

Applicability of fly ashes from a fluidized bed combustion of peat, wood and wastes for concrete

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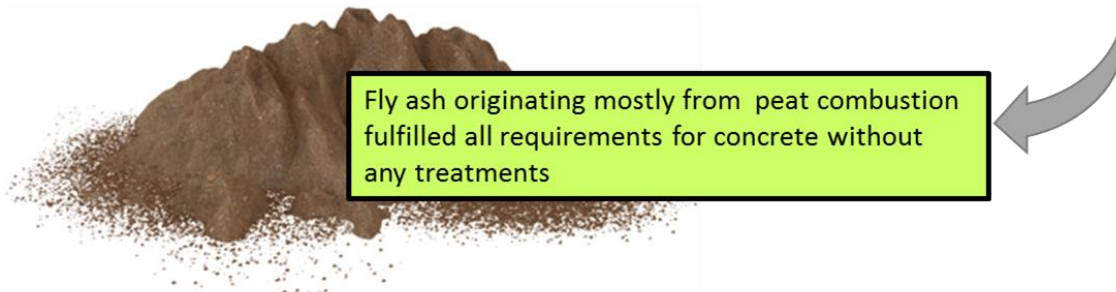
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Highlights

- ✓ Five different fly ashes from fluidized bed combustion
- ✓ Comparison of their characteristics to concrete standard
- ✓ Fly ash originating mostly from peat combustion fulfilled all requirements
- ✓ Potential material to partially replace cement in concrete

Graphical abstract

	FA1	FA2	FA3	FA4	FA5
Fuel	Forest residuals (40%), recycling waste (50%), sludge from the paper making industry (20%)	Sludge from paper making industry (85%), recycled wood (15%)	wood (50%), forest residues (40%), recycled wood (10%)	Forest residuals (60%), peat (30%), wood waste (10%)	peat (80%), wood (20%)



Abstract

Five different fly ashes originating from fluidized bed combustion of peat, wood and different type of wastes was studied by their chemical and physical characteristic to find out how they fulfill the requirements for concrete set by European EN 450-1 standard. Fly ash originating mostly from peat combustion is the only fly ash fulfilling all requirements for concrete without any treatments. For other studied fly ashes some chemical and physical characteristics are exceeded: most probably free CaO, sulfate, chloride, and fineness. Also the sum of main components (SiO_2 , Al_2O_3 , Fe_2O_3) failed for other ashes than the one originating from mostly peat combustion. However, it should be kept in mind that requirements set by European standard is more restrictive than similar in America and some mechanical treatments are possible way to increase their utilization potential.

Keywords: recycling, mortar, reuse, standard, sustainability, utilization

1. Introduction

Biomass is a sustainable energy source used to produce electricity and heat. The use of renewable energy is encouraged by the political goals of European Union, such as “The 2030 climate and energy framework”, which has set the target to increase the share of renewable energy sources to at least 27 % of EU energy consumption by 2030 [1]. Biomass, i.e., wood, bark, and other forest residues, is sometimes co-fired with peat and different type of wastes, like paper sludges and recycling waste. Among combustion methods, fluidized bed combustion (FBC) is efficient and commonly used due to its ability to utilize low-grade fuels with fluctuating quality, composition, and moisture content, or mixtures of fuels, in situ capture of SO_x, and low NO_x emission [2]. However, the combustion residue, i.e. fly ash, has limited utilization potential, unlike ashes from pulverized coal combustion, and until recently these types of fly ashes have been mainly disposed of. However, disposal is becoming more and more restricted and expensive; therefore, additional applications in which fly ashes could be utilized efficiently are in demand.

On the other hand, cement industry has pressures to decrease CO₂ emissions and therefore different substitutional industrial sidestreams has been studied intensively. Coal fly ash from pulverized combustion as a cement replacement material is already widely studied and adopted by the concrete industry to partially replace cement produced from traditional raw materials [3–6]. However, since energy industry is all the time increasing the usage of renewable energy sources, it is reasonable to study fly ashes originating from the combustion of renewable sources [7–9]. The use of biomass fly ash as cement replacement material has been studied in many papers [10–25], but fluidized bed combustion is mentioned as a burning method only on few cases [18,20,26].

