

Lucie BARTOŇOVÁ *, Zdeněk KLIKA **, Jana SEIDLEROVÁ ***

**LEACHABILITY OF SELECTED TRACE ELEMENTS
IN LIGNITE AND ITS COMBUSTION PRODUCTS**

**VYLUHOVATELNOST VYBRANÝCH STOPOVÝCH PRVKŮ
V HNĚDÉM UHLÍ A PRODUKTECH JEHO SPALOVÁNÍ**

Abstract

For lignite and lignite combustion products a sequential leaching procedure was applied to identify and to define associations of Cr, Co, Ni, Cu, As, Se and Pb in samples tested and to gain insight into their behavior during combustion process. The samples were leached by NH₄OAc, HCl, HF and HNO₃ and concentrations of these elements in leachates were determined by ICP-AES and FL AAS methods. Direct element analysis of solid samples was performed by an XRF method. By application of XRD analysis quartz and kaolinite were determined for lignite, while quartz, anhydrite, calcite, mullite, portlandite, lime and anatase were determined for ash samples. Vast majority of Se, Co and Ni was associated with clay minerals both in lignite and in ash samples (the only exception was high percentage of insoluble Ni in a bottom ash sample). Predominant associations for Cr were aluminosilicate minerals and those of organic affinity in both lignite and ash samples. Lead was associated in lignite sample above all with clay minerals, while in combustion products it was distributed quite evenly among the five leaching procedure stages. Leaching behaviour showed a prevalent HCl solubility for lignite and lignite ash samples indicating probably abundance of As-bearing sulphides, oxides or arsenates. Most of Cu was extracted by HCl and HF from all the samples tested indicating sulphides and associations of aluminosilicate minerals.

Abstrakt

Za účelem popisu asociací Cr, Co, Ni, Cu, As, Se a Pb v hnědém uhlí a produktech jeho spalování byly tyto vzorky postupně louženy pomocí NH₄OAc, HCl, HF a HNO₃. Obsahy prvků ve výluzích byly stanoveny metodami ICP-AES a FL AAS, v pevných vzorcích metodou XRF. Metodou XRD byl v uhlí identifikován křemen a kaolinit, v produktech jeho spalování byla prokázána přítomnost křemene, anhydritu, kalcitu, mullitu, portlanditu, CaO a anatasu. Podstatná část Se, Co a Ni byla asociována s křemenem a kaolinitem / mullitem v hnědém uhlí i popelech, kde je navíc pravděpodobná i asociace s amorfni skelnou hmotou. V hnědém uhlí byla zjištěna výrazná afinita Cr k organické hmotě (55%), křemeni či kaolinitu a asociace s mullitem či amorfni skelnou hmotou byla zjištěna u vzorků popelů. V hnědém uhlí byla zjištěna dominantní asociace Pb s křemenem či kaolinitem, zatímco u produktů spalování nebyla zjištěna jednoznačně převládající afinita. Z extrakčního chování As v hnědém uhlí vyplynul jeho převládající výskyt v sulfidech, oxidech či arseničnanech, u Cu byla v hnědém uhlí zjištěna afinita se sulfidickými minerály, zatímco asociace s křemenem, mullitem či amorfni skelnou hmotou byla pozorována u produktů spalování.

Key words: lignite, lignite ash, trace element, sequential leaching, combustion, fluidised bed boiler.

Introduction

Solid fossil fuels, lignite and bituminous coal are still dominant raw sources for the electricity production in the Czech republic [1]. Until 2020 the large proportion of the electricity generation in Czech republic will be covered especially by the combustion of brown coal in thermal power stations. Even if the combustion technology is chosen with respect to the relatively high ash content of Czech coals, the problems of mineral matter behaviour during the combustion process is still considered to be environmentally significant [1,2]. That is why this second part of the two-piece set is devoted to the leaching behaviour of the trace elements from the lignite and lignite combustion products, while the first one was related to

* Mgr., Ph.D., VŠB-Technical University, Ostrava-Poruba, 17. listopadu 15, 708 33

** Prof., Ing., CSc., VŠB-Technical University, Ostrava-Poruba, 17. listopadu 15, 708 33

*** Doc., Ing., CSc., VŠB-Technical University, Ostrava-Poruba, 17. listopadu 15, 708 33

bituminous coal and ash samples that came from the combustion of this bituminous coal [3]. Generally, there are two main reasons why leaching experiments are usually undertaken: many authors use leaching tests to elucidate mobility of the elements from the combustion products to the environment [4-9]. Some others prefer to gain insight into affinity of the elements in coal and ash samples [9-14], metallurgical wastes [15] and other materials. Detailed knowledge of the associations of elements in coal and ash samples is significant for better understanding volatility of the elements during the coal combustion [9-14]. It is generally accepted that affinity of trace elements to organic and inorganic matter (crystalline / noncrystalline phases) is closely connected with their volatility during the combustion process [6,16-20]. In this work sequential leaching procedure was used in order to describe the associations of trace elements in lignite and ash samples and also to obtain some other information on the behaviour of elements during the combustion process. Sequential leaching tests were applied to lignite and corresponding combustion products collected at Tisová power station (equipped with fluidised-bed boiler and fabric filter). Lignite was combusted at the temperature of about 850°C in atmospheric circulating fluidised-bed boiler (ACFBB) with addition of limestone in order to decrease gaseous sulphur emissions. For the study seven potentially hazardous elements were selected: Cr, Co, Ni, Cu, As, Se, and Pb (they were selected also according to their different volatility during the coal combustion). The paper constitutes the continuation of our previous contributions [21,22] that dealt with the mass balances of the elements and of mineral matter during the combustion of the lignite at the same power station.

Experimental procedures

Analytical methods

Chemical analysis of solid samples was performed by X-ray fluorescence analysis (SPECTRO) equipped with energy-dispersive detector Si(Li) and polarised beams. Before the analysis samples were ground (planetary agate mill), homogenized, mixed with wax (4 g/ 0.9 g) and pressed to obtain pellets. This method was applied to lignite and ash samples as well as to the solid residues of lignite after the leaching tests (if the amount of the residues was sufficient). Regarding the fact that insoluble residues of the ash samples after the leaching test was often not of sufficient quantity to prepare the XRF pellet, these residues must have been totally dissolved using microwave digestion unit (Plazmatronika, BM -1S) by mixture of acids - HNO₃, HCl and HClO₄ (1:1:0,5) prior to ICP-AES analysis. Mineral phases were determined by powder X-ray diffraction analysis (INEL) equipped with Lindemann capillary as a sample holder, Ge-primary monochromator and wide-angled position sensitive detector (CPS 120); CuK_{α1} radiation was used. Selected trace elements (Cr, Co, Cu, Ni, As, Se and Pb) in NH₄OAc, HCl, HF and HNO₃ leachates were analysed using flame AAS method (PERKIN ELMER 3030) and ICP-AES technique (JOBIN YVON 24). The same methods were used for totally decomposed solid residues after the leaching tests. Solutions containing HF or HCl were brought to dryness (on hotplate) and then dissolved in 2% HNO₃ before analysis. Due to very low contents of Hg in the samples AMA 254 equipment was preferred to XRF method for the determination of the element. Ash content and L.I. values of the samples were determined gravimetrically at 815°C using muffle furnace. Standard reference material (coal standard ILL6, USA) undertook all the leaching procedures and analytical measurements in order to verify the accuracy of the procedure.

