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Distribution of Trace and Major Elements in Lignite and Products of Its Combustion-Leaching Experiments and Cluster Analysis

Aleksandar Popovic , Dragana Djordjevic
*University of Belgrade
Serbia*

1. Introduction

One of the strategic issues for contemporary manhood is production of a sufficient amount of energy for further technological development. Despite numerous attempts to use new, practically inexhaustible energy sources, such as solar energy (Li, 2002), wind energy (Belanger & Gagnon, 2002) and high and low tides (Omer, 2002), for example, instead of conventional sources, i.e., coal, petrol or gas, the latter ones, nevertheless, remain unavoidable factors in balancing the energy demands of most countries, including Serbia, at the beginning of the 21st century.

On the basis of investigations of coal genesis, its composition, as well as general characteristics of coal deposits, coal can be defined as a combustible sedimentary rock, originating mainly (some coals are algal) from residues of terrestrial and aquatic plants, and of minerals (< 50 %) (Wood et al., 1983). Chemical and physical characteristics of coal are predetermined by the nature of precursor plants, the amount of inorganic material, and by the nature, intensity and duration of biochemical and geochemical processes that are responsible for coal formation. Almost all natural elements have been found in coal (Finkelman, 1993), in variety of forms (Eskenazy & Valceva, 2003; Yudovich & Kertis, 2005), which are responsible for the coal's technological, economical but also ecological impact. Elements can be variously associated (Font et al., 2005). Further, association types may vary within the same deposit (Kuehn & Kurzbach, 1992; Vyazova & Kryukova, 1997).

During coal combustion in power plants, practically only the organic part of coal burns, producing carbon dioxide and water, i.e. its vapor. The inorganic components of coal mainly do not burn, but remain in the ash, which is a by-product of combustion. Since coal, by definition, contains more than 50 % of organic substances, which are not found in the ash, or are found in the very low concentrations, it is clear that the main part of the inorganic components of coal, including trace elements, is concentrated in the ash. During combustion different processes occur, which influence the non-uniform distribution of the elements and phases in different fractions of the combustion products (Xu et al., 2004; Goodarzi, 2006; Ward & French, 2006). One of the basic mechanisms which are present is "evaporation-condensation" (Schultz et al., 1973). Namely, during coal combustion at high temperatures certain elements evaporate. At the lower temperatures, which are typical for the higher parts of the reactor in which the combustion occurs, part of the substances which

had evaporated condenses, and, as a rule, this occurs on the smaller particles which are present in the higher parts of the reactor. Therefore, the fractions which contain the smallest particles of ash are, in the number of cases, enriched with elements the compounds of which are the most volatile. Normally, parts of these most volatile compounds do not condense but are released into the atmosphere, together with the gases which are formed during the combustion (Pacyna & Pacyna 2001; Pavlish et al., 2003).

The chemical composition of ash obtained by coal combustion can be related to the conditions in the original paleo-environment, to geochemical processes occurring during and after the formation of the coal deposit, but also to the technical conditions during coal combustion. It is well documented that coal fly ash characteristics vary with different feed coals, utility systems, and operating parameters; however, coal fly ash characteristics can be expected to be consistent within a range from a single electric generation facility given a consistent feed coal. It often happens that after coal has been combusted in the power plant, ash with a completely different distribution of microelements has been obtained.

Since only a marginal portion of the ash is being used world-wide (Jones et al., 2006; Yunusa et al., 2006), most of it is usually stored in huge coal ash dumps, either in the dry or wet state (Sushil & Batra 2006). Storage of wet coal ash usually prevents the wind from dispersing it, but increases the time necessary for the leaching of various elements (Iturbe et al., 1996). Coal ash in the environment (on the dump; airborne particles deposited on the soil surface, etc.) is exposed to various influences, and solubilization processes occur, sometimes transforming almost insoluble elements to soluble species thus leading to pollution of water and soil (Gupta, 1999).

The quality of waste waters from landfills depends on the quality of the coal, the methods of combustion, the quality and quantity of the "input" water, the quality of the process which is used for the removal of fly ash from the gases resulting from coal combustion (Chu *et al.*, 1978), and on the manner of ash transportation. (Rokita, 1990). As can be seen, the qualities of waste waters are not only dependent on the chemical composition of the coal, which determines the chemical composition of the resulting ash. In order to predict pollution from ash landfills, computer programs have been written which simulate the release of potentially harmful substances under different conditions (Tucek & Konecny, 1975), as well as the content of surface water in the neighborhood of the landfill (Donslund & Eriksen, 1990). Different tracers, i.e. isotopes of strontium and lead (Hurst *et al.*, 1993), sodium bromide, i.e. bromide ion, and lithium were used for the determination of the dispersion of pollution. Distribution of trace and major elements, especially in more mobile and accessible fractions, in ash and slag during coal combustion, is one of the major factors influencing their ability to pollute surrounding waters (Marquenie and Simmers, 1988; Jankowski et al., 2006).

In order to examine and compare distribution of some trace and major elements in lignite and products of its combustion as well as influence of high temperature process on distribution of elements in "Nikola Tesla A" power plant, we performed sequential extraction of lignite as well as ash and slag obtained by its combustion in situ. Sequential extraction is a powerful tool for predicting the behavior of trace elements under various environmental conditions (changes of pH, redox-potential etc.). The use of extraction (Piekos & Paslawska, 1998; Mukherjee & Borthakur, 2004; Senior et al., 2004) and sequential extraction (Fernandez-Turiel et al., 1994; Goodarzi, 1994; Hlavay et al., 1995; Querol et al., 1996) for analysis of coals and coal combustion by-products is being widely used on samples from all over the world including samples of coal, fly and dump ash from Serbia (Popovic et al., 2000; Popovic et al., 2001; Polic et al., 2005; Popovic & Djordjevic, 2005).

