Primljen / Received: 17.4.2020.
Ispravljen / Corrected: 16.9.2020.
Prihvaćen / Accepted: 10.11.2020.
Dostupno online / Available online: 10.1.2021.

Feasibility of using pozzolanicity tests to assess reactivity of wood biomass fly ashes

Authors:

Karmen Kostanić Jurić, MCE
Tomting 2010 d.o.o., Hrvatska
karmen.kostanic@tomting.hr

Ivana Carević, PhD. CE
University of Zagreb
Faculty of Civil Engineering
ivana.carevic@grad.unizg.hr

Assist.Prof. **Marijana Serdar**, PhD. CE
University of Zagreb
Faculty of Civil Engineering
mserdar@grad.hr

Prof. **Nina Štirmer**, PhD. CE
University of Zagreb
Faculty of Civil Engineering
nina.stirmer@grad.unizg.hr
Corresponding author

Research Paper

Karmen Kostanić Jurić, Ivana Carević, Marijana Serdar, Nina Štirmer

Feasibility of using pozzolanicity tests to assess reactivity of wood biomass fly ashes

Pozzolanic activity of materials can initially be assumed from the quantity of the pozzolanic oxides SiO_2, Al_2O_3 and Fe_2O_3. Some of the methods for assessing pozzolanic reactivity of materials include measurement of CaO consumption (Frattini test), decrease in electrical conductivity and pH of a solution containing pozzolanic material, or measurement of an increase in strength of mortar with replacement of cement by pozzolanic material (strength activity index, SAI). The above-mentioned pozzolanicity tests are used in this study to evaluate reactivity of wood biomass fly ashes (WBA-F). The results presented in the paper show that only the SAI method can fully reveal the hydraulic and pozzolanic activity of WBA-F.

Key words:
wood biomass fly ash, Frattini test, electrical conductivity, strength activity index, pozzolanic reactivity

Prethodno priopćenje

Karmen Kostanić Jurić, Ivana Carević, Marijana Serdar, Nina Štirmer

Primjenjivost metoda za ispitivanje pucolaniteta za procjenu reaktivnosti letećih pepela drvne biomase

Pucolanska reaktivnost materijala inicijalno se može pretpostaviti iz količine pucolanskih oksida, SiO_2, Al_2O_3 i Fe_2O_3. Neke od metoda za određivanje pucolanske reaktivnosti materijala uključuju mjerenje potrošnje CaO (Frattini test), smanjenje električne provodljivosti i pH-vrijednosti otopine koja sadrži pucolanski materijal ili mjerenje porasta čvrstoće morta s pucolanskim materijalom kao zamjenom dijela cementa (indeks aktivnosti, SAI). U ovom istraživanju primijenjena su navedena ispitivanja pucolaniteta za procjenu reaktivnosti letećeg pepela drvne biomase (PDB-a). Prikazani rezultati upućuju na to da samo SAI metoda može u potpunosti otkriti hidrauličku i pucolansku reaktivnost PDB-a.

Ključne riječi:
leteći pepeo drvne biomase, Frattini test, električna provodljivost, indeks aktivnosti, pucolanska reaktivnost

Vorherige Mitteilung

Karmen Kostanić Jurić, Ivana Carević, Marijana Serdar, Nina Štirmer

Anwendbarkeit von Puzzolanprüfverfahren zur Beurteilung der Reaktivität von Flugasche aus Holzbiomasse

Die Puzzolan-Reaktivität des Materials kann zunächst aus der Menge der Oxide SiO2, Al2O3 und Fe2O3 des Puzzolans angenommen werden. Einige der Methoden zur Bestimmung der Reaktivität von Puzzolan-Material umfassen die Messung des CaO-Verbrauchs (Frattini-Test), die Verringerung der elektrischen Leitfähigkeit und des pH-Werts einer Lösung, die Puzzolan-Material enthält, oder die Messung der Erhöhung der Mörtelfestigkeit mit Puzzolan-Material als Ersatz für einen Teil des Zements (Aktivitätsindex, SAI). In dieser Studie wurden die obigen Puzzolanitätstests angewendet, um die Reaktivität der Flugasche aus Holzbiomasse (PDB) zu bewerten. Die vorgestellten Ergebnisse legen nahe, dass nur die SAI-Methode die hydraulische und puzzolanische Reaktivität von PDB vollständig erfassen kann.

Schlüsselwörter:
Flugasche aus Holzbiomasse, Frattini-Test, elektrische Leitfähigkeit, Aktivitätsindex, puzzolanische Reaktivität

1. Introduction

The use of wood biomass as a renewable energy source (RES) results in generation of wood biomass ash (WBA) as waste in power plants. Many researchers compared WBA fly ash (WBA-F) with coal fly ash and expected a positive pozzolanic reaction [1, 2]. According to the literature review, the sum of pozzolanic oxides in wood biomass fly ash can vary between 19.8 % [3] and 80.66 % [4], implying that some of the WBAs studied may be pozzolanically reactive. However, studies on the use of WBAs in cement mixes have shown that some WBAs exhibit both hydraulic and pozzolanic behaviour [1]. During chemical analysis of 28 different wood and woody biomass samples, Vassilev et. al. [5] established that CaO is dominant in the composition, with an average value of 43 wt. %. Several authors [6] have shown that, besides pozzolanic behaviour, a hydraulic behaviour can also be expected due to high CaO content among the tested WBAs compared to the reactivity of known mineral admixtures. The estimation of pozzolanic reactivity by various authors often leads to contradictory results. For example, pozzolanic activity of bottom WBAs and three fly WBAs tested with the Frattini method according to EN 196-5 [8] was evaluated negatively [9], regardless of a significant amount of pozzolanic oxides in one of the ashes (56.01 %) [10]. Rajamma et al. [7] showed the pozzolanic activity of fly WBA with a 53.2 % pozzolanic oxide content. Testing the pozzolanic reactivity with indirect methods (Strength Activity Index) showed a positive [11] and negative result [12], depending on characteristics of WBA used in the test. It can be concluded from this that the reactivity of WBA with a high calcium content, and its influence on the properties of cementitious materials, has not as yet been systematically researched.

