

# Biomass ash as a potential material for civil engineering

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## Abstract

*With the gradual phase-out of coal-fired power plants and the growing emphasis on renewable energy sources, biomass ash is becoming one of the potential alternative sources of raw materials for civil engineering. While fly ash from coal has long been used as a mineral admixture in cement and concrete, fly ash produced by the combustion or co-combustion of biomass presents a new challenge. Its chemical and mineralogical composition varies significantly depending on the type of biomass and combustion technology, which complicates its direct use in cement composites. This work focuses on the characterization of biomass fly and bottom ash from various combustion processes from the Czech Republic. It presents their chemical and phase composition and compares them with fly ash (FA) and FBC ash as well as with the requirements for materials used in construction.*

*Analysis indicates that the fly ash meets the requirements of EN 450-1 standard, while biomass ashes generally do not, mainly due to their increased content of alkalis, sulfates, chlorides, and calcium-bearing phases. Despite these limitations, mineralogical composition confirmed a high proportion of amorphous phase in biomass ashes, which indicates potential pozzolanic activity. In terms of physical properties, biomass ash requires further processing, such as grinding, to achieve a suitable particle size for use as a supplementary cementitious material (SCM).*

**Keywords:** fly ash, biomass ash, fluidized bed combustion ash, X-ray diffraction, X-ray fluorescence, particle size analysis

## Introduction

The utilization of coal ash in the construction industry, especially in concrete, represents a significant opportunity to improve the sustainability and efficiency of building materials. Ash which is a by-product of fossil fuel and biomass combustion, has properties that are strongly influenced by the combustion technology used<sup>1-3</sup>. Classical pulverized coal combustion (PCC) produces fly ash with a high proportion of amorphous glass phases and a minor proportion of crystalline phases, mainly mullite<sup>4-7</sup>. The amorphous phase has pozzolanic properties<sup>8</sup>, which can contribute to the mechanical strength of cement mixtures<sup>1,9</sup>. Fluidized bed co-combustion (FBC), which includes fly ash (FBC FA) and bottom ash (FBC BA), occurs at lower temperatures<sup>10,11</sup> and leads to the formation of non-glassy amorphous phases that increase the reactivity of these ashes<sup>12</sup>. FBC FA differs from FA in its irregular particle shape, higher content of free lime and sulphates, and crystalline structure<sup>10,11,13</sup>. However, these samples have the potential to be used in the construction industry as alternative binders<sup>14,15</sup>.

Fly ash can be used as a cement replacement, bringing several benefits, including lower CO<sub>2</sub> emissions, which are significant in combating climate change<sup>16,17</sup>. One way to reduce the carbon footprint of cement is to partially replace Portland clinker with supplementary cementitious materials (SCM)<sup>9,18</sup>, which also include ash. For the effective use of FA, they must meet certain standards, especially regarding the content of silica, alumina, and iron oxides. Classification according to the EN 450-1 standard<sup>19</sup> ensures that the FA meets the required parameters for use in cement, while

tests according to EN 196-1<sup>20</sup> and EN 206+A1<sup>21</sup> standards verify their suitability for specific applications, especially in terms of strength and durability.

Fly ash from co-firing is also subject to the requirements of EN 450-1, which specifies the conditions and applies to any coal fly ash co-fired with materials defined by the standard. According to the standard EN 450-1, in the case of fly ash originating from co-firing, the minimum share of dry coal must be 60%, whereas if the co-fired material is wood, the minimum share of dry coal is 50%. The standard also specifies other co-fired materials, such as biomass. If the fly ash meets the requirements of EN 450-1, it can, in addition to previously mentioned applications, be used for soil treatment according to EN 16907-4<sup>22</sup> or as fly ash for hydraulically bound mixtures according to EN 14227-4<sup>23</sup>, which includes use in the construction of roads, airports, and other traffic areas.

The transition to biomass as an alternative to coal combustion represents another step towards more sustainable energy and construction solutions<sup>18,24</sup>. Biomass, due to its renewable behaviour, offers the possibility to reduce dependence on fossil fuels, which is important for energy safety and sustainability. However, to ensure the effective integration of biomass combustion ash (BMA) into the construction industry, it is necessary to perform a thorough analysis of its chemical composition and physical properties. The physical and chemical properties of BMA depend on the characteristics of the input biomass, the type and conditions of combustion, the proportion of individual plant components, and many other factors<sup>24–26</sup>.

