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 synergistic mercury bound to organic matrix, by elemental Hg0, mercury bound to crystal lattice of sulfides and silica minerals. The thermocan skiing 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 thermocan skiing 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 900°C was applied (Fig. 1b). The experimental setup makes the possibility of real-time recording of the dynamic behavior of the mercury evaporation from solid samples as a function of time and temperature.

The thermocan skiing 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°C/min
- Sample weight: 0.2 – 30 mg
- Particle size: 1 mm
- Carrier gas: air

The measurement procedure demonstrates quite good reproducibility of the thermograms (Fig. 2).

Fig. 2. Reproducibility of the thermograms of anthracite. Three runs, total Hg concentration in 685 ppb.

Fig. 3. Thermograms of pyrites and coal.
a) hot thermal pyrites, Afghura, Kazakhstan
b) pyrite-bearing coal, South Africa. Black line mercury signal blue line non-selective absorbance proportional to SO2 concentration.

In both spectra, the low-temperature peaks (100-200°C) are obviously caused by the release of admixed elemental mercury (Hg0). The break of the pyrites crystal lattice destruction is clearly identifiable by the beginning of the SO2 release (Fig. 4) at the temperature of 350-360°C. The FeS2 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 thermocan skings in pyrite
It was found out that significant part of mercury in productive coal horizon is accumulated in sulfides, mainly in pyrite, FeS2, FeS. Therefore, it is interesting to compare the mercury thermoscans of pyrite and pyrite-bearing coals (Fig. 3).

Fig. 4. Thermograms of three types of coal having similar total mercury concentration.
A) anthracite, 570 ppb (Voronezh); B) coal, 980 ppb (Ivolya); C) coal, 620 ppb (Malakhovka).

Different proportions of mercury are released from these coal samples with low- (120-180°C), mid- (300-450°C), and high- (450-650°C) temperature intervals. Thermocan skiing demonstrates different distribution of low- and high-temperature mercury species in bituminous coal from Voskod and Highfield coals of South Africa (Fig. 5).

Fig. 5. Thermograms of bituminous coal from Voskod and Highfield Coals, South Africa, ppb.
A) coal 580 ppb (both species); B) coal 195 ppb (mid- and high- temp. species).

Obviously, these coals require different pre-treatment combustion 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.

Fig. 6. Mercury accumulation in organic matrix. Bituminous coal from Voskod deposit, South Africa. Sample weight: 0.9 ppm; total Hg 106 ppb.

Conclusion
1. Total mercury concentration in the studied coals varies in a range of 〈 2 ppm to 2 ppm. In productive layers, mercury is accumulated in sulfides and coal matrix.

2. The thermocan skiing data show the presence of various mercury thermoscans in coals enabling to determine the low-, mid-, and high-temperature mercury species in coal.

3. Mercury in pyrite exists as elemental Hg0, releasing at the low temperature, and included into crystal lattice of FeS2, escaping with its destruction starting at 350°C.

4. The spot mercury accumulation up to 0.45 wt.% in coals was found in organic matrix, sulfides, iron oxides, and as oxides and hydroxides, clay minerals and phosphates.

5. The thermocan skiing technique gives additional information about mercury speciation in coal. This is useful for better understanding of the mechanism 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.

References


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Appendix
Sample samples: coal (0.5 mm); Co. fuel (0.5 mm); Co. fuel (0.5 mm); Co. fuel (0.5 mm); Co. fuel (0.5 mm).

Appendix A: Thermocan skiing and Mercury in coals.

Appendix B: Mercury thermoscans of coal an organic matrix.

Appendix C: Mercury in coals.