When Portland cement reacts with water, C-S-H gel is formed as the main hydration product. During hydration, portlandite is also formed, which contributes to high alkalinity of the solution and protects reinforced concrete from corrosion at the macro level. A hydraulic binder is defined as a material which, when reacting with water, leads to the formation of hydration products and to the transition to a solid structure (hardening in reaction with water) [13]. The estimation of the amount of portlandite (CH) as hydration product is used to estimate the degree of hydration of the hardened cement paste, and it provides information on possible influence on mechanical properties after hardening. Pozzolanic material is characterized by its ability to react with portlandite and form additional C-S-H gel, which fills cavities between cement particles and aggregate, and contributes positively to the mechanical and durability properties of cement composites.

In the scope of this research, WBA-Fs from three different power plants were tested with two standardized and one non-standardized pozzolanic test methods, in order to evaluate their potential as a supplementary cementitious material. The standardized methods included a direct method - the Frattini test, which measured the $Ca(OH)_2$ reduction over time caused by pozzolanic reaction, and an indirect method (strength activity index). A non-standard method was used to measure the change in electrical conductivity of a saturated $Ca(OH)_2$ solution with the addition of biomass ash. The aim of this study was to evaluate feasibility of these common pozzolanic tests to indicate the reactivity of wood biomass fly ashes (WBA-Fs).

2. Materials and investigation methods

2.1. Materials

Pozzolanic reactivity was investigated at three different WBA-F, which were collected at different power plants in Croatia. General information about power plants from which these ashes were generated (type and temperature of combustion, capacity, and type of biomass) is given in Table 1.

A detailed characterization of WBAs used is given in [14]. A summary of chemical composition of WBA-Fs, cement, and particle size distribution, is shown in Table 2 and Figure 1.

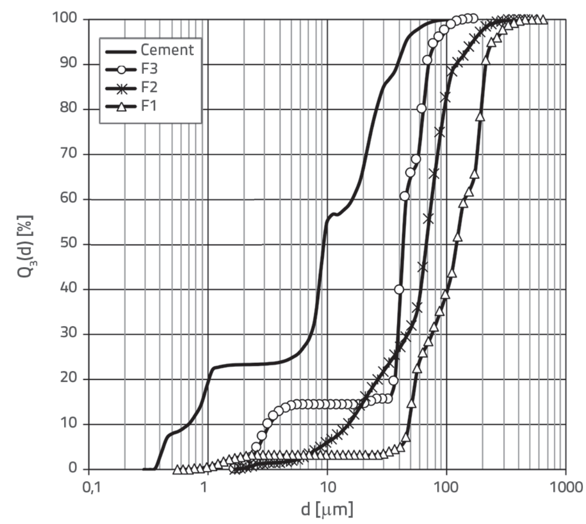

Figure 1. Particle size distribution of WBA-Fs and cement

Table 1. Characteristics of power plants where WBA-Fs were collected

No.	Name	Combustion characteristics			Biomass characteristics
		Combustion type	Combustion temperature [°C]	Power [MW]	Wood biomass type
1.	**F1**	grate firing combustion	800	15	beech, oak, and hornbeam
2.	**F2**	grate firing combustion	500 – 1000	5	beech, oak, fir, and spruce
3.	**F3**	pulverized fuel combustion	700 - 750	16	beech, oak, hornbeam, and mixed wood

Table 2. Chemical composition of tested materials

	CEM	F1	F2	F3	LP	MK	SP
pH	12.86	12.97	13.15	13.25	-	-	-
CaO	59.8	16.25	46.75	51.9	4.21	0.55	0.05
MgO	2.01	4.30	8.26	3.75	1.83	0.36	0.05
Al_2O_3	4.94	10.50	6.16	2.28	26.46	41.18	0.27
TiO_2	0.23	1.17	0.34	0.15	-	-	-
Fe_2O_3	3.15	4.23	2.85	1.47	9.22	1.17	0.21
SiO_2	21.88	39.95	19.8	9.28	51.87	53.53	93.60
SO_3	3.33	0.60	2.73	3.58	0.56	0.02	0.8
P_2O_5	0.22	1.35	1.82	1.84	-	-	-
Na_2O	0.846	1.32	0.646	0.545	0.23	0.08	0.23
K_2O	1.25	4.77	6.05	9.2	1.14	0.83	0.5
LOI	3.6	8.3	3.8	13.8	0.54	1.36	-
Pozzolanic oxides (SiO_2+Al_2O_3+Fe_2O_3)	29.97	54.68	28.81	13.03	87.55	95.88	94.08
Free CaO	2.50	0.50	7.30	13.50	0.08	-	-
Free MgO	0.75	0.50	3.30	3.80	-	-	-

For benchmarking purposes, coal combustion fly ash (FA) [15], commercial metakaolin (MK), and silica fume (SF) [16], were used in certain experiments, in addition to biomass ash, to assess pozzolanic activity.

It can be seen from chemical composition (Table 2) that all three WBA-Fs have a lower proportion of pozzolan oxides compared to fly ash from coal combustion (FA). Out of the three WBA-Fs, sample F1 has the highest content of pozzolanic oxides. Samples F2 and F3 have a higher CaO content, similar to the cement sample. In addition, samples F2 and F3 have a higher content of free CaO. Particle size distribution results show that all three tested WBA-Fs have coarser particles compared to cement.

