INDUSTRIAL WASTE UTILIZATION IN BUILDING MATERIAL INDUSTRY

UPOTREBA INDUSTRIJSKOG OTPADA U INDUSTRIJI GRAĐEVINSKIH MATERIJALA

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Abstract: Paper presents some aspects of industrial waste utilization, like fly ash from thermal power plants and slag from metallurgical processes, in building material industry, especially in cement and concrete production. Fly ash and metallurgical slag, which can have cementitious or pozzolanic properties, must have appropriate chemical, physical and mechanical characteristics for this utilization. Some data about fly ashes and cooper slag in Serbia are presented. Also, some Serbian and international standards which follow this utilization are presented. Beside this, grinding can be applied as technological process in the aim of better utilization of fly ash and slag.

Key words: fly ash, metallurgical slag, characterization, standards, cement, concrete, grinding

1. INTRODUCTION

The four largest producers of electricity in Serbia, thermal power plants Kostolac A and Kostolac B in Kostolac and Nikola Tesla A and Nikola Tesla B in

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Apstrakt: U radu su prikazani neki aspekti primene industrijskog otpada, kao što je leteći pepeo termoelektrana i šljaka iz metalurških procesa, u industriji građevinskih materijala, posebno u proizvodnji cementa i betona. Leteći pepeo i metalurska šljaka, koji mogu imati pucolanska svojstva, moraju imati odgovarajuće hemijske, fizičke i mehaničke karakteristike za ovu upotrebu. Prikazani su i neki podaci o letećim pepelima i metalurskoj šljaci u Srbiji. Takođe, prikazani su i neki srpski i međunarodni standardi koji prate ovu upotrebu. Pored toga, mlevenje može da se primeni kao tehnološki proces u cilju boljeg korišćenja letećeg pepela i šljake.

Ključne reči: leteći pepeo, metalurska šljaka, karakterizacija, standardi, cement, beton, mlevenje

1. INTRODUCTION

The four largest producers of electricity in Serbia, thermal power plants Kostolac A and Kostolac B in Kostolac and Nikola Tesla A and Nikola Tesla B in
Obrenovac, utilize lignite as the primary energetic fuel. Total installed capacity of thermal power plants in Kostolac and Obrenovac are 1006 MW and 2888 MW, respectively.

Based on several years of practical experience, it is established that 1.4 kg - 1.5 kg of coal is necessary to combust for production of 1 kWh of electricity (Brzaković, 2002).

As the coal burns, it produces emissions (gases like carbon dioxide, sulphur dioxide and nitrogen oxides) and ash. The gases, together with the lighter ash (fly ash), are vented from the boiler up the stack. Huge air filters called electrostatic precipitators remove nearly all the fly ash (also so-called electrofilter fly ash) before it is released into the atmosphere. The heavier ash (bottom ash) collects in the bottom of the boilers and is removed (http://www.centreforenergy.com).

In thermal power plants Kostolac and Nikola Tesla in Serbia about 90% of produced ashes are represented as fly ash, while max. 10% is represented as bottom ash. Fly ash has great fineness (below 0.5 mm), while the bottom ash is a granular material, much coarser than fly ash, removed from the grid of the bottom of boiler.

Thickened tailing technology for ash depositing is applied in practice few years ago in TPP Kostolac B and TPP Nikola Tesla B. Bottom ash is crushed in toothed roll crushers to 100% -5 mm, and then mixed mechanically or hydraulically with water and fly ash in solid to liquid ratio of 1:1, i.e. in 50% of solids. After that, mixture was hydraulically transported with series of centrifugal slurry pumps through pipeline in the form of thick hydromixture to open ash disposal sites. Taking into consideration the enormous annual production of fly and bottom ashes in TPP Kostolac B and TPP Nikola Tesla B (more than 1.4 million tons and 1.75 million tons, respectively), these ashes are the major polluters of the environment - land, water and air.

