Co-benefit of catalytic denitrification for reduction of mercury emissions

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Keywords: Catalytic Denitrification, Gas Cleaning, Mercury Emission, Mercury Removal

1. Introduction

1.1. Mercury facts

Mercury is a chemical element with symbol Hg, formerly named „quicksilver". It has been known and used since ancient times. Mercury is one of the only two elements that are liquid under standard conditions. It is used in products like: fluorescent lamps, batteries, cosmetics, electrical equipment, measuring instruments (thermometers, pressure gauges), dental filling and many others. Mercury compounds are also widely used in agricultural chemistry (pesticides, biocides).

Despite its popularity and a wide variety of applications mercury is poisonous to living organisms and environment with mercury toxicity most commonly affecting neurologic (e.g. brain) and renal organ systems. After intake, mercury excretion is a long-term one – the half-life of mercury is within the range of several years – causing not only direct poisoning but also passing along the food chain.

The most well-known example of severe mercury poisoning was the dumping of mercury compounds (methyl mercury) into Minamata Bay in Japan. In the 60' last century Minamata Bay became polluted by akylmercury compounds contained in wastewater discharged into the bay. Polluted fish and shellfish resulted in mass toxicosis, with permanent and irreversible damage to brain (especially in children) or deaths. The name of the Minamata Bay has become a symbol of the efforts to control and decrease the level of mercury in the environment. The UN Convention on Mercury that is being developed under the auspices of UNEP is popularly referred to as the *Minamata Convention*.

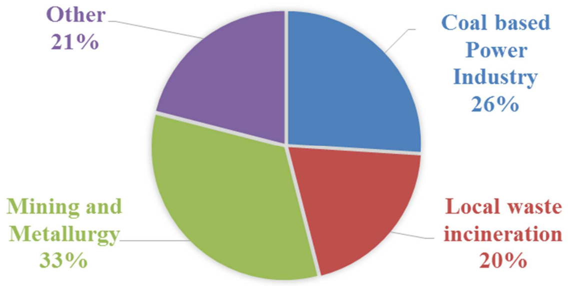

Figure 1. Sources of mercury emissions [1]

The largest sources of mercury emissions within the aforementioned groups include:

- ✓ Cement Production – 9%;
- ✓ Chemical Industry (especially Chlor-alkai) – 2%;
- ✓ Waste Incineration – 2%;
- ✓ Gold Mining & Jewellery – 29%.

Total estimated global anthropogenic mercury emissions are 1920 tons.

1.2. Global mercury emissions from fossil-fuel fired power plants

The estimated global mercury emissions from coal fired power plants is 500 t/year. Figure 2 presents data on emissions in selected countries, or regions, in 2005.

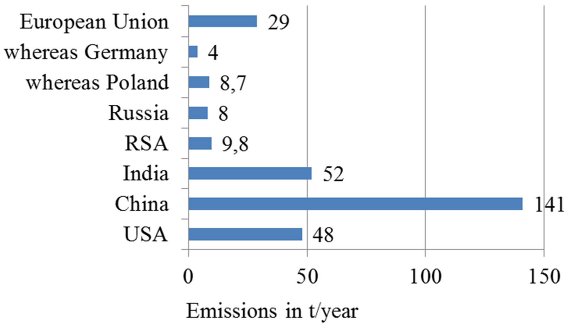

Figure 2. Annual global mercury emissions from coal-fired boilers [1]

With regard to the aforementioned comparison some important information should be pointed out:

- ✓ Emissions in EU member states in 1995 amounted to 52 t/year. Emissions from coal-fired power plants decreased from 52 to 29 tons mostly due to wide applications of desulphurisation and denitrification systems in power plants. The later part of this study indicates that a "co-benefit" of Selective Catalytic Reduction (SCR) and WFGD systems as well as efficient de-dusting technologies is a dramatic reduction of Hg emission. This effect may be observed in EU.
- ✓ Since coal-fired boilers in China are in principle equipped with FGD and SCR systems, significant reduction in Hg emission may also be expected there.
- ✓ Mercury emissions in Poland shall be verified soon. The aforementioned value has been explained in this section.

1.3. Mercury emissions from coal combustion in Poland

The first and most advanced EU normative act will implement mandatory and continuous monitoring of Hg emission. Such provision has been included inter alia in the new IED Directive.

In case of Poland, implementation of emission monitoring will update the current emission values which often vary depending on the source of publication.

