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Characterization of harvest residues ashes and ceramic waste powders originating from Vojvodina as potential supplementary cementitious materials

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ABSTRACT

Traditionally, residential buildings in Vojvodina have masonry walls. Various types of mortar of mineral origin are most often used for joining masonry elements and finishing. The total amount of mortar for the construction of one building is not negligible. The estimated annual consumption of mortar in Vojvodina is about 198 thousand tons i.e. 27 thousand tons of cement and about 31.5 thousand tons of hydrated lime. It can easily be seen conventional mortars based on cement and lime are unacceptable in the light of environmental protection and sustainable development in the contemporary construction industry. Therefore, there is a need for research and development of new, alternative types of binders, based on locally available renewable and/or waste materials. The ceramic masonry elements and tiles industry generates ceramic waste during the production process. This waste, in powder form, could potentially be used as supplementary cementitious material (SCM). Biomass ash, generated by the combustion of harvest residues, as a renewable energy source, is another alternative to cement in modern building composites. This paper emphasizes the physical, chemical, and pozzolanic characteristics of the available agro-waste ashes and ceramic waste powder, originating from Vojvodina. The results indicate relatively high pozzolanicity of all tested ceramic powders and biomass ash based on cob corn, owing to their high fineness and reactive silica content. Furthermore, a catalogue of collected waste materials, illustrating basic data on the raw materials, processing method, landfilling, available quantities, and their tested properties is given.

1 Introduction

The carbon emission resulting from cement clinker production has always been a concerning issue among sustainability researchers, as well as among cement-based composites technologists, mainly due to the growing alarm about global warming.

With an increasing demand for sustainability in the construction sector in the 21st century, the development of cement-based composites incorporating waste materials originating from agriculture and industry attracts wide interest. The utilization of such waste in cement-based composites shows immense potential as an alternative material and brings various environmental, economic, and technological benefits. Incorporating agricultural and industrial waste for developing green and sustainable cement-based composites is promising with regard to promoting a cleaner environment, reduction of a high level of greenhouse gas emissions, and mitigating the environmental burden of concrete production. From the aspect of economic development, this substitution results in considerable savings due to the reduction of high disposal costs of agricultural and industrial waste as well as the exploitation and preparation costs of raw materials (clay and limestone). Thus, reusing these waste materials saves natural resources, contributes to sustainability, and decreases the dumping of these wastes into landfills.

Substantial quantities of biomass waste from harvesting (leaves, straw, stalk, etc.) are generated every year. About 30% of the annual production of biomass waste is used as animal food or as fertilizers. The rest can be utilized as a renewable energy source. Within the combustion process, 2-10% of biomass ash is generated as a by-product. The utilization of biomass, as an energy source, increases worldwide so does the amount of biomass ash as waste material. Unfortunately, biomass ash is usually put down in open dumps resulting in disposal problems, such as air, water, and ground pollution. Thus ideas for its use are welcomed.

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Generally, ceramic waste can be collected in brick, block, and roof tiles production of red pastes, or in sanitary ware, wall, and floor tiles production from white pastes. These materials can be found in construction and demolition (C&D) waste, also. The ceramic wastes are highly durable and resistant, both chemically and physically to harsh environmental conditions. Unfortunately, much ceramic waste is deposited in landfills, just a small portion is crushed and used in covering sports fields and in gardening and negligible amounts are used in the manufacture of mortar or concrete to replace cement or aggregates.

Traditionally, residential buildings in Vojvodina have brick walls, whether they are individual or multi-family. During the construction, various types of mortar of mineral origin are most often used for joining masonry elements and finishing. The total amount of mortar for the construction of one building is not negligible. For example, about 12 m^3 of mortar, or 20 tons (average consumption 0.4 t/m^2) is used for masonry and plastering of a residential unit with a usable area of 50 m^2. If it is taken into account that, according to the data of the Statistical Office of the Republic of Serbia, Statistical Yearbook 2020, 6266 apartments were completed in the area of Vojvodina in 2019, with a total area of 494049 m^2, the estimated annual consumption of mortar is about 198 thousand tons.

The usual mixing proportion of mortar components is 1:2:5, by volume (cement: lime: sand), so 1 m^3 of mortar requires about 230 kg of cement and about 270 kg of hydrated lime. With regard to the above-mentioned needs of mortar, the consumption of component materials is about 27 thousand tons of cement and about 31.5 thousand tons of hydrated lime annually.

Both binding materials are obtained in technological processes in which large amounts of natural non-renewable resources (limestone and clay) and fossil fuels (coal, oil, and natural gas) are consumed. It is well known the production of 1 t of cement clinker needs about 1.5 t of raw materials (limestone and clay) and the production of the same amount of lime requires about 1.4 t of limestone. During the thermal treatment of these raw materials, a significant amount of CO_2 is emitted into the atmosphere. It is estimated that during the production of 1 t of cement and 1 t of lime, about 0.6 t of CO_2 and 0.8 t of CO_2 are released, respectively. Based on these data, it can be easily estimated that the annual mortar production consumes 40.5 thousand tons of limestone and clay for cement production and 44.1 thousand tons for limestone to obtain lime. It means, that about 41.5 thousand tons of CO_2 are emitted into the atmosphere.