Leaching procedure

Due to its relative simplicity we prefer the method being used (sometimes with little modifications) by [11,13,14] for both coal and ash samples. Since the leaching procedure is described in detail in our first paper [3], only a brief description is given below. Duplicate 5 g samples (ground to < 0,09 mm particle size) were sequentially leached at room temperature with 35 ml each of 1M ammonium acetate (NH₄OAc), 3M hydrochloric acid (HCl), concentrated hydrofluoric acid (HF) and 3M nitric acid (HNO₃). Each suspension was shaken in polypropylene tube for 18 hours on shaking equipment.

Each sample was separated into 5 fractions, interpretation of which is as follows [11,13,14]:

- Stage 1:** 1M NH₄OAc removes exchangeable cations or loosely bound ions that may be organically associated or adsorbed on clays
- Stage 2:** Dilute cold HCl dissolves carbonates and monosulphides
- Stage 3:** Concentrated cold HF removes ions with association to aluminosilicate minerals
- Stage 4:** Dilute cold HNO₃ is used to dissolve disulphides (pyrite)

Stage 5: Solid residue contains elements bound to organic matter itself or associated with minerals shielded in it and probably to some insoluble minerals (e.g. chromite)

Samples

Lignite was combusted at Tisová power station together with limestone at about 850°C. The plant was equipped with circulating fluidised-bed boiler and with fabric filter as a particulate control device. The influence of the technical parameters, mass balance, mineralogy and particle size of the ash samples on the element distribution among the combustion products have already been discussed in our previous papers [21,22]. So this article deals with the assessment of the leachability of several potentially hazardous elements [23] - Cr, Cu, Ni, Se, As, Pb, and Co - in the lignite and the lignite combustion products. Moreover, Cr and Cu were selected owing to their typical volatile behaviour during the combustion process, As and Se for their low volatility. Ni, Pb and Co represent intermediate behaviour. Lignite (C), bottom ash (BA) and fly ash (FA) samples were collected over approximately a 6-hour period at regular time intervals (every 30 minutes). Then the 30 minutes' samples were mixed and subsampled to produce 0,5-1,0 kg average sample that was ground and milled (in agate mill). The lignite was dried at room temperature as well. After homogenisation average samples from each the material were prepared for both the direct analysis and for the leaching experiments. The samples of BA and FA were also separated into three particulate – size fractions using sieves.

Chemical composition of lignite, bottom ash and fly ash samples

X-ray fluorescence method was used for determination of sulphur, major element oxides, and trace elements in the lignite, limestone and ash materials and the results obtained are given in Table 1. Sulphur and major oxide contents are expressed in [wt%] and trace elements in [ppm]. Ash content values [wt%] are given for the lignite, while values of loss on ignition (L.I.) in [wt%] are related to the limestone and ash samples.

TABLE 1. Major element oxides [wt%], sulphur [wt%], and trace elements analysis [ppm] of lignite, limestone and the lignite combustion products.

	Lignite	Limestone	BA	FA
A^d or L.I.[wt%]	29.87	42.77 ^{*)}	7.59 ^{*)}	2.97 ^{*)}
SiO₂	11	1	26	34
TiO₂	2	0.02	4	7
Al₂O₃	8	< 0.2	16	28
Fe₂O₃	1	0.1	2	3
CaO	0.4	52	28	16
K₂O	0.07	< 0.03	0.1	0.2
S	1	< 0.006	3	4
Cl [ppm]	155	155	189	186
V	239	< 0.9	277	631
Cr	56	< 1.2	98	154
Co	8	< 3.0	10	19
Ni	27	5.7	36	80
Cu	186	3.3	182	577
Zn	42	24	59	96
Ge	6	< 0.9	10	13
As	14	< 0.3	24	28
Se	4	< 0.2	1	14
Br	4	1.7	0.9	8
Sn	4	1.4	11	11
Sb	0.4	< 0.1	0.7	1.2
W	8	< 3.7	10	22
Hg	1.580	0.001	0.005	1.18

Pb	10	12	17	28
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Lignite analysis is quoted on a whole-coal basis.

*) loss on ignition (L.I.)

Mineral composition

X-ray diffraction analysis was used for the determination of mineral phases in lignite and ash samples. Mineral composition of the ash samples was studied in the three particulate-size fractions of both BA and FA (BA: <0.04 mm, 0.4-2.0 mm, > 2.0 mm; FA: < 0.04 mm, 0.04-0.09 mm, > 0.09 mm). Diffractograms obtained for the particulate-size fractions of BA and FA are shown in Fig. 1. Identified minerals are given (in a semi-quantitative scale) in Table 2 (lignite and particulate – size fractions of BA and FA). The dominant minerals present in lignite there are kaolinite and quartz and a little content of pyrite and Ti-bearing minerals is expected too (see also Table 1). During the combustion kaolinite was transformed into metakaolinite and mullite.

FIG. 1. X-ray diffractograms of particle-size fractions of BA (A) and FA (B)
(1-Anhydrite, 2-CaO, 3-Portlandite, 4-Quartz, 5-Calcite, 6-Mullite, 7-Anatas)

