Peculiarities of mercury distribution in coals

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Introduction

The mercury concentration in coal varies in a wide range from less than 1 ppb to 300 ppm [1, 2]. Mercury speciation in coal can be represented by syngenetic mercury bound to organic matrix, by elemental Hg(0), mercury bound to crystal lattice of sulfides and silica minerals. The thermospeciation analysis based on real-time detection of the mercury release from a sample during its gradual heating is applied to reveal mercury species having different bond energy with coal matrix.

Experimental setup

The standard **RA-915M** mercury analyzer coupled with attachment (Lumex Instruments), **Fig. 1a** was used for total mercury determination and for thermoscanning of solid samples [3, 4].

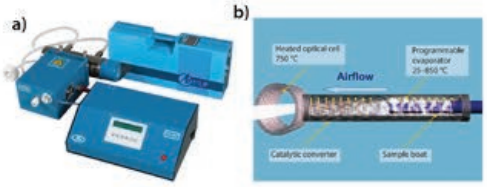

Fig. 1. Lumex RA-915M ZAAS system - a); PYRO-915 double-section atomizer enabling gradual sample heating - b).

The special mode of continuous, quasi-linear increase of the PYRO-915 atomizer temperature from ambient to 900ºC was applied (**Fig. 1b**). The experimental set enables the possibility of real-time record of the dynamic behavior of the mercury evaporation from solid samples as a function of time and temperature.

The thermoscanning procedure

As a result of the measurement procedure optimization, the following measurement procedure for coal samples was used:

- Linear sample heating with a gradient of 0.8 ºC/s,
- Sample weight: 200 ± 30 mg,
- Particles size: up to 1 mm,
- Carrier gas: air.

The measurement procedure demonstrates quite good reproducibility of the thermospectra **Fig. 2**:

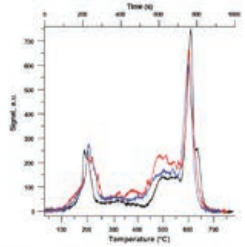

Fig. 2. Reproducibility of the thermographs of anthracite. Three runs , total Hg concentration in 885 ppb.

Total Hg concentration in the anthracite sample is 885 ppb. Mercury is released from anthracite in following temperature intervals:

30–300 °C	300–550 °C	550–800 °C
180 ppb	265 ppb	440 ppb
20%	30%	50%

Mercury thermospecies in pyrite

It was found out that significant part of mercury in productive coal horizons is accumulated in sulfides, mainly in pyrite, FeS_2 [1, 2]. Therefore, it is interesting to compare the mercury thermospectra of pyrite and pyrite-bearing coals (**Fig. 3**).

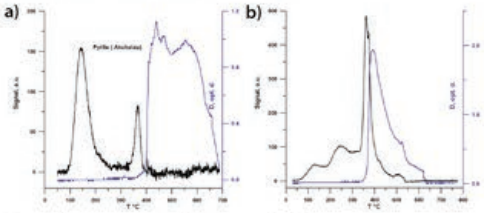

Fig. 3. Thermospectra of pyrites and coal.
a) hydrothermal pyrite, Akchatau, Kazakhstan;
b) pyrite-bearing coal, South Africa. Black line: mercury signal; blue line: non-selective absorbance proportional to SO_2 concentration.

In both spectra, the low-temperature peaks (100–200 °C) are obviously caused by the release of adsorbed elemental mercury Hg(0). The outbreak of the pyrite crystal lattice destruction is clearly identified by the beginning of the SO_2 release (blue line in **Fig. 4**) at the temperature of 350–360 °C. The FeS_2 destruction is marked by sharp peak of mercury emission. It is evident that main portion of mercury in the coal sample arises from the pyrite inclusions.

Mercury thermospecies in coals

The analyses of various types of coals from 35 deposits in Russia, Ukraine and South Africa reveals variously shaped mercury thermospectra (**Fig. 4**). Total mercury concentration in the studied coals varies in a range of less than 2 ppb up to 2 ppm.

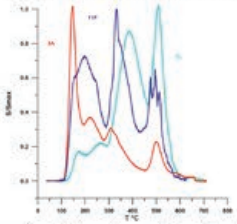

Fig. 4. Thermographs of three types of coal having similar total mercury concentration.
3A – anthracite, 470 ppb (Rovenki); 11F – fat coal, 580 ppb (Lvov); 1L – lean coal, 620 ppb (Makeevka).

Different proportions of mercury are released from these coal samples within low- (120–180 °C), mid- (300–450 °C), and high- (450–650 °C) temperature intervals.

Thermoscanning demonstrates different distribution of low- and high- temperature mercury species in bituminous coal from from Vaal and Highveld coal fields of South Africa [5] (**Fig. 5**):

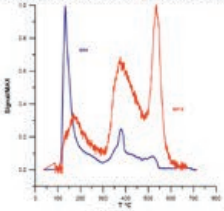

Fig. 5. Thermospectra of bituminous coal from Vaal and Highveld Fields, South Africa. ppb.
SA4 – Vaal Field (540 ppb): low-temp species;
SA10 – Highveld Field (195 ppb): mid- & high-temp species.

Obviously, these coals require different pre-combustion treatment to reduce mercury content.
The scanning electron microscopy and electron probe microanalysis reveal peculiarities of mercury and other chemical elements distribution in organic matrix and inorganic impurities.

The mercury accumulation in coals was found in organic matrix, sulfides, iron oxides and hydroxides, clay minerals and phosphates (**Fig. 6**):

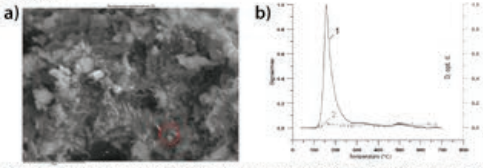

Fig. 6. Mercury accumulation in organic matrix. Bituminous coal from the Vaal deposit, South Africa. Sample 8V: total Hg 106 ppb. a) Micrograph of the sample. At point 58 (circled) the Hg concentration is 0.37 wt.%; b) Mercury thermospectrum.

Conclusion

- Total mercury concentration in the studied coals varies in a range of < 2 ppb to 2 ppm. In productive layers, mercury is accumulated in sulfides and coal matrix.
- The thermoscanning data show the presence of various mercury thermospecies in coals enabling to determine the low-, mid-, and high-temperature mercury species in coal.
- Mercury in pyrite exists as adsorbed Hg(0) releasing at the low temperature, and included into crystal lattice of FeS_2 escaping with its destruction starting at 350 ºC.
- The "spot"mercury accumulation up to 0.45 wt.% in coals was found in organic matrix, sulfides, iron oxides and hydroxides, clay minerals and phosphates.
- The thermoscanning technique gives additional information about mercury speciation in coal. This is useful for better understanding of the regularities of mercury geochemistry, causes of mercury enrichment in coals, and also for enhancement of the coal pre-treatment technology before combustion to reduce mercury emission to environment.

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Acknowledgements

The authors are thankful to Dr. Ludmila Haponych, Coal Energy Technology Institute (Kiev), for coal samples from Ukrainian coal mines.This study is supported by the National Research Foundation of South Africa and the Russian Foundation for Basic Research, Joint Science and Technology Cooperation in Basic Research, Project No 14-05-93961.