- ✓ Poland's National Inventory Report (Greenhouse Inventory) 2009–2010 – published by the National Centre of Emissions Monitoring (KOBiZE) includes the following values as for 2010:
  - Combustion processes in energy generation and transformation system – 8.7 t/year;
  - Non-industrial combustion processes – 1.8 t/year;
  - Industrial combustion processes – 3.5 t/year;
  - In total – 14.0 t/year.

Total mercury emission from all sources – 14.8 t/year.

The report indicates increased mercury emission in 2010 by 4.4%.

- ✓ Data in the MERCPOL project indicate mercury air emissions in 2008:
  - from combustion by energy sources (energy and heat generation) – 16 t/year.

Total mercury air emissions – 21.2 t/year.

The report indicates possible verification and decrease in reported values.

- ✓ In an interesting study "ENERGOPOMIAR" Sp. z o.o. estimated mercury transport into fossil-fuel (lignite and hard coal) fired power plants (ca. 21 t/year) and percentage of mercury emission (from sample facilities of ca. 38–90%). The results of estimations confirm the value of mercury air emission amounting to ca. 10–15 t/year during coal combustion by energy sector and industrial sector.

2. Current and expected mercury emission regulations and thresholds

2.1. International Mercury Convention

In 2001, during 21st session of the United Nations Environment Programme (UNEP) Governing Council (GC) initiated action towards international control and reduction of mercury emissions. The final stage of works on Mercury Convention involving negotiations of its final content started in 2010. On 10th October 2013 International Mercury Convention was signed at the Minamata Bay in Japan. After ratification of the Convention by at least 50 countries it will become effective.

The Minamata Convention provides for the following:

- ✓ Obligatory control of mercury air emission from respective sources – Inter alia: coal combustion, heavy metal production (lead, zinc and copper), waste incineration plants, cement production, gold mining industry;
- ✓ Determination of requirements for new and existing sources of emission; BAT/BEP guidelines;
- ✓ Corrective actions – national action/implementation plans;
- ✓ Implementation of emission thresholds;
- ✓ Obligatory emission inventory reports.

It should be emphasised that UNEP Mercury Convention is not the only international document providing for reduction of Hg emission. The respective provisions are also included in the following documents:

- ✓ Montreal Protocol that Deplete the Ozone Layer;
- ✓ The Basel Convention on the Control of Transboundary Movements of Hazardous Wastes;
- ✓ Rotterdam Convention.

Supporting resolution of the Convention, the European Union has been actively participating in preparatory works. Therefore it is not surprisingly that many of the conditions and regulations included to the convention reflect to the one of most important environmental document of EU: BAT Reference Document for the Large Combustion Plants.

2.2. Best Available Techniques (BAT) Reference Document for the Large Combustion Plants

Industrial Emissions Directive 2010/75/EU

Conclusions included to this document will represent the firm and obligatory conditions for mercury emissions valid within European Union. The document is expected to become effective as of 2017 and the emission limits will be mandatory starting from 2021.

Emissions limits defined by the BAT Reference Document are:

- ✓ For coal fired boiler < 300 MWth: 1 – 9 µg/Nm^3 (existing) and 1 – 3 µg/Nm^3 (new)
- ✓ For coal fired boiler ≥ 300 MWth: 1 – 4 µg/Nm^3 (existing) and 1 – 2 µg/Nm^3 (new)
- ✓ For lignite fired boiler < 300 MWth: 1 – 10 µg/Nm^3 (existing) and 1 – 5 µg/Nm^3 (new)
- ✓ For coal fired boiler ≥ 300 MWth: 1 – 7 µg/Nm^3 (existing) and 1 – 4 µg/Nm^3 (new)

For units ≥ 300 MWth permanent Hg-emission measurement must be installed.

2.3. Other applicable EU documents

After implementation of the European Strategy on Mercury in 2005 (and its ratification in 2011) EU has implemented several regulations on mercury emissions:

- ✓ Regulation (EC) No 1907/2006 of the European Parliament and of the Council of 18 December 2006 concerning the Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH), establishing a European Chemicals Agency
- ✓ Commission Regulation (EU) No 847/2012 of 19 September 2012 amending Annex XVII to Regulation (EC) No 1970/2006 of the European Parliament and of the Council on the Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH) as regards mercury;

- ✓ Commission Regulation (EU) No 848/2012 of 19 September 2012 amending Annex XVII to Regulation (EC) No 1907/2006 of the European Parliament and of the Council on the Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH) as regards phenyl mercury compounds.