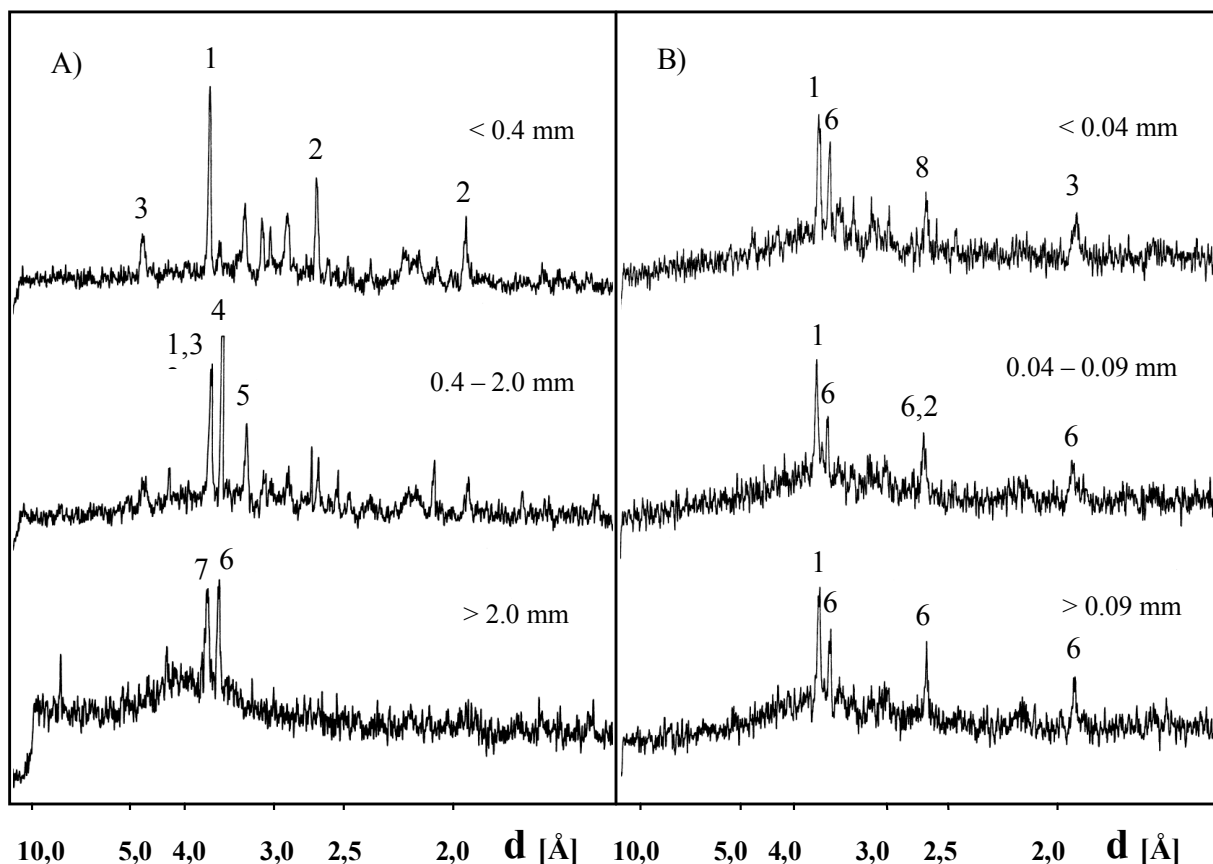


TABLE 2. Semiquantitative content of mineral phases in lignite, BA and FA particle-size fractions

	Lignite	BA (mm)			FA (mm)		
		<0.4	0.4-2.0	>2.0	<0.04	0.04-0.09	>0.09
Quartz	++	(+)	+++	+++	++	++	++
Anhydrite	-	+++	+++	-	++	++	++
Kaolinite	+++	-	-	-	-	-	-
Calcite	-	++	++	-	-	-	-
Mullite	-	?	?	?	++	++	++
Portlandite	-	++	++	-	-	-	-

CaO	-	++	++	-	+	+	+
Anatase	-	-	+	++	++	++	++

Note: +++ > 10%, ++ 5-10%, + 2-5%, (+) ?

Anhydrite, calciumoxide, portlandite, calcite and mullite were identified in the finer bottom ash fractions (< 2 mm), while quartz and anatase were dominant phases identified in the coarsest fraction of BA (>2mm). Unlike the bottom ash the mineral composition in the fly ash fractions is relatively invariable. Major mineral phases observed in FA are anhydrite, calciumoxide (lime), quartz, mullite and anatase. Abundance of these minerals in FA is in a good agreement with chemical analysis results (e.g. TiO₂ content in the coarse fraction of BA and in all fractions of FA is approx. 7.1%). The chemical analysis of the particulate-size fractions has already been presented in our previous works [21,22]. Calcite, lime, portlandite and anhydrite are minerals abundant in the combustion products, whereas in lignite relatively low content of Ca-bearing minerals was observed (see Table 2). Presence of CaO in the combustion products can be explained by big redundancy of limestone above the stoichiometric ratio to sulphur.

Results and discussion

Reproducibility of the leaching procedure

Sequential leaching procedure of all the samples was performed by each of the solvents in duplicate. In general, the most consistent data was obtained for Cu, Ni, Co, and Cr. Quite worse reproducibility obtained for Pb, As and Se, could be brought about probably by very low concentrations of these elements in measured samples. Reproducibility of Cu (and also that of Ni, Co, Cr) and reproducibility of Pb (approx. represents also that of As and Se) is given in Figs.2A and 2B, respectively. In both Figures reproducibility is expressed as µg of Cu (Pb) leached by given solvent (or present in solid residue) from the total amount of the element present in 1 g of parent sample before the leaching procedure, i.e. in ppm.

FIG. 2A. Comparison of two independent parallel Cu analyses

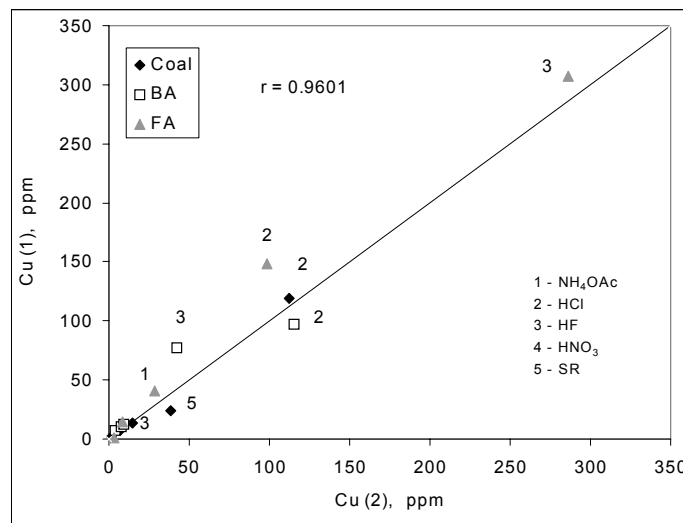
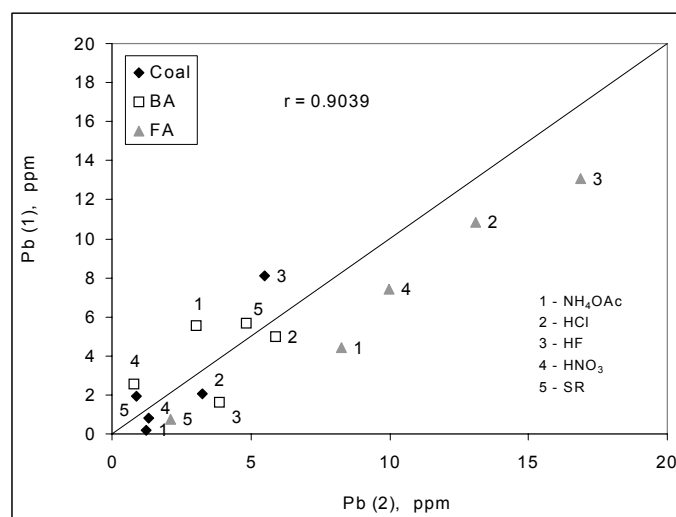


FIG. 2B. Comparison of two independent parallel Pb analyses



Sequential leaching results

For better understanding the behaviour of the elements during the lignite combustion the samples of lignite, BA and FA were sequentially leached by the following four solvents: 1) 1M NH₄OAc, 2) 3M HCl, 3) concentrated HF and 4) 2M HNO₃. Insoluble solid residue made us the fifth sample. The major results obtained by the leaching tests are given in Table 3. Table 3.1. relates to the sequential leaching data of the lignite sample, Tables 3.2. and 3.3. to BA and FA, respectively. The first five columns of Tables 3.1.-3.3. contain percentages of each element leached by a given leaching solvent or present in solid residue. In the sixth column of the tables the sum of the element determined in stages 1-5 is expressed in ppm (i.e. in µg of the element per 1g of the original sample before the extraction). Total amount of the element in the parent sample before the leaching is given in Table 1 and also in the 7-th column of Tables 3.1. –3.3. for the comparison with the 6-th column.

TABLE 3. Percentages of the elements in the five separation stages of sequential leaching for unfractionated coal, BA and FA samples.