Beside fly ashes, large deposits of copper slag located in Serbia in Bor. Metallurgical slag from pyrometallurgical process of smelting ore and copper concentrate in Bor Copper Mine smelting plant represents a significant economic potential, as well as big ecological problem. Approximately about 16,500,000 tons of slag and 700-1000 tons of daily produced slag in Bor Copper Mine smelting are deposited in smelter slag dumps for over 100 years of ore exploitation in Bor Copper Mine (Stanojlović et al. 2008).

This paper presents some aspects of fly ash and metallurgical slag utilization, especially copper slag, in the building material industry (in cement and concrete production), with the retrospection of the standards followed this usage. Paper presents some data related to characterization of fly ashes from thermal power plants Kostolac B and Nikola Tesla B.

2. UTILIZATION OF FLY ASH AND METALLURGICAL SLAG IN BUILDING MATERIAL INDUSTRY

In 30's of the last century in the United States fly ash was added to cement in the construction of big large dams. Application of fly ash has more positive aspects, which are reflected primarily in reducing the cost of deposit, as well as protecting the environment. The most important application of ashes is in the building material industry, mining (for filling abandoned mine shafts, open pits), agriculture (for land
reclamation and fertilization), metallurgy (for production of steel and other metallurgical sintered products), water treatment (for filters), gas desulphurization (producing of aqueous suspension), for the production of oxide-aluminum and aluminum (extraction of mullite for aluminum production) (Brzaković, 2002).

Today, fly ash – the most commonly used coal combustion product – is a remarkable material that cost-effectively improves the performance of products it is added. So, fly ash is also a cost-effective resource and using fly ash makes a positive contribution to the environment (http://www.flyash.com).

Fly ash has the largest application in the production of cement, hydraulic lime, various types of concrete, lightweight sintered aggregate, brick products, in road construction. The reason of the fly ash usage is not only in the reducing of costs, but it seems in the fact that the ash, if it is used for the production of cement, for example, reduces the heat that is released during hydration of the cement, affects the consistency and strength as well as resistance to aggressive (corrosive) water. In road construction, for example, fly ash mixes with lime and represented material that is easily processed and compacted, become strong relatively fast and it has high compressive strength and slightly susceptible to erosion and the impact of frost. In mixture with lime ash can be used in road construction of embankment, the lower of carrying layers and subgrade of pavements, repairs to roadways (Brzaković, 2002).

Concrete containing fly ash is easier to work with because the tiny, glassy beads create a lubricating effect that causes concrete to flow and pump better, to fill forms more completely, and to do it all using up to 10 percent less water. Because the tiny fly ash particles fill microscopic spaces in the concrete, and because less water is required, concrete using fly ash is denser and more durable. Fly ash reacts chemically with lime that is given off by cement hydration, creating more of the glue that holds concrete together. That makes concrete containing fly ash stronger over time than concrete made only with cement (http://www.flyash.com).

The utilization of fly ash across European countries is different and is nearly based on national experience and tradition. In 2010 about 14 million tones of fly ash were utilized in the construction industry and for production purposes in underground mining. Most of this fly ash was used as concrete addition in road construction, as raw material for cement clinker production, in blended cements, in concrete blocks and for infill (that means filling of voids, mine shaft and sub-surface mine workings). In 2010, about 1.9 million tones of bottom ash were used in European countries in the construction industry. Out of this about 42% was used as fine aggregate in concrete, about 42% in road construction and filling applications and about 10% in cement production (Caldas-Vieira and Feueborn, 2013).

Because fly ash use displaces cement use, it also reduces the need for cement production – a major energy user and source of "greenhouse gas" emissions. For every ton of cement manufactured, about 6.5 million BTUs or 1904 kWh of energy are consumed. For every ton of cement manufactured, about one ton of carbon dioxide is released. Replacing that ton of cement with fly ash would save enough electricity to power the average American home for 24 days, and reduce carbon dioxide emissions equal to two months use of an automobile. Experts estimate that cement production contributes to about 7% of carbon dioxide emissions from human sources. If all the fly ash generated each year were used in producing concrete, the reduction of carbon
Dioxide released because of decreased cement production would be equivalent to eliminating 25% of the world's vehicles (http://www.flyash.com).

