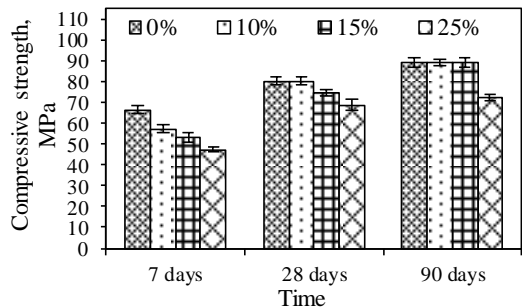


Fig. 14. Compressive strength of slag cement samples with 0-30 wt.% AFA additive after 7, 28, and 90 days of hydration

Therefore, in the next research stage, a part of Portland cement was replaced by the AFA additive in the slag cement.

The system 60 wt.% slag – (40-x) wt.% OPC – x wt.% activated biomass fly ash

In this part of the research, the activated biomass fly ash was used in 5, 10, 15, 20, and 25 wt.% replacement of Portland cement in the slag cement, when the slag part in the mixtures was constant and constituted 60% by weight.

The results of calorimetric analysis (Fig. 15) showed that with the growing amount of the AFA additive in the samples from 5 to 15 wt.%, the second exothermic peak appeared earlier (9 h 18 min and 8 h 48 min, respectively) than in the samples without additive (9 h 22 min); whereas, in the samples with 25 wt.% AFA additive, this maximum was obtained later (10 h 21 min) (due to a very low

amount of OPC). The third peak (associates with hydration of the slag component) in the pure slag cement sample was less intense than the second maximum; in the sample with 5 wt.% AFA additive, it remains the same; whereas, in samples with 15 and 25 wt.% AFA additive, the third peak was more intense than the second maximum. In addition, in samples with 5 and 15 wt.% AFA additive, the third maximum appeared earlier (respectively, after 15 h 12 min and 14 h 51 min) than in the pure slag cement sample (15 h 37 min). Therefore, it can be assumed that the AFA additive (except for the sample with 25 wt.% of AFA) accelerates the initial hydration of blast-furnace slag cement and promotes hydration of the slag component.

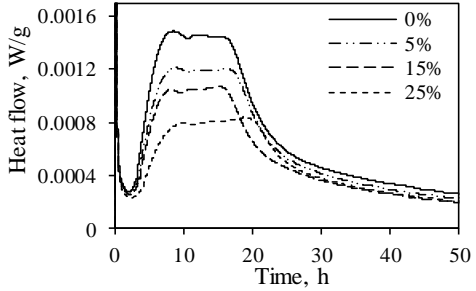


Fig. 15. Calorimetric curves of the thermal flow in the samples with different amounts of the AFA additive

The investigation of the compressive strength of the blast-furnace cement samples with the AFA additive showed that this material had a negative effect on the early compressive strength of samples (Fig. 16). When 5–25 wt.% AFA was blended in the samples, the compressive strength of all the samples was lower than 66 MPa. Nevertheless, at a later period of hardening (after 28 and 90 d of hydration), AFA additive (up to 10 wt.%) increases the compressive strength of the samples.

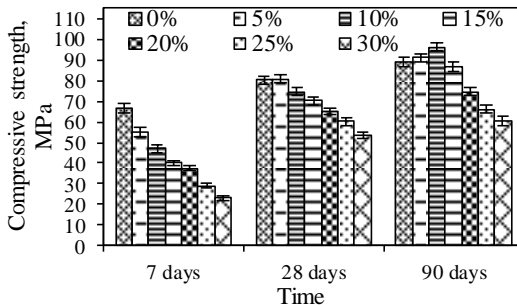


Fig. 16. Compressive strength of blast-furnace cement samples with different amounts of the AFA additive after 7, 28, and 90 d of hydration

