PROPERTIES AND POSSIBLE APPLICATION OF HARVEST RESIDUES ASH IN CEMENT BASED COMPOSITES

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Summary: *Utilization of less-expensive and locally available by-products as a mineral admixture in cement-based composites brings multiple benefits to the costs, the technical properties of concrete as well as to the environment. The aim of this research was to investigate the possibility of application of locally available waste materials: harvest residues biomass ashes as SCMs. The study included analysis of the availability of these ashes in AP Vojvodina, testing of their chemical composition and pozzolanic activity. Based on the obtained results, recommendations for potential application of biomass ashes in cement-based composites, as SCMs, are provided.*

Keywords: *Harvest residues, ash, SCM, pozzolanic activity*

1. INTRODUCTION

The process of manufacturing the Ordinary Portland Cement (OPC) is associated with adverse consequences on the environment, as it consumes considerable quantities of natural resources and releases approximately 8% of global antropoghenic CO_2 emission to the atmosphere. Researchers all around the globe are exploring the possibilities to replace some proportion of OPC with alternative materials from other industries that once were considered as waste and sent to the landfills. Known as Supplementary Cementitious Materials (SCMs), by-products, such as: fly ash, silica fume, slag, rice husk ash are already being used as cement replacement materials at a growing pace in the construction sector.

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This results in reducing the potential environmental burden and, in some cases, enhancing the mechanical and durability properties of cement-based materials.

Currently, concrete is dominantely used building material with more than 10 billion tons produced annually in modern industrial society [1]. During cement and concrete production, in addition to CO_2 emission, several other issues, such as the use of energy, natural resources (primarely aggregate) consumption, C&D waste, contribute to the common environmental impact that OPC concrete is not friendly enough or appropriate with the needs of sustainable development.

In this light, the concept of 3Rs (Reduce, Reuse and Recycle) is becoming more and more employed in the construction and manufacturing sectors [2]. The potential of Serbia in the RES is about 6 million tons per year. By utilization of this potential, the use of fossil fuels can be significantly reduced. Biomass has the greatest potential which presents 64% of all RES, and is about 3.3 million tons per year. In the structure of planned primary energy production in Serbia for 2014, RES participated with 1,819 million tons per year, which accounted for about 17% of domestic primary energy production. In this, the highest share had solid biomass - 58% [3]. Greatest potential of biomass in Serbia lies in the agricultural residue and wood biomass, a total of about 2.7 million tons (1.7 million tons in the remains of agricultural production and about 1 million tons in wood biomass) [4].

In the process of harvest residues combustion, the significant quantities of biomass ash are generated. These ashes are not further utilised, but disposed of on the landfills and companies which are involved in this process pay considerable high price for their storage, transportation and disposal. The aim of this research was to investigate the possibility of application of locally available waste materials: harvest residues biomass ashes as SCMs. The study included analysis of the availability of these ashes in AP Vojvodina, testing chemical composition and pozzolanic activity, mainly influenced by their chemical composition.

2. AVAILABILITY OF HARVEST RESIDUES ASHES IN AP VOJVODINA

In recent years, companies all across AP Vojvodina are shifting from traditional energy sources (primarily fossil fuels) to locally available renewable sources, such as biomass. In addition to the economic aspects of this form of sustainability, biomass is considered as carbon neutral source; hence its utilization as an energy source will not contribute to net emissions of CO_2 into the atmosphere, as opposed to fossil-based products.

It is estimated that the total potential of biomass from agriculture in Serbia is about 13 million tons per year. More than half of the resources lie in corn biomass, more than a quarter in straw of cereals, and the rest of about 15% in harvest residues of sunflower, soybean, oilseed rape or residual the remains of orchards and vineyards. It is estimated that about half of harvest residues at large agricultural farms can be used for energy purposes, while only about 20% harvest residues, generated on relatively small private farms, can be used for energy purposes.