Biomass ashes show significant heterogeneity in composition, which is a key difference compared to coal ash<sup>27,28</sup>. Silicon dioxide (SiO<sub>2</sub>) dominates in ash from rice husk and rice straw<sup>27,29,30</sup>. A high proportion of SiO<sub>2</sub> is also found in agricultural residues such as wheat straw and in energy crops. Phosphorus (P<sub>2</sub>O<sub>5</sub>) occurs most abundantly in ash from animal-derived materials, especially bone meal<sup>27</sup>. Considerable amounts are also present in blue-green algae ashes, agricultural residues, and certain energy crops. Calcium (CaO) is the main component of ash from woody biomass, such as bark, wood chips, and sawdust, where it forms the dominant fraction<sup>27,28,31</sup>. Chlorides appear in elevated concentrations in straw and animal waste<sup>27,28</sup>.

The aim of this work was to provide basic information about biomass ash and compare its properties with FA and FBC ash produced by coal combustion. The research focused on X-ray fluorescence (XRF) to determine chemical composition, X-ray diffraction (XRD) to identify mineralogical composition, and particle size distribution analysis (PSD) to understand physical properties. Thanks to these analyses, it was possible to gain deeper insights into the properties of various ash and their potential for use in the construction industry.

## Materials and methods

Ash samples from various locations in the Czech Republic and from various types of coal and biomass combustion and co-combustion were selected as input materials. FA was obtained from the power plant in Tušimice (TU), while FBC ash from fluidized bed combustion of coal comes from Ledvice (LE). Another raw material that was analyzed was ash from FBC co-combustion of coal and biomass (CC-BMA) from the power plants Poříčí (PO) and Hodonín (HO). Additionally, ash from pure biomass from grate combustion (GC-BMA) from Jindřichův Hradec (JH) was analysed. Sampling of all materials was carried out in 2022. The specifications of locations, combustions, and combustion products (ashes) are provided in Table 1.

All samples were dried at 40 °C to constant weight before analysis, and for XRF and XRD analysis, the samples needed to be properly ground. X-ray diffraction (XRD) was performed on a  $\theta$ - $\theta$  X'Pert3 Powder diffractometer (PANalytical, Netherlands). Samples for XRD were measured by semi-quantitative analysis and quantitative Rietveld analysis using internal standard ZnO (10%). The results were evaluated using HighScore Plus 5 software. X-ray fluorescence (XRF) was performed on an X-ray spectrometer ARL 9400 XP (Thermo ARL, Switzerland). The particle size distribution was measured on a laser particle size analyzer, Bettersizer ST (Dandong Bettersize Instruments Ltd., China).

**Table 1: List and characterisation of locations and produced ash**

Sample	Location	Method of combustion	Type of ash
FA	power plant Tušimice (TU)	PCC of coal*	fly ash
FBC FA	power plant Ledvice (LE)	FBC of coal**	FBC fly ash
FBC BA			FBC bottom ash
CC-BMA FA (PO)	power plant Poříčí (PO)	FBC co-combustion (80 % coal + 20 % biomass)**	BMA fly ash
CC-BMA BA (PO)			BMA bottom ash
CC-BMA FA (HO)	power plant Hodonín (HO)	FBC co-combustion (80 % coal + 20 % biomass)**	BMA fly ash
CC-BMA BA (HO)			BMA bottom ash
GC-BMA FA+BA	Energetické centrum s.r.o. Jindřichův Hradec (JH)	grate combustion (hay and straw)	BMA fly ash + bottom ash