It was found that the Portland cement replacement by the AFA additive promoted the formation of gismondine ($\text{CaAl}_2\text{Si}_2\text{O}_8 \cdot 4\text{H}_2\text{O}$) (Fig. 17). The intensity of these peaks grew with the increasing amount of additive from 5 to 25 wt.% and

lengthening the time of hydration up to 90 days. Furthermore, in all the X-ray patterns of samples, after 28 d of hydration, the diffraction peaks of new CSH ($\text{Ca}_2\text{SiO}_4 \cdot 0.5\text{H}_2\text{O}$) (*d-spacing*: 0.329, 0.277, 0.267, 0.225 nm) with a high C/S ratio ($\text{C/S} = 2$) could be identified. When hydration time was prolonged up to 90 days, the most intense peaks of this compound were fixed in the samples with 5 and 15 wt.% AFA additives.

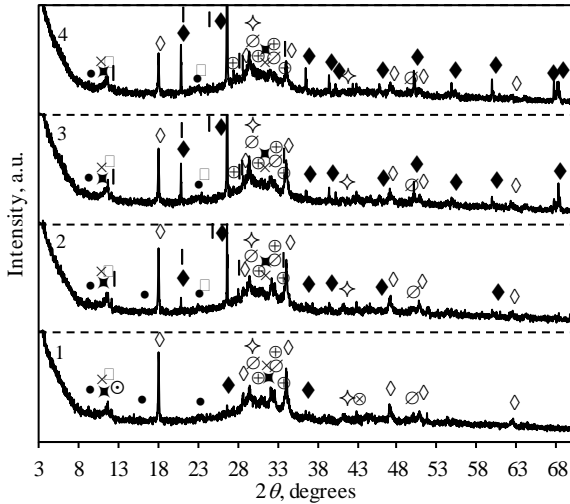


Fig. 17. X-ray diffraction patterns of blast furnace cement samples with AFA additive cured for 28 days under normal conditions: 1 – 0 wt.% AFA, 2 – 5 wt.% AFA, 3 – 15 wt.% AFA, 4 – 25 wt.% AFA. Indexes: \diamond – Portlandite ($\text{Ca}(\text{OH})_2$); \blacklozenge – Quartz (SiO_2); \diamond – Tricalcium silicate (Ca_3SiO_5); * – Dicalcium silicate (Ca_2SiO_4); \circ – Calcium silicate hydrate ($\text{Ca}_{1.5}\text{SiO}_{3.5} \cdot x\text{H}_2\text{O}$); \oplus – Calcium silicate hydrate ($\text{Ca}_2\text{SiO}_4 \cdot 0.5\text{H}_2\text{O}$); \bullet – Ettringite ($\text{Ca}_6\text{Al}_2(\text{SO}_4)_3(\text{OH})_{12} \cdot 26\text{H}_2\text{O}$); \blacksquare – Monocarboaluminate ($\text{Ca}_4\text{Al}_2\text{O}_7\text{CO}_2 \cdot 11\text{H}_2\text{O}$); $\bar{}$ – Gismondine ($\text{CaAl}_2\text{Si}_2\text{O}_8 \cdot 4\text{H}_2\text{O}$); \blacktriangle – Hydrocalumite ($\text{Ca}_2\text{Al}(\text{OH})_7 \cdot 3\text{H}_2\text{O}$); \times – Tetracalcium aluminate hydrate (C_4AH_{13}); \odot – Brownmillerite ($\text{Ca}_4(\text{Al}, \text{Fe})_2\text{O}_{10}$); \diamond – Calcite (CaCO_3); \otimes – Periclase (MgO)

Table 5. Thermogravimetry analysis results of blast-furnace cement samples with AFA additive cured for 7, 28, and 90 d under normal conditions

Amount of additive, wt. %	Mass loss, wt. %					
	After 7 d of hydration		After 28 d of hydration		After 90 d of hydration	
	80–200 °C	435–465 °C	80–200 °C	435–465 °C	80–200 °C	435–465 °C
0	2.59	0.52	3.69	0.75	4.47	1.22
5	2.55	0.31	3.75	0.76	4.81	1.29
15	1.80	0.23	3.10	0.38	4.24	0.78
25	1.31	0.20	2.59	0.22	3.73	0.48

The conditional high mass loss at 80–200 °C in samples with the AFA additive after 28 and 90 d of hydration is mostly associated with the formation of an additional quantity of CSH and once again indicated that this additive activated slag and promoted the hydration reaction (Table 5). However, the reduction of the amount of CH in the hydrated samples with the AFA additive showed that the AFA additive activated the reaction between the portlandite and amorphous slag components (pozzolanic reaction).

