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## DEVELOPMENT OF A PILOT PLANT FOR REDUCTION Hg EMISSION FROM LARGE POWER PLANT

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**Abstract**

This paper deals with the implementation process of the project of the Technology Agency of the Czech Republic (TAČR) ALFA TA04020723 "Development of a pilot plant for monitoring of Hg emissions reduction from large and medium capacity energy sources". The project currently responds to the emerging EU BAT legislation, which sets emission limits for Hg concentration in flue gas. The subject of the paper is presentation of the project's results for 2015. The scope of project activities in 2015 included measurements in energy facilities while defining the balance of Hg concentrations in the combustion products. The project's main objective in 2015 was to build and commission the pilot plant for the oxidation of the free form of Hg<sup>0</sup> into the oxidized form of Hg<sup>2+</sup>.

**Introduction**

Efforts for global environmental protection are primarily focused on the area of emissions. The reason is that emissions of pollutants emitted into the atmosphere are carried by wind, thus contaminating the environment regardless of regional boundaries. Therefore, the EU focuses its efforts to protect the environment on air emission limits. In contrast, solid wastes are usually dealt with at national level through national laws and regulations.

Based on their proven harmful effects on living organisms, limiting mercury emissions emitted into the atmosphere is currently a hot topic addressed internationally. This mainly involves mercury emitted from the combustion of solid fossil fuels. The EU is preparing a new document called "Best Available Techniques (BAT) Reference Document for the Large Combustion Plants" which sets emission limits for mercury concentrations for both new and existing facilities. The emission limits are listed in the following table; in 2015 these limits were tightened significantly. For existing facilities burning coal, with a thermal power greater than 300 MWt, the existing value of 6 µg/Nm<sup>3</sup> was changed to the stricter 4 µg/Nm<sup>3</sup>. For combustion plants burning lignite, with a thermal power greater than 300 MWt, the limit was also changed to a stricter value - from the original 10 µg/Nm<sup>3</sup> to 7 µg/Nm<sup>3</sup>. The updated emission limits for Hg concentrations are shown in the following table.

Table I

Emission Limits for solid fossil fuels

Combustion facility of rated heat intake (MW <sub>t</sub> )	Hg emissions (µg/Nm <sup>3</sup> )		rated period	monitoring
	new source	existing source		
coal: anthracite and bituminous coal				
< 300	1 - 3	1 - 9	average taken from samples gathered during one year period	four times a year
> 300	1 - 2	1 - 4	year average	Continual
coal: sub-bituminous and lignite				
< 300	1 - 5	2 - 10	average taken from samples gathered during one year period	four times a year
> 300	1 - 4	1 - 7	year average	Continual

The BAT legislation will come into force in 2017. Subsequently, EU Member States will have four years to transpose the results of the document into their respective national legislations. In 2021, the stated emission limits will be mandatory for all combustion plants with a rated thermal power greater than 50 MW<sub>t</sub>.

The main objective of the project is the identification and subsequent proposal of a concept design for the issue to achieve the projected Hg emission limits with the selected representative energy sources combustion solid fossil fuels in the Czech Republic, and the application of the draft technical design to achieve the projected future emission limits for mercury arising from the combustion of solid fossil fuels in existing power plants, including assessment of its impact on operational economy.

### Analysis of fuel resources

In 2014, selection of fuels was performed, followed by analyses to determine Hg concentrations in dry matter. Based on the information on oxidation of Hg<sup>0</sup> to Hg<sup>2+</sup>, where Hg is firstly oxidized with chlorides, new analyses of the same types of fuels were performed in order to determine not only Hg concentrations, progress of Hg concentration on more samples taken in the course of the year, but also Cl concentrations.

Cl concentration has a profound effect on the oxidation of the atomic form of mercury Hg<sup>0</sup> to the oxidized form of mercury Hg<sup>2+</sup>. In literature there are descriptions of various catalytic oxidation mechanisms. However, these effects could also be explained by the simple oxidation of hydrogen chloride where reactive chlorine is formed which then reacts with atomic metallic mercury. This reaction is similar to the formation of persistent pollutants such as PCDD/F; HCl oxidation is the so-called Deacon reaction and is used to produce chlorine industrially from waste hydrogen chloride. This principle explains the formation of the oxidized form of mercury even during coal combustion in a mild oxidizing atmosphere.

On the basis of knowledge of Hg oxidation due to the concentration of Cl contained in fuels, an analysis of coal samples was performed and the concentration of Cl was determined.