Taking into account the results of the previous analysis, it can be seen that conventional mortars based on cement and lime are unacceptable in the light of environmental protection and sustainable development in the contemporary construction industry. Therefore, there is a need for research and development of new, alternative types of binders, based on locally available renewable and/or waste materials.

This paper presents a part of the writers' activities in the realization of the project "Development of new binders based on agricultural and industrial waste from the area of Vojvodina for the production of eco-friendly mortars", and includes a short review of current research on the application of biomass ash and ceramic waste powder as SCMs, data on the availability of those materials in Vojvodina region, characterization and cataloging of collected samples.

2 Literature review

2.1 Review on the application of biomass ashes in masonry mortars

The pozzolanic materials contribute to the strength of cement-based composites in two ways, firstly due to the filler effect (packing of smaller particles and filling the voids in the structure) and secondly owing to their pozzolanic reactivity. Biomass ashes are generally rich in amorphous silica and can be a potential cement substitute, with proper processing before their application.

Several researchers have introduced agricultural wastes, in form of ash, as a partial replacement of cement or as an alkaline activator including rice husk ash (RHA) [1], olive waste ash (OWA) [2], sugar cane bagasse ash (SCBA) [3], corn cob ash (CCA) [4], palm oil fuel ash (POFA) [5], wheat straw ash (WSA) [6], soya straw ash (SSA) [7], almond shell ash (ASA) [8], cornstalk ash (CSA) [9], barley straw ash (BSA) [10], etc.

From the earlier research studies, it is noticed that different processing conditions have a remarkable influence on the pozzolanic performance of these ashes. A simple processing method (such as a sieving process) helps convert them into reactive pozzolans. Further grinding of the sieved biomass ash to the cement fineness led to even higher pozzolanicity index, signifying superior pozzolanicity of the ash [11]. Grinding results in a reduction of particle size and an increase in the specific surface area of the particles. As a result, a greater number of nucleation sites for the pozzolanic reaction is available and the reactivity is enhanced, too. Rithuparna et al. [12] reported that grinding of RHA and SCBA for the respective optimum duration is sufficient to improve their pozzolanic performance, while further increase in the grinding duration leads to only a marginal increase in the reactivity.

Rithuparna et al. [13] investigated the influence of high-volume cement replacement (for up to 80%) by palm oil clinker powder in cement – lime mortar. The results indicate that up to 40% of cement could be replaced to obtain the requisite compressive strength of masonry mortar. Similar recommendations were given by Šupić et al [6], whereas research findings highlight the possibility of replacing cement with slag (50%), fly ash (30%) or wheat straw ash (30%) while maintaining its performance and improving the economic and environmental impacts of masonry mortar production. Lertwattanaruk et al. [14] developed a masonry mortar based on four types of waste seashells, including short-necked clam, green mussel, oyster, and cockle as cement replacement (5%, 10%, 15%, or 20% by weight). All mortars containing ground seashells yielded adequate strength, lower drying shrinkage and lower thermal conductivity compared to the conventional cement, indicating a good perspective for their utilization as SCMs in masonry mortar formulations.

In recent years, the scientific community has studied the incorporation of biomass ashes in cement-based mortar and concrete as SCMs, while the recent trend indicates a high interest in using these materials as alkaline activators. Raw materials with a strong alkalinity are generally used as activators, hence biomass ash that is rich in potassium can act as one environmental-friendly alternative. The results are promising and mostly demonstrate the viability of using biomass ashes in the activation of coal fly ash (FA) and granulated blast furnace slag (GBFS) and the reduction in the consumption of commercial chemical reagents for alkali-activated materials (AAM) preparation [2],[4],[8],[17].

Nevertheless, the common concern with regards to the suitability of biomass ashes used as cement substitutes is the uniform long-term quality and, consequently, long-term durability of the produced cement-based composites. Therefore, the overall durability-related properties of such composites are still to be experimentally verified, documented and discussed at large.

2.2 Review on the application of ceramic waste powder in masonry mortars

There are two possibilities of utilization of ceramics waste in mortars or concrete, like a fine aggregate for partial or total substitution of natural aggregate, and as a pozzolanic material for partial replacement of cement or as active mineral addition for lime mortars. The use of ceramic waste as an aggregate in lime mortar has been known long ago, and that type of masonry mortar is called "Surkhi". However, the studies on the application of ceramic waste as pozzolanic materials in mortars are limited in comparison to concrete.

Various ceramic wastes may become a significant part of cement-based composites due to stability and high resistance to biological, chemical, and physical degradation [18]. Also, it is an inexpensive, abundant, and environmentally friendly material. As it is rich in aluminosilicates, ceramics are the appropriate supplements for cement materials that can improve the mechanical strength and durability performance of mortars and concretes. It is essential to emphasize that ceramic waste may be used in the construction industry without extensive prior preparation.