Based on the physical, chemical and morphological properties, it is reported that harvest residues ash, generated by combustion of agricultural biomass, has a noticeable potential for use as a pozzolanic mineral admixture and/or as an activator/binder in cement-based materials: mortar and concrete [5]. Compared to well-known pozzolanic materials, such as fly ash, where significant research has already taken place and high use are already reported in several countries, commercial utilization of harvest residues ash is not so widely reported.

Based on the research, most of the harvest residues ashes produced are either disposed of in landfill or recycled on agricultural fields or forest, while the companies which combust biomass as an energy source pay considerable price for the transportation and landfilling of these ashes. A brief overview of the available types and quantities of generated biomass ashes in AP Vojvodina is presented in Table 1.

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	wheat straw 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 silo waste melasa	700-900°C	1. ash from boiler furnace 2. ash from multiciklon 3. fly biomass ash	**1100**
The Veterinary Institute Subotica	agro pellets of wheat straw and soya straw	450-550°C	1. ash from boiler furnace 2. ash from multiciklon 3. fly biomass ash	240
Hipol Odžaci	agro pellets of soya straw	800-1000°C	1. ash from boiler furnace 2. ash from multiciklon 3. fly biomass ash	700
Victoria Starch Zrenjanin	agro pellets of wheat straw and soya straw	unknown	1. ash from boiler furnace	9
Almex-IPOK Zrenjanin	agro pellets of wheat straw and soya straw sunflower husk	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	**≈ 4.200 tons**

Harvest residues ashes can potentially be used as mineral additive and/or aggregate in cement based composites, depending on the chemical composition and pozzolanic activity of these ashes. Experimental research of biomass ashes as potentially building materials should result in guidelines relevant for its further use of biomass ashes as a mineral additive in cement-based composites. To achieve this goal, further investigations will include determination of biomass ash influence on basic properties of mortars and concretes. First step in this process is to analyse chemical composition of available biomass ashes and it influence on their pozzolanic activity.

3. CHEMICAL COMPOSITION OF HARVEST RESIDUES ASHES

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

- Wheat straw ash (WSA), “Mitrosrem” Sremska Mitrovica,
- Wheat and soya straw ash (WSSA), „Soya-protein“ Bečej,
- Soya straw ash (SSA), „HIPOL“ Odžaci,
- Oil rapeseed ash (ORA), „Knot-Autoflex“ Bečej,
- Silo waste ash (SWA), „Victoria Oil“ Šid,
- Sunflower husk ash (SHA), „Soya-protein“ Bečej,
- Wheat straw and sunflower husk ash (WSSHA), „Soya-protein“ Bečej,
- Cob corn ash (CCA), „Sava Kovačević“ Bečej.

The chemical compositions of OPC and biomass ashes are given in Table 2. The chemical compositions was determined in accordance with SRPS EN 196-2 [6]. Obtained chemical composition of pure wheat straw ash points out relatively high total content of SiO_2 (~70%). All the other biomass ashes with combination of WSA are characterized with moderate silica content. Soya straw, oil rapeseed and cob corn ashes have lower silica content which should result in poorer pozzolanic activity of these materials. Sunflower husk ash has SiO_2 in traces; hence it cannot be used as SCM.

Table 2. Chemical composition of OPC and biomass ashes

Material (%)	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Na_2O	K_2O	SO_3	P_2O_5	LOI
Cement	21.25	5.55	25.3	61.6	2.37	0.25	0.72	3,75	-	1.77
WSA	**69.13**	1.12	0.73	5.78	2.50	0.11	13.03	0.20	1.72	5.18
WSSA	**56.36**	2.03	1.53	7.13	3.54	0.20	20.02	0.18	3.72	4.85
SSA	**32.62**	4.58	1.46	15.78	8.33	0.85	20.96	0.47	3.72	10.73
SWA	**43.66**	5.41	2.06	15.89	5.05	0.97	14.09	0.76	4.82	6.41
ORA	**32.37**	6.32	2.45	14.00	2.91	0.89	17.85	3.78	1.44	17.61
SHA	**5.34**	1.19	1.03	12.96	9.94	0.68	44.76	9.71	-	12.64
WSSHA	**44.12**	1.99	1.93	10.94	4.91	0.26	16.24	0.45	5.43	13.05
CCA	**18,31**	0,25	1,59	3,45	2,29	0,00	32,36	0,52	8,92	20,59