The reason for small amount of studies is that the use of pure biomass fly ash as a partial cement replacement material is not allowed by American standard ASTM 618 [27] and European standard EN 450-1 [28] which are the standards governing the use of fly ashes as a mineral admixtures in concrete. The standards set several chemical and physical required properties for fly ash to be used in concrete (Table 1). EN 450-1 applies to ashes originating from pulverized combustion where the coal content must be over 60% or over 50% when coal combustion takes place with pure wood. However, it is reasonable to expect that in the future extension of the current regulations to the use of fly ash from biomass pulverized or fluidized bed combustion in concrete should be limited to those fly ashes meeting the physical and chemical requirements as specified in the ASTM C 618 or EN 450-1 standards, and therefore these limit values can be used now to provide a guideline for all type of fly ash utilization in concrete.

The comparison of physical and chemical characteristic of biomass and co-fired fly ashes for reuse as a mineral admixtures in concrete according to the ASTM and EN requirements is studied in few papers [11,18,29–32]. Typically co-combusted ashes fulfill requirements without any treatments but biomass fly ash often need some treatment before the limits from the standards is fulfilled. However, there are no comprehensive publications how fly ashes originating from fluidized bed combustion of wood, peat and wastes meet the concrete standard requirements. Therefore this study aimed to establish whether fly ashes from fluidized bed combustion of peat, wood and different type of wastes fulfills the requirements set by European EN 450-1 standard. EN 450-1 standard was selected for comparison since it is stricter and less permissive compared to American specifications. Five different fly ashes from five different Finnish power plants all having fluidized bed combustor were studied.

Table 1. Chemical and physical characteristics for fly ashes to be used in concrete application (SFS-EN 450-1 and ASTM C 618).

Characteristic	Limit value [wt.%]	
	SFS EN 450-1	ASTM C 618
Loss on ignition at 950°C	A <5, B <7, C <9	< 6

SiO₂, Al₂O₃, Fe₂O₃	> 70	F > 70, C > 50
Chloride	< 0.1	-
Sulphate as SO₃	< 3	< 5
Free CaO	< 1.5	-
Tot. alkalis (Na+K)	< 5	-
MgO	< 4	-
P₂O₅	< 5	-
Fineness (45 µm)	S < 12, N < 40	< 34
Activity index 28 d	> 75	-
Activity index 90 d	> 85	-

2. Material and methods

2.1 Fly ashes

Fly ashes from five different Finnish power plants were studied. The power plants have fluidized bed boilers. However, the power plants use different mixtures of fuels (see Table 2). Fly ash samples were collected from electrostatic precipitators (FA1, FA2, FA3, and FA5) and silo (FA4). FA1 is originating from combustion of different wastes: forest residuals, recycling waste and sludge from papermaking industry, and on the other hand, FA5 is originating almost totally from peat combustion having only minor amount (20% or less) wood in its fuel.

Table 2. Information about of studied fly ashes.

	FA1	FA2	FA3	FA4	FA5
Fuel	Forest residuals (40%), recycling waste (50%), sludge from the paper making industry (20%)	Sludge from paper making industry (85%), recycled wood (15%)	wood (50%), forest residues (40%), recycled wood (10%)	Forest residuals (60%), peat (30%), wood waste (10%)	peat (80%), wood (20%)
Collection	ESP	ESP	ESP	Silo	ESP

2.2 Materials for mortars

The cement used in this study was Portland cement type CEM I 52.5 R- SR5 from Finnsementti (Finland). Sand used as an aggregate material was sieved natural silicon sand from Fescon (Finland), having a particle size of 0.5–1.6 mm. A polycarboxylate-based super plasticizer agent (Sem®Flow ELE 20, Semtu) was used to adjust the consistency of mortar mixtures.

