



Self-hardening of fly ashes from a bubbling fluidized bed combustion of peat, forest industry residuals, and wastes



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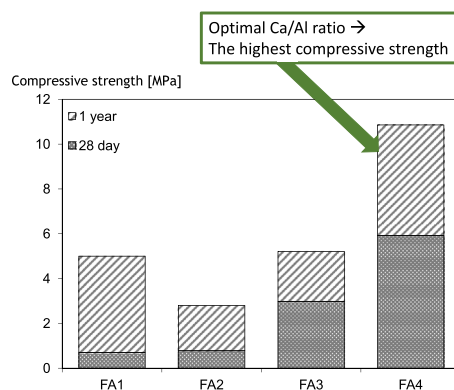
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HIGHLIGHTS

- One month and year hydration for fly ashes from bubbling fluidized bed combustion.
- The amount of selectively soluble components predicts hardening potential well.
- Ettringite and different Ca–Al phases are the main hydration products.
- Ca and Al are the most important components for strength production.

GRAPHICAL ABSTRACT



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ABSTRACT

More and more biomass fly ash is produced because of the increasing usage of renewable energy sources. Therefore, novel applications in which biomass fly ashes can be utilized efficiently are needed. One interesting option is to use biomass fly ashes in hardening applications such as earth construction. In this study, the self-hardening of fly ashes from a bubbling fluidized bed combustion of peat, sludges from the papermaking industry, forest industry residuals, and other wood wastes was investigated. The self-hardening compressive strength of fly ashes after 28 days and one year of hardening was measured for four different fly ash samples. The compressive strength for self-hardening samples was dependent on reactive calcium, aluminum, silicate, and sulfate content, but calcium (Ca) and aluminum (Al) seemed to be the most important components. According to the X-ray diffraction measurements, the main reaction products are ettringite, hydrocalumite, monocarboaluminate, and various types of Ca–Al phases.

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1. Introduction

Biomass energy can be considered sustainable when the consumption of the biomass is less than its rate of growth and if the biomass intakes more carbon dioxide (CO₂) during its lifetime than it releases during firing [1]. Biomass fly ash is generated as a by-product of the combustion of biomass in power plants, pulp and paper mills, and other biomass burning facilities. About 7 million tons of biomass ash is produced in Europe annually, and the amount is increasing because of the EU 20–20–20 energy policy target [2] and the increase in incineration of sewage sludge. Despite the fact that biomass fly ash is possible to be recycled in many ways (e.g., forest fertilizing [3]) and that the disposal costs are increasing, most of it is still landfilled. Therefore, novel applications in which biomass fly ashes can be utilized efficiently are needed.

A special characteristic of fly ash that originates from a fluidized bed combustion is its self-hardening or self-cementitious property, which enables fly ash to react in water and to produce reaction products similar to hardened Portland cement [4–6]. The main observed hydration products are ettringite, calcium silicate hydrate gel, portlandite, and gypsum [4–9]. This self-hardening property makes fly ash an interesting raw material for soil stabilization [10–12], earth construction [13], mine backfilling [14], and concrete applications [15–18], for instance, to replace Ordinary Portland cement or other Calcium-rich primary materials. The use of waste materials in concrete materials as a substitute for primary Portland cement contributes to lower CO₂ emission and to save on primary materials. However, the use of fly ash in applications in which self-hardening plays an important role is only occasional, as the properties of biomass fly ash and thus its reactivity vary depending on the origin and properties of fuel and combustion conditions [19–21].

Illikainen et al. [7] studied the self-hardening properties of two different biomass fly ashes from the co-firing of peat and wood in a circulating fluidized bed combustion (CFBC) and the co-firing of peat and forest industry residuals in a bubbling fluidized bed combustion (BFBC), and found the latter to have better self-hardening properties due to the higher amount of reactive calcium (Ca), aluminum (Al), and silicon (Si). Moreover, fly ash properties varied depending on the peat and wood ratio. The current study focuses on biomass fly ash from BFBC with different mixtures of fuels and therefore different types of fly ashes. This study aims to gain more understanding of the reactivity and self-hardening properties of fly ash originating from the combustion of different fuel mixtures. The chemical and physical compositions and the reactive components of fly ash were analyzed. The mineralogical changes during hydration and the compressive strength after 28 days and one year of hydration were also measured.

