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Correlation between physical and chemical properties of wood biomass ash and cement composites performances

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HIGHLIGHTS

- 6 fly ashes from untreated wood biomass were investigated as SCM.
- Statistical analysis was used to determine influence of WBAs on cement composites.
- Desirability functions were used to define an acceptable content of WBA.
- Alkalis in WBA and LOI significantly influence on properties of tested composites.

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ABSTRACT

Wood biomass is a viable alternative to coal, while the ashes generated from biomass combustion appear as a serious environmental and economic issue. This research focuses on use of wood biomass ashes (WBA) as a supplementary cementitious material. Fly WBAs, originating from 6 power plants, were used as collected to replace 5, 10, and 15 wt% of cement in pastes and mortars. Statistical analysis was performed to quantify the effect of WBAs physical and chemical properties on the properties of composites with different WBA content. Analysis showed significant contribution of alkalis and LOI values on properties of WBA cementitious composites.

1. Introduction

Even though cement has a key role in meeting the rising global construction needs, the modern cement industry is facing numerous hardships while trying to reduce energy and raw material needs, as well as offsetting its carbon footprint. According to the International Energy Agency [1], the cement industry should be turning towards boosting energy efficiency and application of alternative materials, using it as fuel or raw materials. With these challenges ahead, using supplementary cementitious materials (SCMs) in order to reduce cement content in concrete is now under the spotlight [2]. Completing ambitious climate and energy goals until 2030, which include further reduction of overall greenhouse gas emissions and fossil fuels dependence, is crucial to ensure a thorough transformation of the European energy system. In order to do that, Europe plans to eliminate coal-burning power plants by 2030, relying on the ability of renewable energy sources to fill the gap left by the coal cutback. While meeting the target of renewable energy share of at least 32% by 2030, set by the Directive 2018/2001, a stable and continuous supply of energy needs to be enabled by different types of renewable energy such as solar energy, energy of the wind, geothermal and hydrothermal energy, bioenergy etc. [3,4]. Precisely, bioenergy and biomass could make a substantial contribution in establishing low-carbon energy system, provided that the biomass is produced and used in a sustainable manner [5,6]. The fact that wood biomass is considered to be a CO_2-neutral source of energy on account of releasing nearly equal amount of CO_2 by burning as it absorbs while growing, places it among the top biomass-source potentials for energy production in the EU with a majority share of 59% of all renewables [5,7]. Besides that, a large-scale industrial application of biomass in energy plants for heat and electricity production is expected to triple by 2035, compared with the levels from 2008 [8]. Even now, the expansion of wood biomass power plants is already resulting in sizeable amounts of wood biomass ash (WBA).

Considering that around 3% of WBA is being generated during combustion of 1 t of the wood biomass [9], an average electrical

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output of 1.5 MWh/ton of biomass and renewable electric production of 483 TWh indicate that around 10 million tons of ashes are globally produced from using biomass for electricity production [10–12]. These numbers are a strong indicator of the essential need for strategic and sustainable management of the waste ashes. Current WBA management practice in Europe is largely based on disposing WBAs on landfills as well as using it as soil amendment/fertilizer, most times without any form of control, which is a paramount environmental and economic issue [6,10,13–17]. Due to lack of disposal sites and the ease of air contamination with fine particles transported by wind, causing respiratory health problems to residents near the landfill, the disposal of wood ash in landfills should be properly managed. Leaching of heavy metals from the WBA or washing out of landfills during rain, which can lead to contamination of groundwater resources also represents a major problem [14,18,19]. By adopting the new "Circular Economy Package", which among other things includes the amending Directive 2018/851 on waste and the Directive 2018/850 on the landfill of waste, European Union is strongly supporting the minimization of waste landfilling [20,21]. Therefore, planned and responsible management of the WBA is a very topical issue that requires an adequate solution. Hence the costs of landfilling will unquestionably rise in future, due to additional disposal sites crisis and stringent EU landfill directives [11]. Therefore, novel concrete containing waste materials represents a feasible application of WBA, at the same time solving the problem of industrial waste disposal along with reducing the amount of cement required [18]. To avoid exceeding the benefits of using this waste material as partial cement replacement, WBA should be utilized nearby the energy plant where it originates from, taking into account CO_2 emissions due to transportation [22]. In this respect, it is important to stress the high variability of WBAs chemical composition, which depends on the raw material itself. Although research studies reported until now have demonstrated that WBA can be used in the cement composites [13,23–26], there is still a necessity for a multidisciplinary and comprehensive approach to fully understand the chemical and microstructural characteristics of WBA and their impact on properties of cement composites.

WBA being a complex blend of inorganic and organic matter, its volume, characteristics and quality fluctuate even more than conventional coal ash, depending on various parameters [27]. The variable chemical composition of WBA differs from that of coal fly ash, presently a widespread form of Portland cement substitute [28]. Therefore, the existing regulations for using fly ash in cement EN 450-1 [29] can be applied to WBA only as guidelines. Considering the lack of standardised quality parameters in SCMs usage, demonstrating that mechanical performance and durability of cementitious composites containing alternative binding materials are not deteriorated is therefore of utmost importance [11]. Accordingly, quality control of biomass ash production and application is essential, even in comparison with coal fly ash, commonly used in cement and concrete production desipte its chemical oscilations [13]. Providing a detailed insight on the impact of WBA on mechanical and durability properties of cement composites is recognised as the initial step in defining the lacking guidelines for accepting WBA as a new raw material in the construction sector. Accordingly, the main objectives of this research were defined as a need: (a) to show the influence of physical and chemical properties of WBA used as a partial cement replacement on mechanical and durability properties of cement composites; (b) to define an acceptable content of WBA used as a partial cement replacement which would not impair the quality of cement composites.

Investigation was conducted on fresh and hardened pastes and mortars with different content of WBAs from separate origin. WBA utilized in this research were collected from 6 power plants located in Croatia with different types of combustion technology (grate combustor, pulverized fuel combustor and bubbling fluidized bed combustor). Basis for evaluation of mechanical and durability performance of cement pastes and mortars with different content of WBA as cement replacement (5%, 10% and 15%) was detailed WBA characterisation presented in [11].

2. Materials and methods

Specimens were produced using cement CEM I 42.5 R, potable water and standard sand complying to EN 196-1 [30]. Wood biomass fly ash (WBA), collected from six different power plants in Croatia, was used as partial cement replacement. WBA was collected from October till January, characterization was done from January till April and finally cementitious composites were prepared in May/June. During the experimental work, WBAs were sealed in plastic bags and then stored in closed plastic containers. Summary of chemical and physical properties of WBAs and cement used, as well as inputs from power plants (average temperature, biomass and technology used), are presented in Tables 1 and 2. More detailed characterization of used WBAs (chemical composition, particle-size distribution, particle morphology, heavy-metal content and mineralogical composition) is published by Carević et al. [11]. Particle size distribution of WBAs and cement is presented on Fig. 1.

2.1. Mix design

Thirty-eight mixes, divided into three groups, were prepared as follows:

a) *Two reference mixes*: Cement paste (P0) according to EN 196-3 [31], with 500 g of CEM I 42.5R and 125 g of water & Mortar (M0) according to EN 196-1 [30], with the mass ratio of CEN standard sand, CEM I 42.5R and water equal to 3:1:0.5;
b) *Group I*: 18 paste mixes with six different types and contents of WBA;
c) *Group II:* 18 mortar mixes using six different types and contents of WBA.

WBA was used as cement replacement by mass of 5%, 10% and 15%. For preparation of paste mixes, water amount was determined as a prerequisite to achieve a standard consistence.

Mixes were designated as: a) P_i-5, P_i-10, P_i-15 for pastes, b) M_i-5, M_i-10 and M_i-15 for mortars, where *i* is number of the WBA-F sample. Reference mixes with 0% WBA were denominated as P0 and M0.

2.2. Specimens and test methods

Fresh state properties for both, pastes and mortars, were determined immediately after mixing. After casting, the specimens were kept covered at laboratory conditions for 24 h until demoulding, to prevent water evaporation. After demoulding, the specimens were in mist room at 20 ± 2 °C and RH $\geq$ 95%, until testing. Different curing procedure was followed only for the drying shrinkage testing; specimens were stored at 20 ± 2 °C and RH 60 ± 10% until testing at the age of 365 days.

Table 3 shows the standards used for testing the paste and mortar properties. Compressive strength was tested at the age of 7, 28 and 90 days, while drying shrinkage was measured after 1, 3, 7, 14, 28 and 56 days and afterwards monthly until 365 days. Capillary absorption was tested at the age of 28 days. For testing mortar properties in hardened state, 3 specimens were prepared per each mix and per each age.

