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## A COMPARATIVE STUDY OF REMOBILIZATION OF TRACE ELEMENTS DURING COMBUSTION OF OIL SHALE AND COAL AT POWER PLANTS

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*On the basis of results from instrumental neutron activation analysis of trace elements in oil shale, coal and their combustion ashes at power plants, it has been confirmed that these elements are remobilized during the combustion process.*

### Introduction

Instrumental neutron activation analysis (INAA) was applied to measure the concentrations of 40 chemical elements in oil shale and coal and in the products of their combustion at power plants, the latter consisting of ash from different points in the furnace and stack, including fly ash. Special attention was paid to the fine fractions of fly ash, since micron and submicron particles are responsible for the long-distance transport of air contaminants. The detection limits of all measured elements which were studied were lower than their mean amounts in the earth's crust (this latter value is K).

Concentrations of heavy metals, including radioactive U and Th, and Cr, Co, Ni, Zn, Mo, Cd, Hg, etc., and toxic nonmetals - As, Se, Br, Sb - were determined in the initial fuel and its combustion products at two large power plants. The first one - the Baltic Power Plant (Estonia) - is oil-shale-fired, the second one in Chengdu (China) is coal-fired. There are many similar features in the changes of the trace element composition of combustion products of both oil shale and coal. Fly ashes are mostly enriched with volatile elements. Consequently, it is evident that the

remobilization of trace elements has taken place. The behaviour of these elements, as revealed by INAA, corresponds to the model of volatilization and condensation processes occurring during combustion of solid fuel.

Solid fossil fuels - oil shale and coal - will remain the most economic, generally acceptable and readily available fuel for power production in vast regions of the world well into the future. The total world resources of oil shale are estimated to be 11.5 Ttons and Estonian kukersite comprises 2.1 Gtons of this resource. The annual oil shale production in Estonia is about 30 Mtons, of which 20 Mtons are used in power plants.

Coal resources are abundant, as compared to other fossil fuels. On a world scale, the availability of oil and gas can be measured in decades, whereas identified coal reserves are sufficient for many hundred years. This ensures long-term availability of coal at an increasingly competitive cost.

The total annual output of coal in the entire world is presently about 3.5 Gtons. The leading countries in coal production are China, USA and Russia. China produces 1 Gton of coal annually, it makes up 75 % of China's total energy supply. In China, 70 % of particulate emissions and 90 % of discharged sulphur dioxide originate from coal burning.

Medlin and Simon [1] have pointed out that for a complete characterization of a solid fuel, not only economically important parameters, but also the entire list of chemical elements present in the fuel have to be determined. Minor and trace elements are to be included in this list, too. In fact, the minor and trace elements in coal are remobilized during mining and combustion and consequently may be released into the environment. The authors of the present paper consider a complete analysis of fuel combustion products also very essential. Although many elements are present in coal only in trace amounts, burning large amounts of coal may cause a relatively extensive contamination with trace toxic elements. For example, about 50 thousands tons of arsenic, a toxic trace element, is released into the global environment every year as a result of coal combustion [1].

Practically every improvement in the technology of fossil fuel combustion is accompanied by some changes in the composition of combustion products - whether in the ash from different points in a power plant or the fly ash. Modernization of the equipment for removal of suspended particles (e.g. cyclones, precipitators, filters) also has an effect on the composition of ash. This is especially true with fly ash, where some redistribution of chemical elements between different phases occurs. To observe these changes a multielement and sensitive analytical technique has to be used.

In the study of combustion products from solid fuel, special attention must be paid to fine fractions of fly ash. The settling rate of small particles is very low, and they may therefore remain in suspension for several days. Consequently, micron and submicron particles are responsible for the long-distance transport of air contaminants. Fine-size particles may penetrate into the lungs and stay there ("respirable" particles). It has been

observed that small particles usually contain the highest amounts of some toxic chemical elements, evidently being more harmful to man than larger particles.

The aim of the present work was to use INAA to investigate changes in the elemental composition of solid fuel and its combustion products at consecutive stages of combustion.

