CONCENTRATION OF TRACE ELEMENTS IN SOME COALS FROM REPUBLIC OF MACEDONIA, WITH EMPHASIS ON THE POTENTIALLY HAZARDOUS

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Abstract:
In this paper the results obtained for concentration of the trace elements in some coals from the Republic of Macedonia are given. It became possible to determine the dependence between some of them. The representative sample was analyzed for proximate analysis as well as for the trace elements. AES-ICP techniques were used in determination of the trace elements in the coal. Five samples of the coal were analyzed for the presence of Ba, Cr, Pb, Zn, Cu, Ni, Mo, V, Se, Ag and Co. The results show that the content is in a range about Ba (83-298), Cr (12-29), Zn (8-89), Cu(4.4-27), Pb (1.8-8.7), Ni (7.8-17.5), Co (1.9-9.7), Mo (0.4-2.8), V (14-57), As (6.5-26), Se (1.7-7.0). The concentrations of all trace elements in these coals are unremarkably, falling well within the range of the World class coals. These data do not indicate any potential for economics by-product, technological problems or environmental or health concerns.
Keywords: Trace elements, coals, AES-ICP.

1. Introduction

Coal is a very complex heterogeneous material of organic and mineral fractions and the modes of occurrence of the trace elements in the coal are influenced by the depositional environment and the geological processes prevailing during the formation of the coal beds. Although most trace elements are associated with mineral matter many of them appear to have an organic affinity arising from their association with the original plant material from which the coal was formed.

The trace elements in the coal play an important role in its mining, treatment and usage. They can be associated with specific minerals or with organic 'coaly' matter. The sources of the trace elements include biological material (plants, algae and bacteria) that is the precursor of the coaly material, water in the peat swamp and mineralogical material washed or blown into the swamp.

[Swaine (1975), (1980), (1990), (1994)] discussed the concentration, origin and enrichment of the trace elements in the coal. [Gluskoter *et al*. (1973), (1977), (1981)] described the affinity of the trace elements according to their association with organic or inorganic materials in the coal. [Finkelman (1981), (1982), (1994)] pointed out that in a low rank coals such as lignite and sub-bituminous coal, the trace elements like Na, Mg, Ca, Sr, and Ba are usually associated with organic constituents in the coal. [Finkelman (1982)] then studied the modes of occurrence of the trace elements in detail. [Pareek and Bardhan (1985)] had studied the association of the trace elements with macerals and found out that Cu, Ni, Co, V, Ga, and B are usually associated with vitrinite, although Cu and Ni can originate from both organic and inorganic sources. [Martinez-Tarazona *et al.* (1992)] believed that most of the trace elements in bituminous coal were concentrated in detritus and digenetic minerals.

[Lu *et al*. (1995)] investigated the distribution of the trace elements of the coal in China. [Spears and Zheng (1999)] studied the origin of the elements in UK coal, whereas [Helle *et al*. (2000)] completed the chemical characterization of coals from Chile.

The most of the trace element content in coals is associated with three major minerals: pyrite, kaolinite, and illite. However, the minerals in coal are not uniform, either in chemical composition or physical properties (such as particle size and density) [Davidson M. (1996)].

The trace elements in the coal such as, Zn, Cd, Pb, Mo, Ni, As and Se, are important concern for land disposal due to their environmental significance [Keefer, (1993)],[Spears, *et al.* (1999), (2000)], but the ultimate impact of each trace element will depend upon its state in Coal Combustion Residues (CCRs) and toxicity, mobility and availability in the ecosystem.

2. Materials and methods

In this research, five samples are examined. The method used for the analysis of trace elements was AES-ICP method. First of all, the samples were burning on 950ºC to constant weight and then the resulting ash is subjected to the next treatment.

- *The procedure*

Before treatment, for digestion we weighed 0,5 g with accuracy of +/-0,0001g sample Teflon vessel and add 5 mL of 68%, p.a.., HNO3 and kept for digestion on temperature of 150oC, until approximately 1mL of leaves the nitrogen acid. Then, Teflon vessel is cooled to room temperature.

- *Digestion with HF and HClO4*

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. Finally the results are measured in terms of the initial mass of coal.

3. Results and discussion

Table 1 shows the content of major oxide of investigated coals. In table 2 is presented the content of the trace elements of investigated coals.