2.2. Methods

2.2.1. Frattini test

The Frattini test, as described in EN 196-5:2011 [8], was used to assess pozzolanicity of WBA-F as a supplementary cementitious material and as a pozzolanic cement. In the first case, the test was carried out with the 85 % cement and 15 % WBA-F mixture, while in the second case the test was conducted with pure WBA-F. As WBA-Fs have a high content of CaO, it was hypothesized that they are mainly hydraulically active and that a super-saturation of the available calcium ions could occur when they are added to Portland cement. Therefore, the Frattini test was performed on WBA-F following the procedure similar to that used for pozzolanic cements.

20 g samples (cement/WBA-F mixture or pure WBA-F) were diluted in 100 ml of distilled water and conditioned at 40°C, with the test being carried out after 7, 15, and 37 days. The sample was vacuum filtered through Büchner funnel using filter paper with a pore diameter of 2 μm to separate solids from aqueous substances. 50 ml of the filtrate was homogenized with five drops of the methyl orange indicator prepared beforehand. According to the standard, the titration of standard 0.1 mol/l of hydrochloric acid in the burette of known volume reaches the end point when the indicator in solution changes from clear to light yellow, indicating pH neutralization. This allows calculation of free hydroxyl ions in solution before titration from known volumes and the molar concentration of hydrochloric acid. To determine $[Ca^{2+}]$ in solution, the alkalinity was adjusted to pH 12.5 ± 0.2 by adding NaOH. EDTA solution and 1.0 g murexide indicator were used in the second titration to determine the CaO concentration in ml/l, analogous to the determination of $[OH^-]$. The colour change in the first titration was pale, but the reaction endpoint between EDTA and CaO exhibited a significant change from pink to violet colour.

The test results are expressed as the concentration of calcium ions (expressed as calcium oxide) and the alkalinity of the aqueous solution in contact with the cement hydrate after a fixed period of time, compared with the saturation concentration of calcium ions (expressed as calcium oxide) as a function of the hydroxyl ion concentration at 40° C. Test results below the portlandite saturation curve indicate the removal of Ca^{2+} from the aqueous solution (the solution becomes unsaturated in portlandite), which is then attributed to the pozzolanic activity of the material added to the cement. Results lying on the line indicate zero pozzolanic activity, while results above the line do not correspond to pozzolanic activity. It should be noted that this procedure assumes that no other source of soluble calcium is present in the system, since leaching of calcium would invalidate this approach.

2.2.2. Electrical conductivity (EC)

If a reactive pozzolanic material is added to the saturated lime solution, the conductivity is expected to decrease over time due to ion consumption by pozzolanic reaction [17-19]. Based on this hypothesis, an experimental indirect method for rapid detection of the pozzolanic activity of natural pozzolans was developed [19]. The method involves periodic monitoring of the electrical conductivity and pH of a saturated $Ca(OH)_2$ solution into which a controlled amount of pozzolanic material has been added. This indirect method of assessing pozzolanic activity starts with preparation of a saturated calcium hydroxide solution. $Ca(OH)_2$ was mixed with distilled water and added to oven where it was heated to a temperature of 40 ± 1°C. Samples of 4g BWA-Fs were homogenized with a 40 mL solution. During a period of four hours, a Lab 850 Schott pH-meter was used to determine the pH-value, while the PCD 650 Oakton was applied to measure electrical conductivity of the solution. A drop in pH value indicates a reaction between WBA-F and OH^- anions, and the EC value depends on the concentration of free Ca^{2+} and OH^- ions in the solution. A decrease in these values over time can be attributed to the pozzolanic reaction between SCM and free ions.

2.2.3. Strength activity index (SAI) test

The test procedure is described in European Standard EN 450-1 [20] for coal fly ash. The test result is expressed as a compressive strength ratio between mortar prisms with supplementary cementitious material (A) and reference prisms made of Portland cement (B). The strength activity index SAI = A/B*100 is expressed in percent. In this research, mortar prisms 40 x 40 x 160 mm were cured at 7, 28, and 90 days and, after each period, A and B prisms of the same age were subjected to pressure to determine the strength. According to EN 450-1, the SAI test of no less than 75 % at 28-day compressive strength, and 85 % at 90-day compressive strength, with cement substitution of 25 %, indicates pozzolanic reactivity. According to ASTM C618, an activity index greater than 75 % after 7 and 28 days, for 20 % cement substitution with coal fly ash, is interpreted as pozzolanic reactivity. According to BS 3892, a result of more than 80 % for 30 % replacement [21] is considered a proof of pozzolanic reactivity.
In this study, mortar prisms were made with CEM I 42.5 and standard quartz sand in a ratio of 1:3 with a water-binder ratio (w/b) of 0.50, while 15 % of cement was replaced by WBA-Fs. It is obvious that this is a lower substitution level compared to the substitutions of 20 to 30 % of cement by coal fly ash as required by the above mentioned standards [20]. However, due to workability issues, 15 % of cement replacement by WBA-F was a maximum that could be reached without the use of chemical admixtures, as these admixtures would hinder the effects of WBA-F [6]. In addition, the authors of a previous research [22-24] concluded that 10-15 % of the cement replacement by WBA-F was the maximum value, due to the higher amount of free CaO and free MgO in WBA-F samples. However, since the calculated SAI values were not obtained on the same quantities of cement substitute as required by the standards, the SAI values in this study were used only for comparison purposes and not for acceptance according to these standards.

3. Results and discussion

3.1. Frattini test

Frattini test results at 7, 15 and 37 days for F1 ash (results labelled respectively as MF1-7, MF1-15, and MF1-37), for F2 ash (results labelled respectively as MF2-7, MF2-15, and MF2-37) and for F3 ash (results labelled respectively as MF3-7, MF3-15, and MF3-37) as a 15 % cement replacement, are shown graphically in Figure 2. According to the standard, the tests should be performed after 7 and 15 days. However, in this study, the measurement was continued until the sample age of 37 days since WBA delays setting times and extends heat of hydration development [2, 10, 25].