Table 1
Chemical and physical properties of WBA-F samples and cement.

	CEM I	F1	F2	F3	F4	F5	F6	Criteria according to EN 450–1
Technology used		Grate combustor	Pulverized fuel combustors	Pulverized fuel combustors	Grate combustor	Grate combustor	Bubbling fluidized bed	
Average temperature (°C)		800	700–750	700–750	700–950	800	850	
Additive used		–	–	–	–	–	Quartz sand	
Type of the biomass mostly used		Oak, hornbeam	Beech, oak, hornbeam, poplar, cherry	Beech, oak, hornbeam	Beech, oak, abies, picea	Beech, oak, hornbeam	Beech, oak, hornbeam, poplar	
P_2O_5 (mass %)	0.22	2.76	2.60	1.84	1.82	1.35	4.03	≤ 5
CaO (mass %)	59.80	67.85	48.70	51.90	46.75	16.25	47.35	–
MgO (mass %)	2.01	4.31	4.79	3.75	8.26	4.30	4.71	< 4
TiO_2 (mass %)	0.23	0.05	0.15	0.15	0.34	1.17	0.25	–
SO_3 (mass %)	3.33	1.26	4.77	3.58	2.73	0.60	3.95	≤ 3
Na_2O_{eq} (mass %)	1.67	3.71	10.90	6.60	4.63	4.59	4.72	≤ 5
Pozzolanic oxides ($SiO_2 + Al_2O_3 + Fe_2O_3$)	29.97	5.37	12.29	13.03	28.81	54.68	19.70	≥ 70
Free CaO (mass %)	2.50	23.50	8.60	13.50	7.30	0.50	8.80	< 1,5
Free MgO (mass %)	0.75	4.00	4.20	3.80	3.30	0.50	4.50	–
Cl^- (mass %)	0.04	0.04	0.06	<0.003	0.04	0.04	<0.003	< 0.10
LOI (950 °C)	3.6	19.1	13.4	13,8	3.8	8.3	12.7	≤ 9
pH	12.86	13.34	13.37	13,25	13.15	12.97	13.22	–
Density (g/cm^3)	3.1	2.47	2.59	2,59	2.59	2.63	2.33	–
Bulk density (kg/m^3)	n/a	0.59	0.38	0,38	0.91	0.61	0.55	–
d_{50} (μm)	9.6	31	18.2	43,3	71.9	120.7	17.8	–
% passages through sieve 21.23 μm	70.4	30.17	69.21	14.5	16.14	3.18	5.3	–

Table 2
Heavy metal content in WBA and cement (mass%) [11].

Heavy metal	WBA designation						
	CEM I	F1	F2	F3	F4	F5	F6
Zn (mg/kg)	182.4	26	1850	71	98.5	314.7	139
Cd (mg/kg)	0.93	2.42	3.1	1.5	3	2,6	6
Cr (mg/kg)	63.9	20.7	50	26.2	26.1	123	61.7
Ni (mg/kg)	68.7	17.4	79.6	22	12.9	170.3	35.2
Pb (mg/kg)	1.9	<0.04	79.9	5.9	5.9	101.4	37.8
Mn (mg/kg)	617.3	2098	6565	2609	501.4	1660	942
Co (mg/kg)	7.9	<0.04	11.2	4	3.5	26	15.8
Ba (mg/kg)	236.7	1124	588.8	1089	72.7	1437	545
Bi (mg/kg)	<0.02	31.5	44.8	24.6	10	2.8	25.2
Sr (mg/kg)	1775.4	492.5	408.5	548.7	46.6	314.7	485
Cu (mg/kg)	30.6	65.9	84.4	44.6	3.5	79.7	56.1
Hg (mg/kg)	0.042	<0.003	<0.003	0.006	<0.003	0.01	0.189

2.3. Statistical analysis of the results

Statistical analysis of the results was performed to quantify the effect of WBAs physical and chemical properties on the properties of cement composites with WBA in fresh and hardened state.

To determine the effect of the WBA type and content on the properties of the composite, it was taken into account that the binder is a mixture composed of two components (CEM I + WBA). Accordingly, physical and chemical properties of the binder are expressed with regard to WBA content according to the following equation:

$$X_i = X_{cem} \times (\%/100)_{cem} + X_{WBA} \times (\%/100)_{WBA} \qquad (1)$$

where:

X_i - expressed value of observed physical or chemical property
X_{cem} – value of the physical or chemical property for cement
X_{WBA} – value of the physical or chemical property for used WBA
$(\%/100)_{cem}$ – content of cement in the mixture, expressed in percentages
$(\%/100)_{WBA}$ – content of WBA in the mixture, expressed in percentages

For example, for the P4-5 mixture, the content of free CaO was determined by taking into account 95% share of free CaO in cement and 5% share of the same mineral in F4; i.e. 0.95*2,5 + 0.05*7.3 = 1. 615 (%, mass).

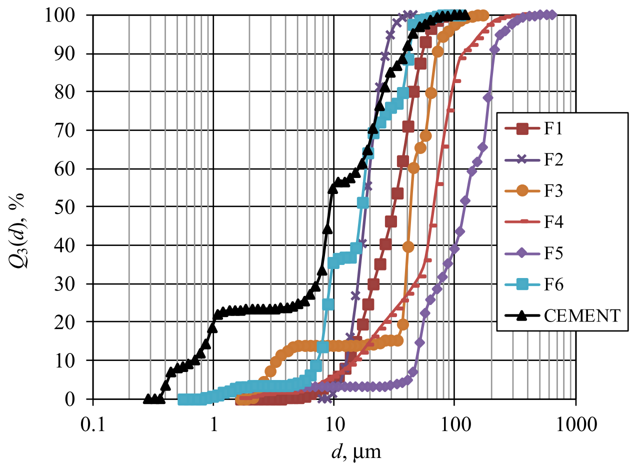


Fig. 1. Particle size distribution of WBA and cement.

Table 3
Test methods for investigation of fresh and hardened state properties of pastes and mortars.

Property	Standard
Standard consistency	EN 196-3:2016
Setting time	
Soundness	
Temperature	
Density	EN 1015-6:2000/A1:2008
Temperature	HRN U.M1.032:1981
Air content	EN 1015-7:2000
Consistence by flow table	EN 1015-3:2000/A1:2005/A2:2008
Compressive strength	EN 196-1:2016
Capillary absorption	EN 13057:2003
Drying shrinkage	EN 12617 - 4:2003

Data normality (normal distribution) was verified by using Shapiro-Wilk test [32]. Based on the results of Shapiro-Wilk test, i.e. verification that this is not a normal distribution of data, further analyses were undertaken by using Spearman's Rank correlation coefficient [33,34,35] in accordance with the following expression:

$$r_s = 1 - 6\sum_{i=1}^{n} \frac{d_i^2}{n(n^2 - 1)} \tag{2}$$

where:

r_s – Spearman's Rank correlation coefficient
d – difference between rank values of two observed variables
n – of different series.

Values of the Spearman's Rank correlation coefficient can range from −1 to + 1 and are indicative of the intensity or strength of the relationship between two values which are in correlation. In the discussion, only dependencies with correlation coefficient value greater than 0.5 were considered. The moderate correlation corresponds to a correlation coefficient equal to ± 0.5 to ± 0.69, high correlation from ± 0.7 to ± 0.89 and strong correlation from ± 0.9 to ± 1.00 [34,36].

Further, to detect which of the investigated WBA has the ability to fulfil the set criteria, the desirability functions were used. The desirability functions reflect the levels of each response in terms of minimum and maximum desirability. A desirability function (d_j) varies over the range of $0 \leq dj \leq 1$. Individual responses are described using following equations, where the maximized individual response is defined by:

$$d_j = \left[\frac{Y_j - minf_j}{maxf_j - minf_j}\right]^t \tag{3}$$

or the minimized individual response by:

$$d_j = \left[\frac{max_j - Y_j}{maxf_j - minf_j}\right]^t \tag{4}$$

where d_j, Y_j, min f_j and max f_j are the individual desirability functions, the current, the lowest and the highest values of jth response included in the optimization [37]. The power value t is a weighting factor of the jth response.

By using an overall desirability function (D), which presents the geometric mean of the individual desirability functions (d_j), the multi-objective optimization problem can be solved:

$$D = (d_1 \times d_2 \times d_1 \times \ldots\ldots\ldots \times d_m)^{\frac{1}{m}} \tag{5}$$

where m is the number of the responses. The maximum value of D gives the optimum solution.