2. Materials and Methods

Eight samples of milled lignite, ash and slag obtained by lignite combustion were subjected to a five-step sequential extraction procedure. The procedure itself comprised of the following sequence of extractants:

Phase I: Distilled water (weakest extractant - the amount of elements extracted in this step is the least that can be expected, regardless of the type of water used for ash transport to the dump);

Phase II: 1 M ammonium acetate (this extractant should dissolve the fractions of elements that are bound to the particle surface with stronger bonds than the fraction washed with distilled water);

Phase III: 0.2 M ammonium oxalate / 0.2 M oxalic acid (imitation of reductive dissolution of iron and manganese oxides, which are important microelement scavengers);

Phase IV: 30 % H₂O₂, 0.01 M HNO₃ on a water bath at 85°C, in order to dissolve organic/sulfide matter, with subsequent desorption of eventually re-adsorbed elements, by application a 3.2 M ammonium acetate solution washing for 30 min.

Phase V: Digestion with 6 M HCl bath at 85°C, introduced in order to obtain additional information on the crystalline iron oxides and silicates.

The elected sequence of extractants was, with some alterations, mostly used for examination of coal and combustion product samples (Gupta, 1999; Senior et al., 2004; Jankowski et al., 2006), and it is remarkably similar to the sequence of extractants used for sediments and soils.

After washing, the residuals were treated with the next extractant. The combined extracts and washings after each extraction step were concentrated and the trace elements were analyzed by a "SpectrAA-20+ Varian" atomic absorption spectrometer.

The available data sets were analyzed using the SPSS 10.0 statistical program (Descriptive Statistics and Classify Hierarchical Cluster).

3. Results

Average concentrations and standard deviations of concentrations of extracted major and trace elements from lignite, ash and slag obtained by lignite combustion in "Nikola Tesla A" power plant are shown in Tables 1-3.

4. Discussion

4.1 Lignite

The macro and microelements contained in coal are differently distributed (Tables 1-3, Figure 1). It should be mentioned that during applied sequential extraction process the solid phase is not totally destroyed. As opposed to the organic component dissolved in the fourth phase of extraction, the total mineral component is not dissolved, which means that all the macro elements and some of the microelements may have an additional mineral component, besides the one determined by the extraction. However, it is obvious from the results obtained by extraction that most elements are contained in the inorganic phase of coal, even inside the extractable part.

The investigated macro elements can be separated on the basis of their fraction in the organic phase into elements which are dominantly extracted from the organic phase (aluminium 58.56

$\pm 11.31\%$ and silicon $58.36 \pm 11.66\%$) and into elements which are dominantly extracted from the inorganic component, even in an extracted fraction of coal (iron 60.76% of the totally extracted elements is released in the third phase of the extraction). It is interesting to note that two macro elements, magnesium and potassium, can not be precisely categorized. Actually, a larger amount of potassium and approximately the same amount of magnesium were released in the fourth phase of the sequential extraction, compared with the sum of the amounts extracted in the third and the fifth phase, however, more than 50% of the extracted amounts are released in the first two phases of the sequential extraction. Since it is not possible to determine the origin of adsorbed and ion-exchangeable fraction using the applied technique, i.e. it is not possible to say whether the adsorbed and ion-exchangeable potassium and magnesium are connected with the organic or with the inorganic fraction of coal, there is no precise conclusion about that whether these two elements in the extractable fraction of coal are distributed dominantly in (or with) the organic or in the mineral phase.

Mg	Phase I		Phase II		Phase III		Phase IV		Phase V		Total
	ppm	%	ppm	%	ppm	%	ppm	%	ppm	%	
Average	2.35	0.08	373.9	12.23	32.91	1.08	314.6	10.29	2333	76.32	3057
St.deviation	0.50	0.02	91.9	3.01	7.50	0.25	50.4	1.65	1082	35.41	1233
Average	163.6	19.27	321.0	37.80	43.68	5.14	184.0	21.67	136.9	16.12	849.2
St.deviation	43.7	5.14	3.4	0.40	2.52	0.30	92.7	10.91	58.1	6.84	200.4
Average	125.0	11.17	285.2	25.49	38.21	3.42	119.0	10.64	551.4	49.29	1119
St.deviation	4.7	0.42	4.2	0.37	21.33	1.91	22.4	2.00	12.9	1.15	66
Al	Phase I		Phase II		Phase III		Phase IV		Phase V		Total
	ppm	%	ppm	%	ppm	%	ppm	%	ppm	%	
Average	103.9	1.30	205.2	2.56	2699	33.71	449.2	5.61	4548	56.81	8005
St.deviation	69.7	0.87	130.7	1.63	757	9.46	209.8	2.62	674	8.42	1842
Average	49.49	2.99	0.05	0.00	431.9	26.09	969.4	58.56	204.5	12.35	1655
St.deviation	35.17	2.12	0.10	0.01	18.7	1.13	187.2	11.31	76.5	4.62	318
Average	3.65	0.15	0.85	0.04	1154	48.20	805.1	33.63	430.6	17.99	2394
St.deviation	3.46	0.14	0.49	0.02	1632	68.16	53.6	2.24	17.8	0.74	1707
Si	Phase I		Phase II		Phase III		Phase IV		Phase V		Total
	ppm	%	ppm	%	ppm	%	ppm	%	ppm	%	
Average	66.3	4.71	399.3	28.38	151.2	10.75	369.6	26.27	420.4	29.88	1407
St.deviation	31.7	2.25	62.5	4.44	35.0	2.49	64.48	4.58	19.5	1.39	213
Average	254.7	5.92	124.2	2.89	229.6	5.33	2512	58.36	1184	27.50	4304
St.deviation	67.8	1.58	20.4	0.47	31.3	0.73	502	11.66	469	10.90	1091
Average	114.3	2.51	174.2	3.83	104.6	2.30	1124	24.71	3032	66.65	4548
St.deviation	5.9	0.13	10.2	0.23	18.9	0.42	45	0.99	268	5.89	348
K	Phase I		Phase II		Phase III		Phase IV		Phase V		Total
	ppm	%	ppm	%	ppm	%	ppm	%	ppm	%	
Average	37.49	2.12	20.24	1.14	560.7	31.70	130.2	7.36	1020	57.68	1769
St.deviation	5.94	0.34	3.47	0.20	56.68	3.20	27.5	1.55	456	25.78	550
Average	33.13	20.01	59.30	35.81	16.32	9.85	45.27	27.34	11.57	6.99	165.6
St.deviation	3.72	2.25	30.81	18.61	2.55	1.54	23.10	13.95	2.87	1.73	63.0
Average	27.54	6.54	91.58	21.76	178.2	42.33	0.00	0.00	123.6	29.37	420.9
St.deviation	0.18	0.04	6.92	1.64	235.5	55.95	0.00	0.00	16.83	4.00	259.4
Fe	Phase I		Phase II		Phase III		Phase IV		Phase V		Total
	ppm	%	ppm	%	ppm	%	ppm	%	ppm	%	
Average	0.33	0.01	177.8	2.90	2832	46.15	272.9	4.45	2853	46.50	6135