Fuel selection for carrying out analyses in order to investigate mercury concentration was based on several criteria:

- coverage of wider spectrum of fossil fuels used in large and extra-large combustion sources
- expected sufficient availability in the future, i.e. sufficient and reachable supplies
- real usability in the conditions of the Czech Republic, especially with respect to transportation options.

Based on the criteria stated above, following types of lignite we selected after carrying out the analyses. 3 samples weighting 1 kg each were taken from each type of the lignite. Samples of the lignite were further analyzed in the Coal research department in Most.

- North-Bohemian coal plateau – Nástup Tušimice mine and Bílina mine  
Nástup Tušimice mine (DNT) – sample "Industrial mixture" - PS2  
Bílina mine (DB) - sample "Rough gravel" HP1, "Industrial mixture" PS1 a PS2
- Mostecká coal plateau  
Vršany mine - sample – sample "Industrial mixture" PS3
- Sokolovská coal plateau  
Jiří mine – sample DT - NS II

Analyses results are shown in the following Table II.

Table II  
Hg concentrations in fuel – lignite

Mine	Fuel type	Analyses – 2014		Analyses – 2015	
		Wtr % by weight	Hg mg/kg <sub>dry m</sub>	Wtr % by weight	Hg mg/kg <sub>dry m</sub>
Bilina mine	HP1	27.43	0.157 ± 0.011	28.06	0.257 ± 0.019
	PS1	26.44	0.182 ± 0.013	24.75	0.180 ± 0.013
	PS2	24.42	0.200 ± 0.015	25.73	0.212 ± 0.15
	HP1	28.1	0.153 ± 0.011	27.73	0.107 ± 0.008
	HP1	27.3	0.176 ± 0.013	29.49	0.222 ± 0.016
	PS2	25.11	0.325 ± 0.024	25.76	0.284 ± 0.021
	PS2	25.49	0.259 ± 0.019	24.23	0.283 ± 0.021
	PS1	26.42	0.225 ± 0.016	24.63	0.275 ± 0.020
	PS1	27.62	0.158 ± 0.012	26.90	0.159 ± 0.012
DNT	PS2	28.95	0.233 ± 0.017	31.13	0.188 ± 0.014
	PS2	28.75	0.218 ± 0.016	31.88	0.197 ± 0.014
	PS2	29.66	0.256 ± 0.019	30.93	0.225 ± 0.016
Jiří mine	PS2	34.89	0.510 ± 0.040	33.18	0.572 ± 0.042
	PS2	34.05	0.358 ± 0.026	40.24	0.441 ± 0.032
	PS2	34.21	0.540 ± 0.040	34.63	0.432 ± 0.032
Vršany	PS3	26.19	0.192 ± 0.014	28.6	0.237 ± 0.017
	PS3	26.5	0.284 ± 0.021	28.03	0.273 ± 0.020
	PS3	25.98	0.256 ± 0.019	28.26	0.275 ± 0.020
Mibrag	PS	-	-	45.8	0.290 ± 0.019

