



Effects of high-temperature fly ash and fluidized bed combustion ash on the hydration of Portland cement



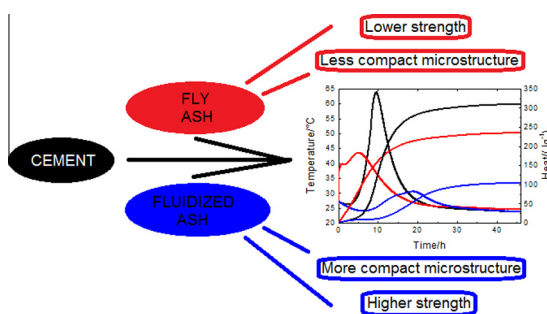
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HIGHLIGHTS

- This work is aimed at the comparison of the fly and fluidized bed combustion ash.
- For fluidized, another peak appears on the calorimetric curve.
- Another peak is mainly due to reaction of free lime.
- The hydration can be slowing down or accelerating by different ash.
- Some pastes with fluidized ash have better strengths than pure PC.

GRAPHICAL ABSTRACT



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ABSTRACT

This work is aimed at the comparison of the effects of high-temperature fly ash and fluidized bed combustion ash on the hydration of Portland cement and compressive strength of resulting materials. Two samples of high-temperature fly ash (FA), one sample of fluidized bed combustion ash (FBCA) and one sample of fluidized filter ash (FFA) were selected for this work. The pastes were prepared with the same water-to-binder ratio (0.4). The replacement of cement was 10, 20, 40 and 60 wt.%. The influence of ashes on the hydration of ordinary Portland cement (OPC) was measured by means of isoperibolic calorimeter. The compressive strength was determined after 1, 7 and 28 days of curing. The hydration slows down with increasing amount of fly ash, due to lower reactivity of FA compared to OPC. For fluidized ash, the hydration is accelerated through free lime. When comparing calorimetric curves with mechanical properties, it was found out that for the pastes with the same OPC replacement, the samples with the highest developed heat also achieved the highest strength after one day of hydration. After 28 days of hydration some samples achieved even higher strength than OPC paste.

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1. Introduction

Portland cement is a hydraulic binder produced by grinding cement clinker and minor amounts of gypsum [1]. Clinker phases are tricalcium silicate (abbr. $C_3S - 3CaO \cdot SiO_2$ or Ca_3SiO_5 , alite), dicalcium silicate (abbr. $C_2S - 2CaO \cdot SiO_2$ or Ca_2SiO_4 , belite), tricalcium aluminate (abbr. $C_3A - 3CaO \cdot Al_2O_3$ or $Ca_3Al_2O_6$, celite) and

calcium aluminoferrite (abbr. $C_4AF - 4CaO \cdot Al_2O_3 \cdot Fe_2O_3$ or $Ca_4Al_2Fe_2O_{10}$, brownmillerite) [2]. Sulphate ions from gypsum ($CaSO_4 \cdot 2H_2O$) influence the reaction kinetics of C_3A and $Ca(OH)_2$ (CH, portlandite), to form ettringite ($C_6A\bar{S}_3H_{32}$), associated with the retarding effect. In the absence of $CaSO_4$ or other regulators of setting, C_3A responds to hydration very quickly to form stable C_3AH_6 , which results in too rapid, so-called “quick” setting. In contrast there is a “false” setting in the case of large content of sulphate ions compared to aluminate ions [3,4].

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The pozzolanic activity is characterized by the activation of pozzolans through cement hydration. During the hydration process, up to 28 wt.% of ordinary Portland cement is converted to calcium hydroxide [5–7]. Indeed, amorphous SiO_2 contained in the pozzolan reacts with calcium hydroxide in water to form hydrated calcium silicates [1,8]. From the family of pozzolanic materials the most commonly used for many construction applications are fly ash (FA), granulated blast furnace slag, silica fume, etc. [9–11]. Also, the use of fly ash as a cement replacement reduces the overall CO_2 footprint of concrete [10].

There are different types of fly ash resulting from the coal source and combustion technology. They can be divided into two groups: high-temperature fly ash and ash from fluidized bed combustion [12].

Fly ash is the by-product of the combustion of pulverized coal and is collected by mechanical and electrostatic separators from fuel gases of power plants where coal is used as fuel. The disposal of fly ash is one of the major environmental issues as dumping of fly ash as a waste material may cause severe environmental problems/hazards. The combustion of pulverized coal requires subsequent flue gas desulphurisation, which is performed with lime or limestone and the product is mostly calcium sulphate dihydrate (gypsum) [13,14].

