

Reduction of mercury emissions from coal combustion in the Czech Republic

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Abstract. Under the new legislation, in force since 2021, mercury emission limits for large combustion plants (LCP) are determined. This paper describes formation of mercury during coal combustion process and present methods of removing mercury from flue gases. This paper also reviews the fuel base of the Czech Republic and current measurement results of mercury emissions from some important LCPs in the Czech Republic. Measurement shows that most LCPs in the Czech Republic do not meet these emission limits and it leads to find out technical and economic solution.

1. Introduction

In terms of proven ecotoxicity and accumulation, global mercury (Hg) issues are addressed in recent years. The researches relate the harmfulness of individual forms of Hg to human health, sources of Hg that discharge it into the food chain as well as into the air. One of the most significant sources of Hg emissions are fossil fuel burning units. For these reasons, the EU has also newly revised the emission limits for Hg concentrations for LCP, it means for units with a thermal input higher than 50 MWt. New legislation will come into force in the second half of 2021. In the Czech Republic Hg emissions have not been legislatively established. Only once a year, the Hg measurement was carried out according to Czech technical standard (ČSN). However, this has changed with the new legislation. Every LCP has to solve in a relatively short time several issues. It means how much Hg emissions are emitting from LCPs and in case of failure to meet the required limit, find measures to meet the emission limit. Another sector linked to the new legislation is the measurement of Hg emissions. The actual determination of Hg emissions is both specific and novelty. Hg emissions are nowadays a highly discussed topic at all levels in the Czech Republic.

2. New emission limits valid from 2021

Commission implementing decision (EU) 2017/1442 of 31 July 2017 establishing best available techniques (BAT) conclusions, under Directive 2010/75/EU of the European Parliament and of the Council, for large combustion plants. There are also new emission limits for mercury. See table 1. Hg emission limits are divided by type of fuel for new and existing sources and by heat input. Sources of thermal input below 300 MWt will show mercury emissions four times a year from the average of samples obtained over one year. Sources with thermal inputs more than 300 MWt will then report an annual average of continuous measurement.



Table 1. Mercury Hg emission limits.

Heat input [MWt]	New plant		Existing plant	
	Hg (coal)	Hg (lignite)	Hg (coal)	Hg (lignite)
< 300	< 1 - 3	< 1 - 5	< 1 - 9	< 1- 10
≥ 300	< 1 - 2	< 1 - 4	< 1 - 4	< 1- 7

3. Mercury in the process of coal combustion

During the coal combustion process, mercury is released into flue gases in three forms.

- Gaseous oxidized mercury (Hg^{2+});
- Gaseous elemental mercury (Hg^0);
- Mercury bound to particles (Hg_p).

Each of Hg forms has its specific properties that influence their formation and reduction during the combustion process. The amount of Hg emissions emitted from individual large combustion plants is then dependent on the type of fuel and the emission control devices. Gaseous Hg^{2+} is water soluble. Therefore in the atmosphere it can be removed by rainfall or moisture. Hg^{2+} presented in flue gases can be removed by wet flue gas desulphurization systems (WFGD). It all results in that the Hg^{2+} represents only 3-5% of the total mercury in the atmosphere. Gaseous Hg^0 stays in the atmosphere in average of 0.5 - 2 years. It is long enough for transporting around the world. First it is necessary to oxidize Hg^0 to Hg^{2+} . This oxidation is important for reducing Hg^0 . For that reason Hg^0 is major problem for large combustion plants. Mercury bound to particles Hg_p is adsorbed onto surfaces – slag, fly ash. This form can be easily captured by dust control devices (precipitators or baghouses). Figure 1 shows the formation of individual forms of mercury in the flue gases from the combustion process.