The aforementioned documents refer to production, utilisation, import, and disposal of products containing mercury. Until the present moment, no explicit regulations have been implemented as regards mercury emission during fuel combustion in power generation. Such regulations have already been implemented in some of the EU member states, e.g. Germany or the Netherlands.

2.4. Mercury monitoring in Canada and the United States of America

As early as in 2000, after a long-term research, the United States Environmental Protection Agency (EPA) provided scientific and legal framework confirming “suitability and necessity” of reducing mercury emissions from power plants.

The government prepared appropriate program of mercury emission reduction in power industry; however, the process was suspended by a court decision and returned to EPA with a request to prepare standards corresponding to current state of the art and legal regulations.

After verification “Mercury and Air Toxics Standards MATS” standard was published on 16 March 2011 as a draft and on 16 December 2011 in its final form.

MATS is applicable, without any exclusions, to all facilities with capacity of MWe and higher. Emission values have been adapted to the average value achieved by 12% of power units with the highest degree of emission reduction.

MATS provides for the following maximum values of mercury air emissions:

- ✓ as regards the existing hard coal fired facilities – 1.8 g/GWh
- ✓ as regards new hard coal fired facilities – 0.08 g/GWh

The existing facilities must be capable of meeting MATS within 4 years.

Canada has implemented “Canada-Wide Standards for Mercury Emissions” standard that was published in the period of 5-6 June 2000 by CCME Council of Ministers in Quebec City and became applicable to all states. In 2006 this standard was completed with a part concerning emissions from fossil-fuel fired plants. The standard provides for the following:

- ✓ as regards the existing facilities specific emission thresholds have been implemented in each state. Reduction of emission from the existing power plants in the period of 2003/04 and 2010 is 52%;
- ✓ as regards new facilities reduction of emissions is 75–85% compared to mercury contained in fuel and does not exceed 3–8 kg/TWh in case of hard coal (depending on the type) and 8 kg/TWh in case of lignite.

3. Mercury emissions and possible reductions in the process of coal combustion

3.1. Forms of mercury emissions and their formation in the process of coal combustion

Mercury occurs in flue gas of a coal-fired boiler, both inside the boiler and downstream, in the three following forms:

- ✓ Gaseous elemental mercury Hg^0;
- ✓ Gaseous oxidized mercury Hg^{2+};
- ✓ Particulate-bound mercury Hg_p – with solids like ash or unburned coal.

Natural mercury in coal deposits most often has a form of mercuric sulphates formed during combustion process. Mercury content depends on particular deposits, whereas in Poland the average mercury content in hard coal is within the range of 50–150 ppb, while in lignite it is between 120 and 370 ppb. Large coal mining sites are characterized by high levels of mercury content:

- ✓ Hard coal from “Bogdanka” coal mine – 561 ppb;
- ✓ Lignite from deposits of KWB Bełchatów coal mine – 1030 ppb or
- ✓ KWB Turów coal mine – 947 ppb.

For the purpose of comparison – mercury content in US coals is between 30–670 ppb, where the average value for hard coal is 70 ppb, and for lignite it is 118 ppb.

During the process of coal combustion at temp. of ca. 1500°C mercury contained in coal is volatilized to elemental mercury (Hg0). As the flue gas is cooled a series of complex reactions with other combustion products begin to convert Hg0 to other forms. Mercury conversion is affected by the following elements of flue gas:

- ✓ CO2, H2O, SO2, NOx, N2;
- ✓ HBr, HCl;
- ✓ fly ash and unburned coal.

As the flue gas is cooled, Hg^0 oxidation to Hg^{2+} occurs on boiler heating surfaces. Main forms of oxidized mercury are: HgBR2, HgCl2, HgO, HgSO4.

The most intensive Hg0 oxidation reaction takes place on the surface of SCR catalysts.

As the flue gas continues to be cooled down, starting from air pre-heaters, mercury forms compounds with solid particles contained in flue gas, such as fly ash or unburned coal. Mercury compounds are referred to as Hg_p.