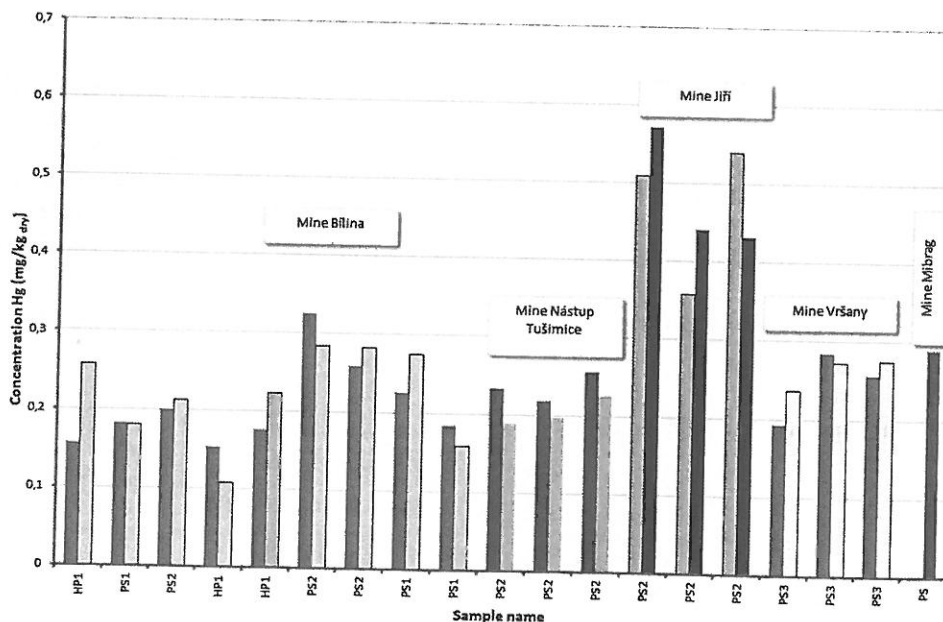


Figure 1. Overview of mercury content in various fuels analyzed in 2014 and 2015

The results show that Hg concentrations in the coal samples taken in 2014 and 2015 differ only to a minimum degree. The greatest Hg concentration was found in the coal sample taken from the Jiří mine, where the average value is 0.482 mg/kg<sub>dry</sub>. The lowest Hg concentration was found in the coal sample taken from the Nástup Tušimice mine, namely 0.203 mg/kg<sub>dry</sub>. Based on the decision of the Czech government not to continue mining in the ČSA mine, no samples were available for the analyses.

The results of chlorine concentrations are shown in the following table.

Table III  
Cl concentrations in fuel – lignite

Mine	Fuel type	Cl %	Mine	Fuel type	Cl %
Bílina mine	HP1	0.0065 ± 0.0007	Jiří mine	PS2	0.0088 ± 0.0009
	PS1	0.0081 ± 0.0008		PS2	0.0120 ± 0.0012
	PS2	0.0034 ± 0.0003		PS2	0.0077 ± 0.0008
	HP1	0.0137 ± 0.0014	Vršany	PS3	0.0093 ± 0.0009
	HP1	0.0097 ± 0.0010		PS3	<0.0010
	PS2	0.0052 ± 0.0005		PS3	0.0079 ± 0.0008
	PS2	0.0077 ± 0.0008	Mibrag	PS	0.0162 ± 0.0016
	PS1	0.0034 ± 0.0003			
	DNT	PS1	0.0091 ± 0.0009		
		PS2	0.0222 ± 0.0022		
PS2		<0.0010			
PS2		0.0032 ± 0.0003			

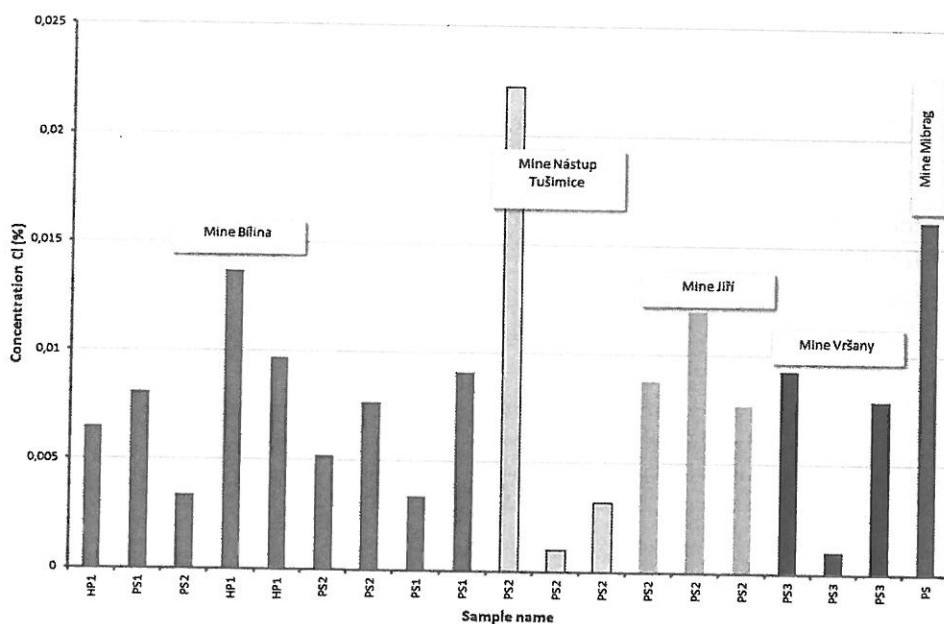


Figure 2. Overview of Cl content in various fuels.

### Measurements in Power plant

The first measurement test of Hg concentrations within the framework of the research project was carried out on Unit 2 of the Dětmarovice Power Plant. The following text contains the results of analyses of solid samples taken, namely of coal, slag, fly ash taken from under the air heater, fly ash taken from individual sections of the electrostatic precipitator (next only ESP), gypsum suspension. Furthermore, the following text also contains the tabulated results of analyses of the flue gas sampled before ESP, after ESP and at the outlet from flue gas desulphurisation (next only FGD), i.e. at the stack inlet. Flue gas was fed into the Hg sorption system. The ASTM-D6784 method - "Ontario Hydro Method" - was chosen here because this globally recognized method guarantees the identification of Hg<sup>0</sup>, atomic mercury and oxidized mercury Hg<sup>2+</sup>. (The conventional method pursuant to ČSN EN 13211 was assessed as insufficient for this purpose because it does not allow Hg specification).