TABLE 3.1 Lignite

	1M NH ₄ OAc	3M HCl	conc. HF	2M HNO ₃	Solid residue	Sum	CH.A.
	[%]					[ppm]	
Cr	0.6	8	25	12	55	50	56
Co	3	20	61	3	12	10	8
Ni	1	28	49	9	13	33	27
Cu	1	68	8	4	18	170	186
As	0.3	35	26	26	14	13	14
Se	0.1	2	85	11	2	3	4
Pb	6	21	54	8	11	13	10

TABLE 3.2 Bottom ash

	1M NH ₄ OAc	3M HCl	conc. HF	2M HNO ₃	Solid residue	Sum	CH.A.
	[%]					[ppm]	
Cr	1	7	15	7	71	119	98
Co	17	22	56	6	0	12	10
Ni	7	9	22	2	59	47	36
Cu	3	55	31	5	6	192	182
As	0.01	83	16	1.0	0.6	30	24
Se	0.7	0.3	94	5	0.05	2	1

Pb	22	28	14	9	27	19	17
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TABLE 3.3 Fly ash

	1M NH ₄ OAc	3M HCl	conc. HF	2M HNO ₃	Solid residue	Sum	CH.A.
	[%]					[ppm]	
Cr	3	10	49	31	8	179	154
Co	4	11	81	4	0	20	19
Ni	6	13	71	4	7	122	80
Cu	7	26	63	3	0.4	469	578
As	3	64	30	2	0.5	44	28
Se	0	0.2	97	3	0	16	14
Pb	15	28	35	20	3	43	28

Chromium

In lignite the content of Cr is 56 ppm. During the lignite combustion it was redistributed between bottom ash (98 ppm) and fly ash (154 ppm). Major experimental data are illustrated in Fig. 3. In the lignite sample about 55% of total Cr was not leached by any solvent indicating major association to organic matter. Percentage of Cr removed by NH₄OAc and HCl is altogether less than 10% which suggests that chromium was not bound as exchangeable ion and its affinity to monosulphides and carbonates was negligible. There is also minor association of Cr to kaolinite or quartz (25%). Similarly as in case of lignite, in BA large percentage of unleached Cr was observed (71% of total Cr) in insoluble residue. Regarding the fact that BA was nearly free of organic matter, association of Cr with insoluble oxides (i.e. chromite) or with amorphous glassy phase (having been generated during the combustion) seems to be more probable [12,14]. Affinity to anatase cannot be excluded too. Leaching behaviour of Cr from FA quite differs from that of lignite and BA: large percentage of Cr was removed by HF (49%) indicating probably major association to glassy amorphous phase. Proportion of non-crystalline phases in two ash samples (having been prepared in laboratory at 850°C) was indirectly determined to be about 50% and 85% [20]. Only 8% of total Cr remained unleached in the solid residue.

Cobalt

The sample of lignite tested contained 8 ppm of Co, BA approx. 10 ppm and FA about 19 ppm. Thus, there is an enrichment of Co in FA vs. BA. Fig. 4 documents the leaching behaviour of Co, which can be summarized as follows: the total proportion of Co that was leached out from the lignite sample makes up 88%, i.e. 12% of Co was associated with the organic matter. Most of Co was removed by HF (61%) indicating major affinity with kaolinite or quartz in the lignite. Minor percentage (about 20%) of Co was HCl-soluble, which could suggest association with carbonates and / or monosulphides. Approx. 3% of Co extracted by each NH₄OAc and HNO₃ indicates that Co was not bound as exchangeable ion and its affinity with pyrite was negligible. Most of Co from BA and FA samples was leached out by HF (56 and 81%, respectively), which is a trend similar to that of lignite, where association with glassy amorphous phase was the most dominant feature as well. On the contrary, 12% of organically bound Co in lignite has dropped during the combustion to almost 0%, which reflects very low content of organic matter in the combustion products.

FIG. 3. Distribution of Cr (%) in the five separation stages of sequential leaching for the lignite and ash samples. 1) 1M NH₄OAc 2) 3M HCl 3) conc. HF 4) 2M HNO₃ 5) Solid residue.

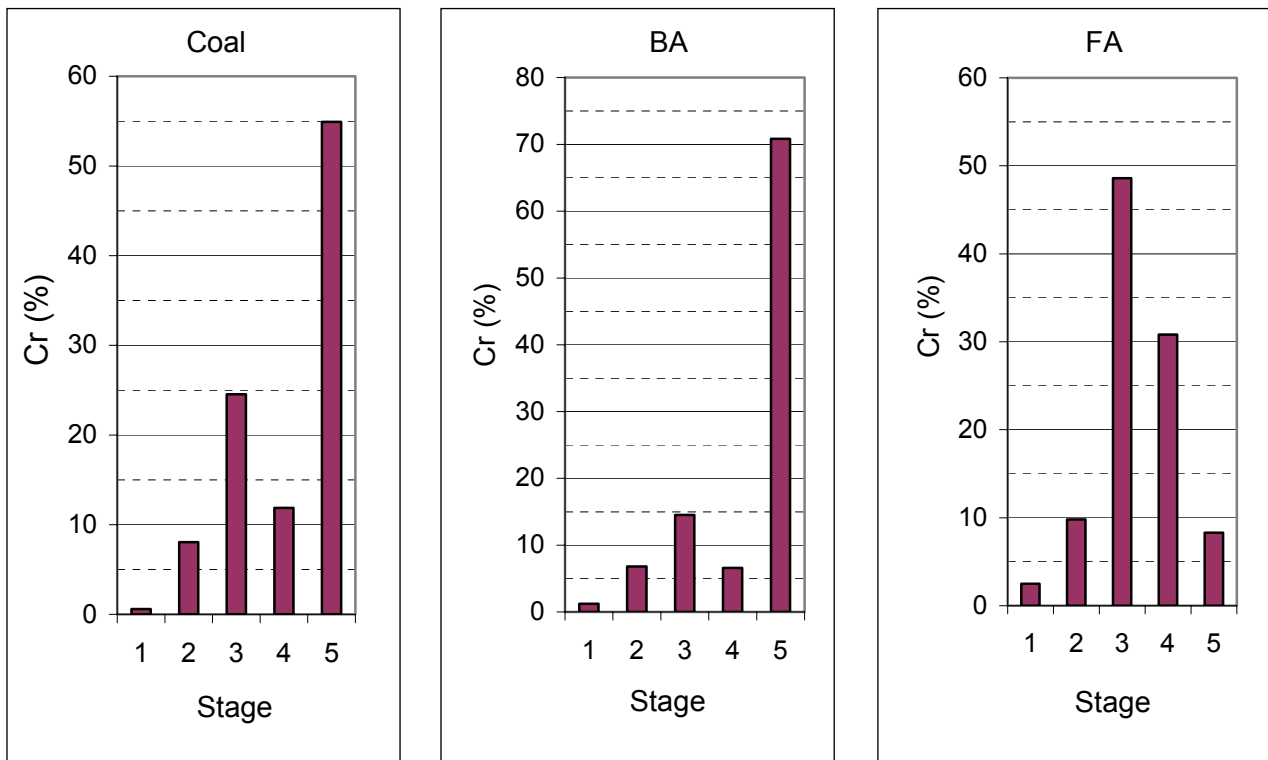
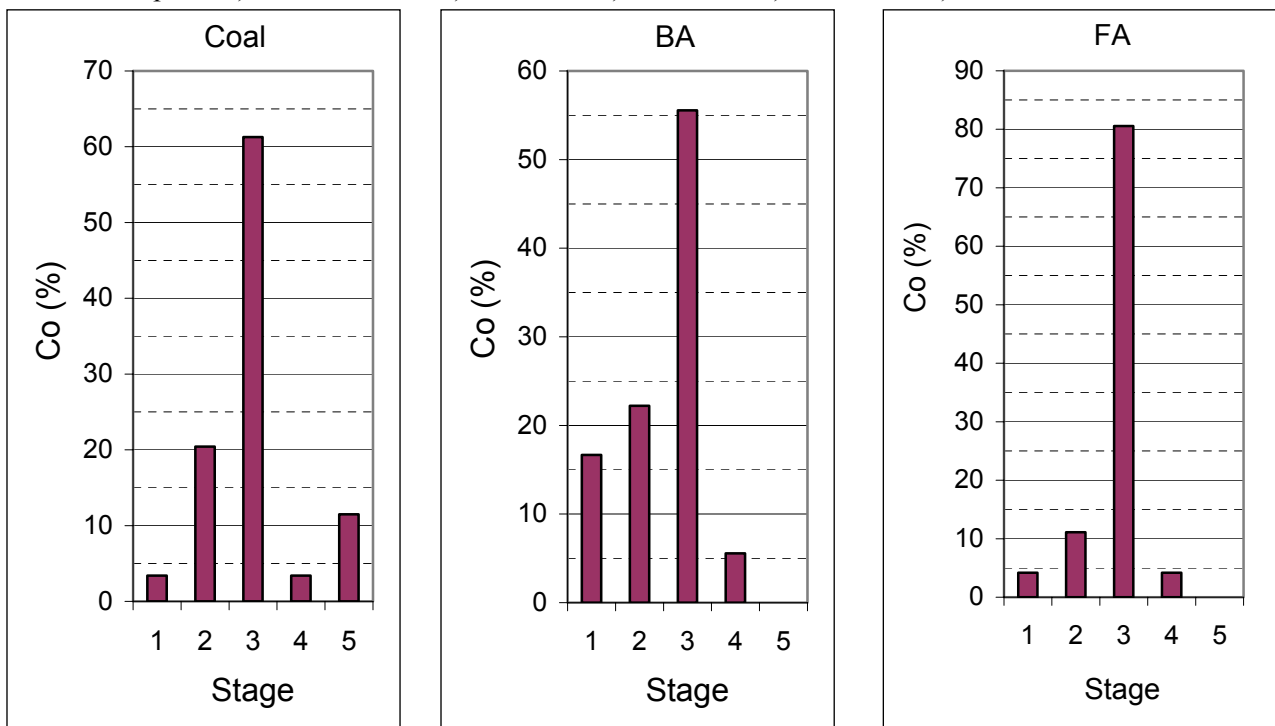


