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# Volatility of Cu, Ni, Cr, Co, Pb, and As in Fluidised-Bed Combustion Chamber in Relation to Their Modes of Occurrence in Coal

L. Bartoňová, and Z. Klika

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***Abstract*****—**Modes of occurrence of Pb, As, Cr, Co, Cu, and Ni in bituminous coal and lignite were determined by means of sequential extraction using $NH_4OAc$, HCl, HF and $HNO_3$ extraction solutions. Elemental affinities obtained were then evaluated in relation to volatility of these elements during the combustion of these coals in two circulating fluidised-bed power stations. It was found out that higher percentage of the elements bound in silicates brought about lower volatility, while higher elemental proportion with monosulphides association (or bound as exchangeable ion) resulted in higher volatility. The only exception was the behavior of arsenic, whose volatility depended on amount of limestone added during the combustion process (as desulphurisation additive) rather than to its association in coal.

***Keywords*****—**Coal combustion, sequential extraction, trace elements, volatility.

## I. INTRODUCTION

COAL is important world energy component and will be widely used also in near future due to its relatively abundant reserves. But coal combustion is still accompanied by many problems. One of the most significant one is the problem of trace elements emissions, because it has great impact on surrounding environment and consequently also on human health. That is why the study of trace elements behavior during coal combustion is of high importance [1]. But environmental risk coming from the toxic elements depends not only on total amount of the elements in coal, but also on their modes of occurrence. Hence numerous studies were focused to the determination of elemental associations in coal and many direct and indirect methods are being used for the elemental affinity determination [2]-[6]. One of the most common indirect methods is using sequential extraction procedure [7]-[10].

This work is focused to the determination of elemental associations in two coals (of different rank) and in particular to the evaluation of the results in terms of these elements volatility during these coals combustion in two circulating fluidised-bed power stations. This work constitutes an extension of our previous research in the same power stations dealing with calculation of trace elements emissions or unburned carbon study in solid combustion products [11], [12].

## II. EXPERIMENTAL

### A. Combustion Units, Samples and Methods

In this work, the attention was paid to the samples of two coals of different rank – the bituminous coal (combusted at Poříčí power station) and the lignite (combusted at Tisová power station). Both power stations are equipped with circulating fluidized bed and the coals were combusted there with limestone owing to the desulphurisation of emissions. Combustion temperature was about 850˚C in both power stations. In each power station the samples of coal, limestone and bottom ash were collected, from which average analytical samples were prepared for this study.

Analysis of studied elements in the samples of coal, limestone and bottom ash was performed by means of X-ray fluorescence spectrometry on SPECTRO XEPOS. This method was used also for the analysis of the insoluble residues obtained after the leaching tests. Analyses of leachates in $NH_4OAc$, HCl, HF and $HNO_3$ (for Cr, Co, Cu, Ni, As, and Pb content) were performed using flame AAS method (PERKIN ELMER 3030) and ICP-AES technique (JOBIN YVON 24). Solutions containing HF or HCl were brought to dryness (on hotplate) and then dissolved in 2% $HNO_3$ prior to the analyses themselves. Ash content and LOI values of coals and limestone samples were determined gravimetrically at 815$^o$C using muffle furnace.

### B. Leaching Procedure

In this work the leaching procedure described and used by Finkelman et al. [7] and other researchers has been adopted.

Duplicate 5 g samples (< 0.09 mm) were sequentially leached (shaken for 18 hours at room temperature) with 35 ml each of 1M ammonium acetate ($NH_4OAc$), 3M hydrochloric acid (HCl), concentrated hydrofluoric acid (HF) and 3M nitric acid ($HNO_3$). The total volume in the flask was made up to 50 ml with deionised water. Solid residue after $HNO_3$ stage was rinsed properly with deionised water and dried at 105ºC.

Using the experimental procedure described above from

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L. Bartoňová is with VŠB-Technical University of Ostrava, Faculty of Metallurgy and Material Engineering, Department of Analytical Chemistry and Material Testing, Ostrava – Poruba, Czech Republic (420-59-699 1514, fax. 420-59-699 1665; e-mail: lucie.bartonova@vsb.cz).