Determined individual and overall desirability functions were used to summarize the influence of investigated WBAs on both pastes and mortars properties.

3. Results

3.1. Effect of WBA on cement paste properties

Cement paste properties for mixes prepared with different types and content of WBA are shown in Table 4. Water amount presented represents the water quantity needed to achieve standard consistency of cement paste. Temperature, initial and final setting, as well as soundness were further tested on cement pastes with standard consistency.

The results (Table 4) show that mixes with WBA have an increased water requirement, with an average increase of 10% compared to the reference mix. Increased water requirement follows the increase of WBA content in the mix, which is in line with conclusions shown in [38,39]. This is especially true for ashes designated as F2 and F3. Fast loss of workability was observed for pastes during mixing, and an increase of F2 content to 15% results in an increase of water requirement of up to 53%.

Increased temperatures compared to the reference mix were recorded for all pastes with WBA, and this is especially the case for mixtures with F1, F2 and F3. Maximum increase of temperature of up to 5 °C was recorded for these mixtures.

Although it is a widely accepted fact that higher paste temperatures in fresh state lead to quicker setting [40], this trend was not observed for the pastes containing WBA. Test results for the initial and final setting show that the presence of WBA in the mixture affects the delay in the start and the end of the setting, compared to the reference (P0) mix. This is especially pronounced for pastes containing WBA designated as F1, F2, F3 and F4, in all tested shares.

Due to high content of the free CaO and free MgO in the composition of the WBA, soundness was tested according to EN 196-3 [31], Table 4. Based on the soundness test results, all tested cement paste mixes met the criteria of maximum distance between the ends of the needles of Le Chatelier's rings of 10 mm, complying to EN 450-1 standard [29].

3.2. Effect of WBA on mortar properties

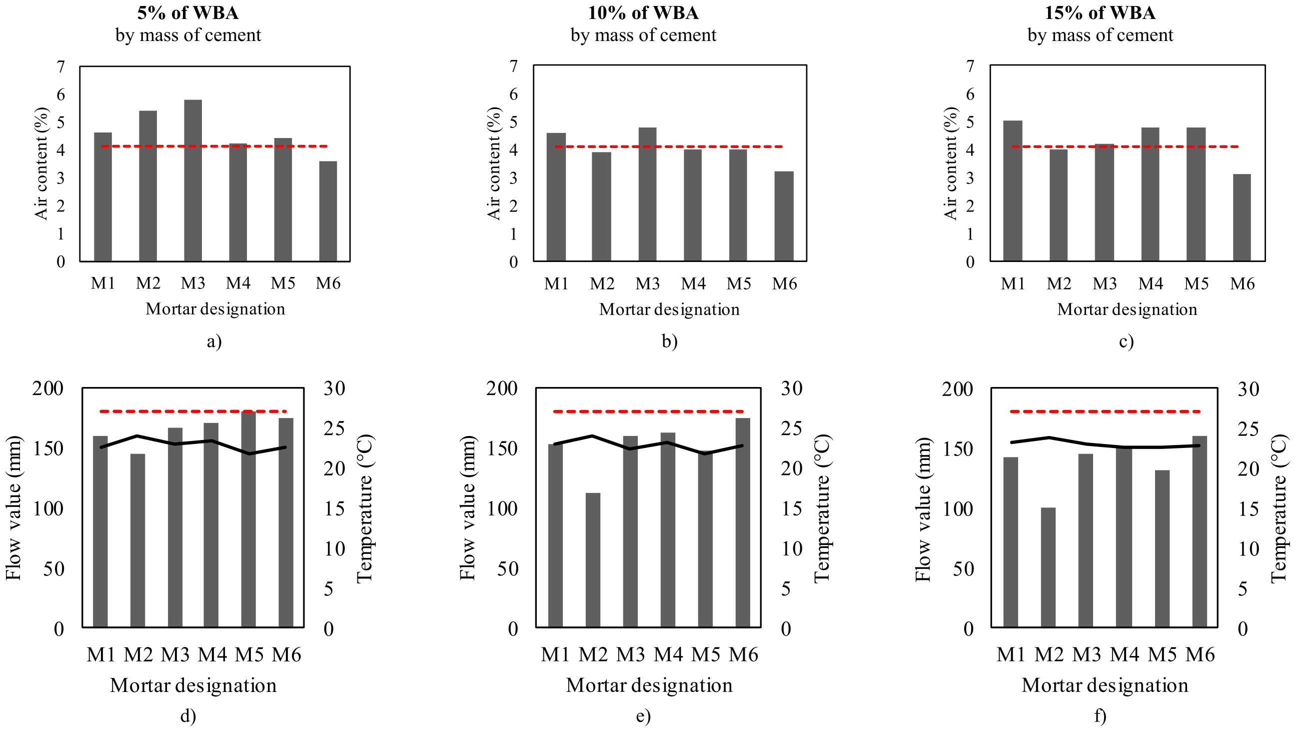
Replacing cement with WBA leads to increased pore content in fresh mortar. However, it must be pointed out that the greatest (maximum) increase of 13.8% compared to the reference mortar was seen in mortars with lowest WBA content (Fig. 2a–c). Mortars with ash designated as F1, F2, F3 particularly stand out in this regard. Further increase of WBA content in mortar does not have any significant effect on the pore content in fresh mortar.

Consistency of mortars decreases proportionally to the WBA content in mixes; specifically, the mortar consistency on average decreased by 8, 16 and 32% for 5, 10 and 15% of cement substituted by WBA, respectively (Fig. 2d–f). Loss of workability as a consequence of using WBA is in line with current research on the same topic [13,14,24,24,39,41–48]. Significant decrease in workability was observed for M2 mortar where the loss of workability was 19, 38 and 44% compared to the M0 mix. Decrease in workability cannot be attributed to the increase in temperature of fresh mortar due to the fact that the greatest temperature increase was observed for mixtures with 15% WBA content in the total cement mass, and it amounts to only 3% compared to the reference M0 where temperature was 22.3 °C.

Results of compressive strength testing performed in accordance with EN 196-1:2016 [30] standard with different WBA con-

Table 4
Influence of type and content of WBA on cement paste properties.

Mix designation	WBA content (%)	Water amount (g)	Temperature of paste (C)	Initial setting time (min)	Final setting time (min)	Soundness (mm)
P0	0	141.5	21.3	195	255	4
P1-5	5	147.6	25.5	265	295	5
P2-5	5	149.3	24.2	265	295	0.5
P3-5	5	147.6	25.8	265	295	3
P4-5	5	147.7	22.4	245	305	0
P5-5	5	143	21.9	190	250	2.5
P6-5	5	144	23.5	195	255	4.5
P1-10	10	154	24.6	295	325	0
P2-10	10	182	26.3	225	315	2.5
P3-10	10	155.1	23.9	230	290	1
P4-10	10	141.1	24.8	235	265	3
P5-10	10	146.1	24	185	245	2.5
P6-10	10	147.6	22.6	200	230	2.5
P1-15	15	161.1	25.2	250	310	8.5
P2-15	15	217	24.8	305	365	2
P3-15	15	166	25.2	215	335	2.5
P4-15	15	141.5	24.5	245	275	2
P5-15	15	151.1	23.2	200	230	4
P6-15	15	157.7	25.7	210	270	3



a) b) c)

d) e) f)

Fig. 2. Influence of WBA on properties of mortar based on WBAs type and content: a, b, c) Air content, d, e, f) Consistence (by flow table) and temperature (black line). ** red dashed lines in Figures a, b, c) represent air content of reference mix and in Figures d, e, f) flow value of reference mix.

tent are shown in Fig. 3. Compressive strength values for the samples with WBA have been compared to the strength of the reference mix (M0).

In all mixes, compressive strength after 7 days has decreased by 4.17% (M5-10) up to 30.04% (M2-15), i.e. on average by 12, 15 and 22% for mixes in which the cement was replaced with 5, 10 and 15% of WBA, respectively compared to the reference mortar. At the age of 28 days, in mortars with 5 and 10% WBA content, compressive strength remains the same or is increased by up to 11.78% (M6—5), except for the M2 specimen, whose compressive strength is up to 11.23% lower for the M2-5 mix i.e. 16.75% lower for M2-10 mix. Compressive strength of all mixes with 15% WBA content has decreased by 9.82% (M5-15) i.e. by 25.10% (M1-15) compared to the reference mix at the age of 28 days. After 90 days, compressive strength of specimen with 5% WBA has increased (M1-5, M4-5, M6-5) or decreased by 1.81% (M5-5) to 6.05% (M3-5), whereas other samples with 10 and 15% WBA content register a drop in the range from 1.26% (M4-10) to 30.69% (M1-15).