St.deviation	0.10	0.00	47.7	0.78	54	0.87	150.4	2.45	1166	19.01	1418
Average	8.81	0.30	0.08	0.00	1761	60.76	746.5	25.76	382.0	13.18	2898
St.deviation	4.47	0.15	0.10	0.00	17	0.57	284.4	9.81	154.0	5.31	460
Average	0.49	0.03	0.00	0.00	942.0	49.70	325.5	17.17	627.5	33.11	1895
St.deviation	0.57	0.03	0.00	0.00	1331	70.21	9.9	0.52	116.4	6.14	1458
Cr	Phase I		Phase II		Phase III		Phase IV		Phase V		Total
	ppm	%	ppm	%	ppm	%	ppm	%	ppm	%	ppm
Average	0.97	1.98	2.85	5.81	5.21	10.62	2.11	4.30	37.91	77.29	49.05
St.deviation	0.35	0.71	1.01	2.05	3.83	7.81	1.26	2.56	23.87	48.66	30.31
Average	0.11	0.92	0.37	3.20	1.01	8.86	7.84	68.61	2.10	18.41	11.42
St.deviation	0.12	1.02	0.68	5.98	0.09	0.75	1.51	13.23	1.52	13.32	3.92
Average	0.64	8.34	0.04	0.52	1.20	15.65	3.58	46.61	2.22	28.88	7.67
St.deviation	0.89	11.62	0.01	0.18	1.64	21.39	1.04	13.55	0.15	1.94	3.73

Table 1. Average concentrations and standard deviations of extracted magnesium, aluminium, silicon, potassium, iron and chromium (ppm) from samples of lignite (first two rows), ash (second two rows), and slag (third two rows) obtained by lignite combustion in “Nikola Tesla A” power plant

Mn	Phase I		Phase II		Phase III		Phase IV		Phase V		Total
	ppm	%	ppm	%	ppm	%	ppm	%	ppm	%	ppm
Average	3.16	1.31	10.55	4.39	8.32	3.46	24.77	10.30	193.7	80.54	240.5
St.deviation	0.76	0.32	3.47	1.44	4.75	1.98	10.41	4.33	80.7	33.56	100.1
Average	1.54	0.86	11.12	6.20	72.00	40.11	14.87	8.28	80.0	44.55	179.5
St.deviation	0.34	0.19	3.40	1.89	25.08	13.97	8.70	4.85	28.0	15.62	65.6
Average	0.07	0.04	4.25	2.65	53.58	33.37	11.89	7.40	90.78	56.54	160.6
St.deviation	0.01	0.01	2.05	1.28	67.35	41.95	0.62	0.38	10.34	6.44	80.4
Ni	Phase I		Phase II		Phase III		Phase IV		Phase V		Total
	ppm	%	ppm	%	ppm	%	ppm	%	ppm	%	ppm
Average	0.13	0.19	1.54	2.23	11.91	17.28	9.18	13.33	46.15	66.98	68.90
St.deviation	0.03	0.04	0.17	0.25	1.16	1.68	1.93	2.80	5.22	7.57	8.51
Average	0.14	0.49	0.06	0.23	15.57	56.80	8.44	30.80	3.20	11.67	27.41
St.deviation	0.03	0.10	0.02	0.05	1.07	3.92	2.79	10.19	1.52	5.56	5.43
Average	0.02	0.07	0.05	0.23	7.84	36.23	5.30	24.51	8.43	38.96	21.63
St.deviation	0.01	0.03	0.00	0.00	11.04	51.04	0.17	0.78	0.97	4.48	12.18
Cu	Phase I		Phase II		Phase III		Phase IV		Phase V		Total
	ppm	%	ppm	%	ppm	%	ppm	%	ppm	%	ppm
Average	0.06	0.20	2.18	7.31	6.49	21.80	3.12	10.47	17.93	60.22	29.78
St.deviation	0.03	0.09	0.44	1.46	1.76	5.91	1.30	4.35	3.94	13.23	7.46
Average	0.08	0.58	0.02	0.15	8.57	65.97	1.44	11.09	2.89	22.21	12.99
St.deviation	0.01	0.10	0.01	0.06	0.97	7.49	0.36	2.80	1.44	11.10	2.80
Average	0.04	0.36	0.02	0.21	1.47	15.21	1.25	12.98	6.86	71.24	9.63
St.deviation	0.01	0.07	0.00	0.00	2.06	21.37	0.10	1.03	0.20	2.06	2.36
Zn	Phase I		Phase II		Phase III		Phase IV		Phase V		Total
	ppm	%	ppm	%	ppm	%	ppm	%	ppm	%	ppm
Average	0.13	0.49	1.44	5.48	0.81	3.09	3.10	11.79	20.81	79.15	26.29
St.deviation	0.08	0.29	0.10	0.38	0.09	0.35	1.63	6.21	4.42	16.83	6.33
Average	3.80	11.91	1.70	5.33	13.24	41.51	2.98	9.33	10.19	31.93	31.90
St.deviation	2.66	8.32	2.72	8.51	2.93	9.18	0.96	3.00	4.69	14.69	13.94
Average	0.42	2.19	0.23	1.21	4.27	22.52	12.38	65.28	1.67	8.81	18.97

