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

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Abstract

The contribution introduces the project TAČR TA04020723 „Development of a pilot plant for monitoring of Hg emissions reduction from large and medium capacity energy sources“. The project responds to the new EU BAT legislative, where both emission limits for Hg concentration in flue gas and continual Hg concentration measurement requirements are stated. The objective of the contribution is an introduction of the project and the results gained in 2014. Analyses of certain lignite and coal samples were done to specify the Hg amount and balance of other compounds concentration was calculated with regard to the specifics of combustion process of a particular power source. At the end of 2014, a measurement was carried out at the large power plant. Hg concentrations were measured in the combustion products and were compared with balance calculation.

Introduction

Effort for global protection of air environment is realized in the field of emissions. Reason for this is the fact, that emission of pollution exhausted in the air are transported by wind away, contaminate the surroundings regardless of regional borders. Therefore, EU also focuses its pursuit of environment protection on limit of emissions exhausted into the air. On the other hand, solid wastes are usually treated on the national level via regulations and acts.

Based on proved negative effects on livestock, actual topic addressed on international level is the lowering of mercury emissions exhausted into the air. Mercury concerned is mercury emitted during combustion of fossil fuels. Mercury in the living environment present serious health risk, and therefore its occurrence in the environment is watched carefully. Mercury is strongly neurotoxic and accumulates in food chains. Mercury gets into the human body mainly by inhaling its vapors, which have comparatively long half-life of permanence in atmosphere, where they appear in elementary form, (Hg^0), as oxides (Hg^{2+}) or bound to very fine-grain particles in aerosols. Its presence in human body results in damages to nervous system, kidneys, respiratory ways, damage of blood production and another diseases.

Therefore the newly prepared documentation in the EU called „Best Available Techniques (BAT) Reference Document for the Large Combustion Plants“, that sets emission limits for mercury concentration both for existing and new devices. Emission limits are sets in the following table:

Table I Emission limits

Combustion facility of rated heat intake (MW_t)	Hg emissions ($\mu\text{g}/\text{Nm}^3$)		rated period	monitoring
	new source	existing source		
coal: anthracite and black bituminous				
< 300	0.5 - 5	1 - 10	average taken from samples gathered during one year period	4times a year
> 300	0.2 - 2	0.2 - 6	year average	Continual measurement
coal: sub-bituminous and lignite				
< 300	1 - 10	2 - 20	average taken from samples gathered during one year period	4times a year
> 300	0.5 - 5	0.5 - 10	year average	Continual measurement

Presented confirmed base measurements will be implemented into legislation of EU member states after 2019. In The Czech Republic, actually no continual measurement of mercury concentration in flue gas is carried out and no technological solution or facility aiming for emission reduction of mercury in flue gas is in place.

Projects objectives

Objectives of the projects are to identify actual distribution of emitted mercury and subsequently to design solution of the problem in order to reach expected emission limits. Actual condition will be verified on chosen representative energy sources combusting fossil fuels in the Czech Republic. Design of technical economical solution for reaching expected future emission limit of mercury will be tested on pilot unit, that will be using catalytic effects of the SCR method. Optimal conditions will be investigated, when necessary level of denitrification has been reached and mercury has been sufficiently oxidized at the same time. Results of this project solution will verify assumptions, on which the principle is based and new technical documentation of changes in existing facilities will be carried out or preliminary documentation of new facilities for mercury emissions elimination will be carried out. Necessary analytical methods for checking of the emission limits will be verified as a part of the project.

Hg forms

During coal combustion at temperatures of 700-800°C decomposition of mercury compound is taking place while elementary mercury Hg^0 is formed. This mercury leaves the combustion chamber in the form flue gas flow. After the flue gas is cooled while going through heat-exchange surfaces (on 200-250°C) of mercury reacts with present halogens, in particular with $HgCl_2$, eventually Hg_2Cl_2 . Mercury is also trapped on the surface of escaping ash (Hg^p), which is subsequently eliminated in ash separator. Remaining part is then emitted in the air. See fig n.1.

