Harvest Residues Ash and Ceramic Powder as Pozzolanic Materials for Developing Sustainable Building Materials

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Abstract. As the global population increases, a large amount of solid waste generates along, occupying large landfill sites for its disposal. Conversion of this waste into other alternative resources will reduce the load on non-renewable building materials and help in solving the landfilling problem. Incorporating mainstream wastes, such as: fly ash, blast furnace slag, rice husk ash, recycled aggregate and bricks in mortar or concrete has become one of the green ways to deal with waste from the agriculture and industry. Maintaining sustainability at the centre of this paper, two types of waste materials have been selected for the study. First is ceramic waste powder obtained from broken or distorted ceramic waste products, and the second is harvest residues ash from the agricultural biomass combustion. The present study aims at evaluating basic chemical, physical and pozzolanic properties of collected cement-alternative materials - phase 1 and testing mechanical and durability properties of concrete (compressive strength, water impermeability and wear resistance) produced with high share of these wastes. The results indicate that optimal types of industrial and agricultural waste materials can be effectively used in the concrete industry as cement substitutes up to the 50% replacement level, while maintaining satisfying concrete's performance and meeting the principles of sustainable development.

Keywords: Ceramic Powder · Harvest Residues Ash · Cement-Alternative · Green · Pozzolanic · Concrete

1 Introduction

The consumption and depletion of natural resources has become a significant sustainability issue for the construction industry. Enormous quantities of construction and demolition (C&D) waste is produced annually in Serbia. Due to no specific handling and utilization plan of C&D waste (apart from low grade application in road structures), these are sent to landfills, losing thereby a large quantum of material having a great potential to be reused and recycled in the new construction.

One of the most efficient methods is to utilize recycled concrete as an aggregate in new concrete, i.e., in place of new building materials, following recommendations and specifications concerning its utilization [1].

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The environmental impact generated by the construction industry is not only related to the natural resources unsustainable consumption and generated waste. Each year, over 4 billion tons of cement are produced. Within this process, carbon dioxide – CO_2 – the gas responsible for the greenhouse effect, is emitted. Annual production of over 4 billion tons of Portland cement is responsible for 8% of the world's total CO_2 emissions [2]. An alternative to reduce the amount of clinker in cement is the use of locally available waste materials, originating from industry and agriculture, whether with filler effect, pozzolanic additions, or cementing agents.

Application of agricultural biomass ashes and ceramic debris powders currently stands out among the studies that seek the application of new materials that can be used as mineral additions in concrete [2–5]. Using these finely ground materials alters the concrete microstructure due to small particles that might occupy empty spaces, which results in a refinement of pores of the hydrated matrix by the filler (packing) effect [6]. Also, the fine particles act as nucleation sites for cement grain hydration. With reactive mineral additions (containing sufficient reactive silica), there is the effect of pozzolanic reactions, which originates secondary C-S-H gel that precipitates in the larger empty spaces of the paste, modifying the concrete porous structure. This process reduces the matrix permeability by filling the pores with additional reaction products (pore buffering).

In Vojvodina, northern province of Serbia, large amounts of biomass ash are created as waste products during direct harvest residues combustion, pyrolysis, gasification, hydro gasification, liquefaction and alcoholic fermentation, estimated at 5.000 tons per year [7]. They are most commonly disposed of in landfills or recycled on agricultural fields. Considering that the disposal costs of waste and biomass ash volumes are ever-increasing, a sustainable ash management has to be established.

Another available resource is ceramic debris. A large quantity of ceramic waste is produced during manufacture of ceramic products in Vojvodina, estimated at 10.000 tons per year. A small part is used in different applications, while a huge amount is sent to landfills. Hence, there is a need for ceramic industries to find an alternative way for ceramic waste disposal.

The objective of this study is to analyze the possibility of application of collected types of biomass ashes and ceramic debris powders, as supplementary cementitious materials (SCMs) in the production of cement-based concrete. First stage of experimental research included characterization of SCMs, whereas all relevant chemical, physical, mechanical and pozzolanic properties were tested and assessed, in accordance with the relevant standards. Based on the characterization results, optimal types of biomass ash and ceramic powder were chosen and further utilized as cement substitutes, up to the 50% replacement level, in the production of concrete.

2 Experimental Research

2.1 Component Materials

Cement
Ordinary Portland cement (OPC), originating from the Lafarge cement factory in Beočin, Serbia, was used. The cement has a specific gravity of 3.1 g/cm^3 and the Blaine fineness of 4000 cm^2/g.