Beside fly ash, blast furnace slag is a nonmetallic coproduct produced in the process of production of iron, when iron ore, iron scrap and fluxes (limestone and/or dolomite) are charged into blast furnace along with coke for fuel. It consists primarily of silicates, aluminosilicates, and calcium-alumina-silicates. Different forms of slag product are produced depending on the method used to cool the molten slag. These products include air-cooled blast furnace slag, expanded or foamed slag, pelletized slag, and granulated blast furnace slag. All these slags may be used in building material industry. Air-cooled blast furnace slag (ABS) has been used as an aggregate in Portland cement concrete, asphalt concrete, concrete, asphalt and road bases. Granulated blast furnace slag (GBS) has been used as a raw material for cement production and as an aggregate and insulating material. Granulated slag has also been used as sand blasting shot material. Ground granulated blast furnace slag (GGBS) is used commercially as a supplementary cementitious material in Portland cement concrete (as a mineral admixture or component of blended cement). Beside these, pelletized blast furnace slag has been used as lightweight aggregate and for cement manufacture. Foamed slag has been used as a lightweight aggregate for Portland cement concrete (http://www.fhwa.dot.gov).

Steel making slag is produced during the conversion of hot metal to crude steel in a basic oxygen furnace of during of melting of scrap in an electric arc furnace. Basic oxygen furnace slag (BOS), electric arc furnace slag (EAF S and EAF C) and secondary metallurgical slag (SECS) are identified (http://www.euroslag.com).

The use of ferrous slag – crystalline or vitrified – instead of natural rocks such as limestone or granite not only saves the energy that may be required to mine natural aggregates, but also eliminates the negative impacts associated with mining such as effects on biodiversity or disruption of the landscape. In the case of cement manufacture, the use of granulated blast furnace slag, instead of clinker reduces the overall process CO₂-emissions as a result of fuel savings and avoidance of sintering limestone or other calcareous materials. Calculations made by the German FEnS – Institute for Building Materials Research have shown that CO₂-emissions were reduced by about 22 million tones in the cement industry (hence in the industry as a whole) in Europe in 2008, because of the use of 24 million tones of granulated blast furnace slag. The reduction is equivalent to the Kyoto objective of countries like Belgium and Netherlands together. Thus, blast furnace slag contributes positively to the sustainability of the whole European industry and in the fight against climate change (http://www.euroslag.com).

In Europe in 2010 about 25.6 million tones of blast furnace steel slag was used for cement production and concrete addition (66% from total purposes). From the total production of steel slag (about 22.3 million tones in 2010 in Europe) 6% was used for cement production and 48% for road construction (http://www.euroslag.com).

Besides slag from metallurgical process of iron, copper slag is the waste material of matte smelting and refining of copper such that each ton of copper generates approximately 2.5 tons of copper slag presents potential secondary raw material. Copper slag is one of the materials that is considered as a waste which could have a promising future in construction industry (as portland cement substitution...
and/or as aggregates. Cooper slag is widely used in the sand blasting industry, in the manufacture of abrasive tools and as abrasive media to remove rust, old coating and other impurities in dry abrasive blasting. Cooper slag can successfully replace fine aggregate in concrete (up to 75% replacement) (Chavan and Kulkarni, 2013).

3. CHARACTERIZATION OF FLY ASH AND METALLURGICAL SLAG RELEVANT TO THEIRS UTILIZATION IN BUILDING MATERIAL INDUSTRY

Depending on the type of coal and type of boiler, siliceous, silico-calcareous or calcareous fly ashes with pozzolanic and/or latent hydraulic properties are produced throughout Europe. According to chemical composition, fly ashes produced in mostly thermal power plants in Serbia belong to group of siliceous fly ashes.