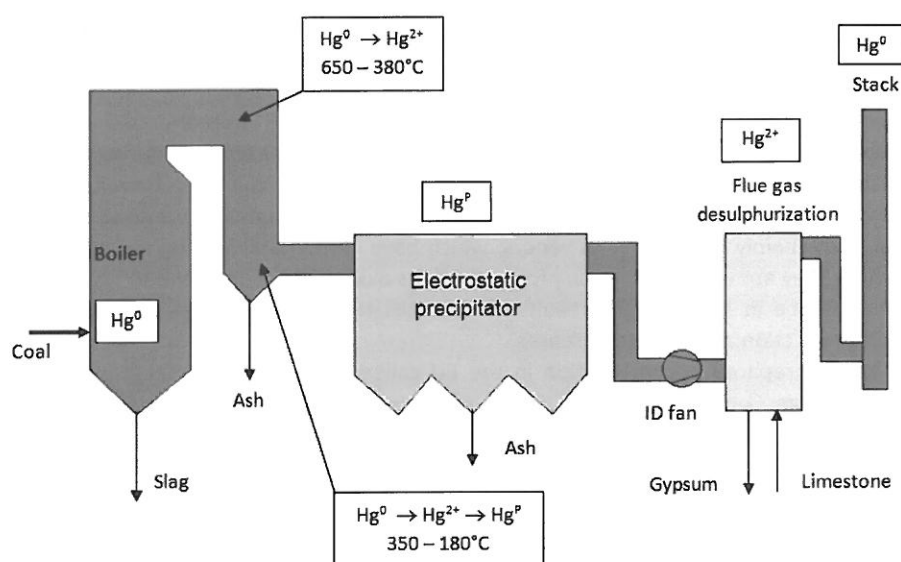


Figure 1. Scheme Hg distribution in the flue gas.

Mercury is then present in the flue gas in metallic form as atomic Hg^0 , oxidized as Hg^{2+} ($HgCl_2$, Hg_2Cl_2 or HgO) or further adsorbed; Hg^p . Oxidized form can be eliminated by wet or dry desulphurization of flue gas. On the other hand, elimination of elementary mercury is very difficult and escapes into the air. Resulting from continuous measurements, 15 % of total mercury entering as a part of the fuel is trapped on the ash and 5 to 10% of mercury goes. The rest is emitted with the flue gas into the air. This situation of emissions is fulfilling actual limits, but the expected change of limit concentration raises the necessity of redistribution of mercury and its compounds.

Methods for mercury concentration reduction in the flue gas

Following methods can be used industrially for reduction of mercury concentration> As one of the most widely used methods of heavy metals adsorption but also of persistent agents (PCDD/F), adsorption using carbon sorbents is used. This technology is commonly used for purification of flue gas from incinerators Sorbent is added together with an additive ($Ca(OH)_2$, $NaOH$, $NaHCO_3$ etc.) into the stream of flue gas during semi-dry or

dry method of purification.. Contaminated carbon sorbent together with purification products is trapped by ash separator.

Another method of Hg concentration reduction is using the BBA method (Boiler bromide addition). The core of the method is the addition of halogenides into the combustion place. As a result of the additive, mercury is oxidized into soluble forms, so entrapment rate of mercury is increased in subsequent facilities formed by filters and wet purification of flue gas. The method is very debated with respect to creation of not only halogenides of mercury creation, but also of other persistent agents, in particular polybrominated dibenzodioxins and dibenzofurans.

Another method is to use catalyser primarily designed for elimination of emissions of NO using SCR method. (Selective Catalytic reduction) It is assumed, that increased oxidation of gaseous Hg^0 will take place in comparison with actual condition without catalyser. Subsequently, Hg^{2+} can be trapped in existing desulphurization facilities. Implementation of catalytic reduction into flue gas mains and requested division of mercury is shown on Figure n.2.