FIG. 4. Distribution of Cr (%) in the five separation stages of sequential leaching for the lignite and ash samples. 1) 1M NH₄OAc 2) 3M HCl 3) conc. HF 4) 2M HNO₃ 5) Solid residue.



Nickel

The Ni content in lignite, BA and FA were 27 ppm, 36 ppm and 80 ppm, respectively. The enrichment in FA relating to BA was observed similarly as in case of Co and Cr. Major results are also shown in Fig. 5. The main conclusions are summarised below: as for the lignite, leaching behaviour of Ni is of the same trend as in case of Co. The total amount of Ni leached out from the sample was 87% and corresponds to inorganic associations of Ni. Unleached 13% of Ni relate to organic associations. Most of Ni was removed by HF (49%) and by HCl (28%) suggesting dominant quartz and kaolinite affinity and carbonates / monosulphides associations. Proportion of NH₄OAc- and HNO₃-extractable Ni was not of greater significance (it is

attributed to Ni that is bound as an exchangeable ion or associated with pyrite). Leaching behaviour of Ni from BA was very different from that of lignite. Large proportion of Ni in BA was not leached by any of the solvents (59%). Regarding the fact that there is a very little amount of the organic mater in BA, Ni must have been bound in acid - insoluble compounds. Prevalent association of Ni in FA sample was above all to glassy amorphous phase, since 71% of total Ni was removed by HF. Other affinities of Ni were not of greater significance in FA.

Copper

XRF analysis results showed similar content of Cu in the lignite and BA (approx. 185 ppm), while FA contained quite higher amount of Cu (578 ppm) indicating enrichment of Cu in FA vs. BA. Leaching procedure results are summarised in Fig. 6. Most of Cu (68%) in lignite was in HCl-soluble form, which suggests carbonates and / or monosulphides association. About 18% was not extracted and this proportion relates to organically bound Cu, an abundance of Cu-bearing shielded minerals in organic matter is possible too. Percentages of Cu leached by NH_4OAc , HF, and HNO_3 are negligible. Fig. 6 suggests some common features in leaching behaviour of Cu from BA and FA. Both ash samples showed negligible proportions of NH_4OAc , HNO_3 , and in solid residue, thus, Cu was not bound organically. The difference was observed in distribution of Cu between HCl and HF leachates. In BA larger quantity of Cu was leached out by HCl (55%), while for FA greater amounts HF-soluble Cu was observed (63%). Affinity with glassy amorphous phase and that with HCl-soluble compounds were dominant features of leaching behaviour of Cu in the ash samples.

FIG. 5. Distribution of Ni (%) in the five separation stages of sequential leaching for the lignite and ash samples. 1) 1M NH_4OAc 2) 3M HCl 3) conc. HF 4) 2M HNO_3 5) Solid residue.