\* PCC = Pulverized Coal Combustion; \*\* FBC = Fluidized Bed Combustion

## Results and discussions

### X-ray fluorescence analysis (XRF)

The chemical composition of the ashes is very diverse and is presented in Table 2. The ashes are rich in silica ( $\text{SiO}_2$ ), alumina ( $\text{Al}_2\text{O}_3$ ), and iron oxide ( $\text{Fe}_2\text{O}_3$ ). The  $\text{SiO}_2$  content ranges from 31.50% to 69.02%. The content of  $\text{Al}_2\text{O}_3$  ranges from 1.83% to 32.80%, and for  $\text{Fe}_2\text{O}_3$  it ranges from 0.83% to 9.40%. Classical pulverized coal combustion FA (TU) is characterized by an iron oxide ( $\text{Fe}_2\text{O}_3$ ) content of 9.40%. The silica ( $\text{SiO}_2$ ) content is 50.00% and the alumina ( $\text{Al}_2\text{O}_3$ ) content is 32.80%. FBC FA and FBC BA (LE) are characterized by silica ( $\text{SiO}_2$ ) content of 36.20% to 42.45%, alumina ( $\text{Al}_2\text{O}_3$ ) content of 27.51% to 32.5%, and iron oxide ( $\text{Fe}_2\text{O}_3$ ) content of 3.57% to 4.11%. All CC-BMA (PO) and (HO) are characterized by silica ( $\text{SiO}_2$ ) content ranging from 39.43% to 69.02%, alumina ( $\text{Al}_2\text{O}_3$ ) content of 9.67% to 10.78 % and iron oxide ( $\text{Fe}_2\text{O}_3$ ) content of 2.03 % to 5.04 %. GC-BMA FA+BA (JH) shows silica ( $\text{SiO}_2$ ) content of 31.5% and the lowest content of alumina ( $\text{Al}_2\text{O}_3$ ) at 1.83% and iron oxide ( $\text{Fe}_2\text{O}_3$ ) at 0.83%.

In terms of using ashes in concrete, according to the standards EN 450-1, the ash must contain more than 70%  $\text{SiO}_2 + \text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3$ , which is not met by the FBC BA, CC-BMA and GC-BMA samples. The amount of alkalis  $\text{Na}_2\text{O}_{\text{eq}}$  ranges from 0.73% to 19.12%, which means that part of the ashes do not meet the standard requirement for the total amount of alkalis, which must be less than 5%. Sample GC-BMA (19.12%) does not meet the standard requirement for the total amount of alkalis. The limit for CaO was met only by the FA and CC-BMA BA (HO) samples, the other samples had a content higher than 10%, as specified by the standard. The limit for MgO (<4%) was exceeded by the CC-BMA FA (HO) sample. The limit for  $\text{SO}_3$  was met by all samples from CC-BMA, the other samples had a content higher than 3%, as specified by the standard. The chloride content (<0.1%) does not meet the GC-BMA FA+BA sample with content 4.77% and CC-BMA FA from PO and HO. The other samples meet or are below the detection limit for chloride. The limit for  $\text{SiO}_2$  (>25%) was met by all samples. The limit for  $\text{P}_2\text{O}_5$  (<5%) was exceeded by the GC-BMA FA+BA (JH) sample.

FA has the most balanced chemical composition and is the only one that meets all the limits according to EN 450-1 standard. On the contrary, FBC BA sample, CC-BMA FA, CC-BMA BA and GC-BMA FA+BA have excessively high CaO,  $\text{SO}_3$ , or chloride and alkali contents and therefore do not meet the requirements of the standard. Chloride content could potentially be reduced by leaching, which is a commonly suggested method for removing soluble salts and heavy metals<sup>32</sup>. The results of the

BMA analyses are in good agreement with the work of Formáček et al.<sup>26</sup>, who analysed the Czech BMA from 2021. The results show only slight variability in the chemical composition of BMA for the same location and the same type of combustion and biomass.

### ***X-ray diffraction analysis (XRD)***

Table 3 shows the phase composition via XRD, which is similarly diverse as the chemical composition from the previous table. All samples contained a high content of amorphous phase, which, according to the XRF results in Table 3, is likely to consist mainly of aluminosilicates. The range of amorphous phase content is 30.9% to 66.7%. The highest content of the amorphous phase, which is crucial in terms of pozzolanic activity, was recorded in samples from the grate combustion of pure biomass (GC-BMA FA+BA). The main crystalline phase in most samples is quartz, with a content of 1.6% to 55.7 %. Most materials also contain calcite, free lime anhydrite and iron minerals.