Knowledge about mercury transformation processes is essential to the process of emission reduction. Elemental mercury Hg0 occurs in almost 100% of air emissions, whereas majority of oxidized mercury and mercury compounds (particle-bound mercury), thanks to their solubility, may be captured by flue gas cleaning systems. Figure 3 illustrates schematic transformation of mercury:

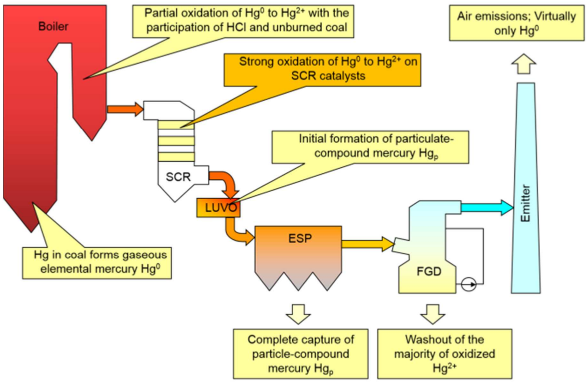

Figure 3. Mercury transformation mechanisms in the process of combustion and flue gas cleaning – according to Niksa and Fujiwara [2]

3.2. Control of mercury emissions in combustion of coal for energy generation purposes

Hg emission control techniques may be divided into three groups:

1. Emission control by reduced quantity of combusted fuels

   Although it may seem to be obvious, most publications indicate a simple relation between quantity of combusted coal and values of emissions. Since the emission value is proportional to coal combustion, then any improvements in boiler efficiency will result in measurable reduction of emission. In order to reduce mercury air emissions the first step thus should be operations aiming at optimized energy generation processes, improved efficiency of a boiler and simultaneous reduction of fuel consumption.

   Hg emission reduction resulting from improved efficiency is a side-effect with no investment or operational costs assigned to it.

2. Emission control via denitrification, de-dusting and desulphurisation systems

   Boiler units are always equipped with flue gas cleaning systems that are planned and implemented in order to reduce emissions, whereas their role is not to remove Hg from flue gas. Their use in mercury emission reduction is referred to as "co-benefit". This method results in no additional costs provided that required effects can be obtained. .

   Efficiency of "co-benefit" to a great extent depends on forms of Hg and may be shortly characterized in the following way:

   <u>NOx reduction</u>

   - Low emission burners – do not directly affect Hg emission. However, frequent and unintentional increase in quantity of unburned coal may result in slightly increased absorption of Hg, analogical to that of activated charcoal.
   - SNCR – no positive impact of SNCR system on Hg reduction is known. Ammonia slip in flue gas which is typical of SNCR process results in concurrence of mercury reactions with chloride, sulphur and bromine and formation of ammonia compounds. Negative effects of high ammonia slip, such as contamination of LUVO, worsened quality of Ely ash and other, do not counterbalance possible increase in ESP efficiency.
   - SCR – in the beginning of the 90's it was discovered that SCR catalysts were capable of volatizing elemental mercury (Hg0). Owing to that, SCR systems combined with FGD, has been the most efficient mercury control technique without additional investment and operational costs. Owing to co-benefit it is possible to volatise Hg0 up to 85% and achieve total emission reduction of ca. 90%.

   <u>FGD (Flue Gas Desulphurisation)</u>

   - FGD systems allow for almost complete removal of oxidized mercury (Hg2+). Oxidized mercury is easily soluble and reacts in FGD reactor. Also particle-compound mercury (Hgp) which has not been removed by de-dusting system, will be captured by FGD.
   - Wet FGD systems have limited capacities of reducing elemental mercury. Thus, their efficiency depends on degree of mercury oxidation. Efficiency of Wet FGD may vary within the range of 10–90%, whereas the higher values are achieved in combination with SCR.
   - Dry and Semi-Dry FGD allow for similar level of mercury emission reduction as in case of Wet FGD. In addition, majority of semi-dry FGD systems are based on additives, such as activated charcoal, sorbalite, etc., which facilitate mercury adsorption. Although additives generate costs and must be recognized as specific control measure, instead of co-benefit, technical possibilities of mercury emission reduction by semi-dry FGD combined with SCR and bag filter – are the greatest ones.
   - Wet FGD process that is used to remove Hg2+ must be adequately verified and adapted. As a result of unfavourable reactions during formation of H2S and HgS, Hg2+ may be reduced to Hg0. As a result, instead of being reduced mercury emissions may increase – the so-called re-emission or secondary emission. Magnesium-based FGD is the most vulnerable to such phenomenon.

     So as to avoid the aforementioned phenomenon, suitable reagent concentration must be prepared and the course of the reaction must be controlled.

