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The ash from fluidized bed combustion as a donor of sulfates to the Portland clinker

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Abstract

The paper deals with possibilities of using solid residues from fluidized bed combustion of coal, bed and filter ash in the production of composite Portland cements. The ash from fluidized bed combustion contains a high amount of CaO, in the form of free lime or $CaSO_4$ (anhydrite), so it could be used as a possible donor of sulfates to the Portland clinker instead of usually used gypsum. At first, the chemical composition of collected ashes was determined by X-Ray Fluorescence and the ongoing hydration process was monitored by isoperibolic calorimetry. Then samples containing mixtures of Portland clinker and ash were prepared. Their respective compressive strength and flexural strength were analyzed and observations were made on the hydration and composition of products of the hydration reaction detected by X-Ray diffraction. Finally, the results of selected mixtures were verified with prepared standardized mortars.

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Keywords: Portland clinker; fluidized bed combustion ash; compressive strength; flexural strength; reaction of hydration.

1. Introduction

The main fossil fuel for production of the electric energy in thermal power plants is coal. During a combustion process, a high amount of solid residues is formed. Chemical, physical and mineralogical properties of the residues differ depending on a type of coal and a type of combustion process [1,2,3]. There are two main types of the combustion process, a high-temperature combustion and a fluidized bed combustion [4]. The advantage

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of the fluidized bed combustion is that the desulfurization process is situated in a boiler. On the other hand at high-temperature combustion special technological equipment is needed, because desulfurization is situated after the combustion process [5,6,7,8]. Limestone ($CaCO_3$) is added directly to the boiler as a desulfurization additive. The calcium sulfate ($CaSO_4$) is formed by the reaction of the limestone particles with sulfur dioxide (SO_2). The solid residues from the fluidized bed combustion contain noncombustible constituents of coal and products of desulfurization, so particles of $CaSO_4$ [9]. The high amounts of SO_3 and CaO are the reason why fluidized bed combustion ashes differ from high-temperature combustion ashes. For that matter fluidized bed combustion ashes should not be used as an additive to concrete [10].

There are some studies where hydration behavior and properties of mixtures prepared from cement and fluidized bed combustion fly ash were observed [11,12]. Ash was added in small amounts and as a replacement of high temperature fly ash. In both cases the addition of ash caused the increase in mechanical properties.

The main additive, which is mixed with Portland clinker to make Portland cement, is gypsum ($CaSO_4{\cdot}2H_2O$). It retards hydration of C_3A ($3CaO{\cdot}Al_2O_3$, tricalcium aluminate), one of the main phases of cement, and allows workability of Portland cement. In this work, the fluidized bed combustion ash is added to the Portland clinker as a donor of sulfates and also as partially substituent of the clinker. Using the secondary raw materials in the production of cement has ecological and economic advantages [13]. In mixtures presented in this work mass ratio between the clinker and the ash from 90:10 to 10:90 was applied. Fluidized bed combustion ashes, bed and filter ashes, from two thermal power plants in The Czech Republic, was used. The mechanical properties and the process of hydration reaction were monitored on the prepared mixtures.

2. Experimental

2.1. Methods

Saccharate method was used to determine a content of free lime in collected ashes. A sample of ash was mixed with saccharose and water. The mixture was filtered and a filtrate was titrated by hydrochloric acid solution on phenolphthalein. The content of free lime (CaO) was calculated according to the formula:

$$\%\ CaO = \frac{c \cdot V \cdot M}{m \cdot v} \tag{1}$$

where c is a concentration of hydrochloric acid solution ($mol{\cdot}dm^{-3}$), V is a volume of the hydrochloric acid solution (dm^3), M is a molar weight of CaO ($g{\cdot}mol^{-1}$), m is a weight of the sample of ash (g), v is a stoichiometric ratio of reaction.

Mechanical properties, compressive and flexural strength, were measured on the complex device for strength tests on building materials DESTTEST 3310 (Betonsystem). Flexural and compressive strength were measured on each testing prism. Dimensions of prisms from pastes were 20×20×100 mm, and from mortars 40×40×160 mm. Prisms were preserved in a humid environment. Strengths were measured after 1, 7 and 28 days.

