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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.