2.3 Methods

2.3.1 Analysis of fly ashes

The particle size distribution of the fly ash samples was measured with the laser diffraction technique (Beckman Coulter LS 13320) using the Fraunhofer model and the wet procedure using water. The main chemical components of fly ash were determined using an 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% LiB₄O₇ and 34% LiBO₂). The free CaO content was determined using the methodology described in [33]. 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. Loss on ignition (LOI) at 950 °C was measured by thermogravimetric analysis using Prepash Precisa Gravimetrics AG “prepASH automatic drying and ashing system”.

2.3.2 Mortar preparation

The control sample was prepared using cement, tap water, and sand. Fly ashes was used to replace 20% of the cement. Preparation of mortar samples was done according to cement standard EN 196-1 [34] with slight modifications. Modifications included the flow table test done before molding the samples. Additionally, adjustments were made to mortar consistency using super plasticizer in the samples. Consistencies of fresh mortar mixtures were evaluated using a flow table test described in mortar testing standard [35]. The consistency was evaluated to ensure the proper rheology of the mortar mixtures, i.e. spread values 17 mm ± 2 mm, and to measure if super plasticizer is necessary to use. The design of the mortar mixtures is presented in Table 3. All mortar specimens fabricated were cured in water for 28 and 90 days prior to being tested.

Table 3. Mortar mix design.

	Cement [g]	Fly ash [g]	Sand aggregate [g]	Water [g]	Super plasticizer [ml]
Control	450	0	1350	225	0
FA1	360	90	1350	225	0.5
FA2	360	90	1350	225	1.0
FA3	360	90	1350	225	1.5
FA4	360	90	1350	225	1.0
FA5	360	90	1350	225	2.0

2.3.5 Mortar strength measurements

Flexural strength was measured from 40 × 40 × 160-mm mortar prisms and broken halves were used for unconfined compressive strength measurements. The strengths for the samples were measured after 28 and 90 days of curing using a Zwick testing machine with a maximum load of 100 kN employing a loading force of 2.4 kN/s. The reported compressive strengths of mortar are the average of the replica specimens tested. The results are presented here as an activity index according to EN 450-1 standard. The activity index is calculated as a percentage of compressive strength of mortar containing fly ash to control mortar.

3. Results and discussion

3.1 Fly ash composition

Five different Finnish fly ashes were studied, and since power plants use different mixtures of fuels, the fly ash samples differed highly in their properties (see Table 4). CaO content varied from 10 % to 55% depending on the used fuel. Fuel of FA2 is composed of mostly sludge from paper making industry which contains a lot calcium [36–38]. Also FA1 contains a lot of CaO since its originating partly from paper industry sludge combustion. On

the other hand, fuel of FA5 is composed mostly of peat and therefore it has low Ca content. FA3 and FA4 contains CaO around 20% since their wood content is higher than of FA5.

In addition to CaO, also SiO₂ content differs greatly: FA1 and FA2 contains 25 % of SiO₂, but FA3, FA4 and FA5 all over 40%. This is natural since SiO₂ is coming from peat and forest residues [37,39]. Fe₂O₃ content is low (< 6%) for all ashes, except for FA5: 45%. FA5 is originating mostly from peat combustion which is the reason for exceptional high Fe content [40]. All fly ashes contained couple percent of Na₂O, K₂O, MgO and P₂O₅, except FA3 contained as much as 6.5% of K₂O, since its originating totally from wood combustion. On the other hand, FA2 has exceptional low Na₂O, K₂O, and P₂O₅ contents since it is not originating from combustion of peat or forest residues. Sulfate content of FA1 is really high: 7.7 %. Also for FA3 it is over 6 %. For other ashes it is below 3%.

Table 4. Chemical composition of studied fly ashes.

