Effect of free Cao and MgO from wood biomass ash on cementitious composites

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Abstract. Wood biomass ash (WBA) presents a great potential for future applications as supplementary cementitious material (SCM). Considering the variable chemical composition of WBA, the influence of free CaO and free MgO in cementitious composites with WBA as SCM should also be investigated, as certain mechanical properties and durability of composites may be negatively affected. The influence of 10 different fly WBA from Croatian power plants, varied in proportions of 10, 20 and 30% as SCM, on standard consistency, initial and final setting time and volume stability of cement pastes was tested. The results show that during the transport of WBA there was carbonation and hydration of free CaO and MgO, which stabilized and partially influenced the volume stability and setting time of cement pastes, so the content of alkali, pozzolanic oxides and LOI should also be considered in the analysis.

Keywords: Wood biomass ash, supplementary cementitious material, setting time, soundness, free CaO, free MgO.

1 Introduction

The cement industry is responsible for 5-9% of global CO_2 emissions [1], [2], with 40% being the energy required to operate the cement plant and 60% being the result of the chemical reaction of decomposition of $CaCO_3 \rightarrow CaO + CO_2$ [3], [4]. Current research is mainly focused on the search for new binders and/or pozzolanic materials as supplementary cementitious materials (SCM) [3], [5], since in this way it is possible to reduce CO_2 emissions by 30-40% without significantly affecting concrete properties [4], and to contribute to the reduction of waste generation and find an environmental and economic solution for both industries. Materials from waste generation from municipal solid waste (MSW) incineration, biomass and sewage sludge are of particular interest, and the possibilities of using these types of ash in the production of bricks, mortar and concrete are being investigated as part of the HORIZON - AshCycle project, with the focus of this research being on wood biomass ash (WBA)..

It is known that fly WBA is characterized by a highly variable chemical composition, which is influenced by the type and origin of biomass, the technology and temperature of combustion, the place of collection, and the method of storage [6], so its use as SCM requires detailed characterization. The fine particles of fly WBA may contain pozzolanic oxides on the one hand and harmful components such as alkalis, free CaO and MgO, and biological residues on the other hand, which may negatively affect the mechanical properties and durability of concrete [7], [8], [9]. There are few studies in which the content of free CaO and MgO was determined and it's influence on the properties of cement composites was investigated [10], [11], [12], [13]. However, the influence of free CaO and MgO in WBA cannot be neglected as they are present in significant amounts. Free CaO and free MgO can have a negatively effect on volume stability, i.e., cause expansion of cement-based materials due to the delayed hydration of these two oxides in the "dead-burned" state. CaO is inherently more reactive than MgO, and its hydration product $Ca(OH)_2$ is more soluble than $Mg(OH)_2$ [14]. As a result of the large volume expansion of CaO and MgO particles due to their hydration, but after the microstructure is already networked, internal stresses occur in the material and it's cracking [15]. This type of expansion mechanism due to the large amount of free CaO and MgO in WBA is proposed by some authors to mitigate the problem of autogenous shrinkage [16], while in Japan expansive admixtures with a large amount of crystalline CaO are used to achieve controlled strains under confinement in reducing concretes [17]. The results of volume stability tests on concrete specimens with WBA indicate an acceptable percentage of up to 30% as a substitute for cement [18], [19]. Certain studies pointed out the possible influence of a high proportion of free CaO in the ash [20], [21] on a shortened setting time, while on the other hand a higher MgO content in the binder causes a delay in the setting time [10]. According to [20], [21], [22], a high content of free CaO can have a negative effect on workability because the hydration reaction of CaO is rapid and can absorb a large amount of water, leaving the paste with insufficient water for lubrication. It has been observed that free CaO can affect the higher temperature of the paste with a higher percentage of WBA because it is very reactive. Previous studies have shown the importance of investigating the influence of free CaO and free MgO in WBA when used as SCM.

The main objectives of this research were: a) to investigate the influence of 10 different fly WBAs on the standard consistency, setting time and volume stability of cement pastes as SCM and b) to determine the optimum proportion (%) of replacement of WBA as SCM with respect to the tested properties. Due to similar problems for coal fly ash, all results were compared with the criteria of the standard EN 450-1 [23], which limits the content of free MgO to 4.0% and CaO to 1.5% by mass.

2 Experimental procedure

For this study, a total of 31 cement pastes were prepared – one reference (with 100% cement) and 30 pastes in which WBA was used as SCM in various proportions of 10, 20 and 30% according to EN 196-3. Portland cement CEM II/A-S 42.5R and 10 locally available fly WBAs from 10 different biomass power plants in Croatia, whose designations are listed in **Table 1**, were used in all pastes. The cement pastes were prepared according to the standard EN 196-3 from 500 g of cement and 125 g of water, varying different proportions of water to achieve standard consistency, using a Vicat apparatus. Standard consistency is achieved when the distance between the plunger and the base -

plate is 6 ± 2 mm. After reaching the standard consistency, the setting time was tested according to the Vicat method and the volume stability with Le Chatelier rings (soundness test). The results of the setting time and volume stability tests were compared with the criteria specified in the standard for coal fly ash EN 450-1. In other words, the initial setting time should not be longer than twice the setting time of the reference mix, while for volume stability it is specified that the distance between indicator points should not be greater than 10 mm.

