Wrocław, 23.05.2022 r.

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Title: The influence of combustion conditions and fuel properties on mercury emission during combustion of pulverised coal

ABSTRACT OF THE PHD THESIS

This doctoral dissertation addresses the selected issues related to the influence of the physicochemical properties of solid fuels – mainly Polish commercial and industrial steam coals - and combustion conditions on the mercury releases accompanying the operation of thermal power plants equipped with pulverised coal-fired boilers. The presented studies and laboratory tests, carried out in the framework of the discussed PhD thesis, focused on the primary (pre-processing) methods dedicated to the mercury emissions reduction (i.e. via proper selection of fuel and modification of combustion process) as well as on the calculations, quasi-empirical simulations and direct measurements of mercury concentration and speciation in flue gases from the abovementioned types of the coal-fired power units.

The dissertation consists of 9 chapters: 1) four devoted to the literature review, the identification of scientific and technological deficiencies or inaccuracies in a field of mercury emission from coal-fired power plants and a description of the phenomena accompanying mercury transformations during pulverized-coal combustion, 2) one introducing the purpose, scope and thesis of the dissertation, and 3) four which refer to the applied or developed methodology as well as the results and conclusions of the conducted laboratory tests and analyses. The work refers to 166 references and contains 25 tables and 78 various types of graphics, diagrams, photos and charts.

The first chapter focuses on indicating the purposefulness of undertaking different research and development works related to the problem of mercury emissions from solid fuel combustion processes, carried out in relation to the needs of modern commercial, industrial and municipal power units, as well as the implementation of the Clean Coal Technologies (CCTs). In the second chapter, the gathered observations and identified issues were associated with the range of migration of mercury compounds, the annual emissions of this pollutant annual caused by the power sector, the common presence of this element in the most important fuels and carbon-based energy sources and the possibility of limiting or controlling the levels of mercury releases from combustion processes by adopting the proper composition of fuel and selecting the favourable parameters of the combustion process. Subsequently, in the third chapter of the dissertation, the nature of mercury phenomena which occur during the combustion of pulverised solid fuels and the related possibilities of controlling mercury concentrations in the emitted flue gases are discussed. It was recognised that, apart from the fuel itself (the composition which directly affects the quantity of mercury releases and the mercury speciation in boiler flue gas), adequate modifications of selected combustion parameters may have a significant, favourable impact on the reduction of mercury emissions or releases from combustion chamber. Moreover, a significant variations of the mercury concentrations observed in the boiler and emitted flue gases as well as of the mercury-reduction efficiencies of different air pollution control devices proved the influence of both fuel and combustion parameters on all mercury-associated issues within coal-fired units.

The first three chapters confirmed the presence of a number of contradictory or only tentatively or conditionally justified scientific theses and observations related to the reduction of mercury emissions via primary methods – the interesting alternatives to more widespread secondary ones. Moreover, numerous literary deficiencies and inaccuracies drastically reduce opportunities for reliable assessment or comparisons of the abovementioned fuel and process aspects on mercury releases from pulverised

furnaces and suggest a need for more comprehensive laboratory tools and calculation algorithms for the classification of solid fuels, combustion technologies and primary methods process parameters from the point of view of mercury emissions. A brief summary of all identified scientific challenges is presented in the fourth chapter.

The abovementioned observations and literature deficiencies were also used to formulate the objectives (scientific and practical), 5 main theses and, in relation to them, the scope of laboratory tests and analyses within the dissertation. It was described in chapter five. The main scientific aim of this work was to determine the influence of the type of fuel (its physicochemical properties - mainly mercury, chlorine and sulphur content) and selected combustion process parameters (mainly size of coal particles and air–fuel ratio) on the speciation and concentration of mercury in flue gases when burning pulverised coal or mix of coal and biomass.