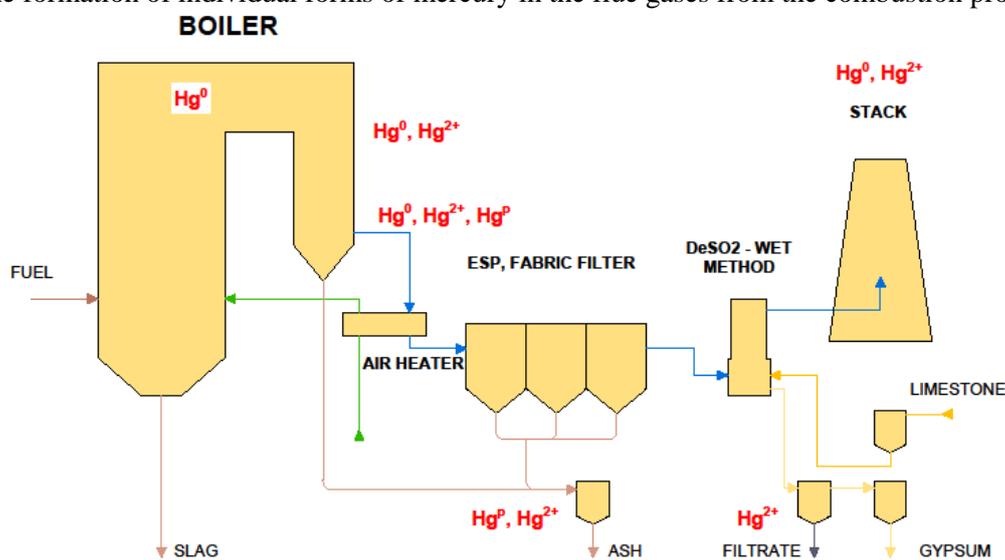


Figure 1. Forms of mercury emissions during coal combustion.

4. Fuel base of the Czech Republic

Mercury is in trace amounts already in the coal. The amount of Hg varies depending on the type of coal (black, brown) and the origin of the coal. Another important factor is the content of halogens in the coal, especially the content of chlorine (Cl). Chlorine is very important for the oxidation of Hg^0 to Hg^{2+} during the combustion processes.

Knowledge of fuel is the basic input information. In LCPs in the Czech Republic, mainly lignite is burned. Table 2 shows the lignite sample analyses (content of Hg and Cl), which are the most used in the Czech Republic.

Table 2. Analysis of lignite samples.

Lignite sample from quarry	Hg mg/kg _{dry}	Cl % _{dry}
<i>Bílina</i>	0.22	0.0074
<i>Nástup Tušimice</i>	0.203	0.0088
<i>Jiří</i>	0.482	0.0095
<i>Vršany</i>	0.262	0.0061

For comparison, a sample of black coal was also analysed. The results of the analysis shows that Hg content is 0.516 mg/kg_{dry} and Cl content is 0.19 %_{dry}.

It is obvious from the analysis of coal burned in the Czech Republic that the content of Hg in lignite is lower than in black coal. Similarly, the content of Cl is significantly higher for black coal than for lignite. However, the resulting value of Hg emissions from LCP does not affect only the amount of Hg in coal. Another factor is the combustion process itself and the choice of the flue gas cleaning method, especially the choice of denitrification system and desulfurization system.

5. Methods of removing mercury from flue gas

For reducing mercury concentrations in flue gases from solid fossil fuel combustion, the development is focused on two main areas. The first area is the development of techniques and technologies designed to promote the oxidation of Hg⁰ itself to Hg²⁺ in the flue gas and the subsequent removal of the Hg²⁺ by means of scrubbing in the FGD systems. The second area is the development of sorbent and associated systems for the sorption of Hg on sorbent surfaces.

The following technologies and methods are available to control mercury Hg emissions.

5.1. Sorbents

- Activated carbon – by adding active carbon, it is possible to reduce the Hg concentration by as much as 90%. Activated carbon is added in front of the dust control device.
- Addition of sorbents based on halides, bromides, iodides. Sorbents are added both to the combustion chamber and then as the activated carbon before the dust control device. It is also possible to use zeolite-based sorbents for capturing mercury.

5.2. Oxidation on the catalyst layer

- The oxidation occurs on a catalyst layer primarily designed to reduce the NO_x emissions. Selective catalytic reduction (SCR) technology must be combined with the dust control device and FGD system using a wet method. SCR technology oxidizes the Hg⁰ to Hg²⁺. This fact allows us to subsequently removed Hg in the WFGD reactor. It is important that flue gas contains sufficient amount of Cl to oxidize mercury in the presence catalyst.

Mercury emission control system must be carried out in various combinations. The following table 3 and table 4 shows technological possibilities of reducing Hg emissions.

Table 3. Technologies used to reduce pollutant emissions and their effect on Hg reduction.