### Results of product analyses

During the measurement tests, samples of fuel, slag and fly-ash were taken from under the air heater, ash samples from individual sections of the ESP and gypsum suspension sample from the wet flue gas desulphurisation technology - FGD. The results of the sample analyses are given in the following tables.

Table IV

Hg concentrations – fuel, slag, ash, gypsum suspension

Sample	Hg (mg/kg <sub>dry,m</sub> )	Average Hg (mg/kg <sub>dry,m</sub> )	Sample	Electrostatic precipitator section				Air heater
				Section I	Section II	Section III	Section IV	
Sample 1 - fuel	0.094	0.109	Sample 1	0.323	0.748	0.736	0.558	0.021
Sample 2 - fuel	0.069		Sample 2	0.286	0.594	0.555	0.530	0.016
Sample 3 - fuel	0.088		Sample 3	0.296	0.797	0.768	0.451	0.014
Sample 4 - fuel	0.183		Sample 4	0.349	0.640	0.783	0.440	0.020
Sample - Slag	0.002	0.002	Sample 5	0.212	0.616	0.826	0.827	0.014
Gypsum suspension	0.101	0.101	<b>Average value</b>	<b>0.293</b>	<b>0.679</b>	<b>0.734</b>	<b>0.561</b>	<b>0.017</b>

### Result of flue gas analyses

Using isokinetic sampling, flue gas samples were taken before ESP, after ESP and at the outlet from FGD. Subsequently, the sampled flue gas was fed to the Hg sorption system. The output emission limit pursuant to the BAT legislation under preparation is 4 µg/Nm<sup>3</sup>.

Table V

Hg concentrations - flue gas (µg/Nm<sup>3</sup>)

Sampling point	O <sub>2</sub> concentration = 6%			
	Hg <sup>0</sup>	Hg <sup>2+</sup>	Hg <sup>(p)</sup>	Hg <sup>(total)</sup>
Sample 1 - Before ESP	0.72	6.66	6.75	14.13
Sample 2 - Before ESP	2.48	5.92	9.20	17.60
Sample 3 - Before ESP	0.55	6.21	4.55	11.31
Sample 1 - After ESP	0.77	8.65	0.01	9.43
Sample 2 - After ESP	0.74	6.23	0.00	6.97
Sample 3 - After ESP	0.71	6.75	0.00	7.46
Sample 1 - After FGD	1.40	5.59	0.01	<b>7.00</b>
Sample 2 - After FGD	1.28	4.83	0.00	<b>6.11</b>
Sample 3 - After FGD	1.29	3.33	0.01	<b>4.63</b>

### Pilot plant

The main objective of the project, and not only in 2015, is the production and commissioning of a pilot plant to study the influence of the actually available methods on the oxidation of atomic mercury Hg<sup>0</sup> into the oxidized form Hg<sup>2+</sup>. Oxidation of Hg<sup>0</sup> into the oxidized form Hg<sup>2+</sup> will take place at the catalyst layer. The pilot plant consists of several parts. The flue gas sampled from the flue gas duct is fed into the reactor via electrical heating, measuring section. A plate-type catalyst with the dimensions of about 320 x 320 x 700 mm is used for the oxidation of the atomic form of Hg<sup>0</sup> into the oxidized form. The reactor is also equipped with a flue gas flow deflector, blow-off nozzles and a measurement device. The whole reactor is stored in a supporting steel structure and the sections can be modularly stacked on each other. The flue gas flow deflectors serve to unify the speed profile across the reactor cross section. Due to the possible deposits of dirt, particularly on the leading edges of the catalyst plates, each module of the reactor is equipped with blow-off nozzles positioned about 350 mm above the plane of the catalyst. Blowing of the catalysts is carried out at appropriate time intervals separately for each module. These intervals will be determined based on experience with the operation of the reactor, and their setting is possible using electronic timers at the individual solenoid valves on the distribution battery. The reactor is provided with an inspection hole, which is equipped with a blow-off device for the case of fouling. The inspection hole is primarily used to check fouling of the leading edges of the catalyst plates. Flue gas discharged at the bottom of the reactor is fed to the measuring section and then to the flue gas fan, which is designed to cover pressure losses in the duct and the catalyst itself. A diagram of the whole system and the layout are given in the Annexes to the interim research report.