Technological recommendations for the possibility to apply biomass fly ash as additive in the binding materials production

The main indicator that can demonstrate the benefits of using AFA in the cement production is the reduction of CO₂ emissions, when a portion of Portland cement clinker is replaced with a biomass fly ash additive. Therefore, based on the estimated raw materials and clinker chemical composition, the reduction of CO₂ emissions was estimated in the plan to produce 200000 tons of CEM II Portland cement and 100000 tons of slag cement with the AFA additive per year. The preliminary calculations of CO₂ emissions to the environment during the clinker combustion have been made taking into account the amount of CaCO₃ contained in the main component (lime), the reduction in the burning fuel (coal) level and not taking into account the potential losses at various stages of production. The compositions of produced products, i.e., Portland cement with 15 wt.% AFA additive and slag cement containing 60 wt.% slag and 10 wt.% AFA, have been chosen based on the results obtained in the research.

According to the calculations, there are consumed 19963.17 tons less of CaCO₃ per year when 15 wt.% of Portland cement is replaced by the AFA additive on the same production volumes of CEM I and CEM II. Thus, there would be emitted up to 4.47 million m³ less of greenhouse gases per year to the environment. Accordingly, at the planned 100000 tons per year of slag cement containing 10 wt.% of the AFA additive production, there would be consumed 6654.39 tons less of CaCO₃, and there would be released 1.49 mln. m³ less of carbon dioxide to the environment during the clinker combustion than in the production of slag cement without the AFA. In addition, for the production of CEM II and CEM III/A cements, the consumption of the fuel would be up to 4966 tons less per year, i.e., CO₂ emissions would be reduced up to 6.5 mln. m³.

To sum up, it can be argued that the use of biomass fly ash in the production of Portland cement and slag cement would allow reducing up to 12.5 mln. m³ of CO₂ emissions to the environment.

Technological schemes of CEM II and CEM III type binding materials production and application

The production of CEM II and CEM III type binding materials was selected according to the optimal results of the research: mixtures with the composition of

85 wt.% Portland cement, 15 wt.% AFA and 60 wt.% slag, and 30 wt.% Portland cement, 10 wt.% AFA, were the same strength grade cements as without the AFA additive.

As the properties of CEM II and CEM III were determined by mixing the AFA additive to the binding material separately, the cement manufacturing scheme as well provides for such mixing of materials. It may happen, because the cement clinker grinding together with the biomass fly ashes could provide positive results as well, and the mixing operation should not be required; however, further, more detailed studies are needed.

After the cement clinker combustion, Portland cement production process consists of the following steps: storage and preparation of raw materials, milling of the cement components and depositing of dust, mixing cement with the AFA additive and cement storage. All the stages consist of the continuous operation process. The recommended technological scheme for the production of the CEM II and CEM III type cements with the AFA additive are given in Figure 18.

Another way to utilize the biomass fly ash is to use these ashes directly in the concrete units located in each larger city. In this case, another ecological aspect would dominate: biomass fly ashes in each city would be consumed, which currently are landfilled, reducing the environmental pollution. In addition, the costs of transportation of waste (ash) would be significantly reduced, as it would be used in the same city where it was collected. For the use of biomass fly ash in concrete units, two silos (for fly ash and ground fly ash) should be additionally equipped, and a vibrating mill should be built, the capacity of which would match the production of the concrete unit.

The main stages in concrete production are cement storage, classification and storage of inert additives, storage and supply of chemical additives, mixing of concrete, and supplying it to the consumer. The principal technological scheme for the concrete mixing concrete is given in Figure 19.

