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SUSTANABLE SOLUTIONS FOR MANAGING ENVIRONMENTALLY HAZARDOUS WASTE MATERALS: REAPPLICATION OF FLY ASH

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ABSTRACT: *The disposal of the fly ash may pose a significant risk to the environment due to the possible leaching of hazardous pollutants. The only sustainable economic solution for the pollution-prevention of the environment is the reuse of fly ash in building materials. Some of building composites, in which fly ash is combined with refractory components can withstand high temperatures. In this investigation testing composites were based on fly ash mixed with high-aluminate cement. Investigated fly ashes were previously subjected to mechano-activation. The leaching behavior and potential environmental impact of hazardous elements were analyzed. Mineral phase analysis by means of XRD was accented due to the fly ash high dependence on its origin. Crystalline phases were investigated by means of DTA. Scanning electron microscopy was used in microstructure analysis. The leachability of toxic elements was within allowed range, thus investigated fly ashes can be replicated in building materials. Investigated fly ash-cement composites proved to have high physico-mechanical performances, but also good thermo-insulation characteristics. The overall results showed that application of the fly ash in building composites is sustainable solution for managing this environmentally hazardous waste material.*
KEYWORDS: *fly ash, thermo-insulation, toxic elements, reapplication, building composites*

INTRODUCTION

The building materials production is an industry branch which is not completely environmentally friendly because it is constantly depleting natural resources. At the other hand, construction industry is generating large amount of waste that needs to be properly managed in order to avoid pollution and deterioration of landscape. A mutually satisfactory solution should be found in order to create equilibrium between application of the waste material from other industrial branches and reduction of the waste material that construction industry creates. Therefore, the 'three-R' principle (reduction, reuse and recycle) has to be world-wide adopted [1, 2]. Ash from coal combustion is considered as one of the most hazardous environmental polluters. According to estimation, the annual global fly ash production was more than 600 million tons in past 10 years [3].

The generation of combustion by-products is a global problem with severe implications for the environment: elements may leach through the soil to the groundwater; ash might cause air pollution if left on open landfills, etc. EU regulations are focused on the recycling of the coal combustion fly ash and reusing it as a component of added-value products [4]. In addition to the fly ash processing and reapplication in new recycled products, there is also an environmental impact that needs to be evaluated before fly ash reapplication. Namely, there is possibility of toxic metals leaching which could pass through the soil into the ground water, especially when fly ash is used as a construction material. Fly ash may contain some elements of environmental concern, such as arsenic, barium, chromium, cadmium, lead, selenium and mercury, which can limit the potential applications [5-7]. Fly ash usually contains relatively small amounts of heavy metals, particularly volatile metals such as cadmium, zinc and lead [8].

A new possibility for fly ash application could be as raw material for high-temperature application: in thermal insulators or/and refractory material products. As such, fly ash has to adequately answer on mechanical and thermal stability criteria. One of the ways of achieving it is by applying mechanical activation (MA) procedure on fly ash. Fly ash acts as superplasticizing admixture helping the "packing" of composite structure [9]. Superplasicizing ability which leads to reduction of water content needed for optimal mixture consistency and increasing of mechanical strength is only being further enhanced by MA. Although mechanical activation is much more cost effective than application of original sized fly ash results are by far better. Important aspect of construction materials is its behavior at elevated temperatures: its thermo-insulation properties, fire resistance and finally possible refractoriness. The use of fly ash additions in building composites can affect the material behavior when subjected to elevated temperature [10]. Materials that retain a large quantity of water are more desirable for fire protection and thermal exposure. Namely, when these materials are exposed to a thermal source, part of the water evaporates and is transported from the exposed surface to the interior of the material where the water cools and condenses again. Afterwards, a liquid film forms which is displaced towards the unexposed side. Some commercial products, used as thermal insulation or passive fire protection in buildings and industrial installations, have a chemical composition and properties similar to fly ash mixtures [11].