## Experimental

The elemental composition of different combustion products generated at two large power plants burning solid fossil fuel was studied. The first one - the Baltic Power Plant (Estonia) - is fired with oil shale and has a capacity of 1600 MW. The second plant, with a capacity of 330 MW, is coal-fired and is located in the town of Chengdu (China, Sichuan Province). In both cases, the compositions of fuel and of various types of ash and fly ash were determined. Moreover, in China samples of aerosols (urban dust) were also collected at different distances from the power plant for study.

INAA was used with high fluxes of reactor neutrons having an elevated cadmium ratio value. The samples of solid fuel, ash, fly ash and aerosols were packed into quartz vials or into aluminum foil. The average mass of a sample was about 40 mg. The samples, together with a set of multi-element geochemical standards, were irradiated during periods of 10 or 24 hrs. with thermal or epithermal neutrons having a total flux density of  $5 \times 10^{13} \text{ cm}^{-2} \text{ s}^{-1}$ . With the help of standard reference materials (using the internal standard method), the concentrations of the following 40 chemical elements were measured: Na, K, Ca, Sc, Ti, Cr, Fe, Co, Ni, Zn, As, Se, Br, Rb, Sr, Zr, Mo, Ag, Cd, Sb, Cs, Ba, La, Ce, Ne, Sm, Eu, Tb, Ho, Tm, Yb, Lu, Hf, Ta, W, Ir, Au, Hg, Th and U. The spectral lines of radionuclides of these elements, in their gamma spectra, were free from interferences, so INAA is capable of identifying them. The detection limits of all these elements were lower than their mean amounts in the earth's crust (K). The average quantification errors for most of the elements which were studied did not exceed 20 %, including both precision and accuracy parameters.

## Results and Discussion

Figure 1 is a presentation of the data from the INAA study of oil shale composition along with the composition of the combustion products at the power plant in Estonia [2-4]. Ash was analyzed in detail. In addition to the oil shale samples (1), the following samples of ash were studied: furnace bottom ash (2), gas duct ash (3), cyclone ash (4), four-fielded electrostatic precipitator ashes (5-8) and fly ash from the exit gas (9). The values of the mean amounts of the respective elements in the earth's crust, K, are marked by horizontal lines with the indexes  $K_U$ ,  $K_{Th}$ , etc.

