AVAILABILITY OF ALTERNATIVE MATERIALS WITH CEMENTITIOUS PROPERTIES IN SERBIA

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Summary: *The most important environmental concerns in the use of concrete in civil engineering practise are the emission of* CO_2 *during the manufacturing of cement and the consumption of non-renewable resources as raw materials. If an alternative material can substitute at least a portion of the cement, but that does not contribute additional emission to the atmosphere and/or conserves natural resources, and possesses cementitious (binder) properties, then the environmental impact of the concrete industry can be reduced. Based on this premise, SCMs are increasingly being investigated and used worldwide in the production of cement-based composites. This paper provides a review of different alternative materials, available in Serbia, that can be, under certain conditions, used as a binder and replace a part of cement in the concrete industry.*

Keywords: *Biomass ash, fly ash, blast furnace slag, zeolite, emission*

1. INTRODUCTION

PC concrete is the most widely used material for construction of infrastructure on a global basis; and is primarily composed of mined materials which include: limestone, sand and clay that are heated in a kiln to be processed for use. The manufacture of PC consumes a great deal of energy and results in a release of carbon dioxide; it was estimated that production of PC is responsible for approximately 5% of global CO_2 emissions. With a worldwide production of over four billion metric tons of cement in 2014, the replacement of PC with municipal and industrial by-products has the potential to significantly reduce negative impacts of construction (such as climate change) on the global environment [1].
Solid industrial by-products, such as siliceous and aluminous materials, produced during various thermal treatments (fly ash, biomass ash, silica fume, slags, etc.), as well as some

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natural pozzolanic materials (volcanic tuffs, diatomaceous earth, zeolite, etc.), may be characterized as supplementary cementitious materials (SCMs) as they exhibit binder properties.
Activity of SCMs is mainly based on the fact that they possess significant contents of active constituents, principally active silica, that combine with the calcium hydroxide (CH), produced from Portland cement hydration, and form hydration products with binding properties –such as calcium silicate hydrates (CSH) to which the strengthening of cement is attributed [2].
SCMs are increasingly being used worldwide in the cement and concrete industry due to technical, economical and environmental reasons. This paper provides a review of alternative materials in Serbia, that can be utilized as SCM, with the emphasis on their physical and chemical characteristics, which could define the possibility of their application as a binder (cement replacement) in standard cement-based composites. These materials include: fly ash, biomass ash, blast furnace slag and zeolite.

2. A REVIEW OF AVAILABLE SCM MATERIALS IN SERBIA

2.1. Biomass ash

The average yearly quantity of the biomass wastes in Vojvodina amounts to about 9 millions tons barely in the agriculture, and the same potential on the level of Serbia is estimated to almost 13 million tons. The large sector in Serbia utilizes only about 15% of straw, while the individual one utilizes about 50% of straw and 20% of cornstalks. Main problems with respect to the profitable usage of straw and other post-harvest residues are high expenses of their collection (collecting, balling or combustion), transportation from production to the usage cites, as well as their handling and storaging [3].
Biomass as the agricultural by-product is the renewable source of feed and a raw material for the obtaining of energy. The balled biomass can be used in the industrial fireboxes by the direct combustion or by the gasification procedure (Figure 1). However, for broader using of biomass as the energent in the individual furnaces, the biomass has to be still more energetically concentrated, i.e. compressed and brought in the forms that are more convenient for transportation and handling. This is the goal of briquetting and pelletizing of biomass (Figure 2).
As the combustion residue remains only biomass ash, containing mineral substances. Utilization of biomass ash (if containing large amounts of silica in amorphous form) in concrete production can be an alternative solution to the incorporation of the traditionally used supplementary cementitious materials (SCMs). Malešev et al. [4] tested chemical properites of various biomass ashes (Table 1), obtained in Vojvodina and their pozzolanic abilities. According to the chemical composition, mixed wheat and soya straw ash and wheat straw ash contain large amount of silica (over 50%). Testing of

Figure 1 – Rolled biomass bales for combustion in Mitrosrem, Sremska Mitrovica

Figure 2 – Pelletizing of biomass in Victoria Starch, Zrenjanin

pozzolanic properties showed that these ashes have pozzolanic activity of class 5, hence they can be further utilized as SCMs in cement based composites.