The process of hydration reaction was observed by isoperibolic calorimetry, on a device constructed and placed in FCH BUT (Faculty of chemistry, Brno University of technology). Immediately after stirring the mixture, 300 g of it were placed in a polystyrene cup, which was enclosed in thermo-insulation foam container and a thermocouple for measuring temperature during hydration reaction was embedded into the testing mixture. The measurements were ended after 30 hours when the temperature was almost constant.

2.2. Material

Bed and filter ashes from fluidized bed combustion (power plants Tisová and Poříčí K8, The Czech republic) and the Portland clinker (Mokrá, HeidelbergCement, The Czech republic) were used for preparation pastes and standardized mortars. Bed ashes and Portland clinker were fine grounded. To mortars, the standardized fine, medium and coarse sand (ČSN 196-1) was used.

The chemical composition of used ashes was examined by X-Ray fluorescence on the device Xenemetric EX-6600 SSD and is given in Table 1. The content of free lime (CaO) in ashes was determined by saccharate method and is given in Table 2.

Table 1. The chemical composition of used ashes.

Major oxides (%)	Tisová		Poříčí K8	
	Bed ash	Filter ash	Bed ash	Filter ash
SiO_2	31.1	33.9	30.0	31.2
Al_2O_3	21.7	22.4	15.1	16.5
CaO	28.1	22.8	29.1	31.2
Na_2O	0.34	0.66	0.26	0.40
K_2O	0.81	0.67	1.48	1.38
MgO	0.47	0.85	0.82	0.90
SO_3	7.77	5.19	16.10	8.80
Fe_2O_3	3.46	7.17	5.41	7.48
TiO_2	5.45	5.41	1.21	1.53
P_2O_5	0.26	0.31	0.14	0.19

Table 2. The content of free lime in used ashes.

	Tisová		Poříčí K8	
	Bed ash	Filter ash	Bed ash	Filter ash
Content of free lime (*wt.%*)	22.94	9.68	9.57	13.54

2.3. Samples composition

Four series of mixtures were prepared. The composition of mixtures in each series was the same (Table 3), they differ in a type of ash added. Following ashes were used: bed ash from fluidized bed combustion from power plant Tisová (TB), filter ash from power plant Tisová (TF), bed ash from power plant Poříčí K8 (PB), filter ash from power plant Poříčí K8 (PF). The amount of water added to various mixtures was determined from consistency of the paste, made from clinker and water with water to binder ratio 0.35. The water to binder ratio (w/b) is the ratio between the total amount of water (*g*) and the total amount of binder (*g*), which is the sum of an amount of the ash and the clinker used in pastes or mortars.

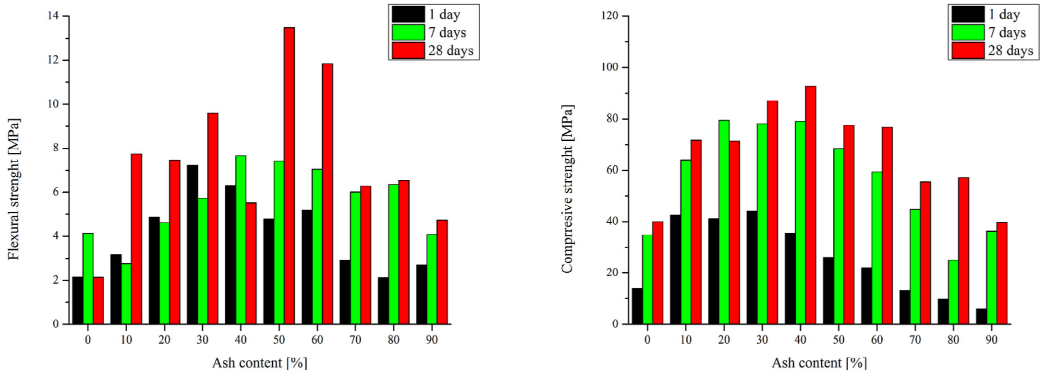
Table 3. The composition of mixtures.

