INVESTIGATION OF FLY ASH HEAVY METALS CONTENT AND PHYSICO CHEMICAL PROPERTIES FROM THERMAL POWER PLANT, REPUBLIC OF MACEDONIA

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Abstract

The main intention of this research was to determinate the contents of heavy metals and physico chemical properties of coal fly ash and to find out if it is possible to reuse it in embankments, soil stabilization, flow able fill, asphalt, geopolymers and so on.

The chemical properties included in this study were: pH, Electrical conductivity, Organic carbon, and Cation exchange capacity. A physical property such as specific gravity was determined.

Four samples of coal fly ash were analysed for the presence of As, Cr, Mn, Pb, Zn, Cu, Ni and Co. We made comparison between concentration of heavy metals in coal fly ash in Macedonia and concentration of these metals in coal fly ash from Spain, Greece, India, Philippines and the UK, given in literatures. The concentration of As in the fly ash from thermal power plant MEC - Bitola in Macedonia is lower than the contents of this element in the fly ash in thermal power plants from the Philippines and the UK. The contents of other heavy metals is in the range same as theirs. Cation exchange capacity (CEC) and ammonium exchange capacity (AEC) values for fly ash from investigation thermal power plant are in the range of 0.19-0.28 meq/ g for CECs and 0.17-0.33 meq/g for AECs. Ec 0.13-0.15mmhos/cm, Organic carbon 3.17-3.85 and specific gravity 2.04-2.37g/cm^3. Every year in Macedonia 900 000 – 1 100 000 t of coal fly ash are produced. Only 10% of coal fly ash is used in cement products which are far below the global utilization rate (25%). We hope that the results of this study will be the basis for further research aimed at increasing the percentage of utilization of coal ash.

Key words: Coal; fly ash; Cation exchange capacity; Organic carbon.

1.Introduction

Fly ash is a very fine powder and tends to stay long time airborne and go long distances. It is the residue of combustion of coal that comprises a wide range of nonorganic particles, low to medium bulk density, high surface area and sandy silt to silt loam texture [Kumar, V., *et al* .(2003)]. Fly ash occurs as very fine spherical particles, having diameter in the range from few microns to 100 microns. Fly ash is ferro - aluminosilicate mineral with major elements like Si, Al and Fe together with significant amount of Ca, Mg, K, P and S, [Aswar, W. R. (2001)].

Fly ash may often contain trace amounts of some heavy toxic metals like Molybdenum, Mercury, Selenium and Cadmium etc. Some metals enriched in fly ash such as Cd, Cr, Ni, Pb and Zn other have intermediate enriched like Al, Fe, Mn, Mg and Si, [Adriano, D.C., *et al* .(1980)].

There are two types of ash generated in thermal power plants: Fly ash & Bottom ash. Fly ash is chemically reactive and finer in texture (0-100 microns). Bottom ash is the heavy and coarse fraction (>100 microns).

Coal fly ash is a complex heterogeneous material consisting of both amorphous and crystalline phases, El – [Mogazi,E., *et.al*.(1988)] [Mattigod, S., *at.al*. (1990)]

It is generally considered a ferroaluminosilicate material, with Al, Si, Fe, Ca, K and Na the predominant elements. Many trace elements in the ash are concentrated in the smaller ash particle sizes [Adriano, D.C., *et.al.* (1980)].

Coal fly ash contains all naturally occurring elements, and is substantially enriched in trace elements compared with the parent coal [Van Hook, R. I.,(1979)].

[Page, A. L., *et. al*. (1979)] have shown that among the elements generally enriched in ashes are As, B, Ca, Mo, S, Se, and Sr.

China is currently the largest producer of fly ash in the world, followed by Russia and USA. In Macedonia, at present, the major portion of fly ash produced goes for disposal in ash ponds and landfills and only a small fraction of it is utilized. Only 10% of coal fly ash is used in cement products**.** The utilization rate (10%) is far below the global utilization rate (25%) [Rai UN, *et.al*. (2004)].

Due to minute particle size and presence of potentially toxic elements like arsenic, chromium, vanadium and antimony, fly ash has been considered hazardous for living organisms. Some heavy metals leach out of the ash ponds and contaminate the soil, surface and ground water.

