



# Silico-aluminous bottom ash valorisation in cement clinker production: Synthesis, characterization and hydration properties



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## HIGHLIGHTS

- Silico-Aluminous Bottom Ash was successfully recycled in kiln feed.
- Raw meals particle size was reduced with the increment of SABA addition.
- Clinker main mineralogical phases weren't negatively affected by SABA presence.
- All syntheses satisfied the requirements for the strength class 52.5 as per standard EN 197-1.

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## ABSTRACT

The utilization of Silico-Aluminous Bottom Ash (SABA), derived from bituminous coal combustion in power plants, was investigated as a raw material in the kiln feed for the production of ordinary Portland cement clinker. Three different raw meals were studied, containing natural raw materials with 0, 3 and 6 wt% of SABA. The raw mixes reactivity was assessed in terms of unreacted lime content, following sintering at 1200, 1350, 1400 and 1450 °C. Clinkers produced at 1450 °C, were characterized through means of chemical analysis, X-ray diffraction (XRD) and scanning electron microscopy (SEM). The characterized clinkers were used to produce cement specimens by co-grinding with suitable amount of gypsum. Accordingly, cement quality was evaluated by determining setting times, standard consistency, expansibility and compressive strength at 2, 7 and 28 days. XRD and TG/DTG analysis were used for the hydration study evolution after 28 days of curing. SABA presents a promising alternative in waste valorisation practice, as it can readily be used in the raw kiln feed as a partial replacement of ordinary raw materials.

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## 1. Introduction

Coal remains one of the major fossil fuel resources used in power plants up to this day, a fact that is attributed to its relatively low cost and high availability, as it is the most abundant energy source and exists in large quantities worldwide. The power demand is estimated to increase by 60% before 2030 globally and, with the exception of renewable energy forms, coal still is one of the fastest growing energy forms within developing and developed economies. Approximately 30% of the global primary energy demands is provided by coal combustion in power plants, whereas the corresponding value for electricity generation reaches 42% [1].

It is well known that coal combustion results in large quantities of by-products being generated in power plants; the most important of which are fly and bottom ash, boiler slags and flue gas desulfurization residue. Fly ash accounts for 60 wt% of the coal combustion residue (80 wt% of the ash produced). It is generated during the burn-off of carbon and volatile matter due to the coal impurities (shale, clays, etc.), some of which may become fused in suspension and can usually be collected in the off-gas cleaning system, either by mechanical pre-collectors or electrostatic or bag filters [2,3]. On the other hand, bottom ash (~15 wt% of the combustion residue) is produced from the heavier particles of the agglomerated remaining matter, which are precipitated and accumulated usually in the boiler first combustion chamber; it typically appears as a porous, dark grey and granular material. When sufficient amount is concentrated, bottom ash is removed using

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water jets of high-pressure and it is conveyed for disposal or use, after dewatering and crushing.

The annual coal combustion by-products is estimated to reach 800 Mt worldwide (100 Mt in European states members), which poses a significantly alarming issue. Expected environmental, economical and technical benefits have provided incentive for extensive investigations on valorisation of the mentioned by-products. Although a number of methodologies have been established (mainly in the construction industry), actual utilization does not exceed 50 wt% of total production today [4–6]. This remains a critical issue, as the option of landfilling not only bears the increasing cost of disposal and the potential of soil and water contamination, it also does not meet the criteria of by-products sustainable management. Priority should be given towards preservation of energy and natural resources, with simultaneous minimization of emissions pollutants.

Several investigations have been carried out regarding fly ash utilization in the last three decades, including the use as an additive in cement, in manufacturing of glass and ceramics, as a low-cost adsorbent, as light weight aggregate, as a filler material in concrete and road bases construction, in the production of zeolites, in the synthesis of geopolymers and as a soil amelioration agent in agriculture [7–10]. Concerning bottom ash valorisation, its potential use as a cement additive and as an aggregate in concrete or as a road base material has been reported [11–14]. To the authors' best knowledge, little attention has been given to the possible utilization of bottom ash as a raw material in the raw meal for the production of ordinary Portland cement clinker.