The powdery fraction of ceramic waste, according to some authors could be used as a cement substitute and enhance the composites' performance owing to its pozzolanic properties.

The literature review revealed that there is a lack of research related to the use of ceramic powder as a substitute for cement in masonry mortars.

Pereira et al. [19] examined the possibility of reusing ceramic waste from bricks and tiles of red-clay ceramic industry as partial cement replacement in mortar. An increase in total porosity and a strength reduction with the higher cement replacement level were observed. However, with up to the 20% replacement, compressive strengths obtained at 90 days are equal to or higher than those obtained with a reference mix. It is concluded, that the degree of hydraulicity of the mortar is dependent on powder fineness and bricks firing temperatures.

Based on the review on utilization of ceramic waste as a cement substitute, conducted by Alsaif [20], it is noticed that the majority of properties in fresh and hardened mixtures (whether it is mortar or concrete), in particular workability and compressive strength, are degraded with ceramic waste powder addition at 20%. The durability properties including acid resistance, chloride ion ingress, rapid chloride permeability, electrical resistivity, corrosion and water absorption are nevertheless improved. Generally, cement substitution by ceramic powder is not extremely effective, as improvement appears to be poor, up to 20%, hence the author suggests combined cement and aggregate substitution in order to promote more sustainable performance and saving natural resources.

The literature review revealed that ceramic waste powder can be successfully used with some other waste materials such as FA and GBFS to obtain alkaline activated mortars which are more efficient, produce less CO_2, reduce costs and consume lower fuel than Ordinary Portland cement (OPC) mortars [21]-[22]. Shah et al. [21] studied the bond strength between the alkali activated mortars - AAM (based on ceramic powder, fly ash and slag) as the repair materials and normal concrete, exposed to aggressive environments. Replacement of the slag by the ceramic powder showed remarkable effect to reduce the loss in the bond strength between the AAMs and concrete substrate exposed to elevated temperatures up 900°C, but displayed the lower performance when exposed to the freeze/thaw and wet/dry cycles.

The use of biomass ashes and ceramic powder in the production of masonry mortar has been scarcely studied so far. The aim of the above-mentioned scientific project is to analyze the possibility of the application of locally available waste materials, originating from agriculture and ceramic industry in Serbia, in masonry mortars. For this purpose, an experimental study comprising a characterization of collected materials, as a first step in the project, was carried out.

3 Availability of selected waste materials in Vojvodina

3.1 Availability of biomass ashes

Availability of harvest residues ashes in Autonomous Province of Vojvodina (APV) has been investigated within the realization of the project IPA Interreg ECO Build in the period 2017-2020. At the time, eleven companies were found to use harvest residues as an energy source for obtaining heat energy [23]. In 2022, most of these companies have continued to utilize this renewable energy source (RES) and generate of biomass ashes. A brief overview of the available types and quantities of generated biomass ashes in AP Vojvodina is presented in Table 1. Based on the collected information, the majority of the generated waste is disposed of in controlled landfills and some companies spend considerable resources on the transportation and landfilling of the ashes.

Ashes from two major producers: Soya Protein and Almex Ipok were collected in order to carry out their characterization.

3.2 Availability of ceramic powder

So far, we have collected data from three factories that produce ceramic products for construction purposes, located in the AP Vojvodina region. A brief overview of the types of ceramic waste available and the amount generated during the annual production is shown in Table 2. A small part of the ceramic waste generated is used for sports fields, road filling and gardening, while the rest is disposed of.

4 Characterization of harves residues ashes and ceramic powders

Characterization of selected waste materials, originating from agriculture and ceramic industry in APV was conducted in accordance with the European standard for siliceous fly ash.

Table 1. Available quantities of biomass ashes in AP Vojvodina

Company	Biomass type	Temperature of combustion	Types of biomass ashes	Produced quantities of ash per year (tons)
Mitrosrem Sremska Mitrovica	soya straw	600-650°C	1. ash from boiler furnace 2. ash from multiciklon 3. fly biomass ash	15
Soya Protein Bečej	wheat straw, soya straw and husk silo waste, sunflower husk	700-900°C	1. ash from boiler furnace 2. ash from multiciklon 3. fly biomass ash	1100
Hipol Odžaci	agro pellets of soya straw, wood pellets	800-1000°C	1. ash from boiler furnace 2. ash from multiciklon 3. fly biomass ash	700
Almex-IPOK Zrenjanin	cob corn, soya straw	700-900°C	1. ash from boiler furnace 2. ash from multiciklon 3. fly biomass ash	1100
KNOT-AUTOFLEX Bečej	wheat straw, soya straw	unknown	1. ash from boiler furnace	60
Fishery Lovćenac	soya straw	unknown	1. ash from boiler furnace 2. ash from multiciklon	9
Victoria Oil Šid	sunflower husk	700-1000°C	1. ash from boiler furnace 2. ash from multiciklon	720
Sava Kovačević Vrbas	cob corn	500°C	1. ash from boiler furnace	30
PTK Panonija Mecker farm	wheat straw, soya straw	500°C	1. ash from boiler furnace	60
Total				**≈ 4000 tons**