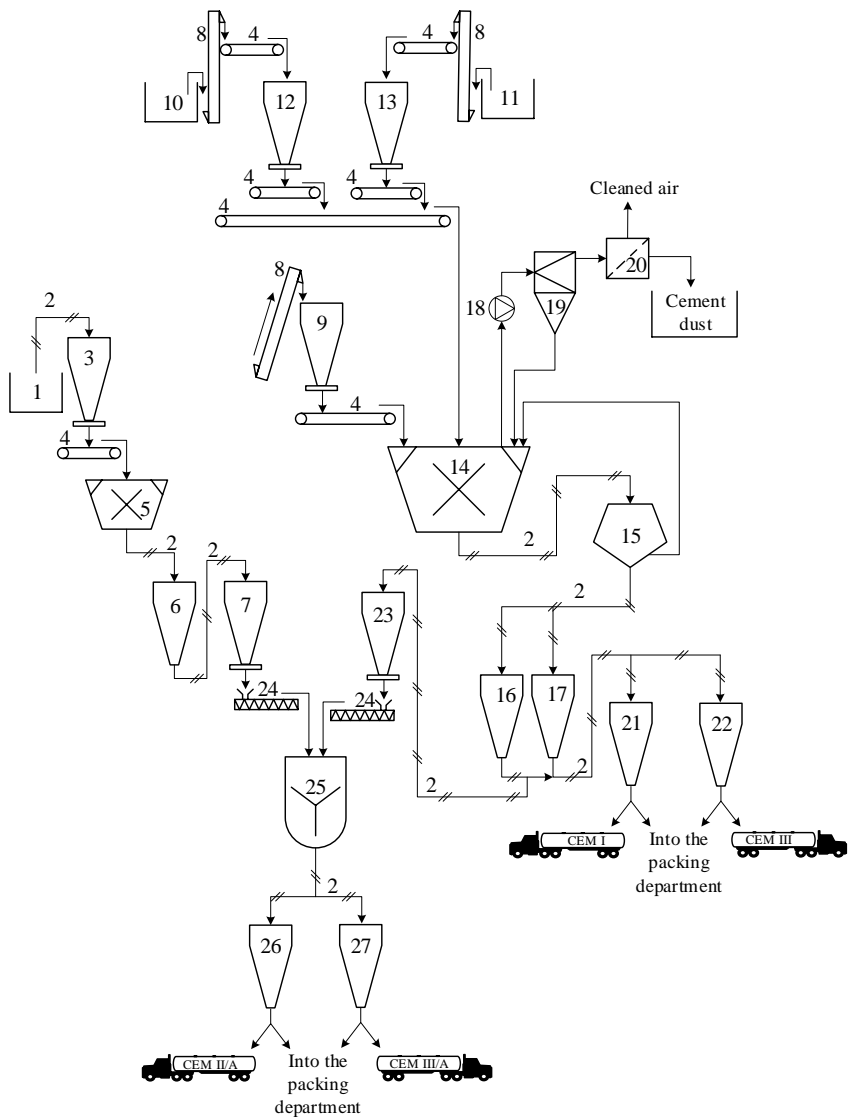


Fig. 18. Principal technological scheme of the CEM II and/or CEM III cement with the AFA additive production. 1 – biomass fly ash receiving hopper; 2 – pneumatic transport system; 3 – biomass fly ash storage silo; 4 – belt conveyor system; 5 – vibrating mill; 6 – ground biomass fly ash intermediate storage silo; 7 – ground biomass fly ash silo with dosator; 8 – elevators; 9 – clinker silo with dosator; 10 and 11 – gypsum and granular blast furnace slag receiving hoppers; 12 and 13 – gypsum and granular blast furnace slag storage silos

with dosator; 14 – cement ball mill; 15 – separator; 16 and 17 – intermediate CEM I and CEM III type cements silos; 18 – ventilator; 19 – ciklone; 20 – sleeve filters system; 21 and 22 – CEM I and CEM III type cements silos; 23 – extra cement silo with dosator; 24 – screw transporter; 25 – double-shaft mixer; 26 and 27 – CEM II and CEM III type cements with AFA additive silos