Siliceous fly ashes are composed of highly aluminosilicate materials, which have a high content of active chemical SiO₂ (over 40%) and a high total content of acidic oxides (SiO₂ + Al₂O₃ + Fe₂O₃), a low content of basic oxides (CaO, MgO), they all give pozzolanic properties. Namely, these ashes must be pozzolanic active, and it's means that fly ashes (finely ground) react with hydrated lime in the presence of water giving insoluble compounds (Ca-silicates and Ca-aluminates), which gives great strengths. Beside this, fly ash must have appropriate physical properties, which are usually represented with particle size distribution, i.e. fineness. If fly ash hasn't sufficient fineness, it hasn't pozzolanic properties when mixed with water and couldn't become strong (Brzaković, 2002). Also, fly ash must have appropriate chemical and mineralogical composition, as well as physical and physical-mechanical properties. This last is usually known as bending strength and compressive strength. Properties of fly ash are important for its use in cement and concrete industry and usually it is defined with standards.

Serbian standard for pozzolanic materials in cement production (SRPS B.C1.018:2001) defines the use of fly ash in the cement industry. This standard provides a classification, technical requirements and test methods of pozzolanic materials used as additive in the cement production. Standard specifies the classification of fly ashes according to the origin (siliceous fly ash classified as artificial pozzolan, mark V) and the classification according to mechanical properties (bending and compressive strengths), in other words pozzolanic activity. Pozzolanic activity is presented with bending strength and compressive strength of mortar test specimens after 7 days of their setting in water. For the highest class of pozzolanic materials, mark 15, bending strength after 7 days must be minimum 4 MPa, while the compressive strength must be minimum 15 MPa. Standard gives the requirements for quality (the impurities, free water, particle size distribution, chemical composition, mechanical properties, radioactivity, expansion). Fly ash must have the appropriate composition, which refers to the content of reactive SiO₂ (min. 25%), reactive CaO (max. 10%), active CaO (max. 2.5%) and loss on ignition (max. 5%). In addition, fly ash must have an appropriate particle size distribution determined by sieving on a series of sieves according to SRPS ISO 565. Fly ash is classified in group 1 of pozzolanic materials, because of its size class -50 mm. Also, fly ash must have the appropriate fineness after grinding, which should be 90%- 94% -0.063 mm.
Foreign standards also define the class of pozzolanic materials and fly ashes, their chemical composition, physical, mechanical and other properties. American Standard ASTM C618 defines two classes of fly ashes for their use in concrete, class C and class F. Class F is pozzolanic fly ash normally produced from burning anthracite and bituminous coals. Class C fly ash is pozzolanic and cementitious fly ash normally produced from burning lignite or subbituminous coal. The chemical requirements in the ASTM specification for class C fly ash are: min. 50% SiO₂ + Al₂O₃ + Fe₂O₃, max. 6% loss on ignition, max. 3% moisture content, max. 5% SO₃. Physical requirements are related to fineness or max. 34% retained on 325 mesh sieve (http://www.undeerc.org).

When cement manufacturers intergrind or blend portland cement with fly ash or natural pozzolans or slag cement, the blended cement is specified under ASTM C595 (AASHTO M 240), Standard Specification for Blended Hydraulic Cements. Among these materials, type IP(X) is indicated as portland-pozzolan (P) cement. In this cement X denotes the targeted percentage of pozzolan expressed as a whole number by mass of the final blended cement. Typical replacement rates for blended cements are 15 to 25 percent (http://www.fhwa.dot.gov).

In United Kingdom pulverized fuel ash or "fly" ash is the fine ash produced in the furnaces of coal-fired power stations. BS EN 450 is a harmonized European Standard for fly ash that replaced the former British Standard BS 3892: Part 1 in January 2007. Three categories of fly ash are permitted under BS EN 450 according to LOI: category A (LOI not more than 5.0%), category B (LOI 2.0% to 7.0%) and category C (LOI 4.0% to 9.0%). There are two categories for fineness: category N (not more than 40% retained on the 45 microns sieve and a limit of +10% on the supplier’s declared mean value permitted) and category S (not more than 12% retained on the 45 microns sieve) (http://www.scotash.com).

Fly ash, beside other additives, such as tuff, slag, gypsum, can be added at different stages of the process of cement production, namely: at feed of the clinker furnace (as one of the raw materials, in addition to the marl, limestone and clay), at feed to the mill for clinker grinding (as pozzolan, slag and tuff) and at the end of the process, when fly ash can mix with cement. In addition, fly ash can be used in factories for the production of concrete, when directly mixed with all the components for the production of concrete. Fly ash is added in the part of clinker grinding process in cement factories in Serbia. In cement factory Titan in Kosjerić in Serbia fly ash is added at the feed of the mill along with tuff and/or slag in different mass ratios (max. 35% by mass of all additives).