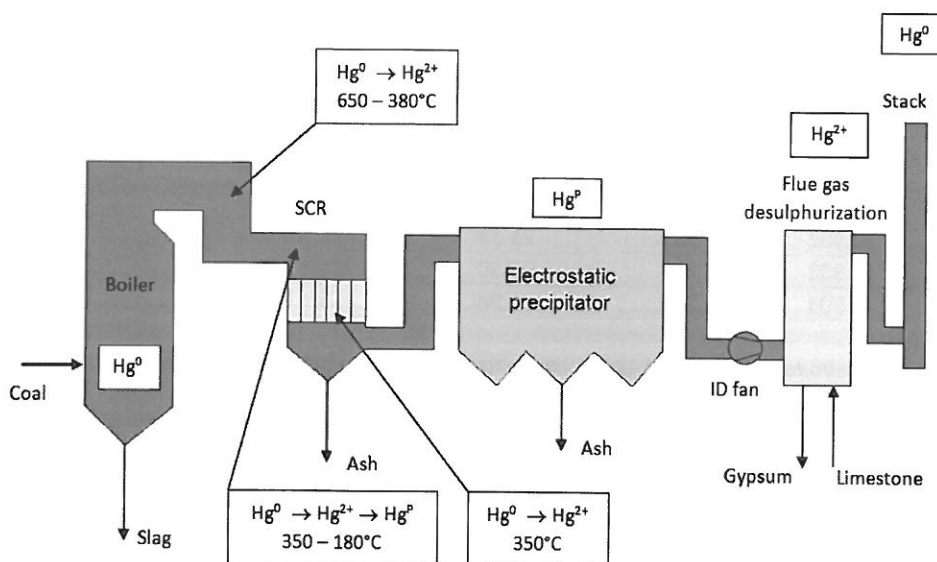


Figure 2. Scheme of Hg distribution in the flue gas using SCR for fulfillment of expected emission limits.

Analysis of fuel composition

In 2013, around 40.6 mil tons¹ of lignite (in 2014 the prediction was 38.5 mil. tons of coal²) in the Czech Republic and the amount is almost completely used as energy fuel both in power plants or heat production facilities. Main areas of coal mining are situated in the area of Podkrušnohoří in Chebská plateau, Sokolovská plateau and North-Bohemian coal plateau.

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.

Lignite

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
Jíří mine – sample DT - NS II

Analyses results are shown in the following Table II.

Table II Hg concentration in different types of lignite

Mine	Sample name	Fuel type	Wtr % mass.	Hg mg/kg dry.
Bílina mine	81887	HP1	27.43	0.157 ± 0.011
	81888	PS1	26.44	0.182 ± 0.013
	81889	PS2	24.42	0.200 ± 0.015
	81893	HP1	28.10	0.153 ± 0.011
	81894	HP1	27.30	0.176 ± 0.013
	81895	PS2	25.11	0.325 ± 0.024
	81896	PS2	25.49	0.259 ± 0.019
	81897	PS1	26.42	0.225 ± 0.016
	81898	PS1	27.62	0.158 ± 0.012
DNT	81899	PS2	28.95	0.233 ± 0.017
	81900	PS2	28.75	0.218 ± 0.016
	81901	PS2	29.66	0.256 ± 0.019
Jiří mine	81890	PS2	34.89	0.510 ± 0.040
	81891	PS2	34.05	0.358 ± 0.026
	81892	PS2	34.21	0.540 ± 0.040
Vršany	81902	PS3	26.19	0.192 ± 0.014
	81903	PS3	26.50	0.284 ± 0.021
	81904	PS3	25.98	0.256 ± 0.019

From the analyses above it follows, that Hg concentration is changing according mining area. According to power generation institute [1] in 2014 33.6 mil. tons of lignite was exploited (Bílina mine – 9.5 mil. tons/year, Nástup Tušimice mine – 12.0 mil. tons/year, Jiří mine – 6.1 mil. tons/year, Vršany mine – 6.00 mil. tons/year) and around 6.41 tons of mercury is released into air by its combustion. Mercury concentration is observed in the long term and its values are stated in the coal catalogue. Stability of mercury concentration in mined coal is obvious from these data. Some variations are caused by changing the mining bed. Result is obvious from the following figure, where analyzed mercury concentrations are compared with mercury concentration stated in available coal catalogues of given mining area.