The FA sample contains a mullite phase (35.0%) which indicates high-temperature combustion of fuel<sup>4,16,17</sup>. It also contains 9 % quartz and 1 % magnetite. FBC ash contains 57 – 61% amorphous phase as well as crystalline phases such as quartz, anhydrite, lime, portlandite, hematite, magnetite and calcite, which agrees with Ohenoja et. al.<sup>10</sup>, who identified the same phases except for magnetite. BMA revealed the presence of amorphous and many crystalline phases. The amorphous phase content ranged from 30.9% to 66.7%. The high amount of lime, portlandite and calcite in FBC and CC-BMA can be explained by the flue gas desulfurization process, in which limestone is added to the boiler<sup>33</sup>. From the perspective of using the ash in cement or concrete, these phases are problematic according to EN 450-1. An interesting finding is the presence of portlandite, which, given the combustion temperature above 850 °C, should not be present in the sample. This mineral probably formed after the combustion process due to the action of air humidity. Regarding the GC-BMA samples, which contained 14.53% CaO according to XRF results, but do not include common calcium-bearing phases in their phase composition, this discrepancy can be explained by the fact that, given the firing temperature of the samples, calcium-bearing phases are present mainly in the amorphous phase. Fly ash from biomass sources such as hay and straw is naturally rich in calcium, and therefore, the high CaO content likely originates from the biomass itself<sup>28,34,35</sup>. The CC-BMA samples contain muscovite and feldspar, both of which are common components of the Earth's crust. In the case of GC-BMA FA+BA sample, two new phases – sylvite (KCl) and arcanite (K<sub>2</sub>SO<sub>4</sub>) – are of particular interest, as they are not typically found in FA. The high content of sylvite, which is the main crystalline phase in GC-BMA FA+BA, probably originates from the biomass itself. Moreover, the ash sample from pure biomass (GC-BMA FA+BA) was found to contain a high amount of the amorphous phase (66.7%), which may positively influence its pozzolanic activity<sup>36,37</sup>. The results of the XRD analysis are again in good agreement with the results of the 2021 analysis of BMA by Formáček et al.<sup>26</sup>. However, the results show some variability in the phase content of BMA for the same location and the same type of combustion and biomass.

**Table 2: Chemical composition of input raw material, XRF [%]**

Sample	Al <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>	Fe <sub>2</sub> O <sub>3</sub>	Na <sub>2</sub> O	K <sub>2</sub> O	MgO	CaO	TiO <sub>2</sub>	P <sub>2</sub> O <sub>5</sub>	SO <sub>3</sub>	Cl <sup>-</sup>	Others
FA	32.80	50.00	9.40	-	1.70	-	1.90	1.24	-	-	-	2.96
FBC FA	32.50	42.45	4.11	0.28	0.93	0.96	11.90	2.38	0.22	3.89	-	0.38
FBC BA	27.51	36.20	3.57	0.16	0.86	0.84	22.00	2.29	0.18	6.09	-	0.30
CC-BMA FA (PO)	9.67	39.71	4.45	0.89	3.93	3.63	29.32	0.76	2.66	2.99	0.21	1.78
CC-BMA BA (PO)	10.63	51.79	2.71	0.78	3.26	1.67	26.29	0.78	0.89	0.46	0.02	0.72
CC-BMA FA (HO)	10.78	39.43	5.04	1.31	4.42	4.40	26.75	0.77	2.48	2.83	0.48	1.31
CC-BMA BA (HO)	10.78	69.02	2.03	1.59	4.41	1.45	8.92	0.29	0.89	0.14	0.09	0.39
GC-BMA FA+BA	1.83	31.50	0.83	0.70	28.00	3.01	14.53	0.13	7.54	6.72	4.77	0.44

