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CHEMICAL CHARACTERIZATION OF FLY ASH SAMPLES FOR FURTHER USE IN SEISMIC GEOTECHNICAL ENGINEERING

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A b s t r a c t: Fly ash is a product resulting from coal burning. Usually, it is deposited in landfills and some portion is used in cement industry. Worldwide there is tendency for greater use of these materials for various purposes to reduce such landfills. It has been greatly examined for use in civil engineering, especially for soil improvement in road construction. While the physico-mechanical properties are widely researched, there are less studies for the aspect of soil dynamics. The chemical properties of fly ash depend on the composition of coal, as well as the technology of burning. Therefore, the chemical composition of fly ash must be examined for its suitability for further use. This paper represents the first experimental stage consisting of chemical characterization of fly ash samples, before their further use in the second experimental stage dedicated to dynamic properties of soils improved with fly ash.

Key words: fly ash, chemical characterization, suitability, soil improvement

ХЕМИСКА КАРАКТЕРИЗАЦИЈА НА ПРИМЕРОЦИ ОД ЛЕТЕЧКА ПЕПЕЛ ЗА ПОНАТАМОШНА УПОТРЕБА ВО СЕИЗМИЧКОТО ГЕОТЕХНИЧКО ИНЖЕНЕРСТВО

А п с т р а к т: Летечка пепел е продукт од согорувањето јаглен. Вообичено се депонира, а дел се користи во цементната индустрија. Во светски рамки има тенденција за поголема употреба на вакви материјали за различни цели за да се намалат депониите со ваков материјал. Овој материјал е многу истражуван за употреба во градежништвото, особено за подобрување на почви во нискоградба. Додека физичко-механичките својства се опширно истражувани, од аспект на динамички својства на почвите има помалку студии. Хемиските својства на летечка пепел зависат од составот на јагленот, како и од технологијата на согорување. Затоа хемискиот состав на летечката пепел мора да се испита дали е соодветен за понатамошна употреба. Овој труд ја претставува првата експериментална фаза која се состои од хемиска карактеризација на примероци од летечка пепел, пред нивна понатамошна употреба во втората експериментална фаза посветена на динамичките својства на почви подобрени со летечка пепел.

Key words: летечка пепел; хемиска карактеризација; подобрување на почви

INTRODUCTION

In North Macedonia, the greatest parof the produced electricity is from the Coal Power Plants (CPP) in Bitola and Oslomej. Furthermore, the geological investigations show that in the country there are new potential coal detabtabposits. It means that more fly ash will result from the electricity production before turning to massive energy production from renewable resources such as solar energy. It can be concluded that for protection of the environment, a solution has to be found for the use of coal ash, which is produced in the country, instead of its deposition. It would mean reduction of costs for the Public Enterprise for Power Plants in North Macedonia (ESM), which otherwise must do expropriation for landfills, transportation and deposition of the coal ash.

The regions of the cities Skopje and Ohrid are the most interesting from aspect of investigation of the seismic properties of the materials and their improvement, due to dense population, composition of the natural soil and the degree of saturation. Considering that it is of high importance to detect the problems before large catastrophes occur and to find solutions for them, it is recommended to convey investigation of the potential of the fly ash as improvement material to natural soils. The Institute of Earthquake Engineering and Engineering Seismology (IZIIS) has performed numerous studies for these regions and owns significant data for the properties of the natural ground.

The results in this paper are part of PhD study which involves laboratory tests for chemical characterization of the materials in the first stage, as well as seismic tests at a later stage which will help to estimate the dynamic properties of fly ash soil improvement for seismically vulnerable structures in critical tectonic zones.

FLY ASH FROM CPP BITOLA

At the moment the fly ash in CPP Bitola originates from coal deposits "Suvodol" and "Brod Gneotino", which belong to the Pelagonian Tertiary basin. According to Andreevski (1995), based on the comparison of the qualitative parameters of the coal from the deposits "Suvodol" and "Brod Gneotino", it is almost identical. The coal from "Suvodol" is classified as lignite with variable content of resinite with vitronite, xylite, clayey component and pyrite in its petrographic composition (Rudproekt, 2009; Geohydroconsulting (2018) prepared a geological elaborate based on thorough investigations for the deposit "Brod Gneotino". The elaborate classifies the coal in the deposit as soft brown coal – lignite, with organic and inorganic origin and low heat content. It is very important to note that Andreevski (1995) mentioned the high variation of the content of fly ash from coals especially lignite and the big amount of fly ash resulting from this type of coal. The fly ash in CPP Bitola is mixed and it is not known exactly in which order it has been deposited, so it can be expected to have different properties at different locations of the landfill. The power plant Bitola burns 5-6 million tons coal per year, resulting in 1–2 million tons per year of fly ash, boiler ash and bottom ash, from which the bottom ash is being burnt twice for better use of the coal potential (Murtanovski et al., 2019). At present, only 10-15% fly ash is regularly used only by the cement industry (Vladicevska and Momirov, 2019).