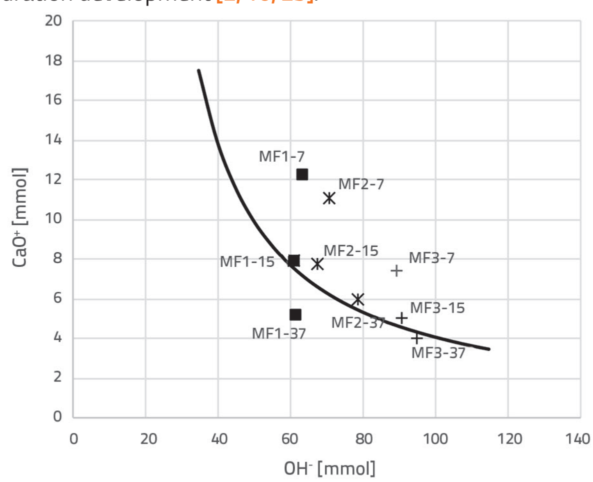

Figure 2. Results of Frattini test for 15 % cement replacement with WBA-Fs

According to Figure 2, all three ashes showed a supersaturation in portlandite after 7 days and thus no pozzolanic activity. After 15 days, all three samples were near the portlandite saturation line, indicating near zero activity. Finally, after 37 days, only MF1 met the criteria according to EN 196-5:2011 [26]. The MF3 blend was slightly below the line after 37 days, while MF2 was still above the portlandite saturation line after 37 days. The highest removal of Ca^{2+} ions was therefore registered in the case of F1, the ash with the highest content of pozzolanic oxides (54.68 %). This higher amount of pozzolanic oxides was able to bind calcium ions from the solution, which indicates pozzolanic activity of this ash after 37 days. The same can be observed with ash F3, but to a lesser extent.
Tested WBA-Fs have a large amount of free calcium oxide in their chemical composition, which is larger than usual for pozzolanic materials. When they were added to replace cement, the amount of available calcium oxide was potentially too high to be absorbed by a relatively small amount of pozzolanic oxides available in these ashes. The question remains as to what happened before 7 days, since there seems to be less Ca^{2+} ions

Table 3. $[CaO^+]$ reduction in [%]

	Sample	Days	$[OH^-]$ mmol l^{-1}	[CaO] mmol l^{-1}	Theoretical max. [CaO] mmol l^{-1}	[CaO] reduction [%]
Pure ash in water	**F1**	7	36.6	11.9	16.2	26.6
		15	32.5	6.9	20.0	65.5
		37	n.p.	n.p.	n.p.	n.p.
	F2	7	94.2	4.4	4.4	0.4
		15	115.8	3.3	3.5	6.4
		37	n.p.	n.p.	n.p.	n.p.
	F3	7	n.p.	n.p.	n.p.	n.p.
		15	n.p.	n.p.	n.p.	n.p.
		37	n.p.	n.p.	n.p.	n.p.
Blend of Portland cement and ash	**MF1**	7	63.6	12.3	7.2	0 (-70.1 %)
		15	61.2	7.9	7.6	0 (-4.3 %)
		37	61.6	5.2	7.5	30.8
	MF2	7	70.8	11.1	6.3	0 (-77.0 %)
		15	67.4	7.8	6.7	0 (-16.8 %)
		37	78.8	6.0	5.5	0 (-9.4 %)
	MF3	7	89.5	7.5	4.7	0 (-58.6 %)
		15	91.0	5.0	4.6	0 (-8.6 %)
			95.0	4.0	4.4	8.6 %

in samples F2 and F3 after 7 days, although they have a higher amount of free lime available. Since the hydraulic reaction is fast [27], faster than the pozzolanic reaction, it is possible that these calcium ions were already absorbed during the hydraulic reaction between free lime and water. In any case, it can be concluded from the results of the Frattini test carried out on WBA-F and cement blend that certain pozzolanic reactivity does exist in the case of F1 ash and perhaps even in F3 ash. However, if pozzolanic reactivity is found, it is rather slow.

The addition of biomass ash to Portland cement showed a supersaturation of calcium ions which could not be absorbed by available pozzolanic oxides. It was therefore decided to test the ashes according to the procedure for pozzolanic cements, i.e. to test the pure samples of WBA-F itself according to the Frattini method. The results for the ashes F1 and F2 after 7 and 15 days are shown in Figure 3. The results for ash F3 are not shown in the Figure, as they did not stabilize over time and the values were well outside the solubility curve.

As can be seen in Figure 3, F1 ash exhibits a significant CaO^+ reduction, which is higher than when mixed with cement (Figure 2). This can be explained by an excessively high CaO content in a blend of ash and cement. Based on the results for pure sample, it can be assumed that F1 initially reacted alone with the water-consuming free lime to form portlandite, and that portlandite subsequently reacted with available pozzolanic oxides. On the basis of the results, it could therefore be concluded that F1 meets requirements for pozzolanic cements. The results for F2 exceeded the value of 90 mol/l [OH -], for which a solubility curve is given in the standard EN 196-5:2011 [26]. Nevertheless, the values for F2 were near the saturation line after 7 days and moved below the line after 15 days, which also indicates a hydraulic reaction due to high calcium content and potential pozzolanic reaction between residual CaO reacting with unbound pozzolanic oxides at later ages (15 days).