Table 1 Data for the chemical analysis of the coal samples from the Republic of Macedonia

	Pelister	Suvo dol 2	Suvo dol 3	Granit	Mariovo
	w/%				
SiO_2	22.05	19.97	9.85	12.15	11.95
Al_2O_3	14,33	2,11	5,25	9,19	2,43
CaO	2,72	3,05	3,56	1,76	6,73
MgO	2,91	1,35	2,11	1,88	2,30
FeO	2,76	1,06	1,43	1,97	0,84
Na_2O	0,496	0,068	0,190	0,232	0,112
K_2O	1,87	0,43	2,79	3,47	0,28
MnO	0,031	0,043	0,060	0,019	0,017
P_2O_5	0,058	0,425	0,058	0,037	0,182
TiO_2	0,417	0,067	0,191	0,282	0,103
Loss. Ig	52,27	71,36	74,56	69,02	74.85
Suma	99.91	99.93	100.05	100.01	99.78

Table 2 The trace element content (ppm) of the Macedonian coals

	Pelister	Suvo dol 2	Suvo dol 3	Granit	Mariovo
	mg/kg				
Sr	109	146	196	1176	224
Ba	298	87	166	172	83
Cr	41	13	17	29	12
Zn	55	89	20	38	8
Cu	27	7,0	11	19	4,4
Pb	8,7	2,1	5,5	6,3	1,8
Ni	9,5	8,4	13,4	17,5	7,8
Co	9,7	5,9	3,9	6,5	1,9
Mo	2,1	1,9	0,4	2,8	1,7
V	57	14	22	40	17
As	26,0	11,3	16,3	41,6	6,5
Se	7,9	6,70	4,1	4,0	1,7

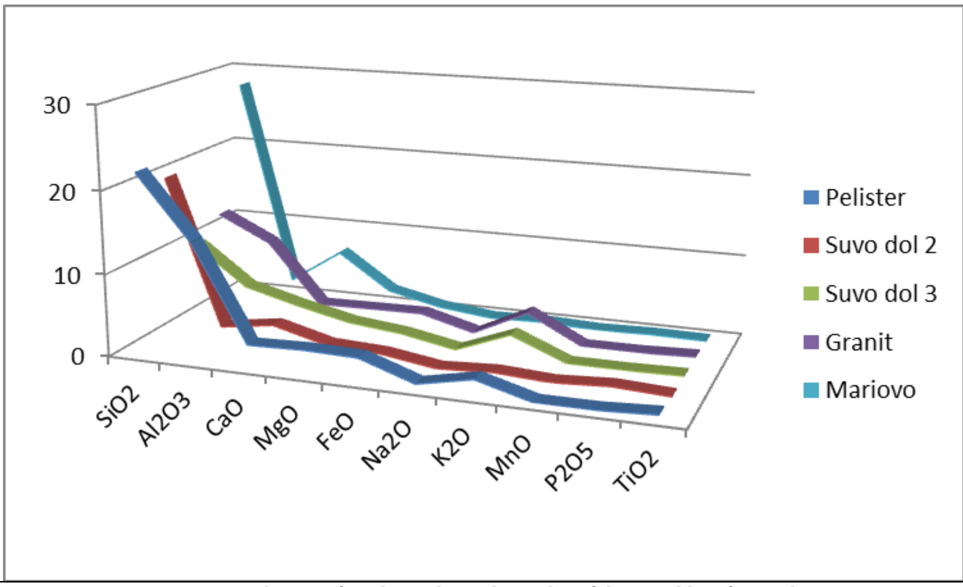

Figure 1. Distribution of oxides in the coal samples of the Republic of Macedonia

Fig 1 shows that the content of oxide in all samples is almost identical with the exception contention of SiO2 and Al_2O_3 which is highest in Pelister and Suvo dol 2 coals.