Cementitious Materials
The following materials were collected and tested within this study:

- Mixed wheat straw, sunflower husk, and silo waste (B1), “Soya-Protein” Bečej,
- Mixed cob corn and soya straw ash (B2), “IPOK” Zrenjanin,
- Ceramic masonry blocks waste (CP1), “NEXE-Stražilovo” Petrovaradin,
- Ceramic roofing tiles waste (CP2), “NEXE-Polet” Novi Bečej,
- Ceramic roofing slipware tiles waste (CP3), “Wienerberger doo” Kanjiža.

Biomass ashes were roughly sieved, through a 4 mm sieve, to separate unburnt straw and other large impurities. In order to obtain a material with a satisfactory level of fineness, all SCMs were ground in a laboratory ball mill for 6 h.

Aggregate
Natural river aggregate was used as fine aggregate, while recycled concrete aggregate (RCA), with the maximum grain of 16 mm was utilized as coarse aggregate in all concrete mixtures. The sieve analysis of river and recycled concrete aggregate and their physical properties were tested in accordance with the standards: SRPS EN 933-1, SRPS EN 1093-3 and SRPS EN 1097-6. The results are presented in Table 1.

Chemical Admixtures
Superplasticizer “Sika ViscoCrete 3070” (SP) was used for the production of concrete mixtures with comparable workability.

2.2 Methods

The chemical composition of collected materials was determined using energy dispersive X-ray fluorescence spectrometer (EDXRF 2000 Oxford instruments) according to EN 196-2 and ISO 29581-2.

The specific surface area was determined according to the Blaine air permeability method given in EN 196-6, which is widely used for the fineness determination of hydraulic cement.

Initial and final setting time, as well as soundness, were determined in accordance with EN 196-3.

The pozzolanic activity was tested on samples prepared according to the procedure given in SRPS B.C1.018. Mortars were prepared with SCM, hydrated lime, and CEN standard sand, with the following mass proportions: m_{hl}: m_{scm}: m_{qs} = 1:2:9 and water – binder ratio 0.6 (where: m_{hl} – the mass of hydrated lime; m_{scm} – the mass of waste material; m_{qs} – the mass of CEN standard sand). After compacting, the samples were

Table 1. Sieve analysis and physical properties of aggregates.

Sieve size (mm)	NA	RCA	
	0/4 mm (% of passing)	4/8 mm (% of passing)	8/16 mm (% of passing)
16	100	100	99.9
8	99.9	97.4	5.3
4	92.9	11.4	0.9
2	77.2	1.9	0.7
1	65	0.9	0.6
0.5	48.8	0.6	0.6
0.25	8.2	0.3	0.3
0.125	0.4	0.1	0.1
Pan	0.0	0.0	0.0
Specific gravity (g/cm^3)	2.65	2.29	2.28
Water absorption (%)	1.0	6.2	5.5

Note: High water absorption of RCA indicates the need to provide the additional mixing water

hermetically sealed and cured for 24 h at 20 °C, then for 5 days at 55 °C. Subsequently, 24 h period was allowed for the samples' cooling to the temperature of 20 °C, followed by compressive and flexural strength tests.

The activity index was examined according to EN 450-1, 2014. The preparation of specimens and determination of the compressive strength were carried out in accordance with EN 196-1.

The compressive strength of concrete was tested after 28 days of water curing. The test was carried out according to SRPS EN 12390-3.

Depth of water penetration under pressure was determined at the age of concrete of 28 days. The test was conducted in accordance with SRPS EN 12390-8.

The wear resistance of concrete was tested on square-shaped specimens, 150 mm long, 50 × 50 mm cross-sectional. Samples were cut from 150mm edge cubes. The test was performed at the age of 60 days of concrete, according to the 'wide wheel' method, described in EN1338.

2.3 Composition of Concrete

For this study, a total of seven concrete mixtures were prepared. Optimal types of ceramic powder and biomass ash were chosen as cement replacement in levels: 10%, 30% and 50%. The mixture, prepared with cement, was labelled as C – reference mixture. In the next six mixtures, cement was replaced by ceramic powder and biomass ash: CP10, CP30, CP50 and B10, B30, B50, respectively. The mix proportions are presented in Table 2.

The composition of concrete mixtures for all types of aggregates was determined based on the following conditions:

- The total amount of binder (cement and SCM) is 400 kg/m^3,
- The water to binder ratio (w/b) is 0.45,
- Superplasticizer was used for flow correction in the range of 0.2–0.3% (%mass cement + SCM),
- The additional amount of water was determined based on the water absorption of RCA.

Table 2. Mix proportions of concrete: quantities (kg/m^3).