Z. Klika is with VŠB-Technical University of Ostrava, Faculty of Metallurgy and Material Engineering, Department of Analytical Chemistry and Material Testing, Ostrava – Poruba, Czech Republic (420-59-699 1548, e-mail: zdenek.klika@vsb.cz).

each sample four leachates and solid residue were obtained. Interpretation of dissolved mineral phases in the leachates and of insoluble solid residue can be described as follows [7]:

| | |
|---|---|
| Stage 1: | 1M $NH_4OAc$ solution dissolves loosely bound ions and exchangeable cations |
| Stage 2: | Dilute cold HCl removes monosulphides and carbonates |
| Stage 3: | Concentrated cold HF dissolves ions with silicate affinity |
| Stage 4: | Dilute cold $HNO_3$ is used to remove pyrite and other disulphides |
| Stage 5: | Solid residue contains elements bound to insoluble minerals (e.g. chromite) and elements with organic association |

### *C. Calculation of $R_i$ Values*

Input mass flow of total inorganic matter into power station (contained in coal and limestone) can be described by (1):

$$m_{IN} = m_C . A_C + m_L . \left(1 - LOI_L\right) \tag{1}$$

where m is mass flow in kg per hour of coal (C), limestone (L) or average input mineral matter (IN) and $LOI_L$ is loss on ignition of limestone and $A_c$ is ash content in coal.

And concentration of the i-th element in this input inorganic-matter mass flow $w_{IN,i}$ can be expressed as follows (2):

$$w_{IN,i} = \frac{m_C . w_{C,i} + m_L . w_{L,i}}{m_{IN}} \tag{2}$$

where $w_i$ values are the concentrations of the i-th element in coal (C), limestone (L) and average input mineral matter (IN).

Redistribution of the elements within the fluidised-bed combustion chamber was evaluated using *Redistribution coefficient* of the i-th element $R_i$ based on the concentrations of this element in average input inorganic matter and bottom ash (collected underneath the fluidised-bed). Values of redistribution coefficient $R_i$ were calculated using the (3) and correspond to the percentage of the i-th element being volatilised out of the input mineral matter (in coal and limestone) in the combustion chamber resulting in the depletion of this element in bottom ash.

$$R_i = \frac{w_{IN,i} - w_{BA,i}}{w_{IN,i}} . 100 \tag{3}$$

where $w_{BA,i}$ is the concentration of the i-th element in bottom ash.

## III. RESULTS AND DISCUSSION

Mass flows of coal, limestone, bottom ash and average input inorganic matter as well as the concentrations of studied elements and ash contents in these materials are given in Table I (Poříčí power station) and Table II (Tisová power station). Using these data the $R_i$ values given in the last column of Tables I and II were calculated.

TABLE I
MASS FLOWS, ELEMENTAL CONCENTRATIONS AND $R_I$ COEFFICIENTS FOR POŘÍČÍ POWER STATION

| | Poříčí power station – bituminous coal combustion | | | | |
|---|---|---|---|---|---|
| | Bitum. coal $w_{C,i}$ (ppm) | Limestone $w_{L,i}$ (ppm) | Bottom ash $w_{BA,i}$ (ppm) | Input inorg. matter $w_{IN,i}$ (ppm) | $R_i$ (%) |
| m (kg/hr) | 42408 | 1141 | 5758 | 14086 | - |
| Ash (%) | 31.66 | 57.83 | 97.86 | 100.00 | - |
| Cr | 42 | <1.3 | 88 | 126 | 30 |
| Co | 9 | <3.4 | 14 | 27 | 47 |
| Ni | 34 | 5.9 | 48 | 103 | 53 |
| Cu | 43 | 2.0 | 91 | 130 | 30 |
| As | 7.1 | 1.9 | 9.4 | 22 | 56 |
| Pb | 39 | 6.8 | 53 | 117 | 55 |

TABLE II
MASS FLOWS, ELEMENTAL CONCENTRATIONS AND $R_I$ COEFFICIENTS FOR TISOVÁ POWER STATION

| | Tisová power station – lignite combustion | | | | |
|---|---|---|---|---|---|
| | Lignite $w_{C,i}$ (ppm) | Limestone $w_{L,i}$ (ppm) | Bottom ash $w_{BA,i}$ (ppm) | Input inorg. matter $w_{IN,i}$ (ppm) | $R_i$ (%) |
| m (kg/hr) | 84179 | 8520 | 2490 | 27436 | - |
| Ash (%) | 26.80 | 57.23 | 92.41 | 100.00 | - |
| Cr | 56 | <1.2 | 98 | 172 | 43 |
| Co | 8.1 | <3.0 | 10 | 26 | 61 |
| Ni | 27 | 5.7 | 35 | 86 | 59 |
| Cu | 186 | 3.3 | 182 | 571 | 68 |
| As | 14 | <0.3 | 24 | 43 | 44 |
| Pb | 9.7 | 12 | 17 | 34 | 50 |

It should be pointed out that $R_i$ values represent the volatility of the elements directly in the fluidised-bed combustion chamber in contrast to the volatility of the elements usually calculated for the whole power station where also adsorption / condensation of volatilised elements in flue gas (approaching the particulate control device) occurs and significantly decreases the calculated percentages of elements.

The sequential extraction procedure described above was applied to the samples of bituminous coal and lignite producing the leachates in $NH_4OAc$, HCl, HF and $HNO_3$ as well as the solid residue. The percentages of the studied elements (Cr, Co, Ni, Cu, As, and Pb) in the particular leachates and in solid residue is shown for both coals in Figs. 1-6.