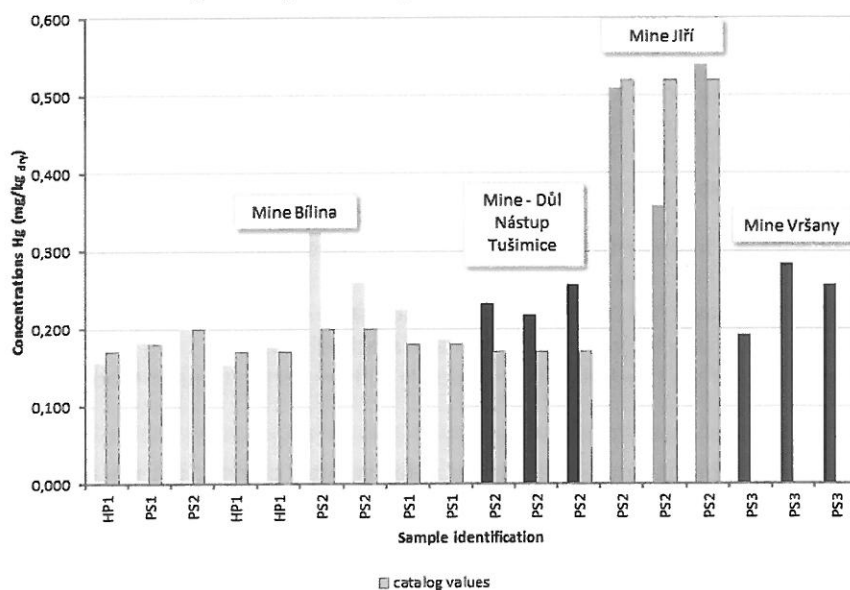


Figure 3. Comparison of cataloged Hg concentrations with analyzed concentrations in taken samples.

Coal

Coal is mined in deep mines and in 2013 8.6 mil tons was exploited in the Czech republic. In Karviná mine 2.62 mil. tons was mine, in Darkov mine 2.65 mil. tons was mined and in ČSM mine 2.48 mil. tons was mined and in

Paskov 0.86 mil. ton was mined. Samples of coal were analyzed and Hg concentration was within range from 0,109 mg/kg_{dry matter} to 0,152 mg/kg_{dry matter}.

Discussion of measures

For measurement design it is necessary to base them on balance calculations, which point to concentrations of observed samples with knowledge of usual combustion mode in chosen sources. Knowledge of these concentrations then give the notion of analytical methods and procedures of samples taking in single points of flue gas flows. They subsequently the baseline for mathematical models of processes involved in mercury distribution as a main observed element. Balance calculation is an essential part of relevant data set for facility design and for measurements for change in distribution of mercury along flue gas mains.

Balance compounds then must be set and these should be compliant with observed elements. This choice has to be harmonized with measurement equipment available, so we can carry out the balance calculation also based on the experimental data. Another essential part of balance calculation is a technology-balance scheme. Lets assume a boiler combusting lignite as a source of energy. Dross is produced as part of ash products. Compliant with scheme on Figure 2., catalytic denitrification SCR unit is equipped in the flue gas mains, at temperatures 350 to 400°C. Flue gas then goes through recuperation exchanger (LUVVO), where part of the ash parts is trapped. Main part of the fine ash is separated in electric separator. Flue gas with main part of the fine ash eliminated are the led into the process of wet desulphurization. Desulphurization is carried out using a calcite and energoplaster is formed. Technology-balance scheme is shown on the Figure 4 following. Single arrows denote the mass flow direction and each flow is denoted by a number.