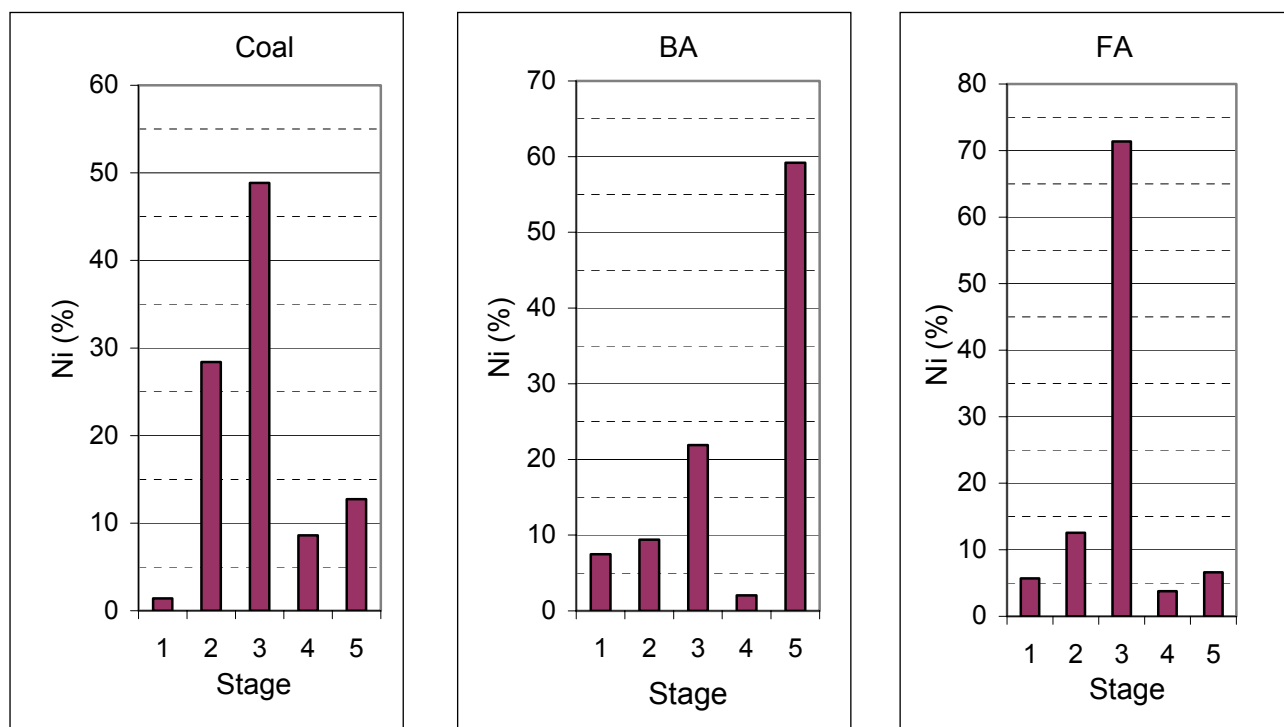
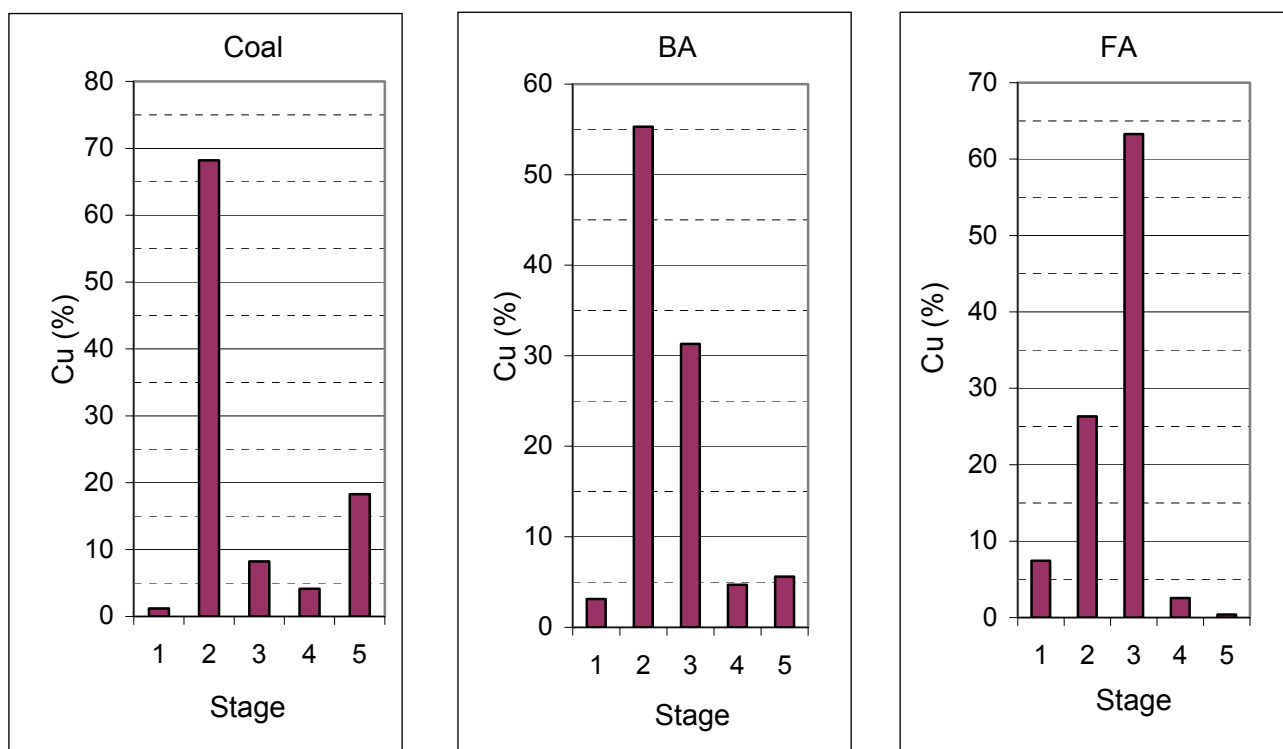


FIG. 6. Distribution of Cu (%) in the five separation stages of sequential leaching for the lignite and ash samples. 1) 1M NH_4OAc 2) 3M HCl 3) conc. HF 4) 2M HNO_3 5) Solid residue.



Arsenic

In the lignite the concentration of As was 14 ppm and during the combustion it was distributed quite evenly between BA (24 ppm) and FA (28 ppm). Fig.7 documents leaching behaviour of As that can be summarised as follows: in the lignite sample As was distributed rather evenly among HCl (35%), HF (26%) and HNO₃ (26%) leachates indicating sulphides affinity and association with quartz or kaolinite. Even if pyrite was not identified by direct XRD analysis, presence of As in it is possible. Concentration of As in pyrite can reach e.g. 1,6% [24], and therefore very low content (e.g. 0,09 %) of FeS₂ can bear all As present in the studied coal (14 ppm). Unfortunately, direct determination of pyrite of so low content is very difficult to determine. Approx. 13% of total As was not extracted by any of the solvents, which can be interpreted as minor affinity to organic matter itself or abundance of shielded As-bearing minerals. No exchangeable As was observed in the lignite. Distribution of As among the five stages of sequential leaching procedure obtained for the combustion products differs quite a lot from that of lignite. The dominant feature is increased proportion of As in HCl-leachable form in BA (83%) and FA (64%) samples, whereas percentage of HF-soluble As have not changed significantly (16 and 30%, respectively). We interpret this observation through the thermal transformation of As-bearing sulphides to the compounds soluble in HCl (probably oxides or arsenates that are HCl-soluble [11,13]). Percentages of As in NH₄OAc- and HNO₃-extractable form and in solid residue are negligible (each less than 3%).

Selenium

Redistribution of Se during the combustion from the lignite (4,4 ppm) between BA (1,2 ppm) and FA (14 ppm) reflects the volatile behaviour of Se. That is why FA is considerably enriched in Se relating to BA. Major data from the leaching behaviour of are given in Fig. 8. Fig. 8 illustrates the dominant feature in leaching behaviour of Se in the lignite – dominant solubility in HF (association with kaolinite and / or quartz – 85%). There is also minor affinity of Se to pyrite (11% in HNO₃-extractable form). Even if it is improbable to effect the total mass balance of Se, also lead selenide is another alternative for HNO₃-soluble Se [14]. Other affinities of Se are not of greater significance (less than 4% altogether). After the combustion process mobility of Se has not changed at all – vast proportion of Se in BA and FA was leached out by HF (94% for BA and 97% for FA). Solubilities of Se in other solvents as well as its abundance in solid residue were neg-

ligible. Since Se belongs to the group of the most volatile elements, only Se that was bound very firmly (e.g. with glassy amorphous phase) remained in the combustion products. Other forms of Se were volatilised.