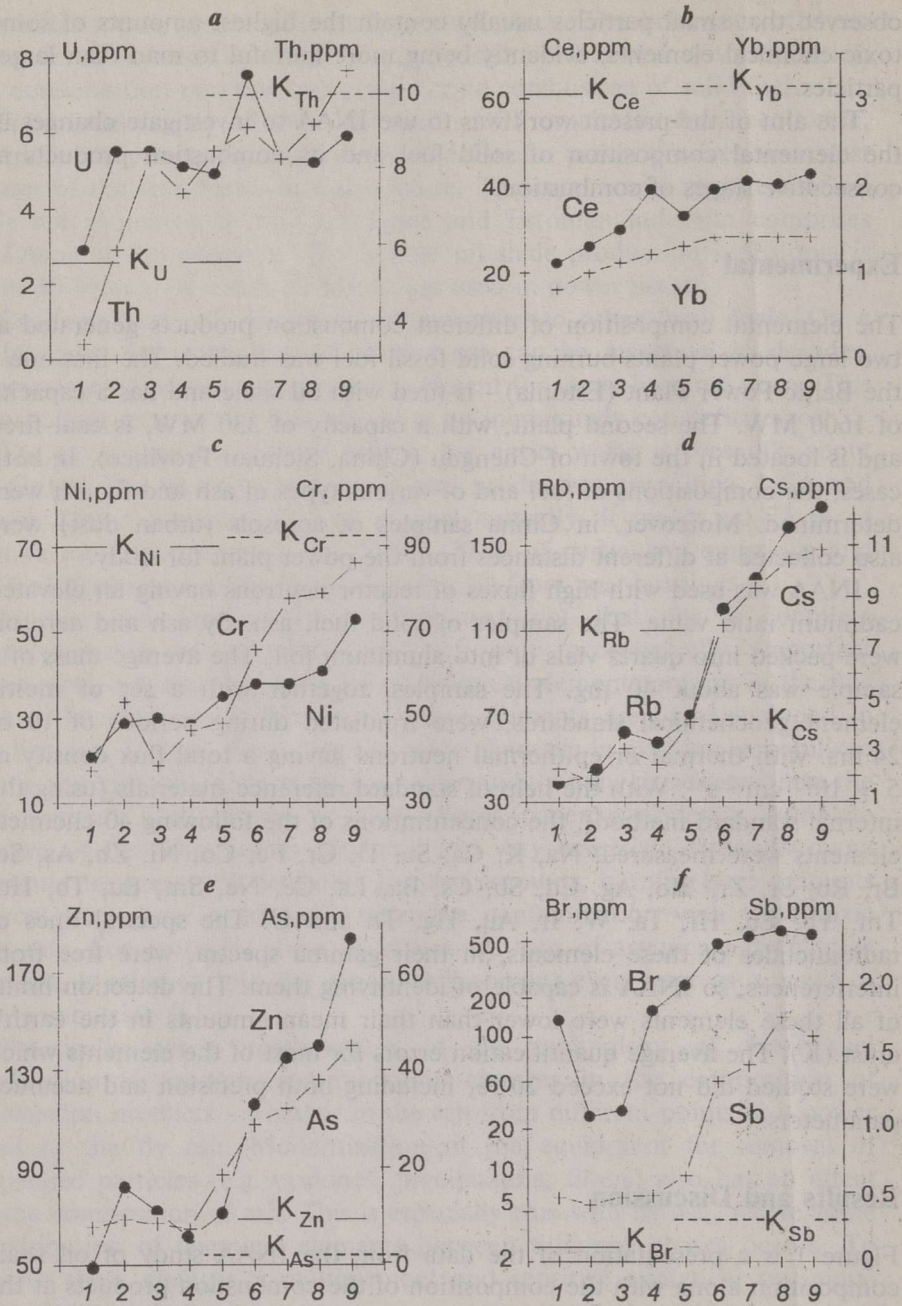


Fig. 1. Elemental concentrations for (a) U and Th; (b) Ce and Yb; (c) Ni and Cr; (d) Rb and Cs; (e) Zn and As; (f) Sb and Br, as measured by INAA of oil shale and its combustion products. 1 - oil shale, 2 - furnace bottom ash, 3 - gas duct ash, 4 - cyclone ash, 5-8 - electrostatical precipitator ashes, 9 - fly ash from exit gas

The K values were taken from a review compiled by Ovtchinnikov, published in 1990 [5].

Conversion of oil shale into the furnace bottom ash is accompanied by an increase in the contents of U, Th and rare earth's elements (REE). The concentrations of U, Ce and Yb in the other types of ash are virtually the same. Only the concentrations of Th are slightly higher in fly ash. Absolute amounts of the REE in ash are small, less than their mean amounts in the earth's crust.

Furnace bottom ash contains more nickel and chromium than the initial fuel. The concentrations of these elements increase in the overhead ash from the boiler along the ash duct and achieve maxima in the fly ash in the exit gas. However, the contents of Ni and Cr never reach their corresponding K values.

The next diagrams in Fig. 1 are related to volatile chemical elements. The concentrations of the rare alkaline metals - Rb and Cs - in the furnace bottom ash are practically the same as in oil shale, but the ash samples taken along the track of its collection at the power plant show a gradual increase in Rb and Cs amounts. The concentration of these metals exceed their K values in ash samples from the last fields of a precipitator and in fly ash from the exit gas.

A similar behaviour is demonstrated for zinc and arsenic. The ash samples from the last fields of a precipitator and from the exit gas are characterized by Zn and As concentrations which are many times higher than their  $K_{Zn}$  and  $K_{As}$  values. As to the last diagram, where the changes in the content of Sb and Br are shown, one can see that the concentrations of these elements also increase gradually along the ash collection track. There is only one difference, namely in the behaviour of Br. The combustion of oil shale proceeds in a manner that leads to a sharp decrease of the content of Br in the furnace bottom ash. The concentrations of Sb, and especially Br, in all samples studied significantly exceed the mean concentrations of these elements in the earth's crust.