MATERIALS AND METHODS

The fly ash used in the investigation originates from the filter systems of coal-fired power plant in Serbia - "Nikola Tesla-Tent A". The fly ash was collected directly from the filter of the power plant. Afterwards the fly ash was transported to a special closed silo for storing. Mechanical activation (MA) of the fly ash was performed by means of laboratory vibrational mechano-activator - planetary ball mill type "Retsch-PM4". 2 kg batch size was used for milling. Material to media ratio of 1:35 was maintained during milling. The fly ash samples were milled for 60 min. Maximal grain size of fly ash was reduced to 0.83 mm by MA. Calcium-aluminate cement (CAC Secar 70/71, Lafarge) was used in the investigation. The composite (labeled as CFA) contained 30 % of fly ash and 70 % of cement.

X-ray fluorescence (XRF) technique was used to conduct chemical element analysis in composites. Analysis was performed by means of XRF spectrophotometer ED 2000 - Oxford. The differential thermal analysis (DTA) of the composites was performed with a Shimadzu DTA – 50 apparatus. The sample was heated under an air atmosphere from 20 up to 1100 °C at heating rate of 10 °C/min. X-ray powder diffraction (XRD) patterns were obtained on a Philips PW-1710 automated diffractometer using a Cu tube operated at 40 kV and 30 mA. All the XRD measurements were performed at room temperature in a stationary sample holder. Potential mobility of trace elements from the composite was determined by means of the batch leaching test, procedure conducted according to Serbian Standard SRPS EN 12457 (1-4) (equivalent to EN 12457 (1-4)). The leaching test was performed at a liquid/solid ratio of 10 L/kg with a stirring time of 24 h and deionized water as the leachant.

RESULTS AND DISCUSSION

The chemical composition analysis – major and minor elements of the investigated composite CFA is presented in Table 1 and trace elements found are given in Table 2. The investigation showed that composite consists mainly of silica, alumina and calcium oxides. Application of fly ash increased SiO_2 content in the composite in comparison with starting composition of applied cement.

Table 1. Chemical analysis of the composite CFA – major and minor elements

Oxide	SiO_2	Al_2O_3	Fe_2O_3	TiO_2	CaO	TiO_2	SO_3	Na_2O	K_2O
(%)	16.08	55.30	1.91	0.16	22.93	0.92	0.17	0.35	0.345

Table 2. Chemical analysis of the composite CFA - trace elements

t.e.	Pb	Zn	Zr	Cu	Ni	Cr	Ba	Sb	Se	Sr	Co	V	W
mg/kg	22.9	23.3	12.8	6.7	16.3	64.4	33.0	0.013	1.0	61.8	16.1	45.4	2.7

Processes taking place during composite thermal treatment from 20 up to 1100°C were identified by means of DTA method (Figure 1).

The thermal treatment of fly ash normally comprises three separate "regions" that are monitored by three individual peaks. The first peak below 200 °C is attributed to the evaporation of moisture. Such peak normally corresponds to the volatilization of the water mechanically bonded in form of H_2O molecule. The second "region" occurring within the temperature range 400–700 °C incarnates polymorphic transition. Peak showing at approximately 500°C is exothermic, corresponding to the transformation of organic matter, the decomposition of $CaCO_3$ and the burning of residual coal present in the fly ash. Also, it is known that β-quartz undergoes transformation to α-quartz at 573°C, thus a weak endothermic effect that follows exothermic peak can be assigned to the presence of quartz in fly ash. The third "region" represents the beginning of the fusion of fly ash. The endothermic peak at approximately 900 °C is induced by presence of alumino-silicates.