**Table 3: Phase composition of input raw material, XRD [%]**

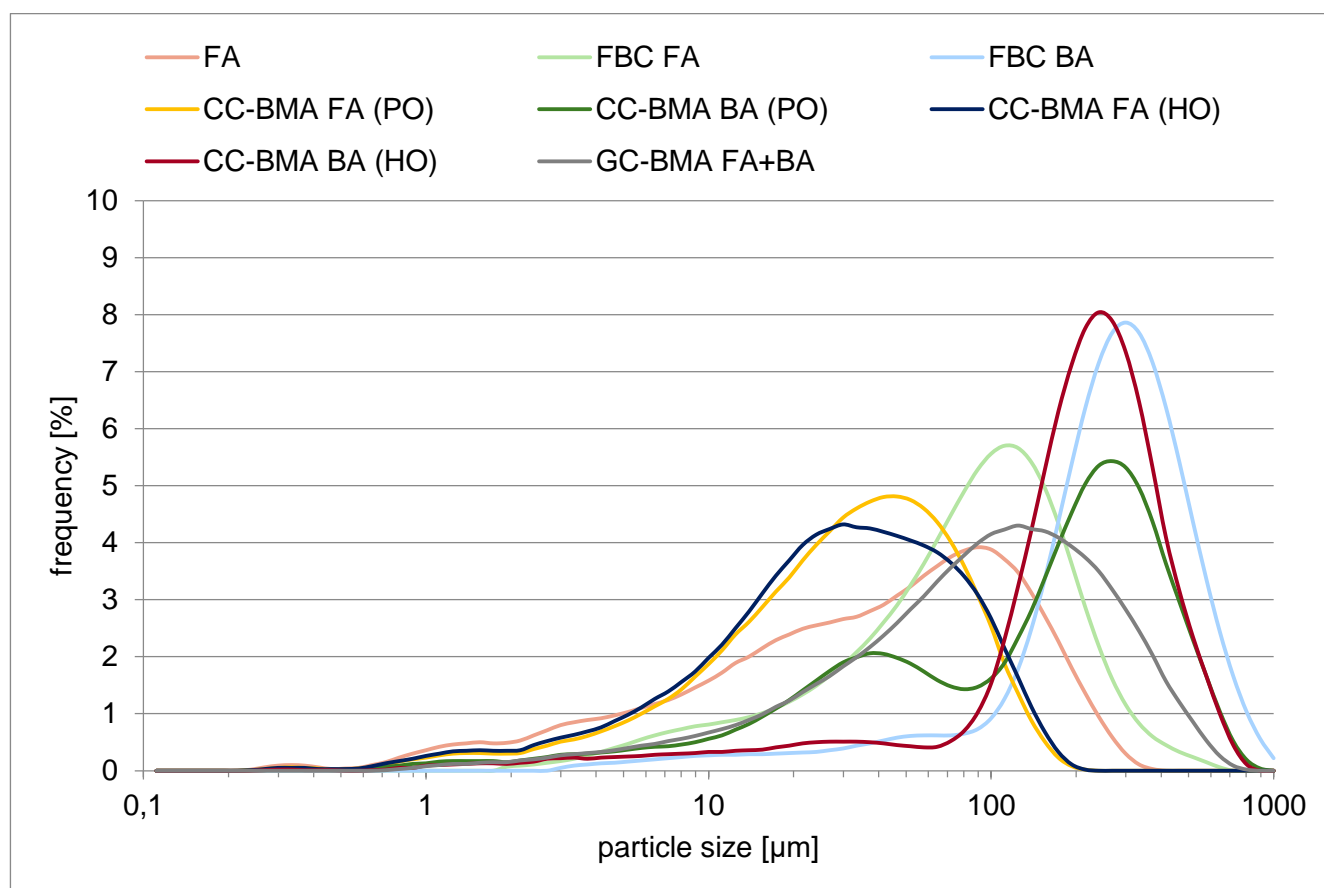
Sample	Amorph.	Quartz	Calcite	Lime	Anhydrite	Magnetite	Hematite	Mullite	Muscovite	Albite	Orthoclase	Akermanite	Sylvite	Arcanite	Portlandite	Others**
FA	54.0	9.0				1.0	1.0	35.0								
FBC FA	60.5	6.5	2.5	6.0	14.0	0.5	2.0								2.0	6.0
FBC BA	57.0	8.0	2.0	5.0	19.0	1.0	1.0								7.0	
CC-BMA FA (PO)	39.8	29.2	1.9	7.9	2.1	0.5			1.6	0.8	0.7				7.7	7.8
CC-BMA BA (PO)	35.6	32.8	2.5	3.0						8.7	1.4	4.2			11.8	
CC-BMA FA (HO)	33.4	30.9	6.5	2.3	2.3	1.2			1.2	12.0	3.7	3.7			2.4	0.4
CC-BMA BA (HO)	30.9	55.7		*					0.6	9.8	2.8					0.2
GC-BMA FA+BA	66.7	1.6								2.4			12.1	14.1		3.1

\*traces \*\* the *Other* category for BMA samples includes phases that appeared sporadically or in small quantities in the input materials (especially leucite, basanite, cristobalite, anorthoclase, hydroxyapatite, wollastonite, periclase, nahcolite, anorthite, graphite, magnetite, and gypsum).