These heavy metals have been known to limit the survival and growth of plants and microbial population [Helfferrich, F. (1962)].

This study investigates select heavy metals content of fly ash from thermal power plant in Macedonia and compares it to the data available with coal fly ashes from other countries. It was also determined the values from CEC and AEC, Electrical conductivity, Organic carbon, Cation exchange capacity and specific gravity, given as data, are important for reuse on coal ash.

According to ASTM C 618, two major classes of fly ash are classified on the basis of their chemical composition resulting from the type of coal burned in thermal power plants. It can be classified as Class F produced from burning of bituminous and anthracite coal. It has CaO less than 10%. Class C is generally produced from burning of sub bituminous or lignite coal. It has CaO greater than 10%.

2.Materials and methods

For our reasearch we took four samples. The fly ash samples were light grey in colour and irregularly shaped.

The method used for the analysis of heavy metals was AES-ICP.

Procedure

Before treatment for digestion

We weighed 0,5 g with acurace of +/-0,0001g sample teflon vessel and add 5 mL of 68%, p.a.., HNO_3 and kept for digestion on temperature of 150^{o}C, until approximately 1mL of leaves the nitrogen acid. Then, teflon vessel are cooled to room temperature.

Digestion with HF and $HClO_4$

HF 5,0 mL and 1,5 mL perchloric acid are added to the samples in teflon vessel. The mixture is heated on electric hot plate until dense white fumes of perchloric acid appear. The content in vessel should not evaporate. When the first digestion is finished, teflon vessel is left to cool and the process is repeated twice, after which 2,5 mL nitric acid and 5 mL water is added to dissolve the residue. At the end, a clear solution is put in the flask weighed 50 mL, the flask is supplemented to the calibration line.

The procedure for determining the quantity of exchangeable cations of so-called "exchangeable sites " in fly ash include replacement of exchangeable cations in fly ash with ammonium cations, NH_4^+, and subsequent determination of their concentration [Daniels, W.L., *et.al*.(1993)].

5g sample are weighed in erlenmaer, 25mL 1M ammonium acetate are added. Then they are mixed and shacked for 1 hour on speed 500rpm on the shaker. After that, suspension is decant.

Then 20mL ethanol are added in erlenmeyer. The extract is collected in the flask 100mL and supplemented with deionized water. The concentration of exchangeable cations is determined by AES-ICP. The measured mass concentrations of exchangeable cations are transferred in milliequivalents na 1 g of sampple. From the obtained milliequivalents per gram of sample are calculated sum of the four exchaneable cations. Σ (Na^+, Ca^{2+}, Mg^{2+}, K^+) / meq g^{-1}

Specific gravity is defined as ratio of the weight of a given volume of fly ash solids at a given temperature to the weight of an equal volume of distilled water at that temperature. Specific gravity of the ash sample was determined using a specific gravity bottle. pH was determined in fly ash /water (1:2.5) suspension with a pH meter. Organic carbon was estimated by rapid dichromate oxidation method [Walkley, A and Black, C. A. (1934)].

3. Results and discussion

Table 1 Data for the chemical analysis of coal fly ash samples from termal power plant of Macedonia compared with the average chemical analysis of the fly ash samples from termal power plants in Virginia.

	1	2	3	4	Virginia
	%				
SiO_2	46.83	48.61	44.85	40.49	43.04-62.8
TiO_2	0,621	0,516	0,596	0,581	nd
Al_2O_3	25,9	24,2	23,2	24,9	22.0-28.0
CaO	6,86	8,30	11,48	13,20	0.62-3.08
MnO	0,190	0,273	0,326	0,376	nd
FeO	8,96	8,04	8,62	9,49	4.1-12.4
MgO	2,99	2,64	3,53	3,99	nd
Na_2O	1,50	1,20	1,17	1,21	nd
K_2O	2,56	2,06	1,87	1,92	nd
P_2O_5	0,343	0,405	0,410	0,388	nd
Suma	99.96	99.75	99.93	99.91	
	ppm				
Sr	471	591	777	993	nd
Ba	715	746	737	833	nd
Cr	114	93	99	101	nd
Zn	192	164	162,95	170,98	82-222
Cu	79,55	61,23	77	80	123-229
Pb	50	45	44	43	nd
Ni	65	58	68	66	nd
Co	26	22	24	25	nd
Cd	1,42	0,94	1,32	0,91	nd
As	11,03	14,14	12,43	5,75	nd

Table 1 shows that the contents of SiO_2, FeO and Al_2O_3 are approximately same with the contents of these elements in coal fly ash in Virginia, while the content of CaO is higher. Fig. 1 shows that the concentration of oxides is nearly identical in all 4 samples.

