

SEQUENTIAL EXTRACTION OF COAL AND UNBURNED CARBON FROM CIRCULATING FLUIDISED-BED POWER STATIONS

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Abstract

This work deals with modes of occurrence of Cu, Co, Cr, Ni, Pb, As and Se in coal and unburned carbon – waste material present in ash after coal combustion at fluidised-bed power stations. Associations of these elements were determined by sequential extraction using 1M ammonium acetate, dilute HCl, concentrated HF and dilute HNO₃. The results obtained for unburned carbons suggested that about 60% of each element was either soluble in HF or acid-insoluble (low danger to the environment). The solubility of these elements in HCl and HNO₃ represent a medium risk to environment – it ranges from 30 to 40%. And as for easily-soluble forms of these elements (significant danger to the environment), less than 1% of Cu, Ni, Cr, Se, and Co and generally less than 3% of As and Pb was bound in this form. Cu was in coals associated with sulphides or organically bound. During the combustion (and thermal decomposition of sulphides) the volatilised Cu was partly captured in aluminosilicate matrix. Ni was associated predominantly with silicatic / aluminosilicatic compounds and sulphides, in unburned carbons it was also bound in the form of insoluble compounds. The most significant affinities of Cr were to pyrite, chromite or direct organic association. Co occurs mainly in silicatic / aluminosilicatic compounds and sulphides. Pb was associated prevalently with sulphides (pyrite, galena), quartz and aluminosilicates. As was bound in monosulphides, arsenates, oxides or silicatic / aluminosilicatic compounds. During the combustion As has been captured in silicatic / aluminosilicatic compounds (e.g. amorphous glassy phase) and insoluble As compounds have been created. Se occurs in coals predominantly in pyrite, quartz and aluminosilicates and in the form of PbSe. In unburned carbons the major part of Se was attributed to silicatic / aluminosilicatic and insoluble compounds.

Key words: coal combustion, trace elements, sequential extraction, unburned carbon, fluidised bed

1. Introduction

Since large proportion of the electricity generation in the Czech Republic is being covered especially by the combustion of coal in thermal power stations, solid fossil fuels are still dominant sources for the electricity production in the Czech Republic. 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].

Abundance of trace elements in coal fuels varies according to the conditions of coal origin, rank and geological history. Thus, they are present in coal in wide concentration ranges ^[2]. Understanding the modes of occurrence of elements in coal is important because it dictates its behaviour and its technological, environmental and economic impact. Knowing the different chemical species is essential for prediction of behaviour of elements during weathering, coal-cleaning process and combustion ^[3-5].

During coal combustion the elements are redistributed among coal combustion products i.e. bottom ash, fly ash and emissions. All solid coal combustion products contain small amount of coal residue – unburned carbon (UC). Even if unburned carbon content in ash samples is about several per cent, owing to vast amount of combustion products that are generated annually the amount of unburned carbon is significant. In recent years, particular attention is paid to the characterization of

unburned carbon particles in order to use this combustion waste as a combustion by-product [6,7]. Since some recent works indicated positive correlation of Hg and unburned carbon content in fly ash [8,9], the capture of volatile elements present in flue gas on unburned carbon particles is rather promising. And this is also the reason why the possibility of utilization of the unburned carbon as low-cost adsorbent is being intensively studied.

Understanding the modes of occurrence of elements in unburned carbon can provide important information for further technological, environmental and economic utilization of this waste material. Moreover, comparison of modes of occurrence of elements in coal and corresponding unburned carbon can help to evaluate the behaviour of elements during the combustion process.

In this work sequential leaching procedure was used in order to describe the associations of trace elements in bituminous coal, lignite and unburned carbon samples. Due to its good reliability and relative simplicity the sequential extraction procedure used by many researchers [4,5,10] was adopted.