Slower strength rate at early age is observed over time for mixes with WBA. Slower rate of strength increase for the mixes containing WBA can be attributed to the pozzolanic reaction [38,43,49], but can also be explained by hydraulic properties of WBA. For example, the authors [50,51] obtained compressive strength of 20 MPa by testing specimen obtained by mixing ground wood biomass ash, peat and water (self-hardening), which confirms the contribution of WBA to the increase of compressive strength [52].

Capillary absorption coefficient was determined for each studied type and WBA content, Fig. 4. Reduction of capillary absorption

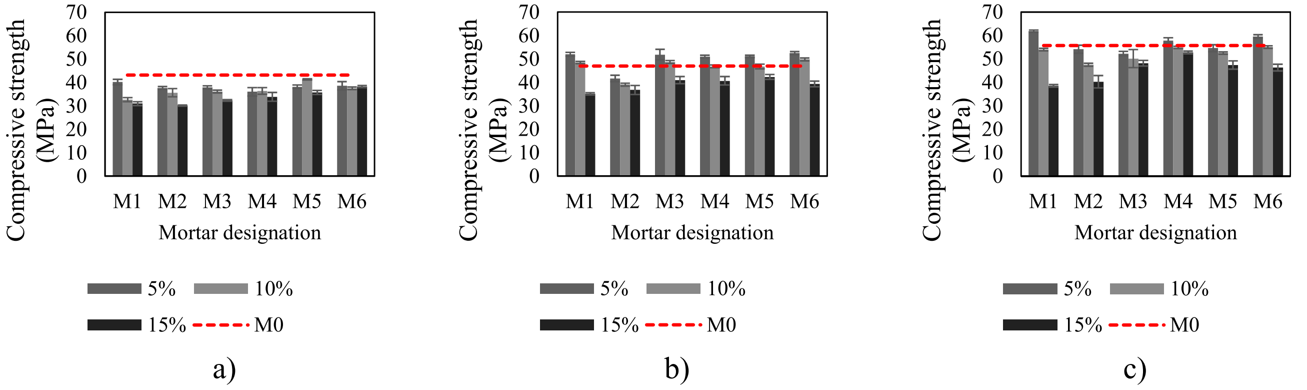


Fig. 3. Compressive strength of mortars of the following ages: a) 7 days; b) 28 days; c) 90 days.

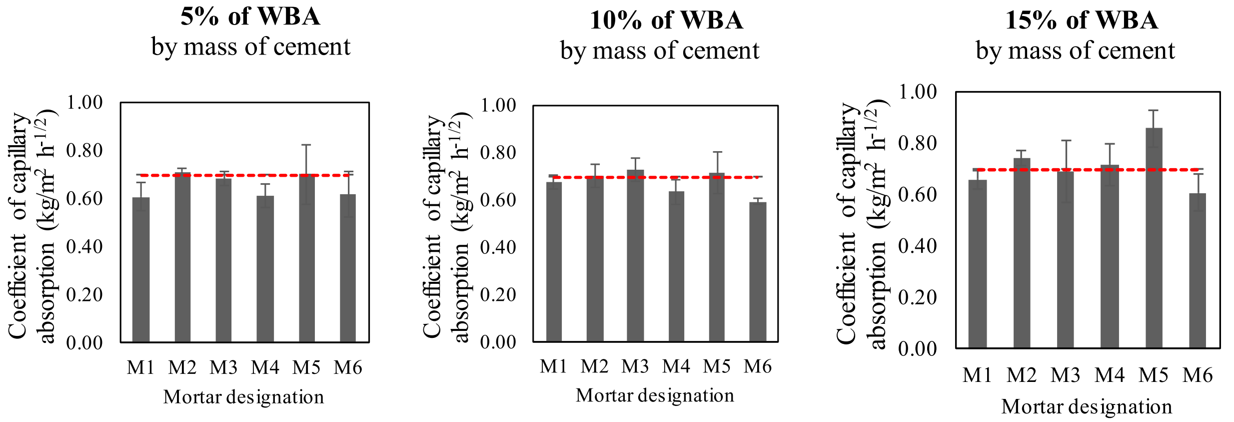


Fig. 4. Influence of WBA type and content on value of capillary absorption coefficient.

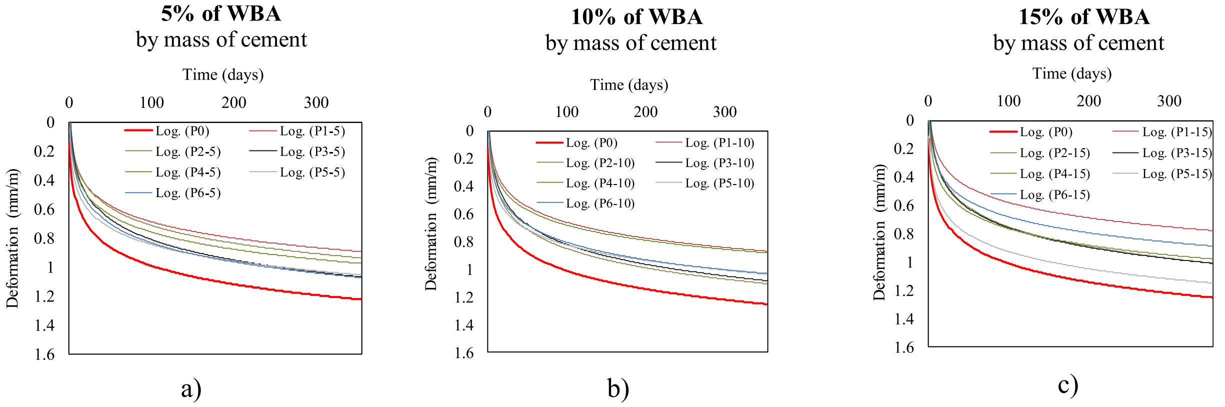


Fig. 5. Influence of WBA content and type on drying shrinkage of mortar during 365 days.

coefficient for 6.04% and 3.25% is observed with an increase of WBA content by 5 to 10%, compared to the reference mix (M0). At 15% of WBAs' content, an average increase of 2.27% in capillary absorption compared to the reference mix (M0) is observed. The aforementioned is in accordance with [49]. However, mortars with 5 and 10% WBA have lower capillary absorption values, whereas increase of WBA content up to 15% has a negative effect on the capillary absorption for all mixes except M6-15.

According to [14,24,53], partial replacement of cement with WBA decreases the values of drying shrinkage. It is considered that lower values of shrinkage are recorded since WBA acts like a filler rather than a binder. The same results are shown on Fig. 5, where three different contents of WBA replacement for cement (5, 10 and 15% by mass of cement) and different technologies of biomass combustion are observed. In all cases the drying shrinkage was reduced when compared to the control mortar (M0) during the period of 365 days. Based on the obtained results it is possible to conclude that partial substitution of cement with WBA (5, 10 and 15% by mass of cement) contributes to an average reduction of overall deformation for 20, 21 and 24% relative to the control mortar after 365 days. Results presented on Fig. 5 are shown using logarithmic trendline.

4. Discussion

Properties of WBA composites are greatly dependent on the physical and chemical properties of WBA. For the purpose of gaining a better understanding of the testing results, a statistical analysis of the effects of chemical and physical properties of WBA was carried (Tables A.1 & A.2).

The statistical analysis determined moderate to strong correlation between the water requirement and setting time with regard to chemical composition and physical properties of the WBA (Table A.1). Increased water requirement in mixes with WBA is linked to the morphology of the WBA [13,54–56,58], high porosity [23,55], large specific area of the particles [57,58], large content of unburned particles [59,60], high content of free CaO [61,62] and other chemical parameters of the WBA [57], Figs. 6 and 7. Furthermore, increase in water requirement is a consequence of high alkali content due to the fact that additional alkali ions accelerate aluminate hydration by decreasing the release of Ca^{2+} ions from the gypsum, thereby causing decreased efficiency of gypsum action during aluminate hydration [63,64], Fig. 7a). Similar mechanism is a consequence of increased content of free CaO and free MgO [65]. Additionally, presence of organic matter (increased LOI values) is conducive for significant absorption of water molecules, decreasing the amount of free water required for achieving desired workability [39,59], Fig. 7b). Larger content of alkalis and magnesium oxide in the binder [14,46,47,58,69,66] and low content of pozzolanic oxides contributes to the delay in setting, especially for pastes with increased WBA content (Fig. 7c–e). Delay of the initial setting can be a consequence of an increased content of heavy metals [67–70]. According to [71], the delay happens due to the conversion of metal hydroxides into new metal hydroxyl compounds; due to this, there is a significant consumption of calcium and hydroxide ions, which causally delays the creation of C-S-H gel and portlandite. It is known that amphoteric metals such as zinc, led and tin are used as setting retardants [71]. Also, higher values of loss on ignition (LOI) can, as a consequence, lead to delayed setting [72].

