

## The lab-scale evaluation of possible mercury speciation in flue gas and mercury emission from combustion of solid fuels

Mercury, the chemical element with a notably detrimental impact on living organisms, has been finally classified by European Union as a dangerous industrial pollutant and included in future pro-environmental EU energy policy. This fact becomes particularly important in Polish economy, where new strict mercury emission standards (Directive 2010/75/EU with the BAT conclusions for LCP), starting from August 18th 2021, will significantly affect the economy of electricity and heat generation within national coal-based power sector. As a result, to adopt the requirements of BAT-AELs related to mercury emissions ( $<1-10 \mu\text{g}/\text{m}^3\text{ref}$ ), a considerable number of power units in Poland will have to be equipped with specific air protection technologies. Due to the natural occurrence of mercury in hard coals, lignites (50-1,000 ppb in dry sample) and other solid fuels (30-3,000 ppb) as well as to specific physicochemical behaviour of mercury during combustion, mercury is always present in flue gases and releases combustion chamber in the gaseous phase. However, when intensive oxidation of mercury within gas duct is promoted, its co-beneficial uptake within popular air protection technologies (flue-gas desulphurisation systems, electrostatic precipitators, bag filters) can be both effective and relatively easy and cheap. What is important, the oxidation rate of mercury vapour strongly depends on the composition of flue gas (primarily on  $\text{SO}_2$ ,  $\text{HCl}$ ,  $\text{H}_2\text{O}$ ,  $\text{NO}_x$  concentrations) –to assess future emission of mercury, it appears to be vital to treat every combination of combustion parameters and physicochemical properties of the fuel individually. Furthermore, while direct measurements of mercury speciation within flue gas duct are time-consuming, cost-intensive and complex, it might be beneficial to develop reliable lab-scale method intended to identify possible mercury releases during the combustion of selected solid fuels. When validated and standardised, it would be used i.e. to forecast future mercury releases from power sector or to select and adjust the parameters of air protection technologies. Moreover, by the proper identification of Hg speciation in flue gases, including individual physicochemical properties of various solid fuels (hard coals, lignites, biomass, RDF-type fuels), the accuracy of all national and local environmental assessments may be significantly improved.

In this work novel lab-scale evaluation method dedicated to the assessment of possible mercury oxidation rate and concentration in flue gasses from pulverised fuel boiler is presented. It consists in the absorption of oxidised gaseous mercury (in water) from flue gas released in the calorimeter bomb, where a sample of fuel is decomposed in the atmosphere of oxygen, and calculation of mercury mass balance. This procedure seems to be more accurate to identify the differences in mercury speciation than physicochemical analysis of fuel alone. Importantly, by the implementation of constant time of combustion and cooling, it seems to be fully repetitive. Moreover, to simulate the operation of existing power station, analysed method was coupled with the mathematical model of solid fuel fired combustion chamber and flue gas duct, that was designed and published by the author in his previous papers.

To highlight the impact of the type of solid fuel on the efficiency of mercury uptake system, 11 solid fuels (hard coals, lignite and biomass) were investigated –both ultimate (using i.e. LECO TruSpec CHNS, LECO AMA254 and Dionex ICS-1100 equipment) and proximate (moisture, ash, volatile –using PN/EN standards) analysis was conducted. Then, all samples were analysed (sample of 1 g in air-dry state was combusted in 350-ml calorimeter bomb. To identify the concentrations of total mercury in fuels, substrates, absorbent and ash, CV-AAS analysers was used. Moreover, both chloride and sulphates were identified using ion chromatography.

### Summary

Conducted tests proved that the significant variations in mercury oxidation rate and speciation in flue gasses during the combustion of different hard coals, lignites and biomass occur. Possible mercury concentrations in raw flue gas ( $>7000^\circ\text{C}$ ) vary between 4 and  $75 \mu\text{g}/\text{m}^3\text{ref}$ . The lowest shares (less beneficial) of oxidised forms of Hg were identified in case of investigated lignites (26-58%), while the highest –in selected hard coals (up to 90%) and biomass (up to 98%). That can be observed, that there was no core principle concerning the impact of the group of fuels on mercury oxidation –even though only subtle variations in chlorine, mercury, sulphur and

ash contents in fuels. It highlights the fact, that due to extremely complex nature of mercury transformations in flue gas leads to the need of individual assessments for every source of energy. Furthermore, mercury transformation in flue gas seems to be very sensitive to the specific composition of solid fuel, therefore the implementation of particular coal or biomass should be preceded by individual lab-studies. What is important, strong similarity between the obtained results and tests conducted in full scale power units may be observed.

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