Sequential leaching test was applied to samples collected at two circulating fluidised-bed (CFB) power stations which combusted lignite and bituminous coal together with limestone and at two combustion tests at CFB power station which co-combusted coal and wastes. At all the power stations always parent coal and unburned carbon (UC) from bottom ash were studied. Owing to different volatility and potentially hazardous effect the following seven elements were selected for this study: there are Cr, Co, Ni, Cu, As, Se, and Pb.

2. Materials and methods

2.1 Combustion facility and samples

In this work attention was drawn to modes of occurrence of 7 elements in 4 coal and 4 unburned carbon samples collected at Poříčí, Tisová and Energetika Frantschach Štětí power stations. All the power stations are equipped with circulating fluidised bed and coal is combusted there at 850°C together with limestone due to desulphurisation of flue gas. Description of combustion has already been reported [11]. In Poříčí power station bituminous coal and in Tisová power station lignite was combusted. In Energetika Frantschach Štětí lignite was co-combusted also with wastes - in test 1 with wood and tree bark, in test 2 with wood, tree bark, sewage sludge, waste rubber, fabric and paper.

The samples were taken at regular time intervals (30 min) over approximately a 6-h period after the fluidised-bed boiler reached a steady state. After homogenisation representative samples from each material were prepared for analysis. As the unburned carbon grains were of several millimetres in size, they were separated from bottom ash by hand.

2.2 Analytical methods

Chemical analysis of solid samples was performed by energy-dispersive X-ray fluorescence analysis on SPECTRO X-LAB.

Mineral phases were determined by powder X-ray diffraction analysis on INEL equipment using low-temperature ashes prepared from the samples at 300°C.

Cr, Co, Cu, Ni and Pb in solutions were determined by AAS method on SPECTRAA-30/40 VARIAN, As and Se were determined by ICP-AES method (Jobin-Yvon 24). Solutions containing HF or HCl were brought to dryness (on hotplate) and then dissolved in 2% HNO₃ before analysis.

Ash content and L.O.I. values of the samples were determined gravimetrically at 815°C using muffle furnace.

2.3 Leaching procedure

Owing to its relative simplicity and good reliability we adopted the sequential extraction method described in literature [4,5,10]. This method was applied to both coal and unburned carbon samples, which enables mutual comparison of results obtained.

Duplicate 5 g of the samples (< 0,09 mm) were suspended in 250 ml PP bottle (at room temperature) with 35 ml of ammonium acetate (1 mol dm⁻³) and shaken for 18 hours. Then the suspension was centrifuged and the supernatant solution was transferred into a 50 ml volumetric flask. After two washings of the solid residue with 5 ml of deionised water the leachate was stabilised by 1 ml of concentrated HNO₃. The total volume in the flask was made up to 50 ml with deionised water. The procedure was then repeated using hydrochloric acid (3 mol dm⁻³), concentrated hydrofluoric acid (48%) and nitric acid (2 mol dm⁻³). The solid residue after HNO₃ stage was rinsed thoroughly with deionised water and dried.

All glassware used for the procedure was previously soaked in 20% HNO₃ and rinsed with deionised water. All reagents used were of analytical grade or better and were checked for possible trace metal contamination.

According to the experimental procedure described above, each sample was separated into 5 fractions. Interpretation of dissolved mineral phases in individual solutions and in solid residue has been adopted from the literature [4,5,10].

Ammonium acetate solution (1 mol dm⁻³) - removes exchangeable cations, loosely bound ions that may be organically associated or ions adsorbed on clays, it also dissolves some calcite.

Dilute cold HCl (3 mol dm⁻³)- is generally used to dissolve carbonates, monosulphides and acid soluble oxides.

Concentrated cold HF- dissolves silicatic and aluminosilicatic compounds

Dilute cold HNO₃ (2 mol dm⁻³)- removes disulphides (pyrite).

Solid residue- contains organically bound, "shielded" or insoluble minerals.

3. Results and discussion

3.1 Mineral analysis of coals and unburned carbons

The most abundant minerals in all the samples studied were quartz (5-10%), kaolinite and mica (2-5%). Very low content of anhydrite and anatase were identified as well.