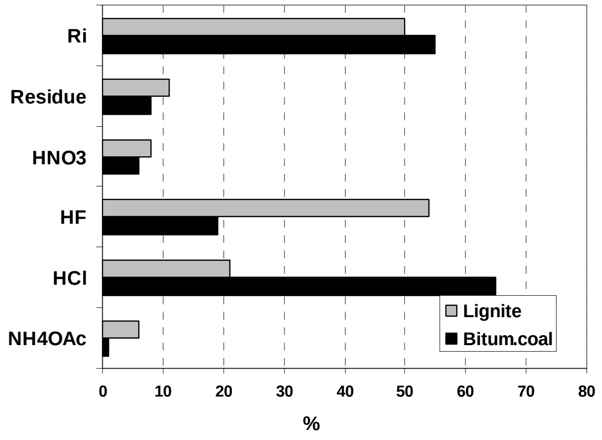

Fig. 1 $R_i$ values as well as percentages of Pb in the four leachates and solid residue for the bituminous coal (combusted in Poříčí) and the lignite (combusted at Tisová power stations)

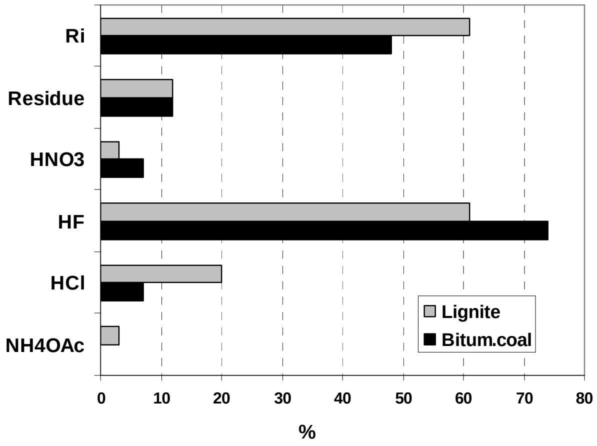

Fig. 2 $R_i$ values as well as percentages of Co in the four leachates and solid residue for the bituminous coal (combusted in Poříčí) and the lignite (combusted at Tisová power stations)

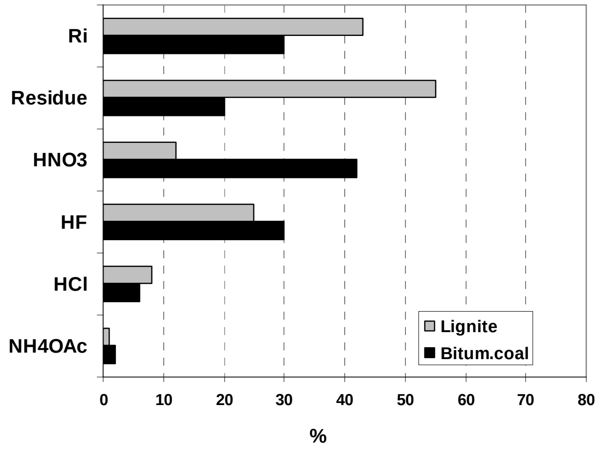

Fig. 3 $R_i$ values as well as percentages of Cr in the four leachates and solid residue for the bituminous coal (combusted in Poříčí) and the lignite (combusted at Tisová power stations)

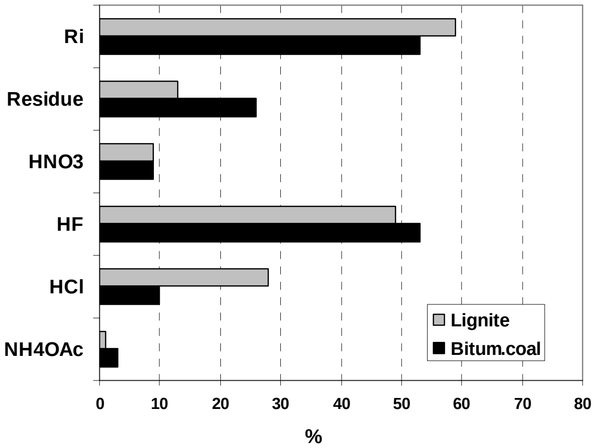

Fig. 4 $R_i$ values as well as percentages of Ni in the four leachates and solid residue for the bituminous coal (combusted in Poříčí) and the lignite (combusted at Tisová power stations)