   <u>De-dusting</u>

   De-dusting system allows for removal of particle-compound mercury (Hg_p).

3. Specific mercury emission reduction techniques

   If the aforementioned techniques turn out to be insufficient in order to achieve the objectives, or if emission thresholds exceed technical capacities of co-benefits, then specific control measures must be implemented in order to reduce mercury emission.

All specific techniques are related to investment expenditure and increased operational costs.

Specific mercury emission control techniques include:

- pre-combustion coal treatment (mechanical, chemical and thermal);
- sorbents and additives;
- application of wet ESP;
- other techniques, most often combining reduction of several substances (majority of them still under research and development).

4. The use of selective catalytic reduction in reduction of mercury emission

4.1. Mercury air emission reduction mechanism when applying Selective Catalytic Reduction of Nitric Oxides (SCR)

Reduction of mercury air emission as a result of SCR technique has been among the most efficient "co-benefit" techniques. However, it should be noted that SCR system does not remove mercury; instead elemental mercury (Hg^0) is volatized to particle-compound mercury (Hg^{2+}). Only in the subsequent steps oxidized soluble mercury is removed in FGD system.

Mercury air emission reduction mechanism when applying Selective Catalytic Reduction of Nitric Oxides (SCR).

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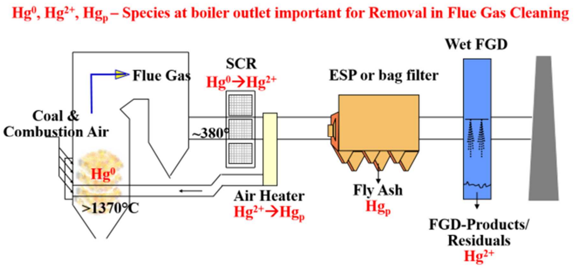

Figure 4. Reduction of mercury emission combined with SCR, ESP and FGD

4.2. Mercury oxidation on the surface of SCR catalysts

Mercury reactions occurring on SCR catalysts have been determined based on the Langmuir-Hishelwood Model consisting of 4 stages: Adsorption, Surface diffusion, Surface Reaction and Desorption.

A simplified model has been presented in Fig. 5.

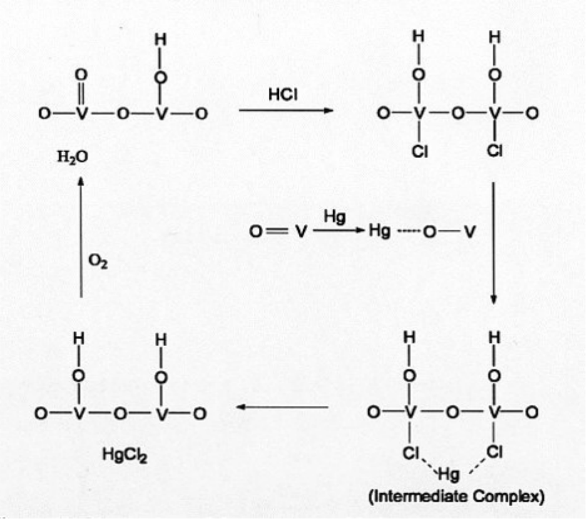

Figure 5. Hg0 oxidation on the surface of titanium-vanadium catalyst [3]

The aforementioned figure illustrates respective stages of heterogeneous catalysis involving mercury and hydrogen chloride. At stage 1 HCl particles are absorbed on surface of activated metals of the catalyst. At stage 2 reactive chlorine (Cl) atoms are generated which then bind with Hg0 (stage 3). The entire process ends up at stage 4 – regeneration of activated centres of catalyst through hydrogen atom oxidation from their surface.

The entire process corresponds to the following chemical reaction:

$$2\ Hg + 4\ HCl + O_2 \rightarrow 2\ HgCl_2 + 2\ H_2O$$

4.3. Boundary conditions for catalytic oxidation of mercury in SCR system

The course of catalytic oxidation of mercury also indicates boundary conditions necessary for its proper course. These are:

- ✓ Appropriate chloride content in flue gas. According to Polish regulations, this condition is met by majority of combusted coals. Additional factor positively affecting appropriate chloride content in flue gas is biomass co-combustion, since majority of biomass fuels are characterized by high content of chloride compounds.
- ✓ „Free" surfaces of the catalyst, i.e. not involved in denitrification reaction. Since the catalytic denitrification and oxidation of Hg depend on the same activated surfaces, both reactions cannot occur simultaneously. Laboratory tests have indicated that ammonia particles are bound on the catalyst surface as the first ones. Then, only after NH_3 content in flue gas has been reduced, catalysts become more active with regard to mercury. This condition is met by each SCR system since the initial relation of NH_3/NO at stoichometric composition near perfect 1 decreases as it flows through subsequent layers of the catalyst. Efficiency of mercury reduction by SCR increases simultaneously with de-

creasing the limit of target NOx content in flue gas.