However, WBA content used as a cement substitute in this paper is still sufficiently low for the potentially "negative" chemical composition of WBA to be "overpowered" by a larger content of cement. This is especially confirmed by testing of soundness of pastes containing WBA where all tested pastes have met the criterion of maximum distance between the ends of the needles of the Le Chatelier rings in accordance with the standard EN 450-1 [29], despite the fact that the values of free CaO values for all used WBAs, with the exception of WBA 5, are greater than limit values according to the referred standard (<1.5% for free CaO, and <4% for MgO). One of the explanations would be that WBA was stabilised in period between ash collecting and mixing as reported by [73]. Namely, chemical reactions when WBA is in contact with water and CO_2 from the air are resulting in the formation of $Ca(OH)_2$ and of $CaCO_3$ [74,75]. Lime is sensitive to atmospheric moisture and carbon dioxide [76–78] and therefore its stabilization could show the alteration in the mineralogy structure of the material [73,74,79]. This however has a positive influence of the composite volume stability, since higher contents of free CaO induce swelling and cracking. It is likely that transportation and storage of the WBA before reaching the concrete plant contributes to its stabilization. Results in this research are in line with [73] where, all tested cement composites satisfied the volume stability test after WBA stabilization (maximum free CaO content in stabilized WBÁ samples were 20.49%).

Statistical analysis of test results showed a correlation between the free CaO and compressive strength of mortar at early age, Table A.2. With an increase of WBA and free CaO content, early-age strength decreased in accordance with [62,80,81]. Content of

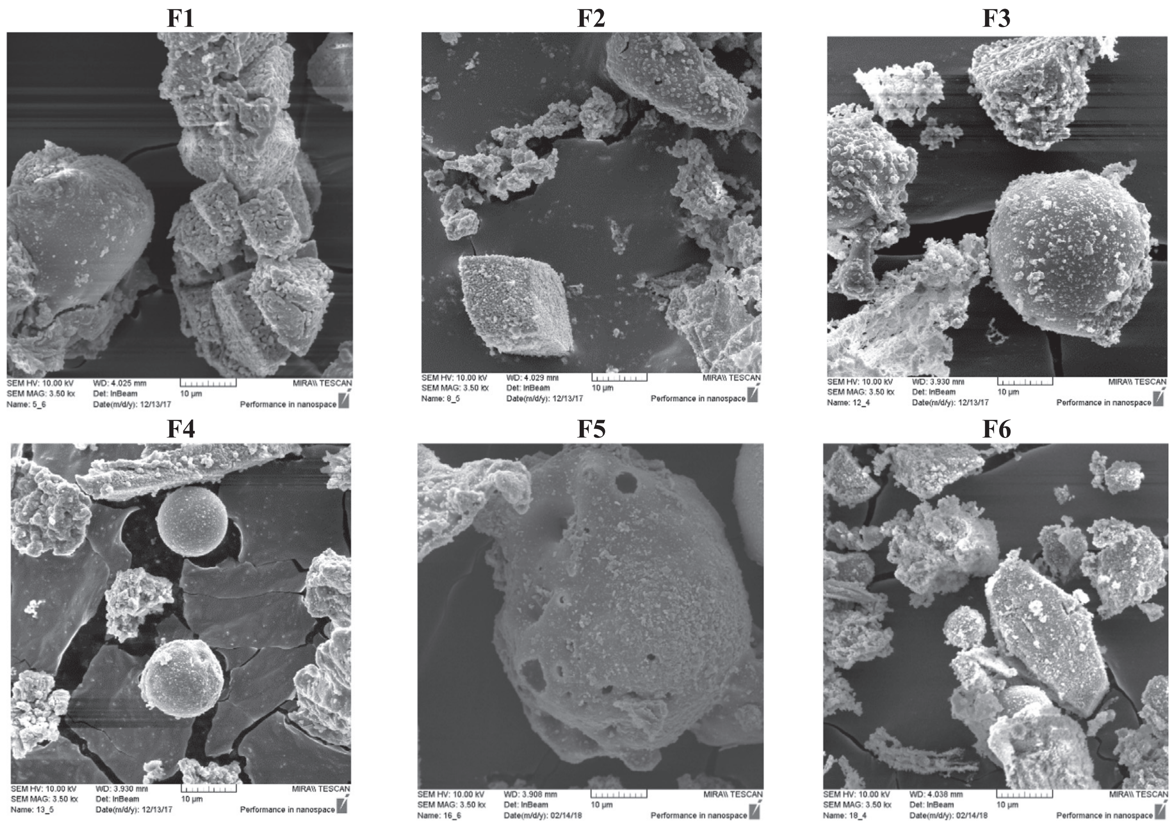


Fig. 6. Micrographs of WBAs (magnification SEM_MAG = 3500x).

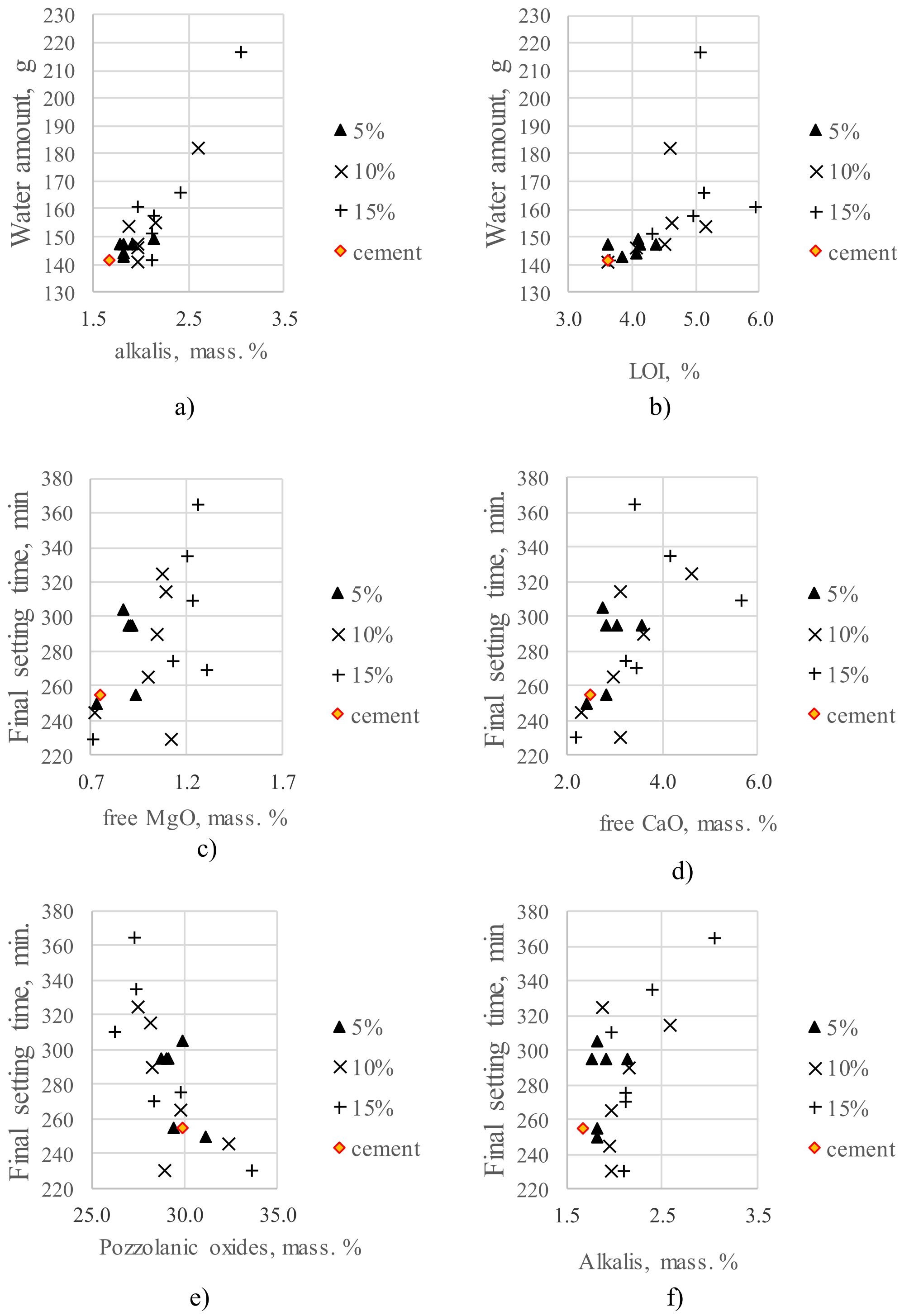


Fig. 7. Effect of chemical characteristics and WBA content on workability: a) alkali content, b) LOI content, and paste setting time: c) free CaO content, d) free MgO content, e) pozzolanic oxides content, f) alkali content.