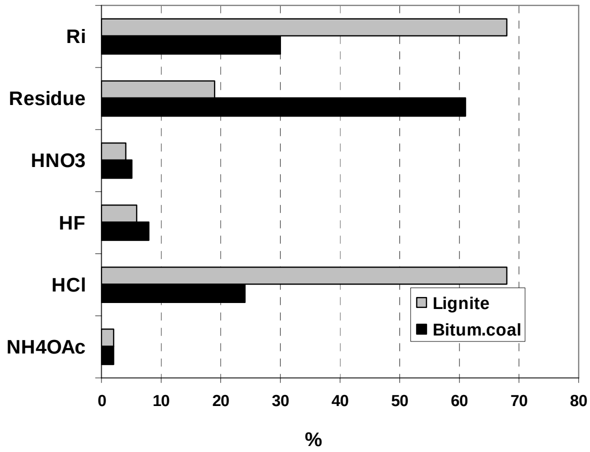

Fig. 5 $R_i$ values as well as percentages of Cu in the four leachates and solid residue for the bituminous coal (combusted in Poříčí) and the lignite (combusted at Tisová power stations)

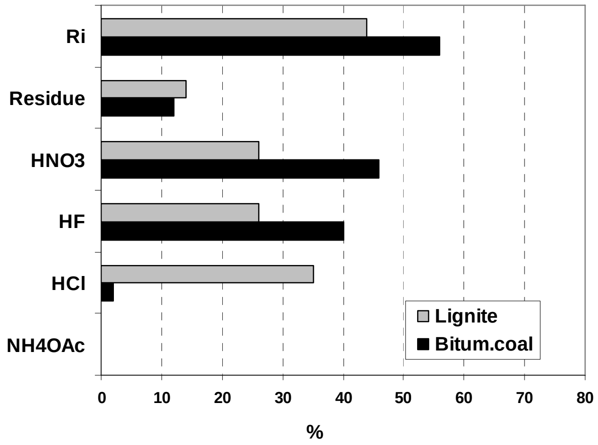

Fig. 6 $R_i$ values as well as percentages of As in the four leachates and solid residue for the bituminous coal (combusted in Poříčí) and the lignite (combusted at Tisová power stations)

Figs. 1-6 were constructed for easier and more transparent evaluation of the effect of elemental mode of occurrence on the behavior of elements during the combustion process. Since the combustion technology and combustion temperature in both power stations were rather similar, the comparison of the behavior of the elements bound in two different coals was possible. Particular attention was paid to the percentages of the elements leached with HF, because silicate-associated elements are thought to show the least volatility.

In Fig. 1 the behavior of Pb is documented showing higher percentage of Pb leached by HF in the lignite (non-volatile silicate association) and higher leachability of this element by HCl in the bituminous coal (affinity to monosulphides, the most likely to galena). Calculated volatilities ($R_i$ values) correspond well with these results because higher association of Pb to silicates in the lignite decreases Pb volatility during this lignite combustion (when compared to higher volatility of Pb in the bituminous coal with higher percentage of Pb in the form of galena).

Results documented by Figs. 2-6 suggest that higher proportions of Cu, Ni, Cr, Co, and As leached by HF was obtained for bituminous coal (combusted in Poříčí power station). On the other hand, in the lignite higher percentages of these elements was leached by $NH_4OAc$ and by HCl, which corresponds with easily volatile fraction of these elements. In case of Cu, Ni, Cr and Co these results are in a good agreement with calculated $R_i$ values that were lower for the bituminous coal where the elements showed significant silicate association.

However, the behavior of As showed the opposite trend – even if in the lignite low silicate association and considerable monosulphides association was observed, the volatility ($R_i$) calculated for this coal combustion was lower. This observation could be explained through the different amount of limestone added during the combustion in these two power stations. In Tisová power station the lignite (with higher sulphur content of 1.34%) was combusted and the amount of limestone added during the combustion was therefore considerably higher ($m_L/m_C = 0.101$). Sulphur content in the bituminous coal was lower (0.5%) and therefore the amount of limestone added during the combustion was not so high ($m_L/m_C = 0.027$). Thus, about four-times higher amount of limestone added to the lignite during the combustion at Tisová power station created rather good conditions for the decrease of As volatility (producing probably solid calcium arsenate remaining in bottom ash). Therefore the behavior of As is different in comparison with Cu, Ni, Cr and Co, because the interactions of these elements with Ca-bearing minerals are known to be of minor significance.

## IV. CONCLUSION

Comparison of elemental (Cu, Ni, Cr, Co, Pb, and As) modes of occurrence in two coals was evaluated in relation to the volatility of these elements during the combustion of these coals (with limestone) in fluidised-bed power stations.

It was found out that with increasing percentage of the elements bound to silicate minerals their volatility decreased - and vice versa - with increasing proportion of the elements bound as exchangeable ion or in monosulphides, their volatility increased.

The only exception of this rule was behavior of As due to its interactions with Ca-bearing minerals (creating most likely calcium arsenate), which had significant influence on the decrease of arsenic volatility.

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