Low content of pyrite can be expected in all the coals but the amount in these samples fell below the detection limit of the X-ray diffraction spectrometer. In unburned carbons the occurrence of amorphous glassy phase is expected as well (due to its non-crystalline character it was not able to be determined by X-ray diffraction method.)

Sequential extraction of coals and unburned carbons

Using the sequential extraction procedure described above the modes of occurrence of Cu, Ni, Co, Cr, Pb, Se, and As were studied and compared for parent coal and corresponding unburned carbon collected at three power stations at four combustion tests.

Total amounts of given elements in 4 extracts and solid residue were compared with original contents of these elements in the samples prior to extraction in order to test the correctness of the procedure. Relative error obtained for all the elements in all these samples did not exceed 15%.

For general evaluation of the leaching behaviour of the particular 7 elements Figures 1-7 are given below, while Table I comprises contents of the elements in the solid samples prior to extraction and the concentrations of the elements in given leachates, which has importance for the environmental impact.

The contents of the elements in the four coal samples studied (Table I) were also compared with the data published by Bouška and Pešek [12], where average contents of many elements were calculated from several thousands of world subbituminous-and-lignite coal samples. As for the elements studied in this work – there are the following contents reported by Bouška and Pešek: Cu – 35.3 ppm, Ni – 57.2 ppm, Cr – 54.5 ppm, Co – 32 ppm, Pb – 11.1 ppm, As – 33.3 ppm and Se – 1.7 ppm. The data given in Table I indicate that contents of Cu (186 ppm) and Se (4,4 ppm) in lignite combusted in Tisová are somewhat high. On the other hand, the contents of other elements are lower than values given by Bouška and Pešek [12].

The most significant results are described below:

Arsenic

Fig. 1 indicates that in lignites (Energetika Štětí – test 2, Tisová power station) As was predominantly associated with monosulphides, arsenates and oxides soluble in HCl and also with pyrite, which is in agreement with conclusions of other researchers [4,5]. In bituminous coal the prevalent occurrence of As in pyrite was observed even if solubility in HF is still quite significant – about 40% of As was bound in quartz, kaolinite or mica.

When compared unburned carbons with parent coals, an increase of As percentage bound in silicatic compounds was found, which was the most significant in Energetika Štětí where solubility of As in HF increased from 7% (lignite) up to more than 50% (unburned carbon). In all the unburned carbons also a decrease in solubility in HCl and HNO₃ was observed indicating thermal decomposition of sulphides/disulphides followed by a release of As. Unburned carbons from Tisová and Poříčí power stations show even negligible solubility of As in HNO₃, which corresponds with total liberation of As from pyrite during the combustion process. In lignites the slight increase of the percentage of unleached As was also observed (compared to coal), thus, the creation of insoluble compounds of As during the combustion is probable.

Table I. Concentrations of the elements in leachates (mg/dm^3) and in solid residues (ppm) as well as total content of the elements in the samples prior to extraction (ppm).