	FA1	FA2	FA3	FA4	FA5
CaO	36	55	21	22	10
SiO ₂	26	24	44	46	46
Al ₂ O ₃	12	14	7.4	11	9.7
Fe ₂ O ₃	3.9	0.7	2.6	5.9	25
Na ₂ O	2.9	0.4	2.1	1.9	1.0
K ₂ O	1.9	0.4	6.5	2.4	1.2
MgO	2.7	2.9	3.4	3.9	1.8
P ₂ O ₅	1.8	0.2	3.0	1.5	2.7
TiO ₂	1.5	0.3	0.8	0.3	0.2
SO ₃	7.7	0.5	6.3	2.9	1.9
Cl	1.8	0.3	0.3	0.1	0.06

3.2 Loss on ignition at 950°C

Loss on ignition (LOI) is the term used to specify the amount of unburned carbon, and it is generally related to the amount of carbon or unburned coal constituents in the fly ash. The standards EN 450-1 set the maximum limits for LOI since the carbonaceous solids of fly ash may affect mechanical properties and air entrainment of cement and concrete, and therefore high LOI can invalidate the use of the ash in concrete application [41]. Loss on ignition for fly ashes studied here are presented in Fig 1. As can be seen, Class A requirement is fulfilled for FA1, FA4 and FA5. FA3 fulfills Class B requirement. FA2 has exceptional high LOI which is explained, not with high unburnt carbon but, with high CaCO₃ content: high LOI at 950 °C is due to the decomposition of CaCO₃ at around 850 °C.

Loss on ignition [wt%]

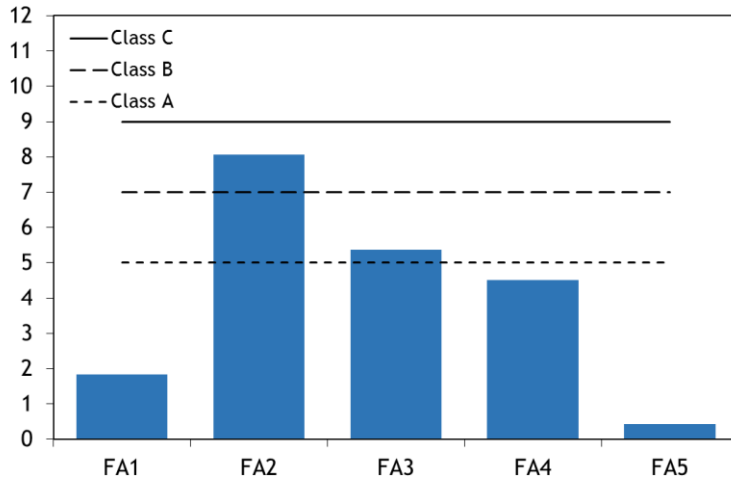


Fig 1. Loss on ignition at 950 °C for studied fly ashes. Lines present the requirements according to EN 450-1: Class A < 5%, Class B < 7%, and Class C < 9%.

3.3 Fineness (45 µm)

The fineness of fly ash according to EN 450-1 is usually measured with 45 µm mesh sieve, and expressed as the mass proportion in percent of the ash retained on sieve. In this study, the fineness is measured using laser diffraction analyzer and expressed as a cumulative coarser which means the mass proportion of the ash being coarser than 45 µm. As presented in Table 1, at class N the fineness shall not exceed 40 % by mass, and at class S shall not exceed 12 %. FA1, FA2 and FA4 exceed both limits (see Fig 2), and therefore they need a grinding procedure before using in concrete. Instead FA3 fulfills the class N fineness requirement and FA5 fulfills the class S fineness requirement so these ashes can be used in concrete without grinding treatment.

Fineness > 45 µm [%]