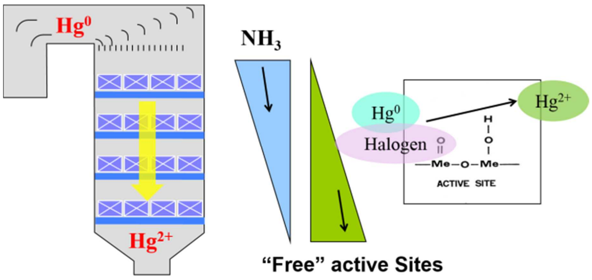

Figure 6. Hg0 oxidation on catalyst surfaces depending on the flux through SCR reactor [4]

4.4. Practical examples of SCR process application in mercury emission reduction

The aforementioned mechanisms of mercury oxidation allowing for its removal in FGD system has been confirmed by practical laboratory tests and on-site research.

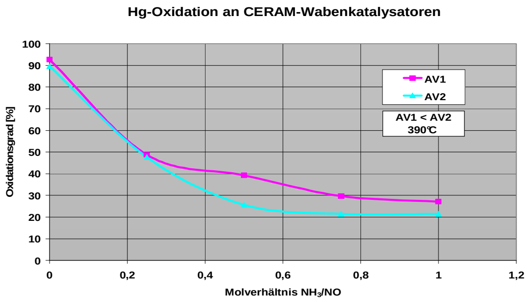

Figure 7. Results of laboratory tests of Hg oxidation on two types of Honeycomb catalysts with different activity [4]

The aforementioned laboratory measurements indicate that:

- ✓ Oxidation degrees amounted to ca. 90%;
- ✓ Higher activity of catalysts (Av) facilitates denitrification re action, however, with earlier Hg oxidation process. The final effect on both catalysts is comparable.

Analogical tests were carried out on several power units. Results of one of such tests have been presented below. This example has been selected by several reasons:

- ✓ Type of coal-fired unit, configuration of flue gas cleaning and type of fuel are comparable with European standard;
  - Power unit capacity: 330 MWe
  - Boiler type: pulverized coal-fired boiler
  - Fuel: hard coal, sulphur content: 0.89%, chloride content: 920 mg/kg
  - Denitrification: high dust SCR, honeycomb catalysts
  - FGD: WFGD
  - De-dusting: Electrostatic Precipitators (ESP)
- ✓ Catalysts provided by Porzellanfabrik Frauenthal were tested jointly with EnBW, e-on Engineering and IFK University in Stuttgart.

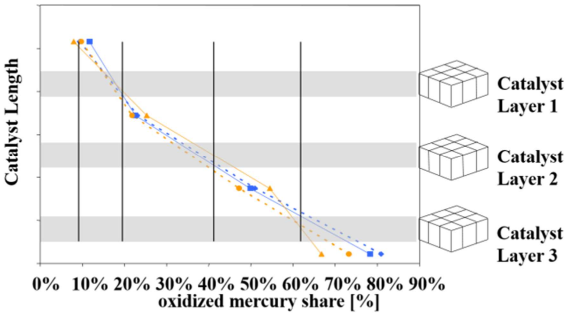

Figure 8. Results of actual measurements of Hg oxidation with various fuels of coal-fired power unit (capacity: 330 MWe) [4]

Measurement results indicate that:

- ✓ At the inlet to SCR the average degree of mercury oxidation is 10%;
- ✓ Degree of oxidation increases after each of 3 catalysts layers (based on laboratory tests);
- ✓ Total average mercury oxidation downstream SCR is 78%.

5. Summary

Application of selective catalytic reduction of nitric oxides in coal-fired boilers results not only in the best effects of NOx reduction (according to BAT/BREF reference documents) but also enables efficient reduction of mercury air emissions at no additional cost.

Current development of international and domestic regulations indicates topicality of this issue. Decisions regarding flue gas cleaning systems in power plants should account for the expected requirements concerning mercury emissions.

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