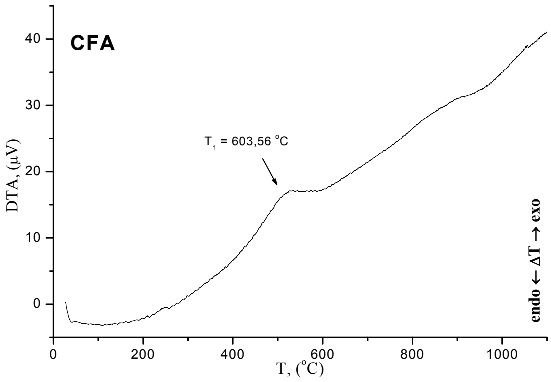

Figure 1. DTA curve of the CFA composite

Detailed interpretation of results obtained for cements is difficult because of complexity of composition of studied samples. The processes of dehydration of individual compounds overlap. In case of CAC the initial amount of water combined with cement is greater than in case of normal Portland cement and a larger amount of this water is retained at elevated temperatures, particularly up to 300ºC. Dehydration of the calcium aluminate and the alumina hydrates is near completion at 500-600ºC which is marked by endothermic peak on DTA curve. The alumina gel passes through several modifications until it is finally transformed at about 1000ºC into a-alumina. CAH_{10} can be finally dehydrated to CA but other hexagonal hydrates produce calcium oxide and $C_{12}A_7$ at temperatures from 600-1000ºC. In this temperature range, solid state reactions between calcium aluminates, alumina and lime are induced. This leads to increase in mechanical strength of CAC due to these reactions, which is represented by small endotherms on DTA curve.

Certain, but not significant quality changes in hydrating system of investigated composite are being caused by the addition of 30% of fly ash. Namely, differences in quantity and quality of hydration products cause small differences in recorded DTA curves of cement and cement-fly ash composite. The first endothermic effect on DTA is slightly shifted towards 120°C as a consequence of fly ash addition. At higher temperatures addition of fly ash does not cause significant differences in quality composition of referent cement pastes. In this way a new binders based on waste material with equally good thermal properties are obtained. Melting is not recorded at the temperature 1100ºC which attributes to good refractory characteristics of composite.

XRD diffractograms of investigated composite as result of the mineralogical analysis are given in Figure 2. Major phases normally present in CAC are: monocalcium aluminate and monocalcium dialuminate. Fly ash samples contain aluminosilicate glass, quartz and mullite. Magnetite, hematite, fluorite and anhydrite are usually present in relatively negligible amounts.

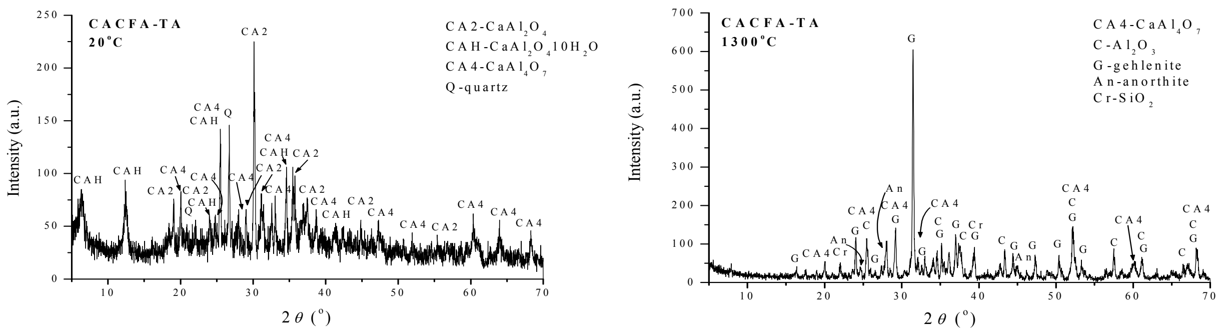

Figure 2. XRD diffractograms of CFA at temperatures 20 and 1300°C

At T = 20°C, phase composition of CFA is as follows: monocalcium aluminate, grossite ($CaAl_4O_7$), calcium aluminium decahydrate ($CaAl_2O_4 \cdot 10H_2O$), quartz and amorphous matter. The most abundant phase is $CaAl_2O_4$, $CaAl_4O_7$ is less abundant. $CaAl_2O_4 \cdot 10H_2O$ and quartz are present in small amount. Crystallinity degree of all present phases is very low. At T = 1300°C phase composition is: gehlenite, Al_2O_3 (corundum), $CaAl_4O_7$, anorthite, SiO_2 (cristobalite). The most abundant phase is gehlenite, while less present phases are $CaAl_4O_7$, corundum and anorthite. There is also possibility of presence of cristobalite but in very small amounts. Crystallinity degree is significantly higher than on the initial sample.