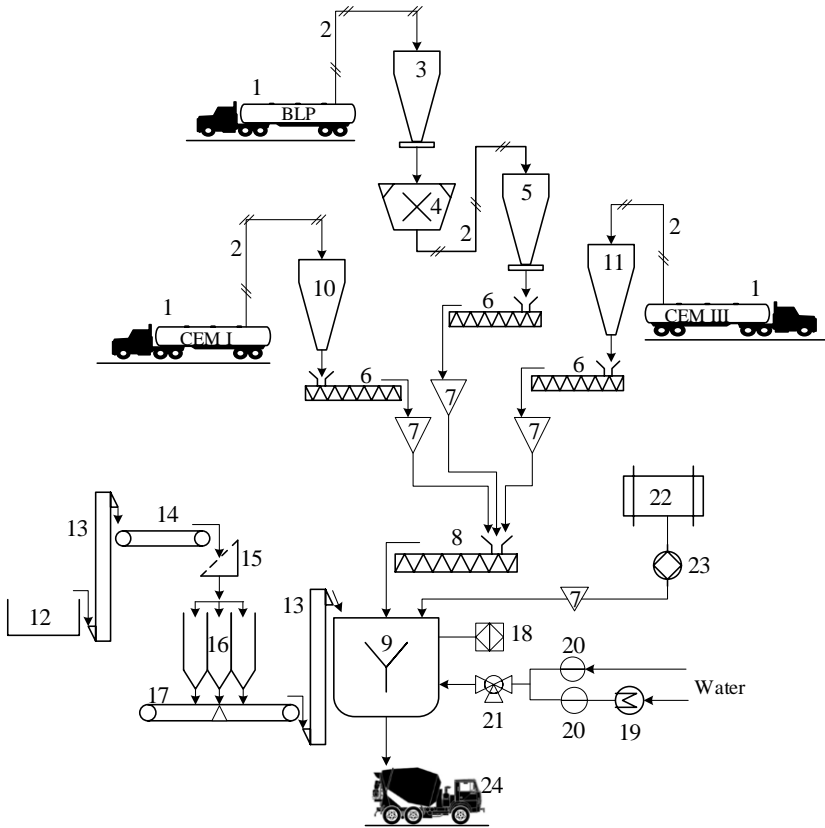


Fig. 19. Principal technological scheme of the concrete production. 1 – cement truck; 2 – pneumatic transport; 3 – biomass fly ash silo with dosator; 4 – vibrating mill; 5 – ground biomass fly ash silo with dosator; 6 – screw transporters; 7 – weight dispenser; 8 – fly ash–cement screw transporter; 9 – concrete mixer; 10 and 11 – CEM I and CEM III type cements storage silos; 12 – filler receiving hopper; 13 – elevator; 14 – belt transporter; 15 – sieves system; 16 – silos of fractionated inert filler; 17 – tape scales; 18 – moisture and temperature gauge; 19 – water heater; 20 – meter for water flow measuring; 21 – water mixing valve; 22 – chemical additive container; 23 – centrifugal pump; 24 – concrete truck