St.deviation	0.19	1.01	0.13	0.67	5.87	30.95	1.26	6.64	0.78	4.10	8.22
As	Phase I		Phase II		Phase III		Phase IV		Phase V		Total
	ppm	%	ppm	%	ppm	%	ppm	%	ppm	%	ppm
Average	1.27	8.64	0.00	0.00	0.14	0.97	0.00	0.00	13.24	90.39	14.64
St.deviation	0.70	4.79	0.00	0.00	0.25	1.71	0.00	0.00	2.98	20.38	3.94
Average	1.58	16.98	0.00	0.03	0.89	9.51	5.10	54.85	1.73	18.62	9.30
St.deviation	0.89	9.56	0.01	0.05	0.59	6.40	1.98	21.25	1.27	13.64	4.74
Average	1.43	29.92	0.01	0.10	0.00	0.00	0.00	0.00	3.35	69.98	4.78
St.deviation	0.35	7.40	0.01	0.15	0.00	0.00	0.00	0.00	0.16	3.40	0.52
Cd	Phase I		Phase II		Phase III		Phase IV		Phase V		Total
	ppm	%	ppm	%	ppm	%	ppm	%	ppm	%	ppm
Average	0.03	20.20	0.03	19.19	0.00	0.00	0.00	0.00	0.10	60.61	0.17
St.deviation	0.01	3.13	0.01	7.09	0.00	0.00	0.00	0.00	0.08	46.95	0.09
Average	0.00	0.00	0.01	4.76	0.00	0.00	0.00	0.00	0.15	95.24	0.16
St.deviation	0.00	0.00	0.01	3.17	0.00	0.00	0.00	0.00	0.00	0.00	0.01
Average	0.00	0.00	0.01	100.0	0.00	0.00	0.00	0.00	0.00	0.00	0.01
St.deviation	0.00	0.00	0.01	141.4	0.00	0.00	0.00	0.00	0.00	0.00	0.01

Table 2. Average concentrations and standard deviations of extracted manganese, nickel, copper, zinc, arsenic and cadmium (ppm) from samples of lignite (first two rows), ash (second two rows), and slag (third two rows) obtained by lignite combustion in "Nikola Tesla A" power plant

Concerning the microelements, they can be classified into three groups. The elements having a predominant part of their extractable component associated with the organic fraction of coal are in the first group, i.e., chromium (68.61 ± 13.23 %) and arsenic (54.85 ± 21.25 %). The elements having a significant (although less than 50 %) amount of their extractable component connected with the organic phase are in the second group, the main representative being nickel (30.80 ± 10.19 %). The organic component of the other investigated elements, which are in the third group, are present in only a small amounts in the organic fraction, i.e., manganese (8.28 ± 4.85 %), copper (11.09 ± 2.80 %), zinc (10.19 ± 4.69 %), cadmium (0.00 ± 0.00 %) and lead (10.38 ± 3.10 %) of the total extracted amount. The fact that most of the elements are indisputably connected with the inorganic fraction of coal is not unexpected taking into consideration the large amount of ash remaining after the combustion of coal. The elements which are prevalently connected with the inorganic component, can be divided into groups based on the difference of their extractability in the third and fifth phase of the sequential extraction of the coal. The first group contains elements the extractable fraction of which is connected with the inorganic component and is concentrated in the third phase of the sequential extraction. The second group contains elements the extractable fractions of which, except the part which is organically associated, are mostly present in the fifth phase of the sequential extraction, which is the most difficult to dissolve. Nickel (56.80 ± 3.92 % extracted in the third and 11.67 ± 5.56 % extracted in the fifth phase of the sequential extraction), copper (65.97 ± 7.49 % extracted in the third and 22.21 ± 11.10 % extracted in the fifth phase of the sequential extraction) and iron (60.76 ± 0.57 % extracted in the third and 13.18 ± 5.31 % extracted in the fifth phase of the sequential extraction) belong to the first group. Cadmium (0.00 ± 0.00 % extracted in the third and 95.24 ± 0.00 % extracted in the fifth phase of the sequential extraction) and lead (1.26 ± 2.52 % extracted in the third, and 88.36 ± 44.81 % extracted in the fifth phase of the sequential

extraction) belong to the second group, while zinc (41.51 ± 9.18 % extracted in the third and 31.93 ± 14.69 % extracted in the fifth phase of the sequential extraction) and manganese (40.11 ± 13.97 % extracted in the third and 31.93 ± 14.69 % extracted in the fifth phase of the sequential extraction) lie between these two groups.