Fluidized-bed-combustion (FBC) ash is a by-product from coal-fired power plants which shall economically reduce air emissions to meet requirements of the Clean Air Act. The principle of fluidized bed combustion technology is the combustion of coal with sorbent, which is added to the combustion chamber according to the sulphur content in coal. Ground limestone is often used for the purpose of sorbent. This is the reason for higher content of CaO in these types of ash. The combustion proceeds at the temperature of about 850 °C [15,16]. The physical and chemical composition of fluidized ashes is similar to that of Portland cement, however the resulting materials attain only low compressive strengths thus they are used just as pozzolan in concrete applications.

Ash from fluidized combustion of coal comes from bed (fluidized bed combustion ash FBCA) and filter (fluidized filter ash, FFA). Coarse bed ash falls through the fluid ring grate during combustion. The particles have higher mass and larger size. This ash contains higher amount of soft burnt lime and anhydrite. Filter ash consists of small light particles which are entrained with combustion flue gas to the chimney section. They are separated from the flue gas on electric precipitators [12].

The essential differences between these types are mainly higher content of SO_3 , highly reactive free CaO and sometimes higher loss on ignition of ash from fluidized bed combustion. While traditional high-temperature FA has mostly only pozzolanic activity, fluidized ash can set and harden by simple mixing with water without any other additives and ingredients. The binding properties of fluidized ash depend mainly on the amount of present anhydrite and free lime which was softly burnt in the process of coal combustion and therefore is highly reactive [12,15–17].

Fluidized ash cannot be applied according to EN 450-1 (European Committee for Standardization, 2005, [18]) because it does not meet either the basic definition or the characteristics of FA in concrete or required technical criteria. The use of fluidized ash for concrete is not allowed according to EN 206-1 (European Committee for Standardization, 2000, [19]), but this ash may be used for example as a replacement of gypsum [15,20].

The application of FA in concrete brings thermodynamically favorable surface for the crystallization of portlandite, hence resulting in “smoother” microstructure, which can contribute to higher strength of resulting material [21]. Other positive effect is the improvement of workability, abrasion, heat evolution, shrinkage and chemical resistance of resulting concrete [22].

An important property of all hydraulic binders is the release of heat during the reaction with water [23,24]. The measurement of heat evolution by isoperibolic calorimeter can monitor all reactions occurring during hydration in real time and in real conditions [24–26]. Despite high complexity of cement system, the data obtained from calorimetric measurements provide an indispensable insight which can be used to characterize the behavior of different kinds of cements or other binders and especially of their mixtures with different constituents [26].

The effect of FA on hydration reactions can be characterized by the delay of hydration [27] and reduced intensity of heat evolution rate compared to OPC. Nevertheless, increased content of fly ash and higher water-to-binder ratio (w/b) result in a prolongation of setting time of the mixture [28]. The decrease of total amount of released heat [29] prevents massive constructions from thermal cracking.

The present article is aimed at the study of the effects of high-temperature fly ash (FA) and both types of fluidized ash (FFA and FBCA) on the hydration of Portland cement. Also, the comparison of their influence on the compressive strength of the resulting material is presented. Although, some of these materials (FA) are currently in use, the lack of information about them is still large. Especially the potential for relevant applications of fluidized bed combustion ash is still searched. New knowledge about the behavior of these materials in combination with cement may help enhance current applicability and assist in the search for new applications of these materials.

2. Methods

2.1. Isoperibolic calorimetry

The data were collected by isoperibolic calorimeter constructed and placed at FCH BUT (Faculty of Chemistry, Brno University of Technology) and the resulting heat was obtained by numerical integration and by multiplying by the integration constant of calorimeter which was obtained from calibration. The construction of used calorimeter was based on the work [30]. This kind of calorimeter was primarily developed by German Academy of Sciences in Halle. In this work an upgraded version with 16 cells was used. The detailed description of this calorimeter is reported in [26].

The calculation of heat generated during the hydration of cement paste enables to make some presumptions – the uncertain one is that the heat capacity of the system (H_2O and cement) does not change during the experiment due to either the temperature change or the physico-chemical changes in the system. In [31], this assumption is used in the calculation of temperature change of concrete. This presumption makes it possible to neglect the influence of heat capacity of the system if the temperature of starting material and the temperature at the end of experiment are equal.

The quantitative determination of generated heat is possible thanks to the integration according to Tian equation [32].

2.2. Mechanical properties measurement

The mechanical properties of materials are often the key factor for their use in practice. The most frequently observed parameter is the compressive strength.

The prepared samples were tested for compressive strength using the press DESTTEST 3310 (Czech Republic). To keep the consumption of raw materials at low level, the tests were performed using the prisms with the dimensions of $20 \times 20 \times 100$ mm. The strengths were measured after 1, 7 and 28 days.

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