Table 2. Available quantities of ceramic waste in some factory of ceramic products in AP Vojvodina

Company	Type of ceramic products	Temperature of combustion	Produced quantities of ceramic waste per year (tons)
AD Polet IGK, NEXE Novi Bečej	roof tiles	cca 1020°C	3600
Ciglana Stražilovo (NEXE, Sremski Karlovci)	masonry block, ceiling block	cca 880°C	1500
WIENERBERGER doo Kanjiža,	roof tiles	1040-1070°C	1000

4.1 Materials and Methods

4.1.1 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

For experimental investigation of chemical and physical properties and pozzolanic activity, the following materials were collected and tested:

- Mixed wheat straw, sunflower husk, and silo waste (BA1), „Soya-protein“ Bečej,
- Mixed cob corn and soya straw ash (BA2), „IPOK“ Zrenjanin,
- Ceramic masonry blocks waste (CP1), „NEXE-Stražilovo“ Petrovaradin,
- Ceramic roofing tiles waste (CP2), „NEXE-Polet“ Novi Bečej,
- Ceramic roofing tiles waste (CP3), „Wienerberger doo“ Kanjiža.

The harvest residues ashes were roughly sieved, through a 4mm sieve, to separate unburnt straw and other large impurities. In order to obtain a material with a satisfactory fineness (equal to or higher than cement), both harvest residues ashes and ceramic waste were ground in a laboratory ball mill for 6h.

4.1.2 Methods

The chemical composition of collected materials was determined using energy dispersive X-ray fluorescence spectrometer (EDXRF 2000 Oxford instruments) according to SPRS EN 196-2:2015 [24] and ISO 29581-2:2010 [25]. The representative samples were pulverized in a laboratory vibratory mill prior to the testing.

The particle size distributions were determined by the laser diffraction method by using a Malvern Mastersizer 2000 particle size analyzer that can analyze particles between 0.01 and 2000µm. The Malvern Mastersizer 2000 records the light pattern scattered from a field of particles at different angles. The recorded intensity at a certain angle is the sum of the intensity of light scattered from the surface of the particles and the intensity of the secondary scattered light because of refraction while passing through the particle, and this is important for particles smaller than 50µm. Applied Mie light scattering theory assumes that particles are spheres, and thus, the results obtained for particle diameters specifically correspond to equivalent sphere diameters. The measurements were performed with an automated dry dispersion unit Scirocco 2000.

The specific surface area was determined according to the Blaine air permeability method given in SRPS EN 196-6:2019 [26], which is widely used for the fineness determination of hydraulic cement. The test is based on the principle of resistance to airflow through a partially compacted sample of powder material.

Initial and final setting time, as well as soundness, were determined in accordance with SRPS EN 196-3:2017 [27]. The method is used for assessing whether the abovementioned physical properties of an SCM material are in conformity with the requirements given in SRPS EN 450-1:2014 [28].

The pozzolanic activity was tested on samples prepared according to the procedure given in SRPS B.C1.018:2015 [29]. 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 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 SRPS EN 450-1:2014 [28]. The preparation of specimens and determination of the compressive strength were carried out in accordance with SRPS EN 196-1:2017 [30].

4.2 Chemical composition

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

The content of oxides SiO_2, Al_2O_3, and Fe_2O_3 has the greatest significance for the potential pozzolanic activity of cementitious materials. Obtained chemical composition of all ceramic powders indicates the relatively high participation of major oxides, satisfying the criterion given in [28] (>70%). Ceramic powders are characterized by low alkali content, whereas the total amount of alkalis (Na_2O+0.658 K_2O) doesn't exceed the limiting 5%, hence the possibility of alkali-silica reaction (ASR) is minimized.

Although both types of biomass ashes have lower amounts of important oxides (below 70%), BA2 is characterized by considerably higher silica content, which should influence its pozzolanic activity. Table 3 shows that the alkali content (Na_2O+0.658 K_2O) of BA1 and BA2 is 15.19% and 8.62%, respectively. The increase in the alkali content of the binder increases the probability of alkali-aggregate reactions; hence this mechanism should be experimentally verified.