CONCLUSIONS

1. Biomass fly ash is not homogeneous and does not have pozzolanic properties, but at the early stage of hydration of the Portland cement, their addition causes a shorter induction period of hydration and accelerates the recrystallization of ettringite to monosulfohydroaluminate (AFm). It was found that this additive significantly reduces the compressive strength of standard OPC samples after 7 and 28 days hardening. Therefore, the untreated biomass fly ash is not suitable for use as an additive in the Portland cement.
2. Tribochemically activated biofuel fly ash (AFA) performs the function of microfill during the Portland cement hydration and acts as a center of crystallization. Due to it, the hydration process of cement minerals is accelerated, and the compressive strength of the samples is increased. Additionally, the AFA additive accelerates the recrystallization of ettringite into the AFm. The activated biomass fly ash can be used as an additive for the Portland cement, as the samples with up to 15% of cement replacement by the AFA additive exhibited a greater compressive strength.
3. Activated biomass fly ash additive inhibits the reaction of alkali and active silicon dioxide and harmful expansion of samples, as in the early stages of hydration in samples with the AFA additive, the permeability to aggressive liquids of the cementitious stone decreases, and at the same time, the decomposition of the cement stone structure is blocked due to the faster formation of cement hydrates.
4. AFA increases the resistance of cement stone to the sulfate attack as in the samples with the AFA additive the calcium aluminate hydrates, which are the cause of sulfate attack, are less common. Moreover, the addition of AFA slows down the calcium silicate hydrate decalcification process during the sulfate attack, as the ash additive is strongly alkaline ($\text{pH} = 12.89$), and it supplies an additional amount of alkali in the cement system.
5. AFA accelerates the initial slag cement hydration process and activates the latent hydraulic properties of granular blast furnace slag. During the hydration process of the slag cement with the AFA additive, more gismondine and calcium silicate hydrates are formed, which compensate the dilution effect of the binding material (OPC). In the samples of slag cement with the AFA additive, the pozzolanic reaction proceeds slow and occurs in the later period of hardening.
6. New compositions of the composite cements are developed, and technological recommendations for the use of biomass fly ash additive are proposed, according to which the biomass fly ash utilization in the Portland cement and slag cement production would allow to reduce the CO_2 emissions up to 12.5 million cubic meters per year and/or consumed biomass fly ashes, which are currently landfilled.

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REZIUOMĖ

Temos aktualumas

Šiomis dienomis intensyviai vystantis statybos pramonei, pastoviai auga įvairių rišamųjų medžiagų poreikis. Daugiausiai pasaulyje yra suvartojama betono, kuriam gaminti naudojamas cementas. Cemento pramonė pasižymi itin didelėmis energijos sąnaudomis ir didele oro tarša išmetamu anglies dioksidu bei kitais degimo produktais. Siekiant sumažinti aplinkos taršą ir patenkinti vartotojų poreikius, ieškoma naujų alternatyvų įprastiniam portlandcemenčiui.

Kita vertus, griežtėjant ES aplinkos ir oro taršos mažinimo taisyklių reikalavimams (2008/50/EB), vis plačiau naudojami atsinaujinantys energijos šaltiniai bei ieškoma naujų pramoninių atliekų antrinio panaudojimo galimybių. Vienas iš šių šaltinių yra biokuras, kurio deginimo metu regeneruojama šilumos energija. Didėjant biokuro panaudojimo apimtims, susiduriama su kita problema – biokuro lakiųjų pelenų utilizavimu. Nepaisant to, kad pelenų sudėtyje yra gausu mikro- ir makroelementų, naudingų augalų augimui, tačiau dėl sunkiųjų metalų buvimo atliekoje, dirvožemių tręšimas biokuro pelenais yra ribojamas ir atlieka kaupiama sąvartynuose. Biokuro lakieji pelenai galėtų būti panaudojami kaip mineralinis priedas ar aktyvatorius/rišiklis cemento pagrindu pagamintose rišamosiose medžiagose, tačiau, kaip pabrėžia daugelis tyrėjų, dėl didelės biokuro žaliavos įvairovės ir deginimo metu taikomo skirtingo technologinio proceso, pelenų sudėtis kinta ir kiekvienu atveju reikalingi išsamūs tyrimai.