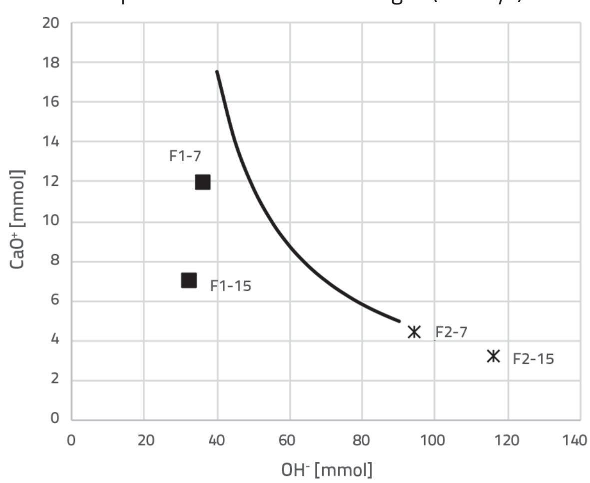

Figure 3. Results of Frattini test for pure samples

Based on the comparison of the ash-cement mixture and pure ash results, it can be concluded that an excessive amount of CaO was available and reactivity was impaired when these

Table 4. pH test results

Time [h]	F1		F2		F3		LP		MK		SP	
	pH	Δ	pH	Δ	pH	Δ	pH	Δ	pH	Δ	pH	Δ
0	12.20	0.00	11.92	0.00	12.20	0.00	12.00	0.00	12.30	0.00	12.30	0.00
0.5	11.86	-0.34	12.20	0.28	12.17	-0.03	12.10	0.10	11.80	-0.50	11.70	-0.60
2.5	11.97	-0.23	12.20	0.28	12.12	-0.08	12.00	0.00	11.67	-0.63	10.27	-2.03
25	11.96	-0.24	12.10	0.18	12.12	-0.08	11.70	-0.30	10.50	-1.80	9.40	-2.90

samples (F1 and F2) were used together with cement. The small available amount of pozzolanic oxides in the ash was fully exploited by the CaO available in pure WBA-F samples. However, once WBA-F was mixed with cement, its contribution to the consumption of free Ca^{2+} was less significant.

The standard EN 196-5:2011 [26] only provides $Ca(OH)_2$ solubility data at 40 °C when [OH^-] is between 35 and 90 mmol/l. Therefore, a theoretical maximum [CaO^+] concentration can be calculated for materials within this range using the formula given in EN 196-5 as follows: MAX [CaO^+] = 350/([OH^-]-15). In this way, the calcium concentration measured in the CaO^+ sample can be compared with the maximum theoretical concentration and the results can be expressed as a percentage of the removed CaO^+ relative to the theoretical maximum [CaO^+] for the corresponding [OH^-]. If the theoretical MAX[CaO^+] is lower than the measured one then, according to [21], the negative results should be normalized to 0 % of the removed [CaO^+]. The calculated [CaO^+] reduction results are given in Table 3. Negative values were normalised to zero. However, these negative values are shown in brackets to highlight the trend, i.e. an increase in values over time, clearly pointing to consumption of CaO.

An example of CaO reduction is given as follow: After 7 days, the Frattini test for F1 yielded [OH] = 36.6 $mmoll^{-1}$ and [CaO] = 11.9 $mmoll^{-1}$. Theoretical max. [CaO] was 16.2 $mmoll^{-1}$ calculated according to formula MAX[CaO^+] = 350/([OH^-]-15). Value 26.6 % as [CaO] precent reduction was calculated as Theoretical max. [CaO]-measured [CaO]/Theoretical max. [CaO] respectively for sample F1 after 7 days 26.6 % lime is utilized in the the pozzolanic reaction. Based on the values of [CaO^+] reduction, it can be observed that the ash F1 mixed with cement (MF1) and tested with this method showed a lower reactivity (lower efficiency in [CaO^+] reduction) compared to a tested sample of pure F1. F2 showed a very low CaO^+ reduction after 7 days, which increased after 15 days, whereas with ash F3 it was not possible to measure and calculate the [CaO^+] reduction. One of the explanations could be that the ash F3 reached a supersaturation with calcium oxides and therefore this test method could not be used.

3.2. Electrical conductivity

Pozzolanic reaction leads to a reduction of free Ca^{2+} and OH^- ions, which should lead to a decrease in the pH-value and EC pH-values [18]. For this test, silica fume, metakaolin, and coal fly ash, were used to compare the trend of behaviour with the WBA-F samples tested. The electrical conductivity monitoring results are shown in Figure 4, while the pH monitoring results are given in Table 4. Table 4 also shows changes of pH value from time zero (Δ).

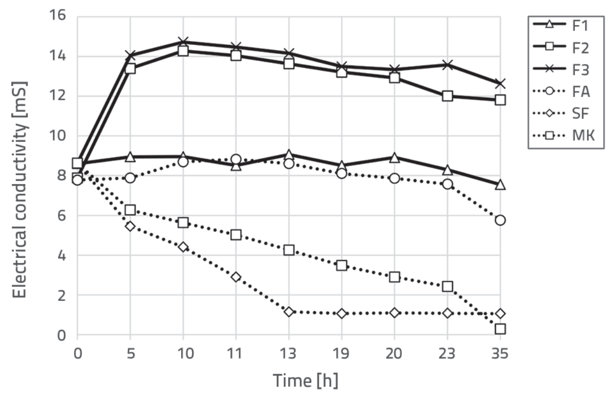

Figure 4. Electrical conductivity test results

Three distinct types of behaviour can be defined based on results shown in Figure 4:

- Silica fume and metakaolin, as typical pozzolanic materials, showed an immediate decrease in electrical conductivity and pH over time, which is consistent with previous studies [17, 19],
- FA and F1 showed similar behaviour in this test, a slight and slow decrease in electrical conductivity and pH values over time, although the proportion of pozzolanic oxides in the FA sample is greater compared to the F1 sample [15, 28],
- F2 and F3 showed an increase in electrical conductivity and pH value during the first 5 hours, and a slight decrease in both values after 5 hours, indicating an initially high availability of free Ca^{2+} and OH^- ions and, finally, slow reaction during later hours. However, if we look at only the part of the curve after 5 hours, when the values of electrical conductivity start to decrease, this decrease was higher in F2 compared to F1 and F3.