Mix	Binder	OPC	B2	Water		NA	RCA		SP
				m_v	$m_{v,add}$	0/4	4/8	8/16	
C	400	400	-	180	40.4	841	313	495	0.8
CP10	400	360	40	180	40.3	838	312	493	0.8
CP30	400	320	80	180	40.0	832	310	489	1.0
CP50	400	200	200	180	39.7	826	308	486	1.2
B10	400	360	40	180	40.2	837	312	492	0.8
B30	400	320	80	180	39.8	828	308	487	1.0
B50	400	200	200	180	39.3	819	305	482	1.2

Cube specimens with 150 mm edge were casted for testing of compressive strength and depth of water penetration under pressure. After casting, all of the specimens were left in their casts for 24 h and then unmolded and cured until required for testing.

3 Results and Discussion

3.1 Characterization of Cementitious Materials

Chemical Composition

The chemical compositions of OPC and selected materials are given in Table 3.

Summarized results of chemical properties of ceramic powders, requirements in relevant standards, as well as criteria fulfillment are given in Table 4.

All ceramic powders fulfill the criterion for total amount of oxides: Al_2O_3 and Fe_2O_3, as well as reactive SiO_2 content which is expected to result in their satisfactory pozzolanic activity.

Biomass ashes are characterized by an insufficient share of important oxides. However, B2 satisfies the criterion for amorphous SiO_2 content, hence it could contribute to the properties of the hardened cement-based composites through pozzolanic activity.

Results indicate that both types of biomass ashes are characterized by high alkali content, i.e., potential trigger of alkali-silica reaction (ASR) between alkaline cement

Table 3. Chemical composition of OPC, biomass ashes and ceramic powders.

Material (%)	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Na_2O	K_2O	SO3	P_2O_5
OPC	17.34	4.53	20.64	50.26	1.93	0.20	0.59	3.06	0.00
B1	20.21	1.83	1.74	13.42	8.30	0.00	23.091	2.88	7.78
B2	45.76	5.92	3.37	14.08	8.30	0.00	13.10	1.26	2.81
CP1	60.86	16.38	6.81	9.38	3.89	0.77	2.39	0.80	0.14
CP2	61.88	16.46	7.40	4.90	3.66	1.63	2.81	0.08	0.20
CP3	59.03	15.81	6.64	5.65	4.20	1.50	2.50	0.07	0.16

Table 4. Chemical composition of biomass ashes and ceramic powders - criteria fulfillment.

Chemical Requirements (EN 450-1)	Criteria	Standard	CP1	CP2	CP3	B1	B2
Total amount of oxides: $SiO_2 + Al_2O_3 + Fe_2O_3$ (%)	≥70%	EN 196-2 EN 450-1	84.1	85.7	81.5	23.8	55.1
Loss of ignition (%)	A: Max 5% B: Max 7% C: Max 9%	EN 196-2 EN 450-1	3.3 Class A	0.3 Class A	1.0 Class A		
Chloride content (%)	≤0.1%	EN 196-2 EN 450-1	0.002	0.003	0.000	0.338	0.502
Sulphate content (%)	≤3%	EN 196-2 EN 450-1	0.80	0.08	0.07	2.88	1.26
Free CaO content (%)	≤1.5%	EN451-1 EN 450-1	6.45	4.69	5.65	5.96	11.34
Reactive SiO_2 content (%)	≥25%	EN197-1 EN 450-1	50.26	31.32	48.01	18.78	35.19
Total amount of alkalis (%) $Na_2O + 0{,}658\ K_2O$	≤5%	EN 196-2 EN 450-1	2.34	3.48	3.15	15.19	8.62
Phosphate content (%)	≤5%	ISO 29581-2 EN 450-1	0.14	0.20	0.16	7.78	2.81

paste and amorphous silica, which is found in many common aggregates. Hence, this reaction should be experimentally verified for each utilized aggregate.

Biomass ashes exceed the limit value for the chlorides content, as well. Absorping chloride ions can threaten the condition of passivity of cement-based material.

All tested materials exceed the limit value for free lime content. Free lime can cause a delayed expansion and compressive strength reduction of cement-based composites, which could result in a serious deterioration of structures built. Hence, durability properties of such composites should be experimentally verified.

Physical, mechanical and pozzolanic properties of ceramic powders are listed in Table 5. The specific surface area of CP1 and CP2 is higher compared to CP3, probably due to the higher temperature and, consequently, denser structure ceramic roofing slipware tiles are produced at. The inclusion of all cement substitutes slightly retarded the setting time, as can be anticipated for the use of SCMs. Ceramic powders CP1 and CP2 show a pozzolanic activity of Class 10, while CP3 demonstrates a pozzolanic activity of Class 5. All ceramic powders meet the requirements for activity index, at ages of 28 and 90 days.