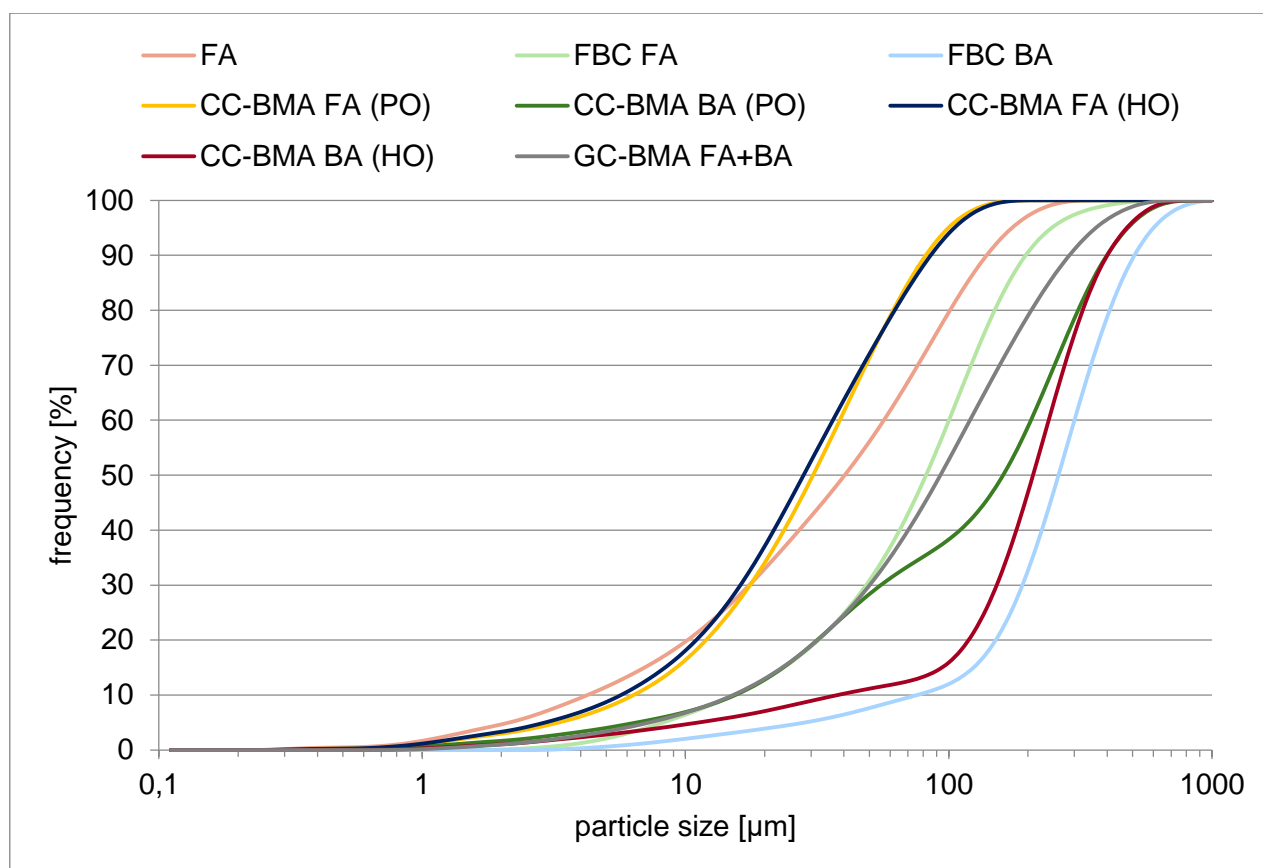
### Particle size distribution (PSD)

Figure 1 shows the particle size distribution of ash. The results are consistent with general principles of combustion in boilers, where bottom ash (BA) consists of larger and coarser particles, while fly ash (FA) contains finer particles that are able to be carried by the flue gas stream<sup>38</sup>. The FA is characterized by a median particle size of 40.29  $\mu\text{m}$ , and its particle size distribution is relatively wide, ranging from submicron particles up to 372.70  $\mu\text{m}$ . The fluidized bed combustion fly ash (FBC FA) is characterized by a higher median particle size compared to conventional FA, while exhibiting a narrower particle size distribution. The median particle size of FBC FA is 82.06  $\mu\text{m}$ , whereas that of FBC BA is 261.50  $\mu\text{m}$ . From the curves, it can be seen that samples from HO, particularly CC-BMA FA (HO), contain fine particles with a median particle size of 24.14  $\mu\text{m}$  and with a wide particle distribution. CC-BMA BA (HO) contains particles with a median particle size of 209.00  $\mu\text{m}$  and with a narrow particle distribution. Samples from PO show a similar particle size distribution to samples from HO. CC-BMA FA (PO) contains fine particles with a median particle size of 30.53  $\mu\text{m}$  and with a wide particle distribution, and CC-BMA BA (PO) contains particles with a median particle size of 161.00  $\mu\text{m}$  and is characterized by a double peak, which refers to the presence of two fractions. The GC-BMA FA+BA (JH) shows a very wide particle distribution, with a median particle size of 93.09  $\mu\text{m}$ . Similar findings were also reported by Formáček et al.<sup>26</sup>. This particle size distribution of BA indicates the need for further processing (grinding) of these types of ash so that they fulfil the function of a fine filler<sup>39</sup>.