BAT technology	Primary use	Reduction of Hg
Bag filters	To remove dust	Reduction of only Hg _p
ESP	To remove dust	Reduction of only Hg _p
SCR	To reduce NO _x emissions	It is necessary to combine SCR with the wet flue gas desulfurization (WFGD)
Dry or semi-dry desulfurization	Especially for removal of SO _x , HCl and HF in flue gas	-
WFGD		Reducing Hg ²⁺

Table 4. Technologies used to reduce Hg emissions.

BAT technology	Reduction of Hg	Comment
Fuel choice	Choosing a fuel with low ash content and / or Hg	Limited by local conditions, availability of other fuels and energy policies
Sorbent - Halides	Oxidation of elemental Hg ⁰ to the oxidized form	Adding into combustion chamber or in front of dust control device. It is necessary in combination with WFGD
Sorbent – activated carbon	Mercury capture on sorbent surface	Dosing in front of dust control device in combination with flue gas desulphurization using a semi-dry method
Fuel pre-treatment	Washing, forming mixtures to reduce the Hg content of the fuel or increasing the efficiency of Hg separation from flue gas	Applicability is highly dependent on specific conditions

6. Measuring and status of current mercury emission in the Czech Republic

6.1. Black coal-fired combustion plants

Selected LCP burning black coal equipped with pulverized boilers, followed by ESP and WFGD system. Part of the source is ecologized and 2 of 4 boilers are equipped with SCR technology.

Measurement was carried out on the boiler without SCR and then on the SCR boiler. Without SCR was average Hg concentration in the flue gas 5.92 µg/Nm³. With SCR was average Hg concentration 5.44 µg/Nm³. However, the emission limit value for Hg on a black coal-fired block with a heat input

more than 300 MWt is $4 \mu\text{g}/\text{Nm}^3$. The emission limit was exceeded in both cases. The Cl concentration was around 50-80 ppm for both measurements.

6.2. Lignite coal-fired combustion plants

Mercury emissions were measured on the following selected LCP with thermal input more than 300 MWt. [3] For these energy sources new legislation sets an emission limit of $7 \mu\text{g}/\text{Nm}^3$.

LCP number:

- 4 pulverized boilers, with ESP and WFGD system.
- 2 pulverized boilers and 2 grid boilers with ESP and FGD by a semi-dry method.
- Lignite in combination with biomass in 2 boilers with circulating fluidized bed with a fabric filter. FGD system is based on the dry additive method.

Results of Hg concentration measurements are shown in the following table 5.

Table 5. Concentration of Hg in flue gas – lignite.

LCP n.	Fuel	DeSO _x technologies	Hg $\mu\text{g}/\text{Nm}^3$	Emission limit $\mu\text{g}/\text{Nm}^3$
1.	Lignite	WFGD	15.0 – 24.0	7.0
2.	Lignite	Semi-dry FGD	18.0 – 26.0	7.0
3.	Lignite/biomass	Dry additive method fluidized bed boiler	0.2 – 2.0	7.0

The values in table 5 shows a high exceedance of approved emission limit. Emission values differ is based on fuel, type of boiler (combustion process) and use of emission control systems.

7. Conclusion

Based on commission implementing decision (EU) 2017/1442 for LCPs are set the Hg emission limits. Mercury emission is currently the most discussed topic in the Czech Republic's energy sector.

Measurement results from some LCPs in the Czech Republic shows that most of them do not meet the emission limits. These LCPs will have to implement measures that will reduce mercury emissions to the desired value. For each LCP, the method leading to the reduction of Hg emissions will vary according to fuel, combustion process, emission control device and investment and operating costs of selected method. LCPs of the Czech Republic have a relatively short period of time to install measures to reduce mercury emissions.

These measures are associated with substantial investment costs that may be critical to the continued operation of the facility. Research and measurement in the field of mercury is an important part of further developments leading to the reduction of mercury emissions.

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References

- [1] Frolka P 2016 *BREF Large combustion plants XVII* Forum for information exchange about BAT: MPO
- [2] Vávrová Z 2015 *Design of Treatment Facilities for Research in Mercury Emissions from Coal Combustion* (Ostrava: Technical University of Ostrava)
- [3] Technical reports - Accredited workplace for diagnostics and operation of power generation equipment Centrum ENET

- [4] Best Available Techniques (BAT) 2016 Reference Document for Large Combustion Plants: Industrial Emissions Directive 2010/75/EU Bureau
- [5] Pilař L, Szeliga Z and Zbieg R Monitoring conversions of Hg⁰/Hg²⁺ in flue gas from energy sources