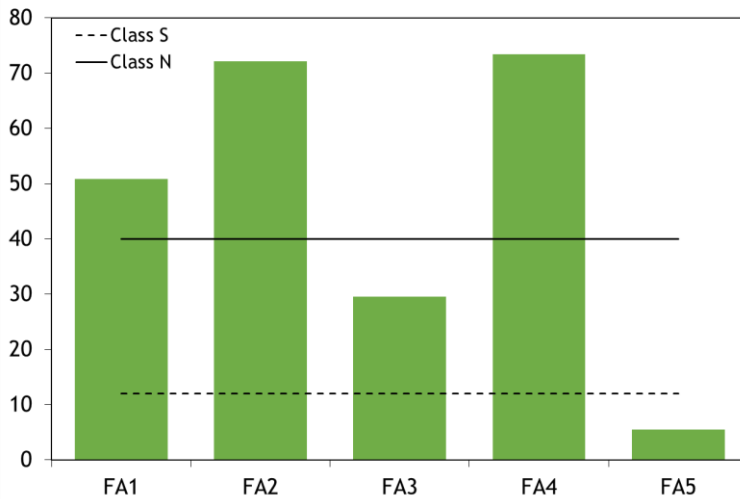


Fig 2. Fineness of the studied fly ashes expressed as the mass proportion of the ash being coarser than 45 µm. Dashed lines present the requirements according to EN 450-1.

3.4 Fly ash main components (SiO₂, Al₂O₃, Fe₂O₃)

According to 450-1, for fly ash to be used in concrete the sum of the contents of SiO_2 , Al_2O_3 and Fe_2O_3 shall not be less than 70 % by mass. For the fly ash samples FA1, FA2, FA3 and FA4, the sum of Al+Si+Fe was below the limit (see Fig 3). The sum for FA1 and FA2 was around 40%, for FA3 50% and for FA4 the sum was 60%. Only exception is FA5 which fulfills the requirement evidently: the sum was 81%. The reason for this difference is that FA5 has high content of SiO_2 and Fe_2O_3 since it is originating 80% from peat combustion. However, from Table 1 it is possible to see that ASTM C 618 standard requires the sum to be more than 50% (Class C). In the case of American standard, FA3 and FA4 fulfills the Class C requirement.

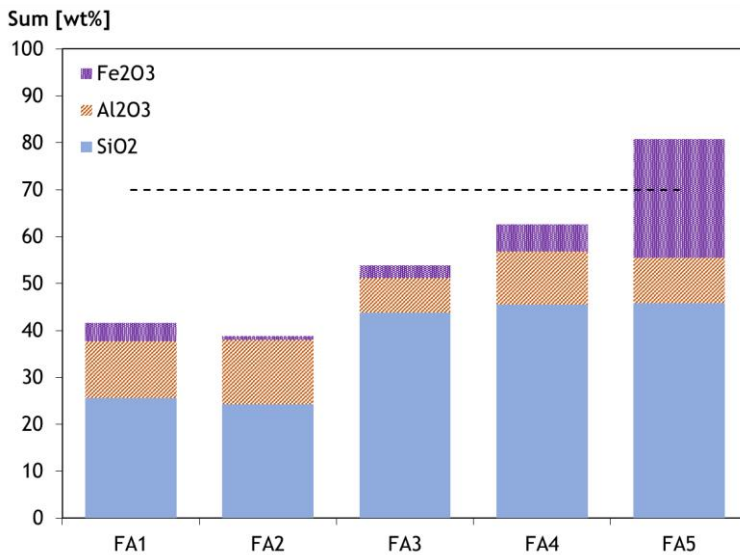


Fig 3. Sum of Al+Fe+Si for studied fly ashes. Dashed line presented the minimum value for the sum according to EN 450-1.

3.5 Chloride and sulfate

Sulfates and chloride can cause corrosion for steel reinforced structures, and they can reduce durability by deterioration of the microstructure [18], so therefore their content in concrete is limited. When the chloride and sulfate composition of studied fly ashes is compared to SFS-EN 450-1 limit values (Fig 4), it can be noticed that FA1 exceeded the limits substantially. FA2 exceeded the limit for chlorine content but fulfills the requirement for sulfate content. FA3 exceeded both limits. FA4 fulfilled the both requirements being barely below the limit values. As with FA4, also FA5 fulfills the both limit being clearly below the limits. As a conclusions for chloride and sulfate it can be said that if fuel contains more than 30% peat, Cl and SO_3 requirements are most probably fulfilled since those elements are coming to the fly ash from wood combustion. However, it should be noted that American standard (see Table 1) does not restrict chloride content at all, and moreover, the sulfate limit for both classes C and F is more (5 wt%) than the limit by European regulation (3 wt%).