Sample	CL	A	B	C	D	E	F	G	H	I
Ash (*wt.%*)	0	10	20	30	40	50	60	70	80	90
Clinker (*wt.%*)	100	90	80	70	60	50	40	30	20	10

The clinker to ash ratio in mortars was same as in pastes. Fine, medium and coarse sand was used to prepare mortars. The types of sand were in ratio 1:1:1. The sand to binder ratio in mortars was 3:1.

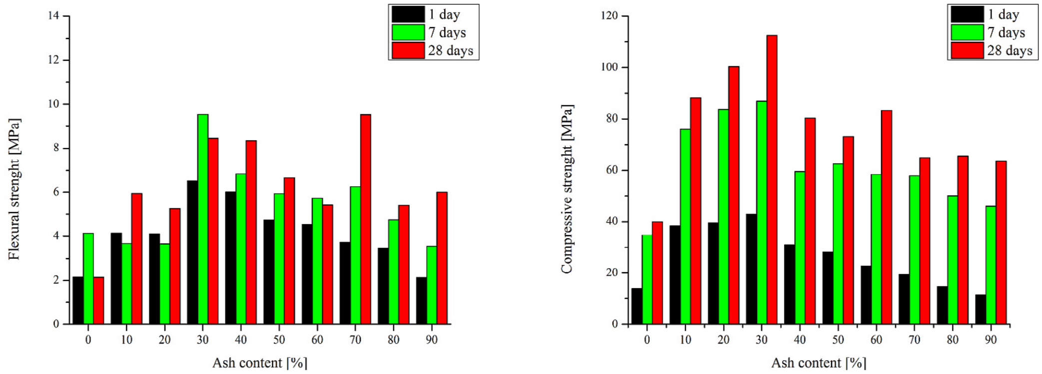
3. Results and discussion

The time dependence of compressive and flexural strengths of the pastes prepared from the Portland clinker and fluidized bed combustion ashes measured on testing prisms after 1, 7 and 28 days are presented in Fig. 1, Fig. 2, Fig. 3 and Fig. 4.



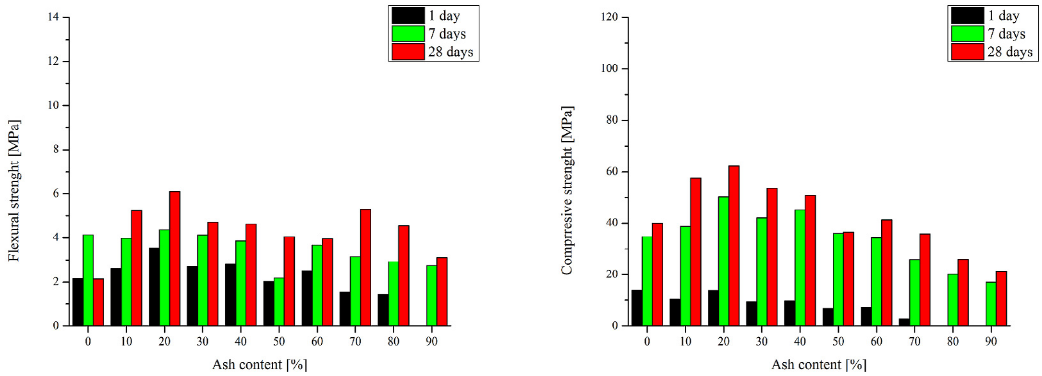
(a) (b)

Fig. 1. Dependence of flexural (a) and compressive (b) strength of pastes with TB on time.