4.3 The particle size distribution

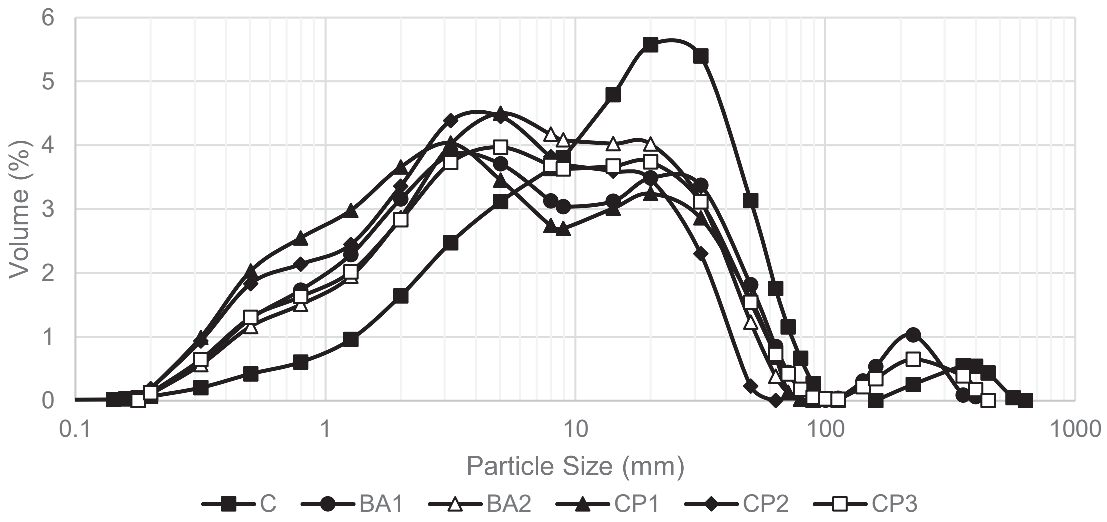
The results were recorded as particle volume percentages and presented as cumulative curves in Figure 1.

The particle size distribution shows that all tested waste materials include finer particles than cement, as a result of the effective grinding procedure and, consequently, the increase in specific surface area of particles. Size frequency distribution (presented as a volume percentage) indicates that all tested waste materials are mostly uniform in particle size.

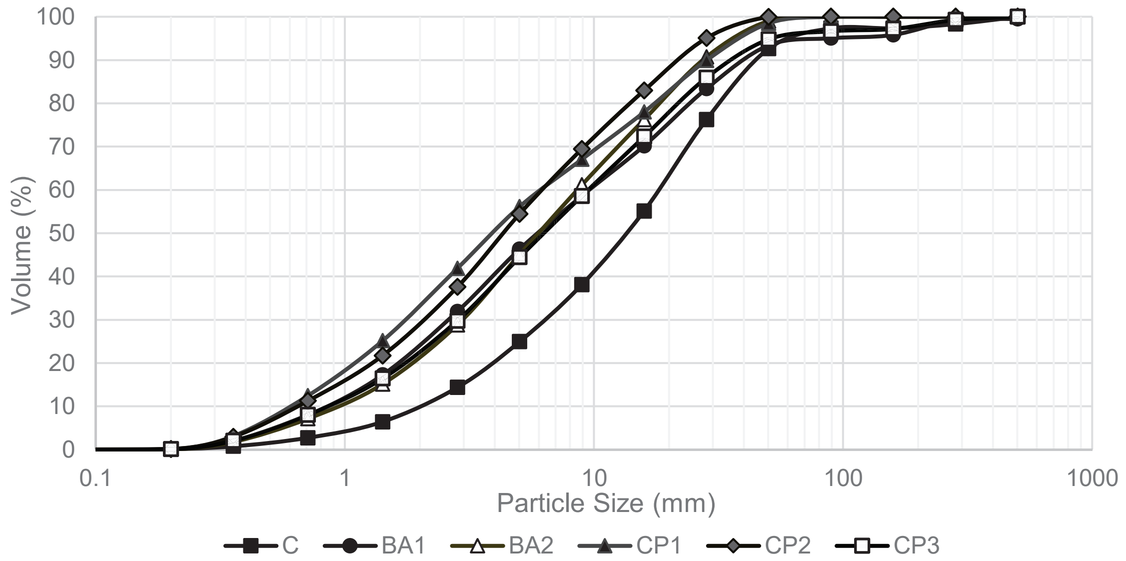
Table 4 lists the values of d10 (median particle diameters corresponding to 10% of the cumulative passing by volume), d50 (median particle diameter corresponding to 50% of the cumulative passing by volume), and d90 (median particle diameter corresponding to 90% of the cumulative passing by volume) for all tested binder samples.

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	SO_3	P_2O_5	SiO_2+ Al_2O_3+ Fe_2O_3
OPC	17.34	4.53	20.64	50.26	1.93	0.20	0.59	3.06	0.00	/
BA1	20.21	1.83	1.74	13.42	8.30	0.00	23.09	2.88	7.78	23.78
BA2	45.76	5.92	3.37	14.08	8.30	0.00	13.10	1.26	2.81	55.05
CP1	60.86	16.38	6.81	9.38	3.89	0.77	2.39	0.80	0.14	84.05
CP2	61.88	16.46	7.40	4.90	3.66	1.63	2.81	0.08	0.20	85.74
CP3	59.03	15.81	6.64	5.65	4.20	1.50	2.50	0.07	0.16	81.48



a)



b)

Figure 1. Particle size distribution of cement and tested waste materials: a) volume percentage and b) cumulative curve

Table 4. Median particle diameters of binder samples

	d_{10} (μm)	d_{50} (μm)	d_{90} (μm)
OPC	2.305	15.254	49.698
BA1	0.956	6.622	43.963
BA2	1.054	6.684	30.720
CP1	0.683	4.342	31.845
CP2	0.727	4.842	24.338
CP3	0.958	7.025	39.145

The median diameter of particles, d90, for OPC corresponds to 49.7μm and is the highest value among tested SCM. As for the other characteristic passing, differences between OPC and other tested materials in particle diameters are more pronounced. Ceramic powders CP1 and CP2 are characterized by the lowest median diameters of particles for characteristic passing, which indicates that these are finer powders, hence it is expected that these SCMs contribute to the filler effect.