For potential use of biomass ashes as SCMs, total content of SiO_2, Al_2O_3 and Fe_2O_3 is of the greatest importance. According to EN450-1 [7], total sum of these oxydes should exceed 70%. Results are shown in Figure 1.

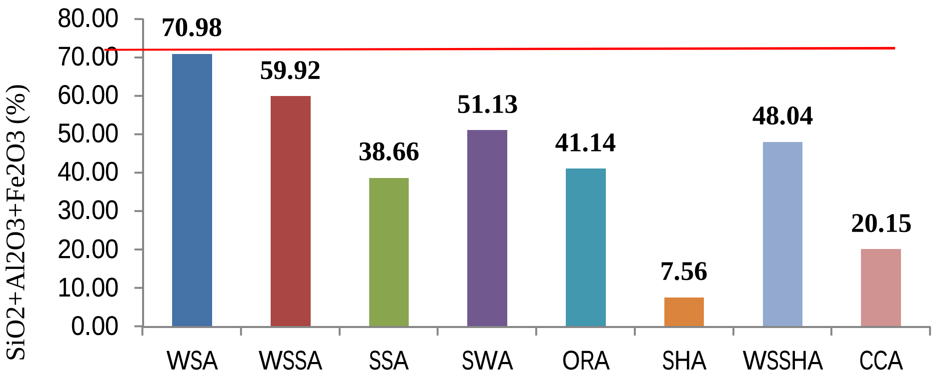

Figure 1. Total content of SiO_2, Al_2O_3 and Fe_2O_3 in biomass ashes

Results indicate that only WSA satisfies the criterion. As the content of wheat straw ash decreases, silica content decreases along. Total content of important oxides of all biomass ashes with the exception of SHA is in the range of 40-70%. Thus, these materials could be used as active mineral additives up to the certain cement replacement levels in cement based composites.

It should be noted that all biomass ashes have relatively high alkali content, especially SHA. In alkali-silica reaction (ASR), aggregates containing reactive silica could react with these alkalis in concrete to form a gel that swells and induces expansive pressure to damage concrete. Although research has shown that most of the utilized aggregates in Serbia are non-reactive, ASR in cement based composites containing biomass ashes should be verified.

4. POZZOLANIC ACTIVITY OF HARVEST RESIDUES ASHES

The pozzolanic activity has been studied on specimens prepared according to the procedure given in SRPS B.C1.017-2001 [8]. The class of pozzolanic material was determined based on 7 day compressive (f_p) and flexural (f_{zs}) strength of standard mortar prisms [9]. Mortars were prepared with biomass ash, slaked lime and standard sand, (Figure 18), with following mass proportions: m_{sl}:m_{bash}:m_{qs}=1:2:9 and water/binder ratio 0,6 (where: m_{sl} – mass of slaked lime; m_{bash} – mass of biomass ash; m_{ss} – mas of CEN standard sand). After compacting (Figure 19), specimens were hermetically packed and cured 24h on 20^0C, then 5 days on 55^0C. After cooling of specimens in next 24h up to 20^0C, compressive and flexural strength were tested.

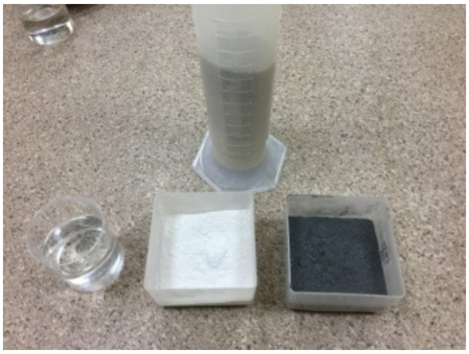

Figure 18. Component materials for testing of pozzolanic activity

Figure 19. Standard mortar prisms for testing of pozzolanic activity

Results of tested pozzolanic properties of collected biomass ashes are given in Table 3.