free CaO does not have a significant impact on compressive strength of older specimen. However, compressive strength also decreases with the increase in the content of alkalis in the WBA composition [63,64,82], Fig. 8 a). At the same time, increase in the content of pozzolanic oxides has the opposite effect, Fig. 8b). This is confirmed by the compressive strength analysis, where mixes with WBA designated F4, F5 and F6 attain greatest compressive strength values, particularly for 15% WBA content, and these are precisely the ashes with the greatest pozzolanic oxide (F5) content and chemical composition which is very similar to cement (F4 and F6). In capillary absorption testing, there is a noticeable dependency with the alkali values and particle size median (d_{50} is the value from which 50% of particles are smaller), Fig. 8c) and d), i.e. greater values of alkalis and larger particles lead to increase in capillary absorption.

In general, it can be concluded that statistically, the impact of certain heavy metals is moderately significant. Current research show that “storing” waste materials in cement composites can lead

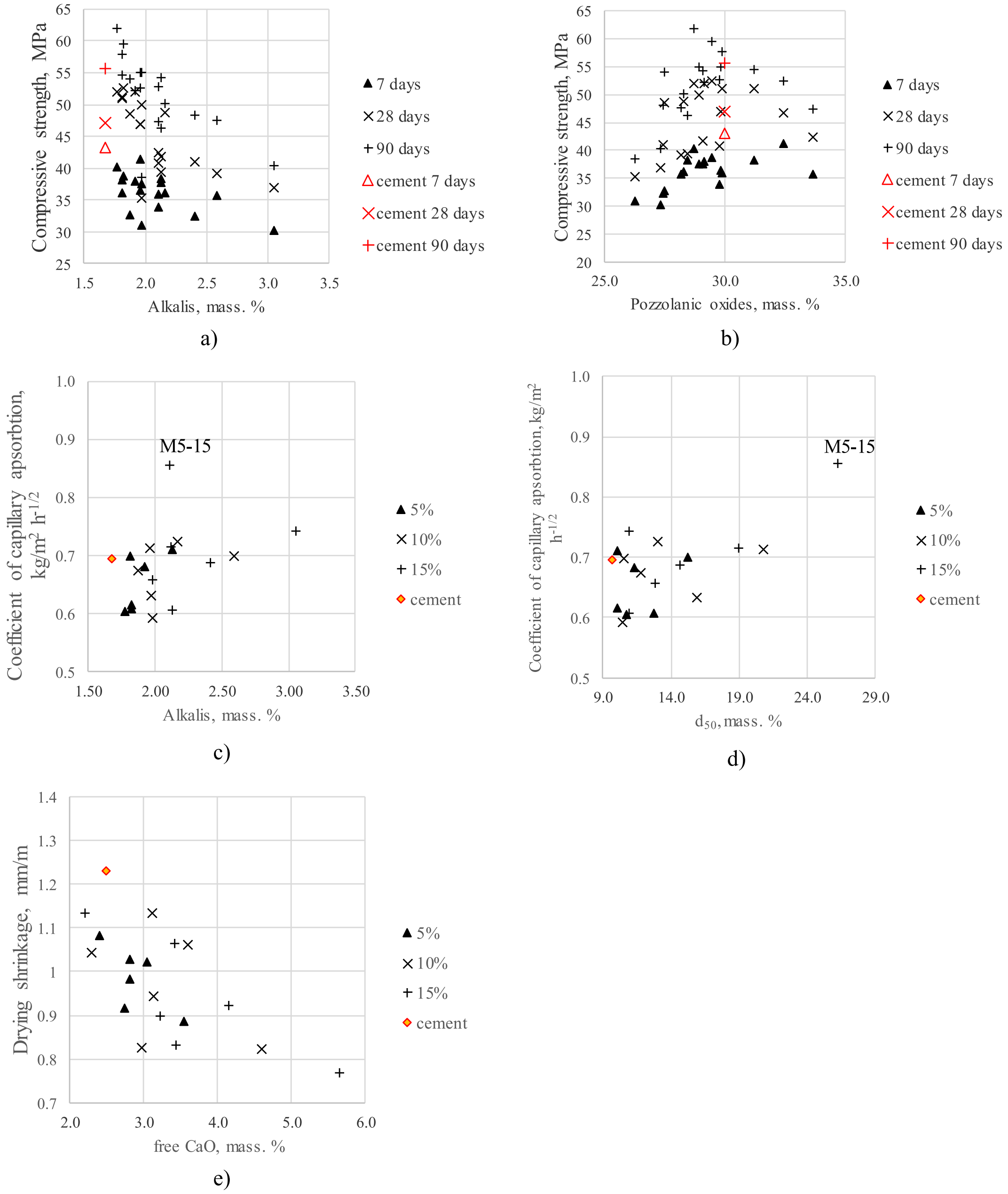


Fig. 8. Compressive strength of mortars at different ages compared to: a) alkali; b) pozzolanic oxides; Capillary absorption compared to: c) alkali; d) WBA size; Drying shrinkage compared to: e) free CaO.

to a change in cement composite properties, as for example it can affect the setting time or compressive strength [67,68,83,84], depending on the type of metal. For example, compressive strength decreases [67,83,84] with increased content of zinc in cement composites. Although during hydration heavy metals can become immobilized in cement matrix of the C-S-H gel or form new compounds for WBA applications in the construction sector, it is necessary to investigate the ecological impact of cement composites with WBA with the leaching test. In addition to impact on compressive strength, according to Table A.2, the impact of certain heavy metals (Zn, Cr, Ni, Pb and Co) on shrinkage was observed: increase in the content of aforementioned heavy metals also increases shrinkage although the total shrinkage value is still smaller compared to the reference mix (M0). At the same time, increased content of free CaO in WBA lead to a decrease in total shrinkage which is in line with the assumptions shown in [13], Fig. 8e).

Finally, optimal types and content of WBA have been confirmed by desirability functions, while taking into account all tested mortar properties. Eight factors were considered for selecting the optimal WBA type and content: water requirement, final setting, consistence, compressive strength (7, 28 & 90 days), coefficient of capillary absorption and drying shrinkage. These factors were used to calculate individual desirability functions. Water amount, final setting, temperature, coefficient of capillary absorption and drying shrinkage were minimized, while consistence and compressive strength were maximized. The individual and overall desirability functions are shown in Table A.3 and Fig. 9.

Analysis of the desirability indexes confirmed that WBAs designated as F6, F4 and F3 can be used as a SCMs in mortar with con-

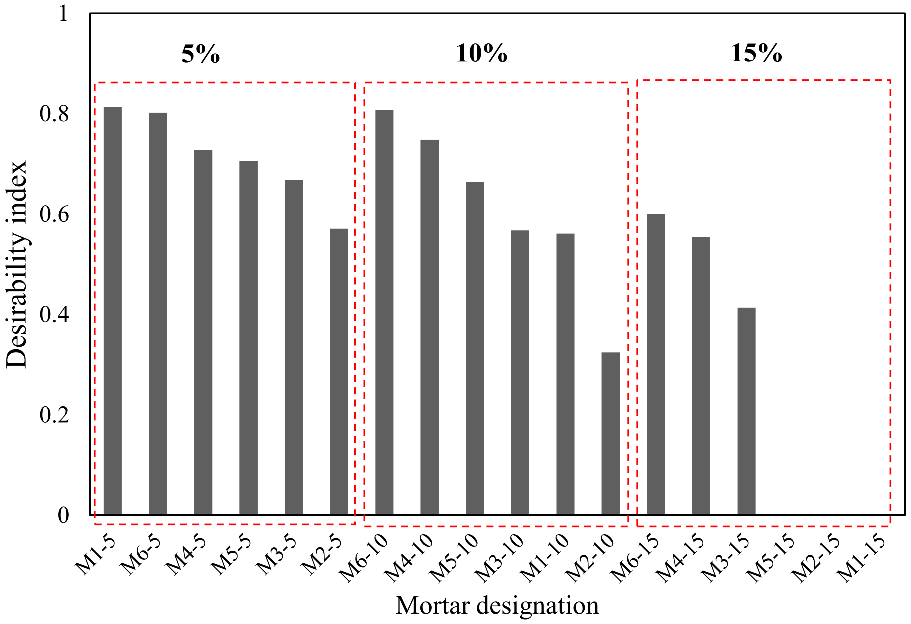


Fig. 9. Desirability index for investigated mortars.