Table 5. Physical properties of biomass ashes and ceramic powders.

	Criteria	Standard	CP1	CP2	CP3	B1	B2
Specific gravity (g/cm^3)	/	SRPS B.B8.032	2.62	2.61	2.59	2.36	2.44
Specific surface area (cm^2/g)	/	EN 196–6	13815.0	11064.0	6200.0	8120.0	8090.0
Pozzolanic activity	$f_{cs} \geq 5MPa$ $f_{fl} \geq 2MPa$	SRPS B.C1.018	Class 10	Class 10	Class 5	Class 5	Class 5
Activity index (%)	$AI_{28} \geq 75\%$ $AI_{90} \geq 85\%$	EN 450-1	$AI_{28} = 100$ $AI_{90} = 104$	$AI_{28} = 90$ $AI_{90} = 107$	$AI_{28} = 90$ $AI_{90} = 98$	$AI_{28} = 68$ $AI_{90} = 79$	$AI_{28} = 102$ $AI_{90} = 115$
Initial setting time (min)	≥ 60	EN 196-3 EN 197-1 EN 450-1	160	160	165	25	165
Final setting time (min)	≤ 2 times the setting of the cement	EN 196-3 EN 197-1 EN 450-1	$220 \leq 2 \times 190$	$210 \leq 2 \times 195$	$225 \leq 2 \times 195$	$45 \leq 2 \times 195$	$285 \leq 2 \times 195$
Soundness (mm)	≤ 10	EN 196-3 EN 450-1	0.6	0.5	0.5	0.6	1.0

Both types of biomass ashes are characterized by relatively high level of fineness, whereas the specific surface area is twice the size of the cement value. The presence of B1 significantly accelerated the setting time of cement paste. The initial setting time was shorter than an hour, hence this material doesn't satisfy the criterion. Biomass ashes have pozzolanic activity of Class 5, while B1 exhibited both activity index values below the required limits.

As tested materials showed negligible expansion - up to 1 mm; hence the soundness criteria are fulfilled.

Based on the obtained results, it can be noted that, amongst ceramic powders, CP1 is characterized with greater pozzolanic activity, higher activity index and higher level of fineness. B2 displayed superior performance over the other type of biomass ash, especially considering activity index.

Therefore, CP1 and B2 have been chosen as cement substitutes in the next phase of experimental research, i.e., concrete production.

3.2 Compressive Strength of Concrete

Compressive strength of reference concrete and concretes incorporating chosen SCMs was tested at the age of 28 days. Results are shown in Fig. 1.

As the SCM content increased, the compressive strength of concrete gradually decreased up to the replacement level of 50%, which might be attributable to the dilution effect, especially at higher replacement levels (fewer cement particles available for hydration, decreased number of the hydration products and increased porosity and permeability of the mix). Regarding biomass ash-based concretes, the relative compressive strength of blended concrete decreased by 13%, 19% and 26% for replacement levels of 10%, 30% and 50%, correspondingly. As for the concretes incorporating ceramic powder, similar trend was observed: compressive strength of blended concrete was decreased by 13%, 19% and 26% for replacement levels of 6%, 10% and 32%, respectively.

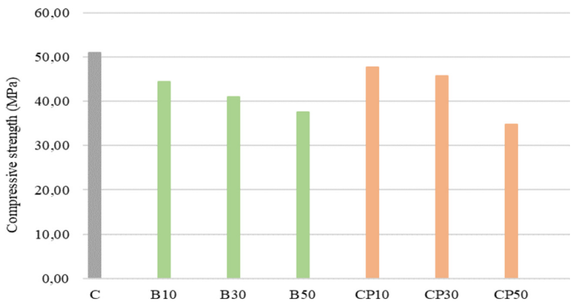

Fig. 1. Compressive strength of concrete.

Considering that all types of concrete achieved strength class equal or higher than C25/30, which is predominately used in concrete structures in Serbia, it can be stated that structural concrete can be produced by utilizing large volume of biomass ash and ceramic powder as cement substitutes. In addition, the pozzolanic reactivity of SCMs could significantly contribute to the strength attainment in the later ages.

3.3 Water Impermeability of Concrete

Figure 2 illustrates the results of depth of water penetration under pressure, while the absorbed mass of water of all tested concretes is displayed in Fig. 3.

The results indicate a continuously decreasing trend in the depth of water penetration under pressure of SCM blended concrete and, at the same time, higher rate of water absorption. Such trend can be explained by the filler effect and pozzolanic property of the incorporated alternative cementitious materials.