4.4 Density and specific surface area

Physical properties: density and specific surface area are shown in Table 5.

Table 5. Density and specific surface area of OPC, biomass ashes and ceramic powders

Material	Density (g/cm^3)	Specific surface area by Blaine (cm^2/g)
OPC	3.10	4000
BA1	2.36	8120
BA2	2.44	8090
CP1	2.62	13815
CP2	2.61	11064
CP3	2.59	6200

Specific surface area is an indicator of material fineness, which influences material's reactivity. Finer particles of cementitious materials can a) have great impacts on cement hydration, including the physical and chemical effects; b) lead to an increase in the effective water-cement ratio; c) serve as nucleation cores for hydration; d) improve a pozzolanic effect and e) dilute cement particles in paste, which provides relatively more space for the formation of hydrates from cement particles, leading to the filler (packing) effect.

After grinding in a laboratory ball mill for 6 h, the specific surface area (Blaine) of all tested cementitious materials significantly exceeded the reference cement value of 4000 cm^2/g.

The ceramic powder obtained by grinding of ceramic waste from masonry elements (CP1 and CP2) displayed the highest fineness value, while the roofing tiles powder (CP3) showed the lowest specific surface area, probably due to the higher temperature of ceramic tiles production and, consequently greater material hardness.

Both types of biomass ashes are characterized by the same fineness, whereas the specific surface area is twice the size of the reference cement value.

4.5 Setting time

The initial setting time, as specified in [28], shall not be more than twice as long as the initial setting time of a 100% reference cement paste (by mass) - criterion 1. The initial setting time, should not be shorter than 60 minutes - criterion 2 (for cement type CEM I 42,5R). All types of tested materials fulfill these criteria. The results are given in Table 6.

The overall effect of ceramic powders and biomass ash BA2 on the setting time of cement paste was proven to retard the setting time, as expected when it comes to SCMs. Both initial and final setting times were extended in relation to the setting time of OPC. In addition, BA2 has a considerably increased final setting time, which may be caused by the presence of unburnt organic substances - straw remains.

The presence of BA1 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.

4.6 Soundness

According to the criteria given in [28], the soundness shall not be greater than 10 mm. As all types of tested materials showed negligible expansion, up to 1 mm, the criteria are fulfilled. The results are given in Table 7.

4.7 Pozzolanic activity

Pozzolanic material class was determined based on 7-day compressive (f_c) and flexural (f_f) strength of standard mortar prisms. Results revealing the pozzolanic properties are given in Figure 2.

Table 6. Initial and final setting time

	The Initial Setting Time (Minutes)	The Final Setting Time (Minutes)	Criterion 1	Criterion 2
OPC	140	190	Yes	/
BA1	25	45	Yes	No
BA2	165	285	Yes	Yes
CP1	160	220	Yes	Yes
CP2	160	210	Yes	Yes
CP3	165	225	Yes	Yes

Table 7. Soundness

	Expansion (mm)	Criterion
OPC	0.8	Yes
BA1	0.6	Yes
BA2	1.0	Yes
CP1	0.6	Yes
CP2	0.5	Yes
CP3	0.5	Yes