Thus, the results obtained by using INAA in the study of variations in the elemental composition of oil shale products confirm the model of volatilization and condensation processes proposed previously [6]. According to this model, volatile components are vaporized during combustion and later they condense on the surface of the ash particles during cooling. Since finer fractions of fly ash have a larger specific surface, those particles would be enriched by these volatile compounds.

Figure 2 demonstrates the results of the present study carried out at the coal-fired power plant. One can observe the changes in the concentrations of some elements beginning from coal (1), to furnace bottom ash (2), gas duct ash (3), cyclone ash (4), and finally, to fly ash (5). In addition, the mean concentrations of the same elements, as measured in aerosols collected at distances of 1.5 km (6) and 2 km (7) from the power plant are presented.

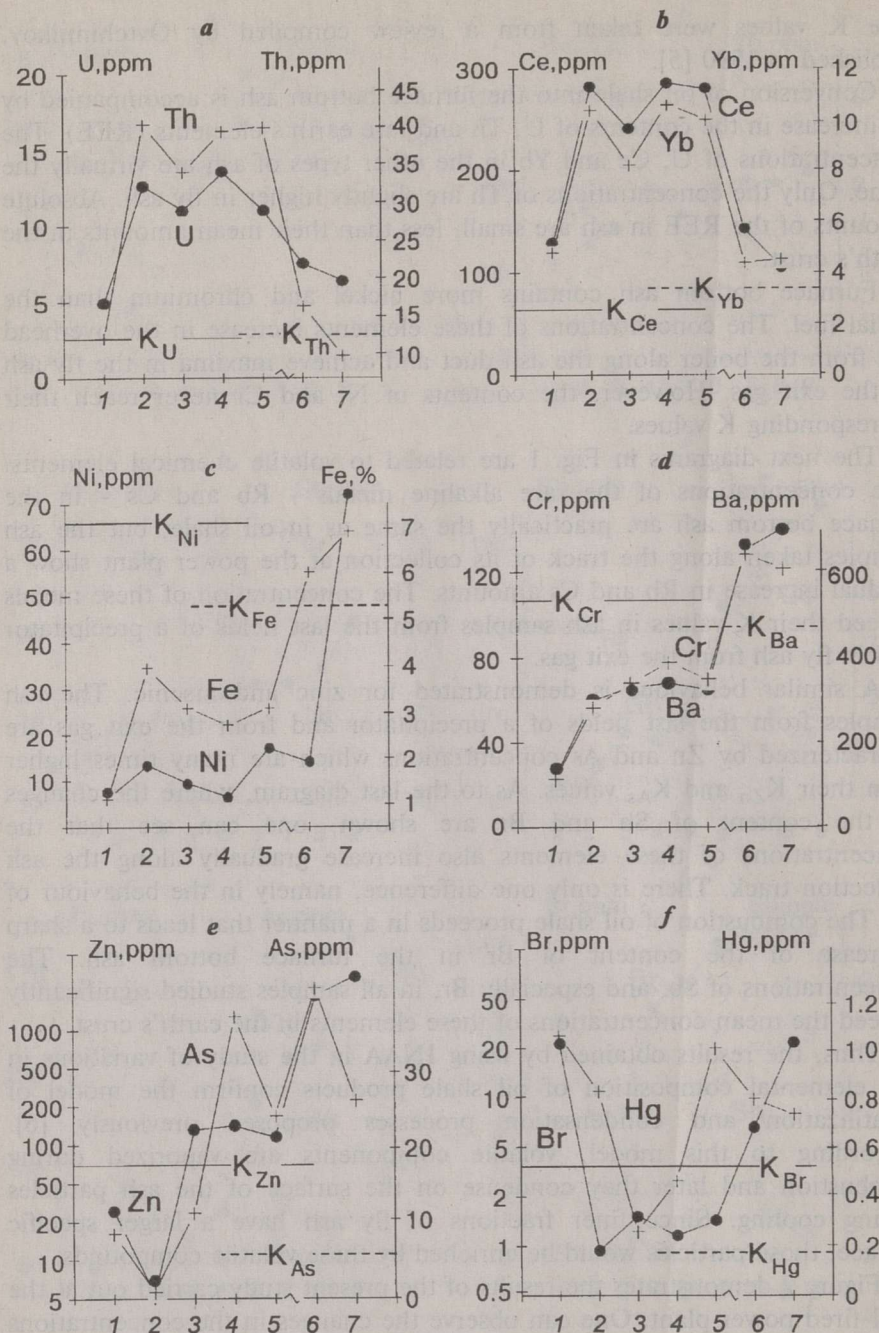


Fig. 2. Elemental concentrations for (a) U and Th; (b) Ce and Yb; (c) Fe and Ni; (d) Cr and Ba; (e) Zn and As; (f) Br and Hg, as measured by INAA of coal, its combustion products and air-transported aerosols. 1 - coal, 2 - furnace bottom ash, 3 - gas duct ash, 4 - cyclone ash, 5 - fly ash from exit gas, 6 - aerosols taken at 1.5 km from the power station, 7 - aerosols at 2 km from the station

The behaviour of two radioactive elements - U and Th - during coal combustion is practically the same. The content of U and Th in furnace bottom ash exceeds their content in coal. The concentrations of these elements in ash are also rather high, but the two radioactive elements are absent in the aerosol samples taken at the distances of 1.5 and 2 km. Consequently, it is apparent that U and Th primarily remain near the power plant.

The rare earth's element (REE) patterns are similar to those of U and Th. Figure 2 shows the changes in the concentrations of one light and one heavy REE, Ce and Yb, respectively. As in the case of U and Th, the concentrations of the REE in coal are higher than their mean amounts in the earth's crust. Furnace bottom ash and overhead ash are highly enriched with REE, but the contents of these elements in distant aerosols are close to their mean concentrations in the earth's crust. Evidently, the radioactive and rare earth's elements are not transported far from the power plant.