2. Materials and methods

2.1. Materials

Fly ashes from four different power plants were studied. All of the power plants have bubbling fluidized bed boilers. However, the power plants use different mixtures of fuels, and therefore the fly ashes differ in properties. Fly ash samples were collected from

Table 2
Mixture design and parameters.

	FA1	FA2	FA3	FA4
Ash (g)	1824	1458	1190	2081
Water (g)	1000	1000	1000	1000
Water-to-binder ratio (–)	0.55	0.69	0.84	0.48
Spread (mm)	145	135	130	148

electrostatic precipitator (ESP) units or silos. Information about the fuel composition of the studied samples is presented in Table 1.

2.2. Methods

2.2.1. Analysis of fly ashes

The particle size distribution of the fly ash samples was measured with laser diffraction technique (Beckman Coulter LS 13320) using the Fraunhofer model and wet procedure reported as a volumetric median size (d_{50}). A specific surface area measurement was based on the physical adsorption of gas molecules on a solid surface using Micrometrics ASAP 2020, and the results were reported as BET isotherm. The main chemical components of fly ash were determined by Omnia Pananalytix Axiosmax 4 kV X-ray fluorescence (XRF) from a melt-fused tablet. The melt-fused tablet was produced from 1.5 g of fly ash melted at 1150 °C with 7.5 g of X-ray Flux Type 66:34 (66% Li₂B₄O₇ and 34% LiBO₂). To assess the hydraulic reactivity of the fly ashes, the selective dissolution method [22–24] was utilized. This method determines the fraction of each component that is available for hardening reactions [7]. The reactive lime (CaO), quartz (SiO₂), and aluminum oxide (Al₂O₃) were determined as their solubility to a solution consisting of ethylenediaminetetraacetic acid and triethanolamine solutions with pH adjusted to 11.6 ± 0.1 with the addition of NaOH, where the concentration of soluble CaO, SiO₂, and Al₂O₃ were determined using the inductively coupled plasma technique. The free CaO content was determined using the methodology described in SFS-EN 451-1:2004. The free calcium oxide describes the dissolved amount of CaO in a specified mixture of butanoic acid, 3-oxo-ethyl ester, and butan-2-ol during 3 h boiling time. Field-emission scanning electron microscopy (FESEM, Zeiss Ultra Plus) was used to visualize the fly ash samples. The FESEM sample was prepared by adding a thin layer of fly ash on the coal sticker. The samples were sputter-coated with platinum, and a low voltage (3 kV) was used when imaging the samples. Identification of the crystal phases of powdered samples was made using the Siemens 5000 X-ray diffractometer (XRD). Step interval, integration time, and angle interval used were 0.04°, 4 s, and 10–70°, respectively.

2.2.2. Preparation of samples and measurement of mechanical strength

Test specimens for studying the self-hardening properties of ash samples were prepared in cylindrical containers 33 mm in diameter and 70 mm in height. Fly ash was mixed for 2 min with water to produce a spread between 100 mm and 150 mm measured using a flow table described in EN 1015-3:1999. The water-to-binder ratio of the different ash mixtures varied between 0.48 and 0.84

Table 1
Fuel compositions of the studied fly ashes.

Sample name	FA1	FA2	FA3	FA4
Fuel	Peat (70%), forest residuals (30%)	Peat (30%), forest residuals (60%), wood waste (10%)	Sludge from the papermaking industry (85%), recycled wood (15%)	Forest residuals (40%), recycling waste (50%), sludge from the papermaking industry (10%)
Sample collection	ESP-A	Silo	ESP-A	Mixture of ESP-A and B

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