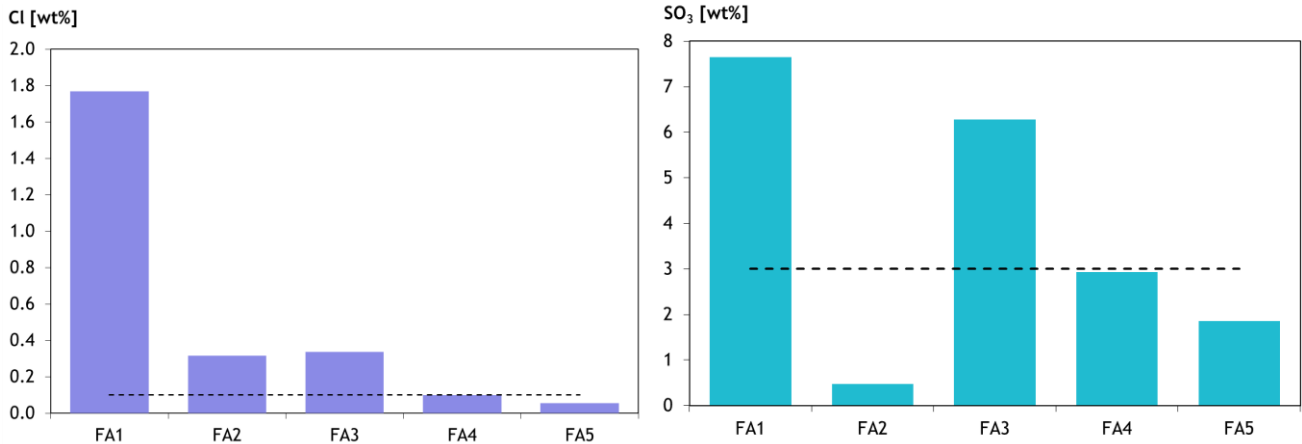


Fig 4. a) Sulfate, and b) chloride content for studied fly ashes. Dashed line presents the maximum values according to EN 450-1.

3.6 Free CaO

When the free CaO content of studied fly ashes is compared to SFS-EN 450-1 limit value (Fig 5), it can be noticed that the limit is exceeded by all other fly ashes than FA5 which Free CaO content is really low. FA1 and FA2 originating from paper industry sludge combustion had really high free CaO content. On the other hand, FA3 and FA4 originating mostly from wood combustion had free CaO content of 3.2 and 3.7 %, respectively. FA5 originating mostly from peat combustion had no free CaO at all. Too high free lime content fly ash may affect both mechanical properties and durability of concrete [42,43]. On the hand, it is noted in [44] that higher free lime in fly ash leads to early setting and higher compressive strength, especially at early age. They also noticed that when the free lime content is too high (>4.5%), the increase of compressive strength becomes less significant, but however the compressive strength results of mixtures with fly ashes having free lime content up to 4.51% satisfy standards. Therefore it can be estimate that at least FA3 and FA4 could bring improved properties for mortar. It should be noted that American standard (see Table 1) does not restrict free CaO content at all, therefore all ashes could be used if physical requirements are fulfilled.