Figure 2 also shows the changes in the concentrations of the elements of the iron group (Fe, Ni, Cr), and the behaviour of Ba. Furnace bottom ash and fly ash are both enriched with all these elements as compared to the initial coal. However, in contrast to the previous cases, the amounts of Fe, Ni, Cr and Ba in aerosols are very high as compared to the ash remaining at the station. One can give two explanations for this phenomenon. First, it may be caused by the presence of iron and other elements present in fine particles within the exit gas which are capable of long-distance transport. However, this reason is quite improbable, because only volatile elements are known to be concentrated on small particles, whereas compounds of Fe, Ni, Cr and Ba are, as a rule, not volatile. So the second explanation is more likely: the source of these elements is not the power plant but some other plant in the industrial zone within the same town. It is worth noting that the concentrations of Fe, Ni, Cr and Ba both in coal, and in the products of its combustion, are less than the corresponding values in the earth's crust. In the aerosols which were sampled, the amounts of these elements exceed the values of  $K_{Ni}$ ,  $K_{Cr}$ , etc.

Figure 2 shows further the changes in the concentrations of some volatile elements - Zn, As, Br and Hg. The content of Zn in coal is less than its  $K_{Zn}$  value; the content of As, Br, and especially of Hg, in this fuel are higher than their mean amounts in the earth's crust. Furnace bottom ash contains reduced amounts of these elements as compared to coal. The concentrations of the volatile elements studied are higher in the ash than in the initial fuel. As to the urban dust (aerosols), the concentrations of these elements are elevated, especially the concentration of Zn.

The behaviour of volatile elements corresponds to the model of volatilization and condensation processes. One can see that the main features characterizing the changes in the concentration of elements are similar to those for oil shale.

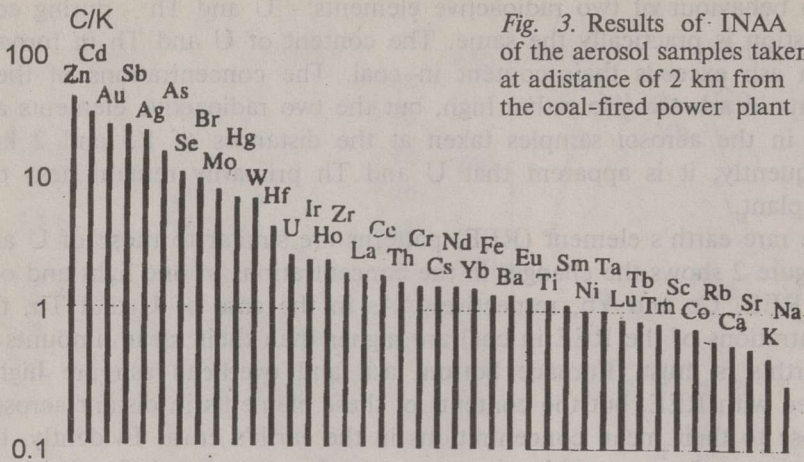


Fig. 3. Results of INAA of the aerosol samples taken at a distance of 2 km from the coal-fired power plant