Pb	Phase I		Phase II		Phase III		Phase IV		Phase V		Total
	ppm	%	ppm	%	ppm	%	ppm	%	ppm	%	
Average	0.21	1.39	0.15	0.98	0.00	0.00	0.03	0.20	14.91	97.43	15.31
St.deviation	0.06	0.38	0.13	0.82	0.00	0.00	0.02	0.11	5.40	35.28	5.60
Average	0.00	0.00	0.00	0.00	0.10	1.26	0.83	10.38	7.03	88.36	7.95
St.deviation	0.00	0.00	0.00	0.00	0.20	2.52	0.25	3.10	3.56	44.81	4.01
Average	0.00	0.00	0.00	0.00	0.00	0.00	2.32	22.73	7.89	77.27	10.21
St.deviation	0.00	0.00	0.00	0.00	0.00	0.00	0.13	1.25	0.32	3.12	0.45

Table 3. Average concentrations and standard deviations of extracted lead (ppm) from samples of lignite (first two rows), ash (second two rows), and slag (third two rows) obtained by lignite combustion in "Nikola Tesla A" power plant

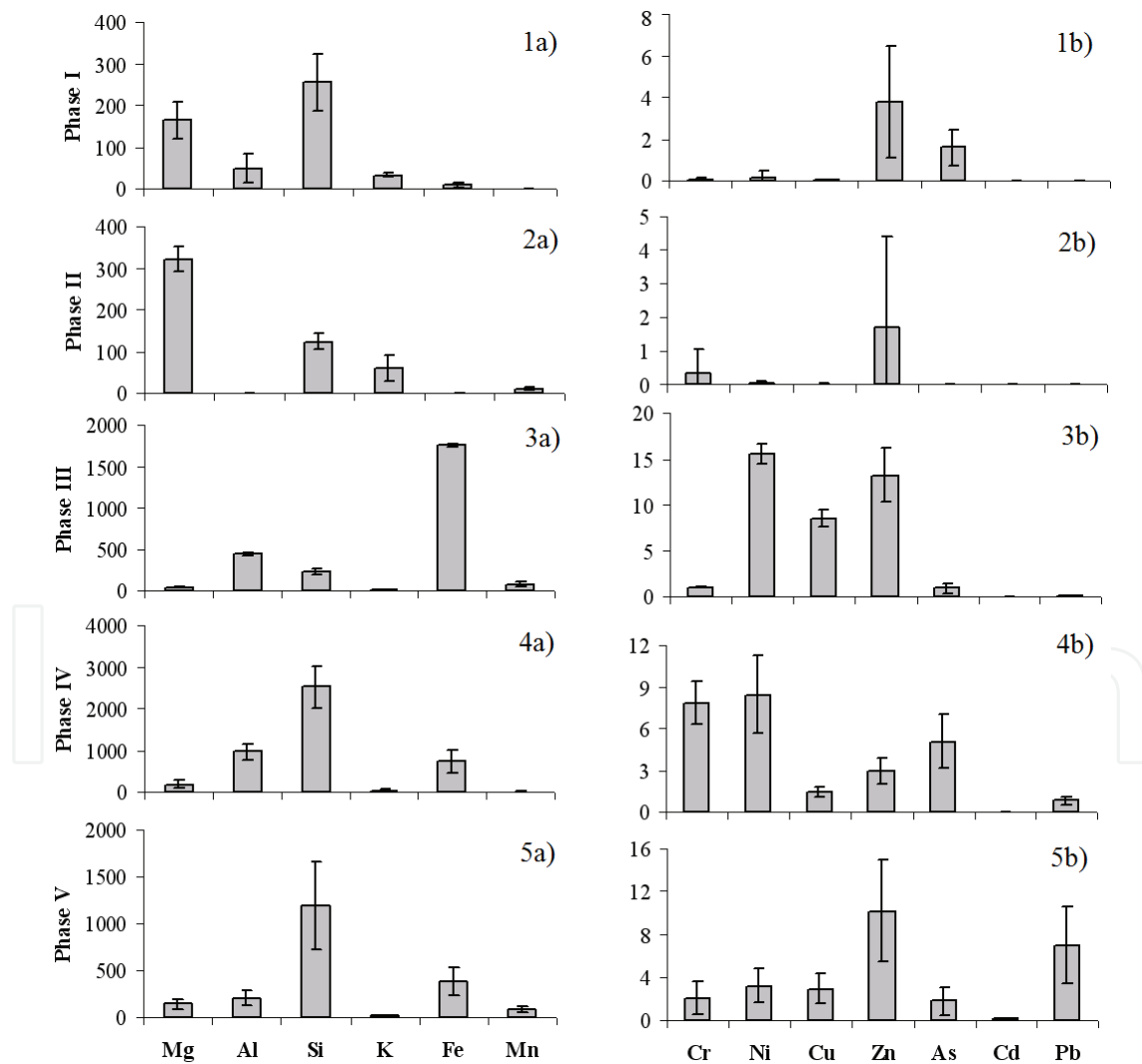


Fig. 1. Average concentrations and standard deviations of a) macro elements and b) microelements (ppm) extracted from samples of lignite

The question arises as to the origin of the adsorbed and ion-exchangeable fraction in the investigated samples of coal. These two fractions of different elements certainly existed in the original samples of coals but it is questionable whether the adsorbed and ion-exchangeable elements, which were present in the original coal, were also present in the coal used in the thermo-electric power plant, or whether these fractions present during the combustion of the coal were of a more recent origin. Taking into consideration that the coal had been exposed to rain after its mining, i.e., in stock piles and during transportation, it is probable that most of the elements which were present in the original "easily extractable" fractions of coal were rinsed out long before the combustion process, and that the adsorbed and ion-exchangeable elements, which were found in the experiment, were there as a consequence of sorption occurring during transportation, storage and grinding of the coal.