XRD analysis of the composite pointed out to certain phase changes occurring with increasing temperature. The XRD spectra in all cases were very complex, usually containing 40–60 peaks. The XRD patterns revealed that with an increase of sintering temperature, more complex aluminosilicates were newly formed. It is possible that simple minerals were gradually incorporated into the complex aluminosilicates when the sintering temperature increased. The original ash contains a significant amount of siliceous glass together with the crystalline phases - quartz, hematite and mullite. Sintering reduces the amount of glassy phase and quartz, and promotes formation of anorthite, mullite, hematite and cristobalite. However, the diffraction peaks of these compounds in sintered samples were broad or poorly developed and in some cases overlap. It was observed that, the peak intensities of these compounds slightly increase and their crystallinity improves with increasing temperature. The formation of rankinite, gehlenite, anorthite and cristobalite in the composites is important because they are thermally stable (i.e. have high melting point) and therefore they contribute to the thermal stability of the concrete mixtures. Although most of the peak intensities of these compounds are relatively small - when gathered and combined with peaks of refractory aggregate minerals they influence creating heat enduring material. These results are in a good agreement with the retained compressive strength after exposure to high temperatures.

The results of the leaching test performed on the composite and comparison with cement sample without addition of fly ash is given in Figure 3. It can be seen that level of toxic elements – Cu, Zn, Se and Cr is lower in the composite than in cement. Addition of fly ash increased level of Pb, Ni and As, while the level of Sb did not change.

CONCLUSIONS

The developed fly ash-cement composite seems to be a promising thermal-insulation and high temperature resistant material which can be used as bonding agent in concretes or mortars for structures and structural elements that are exposed to high temperatures. The investigation highlighted following:

1.) *Mechano-activation promoted long-term strength enhancement and improved over-all performances of investigated composites by minimizing the chemical and microstructural incompatibility of fly ashes and employing it as superplasticizer.*
2.) *Fly ash, as raw material, showed positive thermal insulation or temperature protection properties and behavior in the cementitious composite.*

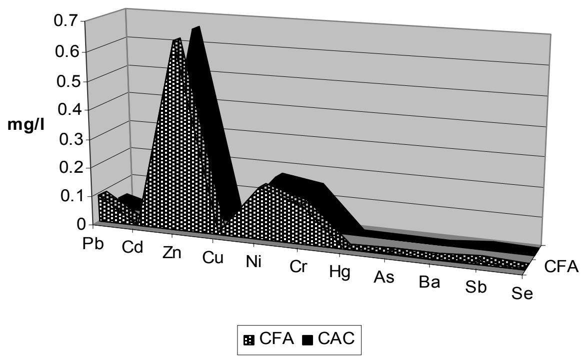

Figure 3. Results of leaching test performed on CFA and CAC samples

3.) *DTA pointed to the slight shifting of the high temperature peaks (above 900 °C) which means that mechano-activation influenced decreasing of fly ash sintering temperature. Melting of the material is not recorded at the temperature 1300 °C which attributes to good refractory characteristics investigated composite.*
4.) *XRD showed that crystallinity of the composite improved with increasing temperature. The formation of rankinite, gehlenite, anorthite and cristobalite in the composites is important because they are thermally stable and therefore they contribute to the thermal stability of the composites.*
5.) *Despite the level of toxic elements in fly ash composition it is safe to reapply this nus-product in building materials. Potentially toxic and/or leachable elements in leachate of fly ash based building composite were under upper value limit assigned by official regulative. The following potential pollutants – Pb, Cd, Zn, Cu, Ni, Cr, Hg, As, Ba, Sb and Se are proved to be of low concern when fly ash is exposed to standard environmental conditions approximated by laboratory batch water leaching test.*
6.) *As the leaching tests carried out on the composite denied possibility of potential larger scale transition of toxic elements from the building material in contact with water, this fly ash reapplication might be regarded as safe process.*

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