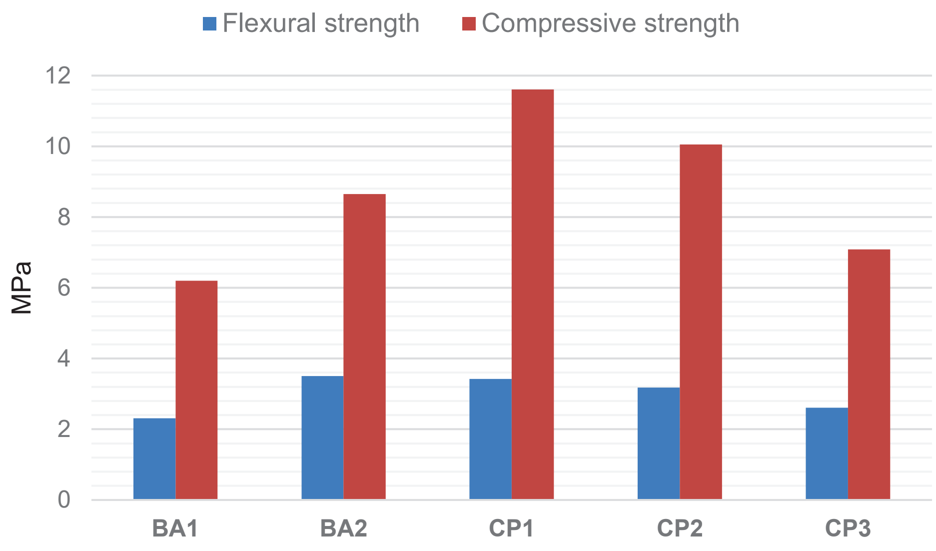


Figure 2. Pozzolanic activity of tested waste materials

Testing of pozzolanic properties showed that both types of biomass ashes, as well as CP3 have pozzolanic activity of Class 5, while ceramic powders CP1 and CP2 have pozzolanic activity of Class 10.

Higher silica content, as well as the increased level of fineness, contributed to the high pozzolanic activity of ceramic powders CP2 and CP3.

4.8 Activity index

Results of the testing activity index (AI) are presented in Figure 3. According to the criteria given in [28], the activity index at 28 days and at 90 days shall not be less than 75% and 85%, respectively.

The data clearly shows that BA2 and all ceramic waste powders met requirements after 28 and 90 days, achieving values greater than 75% and 85%, respectively. It can be observed that BA2 and CP1 displayed a high early strength index as well (equal or greater compressive strength concerning the reference cement sample), thanks to the simultaneous effect of the pozzolanic activity and the dilution effect. The Index of activity after 90days of these four waste materials reached at least 100%. The notable increase in compressive strength after 90 days, indicated the existence of pozzolanic reaction in these SCM.

As a final we emphasize four of the five tested SCM fulfill both criteria for AI. Only BA1 exhibited both activity index values below the required limits. Although the value obtained for this ash after 90 days shows certain delayed pozzolanic activity, the results in total are not satisfactory due to a lack of reactive silica

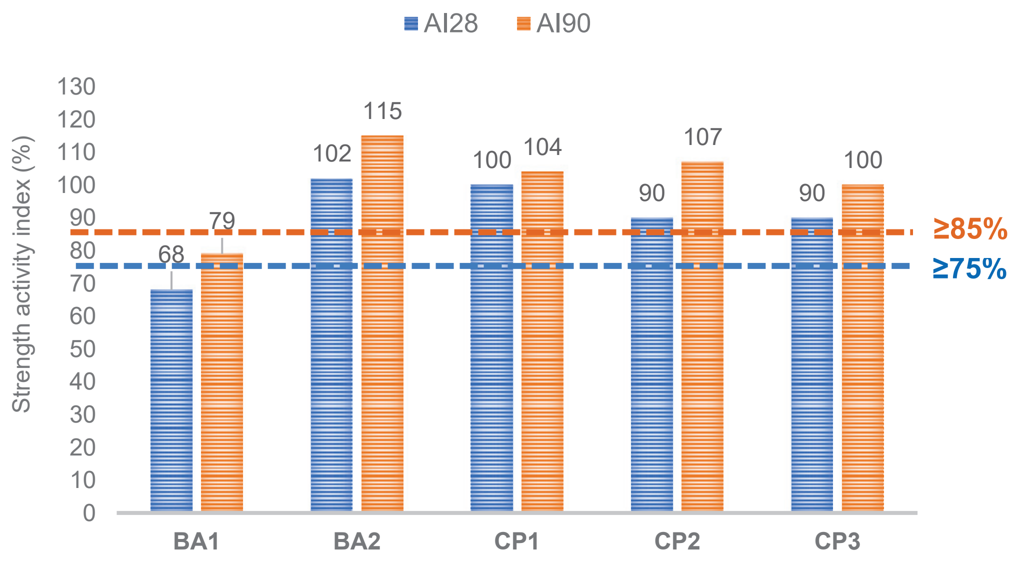


Figure 3. Activity index of tested waste materials

5 Catalogue of harvest residues ashes in AP Vojvodina

The obtained results of listed properties of collected waste materials are presented through the catalogue, given below.

5.1 SCM type BA1 - Mixture of wheat straw, sunflower husk and silo waste ash: basic properties

Mixture of wheat straw, sunflower husk and silo waste ash, before sieving and grinding

Mixture of wheat straw, sunflower husk and silo waste ash, after sieving and grinding

Material origin	Soja Protein, Bečej
Basic data on the material	Bottom ash, roughly sieved through a 4mm sieve
Available amount per year	1100 tons
Disposal	Deported to city landfills
SiO_2 + Al_2O_3 + Fe_2O_3 (%)	23.78%
Specific gravity	2360 kg/m^3
Blaine fineness	8120 cm^2/g
Soundness	Satisfactory
Setting time	Initial: 25' FInal: 45'
The pozzolanic activity	Class 5
The activity index	I_{28} = 68% I_{90} = 79%