4.2 Filter Ash

Fly ash is the most important product obtained by coal combustion. High temperature during combustion in power plants enables melting, crystallizing as well as sintering process of aluminosilicates and generation a new structures that are procuring their chemical property. Since only a small part of organic substances remain in the ash, it would not be realistic to expect fly ash to contain elements the dominant fractions of which are associated with organic component of coal. Thus, it is logical that the highest concentrations of all the investigated elements exist in the extraction phases in which the inorganic matrix of the ash particles dissolve. On the basis of their extraction characteristics, the elements present in the ash (Tables 1-3, Figure 2) can be divided into those which are to a significant degree still associated with the organic component of the ash (silicon - 26.27 ± 4.58 %), those which are to a small extent bonded to the organic component (magnesium - 10.29 ± 1.65 %; manganese - 10.30 ± 4.33 ; nickel - 13.33 ± 2.80 %; copper - 10.47 ± 4.35 %; zinc - 11.79 ± 6.21 %), those which are to minimal extent associated with the organic component of the ash (aluminum - 5.61 ± 2.62 %; potassium 7.36 ± 1.55 %; iron - 4.45 ± 2.45 % and chromium 4.30 ± 2.56 %) and those which, practically, do not exist in a form bonded to the organic component of the ash (arsenic, cadmium and lead).

When the amounts extracted in the third and fifth phase are compared, larger amounts of all the investigated either macro- or microelements were extracted in the last phase, and only for five elements (aluminum, silicon, potassium, iron and copper) is the ratio of these amounts less than 3:1 in favor of the concentration dissolved in the fifth phase of the sequential extraction. It should be noted that higher concentrations of silicon, manganese and zinc were extracted in the fourth than in the third phase of the sequential extraction. This was also true for magnesium but there is a possibility that the results of the extraction of this element in the third phase were influenced more by the applied extraction mean (extraction with oxalate will yield non-soluble magnesium oxalate) than by the nature of the substrate by itself.

4.3 Slag

The arrangement of the elements in the slag, shown in Tables 1-3 and Figure 3 is the most irregular and it is difficult to give any precise classification of the investigated elements, such as the ones made in the case of coal and fly ash.

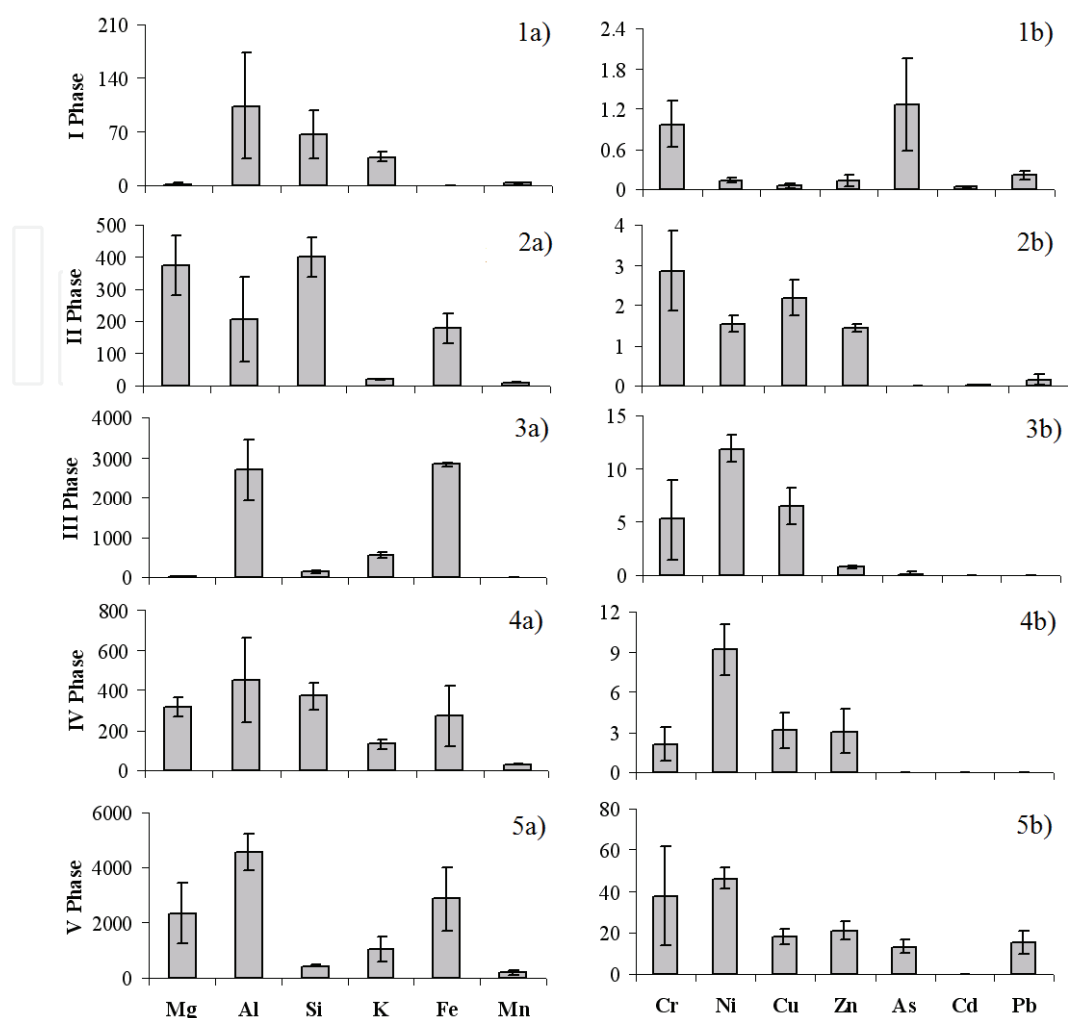


Fig. 2. Average concentrations and standard deviations of a) macro elements and b) microelements (ppm) extracted from samples of filter ash