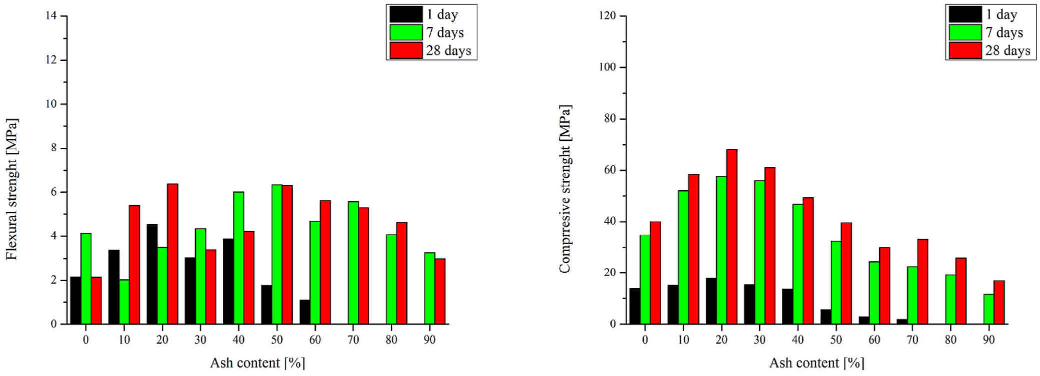
(a) (b)

Fig. 2. Dependence of flexural (a) and compressive (b) strength of pastes with PB on time.



(a) (b)

Fig. 3. Dependence of flexural (a) and compressive (b) strength of pastes with TF on time.



(a) (b)

Fig. 4. Dependence of flexural (a) and compressive (b) strength of pastes with the PF on time.

Generally, we can say, that reached strengths increase with increasing time of curing and the highest values reached the pastes with a content of ash from 10–50 wt.%.

Flexural strengths of all pastes made with bed ash from Tisová (Fig. 1) after 28 days exceeded value 6 MPa. The highest value was measured on the mixture with the content of ash 50 wt.% and it is almost 14 MPa. The compressive strengths (Fig. 1) of all pastes after 28 days were higher than the compressive strength of clinker itself. This fact is due to an absence of sulfate ions, which are needed to form ettringite, as is also described in work of Quennoz,et al. [14]. The values of the compressive strength of all pastes after 28 days were higher than 40 MPa, the highest values exceeded 80 MPa. The strengths increased with growing quantity of ash, but after they exceeded the 40 wt.% content of ash the strengths were decreasing. The amount of added ash is equal to 3% content of sulfates in the mixture, what is the optimal quantity which positively influenced the compressive strength of cement paste prisms, as also published Lerch [15]. So we suggest the similar mechanism in the strength development due to the addition of fluidized bed combustion fly ash to the clinker in corresponding amounts.

Navazze et al. [16] also deals with an addition of fluidized bed combustion ash to the Portland cement. They observed that the strengths of pastes made with the addition of ash were after 91 days higher than the cement itself. The increase was caused by added amount of free lime. Our experiments show higher strengths for pastes with addition of ash with lower amount of free lime (Poříčí), so the effect of addition of free lime to clinker is probably opposite compared to the cement.

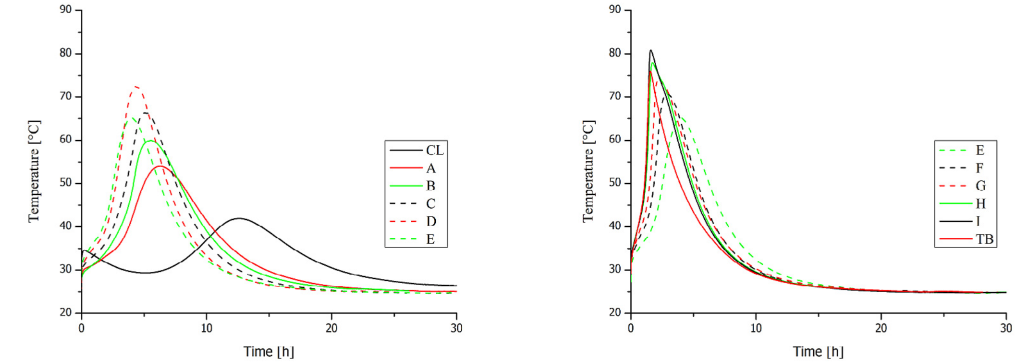
The values of flexural strengths of the pastes made with bed ash from Poříčí K8 (Fig. 2) were after 28 days between 5 and 10 MPa. So they were slightly lower compared to the pastes with ash from Tisová. The values of compressive strengths (Fig. 2) were for all pastes higher than 60 MPa, and the highest measured value was 112 MPa, i.e. for paste with 30% content of ash. In comparison to bed ash from Tisová, Poříčí bed ash has higher content of sulfates (Table 1) so the quantity of added ash needed to reach an optimum amount of sulfates and the highest strengths is lower. Again, strengths of all pastes are significantly higher than the strength of the clinker, which is caused by the absence of sulfate ions [15].