	Poříčí coal	Poříčí UC	Tisová coal	Tisová UC	Štětí 1 coal	Štětí 1 UC	Štětí 2 coal	Štětí 2 UC
A ^d [%]	31.7	37.4	26.8	52.7	24.5	62.3	26.4	65.5
Cu	*43.0	*76.1	*186.0	*547.6	*14.4	*50.3	*13.3	*55.4
NH ₄ OAc	0.1	0	0.2	0.2	0	0	0	0
HCl	1.1	1.8	12.6	24.3	0.9	1.2	0.8	1.8
HF	0.3	1.5	1.5	25.8	0.2	1.8	0.1	2.9
HNO ₃	0.2	0.6	0.7	4.0	0.1	0.5	0.4	0.5
Residue	42.2	44.3	49.5	131.7	3.0	19.7	1.4	12.4
Ni	*34.1	*43.7	*27.0	*54.4	*13.4	*50.8	*10.6	*36.0
NH ₄ OAc	0.1	0	0	0.1	0	0.1	0	0
HCl	0.3	0.5	0.7	1.1	0.5	0.2	0.4	0.8
HF	1.8	2.4	1.2	1.5	0.3	2.8	0.4	1.5
HNO ₃	0.3	0.4	0.2	0.7	0.2	0.7	0.2	0.4
Residue	13.2	22.0	4.8	47.3	1.6	38.2	1.5	16.1
Cr	*42.0	*61.5	*56.0	*107.2	*28.3	*91.7	*22.0	*92.4
NH ₄ OAc	0.1	0	0	0	0	0	0	0
HCl	0.3	0.5	0.4	2.0	0.1	1.1	0.2	1.5
HF	1.1	2.3	1.3	1.7	0.4	4.2	0.3	2.5
HNO ₃	1.6	2.4	0.6	1.8	1.2	2.2	1.0	4.3
Residue	10.9	16.7	41.0	116.3	19.0	45.3	13.5	29.7
Co	*9.0	*11.7	*8.1	*16.3	*4.6	*11.5	*5.3	*11.5
NH ₄ OAc	0	0	0	0	0	0	0	0
HCl	0.1	0	0.2	0.4	0.2	0.2	0.2	0.2
HF	0.7	1.2	0.5	0.6	0.1	0.5	0.2	0.7
HNO ₃	0.1	0	0	0.4	0.1	0.2	0.1	0.3
Residue	1.6	0	1.4	3.5	0.5	7.0	0.7	3.0
Pb	*38.7	*44.0	*9.7	*26.0	*10.7	*29.3	*8.9	*34.2
NH ₄ OAc	0	0	0.1	0	0.1	0	0	0.1
HCl	2.2	1.0	0.2	0.3	0.4	0.8	0.3	0.6
HF	0.6	1.0	0.5	1.1	0.2	0.8	0.2	1.1
HNO ₃	0.2	1.1	0.1	0.7	0.3	1.5	0.3	1.4
Residue	4.0	28.6	1.6	9.9	1.3	3.4	1.2	8.3
As	*7.1	*5.6	*14.0	*12.4	*71.2	*120.5	*35.5	*70.1
NH ₄ OAc	0	0	0	0	0	0.1	0	0
HCl	0	0	0.4	0.3	4.5	3.1	2.3	0.8
HF	0.3	0.4	0.3	0.5	0.5	4.6	0.3	3.6
HNO ₃	0.3	0	0.3	0	2.5	2.1	1.1	1.1
Residue	1.3	0.7	2.6	8.0	6.1	60.6	3.9	47.4
Se	*1.2	*1.0	*4.4	*4.8	*0.9	*1.4	*0.7	*1.0
NH ₄ OAc	0	0	0	0	0	0	0	0
HCl	0.02	0.04	0.02	0	0	0	0	0
HF	0.08	0.06	0.42	0.42	0.02	0.02	0.01	0.01
HNO ₃	0.03	0	0.06	0.03	0.05	0.01	0.04	0.02
Residue	0.15	0	0.15	0.65	0.35	2.55	0.33	1.73

* total concentration of the element in the sample prior to extraction (ppm)