Fly ashes from TPP Nikola Tesla B and TPP Kostolac B belong to type of siliceous fly ashes and contents more than 45% chemically active SiO₂ (44.82% - 47.46% for TPP Kostolac B and 50.57% - 61.63% for TPP Nikola Tesla B). These ashes are characterized with high content of acid oxides (SiO₂ + Al₂O₃ + Fe₂O₃) (over 75%), low content of alkaline oxides (3.02% - 8.35% CaO and 3.74% - 8.7% MgO) and a low loss on ignition (1.1% - 4.1%), which is below 5% as defined in the standard. These ashes are characterized by high fineness, where fly ash from TPP Nikola Tesla B have greater fineness than fly ash from TPP Kostolac B. Particle size distribution have shown that d₅₀ are from 0.025 mm to 0.135 mm for TPP Nikola Tesla B, and from 0.075 mm to 0.20 mm for TPP Kostolac B. But, the masses of reference size class
(-0.045 mm) is mostly below (about from 6% - 60%) the requirements according to international standards (European EN450 Fly ash or American ASTM C618 for fly ash class C) (Kostović et al. 2008).

According to Serbian standard (SRPS B.C1.011:2001) which is harmonized with European standard EN197-1:2000, fly ashes, as artificial pozzolans, and slags can be a component of 6 types of cements, including:

- Portland cement with the addition of slag; the content of slag varies from 6% to 35%; marked as PC 20S and PC 35S according to Serbian standard or CEM II/A-S and CEM II/B-S according to European standard;
- Portland cement with the addition of artificial pozzolan (fly ash); the content of fly ash varies from 6% to 35%; marked as PC 20V and PC 35V according to Serbian standard or CEM II/A-V and CEM II/B-V according to European standard;
- Portland composite cement; the content of slag and/or fly ash and/or limestone varies from 6% to 35%; marked as PC 20M and PC 35M according to Serbian standard or CEM II/A-M and CEM II/B-M according to European standard;
- Metallurgical cement; the content of slag varies from 36% to 95%; marked as M35K, M20K and M5K according to Serbian standard or CEM III/A, CEM III/B and CEM III/C according to European standard;
- Pozzolanic cement; content of artificial pozzolan (like fly ash) and natural pozzolan, varies from 11% to 55% ; marked as P35 and P55 according to Serbian standard or CEM IV/A and CEM IV/B according to European standard;
- Composite cement; content of slag and natural or artificial pozzolan varies from 18% to 50%; marked MP 30 and MP 50 according to Serbian standard or CEM V/A and CEM V/B according to European standard.

Many authors investigated the possibility of fly ash utilization in building material industry. Different investigations showed that particle size distribution and fineness are the most important parameters of fly ash for its utilization. So, ground coarse fly ash was replaced with 20% by weight the portland cement. It has been demonstrated that the fineness of fly ash, not the chemical composition, was the major factor affecting the strength activity index of ground coarse fly ash – cement mortar (Kiaititkomol et al. 2001).

The beneficial effect of grinding of fly ash, may increase utilization of this by-product in precast and ready-mix concrete industry. Incorporation of fly ash with different fineness values and ratios also decreased the expansion to harmless levels of cement mortars due to alkali/silica reaction (Aydin et al. 2010).

Increasing the fineness of fly ash increases the strength and reduces water absorption (by 15%) and, hence, grinding is an effective way to enhance the performance of fly ash received from thermal power plant (Naganathan and Linda, 2013).