The usage of filter ash to prepare pastes entails lower values of strengths. Pastes made with fluidized bed combustion filter ash from power plant Tisová (Fig. 3) had after 28 days flexural strengths about 4–5 MPa, the highest value was 6 MPa, for paste with the content of ash 20 wt.%. The same paste has the highest value of the compressive strength, 62 MPa after 28 days.

Pastes made from filter ash from power plant Poříčí K8 (Fig. 4) had comparable values of the flexural strength to pastes with filter ash from Tisová. The compressive strengths are comparable too. Lower strengths then clinker had pastes with the content of ash higher than 50 wt.%.

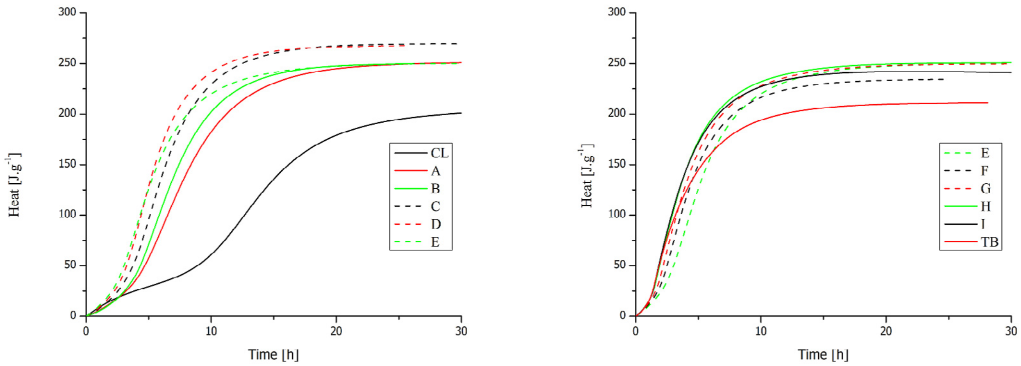
The lower values of strengths of mixtures with filter ashes are probably due to slightly different chemical composition and the higher amount of water needed to prepare the mixture with demanded consistence.

Mixtures with the highest content of bed ash and the highest strength were selected for tests on mortars. The measured values showed the same trends as in pastes. Flexural strengths of mortars after 28 days were about 7 MPa. Compressive strengths were about 40 MPa, what is due to the high content of fly ash satisfactorily.



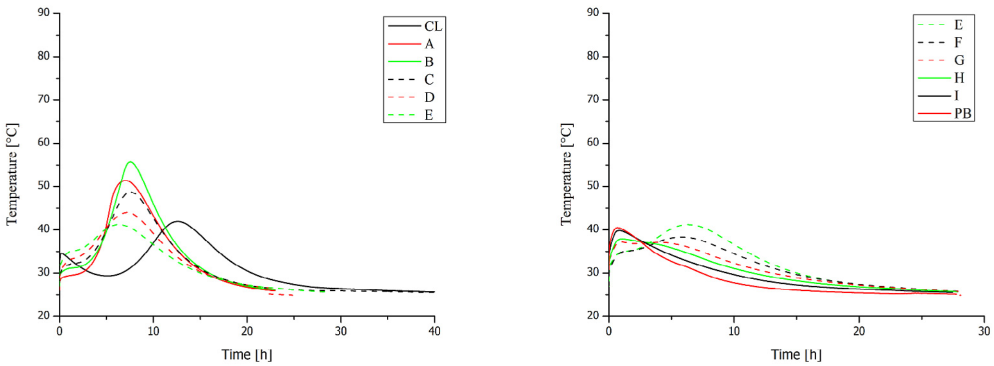
(a) (b)

Fig. 5. Differential calorimetric curves of pastes with 0–50% (a) and 50–100% (b) content of the TB.