Chapter six presents the results of laboratory tests undertaken in order to assess the influence of the type of solid fuel and its properties on mercury emissions. The conducted physical and elemental analysis showed a significant differentiation in the values of the most important physicochemical values - calorific value, ash, mercury, sulfur and chlorine content - involved in the formation of speciation (leading to obtaining the rate of oxidized gaseous forms of the element between 20% and 99%) and concentrations (from 4 to nearly 74 $\mu g/m^3$ in the reference state) of mercury in the flue gases released from the pulverized coal-fired combustion chamber. It was proved that there is no significant correlation between the mercury content and other analysed fuel performance properties mentioned above as well. The observations were confirmed thanks to the use of a original, new laboratory test involving combustion of a small sample of solid fuel in a calorimetric bomb and performing a mass balance of mercury in substrates and products. It was proven that fuels containing relatively small amounts of chlorine and high amounts of sulphur (like selected Polish brown coals), in contrast to the tested hard coals and biomass (with some exceptions, which, additionally, suggests the individual intensity of mercury transformations in the case of every fuel, independent e.g. of the carbon content) should be characterized by unfavourable mercury speciation in the flue gas, which could be partially eliminated e.g. by adding biomass (co-combustion of biomass and steam coal was also covered during the proposed tests).

Chapter seven focuses on examining the impact of combustion conditions on the possibility of mercury emissions from the combustion processes. As part of the undertaken analyses, the mechanisms of mercury releases from the fuel during pyrolysis and degassing were identified, and the possibility to remove, in the case of selected brown coals, more than 80-90% of mercury compounds from the solid fuel during preliminary thermal treatment carried out at temperatures below 300°C (due to the risk of increased fuel degradation, it is suggested to proceed a valorisation in an oxygen-free atmosphere). This fact was confirmed by a large-scale laboratory measurements using an original test stand dedicated to identify mercury speciation and concentration in flue gases. Further, the analysis of ashes from two real coal-fired power units proved 1) the legitimacy of obtaining fine fuel grinding, 2) refraining the generation of increased (unjustified) loss of ignition and 3) extending the contact time of fine fly ash particles with the flue gas (or harnessing their reintroduction into the flue gas tract) in view of the high capture rate of mercury vapors on fly ash.

The eighth chapter presents the original calculation tools or algorithms enabling the estimation of the releases and emission of mercury from pulverised-fuel combustion processes on the scale of large power units. The algorithm created as a part of this work, based on stoichiometric calculations, can be considered as a useful both in determining the expected concentrations of mercury in flue gases and in identifying the air emission factors of this element from the combustion process depending on the applicable emission standards (e.g. BAT-AELs) and unit efficiency. In turn, the calculations undertaken in the FactSage software confirmed the influence of the air–fuel ratio and the type of fuel used on the chemical equilibrium curves, and thus indirectly also on the intensity of mercury oxidation processes in real conditions. The physicochemical properties of solid fuels and process parameters, as demonstrated by the performed calculations, closely correspond to the temperatures prevailing in the combustion process as well, and thus also with the possibility of rapid cooling of the flue gases (which favours the formation of oxidized forms of gaseous mercury). In the dissertation the risk of a decrease in net efficiency resulting from the integration of the low-temperature pyrolysis process, and thus also an increase in carbon dioxide emissions per unit of generated electricity, was identified and estimated. For this purpose, a model of the water-steam cycle of a 200 MW class power unit was prepared in the Aspen Hysys environment (the decrease in efficiency, after optimization of the heat extraction, amounted to approx. 2 percentage points). Finally, some technical solutions were proposed to reduce the negative impact of the abovementioned valorisation method.

The last chapter summarises the undertaken analyses and observations, confirming all the previously formulated objectives and theses of the dissertation. A brief discussion of the results is provided as well. Thus, the scientific and practical usefulness of this work was proved in the perspective of the development of Clean Coal Technologies and the recognition of coal-based fuels as technically and ecologically justified in the future structure of commercial, industrial and municipal power sector.