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The fungistatic properties and potential application of by-product fly ash from fluidized bed combustion

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HIGHLIGHTS

- Fluidized bed combustion ashes have fungistatic properties according to ČSN 72 4310.
- Pulverized coal combustion fly ash does not have fungistatic effect.
- Fungistatic fluidized bed combustion ashes possess potential for antimicrobial applications.

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ABSTRACT

The article deals with the evaluation of antifungal effect of Fluidized Bed Combustion Fly Ash (FBCFA) and Bottom Ash (FBCBA) by-products compared with the performance of conventional pulverized coal combustion fly ash (FA). The antifungal effects were evaluated using the procedure given in the Czech standard ČSN 72 4310. A blend of the *Aspergillus niger*, *Chaetomium globosum*, *Penicillium funiculosum*, *Paecilomyces variotii* and *Gliocladium virens* fungi was used in the experiments. The scale for the evaluating of mould resistance was from 0 to 5 depending on the degree of fungi growth, where a value of 0 means that there is zero growth of fungi and so the product possesses the fungistatic properties. Contrary to "conventional" FA which demomstrated the highest fungi growth degree of 5, the study confirms the attainment of fungistatic propeties by FBC by-products. I tis expected, that the incorporation of fungistatic ash can increase the antimicrobial properties of construction materials.

The literature review has revealed a number of potential applications for FBC ash in the construction industry including the production of cement mixtures, binders, geopolymers, mortars, concretes. However, there are no relevant standards for utilization of FBC ash in such applications.
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1. Introduction

There are many types of coal combustion boilers and combustion techniques employed by the power utilities [1]. The conventional combustion of pulverized coal in power plants is realized at a relatively high temperature of around 1200–1500 °C [2] or can even reach up to 1700 °C [3], resulting in elevated NO_X and SO_X emissions and generating solid residues called coal combustion products (CCP), which are further described as fly ash, bottom ash, boiler slag and flue gas desulfurization material. The bottom ash (BA) is commonly composed of relatively coarse ash particles collected from the bottom of boilers; slag is molten and cooled crystalline inorganic material and flue gas desulfurization material is commonly a mixture of gypsum ($CaSO_4{\cdot}2H_2O$) and calcium sulfite ($CaSO_3$). Fine and ultra fine particles of fly ash (FA) are composed mainly of amorphous or glassy aluminosilicates. The FA from the pulverized coal combustion (PCC) process are commonly in a form of glassy spheres, cenospheres and pleurospheres, due to high operating temperatures used in the boilers. This FA has pozzolanic activity [3] and complies with European standards EN 197–1 [4], EN 450–1 [5] and is classified by the American Specification ASTM C-618 [6] as Class F. The Class F FA types are suitable for cement production [4] and are commonly used as a supplementary cementitious or pozzolanic (type II) additives to concrete [5,7]. The EN 197-1 [4] defines two types of fly ash suitable for production of cements: siliceous fly ash (Class V) or calcareous FA (Class

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W). The former has pozzolanic properties; the latter may have, in addition, hydraulic properties, therefore it is considered as a supplementary cementitious material (SCM). Siliceous FA (V) is a fine powder with mostly spherical particles and consists essentially of reactive silicon dioxide (SiO_2) and aluminium oxide (Al_2O_3). Calcareous fly ash (W) consists essentially of reactive calcium oxide (CaO), reactive SiO_2 and Al_2O_3.

The EN 450-1 defines FA for concrete applications as a fine powder with mainly spherical, glassy particles possessing pozzolanic properties and consisting essentially of SiO_2 and Al_2O_3 with the content of reactive SiO_2 of at least 25%. The content of reactive calcium oxide (CaO) shall not exceed 10% and the content of free calcium oxide (CaO) shall not be greater than 2.5%. Furthermore, the sum of $SiO_2 + Al_2O_3 + Fe_2O_3$ shall not be less than 70% (similarly to ASTM C-618). Based on the loss on ignition (LOI), FA are further divided into three main classes such as Class A with max. 5% LOI, Class B with max. 7% and Class C with max. 9%. The ASTM C-618 [6] divides FA into two main classes. The first Class F is low-lime (pozzolanic) with a sum of $SiO_2 + Al_2O_3 + Fe_2O_3$ of at least 70%, the SO_3 content of max. 5%, LOI of max. 6% and available alkalis of max. 1.5%. The second type is high-lime Class C fly ash (self-cementing) with a sum of $SiO_2 + Al_2O_3 + Fe_2O_3$ of at least 50%, the SO_3 content of max. 5%, LOI of max. 6% and available alkalis of max. 1.5%.