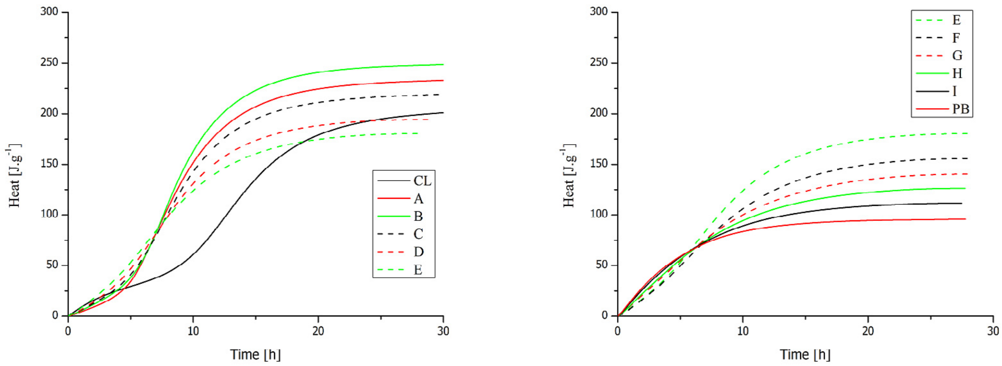
(a) (b)

Fig. 6. Integral calorimetric curves of pastes with 0–50% (a) and 50–100% (b) content of the TB.



(a) (b)

Fig. 7. Differential calorimetric curves of pastes with 0–50% (a) and 50–100% (b) content of the PB.



(a) (b)

Fig. 8. Integral calorimetric curves of pastes with 0–50% (a) and 50–100% (b) content of the PB.

The calorimetric curves presented on Fig. 6 and Fig. 8 show, that process of hydration of ashes is dependent on the content of free lime, which exothermally reacts with water. The experimental data were in good agreement with data published here [17]. The temperature and the heat of hydration increase with the increasing content of free lime. So, the bed ash from power plant Tisová (TB) achieved during hydration reaction higher temperature and higher amount of heat in comparison to bed ash from Poříčí K8 (PB).

The maximum reached temperature (Fig. 5) increases with the increasing amount of the fly ash in the mixture. For the mixture with 90% content of fly ash the temperature was higher than for the pure fly ash. The total released heat for all pastes made with bed ash from Tisová (Fig. 6) was similar and was higher than for the pure ash and the pure clinker.

The behavior of cement mixtures was published elsewhere [17,18,19]. They studied hydration reaction of mixtures made from cement and fluidized bed combustion ash and observed that the increasing addition of ash conversely caused the retardation of hydration.

The Fig. 7 and Fig. 8 show that the maximum reached temperature and the total released heat for pastes made with bed ash from Poříčí K8 decrease with increasing amount of the bed ash. It is due to the fact, that the total released heat for the pure bed is about two times lower than for the pure clinker.

4. Conclusion

The work was focused on the utilization of fluidized bed combustion fly ash from two thermal power plants in The Czech republic as a donor of sulfates.

From the experimental observations, the highest values of compressive strengths were measured on pastes with the ash content from 20 to 60 wt. %. Inconsiderable high values of strength reached mixtures with a higher ash content. The strengths were more than 60 MPa. These values were measured on the mixtures containing 80 wt.% of ash, too. The highest value of compressive strength was measured on pastes with 30% content of fluidized bed combustion fly ash from power plant Poříčí K8 and it reached 112 MPa after 28 days.

When the filter ash was used, the highest values of compressive strength reached mixtures with the content of ash from 20 to 40 wt.%. The compressive and flexural strengths measured on the pastes with filter ashes were lower in comparison with the mixtures with bed ashes. The larger surface area of filter ash caused need of higher volumes of mixing water, which could be a possible disadvantage of their application.

From measured calorimetric curves, we can see the affected process of hydration reaction of ashes by the content of free lime. Mixtures made using bed ash from Tisová reached the similar values of total released heat. The released heat of bed ash from Poříčí was about two times lower than released heat for the Portland clinker. We can also see the dependence of ash content on the calorimetric measurements. So the released heat and the maximum reached temperature decreased when the content of ash increased.

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