The absolutely dominant bonding to the organic phase of slag (in relation to the totally extracted, and not absolute amount) is by zinc ($65.28 \pm 6.64\%$) and relatively dominant by chromium ($46.61 \pm 13.55\%$). Three elements, potassium, arsenic and cadmium, are not bound to the organic phase of the slag, while different amount of the other elements are associated with the organic phase. There are still relatively high amounts (compared with the average amount of organically bound elements in fly ash) of aluminum ($33.63 \pm 2.92\%$), silicon ($24.71 \pm 0.91\%$), iron ($17.17 \pm 0.52\%$), nickel ($24.51 \pm 0.78\%$) and lead ($22.73 \pm 1.25\%$) in the organic fraction. Concerning the inorganic component, higher amounts of four elements, aluminum, potassium, iron and zinc, are extracted in the third than in the fifth phase of the sequential extraction.

4.4 Cluster Analysis of Elements Content in the Lignite and in the High Temperature Product

In order to identify the main associations of elements in the coal, the most common subset of clustering methods that is generally referred to an agglomerative hierarchical method was

used. This method is the most appropriate to evidence correlations between variables. The series of stages is summarized in the dendrogram (Figure 4).

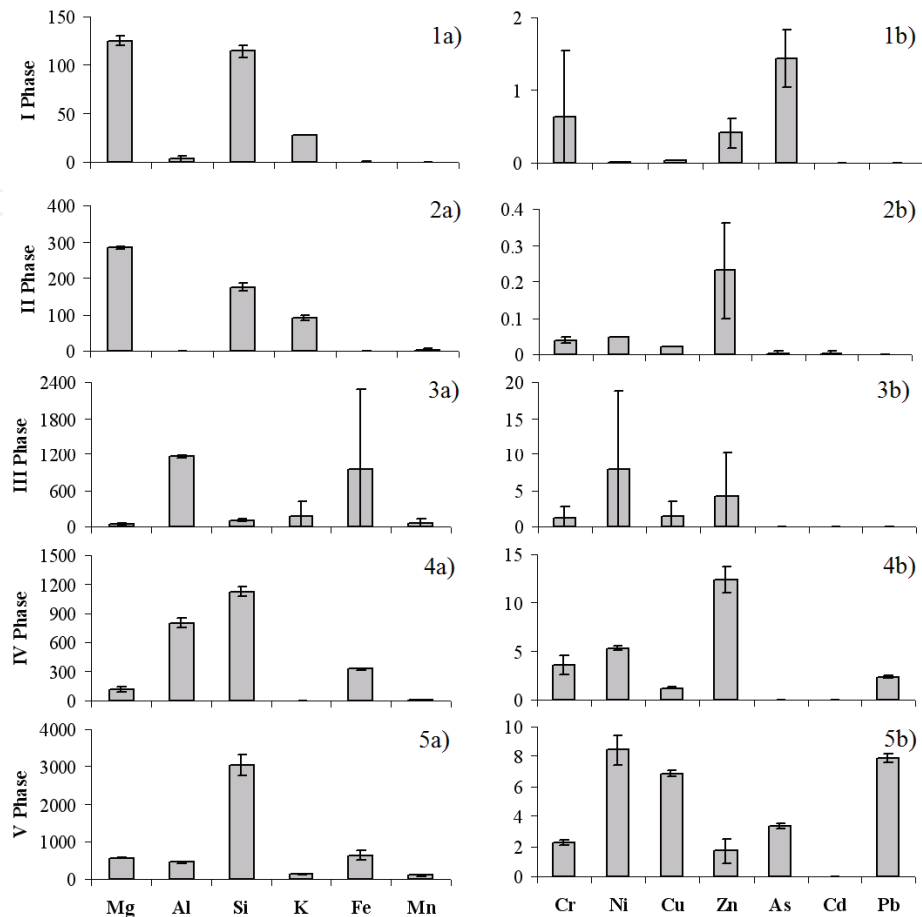


Fig. 3. Average concentrations and standard deviations of a) macro elements and b) microelements (ppm) extracted from samples of filter ash

The lower value is on the axis, the more significant are the associations (Facchinelli et al., 2001; Djordjevic et al., 2004; Relic et al., 2005), i.e. groups of elements in the cluster that are correlated with high significance. As it can be seen, strong associations between the concentrations of different elements leached from lignite and ash are different in their nature, and clearly witness that lignite combustion results in distribution of elements in resulting ash that is different from distribution present in lignite. There is strong association of aluminium, potassium and silicon in the first phase of extraction of lignite (Figure 4-1a), while in same phase of extraction of ash silicon has strong association with arsenic and cadmium (Figure 4-1b). Cluster analysis performed on concentrations leached in the third phase of extraction shows that there is a strong association of aluminium and silicon with magnesium in lignite (Figure 4-3a), while in the ash obtained from lignite aluminium and silicon are associated with potassium (Figure 4-3b). The change in distribution of elements caused by combustion process is also revealed by cluster analysis of associations of elements leached in fourth (e.g. manganese, associated with magnesium and iron in lignite (Figure 4-4a), but with iron and aluminium in ash (Figure 4-4b)) and fifth phase of sequential extraction (for example, magnesium, associated with iron and copper in lignite (Figure 4-5a), but with chromium and arsenic in ash (Figure 4-5b)). Cluster analysis thus demonstrates

an influence of high temperature process of coal combustion on elements associations.