Different authors (Angjusheva et al., 2019; Vladicevska and Momirov, 2019) mention the factors influencing the valorization of fly ash: physico-chemical properties, technical performances and ecological compatibility. Therefore, it is needed to characterize the fly ash from geometric, structural and chemical point of view. The fly ash is a heterogeneous material, and it must be characterized before each use (Angjusheva et al., 2019).

The sampling for the current study was done in August 2019. Two types of fly ash were sampled, old fly ash from a deposit more than 5 years old and new fly ash at the place of current deposition of the fly ash from the power plant. The sampling was done with representatives from ESM.

In order to have a detailed description of the material, chemical and mineralogical characterization of the fly ash was done at the Mining and Metallurgy Institute (IRM) in Bor, Serbia, at the end of October and the beginning of November in 2019. The testing program included the most important features for which knowledge is necessary. The main reason for these tests is to determine the following: class of the fly ash and thus its cementing ability, consisting minerals in order to know the stability of the material from aspect of further chemical weathering which affects the physico-mechanical properties of the materials, presence and quantity of any hazardous elements which might cause contamination to the environment.

CHARACTERIZATION OF FLY ASH

For detailed physical characterization of the samples, the particle size distribution is determined. The new fly ash is sandy silt with a little clay. For comparison the old fly ash is also sandy silt, but contains higher percentage of sandy fraction, lower percentage of silt, and has no clayey component.

In order to determine the potential of the fly ash to pollute the environment, tests were conveyed in order to detect the presence of toxic elements. There are different methods to register macro elements for example Cu, As, Pb, Cd and a separate method to determine the value of trace elements present such as Hg.

For both new fly ash and old fly ash duplicate samples were prepared as well as one control sample. The prepared samples were tested with Spectro Blue ICP-OES (Inductively coupled plasma – optical emission spectrometry) and Spectro Ciros Vision ICP-OES. Using these instruments, the presence of heavy metals is determined, and the results are expresses as content of oxides, which helps define the class of the new and the old fly ash.

According to the standard for definition of the fly ash class ASTM C618 (2019), both new and old fly ash fulfil the requirements for the amount of oxides (Al_2O_3, Fe_2O_3, SiO_2) for Class F (Table 1).

Further more, considering that quartz is the most present mineral and it is stable mineral, it refers to resistance of the fly ash to further weathering.

Table 1

Amount of major and minor elements present in the tested samples

Oxide (%)	New fly ash (sample #1)	Old fly ash (sample #2)
Al_2O_3	23.85	27.28
BaO	0.073	0.066
CaO	3.49	5.30
Fe_2O_3	8.14	7.28
K_2O	3.00	2.24
MgO	1.95	2.37
MnO_2	0.31	0.18
Na_2O	0.89	0.49
P_2O_5	0.20	0.16
SO_3	0.60	0.70
SiO_2	54.61	52.18
SrO	0.035	0.035
TiO_2	0.84	0.88

Based on the amount of present trace elements (Table 2), it can be said that the trace elements present in the new fly ash are within the maximal allowed limits, however the arsenic in the old fly ash (177.7 ppm) is above the allowed value of 50 ppm.

Table 2

Trace elements in the tested fly ash

Element (ppm)	New fly ash (sample #1)	Old fly ash (sample #2)
Be	7.3	6.1
V	128.8	142.0
Cr	105.9	108.7
Mn	1852.3	1044.8
Co	25.5	18.8
Ni	63.1	62.5
Cu	47.7	60.4
Zn	150.0	111.3
As	48.2	177.7
Cd	0.36	0.25
Pb	54.8	32.9
Mo	15.9	10.8
Hg	<0.1	<0.1

Trace elements were determined also for both the new and old fly ash, accompanied by a control sample. According to the obtained results, the fly ash is not toxic.