Considering the filler effect, fine SCM particles (CP and B2 are characterized by high level of fineness) act as micro aggregates, filling the voids in the binder matrix and enhancing the compactness of the concrete structure, leading to the slower rate of water penetration - Fig. 2. On the other side, due to the dilution effect and prolonged pozzolanic reaction, lower amount of hydration products is generated up to the age of

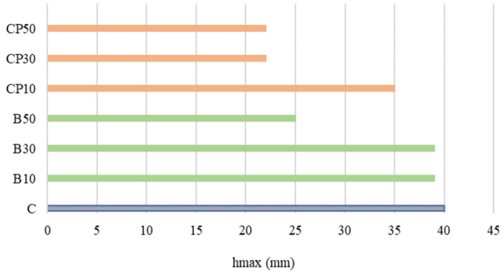

Fig. 2. Depth of water penetration under pressure.

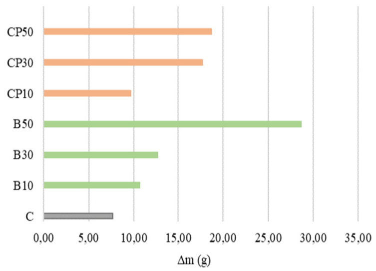

Fig. 3. Absorbed mass of water.

28 days. As a result, the concrete is characterized by a higher capillary porosity, which leads to the higher water absorption of SCM blended concretes - Fig. 3. In the later period, the additional CSH gel produced as a result of pozzolanic reaction could help in filling the pores, reducing permeability and thereby reducing water absorption.

3.4 Wear Resistance of Concrete

The results of testing the wear resistance of concrete are shown in Fig. 4.

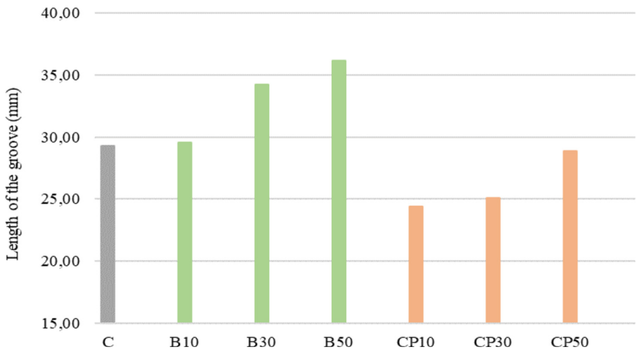

Fig. 4. Length of the groove of tested concretes.

It can be observed that CP improves the wear resistance of cement-based concrete, especially at lower replacement levels. This is probably due to the filler effect, i.e., more compact structure of the binder phase and contribution of the pozzolanic reaction to the additional C-S-H gel formation and subsequent densification of the mix.

Regarding the influence of B2 on the wear resistance of concrete, as the content of biomass ash increases, length of the groove increases along. This is probably due to still an early stage of pozzolanic activity of this type of SCM at the age of testing, i.e. more porous and not sufficiently compacted concrete structure. Considering achieved classes of wear resistance, in accordance with EN 1338, it can be stated that all tested concretes fulfil the criteria for class I, i.e., no measured performances. In that regard, SCMs don't influence the wear resistance of concrete to a great extent.

4 Conclusions

In this study, biomass ash and ceramic powder were adopted as cement substitutes in order to prepare more sustainable concrete. Alongside a significant share of above-mentioned waste materials, utilized as binders, recycled concrete aggregate was used as coarse aggregate in the concrete. According to the research results, the following conclusions are drawn:

- All tested ceramic powders and biomass ash B2 are good SCM candidates, owing to high amorphous silica content and satisfactory level of fineness,
- Due to the dilution effect and early stage of pozzolanic reaction at the 28 days, compressive strength of concretes incorporating SCMs gradually decreased, in relation to the reference concrete. However, 50% SCM inclusions provided satisfactory performance, meeting the class of concrete for structural applications.
- Tested SCMs contributed to lower depth of water penetration under pressure, especially at higher cement replacement levels. This can be attributed to greater compactness of concretes containing large share of fine particles.
- Considering that all concretes belong to the same wear resistance class, it can be noted that SCMs don't have a significant influence on this property of concrete.
- Finely ground ceramic powders and biomass ashes can be used as cement substitutes in concrete production, up to the 50% replacement level, without jeopardizing its physical and mechanical properties to a greater extent.

Although this study provides one specific case of the selected waste materials utilization, the knowledge findings expanded the role of agricultural and industrial waste ash in manufacturing cementitious materials. However, further investigation related to the influence of selected SCMs on the durability properties of concrete is necessary.

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