To satisfy the environmental regulations, high NO_X emissions associated with the PCC process are commonly alleviated using the ammonia-based post combustion NO_X reduction system based on the reactions (1) and (2).

$$4NO + 4NH_3 + O_2 \rightarrow 4N_2 + 6H_2O \quad (1)$$

$$2NO_2 + 4NH_3 + O_2 \rightarrow 3N_2 + 6H_2O \quad (2)$$

The NH_3 used for effective NO_X reduction is an aggressive, irritating and toxic agent, and it is anticipated that a significant number of combustion units will be converted to either selective non-catalytic reduction (SNCR) or selective catalytic reduction (SCR) technologies. For PCC power plants, both techniques use either an ammonia NH_3 based or urea $CO(NH_2)_2$ based reagents. In all cases, some non-reacted ammonia (NH_3) reaches the stack with flue gases (ammonia slip) and much of NH_3 is deposited on fly ash in a form of ammonium salt formed by the reaction occurring with NH_3 and SO_3 from the flue gas [8]. The ammonium sulfate ($(NH_4)_2SO_4$) is a dry pulverous material whereas ammonium bisulfate (NH_4HSO_4) is a sticky, partially liquid material, which can easy adhere to surfaces and accumulate. There is a widespread concern that the presence of ammonia in FA can adversely affect the performance of fly ash in concrete [8]. Specifically, it was found that the compressive strength of mortar and concrete is decreased, and setting time of cement is delayed when the ammoniated fly ash is used, due to the impacts of aggressive ammonium and sulfate ions [8].

Ammonia-based NO_X reduction processes with an excess of applied ammonia can cause the contamination of FA with NH_3 to the levels of 50–300 ppm [9]. In order to assure an adequate performance, the NH_3 content should be less than 100 ppm [10]. For example, in Poland, there are strict NH_3 limits for fly ash at 50 mg/kg and for flue gas desulfurization gypsum at 10 mg/kg [11]. Non-reacted, redundant NH_3 further reacts with gaseous chlorides to form the ammonium chloride (NH_4Cl), which also creates the deposits on fly ash particles [11]. Therefore, the ammoniated FA can not be effectively utilized for cement and concrete and ammoniated gypsum can not be used for cement production and, therefore, these materials are often landfilled.

On the other hand, the circulating fluidized bed combustion (FBC) takes place at a much lower temperature within 800–900 °C [3]. This results in the reducing of NO_X emissions and finer fly ash and a coarser bottom ash. In this respect, the FBC technology is considered to be a more sustainable than conventional PCC method (in regard to the NO_X and SO_X emissions and also elimination of the ammonia-based post combustion NO_X reduction systems), therefore the FBC technology can be a preferred combustion technique in the future. However FBC technology results in some additional problems related to the utilization of fly ash and bottom ash. The fly ash form FBC differs from the PCC ash because it is not fused nor spherical, has a lower content of melt and a higher crystallinity. Furthermore, it is commonly high in a free lime (CaO) and calcium sulfate ($CaSO_4$) [12]. These properties are unambiguously caused by the attributes of the FBC technique [1]. Although FBC material is not covered by the standard specifications, it also contains glassy silicates, has a relatively high surface area and also has the potential to be both pozzolanic and cementitious [13].

The fly ash is routinely used for the production of cement according to EN 197-1 [4] and concrete according to EN 450-1 [5] and EN 206 [7]. Fly ash can be used in concrete as Type I additive, which is mainly inert component such as aggregate filler conforming to EN 12620 [14] or EN 13055-1 [15], or as Type II additive, which is pozzolanic component (an active material contributing to hydration reactions when it meets the requirements of EN 450-1). However, these applications are not allowed for FBC by-products.

The FBC CCPs have considerably higher content of reactive calcium oxide CaO, usually from 15 to 35% and sulphur trioxide SO_3 from 7 to 18%. The FBC ash has lower content of glass phase and higher LOI in comparison to PCC material. Due to chemical and mineralogical composition, and specifically, high content of reactive CaO and $CaSO_4$, the FBC products are characterized by the volume instability, and also interfere with setting and hardening process.

The disposal in landfills has been the most common approach for utilization of ash from the FBC boiler power plants [16]. However, a limited space and increased landfill operation costs, have stimulated the investigation work to develop and demonstrate the environmentally safe applications for these CCPs [17].

Coal combustion products (CCPs) including FBC by-products are utilized in coal mining including mine-filling and reclamation applications as well as for the recultivation and restoration purposes in open cast mines. The mining applications utilized about 52% of the total FBC ash mainly for filling of enclosed voids, mine shafts and subsurface mine workings [18]. The investigation of the long-term performance of CCP based grouts to reduce the acid production in pyrite-rich abandoned mines was performed using the mixtures with different proportions of Class F fly ash, flue gas desulfurization by-product, FBC by-product, and quicklime. A practical experience and cost analysis indicated that using FBC ash in mine grouting applications has definite advantages [19].

Therefore, FBC by-products have only limited practical utilization in building industry. A high degree of expansion occurs upon the hydration of blends with Portland cement; this results in the swelling, reduction of strength development and strength loss. However, construction applications have been identified as one of promising application area [16]. Typically, FBC ash cannot be used as a cement replacement in concrete due to high sulphur content. However, FBC ash can be used for other construction applications that require less stringent specifications including soil stabilization, road base, structural fill, synthetic aggregate and, furthermore, in the case of low free lime as a pozzolanic component for cement replacement [16]. There are the series of Czech Standards related to the application of FBC by-products in construction industry; particularly "ČSN 72 2080" [20] and preliminary standards series "ČSN P 72 2081 from −1 to −16" [21]. The ČSN 72 2080 provides the procedures for determining the chemical,

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