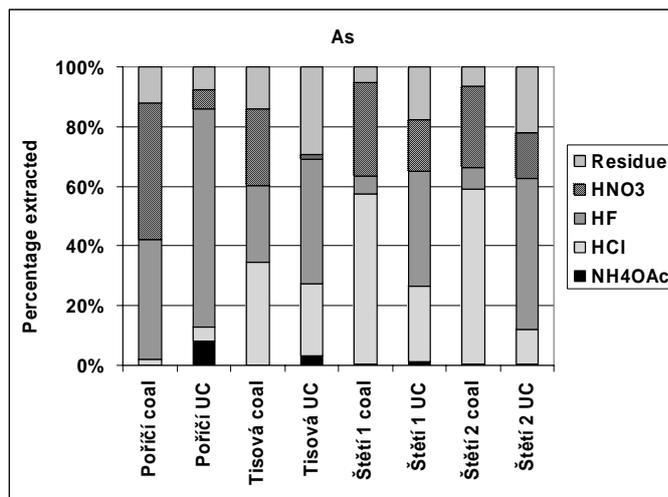


Fig. 1. Percentages of As in the five separation steps of sequential leaching (1M NH_4OAc , 3M HCl, conc. HF, 2M HNO_3 and solid residue) for 4 coals and 4 unburned carbons (UC).

Copper

Affinity of Cu in lignites was prevalently to sulphide minerals while in bituminous coal the highest percentage of Cu was not leached at all (more than 60%), which could reflect either direct organic association of Cu or its presence in the form of insoluble compounds or shielded minerals (Fig. 2). This foundation is consistent with observations described in literature [13].

During the combustion Cu was released from sulphides and was partially captured by aluminosilicate matrix (e.g. amorphous glassy phase), since the Cu solubility in HCl in unburned carbons was lower than that in coals and, on the other hand, solubility in HF increased.

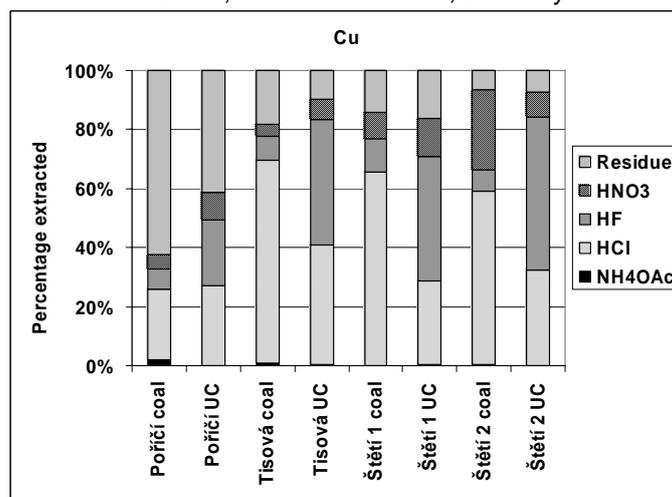


Fig. 2. Percentages of Cu in the five separation steps of sequential leaching (1M NH_4OAc , 3M HCl, conc. HF, 2M HNO_3 and solid residue) for 4 coals and 4 unburned carbons (UC).

Nickel

Leaching behaviour of Ni is given in Fig. 3. In lignites Ni was prevalently associated with sulphide minerals and silicatic and aluminosilicatic compounds (quartz, kaolinite and mica). In bituminous coal Ni showed dominant affinity to Si-containing compounds (more than 50% Ni soluble in HF). Solubility of Ni in HCl and HF is in an agreement with results in literature, however, Palmer and Filby [5] mentioned also the possibility of associations of Ni to oxides soluble in HCl.

Both unburned carbons from Energetika Štětí showed (compared to parent lignites) a decrease in solubility in HCl indicating thermal decomposition of sulphide minerals. On the other hand, solubility of Ni in HF considerably increased, i.e. part of released Ni was captured on silicatic / aluminosilicatic compounds, such as amorphous glassy phase.

Leaching behaviour of Ni in unburned carbon from Tisová power station was similar to that of Energetika Štětí – partial decrease of Ni soluble in HCl and increase of Ni bound in silicatic /

aluminosilicatic compounds. The main difference is a quite high proportion of Ni that remained unleached (nearly 40%) indicating the creation of insoluble Ni compounds.

Association of Ni in unburned carbon from bituminous coal is rather similar to the parent coal – dominant affinity of Ni to aluminosilicates and quartz was observed.