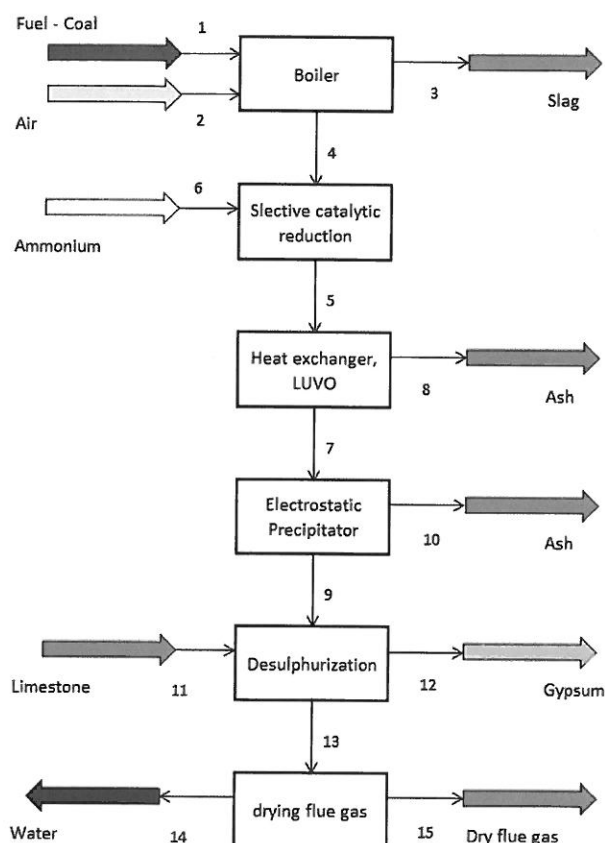


Figure 4. Technology-balance scheme of energetic unit with SCR denitrification and wet limestone purification. Calculation will be carried out with the assumption, that Hg concentration is equal to 0.5 mg/kg in dry fuel. Amount and composition of fuel entering the burning place is given by following table.

Table III Inlet - fuel

Flow no. 1	Fuel
Weight:	245.64 kg
element	X
carbon	0.2634
hydrogen:	0.0232
nitrogen:	0.0048
sulphur:	0.0199
oxygen:	0.0955
chlorine:	7.21E-05
fluorine:	1.19E-04
ash:	0.2829
mercury:	2.04E-07
water:	0.31

X column contains the mass ration of a given element. Along with fuel, air is taken to the combusting place. Amount and composition is shown in Table IV:

Table IV combustion air – inlet

Flow no. 2	combustion air
Weight:	1075.41 kg
element	X
nitrogen:	0.7479
oxygen:	0.2321
water:	0.02

Solution condition for compliance with emission limits for lignite for sources < 300 MW are emissions with limits of 2µg Hg/Nm³. Wet flue gas is formed as a result of the combustion. Analyses is given with respect to dry flue gas and therefore amount and composition of dry flue gas is given in Table V.

Table V Dry flue gas

Flow no. 15	Dry flue gas				
Weight:	1096.822	kg	801.8677	Nm ³	
		X	kmol		
nitrogen:	0.7349		28.788		
oxygen:	0.0428		1.467	4.098	% vol.
ash:	1.00E-05				
mercury:	2.50E-09			3.42E+00	µg/Nm ³
CO ₂ :	0.222		5.535		
CO:	1.29E-04		0.005054	176.463	mg/Nm ³
SO ₂ :	7.30E-05		0.001252	99.892	mg/Nm ³
NO:	5.18E-05		0.001893	70.835	mg/Nm ³

Summary

Analyses of lignite has shown, that mercury concentration varies from 0.2 mg/kg up to do 0.5 mg/kg according to mining area and mine respectively. Mercury content in black coal is roughly half. Based on mathematical model, necessary conditions for mercury redistribution were set with compliance with expected emission limits at the same time. Amount of mercury emitted into the air for combustion of brown air is at the level of 5.4% of total mercury entering the combusting place with the fuel. Remaining part is therefore necessary to be redistributed into outlet streams. It is mostly fine ash and plaster. Amount of dross and fine ash from heat exchanger (LUVA) is negligible in comparison with other streams. Based on calculations, assumed redistribution of mercury between streams is shown on the following chart:

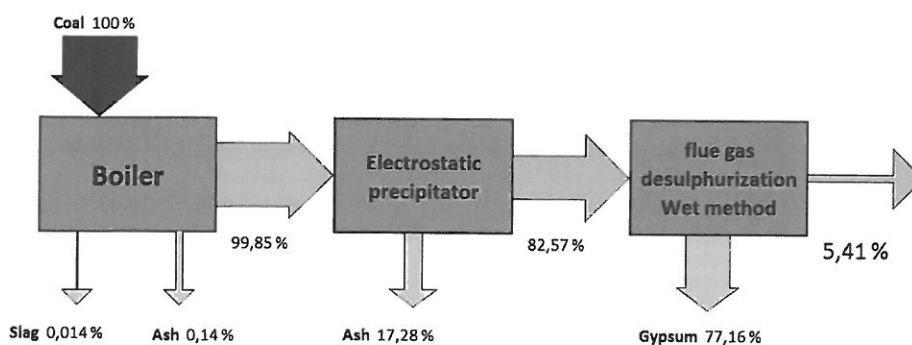


Figure 6. Assumed Hg distribution when using its oxidation on the catalyser for flue gas denitrification using ammonium.

Thermic and concentration conditions have to be found, when catalytic oxidation transforms the atomary mercury into easily separable compounds, especially in wet limestone purification.

Acknowledgment

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