Silico-Aluminous Bottom Ash (SABA), produced in power plants during the bituminous coal combustion, has been ranked in the category of siliceous ashes, where Si, Al and Fe are the three predominant elements. In contrast, calcareous ashes, which derive from lignite combustion, contain higher amounts of calcium. Depending on the nature of coal source, SABA generally consists of 20–60 wt%  $\text{SiO}_2$ , 5–35 wt%  $\text{Al}_2\text{O}_3$ , 5–20 wt%  $\text{Fe}_2\text{O}_3$ , 1–10 wt% CaO, and its loss of ignition may reach 15 wt%. Its main mineralogical phases are quartz ( $\text{SiO}_2$ ), mullite ( $\text{Al}_6\text{Si}_2\text{O}_{13}$ ), hematite ( $\text{Fe}_2\text{O}_3$ ), magnetite ( $\text{Fe}_3\text{O}_4$ ), while it may also contain a glassy matrix rich in silicon and unburnt carbon [15,16].

Concerning cement hydration, SABA is expected to exhibit significant pozzolanic properties due to its high glassy silica content. However, as its CaO content is low, its activation towards the consequent production of secondary CSH compounds requires an

external  $\text{Ca}(\text{OH})_2$  source, such as quicklime, hydrated lime or Portlandite. Concerning clinker production on the other hand, because of its relatively high Si and Al content, it has potential to be used as an alternative source of aluminium and silicon in the kiln raw feed; thus contributing towards preservation of natural resources and minimizing the cost of disposal, by avoiding landfilling.

The aim of the present investigation is the synthesis, characterization and hydration of Ordinary Portland Cement (OPC) clinker produced by partially substituting aluminium and silicon containing raw materials with suitable amount of SABA. Three different raw meals were prepared and studied: one reference containing only natural raw materials and two others with different percentages of SABA substitution (3 wt% and 6 wt%). Following sintering, the clinkers were co-ground with appropriate amounts of gypsum and the produced cements were tested for water demand, setting times, soundness and compressive strengths at 2, 7 and 28 days of curing. In addition, hydration evolution was observed through XRD and TG-DTG analysis throughout the curing process.

## 2. Experimental

### 2.1. Materials & sample preparation

SABA used in the present investigation was collected from a local coal power plant derived from bituminous coal combustion. It appeared as a porous, dark grey, granular by-product, and exhibited a relatively high particle size. Ordinary natural raw materials, specifically limestone, schist, bauxite and silica sand were used to prepare the raw meals. Particle size distributions of all materials were determined by laser scattering technique with a Mastersizer 2000 particle size analyser (Malvern) following ultrasonic-assisted dispersion in high purity ethanol; results are presented in Fig. 1. Furthermore, the bottom ash as well as the natural raw materials used in this study were analysed through means of X-ray Fluorescence (Spectro-Xepos), atomic absorption spectrophotometer (Perkin Elmer 4100) and Inductively Coupled Plasma Mass Spectrometry (ICP-MS X Series II, Thermo Scientific); chemical analysis results are shown in Table 1, whereas SABA trace metals concentrations are presented in Table 2. In addition, X-ray diffraction patterns were collected for SABA and all raw mixes, using a Bruker D8-Focus diffractometer with nickel-filtered  $\text{CuK}\alpha$  radiation

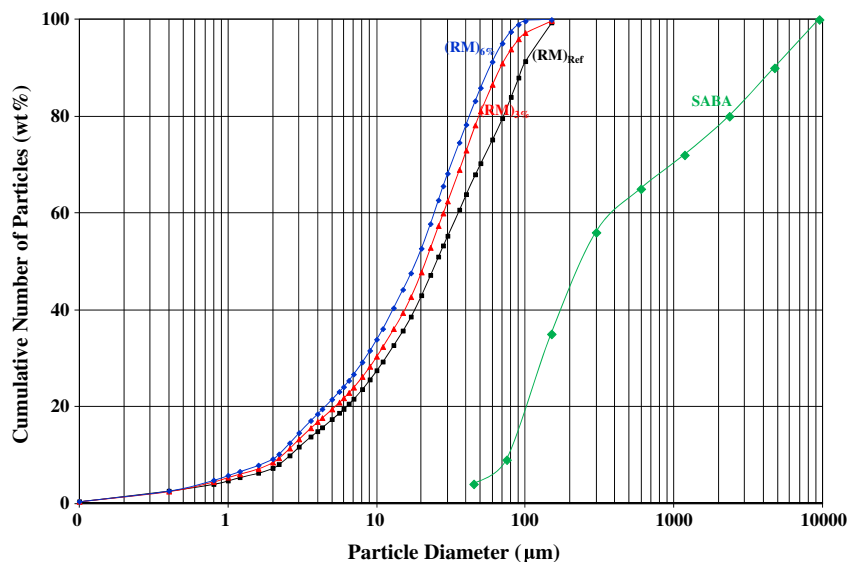


Fig. 1. Particle size distributions of SABA and final raw mixes.

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