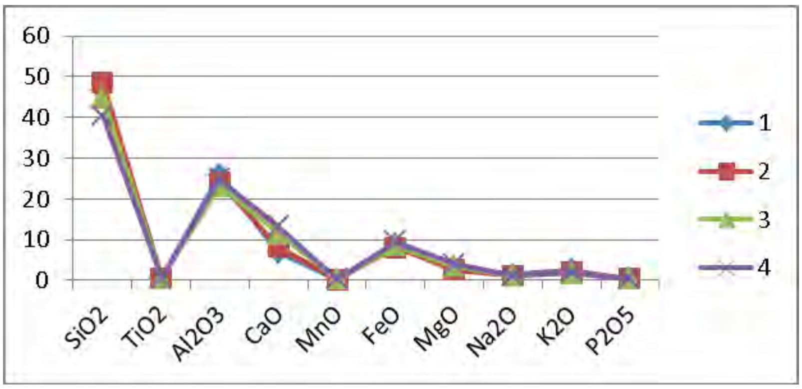

Fig.1 Distribution of oxides in fly ash samples from termal power plant of Macedonia

Trace elements in coal fly ash have been discussed extensively [Adriano (2002)] [Eary *et. Al.*(1990)] [Swaine (1990)(1997)] and their presence is an environmental concern [Hansen et al 2002]. The trace elements in coal ash need to be determined and assessed for potencial effects [Giere *et. Al.*(2003)].

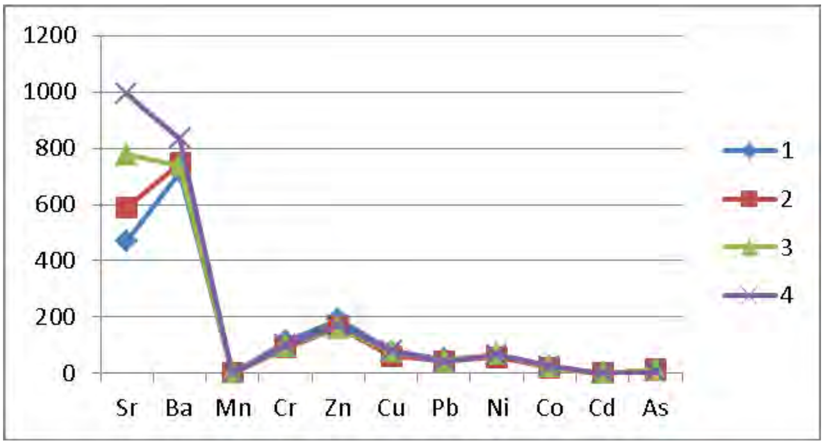

Fig.2. Distribution of trace elements in fly ash samples from termal power plant of Macedonia

Fig. 2 shows that the content of trace elements in all samples is almost identical with the exception of strontium content in which there are small deviations in the lowest value 471 ppm in sample 1 and the highest value 993 ppm in sample 4.

Table 2 . Comparison of values of heavy metals concentration obtained in this study with those values reported in the literature.(n/d indicates that no data were reported)

	Macedonia	**Spain**	**Greece**	**India**	**Philippines**	**UK**
	ppm					
Cr	93-114	134.2	110-160	145.75	6-49	nd
Zn	163-191	221.3	59.6	69.00	23-138	nd
Cu	61-80	71.8	31.8-62.8	83.63	22-34	nd
Pb	43-50	52	123-143	54.50	8-22	17-176
Ni	58-68	87.9	Nd	56.50	6-50	nd
Co	22-26	29.2	Nd	16.88	6-25	nd
Cd	0.9-1.4	Nd	Nd	Nd	<1	0.13-0.82
As	6-14	Nd	Nd	Nd	8.4 - 41.8	40-205