In previous studies [29], this method was evaluated as not being fully reliable for assessing the pozzolanic activity of FA, because of its high content of soluble salts, mostly Na_2SO_4, K_2SO_4 and $CaSO_4$, which cause high conductivity. Potentially similar effect could be expected for F2 and F3, due to their higher SO_3 content. In any case, the method of monitoring changes in electrical conductivity and pH over time revealed that changes

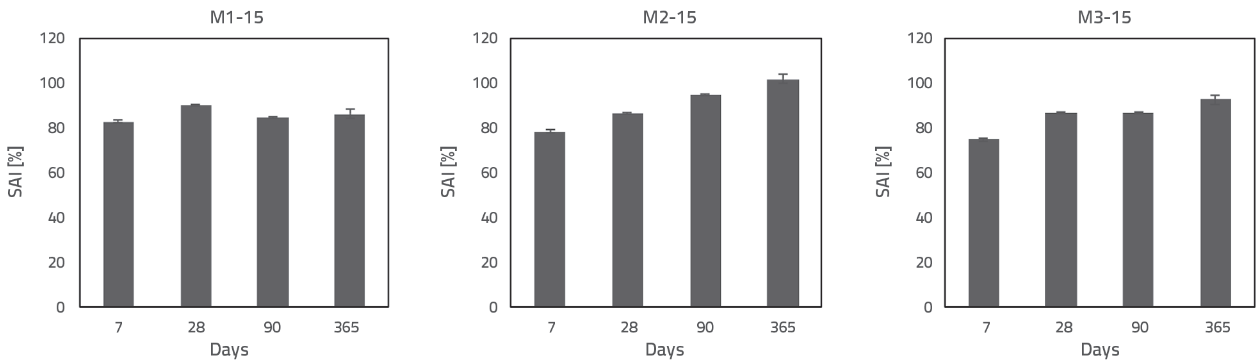

Figure 5. SAI results at 7, 28, 90, and 365 days

in the values were significantly different compared to classical pozzolanic materials, due to high amount of available CaO. Any pozzolanic reactivity available in WBA-F samples was slow and only evident later during the testing period.

3.3. Strength activity index test

Average compressive strength test results and calculated SAI values for three samples, with 15 % WBA-F used as cement replacement and reference mixture with only cement (M0), are given in Table 5. The results are obtained as an average of three specimens for each mix, with average values given in Table 5 and standard deviation indicated in Figure 5. It should be noted that, due to workability issues, only 15 % of cement was replaced with WBA-F, which is lower than the values given in well-known standards for the use of coal fly ash [20, 21].

Table 5. Compressive strength test results and strength activity index

Sample \ Days	7	28	90	365
Compressive strength [MPa]				
M0	43.12	46.99	55.62	56.16
M1-15	32.38	41.00	48.20	52.17
M2-15	33.88	40.69	52.77	57.27
M3-15	35.77	42.37	47.35	48.57
SAI [%]				
M1-15	75.07	87.26	86.66	92.89
M2-15	78.56	86.59	94.88	101.97
M3-15	82.95	90.18	85.13	86.48

The results presented in Table 5 show that, after 7 days, all samples with 15 % cement substitution with WBA-F had lower compressive strength compared to the cement sample. WBA-F mixes reached between 75 and 83 % of mortar strength, which is even lower than the reduced amount of cement in the samples. The trend of SAI for up to 7 days followed the trend in the amount of free CaO and particle size distribution. Mainly, F3 ash that has the highest amount of free CaO and the smallest particles, led to the mortar that had the highest compressive strength after 7 days, while F1 ash that has the lowest amount of free CaO and the biggest particles, led to the mortar with the lowest compressive strength after 7 days. The trend of initial compressive strength values also follows the initial [CaO^+] reduction obtained in the Frattini test. Regardless of a very high initial content of CaO in the ashes F3 and F2, their amount of [CaO^+] after 7 days during the Frattini test was lower than that of the F1 ash. Therefore, it is possible that there was a faster initial hydraulic activity in the case of MF3, which can be attributed to the availability of free CaO and to the finer particles, which react faster compared to bigger particles.

The trend in SAI values changed after 28 days. In this period, it was the compressive strength of MF1 that increased at the highest rate. Such superior increase in compressive strength of MF1 can be correlated to the results of the Frattini test, where the most significant [CaO^+] reduction between 7 and 15 days was evident for F1 and MF1. Finally, at 90 and 356 days, mortar MF2 had a superior increase in compressive strength, reached the full compressive strength of mortar prepared with cement, and even slightly exceeded that value. Such an increase in strength after 28 days could not be expected based on the results of the Frattini test, which was performed until 37 days. According to Li et al. [30], there is a poor correlation of Frattini method with the 28-day relative strength, which was also the case here, indicating that the Frattini method does perform well for purely pozzolanic materials, but cannot cover SCMs that show a (latent) hydraulic nature. Higher compressive strength at the end of the testing period is in accordance with the highest decrease in electrical conductivity of F2, compared to F1 and F3. It is however hard to use a decrease in electrical conductivity during 35 hours as an indication of strength increase at later ages of mortar.

4. Conclusion

Tested WBA-F show a lower amount of pozzolanic oxides compared to the criteria for the assessment of the pozzolanicity of fly ash from coal combustion plants specified in standard EN 450-1 [20]. Based on the sum of the pozzolanic oxides of WBA-F alone, it could be assumed that they do not contribute to the pozzolanic reaction and formation of C-S-H gel. In the present work, pozzolanicity tests (standardised and non-standardised) were applied to WBA-F to verify this assumption.