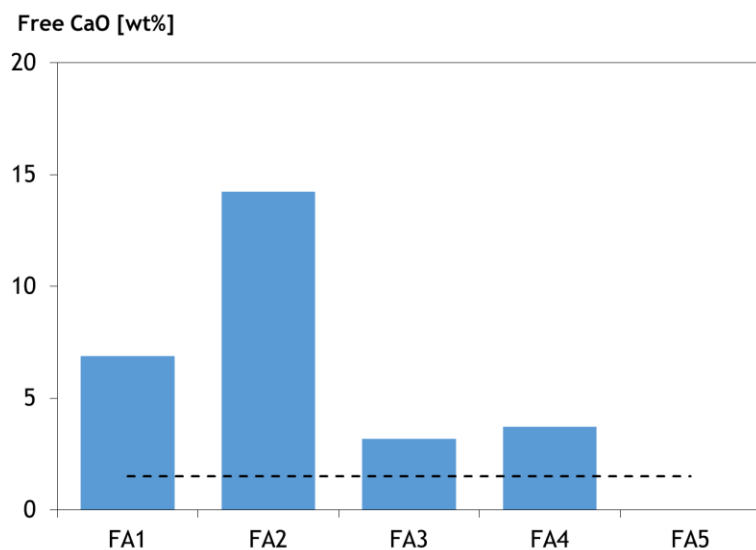


Fig 5. Free CaO content for studied fly ashes. Dashed lines present the requirement according to EN 450-1.

3.7 Total alkalis (Na+K), MgO and P₂O₅

The total content of alkalis (Na+K) is calculated as Na₂O_{eq} and is presented in Fig 6a for studied fly ashes. Only FA3 originating totally from wood combustion exceeded the limit. The content of alkalis is restricted since alkali-silica reaction (ASR) may occur. This reaction produces swelling gel products which exerts an expansive pressure inside concrete [45]. The content of MgO and P₂O₅ are presented in Fig 6 b and 5c, respectively, and it can be seen that the requirements are fulfilled by all studied fly ashes. It should be noted that American standard (see Table 1) does not restrict these three contents at all, therefore all ashes could be used if physical requirements are fulfilled.

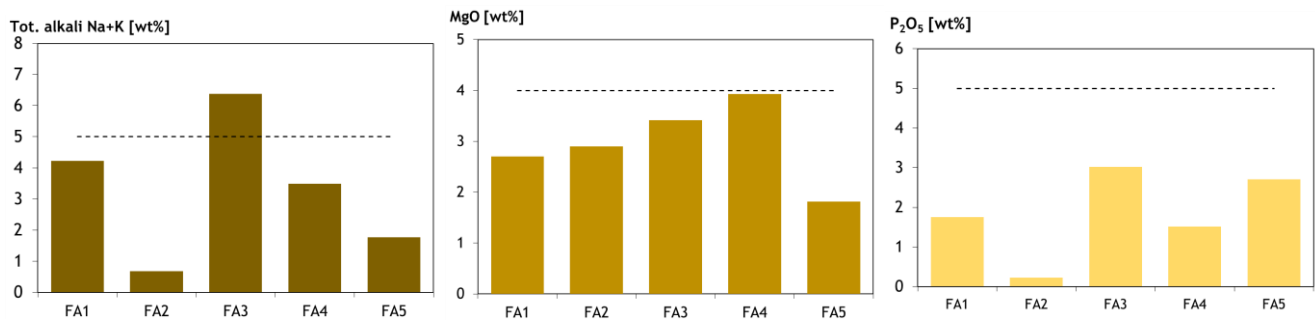


Fig 6. a) Total content of alkalis, b) MgO content, and c) P₂O₅ content for studied fly ashes. Dashed lines present the requirements according to EN 450-1.

3.8 Physical characteristic

The strength results are presented here as an activity index according to EN 450-1 standard. The activity index is calculated as a percentage of compressive strength of mortar containing fly ash to control mortar sample. Therefore, activity index for control sample is 100%, and for mortars containing fly ashes typically below 100%. EN 450-1 sets the requirements so that after 28 d curing the compressive strength should be more than 75% and after 90 d curing more than 85%. Here we replaced 20% of the cement with fly ashes. Compressive strengths of mortar samples at 28 d and 90 d age with various fly ashes are presented in Fig 7a and b. Mortars containing 20 mass-% of fly ashes achieved the required strength (over 75% of the control) at the 28 d age. Only exception was FA4 which did not fulfill the requirement. Two of the mortars containing 20 mass-% of fly ashes achieved the required strength (over 85% of the control) at the 90 d age: FA 2 and FA4. FA1 and FA4 did not fulfill the requirement.