Compared to FA and FBC ash, CC-BMA FA from both locations has finer particles. On the other hand, CC-BMA BA exhibits significantly larger particle sizes. GC-BMA FA+BA has a similar particle size distribution to FA.



**Figure 1: Representation of PSD factions**



**Figure 2: Cumulative particle size curves**

## Conclusion

Ashes produced by various methods during the combustion and co-combustion of biomass were characterized via XRF, XRD and PSD, and were compared with fly ash and fluidised bed combustion FA and BA. Analyses showed that BMA from these processes do not meet the values of current standards in terms of XRF content and granulometry for use as SCM.

In general, biomass ash (BMA), regardless of the combustion technology employed, exhibits elevated concentrations of alkalis, sulfates, calcium-bearing phases, and chlorides. Comparative analysis revealed that BMA contains a lower amount of anhydrite than fluidized bed combustion (FBC) ash and, unlike fly ash (FA), does not contain mullite. X-ray diffraction (XRD) analysis further identified the presence of mineral phases in BMA that are absent in FA and FBC ash, including albite, orthoclase, and akermanite - minerals typically associated with ash derived from biomass co-combustion. Additionally, sylvite and arcanite were detected in ash samples originating from grate combustion of pure biomass (GC-BMA FA+BA). GC-BMA FA+BA is also characterized by a high proportion of amorphous phase, which may contribute to enhanced pozzolanic reactivity and potential applicability as a supplementary cementitious material.

The particle size distribution confirmed that biomass bottom ash is coarser compared to biomass fly ash, which is consistent with conventional coal combustion ashes and is influenced by the combustion process.

## Acknowledgements

*This work was co-financed by the Technology Agency of the Czech Republic under the SIGMA programme TQ03000837. This project was financially supported by the Grant Agency of the Czech Technical University in Prague (SGS22/136/OHK1/3T/11).*

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## **Popílek z biomasy jako potenciální materiál pro stavebnictví**

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### **Souhrn**

S postupným útlumem uhelných elektráren a rostoucím důrazem na obnovitelné zdroje energie se popílek z biomasy stává jedním z potenciálních alternativních zdrojů surovin pro stavebnictví. Zatímco popílký z uhlí jsou dlouhodobě využívány jako příměsi do cementů a betonů, popílký vznikající spalováním nebo spoluspalováním biomasy představují novou výzvu. Jejich chemické a mineralogické složení se výrazně liší v závislosti na typu biomasy a technologii spalování, což komplikuje jejich přímé využití ve stavebních materiálech. Tato práce se zaměřuje na charakterizaci popílků z biomasy pocházejících z různých spalovacích procesů v České republice. Představuje jejich chemické a fázové složení a porovnává je s úletovým (FA) a fluidním (FBC) popílkem, jakož i s požadavky kladenými na materiály využitelné ve stavebnictví.

Analýzy ukazují, že úletový popílek splňuje požadavky normy EN 450-1, zatímco popílký z biomasy je obecně nesplňuje, a to hlavně kvůli zvýšenému obsahu alkálií, síranů, chloridů a fází obsahujících vápník. Navzdory těmto omezením mineralogické složení potvrdilo vysoký podíl amorfni fáze v popílcích z biomasy, což naznačuje potenciální pucolánovou aktivitu. Z hlediska fyzikálních vlastností vyžadují popílký z biomasy další zpracování, například mletí, aby bylo dosaženo vhodné velikosti částic pro použití jako doplňkový cementový materiál (SCM).

**Klíčová slova:** popílek, popílek z biomasy, popílek z fluidního spalování, rentgenová difrakce, rentgenová fluorescenční analýza, analýza velikosti částic