In table 2 is given comparison between concentration of heavy metals in coal fly ash in Macedonia and concentration of these metals in coal fly ash of Spain, Greece, India, Filipini and UK, given in literatures [Fytianos K,*et.al.* (1998)] [Lorens JF,*et.al.* (2001)], [Liao HC,*et.al.* (1999)] [Wadge A, *et.al.* (1986)].
Table 2 shows that the concentration of As in the fly ash from thermal power plant in Macedonia is lower than the contents of this element in the fly ash in thermal power plants of Philippines and UK. The contents of other heavy metals is in range same as their. This is shown graphically in fig.3.

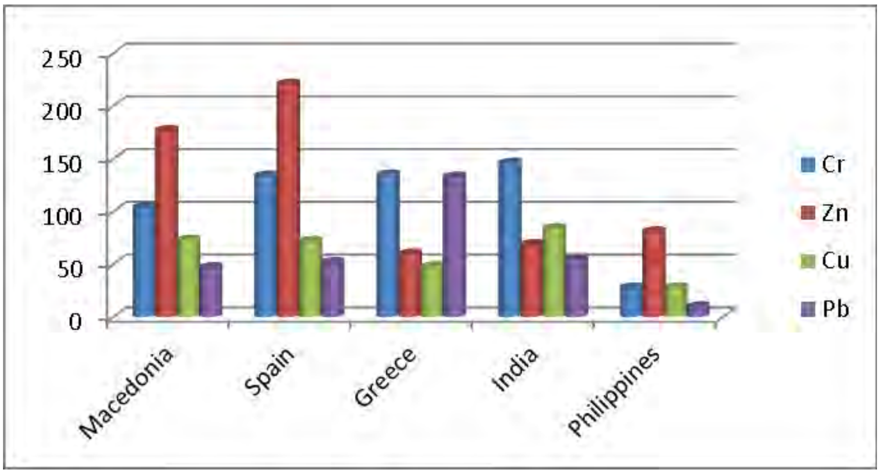

Fig.3 Comparison of values of havey metals concentration in coal fly ash samples from termal power plant of Macedonia, Spain, Greece, India and Philippines

We also determined the correlation coefficient between heavy metals. The results that we obtained showed:
Chromium shows a high correlation coefficient with the following elements (Cr/Zn 0.9502; Cr/Pb 0.9062; Cr/Ni 0.8031; Cr-Co 0.9667).
Zinc shows a high correlation coefficient with Pb and Ni (Zn/Pb 0.9193; Zn/Ni 0.8187).
Cobalt shows a high correlation coefficient with: Co/Zn.0.9453; Co/Pb 0.8088; Co/Ni 0.9130).
The chemical composition of fly ash varies widely, depending on the type of coal burned, the particle size of the ash, and the efficiency of the collectors.
Elements having lower mass can be carried and precipitated with the fly ash (Cu, Zn) while elements having higher mass may settle rapidly after combustion and be enriched in bottom ash (Co). Some elements, like Ni, however show no such preference [Snigdha S.,*et.al.* (2006)].
In table 3 are given data for cation exchange capacity (CEC) and ammonium exchange capacity (AEC). Values for fly ash from research of thermal power plant are in the range of 0.19-0.28 meq/ g for CECs and 0.17-0.33 meq/g for AECs.

Table 3 . Data for CECand AEC value

	Ca	**Mg**	**Na**	**K**	**Suma CECmeq/g**	**NH_4^+ meq/g**
Sample1	0.08	0.08	0.01	0.11	0.28	0.33
Sample2	0.05	0.04	0.01	0.12	0.19	0.18
Sample3	0.05	0.04	0.01	0.13	0.19	0.17
Sample4	0.05	0.10	0.02	0.12	0.24	0.23

pH of the fly ash is directly related to the availability of macro and micro nutrients. pH indicates that whether fly ash is acidic or alkaline in nature. Based on the pH, fly ash has been classified into 3 categories, namely;

- Slightly alkaline 6.5 – 7.5.
- Moderately alkaline 7.5-8.5.
- Highly alkaline >8.5.