FIG. 7. Distribution of As (%) in the five separation stages of sequential leaching for the lignite and ash samples. 1) 1M NH₄OAc 2) 3M HCl 3) conc. HF 4) 2M HNO₃ 5) Solid residue.

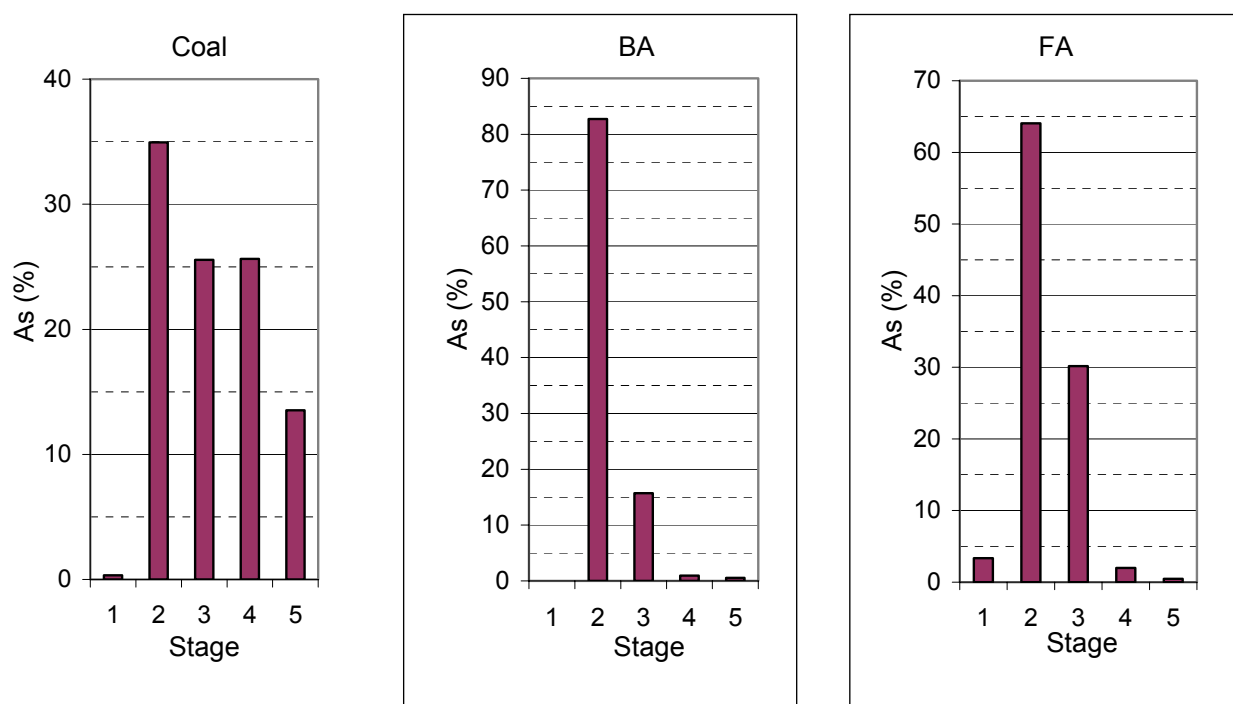
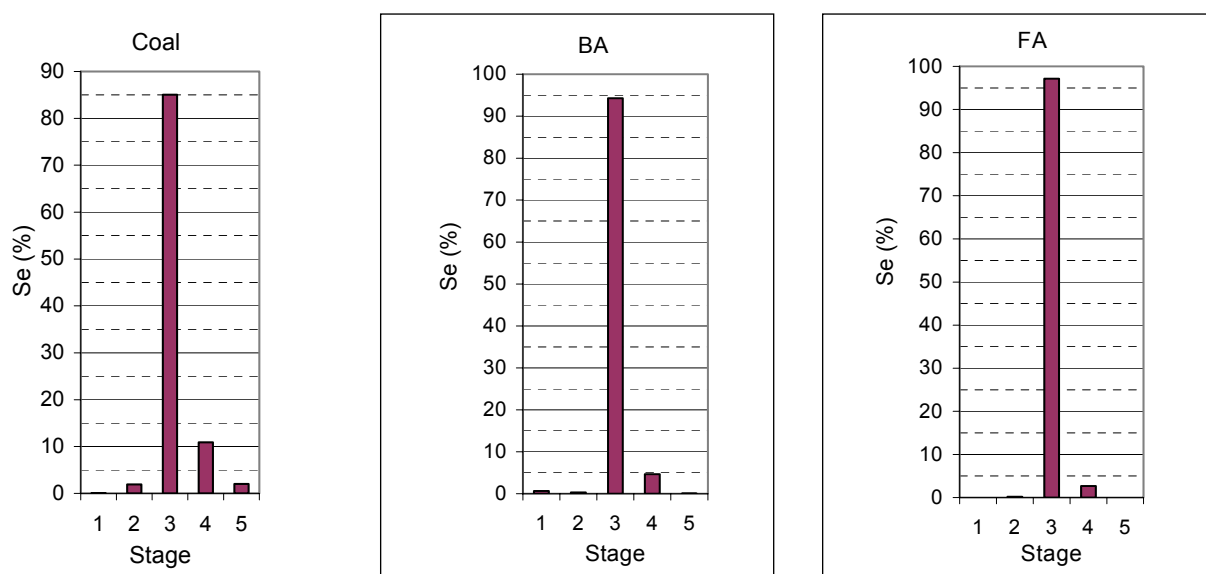


FIG. 8. Distribution of Se (%) in the five separation stages of sequential leaching for the lignite and ash samples. 1) 1M NH₄OAc 2) 3M HCl 3) conc. HF 4) 2M HNO₃ 5) Solid residue.