Table 1 – Chemical composition of tested biomass ashes [4]

Ash	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Na_2O	K_2O	LOI
Mixed wheat and soya straw ash	53.21	4.00	2.69	13.45	1.90	0.41	12.05	10.19
Wheat straw ash	51.93	0.19	1.39	14.28	2.07	0.43	18.43	9.27
Soya straw ash	13.80	1.76	1.45	47.53	7.76	0.07	5.23	18.60
Sunflower husk chimney ash	1.04	0.29	0.79	33.77	8.15	0.48	28.15	21.73
Sunflower husk furnace ash	1.77	0.43	1.25	30.63	11.18	0.32	27.76	19.68

2.2. Fly ash

Fly ash is a mineral by-product formed by combustion of finely crushed coal in the air flow. It is made of fine particles, mainly of silica glass, and these particles are formed using electrostatic separator from gaseous combustion products. Because they are produced and hardened in flue gases, particles of fly ash are characterized by small volume, they are spherical in shape, and measure 0.074 to 0.005 mm in diameter. They are easily movable and can therefore cause a number of problems to the environment. In Europe, fly ash is most commonly used for the production of cement and concrete, for the construction of embankments, for soil replacement, etc [5]. Šešlija et al. [6] tested the mineral and chemical composition of the ash, originating from thermal power plants Nikoa Tesla A (PPNT A), Nikola Tesla B (PPNT B), Kostolac A (PPKO A) and

Kostolac B (PPKO B). Two thermal analysis samples were taken from each thermal power plant. After the research was carried out, it was concluded that the ash by chemical composition belongs to the group of acidic ash, i.e., class F. The chemical composition of the analyzed fly ash is shown in Table 2.

Table 2 – Chemical composition of fly ash [6]

Power plants	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Na_2O	K_2O	LOI
PPNT A1	51.64	21.87	5.54	1.05	3.01	0.57	1.05	6.43
PPNT A2	51.43	22.01	6.03	1.16	2.83	0.43	1.16	7.20
PPNT B1	55.38	22.57	5.46	8.30	2.87	0.45	1.12	2.58
PPNT B2	51.88	22.49	6.61	10.44	3.28	0.58	1.23	2.11
PPKO A1	51.96	23.22	9.82	7.80	2.62	0.44	0.77	2.21
PPKO A2	44.55	20.80	11.23	11.71	2.73	0.50	0.69	4.18
PPKO B1	51.41	22.13	9.98	8.05	2.50	0.48	0.76	3.37
PPKO B2	46.04	21.67	11.44	11.10	2.64	0.51	0.67	1.98

Pozzolanic properties of the materials have not been tested for all types of ash. The only test was done for ash from PPNT A, on both samples, in paper [7]. The paper shows the pozzolanic properties performed according to the standard SRPS B.C1.018, and it has been proved that the ash belongs to class 5. Based on the shown properties, these ashes can be used as a cement replacement or as a mineral additive.

2.3. Blast furnace slag

The slag is a mineral mixture, consisting of materials that have been burnt in the combustion process and other parts of the unburned material which, through the grid, collapses and is rapidly cooled and extinguished in water. Compared with fly ash, slag is a much larger fraction because it moves within the range of 0.425 to 0.075mm.
The mass of the slag is variable and depends on the type of sample, or thermal power plant. Different characteristics depend on the type of coal used in combustion. The chemical composition of slag for PPNT A, PPNT B, PPKO A and PPKO B are shown in Table 3 [6]. According to the chemical composition, the slag samples belong to the same group (acidic ash) as the fly ash, i.e., group F.

Table 3 – Chemical composition of slag [6]

Power plants	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Na_2O	K_2O	LOI
PPNT A	51.06	20.50	6.14	7.27	2.70	0.53	1.23	9.88
PPNT B	52.12	20.97	6.30	5.51	2.30	0.51	1.02	10.50
PPKO A	32.98	12.24	7.56	5.53	1.83	0.48	0.69	36.02
PPKO B	48.91	21.54	11.32	8.87	2.43	0.49	0.74	4.47

The testing of the pozzolanic properties of the slag was carried out. Before testing, the slag was grinded. The results of the study show that slags for all four thermal power plants belong to class 10, that is, the slag has pozzolanic properties. If the slag is used as a supplement to cement, as a substitute, it firstly must be grinded.

2.4. Zeolite

Natural zeolites are microporous materials with crystalline structure. By chemical composition, they represent hydrated aluminosilicate minerals of alkali and alkaline earth metal cations [8]. Due to their honeycomb-like structure with an open cavities [9], natural zeolites have large internal and external surface areas which represent the base of their high pozzolanic reactivity [10]. The application of zeolite as SCM improves some aspects of concrete durability [9].
Worldwide, zeolite is used as cement blending material and mineral admixture. Only in China about 30 million tons of natural zeolite is used per year as a cement blending material [9].
In Serbia, there are high quality zeolite deposits such as Igroš (Figure 3), Zlatokop, Jablanica 1, Toponioca, Beočin (Figure 4), medium to low quality zeolite deposits (Duge Njive, Mečkovac, Katalenac) and zeolite occurrences (Slanci, Kotešica, Tabanović, Lužnica) [11]. Their basic parameters are shown in Table 4. All commercially interesting zeolite deposits are of high quality with zeolite content of 70%, and are related to Miocene volcanic activity [11].