tent up to 15% by mass of cement. Desirability analysis shows that other investigated ashes did not show a potential to be used as a SCMs if replacement level of cement is above 10%, in accordance with their physical and chemical characteristics. Mix M1-15 had a low desirability level for compressive strength of 28- and 90-days age due to exceptionally high value of LOI (19.1%) and free MgO (4.0%), which affected the minimum values of compressive strength. Alkalis had shown significant effect on the setting time and workability (Fig. 7), and in accordance with the above, mix M2-15 has the lowest value of desirability index for fresh properties (water requirement, workability and setting time). Despite the fact that F5 ash is rich in pozzolanic oxides and has physical and chemical properties similar to fly ash from coal, according to the previously published research [11] is best ranked WBA with high potential as a cement substitute. Its physical properties (coarser particles compared to the cement) showed that if they are used in a content greater than 10%, a negative impact on capillary absorption is observed. Due to the high potential of F5, an additional mechanical processing – grinding is recommended before it is used in cementitious composites.

Literature [85] claims that combustion temperature can reach: a) <900 °C in fluidized bed combustor, b) 1000–1200 °C in the grate combustor, and c) around 1600 °C in pulverized fuel systems. Free CaO is usually formed at temperatures higher than 900 °C [74] and its negative effects on long-term properties of cementitious composites have been elaborated previously. Based on the values of free CaO in the WBA samples, it can be concluded that temperatures in the furnace were higher than reported in Table 1. Performed desirability analysis clearly showed the benefits of specific combustor types. WBA designated with F6, coming from fluidized bed combustor, has the optimum behaviour for all three WBA shares. This can be associated with combustion temperatures <900 °C and the fact that this technology uses additive as a bed material, in this case quartz sand, can have beneficial effect on chemical composition of the WBA contributing with a high content of SiO_2 [57,85,86] comparing to other combustion technology. WBA from grate combustor follows this trend, while the lowest composite quality is determined for F2 and F3 coming from the pulverized fuel systems. Those ashes also have the highest alkali content, respectively 10.90% and 6.60%. As it can be seen from this research, alkalis have biggest influence on the tested properties of cementitious materials with WBAs (workability, setting time, compressive strength, capillary absorption).

5. Conclusion

The overall aim of this paper is to quantify the influence of physical properties and chemical composition of WBA on mechanical and durability properties of cementitious composites. Specific aim is to define an acceptable content of WBA, based on aforementioned WBAs characteristics, as a prerequisite for using WBA as a new raw material in construction industry. Based on the performed tests and the analysis, the following was concluded:

- Increase of WBA content in mixes is accompanied by an increased water requirement, i.e. loss of workability, when compared to a mix without WBA. In addition to the morphology of the WBA particles, alkali, LOI and content of heavy metals has the most significant impact on the consistency of pastes and mortars. Therefore, in WBA designated as F2, a significant content of alkali (10.90%), heavy metals (9765.3 mg/kg) and LOI (13.45%) was observed, due to which mixes with WBA designated as F2 showed the greatest loss in workability. Unlike the pastes, the impact of free CaO and free MgO to workability of mortars is partially annulled by the use of aggregates.
- Although higher temperatures of pastes in fresh state have been observed, which are usually associated with accelerated setting, it was established that presence of WBA in mixes affects the delay of the initial and final setting. Although the general trend is indicative of delayed setting, setting time greatly depends on the type and content of the used WBA.
- In all mixes with WBA, a slower strength increase was observed. However, compressive strength increases over time; so that the compressive strength of specimens made with 5 and 10% content of WBA, at the age of 28 days, is comparable to the strength of the reference mix. After 90 days, mixes with 5% WBA designated as F6, F4, F1 achieved compressive strength greater than the reference mix.

- Mortars with 5 and 10% WBA have lower capillary absorption values, whereas increase of WBA content up to 15% has a negative effect on the capillary absorption for all mixes except M6-15.
- Additional positive impact is evidenced by reduced shrinkage of samples with WBA compared to the reference mix without WBA.

When interpreting the results, it should be kept in mind that each chemical and physical property which could affect the properties of the cement composites was analysed individually. Based on the results showed in the paper, the authors consider the 10% of WBA to be an acceptable content with which a part of cement in mortars can be substituted without a significant degradation of characteristics. Additional increase in WBA content would require processing of WBA, such as sieving and/or washing with water, which would reduce the content of alkalis and unburned particles.

CRediT authorship contribution statement

Ivana Carević: Data curation, Formal analysis, Investigation, Writing - original draft. **Ana Baričević:** Methodology, Formal analysis, Writing - original draft, Validation. **Nina Štirmer:** Conceptualization, Writing - review & editing, Supervision, Project administration. **Jelena Šantek Bajto:** Writing - review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A

Table A.1
Correlation matrix of tested properties of cement pastes and physical and chemical properties of WBA.

		Standard consistency (%)	Initial setting time (min)	Final setting time (min)	Temperature of paste (˚C)	Soundness (mm)	CaO	Free CaO	Free MgO	Alkalis	Pozzolanic oxides	LOI	21.23 µm	Cr	Mn	Co	Ba	Bi	Cu
Standard consistency (%)	Spearman Corr.	1	0.307	0.665	0.421	-0.136	0.212	0.506	0.522	0.663	-0.758	0.818	0.073	0.216	0.814	0.049	0.512	0.785	0.663
	p-value	--	0.215	0.003	0.082	0.590	0.398	0.032	0.026	0.003	0.000	0.000	0.772	0.389	0.000	0.848	0.030	0.000	0.003
Initial setting time (min)	Spearman Corr.	0.307	1	0.730	0.442	-0.270	0.611	0.486	0.285	0.116	-0.511	0.285	0.511	0.640	0.265	0.600	0.140	0.439	0.043
	p-value	0.215	--	0.001	0.066	0.279	0.007	0.041	0.252	0.647	0.030	0.252	0.030	0.004	0.288	0.008	0.580	0.068	0.864
Final setting time (min)	Spearman Corr.	0.665	0.730	1	0.548	-0.317	0.550	0.604	0.471	0.342	-0.753	0.516	0.449	0.665	0.563	0.589	0.102	0.654	0.139
	p-value	0.003	0.001	--	0.019	0.200	0.018	0.008	0.049	0.164	0.000	0.028	0.062	0.003	0.015	0.010	0.686	0.003	0.583
Temperature of paste (˚C)	Spearman Corr.	0.421	0.442	0.548	1	0.321	0.336	0.531	0.479	0.340	-0.580	0.473	0.136	0.430	0.348	0.331	0.057	0.573	0.153
	p-value	0.082	0.066	0.019	--	0.194	0.173	0.023	0.044	0.168	0.012	0.047	0.590	0.075	0.157	0.180	0.823	0.013	0.545
Soundness (mm)	Spearman Corr.	-0.136	-0.270	-0.317	0.321	1	0.038	0.012	0.035	-0.229	0.047	0.076	0.240	0.146	0.113	0.120	0.190	0.048	0.091
	p-value	0.590	0.279	0.200	0.194	--	0.882	0.964	0.892	0.360	0.853	0.763	0.338	0.562	0.655	0,634	0.449	0.850	0.719

*Statistically significant values are marked in red, and the correlation interpretations are marked as follow: moderate correlation (from ± 0.5 to ± 0.69) was marked yellow, high correlation (from ± 0.7 to ± 0.89) was marked green and strong correlation (±0.9 to ± 1.00) was marked blue.

Table A.2
Correlation matrix of tested properties of fresh mortar, properties of hardened mortars and physical and chemical properties of WBA.