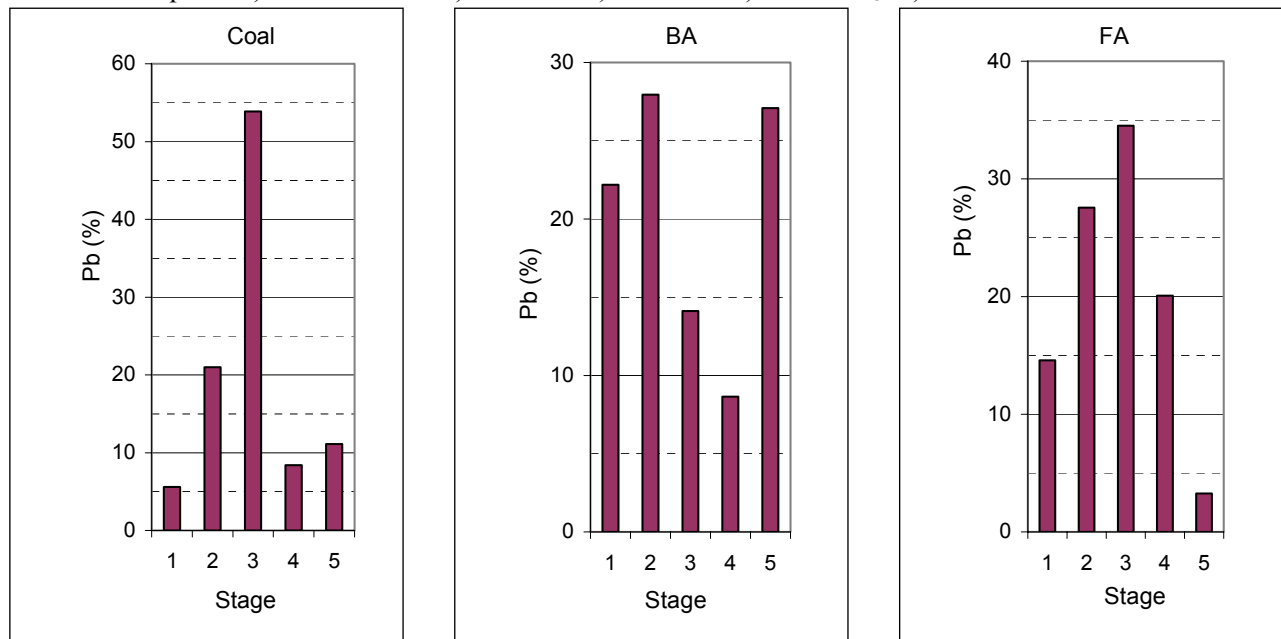


Lead

The sample of lignite contained 10 ppm of Pb, BA about 17 ppm and FA approx. 28 ppm. Leaching behaviour of Pb is documented in Fig. 9. In the lignite sample about 54% of Pb was in HF-extractable form suggesting association with quartz and / or kaolinite. There is also 21% of total Pb that was soluble in HCl, which is attributed to monosulphides / carbonates affinity. Approx. 11% was not leached at all. This can be explained as a minor association to the organic matter itself or abundance of shielded Pb-bearing minerals (e.g. galenite). Rather surprising is the fact that 22% of Pb in BA and 15% in FA were in NH₄OAc-soluble form. Perhaps, this observation could suggest presence of some water-soluble Pb-compounds. In BA,

the distribution of Pb among the five leaching procedure stages is quite even - 22% in NH₄OAc leachate, 28% in HCl leachate, and 14% in HF-leachate. About 27% of total Pb in BA were not leached out at all. This observation can be explained by the presence of insoluble Pb compounds (having been created during the combustion) rather than organic association. In FA sample the dominant proportion was extracted by HF indicating association with glassy amorphous phase.

FIG. 9. Distribution of Pb (%) in the five separation stages of sequential leaching for the lignite and ash samples. 1) 1M NH₄OAc 2) 3M HCl 3) conc. HF 4) 2M HNO₃ 5) Solid residue.



Conclusions-Summary

For lignite, bottom ash (BA) and fly ash (FA) samples successive leaching procedures were applied and the behavior of Cr, Co, Ni, Cu, As, Se and Pb was investigated with the following conclusions: in case of lignite the trace elements were distributed between leachates (mostly inorganic association) and solid residue (above all organic association). In general, the proportion of trace elements in insoluble residue was less than 20%, the only exception was 55% of insoluble chromium. Solubility of all trace elements in NH₄OAc were negligible, less than 6%. Se, Pb, Se, Co and Ni were predominately extracted by HF indicating major aluminosilicate associations. Essential part of Cu was in HCl-leachable form (monosulphides/carbonates affinity) and the same was true for As, although there was also significant solubility in HF and HNO₃ (clay minerals and pyrite associations). In case of combustion products the mobility of Se and Co from ash samples indicated the same dominant feature as in case of lignite. Prevalent proportion of these elements was extracted by HF which suggested a clay mineral association. Most of As was soluble in HCl and this observation could be explained through presence of thermal transformation products of As-bearing sulphides in lignite that were originally HCl- and HNO₃- soluble. Leaching behavior of Cu is more complicated: in BA - it is nearly the same as that of Co (prevalent clay mineral association), whereas in FA the behaviour is similar to that of As (dominant presence of HCl leachable compounds). In BA and FA samples Pb was distributed in the most even manner (betwixt the five leaching stages) among the elements tested, so that there was not any dominant association, but a lot of various affinities was observed. The leaching behavior of Cr and Ni in combustion products was quite similar – in FA large percentage share was in HF-extractable form (aluminosilicate minerals) while in BA vast amount of these elements remained in insoluble form (organic association was not probable due to small proportion of carbon matrix in BA sample).

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Resumé

Vzorky hnědého uhlí a jeho produktů spalování (ložový popel, úletový popílek) byly postupně louženy těmito činidly – NH_4OAc , HCl , HF a HNO_3 , přičemž pozornost byla zaměřena na extrakční chování Cr , Co , Ni , Cu , As , Se a Pb . Obsahy těchto prvků ve výlužích byly stanoveny metodami FL AAS a ICP-AES, v pevných vzorcích metodou XRF. Nejvýznamnější výsledky je možné shrnout do několika bodů: během sekvenční extrakce byla celková množství prvků rozdělena mezi výluhy (anorganická asociace) a pevný zbytek (nejčastěji organická asociace). U vzorku hnědého uhlí byly podíly prvků v nerozpustném zbytku obecně nižší než 20% z celkového množství (pouze s výjimkou 55% nerozpuštěného Cr). Rozpustnost všech prvků v NH_4OAc byla v podstatě zanedbatelná (méně než 6%). Se , Pb , Co a Ni byly v případě uhlí z největší části vyextrahovány pomocí HF , což souvisí s významnou asociací těchto prvků s křemenem a/nebo kaolinitem. Dominantní část Cu byla rozpustná v HCl (afinita k monosulfidům / uhličitánům), což platí i pro As , ačkoli zde byla pozorována i významná rozpustnost v HF a HNO_3 související s afinitou ke kaolinitu, křemeni či pyritu. Co se týče produktů spalování hnědého uhlí (ložového popela a úletového popílku) extrakční chování Se a Co vykazovalo podobné základní rysy jako u hnědého uhlí – převládající část těchto prvků byla vyextrahována pomocí HF (asociace s amorfní skelnou hmotou). Většina As byla rozpustná v HCl , což souvisí s výskytem produktů tepelné transformace sulfidů obsahujících As , které byly původně rozpustné v HCl a HNO_3 . Extrakční chování Cu při vyluhování úletového popílku se velmi podobalo chování Co (dominantní asociace s amorfní skelnou hmotou), zatímco u ložového popela bylo podobné spíše chování As (výrazná přítomnost sloučenin rozpustných v HCl). Ve vzorcích ložového popela a úletového popílku nebyla pro Pb pozorována žádná jednoznačně dominantní asociace, jelikož jeho celkové množství bylo ze všech studovaných prvků rozděleno nejrovnoměrněji mezi jednotlivé výluhy a pevný zbytek. Extrakční chování Cr a Ni bylo vzájemně podobné – v úletovém popílku byla u obou prvků zjištěna vysoká rozpustnost v HF (afinita s amorfní skelnou hmotou), zatímco v ložovém popelu velký podíl těchto prvků zůstal v pevném zbytku po loužení (zde jde vzhledem k malému obsahu organické hmoty v produktech spalování spíše o přítomnost v kyselinách obtížně rozpustných sloučenin než o přímou organickou asociaci).

Recenzent: Prof. RNDr. Peter Baláž, DrSc., Ústav geotechniky Košice