Polycyclic chlorinated biphenyls (PCBs) and Polycyclic aromatic hydrocarbons (PAHs) are toxic organic compounds, which are known to be carcinogen. Therefore, they were also subject to testing. The samples are analysed with gas chromatography-mass spectrometric detector by the method of internal standard. The instrument used for analyses is gas chromatography Agilent 7890B with mass spectrometric detector Agilent 5977A and auto-injector Agilent G4513A. The same instruments are used for analyses of both samples from solid waste and from eluates. Preparation and analysis of eluate is with the aim to determine leachability of harmful elements from ash, and to predict the possibility of negative impact of ash disposal or usage in the environment. Eluate represents extraction of certain elements from the solid samples by means of washing the sample with a solvent. To define the fluid for testing, the pH of the sample has to be determined. The measured pH is 6.89 for the new fly ash and 6.82 for the old fly ash. For leachability testing the moisture content of the samples was determined. The obtained values for the moisture content are 14.35% for the new fly ash and 9.88% for the old fly ash. This can be justified by the fact that the new fly ash contains moisture in order to be transported from the power plant to the location for deposition without producing dust in the air. The registered PCBs and PAHs in the samples are very low and negligible, which means that the fly ash does not represent a pollutant.

Loss on Ignition (LOI) is "the loss in mass of the test specimen when heated under controlled conditions of temperature, time, atmosphere, specimen mass and equipment specifications" (ASTM D7348-13, 2013). It is determined with the apparatus LECO TGA 701 which is thermogravimetric analyser. The samples do not need any complicated preparation procedure and the use of this apparatus is rather simple. However, the testing conditions need to be set in advance according to the standard ASTM D7348-13 (2013). The results are presented in Table 3.

Table 3

Results from TGA

Sample	Average LOI (%)
New fly ash	2.875
Old fly ash	6.820

The amount of Carbon and Sulfur is determined with HORIBA Scientific EMIA – 920V2 Carbon Sulfur Analyzer (Table 4)

Table 4

Percentage of present carbon and sulfur

Sample	C (%)	S (%)
New fly ash	0.643649	0.256627
	0.701711	0.282582
Old fly ash	1.087061	0.301886
	1.190053	0.276291

From the results it can be noticed that the presence of sulfur is rather low, and it is similar in the two materials. However, considering presence of coal, even though it is low the old fly ash shows higher residue of coal than the new fly ash. This refers to insufficient burning of the coal in past and lost coal potential. The difference in color of the two samples also supports this result, more exactly the old fly ash is darker in color.

For determination of the types of minerals present in the crystal phase of the material, XRD method was used. The used apparatus was Rigaku MiniFlex 600 with D/teX Ultra 250 high speed detector and copper anode x-ray tube. According to the obtained graphs which have a lack of peaks, it can be concluded that the material has low crystalinity and is highly amorphous (ures 1 and 2). Both samples have shown presence of SiO_2 – Quartz (red), Fe_2O_3 – Hematite (magenta), $NaAlSi_3O_8$ – Albite (dark blue) and $CaSO_4 \cdot 2H_2O$ Gypsum (light blue). Quartz is the only mineral that survives the coal burning. The rest of the minerals convert into other minerals depending on the burning temperature. Due to the high presence of amorphous particles, significant amount of the present minerals could not be determined with the XRD methodology.