		Air content	Consistency	Temperature	Compressive strength –	Compressive strength -	Compressive strength -	Capillary absorption coefficient	Shrinkage
					7 days	28 days	90 days		
Air content	Spearman Corr.	1.0000	-0.2030	0.0021	-0.2127	0.0259	-0.1286	0.40768	-0.0800
	p-value	--	0.4191	0.9934	0.3969	0.9186	0.6110	0.09308	0.7530
REL CaO	Spearman Corr.	0.3600	0.0837	0.4050	-0.1063	0.2178	0.1992	-0.4448	-0.4610
	p-value	0.1423	0.7413	0.0955	0.6746	0.3854	0.4282	0.06439	0.0540
REL free CaO	Spearman Corr.	0.0830	-0.2211	0.2004	-0.4675	-0.3086	-0.3086	-0.2281	-0.5460
	p-value	0.7434	0.3780	0.4252	0.0504	0.2128	0.2128	0.3627	0.0190
REL free MgO	Spearman Corr.	-0.2874	-0.3161	0.3998	-0.5274	-0.6285	-0.4654	-0.1579	-0.3830
	p-value	0.2476	0.2013	0.1002	0.0245	0.0052	0.0516	0.53148	0.1170
REL sulphates	Spearman Corr.	-0.4513	-0.0796	0.4953	-0.0630	-0.2095	-0.1042	-0.1063	0.2240
	p-value	0.0602	0.7537	0.0366	0.8040	0.4041	0.6806	0.67464	0.3720
REL alkalis	Spearman Corr.	-0.0560	-0.7355	0.4175	-0.5480	-0.7874	-0.7193	0.50464	0.2650
	p-value	0.8253	0.0005	0.0848	0.0186	0.0001	0.0008	0.03269	0.2870
REL chlorides	Spearman Corr.	0.1815	-0.4870	0.4279	-0.2673	-0.3225	-0.0608	0.39429	0.2350
	p-value	0.4710	0.0404	0.0765	0.2836	0.1918	0.8108	0.10542	0.3470
REL pozzolanic oxides	Spearman Corr.	0.0156	0.4225	-0.4870	0.5459	0.4634	0.4551	0.11868	0.2780
	p-value	0.9511	0.0807	0.0404	0.0191	0.0528	0.0577	0.63905	0.2650
REL LOI	Spearman Corr.	0.0176	-0.5124	0.2326	-0.4737	-0.4758	-0.6326	0.01754	-0.1500
	p-value	0.9446	0.0297	0.3530	0.0471	0.0460	0.0048	0.94492	0.5530
REL d_{50}	Spearman Corr.	0.2801	-0.1653	-0.4060	-0.2033	-0.1682	-0.2549	0.50258	0.0240
	p-value	0.2603	0.5122	0.0946	0.4185	0.5046	0.3074	0.03353	0.9260
REL 21.23 µm	Spearman Corr.	0.1027	0.0310	0.5005	0.0609	0.2157	0.3210	-0.0733	0.1970
	p-value	0.6851	0.9028	0.0344	0.8103	0.3900	0.1941	0.77263	0.4330
Zn (mg/kg)	Spearman Corr.	-0.2023	-0.2634	0.0021	0.2405	-0.1992	-0.1558	0.45717	0.6990
	p-value	0.4208	0.2909	0.9935	0.3365	0.4282	0.5369	0.05646	0.0010
Cd (mg/kg)	Spearman Corr.	-0.5550	-0.2211	0.1225	-0.1909	-0.4964	-0.2673	-0.0774	-0.0770
	p-value	0.0168	0.3780	0.6281	0.4479	0.0361	0.2836	0.76017	0.7600
Cr (mg/kg)	Spearman Corr.	-0.3361	0.2283	-0.3531	0.6202	0.3086	0.1496	0.07327	0.6330
	p-value	0.1727	0.3622	0.1507	0.0060	0.2128	0.5534	0.77263	0.0050
Ni (mg/kg)	Spearman Corr.	-0.0934	-0.0919	-0.1620	0.3767	0.1971	0.0175	0.37874	0.8080
	p-value	0.7125	0.7167	0.5207	0.1234	0.4331	0.9449	0.12116	0.0000
Pb (mg/kg)	Spearman Corr.	-0.4166	-0.3275	-0.1061	0.1251	-0.3184	-0.3142	0.48682	0.7190
	p-value	0.0855	0.1847	0.6753	0.6210	0.1979	0.2041	0.04048	0.0010
Mn (mg/kg)	Spearman Corr.	0.2210	-0.7634	0.3894	-0.4427	-0.5088	-0.6388	0.48813	0.3770
	p-value	0.3783	0.0002	0.1102	0.0658	0.0311	0.0043	0.03986	0.1230
Co (mg/kg)	Spearman Corr.	-0.4284	0.0713	-0.3084	0.4861	0.0877	-0.0774	0.17853	0.6660
	p-value	0.0761	0.7787	0.2131	0.0408	0.7293	0.7602	0.47844	0.0030
Ba (mg/kg)	Spearman Corr.	0.2085	-0.4360	-0.2399	-0.2198	-0.2611	-0.5913	0.34365	0.1500
	p-value	0.4064	0.0705	0.3377	0.3808	0.2953	0.0098	0.16263	0.5530
Bi (mg/kg)	Spearman Corr.	-0.1587	-0.5103	0.5545	-0.5583	-0.6202	-0.5294	-0.1022	-0.2280
	p-value	0.5293	0.0305	0.0169	0.0160	0.0060	0.0239	0.68666	0.3630
Sr (mg/kg)	Spearman Corr.	0.1743	0.5950	-0.0789	0.5666	0.7957	0.6491	-0.3746	0.0750
	p-value	0.4892	0.0092	0.7556	0.0142	0.0001	0.0036	0.12561	0.7660
Cu (mg/kg)	Spearman Corr.	-0.1483	-0.6643	0.1952	-0.2487	-0.5728	-0.6409	0.31063	0.3290
	p-value	0.5569	0.0026	0.4376	0.3197	0.0130	0.0042	0.20963	0.1820
Hg (mg/kg)	Spearman Corr.	-0.3466	0.7589	-0.2884	0.8069	0.6386	0.5161	-0.566	0.0590
	p-value	0.1589	0.0003	0.2458	0.0001	0.0043	0.0283	0.01436	0.8160

*Statistically significant values are marked in red, and the correlation interpretations are marked as follow: moderate correlation (from ± 0.5 to ± 0.69) was marked yellow, high correlation (from ± 0.7 to ± 0.89) was marked green and strong correlation (±0.9 to ± 1.00) was marked blue.

Table A.3
Individual and overall desirability functions used for the optimization.

Mix designation	Individual desirability functions								Overall desirability function
	Water amount (g)	Final setting time (min)	Consistence (mm)	Compressive strength (MPa)			Coefficient of capillary absorption (kg/m^2 h$^{-1/2}$)	Drying shrinkage (mm/m)	
				7 days	28 days	90 days			
M0	0.99	0.81	1.00	1.00	0.68	0.73	0.61	0.00	0.00
M1-5	0.91	0.52	0.75	0.78	0.97	1.00	0.95	0.75	0.81
M1-10	0.83	0.30	0.66	0.20	0.77	0.66	0.69	0.88	0.56
M1-15	0.74	0.41	0.53	0.06	0.00	0.00	0.75	1.00	0.00
M2-5	0.89	0.52	0.56	0.58	0.38	0.67	0.55	0.54	0.57
M2-10	0.46	0.37	0.16	0.42	0.23	0.39	0.60	0.21	0.32
M2-15	0.00	0.00	0.00	0.00	0.09	0.07	0.43	0.36	0.00
M3-5	0.91	0.52	0.83	0.60	0.96	0.59	0.66	0.45	0.67
M3-10	0.82	0.56	0.74	0.46	0.78	0.50	0.50	0.37	0.57
M3-15	0.67	0.22	0.56	0.17	0.34	0.41	0.64	0.67	0.41
M4-5	0.91	0.44	0.88	0.46	0.91	0.83	0.94	0.68	0.73
M4-10	1.00	0.74	0.78	0.48	0.67	0.70	0.85	0.88	0.75
M4-15	0.99	0.67	0.64	0.29	0.32	0.61	0.53	0.72	0.55
M5-5	0.97	0.85	1.00	0.62	0.92	0.69	0.59	0.32	0.71
M5-10	0.93	0.89	0.59	0.86	0.67	0.60	0.54	0.41	0.66
M5-15	0.87	1.00	0.39	0.43	0.41	0.38	0.00	0.21	0.00
M6-5	0.96	0.81	0.93	0.65	1.00	0.90	0.91	0.44	0.80
M6-10	0.91	1.00	0.93	0.57	0.85	0.71	1.00	0.62	0.81
M6-15	0.78	0.70	0.74	0.63	0.24	0.33	0.94	0.86	0.60

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