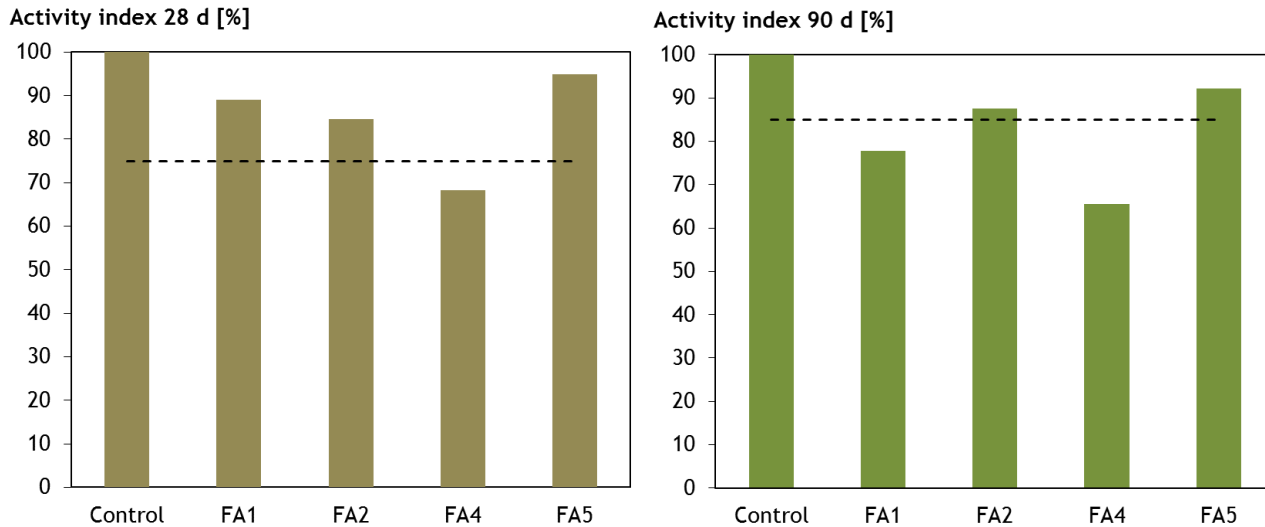


Fig 7. Activity index of mortar samples after a) 28 d, and b) 90 d of curing. Dashed lines present the requirement according to EN 450-1.

Since it seems that most of FBC fly ashes are not suitable for concrete according to EN 450-1 standard, it should be kept in mind that with different mechanical treatments fly ash properties are possible to modify. Classification or fractionation is one interesting option to improve fly ash utilization since there is a strong relationship between fly ash particle size and total heavy metal content in grate-fired systems [46]. On the other hand, an electrostatic precipitator can be used as a classifier in addition to its initial function of collecting fly ash particles from flue gases [7,47,48]. In this study, fly ashes covered the whole fly ash fraction without electrostatic separation. However, detrimental elements content can be too high even after ESP separation and therefore classification afterwards may be necessary. This can be done using an air classifier [49], the centrifugal SPLIT method [50] and sieving [51]. On the other hand, fly ash particle size can be modified by grinding [8]. In the future it is necessary to study the potentiality of different mechanical treatments to improve FBC fly ash properties. It is also necessary to study how FBC fly ashes effect on the water demand and long-time durability of mortar or concrete.

4. Conclusions

Five different fly ashes from fluidized bed combustion of peat, wood and different type of wastes was studied by their chemical and physical characteristic to find out how they fulfill the requirements for concrete set by European EN 450-1 standard. Fly ash originating mostly from peat combustion is the only fly ash fulfilling all requirements for concrete without any treatments. For other studied fly ashes some chemical and physical characteristics are exceeded: most probably free CaO, sulfate, chloride, and fineness. Sulfate and chloride are not problematic if over 30% of peat is used as a fuel since those elements are coming from wood combustion. Also the sum of main components (SiO_2 , Al_2O_3 , Fe_2O_3) failed for other ashes than the one originating from mostly peat combustion. It should be kept in mind that these requirements are set by European standard which is more restrictive than similar in America and some mechanical treatments are possible way to increase their utilization potential. Anyway, fly ashes originating from peat combustion are really promising material to partially replace cement as they are.

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