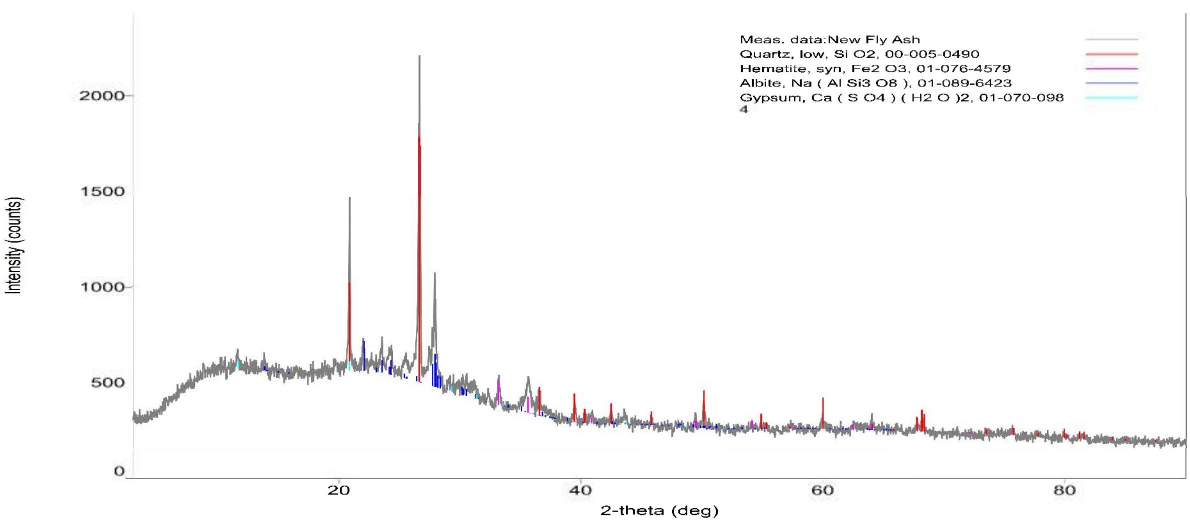

Fig. 1. Results from XRD testing of new fly ash

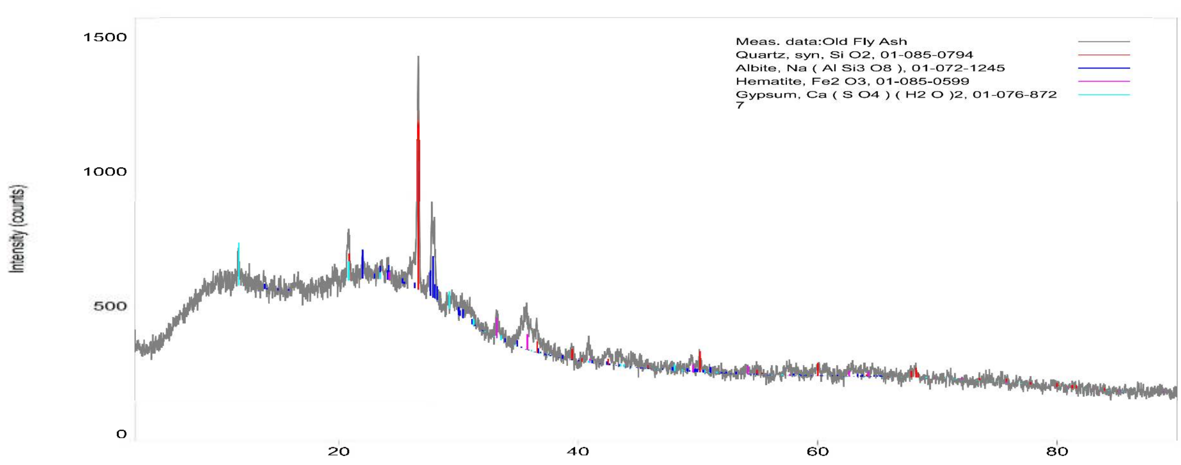

Fig. 2. Results from XRD testing of old fly ash

Scanning Electronic Microscopy (SEM) was used in parallel with Energy Dispersive Spectrometry (EDS). More exactly SEM is used for close observation of the sample particles under different magnification levels. This test is useful to discover the shape of the particles as well as the range of their size. The results from this test can be compared to the XRD results, in order to confirm if the elements discovered with EDS are constituent elements of the minerals registered with XRD. In this study the used apparatus is JEOL JSM-6610LV. It should be noted that since the samples are intentionally coated with gold, this element should be eliminated in the EDS analyses. The idea was to observe the shape of particles. At 500× magnification generally irregular flocculations of particles can be seen, as well as small part of individual particles, with irregular shape, as well as spherical and elongated particles (Figures 3 and 4). However, the SEM images for the analysed fly ash considerably differ from images for fly ash from the literature, mainly lacking majority of spherical cenospheres. As the magnification increases more regular shapes of particles can be observed, solid or hollow (Figures 5 and 6). The unburnt carbon particles are presumably angular.

From the observation of the newly prepared samples with Ultrasound dispersion, it can be concluded that there are still group of attached particles. (Figures 7 and 8) Therefore, it can be said that this method is not applicable for dispersing fly ash particles.

After testing these solid samples, new samples were prepared. Ultrasound apparatus was used with the aim to disperse the flocculation of particles and observe the particles individually. The used apparatus for this is Sonis 3 by Iskra PIO from Slovenia.