Viena iš alternatyvų įprastiniam portlandcemenčiui yra šlakinis cementas. Šios rūšies cementas yra plačiai naudojamas gaminti betonams, kuriems keliami padidinto atsparumo cheminiam poveikiui reikalavimai arba kaip rišamoji medžiaga masyvių konstrukcijų gamyboje. Be to, granuliuoto aukštakrosnių šlako panaudojimas šlakinio cemento gamyboje sąlygoja mažesnes energijos sąnaudas ir CO₂ emisiją į aplinką. Tačiau ši technogeninė atlieka pasižymi latentinėmis hidraulinėmis savybėmis dėl joje esančios amorfinės dalies (stikliška būseną). Aukštakrosnių šlako hidrauliniam aktyvumui padidinti atlieka yra malama ir naudojami aktyvatoriai – šarminės medžiagos (natrio silikatas, natrio hidroksidas), sulfatai ir kt. Biokuro lakiųjų pelenų sudėtyje yra šarminių oksidų, todėl tikėtina, kad pelenų priedas šlakiniame cemente galėtų destabilizuoti šlako stikliškąją dalį hidratacijos metu be papildomo šlako aktyvavimo kitais cheminiais reagentais. Toks biokuro lakiųjų pelenų ir granuliuoto aukštakrosnių šlako kompleksinis panaudojimas sudėtiniuose cementuose ir jų tarpusavio sąveika bei sinerginis poveikis cemento hidratacijos eigai ar cemento akmens stiprumui beveik nėra tyrinėtas.

Taigi, biokuro lakiųjų pelenų panaudojimas mineraliniu priedu portlandcemenčiui ar jų pritaikymas šlakinio cemento hidratacijos aktyvinimui

leistų atrasti naujas biokuro lakiųjų pelenų panaudojimo galimybes bei sumažinti aplinkos taršą.

Darbo tikslas ir uždaviniai

Darbo tikslas – nustatyti biokuro deginimo metu susidarančių lakiųjų pelenų priedo įtaką portlandcemenčio ir šlakinio cemento hidratacijai, fiziniams ir mechaniniams savybėms, bei sukurti naujas kompozitinių cementų rūšis.

Siekiant užsibrėžto tikslo reikėjo išspęsti šiuos uždavinius:

1. Ištirti biokuro lakiųjų pelenų cheminę, mineralinę ir granulimetrinę sudėtis, pelenų morfologiją bei pucolaninį aktyvumą;
2. Ištirti biokuro lakiųjų pelenų priedo įtaką portlandcemenčio hidratacijai ir fiziniams bei mechaniniams savybėms;
3. Sukurti biokuro lakiųjų pelenų aktyvavimo metodą ir ištirti aktyvuotų biokuro lakiųjų pelenų priedo įtaką portlandcemenčio hidratacijai ir fiziniams bei mechaniniams savybėms;
4. Ištirti aktyvuotų biokuro lakiųjų pelenų priedo įtaką portlandcemenčio akmens atsparumui šarminei bei sulfatinei korozijai;
5. Ištirti aktyvuotų biokuro lakiųjų pelenų priedo įtaką šlakinio cemento hidratacijai ir fiziniams bei mechaniniams savybėms;
6. Pasiūlyti biokuro lakiųjų pelenų priedo panaudojimo technologines rekomendacijas.

Mokslinis naujumas

1. Nustatyta, kad tribochemiškai aktyvuoti ir paruošti kaip mikroužpildas biokuro lakieji pelenai portlandcemenčio hidratacijos metu spartina jo mineralų hidratacijos procesą bei didina cemento akmens bandinių stiprį gniuždant, atsparumą šarminei ir sulfatinei korozijoms.
2. Nustatyta, kad aktyvuoti biokuro lakieji pelenai šlakiniam cimente ne tik pagreitina šio hidratacijos procesą, bet ir aktyvina granuliuoto aukštakrosnių šlako latentines hidraulinės savybes.

Praktinė vertė

Sukurtos naujų kompozitinių cementų rūšys bei pasiūlytos biokuro lakiųjų pelenų priedo panaudojimo technologinės rekomendacijos, kuriomis remiantis biokuro lakiųjų pelenų panaudojimas portlandcemenčio ir šlakinio cemento gamyboje per metus leistų iki 12,5 mln. m³ sumažinti CO₂ emisiją į aplinką ir būtų sunaudojami šiuo metu į sąvartynus išvežami biokuro lakieji pelenai.

Ginamieji disertacijos teiginiai

1. Neturintys pucolaninių savybių tribochemiškai aktyvuoti biokuro lakieji pelenai gali būti paversti efektyviu mikroužpildu, kuris spartina portlandcemenčio ir šlakinio cemento mineralų hidratacijos procesą ir didina

cemento akmens stiprį gniuždant.