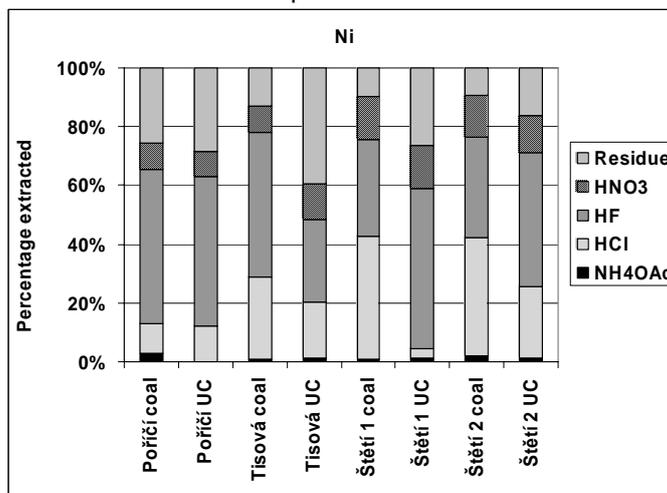


Fig. 3. Percentages of Ni in the five separation steps of sequential leaching (1M NH_4OAc , 3M HCl, conc. HF, 2M HNO_3 and solid residue) for 4 coals and 4 unburned carbons (UC).

Chromium

Major part of Cr in lignites was associated with pyrite and about 40-50% Cr was not leached at all (Fig. 4). Palmer and Filby^[5] explain unleached Cr through its occurrence in form of insoluble chromite, whereas other researchers, as Raask^[14] or Smith^[15], prefer direct organic association of Cr. In bituminous coal Cr was associated mainly with disulphides (pyrite), percentage in solid residue was only 20%.

In unburned carbons major affinity of Cr to aluminosilicate minerals (e.g. amorphous glassy phase) and its presence in unleached fraction was obtained.

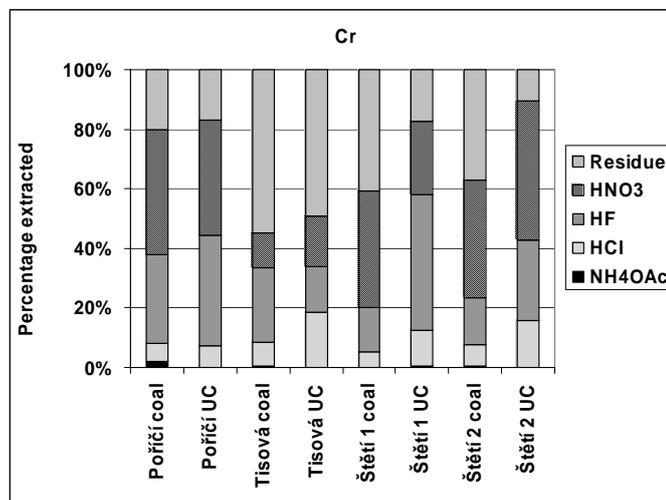


Fig. 4. Percentages of Cr in the five separation steps of sequential leaching (1M NH_4OAc , 3M HCl, conc. HF, 2M HNO_3 and solid residue) for 4 coals and 4 unburned carbons (UC).

Cobalt

Fig. 5 indicates that the modes of occurrence of Co in particular coals are quite variable. Major association of Co with silicatic / aluminosilicatic compounds was observed for bituminous coal and lignite combusted at Tisová power station (60-70%). Both lignites combusted at Energetika Štětí showed dominant association of Co with sulphides. Results published in literature also vary considerably among the samples studied^[3,15].

In all four unburned carbons originated from these coals the major association to quartz and aluminosilicates (amorphous grassy phase) was obtained (at least 40%). When leaching behaviour of Co in unburned carbons was compared with parent coals from Energetika Štětí, the decrease in

sulphides-bound Co and increase of unleached Co was obtained. This behaviour could be explained through thermal decomposition of sulphides and creation of insoluble compounds of Co.