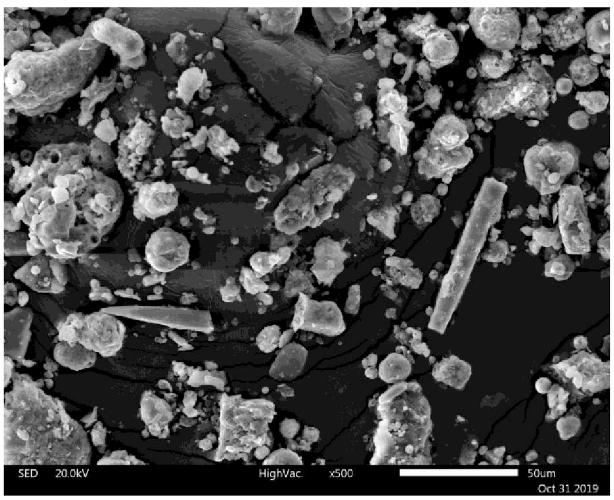

Fig. 3. New fly ash observed with SEM under 500× magnification

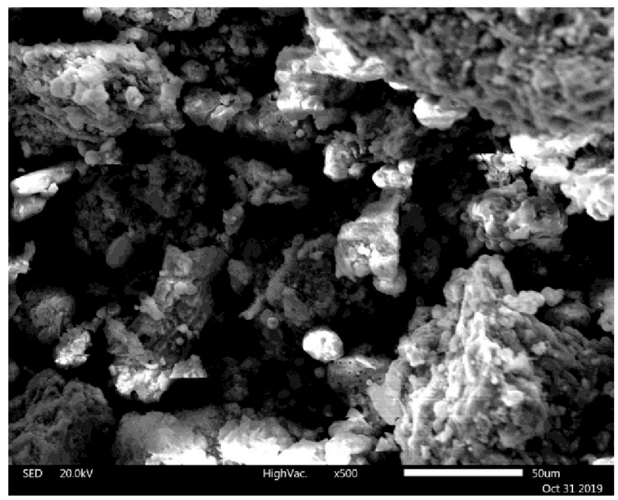

Fig. 5. Old fly ash observed with SEM under 500× magnification

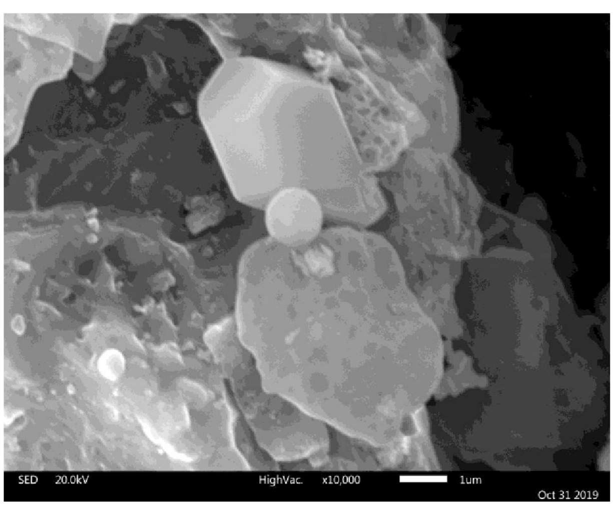

Fig. 4. New fly ash observed with SEM under 10000× magnification

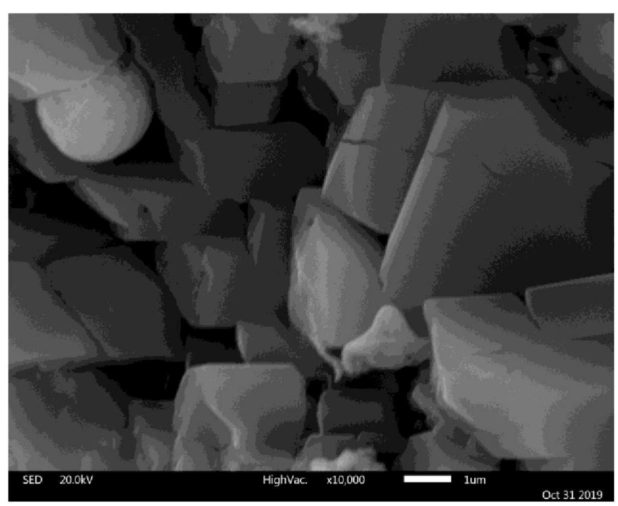

Fig. 6. Old fly ash observed with SEM under 10000× magnification

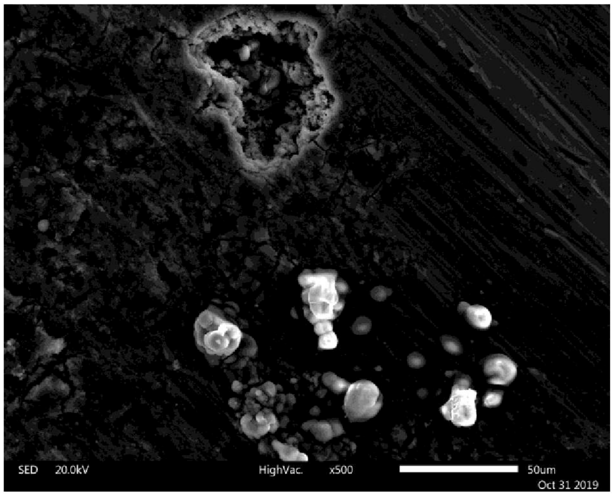

Fig. 7. New fly ash after ultrasound observed with SEM under 500× magnification

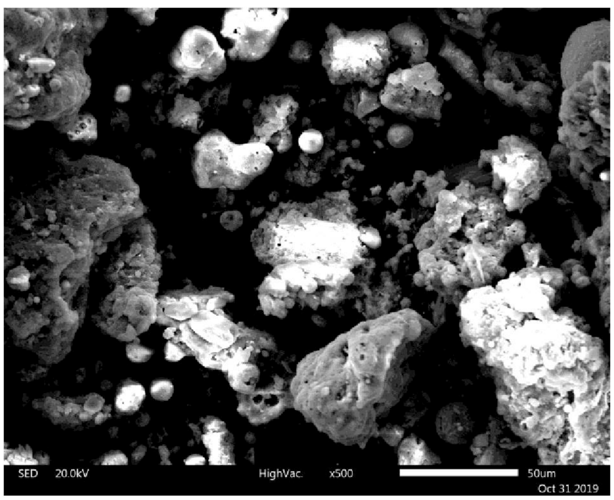

Fig. 8. Old fly ash after ultrasound observed with SEM under 500× magnification

RESULTS AND CONCLUSION

The physical properties of the fly ash refer to a fine material, that is silt. This means that the fly ash can complement the particle size distribution of the natural soil to be improved, such as Skopje Sand. By filling the voids of the sand, the fly ash can provide stability of the soil's skeleton, that is less rearrangement of the particles.

The chemical tests were done to characterize the fly ash. It should be noted that the same tests were conveyed on new and old fly ash.

According to the amount of oxides (Al_2O_3, Fe_2O_3, SiO_2) present in the fly ash, the two samples belong to Class F. However, based on the value for loss on ignition which for both Class C and Class F should be lower than 6%, the new fly ash is categorized into Class F, whereas the old fly ash is an off-specification (does not meet the requirements for Class C or Class F).

Resulting from the leaching tests, it can be concluded that the samples do not contain organic toxic elements and compounds, which means that from this aspect the fly ash is not a pollutant for the environment in which it will be used. Furthermore, based on the comparison between the amount