2. Aktyvuoti biokuro lakieji pelenai aktyvina granuliuoto aukštakrosnių šlako latentines hidraulines savybes ir skatina gismondino bei kalcio hidrosilikatų susidarymą kietėjančioje sistemoje.

IŠVADOS

1. Biokuro lakieji pelenai yra nehomogeniški ir neturi pucolaninių savybių, tačiau veikia kaip kristalizacijos centrai ankstyvojoje portlandcemenčio hidratacijos stadijoje sutrumpindami hidratacijos indukcinį periodą ir paspartindami etringito persikristalinimą į monosulfohidroaluminatą (AFm). Biokuro lakieji pelenai žymiai sumažina standartinių portlandcemenčio bandinių stiprį gniuždant po 7 ir 28 parų kietėjimo, todėl nėra tinkami naudoti kaip priedas portlandcemenčiui.
2. Tribochemiškai aktyvuoti biokuro lakieji pelenai atlieka mikroužpildo funkciją portlandcemenčio hidratacijos metu ir veikia kaip kristalizacijos centrai, spartindami portlandcemenčio mineralų hidratacijos procesą bei didindami bandinių stiprį gniuždant. Be to, aktyvuotų lakiųjų pelenų priedas (ABLP) pagreitina etringito persikristalinimą į AFm. Aktyvuoti biokuro lakieji pelenai gali būti naudojami kaip priedas portlandcemenčiui, nes iki 15 % portlandcemenčio pakeitus ABLP priedu cemento akmuo pasižyminti didesniu stipriu gniuždant.
3. Aktyvuotų biokuro lakiųjų pelenų priedas slopina šarmų ir aktyvaus silicio dioksido reakcijos vyksmą ir žalingą bandinių plėtimąsi, nes ankstyvojoje hidratacijos stadijoje bandiniuose su ABLP priedu vykstant spartesniam portlandcemenčio hidratų susidarymui, mažėja cemento akmens pralaidumas agresyviems skysčiams ir tuo pačiu stabdomas cemento akmens struktūros ardymas.
4. ABLP priedas didina cemento akmens atsparumą sulfatinei korozijai, nes bandiniuose su ABLP priedu susidaro mažiau kalcio aluminatų hidratų, kurie yra sulfatinės korozijos priežastis. Pridedami ABLP sulėtina kalcio hidrosilikatų dekalifikacijos procesą sulfatinės atakos metu, nes tiriamieji pelenai yra stipriai šarminiai (pH=12,89), todėl į kietėjančią cementinę sistemą patenka papildomas kiekis šarmų.
5. Aktyvuoti biokuro lakieji pelenai pagreitina pradinės šlakinio cemento hidratacijos procesą ir aktyvina granuliuoto aukštakrosnių šlako latentines hidraulines savybes. Šlakinio cemento su ABLP priedu hidratacijos metu susidaro daugiau gismondino ir kalcio hidrosilikatų, kurie kompensuoja portlandcemenčio praskiedimo poveikį. Šlakinio cemento su ABLP priedu bandiniuose pucolaninė reakcija vyksta lėtai ir pasireiškia tik vėlesniu kietėjimo laikotarpiu.
6. Sukurtos naujos kompozicinių cementų sudėtys ir pasiūlytos biokuro lakiųjų pelenų priedo panaudojimo technologinės rekomendacijos, kuriomis

remiantis biokuro lakiųjų pelenų panaudojimas portlandcemenčio ir šlakinio cemento gamyboje leistų iki 12,5 mln. m³/metus sumažinti CO₂ emisiją į aplinką ir/arba būtų sunaudojami šiuo metu į sąvartynus išvežami biokuro pelenai.

UDK 666.942.022.3:666.952+666.943.022.3:666.952](043.3)

SL344. 2018-04-16, 2,5 leidyb. apsk. I. Tiražas 50 egz.

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