In Figure 3, the results of INAA of 2 km aerosol samples from the coal-fired Chengdu power plant are shown. One can observe the presence of a group of trace elements in aerosols - Zn, Cd, Au, Sb, Ag, As, Se, Br, Mo, Hg, etc. Most of these elements are volatile. The capability of fine aerosol particles to carry elements of high volatility has also been observed earlier [7]. The high ratio of the concentration of volatile elements in aerosols and in the earth's crust ( $C/K$ ) confirms the technogenic origin of these elements. Actually trace elements like As, Se and Hg can be used as indicators of air pollution caused by coal burning. According to recent studies, about 65 % of anthropogenic emission of mercury to the atmosphere originates from coal burning [8]. Regional variations in anthropogenic Hg concentrations in the environment have been attributed to the deposition of this element, not in the gaseous state, but in particulate form. Selenium is observed to have the highest enrichment level as compared with other elements in coal. A high enrichment level of coal fly ash with arsenic was established by the recent determinations of As in some fine fly ashes.

## Conclusions

Application of INAA to the study of trace element composition of solid fossil fuels and their combustion products, showed many similar features between oil shale and coal. In both cases, a remobilization of elements and volatile compounds takes place, showing a tendency for the materials to accumulate on the surface of the fine particles of ash. INAA is a very effective technique to evaluate different parameters of fuel quality. To characterize coal beds, a set of 128 parameters, including the determination of minor and trace elements was proposed [1]. INAA enables one to determine most of the trace elements, not only in the initial fuel, but also in all products of combustion.



INAA is certainly too expensive for routine measurements. But it is convenient for a detailed study to follow any changes in the elemental composition of the combustion products. These changes may be caused by some essential alteration in technology of solid fuel combustion aimed at improving its efficiency and especially at diminishing the atmospheric pollution by heavy metals and toxic elements. INAA is also useful in different control studies - for example, for inter-laboratory calibration.

## СРАВНИТЕЛЬНОЕ ИЗУЧЕНИЕ РЕМОБИЛИЗАЦИИ ПРИМЕСНЫХ ЭЛЕМЕНТОВ В ПРОЦЕССЕ СЖИГАНИЯ СЛАНЦА-КУКЕРСИТА И КАМЕННОГО УГЛЯ НА ЭЛЕКТРОСТАНЦИЯХ

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### Резюме

При сжигании твердого топлива в котельных агрегатах происходит ремобилизация примесных элементов, и их поведение подчиняется модели «испарение-конденсация» [1, 6]. Цель данной работы — сравнительное изучение ремобилизации примесных элементов в процессе сжигания сланца-кукерсита и каменного угля в котельных агрегатах электростанций.

Пробы топлив и минеральной части продуктов их сжигания были отобраны с технологических узлов тракта золоулавливания котельных агрегатов Прибалтийской ГРЭС (Эстония), работающей на сланце, и электростанции города Чэнду (провинция Сычуань, Китай), использующей каменный уголь. Методом инструментального нейтронно-активационного анализа в отобранных пробах определены концентрации сорока элементов. Данные по сланцу и его золам приведены в работах [2—4]. Концентрации представителей отдельных групп элементов приведены на рисунках 1 и 2. На каждой диаграмме для сравнения даны величины кларковых содержаний соответствующих элементов в земной коре [5].

Сопоставление концентраций элементов на различных этапах отбора проб выявляет одинаковые закономерности в поведении элементов при сжигании как сланца, так и каменного угля. Подтверждается обогащаемость микроэлементами летучих зол обоих топлив и значительное количественное превосходство микроэлементов, особенно Hg, Se и As, в угле и его золах по сравнению со сланцем и его золами.

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