Notwithstanding their lower amount of pozzolanic oxides, a direct test measurement (Frattini method) showed that WBA-F has both hydraulic and pozzolanic properties. When the Frattini test was carried out on a WBA-F and cement mixture, supersaturation with CaO was found, and the pozzolanic reaction was hindered by the amount of CaO available. Nevertheless, after 37 days of measurement, the pozzolanic activity was obvious but slow, exceeding the test time predicted by the standard. When the Frattini test was performed with pure WBA-F, a rapid decrease in the available amount of CaO was observed after 7 and 15 days, due to the hydraulic activity at an early age, and pozzolanic activity at later age. The trend of CaO reduction in the period of up to 7 days correlated well with the first SAI results obtained with mortars containing 15 % cement replacement with WBA-F. Mortars with WBA-F, which showed a higher CaO reduction at an early age, also showed a higher compressive strength at the same age, which was due to their hydraulic activity. In addition, ashes with a higher CaO reduction between 7 and 15 days also showed a higher strength gain between 7 and 28 days. However, strength development at later ages (90 and 365 days) cannot correlate with the Frattini test. Therefore, the Frattini test, as a direct method for measuring pozzolanicity, cannot be used with certainty to fully describe the hydraulic and pozzolanic reactivity of wood biomass ash, since most of its pozzolanic activity is rather slow and becomes apparent at a later age only.

The behaviour of WBA-F in monitoring electrical conductivity also differed compared to classical pozzolanic materials such as silica fume and metakaolin, and was similar to fly ash from coal combustion. In WBA-F, the electrical conductivity increased significantly in the first hours, possibly indicating an increase in Ca+ and Ca- OH ions. After some time, the electrical conductivity began to decrease. The trend of a decrease in electrical conductivity can be correlated to obtain compressive strengths at the end of the test. WBA-F with the highest decrease in specific electrical resistance showed the highest compressive strength after 90 and 365 days. However, it seems difficult to explain how a decrease in electrical conductivity during 35 hours could serve as an indication of an increase in strength at a later mortar age, and this is certainly something that merits further investigation.

In conclusion, only the direct method of measuring compressive strength was able to fully demonstrate the activity (hydraulic and pozzolanic) of fly ash from wood biomass. If the fly ash activity were based solely on the sum of pozzolan oxides, CaO reduction, or loss of electrical conductivity, its compressive strength at a later age would certainly be underestimated. To confirm the hypothesis made in this paper, and to try to fully understand the reactivity of WBA-F, it is proposed to use alternative methods to analyse the reactivity of materials. In the continuation of this research, it is proposed to evaluate the reactivity with the R3 test for the evaluation of pozzolanic and/or hydraulic reactivity, which is validated within the framework of RILEM Technical Committee 267 - TRM. It is also proposed to study hydraulic properties of the WBA-F together with the XRD analysis of mineral phases occurring at different sample ages. Finally, there is an interesting SAI trend for mixtures with WBA-F after 365 days. The results showed a compressive strength gain, which could be explained by a positive contribution of the use of WBA-F. This contribution of WBA-F needs to be further investigated on a microstructural level for the later age of cement composites with WBA-F as cement substitute.

Acknowledgements

This research was performed in the scope of research projects IP-2016-06-7701 "*Transformation of Wood Biomass Ash into Resilient Construction Composites*".

REFERENCES

[1] Omran, A., Soliman, N., Xie, A., Davidenko, T., Tagnit-hamou, A.: Field trials with concrete incorporating biomass-fly ash, Construction and Building Materials, 186 (2018), pp. 660–669, https://doi.org/10.1016/j.conbuildmat.2018.07.084

[2] Wang, S., Miller, A., Llamazos, E., Fonseca, F., Baxter, L.: Biomass fly ash in concrete: Mixture proportioning and mechanical properties, Fuel, 87 (2008) 3, pp. 365–371, https://doi.org/10.1016/j.fuel.2007.05.026

[3] Elahi, M., Qazi, A.U., Yousaf, M., Akmal, U.: Application of wood ash in the production of concrete, Science International (LAHORE), 27 (2015) 2, pp. 1277-1280, https://doi.org/10.13140/RG.2.2.13875.78881.

[4] Udoeyo, F.F., Dashibil, P.U.: Sawdust Ash as Concrete Material, Journal of Materials in Civil Engineering, 14 (2002) 2, pp. 173–176, https://doi.org/10.1061/(ASCE)0899-1561(2002)14:2(173)

[5] Vassilev, S.V., Baxter, D., Andersen, L.K., Vassileva, C.G.: An overview of the chemical composition of biomass, Fuel, 89 (2010) 5, pp. 913–933, https://doi.org/10.1016/j.fuel.2009.10.022

[6] Cheah, C.B., Ramli, M.: Mechanical strength, durability and drying shrinkage of structural mortar containing HCWA as partial replacement of cement, Construction and Building Materials, 30 (2012), pp. 320–329, https://doi.org/10.1016/j.conbuildmat.2011.12.009

[7] Rajamma, R., Ball, R.J., Tarelho, L.A.C., Allen, G.C., Labrincha, J.A., Ferreira, V.M.: Characterisation and use of biomass fly ash in cement-based materials, Journal of Hazardous Materials, 172 (2009) 2-3, pp. 1049–1060, https://doi.org/10.1016/j.jhazmat.2009.07.109

[8] European Committee for Standardization: EN 196-5:2011 Methods of testing cement - Part 5: Pozzolanicity test for pozzolanic cement

[9] Garcia, M.D.L., Sousa-Coutinho, J.: Strength and durability of cement with forest waste bottom ash, Construction and Building Materials, 41 (2013), pp. 897–910, https://doi.org/10.1016/j.conbuildmat.2012.11.081

[10] Berra, M., Mangialardi, T., Paolini, A.E.: Reuse of woody biomass fly ash in cement-based materials, Construction and Building Materials, 76 (2015), pp. 286–296, https://doi.org/10.1016/j.conbuildmat.2014.11.052

[11] Elinwa, A.U., Mahmood, Y.A.: Ash from timber waste as cement replacement material, Cement and Concrete Composites, 24 (2002) 2, pp. 219–222, https://doi.org/10.1016/S0958-9465(01)00039-7

[12] Naik, T.R., Kraus, R.N., McCormick, S.: Recycling of wood ash in cement-based construction materials, The University of Winconsin / Milwaukee, 2001.