of present trace elements in the samples and the maximal allowed limits, it can be said that the new fly ash does not contain excessive trace elements and can be further used. However, due to the value of arsenic present in the old fly ash, it is not recommended to further use this sample.

By conducting a test to determine the percentage of sulfur and carbon present in the samples, it was found out that sulfur is present with less than 1% in both samples, whereas in the old fly ash carbon is around 1% and in the new fly ash it is lower than 1%. Considering that the fly ash will be used in small quantities to improve the natural soil, it can be concluded that the fly ash will not be a risk for the concrete elements of the structures founded in such improved soils and there is no risk for expansion of the soil due to sulfur presence.

Quartz is the only mineral that survives the coal burning. The rest of the minerals convert into other minerals depending on the burning temperature. These conditions in which the minerals convert from primary to secondary are too violent, meaning that normally the materials will not be exposed to very high temperatures or pressures. As shown with multiple tests, quartz is the most present. From mineralogical aspect it is stable mineral, thus it refers to resistance of the fly ash to further weathering. This property of the material is very important for the variability of the physico-mechanical properties with time.

From the observation of the samples with SEM it was noticed that the fly ash consists mainly of groups of attached particles, called flocculations. Ultrasound dispersion was used in order to separate the particles from one another; however, it was concluded that this method is not suitable for dispersing fly ash particles.

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