According to Serbian standard for cement (SRPS B.C1.017:2001), slag is firm mass that originates as byproduct during the pig iron melting. Type of slag depends from type and chemical composition of pig iron and process after the discharge from blast furnace. Standard specifies the classification of slags according to process after the discharge from blast furnace and the classification according to mechanical properties (bending and compressive strengths). Bending strength after 7 days must be
minimum 0.5 MPa or 2 MPa, while the compressive strength must be minimum 2 MPa or 10 MPa, depending from class. Standard gives the requirements for quality (the impurities, free water, particle size distribution, chemical composition, mechanical properties, radioactivity, expansion). Slag must have minimum 66.67% CaO + MgO + SiO2, while grain size distribution varies -4 mm to +80 mm.

In Europe today exists more standards for slag using in the construction sector, beside EN 197-1 for cement, they are: EN 206 (concrete), EN 15167-1 (ground granulated blast furnace slag for use in concrete, mortar and grout Part 1: Definitions, specifications and conformity criteria, EN 14227-12 (Hydraulically bound mixtures - Specifications - Part 2: Slag bound mixtures), EN 12620 (Aggregates for concrete), EN 13139 (Aggregates for mortar), etc. (http://www.euroslag.com).

Cooper slag is iron silicate, Fe2(Si2O4), a by-product of flash smelting in copper manufacture. Flash smelting enables the iron to be removed from the copper ore by reacting with the silicates and floating on the molten copper mass as a slag. The resulting product is extremely hard and abrasive and is widely used in shot blast cleaning of products ranging from iron and steel to concrete and stone. The chemical nature of the copper slag also makes it a potential source of iron and silica in cement manufacture (http://www.bulkmaterialsinternational.net).

The chemical composition of copper slag varies with the type of furnace. The typical composition of smelting slags are: 30% - 40% Fe (as FeO, Fe3O4), 35% - 40% SiO2, up to 10% Al2O3 and CaO, respectively (Shi and Qian, 2000).

According to the available data, copper slag from Bor Copper Mine smelting have the next average chemical composition: 36.62% - 38.45% Fe, 34.04% - 34.76% SiO2, 5.066% - 5.38% Al2O3, 0.892% - 2.03% S. Beside these elements and compounds, slag contains on the average 0.747% - 0.79% Cu, 3.725 g/t - 7.57 g/t Ag and 0.4 g/t - 0.525 g/t Au. Mineralogical investigations confirmed mainly the presence of fayalite and magnetite and also the presence of bornite, chalcopyrite, pure copper, chalcocine, coveline, pyrite (Stanojlović et al. 2008, Čađenović et al. 2012).

Many autors published papers about copper slag utilisation in building material industries. When copper slag is used as a raw material for clinker production, it can act as both iron adjusting and mineralizing component and also improves the grindability of the cinker. When it is used as a cement replacement or an aggregate replacement, the cement, mortar and concrete containing different forms of copper slag have good performance in comparison with ordinary Portland cement having normal and even higher strength. Beside this, by using cooper slag as a partial replacement of cement, substantial amounts of energy required for production of cement will be saved because its use needs only grinding. (Shi et al. 2008).

Other authors established that copper slag in the range of 40% - 50% could potentially replace sand in concrete mixtures. The copper slag was ground in the laboratory into a fine powder to the required size in accordance with standard. For cement mortars, all mixtures with different copper slag proportions yielded comparable or higher compressive strength than the strength of the control mixture (Al-Jabri et al. 2011).

Also, some other authors report about the potential use of granulated copper slag as a replacement for sand in concrete mixes. The experimental investigation
showed that percentage replacement of sand by copper slag shall be up to 40% (Brindha and Nagan, 2010).

4. CONCLUSION

Utilization of fly ash and copper slag in building material industry, especially in cement and concrete industry, has more positive aspects (technological, environmental and economical).

Considering the fact that siliceous fly ashes from Serbian thermal power plants mostly have satisfactory chemical and mineralogical composition and also physical and mechanical properties as pozzolanic aditives for cement and concrete productions, but they haven't necessary fineness (according to reference size class -0.045 mm), it is still necessary that fly ashes are treated in the future. According to published papers, many investigators from other countries confirmed that the copper slag can be used in building material industry. According to this, it can be supposed that copper slag from Serbia can find the usage, but it demands investigations. Further treatment of these industrial wastes demands grinding as technological process according to standard requirements.

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