3 Results and Discussion

3.1 Standard consistency

The standard consistency results (**Table 1**) show that increasing the proportion of WBA as SCM in cement pastes increases the water demand compared to the reference mixture [24], [25], [19], [26], [18], which is mainly related to the irregular shape [27] and larger specific area of the WBA particles [25], [27]. An exception is a mixture with 30% WBA17, where the standard consistency was lower (29%) than when 10% and 20% WBA were used as SCM (31%; 36.2%). The aim of this study is to investigate the influence of free CaO contained in WBA on standard consistency, i.e., water demand, since several studies indicate that it has a negative effect on workability [22], [20],[21] when the free CaO content is more than 1.5% by mass according to EN 450-1. However, this is not the main reason for the high water demand. It is claimed that the hydration of free CaO is rapid and can absorb a large amount of water. Therefore, it is logical that mixes containing WBAs with a high free CaO content will have lower workability because less water is available to lubricate the cement paste after hydration of the free CaO. This applies to all WBAs with a high free CaO content, but not for WBA10, WBA12 and WBA19 with satisfactory free CaO values and yet increased water demand, which requires further testing to determine the reason for this behavior.

3.2 Volume stability

Despite the high levels of free CaO and MgO in WBAs that did not meet the prescribed criterion of EN 450-1 (< 1.5% CaO; < 4% MgO), the majority of the WBAs met the Le Chatelier expansion criterion, which requires that the distance (C-A) between indicator points not exceed 10 mm (**Table 1**). From the results presented in the table, only the mixture with WBA3 did not meet the prescribed criterion when the proportions of 20% and 30% were increased, which can be related to the maximum content of free CaO (26.64%) compared to the other WBAs. Blends with 30% WBA8 and WBA19 also did not meet the criterion, which could be due to the high CaO (15.85%; 4.72%) and MgO contents (5.9%). However, this theory cannot be applied to all other WBAs (WBA1, WBA2, WBA11, WBA16, and WBA17), which met the volume stability criterion despite high free CaO and MgO contents. A possible reason for this is the stabilization of WBAs during the transport of the WBA from the collection point to the mixing process, according to [10], [11], [12]. When WBA with a high content of free CaO and MgO is exposed to atmospheric conditions, carbonation (formation of the product $CaCO_3$) , i.e. hydration (formation of the product $Ca(OH)_2$ and $Mg(OH)_2$ [10] occurs which may lead to changes in structure or mineralogical composition [28], [29]. Therefore, in addition to the type of raw material from which the WBA is obtained, the storage and transport conditions for WBA should also be considered, as it contains significant amounts of free CaO [16]. This could explain the behavior of the WBAs used in this study. It is possible that stabilization of the WBA has occurred and that the mineralogical structure of the WBA has changed, which has had a beneficial effect on volume stability.

3.3 Setting time

Fig. 1 shows the results of setting time tested on cement pastes with different amounts of WBAs as SCM. The initial setting time of cement pastes is higher for all proportions (10, 20, and 30%) of WBA as SCM compared to reference mixture, except for WBA2 at 20% and 30% and WBA17 at 30%. WBA19 (240 min) had the lowest initial setting time at a proportion of 10%, WBA2 (100 min) at a proportion of 20%, and WBA17 (125 min) at a proportion of 30% as SCM. The shortened setting time of WBA19 can be mainly attributed to the low free CaO content, while for WBA2 and WBA17 it may be related to the low MgO content, considering that all other properties that have an influence on such behavior, such as alkali content and LOI, and the lowest content of pozzolanic oxides) are not in accordance with the literature [30], [31], [32], [32], [33]. WBA8 had the longest initial setting time (425 min) at 10% proportion as SCM, which is related to the high content of free CaO (15.8%), MgO (4.72%), alkali (12.76%), and LOI (15.56%) and WBA1 at proportions of 20 and 30% (540 min; 535 min), which can be related to the high contents of free CaO (8.83%) and LOI (20.81%). An exception is the mixture with 10% WBA17, which could not be tested for initial setting time, as it started to set immediately and showed a slight difference between initial and final setting time at 30%. These results are in contradiction with previous studies, as the chemical composition of WBA17 - the largest alkali content of all ashes (33.77%) [11], the high LOI content (19.26%) [34], and the lowest pozzolanic oxide content (1.06%) [10], [12] - indicates the expected longest setting time. However, this cannot be confirmed in this case. The only difference that can explain this behavior of WBA17 is the low MgO content, the lowest compared to other WBAs, since according to the literature [10], a higher MgO content in the binder affects the setting time delay. It should be emphasized that when mixing with WBA11 in all three proportions (10, 20 and 30%) as SCM, the mixing time was reduced to the first 90 seconds due to too fast setting, although the reason could not be determined. However, according to the criterion prescribed in the standard for coal fly ash EN 450-1 [23], the setting time should not be more than twice the setting time (about 320 min) of a mixture with cement only, which is fulfilled for most of the WBA with a proportion of 10%, except for WBA1, WBA2, and WBA8, which is due to the relatively high LOI content (20.81, 20.49; 15.56 wt%). With the increase of the proportion of WBA as SCM to 20% and 30%, most of them do not meet the prescribed criterion, although the increase of the initial setting time at 20% proportion can be tolerated for WBA3, WBA10 and WBA16, as they are slightly different compared to reference mixture. The final setting time is generally higher for