The neutral pH may be generally used in amending both acidic and alkali soils [Kumar, N., *et.al.* (1998)].
In India, fly ash is generally highly alkaline due to low sulfur content of coal and presence of hydroxides and carbonates of calcium and magnesium [Maiti, S.K.,*et.al.* (2005)].
Data value for pH, organic carbon, electrical conductivity and specific gravity are shown on table 4.
pH of fly ash sample was measured as 7.8-9.1; Organic carbon was measured as 3.17-3.85. Electrical conductivity was measured as 0.14 mmhos/cm in the sample and specific gravity 1.96-2.37g/cm^3.

Table 4 data for: pH, Electrical conductivity mmhos/cm, Organic carbon %, Specific gravity g/cm^3

	pH	**Electrical conductivity mmhos/cm**	**Organic carbon %**	**Specific gravity g/cm^3**
Sample1	7.8	0.15	3.17	2.37
Sample2	7.8	0.15	3.59	2.21
Sample3	8.3	0.13	3.85	2.04
Sample4	9.1	0.14	3.41	2.09

This property of fly ash can be exploited to neutralize acidic soils [Elseewi, A.A.,*et.al*. (1978)] [Jastrow, J.D., *et.al*. (1979)]. reported that while addition of fly ash improves soil pH on one hand, it simultaneously adds essential plant nutrients to the soil on the other hand.

[Page, A.L., *et.al.* (1979)] observed that experiments with calcareous and acidic soils revealed that fly ash addition increased the pH. The use of excessive quantities of fly ash to alter pH can cause increase in soil salinity especially with un-weathered fly ash [Sharma, S. (1989)]. In the present study, pH of fly ash sample was measured as 7.8-9.1; it indicates that fly ash was alkaline in nature and can be used for reclamation of acidic soil.

The soluble salt content of fly ash is measured by an assessment of electrical conductivity (EC) of water extract. Electrical conductivity indicates the availability of different ions in the fly ash sample.

In the present study, electrical conductivity was measured as 0.14 mmhos/cm in the sample. Thus it was found that this fly ash could be used as an additive / amendment material in agriculture applications. Organic carbon is the generic name for carbon held within the fly ash, primarily in association with its organic content. In the present study, cation exchange capacity of the fly ash sample was observed as 0.23-0.45 meq/100gm.

Many physical and chemical parameters of fly ash may benefit plant growth and can improve agronomic properties of the soil [Chang, A.C.,*et.al* (. 1977)].

A large number of forestry species such as *Acacia*, *Eucalyptus*, *Dalbergia*and *Casuarina*have shown improvement in growth and biomass production in fly ash amended mine dumps [Paul, B. (2001)].

Fly ash application to acidic soils in coal mine areas increased the yields of different vegetation. Fly ash alone and in combination with press mud showed favorable conditions for growth of tree species.

Two major sectors of fly ash utilization across the globe are cement and concrete. A number of engineering and environmental benefits are also gained by using the ash instead of multiple ingredients for construction works.

Martars made with fly ash can possess properties similar to or even better than some of the commercial products currently used in passive fire protection[Luis F.,*et.al.* (2001)]

4. Conclusions

In general, after summarizing all the facts, which have resulted from this research we could say that, coal fly ash in Macedonia contains moderate quantities of heavy metals and its effects on ground water, soil health and uptake by plants are probably negligible.

The concentration of heavy metals in coal fly ash in Macedonia was less, compared to concentration of heavy metals in coal fly ash from other parts of the world.

On the basis of the results above and discussions of the various physico chemical properties, we can conclude that coal fly ash in Macedonia can be used in agriculture for conjunction with chemical fertilizer to increase the yield of various agricultural crops, the dose of which will depend on the types of crops as well on the types of soils.

Also, this coal fly ash may be used as structural fill material in constructing high way embankments and road bases as ingredient in an ultra high strength concrete (Portland cement) that is almost as strong as steel, in waste stabilization, or in mining applications, for manufacturing concrete bricks, blocks, and paving stone.

We hope that the results of this research will become the basis for further research aimed at increasing the percentage of utilization of coal ash in Macedonia.

5.References

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