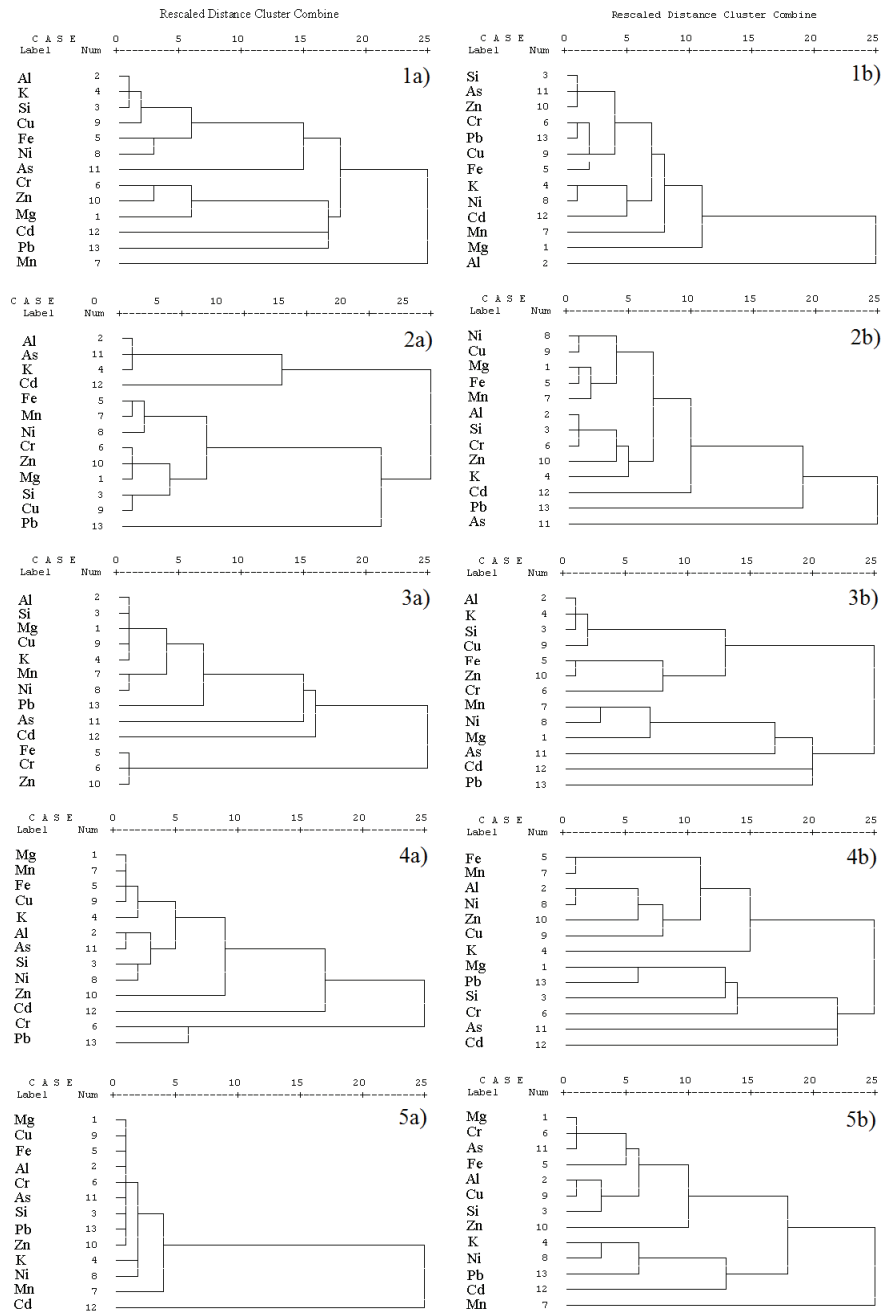


Fig. 4. Dendrograms of cluster analysis for a) lignite and b) fly ash; 1) first phase, 2) second phase, 3) third phase, 4) fourth phase and 5) fifth phase

5. Conclusions

First, it must be emphasized that a larger amount of totally extractable components are present in the ash than in the slag for all the examined elements, except for silicon. It can only be speculated about the reasons for this phenomenon: the cause can be the higher amount of a probably relatively pure organic fraction in the slag, but also the higher content of smaller particles that are carriers of large amount is soluble fractions of element in the ash.

Comparing the characteristics of the extraction of coal, ash and slag, it can be concluded that:

- arsenic (or at least the part which does not leave the system with the combustion gases) during combustion of coal completely transforms to silicates, and this occurs in both slag and ash. The fraction of arsenic which is extracted in the third and fourth phase of sequential extraction of coal disappears during combustion;
- cadmium, which in coal is present in the last extraction phase, is also found in the same phase in ash, while it is not present in slag.
- lead, which was present in coal in the organic phase and in the last phase of the extraction, is present exclusively in the last phase in ash, while lead associated with the organic part is registered in the slag;
- organically bound chromium transfers during combustion mainly to the slag, while chromium, which is bound to the least soluble fraction, goes mainly to the ash;
- both the organic fraction and fraction dissolved in the fifth fraction of extraction are almost equally present in the both lignite combustion products in case of manganese, while the third phase, which is present in coal, transfers almost completely to the slag;
- the fly ash and slag have a similar arrangement of copper (with a somewhat larger amount of the element being extracted from ash in the fifth phase);
- the fraction of nickel soluble in the fifth phase of extraction of coal is almost completely transferred to the ash during combustion;
- organically bound zinc which is left after combustion, and zinc which is bound to the inorganic compounds which are soluble in the third fraction are mainly found in the slag.

Cluster analysis confirmed the difference in associations of trace and major elements in lignite and ash that are caused by transformation occurring during combustion.

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