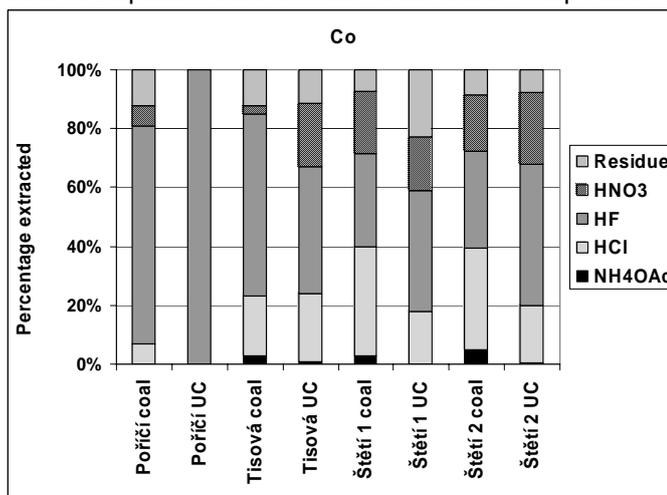


Fig. 5. Percentages of Co in the five separation steps of sequential leaching (1M NH_4OAc , 3M HCl, conc. HF, 2M HNO_3 and solid residue) for 4 coals and 4 unburned carbons (UC).

Lead

Fig. 6 suggests that all the coals studied showed somewhat minor association of Pb with silicatic / aluminosilicatic compounds (no more than 20%). The only exception was the lignite combusted at Tisová power station where the proportion of Pb extracted by HF reaches 50%. In other coals the affinity of Pb to monosulphides (above all galena) and disulphides (pyrite) was observed. Even if Pb bound in PbSe could contribute to the solubility of Pb in HNO_3 , major affinity of Pb to PbSe is not probable due to low Se content in these coals. These conclusions are in agreement with literature [5,13], where galena is thought to be the most important source of Pb in coals.

In unburned carbons from lignites the decrease of proportion of Pb soluble in HCl (galena) and increase of Pb bound in silicatic / aluminosilicatic compounds was observed. Moreover, in unburned carbon originated from bituminous coal also considerable percentage of unleached Pb was determined indicating that Pb was bound in compounds insoluble in extraction solutions.

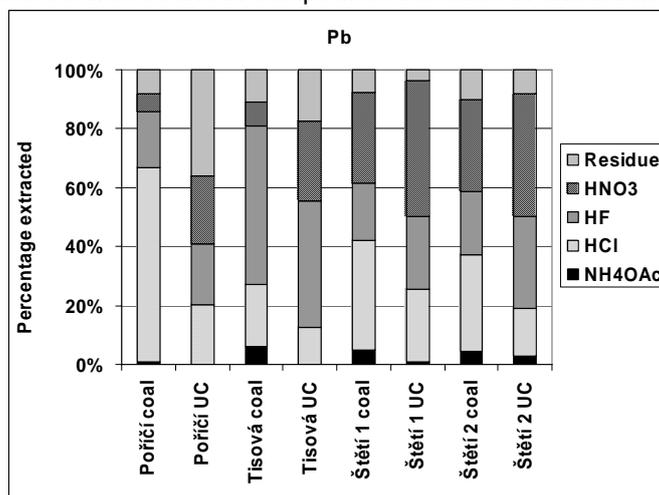


Fig. 6. Percentages of Pb in the five separation steps of sequential leaching (1M NH_4OAc , 3M HCl, conc. HF, 2M HNO_3 and solid residue) for 4 coals and 4 unburned carbons (UC).

Selenium

Leaching behaviour of Se is given in Fig. 7. In coals combusted at Poříčí and Tisová power stations major association of Se (60 and 85%) was with quartz and aluminosilicates (kaolinite and mica), which is in an agreement with conclusion of Swaine and Goodarzi [12]. But otherwise it is not very common [14,15]. In literature the sulphide affinity is supposed to be the most frequent source of Se in coals. In both lignites combusted in Energetika Štětí about 50% solubility in HNO_3 was observed, which could correspond either with affinity of Se to pyrite or its occurrence in form of PbSe that is

soluble in HNO_3 too. About 20-30% of Se was not leached at all indicating its direct organic association or its presence in form of insoluble compounds.