Figure 3 – Deposit Igroš near Brus [12]

Figure 4 – Deposit Općište near Beočin [13]

Zeolite from Serbian deposits are needle-like shapes and are presented in zeolite tuffs in form of very small crystals (0.1-10 µm) in mineral paragenesis with quartz, feldspar, clay minerals, etc. [14].

Table 4 – Zeolite deposits in Serbia – Basic parameters [11]

Deposit	Exploitation method	Depth of zeolite, (m)	Zeolite thickness, (m)	Resources, (Mt)	Reserves, (Mt)	CEC, (meq/100g)
Bečin	Open pit	2-28	14,2	2	0.26 0.15	157 108
Igroš	Open pit	5-20	1,5	0.1	0.05	145
Jablanica 1	Open pit	0-15	18,5	2.2	0.20	168
Toponica	Underground	2-25	2,4	0.5	0.50	140
Zlatokop	Underground	20-30	2	1.3	0.67	164
Katalenac	Open pit	At surface	110	3.4		70
Duge njive	Open pit	At surface	>50	1.1		
Mečkovac	Open pit	At surface	38	1.0		

The quantity of reactive SiO_2 and Al_2O_3 in those zeolites as well as their chemical composition, Si/Al ratio and CEC are shown in Table 5. According to Radosavljević Mihajlović et al. [14] Zlatokop, Toponica and Igroš zeolite deposits are mostly consisted of Ca-clinoptilolite, while Beočin and Slanci are of Ca-heulandite. According to Križak et al [15] in Jablanica 1 deposit clinoptilolite is a dominant mineral.

Table 5- Chemical composition of natural zeolites from Serbian deposits

Deposit	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	K_2O	Na_2O	Si/Al	CEC, (meq/100g)
Bečin [14]	56.0	14.04	1.85	6.20	2.64	2.32	0.52	3.93	166
Igroš [14]	61.62	12.05	2.02	5.44	1.37	0.82	1.00	4.42	123
Jablanica 1 [15]	63.58	13.39	2.58	3.56	2.33	2.70	0.91		168
Toponica [14]	67.50	12.00	1.00	4.91	0.34	1.01	1.13	4.40	140
Zlatokop [14]	64.60	12.40	1.84	4.02	0.80	0.82	0.91	4.71	142
Slanci [14]	64.94	14.08	1.72	4.72	0.78	0.63	0.26	3.91	130

Radeka et al [16] tested puzzolanic activity of natural zeolite from Igroš deposit (previously sieved through a 0,125mm sieve), and it was found to meet criteria for Class 5 according to SRPS B.C1.018:2001, therefore it can be used as SCM in cement based composites.

3. CONCLUSION

Considering that cement industry is responsible for at least 5% of global CO_2 emissions, it is of great importance that at least a portion of the cement can be substituted with an alternative material which possesses cementitious properties, but does not contribute to additional emissions to the atmosphere. Some of those alternative materials, which are avaiable in Serbia, are biomass ash, fly ash, blast furnace slag and zeolite. Since tested soya straw ash and wheat straw ash as well as fly ash from PPNT A and zeolite from Igroš belong to class 5 of pozzolanic activity, and all mentioned slags belong to class 10, it can be concluded that these alternative materials can be used as SCMs.

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РАСПОЛОЖИВОСТ АЛТЕРНАТИВНИХ МАТЕРИЈАЛА СА ЦЕМЕНТНИМ СВОЈСТВИМА У РЕПУБЛИЦИ СРБИЈИ

Резиме: *Када је реч о примени бетона у грађевинарству, најважнија питања заштите животне средине су емисија CO_2 током производње цемента и потрошња необновљивих ресурса као сировина. Ако се алтернативним материјалом може заменити барем део цемента, а да се при томе не допринесе додатној емисији CO_2, и/или да се уштеде природни ресурси, а да такав материјал поседује цементна (везивна) својства, онда се може смањити негативан утицај бетонске индустрије на животну средину. На основу дате претпоставке, СЦМ материјали се све више истражују и користе широм света у производњи композита на бази цемента. Овај рад даје преглед различитих алтернативних материјала који су доступни у Србији, а који се под одређеним условима могу користити као везиво односно замена дела цемента у бетонској индустрији.*

Кључне речи: *Биопепео, летећи пепео, шљака из високих пећи, зеолит, емисија*