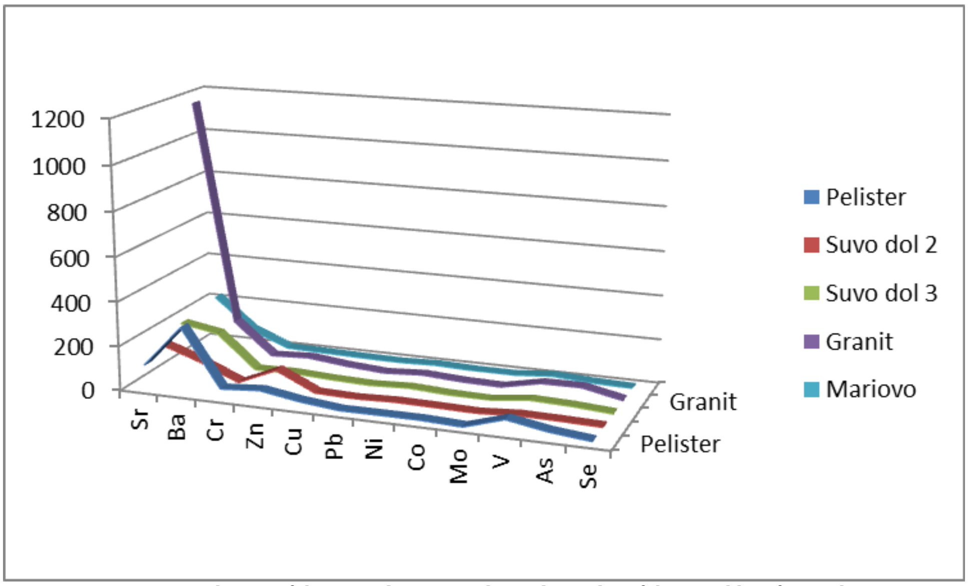

Figure 2. Distribution of the trace elements in the coal samples of the Republic of Macedonia

Fig. 2 shows that the content of the trace elements in all samples is almost identical with the exception content of Ba which is the highest in Pelister coal and content of Sr which is the highest in Mariovo coal.
The results obtained with our research are compared with the World standard value. Table 3 presents the concentration of the trace elements of the coals from Macedonia which is in the range of the World standard value.

Table 3 Trace element content (ppm) compared with the World standard value

Element	ppm	Macedonian coals	Element	Ppm	Macedonian coals
			Ni	0.5-50	7.8-17.5
Ba	20-1000	83-298	Co	0.5-30	1.9-9.7
Cr	0.5-60	12-29	Mo	0.1-10	0.4-2.8
Zn	5-300	8-89	V	2-100	14-57
Cu	0.5-50	4.4-27	As	0.5-80	6.5-26
Pb	2-80	1.8-8.7	Se	0.2-10	1.7-7.9

We also determined the correlation coefficient between some oxides and correlation coefficient between some trace elements. The obtained results are given in the Table 4 and Table 5. They show high levels of correlation.

Table 4 Correlation coefficient between some oxides

Oxides	Correlacion coefficient	Oxides	Correlacion coefficient
Al_2O_3 – FeO	0.9923	FeO- Na_2O	0.9567
Al_2O_3 –TiO_2	0.9950	TiO_2 - FeO	0.9801
Al_2O_3 - Na_2O	0.9696	TiO_2 - Na_2O	0.9684

Table 5 Correlation coefficient between some of the trace elements

Trace elements	Correlation coefficient	Trace elements	Correlation coefficient
Sr-Co	0.8281	Cr-Cu	0.9933
Sr-As	-0.8821	Cr-Pb	0.9342
Cu-Pb	0.9629	Cr-Co	0.8761
Cu-Ba	0.9551	Cr-V	0.9947
Cu-Co	0.8771	Cr-Ba	0.9472
Ba-Pb	0.9676	Zn-V	0.8148
Ba-Co	0.8114	Cu-V	0.9824
Ba-V	0.9415	Ni-As	0.8277
Pb-V	0.9273	Co-Se	0.8846
Co-V	0.8253		

4. Conclusion

After summarizing all the facts, which have resulted from the research performed, we could state that the concentrations of all trace elements in these coals are unremarkably, falling well within the range of the World class coals. The content of Ba is in a range about (83-298), Cr (12-29), Zn (8-89), Cu(4.4-27), Pb (1.8-8.7), Ni (7.8-17.5), Co (1.9-9.7), Mo (0.4-2.8), V (14-57), As (6.5-26), Se (1.7-7.0). These data do not indicate any potential for economics by-product, potential technological problems or environmental or health concerns.

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