The reactor will be provided with thermal insulation with the thickness of 160 mm, where the contact temperature of the surface will not exceed 50 °C at any point.

A diagram of the pilot plant is shown figure 3.

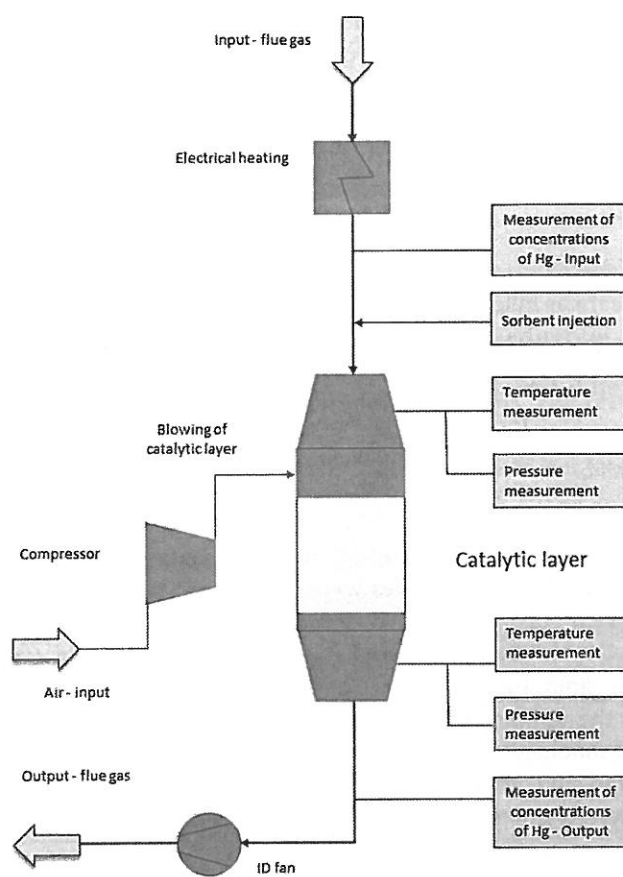


Figure 3. Pilot plant – schema

The parameters of the pilot plant are listed in the following table.

Table VI

Pilot plants parameters

Parameter	Unit	Value
Inlet flue gas amount	Nm <sup>3</sup> /h	400
Flue gas temperature at the inlet to the unit	°C	300 - 350
Catalyst size		
Length	mm	320
Width	mm	320
Height	mm	700
Speed of flue gas passing through the unit	m/s	4.5
Unit size		
Length	mm	1,400
Width	mm	1,400
Height	mm	2,600
Unit weight	kg	570
Unit output (flue gas fan)	kW	5
Flue gas electric heating output	kW	12

## Conclusion

The present article summarizes the results of the first part of project implementation, during which samples of brown coals were taken and analysed for Hg and Cl concentrations. Average Hg concentrations were as follows:

- Coal from the Bílina mine (HP1, PS1 and PS2) 0.220 mg/kg<sub>dry m</sub>
- Coal from the Nástup Tušimice mine (PS2) 0.203 mg/kg<sub>dry m</sub>
- Coal from the Vršany mine (PS3) 0.482 mg/kg<sub>dry m</sub>
- Coal from the Jiří mine 0.262 mg/kg<sub>dry m</sub>
- Coal from the Mibrag mine 0.290 mg/kg<sub>dry m</sub>

Average Cl concentrations were as follows:

- Coal from the Bílina mine (HP1, PS1 and PS2) 0.0074 %
- Coal from the Nástup Tušimice mine (PS2) 0.0088 %
- Coal from the Vršany mine (PS3) 0.0095 %
- Coal from the Jiří mine 0.0061 %
- Coal from the Mibrag mine 0.0162 %

Measurements were carried out at the Dětmárovice Power Plant during which samples of fuel, slag, fly ash and gypsum were taken; in addition, flue gas samples were taken from three sampling points using the sampling method. From the perspective of formation of the various Hg forms, it is obvious that after passing through the ESP the Hg form bound to the Hg<sup>p</sup> fly ash is completely separated. The main result of the measurement is, however, that the emission limit for the Hg concentration of 4 µg/Nm<sup>3</sup>, given by the legislation under preparation, is exceeded in the samples of flue gas discharged from desulphurisation and therefore it will be necessary to implement technology to reduce Hg concentrations. Toward the end of the year, project documentation was prepared and implementation of the pilot plant designed to transform Hg using the catalytic layer was started. At the end of 2015, the pilot unit was put into operation.

## Acknowledgement

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