[13] Snellings, R., Elsen, J., Mertens, G.: Supplementary Cementitious Materials, Reviews in Mineralogy & Geochemistry, 74 (2012), pp. 211–278, https://doi.org/10.2138/rmg.2012.74.6

[14] Carević, I., Serdar, M., Štirmer, N., Ukrainczyk, N.: Preliminary screening of wood biomass ashes for partial resources replacements in cementitious materials, Journal of Cleaner Production, 229 (2019), pp. 1045–1064, https://doi.org/10.1016/j.jclepro.2019.04.321

[15] Skazlić, M., Banjad Pečur, I., Rosković, R.: Properties of self-compacting concrete with high fly-ash content, GRAĐEVINAR, 60 (2008) 11, pp. 945–952, https://doi.org/n/a

[16] Marinković, S., Protić, M., Paunović, S., Nešović, I., Bijeljić, J.: Application of industrial by-products as mineral admixtures for self-compacting concrete, GRAĐEVINAR, 70 (2018) 1, pp. 31–38, https://doi.org/10.14256/JCE.1516.2015

[17] Tironi, A., Trezza, M. A., Scian, A.N., Irassar, E.F.: Assessment of pozzolanic activity of different calcined clays, Cement and Concrete Composites, 37 (2013) 1, pp. 319–327, https://doi.org/10.1016/j.cemconcomp.2013.01.002

[18] Yu, Q., Sawayama, K., Sugita, S., Shoya, M., Isojima, Y.: The reaction between rice husk ash and Ca(OH)2 solution and the nature of its product, Cement and Concrete Research, 29 (1999), pp. 37–43, https://doi.org/10.1016/S0008-8846(98)00172-0

[19] Luxán, M., Madruga, F., Saavedra, J.: Rapid evaluation of pozzolanic activity of natural products by conductivity measurement, Cement and Concrete Research, 19 (1989), pp. 63–68, https://doi.org/10.1016/0008-8846(89)90066-5

[20] The European Committee for Standardization, Fly ash for concrete - Part 1: Definition, specifications and conformity criteria (EN 450-1:2012)

[21] Donatello, S., Tyrer, M., Cheeseman, C.R.: Comparison of test methods to assess pozzolanic activity, Cement and Concrete Composites, 32 (2010), 2, pp. 121–127, https://doi.org/10.1016/j.cemconcomp.2009.10.008

[22] Carević, I., Baričević, A., Štirmer, N., Bajto Šantek, J.: Correlation between physical and chemical properties of wood biomass ash and cement composites performances, Construction and Building Materials, 256 (2020), 30 September, Paper No. 119450, https://doi.org/10.1016/j.conbuildmat.2020.119450

[23] Ukrainczyk, N., Vrbos N., Koenders, E.A.B.: Reuse of Woody Biomass Ash Waste in Cementitious Materials, Chemical and Biochemical Engineering Quarterly, 30 (2016) 2, pp. 137–148, https://doi.org/10.15255/CABEQ.2015.2231

[24] Medina, J.M., Sáez del Bosque, I.F., Frías, M., Sánchez de Rojas, M.I., Medina, C.: Durability of new blended cements additioned with recycled biomass bottom ASH from electric power plants, Construction and Building Materials, 225 (2019), pp. 429–440, https://doi.org/10.1016/j.conbuildmat.2019.07.176

[25] Rajamma, R., Senff, L., Ribeiro, M.L., Labrincha, J.A., Ball, R.J., Allen, G.C., Ferreira, V.M.: Biomass fly ash effect on fresh and hardened state properties of cement based materials, Composites Part B: Engineering, 77 (2015), pp. 1–9, https://doi.org/10.1016/j.compositesb.2015.03.019

[26] The European Committee for Standardization, EN 196-5:2011 Methods of testing cement - Part 5: Pozzolanicity test for pozzolanic cement

[27] Nawaz, A., Julnipitawong, P., Krammart, P., Tangtermsirikul, S.: Effect and limitation of free lime content in cement-fly ash mixtures, Construction and Building Materials, 102 (2016), pp. 515–530, https://doi.org/10.1016/j.conbuildmat.2015.10.174

[28] Vukićević, M., Pujević, V., Marjanović, M., Jocković, S., Maraš-Dragojević, S.: Stabilization of fine-grained soils with fly ash, GRAĐEVINAR, 67 (2015) 5, pp. 761–770, https://doi.org/10.14256/JCE.1281.2014

[29] Payá, J., Borrachero, M.V., Monzó, J., Peris-Mora, E., Amahjour, F.: Enhanced conductivity measurement techniques for evaluation of fly ash pozzolanic activity, Cement and Concrete Research, 31 (2001) 1, pp. 41–49, https://doi.org/10.1016/S0008-8846(00)00434-8

[30] Li, X., Snellings, R., Scrivener, K. et al. (30 more authors): Reactivity tests for supplementary cementitious materials: RILEM TC 267-TRM phase 1, Materials and Structures, 51 (2018) 151, https://doi.org/10.1617/s11527-018-1269-x