In unburned carbons originated from bituminous coal (Poříčí power station) and lignite (Tisová power station) the association of Se with silicatic / aluminosilicatic compounds remained the most dominant. In unburned carbons from Energetika Štětí the occurrence of Se in insoluble compounds prevailed.

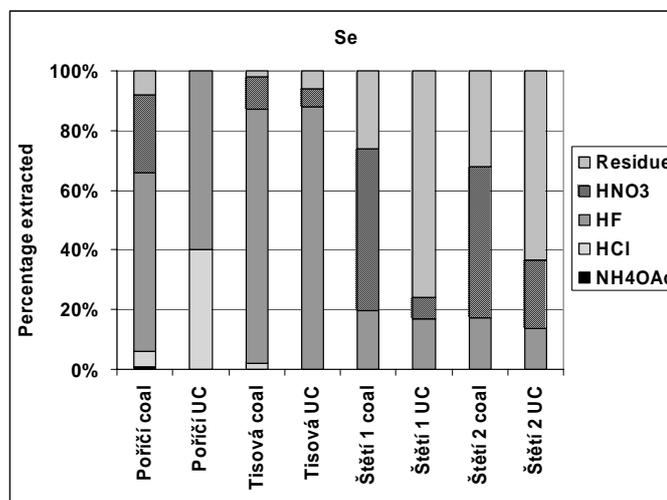


Fig. 7. Percentages of Se in the five separation steps of sequential leaching (1M NH_4OAc , 3M HCl, conc. HF, 2M HNO_3 and solid residue) for 4 coals and 4 unburned carbons (UC).

4. Conclusions

Associations of Cu, Co, Cr, Ni, Pb, As and Se in coals and unburned carbons from 3 circulating fluidised-bed power stations were determined by sequential extraction using 1M ammonium acetate, dilute HCl, concentrated HF and dilute HNO_3 .

Cu was in coals associated with sulphides or organically bound. During the combustion (and thermal decomposition of sulphides) the volatilised Cu was partly captured in aluminosilicate matrix. Ni was associated predominantly with silicatic / aluminosilicatic compounds and sulphides, in unburned carbons it was also bound in the form of insoluble compounds. The most significant affinities of Cr were to pyrite, chromite or direct organic association. Co occurs mainly in silicatic / aluminosilicatic compounds and sulphides. Pb was associated prevalently with sulphides (pyrite, galena), quartz and aluminosilicates. As was bound in monosulphides, arsenates, oxides or silicatic / aluminosilicatic compounds. During the combustion As has been captured in silicatic / aluminosilicatic compounds (e.g. amorphous glassy phase) and insoluble As compounds have been created. Se occurs in coals predominantly in pyrite, quartz and aluminosilicates and in the form of PbSe . In unburned carbons the major part of Se was attributed to silicatic / aluminosilicatic and insoluble compounds.

The modes of occurrence of these elements in unburned carbons themselves provide important information because there is an intensive tendency to find further technological utilization for the unburned carbon particles from coal combustion. The results obtained suggested that about 60% of each element was either soluble in HF or acid-insoluble, i.e. present in the form of low danger to the environment (there are only two exceptions in case of Pb in unburned carbons from co-combustion of coal and wastes). The solubility of these elements in cold dilute HCl and HNO_3 acids represent a medium risk to environment – it ranges usually from 30 to 40% for the elements studied. And as for easily-soluble forms of these elements (significant danger to the environment), less than 1% of Cu, Ni, Cr, Se, and Co was in this form, while in case of As and Pb it was slightly higher – with one exception (8%) it was less than 3%.

Acknowledgement

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