Table 3. Pozzolanic activity of tested biomass ashes

Ash	Biomass type	Pozzolanic activity **CLASS**	Potential cement substitution level (%)
WSA	100% wheat straw	10	50%
WSSA	mixed wheat straw and soya straw	5	25%
SSA	soya straw	/	10%
SWA	silo waste	5	25%
ORA	oil rapeseed	/	10%
SHA	sunflower husk	/	/
WSSHA	mixed wheat straw and sunflower husk	5	25%
CCA	cob corn	/	10%

By analysing obtained results, it can be seen that biomass ash, produced in Mitrosrem by combustion of wheat straw, has pozzolanic activity of Class 10. Biomass ashes, generated from the combination of harvest residues in which wheat straw in included, (WSSA, SWA, WSSHA) have pozzolanic activity of Class 5. As amount of wheat straw decreases, the class of pozzolanic activity decreases, as well. Biomass ashes SSA, ORA, SHA and CCA exhibited low mechanical properties and did not satisfy requirements for neither pozzolanic activity class.

It was also noted that prisms prepared with SHA were friable (no hardening occurred) and could not be tested. This can be attributed to the chemical composition of this type of biomass ash: low silica content and high alkali content, especially K_2O - easily soluble oxide.

Based on the obtained results, recommendations for potential application of biomass ashes in cement-based composites, as SCMs, are given in Table 3, as well.

5. CONCLUSION

Based on the results of presented study, the following can be concluded:

- Available amount of biomass ashes in Vojvodina, is approximately 4200t per year. Regarding the method of ash disposal, a small amount of ash is deposited on the unregulated landfill in the company's circle, and the largest quantity of ash is disposed in containers and transported to municipal landfills.

- Harvest residues ashes can be potentially used as mineral additive and/or aggregate in cement based composites, depending on the chemical composition and pozzolanic activity of these ashes.
- Obtained chemical composition of pure wheat straw ash points out relatively high total content of SiO_2 (~70%), which resulted in high pozzolanic activity of Class 10. All the other biomass ashes with WSA are characterized with moderate silica content and satisfy pozzolanic activity of Class 5. Soya straw, oil rapeseed and cob corn ashes have lower SiO_2 content, while sunflower husk ash has SiO_2 in traces. As a result, these ashes did not satisfy requirements for neither pozzolanic activity class.
- Wheat straw ash can be used as a SCM up to the cement replacement level of 50%; ashes with the incorporation of WSA up to the level of 25%, while the remaining ashes can be used as inert materials up to the cement replacement of 10%. Sunflower husk ash cannot be used as SCM material due to its unfavourable chemical composition, where K_2O is a prevailing soluble oxide.

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СВОЈСТВА И МОГУЋА ПРИМЕНА ПЕПЕЛА ЖЕТВЕНИХ ОСТАТАКА У КОМПОЗИТИМА НА БАЗИ ЦЕМЕНТА

Резиме: *Коришћење јефтинијих и локално доступних материјала као минералних додатака у композитима на бази цемента доноси и економске и еколошке бенефите, а ови материјали могу позитивно утицати и на својства бетона. Циљ овог истраживања је анализа могућности примене локално доступних отпадних материја: пепела жетвених остатака као материјала са цементним својствима (СЦМ). Студија је обухватила анализу доступности овог пепела у АП Војводини, испитивање њиховог хемијског састава и пуцоланске активности. На основу добијених резултата дате су препоруке за потенцијалну примену пепела жетвених остатака у композитима на бази цемента.*

Кључне речи: *Жетвени остаци, пепео, СЦМ, пуцоланска активност*