5.2 SCM type BA2 - Mixed wheat and soya straw ash: basic properties and possible application

Mixture of cob corn and soya straw, before sieving and grinding

Mixture of cob corn and soya straw, after sieving and grinding

Material origin	Almex IPOK, Zrenjanin
Basic data on the material	Bottom ash, roughly sieved through a 4mm sieve
Available amount per year	1100 tons
Disposal	Deported to city landfills
SiO_2 + Al_2O_3 + Fe_2O_3 (%)	55.05%
Specific gravity	2440 kg/m^3
Blaine fineness	8350 cm^2/g
Soundness	Satisfactory
Setting time	Initial: 165' FInal: 285'
The pozzolanic activity	Class 5
The activity index	I_{28} = 102% I_{90} = 115%

5.3 SCM type CP1 - Ceramic masonry blocks powder

Ceramic masonry blocks waste, before grinding

Ceramic masonry blocks powder, after grinding

Material origin	Nexe Stražilovo, Sremski Karlovci
Basic data on the material	Ceramic masonry elements for walls and ceillings (waste)
Available amount per year	1500 tons
Disposal	Landfilled in the surroundings of the factory
$SiO_2 + Al_2O_3 + Fe_2O_3$ *(%)*	84.05%
Specific gravity	2620 kg/m^3
Blaine fineness	13815 cm^2/g
Soundness	Satisfactory
Setting time	Initial: 160' FInal: 220'
The pozzolanic activity	Class 10
The activity index	I_{28} = 100% I_{90} = 104%

5.4 SCM type CP2 - Ceramic roofing tiles powder

Ceramic roofing tiles waste, before grinding

Ceramic roofing tiles powder, after grinding

Material origin	Polet Nexe, Novi Bečej
Basic data on the material	Ceramic roofing tiles waste
Available amount per year	3600 tons
Disposal	Landfilled in the surroundings of the factory
$SiO_2 + Al_2O_3 + Fe_2O_3$ *(%)*	85.74%
Specific gravity	2607 kg/m^3
Blaine fineness	11065 cm^2/g
Soundness	Satisfactory
Setting time	Initial: 130' FInal: 190'
The pozzolanic activity	Class 10
The activity index	I_{28} = 90% I_{90} = 107%

5.5 SCM type CP3 - Ceramic roofing slipware tiles powder

Ceramic roofing slipware tiles waste, before grinding

Ceramic roofing slipware tiles powder, after grinding

Material origin	Wienerberger, Kanjiža
Basic data on the material	Ceramic roofing tiles waste, covered with slipware
Available amount per year	1000 tons
Disposal	Landfilled in the surroundings of the factory
$SiO_2 + Al_2O_3 + Fe_2O_3$ (%)	81.48%
Specific gravity	2587 kg/m^3
Blaine fineness	6200 cm^2/g
Soundness	Satisfactory
Setting time	Initial: 165' FInal: 225'
The pozzolanic activity	Class 5
The activity index	I_{28} = 90% I_{90} = 100%

6 Conclusions and further research

This research aimed to highlight the importance of using waste materials, originating from agriculture and brick manufacture industry to create more sustainable building materials. The following conclusions can be drawn from the experimental study:

- The justification of research into the possibility of applying industrial and agricultural waste materials for the production of masonry and plastering mortar is highlighted
- The feasibility evaluation of using ceramic powder and harvest residues ashes as pozzolanic materials were determined by their physical, chemical, and mechanical characterization tests;
- The chemical characterization of BA2, CP1, CP2, and CP3 indicates their potential of using as mineral additives due to the presence of reactive silica in the chemical composition;
- From the physical tests (Blaine specific surface area test and particle size distribution) all SCMs showed a high level of fineness, as a result of grinding of materials in a laboratory ball mill. Even more, ceramic waste powders CP1 and CP2 may additionally act as filler, improving the packing density of the composite;
- Testing of pozzolanic properties showed that both types of biomass ashes, as well as CP1, have pozzolanic activity of Class 5, while ceramic powders CP2 and CP3 have pozzolanic activity of Class 10; confirming the pozzolanic effect of SCMs on portlandite consumption;
- Regarding activity index, BA2 and all ceramic waste powders (CP1, CP2, and CP3) met requirements after 28 and 90 days, achieving values greater than 75% and 85%, respectively. BA1 exhibited activity index values below the required limits. It was also observed that all mortars incorporating SCMs, apart from BA1, showed equal or better performance in relation to the reference cement mortar. This can be attributed to both pozzolanic reaction and filler effect.

The results indicate a promising light for the sustainable application of industrial and agricultural by-products as a partial replacement for cement to tackle waste disposal problems, to reduce the greenhouse gases impact and to reduce the negative effects on environment. With the satisfactory reactive silica content and high degree of fineness, ceramic waste powder and harvest residues ashes could potentially substitute significant portions of conventional binders in durable composite formulations. Hence, future research should focus on the effect of incorporation of tested materials at different cement replacement levels in cement-based mortars and evaluation of obtained physical, chemical, mechanical and durability properties under optimized conditions.

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