WBA as SCM than for Portland cement. WBA11 exhibited the longest final setting time at 30%, due to the highest LOI content (20.99%), high alkali content (12.76%), and low pozzolanic oxide content (4.27%). At a WBA content of 30%, an excellent correlation was found with the delayed final setting time at a high LOI content (R^2=0.8639).

Table 1. Results of standard consistency, setting time and soundness

WBA ID	WBA share	Depth of penetration (mm)	Standard consistency (%)	Temperature (°C)	Soundness (mm)	Free Cao (wt.%)	Free MgO (wt.%)
-	-	7	27.9	21.1	1	1.45	3.15
	10	5	33.9	23.7	0		
WBA1	20	7	42.6	22.2	1	8.83	3.05
	30	7	46.2	22.5	3		
	10	8	47	21	0		
WBA2	20	8	59	20.6	1	24.60	2.84
	30	8	63	23.1	4		
	10	4	32	23.3	6		
WBA3	20	5	33	23.8	32	26.64	3.56
	30	6	36.2	22.6	37		
	10	8	36.2	23.1	0		
WBA8	20	8	40.8	21.1	2	15.80	4.72
	30	3	44.6	23.7	11		
	10	4	32	21.7	4		
WBA10	20	4	33	22.7	0	0.33	2.56
	30	4	34.2	23.3	1		
	10	7	48	26.9	1		
WBA11	20	4	56	22.1	4	18.14	5.48
	30	4	60	22.5	4		
	10	4	32	22.4	2		
WBA12	20	8	33.2	20.5	1	0.2	5.9
	30	8	35.6	24.2	1		
	10	4	32.4	23.5	0		
WBA16	20	8	35	24	1	15.34	4.53
	30	4	38.4	22.5	4		
	10	4	31	21.4	1		
WBA17	20	5	36.2	21.2	2	15.53	1.19
	30	8	29	27	1		
	10	8	32.4	21.4	0		
WBA19	20	7	35.6	25.1	4	0.2	5.9
	30	4	41	23.9	20		

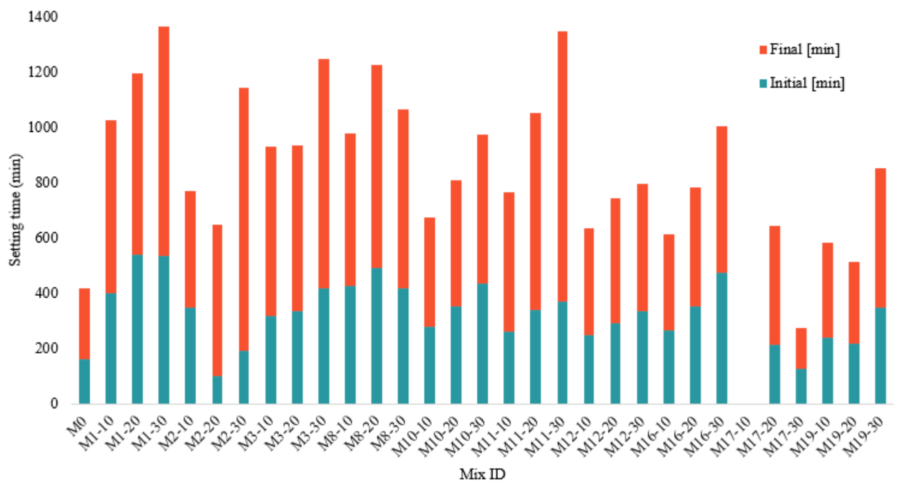

Fig. 1. The influence of different amounts of WBAs as supplementary cementitious material (SCM) on the setting time of cement pastes

4 Conclusion

The results show that free CaO affects the water demand but is not the only factor. As the WBA content increased, the water demand also increased. Most cement pastes with 10 and 20% WBA as SCM met the volume stability criteria according to EN 450-1 despite the high proportions of free CaO and free MgO, indicating the stabilization of WBA by carbonation and hydration during transportation. With an increase of WBA content, the initial and final setting times of the cement pastes increased, which cannot be directly related only to the influence of free CaO and MgO. LOI and pozzolanic oxides had the greatest influence on the prolonged setting time.

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